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SUBJECT: EWA Review of the BWIP Program for Collection and  
Analysis of Hydrochemical Data  
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## **I. Introduction**

The most probable mechanism for transport of radionuclides from the repository to the accessible environment includes the following three steps (Apted, 1983):

1. failure of waste containment
2. hydrothermal interaction of groundwater with the waste form
3. subsequent migration of contaminated groundwater.

The geochemical condition of the repository and the far-field environment is the crucial factor in determining the quantitative importance of occurrences of these steps at the Hanford site.

The measurement of geochemical conditions is critical for assessing the feasibility of a nuclear waste repository in the basalt flows beneath the Hanford site. The geochemical environment at the Hanford site must meet the standards set forth in the performance objectives in the NRC licensing procedures for geologic repositories (10 CFR 60) and the qualifying conditions in the DOE final siting guidelines for geochemistry (10 CFR 960.4-2-2). After acquiring the basic geochemical data, laboratory experiments simulating the placement of the nuclear waste in the basalt environment can be performed.

For the pre-emplacement, containment, and isolation time periods, the temperature, pH, Eh, pressure, and the groundwater and basalt phase composition must be measured or calculated.

These parameters are necessary for evaluating the nature of the basalt-water interactions in the pre-emplacement phase. During the containment period, the stability of the engineered barrier system and the nature of the basalt-water-air interactions will affect repository performance. Finally, radionuclide sorption and solubility must be known to determine the effectiveness of the repository in the isolation time period (Apted, 1983).

The existing geochemical condition of the repository environment is determined by the collection and analysis of groundwater samples from specific intervals of the various stratigraphic units beneath the Hanford site. In this review, EWA evaluates the BWIP program for the collection, analysis, and interpretation of hydrochemical data.

## II. BWIP Hydrochemical Data

Methods for hydrochemical sampling and analysis are outlined in the Basalt Operating Procedures (BOP), Section C-2.4, prepared by the BWIP QA Unit (1982). At present, EWA does not have access to all of this document. However, review of the BOP methods for hydrochemical sampling and analysis, and other phases of field work, including drilling procedures, is a top priority. The integrity and accuracy of hydrochemical data depends strongly on the sampling, handling, and analytical methods. EWA will also seek documentation of sampling and analytical procedures used prior to the issuance of the BWIP BOP in 1982 because a large part of the hydrochemical data for the Hanford site was collected before 1982.

The Site Characterization Report (DOE, 1982) devotes two chapters to the geochemistry and hydrogeology of the Hanford site and its possible effects on the performance of a nuclear waste repository. The regional hydrochemistry was reviewed for the unconfined surficial aquifer (102 representative samples), the Saddle Mountain Basalts (45 samples, mainly from the Mabton Interbed), the Wanapum Basalts (27 samples), and the Grande Ronde

Basalts (18 samples). Each set of data was analyzed for major inorganic composition, trace element content, temperature, Eh, pH, dissolved gas content (for all data except that from the unconfined aquifer), and isotopic chemistry. Vertical and areal differences in chemical composition of the groundwater are noted, based on the zone of sampling and the well location.

"Representative samples" are defined as those samples with anion-cation balances of less than 5 percent. In all DOE work, the anion-cation balance is calculated in this manner (DOE, 1982):

$$(\text{anions} - \text{cations}) / (\text{cations}) \times 100 \quad \pm 5 \text{ percent}$$

The unconfined aquifer is characterized as a calcium-bicarbonate type with wide variability in the chemical composition. Elevated nitrate concentrations were noted and the probable cause is anthropogenic input at the Hanford site. The mean temperature of the groundwater, 19°C, was much greater than the mean air temperature for the site (attributable to warm water from synthetic recharge). The mean measured pH was 7.9. Eh and dissolved gas content were not measured.

Thirty-seven of the 45 samples taken from the Saddle Mountain Basalts are from interbed layers, mainly the Mabton Interbed. The groundwaters of the Saddle Mountain Basalts are principally of a sodium-bicarbonate type. The Mabton Interbed is similar in composition, with slightly higher dissolved solids content. At greater distances from the recharge sources in the Rattlesnake Hills, the groundwater changes from a  $\text{Ca}^{+2}\text{-Mg}^{+2}\text{-HCO}_3^-$  facies to a  $\text{Na}^+\text{-HCO}_3^-$  facies. Sulfate concentrations decrease and total dissolved solids increase. Total dissolved solids and sodium concentrations are expected to increase as the residence time of the groundwater increases (Chebotarev, 1955). Sulfate concentrations are expected to decrease due to sulfate reduction (Hem, 1970). Groundwater temperatures vary for the different layers, but it generally follows the geothermal gradient. Mean pH measured at the surface is 8.4 (controlled by silicate hydrolysis and carbonate buffering) and measured Eh is -0.09 to +0.06. Methane makes up the major mole fraction of the dissolved

gas in the Saddle Mountain Basalts. Samples taken from wells within the Cold Creek Syncline (the reference repository is located within this tectonic structure) have low sulfate and high methane concentrations and this indicates a reducing environment. Outside the syncline, sulfate concentrations are much higher and the methane gas volume percentage is much lower, indicating less reducing conditions.

The Wanapum Basalts are characterized by 27 samples. It should be noted that some of the boreholes from which samples were taken are also open to zones in the Saddle Mountain Basalts. The groundwater is primarily of a sodium-bicarbonate type, although chloride is also a major anion. There are areal differences in the chemical constituents and total dissolved solids concentrations. Samples taken from outside the Cold Creek Syncline have much lower dissolved solids and chloride. Temperature varies with depth, ranging from 19.5° to 41.8°C. The mean pH measured at the surface is 9.3 and Eh is measured at -0.18 to +0.12 volts. Nitrogen gas dominates samples collected outside the syncline and methane gas dominates samples collected within the syncline.

The Grande Ronde Basalt groundwater is characterized by data from 18 samples. Major inorganic ion composition shows that the groundwater is predominantly a sodium-chloride type. Total dissolved solids concentrations are much higher than those of the Saddle Mountain and Wanapum Basalts. Fluoride levels are much higher than expected, but this is attributed to selective leaching of volcanic glass along flow contacts. Longer residence time and higher temperature and pH may also contribute to the elevated fluoride concentrations. Sulfate levels are also very high. This is unexpected in the Grande Ronde groundwaters, which are expected to be reducing because of the high pH and long residence time. Formation temperatures for the Grande Ronde groundwater range from 46.2° to 56.6°C. Mean measured pH is 9.7 (buffered primarily by silica dissociation) and measured potentiometric Eh is -0.22 to +0.21 volts. Nitrogen is the principal dissolved gas measured in the samples; however, in

borehole RRL-2, methane is the principal gas present.

The most recent compilation of hydrochemical data in a BWIP report is available to EWA in Long and WCC (1984). This report focuses on data collected from the candidate repository horizons in the Grande Ronde Basalts. The analytical results of a total of fifteen representative groundwater samples collected from 1980 to 1982 are presented. Mean concentrations of the major constituents of the samples from boreholes DC-6, -12, -14, -15, and RRL-2 again indicate that the Grande Ronde Basalt groundwaters are generally of a sodium-chloride type with high fluoride and dissolved silica. The data presented in the report is considered "representative" because the anion-cation balance is within 5 percent.

The measured pH spans a range of 8.7 to 10.6 and the measured Eh values range from +0.2 to -0.2 volts. Estimated Eh values cited in the report are calculated from equilibrium thermodynamic data and range from -0.54 to -0.37 volts (DOE, 1982). Dissolved gas component distribution and stable and radioactive isotope data is also presented. The main conclusion of the report is that little difference exists between the hydrochemical characteristics of the four candidate horizons in the Grande Ronde Basalts.

EWA has access to the sampling results from specific zones within specific boreholes (the data that is compiled in the two reports previously discussed). This BWIP data covers the major inorganic ions, total dissolved solids, trace elements, Eh, pH, temperature, and the depth of the sampled zone, and the date of the sampling in the borehole. The USGS also makes available groundwater quality records from wells in the Pasco Basin area, and EWA has access to these data as well. The wells are specified with code number describing the township-range-section location of the well or by the BWIP-designated name for wells on the Hanford site. The date of sampling, the major inorganic ion content, total dissolved solids, temperature, pH, and the depth

of the sampled zone are included in the USGS data.

### III. Specific Deficiencies in the Hydrochemical Data

#### III.1 Review of Borehole Reports

The data presented in the SCR (DOE, 1982) and Long (1983) are a statistical summaries of a number of samples from different intervals in different boreholes. The original data appears in reports covering results of drilling, testing and sampling of individual boreholes. One recent report, the Principal Borehole Report, Borehole RRL-2 (BWIP, 1983) was reviewed by EWA (EWA/YIN, July, 1984) and found to be insufficient in regard to the collection and analysis of hydrochemical data. These shortcomings included the following points:

1. Temperature log data in the Grande Ronde Basalts was termed "less reliable due to cross-hole flow."
2. Dye was added to the drilling mud to determine when the borehole had been adequately pre-pumped but there was no explanation of what acceptable levels of the dye in the sample were.
3. Only one groundwater sample was taken from each interval, offering no means for statistical analysis.
4. Major conclusions concerning the boundaries between hydrochemical facies were made based on samples with anion-cation balances and tritium concentrations in excess of prescribed limits.
5. Data was missing in tables containing isotopic data.

Other borehole reports have not been reviewed in depth. From preliminary evaluations, it seems that such shortcomings could be found in other reports because most of the faults found in the RRL-2 report concern inadequate sampling technique. The method for judging the representativeness of a groundwater sample must be available for examination and the methods must be followed by

the BWIP staff. As noted in item 4 above, data was reported in the RRL-2 report that exceeded the limits placed on the anion-cation balance and the tritium concentration. This indicates some degree of sample contamination or analytical error. The use of these methods in other borehole sampling may result in the same problems found in the RRL-2 report.

### III.2 Oxidation-Reduction Conditions and Eh

One of the most serious groundwater sampling difficulties encountered by the BWIP is the accurate measurement or calculation of Eh. The use of potentiometric measurements in the field has given a range of Eh values from about +0.2 to -0.2 volts. The BWIP staff believes that such measurements may only be used to qualitatively indicate general oxidizing or reducing conditions. EWA agrees that these field measurements do not accurately represent the actual oxidation-reduction conditions in the formation groundwater because the Eh is measured at the surface. Also, there are severe problems obtaining accurate Eh measurements by Pt electrodes in dilute groundwaters, such as those at the Hanford site (Langmuir, 1971; Whitfield, 1975).

The Eh has also been calculated thermodynamically assuming certain equilibrium reactions. Iron-bearing minerals in the basalt were assumed to control the oxygen fugacity by reactions of hematite-magnetite and quartz-fayalite-magnetite. Eh values of -0.54 to -0.37 volts were calculated on this basis.

Eh calculations were also performed assuming that an equilibrium reaction between magnetite, groundwater, and hematite controls the redox potential of the groundwater. These methods produced Eh values of -0.43 to -0.41 volts for temperatures of 51 and 300°C.

The difficulty in using mineral pairs or buffers as an indicator of Eh lies in the assumption of complete equilibrium. It is not clear below what temperature such buffers become inoperative. It is highly debated whether such mineral buffers control oxygen fugacity and Eh under lower temperature

conditions, as would be expected in the far-field (Barton and Skinner, 1967 and Heubner, 1971).

Reduction-oxidation couples have not been used by the BWIP to determine Eh. Eh can be defined by a particular redox couple in a solution, although in non-equilibrium natural waters, different redox couples will give different Eh measurements. It is necessary to identify the important redox couple controlling the Eh. A major shortcoming of the BWIP groundwater sampling program is the omission of sampling and analysis for one or both members of a number of potential redox couples for the groundwater. Of the following redox couples only the nitrate species has been analyzed in the data available to EWA:  $\text{Fe}^{+2}/\text{Fe}^{+3}$  (only total iron is measured),  $\text{Cu}^{+}/\text{Cu}^{+2}$ ,  $\text{H}_2\text{S}/\text{SO}_4^{-2}$ ,  $\text{NH}_4^{+}/\text{NO}_3^{-}$ , and also reactions involving these solid phases,  $\text{Mn}^{+2}/\text{MnO}_2$ ,  $\text{Fe}^{+2}/\text{Fe}(\text{OH})_3$ , and  $\text{Fe}^{+2}/\text{Fe}_2\text{O}_3$ , and trace elements such as As (Cherry et al., 1979).

### III.3 Organic Constituents of the Groundwater

The BWIP groundwater sampling program has virtually ignored the presence of organic ligands in the basalt groundwater because drilling fluids have contaminated groundwater samples with respect to organic compounds. However, in the Draft EA (DOE, 1984), the DOE states that extensively pumped basalt horizons produce organic carbon samples that can be considered representative. In these samples, TOC concentrations are between zero and 1 mg/L. Fulvic acid was identified as the main component of a sample analyzed by ONWI (Means, 1980; Means, 1982). Naturally occurring organic ligands, such as the humic and fulvic acids, have been shown to be important multidentate chelating agents for metals and radionuclides. These chelating agents form very strong complexes metals, rare earth and actinide elements. The strong metal-binding capabilities of the multidentate ligands lead to radionuclide mobilization (Means et al., 1978). Boggs and Sietz (1984) report that adsorption of certain actinides was reduced by 25 to 50 percent by the addition of only 1 mg/L of dissolved



organic carbon in a basalt groundwater environment.

In addition to TOC determinations, it is essential that the groundwaters be carefully sampled and analyzed for specific organic components with high metal-binding capability. The ability of these organic components to mobilize radionuclides merits immediate attention from the BWIP staff.

#### III.4 BWIP Sampling Procedure

A large majority of the hydrochemical data available to EWA was collected prior to the introduction of the BWIP BOP (1982). There is no manual or record known to EWA that explicitly describes the groundwater sampling and analytical procedures followed before 1982. Furthermore, much of this sampling was done before the common use of many advances in sampling technology designed to reduce the effect of contamination by drilling and sampling operations, including ultra-filtration and advanced analytical equipment. Sampling and analysis for trace and minor components of the groundwater is particularly susceptible to the slightest contamination, as noted in Long and WCC (1984).

Even hydrochemical data collected after the introduction of the BWIP BOP is suspect--the representativeness of the samples collected at RRL-2 is subject to question because of the high discrepancy in anion-cation balances and high tritium concentrations of some of the samples. Sampling for organic compounds would also be highly susceptible to contamination by materials used during the well drilling.

The proper performance of the analytical methods, especially for the trace elements and organic compounds, is critical to the accurate determination of concentrations of the constituents of the groundwater. Additionally, these procedures must be well documented in the reports so that it can be exactly determined what form of an element or compound is being measured. EWA presently does not have access to the methods used by the BWIP staff for the analyses of the groundwater samples; therefore,

there are certain discrepancies and ambiguities in the data that cannot be resolved.

### III.5 One-time Sampling of Boreholes

In order to provide a higher degree of confidence in the hydrochemical data, the BWIP should have collected multiple samples from each interval in each borehole. As noted before, all the hydrochemical results are from single groundwater samples taken during one-time sampling events, and any single sample is subject to a wide variety of possible conditions that could render it unrepresentative of the formation groundwater. Multiple samples are necessary to guarantee the accuracy of past results. Boreholes that have not been sampled recently should be resampled to assure that past methods provided accurate results. Resampling will also provide an analysis of any possible seasonal change or evolution over time that may occur in the basalt groundwaters.

### III.6 Use of Hydrochemical Data in Geochemical Models

EWA plans to use widely recognized geochemical mass transfer and equilibrium speciation models, such as PHREEQE, EQ3/6, MINTEQ, and WATEQF, to analyze the hydrochemical data gathered at the Hanford site and to evaluate the current BWIP conceptual groundwater models in terms of theoretical geochemical mixing. Modifications of the current geochemical models may also be considered to incorporate new factors that may be encountered in the repository environment (e.g. radionuclide speciation data). However, the current BWIP hydrochemical data base does not provide the full set of parameters necessary for input to the models.

Specifically, alkalinity and oxidation-reduction couples are missing from the data base and are needed in the PHREEQE model. The oxidation-reduction couples are particularly important to the model because they are used to determine the Eh of the system.

Without redox couples or some other accurate method of estimating the Eh, the usefulness of the PHREEQE model will be limited by the Eh data. Any results will be subject to large error because Eh is important in controlling the reactions in the system.

The concentrations of seven constituents of the groundwater needed by the WATEQF model are not presented in the hydrochemical data available to EWA, including  $H_2S$ ,  $NH_4$ ,  $PO_4$ , Sr, and Br. This program also requires accurate estimates of the Eh of the system to correctly calculate the speciation of the groundwater samples.

#### IV. Conclusion

The problems occurring during the sampling, analysis, and dissemination of the hydrochemical data for the Hanford site have been described in this report. Many of these comments appeared in a previous EWA review of the Principal Borehole Report, RRL-2 (EWA/YIN, July, 1984). More specific comments concerning actual sampling and analysis techniques will follow when the BWIP BOP becomes available to EWA.

The deficiencies in the hydrochemical data base inhibit its ability to provide data on the basalt-groundwater system that will contain the repository. Critical parameters, such as the redox conditions, have not been adequately characterized by the sampling and analysis methods. Standards for determining the "representativeness" of a sample have been set using the anion-cation balance and tritium concentrations and these standards have been exceeded in data presented in the reports. The BWIP BOP was published in 1982, but most of the sampling of the boreholes had been done before 1982.

It is imperative that more sampling be performed at the Hanford site to assure the accuracy of past sampling and analysis and to include sampling for new parameters, such as important redox couples and organic compounds that can mobilize radionuclides by their high metal-binding capability.

EWA plans to review any future sampling programs to ensure that the proper sampling techniques are being used and that the

required parameters are being properly measured or adequately estimated. The hydrochemical data base is the foundation of all laboratory study on the behavior of the radionuclides and the performance of the engineered waste package, in the basalt-groundwater environment.

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