STABILIZATION OF DREDGED SLUDGE BY CHEMICALLY AND MINERALOGICALLY DIFFERENT ADDITIVES

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1. ABSTRACT

Sludge from the harbour of Hamburg which was highly contaminated with heavy metals and organic toxicants has 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 proton-induced X-ray emission microprobe (PIXE) indicates that new minerals have been formed. These new mineral formations stabilize the material and change, as confirmed by chemical extraction methods and different leaching tests, the phase specific bonding of heavy metals by incorporation into silicates, carbonates, sulfates, and hydroxides.

2. INTRODUCTION

The quantity of sediment which is dredged from the harbour of Hamburg amounts to about 2 million m³ per year. The possibilities of disposal of these materials are severaly limited because of the high concentration of heavy metals and organic toxicants. At present upland deposition is favoured. This alternative demands minimization of emissions from leachates into the groundwater, which can be achieved by both hydraulic measures and by reducing mobility of pollutants. With respect to critical heavy metals, which are in part weakly bound to the original sludge particles, it is assumed that their bonding strength can be positively influenced by chemical additives.

3. SAMPLE PREPARATION AND TEST METHODS

The dredged harbour sludge is primary classified by a combination of hydrocyclone and up-stream separation in uncontaminated sand and highly contaminated mud fraction, which is dewatered up to stiff consistency (40-50 w/w percent dry substance).

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 are added in different mixing ratios (5-20 w/w percent). The mixtures are 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 are air-dried.

By means of polarization microscopy, mineral content, structure, and texture have been analyzed.

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For qualitative and semi-qualitative analysis of mineral phases X-ray diffraction has been applied. The surface topography indicating stabilization mechanism has been investigated by scanning electron micoscopy. 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 chemical bonding and the bonding 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.

4. RESULTS

Compared to untreated air-dried sludge with its porous texture, in solidified samples, especially those being 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. Often the sludge particles are 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 (Figures 1-2).

FIGURE 1. solidification product of sludge/waste kiln dust/gypsum (thin section) : newly grown radial gypsum crystals filling micropores

FIGURE 2. solidification product of sludge/cement (scanning electron micrograph): "bridging" by fine fibrous calcium silicate hydrate

The physical parameters confirm the results of microscopical investigation. Crushing stength, shearing strength, bending tensile strength, and compressive modulus of elasticity attain best results in mixtures with high amounts of cement. Crushing strength of 0,94 N/mm² in cement mixtures lies above the minimum standard for upland deposition. Good results (0,58-0,89 N/mm²) have been obtained when mixtures of coal fly ash and lime or lime and gypsum were added.

Titration curves (Figure 3) show that by admixing calcium carbonate the pH-value is kept constant for the longest period of acid addition at pH 8. Solidification products containing gypsum or coal fly ash have 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 value in solidified samples of sludge/calcium hydroxide and sludge/lime even after the fourth addition of acid rapidly increases, the pH-value of sludge/cement linearly decreases.

Results from a six-step sequential extraction procedure 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 bonding strength of cadmium is reinforced, which means that the organic/sulfidic fraction respectively have increased. The same effect can be observed in case of lead, when cement, and calcium hydroxide or mixtures of red mud and lime are used as stabilization agents (Figure 4).

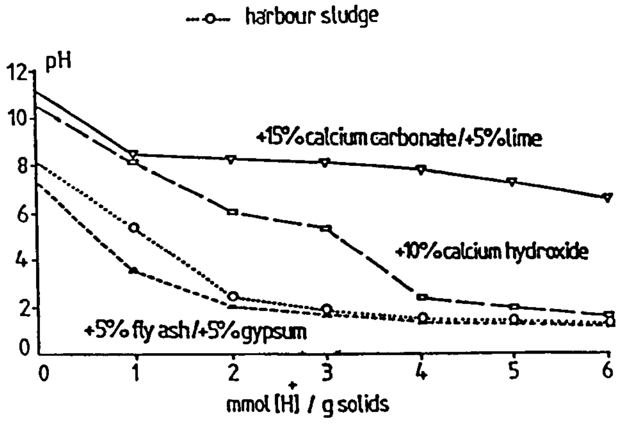

FIGURE 3. pH-titration curves for suspensions showing effects of additives on chemical stability of harbour sludge

For copper best results were obtained with coal fly ash and coal fly ash/gypsum or waste kiln dust mixtures. In coal fly ash/gypsum mixtures also the bonding strength of nickel was reinforced. Other heavy metals like chromium, zinc, and manganese are in untreated sludge more stably bound (organic/ sulfidic fraction) than in solidified samples, where e.g. zinc shifts to the carbonatic fraction. This fraction is considerably less stable in case of pH-lowering or complexation with organic degradation products, but shows at the same time a higher buffer capacity. One has to take into account that the additives may cause additional contamination of the solidified products. Red mud e.g. effects a considerable increase of extractable iron and chromium, whereas slightly contaminated additives like gypsum cause dilution effects. Essential is the phase specific bonding of the heavy metals in the additive.

First leaching tests generaly confirm the results of the sequential chemical extraction. During preliminary leaching tests (German standard methods: DEV S4) on solidified lime/sludge and calcium hydroxide/sludge samples high mobilization ratios of lead and cadmium respectively were found. Considerable amounts of manganese have been leached out from gypsum/coal fly ash mixtures. An altogether stable bonding of all heavy metals was attained by a mixture of coal fly ash and a special cement. The leaching ratio of all solidification mixtures varies between 0,025 % for cadmium and 0,0025 % for iron. This means that drinking water standards are only partly exceeded, as for e.g. chromium. The limit value for zinc is attained in no mixture. Regarding these results, one has to take into account that for eluation a grain size of 0-2 mm simulate extreme conditions. In order to get more precise information, at present column leaching tests with a solid/ liquid ratio of 1:100 and defined grain size are carried out.

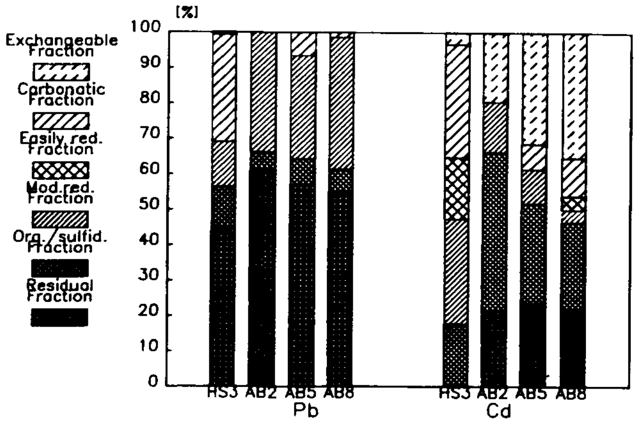

FIGURE 4. sequential extraction results for lead and cadmium on untreated sludge (HS3), sludge/special cement (AB2), sludge/ waste kiln dust/coal fly ash (AB5), sludge/waste kiln dust/ gypsum (AB8)