HYDROGEOGEOCHEMICAL CHARACTERIZATION OF EFFLUENT FROM MINE WASTE ROCK, CLUFF LAKE, SASKATCHEWAN[1]

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Abstract. The interaction between geochemical and hydrological processes in waste rock was evaluated in an instrumented waste rock pile as part of ongoing studies into the scale-up of water chemistry predictions. Sulfate and metal concentrations were determined in both pore water and outflow waters collected in sixteen basal lysimeters over a four-year period. The waste rock contained approximately 0.5% sulfur as pyrite/pyrrhotite and was acid generating. The correlation between outflow rate and concentrations was negative during times when macropore flow was active and positive over longer periods. Sulfate concentrations greater than 40,000 mg/L and elevated metal concentrations including cobalt, manganese, nickel, strontium, uranium and zinc were observed in the acidic (pH ~ 3.6) pore water and outflow water. Over the four–year experiment approximately 5% of the initial sulfur was released at the base of the pile. Predicted sulfide oxidation rates determined from laboratory experiments were up to four times higher than the rates inferred from the field experiment (0.1 mg SO_4^{-2}/kg rock/week to 19 mg SO_4^{-2}/kg rock/week). A lower-permeability cover placed on the surface of the waste rock pile three years after the experiment started induced a decrease of the dissolved load in the effluent from a pre-cover average of 4.8 mg SO_4^{-2}/kg rock/week to 1.2 mg SO_4^{-2}/kg rock/week.

Additional Key Words: acid rock drainage, geochemistry, mass loading.

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Introduction

Sulfide-bearing waste rock is often disposed of in large piles on the ground surface, exposing the rock to atmospheric O_2 and creating a potential environmental hazard. The oxidation of sulfide minerals in mine waste can lead to the release of acidic solutions containing elevated concentrations of metals. It is difficult to predict the intensity and duration of chemical mass loadings to the environment from mine wastes because of the heterogeneous character of mine wastes and the complexity of interactions between fluid flow processes and chemical weathering. The objective of the work presented here was to better understand the hydrologic and geochemical processes that control the release of chemical mass from waste rock and to preliminarily assess the effects of a compacted surface cover on flow and SO_4^{-2} release. We characterized the aqueous and solid-phase geochemistry of an experimental waste rock pile at Cogema Resources Inc.'s Cluff Lake U mine in Saskatchewan, Canada. Here we present the results of our geochemical investigation, focusing on the primary and secondary mineral phases and the chemistry of the pore water and outflow water. We used measured water flow rates and aqueous concentrations, as well as solid phase chemical characteristics, to estimate field-based metal and SO_4^{-2} release rates.

Site Description

The Cluff Lake mine is located in northern Saskatchewan, Canada, approximately 700 km north of Saskatoon (Fig. 1). This area has a continental, semi-arid climate with an average frost-free period of 90 days. Cluff Lake has an average annual precipitation of 450 mm with approximately 311 mm of the precipitation as rain. The region lies within the southwestern part of the multi-ring Carswell Meteorite Impact Structure, which is located in the western part of the Athabasca Basin. The Carswell Structure hosts a number of unconformity-type U deposits that contain a very high-grade U ore.

Materials and Methods

Waste rock pile experiment

The experimental waste rock pile was built in 1998 on top of a larger waste rock pile (Nichol et al., 2000). The five-meter high pile was constructed on an 8 m x 8 m cement pad that was contoured into sixteen 2 m x 2 m contiguous lysimeters (Fig. 2 and Fig. 3). Impermeable walls of 60 mil HDPE-lined plywood were constructed around the five-meter-high sides of the pile to ensure all seepage passed through to the basal lysimeters. Heat-traced, two-inch PVC pipes were used to connect each lysimeter to a tipping bucket flow gauge located in an adjacent instrumentation hut (Nichol, 2002).

The waste rock used in the experiment was mined from the Dominique Janine (DJ)-Extension open pit in fall of 1996 (DJX waste rock) and was exposed to natural weathering conditions at the Cluff Lake mine site until its placement in the constructed pile experiment in the summer of 1998.

Instruments were installed in the waste rock pile during its construction along three vertical profiles. Instrumentation included TDR probes (time domain reflectrometry, Nichol et al., 2002) to measure the water content, TC (thermal conductivity) sensors to measure the matric suction, thermistors to measure the in-situ temperature, and suction lysimeters for manual extraction of in-situ water samples (Nichol et al., 2000).

Figure 1. Map of Canada with the Cluff Lake mine site in northern Saskatchewan.

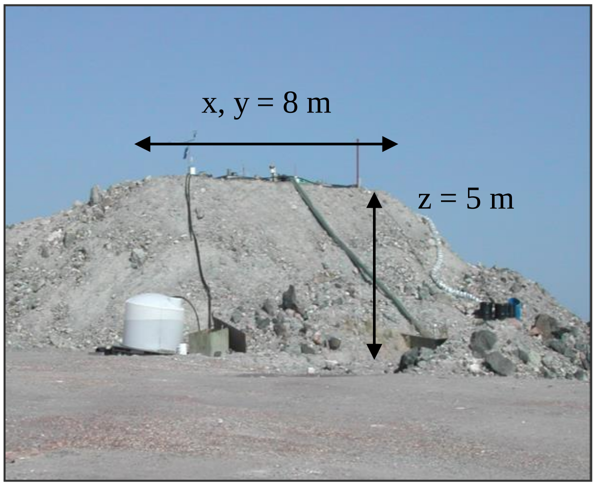

Figure 2. Waste rock pile experiment at Cluff Lake mine site, Saskatchewan.

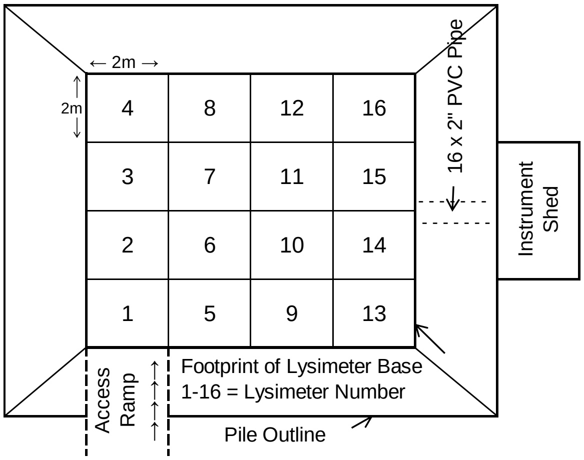

Figure 3. Plan view drawing of experimental waste rock pile showing the 16 lysimeters at the base (not to scale).

Sampling procedures and other tests

Internal pore water and lysimeter outflow water samples were collected from the constructed pile between September 1998 and June 2004. The outflow water was collected in the instrumentation hut on a biweekly basis and at higher frequencies during and after tracer tests and artificial rainfall tests (Nichol, 2002). Pore water was extracted from within the pile several times per year using suction lysimeters located at six different depths: 0.2 m, 0.5 m, 1 m, 1.75 m, 3 m and 4.5 m. More than 2500 water samples were analyzed for SO_4^{-2} using ion chromatography and 165 samples were analyzed for a suite of dissolved metals using inductively coupled plasma mass spectroscopy (ICP-MS). Outflow rates were continuously recorded throughout the duration of the study.

A lower-permeability, compacted waste rock surface layer was placed on the pile surface in August 2002. The waste rock pile experiment was carefully deconstructed in May and June of 2004, when internal structures were mapped and solid-phase samples were collected. The total S remaining in the waste rock at deconstruction was determined by Leco Furnace. Primary and secondary minerals were identified using microscopic analyses, X-ray diffraction (XRD) and scanning electron microscope (SEM).

Results

Waste Rock Characteristics

The waste rock was classified as acid generating with NP/AP ratios less than 0.5 (Haug, 2001). Total S contents ranged from 0.44 to 0.76% and the initial SO_4^{-2} S contents were negligible. The dominant oxidizing minerals were pyrite and pyrrhotite. Primary minerals found in the waste rock after deconstruction were quartz, potassium feldspar, albite, muscovite, chlorite, a clay mineral (kaolinite or smectite) and some minor amounts of amphibole, further indicating the absence of buffering minerals and a negligible neutralization potential. Paste pH was determined for 10 waste rock samples collected at different depths during deconstruction. Values ranged from 3.01 to 3.96, averaging 3.6, and showed no distinct trend with depth. Secondary minerals identified from x-ray diffraction and microscopic analyses include the Fe oxy-hydroxides goethite and ferryhydrite, jarosite, gypsum, hydrated magnesium and aluminum sulfates and annabergite (hydrated nickel arsenate).

Pore and drainage water chemistry

Pore water and outflow water contained elevated SO_4^{-2} concentrations between 400 and 40,000 mg/L, as well as elevated concentrations of metals including Al, Ni, Co, Cu, Fe, Mn, Ni, Sr and Zn (see Table 1). The dissolved metals content of the pore water indicated a general increase with depth and reached a maximum in the outflow water. Iron, which was contained in several secondary minerals observed in the pile during deconstruction, was an exception; Fe was generally at a lower concentration in the outflow water than in the pore water.

Metals such as Mg, Al, Na, Ni, U, Mn, Co, Zn and Cu showed a strong positive correlation with the SO_4^{-2}concentrations in the pore water and outflow water; even though some metals were observed in secondary precipitates (Fig. 4). A strong positive correlation between Cu and SO_4^{-2} could only be observed for SO_4^{-2} concentrations exceeding 5,000 mg/L.

Table 1. Sulfate and metal concentrations in the pore and outflow water.

Depth below surface		**SO4**	**Al**	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Sr**	**Zn**
meters		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
0.20	10th percentile	508	18	0.5	0.8	<0.2	42	1.0	2.8	1.0	0.9
0.50		2676	107	2.6	0.7	0.4	227	5.1	17.3	3.6	1.7
1.00		1859	58	1.4	0.6	0.3	135	3.3	10.3	3.3	0.9
1.75		2708	78	1.8	0.3	4.5	144	3.4	10.8	3.9	1.1
3.00		5932	190	6.8	0.5	6.6	668	16.6	55.1	4.8	2.3
4.50		8882	294	11.5	0.7	2.3	1124	31.3	100.9	5.7	3.2
5.00*		2295	171	6.2	0.5	0.6	827	17.9	42.9	2.9	1.9
0.20	Median	840	29	0.8	1.1	<0.2	59	1.7	4.7	1.6	1.3
0.50		3300	128	3.5	1.3	1.6	300	6.9	25.0	4.6	2.0
1.00		3085	126	3.6	1.0	1.9	283	6.9	35.9	3.9	2.0
1.75		4350	145	4.3	0.5	10.5	388	9.3	31.5	5.1	1.9
3.00		11050	350	14.1	0.8	11.5	1430	40.0	130.5	6.3	3.8
4.50		16700	630	20.7	1.3	8.4	2140	61.1	191.0	7.3	5.4
5.00*		10459	662	18.6	1.0	1.6	2328	53.0	143.1	5.9	5.0
0.20	90th percentile	1608	52	1.5	1.5	<0.1	99	2.9	9.1	2.6	1.9
0.50		3879	157	4.5	1.4	2.9	400	10.0	37.3	5.5	2.7
1.00		6447	267	7.6	1.7	6.7	740	17.2	60.6	4.6	4.0
1.75		14640	685	20.8	1.2	16.8	1948	50.4	174.0	9.2	6.1
3.00		31330	1630	43.5	2.1	24.9	4076	110.3	398.3	8.5	10.4
4.50		35240	1820	41.6	2.1	17.9	4666	112.0	383.8	10.1	9.8
5.00*		20673	2659	67.3	3.1	5.4	8758	213.4	516.2	17.3	20.7

* Water collected at 5m depth is outflow water collected at the base of the pile.

Flow and Chemistry Correlations

Investigations of the relationship between the flow rate and the chemistry of the drainage water revealed a negative correlation between flow rate and concentrations during times when macropore flow was active, and a positive correlation over a longer scale. During active macropore flow, high flow rates correlated with less concentrated outflow water. Slower flow rates correlated with more concentrated outflow water.

The outflow chemistry showed an immediate response to large changes in the flow rate associated with individual rainfall events. A rapid increase in the outflow rate was observed within an hour of large infiltration events. The increase in flow rate was marked by an increase in sulfate concentrations of up to 10,000 mg/L that lasted less than thirty minutes, followed by a slug of relatively fresh, less concentrated water. The initial spike or flush of high SO_4^{-2} water observed in the waste rock pile outflow occurred just prior to the peak in outflow rate. The concentrations in the outflow water then dropped substantially at peak flow levels. After the peak passed and the flow rates stabilized, the SO_4^{-2} and dissolved metals content of the outflow water began to increase towards its long-term average value (Fig. 5).

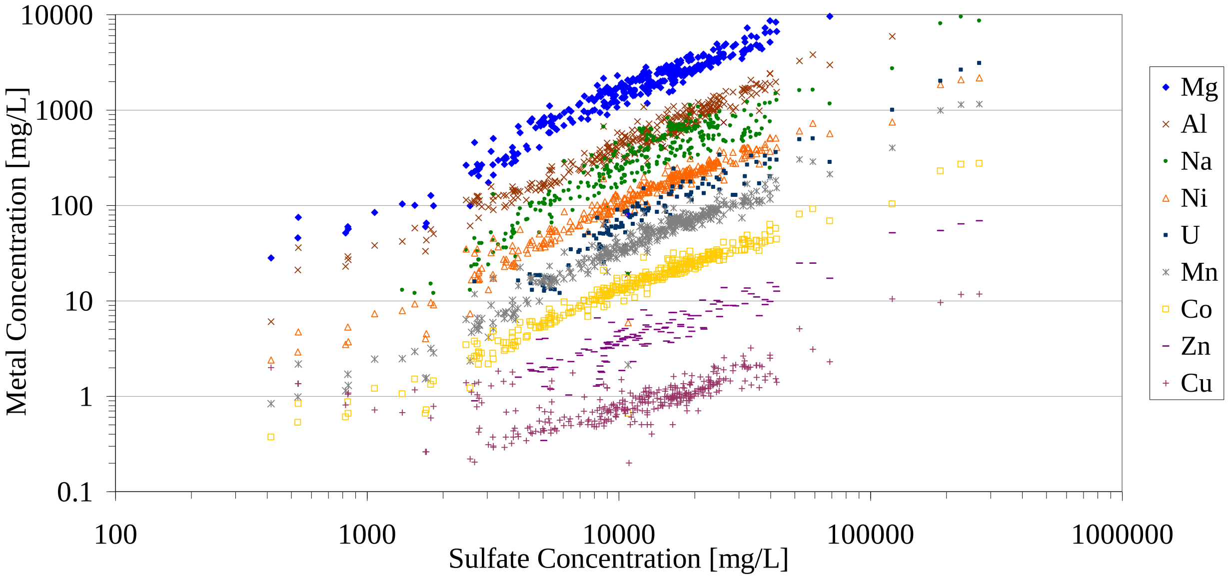

Figure 4. Correlation between selected metals and sulfate concentrations.

On a larger, i.e. monthly or seasonal scale, a positive correlation was observed between the flow rates and the dissolved metals content of the outflow water. A decrease in the flow induced a general decrease in the concentrations in the outflow water (Fig 6).

Loading estimation

The total sulfur content in the waste rock at the beginning of the experiment in 1998 was estimated at 0.45% (Hollings et al., 2001), or assuming a bulk density of 2000 kg/m^3, 2880 kg of S within the experimental pile. The amount of S released at the base of the experimental pile between January 2000 and December 2003 was determined to be approximately 150 kg, or 5% of the initial S (Table 2). Chemistry data from 1998 and 1999 was not included in this calculation because of an insufficient number of analyses. The calculation was based on the flow weighted, monthly average SO_4^{-2} concentrations and the monthly outflow volumes according to the following equation (1):

$$\text{outflow volume [L/month]} * SO_4^{-2} \text{ concentration [mg/L]} = SO_4^{-2} \text{ released [mg/month]} \qquad (1)$$

The amount of S released was calculated for each individual lysimeter and the results were added to determine the total mass loading at the base of the pile. The SO_4^{-2} release rates varied by up to 50% among the sixteen basal lysimeters. For those few months with insufficient samples (mostly winter months), the chemistry was estimated from the flow rate. A correlation factor was derived from the relation between the SO_4^{-2} and outflow rate for the fully recorded months and applied to the months with limited chemistry data.

The total S remaining in the waste rock at deconstruction was determined two different ways: i) by subtracting the SO_4^{-2} recorded in the outflow water at the basal lysimeters (mass loading calculation) from the initial total S content and ii) by averaging total S determinations on fourteen representative waste rock samples collected during deconstruction. Calculation results are presented in Table 2.

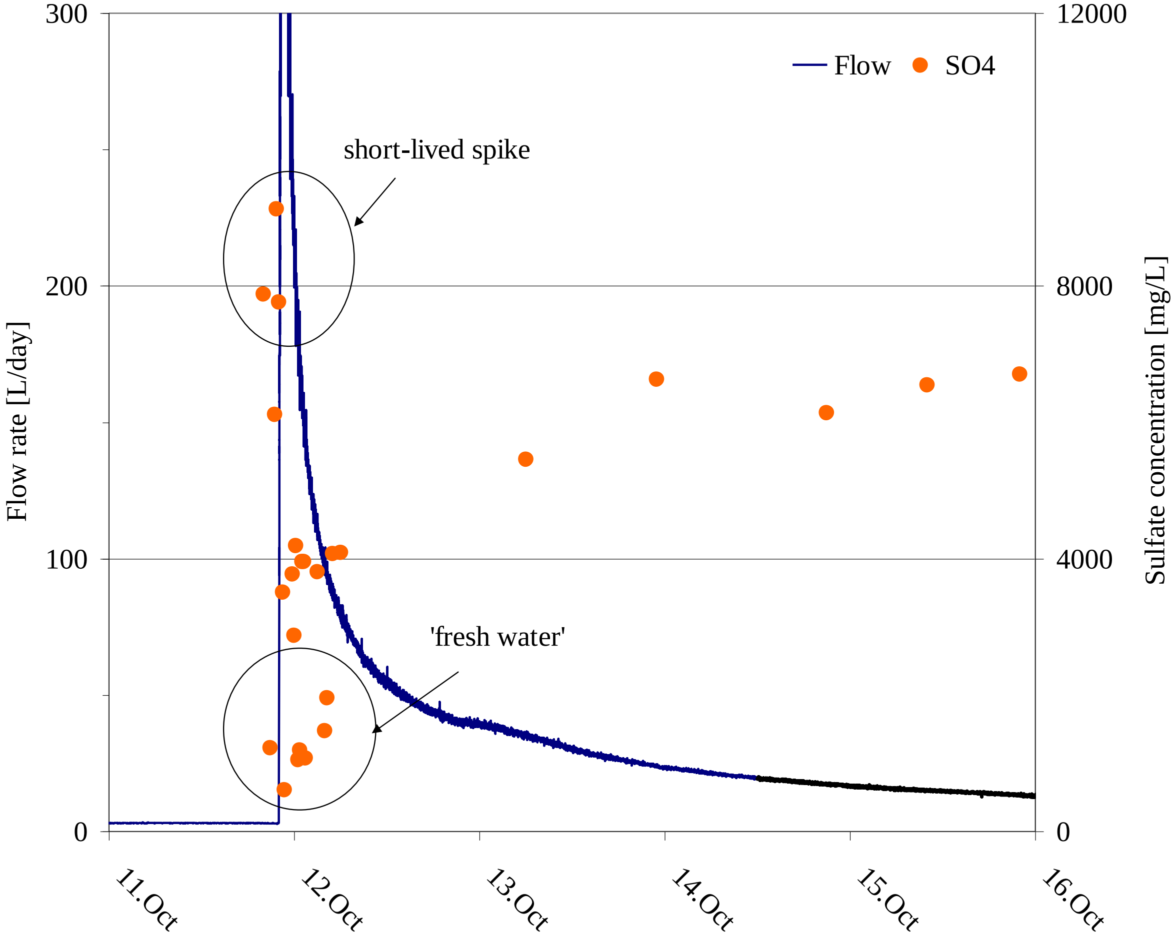

Figure 5. Sulfate concentrations and flow rates for lysimeter 6 during an infiltration event in October 2001.

Table 2. Summary of the total sulfur content in the pile before and after the experiment.

	Prior to experiment	After experiment	
	Leco Furnace	Mass loading calculation	Leco Furnace
Total Sulfur [%]	0.45	0.43*	0.30
Total Sulfur Mass [kg]	2880**	2730	1920**

* Calculated from total S mass (kg) that is obtained from the mass loading estimation.
** Calculated from total S content (%) measured with Leco Furnace.

The time variation in the SO_4^{-2} release rates at the base of the pile is shown in Fig. 6. During the frost-free period from May to October, the combination of elevated flow rates and high SO_4^{-2} concentrations yielded high S and metal loadings at the base of the pile. The rate of SO_4^{-2} release varied between 19 mg SO_4^{-2}/kg rock/week in July 2000 and 0.1 mg SO_4^{-2}/kg rock/week in February 2003.

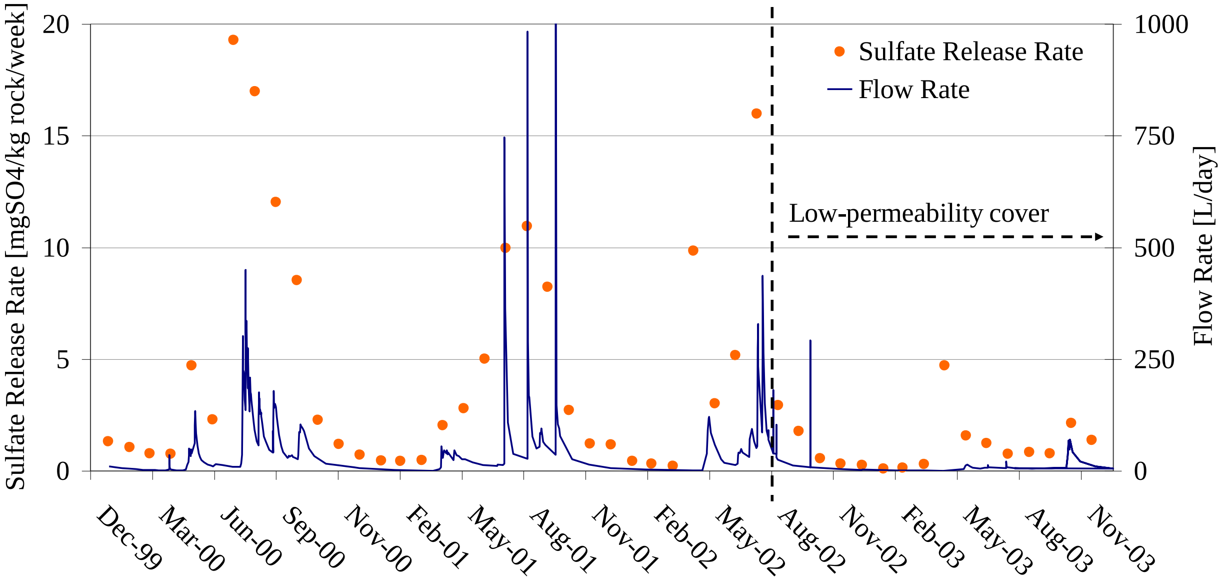

Figure 6. Monthly sulfate release rates and flow rates measured at the base of the pile between December 1999 and December 2003.

Hollings et al. (2001) used kinetic cell tests to estimate the sulfide oxidation rates for five different size fractions of the DJX waste rock placed in the experimental pile. The SO_4^{-2} release rates were determined using three independent methods: O_2 consumption rates in kinetic cells, SO_4^{-2} measurements of kinetic cell effluent after O_2 consumption tests, and humidity cell SO_4^{-2} release rates after ten weeks (Table 3). To correlate these SO_4^{-2} release rates to those observed for the full-scale pile, size-fraction reaction rates were averaged, each weighted by the proportion of that grain size fraction in the field-scale pile. The particle size distribution reported by Nichol (2002) was used for the field scale pile, and it was assumed rock larger than 25 mm, the largest size tested by Hollings et al. (2001), did not react. Application of the laboratory rates to the particle size distribution observed in the field yield a SO_4^{-2} release rate of 14.1 mg SO_4^{-2}/ kg rock/week for the field pile. This value was 3.2 times the average SO_4^{-2} release rate observed in the field from 2000 through 2002 (Table 4). This supports the observations by Malmstrom et al. (2000) that there are large discrepancies between the mineral weathering rates determined in the laboratory and in the field, with lower rates usually observed in the field. The crushing of the waste rock material for the kinetic tests might be a major reason for the elevated release rates observed in the laboratory.

Table 3: Summary of sulfate release rates results observed from laboratory and field experiments.

	Sulfate release rates [mg SO_4^{-2}/kg rock/week]			
	Calculated from O_2 consumption rates	SO_4^{-2} measurements of kinetic cell effluent*	Humidity cell SO_4^{-2} release rates	Experimental waste rock pile
	Hollings et al. (2001)			
Minimum	6.9	3.1	6	0.1
Maximum	70	91	64	19

* Sulfate rinsed from the samples after the O_2 consumption rates.

The lower-permeability compacted surface layer that was placed on the surface of the waste rock pile in August 2002 decreased the outflow rates and in turn decreased the mass loading. The SO_4^{-2} release rates were lower in 2003 compared to previous years (Fig. 5). The average rate of SO_4^{-2} release was four times higher in 2000, 2001 and 2002 prior to cover placement than afterwards (Table 4). Table 4 also summarizes the yearly average sulfate release rates. A general decrease of the mass loading was observed over the duration of the experiment.

Metal loadings were more difficult to quantify because the number of the outflow samples analyzed was limited by time and budget constraints. However, the concentrations of the majority of the metals in the outflow were reasonably well estimated using their strong correlation with the SO_4^{-2} concentration (Fig. 4). Based on this relationship, the metal loading was estimated and the results were summarized in Table 4. The dominant metals in the outflow water were Mg, Al, Na, Ca, Ni, U, and Mn. With the exception of Ca, these metals also indicated the highest release rates, with values between 0.01 and 0.5 mg/kg rock/week. The average release rates for Co and Zn were less than 7 µg/kg rock/week. Average release rates for Cu were not calculated because of the inverse relationship with SO_4^{-2} at lower concentrations.

Discussion and Conclusions

A gradual decrease in the SO_4^{-2} and metal content in the outflow was observed over the duration of the experiment, as shown in Fig. 6. There were at least two possible explanations for this observation. First, the pile was aging such that the inventory of unoxidized sulfide mineral was gradually reduced or coated by oxide surfaces and secondary minerals. An oxidized coating can act to inhibit O_2 from reaching the reaction site and hence, slow down the rate of oxidation (Davis and Ritchie, 1986). Second, a lower-permeability cover was placed on the pile surface in August 2002. The placement of the cover led to reduced flow rates and coincided with reduced concentrations in the drainage water. It is not known, however, if the cover was able to inhibit O_2 transfer into the pile to an extent necessary to reduce sulfide oxidation rates.

Table 4: Average sulfate and metal release rates before and after cover placement and per year.

	Release rate [mg/kg rock/week)]			
	Prior to Cover Placement			**After Cover Placement**
	2000	**2001**	**2002**	**2003**
SO4	5.9	3.8	3.5	1.2
Mg	0.9	0.6	0.5	0.2
Al	0.26	0.17	0.15	0.07
Na	0.17	0.11	0.1	0.04
Ni	0.062	0.040	0.036	0.016
U	0.065	0.041	0.038	0.016
Mn	0.024	0.015	0.014	0.006
Co	0.007	0.005	0.004	0.002
Zn	0.002	0.001	0.001	<0.001

The nature of flow through coarse waste rock can explain the relationships between flow and geochemistry observed in the outflow water. Unsaturated flow in coarse, heterogeneous waste rock exists in the form of matrix flow through the finer-grained fraction of the waste rock, and preferential flow through the coarser-grained fraction. Preferential flow or channeling of flow to spatially distinct areas has been observed by El Boushi (1975), Dexter (1993), Murr et al. (1981), Li (2000), Bellehumeur (2001), Eriksson et al. (1997) and Nichol (2002). Matrix flow was the dominant type of flow for periods with low or moderate infiltration. The voids in the coarser grained material were only episodically wet, and during long periods of dry conditions secondary minerals are likely to precipitate in these voids. The first flush of water through the coarse grained material after a dry period dissolved the secondary minerals and the outflow water became more concentrated. This is likely the reason for the short-lived spike in the outflow chemistry observed immediately after large rainfall events. The following slug of water with relatively low solute concentrations is likely a result of water flowing through the coarse grained material at a velocity such that the water-rock contact time did not allow the accumulation of weathering products in the water.

Our estimate of mass loading at the base of the pile was affected by the high variability in outflow concentrations in response to rainfall events and the limited number of chemical analyses. In addition, the selective sampling of the outflow water used here may not accurately capture the true monthly average because SO_4^{-2} concentrations can change within a few hours in response to infiltration events. However, we considered the observed trends in outflow chemistry in response to infiltration to compute monthly average SO_4^{-2} concentrations.

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