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REVIEW OF GEOCHEMICAL MEASUREMENT
TECHNIQUES FOR A NUCLEAR WASTE
REPOSITORY IN BEDDED SALT

MASTER

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ABSTRACT

A broad, general review is presented of geochemical measurement techniques that can provide data necessary for site selection and repository effectiveness assessment for a radioactive waste repository in bedded salt. The available measurement techniques are organized according to the parameter measured. The list of geochemical parameters include all those measurable geochemical properties of a sample whose values determine the geochemical characteristics or behavior of the system. For each technique, remarks are made pertaining to the operating principles of the measurement instrument and the purpose for which the technique is used. Attention is drawn to areas where further research and development are needed.

INTRODUCTION

This report presents a broad, generalized review of geochemical measurement techniques that can provide data necessary for site selection and repository effectiveness assessment for a radioactive waste repository in bedded salt. Many different types of geochemical data must be acquired by a variety of measurement techniques during these phases of repository evolution.

The geochemical observations required can be classified into two broad categories: baseline site data and monitored site data. The former are generated during exploration and would mainly be used for the selection, evaluation, design and development of a repository site. The latter are generated during and after repository operation and would be used to assess repository effectiveness.

Baseline site geochemical data are used in conjunction with other geotechnical information (IECO, 1979) for the construction of a complete three-dimensional model of the site geologic conditions. Once this model has been sufficiently developed, detailed decisions about where and how to emplace waste can be made.

Monitored site data are used for several purposes. First, the data provide actual operating knowledge about the chemical behavior of the rock and groundwater system at depth. This information can be used as feedback into the original repository design so that appropriate adjustments can be made.

Second, the collection and review of site geochemical data can act as a warning device against possible waste leakage and other possible adverse effects. As time passes and more and more information is collected, a general

understanding of normal behavior is developed so that abnormal behavior can be recognized quickly. Finally, monitored geochemical behavior provide a realistic data base to assess a repository's capabilities for (1) long-term containment and (2) unobstructed waste retrieval. In particular, the interaction between rock and groundwater can be more fully evaluated by pilot testing during repository characterization.

The purpose of this report is two-fold. First, it is to present available geochemical measurement techniques that can be used to collect data for siting and monitoring nuclear waste repositories in bedded salt. Second, it is to assess techniques, whenever possible or appropriate with regard to their reliabilities, measurement limitations, superiority with respect to comparable techniques, and research and development needs.

Tables initiating the two main chapters on solid and liquid phases list the parameters required to geocchemically evaluate a repository. For each parameter measurement techniques are listed as well as: remarks pertaining to the operating principles of the measurement instrument, and the purpose for which the technique is used. Attention is drawn to areas where further research and development are needed.

Geocchemical measurements are subject to both observational and interpretive errors. Observational errors depend upon the accuracy and reliability of the instrument or the observer. Interpretive errors depend upon the experience, knowledge, and judgment of the interpreter. Errors may be reduced by cross-checking with data from different sources (instruments or techniques) which provide comparable precision and accuracy. For example, although automated instrumental techniques provide a larger volume of analyses, it may

be required to conduct a quality assurance program using less productive, but reliable "wet chemical" techniques for chemical analyses of reference standards.

Geochemical evaluation involves both the measurement of chemical properties of rock and water and the evaluation of the effects of those properties on site suitability. Water that enters the storage area may mix with and mobilize some of the nuclear waste. From that point the waste can migrate with the water. The waste-derived species, however, are also subject to geochemical reactions along the flow path. These species can be adsorbed, dispersed, or concentrated, depending upon rock and water chemistry, temperature, pressure, and the manner and rates of flow. Geochemical data from in situ and laboratory tests can be used to predict the effects on waste species as they migrate.

The geochemical parameters listed in this work for solid and liquid phases are those measurable geochemical properties of a sample whose values determine the geochemical characteristic or behavior of the system. The available measurement techniques are organized according to the parameter measured. Each technique is accompanied by remarks explaining pertinent facts about the technique and its application.

A. Solid Phases

The parameters required to characterize the solid phases are listed in Table 1. These parameters are derived from a broad consideration of the preliminary site evaluation criteria as well as the input requirements of various hydrologic, thermodynamic, and transport codes being developed to assess site suitability.

TABLE 1

Solid Phase Parameters

1. Petrology/mineralogy
2. Geochemistry (major and trace elements)
3. Grain size, surface area and nature
4. Cation/anion exchange capacity
5. Distribution coefficient (K_d)
6. Organic constituents
7. Fracture mineralogy/geochemistry
8. Background (natural) and waste radiochemistry

1. Mineralogy/Petrology

A knowledge of the specific mineralogy/petrology of the reservoir rocks is required to interpret sorption characteristics, and to perform the thermodynamic calculations which consider the possible interactions in the rock/water/waste system (McCarthy, et al., 1978). However, the thermodynamic properties of those minerals which exhibit wide ranges in composition are very sensitive to the particular composition of individual specimens being studied. Methods to determine the mineralogy/petrology of reservoir rocks include:

a. Standard Petrographic Microscopy

Thin-section, polished-section and other microscopic studies determine the mineral composition, texture, degree of alteration, microfracturing and crystal structure by use of the petrographic (polarizing) microscope. These allow identification of rock type and origin (Kerr, 1977; Carver, 1971).

d. X-ray Diffraction (XRD)

The distribution and intensity of X-rays diffracted from powdered rock samples allows the identification, determination of lattice cell parameters, and quantitative analysis of mineral phases that are not amorphous. Through the use of a standard reference file of patterns of nearly all known phases compiled by the American Society for Testing and Materials (A.S.T.M.) isolated mineral phases may be identified (Zussman, 1963). The

equipment, techniques, and interpretive procedures are all well established and standardized.

c. Infrared Spectroscopy (IR)

Although this technique is most commonly applied to organic molecules, all covalent bonds show some degree of selective absorption in the infrared, provided the increase in vibrational or rotational energy results in a change in the dipole moment of the molecule. This technique has been applied to the structure of silicates and can provide information concerning structural changes due to radiation damage (metamictization), etc. (Deliens et al., 1977; Ewing, 1969). In the regions of most interest to geologists, however, spectral peaks are rather broad and as a means of mineral identification this technique has a limited application.

d. Scanning electron microscopy (SEM)

Although this technique has a more important application to fracture mineralogy/geochemistry, it can be of value in the identification of small scale phases ($\geq 25\text{\AA}$) which are present in the reservoir rock but are not resolvable by optical microscopy ($\geq 2500\text{\AA}$). In particular it allows determination of crystal habit, texture, surface morphology, etc. which are required for mineral identification (Broers, 1973).

All of the techniques above are laboratory, as opposed to in situ, techniques. A combination of standard petrographic microscopy and

X-ray diffraction should allow adequate determination of the mineralogy/petrology of the repository site.

2. Geochemistry (major, minor and trace elements)

A knowledge of the specific elemental composition of the mineral phases present is required for the thermodynamic codes being used to assess rock/water/waste interactions. It will be necessary to determine the concentration of many, if not all, naturally-occurring elements present in rock-forming minerals if all possible interactions in this complex system are to be considered. There is an enormous variety of techniques available to geochemists to determine elemental compositions. However, only the most generally applicable techniques are considered here. The order is completely arbitrary and is not a ranking of relative merit.

a. X-ray Fluorescence (XRF)

This technique employs a beam of primary x-rays of greater energy than the characteristic x-radiation which it is desired to excite in the sample. The fluoresced x-rays are then detected using either wavelength dispersive (Norris and Chappell, 1963) or energy dispersive spectrometers (Rhodes, 1976). Some 80 elements with atomic number (Z) 10 may potentially be analyzed by this method. With a judicious selection of source (target) and fluoresced x-ray line (K_{α} , L_{α} , etc.) interferences may be reduced or eliminated and sensitivity maximized. It is normally a laboratory analysis with some sample preparation required. Recently borehole sondes

have been developed capable of measuring both induced and natural XRF in situ (Christell et al., 1976). This is a very powerful multi-element, nondestructive analytical technique.

b. Atomic Absorption Spectrometry (AA)

Neutral, unbound "ground state" atoms vaporized by means of a flame or carbon rod will absorb light of a characteristic energy generated by a hollow cathode lamp of the same element. This forms the basis for the AA technique. Some 40 elements can be determined with sensitivities comparable with other techniques (e.g. XRF) and perhaps 70 elements are theoretically possible (Levinson, 1974). The flame AA technique generally requires sample dissolution. The carbon rod (graphite) furnace is required to vaporize solid samples. Most instruments analyze one element at a time and a suite of elemental hollow cathode lamps are required. Recently some multi-element systems have been described (MacLiver et al., 1969) capable of analyzing six elements simultaneously. Matrix effects can severely affect accuracy in some cases. Typically this is a destructive, single element laboratory analysis.

c. Optical Emission Spectrometry (OES)

Ground state atoms excited by arcing between carbon rods return to a lower energy state following appropriate electronic transitions and emit characteristic radiation. This radiation is detected by photographic means and up to 68 elements may be semi-quantitatively determined. Quantitative analysis with densitometers produces analytical sensitivities that are

generally inferior to competitive techniques (e.g., AA). For precision analyses this technique has been largely superseded by the technique below.

d. Direct Reading Optical Emission Spectrometry

This instrument employs the OES principle but uses a suite of photocells to detect emitted radiation. Up to 60 channels (elements) may be measured in a matter of minutes. Using an inductively coupled plasma (ICP) source liquid samples may be analyzed. This is a very useful multielement technique (Levinson, 1974).

e. Nuclear techniques

There are several techniques available that utilize neutron (thermal and fast) or alpha particle bombardment to activate samples and then detect the decay particles (neutrons, gamma rays, or fission particles) to identify the activated elements. These will be considered separately below.

i) Instrumental Neutron Activation Analyses (INAA)

Stable isotopes of the elements when subjected to a neutron flux (either thermal and/or fast) transmute to unstable isotopes whose gamma decay spectrum are well known. This provides a laboratory technique to detect very precisely almost all the naturally occurring elements simultaneously in a non-destructive manner. Preparatory chemistry is generally not required. Recently these techniques have

been applied successfully using borehole sondes with a variety of thermal, fast, and pulsed neutron sources to provide a precise logging technique (Wichman, 1972; Senftle et al., 1976; Christell et al., 1976; and Caldwell et al., 1976).

ii) Delayed Neutron Counting (DNC)

The heavy elements U and Th, when subjected to a neutron flux, fission to produce products which decay by neutron emission. This process may be used to analyze these elements very precisely either in the laboratory (Amiel, 1962) or in situ using borehole sondes (Smith, 1979).

iii) Delayed and Capture Gamma Spectrometry

This is a variation of INAA in which the delayed gammas emitted from metastable transition states of various isotopes are detected and related to the elements producing them. A borehole technique has been developed using this method of analysis (Moxham et al., 1972). Delayed gamma spectrometry has been used for the in situ analysis of elements such as Al, Mn, Na, Mg, Cu and V.

iv) Mössbauer Spectroscopy

Nuclei may be excited by gamma radiation, be transformed to an excited state and then return to ground state by the resonance fluorescence of gamma rays of characteristic energy. This technique has been applied for both

laboratory (Wertheim, 1964) and recently in situ (borehole) analyses (Sowerby, 1973). This technique has been used to measure in situ the elements Sn, Cu and Ni.

v) Fission Track Analyses

This method is similar to DNC in that U and Th are analyzed via their fission products. In this case the fission fragments are recorded directly by a detector (polycarbonate plastic or muscovite) which is chemically etched to reveal the fission tracks. The method has been employed to determine the concentration and distribution of U and Th in a wide variety of materials (Fisher, 1970).

vi) Gamma-Gamma Scattering

This technique is most commonly employed as a borehole density logging technique (Christell et al., 1976). However, the inelastic scattering of gamma rays may be related to the atomic number of the scattering nucleus and hence provide a means of in situ elemental analysis in some situations (Waggoner et al., 1968).

f. SEM/Microprobe

The SEM previously discussed (Sec. A.1.d) may be coupled with either a wavelength or energy dispersive x-ray spectrometer (see A.2.a) to provide a very powerful analytic tool. Although this instrument will be most useful in determining fracture mineralogy/geochemistry, to be discussed later, it may be

employed for whole rock analyses by simply scanning across the sample and integrating the results or homogenizing the sample (Keil, 1973) prior to analysis.

g Visible/Ultraviolet Spectrophotometry

Techniques are available to analyze almost all elements via spectrophotometry. They all involve some amount of chemical processing (samples must be dissolved) and provide single element analysis only (Levinson, 1974). In many cases the methods are quite specific and highly sensitive, while in others interference problems pose severe limitations.

h. Paper and Thin Layer Chromatography

This is a combination of colorimetric analysis and liquid chromatography in which the element analyzed is separated from others by reaction with a suitable compound impregnated on paper or other chromatographic supporting phase to produce a colored band whose width and intensity is proportional to concentration. Frequently some 21 elements including Be, Nb, Ta, Ti, U, Th, Ge, and the Pt group elements are analyzed semi-quantitatively by this method in geochemical laboratories. Chemical preparation is required and elements are determined singly (Ritchie, 1969).

Considering that a large number of major, minor and trace elements will have to be determined in these samples it is desirable to select methods requiring a minimum of sample preparation (if any)

and providing multielement capability provided that the analytical sensitivities are acceptable. Although the more classical "wet chemical" techniques; e.g. uv/visible spectrophotometry, atomic absorption spectrometry, and paper/thin layer chromatography, have been briefly reviewed they are clearly inferior to the more recent instrument techniques in multielement analysis. Specific wet chemical procedures may in some cases provide lower detection limits for particular elements, but they are inappropriate for large scale multielement analyses. Automated multielement instrumental techniques can provide acceptable sensitivities for the majority of elements under study. The three methods that are prominent from this viewpoint are XRF, OES, and INAA. Table 2 compares the sensitivities of these methods. The data shown are just examples of the detection limits achieved in routine geochemical surveys and are taken from Levinson (1974), Van Konynenburg (1979) and R. Ryon (1979). Actual sensitivities achievable depend on sample matrix, specific analytical conditions used, spectrometer resolution, elemental interferences, etc. However, these values are fairly typical for multielement analyses. The INAA values are derived from a high-throughput system using only a short (three minute) irradiation. With a one hour irradiation at a comparable flux (10^{13} n/cm² sec.) the theoretical detection limit is considerably improved, though sample throughput is diminished. Similarly, for the XRF detection limits a short (100 sec) count was assumed. Longer counting times or the use of other lines (K_{α} vs. L_{α}) could considerably improve detection limits for specific elements or groups of elements. Borehole sondes are available for

TABLE 2

Approximate Lower Detection Limit

Element	XRF	OES (ppm)	INAA (ppm)	Element	XRF	OES (ppm)	INAA (ppm)
Ag	25.	.5	7.	Na	130.	--	20.
Al	30.	--	50.	Nb	10.	10.	--
As	4.	1000.	3.	Nd	25.	70.	50.
Au	20.	20.	.01	Ni	6.	5.	--
B	--	20.	--	Os	25.	50.	5000.
Ba	35.	2.	200.	Pb	15.	10.	--
Be	--	2.	--	Pd	20.	2.	--
Bi	15.	10.	--	Pr	25.	100.	--
Cd	30.	50.	50.	Pt	20.	50.	1000.
Ce	25.	200.	15.	Rb	5.	--	50.
Cl	25.	--	200.	Re	25.	50.	10.
Co	5.	5.	2.	Rh	20.	2.	100.
Cr	10.	1.	10.	Ru	10.	10.	100.
Cs	100.	--	1.	Sb	40.	200.	5.
Cu	5.	1.	--	Sc	20.	5.	.03
Dy	20.	50.	.5	Se	5.	--	5.
Er	20.	50.	200.	Sm	20.	100.	.3
Eu	20.	100.	.3	Sn	45.	10.	200.
Fe	8.	2.	1000.	Sr	5.	5.	350.
Ga	4.	5.	100.	Ta	25.	500.	2.
Gd	20.	50.	40.	Tb	20.	300.	.5
Ge	4.	10.	--	Te	60.	2000.	--
Hf	25.	100.	2.	Ti	15.	200.	2.
Hg	20.	--	300.	Tl	10.	2.	1000.
Ho	20.	20.	200.	Tl	20.	50.	--
In	40.	10.	--	Tm	20.	20.	--
Ir	20.	50.	100.	U	15.	200.	.8
La	30.	50.	.3	V	10.	7.	10.
Li	--	100.	--	W	25.	100.	10.
Lu	25.	30.	.1	Y	5.	10.	--
Mg	55.	--	50.	Yb	20.	1.	.8
Mn	10.	10.	.2	Zn	5.	300.	100.
Mo	10.	3.	30.	Zr	5.	10.	--

in situ analysis via XRF and INAA, and both of these techniques provide multielement capability with little or no sample preparation. These two techniques are the most attractive of those discussed.

3. Grain Size, Surface Area and Surface Nature

These related parameters are important for a variety of reasons. In order to more directly relate laboratory distribution coefficients (K_d) to the mass action law equilibrium constants of thermodynamics a knowledge of the distribution coefficients as a function of available surface area (K_A) is required. In addition a knowledge of surface area and its nature provides some insight to the kinetics involved in many of these sorption-desorption reactions, at least in a qualitative sense. Potential methods to study these parameters include techniques previously described: standard petrographic microscopy (Sec. A.1.a) and scanning electron microscopy (Sec. A.1.d); additional methods follow:

a. Ethylene Glycol Method

This standard method to determine grain surface areas has been used for many years to study soils and clays (Bower et al., 1959). According to the Brunauer, Emmett and Teller (BET) theory for adsorption of gases in multi-molecular layers, there is a vapor pressure of a gas from which a uniform adsorbing surface in equilibrium with the gas will adsorb a monolayer. Thus, there should be a vapor pressure of glycol (or any other nonreacting gas) from which particle surfaces under equilibrium

conditions adsorb or retain an amount of glycol approximately equivalent to a monolayer. Empirically derived values for grams of glycol required to form a monolayer per unit area then allow calculation of total surface area.

b. Quantimet

This device couples an image analyzer computer with an optical microscope or SEM to provide automated particle characterization. It can provide grain size and grain area characteristics for unconsolidated sediments and perhaps for mineral grains within consolidated materials (Jowitt, 1971).

4. Cation/Anion Exchange Capacity

In order to relate the surface area based distribution coefficient (K_A) for a particular ion that has been determined in a simple system to that ion's K_A in a complex, multicomponent system (the natural environment), the total cation/anion exchange capacity of the solid phase must be known and assumed to be equal to the sum of all the equivalent concentrations for each competing species on the exchanger. There are many techniques employed to measure this total cation/anion exchange capacity. The laboratory and in situ borehole techniques will be considered separately.

a. Laboratory Techniques

All of the laboratory techniques involve saturating the exchangeable sites with one cation or anion and then allowing the sample to exchange with another cation or anion. The

techniques differ in the elements used and/or the analytical methods used to register the uptake of the exchanged or displaced ion. Table 3 summarizes some of the available techniques. Cation exchange capacity may be estimated by measuring surface area and organic matter content (Curtin et al., 1976; El-Sayed, 1977). It may be influenced by the presence of iron oxides (Herrera et al., 1978). An automatic soil leaching apparatus has been employed to determine exchange capacities (Baker, 1975). The effect of salts of radioactive and nonradioactive elements on cation exchange was investigated by De et al., 1976 and by Ravina et al., 1977. The exchange capacity has also been estimated from infrared (IR) spectra of soils (Ali et al., 1974).

d. In Situ Techniques

A method has been developed to relate cation exchange capacity with the absorbed water in a formation. Once this calibration is achieved then logging for absorbed water via spontaneous potential logs provides an in situ estimate for the cation exchange capacity (Bush et al., 1978).

Although many additional techniques have been proposed, there is no a priori reason to suggest that they should replace the standard methods (Na^+ for cations, PO_4^{3-} for anions) which have been in use for many years (Carroll, 1959). However, some of the automated techniques recently developed do offer a higher sample throughput.

TABLE 3
Cation/Anion Exchange Capacity

Exchanged Ion	Analytical Technique	Reference
NH_4^+	specific ion electrode	Miller et al., 1975
NH_4^+ , Cl^-	specific ion electrodes	Greenhill et al., 1977
Na^+	specific ion electrode	Kennedy et al., 1964
Ba^{+2} , Ca^{+2}	nephelometry	Adams et al., 1979
Sr^{+2}	XRF	Bergseth, 1978
$^{89}\text{Sr}^{+2}$	gamma spectrometry	Abdel-Aal, 1975
NH_4^+ , Cl^-	auto-analyzer	McLeod et al., 1976
$^{140}\text{Ba}^{+2}$	gamma spectrometry	Bache, 1974
^{137}Cs	gamma spectrometry	Beetem et al., 1962
PO_4^{-3}	colorimetry	Dean et al., 1947

5. Distribution Coefficients (K_d)

In solute transport calculations the distribution coefficient is the input parameter which describes the partitioning of solutes between the solid and aqueous phases. K_d is an empirical descriptive parameter. It need have no theoretical or predictive value. Three laboratory and one field method has been used to derive K_d values.

a. Laboratory Methods

i) Batch (static) Method

The vast majority of K_d values presently available for specific elements and radioisotopes have been determined by this method. In a closed system a fixed amount of solid is exposed to an aqueous phase doped with the species of interest and the distribution between solid and liquid phases is monitored through time (Serne et al., 1977; Jenne et al., 1968). A great deal of effort has been expended to determine these values for the species of primary concern in radwaste, i.e., the fission products and the actinides (Ames et al., 1976). At least two problems exist which prevent the direct application of these values to transport model calculations. First, in most cases crushed samples are used. The surface area presented for reaction with the aqueous phase is not representative of the natural environment. Second, the quasi-equilibrium approach

produces aqueous phase concentrations which may not resemble at all the kinetic steady-state condition which is presumed to exist in a natural, dynamic (flow-through) system.

ii) Single-pass Method

The problems presented by a static aqueous phase may be alleviated by using single-pass or flow through apparatus (Hajek et al., 1968). K_d values determined on such systems might be more appropriate for use in transport model calculations. However, problems still remain with the nature of the solid phase; i.e., crushed samples are used.

iii) Core Method

This technique provides the best approximation of the natural environment by using intact cores of the formation being studied and by using a continuous, flow-through aqueous phase (Weed, et al., 1979).

b. Field Methods

i) Two-well Tests

This technique derives relative retardation factors, and hence K_d 's (knowing density and porosity) by using natural flow or an artificial gradient produced by pumping between an injection well and a recovery well. Tritium is

used to identify the water velocity. The arrivals of the species of interest in the injected spike are measured relative to its arrival (Freeze et al., 1979).

It has been observed that measured K_d 's are strongly influenced by the nature of the solid phase. This necessitates measurements for each specific rock unit for which transport model calculations are to be applied. At best, order of magnitude estimates may be obtained from K_d 's derived for various major rock types, e.g., shale, granite, basalt, etc. Although well tracer tests obviously supply the most appropriate K_d values, they are very costly and time-consuming. Batch methods provide rapid estimates, but their direct application to transport model calculations is questionable. In most laboratory experiments the effect of Eh on K_d is not determined. Moreover, for those elements which exhibit more than one oxidative state, the effect should be significant. This is an area where short-term research and development may provide much needed information.

6. Organic Constituents

Sedimentary basins may contain significant amounts of organic material deposited along with the detrital material. The presence of this organic material may have profound effects on the apparent solubilities of compounds or complexes of many elements, and

particularly the radwaste elements. For example, in the micro-environment surrounding organic material the very soluble uranyl ion (frequently present as hexivalent U^{+6} in $UO_2(CO_3)_3^{-4}$) may be reduced to the insoluble tetravalent state (U^{+4}) and be precipitated from solution. Conversely, the solubility of very insoluble actinides, e.g., Pu and Th, may be significantly enhanced by the formation of organometallic complexes with humic/fulvic constituents of this organic material. There are numerous laboratory analytical techniques available to identify and characterize these organic constituents.

a. Combustion Analysis

The total amount of carbon present may be determined by combustion analysis in high-frequency induction or resistance furnaces coupled to CO_2 autoanalyzers (Carver, 1971). These analyses provide total carbon only (including carbonate carbon) and provide no information concerning the structure of actual organic molecules present. Although wet and dry oxidation methods exist to determine organic carbon, the results are not very reproducible.

d. Gas Chromatography

Gas chromatography involves the separation of various components of a volatile mixture by their differing adsorption rates on either solid (GSC) or liquid (GLC) stationary phases. Detectors are available that respond to either concentration in mole fraction of solute in carrier gas (thermal conductivity,

electron-capture, noble gas, or ultrasonic) or to the flow rate in moles per unit time of the solute in the carrier gas (flame ionization). With mixtures of compounds of similar type (adsorption characteristics) but widely varying volatility, temperature programming of the entire column can greatly improve peak resolution. Although the relative retention times are easily used for qualitative analysis, quantitative analysis using peak height or area is possible if mixtures of known substances are used as standards (Ewing, 1969). A comparison of some GC detectors is shown in Table 4. The figures given are average values of comparable items from a number of manufacturers.

- c. Gas Chromatography/Mass Spectrometry or/Infrared Spectrometry
- By using the output from a gas chromatograph as the input for either a mass spectrometer or an infrared spectrometer, precise identification of the separated components is possible. In mass spectrometry the sample (gas) is ionized by collision with rapidly moving electrons and the resulting ions are separated according to their mass/charge ratio by an electromagnetic field and then collected on an appropriately located electrode. Mass spectrometry has proven to be the more useful of the two (Silverstein et al., 1967), primarily because it is able to respond much more rapidly to the GC output than IR scanning, and hence has a better resolution.

TABLE 4

<u>Detector</u>	<u>Minimum Detectable (g/sec.)</u>
Thermal conductivity	10^{-5}
Ultrasonic velocity	10^{-7}
Electron capture	10^{-14}
Noble gas	10^{-12}
Flame ionization	10^{-11}

d. Infrared Spectrometry (IR)

The basic principles involved in this technique have already been described (Sec. A.1.c). However, in the spectral regions corresponding to the IR absorption by organic covalent bonds, resolution is considerably better than in the region of silicate bonds. For organic qualitative analysis, IR is an extremely powerful tool. Standard IR spectra have been generated for almost all known organic compounds (the Sadtler Index) and the list is continuously updated. Although quantitative analysis is possible (Beer's Law calculation) in practice IR is primarily used for qualitative identification and establishment of structure (Szymanski, 1964).

e. Nuclear Magnetic Resonance (NMR)

If a sample is subjected simultaneously to two magnetic fields, one stationary and one varying at some radio frequency, at particular combinations of these fields energy is absorbed by the sample. This absorption can be related to the magnetic dipole nature of the atomic nuclei and observed as a change in the signal developed by a radio-frequency detector. This forms the basis for NMR spectroscopy. As with IR, NMR is of most use as a diagnostic tool in the qualitative identification of unknown substances by providing structural information. Atlases are available of NMR spectra comparable to those for IR and XRD (Silverstein et al., 1967; Harris et al., 1978).

f. Electron Magnetic Resonance (EMR)

Because electrons possess a spin and hence have a magnetic moment, the basic magnetic resonance theory applies equally as well to them as to spinning nuclei. The primary difference is that higher magnetic frequencies are employed. This technique has been used, like NMR, for organic analysis (Ewing, 1969).

For the qualitative identification and quantitative analysis of the organic constituents contained within sediments in a sedimentary basin, a combination of IR and/or NMR plus GC/MS will be required. No one technique will provide all the necessary information.

7. Fracture Mineralogy/Geochemistry

The basic strategy employed for waste isolation involves placement of waste in an aquiclude (e.g., bedded salt) bounded by aquitards (e.g., shale). Hence, before contamination of porous media flow is observed in an aquifer (e.g., sandstone), most waste transport will be through fractures. The mineralogy, and hence geochemistry, along these regions of fracture flow may differ considerably from that of the bulk rock. Analytical methods with very high resolution will be required to study these fracture surfaces. One technique available, SEM/microprobe, has been discussed in previous sections (see Secs. A.1.d and A.1.f). It has been applied specifically for this purpose (Rodgers et al., 1979). Additional techniques are discussed below.

a. Proton Induced X-ray Emission (PIXE)

This technique is exactly analogous to the SEM/microprobe technique, with the exception that protons, rather than electrons or x-rays, are used to excite characteristic x-rays of the elements present. The basic advantage to PIXE is that the x-ray spectral background is low compared to those produced by x-rays or electrons, because the bremsstrahlung radiation yield is considerably lower. This greatly improves the sensitivity. Using a small beam spot, analyses have been made at the 10^{-12} g level and measurements at the 10^{-9} g level are readily achieved (Clark et al., 1979). Although this technique has only recently been applied to geologic materials, it promises to be extremely useful in applications such as the study of fracture mineralogy/geochemistry.

b. Ion Microprobe Mass Analyzer (IMMA)

The basic principles in mass spectrometry were described in Sec. A.6.c. In this application a primary beam of high energy ions (e.g., N^+ , C^+ , O^+) is used to bombard a surface. The surface is eroded by the removal of individual atoms (sputtering) and some of these atoms are charged. Hence the secondary, emitted ions may be analyzed by mass spectrometry (Anderson, 1973). Although the primary ion beam cannot be focused to a spot as small as an electron beam, it actually generates signals from a smaller volume of material within the sample so that thin layers may be analyzed in the absence of

interfering signals from the substrate. This method has been employed for both trace element and stable isotopic analyses (Hintnorne et al., 1979).

The determination of fracture mineralogy/geochemistry may require that all these techniques and possibly others not specified will be needed. This is an area which clearly requires further research and development in order to provide information required to assess site suitability in a geochemical/hydrologic sense.

8. Background (natural) and Waste Radiochemistry

In order to assess depository performance it will be necessary to monitor the activity of the fission products and actinides present in HLW in the reservoir rocks surrounding the depository. A list of the radioisotopes in HLW of interest here is contained in Table 5. After the first few thousand years the bulk of the remaining activity will be due to the long-lived actinides present in HLW. However, many of these actinides (and their daughter products) are members of the naturally-occurring decay series and are already present in the reservoir rocks. During the site selection process it will be necessary to determine baseline values for these radioisotopes.

a. Gamma Spectrometry

Radioisotopes (natural or artificial) which decay by gamma-emission may be measured by their gamma spectra.

TABLE 5

Some Significant Radioisotopes in HLW

Nuclide	Half-life (y)	Decay modes for detection
^{90}Sr	28	β^-
^{93}Zr	1.5×10^6	β^- , γ via daughter
$^{93\text{m}}\text{Nb}$	14	γ (Nb x-rays), e^-
^{99}Tc	2.1×10^5	β^-
^{126}Sn	1.0×10^5	γ via daughter
^{129}I	1.7×10^7	β^- , γ
^{134}Cs	2.0	β^- , γ
^{137}Cs	30	β^- , γ
* ^{210}Pb	20	β^- , γ , α via daughter
* ^{210}Po	0.38	α , γ
* ^{226}Ra	1.6×10^3	α , γ via daughter
* ^{227}Ac	22	β^- , γ
* ^{228}Th	2	α , γ
* ^{228}Ra	6	β^- , γ via daughter
^{229}Th	7.3×10^3	α , γ
* ^{230}Th	8.0×10^4	α , γ
* ^{231}Pa	3.2×10^4	α , γ
* ^{232}Th	1.4×10^{10}	α , γ
^{233}U	1.6×10^5	α , γ
* ^{234}U	2.5×10^5	α , γ
* ^{235}U	7.1×10^8	α , γ
^{237}Np	2.1×10^6	α , γ
* ^{238}U	4.5×10^9	α , γ
^{238}Pu	86	α , γ
^{239}Pu	2.4×10^4	α , γ
^{240}Pu	6.6×10^3	α , γ
^{241}Am	4.6×10^2	α , γ
^{243}Am	7.6×10^3	α , γ
^{244}Cm	18	α , γ

* = naturally-occurring

Activation is not required (Sec. A.2.e.i); the species sought are radioactive. Three types of gamma detectors are routinely in use for laboratory analysis (Adams et al., 1970): NaI(Tl), Ge(Li), and Si(Li). The NaI(Tl) detector and an intrinsic Ge detector (Senftle et al., 1976) have been employed in borehole sondes for in situ analysis. Due to the scattering effects of surrounding rock the Compton continuum (which may be thought of as gamma "background") is much larger in borehole analysis and, hence, sensitivities are much poorer than those achievable in the laboratory. Almost all of the radioisotopes of interest may be detected either directly or indirectly via gamma spectrometry, although with relatively poor sensitivity for those isotopes that decay primarily by alpha emission.

b. Mass Spectrometry

The basic principle of this technique was described in Sec. A.6.c. This technique has been used primarily in detection of the actinides listed in Table 5 via isotope dilution, whereby a tracer isotope of the element being run is added to the sample (Faure, 1977). The method is capable of high precision although a series of spectrometers would be required to analyze the large number of isotopes of interest.

c. Beta Counting and Spectrometry

Of the radioisotopes listed in Table 5 only ^{90}Sr and ^{99}Tc must be determined by beta-counting and ^{129}I is commonly measured by beta-counting. Beta counting involves chemical

isolation of the element sought and then usually a gross beta counting of the isolated fraction. This is necessitated by the fact that beta emissions are not mono-energetic and hence interference from other beta emitting species must be avoided. In practice ^{90}Sr is usually detected indirectly via the daughter ^{90}Y which decays with a more energetic beta energy (Harley, 1967). Fortunately, all the other beta-emitting isotopes of interest may be determined directly or indirectly via the more convenient gamma spectrometry.

d. Alpha Spectrometry

All of the actinides and their daughter products of interest in Table 5 decay via alpha emission. The technique of isotope dilution alpha spectrometry is completely analogous to mass spectrometry, with the exception that the alpha particles are usually detected via silicon surface barrier detectors. Isolation of elemental fractions is required; however, the same basic instrument and detector type and arrangement may be used for all of these radioisotopes. Although radiochemical preparation is required, the sensitivity for the actinides is usually significantly better than that achieved via gamma spectrometry.

In order to measure all of the radioisotopes of interest, gamma spectrometry, beta counting, and probably alpha spectrometry will be required techniques. Although gamma spectrometry is the most generally useful technique, it cannot provide precise analyses for all the radioisotopes of interest.

In this section techniques have been presented to measure the parameters listed in Table 1 which will have to be determined in order to geochemically characterize solid phases. Of the eight parameters listed, six may be adequately evaluated by existing laboratory and in situ analytical techniques. The remaining two parameters, distribution coefficients and fracture mineralogy/geochemistry, can be determined via the existing techniques described in previous sections. However, these techniques may not be adequate to resolve questions relevant to site evaluation of a deep geologic repository. For example, how do laboratory derived K_d 's relate (if at all) to the distribution of species between aqueous and solid phases present in situ (Apps et al., 1978)? It may be required to significantly improve in situ techniques for determining these distribution coefficients. For determining the fracture mineralogy/geochemistry PIXE offers tremendous promise as an analytical technique. However, this technique has only recently been applied to geologic materials and a great deal of further work needs to be done in order to establish its usefulness in this application.

B. Liquid Phases

The parameters required to characterize the liquid phases present are listed in Table 6. Primarily these are required as input for the hydrologic, thermodynamic, and transport codes being developed, although they also provide basic information concerning the hydrology of the site and therefore provide a means of assessing repository performance.

TABLE 6

Liquid Phase Parameters

1. En
2. pH
3. Temperature and pressure
4. Age and sources of waters
5. Conductivity
6. Dissolved gases
7. Colloid size and nature
8. Organic constituents
9. Geochemistry (major and trace element)
10. Alkalinity
11. Background (natural) and waste radiochemistry
12. Diffusion coefficient

1. En

The En of the aqueous system is a measure of the redox state, i.e., oxidation potential. This potential determines (actually, it is a consequence of) the element oxidative states. It is a critical parameter for understanding aqueous speciation and mineral stability for those elements which exhibit more than one oxidation state in geochemical environments. The system En is required input for the thermodynamic codes. Methods to determine En include:

a. Electrodes (Pt or Au)

A reference electrode (calomel) is used to supply a known EMF relative to which the potential generated at an inert electrode (Pt or Au) is measured. This potential is generated by the ions in solution which either donate or accept electrons at the inert electrode surface. To have any significance these probes must be lowered into wells or piezometers or be placed in sample containers that prevent the invasion of air (Wood, 1976). Units are commercially available to perform these functions (Whitfield, 1974). It should be noted, however, that directly measuring En in the natural environment is very difficult. Problems exist with electrode poisoning, kinetic effects, mixed potentials, ionic strength, complex formation, etc. (Stumm, et al., 1970). Direct evaluation of En via inert electrodes may not be possible in many cases. In the case of mixed potentials, there is no system En, because not all of the redox couples present are in equilibrium with each other. Here each couple has its own "En" which may be different from that of another.

b. Dissolved Oxygen

By measuring dissolved oxygen and pH one may calculate the system En using the water dissociation couple (Stumm and Morgan, 1970). Classically, dissolved oxygen is measured by the Winkler titration (Winkler, 1888) or one of the more recent modifications of it (Carpenter, 1965). More recent techniques include compleximetric (Roskam et al., 1963), polarographic (Meyling, 1962), and radiometric (Richter et al., 1962) methods. All of the above require sample collection and analysis without the invasion of air. In situ determination of dissolved oxygen may be made using electrode systems covered with a semi-permeable membrane (Carritt et al., 1959). A wide variety of very sensitive (ppb level) instruments are commercially available which utilize this technique.

c. Redox Couples

Using the same approach as above, it is possible to evaluate the redox level in natural water systems by determining the relative concentrations of the members of one of the redox couples in the system and applying the electrochemical relations in reverse. Such redox couples include: $\text{Fe}^{+2} - \text{Fe}^{+3}$, $\text{Mn}^{+2} - \text{Mn}^{+4}$, $\text{HS}^- - \text{SO}_4^{-2}$, $\text{As}^{+3} - \text{As}^{+5}$, $\text{CH}_4 - \text{HCO}_3^-$, and $\text{NH}_4^+ - \text{NO}_3^-$ (Cherry et al., 1979). The redox domain for which each couple may yield useful results is illustrated in Figure 1.

Figure 1: Redox Couple Domains.

The best estimate of system Eh may be made by computation from analytical information. If equal values of Eh are obtained from each of the redox couples in a multicomponent system, a singular system Eh can be ascribed with very good precision (± 10 mV) (Stumm, et al., 1979). If agreement is poor, then there is no system Eh, and an independent measure for each redox couple of significance must be made for site evaluation purposes.

2. pH

The pH of a system is a measure of the hydrogen ion activity and is required input for the thermodynamic codes. Although titration methods exist to determine pH, they have been largely superseded by electrometric methods using a glass electrode in combination with a reference (calomel) electrode (Garrels et al., 1965). Although in situ devices are available, pH measurements are usually made at the surface on pumped samples. Care must be taken to minimize temperature change with resulting gain or loss of volatiles. With proper sampling and analytic techniques this parameter may be determined with adequate precision and accuracy using the existing electrometric methods.

3. Temperature and Pressure

The temperature and pressure of subsurface waters are easily determined parameters. Temperature may be determined in situ electronically via thermistors and is required to determine mineral stabilities and solubilities. Fluid pressure is required to determine gas solubilities (O_2 , CO_2 , etc.) and hence mineral

stabilities for phases whose equilibria calculations involve gaseous species. Fluid pressure is most easily derived from hydraulic head which may be measured using simple standpipe piezometers or in situ electronic components using pressure transducers or pneumatic devices (Freeze et al., 1979).

4. Age and Sources of Waters

In the recent past a large number of isotopic methods have been proposed and utilized to determine the age and sources of ground waters. These isotopic methods provide information useful for: establishing hydraulic parameters of the regional flow system; distinguishing connate and meteoric waters; determining sources and mixing components; and for groundwater dating which indicates time available for daughter product formation, reaction with waste and host rock, etc. The methods proposed and/or employed to-date are listed in Table 7. As a rule the maximum applicable age range is about five half-lives. However, it naturally depends on the initial concentration and detection limit for each isotope (or amino acid). Many of the methods make specific assumptions about the source function and conservative nature of each isotope (or amino acid) which may require verification. The analytical techniques required to undertake these dating methods follow.

a. Low-level Beta-counting

This technique was described in Sec. A.8.C. The radioisotopes: ^3H , ^{14}C , ^{32}Si , ^{36}Cl , ^{39}Ar , and ^{85}Kr are routinely detected by this technique. In some cases very large samples of groundwater are required, e.g., ^{32}Si and ^{36}Cl , for each

TABLE 7

Methods for Age Determinations and Identification of Ground Waters

<u>Method</u>	<u>Half-life (y)</u>	<u>Emissions</u>	<u>Reference</u>
^3H	12.3	β^-	Freeze et al., 1979
^{14}C	5.7×10^3	β^-	Wigley, 1975
^{32}Si	5×10^2	β^-	Lal et al., 1970
^{36}Cl	3.08×10^5	β^-	Elmoore et al., 1979
^{39}Ar	2.6×10^2	β^-	Loosli et al., 1978
^{81}Kr	2.1×10^5	γ	Davis, 1978
^{85}Kr	10.4	β^- , γ	Loosli et al., 1978
^{18}O	stable	none	Fritz et al., 1976
^2H	stable	none	Freeze et al., 1979
^4He	stable	none	Davis, 1978
^{234}U	2.5×10^5	α	Barr et al., 1973
amino acids (isoleucine)	1.1×10^5 at 20°C	none	Davis, 1978

analysis and they may not prove to be generally applicable. As with all beta-counting procedures, isolation of pure elemental fractions is required for unambiguous measurements.

b. Gamma Spectrometry

This technique was described in Sec. A.2.e.i. Only ^{81}Kr requires this technique, although ^{85}Kr may also be determined by gamma spectrometry. The use of Kr isotopes is a very recent technique in isotope hydrology and further research is clearly required to establish its routine use.

c. Mass Spectrometry

The principles of this technique were described in Sec. A.6.c. It has been applied in this context for determinations of the stable tracers: ^2H , ^4He , and ^{18}O . Deuterium and ^{18}O have been used to identify groundwaters while the accumulation of ^4He from natural decay processes may be used to age date groundwaters. Recently it was suggested that cyclotrons and Van de Graaf accelerators may be used as extremely sensitive mass spectrometers (Muller, 1977). This allows mass spectrometry to be applied to several radioisotopes that previously were only detectable by beta-counting, e.g., ^3H , ^{14}C , and ^{36}Cl . However, the primary advantage is that sensitivity is increased significantly, thus extending the age dating range for each isotope and reducing drastically the sample size required. The application to age dating groundwaters via ^{36}Cl was made by Elmoore et al. (1979). This new technique offers tremendous promise.

d. Alphaspectrometry

This technique was described in Sec. A.8.d. It is used to determine the activity ratio $^{234}\text{U}/^{238}\text{U}$ which has been used to both identify groundwater sources and mixing components as well as date groundwaters (Osmond et al., 1976). Recently it has been applied to the Permian Delaware Basin (Barr et al., 1978). This relatively new technique offers great potential in this application, however, further research is clearly required for its general use.

e. Amino Acid Racemization

The amino acid isoleucine originally exists in living organisms as L-isoleucine. However, with time it undergoes racemization (actually epimerization) to the non-protein amino acid D-alloisoleucine. The rate of this reaction is slow enough to be useful in geochronology. Their application to groundwater dating has been suggested by Davis (1978). Isoleucine and alloisoleucine are separable on automatic amino acid analyzers and the techniques are well established (Bada, 1972). However, unlike radioactive decay, the rate of racemization is strongly temperature dependent and also depends on the physical-chemical environment in which the amino acids are contained. Thus, to be used to age date waters, the rate of the reaction must be evaluated empirically at the appropriate temperature. This technique may be considered a potentially useful one, though a significant amount of research is required.

Although a wide variety of techniques have been proposed to evaluate this parameter, it is clear that a significant amount of further research and development is needed. Certainly more than one method of dating groundwater should be further developed, and hopefully by the use of supplementary methods (e.g., nuclides with different half-lives), interpretive errors would be decreased. Furthermore, most work to date has concentrated on aquifers, whereas few attempts have been made to date systems in largely impermeable rock where fracture flow dominates (Apps et al., 1978).

5. Specific Conductance

Specific conductance is a good indicator of total dissolved solids and may be directly related to it and less directly to ionic strength. In practice ionic strength is usually a derived parameter obtained from the chemical analyses. However, specific conductance is useful in quickly approximating saturation with respect to NaCl in brines, and may be used to identify and distinguish waters from different sources. It is easily measured in situ using conductance cells which may be lowered down a well as the conductance is recorded on a galvanometer (Freeze et al., 1979). This parameter may be adequately determined by existing methods.

6. Dissolved Gases

Dissolved gases can have a significant influence on the subsurface hydrochemical environment. Carbonate mineral equilibria obviously depend on CO_2 content while the system redox state depends on relative concentrations of O_2 , CH_4 , H_2S , etc. In addition,

natural radioactivity produces the gases Rn and He while the waste itself either contains or produces these gases as well as gaseous fission products, e.g., Kr and Ar. These inert gases may well provide a ready means to assess repository performance. Methods based on gas chromatography have been previously described in Secs. A.6.b and c. Additional methods follow.

a. Specific Electrodes

Membrane electrodes of either the polarographic or galvanic type have been developed for H_2S , O_2 and NH_3 . These probes may be used to provide in situ analyses at the ppb level in many cases and are not as susceptible as other chemical techniques to interferences. These probes are commercially available and provide adequate precision and sensitivity for field analyses (APHA, 1975).

b. Lucas Cells

Radon-222, a member of the ^{238}U decay series, may be determined by scintillation counting after gas extraction. Commercial units are available and provide highly precise, selective determination of this radiogenic gas (Lucas, 1957).

Analyses for dissolved gases may be made with acceptable sensitivity and precision using existing methods. Some combination of gas chromatographic and other techniques will be required to analyze all dissolved gases. Analyses for fission product gases will require mass spectrometry.

7. Colloid Size and Nature

Although the compounds of many of the actinides present in radwaste are very insoluble, there is a possibility that transport may occur on the surfaces of colloidal particles (Apps et al., 1978).

Colloids with their high charge/surface area ratio may be the dominant sites for most ion-exchange processes and their physical movement within the reservoir rocks should be evaluated. Some methods to identify and characterize colloids have already been considered in Sec. A.1.d (SEM) and Sec. A.3.b (Quantimet).

a. Coulter Counter

The concentration and frequency distribution of colloidal particles may be determined using a commercially available Coulter Counter. The methods are well established and provide precise data on the size and number of particles present in water samples (Strickland et al., 1968).

Although potentially adequate methods exist to characterize this parameter, it is quite site specific and its potential importance to the transport of radwaste elements will have to be evaluated at each proposed site.

8. Organic Constituents

Many trace elements, including transition metals, heavy metals, rare earths and actinides are known to form relatively soluble complexes with natural organic materials, e.g., humic and fulvic substances (Apps et al., 1978). Recent work has determined the equilibrium

distribution of small organic molecules in natural waters which may also play a role (Thorstenson, 1970). In addition, recent work has shown that organic decontaminants used in radwaste processing (EDTA) may actually serve to mobilize radwaste elements within a repository (Means et al., 1978). Hence, in addition to the necessity to determine the organic geochemistry at each site, the potential for enhanced migration due to synthetic organics associated with radwaste will have to be evaluated. The methods available to determine the dissolved organic constituents present in groundwater have already been described with respect to solid phase organic analysis in Secs. A.6.a through f. These existing techniques provide an adequate means to determine this parameter.

9. *Geochemistry (major and trace element)*

In addition to a knowledge of the chemistry of solid phases present, obviously a knowledge of solution chemistry is required for thermodynamic considerations related to radwaste interactions with canister, back-fill and reservoir rock. Whereas analytical sensitivity is sufficient with present techniques in most cases to determine the chemistry of solid phases, these techniques may not be adequate to determine some of the sparingly soluble elements in groundwaters. This problem will be detailed at the end of this section. Most of the methods described in Secs. A.3.a through h can be applied to analyze liquids. In addition, the following techniques are available.

a. Polarography

The diffusion current generated by reducible species at a dropping mercury electrode is related to the concentration of those species by the Ilkovic equation. This principle forms the basis for a wide variety of techniques collectively referred to here as polarography (Ewing, 1969). Quantitative analysis is obtained either through calibration or the method of standard addition. Because of problems with interferences and mixed potentials in complex solutions, this technique may not prove to be of general use. However, it does provide a means to follow the kinetics of reactions in solution.

b. Specific Ion Electrodes

In situ analyses are possible in drill holes using specific ion electrodes. These electrodes were briefly considered in Sec. B.6.a. At present commercial electrodes are available for measuring at least 18 specific ions (Cd^{+2} , Ca^{+2} , Cu^{+2} , H^{+} , Pb^{+2} , K^{+} , Ag^{+2} , Na^{+} , Br^{-} , Cl^{-} , CN^{-} , F^{-} , BF_4^{-} , I^{-} , NO_3^{-} , ClO_4^{-} , S^{-2} , and SCN^{-}). Although some interferences may occur, research is continuing and this method offers excellent future prospects because of its specific and quantitative nature (Siegel, 1974).

The present analytical techniques may not be adequate to determine the solution concentration of some sparingly soluble elements. For example, dissolved Al typically present at pH 6 to 9 in equilibrium with common rock forming silicate minerals is thought to be present

at the ppb level. This is at or below present analytical sensitivity for the methods considered here. In order to thermodynamically evaluate waste/water/rock interactions this information is absolutely required. In addition, many of the insoluble actinides, e.g., Th, will require processing large volumes of groundwater in order to provide detectable signal even by the nuclear techniques described here. It may not be feasible to acquire large samples from relatively impermeable reservoir rocks. This is an area that calls for further research and development to provide adequate analytical techniques for these elements in groundwaters.

10. Alkalinity

The alkalinity of a water is its quantitative capacity to neutralize a strong acid to a designated pH. Alkalinity of most groundwaters is controlled primarily by the carbonate system and may be calculated from analytical data. However, it is also a parameter that may be determined directly and hence is considered here. It is a required input for the thermodynamic models being developed. Carbonate alkalinity may be calculated by a CO_2 analysis via gas chromatography which was described in Sec. A.6.b. An additional method follows.

a. Titration Alkalinity

The total alkalinity is normally determined by titrating excess base present in a groundwater sample using a standard acid.

This approximates closely to the acid required to titrate a

solution to the pH inflection point near pH 4.5. Endpoint determinations may be made either potentiometrically or by using indicator solutions (APHA, 1975).

The alkalinity of groundwaters may be adequately determined using existing techniques.

11. Background (natural) and Waste Radiochemistry

As a means of assessing repository performance it will be required to monitor the activity of fission products and actinides originally present in HLW which have subsequently entered the groundwater system. Because many of the actinides are naturally-occurring, base-line measurements will have to be made during the site selection process for the repository. All of the methods described in Sec. A.8.a through d are applicable to analyzing groundwater samples. However, whereas these techniques provide adequate sensitivity for rock analysis, in many cases large volumes of groundwater may be required to determine these species in the aqueous phase. As with major and trace element geochemistry, further research and development is required in order to allow analyses of small samples.

12. Diffusion Coefficients

The transport models being developed (Naymik et al., 1978) require as input not only the retardation factor or equivalent distribution coefficient (K_d) previously considered, but also the hydrodynamic dispersion coefficient (D) which combines the effects of mechanical

dispersion (αV) plus molecular diffusion (D^*). Hence, the diffusion coefficient (D^*) must be determined. Solution defined molecular diffusion coefficients may be applied if they are corrected for the reservoir rock tortuosity which may be derived via resistivity measurements (McDuff et al., 1979). Classically two types of experiments have been used to determine effective diffusion coefficients, which can be significantly lower than molecular diffusion coefficients in free aqueous solutions of pure electrolytes (Duursma et al., 1970).

a. Constant Source

Cores of reservoir rock are sealed on all but one exposed end and suspended in a large volume of groundwater doped with the element of interest. After a sufficient period of time the diffusion into the core is measured by sectioning the solid and analyzing for the element of interest. Gamma emitting isotopes of the element of interest are conveniently used for this purpose (Duursma, et al., 1970).

b. Instantaneous Source

In this case a small aliquot of doped groundwater is added at the top of a core and the element's diffusion into the rock is measured. The core is only exposed to the single pulse of tracer and not constantly in contact with it (Duursma, et al., 1970).

The determination of an effective diffusion coefficient by either of these methods is obviously media specific. Values will have to be

derived specifically for reservoir rocks sampled from the repository site under consideration. Order of magnitude estimates may be derived from existing data for various rock types. However, the effects of solution composition may also greatly effect this empirically derived parameter and must be taken into consideration. In addition, the determination of effective diffusion coefficients for elements which interact strongly with the solid phase may have to be made indirectly. This will involve scaling the free solution diffusion coefficient of the strongly adsorbed element to that of a non-sorbing species, e.g., Cl^- , and correcting for sorption using the distribution coefficient (Duursma et al., 1970).

Techniques have been presented in this section to measure the parameters listed in Table 6 which must be determined to characterize geochemically the liquid phases present. Eight of the twelve parameters listed may be adequately evaluated by existing laboratory and in situ techniques. The techniques available to measure the remaining four parameters (water age and sources, geochemistry, radiochemistry, and diffusion coefficients) either do not possess sufficient sensitivity (or require large samples) or their general application and validity has not been well established.

CONCLUSIONS

A consideration of the important role that geochemistry must play in site selection and evaluation brings one to the realization that some definite short-comings exist in our present ability to address this issue. Areas where basic thermodynamic data and/or measurement capabilities are lacking are enumerated below.

1. Several dissolved species crucial to this problem will be present at or below present detection limits, barring the capability of acquiring large sample volumes.
2. Measurements must be made to determine K_A or K_D values for the specific elements and depository materials under investigation. The effects of competing ions must be taken into consideration.
3. Little consideration has been given to the kinetics and mechanisms of sorption and desorption processes. Many conclusions derived from the equilibrium approach may be completely invalid because of these kinetic effects.
4. Basic thermodynamic data for many mineral and dissolved species is lacking; particularly lacking are stability data on complexes of actinides with natural and synthetic organic ligands.
5. Existing and proposed methods for radiisotope age dating of groundwaters must be improved considerably to provide much needed information about the groundwater flow region and transport times.
6. Methods to distinguish fracture mineralogy/geochimistry from whole rock geochimistry must be improved. In many cases fracture flow will dominate and this information is crucial to an understanding of rock/water interactions in these system.

An effort should be made to concentrate research in these problem areas to provide the lacking information or analytical capability on the shortest possible time-scale.

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