

FLOTATION OF CONTAMINATED SOILS AND MINERAL WASTE MATERIALS IN SOIL WASHING PLANTS

Frank Stapelfeldt

Visiting researcher and professor, DEMIN/UFOP
frank@degeo.ufop.br

ABSTRACT

Physical-chemical soil washing plants have proved to be suitable for the treatment of contaminated soils. The principle is based on the fact that soil is liberated by mechanical energy input. The contaminant-soil separation takes place by applying a subsequent combination of classifying and separation processes. Because of the concentration of contaminants in the fine particle fraction, flotation becomes a significant separation process in the particle-size-fraction below 300 µm. Most cases of soil flotation have been made in the treatment of organic contaminants. The flotation of organic contaminants succeeds without any problems caused by the hydrophobic character of the organic contaminant adsorbents and contaminants, i.e. mineral oil carbons and polycyclic aromatic carbons. With the addition of frothers and/or collectors from coal flotation, contaminant recovery of more than 90% are obtainable. Results of a soil washing plant are presented.

About the flotation of heavy metal contaminated soils* are existing only a few investigations. At the Technical University Berlin investigation regarding the flotation of heavy-metal contaminated soils were made. One material to be treated originates from a former steel works on an inner city site. The material is polluted with oxidate lead and zinc compounds. The flotation of the oxidate lead and zinc compounds take place after a preceding sulfidisation and activation with Xanthate as collector. A recovery of maximum 75 % lead and 44 % zinc was obtained for a one step flotation. The recovery of cleaned soil amounted to 92 %.

INTRODUCTION

For the treatment of contaminated soils usually thermal, biological and physical-chemical processes are used. 1996 in Germany 3,45 million-t of contaminated soils and waste material were treated with those processes. About 40 % of this material were treated by physical-chemical soil washing plants (Schmitz & Andel 1997). Contaminants which occur not only include polycyclic appear aromatic hydrocarbons (PAH),

mineral oil hydrocarbons and cyanides but also various heavy metals including mercury. The soil washing processes are working by detaching the contaminants from the soil particles and surrounding them in the finer particle fractions with an adjusted input of mechanical energy. Afterwards, the contaminants are concentrated in the light and/or heavy product of the gravel and sand fractions as well as in the silt fraction. These highly contaminated fractions are separated by a subsequent combination of classification and separation processes. The separation processes are generally based on density separation. There are problems, especially with the selective material separation in the fine particle fraction. Flotation is a solution for these problems.

FLOTATION OF PAH IN A SOIL WASHING PLANT

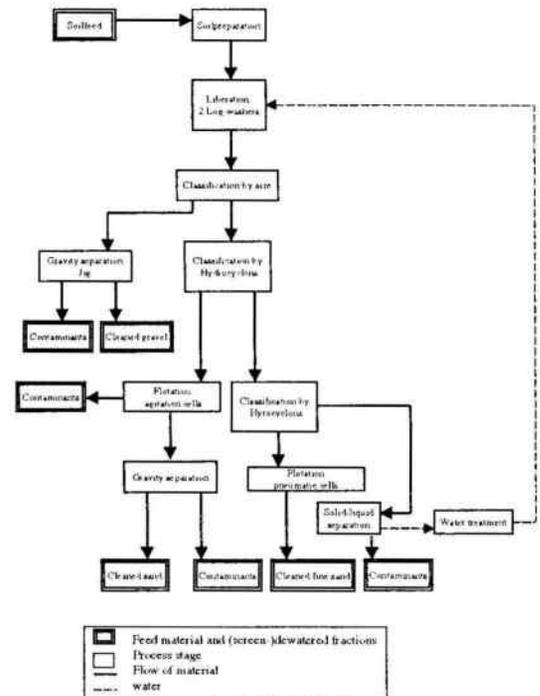


Figure 1: Flowsheet of a soil washing plant.

Figure 1 is showing the flowsheet of a soil washing plant in Berlin. Based on two-shift operations, the annual capacity is 100,000 t. The plant is completely enclosed and encapsulated where possible. It is possible in addition to soil and rubble material, to treat waste materials from all over Germany (Richter et. al. 1997).

After delivery, it is possible to crush the material with a jaw crusher when required. With an impact mill integrated into the process circuit, final particle sizes in the gravel size range can be achieved which is primarily suited for treating material containing slag. The contaminated material is conveyed to two double-shaft log washers connected in series, in which the soil and/or rubble is liberated with water addition. The desagglomerated material is sized at 2 mm and 20 mm. The gravel fraction is separated into highly contaminated light fraction and a clean gravel fraction in a pulsator jig. The fraction < 2 mm is classified in multihydrocyclons. The deslimed fine fraction < 0,1 mm is floated in two pneumatic Ekof flotation cells. The overflow <0,02 mm and the concentrate with highly contaminated fines are sedimented in thickeners. The thickened slurry is dewatered in chamber filter presses. In a multi-cell, modified Sket agitation froth flotation unit the sand fraction 0,1 –2 mm is treated. The contaminants occur in highly concentrated form in the froth product while the tailings are led to the sand fraction as purified material. The coarser soil components containing contaminants, such as substances in the sand size range containing coal and lignite and which cannot be separated by agitation froth flotation, are discharged selectively in fluidised bed separators and subsequently dewatered (Richter et. al. 1997).

Highly contaminated soils from former industry sites are processed in soil washing plants. These include former sites of tar works, gas works and coking plants etc. The soils and building rubbles from this sites are highly contaminated with polycyclic aromatic hydrocarbon (PAH) and other organic contaminants like mineral oil hydrocarbons. In accordance with EPA-the American Environmental Authorities- the term PAH 16 refers to compounds of $C_{10}H_8$ naphthalene to $C_{10}H_{12}$ idenol (1,2,3-c,d) pyrene. The PAH include some long known carcinogenic substances such as benzo (a) pyrene $C_{20}H_{12}$ and benzo(a) anthracene $C_{18}H_{12}$. The extremely low limit values (20 mg/kg) have the consequence that an almost complete removal of PAH must be undertaken from the fractions to be cleaned. Efficient process solutions must always consider the contaminant binding characteristics in the soil matrix. PAH can occur in the soil as follows.

BINDING PROPERTIES OF PAH IN SOIL

Distribution on the surface of soil particles. Here the degree of contamination increases with decreasing particle size, corresponding to the increase of the specific surface.

Selective concentration of soil components with increased contaminant affinity to the PAH, such as root, coal or tar particles.

Independent, solid or highly viscous phase. PAH particles can here occur in form of lumps or pellets. PAH also can be included in soil particles. Here the contaminant can penetrate into the pores and solidify in the course of time.

For the separation of the non-polar PAH in soil washing plants particularly flotation and , because of adhesion at light product fractions, density separation processes provide a good solution.

RESULTS

Pilot test with collectors from coal flotation and frother reagents indicated that at corresponding pH values, a contaminant recovery of > 90 % could be anticipated. Depending on material composition of the feed material, the contaminant recovery is already between 4 and 60% without the addition of collector reagents. Of increased effect is a positive overlapping by the collecting effect of the mineral oil hydrocarbons already present in the soil matrix. In figure 2 the flotation results of several PAH contaminated materials made in a soil washing plant are presented. It can be seen that also highly contaminated feed material of the flotation step can be cleaned to concentrations < 20 mg/kg PAH. Common input concentration of 1000-2000 mg/kg can be decreased to output concentrations under 15 mg/kg PAH.

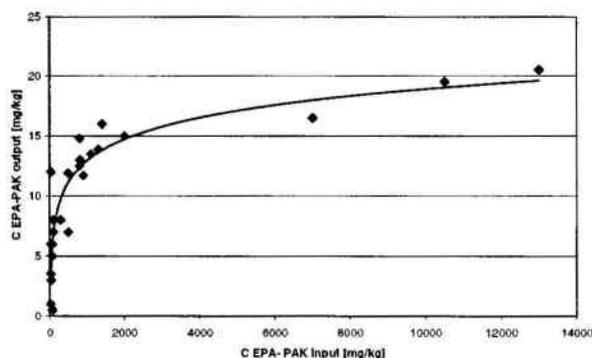


Figure 2: Decontamination results of soils and rubber containing PAH by flotation in a soil washing plant.

FLOTATION OF SOILS CONTAMINATED WITH OXIDATE LEAD AND ZINC COMPOUNDS

About the flotation of heavy metal contaminated soils are existing only a few investigations. But the results were not sufficient for a technical application (Langen et. al. 1994). At the Technical University Berlin investigation regarding the flotation of heavy-metal contaminated soils were made. One material to be treated originates from a former steel works on an inner city site which was polluted with oxidate lead and zinc compounds. The most important waste occurring in steel production refuse is steel slag, flue dust and furnace scale. Flue dusts are frequently accumulated on the works site and therefore are often the cause of inorganic contamination on steel works sites. They contain high concentrations of lead, zinc, nickel, copper, cadmium, chromium, arsenic and alkalimetals. The heavy metals can be washed out of the dust and then absorbed by oxides of iron, aluminium and manganese (Richards et al. 1993).

Sample characterization

The contaminated soil used for the investigations was composed of a mixture of filler material, slag, filter dust and soil. The following minerals were identified by X-ray defraction as main components of the soil with decreasing presence: quartz, >>magnetite, >calcite, zincite and aluminium oxide as well as other iron compounds (including hematite and goethite). The material revealed increasing contents of lead, zinc, cadmium and chromium. Concentrations of lead and zinc were significant and served as main parameters for the investigations. By micro-investigations it was determined that the main part of the lead and zinc contamination occurred in oxidised form or bound by manganese and iron oxides (Stapelfeldt 1998).

Table 1: Particle size distribution and concentration of Pb, Zn, Fe, and Mn in the different fractions.

size fraktion [µm]	M-%	Pb [M-%]	Zn [M-%]	Fe [M-%]	Mn [M-%]
200-250	8,9	0,0654	0,0553	3,16	0,1550
160-200	18,9	0,05	0,0692	4,22	0,1762
100-160	46,6	0,061	0,0837	3,80	0,1856
63-100	19,1	0,0761	0,1118	5,42	0,2287
<63	4,3	0,118	0,2543	7,70	0,2287

After a 1-hour liberation by attrition the particle size range 250 – 63 µm was used for the flotation tests. The soil contained a lead concentration of approx.

600 mg/kg, a zinc concentration of approx. 800 mg/kg and an iron concentration of 5,1 %. The material is characterised by the particle size distribution and element concentration shown in Table 1. The sample size analyses were carried out by wet screening, The contents of the heavy metals are increasing with decreasing particle size.

Flotation tests

The applicability of flotation experience from the processing of mineral raw materials to the objectives of soil decontamination is problematic. On the one hand, the heavy metals occur in various oxidic bonding forms which differ from ore minerals. On the other hand, the application of collectors which are used for acid pH ranges (alkyl sulfates, alcane sulfonates) and collectors which are critical to hardening constituents is only suitable for soils with low contents of carbonates.

The flotation should only take place after a preceding sulfidisation. Xanthates, i.e. potassium amyle xanthate, are the most important collector reagents for the flotation of lead, copper and zinc minerals. The flotation is possible in pH ranges of 5 to 12. In general the flotation conduct of oxidic minerals will be improved by a preceding sulfidisation. For zinc compounds an additional activation with copper sulfate is required and the zinc minerals can be floated together with lead (Schubert 1996).

The investigations were carried out under variation of following parameters: pH-range, condition times and dosages of copper sulfate, xanthate and sodium sulfide, flotation time, particle size range, and multistage. Selected results are presented below. The flotation tests were carried out with a 2 l Humboldt Wedag agitation cell and with 200 g of soil. The used amounts of reagents refer to 1 kg dried soil. The tests were carried out according to the course scheme shown in table 2:

Table 2: Course scheme of the flotation tests

process step	Time
disperse addition of sodium silicate, $c_D = 0,89\text{g/kg}$	$t_d = 300\text{ s}$
sulfidisation addition of sodium sulfide, Na_2S c_{su}	$t_{su} = 900\text{ s}$
activation addition of copper sulfate CuSO_4 , c_{ac} adjusting the respective pH value	$t_{ac} = 300\text{ s}$
addition of collector addition of potassiumamyle xanthat c_{co}	$t_{co} = 300\text{ s}$
addition of frother Flotanol D14, $c_{fr} = 0,2\text{ g/kg}$	$t_{fr} = 120\text{ s}$
flotation	$t_f = 300\text{ s}$

Results

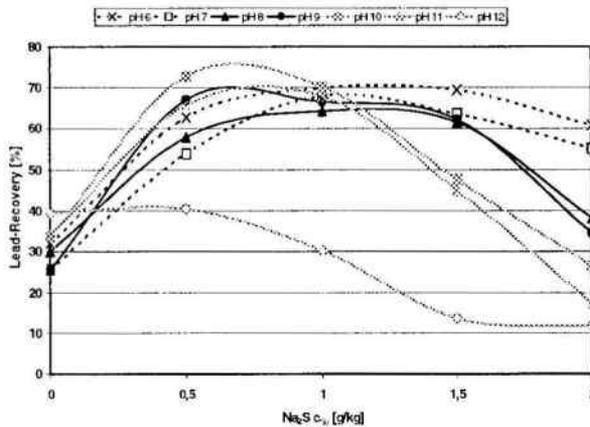


Figure 3: Lead recovery related to different sodium sulfide inputs and pH values.

The results of the investigative tests for the determination of the optimal sodium sulfide amount, dependent on the pH value, are shown in Figure 3 and 4. The activating influence of the sodium sulfide supplement for a pH value of 6-11 and a sodium sulfide amount of 0.5 to 1.5 g/kg as well as the pressuring influence of increasing supplements and high pH values are shown, in figure 3. The lead recovery shows an optimum in the pH area between 9 and 11 and a sodium sulfide amount of 0.5 to 1.0 g/kg. The highest recovery of 73 % was reached at a pH value of 10 and a sodium sulfide amount of 0.5 g/kg. Under the test conditions the recovery of cleaned soil amounted to 95 %. Its upgrading ratio was at 15. At pH values over 11 recovery of lead is significantly less.

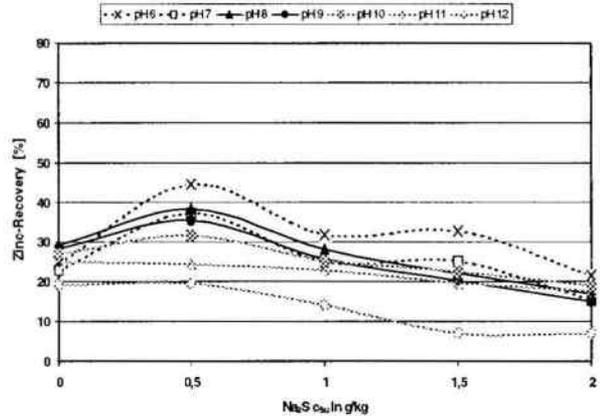


Figure 4: Zinc recovery related to different sodium sulfide inputs and pH values

The recovery and concentration of zinc decrease slightly with the increase in pH values as shown in Figure 5. The highest recovery of 44 % was reached at a pH value of 6 and a sodium sulfide amount of 0.5 g/kg. For the flotation of lead and zinc two different optimal areas can be observed. The next tests were realised under consideration of the optimal conditions for the lead flotation at pH 10 and a sodium sulfide amount of 0.5 g/kg.

In figure 5 the recovery of lead, zinc and mass in the concentrate related to the amount of KAX at pH 10 $t_f = 600\text{s}$ are presented. The recovery of lead does not increase at collector amounts > 1,25 g/kg. The recovery of zinc is significantly increased to approx. 44 % with an increase of the collector. The lead and zinc contents decreased to 150 mg/kg and 450 mg/kg. Without preceding sulfidisation by Na_2S and activation by copper sulfate the recovery for lead and zinc increases only to 61 % and 17 %.

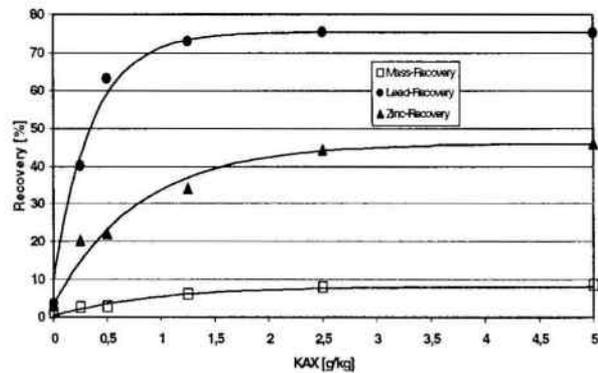


Figure 5: Recovery of lead, zinc and mass in the concentrate related to the amount of KAX at pH 10 $t_f = 600\text{s}$

Tests with increasing particle size ranges show that a selective separation under given laboratory conditions in a size range of 300 - 25 μm is possible. Research of cleaned soil through sequential extraction shows above all that moveable heavy metal fractions are floated. In view of the reuse of soil, this is of significant importance. The flotation kinetic can be described by a first order two class mathematical model

Stapelfeldt, F. Beitrag zur Flotation schwermetallverunreinigter Böden, Dissertation TU-Berlin, 1998

CONCLUSIONS AND OUTLOOK

Most cases of soil flotation have been made in the treatment of organic contaminants. The flotation results of several PAH contaminated materials made in a soil washing plant are presented. It can be seen that also highly contaminated feed material of the flotation step can be cleaned to concentrations < 20 mg/kg PAH. About the Flotation of heavy metal contaminated soils are existing only a few investigations. At the Technical University of Berlin investigations regarding the flotation of soils polluted with oxidate lead and zinc compounds were carried out. The results of the investigations demonstrate that decontamination of heavy metal contaminated soils by flotation is possible and can be implemented in soil washing plants.

REFERENCES

- Lange, M.; Hohberg, H.; Hamacher, B. Möglichkeiten zur Abtrennung von Schwermetallkontaminationen aus Böden. *AufbereitungsTechnik* 35 Nr.1, S. 1 – 12, 1996
- Richards, I.G.; Palmer, J.G.; Barrat, P.A. *The Reclamation of Former Coal mines and Steelworks. Studies in Environmental Sciences* 56. Amsterdam, Oxford, New York 1993
- Richter, R.; Schmidt, A.; Stapelfeldt, F. Sanierung PAK-kontaminierter Böden und Bauschuttmaterialien in physikalisch-chemischen Bodenreinigungsanlagen. *AufbereitungsTechnik* 38 Nr. 4, S.185-193, 1997
- Schmitz, H.-J. Andel, P. *Bodenbehandlungs-anlagen* TerraTech Nr. 5, S.17-20 1997
- Schubert, H. *Aufbereitung fester Stoffe. Band II: Sortierprozesse.* Stuttgart 1996.