

# **Preliminary results from experiments with Cement slurries to control Acid Mine Drainage in Waste Rocks from Brukunga Mine in South Australia**

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## **Abstract**

The use of cements or grouts for geotechnical stabilization of mine voids is well documented, but the effectiveness of cements and grouts in controlling sulfide oxidation has received comparatively little attention from researchers.

In this study, a range of Portland cement slurries were applied directly to waste rocks from the Brukunga Mine in South Australia to test effectiveness in controlling acid mine drainage generation. This paper focuses on the results from three columns used as a control group with no cement application, and another three columns, subjected to application of a cement slurry with a water cement ratio of 1.0.

Cement slurry application caused the pH to increase to almost 12 in the first leach before stabilizing at around 8 after 2 months, at the same time reducing sulfur loads by around 75% and reducing acidity, iron, aluminium, magnesium, copper, zinc and manganese to undetectable levels. These improvements have been sustained for around 8 months since cementing, and monitoring is continuing.

Higher Calcium, sodium and potassium concentrations suggests in the leachates from the cemented rocks indicates that the cement is dissolving slowly whilst neutralizing the acidity produced by the lower rates of pyrite oxidation in these rocks.

Key words: Portland Cement Slurry, Acid Mine Drainage Control

## **Introduction**

The use of cements or grouts for geotechnical stabilization of mine voids is well documented, but the effectiveness of cements and grouts in controlling sulfide oxidation has received comparatively little attention from researchers. Cements have been used for grouting of voids in underground mines (Gynn et al, 2010) as well as a component in covers used to prevent water from flowing through acid producing rocks (Jones and Wang, 1994).

Many studies have investigated the potential of utilizing the useful properties of alkaline industrial waste products such as coal combustion by-products, lime kiln dust and green liquor dregs for controlling acid mine drainage (Bulusu et al, 2007, Perez-Lopez et al, 2007 Sahoo et al, 2013, Makitalo et al, 2015). There is little published work concerning the utility of Portland cement in controlling acid mine drainage.

The Brukunga Pyrite Mine in South Australia was mined between 1955-1972 for pyrite and pyrrhotite resulting in production of 8 million tonnes of waste rocks (Cox et al, 2006). The waste rocks continue to produce acid mine drainage, which is currently treated at a lime treatment plant on-site.

The main objective of this study was to test the effectiveness of directly applying a Portland cement slurry to acid producing waste rocks in reducing acid mine drainage generation.

## **Methods**

Waste rocks and sludge samples were collected from the Brukunga mine in South Australia and the cement used was Cement Australia's General Purpose Cement product.

Six leach columns with 15.5cm diameter and 22.5 cm length were made from PVC pipe. A press on cap with a tap was used to seal the column at the base, and a screw on cap was used to seal the column above.

Each column was filled with 4.78kg of waste rocks from the Brukunga mine ranging from 2mm-26mm in particle size, with 13.6% in the 2-4.75mm size fraction, 69% in the 4.75-13.2mm size fraction and 17.4% in the 13.2-26mm size fraction.

The columns were leached with 1 liter of deionized water each fortnight for 6 months and then kept dry for 49 days before a range of cement treatments (Table 1) was applied to 3 columns with another 3 columns used as a control group.

**Table 1** Cement slurries applied to leach columns.

Columns	Treatment	Cement Composition	Water/Cement Ratio
1	Control	-	-
2	Control	-	-
3	Control	-	-
4	Cement	250g cement, 250g water	1.0
5	Cement	250g cement, 250g water	1.0
6	Cement	250g cement, 250g water	1.0

Immediately before the cement slurries were applied to the columns, the columns were leached with one liter of deionised water to remove a fraction of the sulfide oxidation products that had accumulated over the 49 day dry period.

The cement slurries were prepared in a clean 2 liter plastic beaker. For each column to which a cement slurry was applied, the procedure was as follows. The dry cement powder was first weighed into the beaker and mixed and pounded with a wooden spoon to ensure any lumps were broken up. Deionised water was carefully added whilst the mixture was stirred vigorously to form a homogenous slurry, before the slurry was carefully poured over the rocks in the column with the aim of achieving a uniform coverage over the top surface of the columns and as deep penetration through the columns as the rheological properties of the slurries would allow.

One week after the application of cement slurries, fortnightly leaching was resumed. The fortnightly leaching has been continued for a further 8 months so far, with a 49 day break during the Australian Summer of 2015/16.

Initially leachate samples were collected one day after application of water, but this became problematic after the cement application reduced the permeability of the cemented columns. From 230 days onwards, samples were collected one week after application of water to allow sufficient volumes of leachate to be collected.

pH, electrical conductivity, redox potential and temperature were measured using TPS probes. Titrations were used to measure acidity for samples with a pH < 6.0, and alkalinity for samples with pH >4.0 with a Metrohm 888 autotitrator. Samples were preserved with nitric acid for analysis for Fe, Al, Ca, Mg, Si, Mn, Cu, Zn and S with a Perkin Elmer Optima 8000 ICP-OES and Na and K using a flame photometer. Since November 2015, samples were analysed for sulfate and thiosulfate using a Metrohm 883 Basic Ion Chromatograph.

**Results and Discussion**

*Leachate composition prior to cement application*

Prior to the application of cement, there was little variability in the leachates produced by the 6 columns (Table 2) with total loads of acidity ranging from 57.0 – 67.7 grams of acidity as CaCO3 equivalent for the six of columns, produced over a period of around 6 months.

**Table 2** Average pH, Total Loads of Ca, Mg, Al, Fe, S, Si, Cu, Mn, Zn and Acidity of samples collected from leach columns prior to application of cement slurries. Loads of elements calculated using concentrations measured using ICP-OES

Column	Group	pH	SO4 (g)	Fe (g)	Al (g)	Ca (mg)	Mg (mg)	Si (mg)	Cu (mg)	Mn (mg)	Zn (mg)	Acidity (total) (g)
1	Control	2.37	42.8	11.2	1.9	936	263	295	17	247	668	44.2
2	Control	2.42	38.9	10.6	1.7	604	254	172	15	229	726	42.6
3	Control	2.37	43.7	12.2	1.8	799	264	238	18	231	700	47.3
4	Cement	2.41	39.6	10.8	1.8	721	252	208	15	228	707	43.1
5	Cement	2.43	37.3	10.2	1.8	598	235	136	42	293	615	41.0
6	Cement	2.40	40.4	11.5	1.8	721	205	169	42	272	584	43.5

*Leachate composition after cement application*

Since the application of cement slurries, the leachate compositions of the six columns have diverged (Table 3). The columns to which cement was added have become moderately alkaline (pH ~ 9.0), with reduced loads of sulfur and silicon, and undetectable levels of Fe, Al, Mg, Cu, Mn and Zn, while Na, K and Ca levels are greatly increased. The slightly sulfurous odors of the cemented columns also differ from those produced in the control columns, suggests the presence of sulfide in the cemented columns.

**Table 3** Average pH and total loads of Ca, Mg, Al, Fe, S, Si, Cu, Mn, Zn, and Acidity of samples collected from leach columns after to application of cement slurries. Element loads were calculated using concentrations obtained using ICP-OES for each element except for Sulfur, which was analysed by IC.

Column	Group	Vol (L)	pH	SO4 (g)	Fe (g)	Al (g)	Ca (g)	Mg (mg)	Na (mg)	K (mg)	Si (mg)	Cu (mg)	Mn (mg)	Zn (mg)	Acidity (total) (g)
1	Control	12.6	2.34	64.9	17.9	2.6	0.9	534	29	21	404	26	145	376	64.7
2	Control	12.6	2.36	65.0	18.0	2.7	0.9	520	25	9	339	24	150	479	65.4
3	Control	12.8	2.32	65.2	18.2	2.5	1.0	496	28	9	440	25	136	429	63.8
4	Cement	8.0	9.21	20.6	0.0	0.0	5.5	0	235	872	150	0	0.0	0.0	-1.0
5	Cement	10.1	9.34	20.2	0.0	0.0	5.8	0	250	845	219	0	0.0	0.0	-1.8
6	Cement	3.0	9.26	12.4	0.5	0.2	3.0	0	198	728	18	0	0.07	0.31	-1.2

There is more variation in leachate compositions in cemented columns than in the control group after cementing, due to variations in the degree to which the cemented columns were made less permeable by the cement applications. Column 6 is the least permeable of the columns with only 23% of the water applied to the column draining through the column within a week, which automatically reduces the loads of sulfur, calcium and silicon produced by the column. The reduced permeability of this column also increased the fraction of total sulfur that is present as thiosulfate rather than sulfate in the leachates from this column (Table 4).

**Table 4.** Average Sulfate and Thiosulfate concentrations measured with Ion Chromatography (IC) for 9 samples measured from November 2015 til April 2016.

Columns	Group	SO4 IC	S2O3 IC
1	Control	4844	0.0
2	Control	4902	0.0
3	Control	4818	0.0
4	Cement	1440	220
5	Cement	1380	115
6	Cement	1501	578

*Stability of cement over time*

Cement application resulted initially in a spike of alkalinity corresponding with high pH; over time, the alkalinity and pH declined and stabilized to ~ 8 and ~40mg/L (Figures 1 and 2).

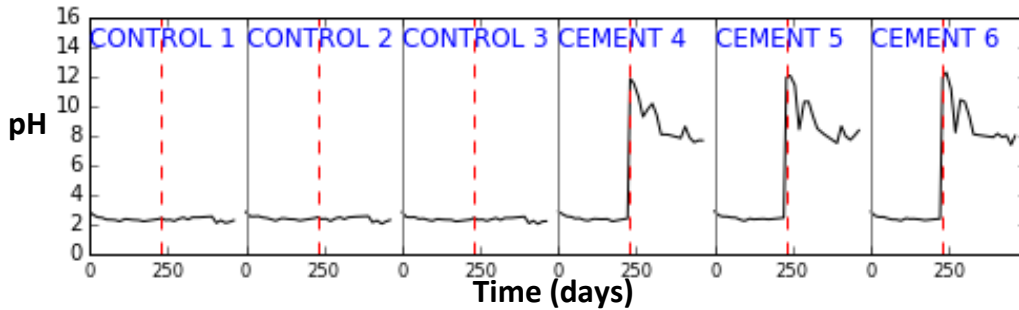


Figure 1. pH

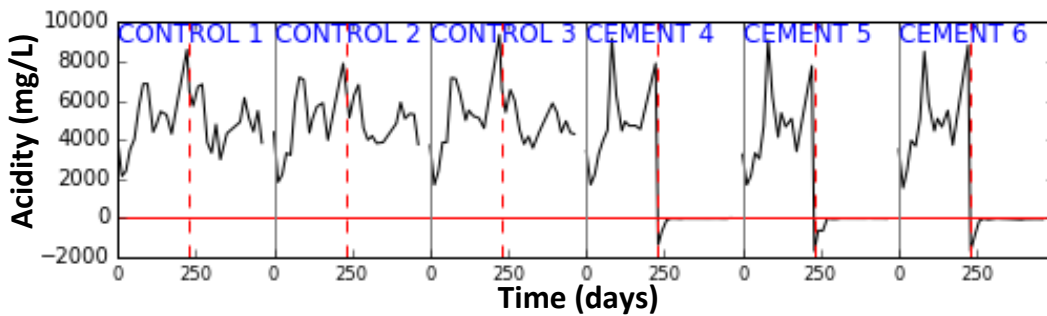


Figure 2. Acidity (mg/L CaCO<sub>3</sub> equivalent), Alkalinity plotted on negative y-axis with the same unit.

Over time column 6 and to a lesser extent columns 4 and 5, have become less permeable as evidenced by decreasing weights of sample collected (Figure 3). To a lesser extent the permeability of columns 4 and 5 have also decreased over time. The higher concentrations of calcium, sodium and potassium in column 6 (Figures 4,5 and 6 respectively) probably reflects enhanced dissolution of these elements from the cement due to the longer contact time.

Assuming constant rates of cement dissolution based on the data in table 3 and using a typical CaO content for Portland Cement of 64% (Guirguis, 1998) predicts that 432 leaches would be required to completely consume all of the calcium in the applied cements. At the fortnightly rate of leaching used here, the calcium of the cements would be completely consumed in around 12 years.

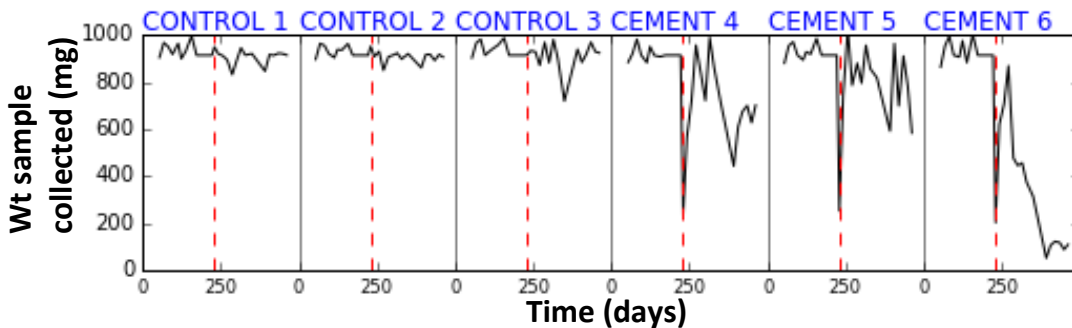


Figure 3. Weight of Leachate sample collected (mg). For the first 230 days, samples were collected after one day. After 230 days, samples were collected one week after water application to allow for the slower rate of drainage in the cemented columns.

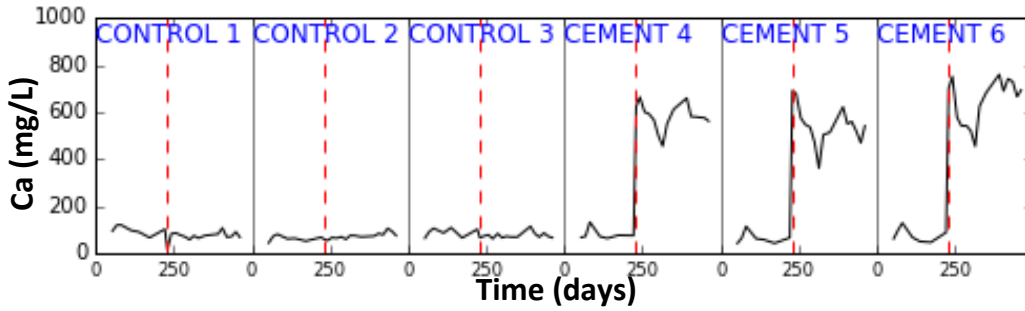


Figure 4. Ca (mg/L)

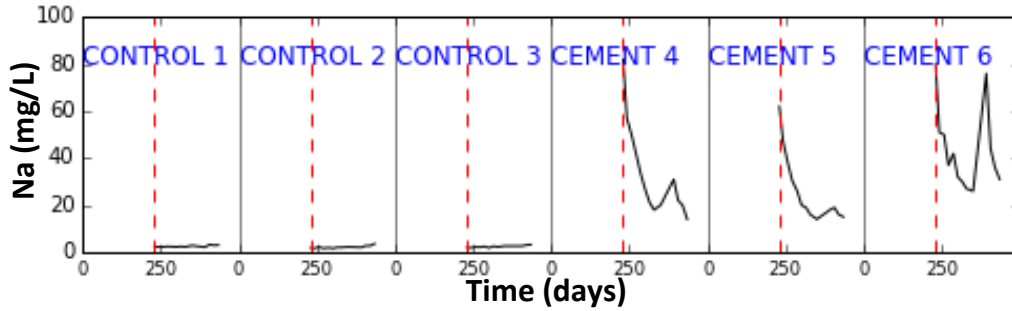


Figure 5. Na (mg/L)

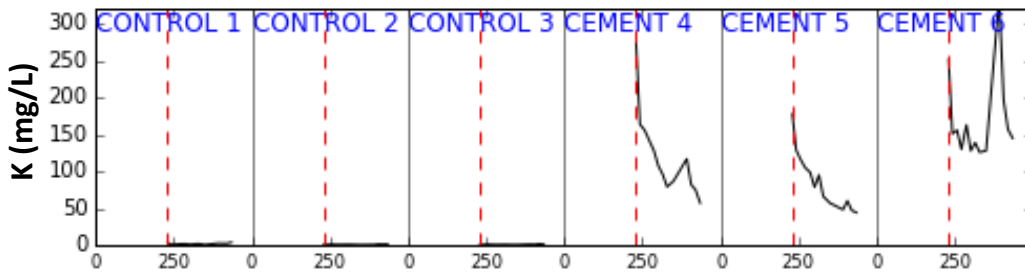


Figure 6. K (mg/L)

Silicon concentrations are higher in the controls columns than in the cemented column, reflecting likely due to sulfuric acid attack of aluminosilicate minerals in the waste rocks. Upon cement applications silicon concentrations decreased in the cemented columns, but in columns 4 and 5 have begun to increase as the pHs in these columns decreased, but this is not the case for column 6; Si is likely being released from the cement matrix, but in column 6, may be re-precipitating (Figure 7).

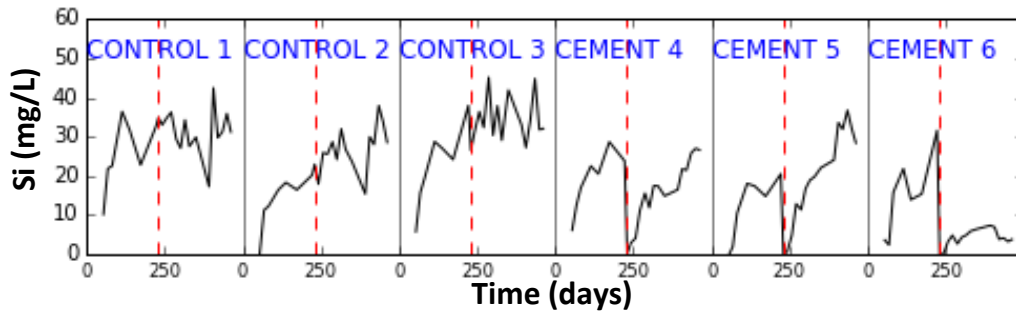
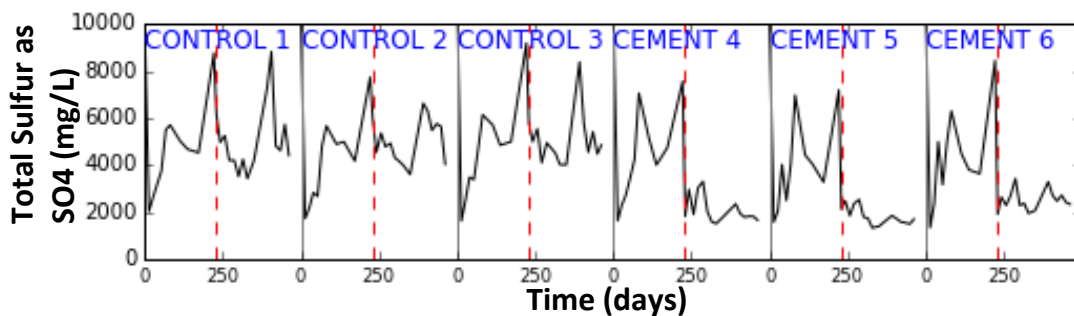


Figure 7. Si (mg/L)

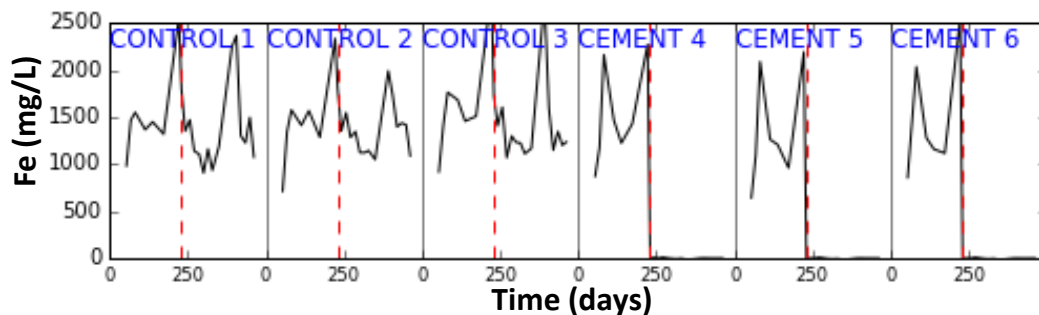
*Rate of pyrite oxidation in cemented columns*

Sulfur concentrations in leachate from the cemented columns appear to be stable at around half the concentrations in the control columns (Figure 8), which suggests that the rate of pyrite oxidation has decreased due to the cement application. It is likely that the lower rate of pyrite oxidation in the cemented rocks is due to direct encapsulation of sulfide surfaces as well as the increased water retention in these columns (Figure 3), which would likely serve as a water barrier to oxygen.

Iron concentrations in the control leachates are over 1g/L, but have been reduced to below detection limit in the cemented columns, which suggests that the iron is being retained in the cemented columns, probably as precipitated ferrihydrite or schwertmannite (Figure 9). The steady release of sulfate in the cemented columns indicates that the precipitation of iron in the cemented columns is not presently inhibiting the oxidation of pyrite.



*Figure 8. Total sulfur as SO4 (mg/L)*



*Figure 9. Fe (mg/L)*

**Conclusions**

Direct application of cement slurries to the Brukunga waste rocks in all cases greatly diminished acidity production and metal loads (iron, aluminium, copper, manganese and zinc).

Calcium, sodium and potassium concentrations are all increased in the cemented columns, which suggests that the cement is dissolving while neutralising the acid being produced by oxidizing sulfides in the waste rocks and leaching sulfate through the cement matrix. The rates of calcium dissolution measured in this experiment suggest that the cements would lose effectiveness after around 12 years due to complete dissolution of the calcium from the cement.

The lower rates of sulfur production in the cemented columns indicate that the continuing pyrite oxidation is occurring at around half the rate of pyrite oxidation in the control columns due to direct encapsulation of pyrite surfaces with cement as well as due to increased retention of water, which may serve as a water barrier to oxygen.

Future work will test the longevity of the cement slurry treatments on the waste rocks and compare the effectiveness of different cement slurry compositions in controlling acid mine drainage.

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