Stabilization of acid generating waste rock with fly ash – immobilization of arsenic under alkaline conditions

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Abstract A fly ash was used to increase pH and decrease arsenic leaching from an acidic mine waste. Both the amended system as well as the control system was leached with ultra pure water. pH in the control increased from 1.7 to 2.7 at the end of the experiment while the pH in the amended system decreased from 12.6 to 11.5. Compared to the control the initial concentrations of arsenic decreased with almost three orders of magnitude in the amended systems. A combination of co precipitation with iron and calcium arsenate precipitation were identified as the major arsenic immobilization mechanisms.

Key Words wood ash, arsenic, acidic mine waste

Introduction

Due to the fact that arsenic is commonly found as an anion (AsO_4^{3-}) in the environment sorption to surfaces decrease at alkaline pH. It is therefore often considered dangerous to alkalise a waste material containing high concentrations of arsenic. Arsenic is on the other hand known to form several insoluble minerals (arsenates) with for instance calcium, barium and iron.

An experiment was thus performed to test the possibility to use an alkaline waste material to both increase pH and decrease arsenic leaching from a highly acidic mine waste. As the alkaline material a wood ash known to contain high available concentrations of both calcium and barium was chosen.

Methods

A highly acidic mine waste (pH 1.7) leaching approximately 200 mg/L of arsenic at a liquid/solid (L/S) ratio (w/w) of two was mixed with ash (50%) in order to increase pH and reduce arsenic leaching. A total amount of 20 g solid material was used in the experiments; the controls consisted of only mine waste and the amended samples consisted of 10 g mine waste and 10 g wood ash. Both the amended systems and the control systems (in duplicates) were run in sequence with ultra pure water as the leachant. Until L/S 18 was reached the incremental steps were 2 and then 10 until L/S 58 was reached. L/S 58 corresponds to over 900 years assuming a waste pile 3 m high and a yearly runoff of 300 mm.

After 24 h on an end-over-end shaker the systems were centrifuged (30 min at 20 000 g) and the water phase filtered (0.40 µm). Wood ash was also leached at L/S 2 and 10 in order to determine the concentrations released from it. At every sampling occasion pH, electrical conductivity and alkalinity (endpoint pH 5.4) was measured immediately after sampling.

Sulphate was determined with capillary zone electrophoresis and elements with ICP-MS. Saturation estimates were performed using PHREEQC and the results were expressed as saturation index (SI), where -0.5 to 0.5 were considered to be in equilibrium with the relevant solid phase. Solid phases such as $Ba(S_{0.77}Cr_{0.23})O_4$, $Ba(S_{0.96}Cr_{0.04})O_4$ (Fällman 1997), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$; log K_{sp} -112), barium arsenate ($Ba_3(AsO_4)_2$; log K_{sp} -23.53) and barium hydrogen arsenate ($BaHAsO_4 \cdot H_2O$; log K_{sp} -5.60; Zhu et al. 2005) were added to the database. Solubility constants for the barium arsenates are much lower than the ones found in the original database.

Results and discussion

Initial pH in the controls were around 1.7 compared to the amended samples with pH around 12.6, indicating equilibrium with portlandite ($Ca(OH)_2$; SI -0.6). This is no surprise due to the large amount of alkaline material. During the experiment pH increased to 2.6 in the controls and decreased to 11.5 in the amended systems. As a consequence of the large amount of wood ash, concentrations of Na, Sr, K, Ca, Rb and Ba increased significantly in the amended systems.

Concentrations of Na, Sr and Ca increased approximately 170—190 times while the concentrations of, for instance, K and Rb increased with over three orders of magnitude. Calcium concentrations, for instance, were initially around 1 000 mg/L in the amended systems compared to around 5 mg/L in the control systems. In the amended systems calcium concentrations decreased to around 100 mg/L and were probably controlled by a combination of calcite ($CaCO_3$) and gypsum ($CaSO_4$). Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) is also a mineral commonly found to control calcium during these conditions (Piantone et al. 2004). Saturation index for ettringite is initially super saturated and at equilibrium at pH below 12. Ettringite is a fine grained mineral capable of sorbing or substitute mainly anionic trace elements. Magnesium concentrations, however, decreased as a result of equilibrium with brucite ($Mg(OH)_2$) in the amended system.

Dissolved barium concentrations seem to be controlled by a combination of witherite ($BaCO_3$) and barite ($BaSO_4$) in the amended systems and by barite in the control systems.

Concentrations of iron was very high in the control systems (2 000—3 000 mg/L) indicating a reductive dissolution of the secondary minerals in the mine waste. Melanterite ($FeSO_4{\cdot}7H_2O$) might, however, act as solubility control for iron(II) after the dissolution. In the amended systems the dissolved iron concentrations were at least three orders of magnitude lower and, according to PHREEQC, in equilibrium with ferrihydrite ($Fe(OH)_3$).

Trace element concentrations in the amended systems were reduced for Co, Ni, Cu, Zn, As, Cd and Pb. Reduction in the amended systems compared to the control systems can be found in tab. 1. Solid phases possibly controlling the trace element concentrations in the amended systems were $Cu(OH)_2$ and $Pb(OH)_2$ due to the very high pH. Corresponding carbonates were found to be sub saturated. Other contributing factors for the immobilization of trace elements were the high pH favourable for sorption even though pH exceeding 12 is known to reduce sorption due to the formation of dissolved hydroxy complexes (e.g. $Pb(OH)_3^-$).

However, two trace elements increased their concentrations significantly during the experiment. Chromium and molybdenum concentrations increased approximately four and 100 times, respectively, in the amended systems compared to the control systems. Initial concentrations in the amended systems were 130 µg/L for chromium and 2 200 µg/L for molybdenum. Since both elements preferably are found as anions it is possible that they have desorbed from the mine waste when the pH increased. A more likely explanation is, however, that they are from the wood ash itself (tab. 2). Geochemical calculations indicated that both chromium and molybdenum concentrations in the amended systems were controlled by solid phases. Likely solid phases for chromium were a mixed barium sulphate chromate analog (e.g. $Ba(S_{0.77}Cr_{0.23})O_4$ (SI 0.5) or $Ba(S_{0.96}Cr_{0.04})O_4$ (SI 0.8)). It is, however, more likely that the hexa valent chromium from the ash has been reduced to Cr(III) by the ferrous iron from the mine waste according to equation 1 (Fendorf and Li 1996).

$$3\ Fe^{2+} + HCrO_4^- + 7\ H^+ \rightarrow Cr^{3+} + 3\ Fe^{3+} + 4\ H_2O \quad (1)$$

Table 1 *Reduction (%) in trace element concentration in the amended systems compared to the untreated control at the first and last sampling as well as total trace element reduction (%) during the whole experiment*

	Conc. reduction (%) first sampling	Conc. reduction (%) last sampling	Total mass reduction (%)
SO_4^{2-}	61	-87	17
Fe	100	100	100
Co	100	99	100
Ni	87	99	93
Cu	100	97	99
Zn	98	96	96
As	100	-14	99
Cd	98	62	59
Pb	-1	83	33

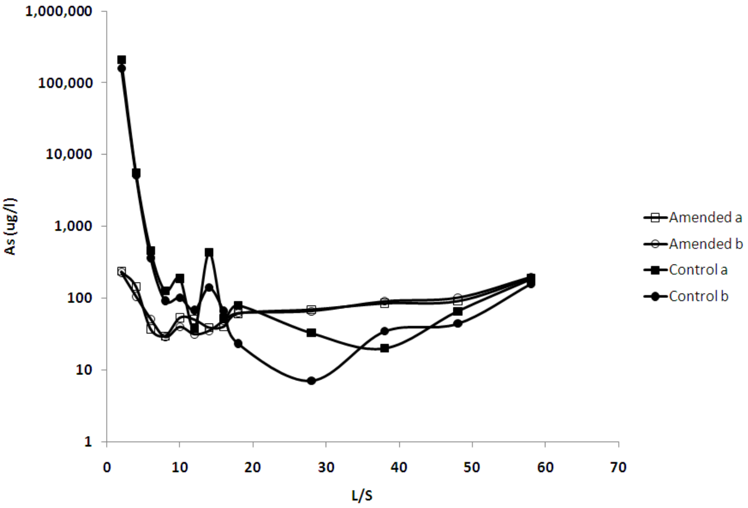

Figure 1 *Concentrations of arsenic in the amended systems (open symbols) and the control systems (filled symbols). Note the logarithmic scale*

Tri valent chromium was then precipitated as the amorphous hydroxide ($Cr(OH)_3$; SI around 0 for the amended systems). This was partly confirmed by the fact that the chromium concentrations found in the amended systems were much lower than the concentrations found in the pure ash water (tab. 2). Molybdenum concentrations were most likely controlled by $CaMoO_4$ (SI decreased from 0.5 at L/S 2 to -1.5 at L/S 58). It was interesting to note that the concentrations of molybdenum were much higher in the amended systems than in the original ash water (tab. 2). This was most likely due to lower concentrations of dissolved calcium concentrations in the amended systems compared to the pure ash water leading to increased $CaMoO_4$ dissolution.

Dissolved arsenic concentrations decreased with almost three orders of magnitude in the amended systems compared to the control systems (fig. 1). The extremely high arsenic concentrations in the control systems were probably due to a reductive dissolution of a complex iron(III) phase. That correlation between log Fe and log As was very strong (r^2 0.80) in the control systems was supporting the hypothesis. This large amount of arsenic was also rapidly being washed from the mine waste as the concentrations rapidly decreased and was only around 150 µg/L at L/S 10 (tab. 2). Geochemical calculations indicated that the dissolved arsenic in the control systems were found entirely (7 orders of magnitude higher As(III) concentrations than As(V) concentrations) as arsenite (As(III)) during the experiment (calculations performed between pe -4 and 4). Dissolved iron was found as ferrous iron according to the calculations (between pe -4 to 4).

Geochemical calculations indicated that arsenic in the amended system was found entirely (11 orders of magnitude higher As(V) concentrations than As(III) concentrations) as arsenate

Table 2 *Element concentrations (µg/L) at L/S 2 and 10 for the amended systems, the control systems and for wood ash only*

	Mine waste		**Wood ash**		**Amended systems**	
	L/S 2	**L/S 10**	**L/S 2**	**L/S 10**	**L/S 2**	**L/S 10**
Ca	4 000	2 300	1 900 000	990 000	1 100 000	88 000
Fe	2 600 000	30 000	23 000	5 700	580	48
As	180 000	150	82	16	230	47
Cu	67 000	2 700	190	64	110	76
Cr	38	2.2	1 100	310	130	61
Mo	20	3.9	1 100	480	2 200	660

(As(V)) during the experiment (calculations performed between pe -4 and 4). Presence of As(V) and Fe(III) in the amended systems indicated more oxidized conditions from the ash water and addition of oxygen cannot be ruled out. In the amended systems arsenic was probably retained by a combination of different mechanisms. One was the massive amount of precipitating or reprecipitating iron (as iron(III)hydroxide) co precipitating the dissolved arsenic again. Another mechanism was the solubility control enforced by the high concentrations of calcium and barium.

Geochemical calculations initially indicated equilibrium or super saturation with respect to $Ca_3(AsO_4)_2{\cdot}4H_2O$ (SI around -2.5) and $Ba_3(AsO_4)_2$ (SI around 19). However, when using solubility constants from Zhu et al. (2005) it became clear that both barium arsenate and barium hydrogen arsenate were well below solubility control (SI between -6 and -9). This indicated that arsenate concentrations were probably not controlled by any solid phase containing barium. Solid phases with iron(III) was also strongly sub saturated ($FeAsO_4{\cdot}2H_2O$; SI around -19). Geochemical calculations have also indicated the presence of ettringite in the amended system. It can therefore not be ruled out that arsenate is substituted for sulphate within ettringite (Mollah et al. 1998).

Conclusions

Results showed that during the right chemical conditions alkaline amendments can even be used to reduce the leaching of arsenic from mine waste. Co precipitation of arsenic with high concentrations of ferrous iron from the mine waste was probably the most important immobilization mechanism. It is however also important that the alkaline material contributes high concentrations of calcium in order to induce solubility control with calcium arsenates. Arsenate substitution with sulphate in ettringite cannot be ruled out.

It has also been shown that the hexa valent chromium from the ash can be reduced and precipitated as $Cr(OH)_3$ in the presence of ferrous iron.

As a final concluding remark; it is also always important to study the two materials together as unexpected effects can appear during the new chemical environment.

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