Geochemical characteristics of a waste rock repository at a western gold mine
by Jason Dwayne Outlaw

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation
Montana State University

Abstract:
This study was conducted to determine the extent of weathering in a large pyritic waste rock repository, characterize its geochemical variations, and correlate the extent of weathering with physical waste rock characteristics. Field sampling activities revealed a highly variable waste rock pile made up of distinct layers of material. Chemical characteristics of waste rock varied greatly between layers throughout the repository. To investigate the associations that may exist between waste rock chemical variables, a correlation analysis was performed on waste rock chemical data. Sample titratable acidity was correlated with soluble SO4 (r = 0.8299), soluble Fe (r - 0.7919), soluble Al (r = 0.9212) and electrical conductivity (r = 0.6720).

The weathering of pyritic waste rock occurs when it comes into contact with air and water. This study revealed that regions of the waste rock dump where this interface occurs were more highly weathered. Samples of waste rock taken from the upper portions of the repository contained greater levels of acidity, electrical conductivity, and water soluble SO4, aluminum and iron. Though weathering may be significantly decreased deep within the repository, chemical data confirmed that weathering may still be occurring at any location within this waste rock pile. The oldest waste rock was found deeper in the interior of the waste rock repository, but it showed the highest degree of weathering. This was supported by data that showed the oldest samples contained greater levels of acidity, electrical conductivity and water soluble SO4, iron and aluminum. Finally, salt formations found within the waste rock repository were found to include copper, magnesium and zinc sulfates.

GEOCHEMICAL CHARACTERISTICS OF A WASTE ROCK REPOSITORY AT A WESTERN GOLD MINE

by

Jason Dwayne Outlaw

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Land Rehabilitation

MONTANA STATE UNIVERSITY
Bozeman, Montana

August 1997

APPROVAL

of a thesis submitted by

Jason Dwayne Outlaw

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

August 21, 1997 — Douglas J. Dollhopf

Date — Chairperson, Graduate Committee

Approved for the Major Department

8-22-97 — [signature]

Date — Head, Major Department

Approved for the College of Graduate Studies

8/25/97 — Joseph J. Fedock

Date — Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library.

If I have indicated my intention to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis in whole or in parts may be granted only by the copyright holder.

Signature Jason D. Outlaw

Date 8-25-97

TABLE OF CONTENTS

TABLE OF CONTENTS -- Continued

LIST OF TABLES

LIST OF TABLES -- Continued

LIST OF TABLES -- Continued

LIST OF FIGURES

ABSTRACT

This study was conducted to determine the extent of weathering in a large pyritic waste rock repository, characterize its geochemical variations, and correlate the extent of weathering with physical waste rock characteristics. Field sampling activities revealed a highly variable waste rock pile made up of distinct layers of material. Chemical characteristics of waste rock varied greatly between layers throughout the repository. To investigate the associations that may exist between waste rock chemical variables, a correlation analysis was performed on waste rock chemical data. Sample titratable acidity was correlated with soluble SO_4 ($r = 0.8299$), soluble Fe ($r = 0.7919$), soluble Al ($r = 0.9212$) and electrical conductivity ($r = 0.6720$).

The weathering of pyritic waste rock occurs when it comes into contact with air and water. This study revealed that regions of the waste rock dump where this interface occurs were more highly weathered. Samples of waste rock taken from the upper portions of the repository contained greater levels of acidity, electrical conductivity, and water soluble SO_4, aluminum and iron. Though weathering may be significantly decreased deep within the repository, chemical data confirmed that weathering may still be occurring at any location within this waste rock pile. The oldest waste rock was found deeper in the interior of the waste rock repository, but it showed the highest degree of weathering. This was supported by data that showed the oldest samples contained greater levels of acidity, electrical conductivity and water soluble SO_4, iron and aluminum. Finally, salt formations found within the waste rock repository were found to include copper, magnesium and zinc sulfates.

INTRODUCTION

Acidity, metal solubilization and salt generation resulting from the weathering of waste rock containing sulfide minerals are common occurrences at hardrock mining operations in western North America and throughout the world. Waste rock is that material that must be removed in order to mine an economically important ore. This waste rock often contains iron-sulfide minerals which, after removal from their oxygen deprived - chemically reduced geologic environment, are placed on site in large repositories. This material is then exposed to air and water, facilitating weathering reactions that can produce acidity, elevated levels of sulfate, and the solubilization of metals. If a sufficient amount of water comes into contact with the repository material, acid rock drainage can occur. Acid rock drainage occurs when the products of sulfide weathering are leached into the natural environment. This can be inhibitory to plant growth and negatively affect aquatic ecosystems.

Due to the large size of most waste rock repository facilities and difficulty of sampling, little is known of the geochemical processes that occur deep within a repository over long periods of time. This study to investigate the geochemical processes deep within a waste rock repository took advantage of waste rock excavation necessitated by an episode of ground movement that took place at the Golden Sunlight Mine located in southwest Montana during 1994. Due to this ground movement, approximately 15 million tons of waste rock were off-loaded from a large repository facility. This study was conducted on the east waste rock complex that underwent excavation from July 1994 to March 1995. This provided a unique opportunity to observe materials and obtain samples from deep within a large waste rock pile.

The Golden Sunlight Mine is located in southwestern Montana approximately 8 km northeast of Whitehall along Interstate 90. (Figure 1) The mine is owned and operated by Placer Dome U.S. Inc. and has been operating since 1981, although historic mining occurred at this site beginning in the late 1800's. The site receives an average annual precipitation of 25.4 to 30.5 cm, mostly as rainfall from April to September (MAPS 1990).

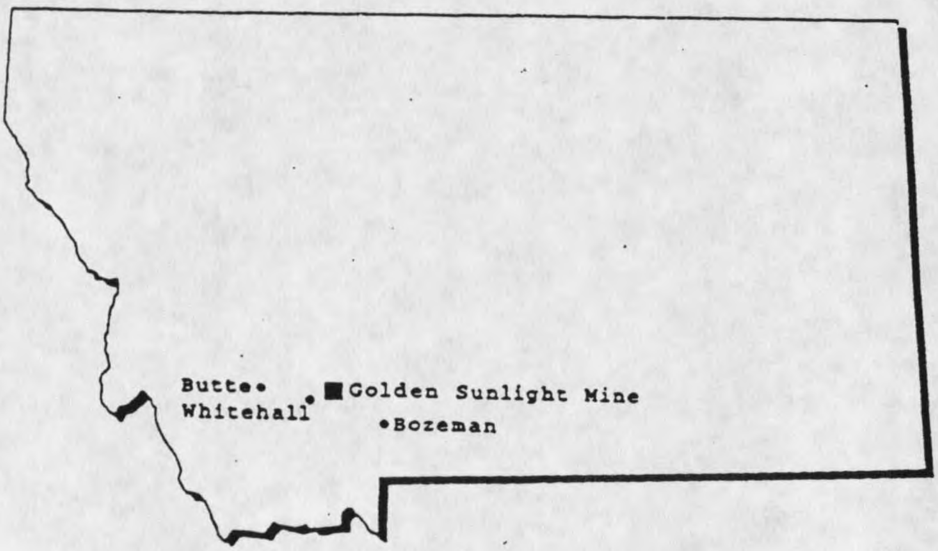

Figure 1. Location of the Golden Sunlight Mine, Whitehall, Montana.

Investigation Objectives

In order better to understand the geochemical weathering that occurs within a large waste rock repository, this investigation addressed the following research objectives:

- determine the extent of weathering in the waste rock repository;
- characterize the geochemical variations in the waste rock repository; and
- correlate the extent of weathering with waste rock particle size distribution.

LITERATURE REVIEW

Pyrite Oxidation

The oxidation of pyrite takes place when the mineral is exposed to air and water. This process involves chemical and biological reactions and is dependent on environmental conditions such as the morphology of pyrite crystals and the presence of water and oxygen.

The oxidation of pyrite by oxygen and water can be expressed in the following widely accepted reactions.

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad [1]$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + ½\ H_2O \qquad [2]$$

$$Fe^{3+} + 3\ H_2O = Fe(OH)_3 + 3\ H^+ \qquad [3]$$

These three reactions can be summarily expressed as Reaction 4.

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+ \qquad [4]$$

Reaction one indicates that the oxidation of pyrite produces ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}) and hydrogen ions (H^+). Ferrous iron produced in Reaction 1 is then oxidized to yield ferric iron (Fe^{3+}) as shown in Reaction 2. Finally, the precipitate $Fe(OH)_3$ is formed from the combination of Fe^{3+} and water (Reaction 3). This third step is a reversible dissolution/precipitation reaction and can serve as a source or sink of solution Fe^{3+} (Evangelou and Zhang, 1995).

While O_2 is the major oxidant of pyrite at neutral to alkaline pH, Singer and Stumm (1970) found Fe^{3+} to be the dominant pyrite oxidant at acidic pH levels (<3.5).

This reaction at pH < 3.5 produces 16 moles of acidity per mole of FeS_2 as shown in Reaction 5.

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad [5]$$

Because Fe^{3+} is the dominant oxidant of FeS_2, Reaction 2, which shows the production of Fe^{3+} from the oxidation of Fe^{2+}, is known as the rate-limiting step in abiotic pyrite oxidation (Singer and Stumm 1970).

When iron-oxidizing bacteria are present in the waste rock dump environment, the rate-limiting step in pyrite oxidation can be bypassed. One such iron-oxidizing bacterium is *Thiobacillus ferroxidans*, an acidophilic iron-oxidizing bacterium that is ubiquitous in geologic environments containing pyrite (Ivarson et. al. 1982). Dugan (1975) and Singer and Stumm (1970) found that iron-oxidizing bacteria such as *T. ferroxidans* can accelerate the rate of Fe^{2+} oxidation by a factor of 10^6.

Other factors influencing the rate of pyrite oxidation are pyrite grain size and morphology. Shellhorn, Sobek and Rastogi (1985) used column leach testing to show an exponential increase in acidity with decreasing particle size (increased relative surface area) of pyritic sulfur refuse. Recent research has shown that pyrite particle morphology has an even greater influence on the rate of oxidation than particle size (Jennings and Dollhopf 1995).

Waste Dump Observations

Temperature profiles of a 20-year-old pyritic waste rock dump in the Northern Territory of Australia were measured by Harries and Ritchie (1980). They found that below 6m, temperatures in the dump remained essentially unchanged through their wet/dry season cycle. Since pyrite oxidation is exothermic, they concluded that this process primarily occurred in the top 5m of the dump with some regions showing oxidation down to 15m.

Harries and Ritchie (1985) also studied the pore gas composition of this Australian waste rock dump. They found that in most regions of the dump, oxygen supply was the oxidation-rate-limiting mechanism. Oxygen levels in this dump were highly variable, ranging from <1% to approximately 20% of atmospheric conditions. In some areas of the dump, oxygen content was near 20% in the top 2m but declined rapidly to <1% as depth increased, leveling off at <1% for depths greater than 5m. In other areas, oxygen content was shown to decrease from near 20% to less than 10% as depth ranged from 0 to 5m, then increased to a maximum of 19% at a depth of 13m. It was determined that the main oxygen transport mechanisms in the dump were likely to be diffusion, due to concentration gradients, and advection, caused by thermal effects and atmospheric pressure changes.

Schafer et al. (1994) performed a monitoring study on a waste rock pile at the Golden Sunlight Mine to compare reclaimed and unreclaimed waste rock dumps. They found that rock particle size gradually increased with depth due to gravity sorting in the end-dumping sequence. Freshly shot waste rock was determined to have a volumetric water content of less than 6 percent. Residual saturation was found to vary between 8 and 12 percent within the dump with residual saturation generally lower near the base of the dump where larger particles are deposited. Fine waste rock produced by vehicle compaction at the top of each bench was found to have a residual saturation level ranging from 15 to 20 percent.

Whitney, Esposito and Sweeney (1995) conducted a study to describe the distribution of secondary alteration minerals within an excavated pyritic mine dump near Central City, Colorado. They identified four mineralogical zones distributed vertically within the dump: a surficial, relatively unaltered zone; a leached zone; a cemented zone in which pore spaces are filled with the minerals copiapite ($Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20\ H_2O$) and coquimbite ($Fe^{3+}_2(SO_4)_3 \cdot 9\ H_2O$); and an interior relatively unaltered zone.

Due to difficulty in sampling material found deep inside waste rock repositories, documentation concerning how waste rock weathers over long periods of time is nonexistent. This geochemical study, analyzing a range of samples collected throughout a large waste rock repository, is unique in this aspect.

MATERIALS AND METHODS

Waste Rock Sample Collection

The field sampling program was conducted simultaneously with excavation of the east waste rock complex. Excavation using electric shovels and 175 ton haul trucks began at the top of the waste rock pile at 1682 m (5520 ft) elevation and continued downward in approximately 12 to 18 m benches to the 1588 m (5210 ft) elevation level. Sampling occurred in 30 test pits that were located along two north-south and two east-west transect lines. The locations of these test pits with elevations are shown in Figure 2. Overall, 121 waste rock samples were collected for geochemical analysis.

Prior to the removal of each bench, transect lines were located by Golden Sunlight Mine survey staff and test pits were excavated to permit sampling. In this manner, sampling occurred along established transect lines at approximately 1.8 m vertical intervals throughout the portion of the east waste rock dump that was excavated.

Test pits were excavated to depths ranging from 3 to 4.6 m. One wall of each test pit was left vertical for logging and sampling while the other was sloped for safety concerns. Distinct layering of waste rock material was observed in the waste rock pile and was defined by changes in particle size and/or Munsell color. Each layer within a test pit was given a unique sample number (for example, TP10GS3 refers to test pit number 10 layer 3). The logs for each test pit are presented in Appendix B. A bulk sample was taken from each layer and transported to Montana State University for analysis. Sample

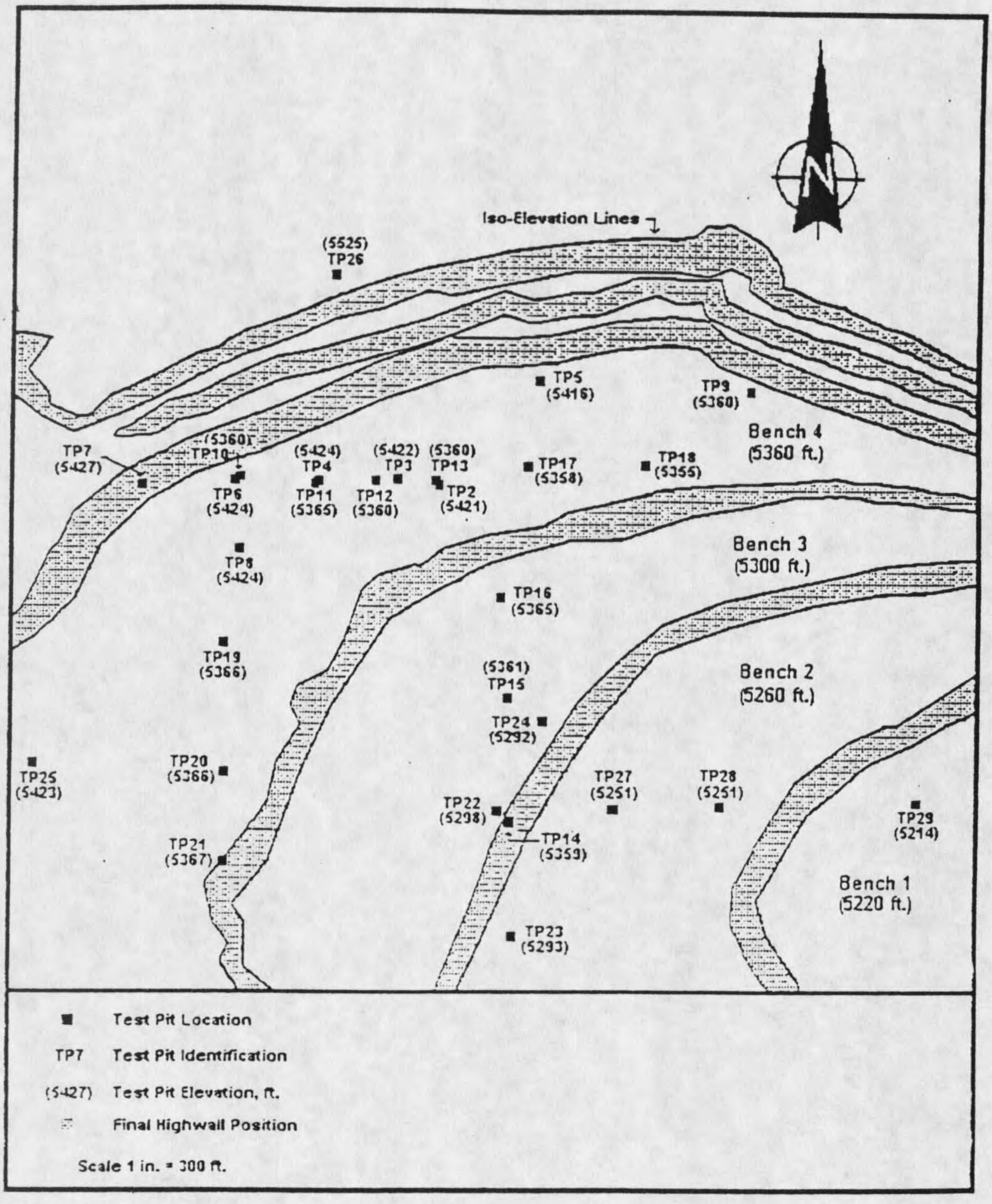

Figure 2. Overhead view of waste rock repository with test pit locations and elevations.

collection occurred concurrently with sample collection by researchers from the University of Saskatchewan who were performing a hydrogeologic study of this waste rock dump. Identical sample identification numbers were used by each university to facilitate data sharing and collaboration.

Analytical Procedures

Bulk samples were analyzed for particle size (ASTM D421-85). Aggregates were broken with a mortar and rubber-tipped pestle, then sieved by hand using metal sieves to obtain a <2mm diameter size fraction. It should be noted that while coarse layers were encountered in the waste rock pile, sampling of very coarse materials (>20 cm diameter) was prohibitive for practical reasons. A portion of the <2 mm diameter size fraction from each bulk sample was used for a 1:1 paste extraction (Methods of Soil Analysis, 1983, Method 10-2.3.2). Due to the low porosity of waste rock samples, a 1:1 paste extraction was chosen to ensure the collection of sufficient extract to analyze the entire suite of chemical variables. In addition, a 1:1 paste ensures that each sample is extracted at the same soil to water ratio, as opposed to the subjective variability involved in preparing a saturated paste. This water extract was analyzed for pH (Methods of Soil Analysis, 1965, Method 60-3.1.2), electrical conductivity (EC) (Methods of Soil Analysis, 1965, Method 62-2.2.3), soluble iron (Fe), aluminum (Al), manganese (Mn) and sulfate (SO_4) (Methods of Soil Analysis, 1965, Method 62-1.3.2.1) and titratable acidity (TA) to pH 7 (Standard Methods for the Examination of Water and Wastewater, p. 2-30). Waste rock of <2mm size was analyzed for potential acidity and sulfur fractionation, including total sulfur

(TS), hot water extractable sulfur (H_2O-S), HCl extractable sulfur (HCl-S), HNO_3 extractable sulfur (HNO_3-S), residual sulfur (Res-S) and neutralization potential (NP) (Modified Sobek et. al., 1978). The hot water extraction is intended to remove sulfur from the readily soluble calcium, magnesium and sodium sulfates. Sulfate sulfur existing in less soluble minerals such as Jarosite ($KFe_3(SO_4)_2(OH)_6$) is removed with the HCl extraction. The HNO_3 extraction serves to extract the sulfide sulfur that exists as pyrite and the residual sulfur is a measure of the organic sulfur in the sample.

The parameters pH, EC, titratable acidity and soluble Fe, Al, Mn and SO_4 were measured by the Soil Analytical Laboratory at Montana State University. To monitor the precision of analysis, laboratory replicates were entered into the sample set at a 10 percent rate. Replicate relative percent difference (RPD) averaged 2.2% pH, 9.1% EC, 5.6% titratable acidity, 8.2% soluble Al, 5.8% soluble Fe, 7.1% soluble Mn, and 4.1% soluble SO_4.

Neutralization potential and the sulfur fractionation parameters were measured by Energy Laboratories, Inc. in Billings, MT. Laboratory replicates were entered into the sample set at a 10 percent rate. Replicate RPD averaged 11.3% neutralization potential, 1.8% total sulfur, 19.9% hot water extractable sulfur, 12.1% HCl extractable sulfur, 2.4% HNO_3 extractable sulfur, and 11.1% residual sulfur.

In order to analyze the data based on age, position, and percent passing a 2mm sieve, the data were divided into three age categories, four elevation categories, and four particle size separation categories. Achieving relatively uniform sample sizes was the basis for the delineation of categories. Measurements below analytical detection limits were adjusted for inclusion in the development of all categories. This adjustment multiplied respective analytical detection limits by a factor of 0.7 to obtain a numerical value (Severson 1979).

In cases where data populations were normal or where data transformations could be applied to normalize populations, a one-way analysis of variance (ANOVA) was conducted using a 95 percent confidence interval. Where the p-value for the observed F statistic was less than or equal to 0.05, the hypothesis of equality of means was rejected. Data sets with unequal means were then subjected to the Student-Newman-Keuls means separation procedure at the 0.05 level of significance.

In cases where data populations could not be normalized through transformation, a one-way ANOVA on ranks was performed using a 95 percent confidence interval. Where the p-value for the observed H statistic was less than or equal to 0.05, the hypothesis of equality of medians was rejected. Data sets with unequal medians were then subjected to the Dunn's separation procedure at the 0.05 level of significance. Results were reported with respect to sample means.

<u>Determination of Sample Ages</u>

Sample ages were determined using drawings supplied by Golden Sunlight Mines, Inc. Drawings for the years 1987, 1988, 1989, 1990, 1992 and 1993 were provided which document the crest and toe position of the repository for each year. Figure 3 shows the waste rock dump study area areal view with the locations of cross-sections. Figures 4, 5, 6 and 7 show cross-sections A-A′, B-B′, C-C′ and D-D′, respectively. These cross-sections show the crest and toe positions of the repository for each year along with the locations of test pits. Test pit 29 was excavated in material placed in 1994. The location of test pit 29 in Figure 5 is shown outside the last toe and crest position due to the unavailability of toe and crest positions for 1994.

Since new material is placed on the repository by end-dumping from the edge, the oldest aged material is found not at the lowest elevations of the repository but farther toward the interior from the edge. This can be seen by examining Figures 4 through 7. Thus, sampling at higher elevations in the waste rock pile encountered not just new material, but materials of varying ages. To support this, a correlation analysis was performed on test pit elevations vs. material age. While the correlation was significant ($p = 0.007$), a low r-squared value of 0.24 hinders interpretation because only 24 percent of the variability in age can be attributed to elevation.