CHEMICAL STABILIZATION AND SOLIDIFICATION OF HEAVY METAL CONTAMINATED DREDGED SLUDGE FROM HAMBURG HARBOUR

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ABSTRACT

Contaminated sludges from Hamburg harbour have been stabilized by means of lime, calcium hydroxide,calcium carbonate, gypsum, trass, waste kiln dust, cement, coal fly ash, and red mud. Analysis of the solidification products by polarization microscope, electron microscope, X-ray diffraction, electron microprobe, and PIXE microprobe indicate that new minerals have been formed which stabilize the material and change, as confirmed by chemical extraction methods and leaching tests, the phase specific bonding of heavy metals.

INTRODUCTION

The quantity of sediments dredged from the harbour of Hamburg amounts to about 2 million m^3 per year. Disposal facilities of these materials are severely limited because of the high concentrations of heavy metals and organic toxicants. At present upland deposition in heap-like form is favoured. This alternative demands minimization of emissions from leachates into the groundwater, which can be achieved by both hydraulic measures and by reducing the mobilities of pollutants. With respect to critical heavy metals, which are in part relativrly weakly bound to the original sludge particles, it is assumed that their bonding strength can be improved by chemical additives.

SAMPLE PREPARATION AND TEST METHODS

The dredged harbour sludge was primarily classified by a combination of hydrocyclone and upstream separation in low contaminated sand and a highly contaminated mud fraction, which was dewatered up to stiff consistency (40-50 w/w percent dry mass).

For solidification non hydraulic, hydraulic, potentially hydraulic, and pozzolanic stabilization agents such as lime, calcium hydroxide, calcium carbonate, gypsum, different types of cement, trass, waste kiln dust, coal fly ash, and red mud were added in different mixing ratios (5-20 w/w percent). The mixtures were then poured into prismatic moulds (40x40x160 mm) and stored in a conditioning cabinet at about 80% humidity and 20 °C for 28 days. Subsequently they were air dried.

After storage the mineral content, structure, and texture of the solidified samples were tested and analyzed by polarization microscopy. For qualitative and semi-quantitative analysis of mineral phases X-ray diffraction has been applied. The surface topography indicating stabilization mechanisms has been investigated by scanning electron microscopy. In order to identify the mineral phases and the balance sheet of materials for determining the migration of material during recrystallization and neomineralization, electron microprobe and proton induced X-ray emission microprobe have been used.

With regard to the mobility of heavy metals as a consequence of acidification, the buffer capacity of the solidified samples has been determined in titration tests. In a six-step sequential extraction procedure the phase specific metal associations and the binding strength of heavy metals have been investigated. Physical parameters for evaluation of the disposal facilities have been supplied by soil mechanical methods and building material tests such as setting behaviour, change of volume, bending tensile strength, and compressive modulus of elasticity.

RESULTS

In comparison to untreated air-dried sludge with its porous texture, in solidified samples, especially those beeing treated with hydraulic additives, scanning electron micrographs show that there is a kind of "bridging" between the sludge particles, consisting of acicular and fine fibrous hydration products. The sludge particles are often coated with hydration products and other new minerals, which also grow into the pores. Admixture of gypsum results in a "framework" of recrystallized gypsum in the micropores. All these findings suggest that solidification and decrease of permeability is caused by the growth of new mineral phases forming an unorientated meshwork (intersertal texture) and thus enclosing the sludge particles.

The physical parameters confirm the results of microscopical investigation. Crushing strength, shearing strength, bending tensile strength, and compressive modulus of elasticity attain best results in mixtures with high amounts of cement. In cement mixtures the crushing strength of 0.94 N mm^{-2} lies above the minimum standard for upland deposition. Good results (0.58 - 0.89 N mm^{-2}) have been obtained when mixtures of coal fly ash and lime or lime and gypsum were added.

Titration curves in figure 1 show that by admixing calcium carbonate the pH value is kept constant at pH 8 for a large range of acid addition. Solidification products containing coal fly ash or gypsum show only small buffer capacities, like harbour sludge itself. By adding calcium hydroxide, lime, and cement, the pH value of the mixture increases leading thus to a decrease of heavy metal solubility. But while the pH values in solidified samples of sludge/calcium hydroxide and sludge/lime after high additions of acid still remain constantly, the pH value of sludge/cement decreases linearly.

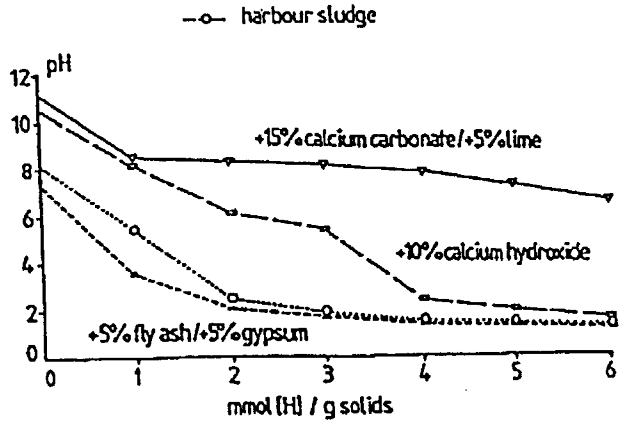

Figure 1. pH titration curves for suspensions showing effects of additives on chemical stability of harbour sludge

Results from a six-step sequential extraction procedure (1) on untreated sludge and solidified samples show that by addition of special cements or mixtures of waste kiln dust and coal fly ash and gypsum, respectively, the binding strength of cadmium is reinforced, which means that the residual fractions increased. A similar effect can be observed in the case of lead with increasing moderately reducing fractions (see fig. 2).

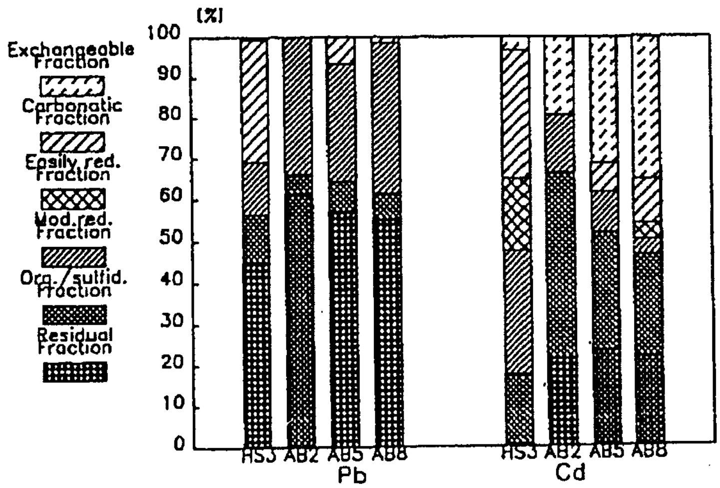

Figure 2. Sequential extraction results for Pb and Cd on untreated sludge (HS3), sludge/special cement (AB2), sludge/waste kiln dust/coal fly ash (AB5), sludge/waste kiln dust/gypsum (AB8)

Copper, nickel, and zinc, which are mainly associated with the organic/sulfidic phases in the original sludge, are shifting to either moderately reducing fractions (Cu), carbonatic or hydroxidic phases (Zn), or carbonatic and cation exchangeable fractions (Ni). The latter phases are relatively unstable, and the metals may become remobilized by lowering of pH or by complexation with organic substances. With respect to the possible impact on water quality, however, the chemical conditions in the deposit have to be considered, i.e. the presence of a relatively high buffer capacity by addition of lime, calcium carbonate, cement, alkaline fly ash, etc., or by formation of new sorption sites e.g. on iron oxyhydrates. In the systems studied here, mobility of chromium is not affected by the additives. The behaviour of lead indicates a decrease of the carbonate fraction in the original material following the addition of lime, gypsum, and lime/red mud mixtures; these shifts should be associated to an increase in chemical stability.

REFERENCES

1. Calmano, W. and Förstner, U. (1983) Sci. Total Environ., 28, 77-90.
2. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung. Verlag Chemie, Weinheim