Effects of calcium on sorption and flocculation of trace metals in leachate from mine waste deposits

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Abstract

At present, treatment of mine waste drainage includes extensively liming. The main reason for this treatment is to raise pH, which is well known to be favourable for precipitation of sparingly soluble trace metal compounds as well as for sorption of cations. The effect of calcium on the processes of metal retention is less known but it could be an important factor in especially the flocculation of metal containing particles.

The development of particles in water containing sulphate, oxidised iron and humic acids in field-like proportions with variable pH, calcium concentrations and ionic strength was measured. The particulate matter content of the samples increased with time, as well as the concentrations of As, Pb, and Cu in the particulate fraction.

The addition of calcium increased the formation of filterable particles in simulated natural water within the studied pH-range. Calcium has a greater effect than sodium. Calcium increased the particle bound amount of arsenic, copper and lead but not zinc.

Introduction

In order to decrease metal loads from mining activities on the environment, processes that favour the removal of metals from the water phase should be studied and the conditions for their occurrences promoted. It is of interest if processes such as co-precipitation, sorption and subsequent sedimentation could be used and incorporated in a passive treatment system as a way to polish mine waste effluents, and as a way to decrease the affected distance in the recipient water from the mine.

At refining plants and mines for sulphidic ore the most important treatment method for the effluent water is liming. In order to neutralise the acid drainage, lime or limestone is used to increase the pH. The high cost and demands for maintenance during extended periods of time mean that this method is not sustainable. The effect of pH on precipitation/co-precipitation/sorption of metals has been studied in numerous contexts including water from mine waste. A high pH will cause a precipitation of sparingly soluble solid trace metals. Precipitation of (oxy)hydroxides of iron in oxygenated waters is fast also at neutral pH-values and co-precipitation of trace metals onto the (oxy)hydroxides may be the result.

Perhaps more emphasised or studied is the sorption of trace metals onto the surfaces of the formed iron particles. Since iron is a major component in drainage from acidic mine waste an increase in pH that is sufficient to precipitate iron will often be sufficient for the removal of trace elements from the water phase. In this way withdrawal of trace metals from the soluble phase is possible without adjustment of pH to such high levels that will give adverse effect on the environment.

Sorption itself is not always sufficient for metal removal from natural waters. The sorption process must take place at a stationary surface. If this is not the case (i.e. for sorption onto particles in running water), the initial sorption process must be followed by a flocculation in order to create particles of a size and density that can make them prone to sediment and thus be removed from the mobile phase.

At closure of a mine site or a refining site other methods than liming have been proposed, such as dry cover or water cover with the purpose of decreasing the air and water flow through the waste and thereby decrease both the weathering and the transport of effluents. These methods are considered to be sufficient to keep the release of metals and acid at

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acceptable values. Such measures may include small doses of lime in the solid waste but the removal of metals should be sufficient without liming of the effluent water. Other factors such as changes in ionic strength and calcium concentrations in the effluent water, could affect the retention of metals in e.g. wetlands or ponds.

Increased calcium concentrations may increase the formation of particles and increase the size of the particles formed. Sholkowitz (1976) and Sholkowitz and Copland (1981) showed that the increased salinity increases the trace metal removal by flocculation of trace metal-DOM (dissolved organic matter) complexes.

Tipping and Higgins (1982) showed that iron in the presence of DOM stabilises colloids as small iron particles coated with organic material. The stabilising of hematite colloids by DOM (fulvic acids) have been confirmed by Ledin et al., (1993). Since calcium may bind to DOM, a high calcium concentration might therefore prevent the forming of DOM-stabilised colloids and instead result in a formation of calcium induced formation of particles with a size sufficient for them to sediment. Calcium may also compete with other metals for binding sites on solid surfaces and DOM (Cowan et al. 1991; and Tipping, 1993). Binding of calcium to DOM is weak (Marinsky et al. 1999) and must thus be present in large excess, to be able to compete successfully for binding sites.

At present, calcium is used in mine water treatment basically because of the effect it has on raising the pH. But there might also be a secondary effect of liming caused by the overall effect of calcium on the scavenging of trace metal containing particles. By measuring the incorporation of trace metals in the particulate the combined effects of a calcium addition may be determined. In order to be able to increase the retention of metals and prevent their transport downstream it is important to be able to tell what mechanism that is acting.

Aim

The aim of this research is to study the effect of calcium additions on the dissolved/particulate fraction ratio for the elements Cu, Zn, Pb and As and the transitions to a sedimenting phase. The processes with which metals are associated to the particulate phase are discussed.

Hypothesis

An increase in calcium concentration generates a corresponding increase in the growth of particles. Calcium has a greater effect on formation and growth than other salts. Calcium increases the particle bound metal fraction for the elements studied.

Material and methods

In order to prevent the contamination of samples all equipment was acid washed with a mixture of hydrochloric acid and nitric acid. Rinsing was done with running Milli-Q water. For some material, like the filters, warm 0,2 % nitric acid was used in order not to disturb the filter performance. This procedure was also performed on containers for test solutions and for mixing and measuring devices as an extra washing step. For a complete description of washing procedures see Sjöblom et.al (2003). Simulated river water resembling concentrations in the receiving water from a former refining site was mixed to yield the following concentrations.

Table 1. Measured average concentrations of main constituents in the mixed waters (mg/L) for fractions greater than 0,4 μm.

Sample	Ca	Na	Fe	SO_4*	TOC	pH
A	69,87	12,31	1,06	167,5	3,43	6,5
B	70,65	12,25	1,03	169,3	3,62	5,5
C	7,52	11,93	1,08	18,0	3,53	6,5
D	7,40	12,01	1,06	17,7	3,55	5,5
E	-	101,60	1,08	187	4,17	6,5
F	-	12,07	1,09	-	4,39	6,5

* Calculated concentration.

The experimental set-up varied the pH and calcium concentrations by one order of magnitude. Sample A had a calcium concentration of 2,0 mmol/L and a pH of 6,5; sample B calcium of 2,0 mmol/L and a pH of 5,5; sample C a calcium concentration of 0,2 mmol/L and pH of 6,5 and sample D a calcium concentration of 0,2 mmol/L and a pH of 5,5. All concentrations of trace elements were kept identical and were analysed at the start of the experiment, giving concentrations of Zn 265 μg/L, Cu 51 μg/L, As 3.6 μg/L and Pb 1.1 μg/L. Sample E was prepared to simulate a

water without calcium, but with the same ionic strength and same pH as sample A. Sample F contained no calcium and had a lower ionic strength than sample A. Replicates of all samples were prepared.

All chemicals were prepared from chemicals of p.a. quality, the TOC content was prepared from Aldrich Humic substances and the resulting TOC-values were recorded. The prepared solutions were buffered with $NaHCO_3$ giving a resulting concentration in the solution of about 2,0 mM. For the adjustment of pH sulphuric acid or sodium hydroxide were used. Stock solutions of humic substances, trace metals, iron and calcium sulphate/sodium sulphate were prepared individually. For the iron solution a stock solution of 1000 mg/l as Fe (III) (soluble at this concentration) was prepared, and 2 ml was diluted to 100 ml and left for 24 h, starting the precipitation of iron hydroxides. Parallel to the preparation of the iron solution, 100 ml of the humic stock solution and 100 ml of the trace metal solution were added to 1000 ml of Milli-Q water and shaken vigorously. This solution was then left for 24 h in order to make the metal ions react with the humic substances. After this time the iron solution together with 500 ml of calcium/sodium sulphate stock solution were added to the trace metal/humic substance solution and mixed after being diluted to a total of 2000 ml. pH was adjusted on separate subsamples prior to the preparation of each sample in order not to contaminant the samples with the pH-electrode, and acid or base corresponding to the sample volume was then added to the sample.

The samples were filtered five times with exponentially increasing time lags between two consecutive filtrations (1 h, 3 h, 8 h, 24 h and 48 h). At the start of each filtration, samples were shaken vigorously and 350 – 400 ml was transferred into the filtration containers. Pre-weighted filters were placed in the filter holder, and the filters were conditioned by filtrating 5 ml of 0,2 % of nitric acid followed by 20 ml of Milli-Q water. After filtration filters were placed in an exsiccator with vacuum to dry for a week.

A sequential filtration was performed with pore sizes of 1,2 and 0,4 µm. A volume of each fraction was acidified with nitric acid for preservation and analysis with AAS and ICP-MS, and after filtration through 0,4 µm a fraction was stored and kept cool for the determination of TOC-analysis. At the same time pH was measured.

Results and discussion

Particle formation

In this study, only data obtained from analyses of the filtration with the greatest pore size (1,2 µm) is reported. The composition of the particles on the filters was analysed as the difference between total concentration in the samples and the filtrate. The particles consisted mainly of Ca and TOC (total organic carbon) and to some extent Fe. When the effect of Ca was ignored, the rest of the solid material on all particle fractions above 0,4 µm was similar; TOC 65–68 %, Na 10–13 % and Fe 20–22 %. A thermodynamic calculation of the solubility of species in the solution was done with MINTEQA2. Ver. 4.0 and saturation with hematite was found for all solutions. No other species exceeded the solubility limit. The thermodynamic calculations showed that the result of oversaturation with respect to iron would yield an iron concentration in the solid phase of about 9 µg/L. This is consistent with the results obtained from solutions containing no calcium, but slightly or much less than the amount that precipitated in the samples with low and high calcium concentrations respectively. In figure 1a and b, the formation of particulate matter as a function of time is described for the different solutions used in the study.

The particle formation is generally higher for high calcium concentrations than for low. A higher pH seems to have a negative effect as seen in figure 1a. This is accordance with Ledin et al. (1993) who found that DOM stabilises colloids at pH-values of about 6 and higher. In samples without calcium addition the particle formation does not display the same sharp initial increase as in solutions with calcium (figure 1b).

Effect of ionic strength.

In figure 2 the particle formation is plotted as a function of ionic strength. It can be seen that the particle formation is increasing with ionic strength, and also that the changes over time are small for the calcium-containing solutions.

However when calcium is changed to sodium the divergence is evident, implying that not only ionic strength affects the formation of particles.

Effect of calcium

It is evident that calcium plays an important role in the incorporation of trace metals in a particulate fraction. Contrary to particle growth a greater increase of the particulate phase occurs at a higher pH as shown in figure 3a-e below for particle bound metals >1,2 µm.

The samples with high calcium concentration clearly contain higher amounts of copper, lead, arsenic and organic carbon bound to particles than the samples with ten times lower concentration. The increase can be as much as 20-33 % for the total organic carbon contents, 42-172 % for arsenic, 30-154 % for copper and 41-147 % for lead at 48 hours after sample preparation. The average values for particulate metals for high and low calcium concentrations after 48 h are shown in table 2 below.

Table 2. Particulate bound trace metals after 48 h in the fraction greater than 1,2 µm as % of total concentrations.

	TOC*	As	Cu	Pb	Zn	Ca
High Ca	~ 75	~ 88	~ 70	~ 73	~ 12	~ 6
Low Ca	~ 59	~ 51	~ 48	~ 64	~ 16	~ 8
Na	~ 31	~ 32	~ 17	~ 47	~ 21	~ 74

* Fractions > 0,4 µm.

In general, the levels of both particulate matter and trace metals (except Zn) in the sodium sulphate sample are much lower than in the calcium sulphate samples. The sodium ion has not the same positive effect on particle growth as the calcium ion.

The sorption and coagulation processes basically regulate the incorporation of trace metal ions in the particulate phase. By comparing the changes of a relative trace metal content in the solid particulate phase for all metals, the dominating process can be determined. If concentrations in the solid phase (particles) increase then sorption should be the dominating process. On the other hand, if the concentrations of trace metals in the solid phase are constant and the amount of particulate matter at the same time increases then flocculation is the dominant process. In figures 4a and b examples of the different behaviour for As and Cu is illustrated.

Initially, the arsenic – mass ratio, especially in samples treated with a high calcium dose, increased tremendously over a short period of time (figure 4a). This can be attributed to the co-precipitation with hematite particles that takes place, or adsorption onto surfaces. In a longer perspective, and all the time for copper (figure 4b), the ratio was fairly constant, indicating coagulation as being the major mechanism.

Zinc has somewhat different chemical properties than other metals in the study and sorption at the pH-values used in the experiment is lower. Several studies shows that the adsorption of Zn (and Cd) are lower in natural (Hamilton-Taylor 1997), or mine drainage waters (Håkansson et al. 1989; Webster et al.1998) than e.g Pb and Cu. It seems from the figure as if the initial sorption of Zn onto particles is restrained by high calcium concentrations and especially at low pH.

Conclusions

When liming is terminated at mining sites it is necessary to predict the effects of a changed composition of main constituents as well as the future pH-development and their effect on metal transport.

The addition of calcium increased the formation of filterable particles in simulated natural water within the studied pH-range. Calcium has a greater effect than sodium. Calcium increased the particle bound amount of arsenic, copper and lead but not zinc.

In order to optimise the design of treatment facilities constructed or natural it is important to know the dominant mechanism for metal retention. This may influence the type of system that should be constructed. Large immobile solid surface areas should be exposed to all parts of the running water if sorption is the dominating process. If flocculation is the dominant process, then particle formation could be facilitated by introduction of e.g. iron rich ground water or mine water.

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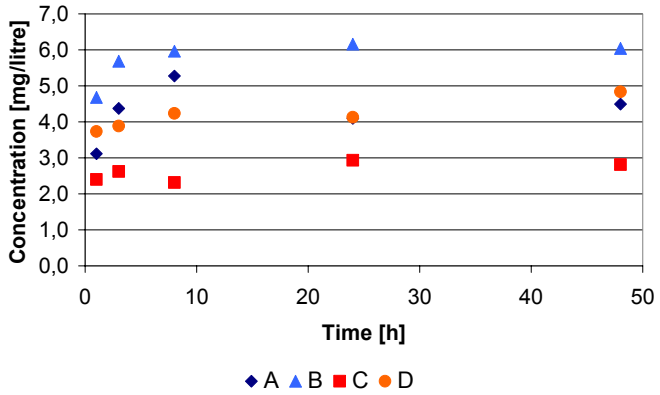
a)



b)

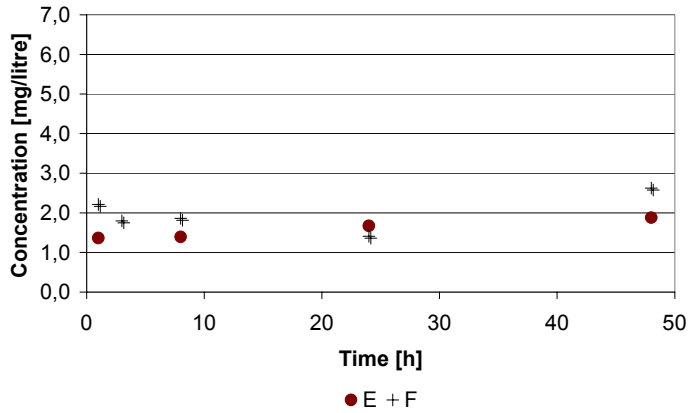


*Figure 1. Growth of particulate matter in samples with **a)** varying calcium concentration and pH-value (A-D), and **b)** without calcium addition (E-F). Filtration through 1,2 µm filter.*

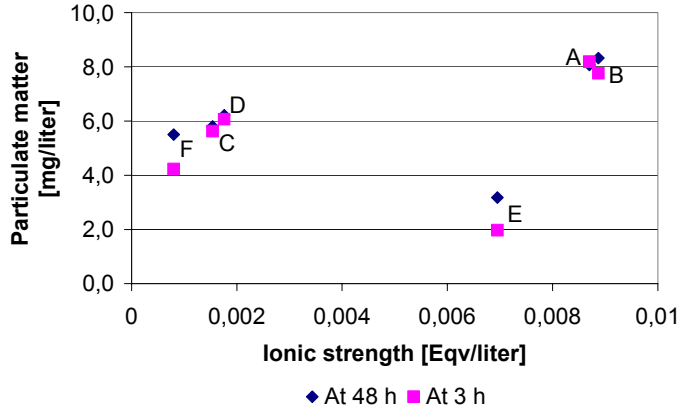
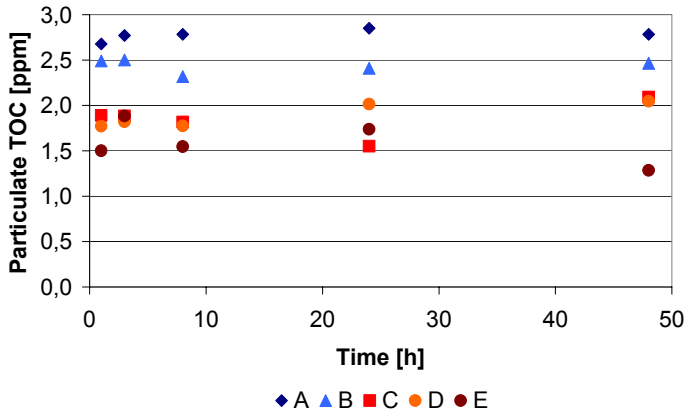
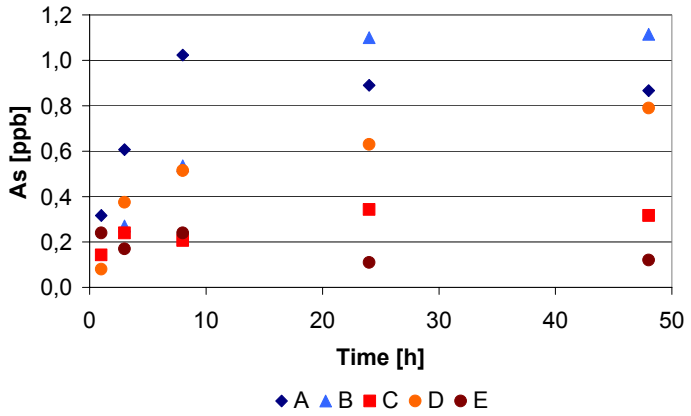


Figure 2. The effect of ionic strength on particle formation. The capital letters in the figure denote the treatment (A-F).

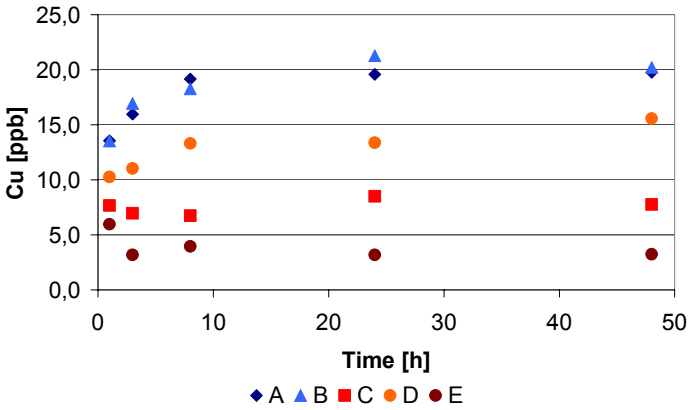
a)


Particulate TOC [ppm]
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
10
20
30
40
50
Time [h]
A B C D E

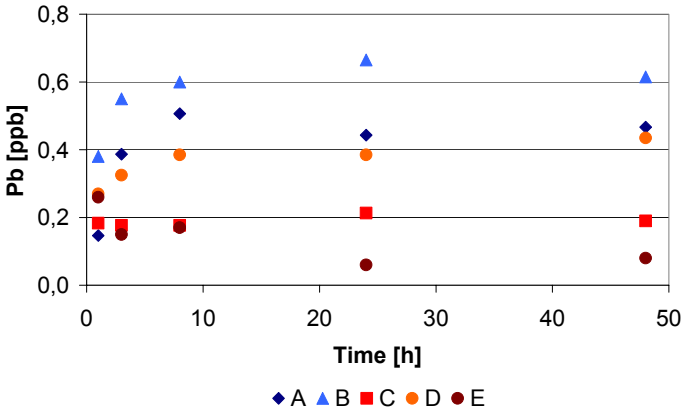
b)


As [ppb]
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
10
20
30
40
50
Time [h]
A B C D E

c)


Cu [ppb]
25,0
20,0
15,0
10,0
5,0
0,0
0
10
20
30
40
50
Time [h]
A B C D E

d)



e)

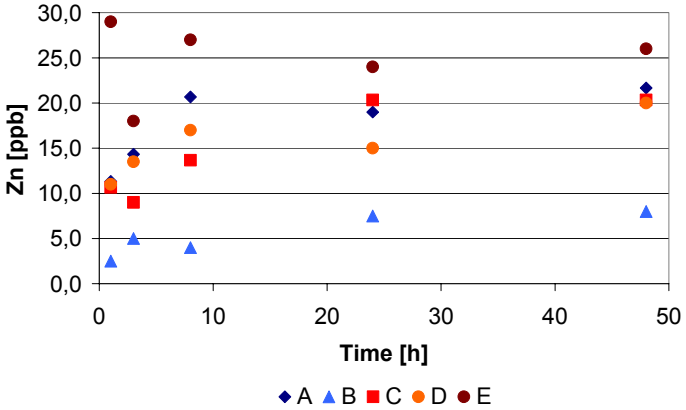
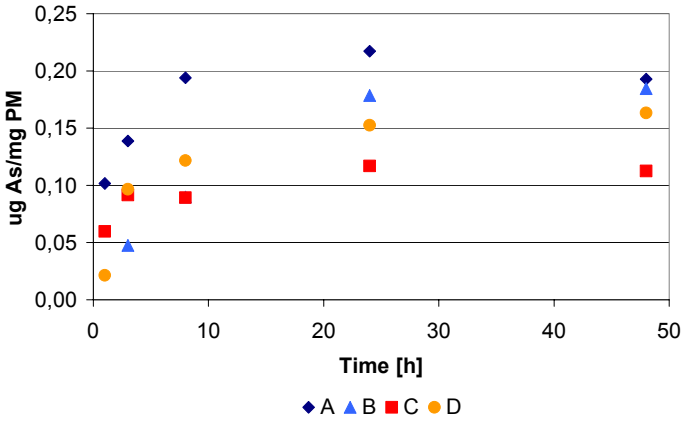


*Figure 3. The effects of calcium on the formation of particulate fractions for **a)** organic carbon, i.e. humic substances, **b)** arsenic, **c)** copper, **d)** lead and **e)** zinc. Capital letters stand for treatment (A-E).*

a)



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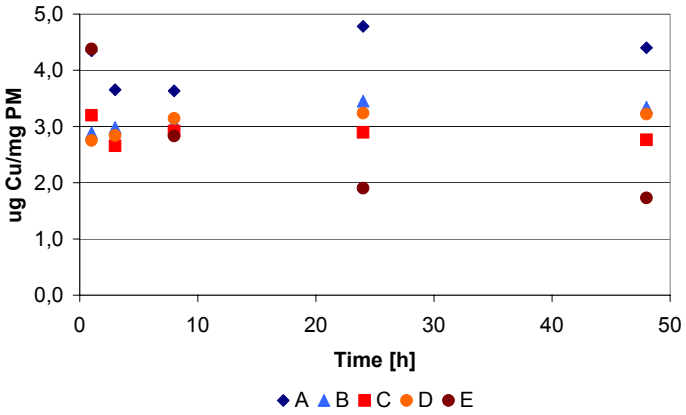

*Figure 4. Relation of particle bound **a)** arsenic and **b)** copper to particulate matter for each treatment (A-E).*