

Prevention of Sulfide Oxidation in Waste Rock using By-products and Industrial Remnants, a Suitability Study

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Abstract Prevention and mitigation of acid rock drainage from mining are decisive for limiting environmental impact. Five by-products and industrial remnants (lime kiln dust, blast furnace slag, granulated blast furnace slag, cement kiln dust and fly ash) were investigated for their suitability to prevent acidity and metal(loid)s during leaching from highly sulfidic (50wt%, sulfide) waste rock in small scale laboratory test cells. Variations in pH and electrical conductivity in leachate allowed differentiation between the different materials. Lime kiln dust (5wt%) and fly ash (1 and 2.5wt%) were observed to be the most suitable materials to prevent acidity and metal(loid)s leaching.

Keywords Prevention measures, metal leaching, waste rock management, by-product, industrial remnant

Introduction

In Sweden, the most common way for treatment of acid rock drainage (ARD) generated by waste rock heaps during operation is active treatment through the addition of alkaline materials in an attempt to raise the pH and attenuate metals of drainage waters. This approach generally includes alkaline reagents with subsequent sludge formation as a result of precipitation of e.g. Me-oxides and gypsum. An alternative would be the treatment of the waste rock in order to mitigate the generation of ARD and thereby reduce the lime consumption and sludge formation during operation. Studies have shown that sulfide oxidation at near neutral pH in the presence of sufficient alkalinity will promote precipitation of secondary minerals such as Fe-oxides on the sulfide surface which with time grow thicker and thereby prevents the sulfides from further oxidation (Huminicki and Rimstidt 2009). Several materials (organic and inorganic) studied were either too expensive or potentially harmful to the environment (Sahoo et al. 2013). In recent years, the focus has shifted towards the use of alternative materials such as by-products and industrial remnants (BPIR) in order to minimize costs. A mapping of BPIRs in Sweden (Alakangas et al. 2014) identified materials with potential to promote secondary mineral formation and/or stabilization/solidification through pozzolanic properties. The materials were further investigated and the results are presented in this paper. The aim of the study was to investigate the suitability of different BPIR to prevent acidity generated by the oxidation of sulfidic waste rock and to immobilize metal(loid)s.

Materials and methods

Highly sulfidic waste rock (50wt% sulfide) from an open pit mine (Zn, Cu, Au, and Ag) currently in operation in the Skellefte field, northern Sweden was used in the study. Waste rock with high sulfide content not typical for all waste rock at the site was used in the study. Mineral characterization showed that pyrite and quartz are the dominating minerals with traces

of muscovite, chlorite and calcite. Other sulfides found are chalcopyrite, bournonite, sphalerite and arsenopyrite (unpubl. data). A more detailed characterization is on-going in order to identify the distribution of trace metals in minerals. Acid Base Accounting test (Swedish standard SS-EN 15875:2011) showed that the waste rock is acid producing with a net neutralization potential (NNP) of -946 ± 167 . The total element composition of the waste rock was determined with the EPA-methods (modified) 200.7 with ICP-AES (Perkin Elmer Optima DV 5300) and 200.8 with ICP-SFMS (Thermo Scientific Element) by the SVEDAC-accredited ALS Scandinavia laboratory in Luleå, Sweden. For analyses of As, Cu, S, and Zn, the samples were dried at 50 °C and digested with 7 M nitric acid in closed teflon vessels in a microwave oven. The other elements were determined after fusion with lithium metaborate followed by dissolution in diluted nitric acid. Five different materials were used as additives to waste rock with the aim to reduce the generation of acid and metal(loid)s during operation. Lime kiln dust (LKD), originating from combustion gasses flowing through the kiln in the production of quicklime by Nordkalk consists of partially calcined material mixed with finely crushed limestone. LKD primarily consists of finely crushed calcium carbonate in combination with quicklime and traces of portlandite and gypsum. Cement kiln dust (CKD) from Cements AB is a fine-grained caustic material originating from combustion gasses flowing through the cement kiln in the production of cement clinker. The main minerals are calcite and quicklime with traces of ettringite, gypsum, and portlandite. Blast furnace slag from Merox AB is produced parallel with iron in the blast furnace. It can be either air cooled (BFS) or water granulated (GBFS) depending on desired material characteristics. The mineralogy of BFS primarily consists of monticellite and akermanite. The minerals in GBFS are undetermined as it is considered amorphous; it does, however, resemble hercynite (personal communication with Merox AB). Fly ash (FA) from the paper mill industry, BillerudKorsnäs, is a fine-grained remnant from the separation of combustion gasses in the incineration of biofuels. The mineralogy mainly consists of calcite, quartz, and hydroxides.

Kinetic leaching

Kinetic testing was conducted using free-draining column leach test methods in HDPE small scale test cells (10L) lined with geotextile at the bottom to avoid clogging. Partly oxidized sulfide-rich waste rock crushed and sieved to a size of 5-30mm and 30-60mm was used (Table 1). Each test cell was irrigated with 600ml of MilliQ water on a weekly basis (based on average annual precipitation in the area). Each cell was leached for several weeks before addition of BPIRs to ensure reasonable similarity regarding pH, EC and metal(loid) concentrations in the different test cells. The alkaline material was added on top of the waste rock in accordance with Table 1 and Figure 1. The amounts of BPIRs added were based on estimated costs for material and transportation (Alakangas et al. 2014). One test cell was kept as a reference. CKD was added to (G)BFS in order to activate (hydrate) the (G)BFS for making use of the materials pozzolanic properties as it has been suggested to bind S in a more stable form than gypsum (Tariq and Yanful 2013).

Leachate was collected at the bottom on a weekly basis the day after irrigation. pH and electrical conductivity (EC) were determined immediately in closed containers to limit oxygen

exposure. The pH and EC were measured using a WTW Multi 3420 multimeter equipped with Sentix® 940 (pH) and TetraCon® 925 (EC) electrodes, respectively. Instruments were calibrated prior to each sampling session. Leachate samples were filtrated (0.22µm, nitrocellulose membrane filter) into high-density polyethylene bottles using vacuum filtration. The bottles had been previously washed with 50% hydrochloric acid followed by 1% nitric acid. The filter equipment was washed in 5% nitric acid and the filters in 5% acetic acid. Samples were stored cold (4°C) and in darkness until analysis.

Table 1 Addition of by-products and industrial remnants on top of waste rock in small-scale laboratory test cells.

Cell	Material	Amount	Waste rock size
1	Reference	-	5-30mm
2	GBFS+CKD	4+1wt%	5-30mm
3	BFS+CKD	4+1wt%	5-30mm
4	LKD	5wt%	5-30mm
5	FA	1wt%	30-60mm
6	FA	2.5wt%	30-60mm
7	FA	5wt%	30-60mm
8	GBFS	5wt%	30-60mm

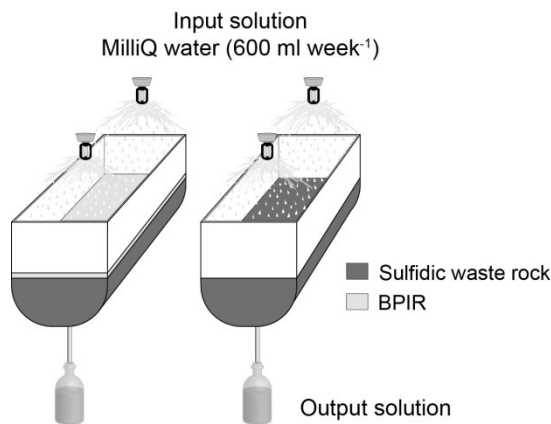


Figure 1 Sketch showing the experimental design of non-saturated small-scale laboratory test cells

Results and discussion

A comparison of the waste rock to the average continental crust show an enrichment of Fe, S, Si, As, Cu, Hg, Sb and Zn (Figure 2). Dominating major elements Fe, S and Si coincide with mineralogical observations of pyrite and quartz as dominating minerals. Trace elements of Cu and Zn are enriched but not to a great extent as As, Hg and Sb (>200 times

higher than average continental crust as suggested by Krauskopf and Bird (1995)). Compared to the waste rock, Ca, K, Mg and U were higher in the BPIRs (Figure 2).

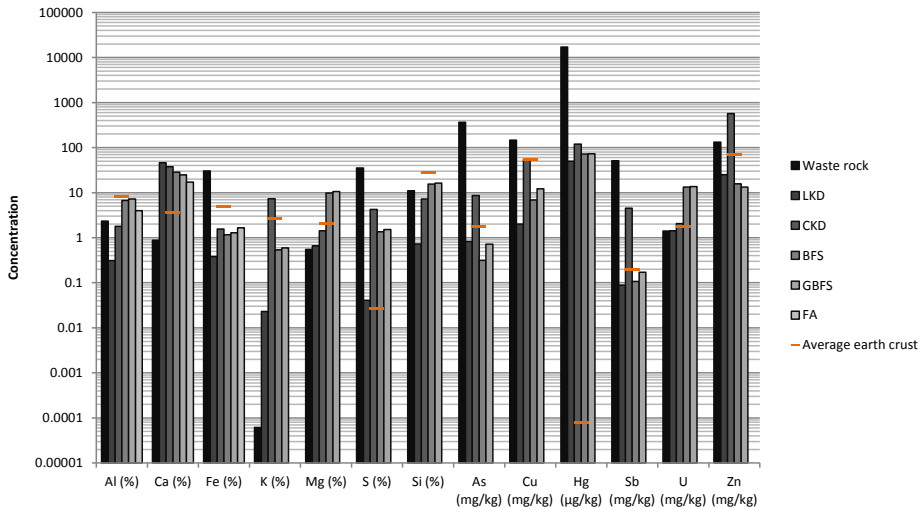


Figure 2 Abundance of selected elements in waste rock compared to those in by-products and industrial remnants used in this study.

Kinetic leaching

Four test cells (1-4) containing waste rock of size 5-30mm were leached for nine weeks before BPIRs were added to three of them (2-4) and one was kept as a reference (1). Cell 1 with solely waste rock displayed a geometric mean pH of 3.5 and EC of 5.2mS/cm during the first 175 days of leaching (Figure 3A) but decreased to 2.5 and EC increased to 9.1mS/cm at the end of the leaching period (Figure 3A). Cell 2 and 3 filled with mixtures of GBFS + CKD and BFS + CKD respectively displayed an initial increase in pH (6.5 and 7.3). The pH did however not remain stable, instead, it declined until day 154. The cells were terminated due to the incapability of maintaining neutral pH (3.8 and 4) (Figure 3B). At the time of termination, the EC had decreased to levels similar to that of the reference cell which suggests that the mixture of GBFS + CKD and BFS + CKD did not contribute to the neutralization. Both cell 2 and 3 showed signs of cementing as explained by Tariq and Yanful (2013) despite that no grinding of GBFS and crushing of BFS to only size 0-4mm occurred prior to testing (grinding/crushing is the conventional way of activating GBFS/BFS for use in cement). The lack of grinding/crushing together with the much lower amount of CKD than reported by Chaunsali and Peethamparan (2013) was hypothesized to ensure slow hydration of (G)BFS to promote the precipitation of C-S-H (calcium-silicate-hydrate) and the subsequent formation of ettringite for a more stable binding of S than that of gypsum. The cementing of (G)BFS and CKD mixtures most likely hindered the dissolution of silicates and carbonates, resulting in a failure to maintaining high pH. This statement is supported by the declining behavior of EC to levels prior to addition of (G)BFS and CKD (Figure 3B).

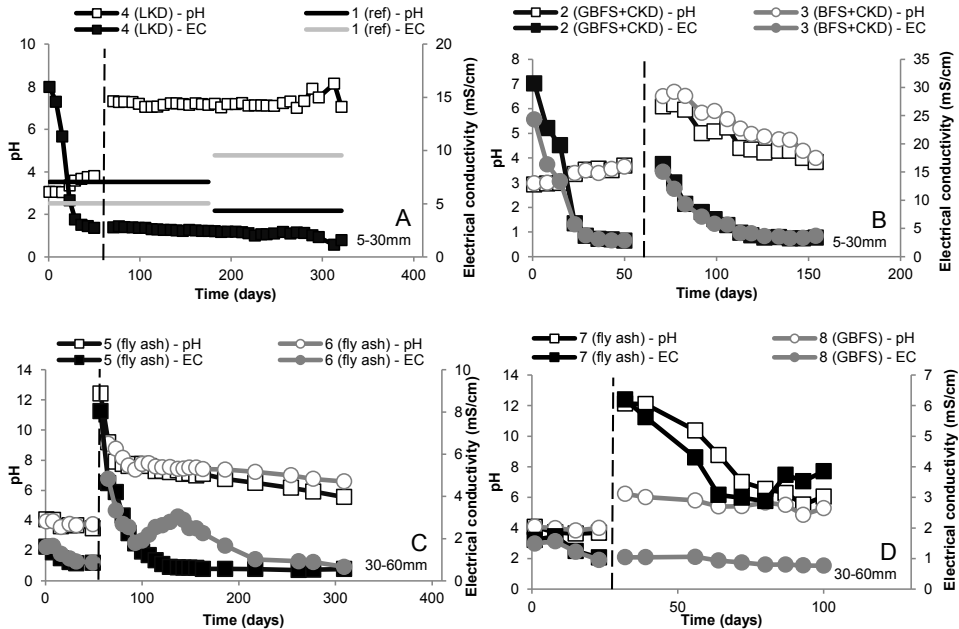


Figure 3 Basic parameters of leachates from non-saturated small scale leaching test cells filled with crushed sulfidic waste rock. **A:** (1) Waste rock (reference), (4) Lime kiln dust (5wt%). **B:** (2) Granulated blast furnace slag (4wt%) + Cement kiln dust (1wt%), (3) Blast furnace slag (4wt%) + Cement kiln dust (1wt%). **C:** (5) Fly ash (1wt%), (6) Fly ash (2.5wt%). **D:** (7) Fly ash (5wt%), (8) Granulated blast furnace slag (5wt%). Dashed line indicates addition of by-products and industrial remnants.

Leachate from cell 4 displayed an initial increase in pH (7.3) after addition of LKD. The pH maintained around neutral (7.0 – 8.1) throughout the time of leaching. No increase in EC was observed after addition of LKD. Compared to before addition of LKD (around 2mS/cm), EC decreased down to 1.1mS/cm at day 321, at the end of leaching period (Figure 3A). Cell 5 and 6 with waste rock of size 30-60mm were leached for six weeks before fly ash were added (1wt% and 2.5wt% respectively). Leachate from cell 5 showed an initial increase in pH to 12.4 the first week after addition of fly ash (day 57) (Figure 3C). No water was possible to percolate through cell 6 probably due to hydration of the fly ash. Over the following weeks, pH dropped to 7.7 and 8.2 for cell 5 and 6 respectively. The pH in both cells declined with time to 5.5 and 6.5 at the end of the leaching period (Figure 3C). The EC in cell 5 declined after addition of 1wt% fly ash until day 129 after which it remained around 0.55-0.65mS/cm until day 277, at end of leaching period (Figure 3C). Cell 7 and 8 with waste rock of size 30-60mm were leached four weeks before fly ash (5wt%) was added to cell 7 and GBFS (5wt%) to cell 8. Leachate from cell 7 showed an initial increase in both pH (12.1) and EC (6.2mS/cm) which declined over time until the cell was terminated at day 100 when the pH had dropped below 6. Cell 7 showed signs of cementing which is the likely reason for not being able to maintain near-neutral pH. Cell 5 (1wt% fly ash) was able to maintain a pH above 6 until day 277 which conclude that a larger volume

fly ash will not necessarily generate better results. Regarding fly ash, it is evident that application (thickness, compaction etc.) may be proven important to avoid cementation. Leachate from cell 8 showed an increase in pH (6.2) after addition of GBFS (5wt%) but no signs of increased EC were found. The pH declined during the time of leaching (4.7 at day 93). Cell 8 showed signs of carbonation. Through personal communication with Merox, it is implied that solely GBFS may require a greater water volume to dissolve than used in this study. The need of excess water was supported by the modified batch leach tests performed prior to the setup of columns for leaching (Swedish standard SS-EN 12457-2) for estimation of easily soluble metal(loid)s in the respective by-product or industrial remnant (unpubl.data).

An initial wash-out of oxidation products and soluble secondary minerals was shown for all cells which reflected the pH (Figure 3A-D). Similar pH, EC, and metal(loid) concentrations were observed for cell 1-4 and 5-8 prior to the addition of BPIRs. The Fe:S molar ratio in the leachate of cell 4 was stabilized around 0.5 after 219 days confirming pyrite oxidation as the primary source of Fe and S, and an indication of accelerated sulfide oxidation (Figure 3A). The increasing sulfide oxidation was accompanied by release of high concentrations of metal(loid)s to the leachate. Release of Cu (19.7mg/L) and Zn (23mg/L) displayed high leachability at day 219, compared to its presence in the waste rock (147mg/kg and 133mg/kg respectively), if similar release rate as day 219 continue all Cu and Zn would be depleted in less than five years. The time until accelerating sulfide oxidation is long considering the high sulfide content in the waste rock (50wt% sulfide) as well as the particle size. The high release rate of metal(loid)s are due to the likely high concentration of ferric ions and bacteria due to the low pH, which both together accelerate the oxidation rate of pyrite (Nordstrom and Southam 1997). In such acidic environment recovery of metal(loid)s could have been an option.

Cell 4, 5 and 6 were those that showed best results in pH and EC development throughout the time of leaching. The average concentration of metal(loid)s in cell 1 (solely waste rock) after day 219 suggest that the sulfide oxidation occurring is significant (Table 2). The addition of LKD shows a significant decrease of metal(loid) concentrations corresponding to >99.9% for As, Fe, U, and Zn. Concentrations of S and Sb are decreased by 94.7 and 98.3% respectively, while Hg shows a decrease of 88.1%. Due to differences in waste rock size, a direct comparison between cell 1 (reference) and cell 5- 6 is not applicable. When the dominant mineral present (pyrite) is acid generating, a particle size reduction can result in lower pH when subjected to column leaching (Lapakko 2006). The size difference between cell 1 and cell 5-6, therefore, suggest that observations in pH in cell 1 are over-estimated compared to that of a *hypothetical* reference corresponding to size 30-60mm. Whether or not the addition of fly ash to cell 5-6 is comparable to that of the reference cell, it can through a comparison of figure 2 and table 3 be concluded that although fly ash is enriched in metal(loid)s it is not necessarily reflected in the chemical composition of the leachate.

Table 3 Concentrations of metal(loid)s in leachate from solely waste rock and from waste rock with the addition of by-products and industrial remnants. 1: Waste rock (reference), 4: Lime kiln dust (5wt%), 5: Fly ash (1wt%), 6: Fly ash (2.5wt%).

Cell	As (µg/L)	Cu (µg/L)	Fe (mg/L)	Hg (µg/L)	S (mg/L)	Sb (µg/L)	U (µg/L)	Zn (µg/L)
1 ¹	10708	11358	7040	0.42	5902	182	228	14532
4 ²	0.22	<0.1	0.0004	0.05	315	3.1	0.28	1.84
5 ³	0.13	0.80	0.63	<0.002	95	1.7	1.1	76
6 ³	0.53	0.28	0.27	<0.002	156	4.0	1.8	45

¹ Average concentration of 102 days of leaching (day 219-321)

² Concentration at day 321

³ Concentration at day 277

In general, a materials suitability for application cannot be determined only by examining the total chemical composition or its leachability in a batch test (unpubl.data) but rather has to be put in context (in this case application to waste rock) before any major conclusions can be made. In this case, it can be concluded that addition of BPIRs that fail to maintain pH during the first 200 days is not suitable for this application.

Conclusion

- Despite high sulfide content in waste rock (50wt%), the sulfide oxidation did not accelerate until 219 days of leaching.
- An increase in the amount of by-products and industrial remnants do not necessarily increase the quality of leachate.
- The most promising industrial remnants are LKD due to the ability to remain pH, EC and lower the metal(loid) concentrations over a longer period of time.

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