

Treatment of historical mining waste using different incineration ashes

Sanna Ekblom¹, Lotta Sartz^{1,2}, Mattias Bäckström¹

¹*Man-Technology-Environment Research Centre, Örebro University, Fakultetsgatan 1, 701 82 Örebro, Sweden, mattias.backstrom@oru.se*

²*Bergskraft Bergslagen AB, Fordonsgatan 4, 692 71 Kumla, Sweden, lotta.sartz@oru.se*

Abstract ARD from historical mining sites in Sweden is a major source for trace elements to surface waters. In order to be able to treat a large portion of these sites cost effective reclamation methods is necessary. Incineration ashes were used in leaching tests to study their effect on a highly weathered mining waste in order to neutralize acidity and immobilize trace elements.

This study shows that ashes can be used to increase pH and decrease trace element mobility from oxidized mining waste. Increased leaching of Cl, Mo and Sb, however, needs to be considered for waste fuel ashes before use.

Key words Antimony, molybdenum, chloride, leaching

Introduction

Mining has been ongoing for centuries in mid Sweden and has had an impact on the environment. Waste deposits with historic sulphidic mining waste are highly weathered, generating acid rock drainage (ARD) with high concentrations of trace elements such as Cu, Zn, Pb and Cd.

Mainly two processes generate acidity and trace elements: (1) sulphide mineral oxidation and (2) hydrolysis of Fe³⁺, Al³⁺ and Mn²⁺ (Akcil and Koldas 2006). Pyrite (FeS₂) is the main acid producing sulphide mineral. Oxidation occurs when pyrite reacts with dissolved oxygen producing acidity as well as dissolved ferrous and sulphate ions. When pH drops, oxidation of ferrous iron to ferric iron is accelerated by microbiological activity. Ferric iron will cause oxidation of pyrite to proceed during anaerobic conditions.

Other common sulphide minerals in mining waste are galena (PbS) and sphalerite (ZnS). Both galena and sphalerite are characterized as non-acid producing minerals, but oxidation and dissolution in acidic conditions will mobilize trace elements.

Neutralisation of ARD with alkaline additives would result in reduced mobility of trace elements (Pb, Zn, Cu, Cd). Major elements such as Fe and Al, frequently found dissolved in the acidic water, play an important role in metal immobilization. When pH increases, formation of iron- and aluminium hydroxide, hydroxysulphate and hydroxycarbonate minerals are favoured, which will act as sorbents for cationic metals (Bigham et al. 2000). Commercial materials such as limestone, slaked lime or sodium carbonate have been used as neutralizing agents with good results but it is rather costly and consumes natural resources. By reusing alkaline by-products, the cost would rapidly decrease and two environmental problems could be solved at the same time. Many studies have been performed

where various alkaline by-products were used, including e.g. residues from pulp and paper industries (Sartz 2010; Jia et al. 2014) and fly ash from coal combustion (Park et al. 2014) with good results.

This paper includes six ashes (fly and bottom ash) from incinerator facilities using three different fuel sources, including household/industrial, contaminated and non-contaminated wood chips. Ashes were mixed with historic sulphide-rich mining waste from Bergslagen, mid Sweden.

The aim is to study alkaline by-products ability to neutralize and stabilize acidic metal-rich mining waste without adding new contaminants to the system and thus reduce the impact on the environment.

Methods

The mining waste was highly weathered and collected from Ljusnarsbergfältet in Kopparberg, Sweden (Sartz 2010). The ore field was discovered in 1624 and was last operated in 1975 before being closed down. Mining focused primarily on copper (chalcopyrite, CuFeS_2) and secondary on iron ore, and later also sphalerite (ZnS) and galena (PbS). Prior to sampling, waste rock aggregates were crushed and sieved into fractions < 13 mm (Sartz 2010).

The study included six ashes originating from different incineration facilities in Sweden (tab. 1).

Table 1 Summary of BFB ashes used in this study (Saqib and Bäckström 2015).

Alkaline material	Abbr.	Waste fuel (%)	Additives
Lidköping bottom	LB	Household + Industrial (70:30)	Ammonia, slaked lime and activated carbon
Lidköping fly	LF		
Nynäshamn bottom	NB	Contaminated wood chips (100)	Ammonia, lime and activated carbon
Nynäshamn fly	NF		
Eskilstuna bottom	EB	Wood chips (100)	Ammonia
Eskilstuna fly	EF		

Distribution of trace elements as well as the chloride content (%) of the ashes were determined in a previous study and can be found in tab. 2 (Saqib and Bäckström 2015). Leached concentration of trace elements in the ashes at liquid/solid ratio (L/S) 2 and 10 can be found in tab. 3 (Saqib and Bäckström 2015).

Table 2 Concentration of trace elements (mg/kg dw) and chloride (%) in the ashes (Saqib and Bäckström 2015).

Location	Ash	Zn	Cu	Pb	Cd	Mo	Sb	Cl
Eskilstuna	Fly	1 290	74	140	12	<6	2	0.6
	Bottom	821	36.7	12	0.3	<6	0.5	<0.1
Lidköping	Fly	8 120	16 400	6 920	97	28	538	21.4
	Bottom	2 490	3 550	563	1.5	24	321	0.5
Nynäshamn	Fly	12 100	864	1 900	21	7	64	4
	Bottom	5 760	1 890	1 730	0.4	<6	22	<0.1

Table 3 Leachable concentrations ($\mu\text{g/L}$) of trace elements from the ashes at L/S 2 and L/S 10 with 18.2 M Ω water (Saqib and Bäckström 2015). Bdl: below detection limit.

Location	Ash	L/S	Zn	Cu	Pb	Cd	Mo	Sb
Eskilstuna	Fly	2	280	10	570	Bdl	300	Bdl
		10	110	35	230	Bdl	38	0.23
	Bottom	2	27	110	16	Bdl	6.70	Bdl
		10	100	29	230	Bdl	7.40	0.32
Lidköping	Fly	2	44 000	830 000	1 300 000	12	1 200	1.7
		10	2 600	3 100	67 000	Bdl	330	0.38
	Bottom	2	19.0	12.0	1.8	Bdl	220	50
		10	22	6.6	15.0	Bdl	31	100
Nynäshamn	Fly	2	3 600	270	30 000	Bdl	200	0.29
		10	2 800	81	12 000	Bdl	80	0.23
	Bottom	2	50	15	52	3.8	54	34
		10	11	6.6	10	Bdl	5.4	16

A 2.5 L container was prepared for each ash by adding 180 g mining waste and 20 g ash (90:10). A reference sample was prepared with 200 g mining waste to achieve the same L/S as the other samples. An addition of 20 g of 18.2 M Ω water was made to the containers giving a starting L/S of 0.1 followed by cumulative L/S of 0.5, 1, 2, 5, 10 and 20. After addition of water the containers were shaken and the liquid phase was removed and filtered (0.40 μm) for analysis every second day. After sampling, electrical conductivity and pH were measured immediately followed by acidity/alkalinity and inorganic anions (chloride and sulphate). For major and trace element analysis samples were acidified with HNO₃ followed by analysis using ICP-MS.

Results and discussion

Leaching of the mining waste from L/S 0.5 to L/S 20 showed a slight increase in pH from 2.5 to 3.7 and acidity of the system dropped from 25 to 0.9 meq/L during the leaching process. Concentration of sulphate was 5.5 g/L during the first sampling occasion and showed a rapid decline after two leaching steps before levelling off. Calcium concentrations stayed rather constant throughout the system while Al and Fe both declined as L/S increased. Initial concentrations of Fe and Al were 154 and 323 mg/L, respectively. Trace elements found in higher concentrations in the mining waste were Cu, Zn, Pb and Cd. At initial L/S (0.5), Cu concentrations were 127 mg/L and decreased to 0.4 mg/L at L/S 20. Zn and Cd also showed declining concentrations from 560 to 0.3 mg/L and 1.7 to 0.001 mg/L, respectively. On the contrary, concentration of Pb stayed fairly constant during the leaching process.

Electrical conductivity (EC) in the samples gave a good idea about the total amount of ions in the leached water. From the start at L/S 0.5, EC quickly decreased. At L/S 2, 74-96 % of the ions were washed out, indicating that a great amount of easily soluble minerals like alkali and earth alkali metal salts were rapidly rinsed out. Sample LF has a significantly higher EC comparing to the others, likely caused by the high chloride content (21 %) (tab. 2).

Changes in pH in all systems are shown in fig. 1. By adding alkaline material to the mining waste, pH increased by 1.5-7 units. All fly ashes as well as Eskilstuna bottom ash were able to increase the pH to between 7 and 9 and showed a buffering capacity ranging from 0.2-0.4 meq/L at L/S 10. NB showed an increased alkalinity from starting L/S at 0.16 meq to 0.76 meq/L at L/S 5 whereas the other system showed an instant decrease. The reason for the increased alkalinity might be due to calcite (CaCO_3) dissolving, which will rapidly elevate the amount of HCO_3^- at near neutral conditions and therefore increasing the alkalinity in the system.

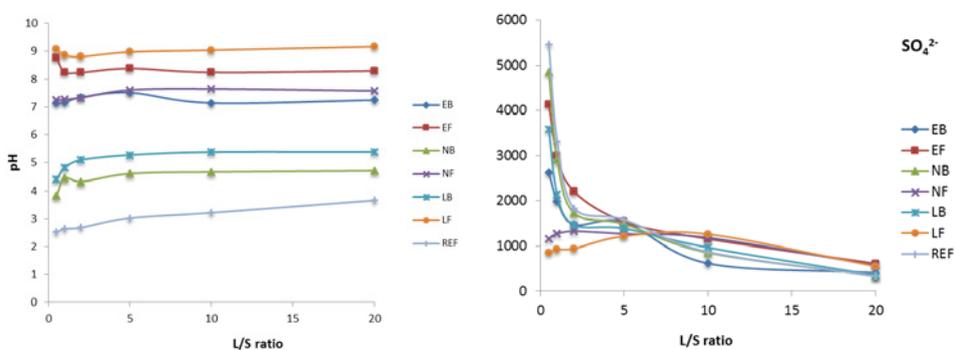


Figure 1 pH and sulphate concentrations as a function of L/S ratio in all systems.

Concentrations of sulphate are shown in fig. 1. Sulphate concentrations in the mixed systems showed a rapid decrease from L/S 0.5-2. After L/S 2, the system reached equilibrium probably due to precipitation of CaSO_4 . The abundance of chloride in the systems is clearly

connected to the ashes since the reference system contained 73 mg/L during the first sampling occasion. Chloride concentrations in several of the mixed systems was diluted to below limit of detection. LF showed an exceptionally high chloride concentration of 28 g/L at L/S 0.5, which can be associated with the high chloride content of the fuel. NF also showed a high chloride concentration at 3 g/L. Chloride concentrations were much lower in the bottom ashes.

Concentrations of calcium in LF and NF were the highest at the initial sampling occasion with 9.6 g/L and 1.8 g/L, respectively, and showed a rapid decrease until L/S 2 where the concentrations leveled out. Addition of lime/quicklime for flue gas treatment is a likely cause of the elevated calcium levels in Lidköping and Nynäshamn fly ashes. The rapid decline in LF and NF is probably due to dissolution of $\text{Ca}(\text{OH})_2$, whereas gypsum (CaSO_4) are at equilibrium causing stabilization of all systems (Gitari et al. 2010).

High concentrations of Al and Fe could be found in the reference system. All mixed systems showed an almost quantitative removal of Fe during the first sampling occasion. Al concentrations in NB and LB (pH ~4-5) were high indicating that precipitation of Al was unsuccessful for the systems where pH did not exceed 5.5.

Trace element immobilization was successful in several systems. Concentrations of Cd and Sb can be seen in fig. 2 and a comparison of the concentrations of Zn, Cu, Pb, Cd at L/S 10 in the reference and the mixed systems are shown in tab. 4. The trace metal concentration shows a decrease by 83.5-100 % at L/S 10 in four of the systems, including all fly ashes and Eskilstuna bottom ash (EB). The remaining systems (NB and LB) showed an increase of over 100 % for Zn and Cd compared to the reference. With pH of 4.7 (NB) and 5.4 (LB) at L/S 10, the systems were not able to immobilize these elements and the elevated concentrations of metals are likely caused by additional concentrations of these elements being released from the ashes. At pH 4.7, the Nynäshamn bottom ash (NB) was partly able to immobilize Cu and Pb from the leachate (around 60-70 %) and Lidköping bottom ash (LB) 5.4 showed a decrease of 90 %. This indicates that a lower pH is required to immobilize Pb and Cu compared to Zn and Cd.

Mo and Sb are trace elements frequently found in ashes as can be seen in tab. 2 and 3. Leached amounts of these elements are higher from the fly ashes compared to the bottom ashes contrary to the other trace elements. It should be noted that the content of these elements are higher in fly ashes in general (tab. 2). For Sb, all system shows at least a 250 % increase in concentration compared to the reference. LF showed the highest increase of almost 200 000 %. Concentrations of Mo from the bottom ashes decreased 11 to 51 % whereas the concentrations increased with around 450 to 2 700 % from the fly ashes. In a previous study it was found that Mo has a higher sorption at low pH compared to high pH as it acts as an anion (Bäckström and Sartz 2011), which might be the case here as well.

Table 4 Concentration of trace elements (Zn, Cu, Pb, Cd, Mo and Sb) in the systems as well as the ashes impact on element mobility compared to the mining waste (%) at L/S 10.

	Zn		Pb		Cd		Sb		Mo		Cu	
	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%
REF	2 580	-	1 780	-	7.64	-	0.027	-	0.240	-	1 840	-
EB	66.7	97.4	1.59	99.9	1.26	83.5	0.198	-558	0.214	11.0	3.34	99.8
EF	6.35	99.8	0.710	100	0.05	99.4	0.837	-2 690	1.57	-552	4.75	99.7
NB	6 550	-154	555	68.9	17.2	-125	0.106	-254	0.177	26.4	783	57.3
NF	28.3	98.9	1.54	99.9	0.17	97.8	6.23	-20 700	1.32	-449	4.38	99.8
LB	5 350	-107	160	91.0	19.7	-158	0.402	-1 240	0.118	51.0	170	90.7
LF	26.4	99.0	3.32	99.8	0.120	98.4	58.7	-196 000	6.72	-2 700	107	94.2

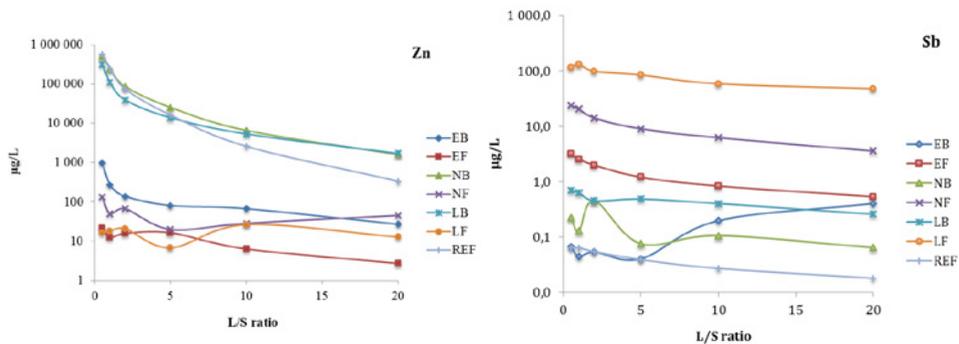


Figure 2 Concentration of zinc and antimony plotted against L/S ratio.

A ratio between concentrations at L/S 2 and L/S 10 was calculated to give an idea about whether the elements were easily washed out or stayed in or on the solid phase through precipitation or sorption. This calculation was used in a previous paper (Sartz 2010). Calculated ratios of trace elements can be found in tab. 5.

Precipitation/sorption behaviour for Ca can be found in all systems. Resemblances with sulphate ratios could indicate equilibrium with gypsum as discussed earlier. Zn and Cd shows comparable ratios for all systems except for LF since equilibrium on a solid phase is reached first at L/S 5. The high ratios of around 30 for Zn and Cd in the reference indicated that the elements originated from easily soluble secondary minerals from the mining waste. NB and LB, with pH under 5.5, also showed washout behaviour for Zn and Cd. The other systems, all with a pH over 7, showed ratios close to or lower than 3, which would indicate that precipitation and/or sorption has occurred. It can be noted that dilution of these elements decrease as the pH increase, likely caused by sorption onto Al and Fe hydroxide, hydroxysulphate

Table 5 Ratios calculated from concentrations at L/S 2 and L/S 10. Green indicating precipitation/sorption, red that dilution/washout occurred and yellow that some precipitation/sorption occurred.

	SO ₄ ²⁻	Ca	Zn	Cu	Pb	Cd	Mo	Sb
EB	2.4	1.4	2.1	1.5	0.8	2.1	1.0	0.3
EF	1.9	1.2	2.5	4.1	1.6	3.5	2.6	2.4
NB	2.0	1.5	13	3.7	2.7	12	0.8	4.3
NF	1.1	1.3	2.3	3.3	1.0	2.6	2.1	2.3
LB	1.5	1.4	7.3	3.3	2.3	6.0	2.1	1.1
LF	0.7	3.6	0.8	1.7	1.1	7.5	3.6	1.7
REF	2.1	1.6	29	12	1.3	30	1.5	2.0

< 3	= Precipitation/sorption
3 – 6	= Some precipitation/sorption occurred
> 6	= Washout/dilution

and hydroxycarbonate previously formed. The ratios for Pb for the reference as well as the mixed systems show precipitation/sorption, indicating that precipitation/sorption of Pb is not as pH dependent as Zn and Cd. In addition to sorption onto Al and Fe compounds, similarities between Pb and sulphate ratios could indicate that they are at equilibrium by formation of anglesite (PbSO₄). The ratio for Cu in the reference is 12 indicating wash out/dilution. The mixed systems have ratios under 4, probably also caused by sorption onto Al and Fe hydroxide, hydroxysulphate and hydroxycarbonate. Mo and Sb ratios in all systems are between 0.3 and 4.3, indicating sorption or precipitation.

Conclusions

Alkaline by-products were used to attempt to stabilize and neutralize highly weathered mining waste. It was concluded that the alkaline additives increased the pH of around 1.5-7 units. Successful immobilization of trace elements originating from the mining waste (Zn, Cu, Pb and Cd) was found in systems with pH between 7 and 9, with a decrease of 83-100 % at L/S 10. Increased leaching of harmful elements as well as chloride from the alkaline by-products was noticed, particularly in the fly ash mixtures. These limitations would need to be considered if these ashes were to be used for this purpose.

Acknowledgements

Viktor Sjöberg is acknowledged for performing the element analysis.

References

- Akcil A, Koldas S (2006) Acid Mine Drainage (AMD): causes, treatment and case studies. *J Clean Prod* 14(12): 1139-1145
- Bigham JM, Nordstrom DK (2000) Iron and aluminum hydroxysulfates from acid sulfate waters. *Rev Min Geochem* 40: 351-403
- Bäckström M, Sartz L (2011) Mixing of Acid Rock Drainage with Alkaline Ash Leachates—Fate and Immobilisation of Trace Elements. *Water Air Soil Pollut* 222(1): 377-389
- Dold B (2014) Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals* 4(3): 621-641
- Gitari WM, Petrik LF, Key DL, Okujeni C (2010) Partitioning of major and trace inorganic contaminants in fly ash acid mine drainage derived solid residues. *Int J Environ Sci Tech* 7(3): 519-534
- Jia Y, Maurice C, Öhlander B (2014) Effect of the alkaline industrial residues fly ash, green liquor dregs, and lime mud on mine tailings oxidation when used as covering material. *Environ Earth Sci* 72(2): 319-334
- Park J, Edraki M, Mulligan D, Jang H (2014) The application of coal combustion by-products in mine site rehabilitation. *J clean prod* 84(1): 761-772
- Saqib N, Bäckström M (2015) Distribution and leaching characteristics of trace elements in ashes as a function of different waste fuels and incineration technologies. *J environ sci* 36(10): 9-21
- Sartz L (2010) Alkaline by-products as amendments for remediation of historic mine sites. *Örebro Studies in Environmental Science* 15, Dissertation, Örebro University, Sweden
- Sartz L, Bäckström M, Karlsson S, Allard B (2016) Mixing of acid rock drainage with alkaline leachates: Formation of solid precipitates and pH-buffering. *Mine Water Environ* 35(1): 64-76