

## On the neutralisation of ARD and acid-generating waste rock by different alkalinity sources – carbonate and/or hydroxide

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**Abstract** Six alkaline waste materials were tested for their neutralising capacity and metal immobilisation ability as amendments to a weathered waste rock. Two of the materials were of carbonate-type: lime mud (LM) and green liquor dreg (GLD) and four were of hydroxide-type: lime kiln dust (LKD), LD-slag (LD), carbonated fly ash (CFA) and a fresh fly ash (FFA). pH achieved by carbonate and ARD reactions (approximately 6) is too low to ensure quantitative sorption of e.g. Zn and Cd. Hydroxide neutralisation reactions however result in higher pH, but lower alkalinity.

**Key Words** alkaline by-products, fly ash, LKD, immobilisation

### Introduction

Treatments of ARD and highly weathered waste rock is the focus for laboratory and field scale studies in Kopparberg, mid Sweden. An effluent water with low pH, high concentrations of Fe(II) and other trace elements as well as low alkalinity could be detrimental for a recipient.

Amendments of alkaline materials to oxidized mine waste prevent the formation of or improve the quality of ARD (Bellaloui et al 1999, Davis et al 1999, Pérez-López et al 2007). Typical pH achieved when a carbonate material is added to mine waste or ARD is 5.5 to 6.9 (Sherlock et al 1995), almost unaffected by the amount added (Sartz and Bäckström 2007, Yin and Catalan 2002). Also, treatments of ARD with ALDs (anoxic limestone drains) produce effluent waters with pH around 6 (Cravotta 2003). A pH of 6 is often too low to ensure quantitative sorption of Zn and Cd (Catalan and Kumari 2005). However, carbonate amended systems can maintain long-term neutral pH conditions, due to a high alkalinity generation (Catalan and Kumari 2005).

Fly ash, due to its content of free lime, can form hard pans through pozzolanic reactions (Ahmaruzzaman 2010, Pérez-López et al 2007). Hard pan formations decrease fluid flow and increase the contact time between fluid and alkaline material. Consequently, mixing in distinct layers should be beneficial for fly ash amended systems. Thorough mixing of weathered tailings using carbonate materials is also a possible method using, for instance, tilling. Mixing ensures a close and even contact between the acid producing waste and the alkaline material. In both cases (layering and mixing) it is economically beneficial to use industrial by-products. Natural resources such as limestone are also conserved.

### Methods

Experiences were used from three different experiments: (1) laboratory scale (50 mL) mixing experiments with waste rock and alkaline by-products mixed at different proportions (0–50%) and shaken with water (Sartz and Bäckström 2007); (2) half scale (30 L) mixing experiments with waste rock and alkaline by-products mixed (10%); (3) meso scale (1.5 m<sup>3</sup>) layered experiments with waste rock and layers of several different alkaline by-products (10–50%) (Bäckström et al. 2010). For detailed information about the different experiments the reader is referred to the respective references.

Oxidized waste rock from the historic mining area Ljusnarsbergfältet in Kopparberg, mid Sweden, has been used for all experiments. Secondary aggregates were crushed and the fraction 0–13 mm was used. Alkaline oxide/hydroxide based materials used in the different experiments were LD-stone (LD), lime kiln dust (LKD), fresh fly ash (FFA) and carbonated fly ash (CFA) while the carbonate based materials were green liquor dreg (GLD) and lime mud (LM). It should, however, be noted that in the oxide/hydroxide based materials there is more or less carbonates as well. This is especially true for LKD and FFA that contain approximately 50% oxide/hydroxide and 50% carbonate. Materials used in the different experiments are from the same batch and comparisons can therefore be made.

Measurements have been made for pH, alkalinity (endpoint pH 5.4) and for major and trace elements (ICP-OES and ICP-MS).

## Results and Discussion

Only experiments where both the exact materials and the exact proportions between mine waste and alkaline by-products have been chosen in order to be able to make direct comparisons.

When comparing the laboratory scale with the half scale (tab. 1) it is apparent that the oxide/hydroxide based materials give a higher pH in laboratory scale compared to the carbonate based materials. This is most likely due to the presence of hydroxides in these materials. It is also obvious that alkalinity is higher for carbonate based materials, both for laboratory and half scale. Alkalinity is higher in the half scale experiments compared to the laboratory scale experiments for LM, GLD, LKD and FFA. This is most likely an effect of lower pH inducing higher rate of calcite dissolution. LD and CFA have lower alkalinity in the half scale experiments suggesting low carbonate content.

**Table 1** Comparison between lab scale (mixed) and half scale (mixed) experiments with respect to pH and alkalinity (meq/L). Numbers indicate the amount (%) of alkaline by-product. REF is only waste rock

Added alkaline by-product	pH lab	pH half	Alk lab	Alk half
LD10 (oxide/hydroxide)	9.5	6.6	0.9	0.3
LKD10 (oxide/hydroxide)	9.0	6.9	0.3	6.3
GLD10	7.2	6.6	4.1	12.4
LM10	7.1	6.6	4.7	13.5
CFA10 (oxide/hydroxide)	6.7	5.1	0.5	0.0
FFA10 (oxide/hydroxide)	7.1	6.3	1.3	5.5
REF	2.9	2.6	0.0	0.0

Laboratory scale experiments compared with meso scale experiments are found in tab. 2. It becomes apparent that pH increases significantly when the amount of alkaline by-products are increased in the laboratory scale but not to the same extent in the meso scale. It is also apparent that increased alkaline addition of oxide/hydroxide materials gives a higher pH increase. This is most likely an effect of availability. In the laboratory scale experiments (shaken) all alkaline material is available for participation in the reactions. In the meso scale experiments the alkaline materials are layered and the available surface for reactions is much lower than the total amount. As the water percolates through the alkaline layers it reaches equilibrium with the solid phase and the thickness of the layer has no significance in the short term perspective. However, in the long term perspective the thickness will have a significant impact on the total neutralisation potential. Due to the generally lower pH in the meso scale compared to the laboratory scale the dis-

**Table 2** Comparison between lab scale (mixed) and meso scale (layered) experiments with respect to pH and alkalinity (meq/L). Numbers indicate the amount (%) of alkaline by-product. REF is only waste rock

Added alkaline by-product	pH lab	pH meso	Alk lab	Alk meso
FFA10 (oxide/hydroxide)	7.1	6.1	1.3	3.5
FFA50 (oxide/hydroxide)	9.7	6.7	0.9	3.7
CFA10 (oxide/hydroxide)	6.7	6.4	0.5	1.8
CFA30 (oxide/hydroxide)	9.7	6.4	0.8	2.1
LM10	7.1	5.7	4.7	5.8
GLD10	7.2	6.0	4.1	7.9
GLD30	7.7	5.8	2.6	3.9
REF	2.9	2.6	0.0	0.0

**Table 3** Comparison between half scale (mixed) and meso scale (layered) experiments with respect to pH and alkalinity (meq/L). Numbers indicate the amount (%) of alkaline by-product. REF is only waste rock

Added alkaline by-product	pH half	pH meso	Alk half	Alk meso
FFA10 (oxide/hydroxide)	6.3	6.1	5.5	3.5
CFA10 (oxide/hydroxide)	5.1	6.4	0.0	1.8
LM10	6.6	5.7	13.5	5.8
GLD10	6.6	6.0	12.4	7.9
REF	2.7	2.6	0.0	0.0

solution of carbonates is higher, resulting in higher alkalinity. Higher alkalinity is possibly a drawback as the total neutralisation potential is depleted at a higher rate.

Comparison between half scale and meso scale experiments is given in tab. 3. Carbonate materials (LM and GLD) have highest pH and alkalinity in the half scale experiments, and as well highest alkalinity in meso scale experiments. Nevertheless, pH in layered meso scale experiments is highest for the two fly ashes; actually, the worst performing system in mixed half-scale experiments (CFA10) is the best performer in layered meso scale experiments.

Measuring of flow rates in the different experiments showed no differences between carbonate or hydroxide materials in the mixed half scale experiments. For the layered meso scale experiments however, the flow rate was at least 2 times slower in hydroxide systems than in carbonate systems, thus indicating hard pan formation in layered fly ash amended systems. The higher pH for the fly ash systems in the layered experiments is therefore suggested due to longer contact time between the alkaline material and the acid leachate.

Trace elements immobilisations are shown in tab. 4. Reductions are strongly connected to pH and it becomes apparent that e.g. fly ash (CFA10) performs much better in layered meso scale than in mixed half scale, probably due to the formation of hard pans. On the contrary, carbonate materials (GLD10 and LM10) perform better when mixed, either in lab scale or half scale, than when layered in the meso scale.

**Table 4** Reduction of trace elements in per cent compared to the reference in the respective experiments. Grey shaded cells represent large differences in reduction between the different experiments

Comparison	Cu		Zn		Cd		Pb	
	lab	half	lab	half	lab	half	lab	half
<b>Comparison 1</b>								
LD10	99.7	100.0	100.0	100.0	99.9	99.9	99.7	98.0
LKD10	99.6	100.0	100.0	100.0	99.9	99.9	99.8	91.2
GLD10	100.0	100.0	99.3	99.7	99.9	98.8	96.6	99.9
LM10	99.9	100.0	99.1	100.0	99.9	99.9	97.8	99.0
CFA10	99.8	100.0	99.8	91.1	99.9	96.5	99.8	83.0
FFA10	100.0	100.0	99.3	99.9	99.9	99.4	98.7	98.3
<b>Comparison 2</b>	lab	meso	lab	meso	lab	meso	lab	meso
FFA10	100.0	98.5	99.3	73.2	99.9	81.4	98.7	98.8
FFA50	99.9	100.0	99.6	99.9	99.9	99.2	99.8	99.0
CFA10	99.8	99.9	99.8	99.9	99.9	99.7	99.8	98.3
CFA30	99.8	99.7	99.6	97.7	99.9	97.7	99.2	97.3
LM10	99.9	100.0	99.1	99.9	99.9	98.6	97.8	87.1
GLD10	100.0	98.7	99.3	93.2	99.9	93.9	96.6	76.3
GLD30	99.7	98.3	97.7	94.3	99.9	91.6	99.0	97.3
<b>Comparison 3</b>	half	meso	half	meso	half	meso	half	meso
FFA10	100.0	98.5	99.9	73.2	99.4	81.4	98.3	98.8
CFA10	100.0	99.9	91.1	99.9	96.5	99.7	83.0	98.3
LM10	100.0	100.0	100.0	99.9	99.9	98.6	99.0	87.1
GLD10	100.0	98.7	99.7	93.2	98.8	93.9	99.9	76.3

### Conclusions

The materials containing sources of alkalinity both from carbonate and hydroxide act as hydroxide materials (high pH and low alkalinity) when all material is available for neutralisation (shaken in lab) and as carbonate materials when mixed in stationary experiments.

Mixing in distinct layers favor fly ash amended systems, while homogeneous mixing of the materials favor carbonate amended systems.

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