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Applications of Portland cement blended with fly ash and acid mine drainage treatment sludge to control acid mine drainage generation from waste rocks

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ABSTRACT

Portland cement is an effective but expensive option for source control of acid mine drainage (AMD); the cost could be reduced by blending the cement with cheap waste materials such as fly ash from coal combustion and sludge produced from neutralization of acid mine drainage with lime. To test how these two additives affect cement performance in reducing AMD generation, blended cement slurries were applied to sulfidic waste rocks from Brukunga, South Australia, in leaching columns monitored for around 1 year. Acidity, metal and sulfate loads decreased greatly (by 80–95%) for all cement applications but the effect varied, depending mostly on the depth of penetration of the cement in the column (a function of slurry viscosity). The fly ash-blended cements penetrated further into the columns than the more viscous surface-capping sludge-blended cements, causing a greater decrease of leachate acidity loads and sulfide oxidation due to better coverage of the waste rocks and more acidity neutralization by cement dissolution. The AMD sludge showed no evidence of releasing its adsorbed heavy metals, but the fly ash released some Si, indicating that it is not chemically stable in the cement. There was little secondary mineral growth in the blended cements; the ettringite in the AMD sludge-blended cement formed from bassanite present in the sludge rather than exposure to acid mine drainage. Overall analysis of the long-term effectiveness of the blended cement applications shows that cement placed as a surface cap on top of the waste rock provides more value, because the slower cement dissolution rates ensure continued effectiveness for many years. Scaling up the results from the laboratory study to the field scale at the Brukunga mine site suggests that benefit/cost ratios in the order of 20–30 might be achieved compared to the present use of lime neutralization for AMD treatment.

1. Introduction

Acid mine drainage (AMD) is a major environmental problem in many countries, resulting from oxidation of sulfide minerals exposed by mining to the atmosphere (Simate and Ndlovu, 2014; Pandey et al., 2007; McCarthy, 2011). AMD can be treated by adding a source of alkalinity, commonly hydrated lime or limestone, which causes pH to increase and precipitates a sludge typically composed of gypsum and Fe and Al hydroxides, as well as adsorbed heavy metals (hereafter referred to as AMD sludge) (Zinck, 2005; McDonald et al., 2006). However since sulfide oxidation in mining wastes may continue to generate AMD for hundreds of years, it is preferable to control this process at the source, and many methods have been developed for controlling AMD generation within waste rock and tailings, e.g. water covers, impermeable covers, alkalinity addition, microencapsulation (Kleinmann, 1990) and biofilms (e.g. Jin et al., 2008).

Portland cement has been used in several different ways in controlling AMD generation. The dissolution of cement in AMD results in neutralization of acidity and this can be exploited in AMD treatment (Ekolu et al., 2014; Jones and Cetin, 2017; Sephton and Webb, 2019). Mixing of cement into tailings can prevent leaching of toxic metals, increase strength and decrease permeability (Jang and Kim, 2000; Deschamps et al., 2008; Hadimi et al., 2016; Yilmaz et al., 2009, 2015). Cement encapsulation has also been shown to slow down pyrite oxidation in laboratory experiments (Ji et al., 2012), although the authors noted that cement may not be appropriate for field application, due to the ‘difficulty of distributing cement to micro- and deep-sites’. In studies of concrete decay owing to the presence of sulfides in aggregates, rates of sulfide oxidation have been found to be relatively slow, with signs of damage emerging over years to decades (Schmidt et al., 2011;

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Rodrigues et al., 2012; Capraro et al., 2017), and sulfide minerals within concrete slabs may be completely protected from oxidation (Shayan, 1988).

However, it is well known that concrete is vulnerable to sulfate attack (Neville, 2004), and sulfide oxidation within concrete aggregates or adjacent to concrete structures may cause staining, cracking and loss of strength (Shayan, 1988; Midgley, 1958; Lugg and Probert, 1996; Thomas et al., 1989; Lee et al., 2005; Hawkins, 2014). The severity of these effects depends on the type of sulfide mineral (Midgley, 1958); pyrrhotite reacts more quickly than pyrite (Chinchón-Payá et al., 2012; Rodrigues et al., 2012; Duchesne and Fournier, 2013; Marcelino et al., 2016).

Due to the relatively high cost and environmental footprint of Portland cement, waste materials with cementitious properties such as fly ash and cement kiln dust have been used instead (Bulusu et al., 2007; Guynn et al., 2007; Park et al., 2014; Skousen et al., 2012), or mixed with Portland cement in concrete dry covers over waste rock piles (Northwest Geochem, 1990, 1996; Lundgren, 1997; Steffen Robertson and Kirsten Inc., 2000) and in mine backfilling (Dudeney et al., 2013). However with relatively little data on the efficacy of Portland cement in controlling AMD generation from waste rocks, its high price cannot be evaluated against the potential value that it provides, and the effects on cement performance of substituting cheaper materials like fly ash are uncertain.

Sephton and Webb (2017) applied Portland cement slurries with different water powder (w/p) ratios to leach columns containing sulfidic waste rocks from the Brukunga Mine, South Australia. Slurries with the lowest w/p ratio partially sealed the top of the column, resulting in a modest decrease in sulfide oxidation rates and reducing the number of fluid pathways so that acidity loads greatly decreased. Cement slurries with higher w/p ratios plugged the columns, greatly decreasing permeability and sulfide oxidation rates and producing leachates with negligible acidity.

This paper presents the results of additional leach column experiments to test whether blending cheaper alkaline waste materials (fly ash and AMD sludge) with Portland cement diminishes or enhances its performance in controlling AMD generation. Fly ash is produced by coal combustion in power stations and is widely available; it has been reported to improve the workability, strength and impermeability of concretes (Skousen et al., 2012) and may improve sulfate resistance (Freeman and Carrasquillo, 1991; Sumer, 2012). AMD sludge was chosen because large amounts are produced at mine sites where there is a lime treatment plant for AMD neutralization, and it has been used in cemented paste backfill (Gabr and Bowders, 2000; Benzaazoua et al., 2006) and mixed with soil or tailings as an oxygen barrier (Demers et al., 2015a, 2015b, 2017). The chemical stability of AMD sludge is improved by addition of alkaline materials such as Portland cement and fly ash (Tseng, 1988; Bricka and Jones, 1993; Connor and Hoeffner, 2010; Li et al., 2001), so the application of AMD sludge-blended cement to waste rocks could be an economical way of controlling AMD whilst also stabilising the metal content of the sludge.

2. Materials and methods

2.1. Study site

The waste rocks used in this study are from the Brukunga mine in South Australia. Brukunga was mined for sulfur from pyrite and pyrrhotite between 1955 and 1972, and over this period around 8 million tons of waste rock were excavated and deposited in dumps, which remain exposed with the sulfide minerals oxidizing and generating acidity (Taylor and Cox, 2003). The average annual rainfall at the site is 575.8 mm, which produces around 100 ML/year of acid mine drainage (average pH 2.8, SO_4^{2-} 7.5 g/L, Fe 1.2 g/L) from the minesite (Department of the Premier and Cabinet, 2017). This is treated on-site by neutralization with lime, forming ~900 t AMD sludge per year composed of gypsum, iron and aluminum hydroxides and other trace metals.

Table 1
Chemical and mineral compositions and acid neutralizing capacities of waste rock, Portland cement, fly ash and AMD sludge used in this study. C3S, C2S, C3A and C4AF are tricalcium silicate, dicalcium silicate, calcium aluminate and calcium aluminoferrite respectively. Note the XRD analysis of the cement was performed over one year after the bag of cement was opened, hence the relatively high calcite content.

	Waste rock -southern dump	Waste rock -high wall	Portland cement	Fly ash	AMD sludge
Si (%)	21.6	23.4	9.21	27.9	0.9
Al (%)	5.5	6.5	2.8	11.3	6.5
Fe (%)	5.1	6.1	1.9	2.0	6.8
Ca (%)	0.9	2.2	45.8	0.7	10.0
Mg (%)	1.6	2.4	1.0	1.2	3.5
K (%)	2.2	1.9	0.8	1.14	0.07
S (%)	6.0	5.5	1.1	0.01	8.4
Cu (ppm)	41	48	49	13	53
Mn (ppm)	297	818	468	432	454
Zn (ppm)	90	1327	113	75.7	2710
quartz (%)	33	33	0	7	0
albite (%)	21	21	0	0	0
muscovite (%)	18	11	0	0	5.5
phlogopite (%)	4.7	18	0	0	0
microcline (%)	5	9.7	0	0	0
pyrite (%)	3.4	3.5	0	0	0
jarosite (%)	7.5	1.1	0	0	0
C3S (%)	0	0	45	0	0
C2S (%)	0	0	20	0	0
C3A (%)	0	0	5.2	0	0
C4AF (%)	0	0	7.5	0	0
calcite (%)	0	0	5.7	0	1.6
portlandite (%)	0	0	0.3	0	0
gypsum (%)	0	0	0.9	0	3.7
mullite (%)	0	0	0	13	0
bassanite (%)	0	0	0	0	25
amorphous (%)	4.7	2	12	78	69
ANC (%) (g $CaCO_3$ eq. kg^{-1})	−12.1	7.7	1078	20	191

2.2. Materials

The waste rock samples were collected from three locations at Brukunga, the southern waste rock dump, the high wall and a small dump composed of a mixture of both (Taylor et al., 2009) (see Sephton and Webb, 2017 for map). The major mineral phases in the waste rocks are quartz, albite, muscovite, phlogopite, microcline, pyrite and jarosite (Table 1).

The waste rock samples vary in degree of weathering (Fig. 1), with the southern waste rock dump material being generally more highly weathered than the high wall material. Highly weathered samples break apart easily and are often yellow or orange in colour (Fig. 1a) due to the presence of secondary jarosite (Table 1). The surface and interior of these rocks are fairly similar in appearance, indicative that oxidation has occurred throughout the rock. Less weathered rock samples are much stronger, bluish-grey in the middle and have a reddish-brown oxidised surface layer. The less weathered rocks also have higher acid neutralizing capacity (ANC), due to the presence of larger amounts of reactive silicate minerals such as phlogopite and microcline (Table 1).

The Portland cement used was from a new 15 kg paper bag of Cement Australia general purpose cement, the fly ash was a commercially available product from Boral Ltd. Named Boral Blue Circle fly ash, and the AMD sludge was collected by Wendy Stanford from the Brukunga water treatment plant in June 2014. The fly ash is predominantly amorphous glass with 13% mullite and 7% quartz, and has a little ANC (Table 1). The AMD sludge used for making blended

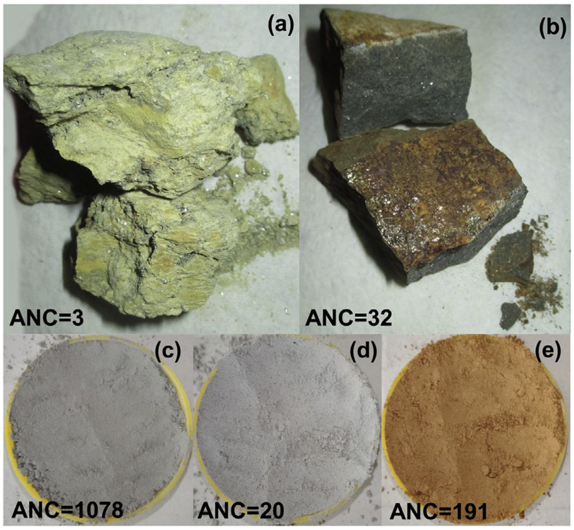

Fig. 1. (2-column) Materials used in the experiments, a. highly weathered and b. Lless weathered Brukunga waste rock, c. Portland cement, d. fly ash, e. AMD sludge. Acid neutralizing capacity (ANC) in g $CaCO_3$ eq. per kg. Diameter of samples in c-e is 50 mm.

cements was dried thoroughly at around 100 °C under a heat lamp, which converted the gypsum ($CaSO_4.2H_2O$) originally present to bassanite ($CaSO_4.0.5H_2O$) (Table 1).

2.3. Leaching columns

Six columns of the same type as in our previous study (Sephton and Webb, 2017), 15.5 cm in diameter and 33–34 cm long made from PVC pipe, were used to test fly ash- and sludge-blended cements. The columns were sealed at the base with a tap outlet to allow for drainage collection, and could be sealed at the top with a screw-on cap, with a 25 mm opening allowing for an oxygen gas sensor to be inserted so that oxygen consumption rates could be measured. These columns were filled with 4.73 kg samples of waste rock with grain size ranging from 2 to 26 mm, with 57.5% from the southern waste rock dump, 21.5% from the high wall and 21% from the small trial dump. The grain size distribution of the rock was selected to minimize the chance of clogging in the columns to allow for reliable collection of leachate samples and to ensure representative samples across all of the replicate columns.

The leaching regime was the same as used for twelve similar columns documented in Sephton and Webb (2017). For the first leaching event, a 1 L graduated cylinder was used to pour enough deionized water into each column to fill it up to the brim (around 4 L). The volume of water added was used as a measure of the total void space in each column, which was later used to calculate the rate of sulfide oxidation from measured rates of oxygen consumption. For this initial leach, the taps at the bases of the columns were initially closed, allowing water to sit in the columns for 24 h to allow for dissolution of soluble salts that had accumulated on the waste rocks. After 24 h, the taps were opened to allow for collection of the leachate in 1 L sample bottles.

The columns were subsequently leached with 1 L of deionized water approximately every two weeks over around six months (twelve times), and then kept dry for around 50 days, before the columns were leached one more time with 1 L of deionized water to remove soluble salts.

The blended cement treatments (Section 2.6 below) were then applied and regular leaching commenced one week after the application of cement slurries; the columns were leached approximately every two weeks over the next 5 months (a further nine times), and subsequently allowed to dry for around 50 days. Leaching every two weeks then resumed (nine times over around 5 months), before the columns were again left to dry for around 50 days. Finally, the columns were leached every two weeks for six weeks (three times).

For all column leaches other than the first, the taps were opened prior to water application so that drainage would immediately accumulate in sample collection bottles placed beneath the column taps. For column leaches prior to cement application, samples were collected one day after water application, while for those after cement application, samples were collected one week after to allow more time for drainage, because some of the cemented columns had become relatively impermeable, as described in Sephton and Webb (2017).

Twenty-two smaller leach columns were used to economically test a wider range of cement slurries with different water/powder (w/p) ratios and different rates of addition of sludge and fly ash, to complement the data obtained from the larger columns. The rates of cement application used in the small columns (94 g powder per kg waste rock) were around twice those for the large columns (53 g powder per kg waste rock) in order to cover the waste rocks more completely (Section 2.5). The smaller columns, 26 mm in diameter and 22.5 cm long, were constructed from transparent vinyl tubing; a piece of polyester fabric was fitted with an annular press-on cap at the base of the column to retain the waste rocks but allow free drainage of leachate. The columns were filled using 106 g samples of waste rocks with grain size ranging from 2 to 4.75 mm, with 55% from the southern waste rock dump and 45% from the high wall. Column leaches for the 22 small columns used 25 ml applications of milliQ water applied with a bottle-top dispenser.

The small columns were leached three times within one week prior to the application of cement to sixteen of the columns; four columns were kept without any cements or treatment to serve as controls. One week after cement applications a regular leaching program commenced, with water being applied every two weeks over the next four and a half months (9 times), before the columns were allowed to dry for around 50 days, then leached again every two weeks for another 4 months (8 times), and left to dry again for 50 days. Finally, the columns were leached every two weeks for one more month (2 leaches). Prior to cement application, leachate samples were collected on the same day as water application since the small waste rock columns drained very fast; after cement application, samples were collected one week after watering to allow for the much slower drainage through some of the cemented columns.

A number of the small columns (7–9, 15–18 and 21–22) became impermeable after cement applications, so 10 ml leachate samples from these columns were instead collected using a pipette from water pooled on top of the cemented waste rock (called supernatant hereafter). Most of these columns were sampled in this manner four times (at 131, 208, 250 and 296 days); columns 9, 10 and 18 were not sampled at 131 days because of insufficient water.

Overall the watering rates used for both large and small columns were equivalent to rainfall of approximately 1 m per year, about double the average annual rainfall at the Brukunga minesite (575.8 mm).

2.4. Preliminary tests with blended cements

The rates of fly ash/AMD sludge addition chosen for the column leaching experiments (25%) were based on preliminary tests to establish the maximum amount that could be added without affecting the physical stability of the cement blend. Fly ash/AMD sludge was mixed with Portland cement and water in different proportions and set in an ice cube tray. The samples were prepared in duplicates, with one of each pair subjected to several wetting/drying cycles by soaking in dionised water in a plastic vial. Cement blends with 50% AMD sludge cracked and fell apart after a few wet/dry cycles whereas those with 25% AMD sludge did not. Cement containing 25% AMD sludge with a higher gypsum content (~15% S) disintegrated after repeated wet/dry cycles; Lerch (1949) found that cement expansion increased substantially when the gypsum content increased from 5 to 7.5 wt % SO_3.

Unblended, 25% fly ash-blended and 25% AMD sludge-blended

Table 2
Cement slurries applied to leach columns (results from large columns 1–12 given in Sephton and Webb (2017). SP indicates that superplasticizer was added as described in the text.

Columns	Powder composition	Mass of H_2O (g)	Water/powder (w/p) mass ratio
Large columns			
1–3	n.a (Control)	n.a	n.a
4–6	250 g cement	200	0.8
7–9	250 g cement	250	1.0
10–12	250 g cement	300	1.2
13–15	187.5 g cement, 62.5 g fly ash	250	1.0
16–18	212.5 g cement, 37.5 g sludge	250	1.0
Small columns			
1–4	n.a (Control)	n.a	n.a
5,6	10 g cement	8	0.8
7,8	10 g cement	10	1.0
9,10	7.5 g cement + 2.5 g fly ash	10	1.0
11,12	8.5 g cement + 1.5 g sludge	10	1.0
13,14	8.5 g cement + 1.5 g sludge	12	1.2
15,16	8.5 g cement + 1.5 g sludge	10 + SP	1.0
17,18	7.5 g cement + 2.5 g sludge	10	1.0
19,20	7.5 g cement + 2.5 g sludge	12	1.2
21,22	7.5 g cement + 2.5 g sludge	10 + SP	1.0

cement paste samples from these preliminary tests were retained as reference samples for mineralogical analyses (Section 2.8).

2.5. Cement slurry applications to leach columns

Cement slurries for application to the leaching columns were prepared by weighing the requisite masses of cement, fly ash or AMD sludge into a clean 100 ml plastic beaker and mixing carefully to achieve a homogenous blend prior to addition of water (Table 2). The sludge was thoroughly dried at 110 °C with a heat lamp prior to being mixed with the cement.

The requisite mass of deionized water was weighed out, added to the powder, and mixed vigorously with a wooden stirring rod to achieve a homogenous slurry before being poured onto the waste rock in the leach column. To test whether the viscosity of the sludge-blended cements could be reduced to allow deeper penetration within the columns, Optimum 380 Superplasticizer from concreteountertopsupply.com was added to some of the AMD sludge-blended slurries at a rate of 0.1 ml per 100 ml H_2O.

2.6. Analyses of leachates

The pH, temperature and electrical conductivity (EC) of the leachates from both small and large columns were measured using TPS brand sensors on the same day as sample collection. One sub-sample from each leachate was used to perform an acidity or alkalinity titration within two days of sample collection; acidity titrations were performed on samples with $pH < 5$ and alkalinity titrations were performed on samples with $pH > 5$. Another sub-sample was filtered with a 0.45 µm nylon filter, treated with a few drops of concentrated HNO_3 and stored in a cold room at 4 °C for later analysis for Fe, Al, Ca, Mg, Si, Mn, Zn, Cu and total S with inductively coupled plasma optical emission spectroscopy (ICP-OES) and for Na and K with flame photometer. For six samples from both large and small control columns, Fe2+ concentrations were obtained using the phenanthroline method with a LaMotte Smart 3 colorimeter and Fe^{3+} were calculated by subtracting the Fe^{2+} concentration from the total Fe concentration.

SO_4^{2-} and $S_2O_3^{2-}$ were measured using ion chromatography (IC) for 90 of 161 leachate samples analysed from the large columns and for 66 of 240 leachate samples analysed from the small columns. For these analyses, a sub-sample was transferred by pipette to an 11 ml ion chromatography sample tube and diluted with a volume of eluent at a rate estimated to bring sulfur species concentrations within the IC working range. The mixture of sample and eluent was then shaken and allowed to react for at least 1 h before being filtered by 0.45 µm nylon filter in order to remove precipitates that formed from the reaction of sample with the eluent.

Charge balance error and saturation indices were calculated using USGS PHREEQC software and the llnl. dat geochemical database (Parkhurst and Appelo, 2013). Charge balance errors were within ± 10% for > 90% of leachates collected from the large columns and > 80% of the leachates collected from the small columns not treated with cement. Most of the leachate samples from the small columns treated with cements had charge balances of less than −10% because these leachates contained significant concentrations of Na and K (not measured for these samples). For these leachate samples, IC analyses of total sulfur exhibited a strong correlation with EC ($r^2 = 0.94$; 46 samples), and this relationship was used to calculate the total sulfur concentrations for the 74 leachate samples which were not analysed for sulfur using IC.

2.7. Analyses of solids

Mineralogical and chemical analyses were performed on dried and powdered sub-samples of waste rocks from the southern waste rock dump and high wall, Portland cement, fly ash and AMD sludge, cemented waste rock obtained from four of the large leach columns and reference samples of unblended cement, 25% fly ash-blended and 25% AMD-sludge blended cement paste (Section 2.4). The cemented waste rock and cement paste samples were broken apart using a hammer or mortar and pestle, and for the samples containing waste rock tweezers were used to remove larger waste rock fragments from the samples so that the samples analysed contained a significant proportion of the cement.

XRD analyses were obtained on a PANalytical X'Pert Pro diffractometer at Federation University, equipped with an incident beam BBHD CoKα monochromator and an X'Celerator linear detector, operated at 40 kV and 25 mA over 5-76° 2θ with a step size of 0.017° 2θ at a rate of 0.08° 2θ per second The samples analysed were 2–3 g in weight and were spiked with zincite at a rate of ~10 wt %, thoroughly mixed by a mortar and pestle and back-loaded into the 27 mm sample holders. Diffrac EVA v. 4.2 and HighScore software were used for phase identification and Siroquant Version 3.0 and Profex version 3.11.1 were used to quantify the major phases and amorphous content of each sample (Degen et al., 2014; Döbelin and Kleeberg, 2015). XRF analyses were obtained using an Olympus Delta Premium DP6000 handheld pXRF with a Rhodium anode at 40 kV, with the samples prepared as pressed pellets using 7 g of powdered sample and 4 drops of PVP glue.

Acid neutralizing capacity (ANC) was measured using a modified version of the method of Ahern et al. (2004). 0.1–1 g of sample were reacted with 25–50 ml of 0.1 M HCl in 50 ml deionized water, boiled for 2 h with deionized water added to maintain volumes at around 50–100 ml, and allowed to stand over night before performing a back titration using 0.25 M and 0.05 M NaOH. The time allowed for the reaction to complete was longer than in the original method in order to allow for measurement of neutralizing capacity associated with silicate minerals.

2.8. Oxygen consumption tests

Oxygen consumption was measured for the large columns only. For each measurement, the tap at the base of the column was closed and the top of the column sealed using the screw on cap; the PASCO PASPORT oxygen gas sensing element with its rubber stopper plugged the hole in the cap. The logger was set to record the oxygen partial pressure every 5 min for 12–60 h. Oxygen consumption rates were measured 13–16 times prior to cement application, and a further 18 times after cement application.

To determine if a correction was necessary for oxygen consumption by the sensor, measurements were made in a column filled with 4.5 kg of quartz gravel. The measured rates (-0.18 mmol/day to $+0.14$ mmol/day) were much less than those in columns with waste rocks (-1 to -10 mmol/day), so no correction was required.

3. Results and discussion

3.1. Control columns

The large control columns produced leachates with similar pH, SO_4^{2-} and Fe concentrations to the average composition of acid mine drainage at Brukunga (Table 3), whereas the small control columns produced leachates with lower SO_4^{2-} and Fe concentrations and higher Fe^{2+}/Fe^{3+} ratios (Table 3). This is probably due to the shorter contact time between the leachate and waste rock in the small columns.

3.2. Penetration of cement through the columns

The cement slurry added to each column penetrated to a different extent depending on its viscosity. The cement slurries with lower w/p ratios and containing AMD sludge were most viscous and penetrated less, tending to form caps (Fig. 2b, f and Fig. 3b,e, h), whereas cement slurries without AMD sludge, or with increased w/p ratios or with the addition of superplasticiser, were less viscous and penetrated deeper, plugging the columns at the base (Fig. 2c–e and Fig. 3c,d,f,g,j). The high viscosity of the AMD sludge is likely due to its bassanite content (~25%; Table 1); addition of bassanite in calcium sulfoaluminate cements has been shown to increase viscosity and shorten cement setting times (García-Maté et al., 2015). The fly-ash blended cement penetrated somewhat less deeply than unblended cement with the same w/p ratio in the large columns (Fig. 2c,e), indicating that fly ash addition may increase slurry viscosity to some extent, but not nearly as much as AMD sludge. The different distributions of cement through the columns had a great influence on acid mine drainage generation, as will be explained in the next section.

Table 3
Average compositions of AMD leachates from large and small control column experiments and field data from acid holding ponds at the Brukunga mine site for the year of 2017 (Department of the Premier and Cabinet, 2017).

Parameter	Large control columns	Small control columns	Brukunga mine site
pH	2.4	3.0	2.8
Eh (mV STD H electrode)	787	605	no data
EC (mS/cm)	4.3	1.1	no data
Acidity (mg/L $CaCO_3$ eq.)	4809	918	no data
SO_4^{2-}(mg/L)	4979	895	5465
Ca (mg/L)	86	28	no data
Mg (mg/L)	50	33	no data
Al (mg/L)	590	48	526
Fe (Total) (mg/L)	1316	206	479
Fe^{3+} (mg/L)	1290	9	no data
Fe^{2+} (mg/L)	26	197	no data
Cu (mg/L)	2.2	0.4	0.5
Mn (mg/L)	18	5.3	35
Zn (mg/L)	50	11.3	24

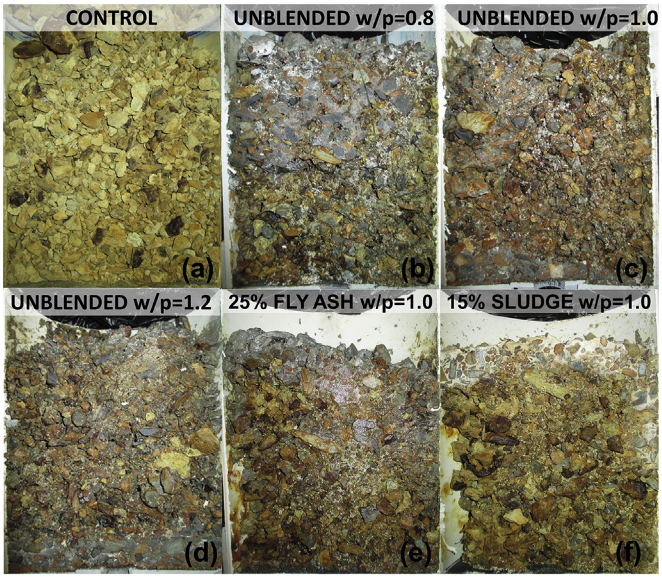

Fig. 2. Photographs of large columns after cutting open showing distribution of cement; column dimensions are approximately 16 cm width by 18 cm height. Figures b–d are for unblended cements from our previous study (Sephton and Webb, 2017).

3.3. Effect of cement applications on acid mine drainage generation

Overall, the application of blended cements decreased sulfide oxidation rates and improved leachate quality, dependent on cement penetration through the columns; the results were mostly consistent with the results of previous experiments using only unblended cements (Sephton and Webb, 2017). The leachate compositions depend ultimately on the cement coverage and how it controls the flow of water through the waste rock, since this determines whether the water makes contact with cement (which releases Ca, Na, K, Si and alkalinity as it dissolves) and/or waste rock containing sulfides (which release H^+ and metals as they oxidise).

In the large columns with fly ash-blended cement, sulfide oxidation rates decreased after cement application to about the same extent as in columns containing unblended cement with the same w/p ratio (Fig. 5a), reflecting the fact that the penetration of the cement was similar. The AMD sludge-blended cement application also caused a decrease in sulfide oxidation rates but to a lesser extent, reflecting the limited penetration of the AMD sludge-blended cement slurry down the column profile. The AMD sludge-blended cement thickly covered ~25% of the waste rock (Fig. 2f), and sulfide oxidation rates decreased by approximately this amount (Fig. 5a).

In columns where the cement penetrated to the bottom (fly-ash blended cement slurries or AMD-sludge blended cements with superplasticiser), the column permeability was reduced so that only a fraction of applied water was collected as leachate (Tables 4 and 5; Figs. 4a, 6a and 7a). Leachate pHs were alkaline or neutral and acidity was negligible, similar to results obtained with higher w/p ratio unblended

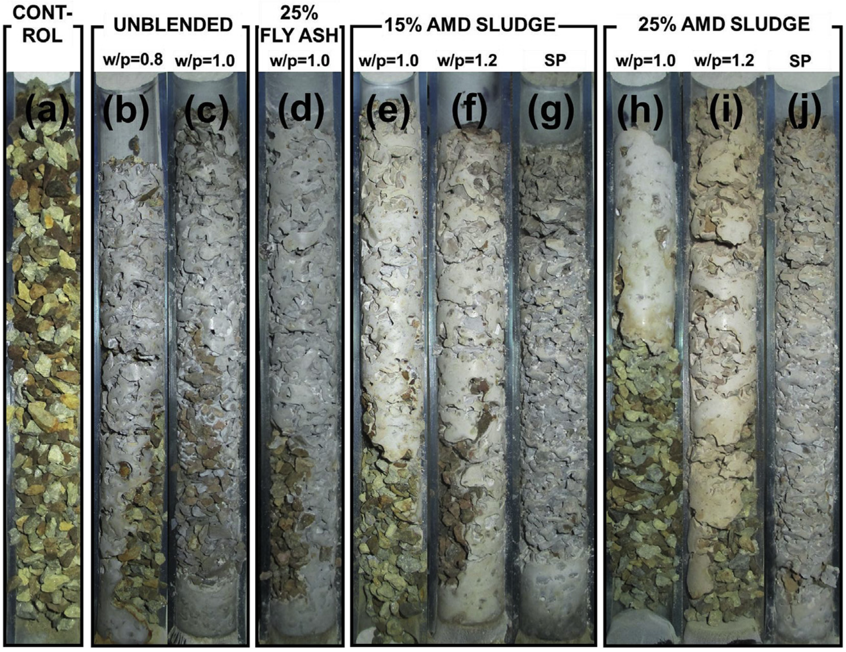

Fig. 3. Photographs of small columns after cutting open showing distribution of cement; column dimensions are approximately 2.5 cm width by 18 cm height. SP = superplasticiser.

cements (Sephton and Webb, 2017).

Sludge-blended cement slurries without superplasticizer penetrated less; an incomplete cement cap typically formed and water flowed readily through the column, so most of the applied water was collected as leachate (Tables 4 and 5, Figs. 4a, 6a and 7a). Because the leachate contacted uncemented sulfide-containing waste rock in these columns, it had low pH and some acidity, similar to leachate from columns containing unblended cement with the lowest w/p ratio of 0.8 (Sephton and Webb, 2017).

In the small columns with 25% sludge-blended cement at a w/p ratio of 1.0 (Fig. 3h), the cap was so thick that virtually no water passed through it for the duration of the experiment (Fig. 7a). The supernatant samples collected from on top of the cement cap contained the lowest solute concentrations because the thick cap effectively prevented any contact between the water and the waste rocks (Table 5). Columns that were rendered impermeable at the bottom rather than at the top released much higher loads of solutes, because the supernatant water was in contact waste rock even though it was covered in cement (Table 5).

A limitation of the column leaching experiment design is that water can only exit the column through the drain at the bottom, so in columns plugged with cement, the water pools on top of the cement. If waste rock dumps were cemented in this way, rain falling on the cemented surface would runoff, resulting in lower contact times with the cemented waste rock than in the present experiments. Hence field trials would be essential for further investigation of the potential of this technique.

3.4. *Leachability of additives (fly ash and AMD sludge) to cement*

Across both large and small column experiments, leachates from the fly ash-blended cement columns contained 1.5–2.5 times higher Si loads (Figs. 8c and 9c) than the other columns, due to release of Si from the fly ash itself (which has a high Si content; Table 1). The fly ash-blended cements in the large column experiment also produced leachates with significantly lower pH than in the small column experiments, where pHs were approximately the same as those from the unblended cement small columns; this is probably due to the higher rate of cement addition used in the latter columns, which made them impermeable. For one of the large columns in the fly ash-blended cement group the pH decreased over time (Fig. 4b), likely due to progressive depletion of acid neutralizing capacity from the fly ash-blended cement.

Determining the leachability of the AMD-sludge is complicated by the fact that its composition is similar to that of the AMD produced by oxidation of the sulfides in the waste rocks (since the former was derived by neutralization of the latter), so dissolution of AMD sludge will produce leachate similar to that resulting from sulfide oxidation. However, AMD sludge-blended cement is acid neutralizing (both AMD sludge and cement have significant ANC; Table 1), whereas the waste rock is acid-producing. Hence oxidation of sulfides in the waste rock will release both acidity and metals, whereas leaching of AMD sludge-blended cement will release metals. The composition of leachate from the control columns was produced only by sulfide oxidation, so on a plot of metal against acidity loads (Figs. 8 and 9), a line from the origin to the control column leachate defines all leachate compositions determined by sulfide oxidation. Leachates that plot above the line have metal concentrations higher than would be expected from sulfide oxidation, and therefore contain contributions from AMD sludge-blended cement dissolution. Figs. 8 and 9 show that leachate compositions plot approximately along the sulfide oxidation line, indicative of negligible release of metals from the sludge-blended cements. This is consistent with the relatively low release of Ca, Si, Na and K from the sludge-blended cement columns (Figs. 8 and 9), indicating that the cement itself was dissolved less than in other columns (and therefore its ANC was less depleted over the course of the experiment).

The chemical stability of the AMD sludge within the cement in the present experiments confirms the results of other studies (Tseng, 1988; Bricka and Jones, 1993), but the results of our preliminary tests (Section 2.5) indicate this depends on the relative proportions of cement and AMD sludge and also on the sludge mineralogy, especially the gypsum/bassanite content. Nonetheless previous studies have shown good results with sludge-blended cements with much higher rates of sludge addition (≥70% sludge and ≤30% cement; Northwest Geochem, 1990), so there may be scope to use higher amounts of sludge especially for sludges with lower gypsum/bassanite content.

Table 4
Amounts of leachates and solutes collected from large leach columns; data for unblended cement columns is from our Sephton and Webb (2017).

Group	Water applied (kg)	Leachate collected (kg)	ave. pH	Acidity (g $CaCO_3$ eq.)	Total S as SO_4^{2-} (g)	Fe (g)	Al (g)	Cu (mg)	Mn (mg)	Zn (mg)	Ca (g)	Mg (g)	Si (g)	Na (mg)	K (mg)
Control	20	18.6	2.3	92	93	26	3.8	40	195	589	1.4	0.77	0.28	53	13
Unblended w/p = 0.8	20	18.2	2.6	11	14.9	1.6	0.4	3.6	17.3	50.2	1.7	0.09	0.09	101	195
Unblended w/p = 1.0	20	11.8	8.1	−2.5	26.9	0.2	0.01	0.07	0.2	0.6	9.1	0.003	0.14	382	1550
Unblended w/p = 1.2	20	11.4	8.7	−3.7	27.6	0.0	0.0	0.1	0.1	0.1	9.3	0.0	0.05	528	1802
Fly ash w/p = 1.0	20	14.5	7.4	−0.3	25	0.05	0.003	0.1	1.6	1.9	8.7	0.02	0.36	310	998
15% Sludge w/p = 1.0	20	17.1	2.5	15	18	2.9	0.5	4.4	22.5	56.1	1.1	0.13	0.08	80	147

Table 5
Amounts of leachates and and solutes collected from small leach columns.

Group	Water applied (g)	Leachate collected (g)	Supernatant collected (g)	ave. pH	Acidity (mg $CaCO_3$ eq.)	Total S as SO_4^{2-} (mg)	Fe (mg)	Al (mg)	Cu (µg)	Mn (µg)	Zn (µg)	Ca (mg)	Mg (mg)	Si (mg)
Control	500	386	0	3.0	266	301	68	16	131	1648	3690	9.9	10.1	0.3
Unblended w/p = 0.8	500	380	0	3.9	54.5	156	14	2.9	16	417	737	22.7	3.2	0.6
Unblended w/p = 1.0	500	5	30	7.3	−2.0	66	0	0	0	0	0.4	12.2	0.1	0.6
Fly ash w/p = 1.0	500	22	40	7.4	−1.2	85	0	0	0.2	0	0	18.2	0.1	0.9
15% Sludge w/p = 1.0	500	377	0	4.8	27	106	5.6	1.6	6	299	566	16.2	2.6	0.1
15% Sludge w/p = 1.2	500	3	40	7.0	3.0	96	0.6	0	0	45	87	22.5	1.2	0.5
15% Sludge w/p = 1.0 with superplasticiser	500	0	40	7.5	−1.2	104	0	0	0	0	0	13.8	0.1	0.6
25% Sludge w/p = 1.0	500	0.2	40	8.5	−4.5	5.2	0	0	0	0	0	1.7	0.1	0.5
25% Sludge w/c = 1.2	500	352	0	5.2	16.2	109	4.7	1.3	5	237	451	23.6	2.9	0.2
25% Sludge w/p = 1.0 with superplasticiser	500	1.2	40	7.7	−0.8	65	0	0	0	0	0	17.0	0.1	0.7

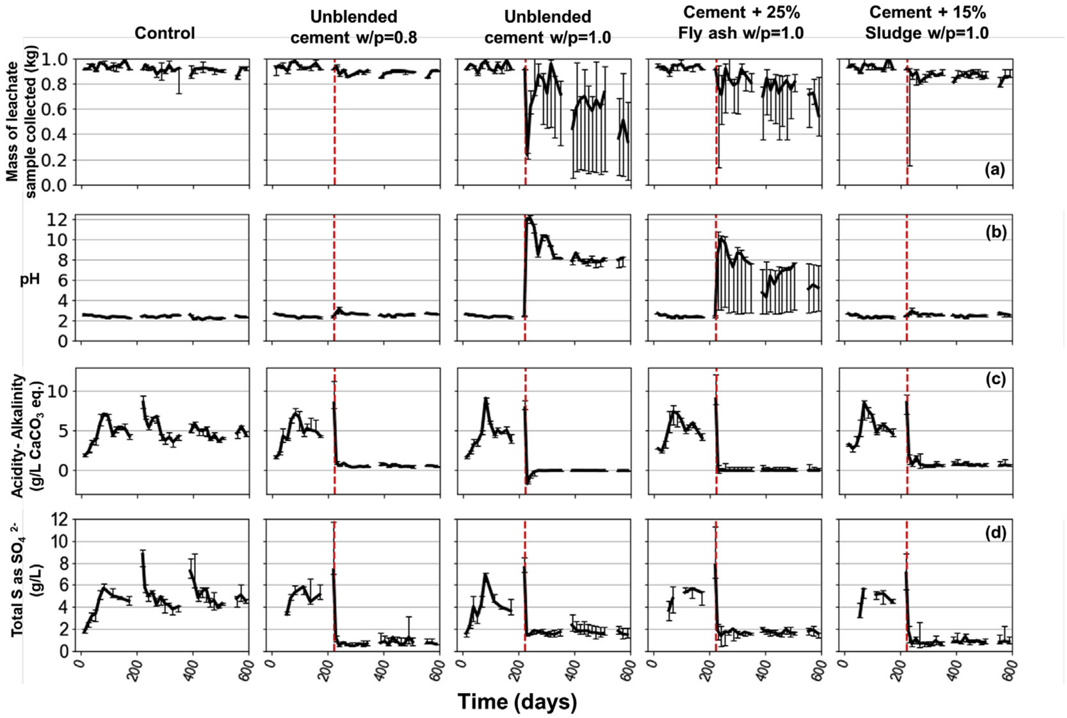

Fig. 4. Time series: a. Mass of leachate collected, b. pH, c. Acidity – alkalinity, d. Total sulfur.

3.5. Secondary mineral formation

Several different secondary minerals were present within the cement after the completion of the experiments (Table 6). To quantify the amounts of these that resulted from AMD attack on the cement, the figures in Table 6 need to be corrected for the varying proportions of waste rock in each sample (Table 7), as well as the amounts of secondary minerals occurring naturally in the cement samples (Table 8). With respect to the latter, it should be noted that the high content of ettringite in the AMD sludge-blended cement probably formed from the reaction between bassanite in the sludge (25%; Table 1) and the cement, which entirely consumed the bassanite:

$$\underset{\text{(bassanite)}}{3(CaSO_4.0.5H_2O)} + Ca_3Al_2(OH)_{12} + 24.5H_2O$$
$$\rightarrow \underset{\text{(ettringite)}}{Ca_6Al_2(SO_4)_3(OH)_{12}.26(H_2O)}$$

The stoichiometry of this reaction dictates that 6 wt % bassanite (the

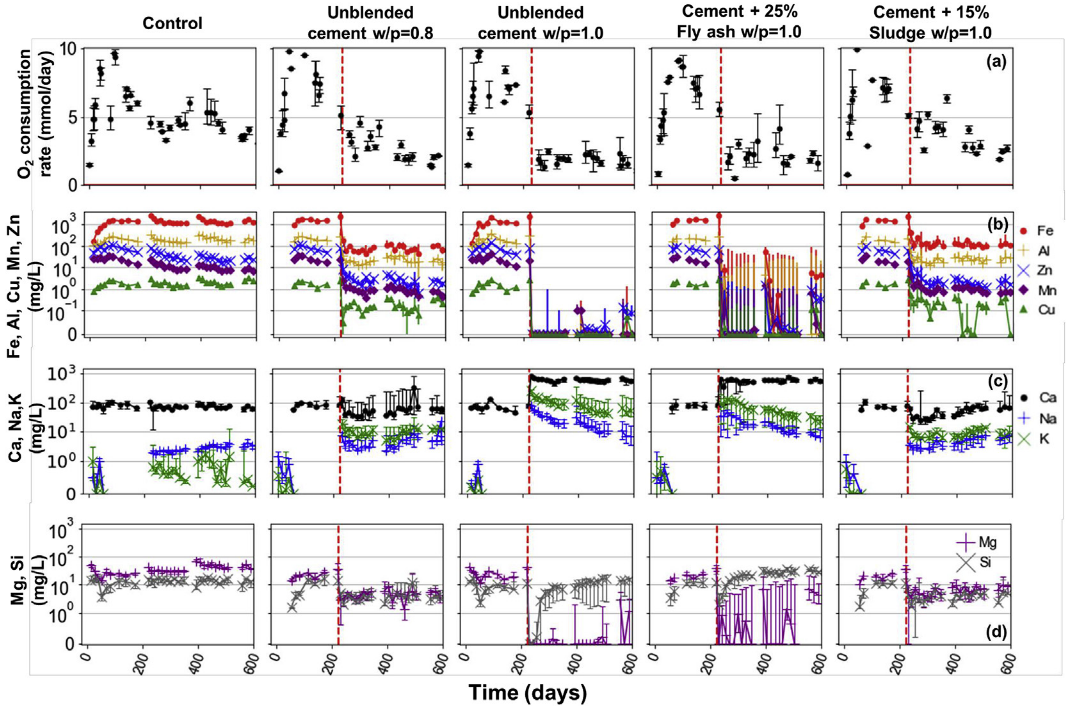

Fig. 5. Time series for large columns: a. Oxygen consumption rates, concentrations of b. Fe, Al, Cu, Mn and Zn, c. Ca, Na and K, d. Mg and Si.

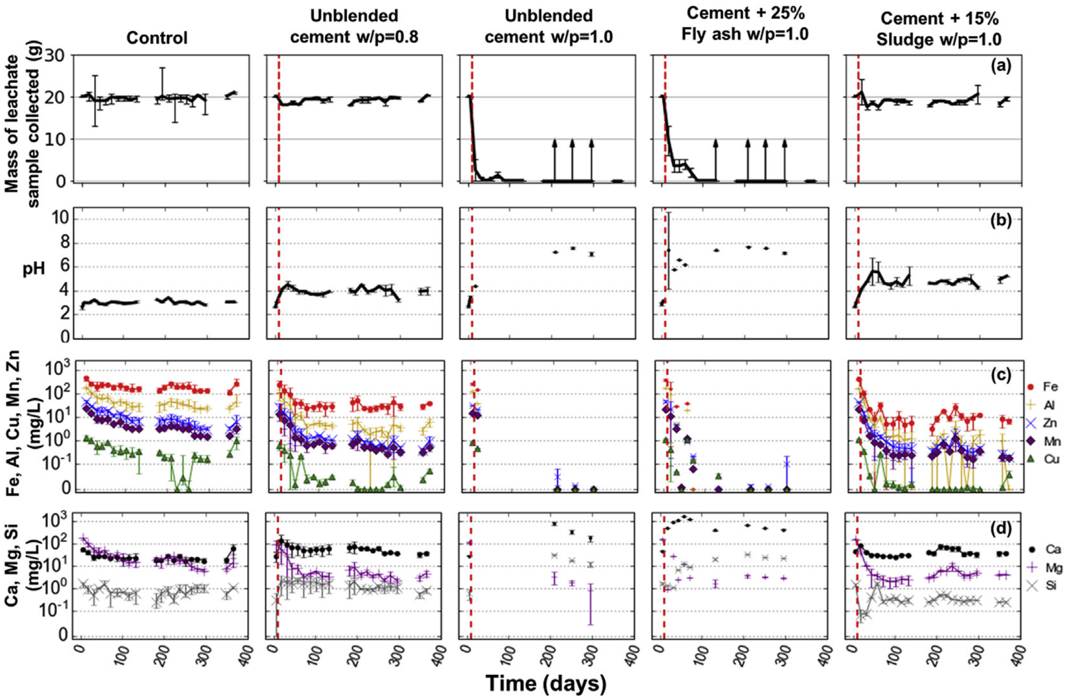

Fig. 6. Time series for small columns: a. Mass of leachate sample collected, b. pH, concentrations of c. Fe, Al, Cu, Mn and Zn, d. Ca, Mg and Si. Vertical arrows in a. indicate when 10 ml supernatant water was collected by pipette (Section 2.4).

amount of bassanite in a blended cement with 25% AMD sludge), would produce 17 wt % ettringite, matching well with the difference between the ettringite content of the 25% AMD sludge-blended cement (22%) and that of the unblended cement sample (6.5%; Table 8).

The amounts of gypsum, ettringite and thaumasite formed from AMD attack on the cement during the experiments were calculated by subtracting amounts of these phases present in the unleached samples (Table 8) from the amounts present in the samples from the cemented waste rock columns (Table 7). The results (Table 9) show significant amounts of ettringite and thaumasite formed in the columns with unblended cements, but not in the columns with fly ash and sludge-blended cements. The lack of secondary mineral growth in the sludge-blended cements is consistent with the relatively low rates of Ca, Na, K and Si being released from these columns, indicative of low rates of cement dissolution (Section 3.4). In the column with fly ash-blended cement the gypsum content was higher, which is consistent with the higher Ca loads from this column, due to the lower leachate pHs which dissolved the cement faster (discussed further in Section 3.6).

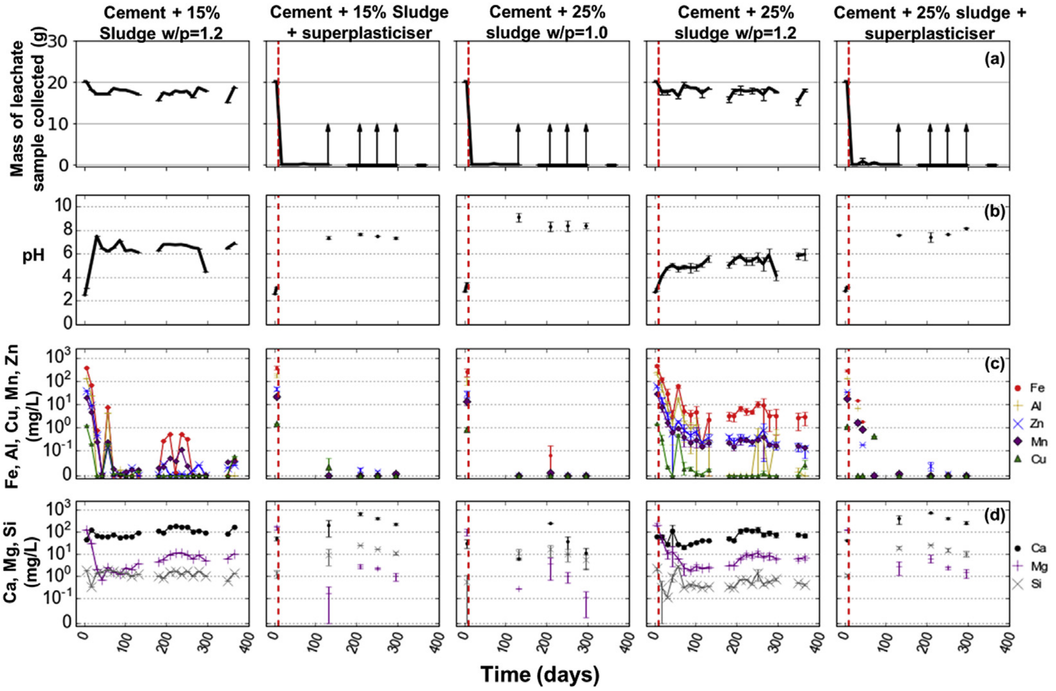

Fig. 7. Time series for small columns (continued): a. Mass of leachate sample collected, b. pH, c. Fe, Al, Cu, Mn and Zn d. Ca, Mg and Si. Vertical arrows in a. indicate when 10 ml supernatant water was collected by pipette (Section 2.4).

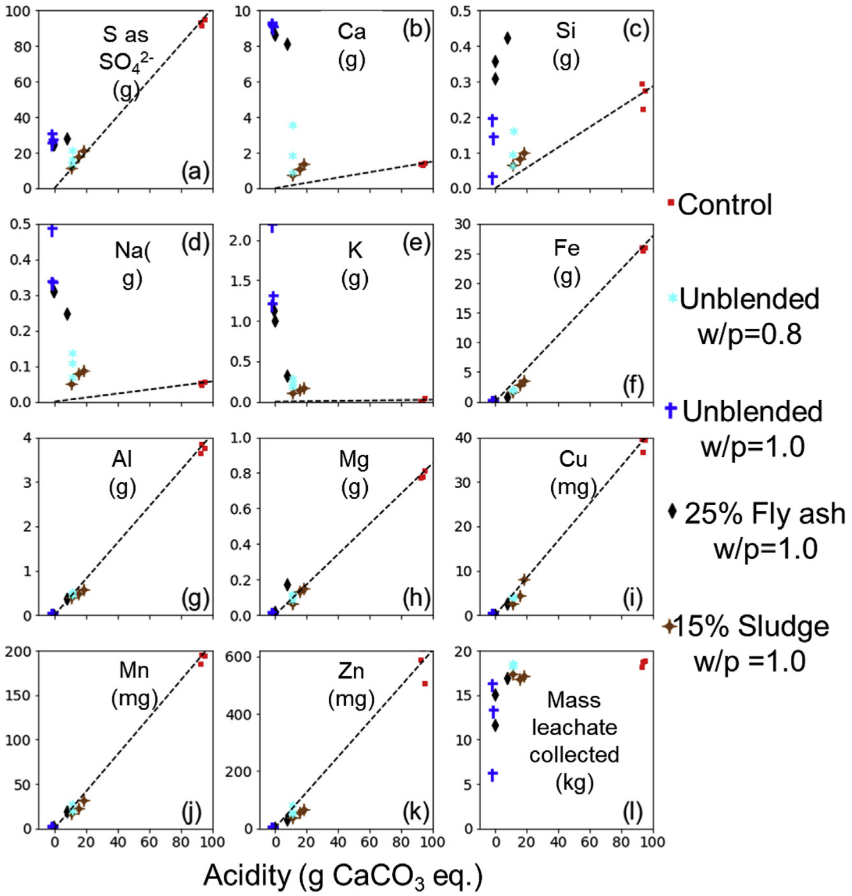

Fig. 8. (2-column, colour) median pH and solute loads in leachates from large columns plotted against acidity loads. Dashed line is from the origin to the median analysis for the three control columns.

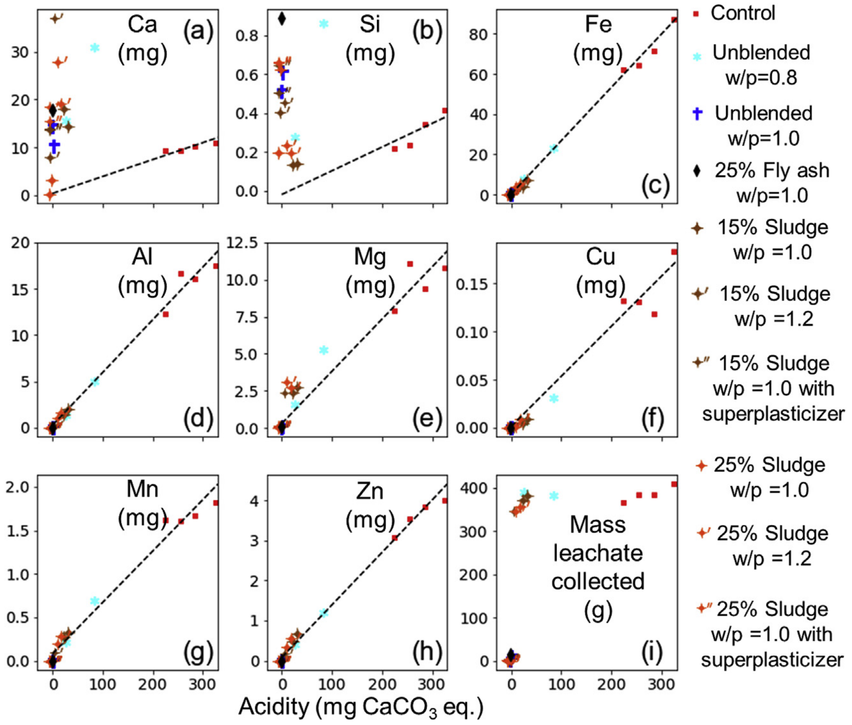

Fig. 9. (2-column, colour) median pH and solute loads in leachates from small columns plotted against acidity loads. Dashed line is from the origin to the median analysis for the three control columns.

Table 6
Quantitative XRD analysis of samples of cemented waste rock from large leach columns. Note that the amorphous component of the samples is assumed to occur entirely within the cement as hydrated Ca silicate and aluminate phases.

Concentration (wt. %)	COL. 4 w/p = 0.8	COL. 7 w/p = 1.0	COL 13.25% Fly ash	COL 16.15% AMD sludge
Amorphous	36.3	44.6	37.9	55.6
Waste rock phases				
Albite	4.9	3.8	6.5	0
Butlerite	0.6	1	0.8	0.3
Chlorite	0.1	0.1	0.2	0
Jarosite	0.2	2	1.6	0.4
Microcline	1.5	4.3	2.5	0.2
Muscovite	1.9	1.6	3.2	0.6
Phlogopite	2.4	1.4	2.8	0.4
Pyrite	0.1	1.3	0.2	0
Quartz	8.7	7.5	12.7	2.1
Total (waste rock)	**20.4**	**23**	**30.5**	**4**
Cement phases				
Aragonite	1.6	3.7	2.9	0
Bassanite	0	0	0	2.5
Calcite	20.5	7.9	21.4	16.5
Gypsum	0.4	0.9	2.6	0.1
Ettringite	9.3	12.6	2.6	15
Portlandite	0	0	0	0
Thaumasite	8.8	4.3	0	1.3
Vaterite	2.7	3	2.1	5
Total (cement) + Amorphous	**79.6**	**77**	**69.5**	**96**

3.6. *Effectiveness and longevity of blended cement applications*

Ca is the dominant solute released from cement dissolution (Tables 4 and 5), as it is the main component of cement (Table 1), so the rate of cement dissolution can be determined using both Ca loads in leachates and amounts of Ca-bearing secondary minerals formed (gypsum, ettringite and thaumasite). Because cement dissolution is incongruent, using leachate loads alone underestimates the degree of cement dissolution, since a significant fraction of the solutes may be stored as secondary minerals.

Ca in cement is present primarily as hydrated Ca silicates and aluminates, along with smaller amounts of portlandite, calcite and gypsum (Table 1); apart from gypsum, all these minerals neutralize 2 mol of H^+ for every mole of Ca^{2+} released. Hence the ANC of cement (as g $CaCO_3$ eq./kg) can be calculated by multiplying its Ca content (in g/kg) by 2.5 (molecular weight of $CaCO_3$/atomic weight of Ca). The cement used in these experiments had 45.6% Ca (Table 1), which converts to 1140 g $CaCO_3$ eq./kg, very similar to the measured ANC of 1078 g $CaCO_3$ eq./kg (Table 1). Therefore the load of Ca released from cement dissolution can be converted to the equivalent loss of ANC from the cement by multiplying by the same factor.

The formation of the secondary minerals ettringite and gypsum removes Ca from solution:

$$3Ca^{2}++3SO_4^{2-}+\underset{\text{(hydrated Ca-aluminate)}}{Ca_3Al_2(OH)_{12}}+26H_2O \rightarrow \underset{\text{(ettringite)}}{Ca_6Al_2(SO_4)_3(OH)_{12}.26(H_2O)}$$

$$Ca^{2+}+SO_4^{2-}+2H_2O \rightarrow \underset{\text{(gypsum)}}{CaSO_4.2H_2O}$$

To account for the amount of Ca removed when determining the rate of cement dissolution, the ANC loss from the cement (as g $CaCO_3$ eq./kg) can be calculated by multiplying the secondary mineral content (as g/kg) by (molecular weight of $CaCO_3$/molecular weight of the mineral) and multiplying by the number of moles of Ca used to form the mineral, i.e. the number of moles of $CaCO_3$ (equivalent) lost from the cement.

The formation of thaumasite directly neutralizes acidity:

$$2\,H_2SO_4+\underset{\text{(hydrated Ca-silicate)}}{Ca_3Si_2(OH)_{14}}+H_2CO_3+8\,H_2O$$

$$\rightarrow \underset{\text{(thaumasite)}}{Ca_3Si(CO_3)(SO_4)(OH)_6.12H_2O}+Si(OH)_4$$

For each mole of thaumasite formed, 4 mol of H^+ are neutralized, which represents 2 mol of $CaCO_3$ eq. Therefore the thaumasite content from XRD analysis (as g/kg) can be converted to equivalent ANC (as g $CaCO_3$ eq./kg) by multiplying by (2 x molecular weight of $CaCO_3$/molecular weight of thaumasite).

The original acid neutralizing capacity (ANC) of the cement applications (Table 1) can be compared with the total loss of ANC over the course of the experiment (represented by Ca in the leachates as well as Ca in gypsum and ettringite), and taking into account the ANC represented by thaumasite (Table 10). Assuming the loss of ANC from the cement over the experiment continues at a constant rate into the future, the time until all of the cement ANC is depleted can be calculated, giving an estimate of cement longevity (Table 10). Because both ettringite and thaumasite contain ANC (due to the OH^- and $CO_3{}^{2-}$ ions within their structures), this calculation assumes that the ettringite and thaumasite formed will eventually be dissolved and thereby contribute to acid neutralization.

Multiplying the longevity of a particular cement application by the reduction in acidity loads (difference between acidity load from those columns and that from the control columns) yields a measure of long-term effectiveness (Table 10). This shows that the AMD sludge-blended cement performed best, mainly due to its higher viscosity; the cement was concentrated at the top of the column to a greater extent than for any of the other cement applications, where it thoroughly covered the waste rocks and dissolved relatively slowly, releasing lower Ca loads than from the other columns (Table 6). The cement cap encapsulated a smaller fraction of the waste rocks than for other cement applications, resulting in a relatively small decrease in sulfide oxidation rates (Fig. 3e), but diverted water away from most of the acid-producing waste rock, so there was a disproportionately small release of sulfate compared to the measured oxygen consumption rates (Figs. 3d and 4a).

An additional factor in the effectiveness of the AMD sludge-blended cement may be due to the reaction of bassanite in the sludge with hydrated Ca-aluminate in the cement to form ettringite. In calcium sulfoaluminate (CSA) cements, ettringite is formed while the cement is still plastic rather than when it has become rigid (Bescher et al., 2016), minimising destructive expansion and cracking (Müllauer et al., 2013); as a result CSA cements have both good sulfate resistance (Taylor, 1997; Singh and Garg, 2002; Grounds et al., 2003; Bescher et al., 2016) and resistance to shrinkage (e.g. expansive cements; Ribeiro, 1998; Evju and Hansen, 2001). Therefore the ettringite in the AMD sludge-blended

Table 7
Calculated gypsum, ettringite and thaumasite content of cement samples from leach columns after correction for variable amounts of waste rock present; w/p is 1.0 unless specified otherwise.

	COL. 4 w/p = 0.8	COL. 7 w/p = 1.0	COL13 25% fly ash	COL. 16 15% AMD sludge
gypsum (wt. %)	0.5	1.2	3.7	0.1
ettringite (wt. %)	11.7	16.5	3.7	15.6
thaumasite (wt. %)	11.1	15.6	0.0	1.3

Table 8

Quantitative XRD analysis of unblended and blended cement paste samples. The composition of 15% sludge blended cement paste was not analysed but interpolated from a and c. All samples were prepared with a w/p ratio of 1.0.

	Unblended cement paste (a)	25% fly ash blended cement paste (b)	25% sludge blended cement paste (c)	15% sludge blended cement paste (d) – interpolated from a and c
gypsum (wt. %)	1.3	1.6	1.0	1.1
ettringite (wt. %)	6.5	5.9	22	18.1
thaumasite (wt. %)	1.6	0	3.5	2.5

cement, which formed from bassanite in the sludge rather than from later exposure to acid mine drainage, probably inhibited the physical disintegration of the cement and thereby increased its resistance to dissolution.

The fly ash-blended cement performed better than unblended cement with the same w/p ratio, but not as good as unblended cement with a lower w/p ratio. The deeper penetration of fly ash-blended cement meant that it decreased sulfide oxidation rates more than other cement applications (Fig. 3e) but dissolved faster, resulting in higher Ca loads and therefore more gypsum precipitation (Fig. 8; Table 6) compared to both the unblended cements with a lower w/p ratio and the AMD sludge-blende cements. The long-term effectiveness of fly ash-blended cement could be improved by using lower w/p ratios to increase the viscosity, resulting in a more concentrated cement distribution and lower rates of deterioration. Applying the cement at a higher rate in order to more completely fill the voidspace would have the same effect.

3.7. Practical considerations of cement application to control AMD generation

The practicalities of using cement to control AMD generation from waste dumps can be illustrated by using the Brukunga mine as an example. The mass, bulk density and gas-filled porosity of the waste rock at Brukunga are 10 Mt, 1700 kg/m^3 and 0.3 respectively (Bennett, 1994), giving a void volume of 1.7×10^6 m^3. The specific volume of cement is 3.17×10^{-4} m^3 kg^{-1} (Taylor, 1997), but this must be corrected for the water/powder ratio used to make cement paste. The w/p ratio used in this study was 0.8–1.2, but a large amount of water is lost as the cement sets; a sample of cement paste prepared with 10 g Portland cement and 10 g of water weighed 14.8 g 2 years later (i.e. 52% water loss). Using a w/p ratio of 0.5 yields a corrected specific volume of cement of 8.17×10^{-4} m^{3}kg^{-1}, which means 2.1 million tons of cement would be required to fill the waste rock dump voids. At Brukunga the cost of Portland cement powder is around $310 per ton, so 2.1 million tons would cost around $651 million. This would not be economical compared to the status quo of lime neutralization at $0.8 million per year (Taylor and Cox, 2003).

If instead the cement filled only voids at the surface of the waste rock dumps (~0.5% of the total porosity), then the cost would reduce to $3.3 million. If the effectiveness and longevity of the cement application are similar to the best outcome achieved in the present study (acidity reduction by 82% and longevity of 118 years; Table 6), and the reduction in treatment costs is proportional to the reduction in acidity generation, the cost reduction resulting from filling the surface voids with cement would be 82 % × 118 years x $0.8 million per year = $77 million savings. Dividing this by the estimated $3.3 million cost of cement application yields a benefit/cost ratio of around 23.

The cost could be reduced and benefit/cost ratio improved by adding sludge to the cement. If sludge substituted for 15% of the cement mass, the required mass of sludge would be around 1470 tons, which is less than the amount of sludge produced by the Brukunga treatment plant every 2 years (Section 2.1). Assuming that adding 15% sludge to the cement decreases the cement cost without decreasing its effectiveness in reducing acidity generation, then the benefit/cost ratio would be increased to around 27.

4. Conclusions

Applications of fly ash-blended and AMD sludge-blended cements to acid-producing sulfidic waste rocks in leaching columns considerably reduced AMD generation, decreasing acidity, metal and sulfate loads in column leachates by 80–95%, similar to the effects of unblended cements. The AMD sludge showed no evidence of releasing its adsorbed heavy metals, but the fly ash released some Si, indicating that it is not chemically stable in the cement. Leachate compositions were mostly determined by the distribution of cement, which is in turn controlled by the viscosity of the cement slurry. Whereas fly ash did not affect slurry viscosity to any great extent, the AMD sludge substantially increased slurry viscosity owing to its significant bassanite content.

Cements with low slurry viscosity (fly ash-blended and unblended cements with higher w/p ratios) penetrated deeply and covered the waste rock more thinly, producing leachates with higher pH and lower acidity and metal concentrations. Cements with higher slurry viscosity (containing AMD sludge or lower w/p ratios) covered the waste rock more thickly at the top of the columns, so the cement was exposed to a smaller surface area of the waste rock, resulting in lower rates of cement dissolution, but leaving some of the waste rock beneath uncemented and able to oxidise and produce AMD. Water that bypassed the cemented rock at the top of the columns flushed relatively small amounts of this AMD from the uncemented rock.

There was significant ettringite and thaumasite growth in the unblended but not blended cement columns. The lack of these secondary minerals in the AMD sludge-blended cements is due to the low rates of cement dissolution, also shown by the relatively small amounts of Ca and Si released from these columns. In the columns with fly ash-blended cement, the lower ANC of the fly ash resulted in lower pH leachates which dissolved the cement faster and released higher Ca concentrations, favoring gypsum precipitation.

The long-term effectiveness of the blended cement applications is greatest for cement placed as a surface cap on top of the waste rock, because the cement dissolves more slowly. Although it would be

Table 9

Calculated gypsum, ettringite and thaumasite content (wt. %) in cement fraction of samples resulting from AMD attack on the cement. The unleached unblended sample with w/p = 1.0 is assumed to be mineralogically the same as an unleached unblended sample with w/p = 0.8.

	COL. 4 w/p = 0.8	COL. 7 w/p = 1.0	COL. 13 25% Fly ash	COL. 16 15% AMD sludge
Gypsum (wt. %)	−0.8	−0.1	2.1	−1.0
Ettringite (wt. %)	5.2	10.0	−2.2	−2.5
Thaumasite (wt. %)	9.5	14.0	0.0	−1.2

Table 10
Estimation of cement longevity using rates of depletion of acid neutralizing capacity (ANC) from both Ca released in leachates and also secondary mineral precipitation, and estimation of long-term effectiveness (see text for discussion of calculations). The Ca loads were obtained over 12 months (August 2015–August 2016), whereas secondary mineral growth was determined in January 2018; it has been assumed that all secondary mineral precipitation took place when the columns were being leached, as the columns were dry after that.

Acid neutralizing capacity (g $CaCO_3$ eq.)	Unblended cement w/p = 0.8	Unblended cement w/p = 1.0	25% fly ash- blended cement	15% AMD sludge-blended cement
Total ANC (g) in cements (Table 1)	270	270	203	236
Acid neutralization associated with sec. mineral precipitation (g/yr)	11.2	18.6	3.2	0
Acid neutralization represented by Ca release in leachates (g/yr)	4.25	22.75	22	2
Total rate of loss of ANC (g/yr)	15.45	41.35	25.2	2
% ANC depleted/yr	5.7%	15.3%	12.4%	0.8%
ANC Longevity (yr)	17.5	6.5	8.1	118
% Decrease in acidity loads	88%	100%	97%	82%
Long term Effectiveness (yrs)	15.4	6.5	7.8	97

necessary to carry out larger scale field trials to further optimize this technique, scaling up the results of the present study to the Brukunga mine site suggest that the benefit of applying a blended cement slurry (in reduced water treatment costs) could outweigh the cost of cement application by a factor of 20–30.

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