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TECHNICAL MEMORANDUM

REPORT ON THE GEOSTATISTICAL ANALYSIS OF MATERIALS SAMPLED FROM THE SOUTH SPOIL AND HILLSIDE WASTE ROCK DUMPS AT THE MIDNITE MINE, WASHINGTON STATE

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Region 10

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Geochemical characterization studies were performed on waste rock samples taken from the Hillside and South Spoil dumps, at the Midnite Uranium Mine, in 1992 and 1994. Details of the sampling and analytical protocols and methods are provided by Altringer and Froisland (1993) and Moore, Price and Gardner (1994). Initial geochemical descriptions were based upon analyses of 2 drill core samples extracted from the South Spoil dump, and 3 drill core samples removed from the Hillside dump. Sampling was attempted at 5 feet depth intervals within each core, down to depths of 165 feet (South Spoil dump) and 132 feet (Hillside dump). The drilling program returned sample sizes of 39 (South Spoil) and 58 (Hillside).

Both dumps were re-sampled, more extensively, in 1994. Eleven drill cores were developed in the South Spoil dump, and 6 drill holes in the Hillside dump. Composites of waste rock were removed at 5 feet intervals, down to depths ranging from 75 feet to 190 feet, varying with location. In total, the 1994 drilling campaign yielded rock sample sizes of 299 (South Spoil) and 109 (Hillside), in addition to those extracted in 1992. For the purposes of initial, exploratory and descriptive analyses, geochemical data from Hillside and South Spoil samples were combined. Subsequent analyses were performed to detect geochemical differences between the samples, using statistically objective criteria.

Geochemical analyses of the samples included a type of acid-base accounting, paste pH determinations, and measurements of total metal and selected metalloid concentrations. Kinetic, humidity cell tests were also performed on selected sub-samples of South Spoil and Hillside waste rock. Moore et al (1994) present the results of these analyses in tables of unprocessed data. No statistical summaries of analyses were performed on the data.

URS Greiner Woodward Clyde (URSGWC) reviewed the 1992 and 1994 data sets, and provided preliminary summaries of "key indicator" geochemical variables (URSGWC, 1999 a & b). The review included an initial assessment of the statistical adequacy of both data sets, and concluded that more formal numerical analyses of the data should be performed. The results of formal numerical analyses would form the basis of recommendations for additional rock sampling and geochemical analysis, if necessary to provide a more reliable description of dump geochemistry and potential drainage quality, and to assist the selection of remedial technologies for dump closure.

This report describes methods of data reduction, transformation and formal statistical analysis applied to both 1992 and 1994 geochemical data sets. Analyses included basic statistical descriptions of waste rock geochemistry, together with multivariate pattern analysis and analysis of variance. In addition to analyses of results generated from static descriptions of acid-base balance and geochemical constituent concentrations in rock samples, results of kinetic testing were subjected to time series evaluation. Analyses of kinetic test data aimed to clarify any uncertainties regarding geochemical weathering of rock over time, and resultant drainage quality.

The overall aim of the analyses was to provide a statistically reliable description of the geochemical characteristics of the South Spoil and Hillside dumps. The results of the analyses would assist decisions with regard to the management of surface run-off and drainage from the dumps, and their final surface reclamation. The development of a statistically reliable description of dump geochemistry using existing data required the following key objectives to be achieved:

- Conversion of large data sets into manageable spreadsheet formats
- Determinations of the statistical distribution of all measured variables
- Identification of appropriate descriptive and inferential statistical methods suited to data characteristics and hypothesis testing
- Determination of necessary data transformations and standardization
- Application of standard, univariate descriptive methods to summarize geochemical variables
- Application of multivariate analytical techniques to -

Identify "key indicator” variables on the basis of variance and/or constancy

Detect underlying structure and pattern

Detect redundancy in individuals (excessive sample size) and their attributes (measured variables)

Reduce the large data sets to "principal components" or “factors” which adequately summarize the important geochemical characteristics of the waste rock samples

Analysis of variance to estimate the geochemical variability and the significance of differences within samples (by depth) and between samples (by drill core), and their interaction, if any.

3.1 DATA MANAGEMENT

URSGWC were presented with two data sets containing both real and integer geochemical measurements, and text characters. Numeric values were presented in various units of measurement, and ratios. A high frequency of missing data or measurements below the analytical limits of detection were evident. Elements of redundancy in measured attributes (high intercorrelation between variables) also existed.

Statistical analysis of the data required that 1992 and 1994 measurements were to be managed such that:

- All measurements below the detection limit would be set to 50% of the limit
- Occasional missing data for a given variable within a sample would be substituted by a mean value for the sample
- Frequent missing data for a variable within a sample would require the removal of the variable from future analysis
- Redundant variables would be removed from the analysis
- All measurements would be converted from integer to real values
- Most constituent concentrations would be converted into mg/kg units
- Several constituent concentrations would be represented as % values, by mass
- Data would be standardized and transformed as required by statistical analytical methods.

Both 1992 and 1994 data sets were converted into Microsoft EXCEL spreadsheet format. All data transformations and descriptive and inferential statistical analyses were performed using the proprietary “Statistica” package. Due to the large sample sizes involved, 1992 and 1994 data sets were managed and analyzed separately. The reduced data sets used in the assessment of static ABA, metal and non-metal analyses are attached as Appendix A.1.

3.2 UNIVARIATE AND DESCRIPTIVE METHODS

The distribution of each measured variable within the 1992 and 1994 data sets was estimated semi-quantitatively from probability curves. Due to the presence of skewed, non-normal distributions for several variables, geochemical measurements were summarized as both means with standard errors, and median values with ranges. The statistical adequacy of the data was inferred initially from distribution patterns and the standard error:mean ratios for each variable. The mean value of a variable was considered to be a reliable estimate of the true population if the standard error $\leq 0.1 \times$ mean.

Global mean and median values were computed for each variable, as well as for each core and each depth interval, for both South Spoil and Hillside dumps. Preliminary trend analysis was performed by plotting measurements of each variable with depth and core location. The within- and between-sample variability of each attribute was summarized using "box and whisker" plots of median and range values.

3.3 MULTIVARIATE PATTERN ANALYSIS

More robust trend and pattern analyses were performed using optimized principal components analysis (PCA). The application of this method also served to identify main sources of geochemical variability and constancy within and between samples, detect redundancy within the data sets, and reduce the two complex spreadsheets to fewer, more manageable, "composite" variables. The purpose of this analysis was to identify key geochemical indicator variables, eliminate "redundant" variables on the basis of high correlations with other variables, and reduce the extent of future geochemical analysis, to the extent possible.

Normal probability plots of each variable revealed non-Gaussian distributions of measurements for several variables, such as calcium concentration and gross acid potential (refer to Figures 3.1a&b). Although measurements of several variables were normally distributed, such as uranium and iron concentrations (Figures 3.2 a&b), overall multivariate normality of the 1992 and 1994 data sets was not evident.

Given the lack of multivariate normality within the data sets, and the orders of magnitude range of measurements between variables, PCA was applied to ranked data. The transformation of measured data to ranks effectively converted PCA from a parametric technique, sensitive to data distribution, to a distribution-insensitive, non-parametric method. VARIMAX rotation of axes was used to maximize the amount of matrix variance accounted for by eigen vector extraction. An eigen vector may be interpreted as a best-fit regression line through a multi-dimensional array of variable axes.

The level of geochemical variance accounted for by each eigen vector was estimated as the eigen value for each principal component. The analysis was optimized by plotting the cumulative eigen value against successive principal components, and subjectively identifying the asymptote of the curve beyond which point additional components (eigen vectors) accounted for little variance within the data set.

Multivariate analysis of the 1992 and 1994 data sets aimed to provide the following information:

- Significance of correlation or association between geochemical variables, and potential sources of information redundancy
- Geochemical similarities or differences between drill core samples and sample depths, and potential for sample combination or removal
- Within and between sample variability and the identification of important "key indicator" variables, based upon variance and/or constancy
- Synthetic, composite parameters which adequately characterize the samples, and which may be used in subsequent analyses in place of a full suite of independent variables.

3.4 ANALYSIS OF VARIANCE

Based upon the results of multivariate analysis and the detection of key indicator variables, formal analyses of variance (ANOVA) were performed on all variables measured in the 1992 survey, and "important" or "key indicator" geochemical variables identified by PCA of 1994 data. The aim of the analyses was to determine the significance of geochemical differences between waste rock cores and sample depths within South Spoil and Hillside rock dumps. From this, the overall two-dimensional homogeneity or variability of the rock dumps could be inferred.

The results of *a priori* tests of data homogeneity, and probability plots of key geochemical variables, indicated that parametric ANOVA could not be applied without data transformation. Therefore, each analysis was performed as a 2-Way ANOVA with interaction, applied to symmetric sets of ranked data, without missing values.

4.1 ACID-BASE BALANCE AND ACID GENERATION POTENTIAL

Descriptive Overview

Statistical descriptions of combined South Spoil and Hillside waste rock geochemistry are summarized in Appendix C2. Initial estimates of variability and reliability were based upon variance (standard error): mean ratios. Summaries of relatively limited 1992 data indicated high levels of variability, particularly with respect to parameters associated with acid-base balance. Less variability was detected in the set of 1994 measurements, probably as a consequence of the larger size of the South Spoil sample. Partitioning of variance between South Spoil and Hillside samples indicated the statistical adequacy and reliability of the South Spoil sample. However, variability in measurements of most geochemical parameters remained high for the Hillside sample, thereby indicating the unreliability of mean values for use as “predictors” for most variables.

Analyses of 1992 and 1994 data, pooled across all cores, indicated mean sample pH values of 7.36 ± 0.067 and 7.37 ± 0.055, respectively. Waste rock paste pH for the combined data sets ranged from 4.15 to 10.4; the most frequent values showing materials from both dumps to be generally circum-neutral to alkaline. Site-specific analysis of 1992 data showed significant variability in pH measurements within several core samples , particularly those sampled from the South Spoil dump. For example, high pH variability was detected within South Spoil core #14 within which measurements varied from alkaline to pH = 4.6. The more acidic materials were located within a mid-elevation zone of 40 - 75 feet depth.

Results of 1994 analyses confirmed variability in the pH of waste rock sampled from both South Spoil and Hillside dumps. Within the context of a generally calcareous waste rock matrix, measurements of $\text{pH} < 6.0$ were considered to be evidence of net acid generation by pyritic waste materials and/or dissociated metals, such as aluminum (Al) and iron (Fe).

Approximately 10% of South Spoil waste rock samples indicated $\text{pH} < 6.0$, down to pH = 4.15. The distribution of acidic materials was predominantly limited to mid- to deep level depths (50 - 145 feet) within the South Spoils dump, although acidity was also detected in several upper horizon samples (0 - 40 feet).

Measurements of pH in Hillside dump samples were also variable (range = 4.6 - 8.3), with about 16% of the sample indicating $\text{pH} < 6.0$. Low pH materials were distributed across all depths within the Hillside dump. The horizontal and spatial variability of waste rock paste pH is summarized in Figure 4.1, in which cores 1 - 11 and 12 - 17 were derived from South Spoil and Hillside dumps, respectively. Paste pH values < 6.0 were invariably associated with materials of low to very low net neutralization potential (NNP) which occurred in both Hillside and South Spoil dumps.

The acid-base balance (NNP) of waste rock samples was calculated as the difference between estimated gross acid potential (AP) and neutralization potential (NP). Acid potential was estimated empirically from measurements of the total sulfur content of rock, as follows:

$$AP = 31.25 \times \%S.$$

Neutralization potentials were inferred from the measured carbonate content of the rock samples, which was likely to underestimate NP. Both of these estimates provided a conservative basis for calculating waste rock NNP, where NNP = NP - AP (t Ca CO_3 equivalent / kt rock). The following diagnostic criteria were applied to the detection of potentially net acid generating materials in both waste rock dumps:

- If NNP $\geq$ +20 t $CaCO_3$ equiv./kt, the material is not net acid generating
- If + 20 t/kt > NNP > - 20 t/kt, the material's net acid generation potential is uncertain (usually requiring additional, kinetic analysis)
- If NNP $\leq$ - 20 t $CaCO_3$ equiv./kt rock, the material is likely to be net acid generating.

Using these criteria, the combined 1992 and 1994 analyses confirmed that approximately 16% of the South Spoil rock samples were net acid generating, whereas <1% of the Hillside materials were confirmed to have net acid generation potential. Although, the majority (>99%) of Hillside materials were classified as having uncertain net acid generation potential, 16% of the rock had already generated acidity (pH<6.0). Additionally, none of the Hillside rock was confirmed to have significantly positive NNP. In this context, Hillside materials differed from South Spoil rock, of which 51% showed confirmed net neutralizing potential. However, the remaining 27% of the South Spoil dump samples were classified as having uncertain net acid generation potential, requiring further analysis. Approximately 10% of these "uncertain" materials showed evidence of actual acid generation (paste pH < 6.0).

Site-specific results of static ABA analysis are summarized in Table 4.1.

Table 4.1
FREQUENCIES OF PROJECTED ACID GENERATION POTENTIALS BASED UPON STATIC ABA ANALYSIS OF WASTE ROCK

Dump Location	Survey Year	Potentially Acid Generating	Non-Acid Generating	Uncertain Behavior
South Spoil	1992	0.13	0.46	0.41
South Spoil	1994	0.18	0.55	0.27
Hillside	1992	0.00	0.02	0.98
Hillside	1994	0.00	0.01	0.99

All measured parameters related to the acid-base balance of waste rock in the South Spoil dump (%S, $\%CO_3$, [Mg], [Ca], Gross AP, Gross NP) showed marked variability within- and between core samples. Consequently, estimates of NNP for South Spoil samples were also highly variable (range = -81 to + 412 kg $CaCO_3$ / t rock [1994 data]). The statistical significance of the differences in acid-base balance between core samples removed from the South Spoil dump was confirmed by two-way analysis of variance. The results of ANOVA confirmed significant differences between South Spoil and Hillside core acid-base balance ($p \ll 0.01$). The results of ANOVA for ABA-related parameters are summarized in Appendix B1.

Although less variable than South Spoil material Hillside samples generally showed lower and more or less constant levels of total S, and therefore lower and more uniform gross AP than South Spoil samples (Figure 4.2).

Generally lower $CaCO_3$ concentrations in Hillside dump materials, and correspondingly lower gross NP of Hillside rock, provided an overall average NNP which was lower than that calculated for South Spoil samples. The comparative variability of ABA parameters measured for both dumps is summarized in Appendix B2. The uniformity and constancy of ABA-related measurements within- and between Hillside rock samples is suspect.

Multivariate Analysis of Acid-Base Balance

More detailed numerical analysis of 1992 and 1994 data indicated significant positive correlations between paste pH measurements and geochemical variables, which generally influence NNP estimates (concentrations of carbonate [CO_3], calcium [Ca] and magnesium [Mg]). Significantly negative correlations were detected between paste pH and generic indicators of acid generation potential (concentrations of total sulfur [S], sulfate [SO_4], Al and Fe). These statistical relationships were mechanistically and intuitively reasonable, and were supported by specific bivariate plots, which indicated approximately linear, inverse relationships between pH and total concentrations of Al and Fe (Figure 4.3). Regression equations developed from these correlations may have predictive value with regard to future net acid generation potential of the waste rock. Similarly, regression analysis of pH and NNP data indicated a quadratic relationship which also has potential predictive value (Figure 4.4).

The results of principal components analysis (PCA) of ranked data (equivalent non-parametric factor analysis) confirmed the significance of relationships between key acid-base balance variables, which are summarized as Pearson Product Moment Correlation Coefficients in Appendix B3.

Evaluation of eigen values and eigen vector coefficients for each factor indicated significant potential for reducing both 1992 and 1994 data sets to fewer, composite variables (principal components). In doing so, future requirements for geochemical and numerical analyses can be reduced and simplified. Multivariate analysis of 1992 and 1994 data sets accounted for > 75% geochemical variance between samples. Two-dimensional ordinations of geochemical variables (eigen vector loadings plotted against the first two principal components) clearly showed close relationships between variables associated with acid generation, and between variables associated with acid neutralization (Figure 4.5).

Ordination of 1992 samples in two-component space provided an overall indication of geochemical similarities and differences between samples, and the wide variation in geochemical characteristics between- and within cores sampled from both dumps (Figure 4.6). As a general rule, ordination diagrams of this type are interpreted on the basis of distances between variables and samples plotted in two-axis space. Geochemically similar individuals within a sample will be located by x-y coordinates which tend to cluster; samples which have different geochemical signatures are separated in two-axis ordination space. Similarly, geochemical variables which are clustered indicate similar distributions within- and between-rock dumps. The most important observation arising from the site ordination shown in Figure 4.6 is the absence of any clear geochemical gradients, which may have been associated with depth effects, and the absence of sample clustering which may have differentiated the Hillside and South Spoil dumps. Site ordinations could not be plotted for the 1994 survey, due to excessive redundancy (repetition) of site data, and high levels of correlation between geochemical variables. This result confirmed over-sampling and analysis of strongly related geochemical variables in the 1994 survey, with particular reference to South Spoil dump characterization.

For both 1992 and 1994 data sets, approximately 75% of the geochemical variability within and between samples (cores) was accounted for by four principal components. Evaluation of factor loadings (correlation coefficients between original and composite variables), explained the principal components of the data sets, as shown in Table 4.2:

Table 4.2
GEOCHEMICAL VARIABLES FOUND TO BE HIGHLY CORRELATED WITH THE PRINCIPAL COMPONENTS OF SOUTH SPOIL AND HILLSIDE DUMP GEOCHEMISTRY

Data set	Principal component 1	Principal component 2	Principal component 3	Principal component 4
1992	NNP, CO_3 , Ca, Mg (39%)	AP, S, SO_4,Cu (22%)	U (10%)	Mn (6%)
1994	NNP, CO_3 Ca, pH (37%)	AP, S, SO_4 (23%)	U (8%)	Mn (7%)

These results showed that most of the geochemical variability within and between the Hillside and South Spoil dumps was accounted for by factors related to the acid-base balance of the samples, with some minor variance accounted for by sample concentrations of copper (Cu), manganese (Mn) and uranium (U). Levels of all other geochemical variables measured in the analysis were relatively constant throughout the samples. Therefore, subsequent analyses were performed only on these "principal" or "key indicator" geochemical variables. Detailed results of multivariate analysis of both 1992 and 1994 data sets are provided in Appendix B4.

4.2 TOTAL METALS AND METALLOID ANALYSIS

Descriptive Overview

Several trace elements of potential importance were removed from both the 1992 and 1994 data sets due to their concentrations mostly being less than the limits of detection set for the geochemical analyses. Elements removed from the analyses, and their limits of detection, are listed in Table 4.3:

Table 4.3
ELEMENTS REMOVED FROM STATISTICAL EVALUATION OF GEOCHEMICAL DATA DUE TO HIGH FREQUENCY OF ANALYTICAL NON-DETECTION

Element	Approximate Detection Limit (mg/kg)
Arsenic As	6,000
Boron B	1,000
Barium Ba	200
Cobalt Co	860
Chromium Cr	700
Molybdenum Mo	1,200
Nickel Ni	5,000
Phosphorus P	15,400
Lead Pb	5,000
Thorium Th	1,800
Vanadium V	800

The detection limits set for the listed trace elements were unusually high. The removal of these constituents from the analyses created a false homogeneity regarding the metal and metalloid geochemistry of rock samples. This apparent homogeneity was reinforced by the relatively uniform distributions of copper (Cu) and zinc (Zn) in the samples. In a statistical sense, the false homogeneity of the 1992 and 1994 data sets limited the metals analysis to relatively common major elements such as Al, Ca, Fe, Mg and Mn, and the trace elements, Cd, Cu and Zn. Due to its ubiquitous distribution and apparent level of enrichment in both dumps, total U concentrations were also included in the analysis.

Total concentrations of Al, Ca, Fe, Mg and Mn measured in 1992 and 1994 surveys fell within ranges expected for native calcareous soils and rocks of the western United States. The analytical detection limits for B, Co, Mo, Ni, Pb and Th were set above the criteria at which constituents may be considered to be at "enriched" concentrations (Bowen, 1979). Consequently, concentrations of these elements could not be identified as being elevated or normal. Concentrations of barium (Ba) in rock samples were generally below detection limits, which were set below the mean crustal abundance for the element. Therefore, Ba can not be regarded as a constituent of potential concern within waste rock at Midnite mine. Although possibly occurring at concentrations below enrichment criteria, the extent to which chromium (Cr) and vanadium (V) exceeded mean crustal abundance, if at all, could not be confirmed. Of the trace elements measured above detection limits, Cu and Cd were occasionally detected at levels which may be considered as elevated to enriched, whereas Zn was found to occur within the normal concentration range. In general, concentrations of total U were found to exceed either the mean crustal abundance of the element, or enrichment concentrations.

Biplot comparisons of constituent concentrations measured across all drill cores and sampling depths in 1992 and 1994 showed potentially significant geochemical variability within and between samples, particularly between core locations. Graphical analyses of both data sets indicated higher average concentrations of Al in Hillside samples, relative to South Spoil materials. Conversely, mean concentrations of total Ca, Cd, Mg, Mn and Zn were higher in South Spoil waste rock. For several elements, notably Cu and U, biplot analyses of 1992 and 1994 data yielded conflicting results. However, on the basis of more extensive analytical data from the 1994 survey, both Cu and U concentrations were found to be higher in South Spoil materials. The variability of constituent concentrations over sampling depth was generally too high to subjectively determine depth trends from biplot graphs. The variability of constituent concentrations over depth is presented as a series of "box and whisker plots of median and range values, in Appendix B6. Linear regression analyses mostly failed to detect any significant, depth-related trends (eg: Figure 4.7). However, the possibility of U and S concentrations decreasing with depth was detected (Figure 4.8).

Multivariate Analysis of Elemental Distribution

Results of PCA applied to ranked data confirmed Al, Ca, Cu, Mg, Mn and U to be the principal sources of metal variability within the reduced data sets. However, the relative importance of these elements is likely to have been inflated by the removal of elements occurring below the selected detection limits, and several trace elements occurring at uniformly low concentrations within the samples. Therefore, the current analysis was unable to detect key metal indicator variables or composite principal components which may be regarded as truly representative of the trace (heavy) metal geochemistry of the waste rock at Midnite mine.

Numerical analyses of metals which influence acid-base balance (Al, Ca and Mg), have been presented in previous sections of this report. For both 1992 and 1994 data sets, both Ca and Mg showed similar distribution patterns with significantly higher concentrations and variability evident in South Spoil materials, relative to Hillside samples.

Concentrations of Ca and Mg in Hillside waste rock were generally lower than expected for "normal" soils and rocks of the western USA, and indicated low acid neutralization potential.

Concentrations of major metals which may contribute to the total acidity of waste rock drainage (Al, Fe and Mn) were found to be highly variable in both South Spoil and Hillside samples. Two-way ANOVA of 1992 data confirmed statistically significant ($p << 0.01$) differences in mean Al concentrations between core samples. Measurements recorded in 1994 showed highest Al concentrations to occur in Hillside materials, and provided a reliable basis for pH prediction in both dumps.

Although mean concentrations of Fe were generally higher in South Spoils materials than Hillside waste rock, the within-sample variance of both dumps was large. Consequently, a statistically significant difference between cores and dumps could not be determined. This observation was also evident in the results of 1994 analyses. Mean concentrations of Mn measured in South Spoil and Hillside samples varied markedly, with concentrations in South Spoil material exceeding those measured in Hillside materials. The differences between cores taken from both dumps was confirmed to be statistically significant ($p<<0.01$). Summaries of variance in major metal concentrations in rock, and of the results of two-way ANOVA of 1992 geochemical data, are presented in Appendix B5.

The most important secondary elements (Cu, Mn and U) were found to account for less geochemical variance in both 1992 and 1994 data sets. This suggested that concentrations of these elements may be more uniformly distributed throughout the samples. These "trace" elements may be regarded as probable constituents of concern due to the elevated levels of Cu and U in both Hillside and South Spoils samples, and the potentially high solubility of U and Mn in both alkaline and acidic run-off and drainage.

Measurements of total U in 1992 samples of both South Spoil and Hillside material indicated general enrichment to concentrations above the upper range expected for normal soils and rocks of the western USA. Mean core concentrations were higher in Hillside than South Spoil waste rock. Both data sets also confirmed a high degree of within- and between sample variability, with differences between samples being statistically significant.

Analyses of trace metals (Cd, Cu and Zn) concentrations recorded in the 1992 survey also showed significant differences between mean core concentrations, and between dumps. Concentrations of Cd and Zn were generally higher in South Spoil, relative to Hillside waste rock, with Cd concentrations in both dumps exceeding mean crustal abundance values. Several samples of waste rock in South Spoil dump contained levels of Cd which may be considered as enriched, relative to conventional crustal abundance indices. Zinc concentrations were generally within the normal range for soils.

Concentrations of Cu varied significantly between sample cores, with highest mean values occurring in Hillside materials. Several samples in both dumps indicated elevated Cu concentrations.

Results of two-way ANOVA of 1992 data are summarized in Appendix B5.

Analysis of Variance of Principal Geochemical Components

Two-way ANOVA with interactive terms was applied to ranked data from 1994 surveys. The analyses focused only on those variables which were found to be significant sources of geochemical variability by multivariate modeling (i.e.: those accounting for greatest variance, and showing highest significant correlations with the first four principal components of PCA). The variables selected for ANOVA, using more comprehensive 1994 data were:

- Ca and Al (highest scores on PCA vector 1)
- S and Cu (highest scores on PCA vector 2)
- U (highest score on PCA vector 3)
- Mn (highest score of PCA vector 4).

These variables may be regarded as key indicator variables which characterize the overall geochemistry and variability within and between waste rock sampled from South Spoil and Hillside dumps.

Results of two-way ANOVA applied to 1994 measurements of concentrations of these variables showed statistically significant differences between sample core locations and depths, for each variable. The significance of differences between and within core samples, for each indicator variable, is summarized in Table 4.8. A more detailed description of sample variability and the results of ANOVA is provided in Appendix B7.

Table 4.8
SUMMARY OF THE RESULTS OF TWO-WAY ANOVA APPLIED TO “IMPORTANT” VARIABLES DETECTED BY PCA

Variable	Effect	F-ratio	Significance	Effect	F-ratio	Significance	Dump
Ca	Core	32.9	P<0.01	Depth	3.9	P< 0.01	SS
Al	Core	27.4	“	Depth	6.6	“	H
S	Core	15.5	“	Depth	6.5	“	SS
Cu	Core	19.6	“	Depth	6.8	“	SS
U	Core	7.4	“	Depth	3.8	“	SS
Mn	Core	24.6	“	Depth	2.5	“	SS

Results of ANOVA supported the preliminary conclusions, based upon variance: mean ratios and ANOVA of 1992 data, regarding the high degree of geochemical variability between core samples, and the probable unreliability of using a mean value for any geochemical variable as a descriptive, diagnostic or predictive tool. The geochemical differences between samples also indicated generally higher concentrations of most key indicator constituents in the South Spoil samples, than in Hillside material. Exceptionally, concentrations of total Al and U were significantly higher in Hillside waste rock than in South Spoil material. This observation suggested that the net acid generating potential of Hillside rock, although currently classified as "uncertain", may be potentially high in waste rock which has poor buffering capacity, and relatively high concentrations of total Al.

4.3 STATISTICAL ADEQUACY OF CURRENT GEOCHEMICAL DATA

At this stage, it can be concluded that South Spoil waste rock was probably over-sampled. South Spoil data also generally showed high levels of information redundancy due to measurement of numerous strongly-related variables. Although analyses of metal and metalloid constituents were limited to a reduced suite of elements, sufficient information was gained to infer the likely quality of rock drainage. In the light of field observations and the inferred probability of acid rock drainage formation, trace metals are likely to occur at elevated concentrations in dump drainage. Several constituents, such as Mn, U, and Zn will be soluble within both acidic and alkaline drainage.

Irrespective of several trace metal constituents being excluded from the analysis, sample adequacy was confirmed for major base metals (Al, Ca, Fe, and Mg), several trace metals (Cd, Cu, Mn, and Zn), and uranium.

Although the results of metal analyses confirmed sample adequacy and reliable estimates of constituent ranges in the waste rock, some uncertainty existed with regard to the net acid generation potential of the waste materials, particularly those sampled from the Hillside dump. However, measurements of pH, Al, and Fe in rock of “uncertain” acid generating behavior indicated the probability of a significant proportion of “unclassified” rock being net acid generating. Field observations of actual acid rock drainage occurring in the vicinity of both dumps support this view. Uncertainty regarding long term behavior of waste rock, and its potential to generate acidic drainage, was resolved by analyses of kinetic test data. Results of kinetic analyses are presented in Section 5 of this report.

Kinetic, humidity cell analyses were performed by the Bureau of Mines on samples of South Spoil and Hillside waste rock, in 1992 and 1994. The tests were performed over a 20 – 24 week period which is regarded as minimal relative to similar large-scale geochemical studies of this type, which run for up to two years. Consequently, the relatively short-term data derived from the humidity cell study is likely to be inadequate for meaningful, predictive time series analysis of drainage quality.

5.1 WASTE ROCK SAMPLING FOR KINETIC ANALYSIS

South Spoil waste rock was sampled from two cores drilled to a maximum depth of 135 feet in 1992, and 11 cores drilled to a maximum depth of 185 feet in 1994. The 1992 and 1994 sampling programs provided a total of 17 and 23 waste rock composites, respectively.

Waste rock from Hillside dump was sampled less extensively with only 2 drill cores from which 3 composite samples were collected in 1992, and 4 composite samples collected in 1994. Sampling depths ranged from 5 - 95 feet (1992) and 0 - 75 feet (1994). The statistical and scientific rationale underlying the sampling protocol remain unclear.

Due to the limited extent of the 1992 sampling program, reported problems with sample collection and the subsequent analysis of samples biased towards fine fraction materials (Moore *et al*, 1994) only the results of kinetic testing of materials sampled in 1994 were used as the basis for predicting drainage quality from both South Spoil and Hillside dumps. Numerical analyses were performed on individual and averaged measurements of drainage quality for each of the four Hillside dump humidity cells. The 23 data sets derived from kinetic testing of South Spoil rock were grouped as shown in Table 5.1.

Table 5.1
DEPTH INTERVAL GROUPING OF WASTE ROCK SAMPLED FROM SOUTH SPOIL DUMP

Group	Depth Interval (feet)	Sample Size (n)
1	0- 20	4
2	21-40	3
3	41-80	8
4	100-135	4
5	140-185	4

Water quality parameters measured in leachates collected weekly, over a period of 20 to 24 weeks, from each humidity cell were:

- **Cations** Al, Ba, Ca, Fe, Mg, Cd, Cu, Mn, Si, Zn, U
- **Anions** SO_4
- **Physico-chemical** Electroconductivity (Ec), RedOx potential (E_h) and pH.

This suite of water quality parameters is not comprehensive, and omits several key anionic and cationic variables which are relevant to Tribal water quality standards, notably:

- Sb, As, Be, Cl, CN, F, Pb, Hg, NO_3 , NO_2 , Se, Ag, Th

However, the range of variables is sufficient for assisting remedial technology selection. In addition to time series analysis of measured variables, numerical analyses were performed on a calculated index of acid rock drainage generation based upon the molar ratio of dissolved Ca and Mg, relative to dissolved sulfate. The ratio provides an indication of the relative rate of sulfur oxidation and CO_3 depletion, though acid neutralization. The following criteria were used as preliminary diagnostic indicators of acid rock drainage potential:

- If $[Mg] + [Ca] : [SO_4] < 2.0$, then relatively rapid S oxidation, acid generation and subsequent neutralization are indicated
- If $[Mg] + [Ca] : [SO_4] > 2.0$, then relatively slow S oxidation is indicated, together with probable CO_3 depletion occurring as dissolution in neutral to alkaline pore water.

Calculations of the rates of sulfide oxidation, acid generation and alkalinity consumption could not be completed, due to a lack of quantitative information regarding dry sample masses and ratio of water to sample mass used within the humidity cells.

5.2 NUMERICAL ANALYSES OF HUMIDITY CELL LEACHATE QUALITY

Basic statistical descriptions of leachate quality from each South Spoil group of cells, and each individual Hillside cell, were summarized using means and ranges for each variable. Changes in leachate quality were compared with U.S. Environmental Protection Agency (EPA) drinking water and Tribal standards.

Changes in drainage quality over time were analyzed graphically, with "best fit" temporal trends fitted by linear, quadratic or polynomial regression analysis, as appropriate. Drainage quality projections were attempted with the use of time series analysis. The time series analysis model selected as the most generally appropriate used a damped exponential smoothing method.

5.3 RESULTS

Acid Drainage Generation

Measurements of leachate pH derived from South Spoil humidity cells were neutral to slightly alkaline. Exceptionally, drainage pH derived from South Spoil wastes sampled at the 100 – 135’ depth interval showed a trend of decreasing pH, down to pH = 6.47. This pH level is marginally below EPA drinking water and Tribal water quality standards, but is indicative of the likely decrease in drainage pH for all samples.

A general tendency for initial increases in drainage pH to be followed by a decrease, was generally evident (Figure 5.1a). A similar averaged trend was also evident for drainage derived from cells of Hillside dump rock (Figure 5.1b). However, the pH of Hillside cell drainage varied with depth, and showed clear evidence of acid generation throughout the depth profile (Figures 5.2 a-d). Lowest drainage pH (pH = 3.83) was generated by Hillside waste rock sampled at the 30-35 feet interval, and was correlated with high sulfate concentrations.

Initial sulfate concentrations were elevated in leachates generated by both South Spoil and Hillside materials. Initially high sulfate concentrations may be indicative of weathering and sulfide oxidation under relatively dry conditions, after which the weathering products are flushed by higher rainfall and infiltration rates. Although the initial sulfate concentrations in drainage were elevated, levels rapidly reduced to fall within Federal and Tribal standards.

The potential for acid rock drainage generation in the Hillside waste rock sample was confirmed by analysis of the molar concentration ratios of $[Mg] + [Ca] / [SO_4]$, estimated from measurements of dissolved Mg, Ca and SO_4 in humidity cell leachates. This preliminary frame of reference indicated that, on average, drainage from both South Spoil and Hillside waste rock cells was characterized by ratios < 2.0, which increased over time (Figures 5.3 a & b). Therefore, acidic drainage may be expected in at least the medium term, from both South Spoil and Hillside waste rock, irrespective of the neutral to alkaline pH of relatively short term drainage collected over 20 – 24 weeks of South Spoil humidity cell testing. Exceptionally, drainage from South Spoil rock sampled at the 140 – 185 feet depth interval, showed rapid increase in the Mg/Ca: SO_4 ratio, to yield estimates > 2.0, usually associated with leachates from non-acid generating materials (Figure 5.4). This observation is consistent with the results of static acid-base accounting, which indicated significant variability in ABA characteristics along the profiles of sample cores, with several occurrences of higher NNP values at mid- to lower depths.

Although the results of drainage analysis from Hillside cells confirmed the net acid generation potential of the rock, aspects of the analysis were suspect. In addition to the small total sample size (n=4), and a minimal depth interval sub-sample size (n=1), changes in ARD-related constituent concentrations over time were identical for each variable (Figure 5.5 a & b). Subsequent analyses of variations in concentrations of all dissolved constituents over time also showed identical distribution patterns (refer to Appendix C2). The overall trend of approximately negative exponential decay in constituent concentrations over time is a theoretically convenient way of describing the changes in cell drainage generated by controlled weathering of varying rock types and geochemical characteristics. However, identical and precise exponential decay responses for all dissolved constituents and rocks of varying mineralogy and geochemistry is highly improbable. Consequently, all results of humidity cell testing performed on Hillside waste rock were graphically summarized for recording purposes, but were removed from further analysis, due to probable unreliability.

Dissolved Constituents

Primary base metal cations and anions related to acid drainage potential

Temporal changes in the concentrations of Mg, Ca and sulfate in humidity cell leachates have been discussed previously in relation to acid rock drainage prediction. In general, dissolved concentrations of each of these constituents decreased over time as a negative exponential series (Figure 5.6 a & b). This type of response is expected in relatively dry climatic environments where weathering products accumulate on rock surfaces, between rainfall events. Rock drainage generated by rainfall and leaching is usually characterized by elevated concentrations of soluble weathering products which decrease with progressive "flushing" from the system. Although an overall decrease in Mg, Ca and SO_4 concentrations was indicated for South Spoils material, each constituent showed post-flushing stabilization towards equilibrium concentrations. This trend suggested relatively slow sulfide oxidation and carbonate consumption which, when expressed as a molar ratio, indicated longer term potential for ARD generation in both dumps. Measurements of drainage pH were highly correlated with concentrations of dissolved sulfate (Figure 5.7). However, the magnitude of ARD generation may be moderated by the buffering capacity of silicates, as well as base metal carbonates. Therefore, analyses of acid-base balance and predictions of long term acid generation, should be performed within a the context of host rock mineralogy. In particular, the ratio of calc – alumino silicates (eg: chlorite and epidote), if present, to other less reactive alumino silicates, such as feldspars, should be considered.

A preliminary evaluation of silicate activity was performed using measurements of dissolved silicon (Si) in humidity cell leachates. Overall, soluble Si concentrations were found to be highly variable over sampling depth interval, and time. As a general trend, soluble Si concentrations in rock leachate were found to increase slightly over time to reach a constant equilibrium level (Figure 5.8). This indicated the probable mobilization of reactive silicates as a consequence of acid generation. However, quantitative estimates of the rates of S oxidation and acid-sulfate release, and rates of consumption of carbonate/silicate buffers could not be calculated from the data provided.

Secondary cations associated with acid drainage potential

The temporal change in dissolved constituents, most likely varying as a function of pH, ionic solution strength and time, is described in Figure 5.9a. When this average trend was smoothed and extrapolated for predictive purposes, solution stabilization towards a final equilibrium condition was confirmed. However, damped exponential smoothing was found to markedly overestimate solution conductivity, as observed when applied to each dissolved constituent (Figure 5.9b).

Concentrations of dissolved Al and Fe in South Spoil and Hillside dump drainage were initially elevated but decreased over time to meet EPA drinking water standards. However, dissolved Al in leachates from all samples exceeded Tribal criteria. This trend was adequately summarized by representative negative polynomial series decay for Al (Figure 5.10).

The temporal behavior of Fe in rock drainage was highly variable. Regression analysis indicated solubility patterns to vary with sample depth. Presumably pre-weathered and leached waste rock sampled from the upper 5 feet of South Spoil dump showed a logarithmic reduction in Fe concentration over time, possibly due to the lower solubility of higher oxidation state (Fe^{3+}) species (Figure 5.11 a). Conversely, unweathered waste rock sampled at depth (140 – 185 feet) showed progressive increase in dissolved Fe concentration over time (Figure 5.11b). Previous static analyses of Al and Fe in both South Spoil and Hillside dumps confirmed a strong inverse relationship between rock paste pH and total Al and Fe concentration. This relationship is explained in terms of the contribution of Al and Fe ion dissociation on the total acidity of waste rock pore water. Although the relationship between pH and dissolved Al was not as clear from the analysis of humidity cell test data, the strong inverse relationship between pH and dissolved Fe concentration was confirmed (Figure 5.12).

Concentrations of constituents dissolved in waste rock leachates are compared with Federal and Tribal standards in Table 5.1.

Table 5.1
COMPARISON OF INITIAL AND FINAL CONCENTRATIONS OF DISSOLVED CONSTITUENTS IN HUMIDITY CELL DRAINAGE WITH EPA DRINKING WATER AND TRIBAL WATER QUALITY STANDARDS

Water quality parameters	Concentration range in South Spoil leachates (mg/l)	Concentration range in Hillside leachates (mg/l)	Federal drinking water standard (mg/l)	Tribal standard (mg/l)
Al	0.183 - 1.825	0.18 - 6.0	0.2	0.05
Ba	0.007 - 0.055	0.005 - 0.032	2.0	2.0
Cd	0.001 - 0.011	0.0015 - 0.024	0.005	0.005
Cu	0.015 - 0.034 *	0.015 - 0.171	1.3	1.0
Fe	0.073 - 2.119	0.16 - 6.77	0.3	0.3
Mn	0.135 - 55.80	0.615 - 71.125	0.05	0.05
U	0.015 - 2.17	0.288 - 30.21	-	-
Zn	0.003 - 0.311	0.036 - 3.62	5.0	5.0
SO_4	30.25 - 2,360	14.75 – 1,357	50	250
pH	6.47 - 8.04	3.83 - 8.31 **	6.5-8.5	6.5-8.5

All dissolved constituents showed a general trend of decreasing concentration over time, except Cu * in near-surface samples of South Spoil waste rock, and pH ** which indicated a parabolic response over time.

Trace Constituents

Patterns of temporal change in trace constituent concentrations in South Spoil cell drainage differed according to metal type and sampling interval. This supported the conclusion that South Spoil waste rock is both geochemically and mineralogically variable. However, an overall trend of decreasing concentrations of trace metals over time was generally evident. This trend could be summarized approximately by any of the decay curves plotted for any depth interval, as shown for Ba, Cd, U and Zn in Figures 5.13 to 5.16. Exceptionally, temporal trends in dissolved Cu concentrations varied markedly over sample depth interval. Although Cu concentrations decreased in drainage collected from rock sampled at mid-level to deep sampling intervals, drainage from near-surface samples showed rapidly increasing concentrations in dissolved Cu after 17 weeks of weathering (Figure 5.17a&b). Nevertheless, initial and final concentrations of Ba, Cu and Zn in leachates generated by South Spoil and Hillside waste rock samples were within Federal drinking water and Tribal standards. Concentrations of Cd in drainage from all samples initially exceeded water quality standards. Exceptionally, Mn concentrations in all drainage samples were consistently elevated above Federal drinking water and Tribal standards.

6.1 STATIC ANALYSES

Preliminary screening of 1992 static analytical data indicated a high level of geochemical variability within the South Spoil and Hillside waste rock samples. The level of variability was less pronounced in the 1994 analysis, probably as a consequence of the large South Spoil sample size. However, variance partitioning confirmed potential unreliability of mean values of geochemical parameters measured in Hillside materials. This suggested that mean values of variables, at least for the Hillside data set, can not be used as reliable summaries of waste rock geochemistry, and that attention should be focused upon ranges and percentiles.

Measurements of parameters associated with acid-base balance and the potential acid-generating behavior of waste rock were significant sources of variance and uncertainty in both South Spoil and Hillside samples. Measurements of all ABA parameters varied widely within and between core samples, and indicated potentially significant differences between the acid-base balances of the South Spoil and Hillside dumps.

Significant uncertainty was associated with the calculated net neutralizing potentials (NNP) of materials sampled from both dumps. Using results of 1994 analysis, 55% of the South Spoil rock samples indicated high NNP associated with a very low probability of ARD generation. However, 18% were confirmed as potentially acid generating materials, with 27% falling within a range of behavioral uncertainty. Approximately 99% of the Hillside samples were also classified as materials of uncertain acid generating behavior. Nevertheless, approximately 16% of these “uncertain” rock types showed evidence of actual acid generation, which corresponded with supporting field observations.

As a general trend, all low paste pH materials were significantly correlated with low NNP. Additionally, significant inverse correlations were detected between pH and a suite of geochemical variables known to influence waste rock acidity. These parameters included S, SO_4, Al and Fe. These relationships have potential predictive value, and may be used to circumvent the need for further ABA analysis.

Results of principal components analysis (PCA) revealed the effects of over-sampling and redundant analysis of South Spoils materials. Although, this redundancy was not evident in either the 1992 or 1994 Hillside data sets, overall geochemical differences between the two dumps could not be confirmed by PCA. This suggested that the geochemical behavior of South Spoil and Hillside dumps is likely to be similar, even though the Hillside rock was inadequately characterized. Of particular importance was that PCA results showed an absence of discrete sample “clustering”, usually indicative of geochemical similarities unique to a group or groups of individuals within a sample. Therefore, it was concluded that discrete rock types can not be identified within or between the dumps, based upon current geochemical characteristics. PCA was also unable to detect systematic gradients which would otherwise indicate spatially dependent trends within or between the samples. However, PCA results did confirm the variability of both rock dumps, and the difficulty in generalizing with regard to geochemical characteristics and behavior. The results of analysis of variance (ANOVA) of 1992 and 1994 data sets confirmed the geochemical heterogeneity of both dumps, although systematic trends could not be determined.

It was concluded that the principal geochemical characteristics of waste rock in both dumps could be summarized in terms of selected acid-base balance parameters and total concentrations of uranium, manganese and copper. Although several key trace elements were absent from the analysis, sufficient reliable information was gained from the analysis to assist the review of remedial alternatives and the selection of appropriate surface reclamation and erosion control methods. It was concluded that total metal concentrations and both actual and potential waste rock acidity were not sufficiently high to limit surface reclamation and erosion control success. However, technology selection should be determined on the basis of water quality objectives and objective cost:benefit analysis of alternatives. The need for further geochemical analyses was not evident in this regard.

6.2 KINETIC ANALYSES

Statistical sampling and technical inadequacies associated with the analysis of Hillside waste rock (1992 and 1994), and South Spoil waste rock (1992) were sufficient to preclude most results of kinetic testing from further consideration. Therefore, the geochemical behavior of Hillside waste rock under weathering conditions, and its potential for acid drainage generation, remain unconfirmed in a theoretical sense. However, review of selected Hillside data associated with drainage pH and key indicators of acid generation potential, showed significant potential for acidic drainage generation. This inference was supported by field observations of actual acid rock drainage generation, high total concentrations of Al and Fe (both of which were significantly correlated with rock acidity), and the occurrence of low pH in up to 16% of “uncertain” rock samples.

Both waste rock sampling and analytical methods applied to South Spoil materials in 1994 were adequate for statistical assessment of leachate data. However, waste rock leachate data derived from South Spoil humidity cell analyses may be regarded as relatively short term, and possibly inadequate for the accurate prediction of long term drainage quality. Regardless of this limitation, measurements of cell drainage pH, and estimates of base metal:sulfate ratios indicated both actual and potential acid generation in South Spoil and Hillside samples. Sulfide oxidation and carbonate consumption appeared to be slow in South Spoil waste rock, but actual rates could not be inferred from the data provided. However, calculated ratios of Mg, Ca, and SO_4 in Hillside and South Spoil leachates indicated longer term acid generation potential.

Time series analysis of change in concentrations of all dissolved constituents generally showed strong evidence of build-up and flushing of weathering/oxidation products over time. Some anomalous variations were occasionally seen, as for Cu, at different sample depths.

Initially high dissolved sulfate concentrations and their inverse correlation with drainage pH suggested progressive sulfide oxidation and rapid removal of soluble oxidation products when flushed. The initial quality of humidity cell leachates was likely to be representative of drainage chemistry following periods of prolonged weathering under relatively dry conditions, followed by significant rainfall events. In this context, the behavior of constituents such as Mn, U and Zn is important, due to their solubility over a range of drainage pH, including alkaline conditions. Results of kinetic testing showed initially high concentrations of each metal, with Mn being elevated above Federal drinking water and Tribal standards throughout the test period.

Several key water quality variables were omitted from the analysis. Those which are relevant to Tribal water quality criteria include:

Sb, As, Be, Cl, Cr, F, Pb, Hg, CN, NO_3, NO_2 , Se, Ag, Th

The absence of these variables from the analysis does not limit the use of existing leachate data in broadly characterizing future rock drainage, using key indicator variables, for the purpose of identifying potential mitigation technologies. Further kinetic testing is not recommended at this stage.

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