

ALKALINE BY-PRODUCTS AS AMENDMENTS FOR STABILIZATION AND NEUTRALIZATION OF OXIDIZED SULPHIDIC MINE WASTE DEPOSITS

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ABSTRACT

Stabilization of oxidized sulphidic mine waste deposits with alkaline by-products could be a way of controlling ARD. Mixtures of alkaline by-products (10% by volume) and oxidized waste rock have been studied during six months in 30 L experimental drums. Alkaline by-products are: lime mud (LM), green liquor dreg (GLD), lime kiln dust (LKD), LD slag (LD), water work granules (WWG), carbonized fly ash (FAE) and fresh fly ash (FAF). The experiments are fed with water once a week to imitate natural precipitation.

pH of the reference (no alkaline amendment) is below 3 and trace metal concentrations are 2000 mg/l, 4 mg/l and 1 mg/l for Zn, Cd and Pb respectively. LKD, LM and LD amended systems (pH 6.7-7.5) are the most efficient for Cd- and Zn-removal (reduction at least 99 % compared to the reference), while GLD (tap pH 6.5) is the most efficient for Pb-removal (99 % reduction compared to the reference). FAE amended system only reaches pH around 5 and accordingly trace metal reduction is rather low. Geochemical simulations using PHREEQC indicate equilibrium with otavite and smithsonite in the WWG and GLD systems, whereas cerrusite is at equilibrium in the LKD, WWG and GLD systems.

Key Words: Fly ash, lime mud, green liquor dreg, lime kiln dust, water work granules, LD slag

INTRODUCTION

Excavation of sulphidic ores exposes sulphide minerals for oxygen and water through air and rainfall. The mechanism is illustrated by the oxidation process of pyrite, by dissolved oxygen (Equation 1) or ferric iron (Equation 3). The regeneration of ferric iron from ferrous iron (Equation 2) is the rate-limiting step for pyrite oxidation (Moses and Herman, 1991). Consequently, acidic, metal-rich discharges (ARD) are often recognized in vicinities of sulphidic mine waste areas.



Precipitation of ferric hydroxides (reaction 4) and aluminum hydroxides (reaction 5) produce acid and take place both at the source and also as the leachates leave the deposit and are supplied with oxygen. pH in a recipient can hence drastically decrease. Precipitation of ferric hydroxides are pH-dependent and if pH < 3, ferric hydroxide will not precipitate and, in the case of pyrite, the oxidation will proceed according to reaction 3.



Pyrite oxidized by ferric iron (reaction 3), which has been replenished from the pyrite oxidation with oxygen (ferrous iron from reaction 1 is further oxidized in reaction 2) is a crucial process in old and highly weathered waste rock piles, since it maintains pyrite oxidation even when the waste is covered, i.e. has an oxygen barrier. Covering of the waste can even make the situation worse (as ferric iron driven oxidation of pyrite produces more protons than the oxygen driven oxidation). This was for instance seen in post remediation monitoring of the coal fly ash and bentonite covered waste rock piles at Bersbo copper mines, Sweden (Karlsson and Bäckström, 2003).

Instead of covering historic mine waste, reactive (alkaline) materials can be tilled down or injected in the pile (Zagury et al., 1997; Davis et al., 1999). This will reduce the pyrite oxidation rate, neutralize the acid produced and immobilize metals (through sorption and/or precipitation). Also, reductive dissolution of secondary iron(oxy)hydroxides and iron(III) mediated weathering of pyrite is avoided. Use of alkaline slags and ashes etc may also result in hard pan formation through pozzolanic reactions. This will in turn drastically decrease the flow rate through the pile and hence increase the contact time between water and the alkaline material. Mixing can either be made using heavy machinery or by injection. By injecting the material as a slurry the historical and cultural values can be preserved to a greater extent since the visual appearance is not changed.

The present experiments simulate chemical changes taking place when a weathered and acidic historic mine waste is mixed with a strongly alkaline material. Accordingly, acid present in the mine waste is neutralized and immobilization of trace metals occurs through sorption and precipitation processes.

MATERIALS AND METHODS

Alkaline materials and mine waste

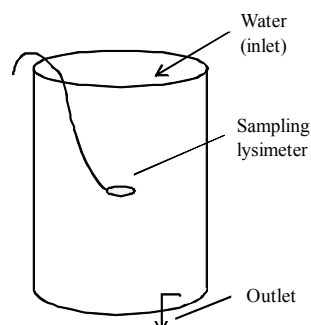


Figure 1 Principal outline of the stabilization systems.

Mixtures of seven alkaline by-products and oxidized sulphidic waste rock were prepared and filled in 30 L plastic drums. Mine waste and the alkaline materials were homogeneously mixed in the drums. The proportion of alkaline material was 10 % by volume in all systems, as this volume was estimated possible to inject in a waste rock pile. A sampling lysimeter was installed in the center of the drums. Tap water is added to from the top and withdrawn at the outlet at the bottom of the drums. A principal outline is shown in figure 1. Since the start of the experiment in November 2009, approximately 10 L has passed the drums, giving an L/S ratio of around 0.3.

In addition to the seven alkalinity amended systems also a reference with no alkaline additive was prepared, giving a total of eight systems. The reference system is however not equipped with a sampling lysimeter. Historic mine waste from Ljusnarsbergsfältet, Kopparberg, Sweden, is used in the experiment. It is a heavily weathered complex sulphidic waste rock and 200-300 years old (Sartz, 2006). Prior to the experiments mine waste aggregates (secondary minerals) were crushed and sieved (0-13 mm). For all materials used in the experiment, abbreviations and origins are listed in table 1. In table 1 also the main type of alkali (carbonate or hydroxide) as well as the neutralizing capacity

(expressed as mmol H⁺/g dw alkaline material to maintain a pH above 6) are shown. In a previous study (Höckert, 2007), the acid producing potential of the mine waste was found to be 41.7 kg CaCO₃/t and 73 kg CaCO₃/t for surface acidity and total acidity respectively. Based on the neutralizing capacity and the density of the alkaline materials, addition of 10 % by volume is more than sufficient for neutralization of surface acidity for LKD, LD and LM amended systems and sufficient for WWG and GLD systems. Acid neutralizing capacity of FAF and FAE amended systems is however lower than the acid producing potential (surface acidity) of the mine waste. During the time span of these experiments, only surface acidity is of interest, for a full-scale injection however, the added amount of alkalinity must be sufficient for neutralization of total acidity. The filled drums were placed indoors for constant temperature and drying/wetting conditions as well as to ensure sampling during winter.

Table 1: Alkaline materials used in the experiment. The origin and abbreviation of each material is listed as well as main type of alkali, capacity to neutralize acid to maintain a pH above 6 (Bäckström and Sartz, 2010) and surface area based on grain size distribution.

Material	Abbr.	Origin	Main type of alkali	Capacity, mmole H ⁺ /g dw	Surface area, m ² /kg
Lime Kiln Dust	LKD	Nordkalk AB, Köping	CaO/CO ₃	15.8	50
Water Work Granules	WWG	Nordkalk AB, Köping	CO ₃	5.8	2.8
LD slag	LD	SSAB Merox AB, Oxelösund	CaO	5.0	5
Green Liquor Dreg	GLD	Korsnäs Frövi, Frövi	CO ₃	16.0	50
Lime Mud	LM	Korsnäs Frövi, Frövi	CO ₃	10.0	35
Fly Ash F	FAF	Korsnäs Frövi, Frövi	OH/(CO ₃)	3.7	25
Fly Ash E	FAE	E.ON, Örebro	OH/(CO ₃)	4.4	40

Educational Project

The experiments are performed as a part of an educational project at the senior level of the nine-year compulsory school. The projects aims at increasing the general knowledge and interest in environmental science, chemistry and geology as well as integrating the secondary school with universities and encourage innovative thinking and use of by-products.

Sampling and analytical

The drums are fed with tap water once a week and water samples are withdrawn both from the center and from the bottom, through the sampling lysimeter (suction cup) and the tap, respectively. pH measurements are performed once a week, while other parameters (alkalinity, electrical conductivity, redox potential, inorganic anions and metals) are measured monthly. Samples for full parameter analysis are immediately filtered through 0.4 µm polycarbonate filters. Samples for element analysis are also acidified to 1% with HNO₃ (suprapur). Electrodes are used for measurements of redox potential, pH and electrical conductivity. Alkalinity is determined through end point (pH 5.4) titration using 0.02 M HCl, anions with ion chromatography and elements with ICP-OES.

Geochemical Calculations

Geochemical calculations were performed using the geochemical model PHREEQC (Parkhurst and Appelo, 1999) with the Minteq database in order to gain information about possible solubility limiting trace element phases. Saturation index (SI) is defined as the logarithmic representation of the ratio between the ion activity product (IAP) and the solubility constant (K_{so}). Positive SI (>0.5) indicates over saturation while negative SI (<-0.5) indicate sub saturation and SI in the range $-0.5 - 0.5$ is considered to be in equilibrium.

RESULTS AND DISCUSSION

pH and Alkalinity

Average and median values for pH and alkalinity are shown in table 2. Almost all amendments, with the exception for FAE, are capable of raising pH to above 6. For tap samples the LKD system has highest pH, followed by LD, LM and GLD. pH in the WWG system was initially rather low, but increased after the second sampling occasion; hence the difference between average and median pH values. Possible explanations for the slow start in the WWG systems are low surface area or low calcite solubility.

Table 2: Average and median values of pH and alkalinity in 30 L mixing experiments with mine waste and alkaline materials. Alkaline amendment in all systems is 10 % (by volume). (n = 8).

		pH average	pH median	Alkalinity (meq/l) average	Alkalinity (meq/l) median
Reference (MW)		2.69	2.68	0.00	0.00
LM	Tap	6.64	6.58	13.51	12.80
	Lysimeter	6.68	6.69	9.47	9.70
LKD	Tap	6.88	6.88	6.28	4.45
	Lysimeter	6.80	6.79	10.23	10.90
GLD	Tap	6.64	6.63	12.35	11.00
	Lysimeter	6.30	6.33	7.83	8.00
WWG	Tap	6.15	6.41	16.68	18.60
	Lysimeter	6.44	6.41	18.40	19.20
LD	Tap	6.61	6.76	0.28	0.20
	Lysimeter	8.48	8.56	0.70	0.60
FAE	Tap	5.08	5.29	0.04	0.00
	Lysimeter	4.56	4.74	0.00	0.00
FAF	Tap	6.34	6.45	5.50	6.00
	Lysimeter	5.35	5.34	0.18	0.20

Lowest pH (both at the tap and in the lysimeters) was noted for the fly ashes (FAE and FAF). This is due to the fact that the addition of fly ashes was lower than the amount required to neutralize the already present surface acidity in the mine waste. In these systems there is also significantly lower pH in the lysimeter compared to at the tap. As the systems works, in principle, as columns neutralization reactions take place first at the top of the systems and work their way down to the bottom, pH will

thus initially be lower at the beginning of the systems with too little alkaline material (FAE and FAF). As the water becomes acid carbonate dissolution increases and pH will increase at the tap at the bottom.

As seen in table 2, alkalinity is very high in the WWG system, followed by LM, GLD and LKD. Although high alkalinity is desired when leachates enter a recipient; very high alkalinity is possibly a drawback as the total neutralization potential is depleted at a higher rate.

For oxide/hydroxide amended systems (e.g. LD) pH and alkalinity is temporary increased at the time of reaction, but as the water continues to percolate through the mine waste the alkalinity is exhausted and consequently leachates will have rather low alkalinity. This in turn will also lower the pH at the tap (table 2). In the case of carbonate materials (e.g. LM), carbonate alkalinity (HCO_3^-) is generated at the time of reaction, which has the ability to exist and buffer pH at much lower pH values than hydroxide alkalinity (OH^-). Therefore, leachates from carbonate amended systems will have higher alkalinity.

LKD behaves more like a carbonate in these experiments, with moderate pH and high alkalinity.

Sulphate and Major Elements

Calcium concentrations was found to be in equilibrium with calcite (CaCO_3) in all carbonate based amended systems (LM, LKD, GLD and WWG) with concentrations around 400-500 mg/l. Sodium concentrations was found to be very high from the GLD (2 500 mg/l) and the FAF (500 mg/l) systems. Also potassium was found to be high from the FAF system with concentrations around 1 400 mg/l. Magnesium concentrations was found to be high from several systems; the highest being from the reference (2 500 mg/l), indicating weathering. Iron concentrations increase in the reference system (figure 2), indicating reductive dissolution of the pre formed ferric iron containing secondary minerals. Iron concentrations in the amended systems are significantly lower (around two orders of magnitude), reflecting the higher pH precipitating iron as (hydr)oxides. Sulphate concentrations (figure 2) are determined by equilibrium (SI -0.3-0.2) with gypsum (CaSO_4) in all systems. Lower sulphate concentrations in the amended systems are thus a direct consequence of increased calcium concentrations from the alkaline materials.

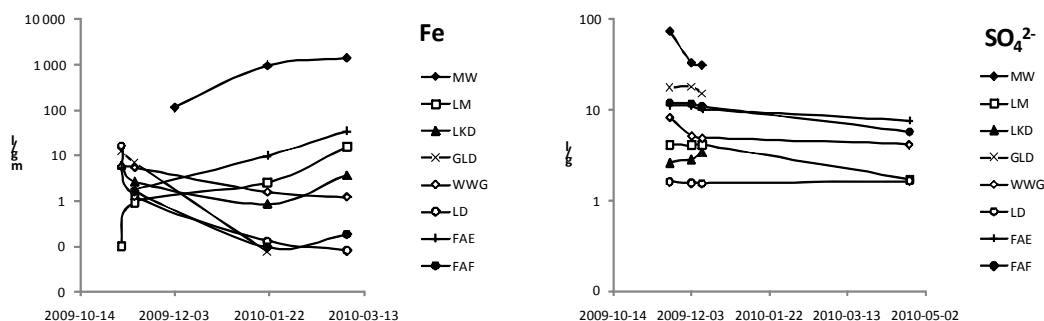


Figure 2: Changes in iron and sulphate concentrations (in mg/l and g/l respectively) from the start of the experiment until the last sampling occasion. Note the logarithmic scale.

Trace Elements

Trace metal reduction (compared to the reference, MW) is strongly connected to pH and hence, almost quantitative removal (>99 %) is found for copper, zinc and cadmium in all amended systems (except FAE) (figure 3). Lead reduction is somewhat lower with a reduction of 95 % in the LKD-system. In the system amended with FAE pH is significantly lower (pH around 5; table 2) and thereby reduces both sorption and precipitation of trace elements. Almost linear relationships between pH and logarithmic trace element concentrations were found when all data was compiled. This indicates that pH is the major driving force for trace element reduction in the amended systems. Also precipitation of different minerals is important for the reduction of trace elements from the amended systems. As shown in figure 4 the respective carbonate minerals are at or close to equilibrium. Saturation for the carbonate minerals are especially found in the systems amended with alkaline materials containing high concentrations of calcite (LM, LKD, WWG and GLD). Sulphate containing minerals such as anglesite (PbSO_4) was not found to be close to equilibrium (SI -1 - -3 in all systems).

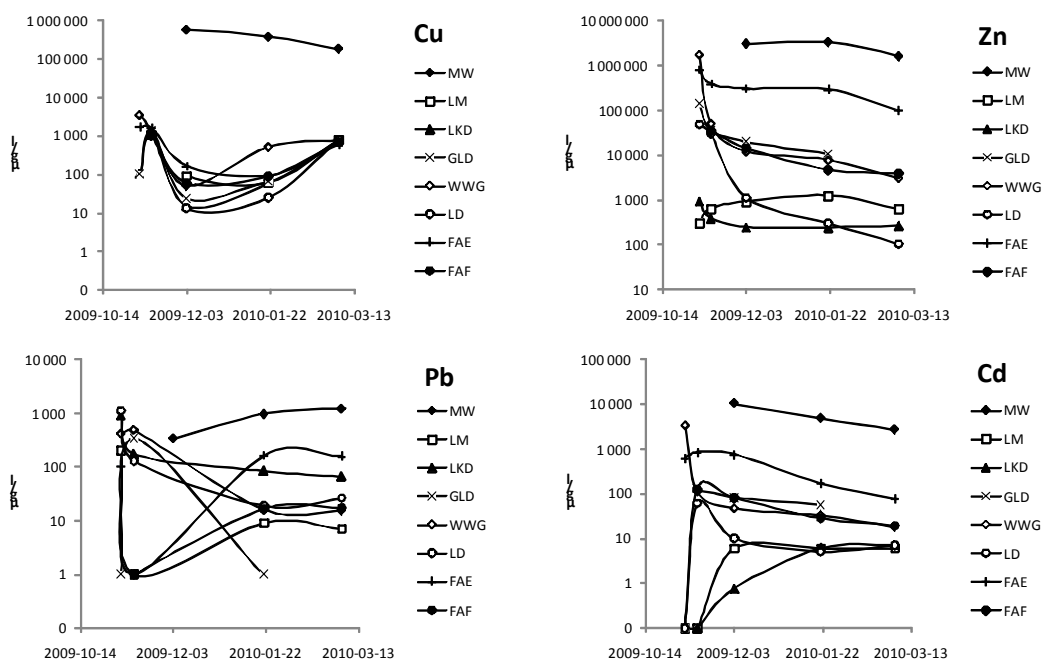


Figure 3: Concentrations (in $\mu\text{g/l}$) of Cu, Zn, Pb and Cd in the reference system (MW) and the amended systems at the bottom tap. Note the logarithmic scale.

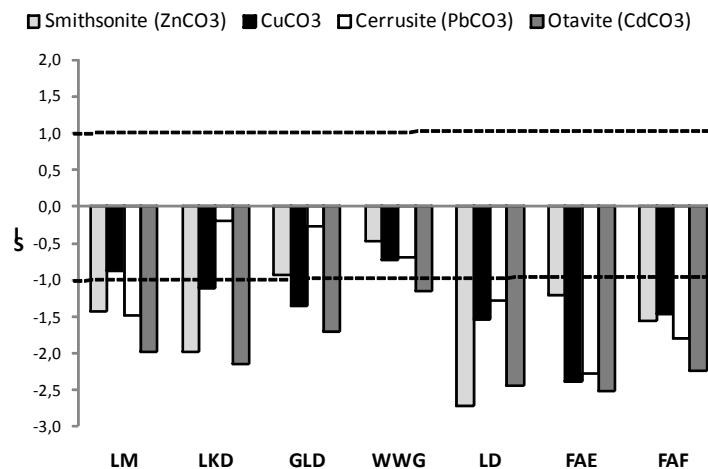


Figure 4: Saturation indices (SI) for metal carbonate minerals of Zn (smithsonite), Cu, Pb (cerrusite) and Cd (otavite) in the different amended systems.

There is also a significant difference between trace element concentrations within the systems (lysimeters) and in the outflowing leachates (figure 5). In general the differences are due to different pH in the lysimeters and at the tap. For instance, trace element concentrations are significantly higher and pH significantly lower within the fly ash lysimeters compared to the leachates.

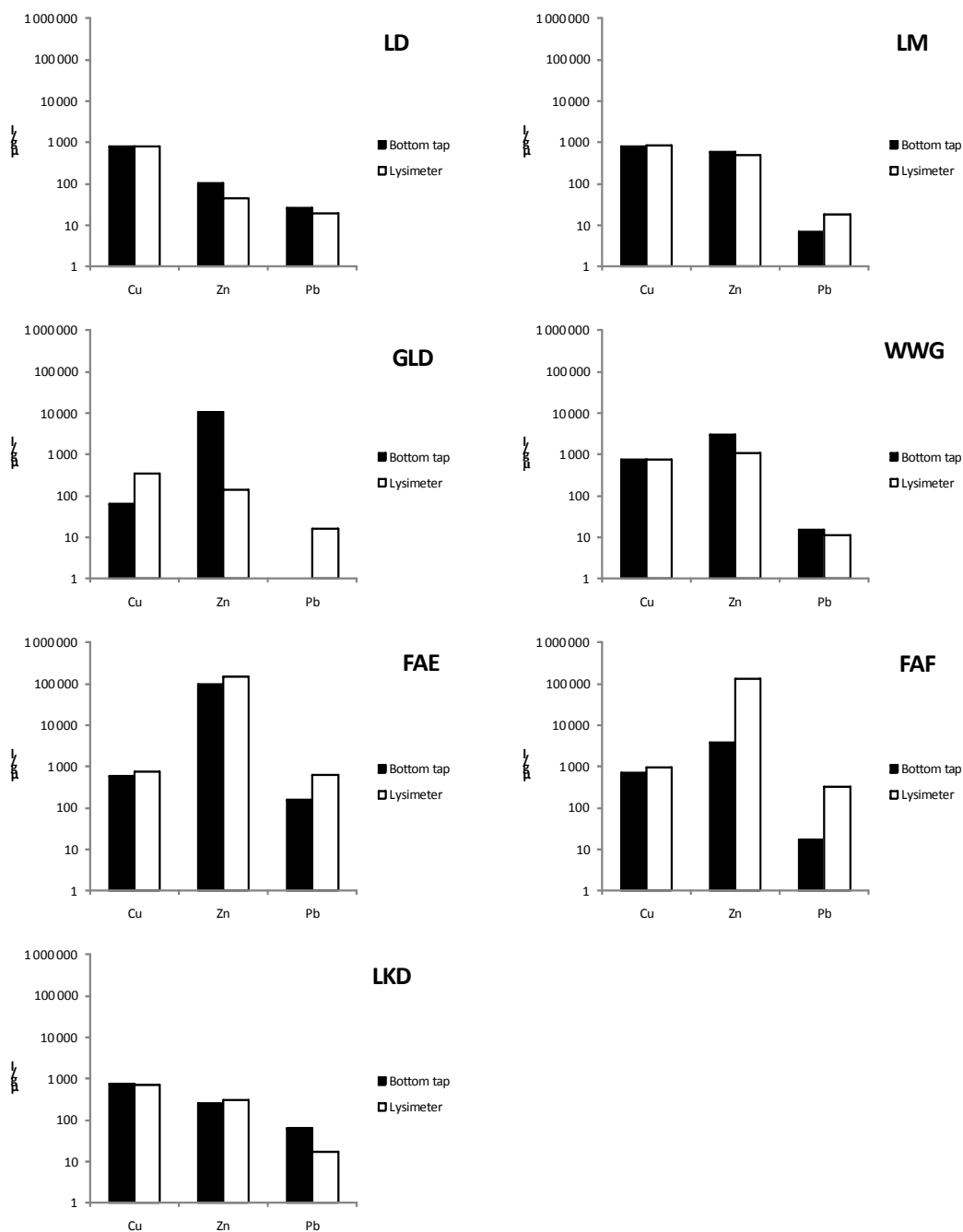


Figure 5: Differences in trace metal concentrations (Cu, Zn and Pb) between bottom tap and sampling lysimeter in the seven amended systems at one sampling occasion. Note the logarithmic scale.

CONCLUSIONS

This study has shown that addition of alkaline by-products to oxidized waste rock will increase pH from below 3 to approximately 7. Trace element reduction will in most cases exceed 99 % compared to the untreated system and major mechanisms behind the reduction are sorption and carbonate precipitation.

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