THE RELATIONSHIP BETWEEN WASTE ROCK GEOCHEMISTRY, AGE AND REACTIVITY[1]

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Abstract. Understanding the relationship between variables controlling the propensity for acid rock drainage in the 4000 acre historic Robinson District near Ely, NV, required a detailed understanding of dump conditions. Profiles of O_2, pH, temperature and specific conductivity were collected from various waste rock dumps that represent a continuum of oxide/sulfide, leached/unleached dumps of different ages from across the site. Young sulfide dumps were characterized by background ambient temperature and rapid oxygen consumption, resulting in the development of a steep oxygen gradient from atmospheric levels at the surface of the dump to near zero levels a few feet into the dump. The temperature of young dumps has yet to increase while recognizable decreases in pH and increases in specific conductivity are just starting. Eventually, the oxidation rate slows, resulting in oxygen levels closer to atmospheric in the dump. During this stage, the pH and SC profiles develop, indicating zones of advanced oxidation and neutralization, and the dump may also develop an elevated temperature gradient. In the mature stage, a sulfide dump exhibits close to atmospheric oxygen levels throughout, similar to an oxide dump profile, but remains exothermic. In conjunction with pH, chemical and SC profiles, these data identified dumps that require remedial measures compared to those that require only minimal action prior to closure.

Introduction

The use of temperature and oxygen profiles in the analysis of historic waste rock dumps provide insight into the kinetics and evolution of pyrite oxidation in different rock types over time. Oxygen profiles reflect the current rate of oxidation, while temperature profiles reflect the history of oxidation in the dump. These profiles, coupled with geochemical and geotechnical data provide an understanding of which dumps are oxidizing, how, and why, and provide information necessary to optimize future dump design and implement appropriate remedial strategies for historic dumps.

The presence of several historic waste rock dumps at BHP Robinson Operations presents an opportunity to gather data from dumps of various ages, providing a time-lapse picture of the evolution of pyrite oxidation in different waste rock types, beginning in the early 1900s and continuing to the present. The layering of waste rock from different eras of mining at the site has resulted in a complex assemblage of dumps. Data gathered in this study were used to characterize the various dumps and determine the basic dump type, history of oxidation, and buffering behavior of the dump.

In addition to characterizing the geochemical behavior of the dumps, these data are being used to develop a refined waste rock model that will expand on traditional 1-dimensional Davis-Ritchie type models (Davis and Ritchie, 1986) to include a 2-dimensional representation of diffusive and convective transport of oxygen within the dump profile.

Pyrite Oxidation

Understanding the evolution of pyrite oxidation in a waste rock dump is the first step towards determining whether or not the dump will produce acid rock drainage (ARD), over what time period, and in what quantities. The common mechanisms for pyrite oxidation are represented by:

$$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \qquad (1)$$
$$\Delta H = 1440 \text{ kJ/mol}$$

$$2\,FeSO_4 + H_2SO_4 + {}^1\!/_2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (2)$$
$$\Delta H = 102 \text{ kJ/mol}$$

$$FeS_2 + Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow 3FeSO_4 + 2H_2SO_4 \qquad (3)$$

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Below a pH of 3, the oxidation of pyrite by ferric ion (Equation 3) becomes faster than oxidation by oxygen (Equation 1). Bacteria such as *Thiobacillus ferrooxidans* catalyze the oxidation of the ferrous ion (Equation 2), increasing the rate of pyrite oxidation by ten to a hundred times under field conditions (Ritchie, 1994). Hence, pyrite oxidation is dependent on a supply of oxygen and water, and results in a release of heat.

The consumption of oxygen and the exothermic nature of pyrite oxidation result in the development of temperature and oxygen gradients that evolve as the oxidation process progresses. Neither profile provides a complete picture by itself, both profiles must be considered in order to form a complete picture of oxidation in a waste rock dump. A new sulfide dump starts out with a background thermal gradient, indistinguishable from an oxide dump, except for a steep oxygen gradient formed as oxidation begins, rapidly consuming all oxygen in the dump. Over time, the dump slowly heats, and the oxygen profile advances into the dump. A mature sulfide dump may have an oxygen profile similar to that of an oxide dump, yet the temperature profile will indicate a substantial heating of the dump caused by years of pyrite oxidation.

The shape of the temperature and oxygen profiles in a dump is controlled by the rate at which oxygen diffuses into the dump and the rate at which it is consumed within the dump. A high oxidation rate will result in release of heat and will be reflected by higher temperatures within the dump. A low oxidation rate may allow nearly atmospheric levels of oxygen to exist within the dump, yet slowly over time the dump will heat up as excess heat from the oxidation reaction builds up inside the dump.

Methods

Two methods were employed to collect temperature and oxygen profiles in the Robinson District, a hand driven soil gas probe, and a down-hole device lowered into open bore holes. Both devices allow collection of oxygen and temperature readings from various depths, with each method having its own advantages.

Soil Gas Probe

A soil probe consisting of a drive point with a retractable gas sampling port on the tip and several three foot sections of pipe was driven into the ground using a slide hammer or sledge. At various depths, an oxygen meter fitted with a sample pump was used to extract pore gas from depth. The readings were monitored until the O_2 level stabilized, then recorded. At the final depth of the probe, a temperature sensor was lowered down the inside of the pipe and temperatures recorded at various depths. The probe was then extracted from the ground using a slide hammer.

This method works best for shallow investigations to depths of less than ten feet. The probe is difficult to advance into boulder-laden waste rock due to the high probability of encountering refusal. In rare instances, the probe can be advanced as much as fifteen feet into a dump, but more typically, refusal is encountered after three feet. Despite these limitations, a shallow probe usually provides enough data to determine whether oxygen levels drop off quickly in the dump, or are at atmospheric levels throughout. The probe can be advanced several times in the same area in a short amount of time, allowing the investigation of spatial variability in the profiles. Another advantage is the lack of any heavy equipment requirements, which allows one person to carry all necessary equipment and reach areas of the mine site that are no longer maintained and may be inaccessible by vehicle.

Eleven soil probe oxygen profiles were collected at seven different locations during the initial field investigation to check the correlation of oxygen profiles with noted dump type and to determine the feasibility of the method (Figure 1, P prefix).

Down Hole Inflatable Packer

The second method used to collect oxygen and temperature profiles consisted of lowering an inflatable packer fitted with temperature and oxygen sampling probes down an open bore hole. At each desired sample depth, the packer was inflated until it filled the open bore, pressing the sample probes against the sides of the hole. The probes were mounted near the center of the packer so that 1½ feet of the hole were blocked above and below the probes. A sample pump attached to an oxygen meter at the surface was used to extract a pore gas sample from the side-wall of the bore hole. The oxygen and temperature readings were monitored until they stabilized, recorded, then the packer was deflated and lowered to the next desired sample depth. The packer was connected to a bundle of cable, wire, and tubing, allowing data collection to a depth of 100 feet, which could be increased to 200 feet or more if required.

The advantages of the inflatable packer method include the ability to collect data to a far greater depth

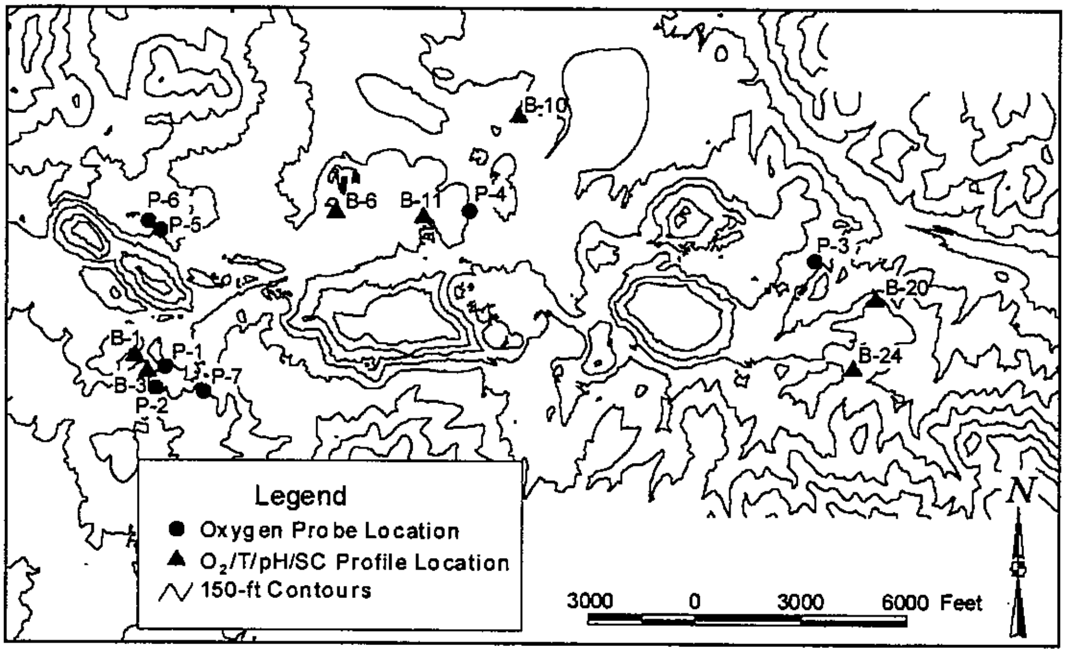

Figure 1. Oxygen and temperature profile locations in the Robinson District.

than with hand-driven surface probes. This feature becomes important in dumps which have been layered during construction, such that a layer of oxide waste rock sits atop a layer of sulfide waste rock. In order to ascertain the oxidation state of the deeper layer, the profiles must extend all the way through the oxide layer and into the underlying layer.

The primary disadvantage is the requirement of having an open bore hole in place prior to sampling. Profiling must be combined with other investigations requiring the drilling of bore holes including exploration and remedial investigations. Open holes should be covered tightly between the time they are drilled and the time the profiles are collected to minimize the infiltration of oxygen into the hole. If a hole has been left uncovered for some time, it may be possible to purge the bore by removing several casing volumes of air from the hole, thereby drawing fresh pore gas to the surface of the bore side-walls. A total of seven down hole oxygen and temperature profiles were collected in various dump types using the open bore holes from the historic waste rock characterization drilling program. Profiles were collected from a variety of waste rock types in dumps of various ages (Figure 1, B prefix).

Waste Rock Core Samples

Waste rock samples collected during the historic waste rock coring program are being analyzed by a State of Nevada certified laboratory for bulk and trace chemistry, and geotechnical parameters bulk density, undisturbed permeability, natural moisture content and grain size distribution.

Results

The results from the soil probe oxygen profiles show that the general nature of the profile is apparent in the first few feet of the dump (Figure 2). The probe that was advanced to a depth of 13 feet (P-2) encountered nearly anoxic conditions not attained at shallower depths.

The results from the down hole investigation agree with the results of the soil probe investigation (Figures 3-4) in that the general trend of the profile is defined in the top 1-2 yards. The oxygen profile observed in Bore B-6 is the only one to deviate significantly at depth from the pattern established at the surface. An unexpected result was observed in profile B-20 where the oxygen profile levels off at 15% of atmosphere through 60 feet of the profile.

Preliminary analysis of the profile data indicates a different evolution of oxygen profiles than was assumed based on the early Davis-Ritchie model (Davis and Ritchie, 1986). Specifically, the abrupt swing from atmospheric oxygen to anoxic conditions across the oxidation zone predicted by the Davis-Ritchie model was not observed in every bore. More commonly, oxygen leveled off at a nearly constant value somewhere between atmospheric and anoxic conditions throughout the bulk of the dump. This

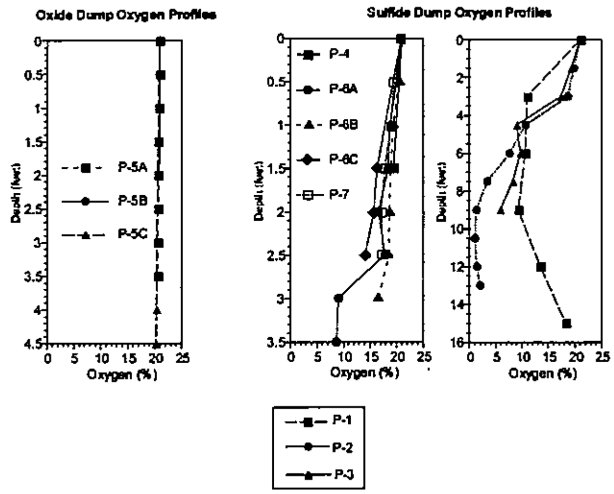

Figure 2. Soil probe profiles from sulfide and oxide dumps.

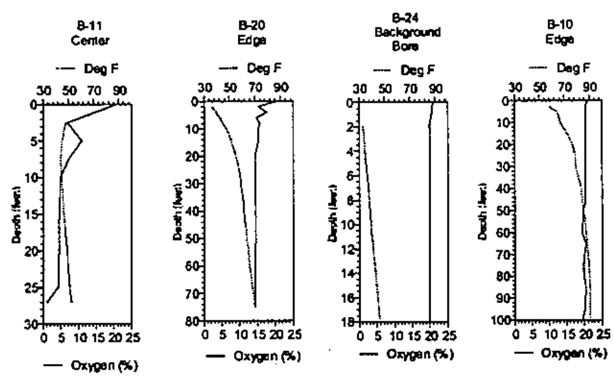

Figure 3. Oxygen and temperature profiles for bores B-11, B-20, B-24, and B-10.

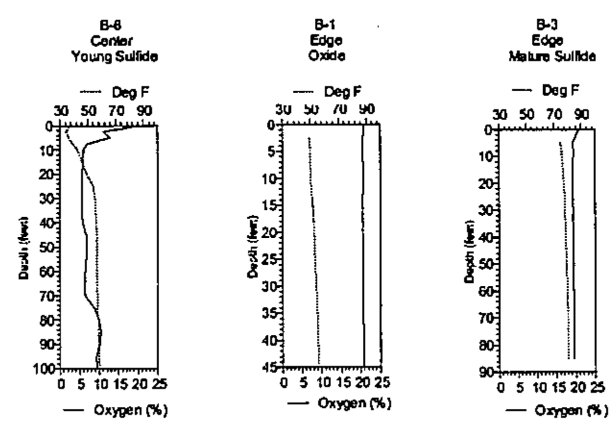

Figure 4. Oxygen and temperature profiles for bores B-6, B-1, and B-3.

result is predicted by more complex models as a result of oxygen diffusion combined with convection drawing oxygen in the toe of the dump (Ritchie, 1994).

Specifically, four different trends were observed in the oxygen and temperature profiles. The background or oxide trend (B-1, B-24), where temperature is low and oxygen is at or near atmospheric levels, and young, intermediate, and mature sulfide trends. The young sulfide trend (B-11, B-6) was marked by low temperature and steep oxygen gradients to near anoxic conditions, while the intermediate trend (B-20) was marked by elevated temperature and oxygen levels between atmospheric and anoxic. The mature trend (B-10, B-3) consists of a highly elevated temperature and near atmospheric levels of oxygen.

The Standard Conductivity (SC) and paste pH profiles followed three general trends, a background trend, and a buffered and poorly buffered trend. The background trend consists of near neutral pH and low SC (B-24), while the buffered trend is marked by pH and SC rising together into the dump (B-3, B-11), as acid is neutralized, dissolving buffering materials. The poorly buffered trend consists of high pH and low SC combined with low pH and high SC (B-1, B-6, B-10, B-20). In this case, the acidic zone coincides with the high SC as a result of dissolution of minerals by the acid without significant buffering occurring.

Discussion

When the results of the temperature and oxygen profiles are merged with the results of the bore hole logging, paste pH and conductivity measurements (Figures 5-6), a complete picture is formed of the state of pyrite oxidation in various waste rock dumps. Preliminary analysis indicates that several variables control the development of the various profiles, which can be simplified as:

1. The availability of oxygen
2. The quantity of pyrite and other sulfides
3. The rate of pyrite oxidation
4. The age of the dump
5. The buffer capacity of the dump rock
6. The location of the profile on the dump

These variables are all controlled by various physical properties of the dump structure and materials, e.g. porosity, permeability, grain size distribution, dump dimensions, mineralogy, water content, and bacterial population, which will be measured and included in a refined model of waste rock oxidation and ARD fate and transport.

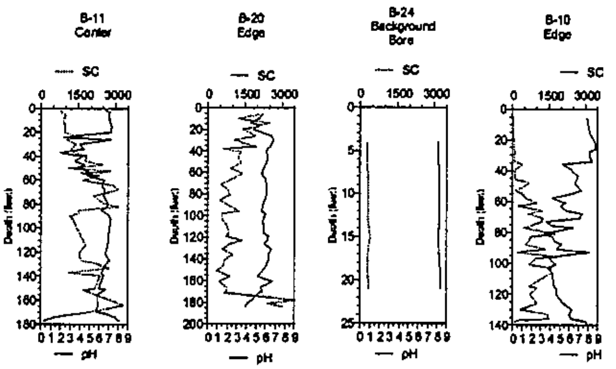

Figure 5. pH and conductivity profiles for bores B-11, B-20, B-24, and B-10.

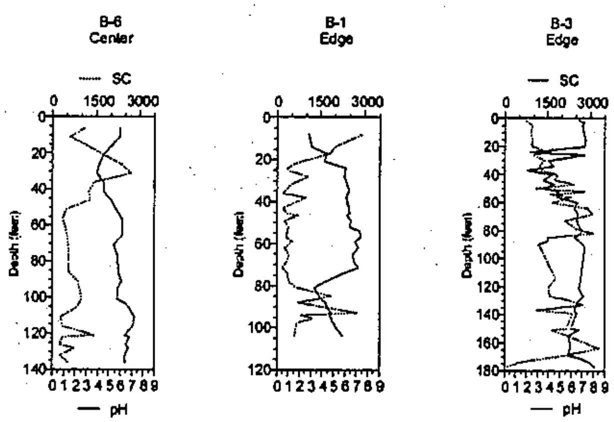

Figure 6. pH and conductivity profiles for bores B-6, B-1, and B-3.

In particular, new insight was gained into edge effects from the sides of the dump, and the appropriate values for the diffusion coefficient of oxygen into the pore space and the diffusion coefficient of oxygen into the waste rock. These observations are being incorporated into the modified Davis-Ritchie waste rock model currently under development. The new model more accurately represents the biogeochemical processes occurring in waste rock dumps, allowing 1) optimization of current and future waste rock dump design, and 2) selection of appropriate alternatives for remediation of historic dumps.

The typical application of the original Davis-Ritchie model consists of a one-dimensional representation of oxidation through a waste rock dump, an application that fails to account for oxygen entering the sides of the dump through diffusion and convection. For dumps with a significant percentage of side exposure, the model will not accurately represent pyrite oxidation, and will in fact under-represent oxidation unless unrealistic values are used in the calibration. The resulting predictions of the future behavior of a dump with this type of application is suspect.

A far more accurate application of the waste rock oxidation model consists of a two-dimensional cross-sectional model which allows diffusion of oxygen into the dump from both the top and the sides, resulting in profiles that match those observed in the field sampling program. The model more accurately predicts pyrite oxidation within a dump, as well as the fate and transport of any oxidation byproducts.

Collection of temperature and oxygen profiles is an important step in creating and calibrating the waste rock oxidation model used to assess the potential development of acid rock drainage in historic, current, and future dumps. Temperature, oxygen, pH, conductivity, and mineralogical profiles collected during the historic waste rock characterization field study are being used to calibrate model parameters to the different types of waste rock found in the Robinson District. In the future, the model will be linked with a previously developed fate and transport model to determine the potential for impact to surface and groundwater presented by various dump designs. The resulting information can be used to determine the optimum design for waste rock dumps and minimize the potential for the development of acid rock drainage.

Literature Cited

Davis, G.B. and Ritchie, A.I.M. 1986. A model of oxidation in pyritic mine wastes: part 1, equations and approximate solution. Appl. Math Model. 10, 314-322.

Ritchie, A.I.M. 1994. Sulfide oxidation mechanisms: Controls and rates of oxygen transport. *Environmental Geochemistry of Sulfide Mine-Wastes* 22, Mineralogical Association of Canada. Chapter 8.