H51B-0803: Groundwater Oxidizing and Reducing Conditions Near Yucca Mountain

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Abstract

Groundwater data from 73 wells in Yucca Mountain region were analyzed to better understand geochemical conditions and to make reducing/oxidizing (Redox) environment comparisons. Major ion chemistry, silica, fluoride and associated saturation indices, determined with PHREEQC, were sequentially examined using the multivariate statistical methods of principal component factor analysis and *k-means* cluster analysis. Analysis of both major ion concentration data and their saturation indices allow simultaneous consideration of arithmetic (raw concentrations) and logarithmic (saturation indices) variables that describe the hydrochemical system and therefore can provide further insight into the system's behavior. The factor analysis of the major ion and saturation indices transforms the variables into a tractable number of descriptive factors that are rotated to summarize the chemical groundwater system and better interpret system variation. Results obtained from these analyses show a good agreement with literatures results. Literature indicates that the saturated zone (SZ) located to the east and south of the Yucca Mountain has reducing conditions, and oxidizing conditions are found elsewhere in the SZ flow system.

Introduction

Study Area

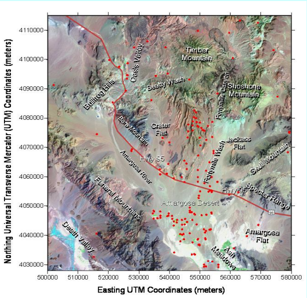
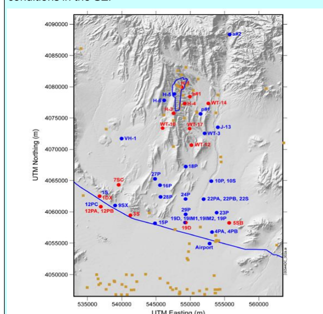


Figure 1. Satellite image of the Amargosa Desert region with the 73 sampling locations overlain.

Yucca Mountain (**Figure 1**), north of the Amargosa Desert, Nevada, is a group of north-trending block-faulted ridges of volcanic rocks (ash-flow and ash-fall tuffs) **[1]**. Amargosa Desert is located in the southern portion of Nye County within the Great Basin, and is part of the Death Valley groundwater basin. Fortymile Wash, an ephemeral drainage, originates in the uplands north of Yucca Mountain, flows southward along the east side of the mountain, and terminates in the northern part of the Amargosa Desert. Yucca Mountain has been chosen as the site of a high-level nuclear waste repository and is expected to hold approximately 77,000 metric tons of radioactive waste. The present climate in the Amargosa Desert region is considered arid to semiarid, with average annual precipitation ranging from less than 130 millimeters (mm) at lower elevations to more than 280 mm at higher elevations **[2]**.

Many authors (i.e., Bill W. Arnold, Arend Meijer, Elena Kalinina, Bruce Robinson, Sharad Kelkar, Carlos Jove-Colon, Stephanie Kuzio, Scott James, and Ming Zhu) **[3]** were assumed that the variations in groundwater redox chemistry in the Saturated Zone (SZ) near Yucca Mountain could have significant impacts on processes associated with the potential transport of redox-sensitive radionuclides from the proposed repository to the accessible environment. Their study examined geochemical data relevant to the distribution of redox conditions in the saturated zone, the relationships between redox state and solubility and sorption coefficients for technetium and neptunium, and sensitivity in transport model simulations. The results, which are based on the direct measurement of reduction/oxidation potentials by using an inert platinum electrode apparatus. Groundwater samples were designated as oxidizing if the concentration of dissolved oxygen (DO) was more than 1.0 mg/l and reducing if (DO) was less than 1.0 mg/l. Reducing conditions in the volcanic rocks of the saturated zone are recognized, located to the east and south of the repository and along the inferred flow paths from the repository as shown in **Figure 2**. The direct measurement of redox conditions in groundwater **Figure 3** has many uncertainties related to factors such as the potential for contamination of samples, instrumentation errors, and apparent inconsistencies due to chemical disequilibrium.

Lindberg and Runnells (1984) presented a comparison of Eh measured using a platinum electrode and Eh calculated from various redox couples using the Nernst equation as shown in **Figure 4**. To identify the oxidizing and reducing locations in the Yucca Mountain region, this study examines the geochemical data that are relevant to the distribution of redox conditions in the SZ.



Source: BSC 2006 [DIRS 178672], Figure 2.1-2, p. F-2.
NOTES: Wells with oxidizing groundwater are shown with blue filled circles, wells with reducing groundwater are shown with red filled circles, and wells in which redox conditions have not been measured are shown with brown filled squares. Wells with both oxidizing and reducing conditions (H-1 and 19-D) are shown with half-filled circles. The repository is outlined in blue in the north-central part of the map, and Highway 95 is shown as the blue line in the southern part of the map.

Figure 2. Map showing locations of wells with oxidizing and reducing groundwater **[3].**

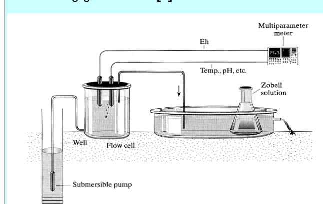


Figure 3. Field apparatus for Eh measurements **[8]**.

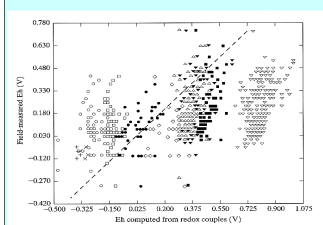


Figure 4. Plot of Eh values computed from the Nernst equation vs. field-measured Eh values **[8]**.

The dashed line represents a perfect correlation between measured and calculated Eh. It is clear that there is little correlation between the values of Eh measured directly via the platinum electrode, and those calculated from the Nernst equation from redox pairs.

Methods

Data Set

Ground water chemistry data were obtained from the Nye County Nuclear Waste Repository Project Office (NWRPO) website as of March 2003 **[4]** and a Los Alamos National Laboratory report **[5]**. Data were compiled into a single database, covering the Amargosa Desert region. The data set consisted of major ion data from 73 sampling locations, presented on **Figure 1**. For the wells that have more than one testing zone, the average of the major ions concentration was taken to reduce the number of sampling locations to 41.

Methods

Hydrochemical Modeling

PHREEQC software was used to calculate the Saturation Indices (SI) for the 41 locations in the region.

Methods

Multivariate Statistical Methods

The Multivariate Statistical Methods (MSMs) applied herein are principal component factor analysis (PCFA) and k-means cluster analysis (CA). PCFA is a dimension-reduction method and CA is a classification method. Using STATISTICA™8, a PCFA was performed on major ion data, Fluoride and Silica data and species near saturation data, obtained by applying PHREEQC to the major ion data, from 41 wells in the Amargosa Desert region, to reduce the number of variables from 20 to a 4. In addition, a rotation of the first four factors was conducted to find relationships among the original variables. From the rotated factors of the ion chemistry, factor scores were generated for each of the 41 wells, thus producing a loading table indicating the decomposition of each of the samples into the 4 rotated factors. Using the same statistical software, the factor scores from the rotated PCFA results were then evaluated with the *k-means* CA to cluster wells with a similar composition into seven separate sample groups, or chemical facies. The *k-means* CA variables are the four factor scores, and the observations are the factor scores for each sampling location.

Methods

Biplot

A biplot is simultaneous bi-variate (factor loadings and factor scores) scatter plot that provides a visual picture of the relationships between and among different ions and sampling locations; in addition, it shows objective sampling location groupings. Each factor, with a certain chemical composition, implies a dominating hydrochemical process, and a clustered group implies a hydrochemical facies with similar genesis, evolution and/or composition **[6]** indicated by the underlying factors. The first two rotated factor loadings for major ions and factor scores for each sampling location, grouped into hydrochemical facies, are presented in the biplot on **Figure 5.** The biplot presented here has two scales: one for factor scores of sampling locations (i.e., bottom and left), and the other for factor loadings of ions (i.e., top and right).

Methods

Locations of Wells with Oxidizing and Reducing Gw on DEM

Surfer™ 8 software was used to plot the location of wells with oxidizing and reducing groundwater in the Digital Elevation Model (DEM) of the study region.

Methods

Logistic Regression

Logistic regression was used to predict independent variables based on categorical dependent variables and to determine the percent of variance in the independent variables explained by the dependent variables. It was also used to rank the relative importance of independent variables related to the dependent variables; to assess interaction effects; and to understand the impact of covariate control variables. The impact of predictor variables is usually explained in terms of odds ratios **[7]**.

Using STATISTICA™ 8, logistic regression was performed using redox state as the categorical variable (dependent variable) and the major ions as the independent variables for the 41 locations in the Yucca Mountain region to rank the relative importance of independent variables that have significant effect on the redox state.

Results

Hydrochemical Modeling

Table 1 Indicates that the groundwater in the area is near saturation with respect to aragonite ($CaCO_3$), calcite ($CaCO_3$), chalcedony (SiO_2), dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), sepiolite ($Mg_2Si_3O_7.5OH:3H_2O$) and amorphous silicate (SiO_2).

Reactions among aqueous species that occur within the same oxidation state as the elements involved (e.g., $CO_2/HCO_3^-/CO_3^{2-}$; SO_4^{2-}/ HSO^{4-}) are rapid and equilibrium can be assumed; in contrast, equilibrium is usually not attained between aqueous species with differing oxidation states (e.g., SO_4^{2-}/HS^-; $HCO3^-/CH_4$). A small number of minerals, usually of relatively high solubility, appear to behave reversibly in natural systems (e.g., calcite, gypsum, halite, and fluorite); most other minerals do not react to equilibrium but can still have an important effect on natural-water chemistry (i.e., primary silicates).

Table 1. Chemical Species Saturation Indices in the Yucca Mountain Region

Species	MV	MV	Mean	St.dev	% NS
Anhydrite	-5.12	-1.68	-2.70	0.69	0.00
Calcite	-1.85	1.08	-0.03	0.47	78.00
Chrysotile	-11.60	5.83	-3.20	2.55	8.00
Dolomite	-4.18	2.31	-0.60	1.10	40.00
Fluorite	-3.45	0.19	-1.10	0.57	16.00
Gypsum	-4.93	-1.46	-2.50	0.70	0.00
Halite	-8.33	-6.44	-7.50	0.48	0.00
Sepiolite	-7.25	3.73	-1.75	1.80	15.00
SiO2(a)	-1.35	0.19	-0.39	0.19	78.00
Talc	-7.11	9.97	1.33	2.60	12.00

Results

MSM, PCFA

Rotated factor loading distributions for each variable are presented in **Table 2**, along with the amount of total proportional variation explained by each rotated factor. High loading indicates a high degree of correlation. Factor 1 explains 27.30% of the variation and is dominated by Ca^{2+} , Mg^{2+} , anhydrate and gypsum, which are typically associated with the dissolution of carbonate. Factor 2 explains 24.10% of the variation and is primarily composed of calcite, chrysotile, dolomite, sepiolite and talc, which are also primarily related to carbonate dissolution. The first two rotated factor represented about 51.40% of the variation, whereas Factor 3 and Factor 4 together explain nearly 35% of the variation with dominant species of Na^+, total alkalinity, TDS and halite in the third factor and silica in the fourth factor. The remaining factors (17) explain only 13.7% of the system and are therefore omitted.

Table 2 Rotated factor loadings for major ions and SI

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Ca	**0.91**	0.15	0.14	0.06
Mg	**0.78**	0.31	0.21	-0.07
Na	-0.15	0.21	**0.94**	-0.02
K	0.45	0.06	0.51	0.59
Cl	0.53	0.08	0.65	0.03
SO4	0.69	0.32	0.49	-0.09
Total Alkalinity	0.30	0.28	**0.83**	0.07
Pseudo TDS	0.47	0.29	**0.80**	0.11
F	-0.50	-0.26	0.53	0.07
SiO2	-0.15	0.17	0.02	**0.94**
Anhydrite	**0.95**	0.03	0.09	0.07
Calcite	0.38	**0.81**	0.25	-0.06
Chrysotile	0.037	**0.97**	0.15	0.06
Dolomite	0.47	**0.80**	0.27	0.08
Fluorite	0.42	-0.37	0.18	0.33
Gypsum	**0.96**	0.04	0.09	0.06
Halite	0.23	0.18	**0.92**	-0.09
Sepiolite	0.07	**0.97**	0.13	0.13
SiO2(a)	0.08	0.07	-0.11	**0.95**
Talc	0.09	**0.97**	0.15	0.13
Variation	5.44	4.87	4.60	2.37
Percentage	27.30%	24.10%	23.10%	11.80%

Results

MSM, CA

Agreement between the derived groups and lithology validates these groups as hydrochemical facies. The dominant redox state in the Yucca Mountain West Face, Fortymile Wash, Amargosa Desert North East, and Yucca Mountain South East is oxidizing. Where as it is reducing in the Amargosa Desert North East and Yucca Mountain East Face as shown in the **Table 3** below.

Table 3
Summary of Redox Conditions Derived by Cluster Analysis of Rotated Factor Scores

Group Name	Number of Sampling Locations	Dominant Redox State
Yucca Mountain West Face	2	Oxidizing
Fortymile Wash	12	Oxidizing
Amargosa Desert North East	3	Oxidizing
Amargosa Desert North West	2	reducing
Yucca mountain East Face	10	reducing
Yucca Mountain South	10	Oxidizing
Yucca Mountain South East	2	reducing
Total Number	41	

Results

Biplot

Figure 5 below shows the principal component analysis biplot with samples grouped into seven hydrochemical facies and relevant major ions and SI. Sampling locations are shown as symbols and ions are shown as vectors with their end located at the factor loading values indicated in **Table 2** for that ion. Each ion vector indicates the direction of increasing ion content in the samples, and their projection onto the factor axis is proportional to their correlation to that factor.

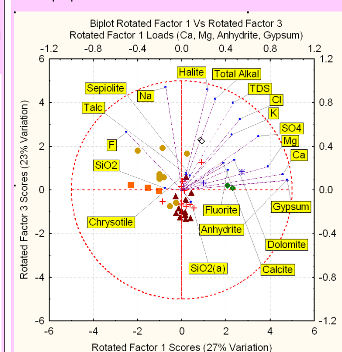


Figure 5. Biplot Rotated Factor 1 Vs Rotated Factor 3

Conclusions

The working hypothesis of this study is that redox conditions are related to the major ion chemistry of the groundwater – even when the ions themselves are not redox-sensitive.

The logistic regression model and the multivariate statistical analysis could be a good tool to determine the redox conditions in the groundwater using major ions data. Work is ongoing to validate this hypothesis.

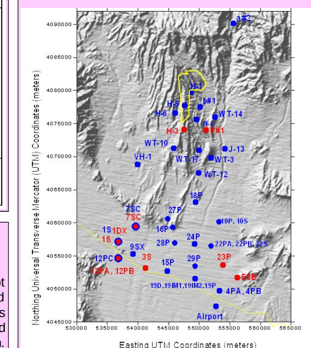
Acknowledgments

The Nye County NWRPO funded this work through a grant provided by the U.S. Department of Energy Office of Civilian Radioactive Waste Management. We also thank the Center for Environmental Resource Management of The University of Texas at El Paso for their funding and support.

Results

DEM

Figure 6 below shows the location of wells with oxidizing and reducing groundwater plotted on a DEM of the study region. Wells with oxidizing groundwater are shown with blue circles, wells with reducing groundwater are shown with red circles.



Wells with oxidizing GW are shown with blue circles, wells with reducing GW are shown with red circles.
Wells with both oxidizing and reducing are shown with red blue circles.

Results

Logistic Regression

The logistic regression model test shows that Na^+, K^+, and TDS as the most relative important independent variables that have a statistically significant relationship to oxidizing/reducing conditions in Yucca Mountain SZ (e.i. their high presence indicates a higher likelihood of finding reducing conditions), as shown in **Table 4**.

Table 4. Logistic Regression Modeled Probability that Redox Condition is Reducing

	Estimate	Standard - Error	Wald - Stat.	p
Intercept	0.57	2.20	0.07	0.80
Ca	0.10	0.08	1.65	0.20
Mg	0.21	0.15	2.04	0.15
Na	0.10	0.05	4.16	0.04
K	0.33	0.16	4.25	0.04
Cl	0.19	0.12	2.68	0.10
SO4	0.05	0.04	1.55	0.21
Total Alkalinity	0.08	0.05	2.55	0.11
Pseudo TDS	-0.08	0.04	4.86	0.03
F	0.84	0.44	3.63	0.06

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