



UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

APR 20 1988

MEMORANDUM FOR: Hugh Thompson, Director
Office of Nuclear Material Safety and Safeguards

FROM: Eric S. Beckjord, Director
Office of Nuclear Regulatory Research

SUBJECT: RESEARCH INFORMATION LETTER NUMBER 15.2, RESULTS OF RESEARCH
ON DATING GROUND WATER FOR HIGH LEVEL WASTE REPOSITORY SITE
CHARACTERIZATION

This research information letter presents a synopsis of ten years of research on ground water dating by Professor Stanley N. Davis of the University of Arizona and his students and other recent contributions to the literature on ground-water dating. The final report of the project (enclosed) is an extended review article which presents both the results of research investigations and an assessment of the state-of-the-art of ground water dating. An ongoing assessment of the state-of-the-art was an integral part of the research. This letter is intended to transmit and briefly explain the research results and the state-of-the-art review, and also to suggest how ground water dating methods can be applied to licensing needs for high level waste repositories such as calculations of ground water travel times. For completeness and to preserve a record of the research, this letter discusses all three media then being considered by the DOE when this work was begun. In addition, a section has been included to describe the applicability of ground water dating techniques to regulating LLW disposal. All of the site specific analysis and regulatory analysis were prepared by Dr. G. F. Birchard, the RES project manager for this work. Dr. Birchard (ext. 23864) is the contact for this work.

A handwritten signature in cursive script that reads "Eric S. Beckjord".

Eric S. Beckjord, Director
Office of Nuclear Regulatory Research

Enclosure: As stated

BB07270029 880714
PDR WASTE
WM-1 PDR

DATING GROUND WATER FOR RADIOACTIVE WASTE DISPOSAL SITE EVALUATION

ABSTRACT

Nuclear Regulatory Commission and Environmental Protection Agency standards require hydrogeologic characterization of a proposed high level waste repository site. Characterization of the hydrogeology for the ten-thousand year regulatory period for high level waste disposal likely will require the use of ground-water dating. The age of ground water is the length of time that the water has been isolated from the atmospheric portion of the hydrologic cycle. The concept of a ground-water age is idealized because all ground water to some extent is a mixture of waters of different ages.

In simple systems relative ages of ground waters from different portions of an aquifer can be determined by a variety of independent methods. The dates obtained are commonly in accord with each other and reflect systematic increases of water ages in downgradient directions. In complex ground water systems, multiple, independent dating methods can be used to develop an understanding of the hydrodynamics of the ground water system. In fact, the ages and relative quantities of mixing waters may be estimated provided that sufficient isotopic and geochemical data are available.

Isotopic and other geochemical dating methods provide direct information on average ground water conditions over long periods of time. This is an important distinction to hydrodynamic measurements which yield only instantaneous parametric values. Thus, geochemical methods are particularly suited to assist in understanding long-term, unperturbed hydrogeologic conditions. Ideally, hydrodynamic and geochemical methods both should be used to develop an integrated understanding of long term flow and transport.

The Cl-36, I-129 and noble gas methods of dating ground waters which were developed in part under this project can provide important data for assessing site hydrology under differing conditions. The Cl-36 method provides unique long-term data on ground water flow for assessment of the tuff site and the Hanford basalt site whereas the I-129 method would provide important data for understanding the origins of brines in bedded and domed salt.

The proposed repository site at Yucca Mountain, Nevada, has a combination of unsaturated and saturated flow. Hydrodynamic calculations are uncertain for the Yucca Mountain flow regime. Chlorine-36 and deuterium/oxygen-18 isotope data will be useful for characterizing flow in the unsaturated zone. Carbon-14 and deuterium/oxygen-18 data have already been used to characterize flow in the saturated zone. Major and minor ion chemistry may be useful for characterizing the degrees of mixing of waters at Yucca Mountain.

1 INTRODUCTION

This project assessed ground water dating from a generic perspective and the report summarized here addresses applicability to a variety of media.

1.0 Preface

This research information letter is a synopsis of ten years of research conducted on ground water dating by Professor Stanley N. Davis of the University of Arizona. The final project report is an extended review article which presents both the results of the research investigations and an assessment of the state-of-the-art of ground water dating. This letter is intended to transmit and explain briefly the research results and the state-of-the-art review, and also to present one way that ground water dating methods can be applied to calculations of ground water travel times for high level waste repositories. For completeness and to preserve a record of research results, this letter discusses all three HLW repository media which were under consideration at the time this work was undertaken. This perspective is important because it establishes the geologic context within which the various methods are applicable. In addition, a final section discusses use of ground water dating in low level waste facility evaluations.

1.1 Regulatory Context

The Environmental Protection Agency (EPA) containment requirements, 40 CFR 191.13, require that high level waste (HLW) disposal systems shall be designed, based upon performance assessments, not to exceed limits for

cumulative releases of radionuclides to the accessible environment for 10,000 years after disposal. The Nuclear Regulatory Commission (NRC) performance objective for the geologic setting in 10 CFR 60.113 requires that: "The geologic repository shall be located so that prewaste-emplacment ground water travel time along the fastest path of likely radionuclide travel from the disturbed zone to the accessible environment shall be at least 1,000 years or such other travel time as may be approved or specified by the Commission."

The demonstrations of compliance with both the EPA containment requirements and the NRC performance objective for the geologic setting require similar understanding of the hydrogeology of the site. The EPA containment requirements mandate calculation of radionuclide release to the accessible environment. A model of hydrologic transport of radionuclides is required to determine radionuclide release, and a ground water flow model is necessary for transport modelling. Such modelling requires detailed hydrologic characterization to predict ground water movement over the ten-thousand year period. The NRC ground water travel time performance objective implies a demonstration that ground water travel times will be greater than one-thousand years. To determine ground water travel times, a model of ground water flow is required. This ground water flow model will require detailed hydrologic characterization of the site.

The following discussion will focus on applying dating of ground water as part of an approach to develop the hydrogeologic understanding of a site necessary for demonstrating compliance with the NRC performance objective for the geologic setting and the EPA containment requirement.

1.2 Background On Ground Water Dating

The age of ground water is commonly defined to be the length of time that the water has been isolated from the atmosphere. This definition is useful for uncomplicated hydrologic systems but it does not reflect the complexity of most ground water systems. Only simple systems which can be compared with flow through a single long pipe can yield nearly homogeneous dates for water sampled from the same general part of an aquifer. Few natural systems approach this type of simple linear, non-mixing or "piston", flow. In addition, most ground water is taken from wells which tap more than one restricted water bearing

zone. Consequently, a sample of water is generally a mixture of waters of different ages, even if the ground water flow approaches idealized piston flows in each zone intersected by the sampling well. Natural springs also are commonly connected to a number of water-bearing zones so that samples of spring water may be mixtures of waters of vastly different ages.

Even though, strictly speaking, all ground water samples have mixed ages, an integrated age or residence time which is determined for a large volume of water can provide useful information. A number of methods are available to determine water ages. For each method one-dimensional piston flow is assumed in data analysis. If several of these methods were to be applied to a single sample of ground water, each method would indicate a somewhat different age. Nonetheless, these differences provide important information concerning the natural flow system. In general, if ages of the same sample determined by various methods are discordant, then some type of mixing is indicated. Further, if enough ages are determined, and hydrodynamic data are available, then the sources, quantities, and ages of waters which have been mixed may be estimated.

Water dating can be useful in a number of ways. The age of water in large basins will give an indication of the water circulation in the basin. Dating of water from the unsaturated zone and from below shallow water tables will provide direct data on recharge rates of ground water. Water ages will be helpful in reconstructing general geologic processes such as formation of evaporites and the dissolution of evaporites and carbonates. Water dating will provide a basis for determining the origins of fluids in evaporites. Lastly, water dating can help predict possible future directions and velocities of contaminant transport in the subsurface. Water dating provides the only reliable direct evidence of average hydrogeologic conditions over hundreds or even thousands of years. Past water movement which can be estimated from water ages is assumed to reflect future probable movement of ground water. Burial of radioactive wastes in geologic repositories requires isolation periods greatly in excess of the length of the historical period of scientific observations. The pattern and velocity of ground water must be projected far into the future without a firm long-term data base from historical measurements. Water dating helps to overcome this lack of accurate hydrologic data from the past and provides, for an undisturbed system, a better prediction of future conditions

than can be achieved by purely hydrodynamically-based models. Water dating provides data which can be useful in predicting the response of a site to hydrologic disturbance.

This study has identified and evaluated nine different methods of dating ground water. These include all of the available and known potential methods. The applicability and accuracy of each method varies from site to site. Although each method may be based on different physical or chemical principles, all of the methods in their elementary forms must generally assume piston flow in order to extract a date from the basic data. A more realistic approach would be to use all the data simultaneously in combination with some hydrogeological model to calculate the ages and the proportions of various waters which may have been mixed by natural or artificial means. These types of models are not addressed here because they are in their infancy.

Selection of wells and springs to be sampled, choice of field sampling techniques, sample handling and storage, analytical procedures, and processing of laboratory data all can have profound effects on the results of field and laboratory measurements and hence on the interpreted water ages, but for purposes of this discussion the assumption was made that adequate quality assurance measures are in place.

2 RESULTS AND FINDINGS

2.1 For Dating Groundwater

For a given site as many useful methods as feasible should be used because each method yields information which is independent of other methods. However, because of the substantial time and money involved in each measurement a careful selection of dating methods considering site characterization needs is required. The selection of methods cannot be defined generically because ground water dating needs are site specific and because methods which are effective at one site may be ineffective at another. The C1-36, I-129 and noble gas methods of dating ground waters, which were developed in part under this project, provide important hydrologic data for site assessment. The C1-36 method provides unique long-term data for site assessment of the basalt and

tuff whereas the I-129 method provides critical data in understanding the origins of brines in bedded (and domed) salt.

2.2 Hydrodynamic Calculations

Laws governing the flow of ground water through permeable material provide a basis for the estimation of the age of ground water. Measurable hydrogeologic parameters such as effective porosity, permeability, and hydraulic gradients yield information on water velocities which, when combined with distances of travel, give indications of the residence time of water in the subsurface. As in all dating methods, uncertainties are large. Most of the uncertainties relate to the heterogeneities found in natural flow systems.

Even if the flow systems were defined with reasonable precision, the relationship between water ages estimated by hydrodynamic methods and those based, for example, on atmospheric radionuclides are not easy to determine. To be sure, a rough correspondence exists among the various methods, but discordance in ages of 10 to 20% are certain to be present under the most ideal circumstances and discordances of 20 to 100% are probably more common. Some of the discordances are related to the differences between the actual paths taken by the water particles and associated dissolved substances and the averaged macroscopic paths calculated by the hydrodynamic equations. This is particularly true if molecular diffusion is not taken into account in the hydrodynamic transport equations, as is almost always the case. Specifically, the problem relates to the movement of water molecules and other dissolved molecules into submicroscopic pores through diffusive processes which are not controlled by macroscopic hydraulic gradients. If a water molecule with a permanent identity existed, this molecule would not travel the macroscopic path but, instead, would actually spend a considerable portion of its time residing in the submicroscopic pores adjacent to the larger openings. The study of these differences between the hypothetical macroscopic pathways (fracture flow) and the actual pathways (fracture plus matrix flow) is a major area of continuing hydrogeologic research.

2.3 Atmospheric Radionuclides

A large number of radionuclides are produced in the atmosphere through the interaction of gases, primarily nitrogen and argon, with high energy cosmic ray particles. Those radionuclides which are mobile in water will travel into the subsurface and can be found in ground water. If the original concentrations of the radionuclides at the surface can be reconstructed, then the age of the ground water can be measured by noting the decrease in concentration which has taken place through radioactive decay.

With the exception of hydrodynamic calculations, the use of atmospheric radionuclides has been the most important method with which to estimate ground water ages. The first studies were made more than 25 years ago using carbon-14. Shortly thereafter, analyses of tritium were used to study ground water of modern origin. These two radionuclides remain the most commonly used today. Within the past 10 years, many other radionuclides of predominantly atmospheric origin have been isolated from samples of ground water. Those studied the most have been silicon-32, chlorine-36, argon-39, krypton-85, and iodine-129.

Numerous difficulties exist with the estimation of water ages from atmospherically-derived radionuclides. These difficulties extend beyond those of hydrogeologic heterogeneities and of molecular diffusion which have already been mentioned. For carbon-14 and silicon-32, complex geochemical models are required to correct for mineral-water interactions. For tritium, owing to the testing of fusion weapons, the source term varies irregularly with time. For silicon-32 and chlorine-36, the original concentrations are strongly dependent on geographic locations of samples. For krypton-85, anthropogenic sources will almost always dominate the concentrations measured. For chlorine-36, argon-39, and iodine-129, subsurface production, in addition to atmospheric sources, can be important.

Despite these problems, dating with atmospheric radionuclides has been used to estimate ground water ages which range from a few years to a few million years. At present, a few gaps in the method exist because radionuclides with appropriate half-lives have not been found in ground water. The most troublesome gaps are in waters 30 to 100 and 30,000 to about 100,000 years old.

2.4 Reconstruction of Climate

Information concerning the climate at the time of ground water recharge is contained in the hydrochemistry of the ground water. If sufficient chemical data related to past climates are accumulated, correlations can possibly be made with known Pleistocene chronologies. This is an indirect method of dating ground water which has considerable promise but which has not been studied by many researchers.

Constituents in ground water which are potentially useful for paleoclimatological reconstructions are total chloride content, deuterium, oxygen-18, and the noble gases. Chloride is concentrated by evapotranspiration so it has a complex inverse relationship with effective precipitation. Distance to the marine shoreline is also a factor because most natural chloride in precipitation has a direct marine source. In many regions, as the shoreline receded in response to the lowering of ocean levels during glacial epochs, the effective precipitation also increased. These two effects combined produced a much lower chloride content in the water entering coastal aquifers during glacial times.

Deuterium and oxygen-18 concentrations decrease in precipitation as temperatures decrease provided topographic and climatological factors, other than temperature, are more or less constant. A number of European workers have been strong advocates of the use of deuterium and oxygen-18 as aids for paleoclimatic reconstructions.

Noble gases dissolved in ground water near the time of recharge are also potentially useful as indicators of paleotemperatures. Unlike the stable isotopes, oxygen-18 and deuterium, the noble gases give a direct measure of temperatures at the intake areas because the solubility of the gases is directly dependent on temperature but the stable isotope concentrations are a complex function of distance from the ocean, elevation, mechanics of precipitation, and past storm tracks as well as atmospheric temperatures.

2.5 Anthropogenic Material

A number of materials of anthropogenic origin are dissolved in present-day rain water. Some of these materials can be detected in ground water of recent origin. The fluorocarbon compounds are a good example. Also, almost all of the krypton-85 and much of the tritium in modern rain water is from anthropogenic sources. Detection of fluorocarbons or elevated concentrations of krypton-85 and tritium in ground water would indicate ages of the ground water of less than about 40 years. In the case of krypton-85 and fluorocarbons, a steady increase of these materials has occurred with time so their concentrations in recent water increase accordingly. Theoretically, precise dating of recent water is possible by using analyses of both krypton and fluorocarbons. Bomb-pulse chlorine-36 is another important anthropogenic constituent which is one of the best markers for water originating as precipitation between 1952 and 1965. The detection of this pulse is useful in determining rates of migration of recent ground water and in measuring rates of recharge in arid soils.

2.6 Other Dating Methods

Geologic reconstruction can sometimes provide information useful to dating ground water at a site. For example, if hydrologic evidence exists that ground water is not older than a given geologic feature or event then dating that feature may provide an upper limit on the ground water age. Uranium disequilibrium methods have been proposed for ground water dating. If radionuclides in the uranium decay series enter ground water out of equilibrium, as is typically the case, then the return to equilibrium may serve as a radioactive clock for ground water dating. This method will not work unless a well defined uranium source such as a uranium ore body or an oxidation reduction boundary exists at the site. Moreover, uranium sorption complicates interpretation of ground water ages.

Chemical disequilibrium and alterations of molecular structure may provide information on ground water history. One of the most promising of this class of methods appears to be isotopic equilibration of the oxygen isotopes in the sulfate ion. Other methods include amino acid racemization and analysis of microgradients in chloride concentration. Chemical disequilibrium methods

suffer from strong temperature sensitivity and complex reaction kinetics. If high chloride concentrations can be associated with a specific geologic event they may provide extremely useful information for ground water dating. If not, diffusion and dispersion need to be well understood for chloride gradients to provide data for ground water dating.

3 DISCUSSION

3.1 Difficulties in Applying Ground Water Dating Methods to High Level Waste Sites

The concepts and methods of ground water dating have been well documented and well developed for aquifer systems. For isotropic saturated porous flow systems where the hydrology may be characterized readily, hydrodynamic calculations will yield ground water travel time values that will agree with geochemical calculations to within about 20%. This degree of precision would appear to be more than sufficient for regulatory purposes. Ground water travel times calculated to be greater than 1200 years would exceed the regulatory requirements given this level of precision. However, geologic repository site selection has focused on identifying sites with very low amounts of ground water flow. The sites identified are in basalt, salt and unsaturated tuff, none of which are thought to have saturated porous flow. Although the ground water travel times are thought to be much greater in the proposed repository sites, the uncertainties in the ground water travel times are much greater than for saturated porous media because the hydrology of the low permeability, fractured rock and salt has not yet been characterized with as much confidence.

The heart of the difficulty in characterizing low permeability rocks is the direct relationship between permeability and the volume of rock that can be characterized hydrologically. A widely spaced set of monitoring wells can be placed around a central pumping well to obtain data for high permeability rocks. However, for low permeability rocks such as dense interiors of basalt flows the radius of influence that can be tested hydrologically may be very small. Volumes of water withdrawn in the basalt site for pressure tests were as small as .51 liters (Thorne and Spang, 1985). The authors did not calculate

the radius of influence for the tests but it does not appear to exceed the radius of rock that has been disturbed by drilling.

If vertical fractures or fracture zones exist they may not be characterized by vertical drilling. Moreover, no matter what the angle of drilling, with the small number of tests that will be undertaken in the above ground stages of site characterization, major fracture zones could be missed completely. Any rock type with very low intrinsic permeability which is susceptible to fracturing, such as tuff, basalt, granite and shale, will be difficult to characterize hydrologically. At such sites a few major fracture zones, which possibly might not be detected by surface geological studies, could dominate the flow of ground water for a site, but could also fail to be detected by hydrologic testing in site characterization. Thus, hydrodynamic calculations based solely upon hydrologic models which use data from standard hydrologic tests may be unreliable for low permeability fractured rocks.

Prediction of ground water flow rates and travel times in unsaturated soil and rock is an area of limited experience. Models of unsaturated flow and transport have not received much field testing. Hence, predicting ground water travel times in an unsaturated tuff repository is highly uncertain.

Geochemical ground water dating can provide additional means for establishing reasonable bounds on ground water travel times for most sites. Geochemical ground water ages may be used to set limits on the acceptable range of hydrologic parameters that may be used in modeling a site. The degree of confidence that may be placed in ground water travel time calculations will depend on the extent to what agreement may be achieved between various geochemical methods and the extent to which the geochemical age dates constrain models of ground water flow at a site.

4.0 CONCLUSIONS AND REGULATORY IMPLICATIONS

4.1 Need for Site Specific Application

The research has demonstrated that geochemical methods of ground water dating can provide very useful information for understanding ground water flow and

determining ground water travel times. Hydrodynamic information alone may be insufficient under certain circumstances for characterizing long term ground water flow. Although Congressional action has focussed investigations on the tuff site, the applicability of these techniques to the other sites previously under consideration is discussed here for completeness in case activities in these media are resumed at some later date. The geochemical methods for dating ground water apply differently to different sites because the salt, basalt and tuff sites are radically different in both their hydrology and geochemistry. Thus the application of ground water dating methods to site characterization needs to be presented on a site specific basis.

4.2 Salt

Standard hydrologic characterization methods are appropriate for the aquifer units in the basins in which bedded salt repository sites such as the proposed site in Texas could be located. Hydrodynamic ground water models are well developed for analysis of flow and transport in sedimentary aquifers. Therefore, hydrodynamic calculations, supported by ground water dating using H-3, C-14 and Cl-36 radiometric methods and deuterium-oxygen stable isotope ratios should provide a satisfactory basis for calculating travel times in aquifer units around a salt repository. In deep parts of the basin, ground water could prove to be quite old so that H-3 and C-14 levels would have decayed to background. However, H-3 and C-14 will prove useful for characterizing recharge areas and C-14 will be useful for dating ground waters up to 50,000 years old. Cl-36 will prove useful for dating flow in the deeper parts of the basin and in areas of discharge or ground water mixing. Deuterium-oxygen data will be useful for discriminating between waters which originated from different recharge areas and under different climatic conditions. Thus, a regional ground water flow model may be established for a salt repository by integrating hydrodynamic and isotopic data. Consistency between the calculations based solely on hydrodynamic data and radioisotopic ages may be used as a measure of confidence in the regional model.

Salt was proposed as a medium for a repository primarily because it has extremely low permeability and is self sealing. These properties make standard hydrologic methods irrelevant to characterizing the movement of fluids in bedded salt. One of the major achievements of this project and related natural

analog investigations has been the development of I-129 as a method of dating and tracing ground water. I-129 measurements may be used to determine the origins of brine pockets and fluids in salt.

To determine the origins of brine pockets they should be characterized chemically; deuterium/oxygen measurements should be made, tritium and C-14 measurements attempted; and I-129 analysis by accelerator mass spectrometry should be undertaken.

The chemical analyses and tritium measurements should be done first to eliminate the unlikely possibility that the water is very young. Next the C-14 and deuterium-oxygen measurements should be undertaken. If the brine is older than 50,000 years old, which is likely, the C-14 levels will be background. Geochemical modeling of the solution and solid phases, and the analysis of trilinear diagrams for Na, K, Mg and Ca and for Cl, Br and SO₄ may be used to develop a model of the evolution of brines and of the mineralogy of bedded salt (Stein and Krumhansl, 1985). If these data and the deuterium-oxygen data support the hypothesis that a brine is very old, I-129 measurements should be undertaken. Because salt contains virtually no uranium, all I-129 in brine may be assumed to have originated from outside of the salt bed, either at the time of salt bed formation for trapped brine or at the time ground water entered the salt. Because brine trapped at the time of formation would be much older than brine which flowed into place, distinguishing between the two origins is simple. Given that the salt beds in Texas are of Permian age, no I-129 could be measured in brine trapped at the time of formation. Because the half-life of I-129 is 16 million years, I-129 would be readily detected if the brine originated from water with an external source. The key to the usefulness of I-129 is that iodine is highly soluble and will remain in the brine. Interpreting Cl-36 data could be impossible because of isotope dilution effects by exchange of brine chloride with chloride in the solid phase. Cl-36 levels would be expected to be well below background. Thus, Cl-36 measurements are not recommended for determining the origins of brines in salt. I-129 data are most useful because of the simple chemistry of I-129 in salt and because of its long half-life.

Only through the process of underground exploration in repository development can a sufficient area of the salt bed be investigated to ensure that brecciated

zones that might transmit water, or large brine pockets which might affect the repository are not present at a salt site. Above ground techniques are simply not able to find such features reliably because they do not sample a large enough area. However, if such a feature is located I-129 dating methods and geochemical modelling can be used to determine the origin of the brine.

To determine ground water travel times from a salt site the results of the regional ground water flow investigations and age dating of brines in the salt unit should be integrated. Young brines within bedded salt would indicate a loss of integrity of the proposed repository unit. Moreover, failure to find brine pockets or brecciated zones does not conclusively prove that they do not exist, confidence for licensing will be gained if ground water travel times from the water bearing strata above and below the salt beds to the accessible environment have travel times greater than 1000 years. If ground water ages in the strata above the proposed repository are discordant and the ground water chemistry also shows evidence of mixing, the site may be a poor one because mixing indicates that vertical ground water flow is occurring and that the potential exists for relatively rapid movement of contaminated ground water to the accessible environment. A mixing model may be used to determine the ages of mixed waters. However, from the regulatory point of view, the absolute ages of the ground waters are not as important as the mixing which is an indicator of significant vertical ground water movement.

If ground water mixing is observed at or near a salt repository site, further investigations may be required to provide hydrologic and geochemical evidence that proves that it is occurring slowly enough not to jeopardize the performance of the site. Evidence that could severely question the suitability of a salt site would be mixing of ground water above or below the salt, particularly if combined with a salt plume, indicating active salt dissolution in the vicinity of the site. Conversely, chemical stratification of ground water and the occurrence of uniform ground water chemistry along the flow paths of ground water in the repository region would be favorable evidence of salt stability which could add support to ground water travel time calculations.

4.3 Basalt

Hydrodynamic calculations for determination of ground water travel times appear to be highly uncertain for the basalt site. Possible estimates for ground water travel times for the basalt site made by the NRC in its review of the DOE's Draft Site Characterization Report ranged from 20 years to 43,547 years (Appendix D, Draft Site Characterization Analysis, NRC NUREG-0960, 1983). Mean travel times ranging from 22,000 to 940,000 years were calculated in the Environmental Assessment, (DOE/RW-0070, 1986) of the Hanford Site, Washington using a different set of parameter values and boundary conditions.

The most difficult hydrodynamic modelling and data acquisition areas appear to be in (1) characterizing the fracture flow and vertical permeability through flow units and (2) determining the boundary conditions for flow at the site. Because the interbeds and flow tops at the basalt site behave as transmissive aquifers, large-scale pump tests, piezometer measurements and standard hydrologic methods for investigating aquifers may be applicable to determining the rate of ground water travel within the flow tops and interbeds. However, because of the high permeabilities and storativities of the aquifer units, large-scale testing may not necessarily detect vertical fracture zones in the basalt flows which could be pathways for vertical ground water flow. Large scale testing will induce large artificial horizontal pressure gradients which causes horizontal ground water flow along the interbeds or along the flow tops being tested. Large scale pumping could reduce pore pressure in vertical fractures. Lower pore pressure could allow the fracture to close, thus lowering the vertical permeability. Thus, vertical flow that would occur under natural gradients or under vertical gradients induced by waste heat might not be well characterized by pump testing. Similarly, tracer testing under natural hydrologic gradients would likely investigate a very small area and under induced gradients would suffer from the same drawbacks stated above as other large-scale hydrologic tests.

Geochemical methods of dating and tracing ground water flow have the potential for significantly improving ground water travel time calculations and site hydrogeology models. Chemical stratification of ground water is evidence that ground water flow is primarily horizontal. Areas lacking stratification in an otherwise stratified system are probable areas of vertical flow. By

correlation of hydrologic head gradients with observed ground water chemistry, the flow of ground water can be traced more confidently. Detailed investigation is needed in areas where both chemical mixing and upward hydrologic gradients are observed. These could be the fastest pathways for the release of radionuclides to the accessible environment. They are probable areas of discharge of deep ground water.

Tritium, C-14, Cl-36, deuterium and oxygen-18 measurements should be undertaken to determine the rates and pathways of ground water flow. Tritium in ground water would indicate the presence of very young waters. Possible sources would be contamination or leakage from drilling operations or rapid downward flow of ground water. C-14 dating of deep ground waters may not be fruitful because levels of dissolved bicarbonate and carbonate are very low in the deep ground water at the Hanford site and because interbeds contain coal and organic rich units which could substantially dilute the small amounts of C-14 present with "dead" carbon. Nevertheless, C-14 dating could be useful in areas of recharge and ground water mixing and in waters which are not too deep.

C-14 will probably be below background levels in most deep Hanford ground waters because of the low abundance of carbonate and bicarbonate and the relatively short 5,730 year half-life of C-14. On the other hand the half-life of I-129 is so long at 16 million years that it is greater than the age of most of the relevant part of the Hanford basalt sequence. The Grande Ronde Formation, in which the repository was planned to be located, is approximately 15 million years old (Hanford Environmental Assessment, 1986) and the overlying units are, of course, younger. Thus, I-129 is unlikely to be useful at Hanford.

The one method with a good chance of providing the data necessary for quantitatively dating the ground water at the Hanford site is the Cl-36 method. It will be applicable to waters if they are sufficiently old because it has a half-life of 301,000 years. Therefore, Cl-36 may be applicable to dating the older waters at the Hanford site. For near surface waters younger than about 50,000 years or for cases in which substantial dilution of old waters has taken place, Cl-36 levels may be indistinguishable from modern levels. For waters younger than 50,000 years old and for mixed waters, C-14 dating may be applicable. The low levels of dissolved carbonate and bicarbonate will

probably constrain the upper limit of C-14 dating to significantly under 50,000 years. Thus, a significant gap may exist between the ages to which C-14 and Cl-36 may apply. For example, it is possible that ages younger than 100,000 years could not be measured by Cl-36 whereas ages older than 30,000 years could not be measured by C-14.

Because basalt has relatively low uranium concentrations in comparison to other rocks found near the earth's surface such as sandstone, shale and granite, in situ production of Cl-36 and C-14 should not be a major problem in age dating. Thus apparent young ages will not be caused by in situ production. The basalt environment appears to be very suitable for applying Cl-36 age dating for three reasons: (1) lack of in situ production; (2) lack of leachable dead chlorine and; (3) the likely age of the waters is in the range of Cl-36.

Difficulties will occur in applying Cl-36 ages to the ground water travel time performance objective. The travel times required by performance objective are 1000 years or greater but the ground waters may be fifty thousand or more years old. Thus uncertainties in the measurement method could obscure local gradients in ground water age. For example, suppose that ground water takes 5000 years to travel from the boundary of the disturbed zone to the accessible environment. Suppose the ground water age is 100,000 years. Chlorine-36 age dating with an accuracy of $\pm 5\%$ at a given confidence level could not necessarily distinguish between waters taken from the boundary of the disturbed zone and those from the accessible environment. However, Cl-36 dating on a regional scale could be extremely useful for establishing the deep ground water flow paths and determining travel times on a regional scale. The uncertainties in the models of regional flow using hydrologic data alone may be greatly reduced by incorporating Cl-36 data. Likewise, C-14 dating will be useful in characterizing regional waters younger than 50,000 years old.

Several features could be looked for at Hanford. The most important is hydrological and geochemical evidence of upward flow. If flow is horizontal significant amounts of water do not flow between basalt flows and several properties would be observed.

- (1) Stratification would be observed in the ground water chemistry with total dissolved solids increasing with depth.

- (2) Ground water ages determined by C-14 and Cl-36 would be distinctly different for each unit and would be increasing with depth.

Because the Hanford site was located near a major river in what would be assumed, based on topography, to be a regional zone of discharge, evidence of mixing would be evidence of upward ground water movement at the Hanford site. Areas of mixing may be identified by several wells where ground water ages determined by C-14 and Cl-36 do not increase distinctly with depth and ground water chemistry is not stratified. If mixing is occurring at Hanford, the hydrologic integrity of the site will be in question unless the rate of mixing is extremely slow. Because waters of many different ages may come together at a regional discharge zone such as a major river, the two component mixing model which could be applied using C-14 and Cl-36 dates would be inadequate. Ground water chemistry and radiometric dating would identify mixing zones but extensive hydrologic testing would be needed to attempt to prove that the rate of flow meets regulatory criteria. Ground water dating methods would be useless in areas where waters from a number of different hydrostratigraphic units mix, and the interpretation of hydrologic testing could be controversial in mixing zones. Avoiding regional discharge areas would lower the risk of rapid release of radionuclides to the accessible environment and would simplify the analysis of ground water travel times and rates of ground water flow.

4.4 Tuff

The proposed repository site in tuff is unique in that it is the only high level waste site proposed in the unsaturated zone. The flow of ground water in unsaturated, fractured rock is poorly understood at present. Models of unsaturated flow are not reliable, and ground water travel times predicted using unsaturated flow models are highly uncertain and subject to controversy. Radiometrically determined ground water ages would provide independent evidence of the rate of ground water flow. Unfortunately, dating unsaturated zone waters is not easy.

The difficulty with radiometric dating in the unsaturated zone is that a number of the commonly used methods are not applicable for unsaturated zone investigations. Tritium may be useful very near the surface to identify recharge areas but it is subject to vapor transport and thus will only be

useful for identifying gross features such as recharge along a desert wash. Vapor transport of tritium could complicate attempts to use it as a quantitative tracer. Likewise, C-14 dating may be made difficult, if not impossible, by the exchange of atmospheric CO₂ with dissolved CO₂ because both air and water are in contact in the unsaturated zone and the system is open with respect to CO₂. If the soil gas is able to communicate with the atmosphere, then modern C-14 in CO₂ will mix with dissolved C-14 producing younger apparent ground water ages than the "true" age. Noble gas isotopic data suffers from the same problem of being open to the atmosphere. Likewise, helium accumulation would certainly fail as a dating method. Uranium series disequilibrium methods would not work because an oxidation/reduction front is required as a starting point for the measurement whereas the unsaturated zone is strictly oxidizing. The tuff and the ground water are too young to use I-129. However, two methods with promise are (1) Cl-36 and (2) deuterium and O-18 analyses for paleoclimatic reconstruction.

Obtaining ground water samples from the unsaturated zone requires use of state-of-the-art methods. Porous cup devices are commonly used in soils but are not designed to be used down deep holes. Investigators have proposed to extract water from core samples for Cl-36 measurements. This approach is adequate provided that drilling activities do not contaminate the core. Special air drilling methods which use no detergents or drilling fluids are required to avoid contamination of unsaturated core.

Chlorine-36, which has a half-life of 301,000 years is not useful for dating waters younger than 50,000 years old because such waters cannot be distinguished from modern waters. In general Cl-36 is useful for dating waters greater than 100,000 years old. Thus Cl-36 data for the unsaturated zone may not necessarily provide precise age data but could indicate that waters are younger than 100,000 years. These data could provide constraints to modelling without giving precise ages. The possibility also exists that Cl-36 ages could show that some unsaturated zone water has specific ages greater than 100,000 years but other water has unspecific ages under 100,000 years. These data could provide precise constraints to modelling matrix diffusion and fracture flow. Cl-36 data combined with chemical analyses of the water samples could provide a basis for predicting whether radionuclides would tend to be transported by fracture or matrix flow. For example, at Rainier Mesa, Nevada,

higher sulfate and chloride contents have been observed in matrix water than in water in fractures (White et. al., 1980). These data have been interpreted as meaning that matrix water is very old but water in the fractures is relatively young. Based upon these data, at Rainier Mesa the primary transport mechanism appears to be fracture flow. Cl-36 age dating of the waters could be used to quantify and substantiate the interpretations reached at Rainier Mesa. Likewise, the combination of data on groundwater chemistry and Cl-36 could be used to quantify and substantiate models of flow at Yucca Mountain.

The primary objective of the ground water dating studies would be to determine the rates of ground water movement along paths of flow in the repository. Isolated fractures connected with local sources of recharge, such as washes or low spots on the mountain, possibly could sustain much more rapid flow than the rock matrix. Samples from single wells may be insufficient to resolve concerns about unsaturated zone travel times. If rapid water flow took place in fractures compared to the tuff matrix, water in the vicinity of these fractures could be significantly younger than the bulk of the tuff matrix.

An approach to start testing the importance of fracture flow at Yucca Mountain would be to identify by geomorphology those fracture zones intersecting the ground surface that are likely recharge zones. Tritium and bomb pulse radionuclides including Cl-36 could be depth profiled in the near surface in and around the most probable recharge areas. Recharge rates could be measured and the significance of fractures in recharge could be evaluated.

When an underground structure is developed at Yucca Mountain, underground faults and fractures most capable of transporting water should be identified. Water samples should be collected by whatever procedure possible from in and around these fracture zones. Water samples should be collected from areas least affected by fracturing and the chemistries and radiometric ages should be determined for unsaturated tuff. A comparison of fracture-affected areas and unaffected areas would help resolve questions about the importance of fracture flow. The data would provide a basis for physical and numerical modelling.

The analysis of the isotopic ratios of water (deuterium and O-18) may indicate that isotopically discrete zones of water are present. For example, if substantial recharge occurred in the Late Pleistocene, then the deep

unsaturated ground water could be relatively enriched in heavy isotopes indicative of recharge under cooler climatic conditions at about 10,000 years ago. If recharge also occurred during the warm and relatively wet period about 5,000 years ago a zone of isotopically light water might also be present. Water isotope ratios become more and more difficult to interpret with increasing age because reconstruction of climates becomes more uncertain and because dispersion could lead to mixing of waters. Therefore, deuterium/oxygen-18 data will be difficult to analyse for waters significantly greater than 10,000 years.

If Cl-36 dating shows that the deep ground waters in the unsaturated tuff are uniformly 50,000 years old and greater, a rate of recharge and inflow of water can be determined by which the 1,000 year ground water travel time performance objective could be met. If waters are much younger, stable hydrogen and oxygen isotopes might be used to identify waters recharged under different climatic regimes. These data, in combination with a ground water flow model, might suffice to determine groundwater travel times.

Saturated zone ground water dating at Yucca Mountain has been undertaken already (White and Chuma, 1987). C-14 dating methods, deuterium and O-18 have been used to try to determine the ages, origins and flow paths of saturated zone ground waters at the Nevada Test Site. These are appropriate methods for characterizing regional ground water flow. With proper correction for C-13 enrichment or depletion, C-14 ages may be determined for the saturated zone at NTS. White and Chuma (1987) present isotopic enrichment/depletion correction procedures.

Difficulties are likely to be encountered in applying C-14 dating and stable isotope data to ground water travel time calculations for the saturated zone at Yucca Mountain. The isotopic data for Yucca Mountain are consistent with glacial period recharge of ground water for the saturated zone below and immediately around the mountain. Uniform ground water ages at Yucca Mountain of about 10,000 years appear to be indicative of a regional recharge event. Determining ground water travel times in the saturated zone without clear age differences and with diffuse recharge will be difficult. However, if water in the unsaturated zone is older than the saturated zone water, a case can be made

that significant recharge is not occurring through the mountain and therefore that NRC travel time criteria are met.

4.5 Low Level Waste Disposal

Ground water dating methods are applicable to characterizing ground water flow at proposed low level waste (LLW) sites. Generic statements about applying dating methods to LLW sites are of limited value because LLW site properties vary greatly between regions. Ground water dating methods should be evaluated in terms of the specifics of hydrogeologic site characterization.

In arid portions of the west tritium infiltration may be a means of assessing the movement of water in the unsaturated zone. A pulse of tritium was produced by atmospheric testing of nuclear weapons. This pulse serves as a time marker for the infiltration and movement of ground water. In more humid areas the tritium pulse may have infiltrated into the saturated zone in which the pulse may serve as a time marker for groundwater flow in the site vicinity.

In arid regions, where a substantial fraction of precipitation evaporates in the unsaturated zone, recharge rates may be estimated from the relationship $R=P(C_{lp}/C_{ls})$ for which R =recharge, P =average annual precipitation, C_{lp} =average chloride concentration of local precipitation, and C_{ls} =average chloride concentration of soil water (Stone, 1985). In areas where runoff occurs the runoff would have to be subtracted from the precipitation. Obviously, chloride enrichment is not a precise tool for determining ground water flow rates but it is a useful tool for assessing evaporation rates in arid regions.

Evaporation enriches soil and ground water in deuterium and oxygen-18. Levels of chloride enrichment should correlate with levels of H-2 and O-18 enrichment.

For many sites the concentration of tritium in water entering the soil is a complex function of time because of episodic atmospheric testing. A much sharper peak in time was produced for Cl-36 because it was produced in quantity only by atmospheric testing over the oceans, in particular fusion bomb tests by the United States over the Pacific Ocean. Therefore, a peak in Cl-36 may be observed in soil water. The Cl-36 peak can serve as a time line in infiltration and transport studies. The major drawback in using Cl-36 data is

that the measurement is expensive and not routine. Sufficient amounts of water must be collected to undertake the measurement.

Another use of the Cl-36 peak could be to characterize differences between fracture flow and matrix flow in the unsaturated zone. If a sufficiently large sample quantity could be collected or if measurement were sufficiently sensitive Cl-36 could be used to develop a better understanding of the physics involved in combined fracture and matrix flow in the unsaturated zone. This problem in physical understanding is particularly acute for the HLW tuff site. The Cl-36 pulse might serve as a marker for resolving questions at the tuff site.

In humid areas in which water moves relatively rapidly through the unsaturated zone, hydrologic tracer tests should be conducted to help to characterize proposed LLW sites. Hydrodynamic methods of dating ground water are preferred where travel times are ten years or less (i.e. less than the half-life of tritium). There is little need to resort to expensive and sophisticated geochemical analysis if simple tracer tests and standard hydrologic tests provide data showing that travel times are under ten years.

However, in humid regions ground water flow in rocks of low to moderate permeability may be sufficiently slow that waters in the saturated zone beneath a proposed LLW site could be hundreds or thousands of years old. Tritium methods can be applied to waters up to 30 years old. The C-14 method could be applied to dating waters several thousand years old up to about 30,000 years of age. The Ar-39 method may be applied in the 50-2000 year gap between tritium and C-14. The atmospheric radionuclides H-3, Ar-39, and C-14 provide data which may support hydrodynamic calculations for LLW sites.

Hydrodynamic calculations may be highly uncertain for very tight clays in which diffusion is the primary means of transport. Disposal of LLW is allowed in the saturated zone under diffusion dominated flow conditions. Under these conditions the C-14 method may provide useful ages. It is possible that Cl-36 dating would be useful if diffusion rates exceed 100,000 years. C-14 or Cl-36 diffusion rates could be used to establish an upper bound on mass transfer rates in undisturbed low permeability clays. These rates could be useful for supporting siting of a LLW site in the saturated zone.

Deuterium/oxygen-18 data would provide additional support to C-14 data for saturated zone water dating for LLW sites. Interpretation of the deuterium/oxygen-18 data would be similar to interpretation discussed previously for HLW sites.

For diffusion controlled LLW sites chemical diffusion gradients provide additional data which may be used to calculate diffusion rates. Knowledge of the diffusion source term and the boundary conditions for the diffusion problem is needed to determine mass transfer rates based on the chemical gradient. A "conservative" solute such as chloride or perhaps sulphate might have a geologically controlled relatively high concentration in a stratum from which diffusion could occur. The diffusion equation could be solved using the concentration profile to determine mass transfer rates.

4.6 Conclusions

The proposed repository site in tuff cannot be investigated by many standard hydrological and hydrochemical methods because the proposed underground facility is located in the unsaturated zone. Assessing groundwater travel times and groundwater transport may be accomplished through dividing the problem into three parts.

1. Characterize infiltration rates using geomorphic principles, by placing devices which measure infiltration in washes, in alluvium covered areas on Yucca Mountain, and in fractures. Long term infiltration rates should be determined using isotopic tracers such as the Cl-36 bomb pulse.

2. Characterize the flow and age of water in the unsaturated zone by hydrodynamic methods. Because the relative contributions of fracture and matrix flow to the rate of transport are very uncertain the hydrodynamic results are likely to be very uncertain. Uncertainties can be reduced by determining Cl-36 ages which will indicate whether waters are extremely old (greater than about 100,000 years). If waters are older than 100,000 years then Cl-36 dates can be determined. If not, a lower bound on the rate of flow can be determined. Moreover, Cl-36 age dating may provide data which could show that fracture flow is not strongly coupled to matrix flow. This is a key issue in site characterization.

If the water is too young to date by Cl-36 then deuterium/oxygen-18 stable-isotope data may provide a basis for estimating the ages of unsaturated ground waters. The Cl-36 and stable-isotope data combined with data on groundwater chemistry, (e.g. sulfate ion concentrations) will likely provide sufficient information to reduce uncertainties significantly in characterizing groundwater flow in the unsaturated zone.

3. Characterize flow in the saturated zone using C-14, deuterium/oxygen-18, and groundwater chemistry in combination with hydrodynamic methods. Unsaturated zone waters should be compared with saturated zone waters to characterize the rate of recharge through the mountain.

The results of (1) hydrologic testing, (2) geochemical analysis of major and minor cations and anions, (3) stable isotope analysis, and (4) radiometric dating should be used together to develop a quantitative model of ground water flow for a site. Ground water travel times can then be determined using this model.

5. REFERENCES

Runchal, A. and T. Maini (1980), "The Impact of a High Level Nuclear Waste Repository on the Regional Ground Water Flow." Int. J. Rock Mech. Min. Sci. & Geomech. Vol. 17, pp. 253-264.

Stein, C. L. and Krumhansl, J. L. (1985), "Chemistry of Brines in Salt from the WIPP Facility, Southeastern New Mexico: A Preliminary Investigation" SAND 85-0897

Stone, W.J. (1985), "Recharge Through Calcrete." in Hydrology of Rocks of Low Permeability, International Association of Hydrologists Memoires, Vol. 17.

Thorne and Spane (1985), "A Comparison of Under-Pressure and Over-Pressure Pulse Tests Conducted in Low-Permeability Basalt Horizons at the Hanford Site, Washington State." in Hydrology of Rocks of Low Permeability, International Assoc. of Hydrologists Memoires, Vol. 17.

U.S. Environmental Protection Agency (1982), "Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High Level and Transuranic Radioactive Waste." Federal Register, V-47, no. 250, pp. 58196-58206.

U.S. Nuclear Regulatory Commission (1983), "Disposal of High Level Radioactive Wastes in Geologic Repositories, Technical Criteria," Federal Register, v. 46, no. 120 pp. 28194-28229.

White, A. F. and Chuma, N. J. (1987), "Carbon and Isotopic Mass Balance Models of Oasis Valley - Fortymile Canyon Groundwater Basin, Southern Nevada." Water Resources Res., V. 23, No. 4, pp. 571-582.

White, A.F., Claassen, H.C., and Benson, L.V. (1980), "The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainier Mesa, Nevada." USGS-WSP1536-Q, Water-Supply Paper, U.S. Geological Survey, Washington, D.C.