Estimation of Immediate Acid and Neutralization Rates within ARD Waste Rock Storage Facilities

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ABSTRACT

The weathering rate of primary silicate minerals in a waste rock storage facility determines dump drainage pH and associated behaviour of contaminants in the later stages of the acid rock drainage (ARD) profile due to their long-term acid neutralization capacity. This long-term non-carbonate neutralization rate (ANRnc) value can be used, for more economical ARD management, to estimate the cover thickness and saturation required to control the acid generation rate (AGR) within the waste storage facility, so that the two parameters (ANRnc and AGR) are matched, potentially providing an initial design target for emplacement and cover design. We previously established two methods to determine the ANRnc in a waste sample: i) silicate mineralogy using the available pH-dependent dissolution rate database from the literature; and ii) long-term column leach solution assays with the ANRnc calculated from cation release. The ANRnc values estimated using the two methods for a given waste show good agreement and reproducibility at pH < 4.

As part of the AMIRA International funded project “Alternative Treatment Options for Long-term ARD Control” (P933A), four case studies were carried out to estimate immediate AGR and ANRnc within weathered ARD waste rock storage facilities using mine site water monitoring data in combination with the waste mineralogical tests. These estimates may represent a useful tool to monitor, plan and ultimately help reduce the effects of ARD at mine sites; i.e. to determine what strategies may be necessary to attempt to reduce the AGR to equal the ANRnc.

This paper focuses on the results from our investigations of AGR and ANRnc within a number of mining waste dumps. Estimates of the evolution of dump profiles were determined with a view towards matching the values of the AGR and ANRnc within the wastes.

Keywords: long-term non-carbonate neutralization rate, acid generation rate, waste rock storage facility, site mineralogy, water quality monitoring
INTRODUCTION

The weathering rate of primary silicate minerals in a waste rock storage facility determines dump drainage pH and the associated behavior of contaminants in the later stages of the acid rock drainage (ARD) profile due to their long-term acid neutralization capacity. Given the abundance of these silicates in most mine wastes, the widespread occurrence of ARD shows that in many circumstances, silicates in the absence of carbonates do not provide neutralizing capacity at a sufficiently fast rate to neutralize acidity resulting from sulfide oxidation (Gerson et al., 2014a, Gerson et al., 2014b). The acid generation rate (AGR) from sulfide oxidation is therefore required to be reduced and the long-term non-carbonate neutralization rate (ANRnc) from dissolution of silicates needs to be measured so that the two parameters can be matched for long-term ARD management. These measurements can potentially provide an initial design target for emplacement and estimation of the cover thickness and saturation required to control the AGR within the waste storage facility. This paper will explain these estimates, their current limitations and their application to real ARD wastes.

We previously established two methods to determine the ANRnc in a waste sample: i) from silicate mineralogy using the available pH-dependent dissolution rate database from the literature (Palandri and Khraka, 2004); and ii) from long-term column leach solution assays with the ANRnc calculated from cation release. The ANRnc values estimated using the two methods for a given waste have shown good agreement and reproducibility at pH values < 4 (Miller et al., 2010). However, it has been noticed that at greater pH, ANRnc values calculated from mineralogy generally exceeded those calculated from leach column testing (Gerson et al., 2014a, Gerson et al., 2014b) possibly due to removal of some cations by precipitation in the leach columns. In a similar approach, Morin and Hutt (2011) compared ANRnc values derived from mineralogy with those obtained from short-term humidity cell tests. They found that the rates calculated from mineralogy were similar to, or substantially less than, the measured values. Most recently, we carried out four case studies to estimate immediate AGR and ANRnc within four weathered ARD waste rock storage facilities.

Site A

Site A is a zinc and lead mine located in Alaska. The site is sufficiently cold to support permafrost. Mean annual rainfall at the mine site is 467 mm with a mean measured ground temperature of -2 °C. The waste dump contains approximately 36 million tonnes (Mt) of potentially acid forming (PAF) waste rock. Acid rock drainage (ARD) from the stockpile is towards a tailings impoundment and is treated to meet specific water quality standards prior to discharge.

Site B

The Bingham Canyon porphyry Cu deposit is located in the Oquirrh Mountains immediately west of Salt Lake City, Utah. Large scale open pit Cu mining began at the Kennecott Utah Copper Bingham Canyon (KUCBC) mine in 1906 and mining is currently planned to continue for more than a decade. Waste rock placement on the eastern margin of the Oquirrh Mountains (Eastside dumps) began in 1953 and is still on-going (Borden 2003; Borden et al., 2006). The total mass of waste rock classified as PAF materials within the Eastside dumps was estimated to be approximately 2.2 billion tonnes up to 2004. Copper concentrations within the placed waste rock have averaged less than
0.1% (Borden, 2003). From 1941, Cu was recovered from the waste rock dumps by active heap leach operations, in addition to beneficiation and smelting operations (Borden et al., 2006), until all leach water applications were terminated in September 2000. Since infiltration into the dumps occurred only from natural rainfall after leaching was terminated, drain down of acidic water (at a flow rate of 45 L/s in 2004) has been collected, treated and used in the process water circuit (Borden et al., 2006).

Site C

The Savage River iron ore mine is located in north-west Tasmania, Australia. To date, mining operations have generated in excess of 50 million m\(^3\) of ore and 300 million m\(^3\) of waste rock since about 1975. Current mining plans allow for the potential of a further 100 million m\(^3\) of waste rock over the next 15 years (Gerson et al., 2014a). However, ARD, emanating from legacy (sulfide-containing) waste-rock dumps at the mine site, which flows into both Main Creek and the Savage River, is impacting the river and its tributaries. The historic B-dump was identified as a significant source of ARD at the site and D-type PAF waste is responsible for the major part of the AMD issues in B-dump. From early 1970 to 1996, about 13 Mt of D-type PAF waste rock was placed into B-dump, from which approximately 40% of the total Cu load emanated, and which flows down the river through Main Creek (Li et al., 2011, Li et al., 2012). To reduce impact to the river, combined water shedding and alkaline (A-type chlorite-calcite schist) covers were constructed over the dump in 2006 for long-term ARD control. It has been reported that the average rainfall infiltration was reduced to 9% by the water shedding cover (Hutchison et al., 2009). The alkaline side cover allows rainwater infiltrating the cover to take up alkalinity from the A-type material, and this alkalinity can then react with, and neutralize, existing acid drainage (Hutchison et al., 2009). It was found that alkalinity from the side cover has been migrating down into the D-type PAF waste below, forming passivating layers on pyrite grains, but it may be some time before the remaining PAF waste in the dump is fully passivated (Li et al., 2011).

Site D

The Mount Whaleback mine is an iron ore mine located in the Pilbara region of Western Australia, six kilometers west of Newman. The mine is majority-owned (85%) and operated by BHP Billiton, and is one of seven iron ore mines the company operates in the Pilbara. Approximately 10 wt% of the total remaining waste rock at the BHPBIO Mount Whaleback Mine has been identified as PAF materials that contain sulfide minerals > 1 wt%; e.g. altered black shale from the Mount McRae shale contains 4 wt% pyrite, 50 wt% chlorite, 27 wt% muscovite, 2 wt% dolomite, 1 wt% hematite and 16 wt% quartz (Webb et al., 2006). The earliest acidic drainage found at the Mt Whaleback site was from seepage at the toe of the W39 Terrace Dump in 1995 (Huys, 2010). There are about 40 Mt of waste rock placed in the dump covering a surface area of 0.51 km\(^2\). Based on the average annual rainfall of 314 mm in the Mt Whaleback area (Newman Aero weather station), the average seepage rate was estimated to be 5.08 L/s (assuming full rainfall infiltration). To manage this ARD, an ARD Dam (clay compacted floor) that is below and adjacent to the dump (capacity = 850 ML; surface area = 0.32 km\(^2\)) was constructed in 1995 to collect the seepage and some surface run-off waters from the mine site.

The aim of this study was to scale up our AGR and ANRnc estimation methodology to these four real waste rock storage facilities using existing mine site water monitoring data in combination with the waste mineralogical tests. This paper describes the results from our investigations of AGR and
ANRnc within the four ARD waste rock storage facilities, as well as combining the AGR and ANRnc to produce estimates of the evolution of the dump profiles towards matching these values within the wastes.

METHODOLOGY

Waste rock sample preparation

Site A and Site B waste rock samples were provided by their respective companies. Site C-dump waste rock sample (D-type, potentially acid forming) was collected through an excavation of the eastern alkaline side cover of the dump in 2010 (Li et al., 2011). A Site D waste rock sample of Mt McRae black shale was collected from WB 0505-403 at the mine site and column leached for 2.5 years. The leached residue solid is expected to have similar mineral composition to that in the W39 Terrace Dump. All the rock samples (particle size < 4 mm) were initially dried in an oven at 50 °C overnight with argon purging, and, dry sieved through a 75 µm screen. For X-ray diffraction (XRD) analyses, all the samples were micronized to -2 µm to reduce particle orientation effects on XRD data collection and corundum (α-Al₂O₃, 15 wt%) was added to each sample as an internal standard to quantify the amorphous content in the sample. Corundum (0.3 g) was added to 1.7 g of pulverised material (-75 µm) and then micronized with 10 mL of ethanol using a McCrone Micronizing Mill for 10 minutes. Each suspension obtained was dried in an oven at 50 °C and stored in a sealed tube prior to XRD analysis.

Silicate mineralogy

The simplest method of estimating ANRnc is to calculate the parameter from the known silicate mineralogy of the waste, determined at the time that the pH and AGR are measured using the available pH-dependent dissolution rate database from the literature. The mineralogy of waste samples was determined by XRD and mineral dissolution rate data used in the study is from Palandri and Kharaka (Palandri and Kharaka, 2004) and Lowson and coworkers (Lowson et al., 2007, Lowson et al., 2005) for chlorite. The methodology of the ANRnc calculation steps is described in detail in Miller et al. (2010).

XRD analyses of solid samples were conducted at the Bragg Crystallography Facility, School of Chemistry and Physics, the University of Adelaide. The data collection was performed on a Bruker D4 Endeavor diffractometer with Co Ka radiation (1.7902 Å) at 30 kV and 20 mA. Diffraction patterns were collected with 0/2θ geometry from 5 to 80 °2θ at 0.02 °2θ increments with a rotating sample stage to ameliorate preferred orientation effects. Phase identification was carried out using the DiffracPlus EVA software (Bruker) with the ICDD-PDF2 database (International Center for Diffraction Data, 2000). Bruker-AXS TOPAS V4.2 software was then used to quantify each phase. Crystal structure information for all the minerals was obtained from the Bruker Structure Database.

Estimations from water quality monitoring data

An alternative method of estimating ANRnc can be formulated using solution assay data from long-term standard kinetic column leach tests of -4 mm crushed waste rocks and tailings (Smart et al., 2002) with the ANRnc calculated from cation release (Na, K, Ca, Mg and Al) (Miller et al., 2010). The ANRnc (mg H₂SO₄/kg/week) formulation was first developed by (Paktunc, 1999) and extended by (Miller et al., 2010) as expressed as Equation 1.
\[
\text{ANR}_{nc}(\text{mg} \text{H}_2\text{SO}_4 \text{Kf}^{-1} \text{week}^{-1}) = \frac{R_f \times 49 \times 1000}{m} \left( \frac{\text{Na}}{M_{\text{w}(\text{Na})}} + \frac{\text{K}}{M_{\text{w}(\text{K})}} + \frac{\text{Mg}}{M_{\text{w}(\text{Mg})}} + \frac{\text{Ca}}{M_{\text{w}(\text{Ca})}} \right) \times 2 + \frac{\text{Al}}{M_{\text{w}(\text{Al})}} \times 3 \right) \quad (1)
\]

where, \( R_f \) is the measured drainage flow rate (L/week), \( m \) is the mass of a waste rock sample in the column (t), \( \text{Na}, \text{K}, \text{Mg}, \text{Ca} \) and \( \text{Al} \) are dissolved metal concentrations in the drainage (mg/L), \( M_{\text{w}} \) is the molecular weight and the factor 49 converts mmol H\(^+\) ions to mg H\(_2\)SO\(_4\).

In this study, Equation 1 was used to calculate immediate ANRnc within a waste rock storage facility using water quality monitoring data from each mine site.

RESULTS AND DISCUSSION

Site A

The waste rock collected in 2008 in the stockpile contains 13.9 wt% pyrite with 3.6 wt% sphalerite as sulphide minerals, 5.5 wt% barite and 0.1 wt% gunningite (sulfate minerals), 60.3 wt% quartz, 10.7 wt% biotite with 2.5 wt% albite, 2.2 wt% muscovite and 1.2 wt% sanidine, and is classified as PAF by the acid-base account (ABA) and net acid generation (NAG) testing. However, our recent XRD analyses on waste rock collected in 2010 in the stockpile but at a different area revealed a different mineral composition of 3.3 wt% pyrite, 3.0 wt% sphalerite, 2.5 wt% galena, 70.3 wt% barite and 20.9 wt% quartz within the waste rock. This suggests that the mineral composition of the waste rock varies significantly across the whole stockpile. Since the recent waste rock sample does not contain any silicates other than quartz the silicate mineralogy of the sample collected in 2008 was used for estimation of mineralogical ANRnc and the ANRnc value of 141 mg H\(_2\)SO\(_4\)/kg/week was obtained for the waste as shown in Table 1 the predominant contribution coming from biotite at the dump pH 2.7.

Water monitoring data for the samples collected from Site A in 2002 were averaged and are listed along with other measured parameters in Table 2 for the ANRnc and AGR (based on dissolved sulfate concentration) estimations. The average pH of these samples was low at 2.5. Solution assay data for a typical sample with pH 2.7 (collected in 2008 at the stockpile) was also used for the estimations (Table 2). Table 2 shows relatively high Mg and Al concentrations in the seep waters and the concentrations increased with weathering (six years), consistent with the dissolution of biotite identified in the waste rock mineralogy (Table 1). A relatively high Ca concentration and low K concentration are most likely due to dissolution of gypsum and formation of jarosite in the stockpile although these two secondary mineral phases were not identified by XRD, probably due to their relatively low content and ultrafine jarosite deposition.

The ANRnc value from leached cations was 0.8 mg H\(_2\)SO\(_4\)/kg/week. The AGR of 2.2 mg H\(_2\)SO\(_4\)/kg/week estimated from sulfate concentrations was about three times greater than the ANRnc in the stockpile in 2008 (Table 3). It is worth noting that the AGR within the stockpile decreased by a factor of five from 10.7 mg H\(_2\)SO\(_4\)/kg/week in 2002 to 2.2 mg H\(_2\)SO\(_4\)/kg/week in 2008 and the AGR/ANRnc ratio for the stockpile decreased from 14 to 3 during the six years of weathering (Table 3). These differences represent the evolution of the Site A waste rock oxidation with time; they suggest the stockpile is over the peak and on the downward path in its AGR/ANRnc ratio vs time profile. In 2008, it was clearly further down the path than in 2002.
Table 1 Calculated ANRnc (mg H$_2$SO$_4$/kg/week) from silicate mineralogy of different waste rock materials.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Site A (ANR at pH 2.7)</th>
<th>Site B (ANR at pH 2.9)</th>
<th>Site C (ANR at pH 3.4)</th>
<th>Site D (ANR at pH 4.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass fraction</td>
<td>ANRnc</td>
<td>Mass fraction</td>
<td>ANRnc</td>
</tr>
<tr>
<td>Quartz (SiO$_2$)</td>
<td>0.603</td>
<td>-</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>Biotite (KMg$<em>{1.5}$Fe$</em>{1.5}$Al$<em>{3}$SiO$</em>{10}$(OH)$_2$)</td>
<td>0.107</td>
<td>1147</td>
<td>0.12</td>
<td>1612</td>
</tr>
<tr>
<td>Albite (NaAlSi$_3$O$_8$)</td>
<td>0.025</td>
<td>479</td>
<td>0.14</td>
<td>472</td>
</tr>
<tr>
<td>Muscovite (KAlSiO$_3$(OH)$_2$)</td>
<td>0.022</td>
<td>42</td>
<td>0.22</td>
<td>21</td>
</tr>
<tr>
<td>Sanadine (KAlSiO$_3$)</td>
<td>0.012</td>
<td>461</td>
<td>0.22</td>
<td>21</td>
</tr>
<tr>
<td>Total Site A</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Site B</td>
<td>434</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Site C (ANR at pH 3.4)</th>
<th>Site D (ANR at pH 4.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass fraction</td>
<td>ANRnc</td>
</tr>
<tr>
<td>Quartz (SiO$_2$)</td>
<td>0.12</td>
<td>1612</td>
</tr>
<tr>
<td>Clinohlore$^#$</td>
<td>0.025</td>
<td>479</td>
</tr>
<tr>
<td>Muscovite (KAlSiO$_3$(OH)$_2$)</td>
<td>0.13</td>
<td>366</td>
</tr>
<tr>
<td>Total Site C</td>
<td>264</td>
<td></td>
</tr>
</tbody>
</table>

$^*$kinetic dissolution rate data from Palandri and Khraka (2004).
$^#$Clinohlore dissolution rate data from Lowson et al., (2005; 2007).

The 2008 ANRnc (2.2 mg H$_2$SO$_4$/kg/week) estimated from seep assays is about two orders of magnitude slower than that (141 mg H$_2$SO$_4$/kg/week) calculated from the mineralogy of the waste rock collected at the same time. The mineralogy estimate assumes a 38-75 µm size fraction with average surface area of 1 m$^2$/g whereas the standard column leach used sieved -4 mm material. It was reported that waste rock in a storage facility commonly contains 10 - 30 wt% of -4 mm materials (Kempton, 2012). Given the particle surface area differences, the difference between ANRnc values estimated using the waste stockpile seep assays and mineralogy/laboratory column leach assays are not surprising. This suggests that a scale factor of the order of 0.01 should be applied to the mineralogical estimate here and in the other case studies below. A closer estimate of the effective surface area in the -4 mm samples is currently being defined.
Table 2 Selected cation concentrations from water monitoring data of waste storage facility at different mine sites for AGR and ANRnc estimation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Site A Year 2002</th>
<th>Site A Year 2008</th>
<th>Site B</th>
<th>Site C</th>
<th>Site D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (L/week)</td>
<td>2,831,198</td>
<td>2,831,198</td>
<td>27,216,000</td>
<td>4,294,080</td>
<td>1,632,960</td>
</tr>
<tr>
<td>Waste mass (t)</td>
<td>17,800,000</td>
<td>33,000,000</td>
<td>22,000,000</td>
<td>3,941,212*</td>
<td>40,091,000</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>2.7</td>
<td>2.9</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Acidity (mg CaCO_3/L)</td>
<td>-</td>
<td>18,000</td>
<td>30,000</td>
<td>300</td>
<td>67</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>3</td>
<td>21</td>
<td>40</td>
<td>19</td>
<td>182</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>5</td>
<td>26</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>235</td>
<td>540</td>
<td>500</td>
<td>226</td>
<td>446</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>445</td>
<td>1,100</td>
<td>10,000</td>
<td>400</td>
<td>693</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>435</td>
<td>610</td>
<td>3,000</td>
<td>55</td>
<td>44</td>
</tr>
<tr>
<td>SO_4 (mg/L)</td>
<td>65,980</td>
<td>25,000</td>
<td>60,000</td>
<td>2,496</td>
<td>4,124</td>
</tr>
</tbody>
</table>

*The type D waste rocks in side cover area.

Table 3 Calculated ANRnc (mg H_2SO_4/kg/week) using water monitoring data from different waste storage facilities at the mine sites.

<table>
<thead>
<tr>
<th>pH</th>
<th>ANRnc</th>
<th>AGR</th>
<th>AGR/ANRnc</th>
<th>ANRnc mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A (2002)</td>
<td>2.5</td>
<td>0.8</td>
<td>10.7</td>
<td>14.2</td>
</tr>
<tr>
<td>Site A (2008)</td>
<td>2.7</td>
<td>0.8</td>
<td>2.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Site B (2004)</td>
<td>2.9</td>
<td>71.7</td>
<td>75.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Site C (2009)</td>
<td>3.4</td>
<td>2.7</td>
<td>2.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Site D (2008-2009)</td>
<td>4.2</td>
<td>0.5</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Site B

The Site B waste rock contains 5 wt% pyrite (sulfide), 3 wt% alunite, 2 wt% jarosite and 1 wt% gypsum (sulfate minerals), 52 wt% quartz, 15 wt% clinocloreh, 13 wt% orthoclase, 2.2 wt% muscovite and 10 wt% muscovite (silicate minerals) and are classified as PAF materials. Based on the silicate mineralogy, an ANRnc value of 434 mg H_2SO_4/kg/week, predominantly contributed from clinocloreh, at the effluent pH of 2.9, was calculated (Table 1).

The typical water quality data reported by Borden et al. (Borden et al., 2006) for the seeps from the dump toe in 2004 show the seep waters were highly acidic (pH 2.9) with high Mg, Al and sulfate concentrations (Table 2). In addition to Al, Fe (250 mg/L), Mn (350 mg/L), Cu (140-600 mg/L) and Zn (170 mg/L) were also significant metals in the water (Borden et al., 2006) that contributed to a high titratable acidity (30 g CaCO_3/L). The high Mg and Al concentration is consistent with the predominant dissolution of clinocloreh at pH 2.9 (Table 1). The ANRnc (72 mg H_2SO_4/kg/week) and AGR (76 mg H_2SO_4/kg/week) within the dumps were calculated. It was found that the ratio of AGR/ANRnc was close to 1 (Table 3). However, in this case the AGR may be underestimated due to formation of gypsum, jarosite and alunite, as identified by XRD. It is well known that the use of effluent sulfate concentration can lead to an underestimation of the AGR arising from pyrite.
oxidation as formation of S containing secondary sulfate minerals may occur. In practice, this can be corrected using oxygen consumption measurements (e.g. using a sulfide oxidation cell). Table 3 shows that the ANRnc (72 mg H$_2$SO$_4$/kg/week) estimated from seep assays is about one order of magnitude slower than that (434 mg H$_2$SO$_4$/kg/week) calculated from the rock mineralogy.

**Site C**

The use of waste dump drainage assays and mineralogy methods to estimate ANR and AGR in the wastes may provide a possible measure for B-dump cover performance in ARD control at the Savage River Mine site. The D type PAF waste rock collected from the eastern side cover of the dump in 2010 was quantified to contain 2 wt% pyrite, 12 wt% clinochlore, 14 wt% albite, 22 wt% muscovite, 41 wt% quartz and 9 wt% amorphous. The mineralogical ANRnc was calculated to be 264 mg H$_2$SO$_4$/kg/week at pH 3.4 and the clinochlore chlorite in the rock contributed most of the ANRnc (Table 1).

B-dump water monitoring data extracted from Koehnken (2010) were used to calculate ANR and AGR (Table 2). Since the B-dump seep between the two Main Creek water monitoring points (Main Creek at Pilot Plant and Main Creek at Dolomite Dam) was predominantly from the side cover area under which there are 30 wt% of total D-type PAF rocks in the B-dump, the D-type waste rock mass of about 3.9 Mt was used for the rates calculation (Table 2). The relatively high Ca and Mg concentrations associated with a low Al concentration in the pH 3.4 seep water suggest some alkalinity from the side cover by the partial dissolution of calcite and dolomite, in addition to the dissolution of clinochlore in the D-type PAF waste rock. The sulfate concentration was low (Table 2), consistent with the partial passivation of pyrite surfaces observed in the cover - D type waste interface which has resulted in a reduced sulfide oxidation rate within the dump (Li et al., 2012, Li et al., 2011). The ANR (2.7 mg H$_2$SO$_4$/kg/week) and AGR (2.8 mg H$_2$SO$_4$/kg/week) in the dump were calculated and the ratio of AGR/ANR was close to unity as expected (Table 3). Again, the ANR is about two orders of magnitude slower than the mineralogical ANRnc of 264 mg H$_2$SO$_4$/kg/week at pH 3.4.

**Site D**

Our recent XRD analysis has identified the mineralogy of the BHPBIO weathered waste rock as containing 25 wt% clinochlore, 45 wt% muscovite, 26 wt% quartz and 4 wt% amorphous. The mineralogical ANRnc was calculated as being 72 mg H$_2$SO$_4$/kg/week at pH 4.2 and the clinochlore in the rock contributed all of ANRnc with a very minor contribution from muscovite (Table 1).

Water monitoring data for five water samples was extracted from a water quality dataset collected at the ARD Dam from March 2008 to August 2009 and averaged for the ANRnc and AGR calculation (Table 2). A dilution factor of 1.6 was used for the calculation according to the Dam surface area and the annual rainfall. Table 1 shows that the average water pH was relatively high at 4.2 with a very low titratable acidity. Since carbonate alkalinity in the water was less than 1 mg CaCO$_3$/L (not shown), high Mg with corresponding Al and Si concentrations in the solution is consistent with dissolution of clinochlore (Mg$_3.6$Fe$_{1.4}$Al$_{2}$Si$_3$O$_{10}$)(OH)$_8$) being the major neutralization mechanism within the dump. The high Ca concentration may have resulted from dissolution of other reactive silicate minerals in amorphous form, e.g. anorthite as a secondary product from gypsum during weathering in the dump. Values of ANRnc (0.6 mg H$_2$SO$_4$/kg/week) and AGR (0.6 mg H$_2$SO$_4$/kg/week) were estimated from the water monitoring data with an AGR/ANRnc ratio of 1.0 (Tables 2 and 3). The ratio of AGR/ANRnc of unity indicates that the AGR was fairly close to the
ANRnc provided by silicate minerals within the W39 Terrace Dump in 2008-2009 and that any further reduction in the acid generation rate will result in less acidic drainage from the dump with a subsequently increased water pH in the ARD Dam. Similar to other dumps, the ANRnc is about two orders of magnitude slower than the mineralogical ANRnc of 72 mg H₂SO₄/kg/week at pH 4.2.

**Combination of AGR and ANRnc as a function of pH**

We previously investigated the influence of the ratio of AGR to ANRnc on the pH of leachate from a number of long-term column leach tests and results are shown in Figure 1. When the AGR/ANRnc ratio approaches 1 the effluent pH starts to increase, but can still be as low as 3 when the AGR and ANRnc are matched (Miller et al., 2010). We have now extended this to include AGR/ANRnc and pH data from this study, which is also shown in Figure 1. The figure shows that the calculated AGR/ANRnc data estimated from each of the ARD waste storage facilities fall within the values measured for long-term column leach tests, suggesting that the estimates made for the facilities are quite reasonable.

![Figure 1](image)

**Figure 1** A comparison of ratios of AGR/ANRnc vs pH for different ARD waste rock storage facilities and columns.

The evolution of ARD within the Site A stockpile can be seen in the data shown in Figure 1. In 2002, the AGR/ANRnc ratio estimated from water assays was around 14, but this had dropped to approximately 3 by 2008, indicating that AGR may well be matched by ANRnc in the future. The AGR/ANRnc was about unity for the other three dumps and these too appear to approaching the matching rate. However, for the Site B dumps, the low pH (2.9) and high acidity conditions suggest that these first-level estimates involve possible overestimation of the ANRnc and underestimation of the AGR. There is still 5 wt% active pyrite along with alunite (3 wt%) and jarosite (2 wt%) in the dumps requiring long-term management.
CONCLUSION

An initial estimation of the immediate AGR and ANRnc within a weathered ARD waste rock storage facility can be achieved using mine site water monitoring data in combination with waste mineralogical tests. Given the possible effects of climate, preferential flow paths and variation of waste rock mineralogy by weathering etc. on the pore water chemistry in a storage facility, the ANRnc estimated by the water monitoring data may sometimes involve large uncertainties. As an alternative, the dump ANRnc can also be simply determined from the mineralogy, at time scales significantly shorter than traditional kinetic methods but this requires refinement of the effective surface area in the estimate. Uncertainties in AGR estimates from sulfate release alone can be reduced by comparison with oxygen consumption measurements. These estimates may then represent a useful tool to monitor, plan and ultimately help reduce the effects of ARD at mine sites; i.e. to determine what strategies may be necessary to attempt to reduce the AGR to match the ANRnc in the long term evolution of the dump.

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REFERENCES


