Characterization of deposited flue-dust slurry from a former Pb-smelter site and release of inorganic contaminants

Thilo Rennert[A], Stephan Kaufhold[B], Matthias Händel[A] and Kai U. Totsche[A]

[A]Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, 07749 Jena, Germany, Email thilo.rennert@uni-jena.de
[B]Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, 30655 Hannover, Germany

Abstract

As a by-product of Cu smelting, a flue dust originally enriched in metal sulphides evolved. The dust was deposited as slurry in unsealed heaps and is characterized by very high contents of toxic metals such as Pb and Zn. We studied a Technosol profile in the Mansfeld region, Germany, developed from deposited flue-dust slurry by means of chemical, mineralogical, and microscopic characterization (SEM-EDX, XRD, FTIR, DTA-MS), by column experiments on contaminant release under water-saturated conditions, and by geochemical modelling. The flue-dust slurry contained large amounts of ash particles, and quartz, Fe oxides, silicates, sulphates and sulphides (in varying states of weathering) were identified. In both open-flow and closed-flow column experiments, high metal concentrations were determined (e.g., $c_{max}(Zn) = 87$ mg/l). The concentration patterns in both experimental column approaches indicated that the transport scale approximated the reaction scale and that contaminant release was near equilibrium. Geochemical modelling indicated the dissolution of sulphates and precipitation of secondary carbonates that prevented the complete dissolution of sulphates, which would have led to even higher aqueous concentrations. The combination of intensive material characterization, adequate column experiments and modelling allowed for a quantitative and qualitative estimation of contaminant release.

Key Words

soil contamination, column experiment, modelling, equilibrium, rate limitation

Introduction

Until 1990, for more than 800 years, a metalliferous Permian marine black shale was mined and smelted in the Mansfeld region south-east of the Harz Mountains, central Germany. The shale is a bituminous rock mainly consisting of quartz, calcite, dolomite, feldspars and further alumosilicates, but also of sulphide ore minerals such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), galena (PbS), sphalerite and wurtzite (ZnS) (Knitzschke 1966). During smelting the shale for Cu production, fine particles evolved as flue dust. The purified flue dust was used as feed stock for a Pb smelter after partial smouldering. After closure of the Pb smelter in 1978, the flue-dust slurry was deposited in unsealed heaps. Deposited flue-dust slurry is characterized by high contents of potentially toxic metals such as Cd (0.4 g/kg), Cu (12 g/kg), Pb (140 g/kg), Zn (180 g/kg) as well as S and C species (S_{tot} 160 g/kg; C_{tot} 110 g/kg) (Weiss *et al.* 1997). Heavy metals in the flue-dust slurry were originally present as sulphides, but they were oxidized when exposed to the atmosphere to the respective sulphates (e.g., anglesite, $PbSO_4$). Flue-dust slurry heaps have been identified as the main contaminant source in local sediments and in lakes (Schubert *et al.* 2003, 2008). Oxidation of sulphide minerals in the uppermost layers of a flue-dust slurry deposit proceeded quickly leading to the increased aqueous concentrations of Cd, Cu, Pb as well as Zn, and mobilization of these metals was explained by higher solubility of metal sulphates compared to the respective sulphides (Schubert *et al.* 2003). Therefore, the aim of this study was i) to intensively characterize a Technosol developed from flue-dust slurry by means of chemical, mineralogical, and microscopic methods, ii) to estimate the contaminant release from the substrates by using column experiments, iii) to identify the phases that control the aqueous contaminant concentrations, and iv) to integrate the characterization results and the release studies with geochemical modelling.

Methods

Characterization

We took three samples from a Technosol profile on the former Pb-smelter site in Hettstedt (Mansfeld region, Germany) in an open pit during a remediation campaign. The samples #1 (from 0-50 cm depth) and #2 (from 51-90 cm depth) originated from deposited flue-dust slurry, whereas #3 (depth > 91 cm) was taken from the underlying sediment (quaternary glacio-fluviatile and fluviatile sand). The samples were intensively characterized by means of chemical composition (total metal contents by digestion and X-ray fluorescence (XRF), C, S, pH), X-ray diffractometry (XRD), Fourier-transform infrared (FTIR) spectroscopy, differential thermal analysis-mass spectrometry (DTA-MS), and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) detection.

Release experiments and modelling

We carried out column experiments at water-saturated flow (q = 0.01 cm/min with de-ionized water as eluent) with columns made of polymethylmethacrylate (length 10 cm, inner diameter 4 cm). The eluates were collected with a fraction collector at an interval of 0.17 to 2.2 pore volumes exchanged. The flow was interrupted for 4 times ranging from 4 h to 21.5 d. The transport regime was characterized by fitting Cl^- breakthrough data from tracer experiments to the advection-dispersion equation. Additionally, we carried out closed-flow column experiments in duplicate with #1 and #2. Here, the solution leaving the column after the passage of the sample was pumped back into the water-storage vessel so that a closed loop was established. The solution in the vessel was sampled after 3, 7, and 10 d.

We used Visual MINTEQ 2.51 to evaluate mineral phases that possibly control the aqueous contaminant concentrations. Prior to the computational runs, we defined systems that considered the aqueous concentrations of Ca, Cd, Cu, Pb, Zn, and SO_4^{2-} after the first flow interruption in the open-flow experiments or at the end of the closed-flow experiments. Furthermore, we defined sulphates of the metals mentioned before (gypsum, $CdSO_4$, $CuSO_4$, anglesite, $ZnSO_4$) as well as $CaCO_3$ as finite phases.

Results

Characterization

Due to their different origins, the samples from the flue-dust slurry largely differed from the underlying sediment. The flue-dust slurry samples were brownish black (10 YR 2/2 (#1) and 10 YR 2/1 (#2)), whereas #3 was light yellow (10 YR 7/4). The flue-dust slurry samples revealed very high contents of As, Cd, Cu, Pb, and Zn (Table 1). In contrast, the underlying layer was less contaminated as the percentage of contaminants analyzed in #3 related to the upper most #1 was low (As, 1.2%; Cd, 6%; Cu, 0.4%; Pb, 0.6%; Zn 2.5%). According to SEM-EDX analyses, in both #1 and #2 quartz, feldspars, (Cu, Pb, Zn) sulphides (in varying states of weathering), sulphates, Fe oxides (e.g., hematite) and Fe silicates were identified. The samples also contained ash particles, which were enriched in Ca, S, and O as well as in Pb, Cu, Fe, Zn, and Co, and remnants of wood and plants. Gypsum crystals were identified in #1, whereas we assume gypsum present in #2 as particles < 1 µm or accumulated at the rims of ash particles. The FTIR spectra of both flue-dust slurry samples were characterized by bands mainly attributed to quartz, gypsum and aliphatic species. The X-ray diffractograms of these samples revealed quartz as the dominant mineral, and gypsum, anglesite ($PbSO_4$) and possibly smithsonite ($ZnCO_3$) as further minerals. Our XRD results largely differed from those previously reported on flue-dust slurry from a deposit in this region (Weiss *et al.* 1997). They noticed that the most prominent minerals were sulphides (wurtzite, sphalerite, galena) that summed up to 43.9%, but also anglesite resulting from sulphide oxidation was detected (6.3%). As shown by DTA-MS analyses, the content of sulphide S in our flue-dust samples was in the range 0.1 to 1 g kg^{-1} confirming that the vast majority of sulphides initially present have been oxidized to sulphates.

Table 1. Chemical characterization of a Technosol developed from flue-dust slurry on a Pb-smelter site.

	#1		#2		#3[b]
	(g/kg)				(mg/kg)
SiO_2	430[a]	nd[b,c]	420	nd	nd
Fe	76.9	77.1	55.9	63.8	21,590
As	1.1	1.3	1.2	1.3	16
Ca	28.6	25.5	21.4	24.7	34,150
Cd	nd	0.1	nd	0.1	6
Cu	8.1	8.2	6.2	6.5	31
Pb	21.3	18.3	22.9	19.4	116
Zn	24.3	24.0	26.2	27.1	613
organic C	149		165		3,600
inorganic C	8		16		10,200
total S	21.3		20.3		1,400

[a] determined by XRF in the first data column for #1 and #2; [b] determined by sample digestion in the second data column for #1 and #2, and generally for #3; [c] not determined

Column experiments

The transport regime was dominated by advection, and we did not identify preferential water flow. In the open-flow experiments, the aqueous concentrations of ions under study (except for Cu) resembled similar patterns as exemplified in Figure 1 for #1. The patterns were very similar for #2 in both experimental approaches (data not shown). Concentrations of toxic metals such as Pb and Zn were on a very high level. The flow interruptions had only minor impact on the concentrations indicating that the transport scale was near the reaction scale of the process inducing the release. In the case of Ca and SO_4^{2-}, the molar concentration ratio varied between 0.98 and 1.13 indicating (near-) equilibrium dissolution of gypsum. In contrast to Cd, Pb, and Zn, the concentrations of Cu distinctly increased after the flow interruption indicating rate-limited Cu release, whereas that of the other metals was near equilibrium. The rapid decrease of concentrations in the course of the experiments was caused by the continuous removal of dissolved ions and replacement with de-ionized water.

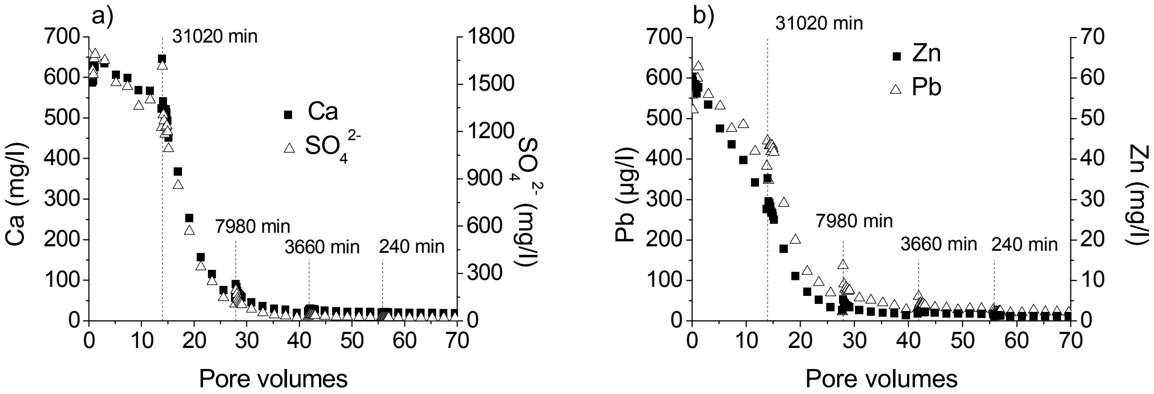

Figure 1. Concentrations of selected substances in the eluates of the open-flow experiment with a Technosol (sample #1): a) Ca, SO_4^{2-}; b) Pb, Zn. Vertical lines indicate the point in time and the duration of a flow interruption.

The closed-flow experiments (Figure 2) confirmed the results of the open-low experiments both quantitatively and qualitatively. The increasing concentrations (except for Cu) that converged to a constant level again indicated that equilibrium between the liquid and the solid phase had established which could be explained by the dissolution of mineral phases. However, the concentration patterns for Cu indicated slow retention of Cu initially mobilized.

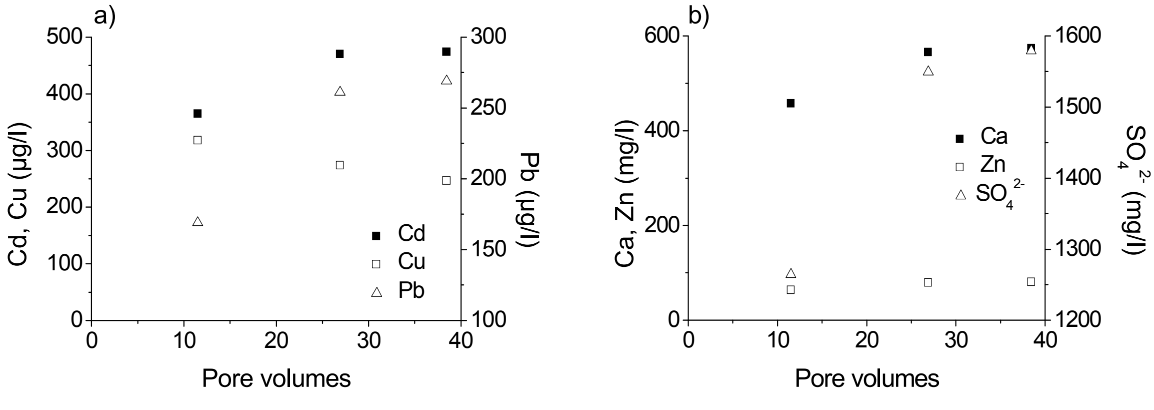

Figure 2. Concentrations of selected substances in the closed-flow experiments with a Technosol (sample #1): a) Cd, Cu, Pb; b) Ca, SO_4^{2-}, Zn.

The proposed dissolution of mineral phases was checked by model calculations. When estimating aqueous concentrations under the assumption of dissolution of sulphates, these modelled concentrations were very similar to those measured except for Cu (Table 2). The measured pHs ranged from 6.7 to 7.5, and the modelled pHs based on the mass balance were only 0.4 to 0.6 lower than the measured ones. In all calculations, the dissolution of gypsum was at equilibrium, and the saturation indices (SI) of the sulphates of Cd, Cu, Pb and Zn, which we defined as finite phases, were < 0 so that these minerals dissolved.

Table 2. Measured (mea.) and modelled (mod.) concentrations of selected elements and sulphate. Measured concentrations refer to those after the first flow interruption in the open-flow experiments and to those at the end of the closed-flow experiments.

Experiment	Ca		Cd		Cu		Pb		SO_4^{2-}		Zn	
	mea.	mod.	mea.	mod.	mea.	mod.	mea.	mod.	mea.	mod.	mea.	mod.
						(mg/l)						
#1 OF[a]	646.0	791.8	0.360	0.652	0.160	0.502	0.440	0.258	1614	1537	35.2	22.8
#1 CF[b]	563.5	747.9	0.470	0.619	0.241	0.431	0.443	0.238	1579	1563	79.3	21.4
#2 OF	441.0	797.4	0.246	0.661	0.182	0.422	0.390	0.241	1487	1603	25.1	23.3
#2 CF	562.5	763.9	0.484	0.637	0.149	0.398	0.311	0.232	1586	1647	82.7	22.3

[a] open-flow experiment; [b] closed-flow experiment

However, the dissolution of sulphates was not complete, because carbonates precipitated as indicated by their SI > 0. According to the calculations, these carbonates include cerussite ($PbCO_3$), otavite ($CdCO_3$), amorphous $ZnCO_3$, and smithsonite, the latter of which we assume present in the samples as deduced from the XRD results. Thus, the modelling strongly indicated an important inhibitory effect of carbonates on the release of toxic metals from deposited flue-dust slurry. For verification, we carried out the same modelling without considering $CaCO_3$. Then, the pH would drop to < 4.5 and the metal concentrations were largely overestimated in all calculations (e.g., Pb by a factor of 10, Zn by a factor > 400). Therefore, our approach resulting in the formation of carbonates following the dissolution of sulphates was capable of reproducing measured concentrations in column experiments adequately. Similar to our modelling results, initially Zn-Cu-Al hydroxides precipitated at a discharge point of another heap of flue-dust slurry and Cu slag in the Mansfeld region that subsequently transformed into a Zn-hydroxide carbonate (Schubert *et al.* 2005).

Conclusion

Deposited flue-dust slurry poses an environmental threat, because initially present sulphides are oxidized to more soluble sulphates as a result of weathering under atmospheric conditions. Therefore, water that passes soils contaminated with such substrates is loaded with dissolved toxic metals. However, complete dissolution of metal sulphates is inhibited by precipitation of secondary carbonates as derived from model calculations that coincide with aqueous concentrations in column experiments.

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