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Subject: NRC Position on the Oxidation-Reduction Conditions of  
the Basalt Groundwater at the Hanford Site.

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## I. Introduction

The redox conditions of the basalt groundwater in both the near- and far-field environments are a critical element in the characterization of the Hanford site geochemistry. The redox conditions are an important aspect in the control of the oxidation states of multivalent radionuclides. The oxidation states of the radionuclides determine the possible species that may form with various ionic constituents and complexes in the groundwater. The speciation of the radionuclide controls its solubility in the groundwater system. Solubility is a crucial factor in determining the amount of radionuclide released from the engineered barrier system. Radionuclide speciation is also an important factor in determining sorption in the near- and far-field environments. Sorption of radionuclides retards migration to the accessible environment.

The NRC position on the redox conditions of the basalt groundwater at the Hanford site is clearly presented in the Site Characterization Analysis of the Site Characterization Report for the Basalt Waste Isolation Project (NRC, 1983). Further information concerning the NRC position on redox conditions was gathered from various NRC reviews of DOE experimental work for solubility and sorption (Kelmers, 1984;

Kelmers et al., 1984; and Meyers et al., 1984) and NRC technical positions papers on solubility and sorption determinations (Apps et al., 1982 and NRC, 1984), and the NRC review of the DOE's Draft EA (NRC, 1985). Section II of this review discusses the important aspects of the redox conditions. The effects of the redox condition on radionuclide solubility and sorption is discussed in Section III. Section IV contains a guide to the methods used to determine the redox potential, as outlined by the NRC. The DOE's current work on redox conditions at the Hanford site and the NRC's evaluation of that work is explained in Section V. Finally, Section VI presents the EWA/YIN conclusions for this review.

## **II. Important Aspects of the Redox Conditions**

The NRC outlines four major aspects of concern related to the redox condition of the repository system: the redox potential (Eh), the redox buffering effect, the redox capacity of the system, and the limiting rates of reactions in re-establishing redox condition equilibrium.

The redox potential is the difference between the potential of the reacting species and that of the standard hydrogen electrode where all reversible redox couples present are in equilibrium. Unless all redox couples present are in equilibrium, the redox potential of a solution cannot be determined, only the redox potential of a particular couple in the solution. Redox potentials for the groundwater can be

determined in four ways: (1) measured directly by colorimetric or other analytical methods; (2) measured directly with electrodes; (3) calculated indirectly with measured concentrations of important redox couples; or (4) calculated indirectly from thermodynamic data. Each of these methods has shortcomings (that will be discussed in Section IV) when applied to the determination of the redox potential of the pre-emplacement groundwater (NRC, 1983).

The redox buffering effect, or "poising," is analogous to the buffering of the acidity of a solution and is related to the system's resistance to change in Eh. This buffering is usually achieved by a chemical equilibrium process which can compensate for addition or removal of the buffered component by adsorbing or generating the buffered component. The Eh of groundwater systems is generally buffered by contact with the atmosphere and reactions involving elemental oxygen. In specific cases, groundwater Eh may be buffered by high concentrations of some redox couple, such as the ferrous/ferric iron species. In the absence of oxygen, the redox potential of the basalt groundwater may be buffered by oxidation-reduction reactions involving iron-bearing minerals (NRC, 1983, p. S-2); however, the NRC disputes the claims by DOE that iron-bearing minerals are actually buffering the Eh, as will be discussed later in this review.

The redox capacity, or reduction capacity, is the resistance to change in Eh in the groundwater system. It is a quantitative measure of the redox buffering effect of the system. It is also a measure of the capacity of the system to control the oxidation state of the radionuclides and the ability of the system to

return to ambient repository redox conditions after the placement of the wastes. Natural waters that are high in iron tend to have high redox capacity. The redox capacity of the basalt groundwaters at Hanford is probably low because of the low iron content (Benson, 1978). In systems with high redox capacities, the measurement of Eh is relatively easy and reproducible, but direct and reliable measurement of Eh exceedingly difficult in poorly poised systems (Langmuir, 1971; Whitfield, 1969; and Stumm and Morgan, 1981). Therefore, the measurement of the redox potential in the basalt groundwaters is not expected to be easy, and the results are likely to be questionable or unreliable.

The rate of reactions involved in the return of the basalt groundwater system to its unperturbed ambient state is an important aspect of the redox conditions of the basalt groundwater. The introduction of oxygen to the system during waste emplacement will cause the groundwater to become relatively oxidizing. Oxidizing conditions are expected to prevail during waste emplacement and for a period of a few hundred years after the sealing of the repository until a re-equilibration occurs. The NRC considers it a priority to determine the rate of this re-equilibration to ambient conditions (the NRC (1983) states that the system will eventually return to reducing conditions--had they conceded that the ambient redox conditions are actually reducing? Such an indication is not given in the strong stance taken by the NRC in their review of the DOE Draft EA (NRC, 1985)). The redox capacity of the groundwater system is a crucial factor in determining the rate of the re-equilibration.

The NRC requests that the following two important points must be addressed by DOE in evaluating the return of the repository to unperturbed ambient redox conditions (NRC, 1983):

- (1) The equilibrium redox condition must be determined, including the identification of redox couples responsible for buffering the system and measurement of the concentrations of these species in the basalt groundwater.
- (2) The rate at which the pre-emplacement equilibrium conditions may be expected to be obtained after closure must be determined.

The NRC feels that a thorough investigation of these two points will result in the determination of useful bounds on the present redox conditions and the length of time necessary to return to unperturbed ambient conditions after waste emplacement.

The NRC (1983) notes that other perturbations to the redox condition of the system may be caused by increased temperature, radiation, and the presence of packing material, canister material, and borosilicate glass. It is postulated that radiation will generate hydrogen peroxide in the near-field. The presence of hydrogen peroxide may increase the redox potential to highly oxidizing levels in the vicinity of the waste package (Braithwaite and Molecke, 1979; Neretnieks, 1982). The effects of these possible perturbations to the groundwater geochemistry must be evaluated for all aspects of the redox conditions.

### III. Dependence of Solubility and Sorption of Radionuclides on Redox Conditions

The solubility and sorption of radionuclides is dependent on the redox conditions of the basalt groundwater system. The rate

at which radionuclides are transported to the accessible environment will be strongly affected by their solubility, the rate and path of groundwater flow, and the sorption reactions between the radionuclides and the minerals in the packing material and the host rock.

The actinides typically exist in various oxidation states under mildly oxidizing or reducing redox conditions. As an example, Apps et al. (1982) note the following common species in simple aqueous systems:  $\text{Ac}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{U}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{UO}_2^+$ ,  $\text{Np}^{4+}$ ,  $\text{NpO}_2^+$ ,  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{PuO}_2$ ,  $\text{Am}^{3+}$ , and  $\text{Cm}^{3+}$ . Actinide radionuclides present in oxidized states are generally more soluble than those present in reduced states (Early et al., 1982) (however, most transition metals, such as Fe and Mn, are more soluble in reduced states (Stumm and Morgan, 1981)). Early et al. (1982) calculated that the solubility of uranium at a redox potential of -0.0 volts was five orders of magnitude greater than the solubility of uranium at -0.4 volts. The uranium solubility was even greater under more oxidizing conditions.

The oxidation state of radionuclides is also important in controlling the formation of complexes with other components of the groundwater. Solubility determinations for actinides are complicated by the formation of complexes and/or colloids with various anions in the groundwater. Most transuranic actinides (especially U, possibly Np) will form strong complexes with  $\text{HCO}_3$  and these complexes have much greater solubilities than the uncomplexed radionuclides. Fluoride, which is present in anomalously high levels in the Grande Ronde groundwater, causes the formation of complexes with reduced oxidation states of Pu,

Np, and Am that significantly increase the solubility of those actinides in the Grande Ronde groundwater environment (Cleveland et al., 1983a and 1983b).

Sorption is an important mechanism for retarding the transport of radionuclides in the near- and far-field environment. Kelmers (1984) and Kelmers et al. (1984) review the DOE experimental work on radionuclide sorption by basalt materials (Salter et al., 1981a; Salter et al., 1981b; Barney, 1982) for the 'key' radionuclides as identified by Barney and Wood (1980). The oxidation state of radionuclides such as Te, Np, and U is identified as a critical factor in the degree of sorption measured in the experiments. Radionuclides present in a reduced state tended to be adsorbed to the basalt materials in greater quantities than the radionuclides present in oxidized states. However, experiments under reducing and oxidizing conditions had only been performed for a few radionuclides. DOE sorption experiments performed under reducing conditions have used artificial reducing agents such as hydrazine, which alter chemical behavior and have been severely criticized by the NRC (Kelmers, 1984). For most of the 'key' radionuclides, sorption experiments have been performed under oxidizing conditions only. For some 'key' radionuclides, no experimental data for sorption has been reported (Kelmers, 1984).

The presence of organic ligands, such as the humic and fulvic acids, in the Grande Ronde groundwater (Means, 1982) may cause very strong complexing of radionuclides. Boggs and Sietz (1984) report that the presence of a small concentration of these

organic compounds (1 mg/l dissolved organic carbon) will substantially reduce the adsorption of Np and Am in a basalt groundwater environment.

In an equilibrium system, the redox potential of the groundwater controls the oxidation state (valence) of multivalent radionuclides; however, the basalt groundwater system is not a system at equilibrium. Therefore, the redox potential indicates only the direction of the redox reaction affecting the oxidation state of the the radionuclides in a non-equilibrium system. The redox capacity of the groundwater system and the kinetics of the redox reactions actually indicate the ability of the groundwater system to impose its redox conditions on radionuclides entering the system (NRC, 1985).

Usually, under reducing conditions, actinide radionuclides are present in reduced oxidation states that generally have lower solubilities and greater sorption onto basalt materials than the oxidized states of the radionuclides usually present under oxidizing conditions. However, the apparent low redox capacity of basalt groundwater and the kinetics of the redox reactions involving radionuclides are likely to inhibit the ability of reducing basalt groundwater to reduce the oxidation states of multivalent radionuclides. The NRC (1985) points out evidence that indicates that the uranium carbonate species can exist in an oxidized valence state in a system with a redox potential as low as -0.4 volts at high pH (Garrels and Christ, 1965; Early et al., 1982; Kelmers, 1984; and Meyers et al., 1984). The basalt groundwater system either does not have sufficient redox capacity to reduce the uranium carbonate species to a reduced valence



state, or the kinetics of this reaction are very slow. According to the NRC (1985), the DOE assumption that the possible reducing conditions present in the basalt groundwater will reduce the oxidation states of the radionuclides to their least mobile form is not valid.

#### IV. Methods Used in the Determination of Redox Conditions

The central issue in characterizing the redox conditions is the determination and interpretation of the redox potential. When combined with knowledge of the temperature, the pressure, the pH, the concentrations of the constituents of the groundwater system, and the mineralogy of the host rock, the redox conditions can be estimated (presuming full equilibration of all aqueous species and redox couples). The difficulty lies in the determination of the redox potential. There are two classes of methods for the determination of the Eh: (1) direct measurements using electrodes, indicators, etc.; and (2) indirect methods using calculation of the Eh from thermodynamic principles or from measured concentrations of redox couples. The determination of Eh for basalt groundwaters by any of these means has proved non-conclusive (NRC, 1983).

Difficulties in attaining an accurate assessment of in situ groundwater conditions have also rendered the characterization of the redox conditions uncertain.<sup>1</sup> Many of the parameters, particularly Eh and pH, can be significantly changed during transport of the sample from depth to the surface. Changes in

temperature and pressure and exposure to the atmosphere can cause increased pH (due to degassing of carbon dioxide) and increased Eh (due to increase in oxygen content).

Direct methods for determining redox potentials include colorimetric methods and electrometric methods. Colorimetric methods use indicators that exhibit different colors when dissolved in solutions of different Eh. The use of colorimetric methods for Hanford groundwaters is limited by the affinity of the indicators for electrons and protons. The Eh of a poorly buffered groundwater will be altered by the reactions involving the indicator. Furthermore, the Eh of the system may also change during the sampling procedure, as mentioned above. The NRC considers that colorimetric methods would be useful only to confirm Eh estimates made by other techniques.

Electrometric methods of measuring Eh directly involve the use of an inert metal electrode (usually platinum) and a reference electrode (usually silver-silver chloride) to measure the transfer of electrons in an oxidation-reduction reaction. An ideal inert electrode would be sensitive only to electron activity and would be equally sensitive to electrons from any redox reaction. Real electrodes, however, are more sensitive to some reactions than to others; also, they are susceptible to surface poisoning effects (Whitfield, 1969) and to mixed potentials (Stumm and Morgan, 1981). The measurement of Eh by electrodes is further complicated by drifting of Eh in poorly buffered systems (Morris and Stumm, 1967), such as the basalt groundwaters. In such poorly poised systems, the determination of Eh can be quite unreliable. Finally, redox potentials

measured by electrodes are valid only if all redox couples in the solution are in equilibrium (Drever, 1982). Again, the NRC (1983) concludes that electrometric methods are useful only for confirming Eh values determined by a variety of methods.

There are two indirect methods for determining the redox potential of a solution. The first method involves a calculation of the Eh through equations based on equilibrium thermodynamic principles. The second consists of measurement of the concentration of various redox couples in the solution and inferring the Eh from the relative concentration of one or more redox couples.

The calculation of the Eh of a solution in equilibrium with multiple mineral phases can be accomplished through the use of equations based on thermodynamic principles. According to the NRC (1983), geochemical computer models are often used to solve these calculations for a complex series of components. The Eh of a solution at equilibrium can be calculated for a groundwater-host rock system. The most useful models are reaction path simulation models, such as PHREEQE (Parkhurst et al., 1980) and EQ6 (Wolery, 1979). Generally, the parameters required for input include temperature, pressure, a thermodynamic data base, and the initial composition of the solution, according to the NRC. The NRC has neglected to mention, however, that either (1) an initial redox potential must be specified so that the relative concentrations of members of redox couples can be calculated in the programs; or (2) the actual concentrations of redox couple members must be specified, to account for electrical neutrality

of the solution. The models perform the calculations along a chemical equilibrium path leading to the minimization of free energy. The output results are given for a number of pre-equilibrium steps as well as the final equilibrium point. Again, full equilibrium of all aqueous species and redox couples is presumed, and this is not necessarily true in many natural systems.

The thermodynamic data base is a critical component of geochemical models. Unfortunately, data for some important elements and compounds are absent or not well known and much of the data available has been measured at temperatures and pressures much lower than the ambient conditions found in basalt groundwaters or those that would be developed in the near-field environment. Additionally, the NRC (1983) noted these deficiencies with reaction path simulation models:

- (1) Organic ligands are not included in the calculations;
- (2) Equilibrium is assumed to be attained when it may not yet be attained;
- (3) Reaction paths calculated by the programs may not be unique;
- (4) The calculations do not account for kinetic effects in the geochemical system.

The NRC concludes that redox potentials calculated by these programs may be questionable unless they agree with other Eh measurements or calculations.

The second indirect method of determining redox potential consists of measuring the concentrations of members of several redox couples in the groundwater. The Eh for each couple can be calculated using the Nernst equation. If the calculated redox

potentials for several redox couples are in agreement, the system may be close to equilibrium and the calculated redox potentials may represent the actual redox potential of the system. Certain redox couples (e.g.,  $\text{Fe}^{+2}/\text{Fe}^{+3}$ ,  $\text{As}^{+3}/\text{As}^{+5}$ ) are sensitive to redox potentials in the range of interest for basalt groundwaters.

The effectiveness of this method is limited by the difficulty in obtaining an unperturbed groundwater sample (as are the direct methods of determining Eh) and by the ability to measure small concentrations of the members of the redox couples in the groundwater samples. Additionally, kinetic factors may invalidate redox potentials calculated through this method (e.g., the sulfide/sulfate redox reaction is extremely slow below 100°C (Ohmoto and LaSaga, 1982)).

In conclusion, the NRC recommends that all methods be employed to determine the redox potential of the basalt groundwaters. If the results of the various methods agree with each other, it is likely that the results give an adequately accurate estimate of the Eh of the groundwater. If not, then the discrepancies between the results must be interpreted. The ultimate goal of this work is to predict the Eh of the basalt groundwater system under post-closure repository scenarios. This will require the use of verified reaction path simulation geochemical codes. The geochemical codes will have to address the kinetics of the reactions involved and the results will have to be verified with experimental data (NRC, 1983).

The NRC's recommendations do not effectively deal with the problem of determining the redox potential in the basalt groundwater. The DOE's characterization of redox potentials has

already revealed a wide range of results from two different methods and the question of which method, if any, has accurately determined the Eh is unanswered. The use of different methods is not likely to clarify this problem. EWA believes that the NRC should require that a bounding range of the Eh of the basalt groundwater be determined, as the NRC recommends for the characterization of many other parameters that cannot be determined without a high degree of uncertainty. In addition, the prediction of Eh for post-closure scenarios using geochemical models will be subject to the same errors that the NRC attributes to the deficiencies in the thermodynamic data base, especially if the models are used to predict Eh in the near-field environment.

#### **V. DOE Determination of Redox Conditions and NRC Comments**

The DOE determination of redox potential in the Grande Ronde groundwater has concentrated on the use of two of the methods explained above: (1) direct measurement of the Eh through electrodes; and (2) indirect calculation of the Eh through thermodynamic principles. Only the redox potentials calculated indirectly are considered accurate by DOE.

Redox potentials ranging from -0.22 to +0.35 volts have been measured in the groundwaters of the Grande Ronde Basalt (DOE, 1982; Early et al., 1982 and 1984). DOE does not expect the measurement of the Eh by electrobmetric methods to be accurate because of the many problems associated with measuring the redox potentials of poorly buffered, non-equilibrium systems as noted

above.

DOE relies on calculation of the redox potential based on thermodynamic principles and assumptions concerning control of Eh and oxygen fugacity by iron-bearing minerals assemblages present in the host rock. Two procedures are outlined in the SCR (DOE, 1982) that are used to indirectly calculate the Eh of the Grande Ronde Basalt groundwater system. These procedures rely on the same thermodynamic principles at the heart of the reaction path simulation geochemical models mentioned previously. The first procedure assumes that the oxygen fugacity of the system can be controlled by iron-bearing minerals in the host rock. Two oxygen fugacity buffers are noted for basalt: hematite-magnetite and quartz-fayalite-magnetite. Assuming pure phases of these minerals are present, the equilibrium constant (determined from the Gibbs free energies of the reactions at equilibrium) is related to the oxygen fugacity. The oxygen fugacity is in turn related to the Eh of the system through the reaction describing the oxidation of water. Using this procedure for temperatures of 510°C and 300°C, redox potentials of -0.54 and -0.37 volts are obtained.

The second procedure involves the calculation of the Eh assuming that the basalt groundwater system is buffered by equilibrium between magnetite, pyrite, and groundwater. Reactions between magnetite, pyrite, and water are combined and simplified to a single reaction. The activity product, the standard potential, the change in entropy, and the change in free energy of the reaction at equilibrium are computed. With the substitution of the the concentration of the sulfate ion into the

equation, these parameters are used to calculate the Eh of this reaction in the system at equilibrium. The calculated Eh for temperatures of 51°C and 300°C are -0.41 and -0.43 volts.

In the SCR, DOE proposed to indirectly calculate the redox potential of the groundwater through measurements of members of various redox couples. However, results of such calculations have not been presented in the Draft EA or any other DOE documents and the groundwater chemistry data that exists for members of important redox couples is very incomplete.

The NRC is not satisfied with the DOE's determination of redox conditions in general, and in particular, of the redox potential. Redox potentials measured by electrometric methods are acknowledged to be imprecise and probably inaccurate, as indicated by DOE in the SCR. The indirect calculations of redox potential are not considered valid because the assumption that iron-bearing mineral assemblages (notably magnetite and pyrite) buffer the oxygen fugacity and control the redox potential has not been verified (NRC, 1983). The NRC points out that the magnetite and pyrite present in the basalt have not been shown to be in sufficient contact with the groundwater or in close enough proximity to each other to control Eh. Additionally, the NRC notes that the concentrations of the dissolved species involved in these reactions may not be large enough to control the Eh (Benson, 1978).

In the Draft EA, the DOE states that the Grande Ronde groundwater is not chemically oxidizing based on assumptions and equations similar to those presented in the SCR (DOE, 1982). The



redox potential calculations are based on thermodynamic calculations assuming equilibrium calculations among observed solid phases and the absence of specific solid phases and dissolved species in the basalt system. Redox potentials as reducing as -0.3 volts are assumed to exist in the basalt groundwater. In this way, the DOE claims that a Potentially Adverse Condition is not present at the site (DOE, 1984, p. 6-96, sect. 6.3.1.2.10).

In their review of the Draft EA, the NRC (1985) presents strong objections to the DOE's conclusions regarding the redox conditions of the pre-emplacement groundwater. The NRC argues that the evidence presented by the DOE is not indicative of redox potentials as reducing as -0.3 volts and that reducing conditions, if they are present, would not necessarily control the solubility and sorption of multivalent radionuclides, as discussed in Section III. The first argument advanced by the DOE is the coexistence of titano-magnetite with secondary ferrous iron-bearing minerals, such as pyrite, and the lack of naturally occurring ferric iron-bearing minerals, such as hematite. However, Benson and Teague (1979) report that a ferric iron phase, possibly hematite, is present within smectite clays, common fracture-filling secondary minerals in the Grande Ronde Basalts. The second argument supporting reducing Eh values is the coexistence of the redox couples sulfide/sulfate and methane/carbon dioxide. However, equilibrium between sulfide/sulfate and methane/carbon dioxide is not expected in the low temperature basalt groundwater. These reactions require biological mediation to be kinetically feasible at low

temperatures and the couples are not generally found to be electrochemically active (Hostettler, 1984; Ohmoto and LaSaga, 1982; Stumm and Morgan, 1981; and Hem, 1975). Finally, the third argument supporting reducing Eh values is the hydrothermal rock/water interaction experiments performed by Jantzen (1983). In citing these experiments, the DOE failed to report the results of tests that more closely simulated repository conditions. Reactions involving deoxygenated Grande Ronde groundwater (GR3) and finely crushed basalt with a high surface area/volume ratio achieved a minimum Eh of about -0.1 volts at a pH of 8.6 and a temperature of 60°C. Tests with crushed basalts of lower surface area/volume ratios produced even more oxidizing redox potentials. Strongly reducing conditions as reported in the EA (-0.4±0.1 volts) were achieved using finely crushed basalt and deoxygenated, deionized water, conditions completely unrelated to the actual basalt groundwater system.

Therefore, the NRC disputes the DOE conclusions concerning the redox potential. Furthermore, the NRC questions the effect of the redox conditions on the oxidation states of multivalent radionuclides. The redox potential does not control the oxidation states of the actinide elements in a non-equilibrium system; rather, it is the redox capacity and the kinetics of the oxidation-reduction reactions in the basalt groundwater system that control the oxidation states. Therefore, the NRC does not expect the basalt groundwater, with its low redox capacity, to be able to reduce the oxidation states of the actinides to their least mobile form.

The question of whether the redox conditions, as interpreted through the data collected by the DOE, are chemically reducing and will maintain radionuclides in their least mobile oxidation states has not been proven by the DOE in the Draft EA, according to the NRC (1985). This has profound implications for many of the other favorable and potentially adverse geochemical conditions in the Draft EA where the control of radionuclide oxidation states by chemically reducing conditions were cited as support for low solubility and high sorption of the radionuclides. The NRC (1985) concludes that the DOE must reconsider the data on the redox conditions and reactions for the basalt groundwater system as well as the findings on the Geochemistry favorable and potentially adverse conditions and the overall qualifying condition for Geochemistry.

#### **VI. Conclusions on DOE and NRC Positions on Redox Conditions**

There are four significant aspects of the redox conditions that must be characterized by the DOE: the redox potential, the redox buffering effect, the redox capacity, and the kinetics of the redox reactions occurring in the basalt groundwater system. The redox capacity and the kinetics of the redox reactions are particularly important in controlling the oxidation states of multivalent radionuclides introduced into the system. The NRC cites evidence that indicates that the basalt groundwater will not be able to control the oxidation states of the radionuclides because of the apparent low redox capacity of the groundwater and slowness of the redox reactions in the system. Therefore, the basalt groundwater is not expected to be able to reduce the

radionuclides to their low solubility, high sorption oxidation states.

The means of determining the redox potential of a solution are generally regarded by the NRC as inconclusive. Nevertheless, the NRC (1983) recommends that all methods be employed by the DOE, and in the case of consensus between the methods, an accurate redox potential is assumed to be determined.

EWA/YIN contends that agreement between the four methods that individually are considered inconclusive is not a defensible technique of determining the Eh. Rather, it would seem appropriate that a bounding range of Eh be established, as is commonly done with other parameters of high uncertainty. The importance of determining the Eh of the basalt groundwater is diminished by the apparent lack of sensitivity of the oxidation states of the radionuclides to the redox potential in a non-equilibrium system with low redox capacity. More consideration must be given to the evaluation of all of the various oxidation states of the radionuclides under both oxidizing and reducing conditions in solubility and sorption experiments, instead of the present concern over the accurate simulation of the redox conditions of the basalt groundwater in the experiments. The kinetics of the redox reactions controlling the rate of return of the post-closure repository conditions to their natural state must be determined.

The NRC review of the DOE Draft EA questions many of the findings on favorable and potentially adverse conditions of Geochemistry. The DOE's assumptions that the basalt groundwater

is chemically reducing and that chemically reducing basalt groundwaters will reduce the oxidation states of the radionuclides to their least mobile forms is the basis of many of these findings. The NRC (1985) disputes the DOE's evidence that the basalt groundwater is chemically reducing and that radionuclides will be reduced to their least mobile oxidation states. The NRC concludes that the DOE must re-evaluate its findings on the Geochemistry conditions in the DOE guidelines, 10 CFR Part 960.

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