FLOODING OF OXIDIZED WASTE ROCK AMENDED WITH ALKALINE BY-PRODUCTS

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ABSTRACT

Leaching of trace elements (Cd, Cu, Pb and Zn) from oxidized waste rock amended with different alkaline by-products was studied during flooding. It has been argued that water covers for oxidized waste would significantly increase leaching through reductive dissolution of the pre-formed hydrous ferric oxides and the associated trace elements.

After approximately three weeks pH in the reference had reached 2.5 and 3.3 in the pore and overlying water, respectively. This can be compared with pH from 6.1 (water works granules) to above 10 (lime kiln dust) in the amended systems. It is clear that the carbonate dominated alkaline by-products have lower pH than the oxide/hydroxide based by-products. However, the systems amended with carbonate based by-products have significantly higher alkalinity.

Cadmium, Cu, Pb and Zn concentrations within the waste decreased with at least 99% compared to the reference. In most systems the surface waters can even be used as drinking water. Cadmium, copper and zinc concentrations are clearly related to pH with decreasing concentrations with increasing pH. Lead concentrations, on the other hand, decrease to pH 8, where the concentrations start to increase slightly again due to the formation of soluble $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ species.

The results indicate that flooding of oxidized waste rock amended with alkaline by-products can be used as a successful remediation technique.

Key words: oxidized waste rock, flooding, fly ash, green liquor dregs, lime mud, slag, lime kiln dust, trace metals

INTRODUCTION

Water covers is a very common method used for modern waste (mainly tailings) in order to reduce further weathering and oxidation of sulfides to a minimum (Vigneault et al., 2001). Due to the significantly lowered diffusion of oxygen in water (around $2*10^{-9}$ m^2/s) compared with in air ($1.78*10^{-5}$ m^2/s), the oxidation is lowered by several orders of magnitude. In the case of pre-oxidized mine waste there is, however, a large uncertainty concerning reductive dissolution of pre-formed secondary iron(hydr)oxides and their associated trace metals. It has been argued that flooding of pre-oxidized mine waste will result in high trace metal concentrations and acid pH due to the dissolution of secondary precipitates (Ribet et al., 1995; Simms et al., 2000; Simms et al., 2001). To avoid this potential disadvantage for pre-oxidized mine tailings protective layers (Simms et al., 2001) or layers with alkaline materials (Catalan and Kumari, 2005) have been suggested (Simms et al., 2001).

Another important factor to consider when flooding mine waste is the water depth in order to avoid erosion and re-suspension due to wind induced waves (Mian and Yanful, 2003).

Laboratory experiments performed on the flooding of pre-oxidized tailings (Simms et al., 2000) showed that even if the pore water quality improved considerably the overlying surface water still had low pH and high metal concentrations after 600 days. Both low pH and high metal concentrations from historical oxidized mine waste can, however, be prevented by the addition of an alkaline amendment (preferably an industrial by-product) (Sartz et al., 2009). Experiments performed by Catalan and Kumari (2005) using lime mud residue covers showed that the quality of the surface water increased.

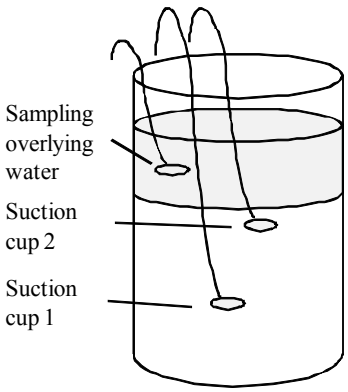
The present flooding experiment aim at simulating flooding of an oxidized waste rock amended with an alkaline material with a permanent water cover (in a natural lake or in a flooded open pit). During the experiment possible reductive dissolution of ferric (hydr)oxides will be studied as well as ongoing oxidation of sulfides.

MATERIALS AND METHODS

Experimental Design

The flooding experiments are designed to simulate the chemical changes taking place when a weathered and acidic historical mine waste is mixed with a strongly alkaline material and flooded with water.

Barrels (PE-plastic) with lid and a total volume of 60 L were used for the experiments. Waste rock and the alkaline materials (approximately 15%, based on the acidity of the mine waste) were mixed in the barrels (Figure 1). Water (18 MΩ) (17-28 L) was then added to the systems resulting in a water level approximately 20 cm above the mine waste/alkaline material mix. Initial liquid/solid (L/S) ratio was found to be around 0.7 except for the green liquor dreg (GLD) system where the final L/S was around 0.4. Sampling was performed, using a 50 mL syringe, through suction cups installed at three levels in each system; (1) L1; 5 cm above the bottom of the barrel, (2) L2; approximately 20 cm below the waste/water interface, (3) a couple of cm above the waste/water interface in the overlying water. Suction cups were sampled top down in order to avoid new water from entering the area surrounding the suction cup prior to sampling. After each sampling a corresponding volume (approximately 0.5 L) of water was added gently to the surface water in order to keep the water volume constant.



System	Alkaline material (%)	Alkaline material	Alkaline chemistry
JT0	0	None	-
JT1	15	WWG	CO_3
JT2	15	FAF	O/OH
JT3	15	GLD	CO_3
JT4	15	LM	CO_3
JT5	15	LD	CaO/OH
JT6	15	LKD	CaO/CO_3

Figure 1: Principal outline of the flooding experiments with the approximate positions of the suction cups (lysimeters; L). Descriptions of the different systems and their alkaline content are also provided.

The historical mine waste, from Ljusnarsbergsfältet in Kopparberg (Sartz, 2006), is heavily weathered and 200-300 years old. Before it was used in the experiments aggregates were crushed and sieved and the fraction smaller than 13 mm was used. Surface and total acidity for the mine waste have been determined to 4.2 and 11.5% as $CaCO_3$ equivalents, respectively (Höckert, 2007). Six different alkaline materials were selected for this study; lime mud (LM), green liquor dreg (GLD) and fly ash (FAF) from pulp and paper industry, water works granules (WWG), lime kiln dust (LKD) and steel slag (LD). A short summary of the different systems can be found in Figure 1.

Sampling and analytical methods

Prior to the start of the experiment the alkaline materials were characterized with respect to free lime and carbonate contents. Total element concentrations were also determined in all materials (including the mine waste) in order to characterize the different constituents from the materials. Sampling was performed after 15 min, 1 h, 2 h, 4 h, 8 h, 1 day, 2 days, 3 days, 4 days, 7 days, 10 days, 15 days, 20 days, 30 days, 40 days and 124 days. The sampling resulted in a total removal of 7.5 L of water adding approximately 0.2 to the initial L/S ratio.

At every sampling occasion pH, electrical conductivity, redox potential and alkalinity was measured immediately. pH and electrical conductivity were measured using a combination electrode and an electrode, respectively, at 25°C without stirring. Calibration of the pH electrode was performed every day at pH 4 and 7. Alkalinity was determined through end point titration to pH 5.4 with 0.02 M HCl during constant air purging. Samples for analysis of elements and Fe(II) were preserved using nitric and sulphuric acid, respectively. Sulphate, chloride and fluoride were determined with ion chromatography. Prior to the analysis the samples were filtered through 0.20 μm polycarbonate filters. Elements (Al, Ca, Cd, Co, Cr, Cu Fe, K, Mg, Mn, Na, Ni, Pb and Zn) were analysed using an ICP-OES. External calibration was used with ^{103}Rh as internal standard. Iron(II) was analysed using a spectrophotometric method. Ammonium fluoride was added to the sulphuric acid preserved samples (masking of Fe(III)), 2,4,6-tri(2´-pyridyl)-1,3,5-triazine (TPTZ; chromophore) and ammonium acetate buffer (pH control). The samples were thoroughly mixed and the absorbance was measured at 595 nm.

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

Alkaline materials

Content of free lime and carbonates as well as total concentrations for the different alkaline materials and the mine waste can be found in Table 1. It is obvious that the alkaline materials have a much higher pH than the mine waste. It can also be found that only LD and LKD have significant amounts of free lime (CaO) while LM, GLD and WWG all have very high concentrations of carbonate. Considering the total available alkaline capacity (both CaO and $CaCO_3$) the following order appears: LM > WWG > LKD > GLD > FAF > LD. However, long term titrations on the alkaline materials show higher total neutralization capacity and the following order: GLD > LKD > LM > WWG > LD > FAF (Bäckström and Sartz, 2010a).

Table 1: Free lime (CaO), content of carbonates (as $CaCO_3$) and paste pH in the alkaline materials as well as total concentrations for all materials (LM, lime mud; GLD, green liquor dreg; FAF, fly ash; WWG, water works granules; LD, LD slag; LKD, lime kiln dust) including the mine waste (MW). BDL, below detection limit. TOC, total organic carbon; LOI, loss on ignition. Gray coloring indicate concentrations significantly higher in the alkaline materials compared to the mine waste.

	MW	**LM**	**GLD**	**FAF**	**WWG**	**LD**	**LKD**
Free lime (%)	-	< 2.4	< 2.4	< 2.4	< 2.4	6.6	14.4
$CaCO_3$ (%)	-	97	72	30	85	5.4	66
pH	3.1	11.8	12.3	12.3	9.6	12.9	12.9
Total conc (g/kg)							
Si	151	0.827	9.16	158	52.2	47.6	19.9
Al	12.5	0.390	4.31	41.4	1.83	6.36	12.6
Ca	27.8	395	295	159	355	286	374
Fe	276	0.336	7.29	19.2	0.505	166	6.20
K	10.1	0.203	3.34	35.1	1.52	0.138	3.73
Mg	34.2	3.06	13.5	11.9	1.39	63.8	17.0
Mn	1.72	0.149	4.60	5.34	0.077	23.9	0.226
Na	1.93	6.69	28.5	11.5	0.615	0.166	0.831
P	0.187	4.48	3.32	8.38	< 0.10	2.46	0.836
Ti	0.341	0.058	0.201	4.62	0.028	7.57	0.448
Total conc (mg/kg)							
Cd	5.6	0.2	3.4	6.6	0.1	0.0	1.6
Co	4.3	0.4	5.5	6.0	0.2	3.3	5.7
Cr	34.5	< 10	127	131	< 10	2 460	24.3
Cu	1 880	0.7	71.9	84.9	3.6	6.7	22.1
Ni	3.3	4.1	81.2	31.2	0.8	61.3	15.8
Pb	6 340	11.1	19.4	64.6	0.3	1.2	24.6
S	28 600	< 80	10 700	7 240	346	355	7 570
Zn	2 270	36.8	1 120	1 200	2.6	5.9	128
TOC (% dw)	1.29	< 2.12	7.35	4.24	< 1.41	< 0.210	< 1.20
LOI (% dw)	12.4	43	44.7	21.5	38.5	4.2	34.4

Reference System

After flooding of the systems, pH decreased to around 2.5 within the pore water of the reference system, while it remained around 3 in the overlying water. This should be compared with the pH obtained at batch leaching at L/S 2 (Table 1). Geochemical calculations indicated equilibrium with gypsum ($CaSO_4$) and fluorite (CaF_2) in the reference system. Trace element concentrations in both the pore and overlying waters are very high as can be noted in Figure 2. On average Cd, Cu, Pb and Zn concentrations are 16, 880, 1.1 and 11 000 mg/l, respectively, in lysimeter 1. In lysimeter 2 the concentrations are somewhat lower, but of the same order of magnitude. In the overlying water the concentrations are significantly lower (approximately two orders of magnitude), except for lead that is only slightly lower. One possible reason for the lower concentrations in the overlying water is, of course, slow diffusion of ions from the solid phase into the water phase. Diffusion is indicated by the fact that the concentrations in the surface water are slowly increasing (Figure 2). Another possible reason is the addition of clean water at every sampling occasion. Lead concentrations are probably governed by a solid phase in the pore water (probably anglesite ($PbSO_4$), that is only slightly sub saturated) thus giving a rather small difference between the pore and overlying water. From Figure 2 it is clear that the concentrations are slowly decreasing. An increase would indicate further oxidation of the sulphides or reductive dissolution of the pre-formed secondary precipitates (mainly hydrous ferric oxides). A decrease in concentrations would on the other hand indicate an initial washing effect or the formation of new sulphides. Preliminary analysis of ferrous iron showed concentrations below detection limit in all systems.

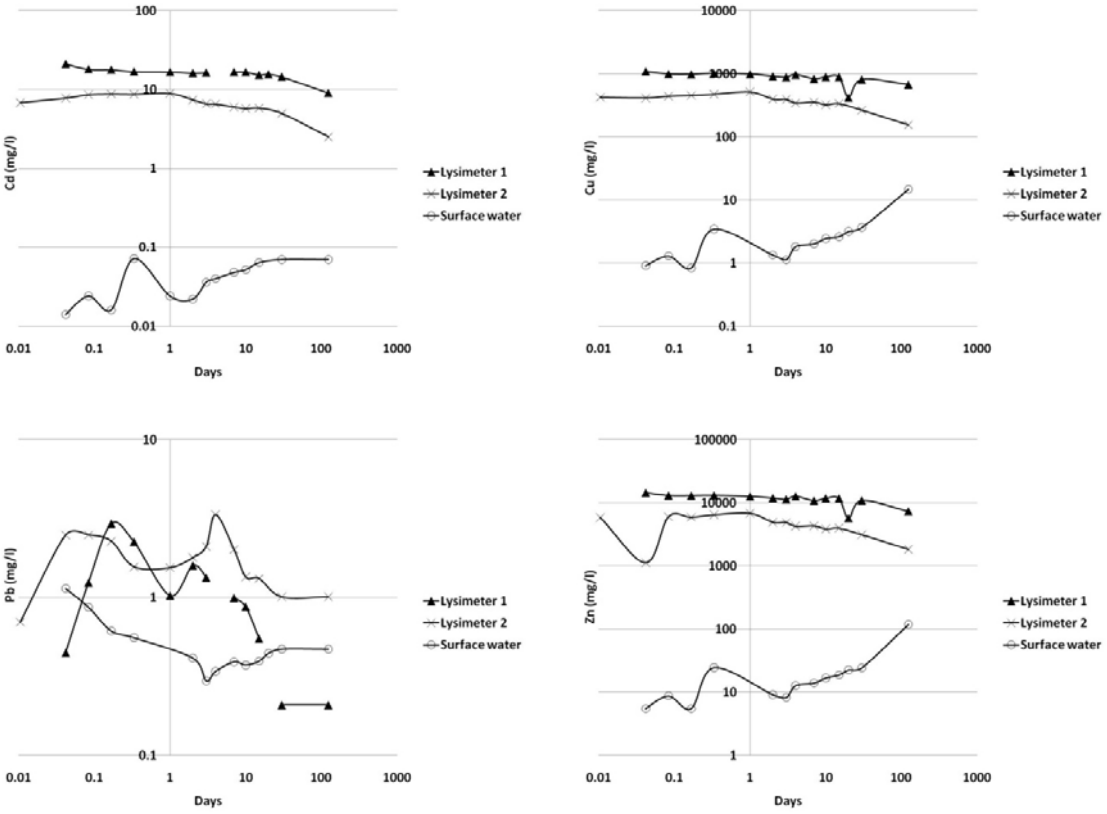


Figure 2: Cadmium, Cu, Pb and Zn concentrations in the reference system. Note the logarithmic scale on both axis.

Amended Systems

During sampling several qualitative observations were made. For instance, 'Was foaming noted in the systems amended with WWG, GLD and LM?' In the LM system the foaming was significant. Visible foaming appears only in the systems amended with materials containing high concentrations of carbonates, indicating formation of CO_2 according to the following reactions:

$CaCO_3 + 2\ H^+ => Ca^{2+} + H_2CO_3$

$H_2CO_3 => H_2O + CO_2(g)$

Geochemical calculations support the presence of calcite ($CaCO_3$) in all amended systems (SI -0.44 to 1.6). Also gypsum ($CaSO_4$; SI -0.4 to 0.1) and fluorite (CaF_2; SI 0.9-1.9) were indicated as solid phases possibly controlling the concentrations of calcium, sulphate and fluoride. After a couple of weeks smell of hydrogen sulfide was noted in the systems amended with LD and LKD. These systems have lowest redox potential (Table 2) and the smell indicates possible formation of new sulphides in the systems. However, at sampling day 124 the redox potential had increased in all systems while pH had decreased approximately 1 unit. The systems had been left for almost three months and it is possible that a new equilibrium condition is forming in the systems. This is somewhat confirmed by the fact that all measured parameters in the different lysimeters in a selected system are becoming more and more alike.

Table 2: pH and redox potential measured in the systems at sampling 15 (after 40 days). Suction cups are listed from the bottom and up (L1, L2 and surface water (SW)).

System		**pH**			**Redox potential (mV)**		
		L1	L2	SW	L1	L2	SW
JT0	Ref	2.54	2.63	3.05	470	440	197
JT1	WWG	6.44	6.42	6.61	5	8	12
JT2	FAF	7.65	7.15	7.00	-49	-44	-2
JT3	GLD	7.03	7.01	7.19	-43	-45	-30
JT4	LM	6.80	6.65	6.81	-51	-99	-89
JT5	LD	9.76	9.08	8.81	-146	-135	-66
JT6	LKD	8.80	9.79	8.67	-75	-68	-46

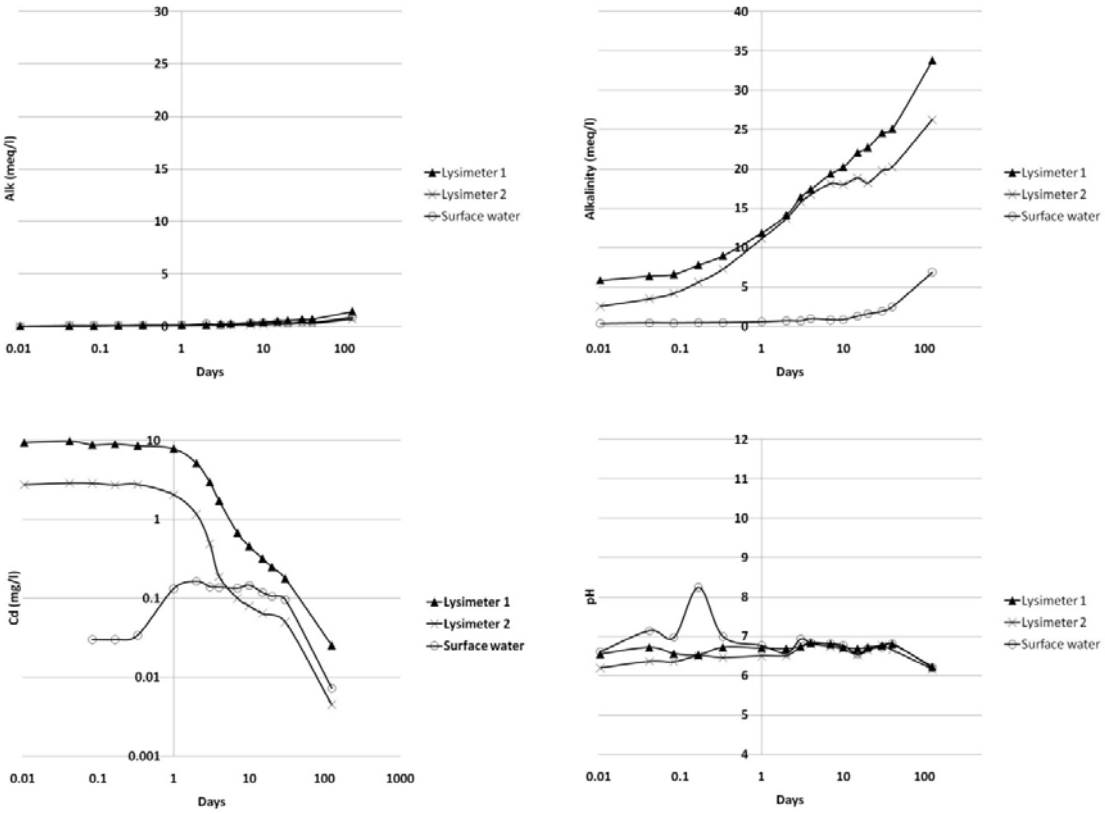


Figure 3: Alkalinity and pH for LD (left) and LM (right). LD represents the typical oxide/hydroxide and LM represents the typical carbonate. Note the logarithmic scale for the days of sampling.

Some interesting observations can be made regarding the different alkaline materials (carbonates and oxides/hydroxides) used in the systems. In Figure 3 pH and alkalinity can be found as a function of time in the systems amended with slag (LD) and lime mud (LM). LD and LM can be considered as typical representatives for oxide/hydroxide and carbonate dominated materials, respectively. While the pH is high in the LD system alkalinity is rather low. In the LM system, on the other hand, alkalinity is very high and the pH is fairly low (between 6 and 7). At acid conditions carbonates react relatively fast with protons, producing HCO_3^- and H_2CO_3, depending on the pH. Calcium carbonates in an acid environment will give a pH up to 6.9 (Sherlock et al., 1995) and a high alkalinity due to the rapid production of HCO_3^- through the following reaction: $CaCO_3 + H^+ => Ca^{2+} + HCO_3^-$. Oxide/hydroxide materials, on the other hand, provide a fairly high pH as long as there is hydroxide left in solution. However, as the hydroxide is the only source for alkalinity measured alkalinity will be rather low at pH below 10. Even though the pH is high in the hydroxide systems the low alkalinity makes the systems vulnerable for sudden increases in acidity. As a consequence of the differences in alkalinity and pH between the carbonate and hydroxide materials rhodochrosite ($MnCO_3$) was found to be in equilibrium in the carbonate dominated systems (systems 1-4) but sub-saturated in the hydroxide systems. Smithsonite ($ZnCO_3$) was also close to equilibrium in the carbonate amended systems while cerrusite ($PbCO_3$) was slightly more sub-saturated (SI around -1.5). However, $Pb(OH)_2$ (SI -0.5-0) was close to equilibrium in the systems amended with highly alkaline materials (systems 5 and 6).

An illustration of the reduction in trace metal concentrations can be found in Figure 4. All other amended systems show similar graphs, but with lower trace metal concentrations. Trace metal concentrations are somewhat higher than found by Catalan and Kumari (2005). However, their system was based on leaching (up to 249 pore volumes) while these experiments are relatively stagnant. Contrary to the reference system (Figure 2) the trace metal concentrations are decreasing with time. This is mainly due to the increase in pH resulting from the dissolution of the alkaline materials added. A summary of the trace metal reduction in the different systems can be found in Table 3.

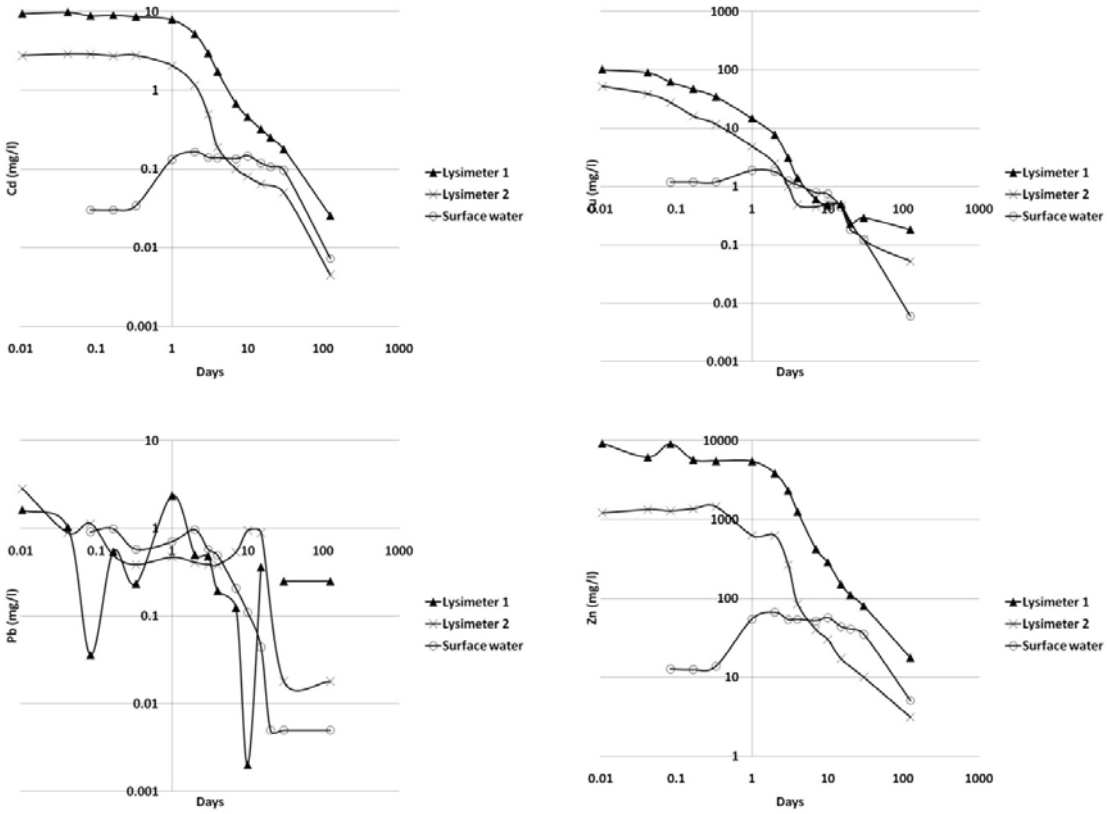


Figure 4: Concentrations of Cd, Cu, Pb and Zn as a function of time in the system amended with water works granules (WWG). This amendment was chosen for illustration as it is the worst performer of all amended systems. After approximately 2 days pH is reaching above 6 in all three lysimeters. Note the logarithmic scale for both axis.

From Table 3 it is clear that the reduction of copper and lead are very good; mainly due to the fact that they are sorbed to surfaces at lower pH than cadmium and zinc (Bäckström and Sartz, 2010b). Somewhat lower reduction of cadmium and zinc can be noted in the systems amended with carbonate based materials (WWG, FAF, GLD and LM) compared to the systems amended with oxide/hydroxide materials (LD and LKD). This difference is due to lower pH and thus lower sorption in the carbonate amended systems. If pH was the only factor affecting the trace metal concentrations in the surface waters a plot between the trace metal concentrations (logarithmic) and pH would form a straight line. In Figure 5 the concentrations of copper and zinc versus pH can be found for all systems including the reference.

Table 3: Reduction (%) in Cd, Cu, Pb and Zn concentrations compared to the reference at day 124 in lysimeter 2 (L2) and in the surface water (SW).

System		Cd		Cu		Pb		Zn	
		L2	SW	L2	SW	L2	SW	L2	SW
JT1	WWG	100	92	100	100	98	98	100	96
JT2	FAF	100	96	100	100	100	99	100	99
JT3	GLD	100	99	100	100	100	99	100	100
JT4	LM	99	96	100	99	100	99	100	98
JT5	LD	100	100	100	100	100	99	100	100
JT6	LKD	100	100	100	100	100	99	100	100

If pH would be the only factor of importance all amended systems would line up in a straight line below the reference system. For copper the line is almost present, except for somewhat higher concentrations in the WWG and LKD amended systems. Concentrations found above the line indicate an addition from the alkaline material itself. This is apparent for zinc in the WWG amended system, but also in the FAF and LM amended systems. This indicates that the alkaline materials may release trace metals when the pH is lowered below their initial pH (Huijgen et al., 2006; Astrup et al., 2006). This would explain the higher zinc concentrations in the WWG amended system compared to the reference system.

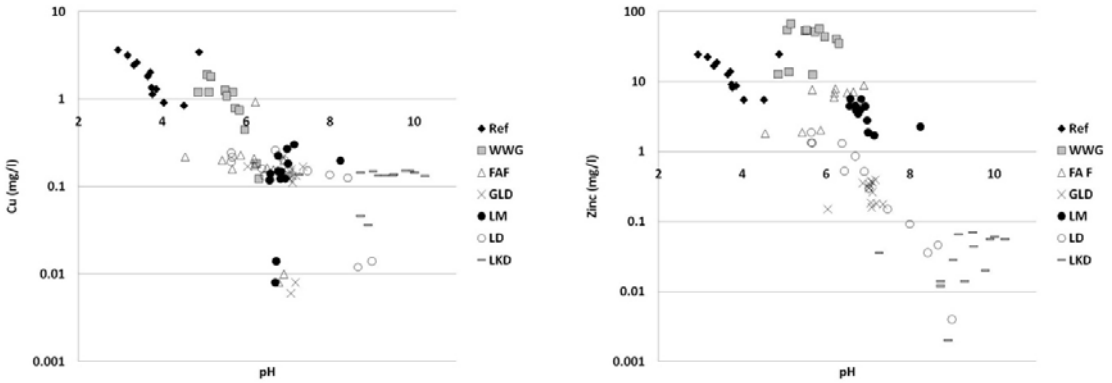


Figure 5: Surface water (SW) copper and zinc concentrations (mg/l) vs pH for all systems. Note the logarithmic scale for the metal concentrations.

Table 4: Concentrations (mg/l) of trace metals in the surface water day 124 in all systems compared with environmental quality (CCME, 2006) and Canadian drinking water criterias. Numbers in bold exceed the drinking water criteria and numbers in grey exceed the environmental quality criteria.

	DW	EQC	MW	WWG	FAF	GLD	LM	LD	LKD
Cd	**0.005**	0.000017	**0.12**	**0.007**	0.001	< 0.001	0.003	< 0.001	< 0.001
Cu	**1**	0.002	**15**	0.006	0.004	0.002	0.12	0.002	0.024
Pb	**0.010**	0.001	**0.47**	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Zn	**5**	0.030	**120**	**5.1**	0.96	0.41	2.7	0.016	0.014

When it comes to the quality of the water from the amended systems comparisons were made with environmental quality and drinking water criterias. From Table 4 it is clear that most amendments (except WWG) even produce water fit for human consumption.

CONCLUSIONS

It is clear that the carbonate dominated alkaline by-products give lower pH than the oxide/hydroxide based by-products. However, the systems amended with carbonate based by-products have significantly higher alkalinity. Cadmium, Cu, Pb and Zn concentrations within the waste decreased with at least 99% compared to the reference. In most systems the surface waters can even be used as drinking water. Cadmium, copper and zinc concentrations are clearly related to pH with decreasing concentrations with increasing pH. Lead concentrations, on the other hand, decrease to pH 8, where the concentrations start to increase slightly again due to the formation of soluble $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ species. Major mechanisms behind the immobilization of trace elements are sorption onto solid phases and precipitation of carbonates and hydroxides. In the long term perspective, formation of sulphides should, however, not be ruled out. The results clearly indicate that flooding of oxidized waste rock amended with alkaline by-products can be used as a successful remediation technique.

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REFERENCES

Astrup, T., Dijkstra, J.J., Comans, R.N.J., van der Sloot, H.A. and Christensen, T.H. 2006. Geochemical modeling of leaching from MSWI air-pollution-control residues. Environmental Science & Technology, 40: 3551-3557

Bäckström, M. and Sartz, L. 2010a. Buffering capacity in several different alkaline by-products – results from a laboratory experiment (in manuscript)

Bäckström, M. and Sartz, L. 2010b. Mixing of acid rock drainage with alkaline ash leachates. 2. Fate and immobilization of trace elements (in manuscript)

Catalan, L.J.J. and Kumari, A. 2005. Efficacy of lime mud residues from kraft mills to amend oxidized mine tailings before permanent flooding. Journal of Environmental Engineering Science, 4: 241-256

CCME, 2006. Canadian Environmental Quality Guidelines for protection of Aquatic life. Summary Table, Update December 2006.

Huijgen, W.J.J. and Comans, R.N.J. 2006. Carbonation of steel slag for CO_2 sequestration: Leaching of products and reaction mechanisms. Environmental Science & Technology, 40: 2790-2796

Höckert, L. 2007. Chemical stabilization of mine waste with sewage sludge and calcium carbonate residues. MSc thesis, Uppsala University, Sweden (in Swedish)

Mian, M.H. and Yanful, E.K. 2003. Tailings erosion and resuspension in two mine tailings ponds due to wind waves. Advances in Environmental Research, 7: 745-765

Parkhurst, D.L. and Appelo, C.A.J. 1999. User´s Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations Report, 99-4259.

Ribet, I., Ptacek, C.J., Blowes, D.W. and Jambor, J.L. 1995. The potential for metal release by reductive dissolution of weathered mine tailings. Journal of Contaminant Hydrology, 17: 239-273

Sartz, L. 2006. History and geochemistry of the Ljusnarsberg mine field – Compilation of present material. MTM 06-16 Rep, Örebro university, 40 pp (in Swedish)

Sartz, L. Bäckström, M. Karlsson, S. and Allard, B. 2009. Stabilisation of acid-generating waste rock with alkaline by-products – results from a meso-scale experiment. In: Securing the Future and 8th ICARD, 23-26 June, 2009, Skellefteå, Sweden (10 pp) (CD-ROM)

Sherlock, E.J., Lawrence, R.W. and Poulin, R. 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environmental Geology, 25: 43-54

Simms, P.H., Yanful, E.K., St-Arnaud, L. and Aubé, B. 2000. A laboratory evaluation of metal release and transport in flooded pre-oxidized mine tailings. Applied Geochemistry, 15: 1245-1263

Simms, P.H., Yanful, E.K., St-Arnaud, L. and Aubé, B. 2001. Effectiveness of protective layers in reducing metal fluxes from flooded pre-oxidized mine tailings. Water, Air and Soil Pollution, 131: 73-96

Vigneault, B., Campbell, P.G.C., Tessier, A. and de Vitre, R. 2001. Geochemical changes in sulfidic mine tailings stored under a shallow water cover. Water Research, 35(4): 1066-1076

Widerlund, A., Shcherbakova, E., Carlsson, E., Holmström, H. and Öhlander, B. 2005. Laboratory study of calcite-gypsum sludge-water interactions in a flooded tailings impoundment at the Kristineberg Zn-Cu mine northern Sweden. Applied Geochemistry, 20: 973-987