Early Indicators of Acid Seepage Generation – a Comparative Study of Long-term Seepage Quality from Two Waste Rock Dumps in the Central Rocky Mountains

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ABSTRACT

Water quality trends are compared between two 30-year old waste rock dumps at a hard rock mine in the Central Rocky Mountains. Both waste rock dumps contain material of similar lithology. One waste rock dump is the primary repository of acid generating material and produced acidic drainage approximately 22 years following construction. The other waste rock dump is the primary repository of non-acid generating material and continues to produce neutral drainage. Comparison of dump drainage evolution reveals precursors to dump acidification. Results suggest decreasing Mo concentrations indicate that internal regions of the dump are becoming acidic. A gradual decrease in Mo concentrations is observed more than a decade before the fist acidic pH is measured. A sudden increase in Zn and Mn concentrations takes place a year before the pH drops from alkaline to circumneutral. The pH is erratic typically ranging from 6.0 to 7.5 for two years before the first acidic pH is measured. Zn, Mn and Cu concentrations fluctuate by over an order of magnitude for the 3 years before the first appearance of acidic drainage.

Key Words: acidic drainage, neutral drainage, prediction, chemical evolution

INTRODUCTION

Management of potentially acid generating (PAG) waste rock is one of the primary environmental challenges of the mining industry. Accurate predictions of drainage chemistry that will occur under various waste disposal scenarios are an essential component in mine planning. Potentially acid generating rock types can be identified by a variety of static and kinetic testwork, however significant uncertainties exist in upscaling experimental results to produce drainage predictions for mine waste facilities. No PAG management strategy is foolproof, and the potential for ARD is difficult to eliminate with certainty when significant quantities of PAG rock are present. For instance, blending PAG waste rock with non-acid generating (NAG) waste rock is a common mitigation approach which has not always proven successful (Morin and Hutt, 2000). Once a mine waste facility is constructed, the geochemical evolution of drainage is to a large degree out of the control of the mine operator. If geochemical trends indicative of impending acidification can be identified in waste rock drainage, a management strategy can be implemented in the years prior to the first appearance of acidic seepage.

Drops in drainage pH from neutral to acidic can take place rapidly. The acidification of drainage water is typically accompanied by a dramatic increase in dissolved metal cation concentrations. More gradual changes in drainage chemistry are expected to take place in the lead up to acidification. The weathering of a waste rock facility is heterogeneous, with some areas weathering relatively quickly compared to others. This is in part, due to the variability in grain size, oxidant availability, and acid generating potential of rock types deposited within a waste facility. The heterogeneity of weathering will result in localized zones becoming depleted of buffering capacity and possibly acidic while other areas remain neutral. If sufficient available buffering capacity remains between the acidic zone and the underlying water table a decrease in pH and alkalinity will not necessarily be observed in the drainage. Furthermore, a localized zone of acidity in a waste rock pile does not alone signify the inevitable development of acid rock drainage (ARD). However, a gradual increase in the geochemical signature of acidic zones can be considered an early indicator of acidic seepage.

The geochemical evolution of drainage from two waste rock dumps at a mine site in the central Rocky Mountains are presented herein. Both waste rock dumps are approximately the same age (30 years) and have been receiving a mix of PAG and NAG rock types present at the mine site, albeit at different ratios. The waste rock dump receiving primarily NAG rock types has remained alkaline, while the waste rock dump receiving primarily PAG rock types became acidic after 22 years. Geochemical trends hypothesized as pre-cursors to acidification are presented for the

acid generating waste rock dump, and compared against trends observed in the non-acid generating dump. The purpose of this comparison is to identify deviations in drainage chemistry of the prior to the first appearance of acidic pH. The non-acid generating waste rock dump provides a control and basis for comparison.

SITE DESCRIPTION

The mine site is a Mo-porphyry deposit in the central Rocky Mountains. The mine consists of an open-pit with two principal waste rock storage facilities. The region surrounding the project area has a sub-alpine climate, typical of high altitude inland mountains of the western United States. The average ambient air temperature at site is approximately 4.2°C. Winters are cold with temperatures ranging from -34°C to -1.1°C. The summer months of June to August are typically cool and dry with temperatures ranging from 10°C to 29°C. The average yearly precipitation is approximately 584 mm, most of which occurs as snowfall in the winter, although shorter duration rain events and thunderstorms are common in the summer months. Hydrology in the region is strongly influenced by snowmelt, which accounts for >70% of annual runoff from catchments surrounding the main pit.

Rock Types

The lithologies present at the mine site can be categorized into three general rock types: Eocene-aged Challis volcanics; Paleozoic metasedimentary rocks of the Copper Basin formation; and Cretaceous plutonic intrusives which host the main ore body. The Challis volcanics in the area are a series of basaltic to dacitic lava flows, tuffs and breccias. The Copper Basin metasediments in the area of are thinly bedded argillites and shales. The Thompson Creek intrusive complex comprises of a number of petrographically and texturally similar phases that intruded during the late Cretaceous. Intrusive lithologies range from biotite granodiorite to biotite quartz monzonite. Molybdenum mineralization is associated with the quartz monzonite intrusive core. Sulfide mineralization is limited to the intrusive and metasedimentary rock types.

A variety of techniques have been used to characterize the mineralogical and elemental composition of waste rock. Samples from all three rock types have been subjected to aqua regia digestion and X-ray fluorescence (XRF) analysis. The mineralogical composition of the metasedimentary and intrusives rock types has been determined by quantitative X-ray diffraction (XRD). The acid generating potential and acid neutralizing potential of these rock types have been characterized by acid base accounting (ABA). The ABA parameters most frequently measured are total sulfur, and Sobek neutralization potential (NP) (Sobek et al., 1978). The median aqua regia results for trace metals are presented in Table 1, and the median XRF results for major elements are presented in Table 2.

Table 1. Median values of aqua regia extraction results of the three rock types composing waste rock.

Rock type	Cu	Mn	Mo	Se	Zn	Ni	Pb	As	Cd	Co	U
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Volcanics	18.4	424	20.7	0.5	54	8.1	18.2	4.9	0.11	8	1.28
Intrusives	38.7	162	364	1.6	41	1.8	68.4	87.5	0.01	3.7	5.45
Metasediments	34.05	380	1.45	2.1	164	27.6	2.4	1.8	0.95	5.15	1

Table 2. Median values of results of XRF whole rock analysis of the three rock types composing waste rock.

Rock type	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	SiO_2	P_2O_5	TiO_2
	%	%	%	%	%	%	%	%	%	%
Intrusives	15.00	1.81	2.66	3.98	0.67	0.04	2.97	73.05	0.10	0.30
Metasediments	12.15	4.87	6.42	2.91	3.36	0.07	1.01	65.55	0.59	0.60
Volcanics	17.14	4.16	4.43	1.19	2.53	0.06	2.98	57.85	0.14	0.64

Sulfide minerals identified with XRD analysis include pyrite and trace quantities of pyrrhotite. Molybdenite is known to occur in the ore zone but was not found by XRD analysis of waste rock samples. The XRD results identified calcite in the metasedimentary and intrusive rock types. The major rock forming minerals identified by

XRD were quartz, plagioclase feldspar, K-feldspar and mica. These three minerals formed more than 90% of the 14 intrusive waste rock samples submitted for XRD. More than 400 samples of each rock type have been tested for acid base accounting parameters. Acid base accounting found a median 'Sobek' neutralization potential of 13.0 $kgCaCO_3$/tonne in the metasediments, 15.1 $kgCaCO_3$/tonne in the volcanics, and 11.8 $kgCaCO_3$/tonne in the intrusives. The median total sulfur present in these three rock types is 0.34 wt. % in the metasediments, 0.28 wt. % in the intrusives, and 0.13 wt. % in the volcanics.

Waste Rock Classification and Dump Construction

The PAG and NAG waste rock dumps are located in two separate valleys adjacent to the open pit. The NAG waste rock dump is the primary repository of non-acid generating waste rock, while the PAG waste rock dump is the primary repository of potentially acid generating material. Both waste rock dumps were opened in 1981 and received waste rock continuously until 1992. The mine site was inactive from 1992 until it re-opened under new ownership in 1994.

Multiple waste rock classification systems have been used over the past three decades. Prior to 1992 waste rock was only classified as volcanic or non-volcanic. In 1996, the mine operator adopted a two rock type classification system which is currently in use. Under the current system, waste rock with NP/AP $\geq$ 1.5 and total sulfur $\leq$ 0.10% is classified as NAG. Waste rock with NP/AP < 1.5 and total sulfur > 0.10% is classified as PAG. In Table 2, the quantity of NAG and PAG material deposited in the two waste rock dumps since 1992 is outlined. The values are based on a block model developed for the site. Waste rock deposited before 1992 is assumed to be NAG if volcanic, and PAG if non-volcanic. In 2006 three borehole samples were drilled through the PAG dump collecting a total of 86 waste rock samples, the median T-S value of was 0.44 wt. % (Stockwell and Dockrey, 2012).

Prior to the 1992, 327 million tons of waste rock was end dumped into a valley adjacent to the main pit. Approximately 23% of the waste rock was classified as non-volcanic (NAG and PAG), and 77% of the material was classified as volcanic (NAG). During this time period waste rock was not segregated within the dump. Since 1992, PAG waste rock has been placed in isolated cells by high-end dumping onto a foundation of NAG material with a minimum separation of 91 m (300 ft) from native ground. Volcanic material is then used as a cover, resulting in the encapsulation of potentially acid generating waste rock (PAG) by non-acid generating volcanic waste rock (NAG) within the NAG dump. The PAG waste rock dump has been constructed by end dumping into a valley adjacent to the main pit and waste rock is not segregated. A 6 m thick volcanic layer (NAG) is deposited on the top of the PAG dump as the dump is constructed.

Table 2. Estimated ABA parameters and running total of T-S, NP, NAG and PAG material deposited in the PAG and NAG dumps.

	NAG Dump				PAG Dump			
Year	**T-S**	**NP**	**NAG**	**PAG**	**T-S**	**NP**	**NAG**	**PAG**
	wt. %	*$kgCaCO_3$/ tonne*	*million tonnes*	*million tonnes*	*wt. %*	*$kgCaCO_3$/ tonne*	*million tonnes*	*million tonnes*
before '92	0.26	19.3	229	68	0.49	14.3	9	18
1994	0.26	19.3	229	68	0.50	13.9	9	20
1995	0.27	19.5	236	68	0.52	13.9	12	28
1996	0.27	19.8	245	69	0.52	13.6	12	33
1997	0.28	19.7	249	74	0.53	13.7	13	34
1998	0.28	19.8	256	76	0.53	13.7	13	35
1999	0.29	19.9	262	76	0.53	13.6	14	37
2000	0.29	19.8	268	83	0.53	13.4	14	39
2001	0.29	19.7	269	84	0.53	13.4	14	39
2002	0.29	19.7	270	85	0.53	13.3	14	39
2003	0.29	19.7	270	85	0.54	13.4	15	44

2004	0.29	19.7	271	85	0.54	13.2	15	53
2005	0.3	19.7	274	87	0.54	13.1	15	55
2006	0.3	19.5	281	97	0.55	13.2	17	61
2007	0.3	19.4	283	99	0.55	12.8	18	83
2008	0.31	19.8	300	100	0.56	12.7	19	90
2009	0.32	19.8	313	108	0.56	12.6	19	93
2010	0.32	19.8	322	111	0.56	12.7	21	107

Water quality sampling

Water quality monitoring of drainage emanating from the toe seeps of the waste rock dumps was initiated in 1990. The field pH and water quality was initially measured 3 or 4 times per year. Prior to 1998 only total (T) concentrations were measured and the detection limit was highly variable, for instance, the detection limit for Mo ranged from 200 µg/L to 10 µg/L. In 1998 dissolved (D) concentrations began to be measured and improved analytical techniques lead to lower detection limits. In September 2000, an onsite laboratory began monitoring, Zn, SO_4, Cu and Mn on a weekly basis for the PAG dump drainage.

RESULTS AND DISCUSSION

PAG Dump Chemistry

The concentrations of selected parameters and pH from 1990 onward are presented in Figure 1 for the PAG dump. Metal cations of concern which have been reported in the highest concentrations include Mn, Cu and Zn are reported in Figure 1a along with SO_4. Oxyanion forming metals and metalloids which have been reported in the highest concentrations are Mo and Se (Figure 1b). The base cations Ca and Mg are reported along with pH and total alkalinity in Figure 1c.

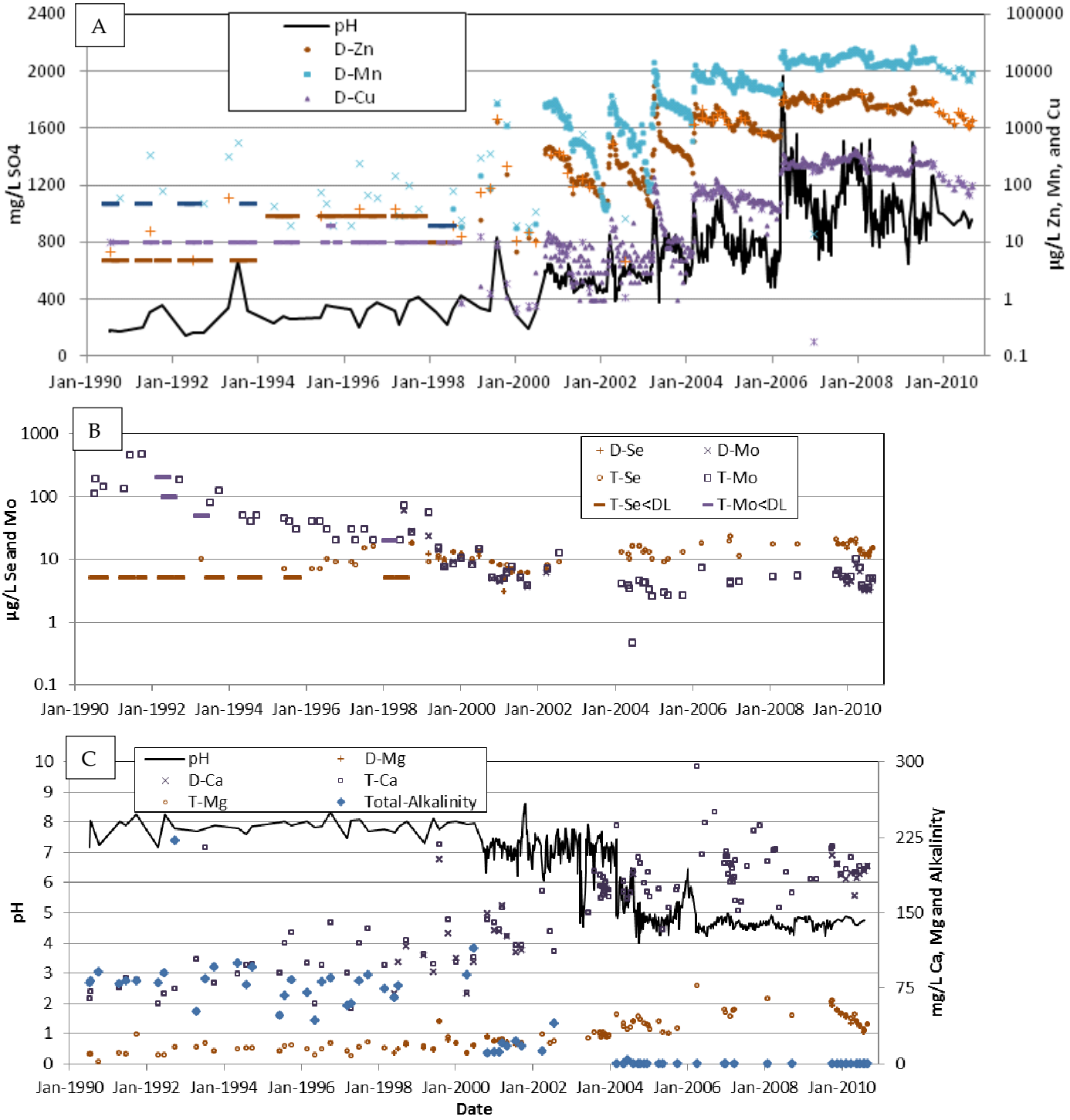

Figure 1. PAG dump drainage chemistry, (a) transition metal cations observed in highest concentrations and SO_4, (b) oxyanion forming metals/metalloids observed in highest concentrations, (c) base cations, alkalinity and pH.

Prior to November 2000, drainage from the PAG dump remained above pH 7. The concentrations of Cu, Zn, and Se were typically below detection limits until October 1998 when detection limits were improved as discussed above. The concentration of SO_4 fluctuates seasonally, with peak concentrations generally occurring during the late summer or early fall. In October 1991, peak SO_4 concentrations were associated with a peak in Mn, Zn and Mo concentrations. The next strong peak in SO_4 concentrations occurred in July 1993. This peak was accompanied by a peak in Mn and Zn, but no peak in Mo took place. From this time point onwards Mo concentrations show a gradual decline while fluctuations in Zn and Mn concentrations remained relatively constant until 1999. Molybdenum briefly rebounded to concentrations as high as 60ug/L in July 1998-March 1999. In August, 1999 T-Mo concentrations drop to below 7 µg/L and typically remain below 10 µg/L hence forth. This drop in Mo concentrations corresponds with the highest Zn and Mn concentrations observed to that time. In August 1999, peaks in Mn and Zn reached concentrations 5 to 23 times greater than that which had been previously observed. From 1999 to 2004 range of Mn and Zn concentrations fluctuates by orders of magnitude while T-Mo typically remained below 10 µg/L.

Instability in the pH became evident in September 2000, shortly after weekly pH measurements were initiated. The pH remained circumneutral until the spring freshet of 2003 when the first acidic pH briefly appeared from the PAG dump seepage. This brief drop in pH to 4.5 was accompanied by a sharp rise in dissolved metal cation concentrations. As peak flows of the 2003 spring freshet subsided, the pH rebounded to more circumneutral values and metal concentrations decreased. During the subsequent spring freshet the pH of dump drainage dropped and became more persistently acidic. The pH began to climb in 2005 following a relatively dry year reaching circumneutral values (pH 6.5) immediately before the 2006 spring freshet. Since the 2006 spring freshet and the onset of persistent acid rock drainage (ARD) conditions, the pH has remained relatively constant typically ranging between pH 4.2 and pH 4.9 with a median value of pH 4.6. The relative size of seasonal fluctuations in Zn, Mn, an Cu after the pH became persistently acidic are much smaller than the fluctuations observed between 1998 and 2004.

NAG Dump Chemistry

The concentrations of selected parameters and pH from 1990 onward are presented in Figure 2 for the NAG Dump. Since the inception of monitoring, total alkalinity has remained between 95 and 165 mg/L and pH has remained neutral to alkaline. Prior to the improvement in detection limits in 1998, the metal cations Cu, Mn, and Zn were typically below detection limits. Since 1998 the concentrations of Zn, Mn and Cu have typically remained below 10 µg/L. Conversely, trends for SO_4, Ca and Mo have been generally increasing since inception of monitoring in 1990. The behavior of Se is somewhat unique. The concentration trends were similar to Mo until 2002. Since 2002 Se has remained relatively constant at approximately 30 µg/L while Mo concentrations have continued to rise.

The dump drainage chemistry does not have distinct geochemical transitions as the PAG dump does. However it does provide a point of comparison for the behavior of the PAG dump. Prior to the acidification of the PAG dump, the two dumps were producing similar SO_4 concentrations, with mean annual concentrations ranging from 180 mg/L to 540 mg/L for the PAG dump, and 160 mg/L to 680 mg/L for the NAG dump between 1990-2000. Despite the similar SO_4 concentrations Zn and Mn were released at higher concentrations from the PAG dump than from the NAG dump over this time period. Furthermore, the metasediments and volcanics which predominantly compose the NAG dump have higher Zn and Mn content then the intrusive waste rock which is predominant in the PAG dump (Table 1). The concentrations of Zn and Mn in NAG dump drainage were typically less than 10 µg/L, making relations to SO_4 difficult to identify.

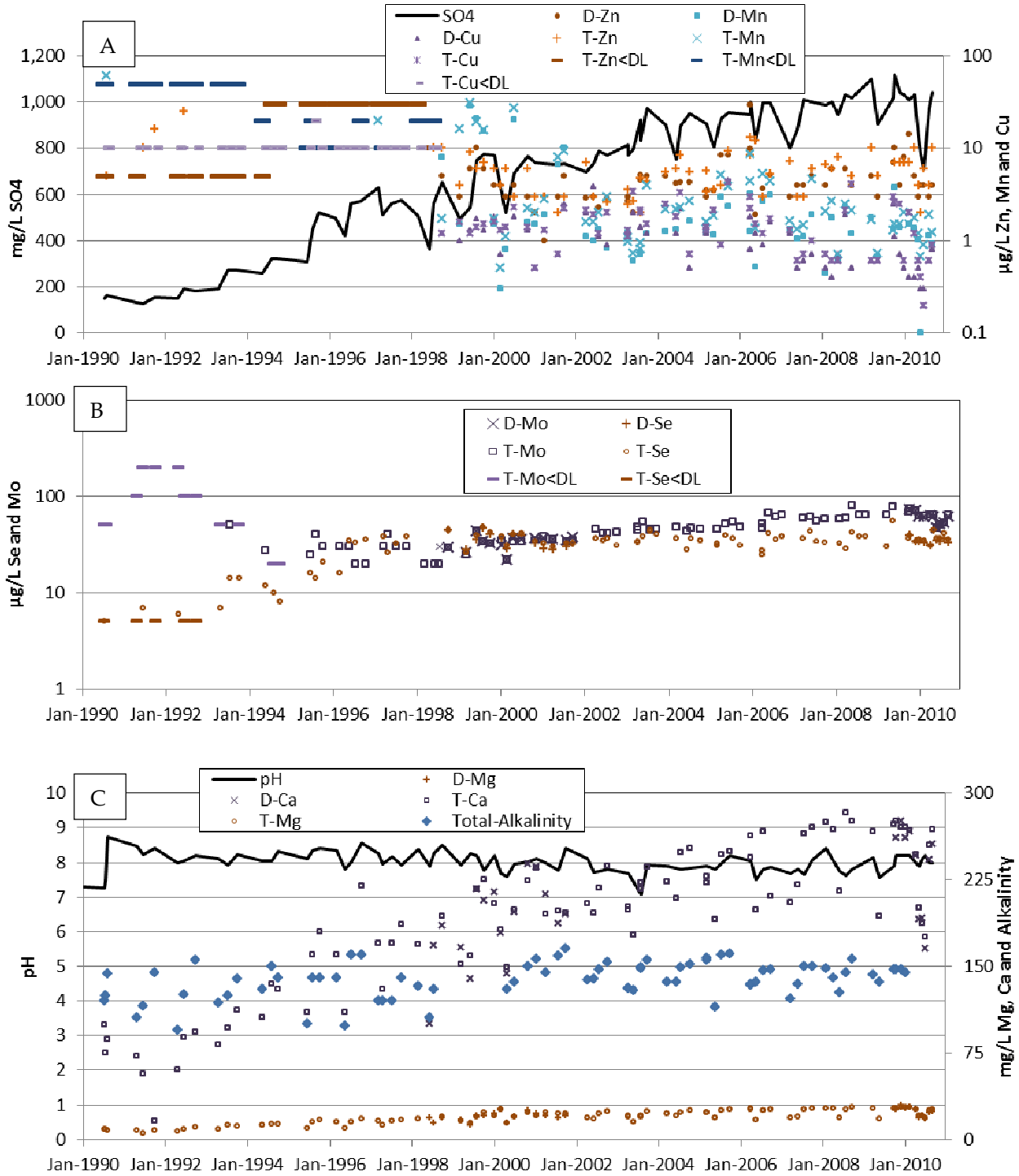

Figure 2. NAG drainage chemistry, (a) transition metal cations observed in highest concentrations and SO_4, (b) oxyanion forming metals/metalloids observed in highest concentrations, (c) base cations, alkalinity and pH.

Molybdenum trends in PAG and NAG dump drainage are markedly different. Between 1991 and 1998 Mo concentrations gradually decreased in the PAG dump seepage, from a peak of 470 µg/L to a minimum of 8 µg/L. Similar to Zn, Mo is released from sulfide oxidation. While sulfide mineral oxidation is expected to accelerate in

acidic regions of the dump, Mo released by oxidation of the sulfide mineral molybdenite would be adsorbed on mineral surfaces under acidic conditions. Therefore, the decreasing trend in Mo concentrations in the PAG dump is interpreted as evidence for acidification of interior regions of the dump. The opposite trend in Mo concentrations is observed in the NAG dump, where Mo has been gradually increasing proportional to increases in SO_4.

Buffering Minerals

In order to identify minerals responsible for pH buffering, PHREEQC equilibrium modeling was conducted with the minteq.v4 database (Parkhurst and Appelo, 1999). The saturation indices (SI) calculated for calcite and gibbsite are presented in Figure 3a, and 3b, respectively. Calcite has been identified to occur in waste rock using XRD. Gibbsite was not identified in waste rock, however it is a common secondary mineral which forms as a result of Al-silicate weathering. Furthermore, gibbsite has elsewhere been shown to buffer drainage at a pH between 4 and 5, similar to that which is observed in the PAG (Blowes et al., 2003). Dissolved aluminum concentrations for both waste rock dumps are presented in Figure 3b as well. A majority of water quality samples collected from waste rock drainage were only measured for total concentrations. Therefore the PHREEQC model was run using totals concentrations, and dissolved concentrations when available to calculate calcite saturation. Only D-Al concentrations are modeled. In Figure 3a, the SI of calcite calculated by total concentrations are nearly identical to those calculated using dissolved concentrations when available. This indicates that total concentrations are sufficient in modeling calcite saturation. Note that the SI of calcite is not plotted for the PAG dump after acidic conditions develop.

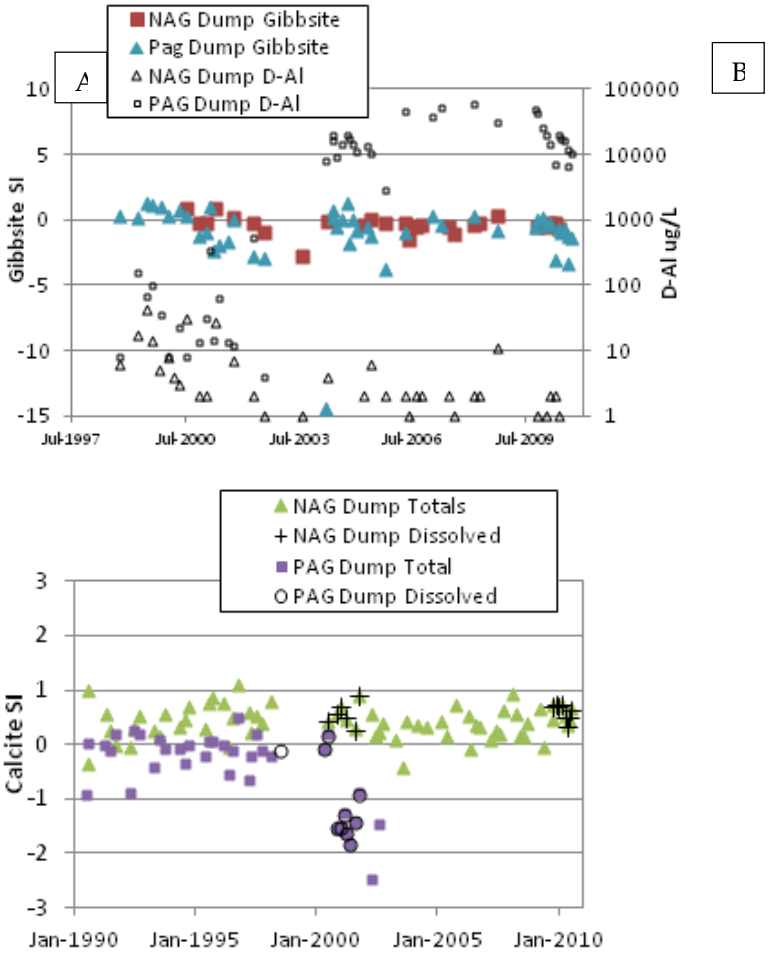

Figure 3. Saturation Indices of Calcite (a) and Gibbsite (b) in the NAG and PAG waste rock dump. The saturation indices of calcite is modeled using both T-Ca and D-Ca concentrations, while the saturation indices of gibbsite is modeled using only D-Al.

The PHREEQC equilibrium model shows that the NAG dump is typically somewhat oversaturated with respect to calcite. This may be due to elevated pCO_2 at the base of the dump. The PAG dump is typically near equilibrium

with respect to calcite prior to 2000. In November, 2000 calcite dropped below equilibrium in the PAG dump drainage, this drop coincided with the beginning of instability in drainage pH (Figure 1). Once persistent acidic conditions developed in the PAG dump after 2004, the pH remained at approximately 4.6. Following acidification, a steep rise in Al concentrations occurred. Dissolved Al concentrations for the PAG dump are plotted in Figure 3b along with the SI of gibbsite. Results for the NAG dump show that gibbsite remained near equilibrium at all time points where D-Al was measured and above detection limits.

Gibbsite generally remaineded near equilibrium in the NAG dump. In the PAG dump, gibbsite was near saturation up until November 2000. After this point a gradual decline in the SI of gibbsite is observed concurrent to instability in pH and the SI of calcites dropping below equilibrium. In 2004 the pH became persistently acidic, Al concentrations increased to approximately 8000 µg/L, and gibbsite returned to equilibrium. In 2005 gibbsite again dropped below equilibrium corresponding to a temporary rebound in pH (Figure 1). In 2006 Al concentrations increase in response to a drop in pH, and gibbsite again returned to equilibrium. The high Al concentrations along with the pH being in a range typical of an Al-buffered system indicate that gibbsite was buffering the pH of the PAG waste rock dump after persistently acidic conditions develop.

EARLY INDICATIONS OF ACIDIC SEEPAGE

The evolution of seepage from the PAG dump can be divided into three stages based on pH, metal concentrations, and buffering mineral phases. The first stage is the neutral pH time period between 1990 and 1998. During this time period the pH was buffered by calcite and remained between 7.2 and 8.3. The second stage is the transitional period between 1998 and the onset of persistently acidic conditions in 2004. This period is distinguished by highly variable metal concentrations, followed by calcite dropping below saturation, instability in pH, and a decrease in alkalinity. The final stage is the onset of persistent acidic drainage buffered by gibbsite. Further evolution of the dump drainage may take place if the gibbsite buffering phase is depleted, as discussed in Stockwell and Dockrey (2012).

Indications of acidic seepage can be found in the first stage in the evolution of the PAG waste rock dump described above. The earliest trend which is considered indicative of future acid generation is a decline in Mo concentrations (Figure 1). This decline in Mo concentrations becomes readily apparent in 1993, which is more than a decade prior to the first appearance of acidic seepage. The decline in Mo concentrations is considered indicative of zones in the interior of the dump becoming acidic, limiting Mo mobility. Conversely, Mo concentrations have risen proportionally to SO_4 concentrations in the neutral pH NAG dump.

August 1999 is considered the beginning of the second stage in the evolution of the PAG dump, as described above. In this stage signals of increased metal leaching and sulfide oxidation become evident. In 1999, a peak in SO_4 concentrations took place which was accompanied by an order of magnitude increase in Zn concentrations and a further decline in Mo concentrations. High Zn concentrations can be leached at a neutral pH, however sudden changes in leaching rates indicate that the dump is becoming more reactive, the inverse behavior of Mo identifies this shift as being related to a decline in pH. The peak concentrations observed in 1999 are short lived, quickly returning to a concentration range previously observed. However, no rebound in Mo concentrations takes place. Conversely, in the NAG dump concentrations of Mn and Zn typically remain below (<10 µg/L). This is particularly noteworthy as the rock types which primarily compose the NAG dump are relatively enriched in Zn and Mn compared to the rock types which compose the PAG waste rock dump. Furthermore, the NAG dump is leaching similar SO_4 concentrations as the PAG dump during this time period.

The pH decreases from alkaline to circumneutral 2 years before the first appearance of acidic pH, and 3 years before the pH becomes persistently acidic. Highly variable Mn, Zn and Cu concentrations continue during this time period. The inability of calcite to buffer the drainage pH is a clear indication that the most affect neutralization potential of the pile is being depleted.

REFERENCES

Blowes, D.W., Ptacek, C.J., Jurjovec, J., (2003). Mill tailings: hydrogeology and geochemistry. In: Jambor, J.L., Blowes, D.W., Ritchie, A.I.M. (Eds.), Environmental Aspects of Mine Wastes, Short Course Volume 31, Mineralogical Association of Canada, pp. 95-116 (chapter 5).

Morin, K.A., Hutt, N.M., (2000). Discrete-zone mixing of net-acid-neutralizing and net-acid-generating rock: Avoiding the argument over appropriate ratios. In: Proceedings from the Fifth International Conference on Acid Rock Drainage, May 20-26, Denver, USA, Volume II, p. 797-803. Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, USA. Page 797

Parkhurst, D.L., Appelo, C., (1999). User's guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculation. USGS, Water-Resour. Invest. Rep. 99-4259.

Sobek, A.A., Schullers, W.A., Freeman, J.R., Smith, R.M. (1978). Field and laboratory methods applicable to overburden and minesoils, EPA 600/2-78-054, 203pp.

Stockwell, J.S., Dockrey, J.W., (2011). Aluminum buffering and geochemical equilibrium of seepage from a mildly acidic waste rock dump – long-term observations and implications for future water quality. In, Proceedings of the 9th International Conference on Acid Rock Drainage, May 20-26, 2012, Ottawa, ON, Canada.