Treatment of acidic and neutral metal-laden mine waters with bone meal filters

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Abstract

This study reports on mine water treatment with apatite containing bone meal filters. Bone meal has earlier been used to immobilize lead, copper and zinc from solution by formation of metal phosphates. Two different mine waters were tested, one neutral and one acidic. Trace elements, especially lead, was efficiently retained by the bone meal in the acidic system. In the neutral system pH was too high for apatite dissolution and the decrease in metal concentrations were thus only due to physical filtering.

Key words: lead, zinc, phosphate

Introduction

By-products as reactive materials to immobilize trace elements in metal contaminated waters are an interesting alternative to raw materials because it saves natural resources and reduces the costs (Hodson 2001; Sartz 2010). Bone meal mainly consists of hydroxyl-apatite $Ca_5[OH|(PO_4)_3]$, lime hydrate ($Ca(OH)_2$) and calcite ($CaCO_3$) (Cheung et al 2002) and has in earlier studies been proven to adsorb both metals and non-metals in contaminated waters. Bone meal immobilizes for instance lead, zinc and cadmium by formation of insoluble metal phosphates (Azab and Peterson 1989; Hodson et al 2001; Abdel-Halim and Shehata 2003; Frogner Kockum et al 2006; Sneddon et al 2006; Nwachukwu and Pulford 2008; Rieuwerts et al 2009) like for instance pyromorphite ($Pb_5(PO_4)_3OH$) (Xu and Schwartz 1994). Previous studies indicated that cadmium and lead was bound to the phosphate in apatite (ion exchange with calcium). In column studies by Frogner Kockum et al (2006) it was shown that lead was partly adsorbed to bone meal, and partly precipitated as lead phosphate.

Adsorption capacities of elements in bone meal follow the following order: Al>Zn>Pb>Cu>Cr>Cd>Co>Ni (Frogner Kockum and Bendz 2007). The ability to reduce concentrations of lead and zinc is especially relevant in mine water treatment, as these elements often are elevated in various mine waters. Earlier analyses of bone meal has shown that the effective surface area is 20.9 m^2/g (Frogner Kockum and Bendz 2007) and that the neutralization potential is largest between pH 4 and 6 (Frogner Kockum et al 2006). Modin et al (2011) however concluded that bone meal may have unsuitable hydraulic properties because of its small particle size (< 2 mm). This means that bone meal filters can stop working due to clogging before reaching the capacity for sorption.

Pilot-scale studies were performed at a waste deposit in Malmö, Sweden. Five tons of bone meal were treating water from an infiltration area of approximately 1°000 m^2 (Ahlquist 2006). Results from the pilot-scale study are shown in Table 1.

Table 1 *Reduction of trace elements in water from a municipal waste deposit. The metal contaminated water was treated with bone meal January 2005 – April 2006 (Ahlquist 2006).*

Trace Element	Reduction (%)
As	63
Cd	94
Cu	91
Hg	94
Pb	97
Zn	74

Methods

Neutral and acid mine waters

Filters were tested for two different mine waters: (1) acidic (pH 3.5-4) mine water with high concentrations of iron and aluminum (6 and 15 mg/L respectively) and (2) neutral (pH 7) mine water with lower concentrations of iron and aluminum (4 and 2 mg/L respectively). Concentrations of lead and zinc were 0.2 and 15 mg/L and 0.7 and 1.2 mg/L for the acidic and neutral mine waters, respectively. In the neutral mine water, lead and zinc were mainly associated with particles (> 0.4 µm). General parameters and major and trace element concentrations are shown in Table 2.

Filter design

Filters had a volume of 1 m^3 and an upflow filter design was used to achieve good contact between the water and the filter material (Figure 1). Before building of the filters some smaller percolation tests were made in order to decide how much of a coarser material that would be needed to obtain the desired hydraulic conductivity. The ratio of bone meal/coarser material was decided to be 20/80. The coarse material used in the filters was iron tailings from a nearby mine. Detailed availability tests on the iron tailings showed it was close to inert, i.e. leaching or addition of contaminants from the filter material was not expected.

The acid filter was in operation during October 2010 to October 2011 (except for the winter months November-March). Flow through the acid filter was 6 L/h to begin with (L/S 0-260 (liquid/solid ratio)) and was then increased stepwise to 60 L/h (L/S 260-1 500) and eventually 500 L/h (L/S 1 500-2 200). The neutral filter was in operation during October 2010 to June 2011, also during the winter months. Flow through the neutral filter was 5 L/h October to December (L/S 0-4 000) and 2.5 L/h January to June (L/S 4 000-10 000).

Samples were collected for analysis of pH, Eh, electrical conductivity, alkalinity/acidity, inorganic anions and major and trace elements at the outlet of the filters (outflow at the top).

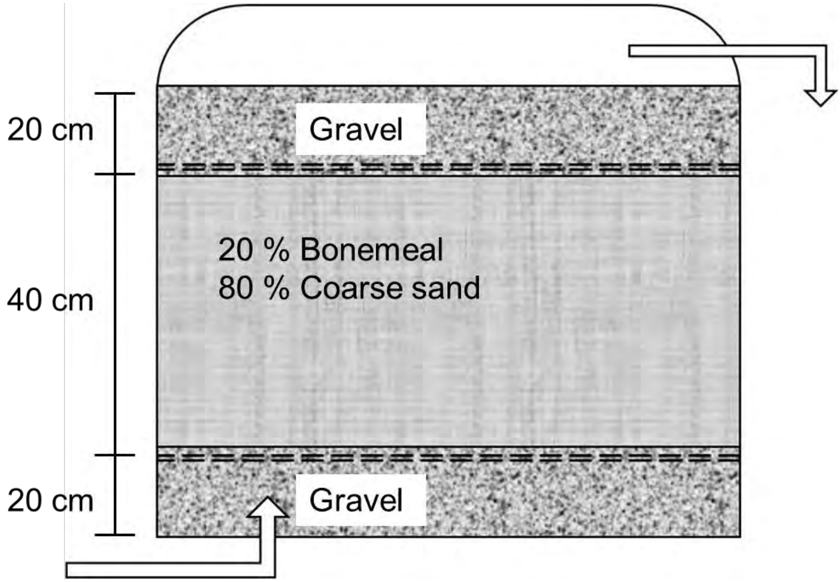


Figure 1 *Schematic of the filter design. Mine water was introduced from the bottom of the filter and samples were taken at the top (outflow).*

Analytical

Electrical conductivity, pH and redox potential were determined immediately after sampling using relevant electrodes. Alkalinity (end-point pH 5.4) and acidity were determined through titration with HCl and NaOH, respectively. Inorganic anions (chloride, fluoride and sulphate) were analysed with ion chromatography. Elemental analysis was performed using ICP-MS.

Results and Discussion

Neutral mine water

The trace elements of highest concern in the neutral mine water were lead and zinc, and the concentration of these metals needed to be reduced before the water could be released to the recipient. When passing through the bone meal filters, concentrations of lead and zinc decreased (Figure 2), but the levels were still unacceptably high to be directly released to recipient. Almost no changes could be seen when comparing general chemical parameters (pH, electrical conductivity etc) before the filter (mine water) to after the filter (Table 2) and the concentration decrease that occurred was probably due to physical filtration, i.e. the metal containing small particles were filtered in the filter.

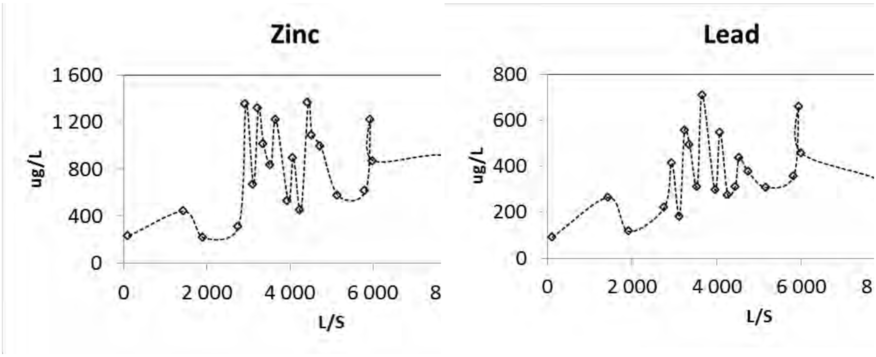


Figure 2 *Zinc- and lead concentrations in the neutral system plotted against L/S ratio. Average concentrations of zinc and lead in ingoing water are shown in Table 2.*

Table 2 *General parameters and major and trace elements at the inlet (ingoing water) and outlet (outgoing water) from the two different systems. The values are average values from the total test period for both filters.*

		Ingoing water		**Outgoing water**	
Parameter	**Unit**	**Acid system**	**Neutral system**	**Acid system**	**Neutral system**
pH	-	4.9	7.3	6.2	7.1
Electrical conductivity	µS/cm	890	270	960	300
Alkalinity	meq/L	0.0	0.6	0.6	0.7
Redox	mV	140	-26	-20	-40
Al	µg/L	15 400	2 000	6 000	1 300
Mn	µg/L	4 600	660	3 000	540
Fe	µg/L	6 000	3 700	3 100	2 300
Pb	µg/L	240	710	53	350
Zn	µg/L	15 000	1 200	5 900	800
Cd	µg/L	22	9.1	13	7.7
Cu	µg/L	1 950	5.7	630	4.7

Acid mine water

When the acid mine water passed the bone meal filter pH increased, alkalinity was added and the redox state changed from oxidizing to reducing conditions (Table 2). Figure 3 shows how concentrations of iron, copper, lead and zinc varied during the entire test period (plotted against L/S ratio). The bone meal filter efficiently reduced concentrations of copper, lead and zinc up to approximately L/S 1 000, where after the concentrations increased (Figure 3). Also, concentration of iron started to increase at the same time. This could imply that the capacity of the filter was exceeded at around L/S 1 000.

The mechanism for immobilization of the trace elements would either be sorption onto secondary iron- and aluminum oxy(hydr)oxides, precipitation as metal phosphates – or carbonates or a combination of sorption and precipitation. Bone meal was less efficient as a zinc scavenger, compared to for instance lead. This was probably due to the pH which was a little bit too low to fully immobilize zinc by sorption and possibly also less likelihood of zinc phosphate formation than lead phosphate formation.

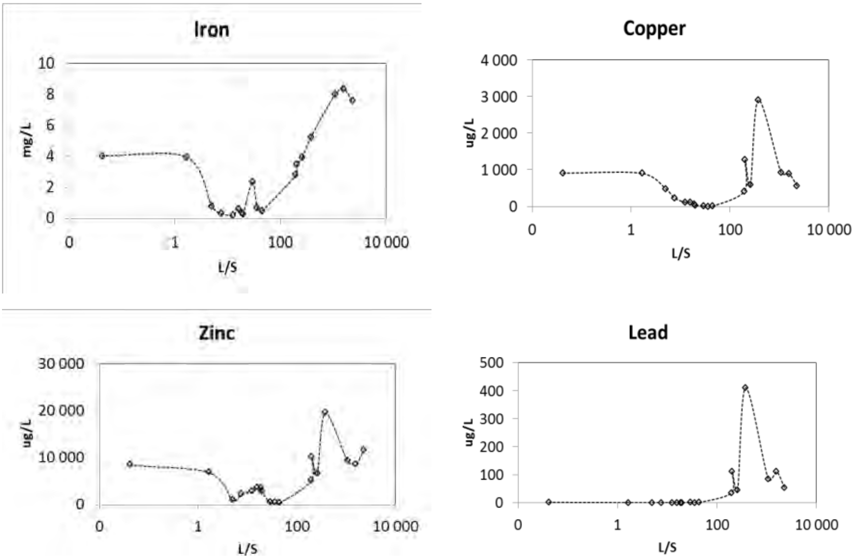


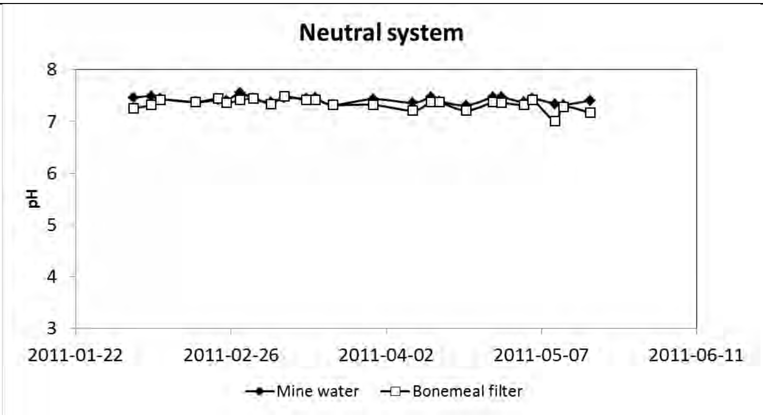
Figure 3 *Iron-, copper-, zinc- and lead concentrations in the acid system plotted against L/S ratio. Average concentrations of the metals in ingoing water are shown in Table 2.*

Comparison between acid and neutral filters

Figure 4 shows variation in pH in ingoing respectively outgoing water for the two filter systems. The large difference in trace element removal between the two systems (acid and neutral) was probably largely dependent on pH, as the high pH in ingoing water in the neutral system did not allow for any dissolution of phosphates from the bone meal and consequently no possibilities for metal phosphate formation. Additionally, the contaminants (lead and zinc) in the neutral mine water were mainly associated with particles (more than 80 %), which makes sorption onto iron- and aluminum phases more difficult.

Table 3 *Removal rate of the trace elements lead, zinc and copper for the two filters. Calculations for L/S and removal rate are based on the mass of bone meal in the filter. The concentration of copper of incoming water in the neutral system was too low to allow any removal rate calculations.*

Element	**Acid water** L/S = 2 280	**Neutral water** L/S = 10 000
Pb	0.25 g/kg bone meal	2.50 g/kg bone meal
Zn	10.6 g/kg bone meal	2.50 g/kg bone meal
Cu	1.90 g/kg bone meal	-



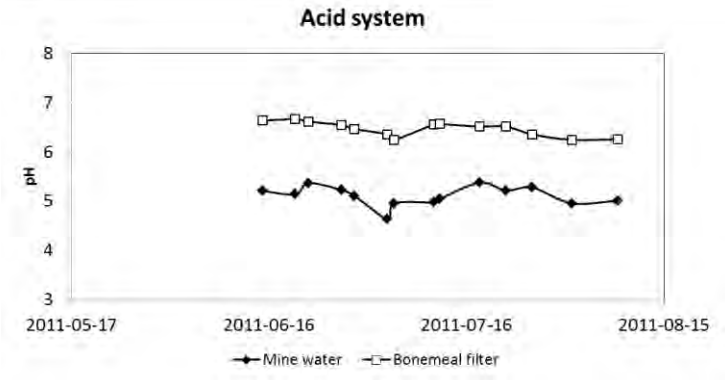


Figure 4 *pH in ingoing mine water and out from the bone meal filters. Top figure shows the neutral system and bottom figure shows the acid system.*

Removal rate for lead, zinc and copper was calculated, the results are shown in Table 3. For lead and zinc, an approximate theoretical capacity of 10 g metal/kg bone meal can be expected, for copper the same figure is 1 g Cu/kg bone meal (Frogner Kockum et al 2006; Frogner Kockum and Bendz 2007).

For the neutral filter, the removal rate was lower than theoretical calculations for both lead and zinc. This was however not surprising, as the lower trace element concentration reduction in the neutral system was not a consequence of exceeded capacity for the bone meal, but more likely due to other factors (high pH in ingoing water and contaminants mainly associated with particles). In the acid system, theoretical capacity was exceeded for copper, while zinc removal was as what would be expected. The maximum (theoretical) removal rate for lead was not reached in the acid system.

Conclusions

Lead and zinc concentrations were reduced with 100 % and 86 % respectively for the acid system, but only with 50 % (lead) and 33 % (zinc) for the neutral system. Lead was efficiently immobilized in the acidic system by a combination of apatite dissolution and subsequent formation of lead phosphate as well as sorption onto iron and aluminum precipitates.

Concentration of zinc was reduced in the acid system, but still rather high. This could be due to a combination of less efficient immobilization of zinc by phosphates, as compared to lead, and also the pH that is a little bit too low to completely immobilize zinc by sorption onto precipitated iron- and aluminum phases.

In the neutral system pH in ingoing neutral mine water was too high for phosphate dissolution from the bone meal. The contaminants were mainly associated with particles, which also affected sorption onto iron- and aluminum phases. Trace element removal was probably largely due to physical separation of metal containing particles in the filter.

Acknowledgements

Thanks to Erik Larsson, Bergskraft Bergslagen, for field assistance.

References

Abdel-Halim SH, Shehata AMA (2003) Removal of lead ions from industrial waste water by different types of natural materials. Water Research 37:1678-1683

Ahlquist M (2006) Utredning av benmjöls förmåga att reducera tungmetaller i lakvatten vid avfallsanläggningen Spillepeng i Malmö. SWECO VIAK AB, 1230573 000, 13pp (in Swedish)

Azab MS, Peterson PJ (1989) The removal of cadmium from water by the use of biological sorbents. Water Science Technology 21:1705-1706

Cheung CW, Porter JF, McKay G (2002) Removal of Cu(II) and Zn(II) ions by sorption onto bone char using batch agitation. Langmuir 18(3):650-656

Frogner-Kockum P, Benz D, Suèr P (2006) Kapacitet av benmjöl som sorptionsfilter. Statens Geotekniska Institut, SGI, 2-0604-0254, 11 pp (in Swedish)

Frogner-Kockum P, Bendz D (2007) Benmjöls kapacitet som filtermaterial för deponitillämpning. Statens Geotekniska Institut, SGI, 2-0705-0324, 11 pp (in Swedish)

Hodson ME, Valsami-Jones E, Cotter-Howells JD, Dubbin WE, Kemp AJ, Thornton I, Warren A (2001) Effect of bone meal (calcium phosphate) amendments on metal release from contaminated soils – a leaching column study. Environmental Pollution 112:233-243

Modin H, Persson K, Andersson A, van Praagh M (2011) Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines. Journal of Hazardous Materials 189: 749-754

Nwachukwu OI, Pulford ID (2008) Comparative effectiveness of selected adsorbant materials as potential amendments for the remediation of lead-, copper- and zinc-contaminated soil. Soil Use and Management 24(2):199-207

Rieuwerts JS, Austin S, Harris EA (2009) Contamination from historic metal mines and the need for non-invasive remediation techniques: a case study from Southwest England. Environmental Monitoring and Assessment 148:149-158

Sartz L (2010) Alkaline by-products as amendments for remediation of historic mine sites. Örebro Studies in Environmental Science 15, PhD Dissertation, Örebro University

Sneddon IR, Orueetxebarria M, Hodson ME, Schofield PF, Valsami-Jones E (2008) Field trial using bone meal amendments to remediate mine waste derived soil contaminated with zinc, lead and cadmium. Applied Geochemistry 23:2414-2424

Xu YP, Schwartz FW (1994) Lead immobilization by hydroxyapatite in aqueous solutions. Journal of Contaminant Hydrology 15(3):187-206