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7-31-84

PRELIMINARY DRAFT

REVIEW OF GEOCHEMICAL CONDITION INFORMATION AT
THE BASALT WASTE ISOLATION PROJECT (BWIP) SITE
(1979 - 1982)

PRELIMINARY DRAFT

8408200475 840731
PDR WASTE
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1. EXECUTIVE SUMMARY

Geochemical conditions at the Basalt Waste Isolation Project site will affect the site performance if radionuclides are released from the waste package itself. The geochemistry of the groundwater and the minerals with which it comes into contact will determine, to a major extent, the mobility of radionuclides and therefore their retardation by the formations through which the groundwater flows. Critical geochemical parameters, including composition of basalt, secondary minerals, and groundwater, groundwater pH and Eh, and formation temperature and pressure, are known with varying degrees of precision. General mineral and elemental composition of the bulk basalts are well known. The secondary mineral composition is less well known despite the fact that secondary minerals are likely to be more important in retardation of radionuclides. Groundwater composition, particularly for deep groundwaters at the potential repository horizon, are not at all well known. Sampling and characterization efforts for these waters have been frustrated by collection difficulties and totally invalidated by evidences of contamination either through drilling of the sampling wells or during collection and processing of the samples. Major compositional features can probably be reasonably estimated from the existing data, but conditions that are dependent on less abundant components, for example, trace element makeup, pH, and

Eh, are in substantial doubt. The contact between groundwater and basalt components is not well known and, consequently, the kinetics of reactions that will control geochemical conditions in the potential repository remain to be determined.

2. INTRODUCTION

This document will review the information available regarding geochemical conditions at the Basalt Waste Isolation Project (BWIP) site. Comments will be directed toward the adequacy of the geochemical information with respect to assessment of the suitability of the site for licensing of a high level radioactive waste repository to be constructed there.

"Geochemical conditions" means the composition of the repository site rocks, minerals, and groundwater as well as the parameters that affect reactions that occur in the system including pH, redox potential, temperature, and pressure. Geochemical conditions and geochemical reactions are closely related. Geochemical conditions are the result of the past geochemical reactions that have occurred. Future reactions that are likely to occur, including those critical to repository performance such as waste package degradation and radionuclide leaching will be affected by geochemical conditions.

2.1 PURPOSE AND SCOPE

The purpose of this review is to summarize the information regarding geochemical conditions at BWIP and to identify gaps in existing knowledge. While neither the US Environmental Protection Agency repository standards, nor the US Nuclear Regulatory Commission repository criteria specify geochemical properties that must be present in a repository, geochemical retardation is generally recognized as contributing to the barriers that will prevent released radionuclides from returning to the biosphere. Return to the biosphere would involve a sequence of events that would include mobilization from the waste package followed by transport through the surrounding medium. Geochemical conditions within that medium would control the rates of mobilization and transport of radionuclides. Therefore, it is expected that characterization of geochemical conditions will constitute a significant component of site assessment and performance prediction.

The scope of this report is limited to review and comment on current information concerning BWIP. The relevance and adequacy of that information to repository performance assessment will be discussed but comments are not intended to refer to the adequacy of the repository itself. Shortfalls in the information base and possible further characterization activities will be suggested in Section 4. References consulted during the preparation of this review are included in Appendix A--Annotated Bibliography whether

or not they are cited herein. Appendix B includes data tables and figures copied from the references consulted.

This review is one of a series of reviews of the BWIP geochemical information base; other reviews in the series deal with radionuclide element solubility and radionuclide sorption at the BWIP site. Together these reviews will provide a complete analysis of current information and needed further characterization for BWIP performance assessment.

2.2 GEOCHEMICAL PARAMETERS

Geochemical conditions are defined for this review as: (1) composition of rocks, minerals, and groundwater, (2) pH and pH controls in the groundwater, (3) oxidation-reduction characteristics of the groundwater, and (4) pressure and temperature conditions. These conditions are expected to form the basis for integrated modeling, assessment, and prediction of site performance with respect to the possible movement of radionuclides through the site toward the accessible environment adjacent to the site.

2.2.1 COMPOSITION OF BASALT AND GROUNDWATER As the principal constituents of the underground system, the minerals and rocks at the potential repository are expected to ultimately determine the geochemical conditions of the site. Important compositional data for the solid phases are the elements present and the stability

of these phases toward reactions with groundwater solutions. Structural and textural conditions cannot be entirely separated from these considerations, however, because they will determine the physical opportunity for reactions to occur. For the more reactive solids, the elemental composition and the species formed upon dissolution are important. The secondary mineralization that occurs along preferred-flow pathways is of greatest significance because of the extent of contact and opportunity for reaction that is possible. Furthermore, where secondary minerals are forming, they indicate saturation conditions in the groundwater with respect to those minerals and therefore provide quite useful information on expected geochemical behavior of radionuclides. Finally, the secondary minerals are most likely to provide the major, if not the only, sorption substrates for radionuclides that may traverse the far-field region of the repository.

The rocks themselves may not be the principal controls on repository performance in the event that groundwater enters the repository. Emphasis is placed on groundwater geochemistry because groundwater is expected to be the transport vehicle for radionuclide movement. Groundwater geochemistry is also an excellent indicator of the chemical reactions occurring between the water and those components of the rock with which it comes into contact. Such reactions may provide information on the expected reactions between the waste package and the surrounding

medium. Groundwater geochemistry is determined by reactions with minerals along the flow pathway, so that composition of exposed surfaces is important. Depending on the relationship between flow rates and chemical reaction rates, the groundwater may or may not be at equilibrium with the surrounding rocks.

Groundwater chemical parameters of interest include overall ionic strength and the elemental makeup of solute species. In addition, the interactions among solutes to form complex species will partly control whether or not the solutions are saturated with respect to those elements. Only with complete information on the pre-development site geochemistry will it be possible to confidently predict the reactions that may occur between waste package components including the waste itself and the rocks and groundwater of the site following repository development.

2.2.2 GROUNDWATER pH CONTROLS Solubility and sorption reactions of solutes in water are highly dependent on the activity of hydrogen ions in the system. The hydrogen ion concentration, represented by pH, is probably the most important single variable characterizing an aqueous system because virtually all chemical reactions are at least partially sensitive to it. Rates of many reactions are greatly affected by pH because of catalysis either by hydrogen or hydroxyl ions. Hydrogen ion can be an important competitor for sorption of cationic species on mineral surfaces and may thus directly affect solution composition. For elements

that may exist in more than one oxidation state, the standard electrode potential is often highly dependent on pH in the solution.

2.2.3 OXIDATION-REDUCTION CHARACTERISTICS The availability (or activity) of electrons in a chemical system is represented by Eh or, less frequently, by pe. Since oxidation or reduction is the loss or gain of electrons, respectively, Eh for a system can indicate the relative abundance of oxidation states for a redox-sensitive element if and when the system has reached chemical equilibrium. Although many naturally-occurring systems are not at complete equilibrium or, more commonly, specific half-cells within natural systems are known to be out of equilibrium, the concept of a "system-Eh" provides a framework for the characterization of geochemical conditions. Chemical species expected to predominate at equilibrium must be considered in performance assessment unless they can unequivocally be shown not to form for kinetic or other reasons. In addition to consideration of thermodynamically expected predominant chemical species, it is also necessary to address the kinetics of the reactions which lead to formation of the predominant species. Repository performance assessment will require the coupling of groundwater dynamic considerations with the geochemical reaction rates.

2.2.4 RELATED GEOCHEMICAL PARAMETERS. Chemical reactions are

sensitive to temperature and pressure, so these parameters will also affect performance assessments of the repository. Temperature affects the rate of almost any chemical reaction, increased temperatures leading to acceleration of the reaction. Thus, to a first approximation, higher temperature systems will attain equilibrium more rapidly and, for complicated systems in which flow and chemical reaction occur simultaneously, higher temperature systems are more amenable to prediction of performance based on equilibria. Temperatures also affect the equilibrium states for many reactions, however, and in general there are fewer data for high temperature reactions. This lack can be partially offset by acceptable schemes for extrapolation of low temperature data to higher temperature.

Pressure effects are generally to shift the equilibrium state of reactions toward a more condensed condition under increased pressure. Reactions leading to a reduced partial molar volume of products compared to reactants are favored by increased pressure, while reactions that yield increased volumes are retarded by increased pressure. In general, pressure compensation is highly predictable and the direct measurement is probably unnecessary for geochemical considerations. It is noted that pressure measurements are often highly important primary data for hydrologic assessment of site conditions and the hydrologic data should provide pressure data that are more than adequate for geochemical assessment. Pressure effects should be included in

the geochemical modeling of the repository.

3. SUMMARY OF EXISTING BWIP GEOCHEMICAL INFORMATION

Geochemical information will be discussed in the context of site geology and hydrology. Geologic and hydrologic conditions determine the relative importance of geochemical parameters and are therefore necessary to allow proper consideration of site geochemistry. In the following sections parenthetical references, such as (Fig. B-1), refer to material copied in Appendix B.

3.1 BASALT GEOLOGY AND HYDROLOGY

The BWIP site is in the Columbia Plateau Basalt Group, a major feature occupying portions of the states of Idaho, Oregon and Washington (Fig. B-1). Up to 5000 feet of basaltic flows, interlayered by weathered and sedimentary series are described in three sections (upper to lower): Saddle Mountains Basalts, Wanapum Basalts, and Grande Ronde Basalts (Fig. B-2). Probable repository horizons are in the oldest and thickest section, the Grande Ronde Basalts. Most emphasis has been placed on the Umtanum Basalt within the Grande Ronde, although flows above the Umtanum in the Sentinel Bluffs Sequence have not been ruled out from consideration.

3.1.1 STRUCTURE AND TEXTURE The BWIP site is in the Cold Creek

Syncline the core of which strikes northwest-southeast (Fig. B-3). To the northeast between the site and the Columbia River lies the Gable Mountain Anticline. To the southwest is the Rattlesnake Hills Anticline. The groundwater basin formed by the Cold Creek Syncline is generally referred to as the Pasco Basin in hydrologic literature.

Columbia Plateau Basalt flows are typically laterally extensive. Intraflow vertical structure is quite distinct and hydraulic permeability is highly dependent on features that are vertically varying within the flow. Long and Davidson (1981) described the general textural and structural character of Columbia Plateau Basalt flows. They noted that interflow structures "exert a strong influence on the hydrologic characteristics." Vesicular flow tops are relatively permeable. Two colonnade (vertically columnar) sections are typically found, separated by a more randomly structured entablature. Groundwater movement in the colonnade and entablature zones is restricted almost entirely to the joints and fractures in these zones because the rock matrix is quite dense and impermeable. Below the lower colonnade is a zone of glassy, sometimes pillowed, rock that forms the base of the flow. Structures and petrographic texture are directly correlated so that Long and Davidson (1981) concluded that petrographic examination of core samples could be used to determine structural attributes of the sampled horizon.

3.1.2 GROUNDWATER MOVEMENT PATTERNS Newcomb et al. (1972) described hydrology within the upper geologic strata at the Hanford site and focus on the unconfined aquifer. The area of interest is centered around the 200-Area where liquid waste disposal has lead to perched zones of contaminated water and has caused the occurrence of "ground-water mounds". Near surface hydrology has also been characterized by monitoring the movement of these contaminants on the Hanford reservation. For example, reports by Eddy (1979) and Eddy and Wilbur (1980) represent an annual series documenting the extent and spread of radioactive contamination in the unconfined aquifer at Hanford. Principal sources of contamination are the past 200-Area liquid waste discharges to cribs and swamps. During the 36 years preceding

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1980 in excess of 6×10^{11} liters of process cooling water have been discharged. The majority of the contaminants are in the upper portion of the unconfined aquifer and are nearing the Columbia River. Tritium, gross beta, and nitrate are the leading mobile species. Wells are also sampled that penetrate 2 deeper aquifers, one in a "semi-consolidated sedimentary material overlying the basalts" and one in the basalt. The basalt aquifer is artesian.

Gephart et al. (1979) discussed the relation of groundwater flow and structure/lithology within the Columbia Plateau, stressing the importance of sedimentary interbeds to major groundwater flow features. Within the Pasco Basin, The Columbia

River Basalt Group consists of the Saddle Mountains, Wanapum, and Grande Ronde Basalts. The confined aquifers present therein are associated with the more permeable interflow and interbed zones and generally located between confining units composed of the dense, columnar portions of the basalt flows. The principal water-bearing or yielding portions of the basalt occur along flow contacts. Here vesicularity and flow brecciation form networks of interconnected vesicles and fissures through which groundwater moves. Gephart et al commented regarding flow at borehole DC1 that results "--suggest horizontal groundwater movement above a depth of 3450 feet (just below the Umtanum) and downward movement below this depth. Apps et al. (1979) noted in wells DC-1, DC-2 and DC-6 that there was a local head minimum within 600 feet below the bottom of the Umtanum with an increasing head below that depth.

Leonhart et al. (1982) reported results of a single tracer (potassium thiocyanate) test of water movement between two boreholes (DC-7 and 8) in a packed zone at the top of the McCoy Canyon Flow. The holes are approximately 55 feet apart. Water was pumped from the packed zone of DC-7 into the packed zone of DC-8. The estimated formation residence time was 170 minutes at a circulation rate of 1 gallon per minute. Recovery of thiocyanate was 60 percent but potassium was lost, apparently by exchange for sodium.

Arnett et al. (1981) applied two-dimensional and three-dimensional groundwater flow models to Grande Ronde Basalt interflow zones in the Cold Creek Syncline. Flow in the models is nearly horizontal and toward the southeast toward Wallula Gap. Travel times to the model boundary exceed 100,000 years for the three dimensional analysis and are over 2 million years in the two dimensional calculations. Arnett, et al. indicated that data still needed include better hydraulic head information up gradient from the repository site and field measurements of vertical hydraulic conductivity.

3.2 COMPOSITIONAL INFORMATION

The chemical makeup of the BWIP repository has been determined in a number of studies.

3.2.1 BASALT COMPOSITION Smith et al. (1980) reviewed the mineralogic and elemental composition of Grande Ronde Basalts. Average compositions of major and minor elements in several of the Columbia Plateau flows are given (Figs. B-4, B-5).

Noonan et al. (1980) analyzed mineral and glass specimens by electron microprobe and compared results for basalts from outcrop collections to those for cored samples. Entablature and colonnade sections were treated separately. They concluded that the reference material (outcrop) is similar in texture and phase composition to core samples.

3.2.2 SECONDARY MINERAL COMPOSITION Secondary minerals described by Smith et al. (1980) include clays (smectite, illite and traces of vermiculite), zeolites (heulandite and clinoptilolite), and polymorphs of silica. Gypsum, calcite and pyrite are noted as rare (Figs B-6, B-7). Ames (1980), in a compendium of results from detailed examinations of mineralogic and elemental makeup of basalts taken from coreholes DD1H-1, DH-2, DDH-3, DH-4 and DH-5, indicates that the top 1000 feet of the basalts are essentially zeolite free and that heulandite is the most common zeolite below 1000 feet. Ames did not mention clinoptilolite, nor did he indicate secondary minerals with redox implications.

Benson and Teague (1979) reported results of 147 scanning electron microscope (SEM) and 170 x-ray diffraction (XRD) analyses of samples from 4 cores performed to examine secondary mineralization in Columbia Plateau Basalts. Electron microprobe and wet chemical methods were also used. Dominant minerals were clay (smectite or iron-rich illite), zeolite (clinoptilolite), and silica (quartz, cristobalite, tridymite, opal). The crystallization sequence varied but usually followed: clay--> clinoptilolite--> silica/clay. Clinoptilolite sometimes showed dissolution features. Vesicle filling was found to be more complex than fracture filling and included minor amounts of erionite, chabazite, analcime, vermiculite, phillipsite, gypsum and calcite.

Wet chemical analyses of iron in the clays indicated Fe(III)-Fe(II) ratios of 3 or 4 to 1 as oxides. Fe(III) oxide weight percent ranged from 10 to 20 and Fe(II) oxide from 3-6 weight percent. The iron is said to occupy a distinct phase, possibly hematite or goethite, within the smectite

Teague (1980) examined the secondary minerals in 39 vesicle and fracture samples taken from two cores through the major basalt groups using SEM/energy-dispersive x-ray (EDAX), XRD, and thin section microscopy. Mineralogy, sequence of crystallization, and connectedness of fissures were sought. Initial phases were almost always clay, rarely clinoptilolite. Distinct overgrowths of silica or clinoptilolite were present, each in about 1/3 of the specimens. Pyrite was found but once. Third and fourth layers included, in addition to the above minerals, heulandite and mordenite. Apatite was found only once. Dissolution evidence was rare and was restricted to clinoptilolite. A generalized crystallization sequence was clay (usually smectite)--> clinoptilolite--> silica/clay. Data on depth dependence and on connectedness were deemed too sparse for interpretation. Vesicles and fractures from the same depths have widely varying amounts of secondary mineralization.

3.2.3 GROUNDWATER COMPOSITION Van Denburgh and Santos (1965) reviewed the physical and chemical suitability of Washington groundwater for use in agricultural, municipal or industrial

applications. In the Columbia Plateau Province, which includes most of Eastern Washington, aquifers are mainly the interbeds and flow tops. Ample water yields from such aquifers have been found, often several hundred gallons per minute and as high as 1500 gallons per minute. In structural basins wells may be artesian.

Data for a large number of wells tapping the upper 1000 feet are presented. Silica concentrations are in the range 40-60 ppm and increase with depth. Iron concentrations are below 0.3 ppm. Sulfate is generally below 30 ppm except where contamination from returnflow of irrigation water from fertilized lands has added to the natural levels. Fluoride reaches 2.8 ppm and is highest in waters that contain high silica and high sodium.

Newcomb (1972) presented a comprehensive discussion of the chemical composition of groundwaters from the Columbia Plateau region based on results of 525 analyses for major components and 100 trace element analyses. Most of the groundwater sampled was discharged from springs or was taken from wells that tap the youngest basalts, the upper 2000 ft. Newcomb indicates that "Passage of the ground water into the oxidizing environment of the atmosphere causes the precipitation of iron oxide at some springs, but there is a general absence of precipitates or encrustations at most springs where water flows from the basalt. Likewise the formation of encrustations and coatings is lacking

at all but a few wells."

Silica concentrations are noted to be generally higher in higher temperature waters, but this relationship is not consistent. There is no correlation of iron content with depth. The major cations are Ca, Mg, Na, and K and bicarbonate is the major anion. Sulfate, chloride, sodium and calcium are noted to be higher in the newly recharged waters that have formed as a result of the Columbia Basin Irrigation Project. Fluoride ranges from 0-2 mg/l, values quite low in comparison to the deeper waters reported elsewhere. Newcomb acknowledged that "...there may be a possibility that such high-fluoride ground water occurs in the basalt at depths below 1000 feet at some places. All evidence for such an occurrence is limited to the LaSala and Doty (1971) data."

Regarding dissolved gases, Newcomb (1972) indicates "The principal readily discernible dissolved gas is hydrogen sulfide, which occurs in small amounts in most of the ground water from wells in the basalt. It seems to be present in greatest amounts in the water from newly drilled wells. The concensus is that the gas diminishes with time as the well is pumped, rather than that the users become accustomed to it and notice it less with time....The concentration of dissolved oxygen is very low in most of the groundwater. A number of determinations, for which no recorded data are available, are know by the author to have found

no oxygen in ground water of the basalt when it was correctly sampled before surface or pump-column aeration....Because most of the ground water is confined under pressure within aquifers that contain fresh, untarnished, and unoxidized iron pyrite and because of the reported determinations of no oxygen, it is assumed that the ground water of the basalt is largely devoid of dissolved oxygen."

Waters from depths greater than 1000 feet have been sampled much less extensively. Hanford area deep wells are shown in Figure B-8 and compositional data are shown in Figure B-9. Apps et al. (1979) planned a comprehensive groundwater geochemical characterization effort involving a very extensive set of chemical and isotopic analyses. Their work was only partially completed and the authors appear to place little credence in the chemical characterization results because of suspected contamination. For example, although some 64,000 gallons of water were pumped from a packed off section of well DC-2 in order to remove local contamination, samples drawn after this "swabbing" contained tritium at about 20% of the Columbia River levels. Although they pumped packed well sections at length and were able to obtain constant conductivity and temperature, normally signs of uncontaminated water, the water still contained diesel oil and "bacterial breakdown odor." The authors express skepticism about possible contamination of earlier well samples.

LaSala and Doty were credited by Apps et al (1979) with having done the only previous geochemical work with deep groundwater from the site.

Average composition and range for ground water from Upper Wanapum were summarized by Gephart et al. (1979) who remarked on the generally poor quality and extremely limited quantity of Grande Ronde Basalt hydrochemical data. Contamination by drilling fluid, poor field sampling, poor laboratory analytical procedures and cross-aquifer communication within the core holes were cited as reasons for the poor data.

Salter et al. (1981) indicated that "There are two distinct groundwaters present in the basalts: a sodium bicarbonate buffered groundwater (pH=8 at 25C) characteristic of the Saddle Mountains and Upper Wanapum Basalts and a sodium-silicic acid buffered groundwater (pH=10 at 25C) characteristic of the Lower Wanapum and Grande Ronde Basalts." For laboratory work most experimentalists use simulated versions of these groundwaters according to recipes GR-1 and GR-2, respectively (Fig B-10). Jones developed a recipe for a synthetic groundwater that approximates the major component composition and pH of water collected from just below the Umtanum horizon in well DC-6. Two stock solutions are prepared. One contains sodium salts of carbonate, silicate, sulfate, fluoride and hydroxide while the other contains chloride salts of sodium, potassium, calcium and

magnesium. Groundwater is simulated by adding aliquots of these stock solutions to distilled water. No effort to control Eh, trace metal ions, gases or organic components was indicated by Jones.

Deutsch et al. (1982) used the geochemical model WATEQ2 with 118 sets of groundwater composition data from Hanford area to estimate saturation indices relative to several minerals. Only few of these sets are for deep (>1000m) wells and their chemistry is said to be quite different from the shallow groundwater. Equilibrium with calcite appears probable, that is, the computed ion activity products are near the measured values, implying saturation. Near saturation with the zeolites, wairikite, and analcime is also inferred. Several minerals for which the solutions appear to be saturated but which are not reported as yet, are found--allophane, MnHPO₄ and, in deep wells where F is high, fluorite.

Ames (1980) suggested that groundwater compositions will be more strongly affected by glassy material than by crystalline components since the former is more soluble. The glassy material is high in silica and contains most of the Cl and F, "because these do not fit well into any of the main stage flow minerals."

3.2.4 GROUNDWATER pH CONTROLS Jacobs and Apted (1981) computed groundwater pH at BWIP based on buffering of groundwater by basaltic glass. They assumed that pH is controlled by silicic

acid at 9.5 ± 0.2 . They concluded that the relatively low mobilities of several actinides in alkaline media are favorable. Newcomb (1972) reported the pH of the prevalent type of groundwater in the upper basalts ranges from 6.5 to 9.2 and most of the values fall between 7.2 and 8.4. Ames and McGarrah (1981) found that fresh basalt or secondary minerals from the Hanford site consistently buffered GR-1 synthetic groundwater to pH values between 8.3 and 8.9.

3.2.5 GROUNDWATER OXIDATION-REDUCTION STATUS Benson (1978) discussed the fundamentals of redox potential, platinum electrode measurements and limitations in practicality of Eh. Eh values are not given by Benson but he suggested that Fe(II)-Fe(III) and the sulfur system are "poorly poised" in Pasco Basin groundwaters. No secondary minerals with redox implications were identified by Benson. Ames and McGarrah (1981), in discussing controls on Eh, investigated several possible poisoning mechanisms including magnetite-hematite, but these were all rejected because, for example, "...the basalt contains no hematite." They concluded that the only poisoning system that seems to fit is magnetite-pyrite which minerals occur at 10-15 weight percent and 1 weight percent respectively. Ames and McGarrah note that the kinetics of reaction with the basalt are slow so that, although the basalt may "try" to control Eh in laboratory experiments, it may be unable to do so. The Eh estimated for the magnetite-pyrite control is between -0.3 and -0.8 v.

Jacobs and Apted (1981) assumed that Eh is controlled by a quartz-pyroxene-magnetite buffer at -0.45 ± 0.05 v. They indicated that the calculated Eh values are in close agreement with field analytical data such as "sulfate:sulfide ratios greater than 1 and dissolved carbon dioxide:methane ratios of about 0.2" as well as the presence of magnetite and pyrite without any hematite. Their conclusion that sulfate would predominate in a reducing system is puzzling, inasmuch as sulfate represents a highly oxidized sulfur species.

3.2.6 RELATED GEOCHEMICAL PARAMETERS Benson (1978) presented a calculated pressure-depth relationship for the BWIP site. He also showed the temperature-depth profiles measured in ca. 6 coreholes at or near (north of) the Hanford site. As noted previously, Apps et al. (1979) reported field pressure tests to provide data for mathematical modeling of ground water flow in deep basalts of the Pasco basin. Gephart et al. (1979) also tabulate pressure values (hydraulic heads) for several wells at Hanford.

Newcomb (1972) indicated that temperature of the ground water is a few degrees higher than the sum of mean annual temperature of its area and the temperature increase due to the earth's thermal gradient down to the aquifer in which the water occurs, although he notes that there are many variations from this generalization. He concludes that nonrepresentative temperatures

were sometimes observed for ground water due to improper techniques and/or inadequate samples.

Smith et al. (1980) indicate a geothermal gradient of ~45 degrees (C)/km based on measured temperatures in wells drilled at Hanford. In the immediate vicinity of the waste, decay heat will increase the temperature, particularly during the first few hundred years after waste emplacement. The highest calculated temperature according to Smith et al. (1980) is near 270 C and occurs at the package-rock interface about 25 years after emplacement. Considerably lower maxima, less than 150 C, appear to prevail 1000 years after emplacement.

4. REVIEW AND COMMENTS ON GEOCHEMICAL INFORMATION

The information summarized previously indicates the range of geochemical conditions at BWIP. It appears that, while much of the existing information is adequate for geochemical assessment of the potential repository, there are certain critical gaps in the existing information.

4.1 BASALT GEOLOGY AND HYDROLOGY

For purposes of geochemical evaluation, the information on structure and texture of the basalt flows at BWIP is adequate. The degree of exposure of basaltic and secondary mineral surfaces

to groundwater and the composition and rates of reaction of those surfaces with groundwater components, however, is largely unknown.

Groundwater ages, the estimated elapsed time since the water was at the surface, can be helpful indicators of the rates of water movement and rates of reaction with minerals along the flow paths. Crosby and Chatters (1965) described the application of carbon-14 techniques to dating groundwater near Pullman, Washington. The results indicate ages of several thousand years for all groundwaters taken from basalts but younger ages for other samples. Isotopic exchange is said to be very limited and apparently of little importance to groundwater dating.

4.2 COMPOSITIONAL INFORMATION

Elemental makeup of the solid constituents is much better known than is the solute composition for groundwater at the repository horizon.

4.2.1 BASALT COMPOSITION The data base for mineral and chemical composition of unaltered Columbia Plateau Basalts described by Smith et al. (1980) appears to be satisfactory for purposes of the BWIP. The primary minerals of the basalts are not likely to significantly detract from adequate repository performance. Indeed, beyond the immediate vicinity of the waste package, it seems unlikely that the primary minerals will have any bearing

whatsoever on the repository. In the near field, where crushed basalt from the site may be used as packing and fresh surfaces may be exposed, the mineral and chemical composition of the basalt may affect the geochemical controls on radionuclide movement. In the zones beyond, where newly-fractured surfaces are absent, the primary minerals will not act, except by diffusion through the quite dense rock matrix. These zones, which are likely to dominate the far-field of the repository, may be subject to a totally different geochemical environment. Because the basaltic matrix is so dense and hydraulically impermeable, mobile groundwater within the basalts may travel for great distances through preferred-flow pathways and remain out of effective geochemical contact with the primary basalt minerals. The mineralogy and surface chemistry of the preferred-flow zones will be far more important in determining the geochemical retardation of radionuclide transport through these zones than will be the primary mineral composition.

4.2.2 SECONDARY MINERAL COMPOSITION Composition of the secondary minerals is generally adequately known. Improved information is needed, however, regarding minerals with redox sensitive components that may reflect the Eh at the time of secondary mineralization. Iron bearing minerals should be better characterized and the oxidation state of iron in the smectite clays should be determined. The identification of nontronite appears to have been based on the abundance of iron in the

smectite. Oxidation state and structural location of the iron have not been reported. Formation and persistence of secondary minerals along fractures or other paths where groundwater is flowing is an important clue to the probable reactions that released radionuclides may undergo. The surface composition and reactivity of these minerals would be much more important to repository performance than would composition or reactions of crushed basalt.

4.2.3 GROUNDWATER COMPOSITION Groundwater composition, particularly for deeper repository horizons, appears to be very poorly known. All recent reports on deep groundwater composition indicate sample contamination due to numerous factors as a major problem. The difficulty in obtaining uncontaminated deep groundwater samples has generally been underestimated. Use of water-based drilling fluids causes contamination that persists even though great volumes of water are pumped from the wells. Air drilling may be less likely to introduce groundwater contamination, although there are questions about the determination of hydraulic parameters in air drilled holes.

Based on the reviews of groundwater chemical composition, it appears that very little can be said about the present geochemical status of groundwater at the BWIP site. The available information deals primarily with the upper Columbia Plateau Basalt zones and data from the deeper zones are

sufficient only to establish that there is a significantly different geochemistry controlling their composition and that extrapolation is not at all certain.

The degree of exposure of surfaces to groundwater and the reactivity of these surfaces with groundwater with respect to sorption, in particular, and chemostat-type buffering of Eh and solution composition, in general, need better definition. Stability of the identified secondary minerals and the relationship of secondary minerals to solution conditions in the groundwater need to be more precisely known. The composition of uncontaminated groundwater from the most conductive horizons in the vicinity of the repository need to be determined and those solid phases that might be at equilibrium with these waters should be better defined. This will require substantial improvement in sampling and analysis than has heretofore been reported. In the absence of such data, however, the geochemical status of the groundwaters that form potential effluents from the repository is uncertain at best.

4.2.4 GROUNDWATER pH In view of the substantial uncertainty regarding groundwater composition, the knowledge of geochemical parameters, especially pH and Eh may be suspect. The values for pH appear to be bounded in all determinations and computations for groundwaters from the Columbia Plateau by about 7.5 to 10.0 and are virtually certain to be alkaline. The assumption of a

value near 8.5 or 9.0, coupled with sensitivity analyses in the range of 1.5 units above and below this value should allow an adequate performance assessment to be made.

4.2.5 GROUNDWATER OXIDATION-REDUCTION STATUS The oxidation-reduction status, is considerably less certain than groundwater pH. The highly reducing conditions that result from theoretical computations are open to question both for the assumptions that are required for the computation and for the kinetic unknowns in the repository site. The choice of minerals to enter into Eh buffer calculations is quite uncertain and the probability of guessing the correct minerals to be used seems low. Furthermore, because of the low permeability of the basalt and the restriction of groundwater to preferred flow pathways, it seems likely that groundwater may remain out of redox equilibrium with respect to the major minerals in the basalt for extremely long time periods. Measured Eh values are subject to question under the best of conditions. With the contamination problems experienced for deep groundwaters at BWIP, the measured Eh values would seem to be unreliable.

Eh at the BWIP potential repository site is said to be strongly reducing (Jacobs and Apted, 1981; Ames and McGarrah, 1981; Smith et al., 1980). Nonetheless, there are significant gaps in the redox system characterization. Measurements of Eh are fraught with uncertainty and specific reports of the results of Eh

measurements are lacking. Computed results must be based on assumptions that demand direct testing before confidence in their accuracy can be engendered. Furthermore, there are site data that are inconsistent with the assertion of "strongly reducing conditions" or system Eh conditions as reducing as less than -0.4 v. The apparent stability of Fe(III) in secondary minerals which should more accurately reflect the geochemistry of mobile groundwater than do primary basalt minerals, suggests a more oxidizing environment. That sulfate exists, much less the dominates the sulfur chemistry in solution, belies the strongly reducing allegations. In the absence of more direct information, it appears that conservatism in performance assessment would require rejection of the alleged strongly reducing conditions until more definitive data are available. In the meantime, both the highly reducing conditions that are theoretically predicted and more oxidizing conditions, perhaps as high as $+0.2$ v should be included in performance assessment.

4.2.6 RELATED GEOCHEMICAL PARAMETERS Pressure information at BWIP is adequate for geochemical assessment. It appears that the range of temperatures that may be expected is so dominated by the wastes themselves that in situ temperatures are less important. Temperatures as high as 270 C may occur near the disposed waste a few decades after emplacement but in the far field or at times greater than 1000 years, when waste package failure may occur, temperatures will be much lower, less than 150 C. Formation

temperatures as high as 60 C may occur naturally at the repository horizon.

5. REFERENCES CITED

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APPS, J., Doe, T., Doty, B., Doty, S., Galbraith, R., Kearns, A., Kohrt, L.B., Lons, J., Monroe, A., Narasimhan, T. N., Nelson, P., Wilson, C. R., and Witherspoon, P. A., 1979, Geohydrologic Studies for Nuclear Waste Isolation at the Hanford Reservation, LBL-8764, Vol 2, Lawrence Berkeley Laboratory, Berkeley, California.

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CROSBY, J. W., III, and Chatters, R. M., 1965, Water Dating Techniques as Applied to the Pullman-Moscow Ground-Water Basin, Bulletin 296, College of Engineering, Washington State University, Pullman, Washington.

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Plateau, Washington: An Integration of Current Knowledge, RHO-BWI-ST-5, Rockwell Hanford Operations, Richland, Washington.

JACOBS, G. K., and Apted, M. J., 1981, Eh-pH Conditions for Groundwater at the Hanford Site, Washington: Implications for Radionuclide Solubility in a Nuclear Waste Repository Located in Basalt, EOS, Transactions of the American Geophysical Union, vol 62, p 1065.

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NEWCOMB, R. C., Strand, J., and Frank, F. J., 1972, Geology and Groundwater Characteristics of the Hanford Reservation of the U. S. Atomic Energy Commission, Washington, Professional Paper 717, U. S. Geological Survey, Washington, D. C.

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SALTER, P. F., Ames, L. L., and McGarrah, J. E., 1981, Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington.

SMITH, M. J., Anttonen, G. J., Barney, G. S., Coons, W. E., Hodges, F. N., Johnston, R. G., Kaser, J. D., Manabe, R. M., McCarel, S. C., Moore, E. L., Noonan, A. F., O'Rourke, J. E., Schulz, W. W., Taylor, C. L., Wood, B. J., and Wood, M. I., 1980, Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt: An Integration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington.

TEAGUE, L. S., 1980, Secondary Minerals Found in Cores DC2-A1

and DC2-A2 Taken from Grande Ronde Basalt Formation, Pasco Basin, Washington, LBL-10387, Lawrence Berkeley Laboratory, Berkeley, California.

VAN DENBURGH, A. S., and Santos, J. F., 1965. Groundwater in Washington: Its Chemical and Physical Quality, Water Supply Bulletin No 24, Washington Division of Water Resources, Olympia, Washington.

APPENDIX-A--ANNOTATED BIBLIOGRAPHY

AMES, L. L., 1980, Hanford Basalt Flow Mineralogy, PNL-2847, Pacific Northwest Laboratory, Richland, Washington.

A compendium of results of detailed examination of mineralogic and elemental composition of basalts taken from coreholes DD1H-1, DH-2, DDH-3, DH-4 and DH-5. Indicates that the top thousand feet to basalts are essentially zeolite free and that heulandite is the most common zeolite below 1000 feet.

Suggests that groundwater compositions will be more strongly affected by glassy material than by crystalline components since the former is more soluble. The glassy material is high in silica and contains most of the Cl and F, "because these do not fit well into any of the main stage flow minerals."

AMES, L. L., and McGarrah, J. E., 1981a. Investigations of Basalt-Radionuclide Distribution Coefficients: Fiscal Year 1980 Annual Report, RHO-BWI-C-108/PNL-3462, Pacific Northwest Laboratory, Richland, Washington.

Reports the determination of distribution coefficients for U, Pu, Am, Tc, Cs, Sr, Se and I on Flow E, Pomona and Umtanum samples from synthetic groundwaters GR-1 and GR-2. Freshly crushed basalt with pieces of iron from the crusher were used. Conclusions regarding sorption were that there were large temperature effects on Kd in the 23 to 300C range except for I & Tc. Uranium Kd increased with increasing temperature while Cs decreased from 23 to 150C and then increased at 300C. Am and Pu Kds increased about 10 fold between 23 and 150C. No discussion of the cause of temperature dependence was found. Pu and Am were 80-90% plated on container walls during the experiments.

Fresh basalt or secondary minerals consistently buffered GR-1 to pH values between 8.3-8.9.

An extended discussion on Eh control indicates that several possible poisoning mechanisms were investigated including magnetite-hematite but these were all rejected because, for example, "the basalt contains no hematite." "The only poisoning system that seems to fit is magnetite-pyrite" which are 10-15 wt-% and 1 wt-%, respectively. The authors note that the kinetics of reaction with the basalt are slow so that although the basalt "tried" to control the Eh in their experiments, it was apparently frustrated in its efforts. The Eh estimated for the magnetite-pyrite control is between -0.3 and -0.8 v.

AMES, L. L., and McGarrah, J. E., 1981b, High-Temperature Determination of Radionuclide Distribution Coefficients for Columbia River Basalts, RHO-BWI-C-111/PNL-3250, Pacific Northwest

Laboratory for Rockwell Hanford Operations, Richland, Washington.

A report on tests of sorption of Cs, I, Sr, Se, Np, Sr, Am, Pu, Tc and U on crushed basalt from GR-1 synthetic groundwater at temperatures of 150 and 300 C. Only Cs results are given. The Kd at 150 is lower than the low temperature Kd but at 300 the Kd is again higher. It is suggested that secondary minerals which form more rapidly at the higher temperature are responsible for capturing the Cs.

APPS, J., Doe, T., Doty, B., Doty, S., Galbraith, R., Kearns, A., Kohrt, L.B., Lons, J., Monroe, A., Narasimhan, T. N., Nelson, P., Wilson, C. R., and Witherspoon, P. A., 1979, Geohydrologic Studies for Nuclear Waste Isolation at the Hanford Reservation, LBL-8764, Vol 2, Lawrence Berkeley Laboratory, Berkeley, California.

NOTE: The only version of this large document that was available for review was a microfiche of exceedingly poor quality. Consequently many details were not noticed and have been omitted.

Field tests to provide data for mathematical modeling of ground water-flow in deep basalts of the Pasco basin were the topic of this report. Discussed were several kinds of tests including: pressure measurements, tracer tests, borehole fracture logging, hydraulic fracturing (stress measurements) and a wide variety of permeability measurements. An extensive groundwater chemistry effort was mounted but with little results.

Wells DC-2, DC-6, DC-8 and DC-11 were involved in the tests. DC-6 is artesian, with 75% of the flow originating at 3650 to 3800 foot depths. Also noted in DC-1, DC-2 and DC-6 was a local head minimum within 600 feet below the bottom of the Umtanum with an increasing head below that depth.

"Gable Mountain Anticline may be acting as a flow barrier separating Cold Creek Valley from the Columbia River Valley to the north and east." The authors agree with LaSala and Doty that Cold Creek Valley deep discharge is to the southeast probably to the Columbia River at or below the Tri-Cities area.

An extended discussion of a large but abortive geochemical characterization effort is presented. A very extensive set of chemical and isotopic analyses was planned, but only partially completed. The authors place little credence in the results because of suspected contamination. For example, some 64,000 gallons of water were pumped from a packed off section of well DC-2 in order to remove local contamination. Samples drawn after this "swabbing" contained tritium at about 20% of the Columbia River levels. The authors express skepticism about possible

contamination of earlier well samples. Although they pumped packed sections at length and were able to obtain constant conductivity and temperature, normally signs of uncontaminated water, the water still contained diesel oil and "bacterial breakdown odor."

In addition to contamination problems, it was noted that the chemical characterization efforts were plagued by sampling difficulties, apparently underestimated analytical costs, techniques not suited to the field and termination of funding for the project.

LaSala and Doty were credited with having done the only previous geochemical work with deep groundwater from the site.

ARNETT, R. C.; Mudd, R. D., Baca, R. G., Martin, M. D., Norton, W. R. and McLaughlin, D. B., 1981, Pasco Basin Hydrologic Modeling and Far-Field Radionuclide Migration Potential, RHO-BWI-LD-44, Rockwell Hanford Operations, Richland, Washington.

Two-dimensional and three-dimensional groundwater flow models applied to Grande Ronde Basalts interflow zones in the Cold Creek Syncline. Flow appears to be nearly horizontal and toward the southeast toward Wallula Gap. Travel times to the model boundary exceed 100,000 years for the three dimensional analysis and are over 2 million years in the two dimensional calculations.

Data still needed include better hydraulic head information up gradient from the repository site and field measurements of vertical hydraulic conductivity.

BARNEY, G. S. 1981, Radionuclide Reactions with Groundwater and Basalts from Columbia River Basalt Formations, RHO-SA-217, Rockwell Hanford Operations, Richland, Washington.

Measured the distribution coefficients of Cs, Sr, Se, Am, Np, Pu and Tc on crushed basalt from Sentinel Gap outcrop samples. Synthetic groundwater was used. Barney noted that "Aquifers at various depths have been observed to have large differences in composition" but he did not elaborate in specific details. For reducing system tests, hydrazine was used to control Eh.

Conclusions were that Cs sorption is by ion exchange, possibly with some interlayer fixation, Sr is bound by ion exchange. Np, on the other hand, is bound by some more specific mechanism. Hydrazine increases the sorption of Np, Barney says due to reduction to NpIV, but bicarbonate diminishes the sorption. A minimum of specific details are given. PuIV is much more strongly sorbed than higher oxidation states.

Barney concludes that Am forms an insoluble compound with Mg

ions since increasing Mg in solution increases Am sorption but bicarbonate or sulfate decrease Am sorption due to complexing.

Technetium was strongly sorbed under reducing conditions.

Selenite was not reduced to selenide by hydrazine as expected. Increased Ca resulted in increased selenium sorption.

"Kinetics studies show that most sorption reactions are relatively fast. However, some groundwater-geologic solid reactions are slow and can influence sorption by dissolution of solid components. These are most important for reactions with secondary minerals which are not near equilibrium with Grande Ronde groundwater. Altered basalt, however, comes very close to being in equilibrium with this groundwater."

BARNEY, G. S., 1982. Evaluation of Methods for Measurement of Radionuclide Distribution in Groundwater/Rock Systems RHO-BWI-LD-47. Rockwell Hanford Operations, Richland, Washington.

Oriented to design of laboratory studies for sorption. Gives detailed recommendations for conduct of sorption experiments. No discussion of field conditions or methods for determining geochemical conditions in the field.

BENSON, L. V., 1978, Secondary Minerals, Oxidation Potentials, Pressure and Temperature Gradients in the Pasco Basin of Washington State, RHO-BWI-C-34, Lawrence Berkeley Laboratory for Rockwell Hanford Operations, Richland, Washington.

Principally deals with the fundamentals of redox potential, platinum electrode measurements and limitations in practicality of Eh. The pressure-depth relationship is calculated for the BWIP site. The temperature-depth profiles measured in ca. 6 coreholes at or near (north) the Hanford site are shown. Eh values are not given but it is suggested that FeII-FeIII and the sulfur system are "poorly poised" in Pasco Basin groundwaters. Poorly poised appears to mean out of equilibrium. Secondary minerals are identified as smectite, clinoptilolite and silica. A high cation exchange capacity is noted for the clay and zeolite. No secondary minerals with redox implications are indicated.

BENSON, L. V., and Teague, L. S., 1979, Distribution and Composition of Secondary and Primary Mineral Phases in Basalts of the Pasco Basin, Washington, LBL-9677, Lawrence Berkeley Laboratory, Berkeley, California.

147 SEM and 170 XRD analyses of samples from 4 cores were performed to examine secondary mineralization in Columbia Plateau Basalts. Electron microprobe and wet chemical methods were also

used.

Dominant minerals were clay (smectite or iron-rich illite), zeolite (clinoptilolite) and silica (quartz, cristobalite, tridymite, opal). Crystallization sequence varies but is usually clay->clinoptilolite->silica/clay. Clinoptilolite sometimes shows dissolution features.

Vesicle filling is more complex than fracture filling and includes minor amounts of erionite, chabazite, analcime, vermiculite, phillipsite, gypsum and calcite.

Wet chemical analyses of iron in the clays indicated FeIII-FeII ratios of 3 or 4 to 1 as oxides. FeIII oxide wt % ranged from 10 to 20 % and for FeII oxide 3-6%. The iron is said to occupy a distinct phase, possibly hematite or goethite, within the smectite

CROSBY, J. W., III, and Chatters, R. M., 1965, Water Dating Techniques as Applied to the Pullman-Moscow Ground-Water Basin, Bulletin 296, College of Engineering, Washington State University, Pullman, Washington.

This is a paper on the application of carbon-14 techniques to dating groundwater near Pullman. Its relevance to the BWIP site is mainly as a technique paper and not for the data presented. The results indicate ages of several thousand years for all groundwaters taken from basalts but younger ages for other samples. The discussion of corrections for isotopic exchange between groundwater and rock is superficial and unsatisfying. No indication that isotopic abundances in the basalt or interbed components are known is given. Corrections are based on C-13/C-12 in marine limestones. Isotopic exchange is said to be very limited and of little importance to groundwater dating.

DEUTSCH, W. J., Jenne, E. A. and Krupka, K. M., 1982, Computed Solid Phases Limiting the Concentration of Dissolved Constituents in Basalt Aquifers of the Columbia Plateau in Eastern Washington, PNL-4089, Pacific Northwest Laboratory, Richland, Washington.

WATED2 used with 118 sets of groundwater composition data from Hanford area to estimate saturation indices relative to several minerals. Only few of these sets are for deep (>1000m) wells and their chemistry is said to be quite different from the shallow groundwater. Equilibrium with calcite appears probable, that is, the computed ion activity products are near the measured values, implying saturation. Near saturation with the zeolites, wairikite and analcime is also inferred. Several minerals for which the solutions appear to be saturated but which are not reported as yet are found--allophane, MnHPO and, in deep wells.

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where F is high, fluorite.

DOVE, F. H., Cole, C. R., Foley, M. G., Bond, F. W., Brown, R. E., Deutsch, W. J., Freshly, M. D., Gupta, S. K., Gutknecht, P. J., Kuhn, W. L., Lindberg, J. W., Rice, W. A., Schalla, R., Washburn, J. F., and Zellmer, J. T., 1982. AEGIS Technology Demonstration for a Nuclear Waste Repository in Basalt, PNL-3632, Pacific Northwest Laboratory, Richland, Washington.

Review and assessment of a "generic" repository in the Columbia Plateau Basalt. Large section on geochemistry, especially modeling, describes possible approaches to geochemical assessment. Notable absence of geochemical data for Columbia Plateau Basalts and the groundwater therein. Apparently relies on the LaSala and Doty (1971) and Van Denburgh and Santos (1965) groundwater data sets. An exercise in making the most interpretation of a minimum of observations without questioning the quality of the observations.

EDDY, P. A. 1979. Radiological Status of the Groundwater Beneath the Hanford Project, January-December 1978, PNL-2887, Pacific Northwest Laboratory, Richland, Washington.

EDDY, P. A. and Wilbur, J. S. 1980. Radiological Status of the Groundwater Beneath the Hanford Project, January-December 1979, PNL-3346, Pacific Northwest Laboratory, Richland, Washington.

These reports are two recent copies of annual documentation of the extent and spread of radioactive contamination of the unconfined aquifer at Hanford. Principal sources of contamination are the past 200-Area liquid waste discharges to cribs and swamps. Notes that over the past 36 years (in 1980) something in

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excess of 6×10 liters of process cooling water has been discharged. The majority of the contaminants are in the upper portion of the unconfined aquifer and are nearing the Columbia River. Tritium, gross beta and nitrate are the leading mobile species. Wells are also sampled that penetrate 2 deeper aquifers, one in a "semi-consolidated sedimentary material overlying the basalts" and one in the basalt. The basalt aquifer is artesian.

EICHOLZ, G. G., and Craft, T. F., 1980, Subsurface Migration of Radioactive Waste Materials by Particulate Transport, Annual Progress Report 1978-1979, School of Engineering, Georgia Institute of Technology, Atlanta, Georgia.

A report on a rather narrowly conceived study of migration of colloids through packed columns of basalt, limestone and "other media." All work done in the laboratory with synthetic systems. Although crushed substrate test materials were effective at removing most of the suspended matter, some particles passed through the columns. Conclusions are that colloidal transport is

possible. Seems a long way from the real world to me.

GEPHART, R. E., Arnett, R. C., Baca, R. G., Leonhart, L. S., and Spane, F. A, Jr., 1979, Hydrologic Studies within the Columbia Plateau, Washington: An Integration of Current Knowledge, RHO-BWI-ST-5, Rockwell Hanford Operations, Richland, Washington.

An excellent discussion of the relation of groundwater flow and structure/lithology within the Columbia Plateau. Indicates importance of sedimentary interbeds to major groundwater flow. "Within the Pasco Basin, The Columbia River Basalt Group consists of the Saddle Mountains, Wanapum and Grande Ronde Basalts. The average total thickness of these basalts is about 5,000 feet. The confined aquifers present therein are associated with the more permeable interflow and interbed zones and generally located between confining units composed of the dense, columnar portions of the basalt flows."

"The principal water-bearing or yielding portions of the basalt occur along flow contacts. Here vesicularity and flow brecciation form networks of interconnected vesicles and fissures through which groundwater moves. Complete closure and fusion of one basalt flow atop another can result in a zone of low density separating the fractures, but unless this interflow contains interconnected vesicles or fractures, its permeability will also remain low. Regarding flow at borehole DC1 -- suggest horizontal groundwater movement above a depth of 3450 feet (just below the Umtanum) and downward movement below this depth.

Average composition and range for ground water from Upper Wanapum given. Notes on the poor data quality and extremely limited quantity for Grande Ronde Basalt hydrochemical data. Cites contamination by drilling fluid, poor field sampling and laboratory analytical procedures and cross-aquifer communication within the core holes as reasons for the poor data.

This is primarily a hydrology document. The geochemistry portions are adequate.

JACOBS, G. K., and Apted, M. J., 1981, Eh-pH Conditions for Groundwater at the Hanford Site, Washington: Implications for Radionuclide Solubility in a Nuclear Waste Repository Located in Basalt, EDS, Transactions of the American Geophysical Union, vol 62, p 1065. ..

Computations of Eh and pH based on buffering of groundwater by glassy portions of basalt. pH is assumed to be controlled by silicic acid at 9.5 ± 0.5 and Eh is assumed to be controlled by a quartz-pyroxene-magnetite buffer at -0.45 ± 0.05 v. Conclusions are that the relatively low mobilities of several actinides in reducing and alkaline media make these parameter values highly

desirable. It is indicated that the calculated Eh values are in close agreement with field analytical data such as sulfate:sulfide ratios much greater than 1 and dissolved carbon dioxide:methane ratios of about 0.2 the presence of magnetite and pyrite without any hematite.

JONES, T. E., 1982, Reference Material Chemistry--Synthetic Groundwater Formulation, RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington.

The recipe for a synthetic groundwater that approximates the major component composition and pH of water collected from just below the Umtanum horizon in well DC-6 is described. Two stock solutions are prepared. One contains sodium salts of carbonate, silicate, sulfate, fluoride and hydroxide while the other contains chloride salts of sodium, potassium, calcium and magnesium. Groundwater is simulated by adding aliquots of these stock solutions to distilled water. No effort to control Eh, trace metal ions, gases or organic components although the potential importance of these parameters to repository performance is discussed briefly.

KOMARNENI, S., Scheetz, B. E., McCarthy, G. J., and Coons, W. E., 1980, Hydrothermal Interactions of Cesium and Strontium Phases from Spent Unreprocessed Fuel with Basalt Phases and Basalts, RHO-BWI-C-70, The Pennsylvania State University for Rockwell Hanford Operations, Richland, Washington.

Work began with the hypothesis that Cs, leached from fuel elements or waste, would form an insoluble pollucite in a basaltic environment. Secondary goal was leaching SrZrO₃. Used

USGS BCR-1 and a section of core from DDH-3. Placed ground basalt together with Cs U₂O₇ and SrZrO₃ and water in a reaction bomb at 300 bars; 200 C for two months or 300 C for a month. Substantial fractions of the Cs were found in solution after the reaction. Uranium was oxidized to VI but no control of oxygen was ever exercised. Results were puzzling to the authors. I find the results of possible relevance to the reaction vessel but not to any postulated repository.

LASALA, A. M., Jr., 1971, Hydraulic Studies of the Basaltic Rock Sequence at Hanford, Conference on Methods of Testing Deep Wells for Feasibility Study of Deep Cavern Storage of High-Level Radioactive Wastes at Hanford, Richland Operations Office, U. S. Atomic Energy Commission, June 3, 1971, U. S. Geological Survey, Water Resources Division, Richland, Washington.

This is a handwritten set of notes on principles of groundwater hydrology with particular reference to Hanford. Hydraulic testing results for well DC-1 are presented graphically. There is no

mention of groundwater chemistry. It is, however, an excellent primer on hydrology.

LEONHART, L. S., Jackson, R. L., Graham, D. L., Thompson, G. M., and Gelhar, L. W., 1982, Groundwater Flow and Transport Characteristics of Flood Basalts as Determined from Tracer Experiments, RHO-BW-SA-220 P, Rockwell Hanford Operations, Richland, Washington.

Reports results of a single tracer (potassium thiocyanate) test of water movement between two boreholes (DC-7 and B) in a packed zone at the top of the McCoy Canyon Flow. The holes are approximately 55 feet apart. Water was pumped from the packed zone of DC-7 into the packed zone of DC-8. The estimated formation residence time was 170 minutes at a circulation rate of 1 gallon per minute. Recovery of thiocyanate was 60 percent but potassium was lost, apparently by exchange for sodium.

LONG, P. E. and Davidson, N. J., 1981, Lithology of the Grande Ronde Basalt with Emphasis on the Umtanum and McCoy Canyon Flows in: Myers, C. W. and Price, S. M., eds., Subsurface Geology of the Cold Creek Syncline, RHO-BWI-ST-14, Rockwell Hanford Operations, Richland, Washington.

Detailed description of textural and structural character of basalt flows. Notes that interflow structures "exert a strong influence on the hydrologic characteristics." Structures and petrographic texture are directly correlated so that the authors conclude that petrographic examination of core samples can be used to determine structural attributes of the sampled horizon.

Generic description of a particular basalt flow from top to bottom:

top--ropy to brecciated, vesicular
upper colonnade with large columns
entablature with small, hackly columns
lower colonnade with large columns
glassy basal zone, may be fractured, vesicular or pillowed.

NEWCOMB, R. C., 1972, Quality of Groundwater in Basalt of the Columbia River Group, Washington, Oregon and Idaho, Water-Supply Paper 1999-N, U. S. Geological Survey, Washington, D. C.

A comprehensive discussion of the chemical composition of groundwaters from the Columbia Plateau. Results of 525 analyses for major components and 100 trace element analyses are presented and summarized. Most of the groundwater sampled is discharged from springs or was taken from wells that tap the youngest basalts, the upper 2000 ft. Newcomb indicates that "Passage of

the ground water into the oxidizing environment of the atmosphere causes the precipitation of iron oxide at some springs, but there is a general absence of precipitates or encrustations at most springs where water flows from the basalt. Likewise the formation of encrustations and coatings is lacking at all but a few wells. Newcomb uses the terms calcium-sodium bicarbonate water extensively, apparently referring to what other authors call a bicarbonate type water characteristic of the upper basalts and which forms the model for the GR-1 groundwater recipe.

Silica concentrations are noted to be in general higher in higher temperature waters but the relationship is not consistent. There is no correlation of iron content with depth. The major cations are Ca, Mg, Na and K and bicarbonate is the major anion. Sulfate, chloride, sodium and calcium are noted to be higher in the newly recharged waters that have formed as a result of the Columbia Basin Irrigation Project. Fluoride ranges from 0-2 mg/l, values quite low in comparison to the deeper waters reported elsewhere. Newcomb acknowledged that "...there may be a possibility that such high-fluoride ground water occurs in the basalt at depths below 1000 feet at some places. All evidence for such an occurrence is limited to the LaSala and Doty (1971) data.

Regarding dissolved gases: "The principal readily discernible dissolved gas is hydrogen sulfide, which occurs in small amounts in most of the ground water from wells in the basalt. It seems to be present in greatest amounts in the water from newly drilled wells. The consensus is that the gas diminishes with time as the well is pumped, rather than that the users become accustomed to it and notice it less with time.....The concentration of dissolved oxygen is very low in most of the ground water. A number of determinations, for which no recorded data are available, are known by the author to have found no oxygen in ground water of the basalt when it was correctly sampled before surface or pump-column aeration.....Because most of the ground water is confined under pressure within aquifers that contain fresh, untarnished, and unoxidized iron pyrite and because of the reported determinations of no oxygen, it is assumed that the ground water of the basalt is largely devoid of dissolved oxygen."

The pH of the prevalent type of ground water ranges from 6.5 to 9.2 and most of the values fall between 7.2 and 8.4. "Temperature of the ground water is a few degrees higher than the sum of mean annual temperature of its area and the temperature increase due to the earth's thermal gradient down to the aquifer in which the water occurs. There are many variations from this generalization;...It has been the author's experience that nonrepresentative temperatures can be observed for ground water through one or both of two types of error involving improper

techniques and inadequate samples."

Newcomb seems to be more sensitive to possible errors in temperature measurements than to errors in chemical analyses. Considering the problems that many later authors identify in the chemical data base this contrast is puzzling.

NEWCOMB, R. C., Strand, J., and Frank, F. J., 1972, Geology and Groundwater Characteristics of the Hanford Reservation of the U. S. Atomic Energy Commission, Washington, Professional Paper 717, U. S. Geological Survey, Washington, D. C.

Newcomb et al. (1972) deal entirely with the upper geologic strata at the Hanford site and focus on the unconfined aquifer. The area of interest is centered around the 200-Area where liquid waste disposal has lead to perched zones of contaminated water and has caused the occurrence of "ground-water mounds". No chemical data are given and no deep geology or hydrology is discussed.

NOONAN, A. F., Frederickson, C. K., and Nelen, J. 1980, Phase Chemistry of the Umtanum Basalt: A Reference Repository Host in the Columbia Plateau, RHO-BWI-SA-77, Rockwell Hanford Operations, Richland, Washington.

This report seeks to show the equivalency of outcrop specimens of Umtanum Basalt to core specimens so that large quantities can be easily collected for experimental use. Mineral and glass phases were analyzed by electron microprobe and compared for the different basalts. Entablature and colonnade sections were treated separately. It is concluded that the reference material (outcrop) is similar in texture and phase composition to core samples. The FeO in the entablature glass from the outcrop is >2x the FeO in the entablature glass from the core.

SALTER, P. F., Ames, L. L., and McGarrah, J. E., 1981a Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington.

Determined the sorption behavior of Sr, Tc, I, Cs, Np, Am, Pu, U and Ra under oxidizing conditions at 23 and 60 C using secondary mineral substrates. Se, Tc, Np and I are not "adequately retarded by secondary minerals." Calls for additional work under "highly reducing conditions."

Also reviewed sorption on Hanford sediments as relevant to sorption on interbed materials.

Notes that "There are two distinct groundwaters present in the basalts: a sodium bicarbonate buffered groundwater (pH=8 at 25C)

characteristic of the Saddle Mountains and Upper Wanapum Basalts and a sodium-silicic acid buffered groundwater (pH=10 at 25C) characteristic of the Lower Wanapum and Grande Ronde Basalts." These are simulated by synthesis according to recipes GR-1 and GR-2, respectively.

Attributes Cs, Sr and Ra sorption to ion exchange and notes sensitivity to ion competition. Pu and Am are highly sorbed while I, Se and Tc are not. States that Np is present as a "neutral bicarbonate species."

SALTER, P. F., Ames, L. L., and McGarrah, J. E., 1981b, The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, Rockwell Hanford Operations, Richland, Washington.

Describes sorption experiments for radionuclides from synthetic groundwaters GR-1 and GR-2 on (presumably crushed) basalts from the Umtanum and Flow E (Grande Ronde) and Pomona (Saddle Mountains) under oxidizing and reducing conditions. Reducing conditions were set by hydrazine additions. Temperatures were controlled in different experiments at 23, 60, 150 and 300 C.

Among the elements tested, Cs was most effectively sorbed under any conditions, followed by Am (ox), Ra, Sr, Np(red). Less sorbed were Pu(red), U(red), Tc(red), Pu(ox) and Np(ox). Little or no sorption of Se(any), U(ox), Tc(ox) or I(ox). Concludes that basalts are capable of strongly retarding all but Se and I among the elements tested.

SMITH, M. J., Anttonen, G. J., Barney, G. S., Coons, W. E., Hodges, F. N., Johnston, R. G., Kaser, J. D., Manabe, R. M., McCarel, S. C., Moore, E. L., Noonan, A. F., O'Rourke, J. E., Schulz, W. W., Taylor, C. L., Wood, B. J., and Wood, M. I., 1980, Engineered Barrier Development for a Nuclear Waste Repository Located in Basalt: An Integration of Current Knowledge, RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington.

Though the title indicates "barrier development", this report contains a large section on site description. Average compositions of major and minor elements in several of the Columbia Plateau flows are given. Secondary minerals are described including clays (smectite, illite and traces of vermiculite), zeolites (heulandite and clinoptilolite), and polymorphs of silica. Gypsum, calcite and pyrite are noted as rare.

Hydrologic data from Gephart, et al. (1979) are repeated and summarized including the ranges and means of composition of groundwaters. Practically all of the data are for the unconfined aquifer although the actual concentrations in any actual

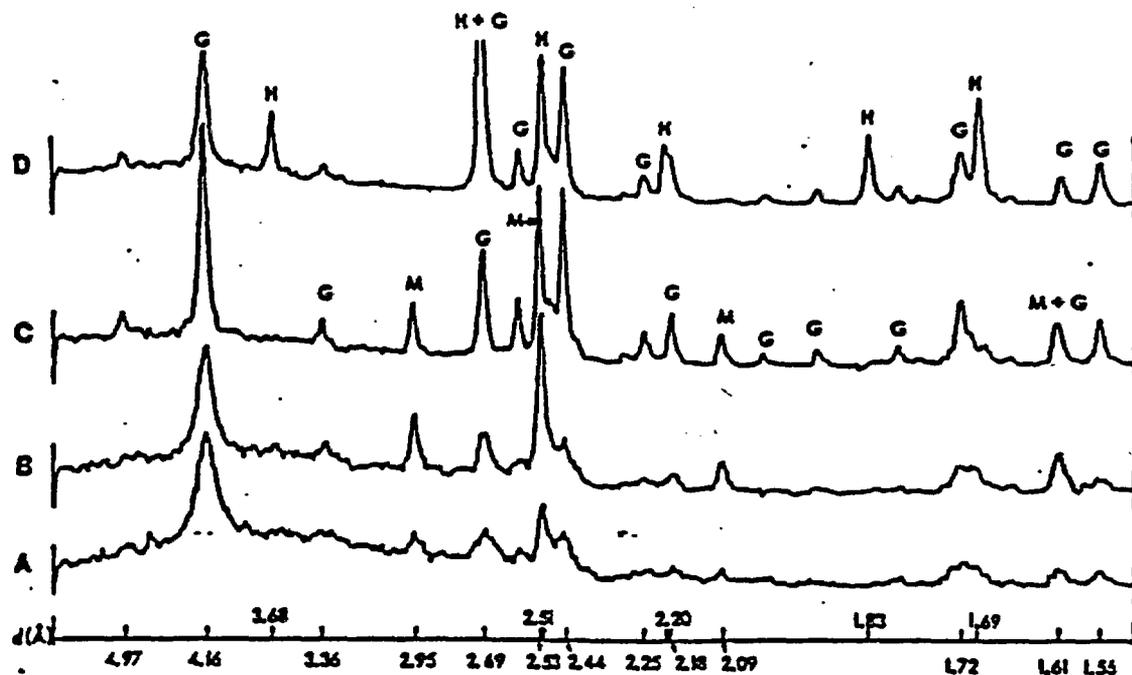


Fig. 2. X-ray diffractogram of precipitates A, B, C, and D after 8 months aging (G = goethite, M = magnetite, and H = hematite).

The NAA results (Table II) showed that the molar ratio (Tc/Fe) of precipitate A was not noticeably different from that of precipitate B, although the initial Tc concentration of solution A was twice that of solution B at the same initial iron concentration. The Tc/Fe molar ratio of precipitate D obtained from the solution, which had the same Tc and Fe concentrations as solution A, was about one-fifth that of precipitate A. The lower molar ratio could have resulted from either lesser isomorphous substitution or dilution by a mineral that did not contain Tc. However, precipitate D started as an iron hydroxide and ferrous sulfide mixture;

TABLE II
Neutron activation analyses results (NAA) for the precipitates after aging 8 months

Precipitate (solutes in initial solution)	Composition (mg/g) ^a			Molar ratio	
	Fe	S	Tc	Tc/Fe	Tc/S
A (FeSO ₄ , high NH ₄ TcO ₄)	579	- ^b	5.1	4.9 x 10 ⁻³	-
B (FeSO ₄ , low NH ₄ TcO ₄)	528	-	3.8	4.1 x 10 ⁻³	-
C (FeSO ₄)	521	-	-	-	-
D (FeSO ₄ , NH ₄ TcO ₄ , Na ₂ S)	558	-	1.1	1.1 x 10 ⁻³	-
E (Na ₂ S, NH ₄ TcO ₄)	-	341	330	-	0.31

^a) Samples were dried at 70°C for 24 h.

^b) Not present or not applicable.

later the ferrous sulfide was recrystallized by dissociation and oxidation to hematite during equilibration as indicated by TEM and XRD. In the other iron precipitates, goethite and maghemite improved their crystallinity but did not recrystallize to form new minerals. Therefore, one could speculate that the Tc associated with ferrous sulfide was released to solution during the ferrous sulfide-hematite transformation and only the Tc incorporated into the goethite phase remained with the precipitate. The Tc/S molar ratio (0.31) of precipitate E is approximately that calculated for the Tc_2S_7 compound (0.29), suggesting that Tc(VII) in the sulfide solution was not reduced to a lower oxidation state to form a sulfide compound. A reduced form of technetium sulfide compounds would be TcS_2 where the molar ratio is 0.5.

DISCUSSION

The experimental results clearly demonstrate that the pertechnetate oxyanion can be removed from solution by both iron and ferrous sulfide. The degree of removal depended on the concentration of ferrous iron and/or sulfide at constant TcO_4^- concentrations (Table I). Equilibration pH also influenced the removal rate, but it is not clear whether the pH influence was related to redox potential of the system or to solubility of the iron precipitates as influenced by pH.

During 8 months of aging, considerable amounts of Tc associated with the precipitates, particularly amorphous FeS, returned to the solution phase as the pH dropped from 8.5 to the 2.2 to 2.6 range, due to hydrolysis and sulfide oxidation. However, a separate experiment did show that most of the Tc remained with the solid phase after 1 month when the aqueous phase was maintained at a pH above 6.5 during sulfide dissociation from the iron phase and subsequent goethite formation (unpublished observation). The precipitation removal of Tc from solution by the addition of ferrous iron or finely ground magnetite is well known and practiced during Tc-bearing waste separation [10]. The particle size and crystallinity differences between minerals formed with and without the presence of Tc indicated that the Tc was incorporated into the goethite and maghemite structure in the sulfide-free ferrous iron system (Figs. 1 and 2) and that the pertechnetate oxyanion in solution was reduced to a lower oxidation state before this structural incorporation. Such a mechanism has been proposed on the basis of redox potential measurements involving Tc(VII)/Tc(IV) and Fe(III)/Fe(II) equilibria and similarity of ionic radii of Fe(III) and Tc(IV) [4]. The ineffectiveness of other hydroxide-forming but nonreducing transition metals including ferric iron for removing TcO_4^- (unpublished data) also indicates that the reduction of Tc(VII) to a lower oxidation state is a prerequisite for incorporation into the iron mineral structure because goethite can grow from both ferrous and ferric iron solutions [11] but Tc is precipitated only when ferrous iron is present.

The Tc-bearing ferrous sulfide, an initial precipitate in the TcO_4^- -ferrous iron-sulfide batch, was unstable under ambient laboratory conditions but could be a stable phase under differing conditions in natural geologic media. Nevertheless, sulfide gradually dissociated from the precipitate leaving behind goethite and hematite (Figs. 1 and 2). The crystallinity of the hematite and the low Tc content of the precipitate after 8 months aging (Table II) suggested that Tc incorporated into ferrous sulfide was liberated to the solution during the ferrous sulfide-hematite transformation. Although determination of environmental conditions necessary

for such a transformation is the subject of another investigation, formation of hematite is not expected to be favored in moderately reducing geologic environments [12].

The blackish precipitate (E) obtained from the TcO_4^- -sulfide batch was a technetium sulfide compound with an apparent Tc/S molar ratio of 0.31 and was insoluble in strong acid and alkaline solutions without strong oxidants. The precipitate appeared to be amorphous Tc_2S_7 , suggesting that Tc(VII) can be removed as a sulfide compound without being reduced to a lower oxidation state. The reported Tc_2S_7 compound has been synthesized in a strong acid solution [6], but formation of such a compound under environmental conditions has not yet been reported. Thermodynamic stabilities and crystal structures of technetium-substituted iron and sulfide minerals is the pertinent subject for further investigation. However, experimental evidences to date have suggested that the mobility of TcO_4^- in waste leachate could be reduced by interaction with ferrous- and/or sulfide-bearing groundwaters and minerals in host rocks or backfill barrier materials under relatively reduced repository environments.

ACKNOWLEDGEMENT

We thank D. H. Newman and B. Fellows, Chemical Technology Division, for providing TEM service and J. Switek for reading the manuscript and offering helpful suggestions. Research was supported by a subcontract with the Office of Nuclear Waste Isolation's Waste Rock Interaction Technology Program, Battelle Memorial Institute, for the U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation. Publication No. 2048, Environmental Sciences Division, Oak Ridge National Laboratory.

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groundwater sample are not given. Deep pH and Eh are calculated according to assumed control by silicic acid and quartz or fayalite-magnetite, respectively.

TEAGUE, L. S., 1980, Secondary Minerals Found in Cores DC2-A1 and DC2-A2 Taken from Grande Ronde Basalt Formation, Pasco Basin, Washington, LBL-10387, Lawrence Berkeley Laboratory, Berkeley, California.

Secondary minerals in 39 vesicle and fracture samples from two cores through the major basalt groups were examined using SEM/EDAX, XRD and thin section microscopy. Mineralogy, sequence of crystallization and connectedness of fissures were sought.

Initial phases were almost always clay, rarely clinoptilolite. Distinct overgrowths are usually present and are silica or clinoptilolite, each in about 1/3 of the specimens. Pyrite was found once. Third and fourth layers include, in addition to the above minerals, heulandite and mordenite. Apatite was found once.

Dissolution evidence was rare and was restricted to clinoptilolite.

A generalized crystallization sequence was clay (usually smectite) → clinoptilolite → silica/clay.

Data on depth dependence and on connectedness were deemed too sparse for interpretation. Vesicles and fractures from the same depths have widely varying amounts of secondary mineralization.

VAN DENBURGH, A. S., and Santos, J. F., 1965. Groundwater in Washington Its Chemical and Physical Quality, Water Supply Bulletin No 24, Washington Division of Water Resources, Olympia, Washington.

A general review from the aspect of suitability of groundwater for use in agricultural, municipal or industrial applications. In the Columbia Plateau Province, which includes most of Eastern Washington, aquifers are mainly the interbeds and flow tops. Ample water yields from such aquifers have been found, often several hundred gallons per minute and as high as 1500 gallons per minute. In structural basins wells may be artesian.

Data for a large number of wells tapping the upper 1000 feet are presented. Silica concentrations are in the range 40-60 ppm and increase with depth. Iron concentrations are below 0.3 ppm. Sulfate is generally below 30 ppm except where contamination from returnflow of irrigation water from fertilized lands has added to the natural levels. Fluoride reaches 2.8 ppm and is highest in waters that contain high silica and high sodium.

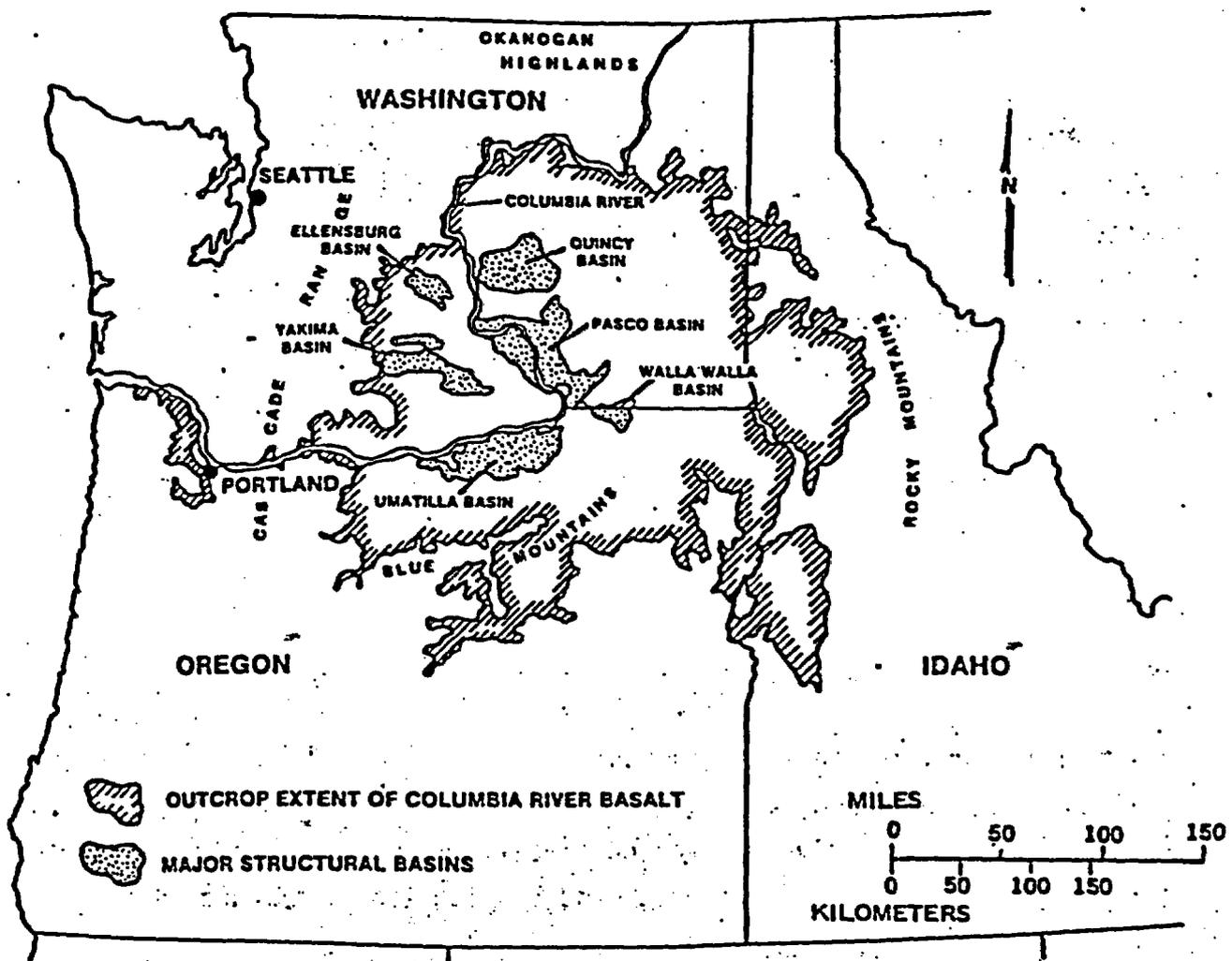


FIGURE 2-5. Distribution of Columbia River Basalt in Washington, Oregon, and Idaho (after Tallman and Others, 1979).

B-1

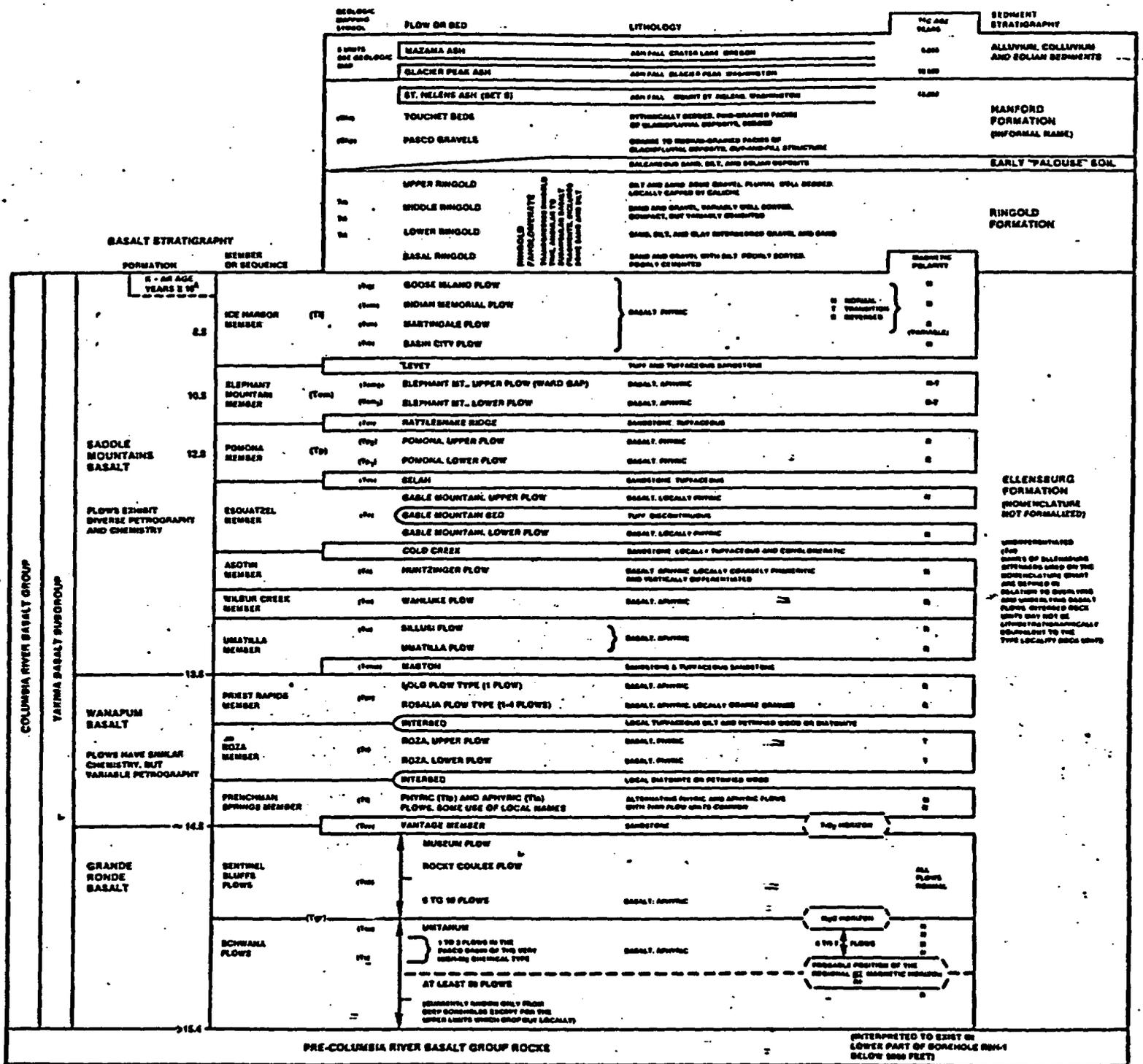


FIGURE 2-10. Pasco Basin Stratigraphic Nomenclature.

B-2

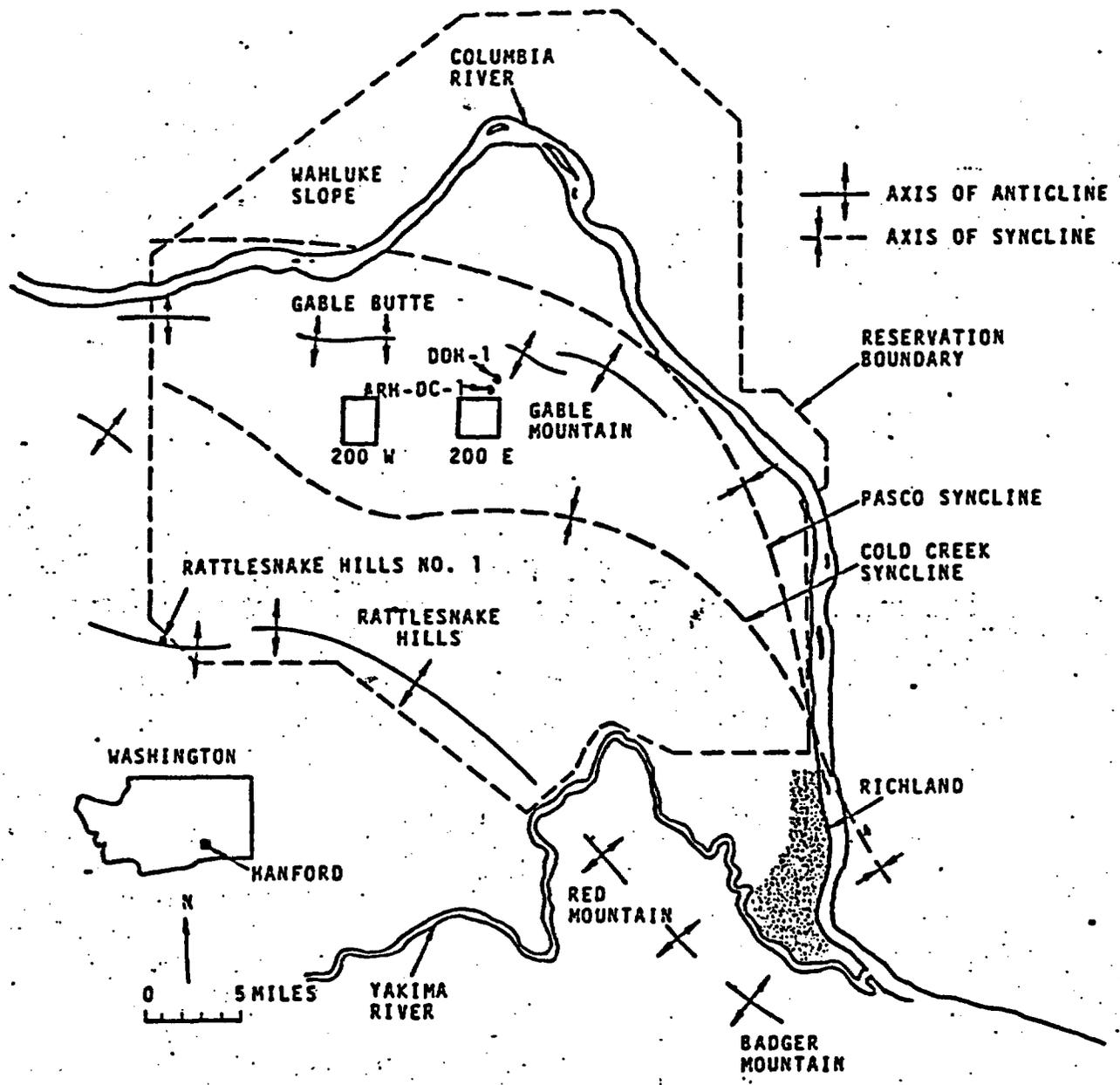


FIGURE 1. Map of the Hanford Reservation, Showing Generalized Geologic Structural Features

B-3

gamma emission from the naturally occurring radioactive isotopes, primarily ^{40}K . Therefore, clay-rich interbeds and basalt flows either markedly higher or lower in K_2O content are readily recognized.

TABLE 2-4. Approximate Major-Element Composition of Basalt Formations in the Pasco Basin.*

Wt%	Grande Ronde	Wanapum	Saddle Mountains	Total Sequence
SiO_2	55.29	51.65	52.22	54.23
Al_2O_3	14.49	13.53	14.44	14.09
FeO^{**}	11.58	14.30	12.24	12.18
MgO	3.97	4.26	5.17	4.17
CaO	7.58	8.15	8.84	7.84
Na_2O	3.04	2.67	2.60	2.92
K_2O	1.69	1.31	1.38	1.58
TiO_2	2.10	3.20	2.47	2.35
P_2O_5	0.37	0.72	0.55	0.46
MnO	0.19	0.22	0.18	0.19

*Values calculated from the average compositions of Columbia River basalt chemical types and approximate unit thicknesses.

** $\text{FeO} + \text{Fe}_2\text{O}_3$, reported as FeO .

The Grande Ronde Basalt in the Pasco Basin has been broadly divided into two units based on its major element chemistry. The upper Sentinel Bluffs sequence of at least 13 flows, totaling nearly 300 m, is chemically characterized by its relatively high-MgO content (5% MgO). The lower stratigraphic sequence, the Schwana, consists of at least 25 flows of markedly lower MgO content (3.5% MgO). The contact between these two major sequences, referred to as the "MgO horizon," is a major chemical marker throughout the Pasco Basin. Within the Schwana sequence there is a single low- K_2O flow which contains from 5 to 6% MgO (also referred to as the very high-MgO flow).

Boreholes just north of the Hanford Site have penetrated at least 800 m of the Schwana sequence intersecting from 15 to 25 separate flows. Chemical stratigraphic correlations have identified 5 chemical stratigraphic units of the low-MgO type. These units were correlated primarily on the basis of vertical variations in TiO_2 and MgO content. The

TABLE 2-15. Average Electron Microprobe Analyses of Minerals and Glass from Selected Flows at the Grande Ronde Basalt Type Section.

(After Camp and Others, 1978.)

Wt%	Mineral							AVc
	Feldspar (41) ^a	Augite (20) ^a	Pigeonite (8) ^a	Ilmenite (4) ^a	Ti-Magnetite (4) ^a	Olivine (2) ^a	Glass 21 ^b	
SiO ₂	55.2	53.6	53.8	0.70	1.0	38.2	74.2	54.1
Al ₂ O ₃	27.2	2.0	0.20	0.50	1.8		13.9	14.6
FeO	0.70	13.5	21.8	46.5	65.2	44.7	1.5	10.4
MgO		13.8	18.0	1.3	1.1	16.2	2.7	5.2
CaO	10.4	16.7	4.8	0.20	0.20	0.30	1.1	8.2
Na ₂ O	5.4							2.21
K ₂ O	0.50						6.8	1.63
MnO				0.20	0.40	0.60		0.04
TiO ₂		0.20	0.30	50.6	30.4		0.30	3.4
P ₂ O ₅		0.40	0.30				0.20	0.15

^aVolume percent.

^bGlass and alteration products.

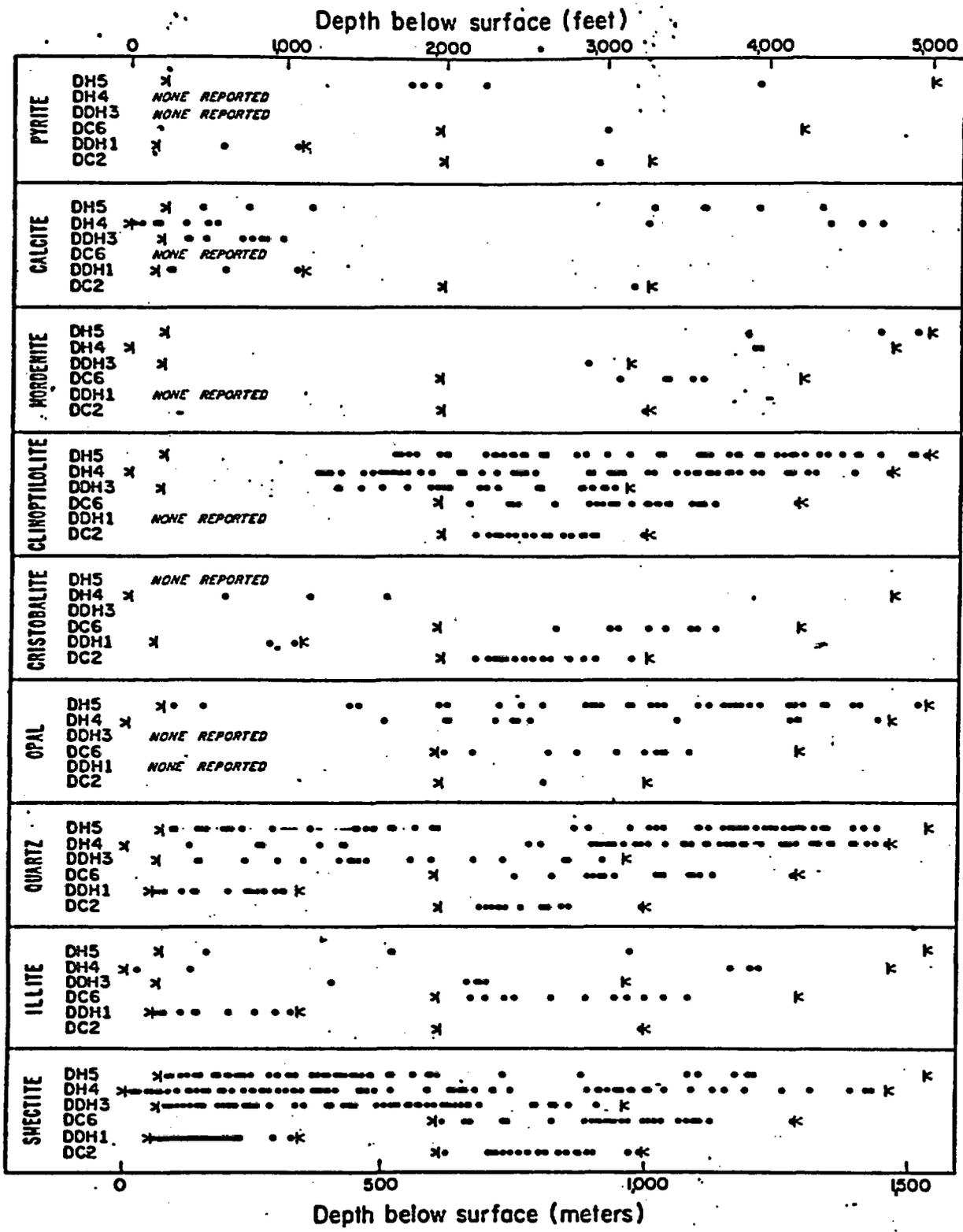
CAV = Average calculated chemical composition for these flows.

2-47

RHO-BMI-ST-7

B-5

Depth of secondary mineral occurrence from XRD data



RCP8002-41

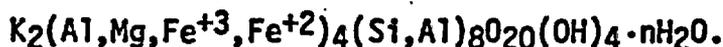
FIGURE 2-21. Approximate Distribution of Major Secondary Minerals as a Function of Depth (after Benson and Others, 1979). Data from DDH-1, DDH-3, DH-4, and DH-5 are from Ames (in press); data from DC-2 and DC-6 are from Benson and Others (1979). (xk) indicates interval of core sampled. Well locations are shown in Figure 2-8.

B-6

The mixed-layered smectite clays recognized are montmorillonite, beidellite, and nontronite, di-octahedral end-members of a solid solution series. These di-octahedral clays fill two-thirds, or slightly more, of the octahedral position (Y) with Al^{+3} - Mg^{+2} (montmorillonite), Al^{+3} (beidellite), or Fe^{+3} (nontronite) and present an approximate generalized chemical formula of:

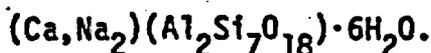


Iron-rich illite contains potassium as the principal interlayer cation rather than calcium and sodium as in the case of smectite. The generalized formula for iron-rich illite recognized in the Pasco Basin basalts is approximately the following:



Only trace amounts of vermiculite have been recognized; the primary chemical difference between it and the smectites and illite is that Mg is the principal interlayer cation.

The zeolites are hydrated aluminosilicates of the alkalis and alkaline earths (Deer and Others, 1967). They are noted for their reversible dehydration, ion exchange, and molecular absorption properties. The principal zeolite mineral recognized is heulandite (or clinoptilolite) with the chemical formula:



Clinoptilolite, although sometimes confused with heulandite, is a separate species somewhat enriched in silica. Minor amounts of mordenite $(Na_2,K_2,Ca)(Al_2Si_{10}O_{24}) \cdot 7H_2O$ have been recognized as a prominent secondary mineral in the Pasco Basin basalts. Also, trace amounts of the following zeolites have been recognized throughout the basalts:

<u>Name</u>	<u>Chemical Formula</u>
Phillipsite	$(Ca,Na,K)_3(Al_3Si_5O_{16}) \cdot 6H_2O$
Harmotome	$Ba(Al_2Si_6O_{16}) \cdot 6H_2O$
Chabazite	$Ca(Al_2Si_4O_{12}) \cdot 6H_2O$
Erionite	$(Na_2,K_2,Ca,Mg)_{4.5}(Al_9Si_{27}O_{72}) \cdot 27H_2O.$

TABLE 2-38. Major Inorganic Composition of Groundwater for Selected Wells Completed in the Grande Ronde Basalt.

(After Gephart and Others, 1979b.)

Anions (mg/l)	Data Source		
	LaSala and Doty (1971)	Apps and Others (1979)	Gephart and Others (1979b)
HCO ₃ ⁻	66.0 (49) ^a	88.0 (51) ^a	43.0 (90) ^a
*CO ₃ ⁻²	52.0 (101) ^a	70.0 (127) ^a	34.0 (52) ^a
Cl ⁻	98.0	148.0	148.0
SO ₄ ⁻²	13.0	96.0	108.0
F ⁻	21.0	ND ^c	37.0
Cations (mg/l)			
Na ⁺	182.0	242.0	250.0
K ⁺	3.3	3.2	1.9
Ca ⁺²	0.8	1.3	1.3
Mg ⁺²	0.0	2.0	0.04
SiO ₂	116.0	115.0	121.0
Total Dissolved Solids	552.0	-- ^b	744.0
pH	10.1	10.1	10.1

^aListed values are corrected for titration of H₃SiO₄⁻ during alkalinity determination. Uncorrected concentrations are shown in parentheses.

^bTotal dissolved solids not determined due to lack of fluoride concentration.

^cND = Not Determined.

B-9

B-10

GR-1
GR-2

} recipes

TECHNETIUM BEHAVIOR IN SULFIDE AND FERROUS IRON SOLUTIONS

SUK Y. LEE AND ERNEST A. BONDIETTI

Environmental Sciences Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee, USA

ABSTRACT

Pertechnate mobile species waste repository precipitation environmental (α -FeOOH) were obtained from observation of the mineral that the Tc was after reduction ferrous sulfide TcO_4^- -ferrous iron to goethite and black precipitate reaction was possible (Tc_2S_7) which solution in the absence of strong oxidants. The results suggested that ferrous- and/or sulfide-bearing groundwaters and minerals in host rocks or backfill barriers could reduce the mobility of Tc through the formation of less-soluble Tc-bearing iron and/or sulfide minerals.

Dave,

For your info.

AG Croff

INTRODUCTION

The leachability of stored high-level radioactive waste from a repository will largely depend on the inherent stability of the waste forms and the reactivity of intruding groundwater. Once radionuclides are leached from the wastes, transport of the dissolved nuclides will be controlled by chemical and hydrogeological retardation factors. Long-lived ^{99}Tc (2.12×10^5 y half life) could occur in many chemical forms in high-level radioactive waste depending on pretreatment prior to disposal. The negatively charged TcO_4^- ion is, however, expected to be a predominant chemical form in aqueous leachate solutions. Since anionic species tend to be poorly retained on silicate minerals, Tc has been identified as a radionuclide that may be difficult to contain in geologic media [1]. But, recent studies [2,3] suggest that TcO_4^- could be chemically reduced to less-soluble oxidation states such as TcO_2 or $Tc(OH)_4$ in the presence of igneous rocks under anoxic conditions. Other experiments indicate that TcO_4^- is reduced by ferrous iron in the absence of an adequate supply of oxygen [4]. Technetium also forms sulfide compounds such as Tc_2S_7 with or without metal sulfide carriers in strong acid solutions [5,6]. Because iron and sulfur are predominant participants in natural redox processes,

studies of TcO_4^- -ferrous iron-sulfide interaction were initiated to provide models for in situ immobilization of leached TcO_4^- .

METHODS

A synthetic brine solution (5 M NaCl) containing NH_4TcO_4 (10^{-5} M) and varying concentrations of Na_2S ($n \cdot 10^{-4}$ M) was prepared. Varying amounts of FeSO_4 ($n \cdot 10^{-4}$ M) were added to 40-ml batches of brine solution and then the pH was adjusted to either 8.5 or 6.3 with HCl or NaOH. After 3 and again after 5 d of equilibration, 2 ml of the solutions was filtered through 0.22- μm membranes and the amounts of ^{99}Tc remaining in solution determined by beta liquid scintillation counting [4].

For the physicochemical characterizations of the Tc-bearing iron, sulfide, and ferrous sulfide precipitates, larger quantities of precipitates were prepared from 200-ml solutions having solute concentrations as follows: (A) 5×10^{-3} M FeSO_4 and 5×10^{-5} M NH_4TcO_4 ; (B) 5×10^{-3} M FeSO_4 and 2.5×10^{-5} M NH_4TcO_4 ; (C) 5×10^{-3} M FeSO_4 only; (D) 5×10^{-3} M FeSO_4 , 5×10^{-5} M NH_4TcO_4 , and 5×10^{-3} M Na_2S ; and (E) 3×10^{-4} M NH_4TcO_4 and 6×10^{-2} M Na_2S . The pH of these solutions was adjusted to 8.5 and the resulting precipitates aged for a month at 70°C and then for 7 months at 25°C . A small portion of each precipitate was taken after both 1 week and 8 months of aging for characterization. The precipitates were washed with demineralized water and 100% ethyl alcohol for x-ray diffraction (XRD) and neutron activation analysis (NAA). The salt-free precipitates were resuspended in water and mounted on grids for transmission electron microscopy (TEM).

RESULTS

By varying both the pH and the amounts of sulfide and/or ferrous iron added to the brine solution containing TcO_4^- , differing amounts of TcO_4^- were removed from the solutions as a result of precipitation with iron, sulfide, and ferrous sulfide (Table I). Although the initial black color of the iron and iron sulfide precipitates changed to brown within 4 d of equilibration, the amounts of TcO_4^- remaining in the solution were not

TABLE I

Percent TcO_4^- removed from brine solutions by precipitates after 5 d equilibration

Initial Na_2S concentration ($n \times 10^{-4}$ M)	Initial FeSO_4 concentration ($n \times 10^{-4}$ M)				
	pH = 8.5				pH = 6.3
	0	1	3	6	3
0	1	1	52	90	0
1.9	3	14	95	88	2
7.5	23	57	95	97	81
15.0	31	66	82	98	95

noticeably affected by the color change. The black precipitates in the solutions containing only Na_2S and NH_4TcO_4 did not change color during equilibration. The loss of TcO_4^- from solutions increased with increasing initial sulfide and ferrous iron concentrations, and the loss was larger when the solution contained both sulfide and ferrous iron. Ferrous iron removed TcO_4^- more effectively than sulfide at pH 8.5, but at pH 6.3, significant amounts of TcO_4^- were lost only when the ferrous iron solution contained a considerable amount of sulfide (Table I).

All five of the precipitates prepared for the characterization studies initially had a black color and removed more than 90% of Tc from the solutions. Precipitates A, B, and C (from the ferrous iron solutions with $5 \times 10^{-5} \text{ M Tc}$, $2.5 \times 10^{-5} \text{ M Tc}$, and without Tc, respectively) gradually changed to a brown color. These precipitates were ferromagnetic both before and after color changes. The black ferrous sulfide precipitate (D) turned bright red, while the technetium sulfide precipitate (E) remained black. After 7 d aging, the black precipitates were examined by XRD and TEM. The XRD indicated the presence of poorly crystalline maghemite ($\gamma\text{-Fe}_2\text{O}_3$) in precipitates A, B, and C, but no x-ray crystalline minerals in precipitate D and E (although precipitate D had a very weak electron diffraction pattern).

The TEM showed that precipitate A (containing Tc) was a mixture of very fine (0.01-0.1 μm) distorted cubic maghemite and lath-like goethite crystals (Fig. 1a). The crystals precipitated without Tc had similar morphology, but their size, particularly goethite crystals, was much larger (0.05-1.0 μm) and their structure appeared to be well ordered (Fig. 1c). Precipitate D, obtained from the TcO_4^- -ferrous iron-sulfide batch, was composed of a mixture of irregular platy ferrous sulfide and acicular iron hydroxide crystals (Fig. 1b).

During 8 months of aging, the initial solution pH of 8.5 decreased gradually to near 2.2 as a result of hydrolysis and sulfate formation; about 40 and 70% of the Tc that had been removed by the iron precipitates (A and B) and ferrous sulfide precipitate (D), respectively, returned to the aqueous phase. The Tc initially removed by sulfide alone, however, remained with the precipitate (E). The XRD, after eight months aging, showed significant improvements in the crystallinity of the minerals in the precipitates (Fig. 2), except precipitate E which remained x-ray amorphous (not shown). Goethite ($\alpha\text{-FeOOH}$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) were major components in precipitates A, B, and C, while goethite and hematite ($\alpha\text{-Fe}_2\text{O}_3$) predominated in precipitate D. The goethite and maghemite lines became weaker and broader (width at half height) as the initial concentration increased, indicating that the added Tc had substituted for Fe in the structure, resulting in a decreased crystallinity. Similar crystallinity changes were observed when goethite was precipitated from ferrous iron-aluminum solutions [7,8,9].

After aging 8 months the morphology of precipitate A (Fig. 1d) as well as precipitate B and C (not shown) did not change although XRD showed improved crystallinity. On the other hand, drastic alterations occurred to precipitate D (Fig. 1e) where hexagonal platy hematite and lath-like goethite appeared to have replaced the irregular platy crystals (x-ray amorphous FeS) observed in the fresh precipitate (Fig. 1b). Precipitate E consisted of very small (about 0.05 μm in diameter), ill-defined circular platy particles (Fig. 1f) that did not produce either characteristic electron diffraction or x-ray diffraction lines. The TEM observations confirmed the XRD results in terms of mineral composition as well as crystallinity of minerals in the precipitates.



Fig. 1. Transmission electron micrograph of (a) precipitate A, (b) precipitate D, (c) precipitate C after aging 7 d, and (d) precipitate A, (e) precipitate D, (f) precipitate E after aging 8 months (bar unit = 0.1 μm).