Fly ash injection into weathered mine waste

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Abstract By adding alkaline ashes through injection to weathered mine waste pH increased approximately 3 units, trace element was immobilized and flow rate decreased due to formation of hard pans. Reduction in trace element concentrations was around 96.9–99.6 % for copper, 94.7–99.7 % for zinc and 22.9–99.8 % for cadmium. For lead the best reduction was 97.3 % and the worst -393 % (increase). MSWI ashes performed worst with low buffering capacity and increase in vanadium and molybdenum concentrations.

Keywords sulfidic mining waste, MSWI ashes, trace elements

Introduction

Due to the known ferric iron driven reaction step of pyrite oxidation, oxygen exclusion alone is not a sufficient method to decrease weathering rates of historic mine waste. By adding an alkaline material, the chemical environment is changed within the deposit: pH is increased and mobilization of common ARD-related trace elements is decreased. Injection and mixing can be performed using alkaline residues such as fly ash, lime mud and green liquor dreg.

The neutralizing capacity of the alkaline material is a key parameter, determining both the neutralizing effect and the longevity of the amendment. An important factor is lowered water flow in fly ash amended systems, due to formation of hydrous Ca-Si-Al minerals (hard pan).

Expected results in larger experiments are decreased flow rates, increased pH and accordingly lowered trace element concentrations in the leachates.

During the last years there has been an increased interest for the use of alkaline residues in mine waste remediation. These alkaline residues include for instance lime mud, green liquor dreg and fly ash, suitable as neutralizers and in sealing layers for mine waste.

It is possible to make an impermeable layer if the alkaline additive reacts with the waste and form hardpans (Li *et al.* 2001). Due to the presence of quicklime (CaO) in alkaline materials pozzolanic reactions and hardpan formation are possible. A hardpan is an impermeable barrier, resulting from the formation of calcium-silicate-gel (CSH) and calcium-aluminate-gel (CAH; Bertocchi *et al.* 2006; Shang *et al.* 2006; Xenidis *et al.* 2002). As a hardpan makes infiltration of oxygen and water difficult, fly ash or quicklime is sometimes incorporated in sealing layers for waste rock and tailings (Hossein *et al.* 1999; Bulusu *et al.* 2007). A hardpan can however also consist of accumulation of secondary precipitates (goethite, gypsum, jarosite) near the surface of an impoundment/pile (Gilbert *et al.* 2003).

Mixing can be done using heavy machinery. One drawback, however, is that the visual appearance of the deposit can be changed. The practical mixing depth may also be insufficient in massive deposits. By injecting the material as a slurry the historical values can be preserved to a greater extent since the visual appearance is not changed.

Injection/stabilization have been used in a historic mining district in the western US, where approximately 2–3.5 Mt of tailings, initially dumped in adjacent creeks, have been *in situ* limed with calcite and $Ca(OH)_2$ or CaO. The alkaline materials were tilled into the waste and it was found that after 10 years pH had increased with two pH units (Davis *et al.* 1999).

The main objective of this study was to investigate the possibility to use fly ashes for slurry injection into oxidized historic waste rock deposits. Both chemical and physical properties of the fly ashes were considered (*e.g.* size distribution, free lime content). pH is a crucial parameter for trace element mobilization and was studied with stabilization experiments of mixtures of fly ash and historic mine waste from the Ljusnarsberg mine field, mid Sweden.

Methods

A number of ten fly ashes were collected in order to do a more detailed study on which type of fly ashes that would be most suitable for injection into weathered waste rock piles. The fly ashes used in the study are shown in table 1.

The mine waste used for the injection study was larger pieces (50–200 mm) of the weathered Ljusnarsberg material. The hand sorted waste rock 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. Remaining waste rock piles are heavily oxidized and covered with secondary precipitates.

Ten 30 L containers were filled with waste rock, together with a pipe (∅ 5 cm) installed in the middle of each container (which was to be used as an injection pipe). The weight of the containers filled with waste rock was approximately 50 kg (Fig. 1).

For the injection, a set of 5 criteria for injection studies stated by Wikman *et al.* (2003) concerning the properties of the alkaline material was followed: (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 may preferably have a sealing effect, *i.e.* allow for

Abbr.	Producer	Facility	Boiler	Fuel	Filter	Additive	D/W	CaO (% dw)
VäP5	Mälarenergi	Västerås	CFB	-	-	-	D	3
VäACV	Mälarenergi	Västerås	CFB	-	-	-	D	4.3
EonW	E.on	Örebro	CFB	Bio	Electro	Limestone, NH_3	W	4.6
EonD	E.on	Örebro	CFB	Bio	Electro	Limestone, NH_3	D	7.1
StE	Stora Enso	Fors	CFB	Bio, PC[3]	Electro	NH_3 (SNCR)	D	8.2
KorW	Korsnäs	Frövi	BFB	W, F, S[1]	Electro	$CO(NH_2)_2$ (SNCR)	W	2.2
KorD	Korsnäs	Frövi	BFB	W, F, S[1]	Electro	$CO(NH_2)_2$ (SNCR)	D	6.4
UppG	Vattenfall	Uppsala	Grate	Mu, In[2]	El+B.F.[4]	$Ca(OH)_2$	W	2.4
UppB	Vattenfall	Uppsala	Grate	Mu, In[2]	El+B.F.[4]	$Ca(OH)_2$	W	<2
Kpbg	Fortum	Kopparberg	Grate	Bio, PC[3]	Cyclone	None	W	4.6

[1]W, F, S: Wood, fiber- and biosludge; [2]Mu, In: Municipal (60 %) and industrial waste; [3]Bio, PC: Bio and pulp chips; [4]El+B.F.: Electro and bag filter

Table 1 *The ten fly ashes used in the study. All ashes came from different Swedish producers. The D/W column states if the ash had been moistened (W: wet) or not (D: dry) before the injection study. Available lime index (CaO, %) was measured according to ASTM C25.*

Fig. 1 *Illustration of the plastic pipe used for gravity injection of fly ash suspensions into the coarse waste rock fraction.*

pozzolanic reactions and hard pan formation and (v) It should not have a particle size exceeding 1 mm.

Before starting the injection, all the moistened ashes (table 1) were sieved through a 1 mm sieve. Injection of the ashes was made by pouring an ash-slurry (a mixture of fly ash and water) through the pipe, which was successively pulled upwards. The fly ash to water ratio (in order to get suitable slurry properties) was determined using a standardized test (SS-EN 445 2007) where slurries of the materials were poured through a funnel with a diameter of 80 mm. A total of 5 kg fly ash was injected into each container.

In order to get a suitable slurry for injection according to the funnel test (SS-EN 445 2007), between 1.5 and 2 L of water was added to 5 kg of fly ash. The results from the injections are shown in table 2, focusing on criteria

Ash	Stable suspension	Too much separation	Hardening	Too rapid hardening	Comments
VäP5	Yes	No	No	No	Easy to form slurry and to inject
VäACV	Yes	No	No	No	Easy to form slurry and to inject
EonW	No	Yes	No	No	Unable to form injectable suspension
EonD	Yes	No	Yes	No	Easy to form slurry and to inject
StE	Yes	No	Yes	Yes	Only 2.5 kg injected due to hardening
KorW	No	Yes	No	No	Unable to form injectable suspension
KorD	No	No	No	No	Some separation, but easy to inject
UppG	No	No	No	No	Some separation, but easy to inject
UppB	No	No	No	No	Some separation, but easy to inject
Kpbg	No	Yes	No	No	Only 2.5 kg injected due to separation

Table 2 *Results from the injections. Columns 2 and 3 concern criteria (i) and columns 4 and 5 concern criteria (iv). Text in red color means that there were difficulties with the injection.*

(i) and (iv) (Wikman *et al.* 2003). Criteria (ii) and (iii) have not yet been evaluated; they will be evaluated at the end of the experiment. The last criteria (v) was evaluated even before the start of the slurry preparations, and it was found that all the ashes that had been moistened (W in table 1) contained agglomerates larger than 1 mm and these were consequently sieved before starting the injections.

To each amended system ultrapure water (1 L) was added every week during one year (2012). After samplings electrical conductivity, redox, pH and alkalinity were measured. Electrical conductivity, redox and pH were measured with suitable calibrated electrodes. Alkalinity was measured by endpoint (pH 5.4) titration with 0.02 M HCl. Elements were analysed with ICP-MS using rhodium-103 as internal standard.

Results

Three of the ashes showed difficulties with keeping an injectable suspension, due to the fact that they were pre-moistened prior to injection. Two other pre-moistened ashes showed some difficulties with keeping the slurries in suspension, but with some gentle stirring the injection was possible. Presence of higher concentrations of carbonates is the most likely cause for this behaviour.

Two of the ashes had a free lime content high enough for hardening (StE and EonD). If the free lime content is too high rapid hardening makes the injection difficult. Hardening of the ash inside the deposit is though desired as it decreases water flow and keeps the fly ash within the deposit (less tendency to be washed out). Problems with injection mainly originated from pre-moistening of the fly ashes, which seem to increase the tendency to separate making it difficult to keep a stable suspension.

Three of the ashes showed difficulties with keeping an injectable suspension, all of these had been moistened before the injection (EonW, KorW and Kpbg). For Kpbg it was only possible to inject 2.5 kg, and for EonW and KorW no slurry at all was achieved and it was therefore not even possible to do the funnel test. The other two pre-moistened ashes: UppG and UppB showed some difficulties with keeping the fly ash slurries in suspension, but as long as the slurry was gently stirred there was no problem with the injection. This was also the case for KorD (table 2).

Two of the ashes had a free lime content high enough for hardening, these were StE and EonD (table 1 for free lime content). Hardening of the StE-ash was however a little bit too fast; it was only possible to inject 2.5 kg before the slurry had filled up and hardened in the injection pipe. Injection of EonD was easily performed with a stable suspension and some hardening, but not as rapid as for the StE-ash.

The two ashes from Västerås, VäP5 and VäACV very easily formed a stable suspension and were as well easy to inject.

	Redox (mV)	El. Cond. (µS/cm)	pH	Alkalinity (meq/L)
Mine waste	456	2 970	2.23	0
VäP5	9.2	17 800	6.22	0.24
VäACV	23	5 290	6.17	0.34
EonD	-4.2	6 840	8.96	1.43
StE	48	7 510	6.05	0.26
KorD	3.7	7 500	9.10	1.38
UppG	75	55 300	5.79	0.18
UppB	49	92 700	6.22	0.12
Kpbg	52	4 850	5.88	0.61

Table 3 *Results from the general chemistry (redox, electrical conductivity, pH and alkalinity) in the injected samples of mine waste with different fly ashes (average values during 2012, n 11).*

Chemical parameters were measured in the leach solutions and also to which degree the fly ash stayed in the container was evaluated. It is important that the fly ash is not washed out too fast and preferably sticks to the mine waste. It was found that in amended samples pH were at least 3 units higher than in the reference system consisting of mine waste only (table 3). Some of the amended systems also had very high electrical conductivity indicating a release of primarily soluble minerals.

Reduction in trace element concentrations was generally good with 96.9–99.6 % for copper, 94.7–99.7 % for zinc and 22.9–99.8 % for cadmium (table 4). For lead the best reduction was 97.3 % and the worst -393 % (increase). Worst performance regarding trace elements was noted for MSWI ashes with bad buffering capacity and low increase in pH. In several systems an increase in for instance vanadium and molybdenum could also be noted. These elements are not present in the mine waste and are thus most likely originating from the ashes.

Conclusions

This study has shown that it is possible to form injectable suspensions with several different ashes. It was harder or sometimes impossible to form stable suspensions with pre-moistened ashes. This is most likely due to the presence of more carbonates in the pre-moistened ashes.

By adding the alkaline ashes through injection to weathered mine waste pH increased approximately 3 units, trace element leaching was in general lowered and flow rate decreased due to formation of hard pans.

Reduction in trace element concentrations was around 96.9–99.6 % for copper, 94.7–99.7 % for zinc and 22.9–99.8 % for cadmium. For lead the best reduction was 97.3 and the worst -393 % (increase). Highest lead concentrations were noted from MSWI ashes. MSWI ashes performed worst with low buffering capacity and increase in vanadium and molybdenum concentrations.

Summarizing, slurry injection of fly ash to weathered mine waste seems to be a promising remediation method if trace element leaching can be controlled.

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	Cu (µg/L)	Zn (µg/L)	Cd (µg/L)	Pb (µg/L)	V (µg/L)	Mo (µg/L)
Mine waste	84200	479 000	1000	1590	0.5	1.2
VäP5	1280	13 900	44.3	946	9.1	107
VäACV	1370	25 400	72.5	200	47.6	74.1
EonD	1410	9 210	23.3	43.2	7.6	144
StE	760	5 960	16.3	834	0.7	0.6
KorD	730	5 720	12.7	405	5.1	7.1
UppG	1850	14 100	76.8	3990	16.6	2.3
UppB	2090	19 500	148	7820	8.6	11.5
Kpbg	2650	22 500	64.4	1600	0.2	5.9

Table 4 *Selected trace element concentrations (averages during 2012, n 4–5) in the amended systems as well as in the reference system (only mine waste).*

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