Properties of alkaline materials for injection into weathered mine waste piles – methods and initial pilot trials

Mattias Bäckström[1,2], Lotta Sartz[2], Erik Larsson[2], Stefan Karlsson[1]

[1]*Man-Technology-Environment Research Centre, Örebro University, SE-701 82 Örebro, Sweden, mattias.backstrom@oru.se*
[2]*Bergskraft Bergslagen, Harald Olsgatan 1, SE-714 31 Kopparberg, Sweden*

Abstract Several alkaline materials were studied with regards to their ability to form stable suspensions with water. Gravitational injection of alkaline materials were performed into weathered mine waste in two different pilot scales (25 L and 1 000 L). When water was added after injection lime mud (LM) was flushed out while lime kiln dust (LKD) and green liqour (GLD) remained within the mine waste. Deconstruction of the pilot systems showed that both materials had penetrated the voids present. LKD and GLD increased pH significantly and reduced trace metal concentratios. It is concluded that both LKD and GLD are suitable for stabilizing acid generating mine waste.

Key Words stabilization, injection, grouting, green liquor dreg, lime kiln dust

Introduction

During mining new mineral surfaces are exposed to oxygen and water. Oxidation of some sulphide (ex, pyrite, pyrrhotite) minerals is an acid producing process (Sartz, 2010). Acid drainage from weathered mine waste piles can affect large areas and cause serious environmental degradation. Addition of alkaline materials ($CaCO_3$, $Ca(OH)_2$, CaO or NaOH) can increase the neutralizing potential of mine wastes and reduce their capacity for acid mine drainage production (Sartz, 2010). In recent years, an increasing number of studies have focused on using less expensive alternative products, such as cement kiln dust (Mackie *et al.,* 2010), lime kiln dust (Bulusu *et al.,* 2007), lime mud from the pulp and paper industry (Chtaini *et al.,* 2001) or fly ash (Pérez-López *et al.,* 2007).

Addition of alkaline materials can be made through injection of a slurry if a stable suspension can be created (Sartz, 2010). A set of 5 criteria for slurry injection was stated by Wikman *et al.* (2003) concerning the properties of the alkaline material: (i) it should be relatively stable in a water suspension, (ii) it must stay in the deposit after injection, (iii) it should be able to fill out the voids in the deposit, (iv) it should preferably have a sealing effect, i.e. allow for hard pan formation and (v) it should not have a particle size exceeding 1 mm.

The aim of this study is to investigate if seven different alkaline (lime kiln dust, lime mud, green liqour dreg, water works granules, LD-stone (slag) and two different fly ashes) by products are suitable for injection into acidic and weathered waste from an abandoned Swedish mine site. Earlier studies have indicated that 15 % by weight is enough to neutralise the present acidity (Sartz, 2010).

Materials and Methods

Mine waste

The Ljusnarsberg mine field was discovered in 1624 and the latest mining period ended in 1975. Approximately 65 large or small pitheads have been found within the central parts of the field. It is estimated that a total area of 500*400 m^2 is affected by mining, ore or waste rock dumps (Sartz, 2010).

The ore was dominated by chalcopyrite ($CuFeS_2$) that occurs as dissiminations, small lenses and veinlets. The chalcopyrite is more or less mixed with pyrrothite (FeS), pyrite (FeS_2) and magnetite (Fe_3O_4) and has quartz, hornblende, actinolite, biotite, chlorite and red garnet as wallrock. From the middle of the 19th century and onwards also galena (PbS) and sphalerite (ZnS) ore was mined (Bäckström and Sädbom, 2008). Remaining waste rock piles are heavily oxidized and covered with secondary precipitates.

Alkaline by products preliminary testing

Seven different alkaline by products were selected for the study: (i) fly ash F (FAF), (ii) fly ash E (FAE), (iii) LD-stone (LD), (iv), water work granules (WWG), (v) lime kiln dust (LKD), (vi) lime mud (LM) and (vii) green liqour dreg (GLD). Two different LKD qualities were used, containing 27 % and 46 % active CaO, respectively.

Preliminary testing (need of crushing and sieving prior to use and the ability to form stable suspensions during mixing with water) FAF and LD did not fulfill criterion (i; stable water suspension); some amendment of cellulose or wood pulp would be required in order to create a stable water suspension. In addition, WWG did not fulfill criterion (v), as the particles were too large. These three materials were therefore excluded from further testing.

Remaining four alkaline materials (LKD, LM, GLD and FAE) were studied in a standardized test (SS-EN 445 2007), where 0.66 L slurries of each material were poured through a funnel (diameter of 8 mm), while recordingthe time.

Small pilot scale trials (25 L)
Alkaline by products suitable for injection were injected into 25 L barrels filled with weathered mine waste (fig. 1). A plastic tube was inserted into the waste rock and slurry was poured until no more slurry could be added. The plastic tube was then retracted 5 cm and the pouring was continued. This was repeated until the plastic tube was fully removed from the waste rock. All trials were performed in duplicates for each alkaline by product. Five minutes after injection the bottom tap was opened in order to study if the injected material remained within the barrel. After 3 days one of the duplicate containers was exposed to a simulated rain of 20 mm. The simulated rain cycle continued for 7 days. Leachate from the bottom tap was collected for chemical analysis (pH, electrical conductivity, alkalinity and trace metals).

Large pilot scale trials (1 000 L)
After evaluation of the first pilot trials (25 L) two alkaline by products (GLD and LKD) were selected for larger pilot trials (1 000 L) (fig. 2). Mine waste was placed around 5 cm diameter tubes in 1 000 L containers. 15 L slurry was added through the pipe and then the pipe was retracted 7—10 cm. This procedure was repeated until the pipe was completely removed from the waste. Approximately 15 % alkaline by products by weight were added to each system (Sartz, 2010). The systems were constructed during the late summer of 2010 and were left exposed to rain and freezing until June 2011 (open bottom tap). In June the tap was closed and leachate was collected after a couple of days and analysed for pH.

Results and Discussion

Physical testing
Results from the preliminary physical testing are presented in tab. 1. The results indicate that only slurries with LM, LKD, GLD and FAE were stable enough to prepare slurries for injection. Addition of cellulose to the slurries might keep the slurries of FAF and LD stable.

Figure 1 *Small pilot trials (25 L) with the plastic pipes for injection.*

Table 1 *Results from the preliminary physical tests on the alkaline by products.*

By product	Needs sieving	Needs cellulose	Optimum funnel time (s)
Lime mud (LM)	No	No	10 s
Lime kiln dust (LKD)	No	No	10 s
Green liquor dreg (GLD)	No	No	10 s
Fly ash E (FAE)	Yes	No	14 s
Fly ash F (FAF)	Yes	Yes	-
LD-stone (LD)	Yes	Yes	-
Water work granules (WWG)	Needs crushing	-	-

Figure 2 *Pilot scale trials 1 000 L during construction (left) and after completion (right).*

Small scale pilot trials (25 L)

LM, GLD and LKD all formed easy to inject, good suspensions during the small pilot trials. However, the FAE suspension separated during injection despite good results during the preliminary testing. FAE could therefore not be evaluated further. The barrels injected with LKD, LM and GLD appeared to have all the voids filled (fig. 2). However, when the bottom tap of the barrels with lime mud (LM) was opened, the slurry poured out. This indicates that the LM slurry, as opposed to the LKD and GLD slurries, did not react with theweathering products on the mine waste. During the following days with addition of water more LM left the system. Thus, LM will probably not form hard pans within a waste pile and the slurry will most likely be drained at the bottom of the waste pile during precipitation events.

Green liqour dreg (GLD) formed a good suspension with water and remained in the mine waste system after injection. However, GLD does not not form impermeable layers within the system as all added water immediatly left the system. Another problem is that the water leaving the system is discoloured (black). Compared to other materials, GLD also demanded much more water in order to obtain a suitable viscosity for injection. This will make it hard to inject required amount of material.

The two qualities lime kiln dusts (LKD) which were tested in the small scale pilot tests (with 27 % and 46 % active CaO). needed no sieving and both formed good suspensions with water.

The low CaO-material (27 %) was easy to inject, while the rapid hardening of the high CaO-material (46 %) made the injection difficult (the suspension started to boil prior to injection). This is consistent with previously reported results on the rapid hardening of LKD grouts with a CaO content of 60.7 % which also led to an incomplete dissolution (Bulusu *et al.,*2007). The LKD injected barrel (low CaO) effectively retained water flow during the initial evaluation period (4 weeks), probably due to hard pan formation. The GLD injected system retained the water flow, but no to nearly the same extent as the LKD injected system.

A couple of days after injection it was apparent that the alkaline by products had filled the voids quite efficiently (fig. 3).

After injections, several rain events were simulated for the systems injected with LM, LKD and GLD. For LM and GLD 11 events were collected and analysed. For LKD only 6 events were analysed due to low permeability. Results from the chemical

Figure 3 *One of the 25 L pilot trials after injection. Different layers with mine waste and alkaline amendment can be seen.*

analysis are found in tab. 2. It is evident that all amendments increase pH in the drainage significantly from around 3 (unamended mine waste; Sartz, 2010) to above 7. From the analytical data it is also evident that LM and GLD contribute carbonate alkalinity while LKD contributes hydroxide/oxide alkalinity (LKD has much higher pH and alkalinity compared to LM and GLD).

Selected results from the analysis of trace metals are presented in tab. 3. Trace metal concentrations in leachates from unamended mine waste were 5.5 mg/L Cu, 2 mg/L Pb and 23 mg/L Zn (Sartz, 2010). It is also apparent that pH is the major driver for trace metal reduction. Metal concentrations were reduced significantly in the injected systems such as follows: 66—99 % for Cu, 96 % for Pb and 68—99 % for Zn.

After analysis of simulated rainwater for around 2 months the small systems were deconstructed in order to inspect how the alkaline by products had filled the voids and how the material was attached to the mine waste surfaces. Some of the observations are visible in fig. 4.

Large scale pilot trials (1 000 L)

In the large scale pilot trials, only LKD with 13 % active CaO was used. Both LKD and GLD were easy to inject and stripes were noticed through the container walls indicating that voids present were filled. After exposure to precipitation it was found that water was not retained in the system amended with GLD. However, in the system amended with LKD very little water left the system indicating formation of impermeable layers in the system. Hard pan formation is thus more likely in a system injected with LKD. Similar behaviour was also noted during the small scale trials. pH in the waters leaving the systems was 7.3 and 12.8 for GLD and LKD, respectively. It is expected that trace element concentrations are reduced significantly due to the high pH as was the case for the small scale trials. Even though the system injected with LKD has a very high pH, possibly harmful to the recipient, hard pan formation will actually decrease the volume of water passing through the waste deposit and the resulting pH downstream the waste deposit will likely be circum neutral after dilution.

Conclusions

This study indicates that the alkaline by products green liquor dreg (GLD) and lime kiln dust (LKD) can be injected into waste rock deposits as slurries. pH significantly increased (from pH 3 to above 7) and as a result trace element concentrations in the drainage leaving the deposit decreased of around 95 % or more. LKD also formed hard pan layers within the deposit and thus minimized the formation of acid drainage. Based on the results from the present study, the amount of active CaO in the LKD has to be lower than 40 % in order to avoid reaction prior to injection. The study also indicated that lime mud (LM) and fly ash (FAE and FAF) were not suitable for injection due to their inability to form stable suspensions.

Acknowledgements

This project is part of the Bergskraft program, and access to laboratory facilities as well as administrative support is gratefully acknowledged. Financial support has been received from regional EU funds and from communities in the Bergslagen region and from Örebro University.
Comments from an anonymous reviewer improved the manuscript and this is greatly appreciated.

Amendment	pH	El. Cond. (µS/cm)	Alkalinity (meq/L)
Lime mud (LM) (n 11)	6.82	1 600	3.04
Lime kiln dust (LKD) (n 6)	12.3	50 000	220
Green liquor dreg (GLD) (n 11)	6.40	3 300	2.83

Presented data are calculated averages.

***Table 2** Results from the chemical analysis of leachate from the small pilot tests (25 L).*

Amendment	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)
Lime mud (LM) (n 11)	0.039	0.084	0.398
Lime kiln dust (LKD) (n 6)	1.85	0.086	0.026
Green liquor dreg (GLD) (n 11)	0.486	0.076	7.32

Presented data are calculated averages.

***Table 3** Results from the trace metal analysis of drainage from the small pilot tests (25 L).*

Amendment	Can be injected	Remain within the waste during precipitation	Hard pan formation
Lime mud (LM)	Yes	No	No
Lime kiln dust (LKD)	Yes	Yes	Yes
Green liquor dreg (GLD)	Yes	Yes	No
Fly ash E (FAE)	No	-	-

***Table 4** Summary over the different alkaline by products used in the small pilot trials.*

Figure 4 *Deconstruction of 25 L pilot trials. Injection with green liquor dregs (left) indicate that all voids have been filled and that impermeable layers have been formed. Mine waste injected with lime kiln dust (right) has formed a solid unit with very low permeability.*

References

Bulusu S, Aydilek AH and Rustagi N (2007) CCB-based encapsulation of pyrite for remediation of acid mine drainage. J Hazard Mater, 143: 609—619

Bäckström M and Sädbom S (2008) Risk assessment of historical mine waste using chemical analysis and ocular mineral/rock classification. Australasian Institute of Mining and Metallurgy, Publication Series 8/2008: 85—90

Chtaini A, Bellaloui A, Ballivy G and Narasiah S (2001) Field investigation of controlling acid mine drainage using alkaline paper mill waste. Water Air Soil Poll, 125: 357—374

Mackie A, Boilard S, Walsh ME and Lake MB (2010) Physicochemical characterization of cement kiln dust for potential reuse in acidic wastewater treatment. J Hazard Mater, 173: 283—291

Pérez-López R, Nieto JM and de Almodòvar GR (2007) Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: column experiments. Chem, 67:1637—1646

Sartz L (2010) Alkaline by-products as amendments for remediation of historic mine sites. Örebro Studies in Environmental Science 15, Dissertation, Örebro University, Sweden

Wikman K, Berg M, Andreas L, Lagerkvist A, Jannes S, Tham G and Sjöblom R (2003) Grouting of fly ash in sanitary landfills. Report 830, Thermal Engineering Research Institute (in Swedish)