MIXING OF WASTE ROCK TO LOWER THE RELEASE OF Mg^{+2} AND SO_4^{-2} AT ARGYLE DIAMOND MINE[1]

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Abstract. The seepage from the Argyle mine waste dumps is mildly acidic and contains high concentrations of magnesium (1400 mg/L) and sulfate (6500 mg/L). Out of the fourteen waste rock types mined, only Pv1 (with relatively low total sulfur content of 0.1 % to 1.0 %) causes a significant release of acidity and solutes. Only Pv5 possesses abundant acid neutralizing capacity and releases significant amount of Ca^{+2} during neutralization reactions. Experiments conducted in the laboratory have shown that when Pv1 is blended with Pv5 (ratio 2:1) a neutral pH solution, with about 1/10 the Mg^{+2} and 1/3 the SO_4^{-2} is released compared to unblended Pv1 or blends made with other waste rock types. Argyle mine has recently implemented controlled co-disposal of these two rock types. The environmental and ecological benefits resulting from of these changes into the waste rock management procedures will be assessed in the coming years.

Introduction

Acid rock drainage (ARD) is the process of acid (H_2SO_4) formation by the oxidation (in the presence of water) of sulfide minerals in waste rocks and tailings. The acid thus formed can enter the environment with the simultaneous mobilization of metal ions, or react with acid neutralizing minerals and, release secondary products such as calcium (Ca^{+2}), magnesium (Mg^{+2}) and sulfate (SO_4^{-2}) ions to the environment.

ARD can be prevented or the composition of the ions released to the environment can be altered by blending different materials so that the acid formed is neutralized, and some of the secondary products are precipitated.

The main ARD problem at the Argyle mine is associated with the waste rock dumps. The seepage from the waste rock dumps, as measured at the toe of the south-east dumps, at gauging station WRDGSOQ, is mildly acidic (pH = 5.2 ± 0.7; acidity = 71 ± 35 mg/L $CaCO_3$) and contains considerable amounts of Ca (295 ± 88 mg/L), Mg (817 ± 322 mg/L) and SO_4^{-2} (3,919 ± 1,524 mg/L). The high acid neutralizing capacity of the receiving environment is evident from the near neutral pH and low acidity values at the gauging station ICIQ1, which is 500 meters south west of WRDGSOQ. The water quality parameters at ICIQ1 are: pH = 7.0 ± 0.6; acidity = 7 ± 3 mg/L $CaCO_3$; Ca = 221 ± 80 mg/L; Mg = 411 ± 163 mg/L and; SO_4^{-2} = 2,141 ± 842 mg/L.

Out of the fourteen different waste rock types that have been mined during the open pit operation, one type (Pv1) is classified as potentially acid forming (PAF), and a second type (Pcl3), although containing measurable sulfur (S) and previously considered to be PAF, has now been categorized as non-acid forming (NAF) (Environmental Geochemistry International - EGi, 2004 A and B). Both these rock types (if not managed properly) can undergo oxidation to produce H_2SO_4 and $MgSO_4$ and therefore, these rocks require special attention. On the other hand, the rock type Pv5 which contains a small amount of sulfides (0.02 to 0.09 %S), also has excess acid neutralizing capacity (ANC). Properties of the waste rock types are summarized in Table 1. It has also been estimated that during the remaining life of the open pit operation, Argyle will generate a further 186 million tonnes of waste rock. Of which 2.75 % will be Pv1, and 1.25% will be Pv5.

Methodology

Waste rock samples with known geochemical properties (for details see Environmental Geochemistry International - EGi, 2004 A and B) were used and composite samples were prepared as detailed in Table 2.

The net acid generation NAG) tests were performed in replicates and NAG solution properties including concentrations of Ca, Mg and SO_4 were determined. Briefly, the NAG test can be described as follows. Accurately weighed (2.5g) pulverized rock sample ($<75\mu m$) was treated overnight with 250 ml of 15 % H_2O_2. The resulting mixture was gently heated until effervescence stops (or for a minimum of two hours). The solution was cooled and adjusted to a final volume of 250ml with demonized water. After recording the initial pH of the solution (referred to as NAGpH), the resulting solution was titrated (to pH 4.5 and 7.0) with a NaOH solution of 0.10 M concentration. The blends were prepared by accurately weighing the

appropriate amounts of different rock types and transferring the weighed sample into the reaction flask.

Table 1.   Elemental composition, paste (1:2, rock:water) pH and EC, and ANC of waste rock types and ore (tailings) from the open pit operation

ELEMENTS	S	ANC	Paste pH	Paste EC	Co	Cr	Cu	F	Mn	Ni	Zn	ARD Class
UNITS	%	Kg H_2SO_4/t		mS/cm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
Rock Type												
Pcd	<0.005	6	6.6	8	48.3	32	85	125	1543	30	178	Barren
Pch	<0.005	2	6.9	26	3.8	14	7	75	159	3	14	Barren
Pcl1	0.007	3	5.6	10	9.8	60	80	410	228	20	28	Barren
Pcl2	<0.005	2	6.3	14	1.1	26	7	93	119	6	6	Barren
Pcl3	0.060	7	6.1	171	10.9	43	140	482	256	16	55	NAF
Pcl4	<0.005	3	6.6	21	0.4	20	2	74	76	2	16	Barren
Pv1	0.507	19	7.7	90	13	117	60	1504	220	43	53	PAF
Pv2	<0.005	5	7.8	19	2.5	20	93	455	32	8	18	Barren
Pv3	<0.005	6	7.7	31	11.6	77	4	1191	234	35	55	Barren
Pv4	<0.005	4	8.3	33	2.8	30	4	302	52	8	18	Barren
Pv5	0.053	115	9.2	150	15.2	35	103	679	1635	29	53	PAF
Pv6	<0.005	3	8.8	57	1	19	2	172	30	6	6	Barren
Pv7	<0.005	6	8.6	29	2.4	28	2	262	42	12	14	Barren
Pv8	<0.005	4	8.1	27	0.7	12	2	195	24	4	7	Barren
COARSE AK1 Tailings	0.039*	74	>8	nd	23.9	160	23	1286	398	325	52	NAF
FINE AKI Tailings	0.044*	89	>8	nd	38.1	240	31	1517	684	477	60	NAF

nd: not determined

The expected amounts of Ca, Mg, and SO_4^{-2} that can be released during the NAG test and relative decrease in the values were calculated using the available data such as the concentrations of these ions in the NAG solutions of individual rocks and blends and the weights of the rocks and blends used for the NAG test. . Appropriate correction was made for the dilution effect due to blending. The results are summarized in Table 3. The paste pH of Pv1 and Pv5 ranged from 7.6 to 8.3, and from 9.0 to 9.3 respectively and paste EC values of the two rock types were relatively small (<201μS/cm). Therefore, it was concluded that any determinations of the paste pH or EC of the blends are of little or no value and hence these tests were not carried out.

Approach

In deciding the suitable blend that can be used to improve the quality of seepage water, the following factors were considered:

- Geochemical properties of different waste rock types produced during the remaining life of the open pit operation;

- Availability and production rates of PAF and NAF materials (mainly Pv1, Pv5); and

- Chemical properties of the NAG soution of the resulting blends (pH, Electrical Conductivity - EC, Ca, Mg and SO_4 concentrations).

Table 2: Composition details of blend samples used

Sample Name	Samples Used	Proportions	Number of Replicates Used
Composite Pv1	Pv1 A, B, C, D, E, F and G	Equal amounts	1
Composite (Pv1 + Pv5 2:1)	Composite Pv1 and Composite Pv5	2:1	3
Composite (Pv1 + Pv5 1:2)	Composite Pv1 and Composite Pv5	1:2	2
Composite (Pv1 + Pcl3 1:2)	Composite Pv1 and Composite Pcl3	1:2	2
Composite (Pv1 + Pcl1 1:2)	Composite Pv1 and Composite Pcl1	1:2	2
Composite (Pv1 + Pv2 1:2)	Composite Pv1 and Composite Pv2	1:2	2

Results and Discussion

It can be seen (from data in Table 3) that:

- Mixing Pv1 and Pv5 (2:1) has produced a non acidic NAG solution (pH=9.3) and increased the Ca concentration in the NAG solution;

- Mixing Pv1 and Pv5 (2:1) has lowered the amounts of Mg (to 1/3 its original value) and SO_4 (to 1/10 its original value) released ;

- Mixing Pv1 and Pv5 (1:2) has produced a non acidic NAG solution (pH=9.2) and lowered the Ca concentration in the NAG solution;

- Mixing Pv1 and Pv5 (1:2) has lowered the released of Mg and SO_4, however, the decrease in Mg release was less pronounced (to ½ its original value) when compared with that of (2:1) blend;

- Mixing Pv1 with other waste rocks such as Pv2 or Pcl3 has not prevented acid production (NAG pH 3.9 – 4.0) or decreased the release of Mg and SO_4;

- Mixing Pv1 with Pcl3 has increased the amount of Mg and SO_4 release.

These observations with regard to the beneficial effects of blending Pv1 with Pv5 can be attributed to high ANC values (19 – 338 kg H_2SO_4/ tonne - EGi, 2004 A and B) arising from the considerable amounts of dolomite that is found in Pv5 (Townend, 2005). Under acidic conditions (when the NAG test is done with Pv1), the dissolution of magnesium bearing silicate minerals (such as chlorite $[(Mg,Fe^{+2},Fe^{+3})_6AlSi_3O_{10}(OH)_8]$) occurs and as a result of this, a solution of high magnesium concentration is formed. The NAG solution of a mixture of Pv1 and Pv5 is alkaline and these conditions do not favor the dissolution of magnesium-bearing silicate minerals. Furthermore, calcium provided by dolomite in Pv5 lowers the SO_4^{-2} concentration in the NAG solution by precipitating gypsum ($CaSO_4$).

Conclusions

Based on these findings, the following changes to the waste rock disposal procedures were implemented:

1) Co-disposal of Pv1 and Pv5:

   To ensure adequate contact between the two units, Pv1 and Pv5 are inter-layered so that there is an approximately 2 meter lift of Pv1 followed by a ½ to 1 meter lift of Pv5.

2) The classification of Pcl1 is being changed to non-adverse (barren) from its previous classification of adverse:

   As such, Pcl1 will no longer require special handling.

3) Pcl3 (which is classified as non acid forming) poses a much lower risk than Pv1 and could be safely dispersed throughout the dumps without special handling as long as it is not within five meters of a final dump surface or the original land surface.

   This has been recommended as Pcl3 will not generate large amounts of magnesium sulfate, but will locally acidify to a pH low enough to inhibit plant growth and rooting. When it cannot be placed as recommended (five meters buffer), then it is being

segregated into specific locations that can be capped at closure (but separate from the Pv1/Pv5 repositories).

It is of particular relevance to note the following findings by the Supervising Scientist, as reported in Annual Reports 2001/02 and 2002/03 and Internal Report 421(Camilleri, C., Hogan, A., McCullough, C. and van Dam, R., 2003).

- A number of aquatic test species were sensitive to low concentrations of $MgSO_4$;

- The toxicity is associated with the Mg^{+2} ion and not the SO_4^{-2} ion;

- Calcium ameliorates magnesium toxicity (for the test species, *Hydra*, as long as the Mg:Ca ration was maintained at 10:1 or below, then Mg^{+2} was not of significant toxicity).

Some diluted seepage from the waste rock dumps flows into the natural environment and as such any measures that lower the concentration of Mg^{+2} and SO_4^{-2} ions in the seepage waters will potentially assist in protect the receiving water ecosystems. The environmental and ecological benefits resulting from these changes into the waste rock management procedures will be assessed in the coming years.

Literature Cited

Camilleri C, Hogan A, McCullough C & van Dam R 2003. Toxicity of magnesium sulfate to local tropical aquatic species: Derivation of a site-specific trigger value. Internal Report 421, June, Supervising Scientist, Darwin. Unpublished paper*.

Environmental Geochemistry International 2004A. Geochemical Characterisation of Waste Rock samples, report prepared for Argyle Diamonds. Unpublished paper*.

Environmental Geochemistry International 2004B. Geochemical Characterisation of Samples from Argyle Diamond Mine, report prepared for Argyle Diamonds. Unpublished paper*.

Supervising Scientist 2002. *Annual report 2001–2002*. Supervising Scientist, Darwin NT. (http://www.deh.gov.au/ssd/about/corporatedocs.html)

Supervising Scientist. 2003. *Annual report 2002–2003*. Supervising Scientist, Darwin NT. (http://www.deh.gov.au/ssd/about/corporatedocs.html)

Townend, R. 2005. Preparation of Four Thin Sections of Four Rock Chip Samples and Brief Petrographic Descriptions. Four XRD identification of Carbonates. Report prepared for Argyle Diamonds. Unpublished paper*.

* Copies of unpublished papers can be obtained from the first author of this publication.

Table 3: Properties of NAG solutions of Pv1 and its different blends with other waste rocks

	NAG (7.0)	NAG (4.5)	NAG EC	NAG pH	SO$_4$	Ca	Mg	SO$_4$	Ca	Mg	Expected		Reduction	
											SO$_4$	Mg	SO$_4$	Mg
Units	kg H$_2$SO$_4$/t	kg H$_2$SO$_4$/t	μS/cm	NONE	mg/kg	mg/kg	mg/kg	mg/L	mg/L	mg/L	mg/kg		%	
Sample Details														
CompPv1	8	5	489	3.2	13673	1752	550	137	18	5.5	13673	550	0	0
Comp(Pv1 + Pv5 (2:1)) Rep 1	0	0	162	9.3	3370	2064	61	34	21	0.6	9115	367	63	83
Comp(Pv1 + Pv5 (2:1)) Rep 2	0	0	160	9.3	3265	2004	34	33	20	0.3	9115	367	64	91
Comp(Pv1 + Pv5 (2:1)) Rep 3	0	0	164	9.3	3511	2133	59	35	21	0.6	9115	367	61	84
Comp(Pv1 + Pv5 (1:2)) Rep 1	0	0	106	9.2	1309	989	79	13	10	0.8	4558	183	71	57
Comp(Pv1 + Pv5 (1:2)) Rep 2	0	0	102	9.2	1330	1061	136	13	11	1.4	4558	183	71	26
Comp(Pv1 + Pcl3 (1:2)) Rep 1	3	1	175	3.9	6046	509	398	60	5	4.0	4558	183	-33	-117
Comp(Pv1 + Pcl3 (1:2)) Rep 2	3	1	189	3.9	6010	516	398	60	5	4.0	4558	183	-32	-117
Comp(Pv1 + Pcl1 (1:2)) Rep 1	2	0	164	4.0	4670	343	224	47	3	2.2	4558	183	-2	-22
Comp(Pv1 + Pcl1 (1:2)) Rep 2	2	0	164	4.0	4787	404	226	48	4	2.3	4558	183	-5	-23
Comp(Pv1 + Pv2 (1:2)) Rep 1	2	0	173	3.9	4781	605	220	48	6	2.2	4558	183	-5	-20
Comp(Pv1 + Pv2 (1:2)) Rep 2	2	1	175	3.9	4922	619	222	49	6	2.2	4558	183	-8	-21