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FLUE DUST FROM COPPER SHALE SMELTING IN CENTRAL GERMANY: ENVIRONMENTAL POLLUTION AND ITS PREVENTION

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ABSTRACT

Copper mining in the "Kupferschiefer district" in Central Germany lasted 800 years. Apart from copper and silver, some 20 other metals of economic significance including zinc, lead, cadmium, tin, molybdenum, germanium, indium and selenium were extracted, with most of these metals being recovered from flue dust. During the 1980s, about 300,000 tons of metalliferous and radioactive flue dust were dumped in unlined basins on mining waste heaps, where they have since been exposed to weathering. The dispersion of metals (Zn, Cd, Cu, Pb) and radionuclides (^{210}Pb, ^{210}Po) into the environment is caused by deflation (particle blow-off), mechanical erosion (rain-water wash-off) and leaching by precipitation. Nowadays metals released from flue dust can be found in the surface water, the groundwater, the soil and lake sediments in the mining district. Leachates from flue dust dumps are extremely enriched in zinc and sulphate. So far only immediate measures have been taken to secure flue dust deposits, and more far-reaching measures are still in the planning stage. New techniques for the immobilisation and recovery of heavy metals from leachates are based on optimising the conditions for the formation of reservoir minerals able to effectively remove metal ions and sulphate from leachates. Lakes in the mining area act as natural sinks for dissolved metals, metalliferous sediments and radionuclides. Their potential to immobilise pollutants should be maintained by avoiding sediment dredging and artificial aeration.

COPPER SHALE MINING IN CENTRAL GERMANY

Copper mining in Central Germany, a traditional mining area, dates back to the 13th century. Initially only surface mining was performed in quarries and open pits. As of the 15th century, underground mining became increasingly important until finally in the industrial era, mining reached depths of more than 1000 m. During 800 years of exploitation in the two major mining districts of Mansfeld and Sangerhausen, more than 2.2 million tons of copper and 11,000 tons of silver were mined (Herbst, 1974). Apart from copper and silver, copper shale processing yielded about 20 other metals including gold, palladium, nickel, zinc, lead, cadmium, tin, molybdenum, rhenium, germanium, indium and selenium.

The large-scale processing of copper shale ore began in the late 19th century when shaft furnaces were put into operation at Eisleben and Helbra. For smelting, copper shale ore was crushed and mixed with coke. Smelting generated three products of economic importance: polymetallic copper stone containing base metals and precious metals, slag used for producing cobble stones (up to 40 million stones per year, Eisenächer and Jäger, 1997) and flue dust scrubbed from the furnace top gas, used as a raw material to produce lead, zinc and rare metals. Each ton of copper shale yielded 35–38 kg of metal, 740 kg of slag, 20 kg of flue dust, and 1500 m^2 of furnace top gas (Lorenz, 1994). Flue gas treatment was introduced back in 1904 for base metal recovery. The procedure included suspending the flue dust in water, dewatering the slurry, and finally depositing the remaining sludge ("Theisen sludge") in basins for further treatment such as carbonisation and selective metal extraction. For more than 70 years this sludge rich in heavy metals (on average 14% Zn, 12% Pb; Table 1) was used as a raw material to produce Zn, Pb, Cd, Ge, Re, Se and other rare metals.

Figure 1. Location of the copper shale mining district in Central Germany (shaded cicle).

MINING AND SMELTING WASTE

In 1990, copper shale mining and smelting in the districts of Mansfeld and Sangerhausen were abandoned for economic and ecological reasons. Nowadays there are about 2000 heaps in the former mining area, most of them dating back to the early days of mining. Two major slag heaps around the former smelters in Eisleben and Helbra contain about 50 million tons of slag, which is partly used as a raw material for road 130 m high contain barren rock from mining. Residues from smelting, such as flue dust, were dumped together with mining waste. From 1978 to 1990, more than 300,000 tons of flue dust was disposed of in unsealed basins and ponds on slagheaps around the former smelters in Eisleben and Helbra.

ENVIRONMENTAL IMPACT

The main pollutants released from the mining and smelting residues are metals (Zn, Pb, Cd, Cu, As), radionuclides (^{210}Pb, ^{210}Po) and sulphate. All these components are remarkably enriched in the smelting residues such as "Theisen sludge" (solidified flue dust), carbonised flue dust and finally metalliferous sludge from leachate treatment. Other kinds of waste namely slag and overburden rocks, have only minor effects on the environment. Mainly fine-grained flue dust with an average particle size of less than 1 micron is subject to erosion by wind and water. Pollutants from flue dust are emitted into the environment by deflation (blow-off), mechanical erosion (wash-off) and selective leaching by precipitation (Schreck and Glaesser, 1998).

Element	%	Element	g/t
SO_3	23.1	Cd	788
SiO_2	17.6	Se	425
C#	10.2	Mo	417
Zn	13.9	Ag	324
Pb	12.1	Tl	310
Sn	1.4	Hg	290
Cu	1.2	Bi	225
As	0.58	Re*	100
Sb	0.39	Ge*	60
Group	**mg/kg**	**Nuclide**	**Bq/kg**
PAH#	1030	^{210}Pb#	4800
PCDD/DF	290	^{226}Ra#	155

Table. 1: Composition of "Theisen sludge" (solidified flue dust). Data from Marquardt et al. (1996), Lorenz (1994)* and UFZ# (unpublished).

All compartments of the environment in the former mining district are affected by extensive pollution by metals derived from mining:

- *Soils* around the former smelters show significant metal enrichments caused by blown-off flue dust. Soil profiles below and along the southern flank of the Helbra slagheap, 0.5–1.5 km away from a Theisen sludge storage basin on top of the heap, exhibit distinctly higher levels of heavy metals in the upper 20 cm of the samples, especially in elevated terrain. The metal ratios in the enriched soil samples correspond to those in Theisen sludge, corroborating the airborne dispersion of metalliferous dust (Marquardt et al., 1996). Farther away from the smelters, anomalous metal enrichments in soils were caused by immissions from ore processing, stretching over a distance of about 1.5 km (As) to 7 km (Cd) in the main wind direction (TÜV Bayern/LUB, 1991). In general, soils in the mining and smelting area of Mansfeld are distinctly enriched in Cu (5.4x), Zn (3x) and Pb (2.1x) compared to average, non-polluted soils in the close vicinity.

- *Lake sediments* about 15 km away from the smelters are highly enriched in heavy metals. Some layers contain up to 2.5% Zn, 0.3% Cu and Pb, fixed as hydroxides/oxides and sulphides (Schreck et al., 1998). A potential danger to the environment comes from the remobilisation of metals in the sediments by changing pH, oxygen content and redox potential. In the past, these sediments have been dredged up several times and deposited in aerated basins, exposing them to weathering. Metals were mobilised and flushed back again into the lake.
- In the mining area, most of the potable water is not obtained from local aquifers but is supplied from a water reservoir in the Harz Mountains, about 80 km to the west. In particular around the former smelters, the shallow aquifers are noticeably polluted by metals (Zn, Cd, As) and sulphate, and are thus not used for drinking water. Sulphate in the groundwater either stems from sulphide mineral oxidation in mining waste or from the leaching of gypsum strata in the subsurface, a side-effect of mining which favours karst weathering. Water from mining galleries is enriched in NaCl and to a minor extent in metals, and is unsuitable for consumption.
- *Surface water* in the mining district is of very different quality. Leachates from mining residues (especially from Theisen sludge) exposed to weathering are highly enriched in zinc (up to 2,600 mg/l) and sulphate (up to 6,750 mg/l, Table 2) and have to be treated. Seepage collection and subsequent water treatment is performed at 3 locations around the former smelter in Helbra. Streams and brooks exhibit elevated contents in heavy metals near outcropping copper shale, near heaps from ore treatment, and downstream of the smelters. As most of the load of pollutants is bound to particles (either as independent particles from copper shale and flue dust or absorbed in hydroxides and adsorbed on clay minerals respectively), the dissemination of metals from mining residues mainly depends on physical weathering and the rate of precipitation.

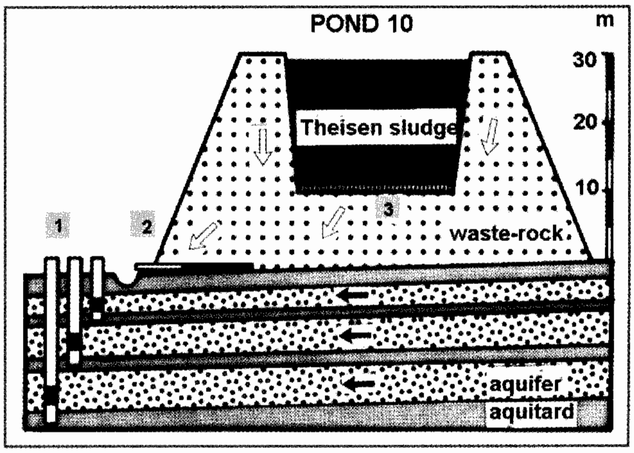
Component (mg/l)	Seepage, Stadtborn well, 1996	Groundwater well 2 (depth 4.77m)	Groundwater well 2A (depth 31.06m)
Zn	2,626	16.54	0.024
Pb	1.9	< 0.0008	< 0.0008
Cu	13.2	< 0.0003	< 0.0003
Cd	2.8	< 0.0003	< 0.0003
As	0.018	0.017	< 0.0003
SO_4	6,750	2,325	247
Cl	314	463	82
NO_3	76	96	0.55
pH	6.2	7.2	6.5

Table 2. Heavy metals and sulphate in surface water and groundwater. Data compiled from Schreck (1997a, 1998). Analyses UFZ: AAS and IC (Böhnisch, Sawallisch).

REHABILITATION AND RESTORATION MEASURES

A comprehensive redevelopment concept for the Mansfeld copper shale mining and smelting district was presented back in 1991 (TÜV Bayern / LUB), only one year after mining had been abandoned. This concept included measures such as the dismantling of the mining installations, the relocation and concentration of flue dust from various unprotected sites all over the area of the smelters to one central, supervised deposit (Pond 10), the capping of highly contaminated production sites and heaps, the final sealing of the central flue dust deposit, the installation of a seepage monitoring system, and finally the restoration and improvement of the leachate drainage and treatment system (Schreck, 1997b).

Today, 8 years later, it must be stated that only immediate measures to prevent the most serious environmental hazards have been carried out. These measures include relocating the majority of the flue dust from various unprotected dumps to a supervised central deposit (Pond 10, Figure 2), temporarily covering dumps and some polluted areas, introducing a basic leachate collection and treatment system, and carrying out a water-monitoring programme. More far-reaching measures are still at the planning stage. The most pressing rehabilitation measure in the former mining district is the imme-



1: Groundwater observation wells. 2: Drainage pipes and drainage channel. 3: Drainage layer. Black arrows: Ground water flow direction, open arrows: Leachate flow direction. From Schreck (1997 b).

Figure 2. Final flue dust deposit, Pond 10. Capacity: about 300.000 tons of sludge.

diate relocation and environmentally friendly disposal of all remaining metalliferous smelting residues in Pond 10. Only this measure will help reduce the metal load of seepage from mining heaps and subsequently improve the quality of both the surface water and the groundwater.

DEVELOPMENT OF NEW POLLUTANT ATTENUATION TECHNIQUES

Highly contaminated leachates are collected and treated with lime on an industrial scale to immobilise metals and sulphate. This procedure results in a non-marketable mixture of Zn (and Cd) hydroxides and gypsum, and the product has to be dumped in a separate basin. One obstructive side effect of this procedure is incrustations of gypsum in pipes, pumps and water reservoirs, necessitating costly repairs.

Nature offers an alternative for the immobilisation of zinc (and other metals) and sulphate from highly polluted leachates. Green incrustations on rocks and leaves can be found in seepage containing metal and sulphate from a flue dust deposit situated on a slagheap (see Table 2). This is glaucocerinite $[Z_n^{8-x}\,Al_x\,(OH)_{16}]\,[(SO_4)_{x/2}\,(H_2O)_9]$, a reservoir mineral with a hydrotalcite structure, first described in the Mansfeld mining area by Witzke (1997). Glaucocerinite is formed from acidic leachates rich in zinc and sulphate that percolate the slag heap. On the way through the heap, the leachates become neutralised and aluminium is dissolved from the glassy component of the slag. These trivalent ions trigger the formation of glaucocerinite. In lab-scale experiments we were able to demonstrate that all the dissolved zinc in the leachates can be immobilised by adding Al^{3+} ions, which sets off the precipitation of glaucocerinite (Figure 3). Field experiments are currently being carried out to test the mineral precipitation process under natural conditions. Ultimately this new immobilisation technique may result in a marketable zinc-containing product, separated from gypsum.

Lakes in mining areas provide a powerful way of immobilising dissolved metals, provided that the reducing conditions of the lake sediments are maintained over the year and the seasonal mixing of the water layers is kept to minimum. Situated about 15 km to the east of the former smelters, the lakes at Mansfeld act as natural sinks for heavy metals and radionuclides derived from mining and processing. Lake sediment profiles show distinct metal enrichments 20–40 cm below the bottom of the lake. In the sediments the zinc content is up to 2.5%, copper and lead are about 0.3%, and arsenic is about 0.2%. Radioactive lead (^{210}Pb) originating from flue dust and metalliferous sludge is also enriched in this layer. One potential danger is metal remobilisation by the aeration of the lake sediments, resulting from the seasonal mixing of the water bodies. Anthropogenic activities, however, may destroy natural immobilisation mechanisms as well. One of the lakes, a sinkhole from karstification, is more than 20 m deep and contains euxinic water. As all the water run-off of the mining area passes through this lake, it would make an ideal sink for metals by the formation of sulphides. Unfortunately this lake is artificially aerated to prevent the offensive smell of H_2S disturbing the residents – and this artificial aeration remobilises metals, which have already been removed from the water by precipitation. Obtaining a better understanding of natural processes would enable such useful systems to be preserved.

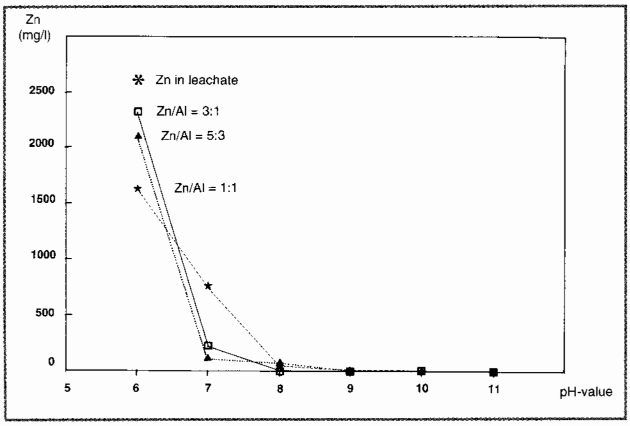


Figure 3. Removal of Zn from leachate by the precipitation of glaucocerinite and zinc oxide, depending on pH. Initial Zn-content in leachate is 2,626 mg/l. Experimental work: T. Witzke. From Schreck and Glaesser (1998).

CONCLUSIONS

Environmental pollution caused by mining usually emerges over a long period of time, sometimes over several centuries. The release of pollutants from mining and smelting waste lasts at least as long unless measures are taken to counteract these processes. In most parts of Europe, especially in Germany, mining has been carried out in populated areas, and conflicts of interest concerning land use are common. Areas once used for mining and metal processing are nowadays employed for various purposes such as small and medium-sized businesses, tourism and recreation, and even agriculture. These new fields of land use call for immediate rehabilitation measures such as the relocation of contaminated mining waste, the capping of dumps and polluted industrial sites, and the long-term monitoring of pollutant emissions from waste.

Environmental protection measures to prevent mining-induced pollution should be taken while mining is still underway. At this stage it is easier and cheaper to mitigate or even to avoid environmental pollution than after the mine has been closed down – when the responsibility for damage is disputable and can only be proved in lengthy legal proceedings, and when money for environmental restoration is scarce.

Nature offers a wide range of possibilities for metal immobilisation, such as the formation of reservoir minerals able to incorporate metals in their crystal lattices, the use of wetlands for metal absorption and precipitation by means of humic acids and changes in pH and redox potential, and finally the advantages of natural lakes and their function as a sink for mining-related pollutants. Natural processes should be put to good use and adapted to the specific needs in the respective target area. Mining waste (limestone, marl) and crushed slag, both of which are abundant around the former smelters, help to neutralise acidic leachates from sulphide oxidation and to trigger the formation of reservoir minerals. The potential of lakes for metal immobilisation should be maintained and thus sediment dredging and artificial aeration should only be employed in exceptional cases.

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