Potential strategies for sustainable control of acid generation from pyrite oxidation

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Abstract Kinetic leach column (KLC) tests were conducted to define the conditions required to control acid and metalliferous drainage (AMD) from a highly reactive, potentially acid forming (PAF) waste. 0.1 wt.% lime addition plus either blending of silicates (25 wt.% K-feldspar and 25 wt.% chlorite), or addition of a non-acid forming (NAF) cover , when watered/flushed with lime-saturated water, greatly reduced acid generation as compared to the control KLC (PAF alone, watered/flushed with Milli-Q), but did not result in circum-neutral pH as required for effective AMD mitigation. In contrast, the combined use of these treatments resulted in leachate pH of >12.

Keywords At-source acid and metalliferous drainage control, Kinetic leach column, NAF cover, Pyrite surface passivation, Reactive silicates

Introduction

Acid and metalliferous drainage (AMD) from both operating and inactive/abandoned mines (Sheoran et al. 2006) is a global environmental problem. In most cases AMD is triggered naturally by the oxidation of sulfide minerals, in particular pyrite—the most abundant sulfide mineral on the earth—through chemical and microbially-mediated reactions with both surface water and oxygen (Erguler et al. 2014). Acidic leachates containing toxic metals/metalloids, such as Fe, Mn, Cd, Pb, As and Se can be released. AMD is a complex and costly environmental issue, due to both the severity and long-lasting nature of the impacts. For the mining industry and governments AMD remediation is expensive with costs in the US and Canada alone estimated to be in the tens of billions of dollars (RoyChowdhury et al. 2015).

Accordingly, cost-effective and sustainable strategies for AMD prevention and remediation are highly desired. Pyrite surface passivating layers, incorporating silicates from the natural dissolution of reactive silicates in real sulfide waste rocks, can be preserved in a continuous, coherent and stable form at pH ≥ 6, and have been found to reduce the pyrite oxidation rate by 50-95% (Zeng et al. 2013). However, in some cases the establishment of these stable surface layers requires initial short-term treatment with greater concentrations of alkalinity than can be obtained from limestone covers. After passivation layers are established, the acid generation rate (AGR) can be reduced significantly so that some carbonates and reactive silicates such as limestone, anorthite feldspar, and hornblende, all commonly found in waste rocks, provide the required matching acid neutralising rate (ANR)(Smart

2015). This forms the fundamental hypothesis of our experimental approach for treatment of a highly reactive potentially-acid forming (PAF) iron ore waste (Mt McRae shale) from the Pilbara region of Western Australia.

The aims of this study were whether in conjunction with lime-saturated watering/ flushing the following treatments could maintain circum-neutral pH as required for the establishment and maintenance of pyrite passivation: (1) lime blending; (2) combined use of silicates (chlorite + K-feldspar) and lime blending; and (3) application of a dolomitic NAF cover in conjunction with lime blending or with both lime and silicate blending.

Materials and methodology

KLC tests setup

Kinetic leach column (KLC) tests were run with lime addition and/or the application of silicate minerals and locally-sourced non-acid forming (NAF) covers, to explore the conditions required to control AMD from the natural PAF waste. All KLC tests other than the control were watered/flushed with lime-saturated water.

Quartz, K-feldspar and chlorite (Geo Discoveries, New South Wales, Australia) were crushed, pulverised and dry sieved to -4 mm size. Setup and daily operation for the KLC (tab. 1) were based on Smart et al. (2002), except that different solutions were used for weekly watering (200 mL) and four-weekly flushing (800 mL). 0.1 wt.% lime was added to all KLC tests, except the control column, to establish a condition favourable for the formation of surface passivation layers on pyrite.

Sample characterisation

All mineral samples (dry-ground to -38 μm) were examined using powder X-ray diffraction analysis as per Qian et al. (2017). The concentration (± 10% error) of major ions from four-weekly KLC leachates was analysed via inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optima 5300 V). Calculations of mineral saturation indices were performed using the PHREEQC computer program, with the Lawrence Livermore National Laboratory database ('llnl.dat'), using E_h, pH, and solution chemistry of the leachates.

Results and Discussion

Sample characterisation

The results of net acid generation (NAG) and acid base accounting (ABA) tests of the two waste rock samples are provided in Tab. 2. The net acid producing potential (NAPP) results demonstrate the correct assignment of PAF and NAF for these two waste types. Quantitative XRD analysis indicated the following compositions (wt.%) for the PAF material - 42 quartz, 22 muscovite, 5 pyrite, 4 K-feldspar, 3 lizardite, and 24 amorphous phase(s), and for the NAF material - 54 quartz, 13 chlorite, 11 dolomite, 10 K-feldspar, 8 siderite, and 4 amorphous phase(s).

Table 1 *The composition (wt.%) of the KLC tests.*

KLC (−4 mm)	Contents	Watering and flushing protocol
control	50% PAF[1] (4.1 wt.% pyrite) + 50% quartz	Milli-Q for all watering/flushing
(1) lime	50% PAF + 50% quartz + 0.1 % lime	
(2) lime+cover	(1) + 400 g NAF cover[2]	Milli-Q watering/flushing prior to flush 1 and lime-saturated water for watering/flushing from flush 1
(3) lime+silicate	50% PAF +25% chlorite +25% K-feldspar + 0.1 % lime	
(4) lime+silicate+cover	(3) + 400 g NAF cover	

[1]Mt. McRae Shale (Undifferentiated); [2]Wittenoom Formation Paraburdoo Member

Table 2 *ABA and NAG test result of PAF and NAF wastes (in kg H_2SO_4 t^{-1}).*

|	ANC	NAG$_7$	MPA	MPA*	NAPP	NAPP*
PAF	2.4	125.0	123.3	117.8	120.9	115.4
NAF	109.3	−	19.3	18.4	-90.9	-90.0

MPA = maximum potential acidity = total S ´ 30.6;
MPA* = CRS ´ 30.6 (CRS from tab. 3);
NAPP = net acid producing potential = MPA–ANC;
NAPP* = MPA*–ANC.

Leachate properties

The pH of the KLC leachates indicate that blending with 0.1 wt.% lime alone or with silicates (KLCs lime and lime+silicate, fig. 1A) provided insufficient neutralisation to maintain circum-neutral pH as required for the formation and maintenance of a pyrite surface passivating layer. The greater leachate pH for lime+silicate as compared to lime, especially over weeks 8–12, suggests that the added silicates may have neutralised a minor amount of acidity from the PAF waste during the 24 weeks.
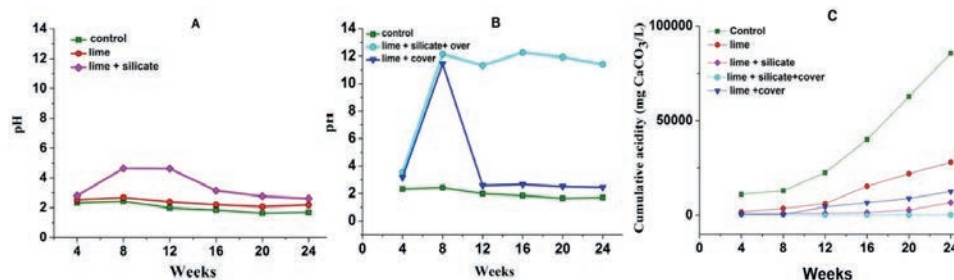
Figure 1 *KLC leachate pH and cumulative acidity profiles during 24 weeks of operation.*

The blending of silicates into the PAF waste in addition to a NAF top cover (lime+silicate+-cover) resulted in basic pH, but the application of the same NAF cover to the lime-blended KLC (lime+cover) gave rise to acidic pH (around 2.5) after 12 weeks (fig. 1B).This again demonstrates the positive role of silicates through neutralisation of acid generated from pyrite oxidation.

Figure 1c shows that the cumulative acidity is greater from the lime and lime+cover KLCs over 24 weeks than from lime+silicate and lime+silicate+cover. This also demonstrates that the blended silicates play a significant role in decreasing the acidity released from the KLCs. In addition, a NAF cover (lime+cover and lime+silicate+cover) decreased the total leachate acidity during the 24 weeks, as compared to the absence of a NAF cover - lime and lime+silicate, respectively - despite the acidic pH for lime+cover after 12 weeks. Only the combined use of blended lime and silicate and a NAF cover with lime-saturated watering/flushing completely inhibited acidity generation across the 24 weeks (fig. 1C).

The results clearly indicate that both silicates and NAF play positive roles in reducing acidity generation from PAF. It is possible that a combined use of lime addition, NAF covers and silicates blending (with saturated lime watering/flushing) may maintain circum-neutral/basic pH enabling establishment and maintenance of pyrite surface passivation, although longer-term testing would be required.

Calculation of acid neutralization rate (ANR) and acid generation rate (AGR)

ANR and AGR were calculated based on the concentration of metals and S (sulfate) released(Miller et al. 2010). For the KLC tests without a NAF cover (fig. 1A) for the periods 8–12 and 12–24 the pH variations were small for these three columns and thus their ANR and AGR were relatively constant and are reported in Tab. 3. For the KLC tests with a NAF cover (fig. 1B) the period 12–24 week maintained almost constant pH (stable ANR and AGR) for ANR and AGR calculations.

Table 3 *ANR and AGR (mmol H2SO4 week⁻¹) calculated using the concentration of cations and S in leachates during different periods.*

		Weeks						
		8–12			12–24			
	control	lime	lime+ silicate	control	lime	lime+ silicate	lime+ cover	lime+ silicate+ cover
AGR	9.53	8.78	7.32	21.12	11.86	8.03	10.47	1.01
ANR (with Ca^{2+})	1.55	7.68	7.13	1.40	6.36	7.39	9.79	6.25
AGR/ANR(with Ca^{2+})	6.15	1.14	1.03	15.08	1.86	1.09	1.07	0.16
ANR (no Ca^{2+})	1.44	1.03	0.36	1.25	1.21	2.18	3.60	0.09

Between weeks 8-12, the AGR of control, lime and lime+silicate was greater than the ANR, consistent with the acidic leachates. The total added Ca^{2+} (31.4 mmol) added to lime+silicate from combined watering and flushing (i.e. 1.4 L per month) with lime-saturated water, assuming a lime solubility of $\approx$1.66 g L^{-1}, was much greater than that released (13.5 mmol) in the leachate, suggesting that the Ca^{2+} retained (17.9 mmol) in the KLC may have precipitated. PHREEQC calculations suggested that leachates were saturated with respect to gypsum (tab. 4).

Table 4 *Gypsum saturation indices calculated for lime+silicate and lime+cover using PHREEQC.*

Column	Weeks	pH	E_h(SHE)	Gypsum (SI)
lime+ silicate	8	4.6	418	0.08
	12	4.6	380	0.14
lime+ cover	12	2.6	617	0.03
	16	2.7	647	0.12
	20	2.5	661	0.10
	24	2.5	702	0.03

SEM-EDS analysis of samples taken from lime+silicate within this time period clearly showed rod-like euhedral crystals containing Ca, O and S, providing further evidence that gypsum precipitation occurred. The precipitation of gypsum can result in inaccurate estimations of AGR based on S concentrations and ANR based on Ca concentrations, but it does not affect the rate difference between ANR and AGR.

During the period of weeks 12–24, lime+silicate+cover gave rise to the lowest AGR and was the only KLC with alkaline effluent. Assuming a lime solubility of 1.66 g L^{-1}, nearly 94.2 mmol Ca^{2+} was applied to lime+cover and lime+silicate+cover KLCs through watering and flushing with lime-saturated water (9 watering and 3 flushing, totalling 4.2 L; tab. 5).The total amount of Ca^{2+} in the leachates from lime+silicate+cover was 37.0 mmol, indicating that 57.2 mmol Ca^{2+}, possibly in the form of calcite (SEM-EDS analysis found Ca carbonate; data not shown) and/or other Ca-containing phases, were retained in this KLC. Note that the sample from lime+silicate+cover was not coated by carbon prior to the environmental SEM-EDS analysis, and thus the detection of Ca, C and O suggests the presence of calcium carbonate, possibly calcite.

For lime+cover (pH <3 during weeks 12–24), 63.0 mmol Ca^{2+} was retained in the KLC, suggesting the possible formation of Ca-containing secondary minerals. It was found that gypsum was the only Ca-containing mineral phase with positive saturation indices (tab. 4). Similar to lime+silicate, rod-like euhedral crystals containing Ca, O and S were also found in lime+cover by SEM-EDS analysis.

Table 5 *Mass balance calculations of Ca2+ for lime+cover and lime+silicate+cover between weeks 12–24.*

	lime+cover	lime+silicate+cover
$Ca^{2+}_{influent-lime}$ [1]	94.2	94.2
$Ca^{2+}_{leachate}$ [2]	31.2	37.0
$Ca^{2+}_{alkalinity}$ [3]	–	9.4
$Ca^{2+}_{neutralised}$ [4]	31.2	27.6

1: Ca^{2+} from watering/flushing with lime-saturated solution;
2: Ca^{2+} in leachate;
3: Leachate Ca^{2+} calculated from alkalinity measured, assuming the alkalinity is in the form of $Ca(OH)_2$;
4: Leachate Ca^{2+} minus alkalinity Ca^{2+}.

Conclusions

Using laboratory-scale KLC tests, combinations of PAF waste blended with lime and silicates, application of natural NAF materials (readily available on-site) as top covers, in conjunction with saturated lime-water watering/flushing have been employed to determine the conditions required to control acid generation from a highly reactive PAF waste material. It was found that an initial 0.1 wt.% lime addition to the PAF waste, even with addition of silicates or a NAF top cover, was not able to maintain leachate pH near or above neutral during 24 weeks of operation. In contrast, the application of both silicates and a NAF cover, together with 0.1 wt.% initial lime addition and flushing/watering with lime-saturated water, maintained a pH of around 12 up to 24 weeks.

The blending of lime combined with a NAF cover substantially reduced the cumulative leachate acidity from the KLC by approximately 65%, as compared to lime addition alone. Similarly, the addition of both lime and silicates in conjunction with a NAF cover significantly reduced cumulative leachate acidity by >90%, relative to the acidity of the same treatment but without silicates addition, demonstrating the positive role of blended silicates in reducing acid generation.

This study suggests that treatment of highly reactive PAF wastes via blending of lime (over 0.1 wt.%), silicates and addition of a NAF cover, when combined with other control measures (e.g. construction of waste rock emplacements using layered and compacted methods), could substantially reduce or eliminate acidity and metal loads in mine drainage. These results highlight to industry the potential for beneficial use of on-site neutralising waste materials and/or lithologies for cost-effective AMD control and mitigation strategies.

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