

HEAVY METAL REMOVAL FROM CONTAMINATED SLUDGES WITH DISSOLVED SULFUR DIOXIDE IN  
COMBINATION WITH BACTERIAL LEACHING

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ABSTRACT

Treatment of dredged sludge from the Hamburg harbour area with sulfurous acid (6%) shows nearly complete removal of Cd, Zn and Mn within the first 10 minutes. Within 1 hour more than 50% of Cr, Ni, Pb and Hg are mobilized; dissolution of Cu and Fe reaches about 40%. The capability of certain bacteria (*Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*) to oxidize sulfur and ferrous iron respectively, while decreasing the pH value from 4-5 to about 2 was utilized for enhancing dissolution of metals from dredged sludge. Acidification with sulfurous acid to pH 4 and following bacterial leaching solubilized the following metal percentages from the dredged material: Cd and Co = 98%, Zn = 95%, Mn = 91%, Cu = 84%, Ni = 66%, Cr = 45%, Fe = 27% and Pb = 17%.

INTRODUCTION

In the coastal regions of the Federal Republic of Germany each year approximately 30 million m<sup>3</sup> dredged sludge are produced during maintenance dredging (ref 1). In the harbour of Hamburg yearly about 2 million m<sup>3</sup> of sludge material has to be dredged (ref 2). Most of the dredged material up to now has been used for filling up low marshlands, to prepare them for the port extension. This relatively economic method cannot be continued as available areas for reclamation are running short and other traditional uses, e.g. in agriculture are now prohibited due to the high concentration of chemical toxicants such as heavy metals (ref 3).

Under long term aspects a feasibility study has been started to find and develop new methods for alternative treatment, utilization or disposal of the dredged material (ref 4). Among the various proposals - however at a lower priority - the solubilization of heavy metals by means of acid treatment has been considered as one possibility for the partial detoxification of the sludge with respect to subsequent agricultural application. Sulfuric and hydrochloric acid have been applied by several authors as the major leaching agents (refs 5, 6, 7) and a complete design for a "detoxification factory" has been established by Müller & Riethmayer (ref 8), initially for the treatment of the dredged sludge from the middle Neckar River (approx. 150.000 m<sup>3</sup>/year).

Based on the experience of an extraction procedure with sulfur dioxide for the treatment of Mn-nodules (ref 9) we initially favoured the use of sulfurous acid mainly because of its lower cost; later we recognized that this leaching agent could open the system for biologically mediated processes, such as bacterial interactions, which may increase the efficiency of metal extraction from such materials at even lower amounts of acid input (ref 10).

METHODS AND MATERIALS

The sulfurous acid procedure was applied to dredged sludge from the Hamburg harbour area as follows:

5 g of the sludge (dry weight) were reacted for 10 min, 1 h, 5 h and 46 h with 50 ml sulfurous acid (6%). Solid matter was separated by centrifuge, washed with dist. water, digested with conc. nitric acid for 2 h and analyzed by atomic absorption spectroscopy. To study the effects of solution pH and solid content 2.5 g, 5 g and 10 g of the sludge

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were reacted with 50 ml leaching solutions for 16 h at pH 1.5, 2, 2.5 and 3 respectively. Percentage of metal solubilization was calculated from the differences in analyses of the head samples and the residues after these leaching tests were completed.

For combined sulfurous acid/bacterial leaching experiments highly contaminated mud - classified by upstreaming water and separated from the sand (ref 11) - was acidified with sulfurous acid to pH 4. The experiments were carried out in 4 cylindrical glass reactors (500 ml) which contained:

- I. dredged sludge (K)
- II. dredged sludge + *Thiobacillus ferrooxidans* DSM 584 (F)
- III. dredged sludge + *Thiobacillus thiooxidans* DSM 622 (T)
- IV. dredged sludge + mixture of *T. ferrooxidans* and *T. thiooxidans* (F + T)

The thiobacilli were supplied by German Collection of Microorganisms, Göttingen. All glass reactors were permanently aerated and kept at  $29 \pm 1.5$  °C.

### RESULTS AND DISCUSSION

Leaching with sulfurous acid shows a very fast removal of all metals investigated. The effect of time on percentage of metal solubilization is illustrated in figure 1. Nearly steady-state metal solubilization starts from times beyond 10 min for Cd, Zn, Mn and Cu. Hg, Ni and Fe slowly increase with time, while after contact time beyond 5 h solubilizations of Pb and Cr decrease again because of oxidation of sulfurous to sulfuric acid and formation of less soluble compounds.

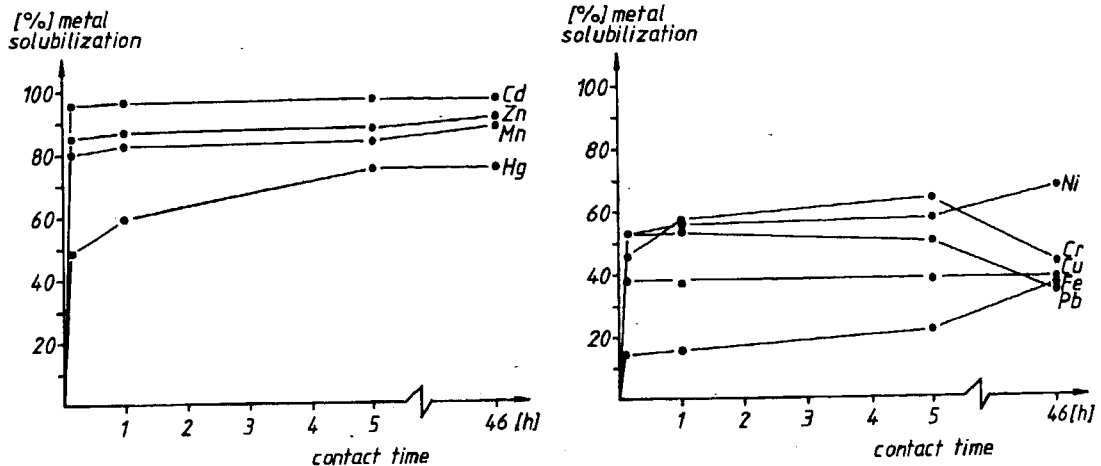


Fig. 1. Effect of time on metal removal from dredged sludge with sulfurous acid (solid content = 10%)

Solubilization rates and ultimate removal efficiencies for all metals increased with decreasing pH and solid concentrations. As examples Cd and Pb solubilizations are depicted in figure 2. There are demonstrated the combined effects of pH and dredged sludge concentration.

As can be seen removal efficiencies for Cd were nearly 100% at pH 1.5 and 5% solid content. At the same pH and 20% solid content Cd removal is only about 60% and at a pH 3 it decreases to 40%. Decrease of Cd solubilization with increasing pH and solid concentration is relatively constant.

This could not be observed for Pb. Differences at various solid contents were much lower at pH 3 and pH 2.5 than at pH 1.5 and pH 2. Between pH 2 and pH 2.5 there seems to be a critical value for Pb solubilization. Maximum Pb removals were 50% and 41% at a 5% solid content for pH 1.5 and pH 2 respectively. These maximum efficiencies dropped to about

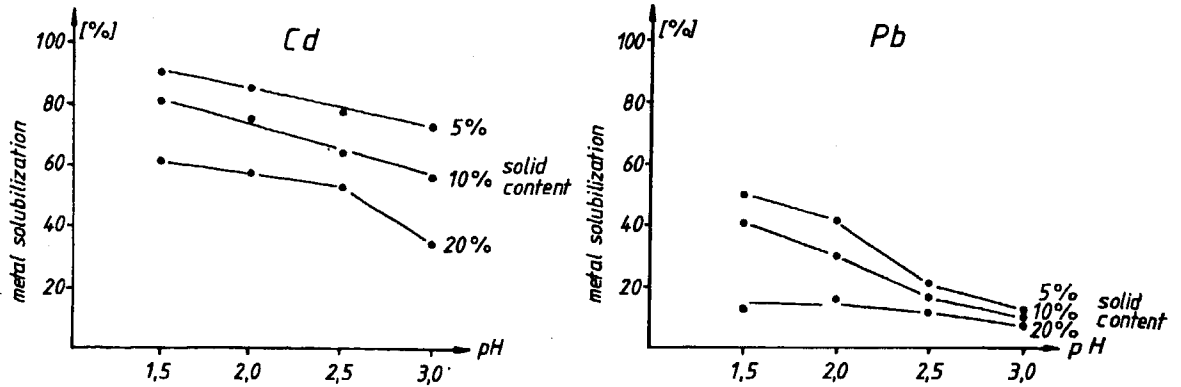


Fig. 2. Cadmium and lead removal from dredged sludge with sulfurous acid (6%) at various solid contents as a function of pH

15% removal at a 20% solid content for the same pH values. Because of formation of  $PbSO_4$  solubilization with sulfurous acid did not exceed 50%.

"Titration curve" for harbour sludge in figure 3 shows that with 40 ml and 70 ml  $H_2SO_4$  per liter of sludge suspension (4% solid matter) a pH 5 and 4, respectively, is established. During the aeration of the suspension sulfurous acid is oxidized to sulfuric acid by lowering the pH by approx. one unit; subsequent bacterial leaching is further reducing the pH as indicated in figure 4. A pH of 2.1 to 2.5 (depending mainly from the solid concentration and initial pH) is levelling off after 10 - 15 days.

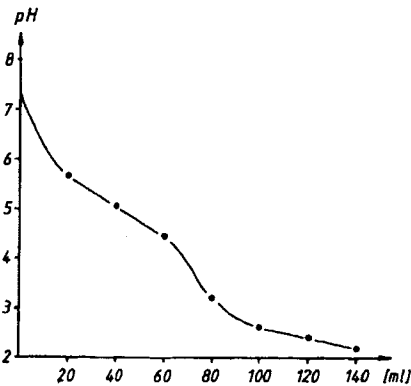


Fig. 3. Sulfurous acid (6%) usage for acidification of 1 l 4% dredged sludge suspension

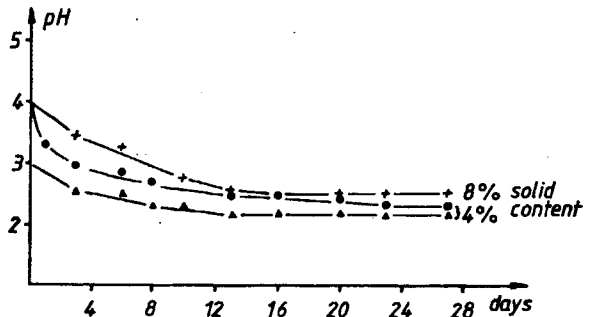


Fig. 4. pH changes in dredged sludge suspensions during bacterial leaching with a mixture of *T. thiooxidans* and *T. ferrooxidans*

As illustrated in figure 5 this effects a more than 90% remobilization of Cd, Zn and Co. Cu is extracted by more than 80% by the combined bacterial leaching with a mixture of *T. thiooxidans* and *T. ferrooxidans* (T + F), whereas the release of Ni and Cr was highest in the *T. thiooxidans*-extract (T). The release of Fe and Pb was less effective and was found at a maximum of 25% for Fe and 15% for Pb in the *T. thiooxidans*-extract.

There is one major advantage of the combined leaching with sulfurous acid and bacteria: the input of acid is characteristically lowered; less than 10% of the acid used in the experiments without bacteria is needed to produce the initial pH of approx. 4 which is prerequisite for start of bacterial activity in the harbour sludge system.

However, it must be concluded that the original objective of decontaminating the dredged

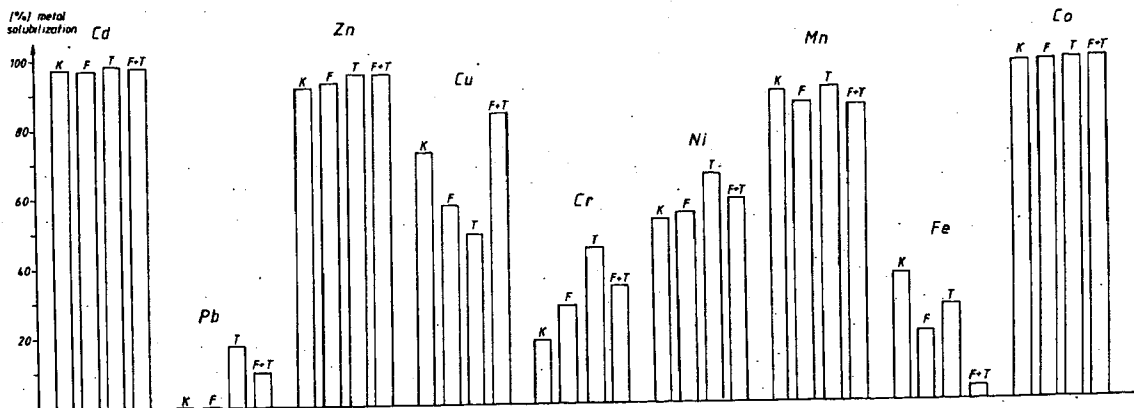


Fig. 5. Metal solubilization from dredged sludge (dry weight = 4%) by bacterial leaching with *T. ferrooxidans* (F), *T. thiooxidans* (T) and a mixture of both (F + T). (K = control sample)

sludge from Hamburg harbour to a quality standard required for agricultural application cannot be reached for Hg (2 mg/kg) and Pb (100 mg/kg) mainly with respect to the limitations of the Abfall- und Klärschlammverordnung (effective since April 1, 1983) of the F.R.G.. On the other hand there are potential applications for waste residues from sulfidic ores (also in the Hamburg area) and for sewage sludges (ref 13), particularly those exhibiting lower contents of the critical metals Hg, Pb and Cr.

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