ASSESSMENT OF LONG-TERM METAL MOBILITY IN HEAT-PROCESSING WASTES

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ABSTRACT. Estimation of long-term release of metals from solids can be made using a test procedure, which combines data from column experiments applying controlled intensification of parameters such as pH-value, redox potential and temperature with results from sequential extraction of the contaminated solids before and after exposure.

1. INTRODUCTION

Typically for systems involving solution/solid interactions, "mobility" reflects the flux of metal species in a certain medium, which contains both accelerating and inhibiting factors and processes. The former influences comprise effects of pH-lowering, redox changes, inorganic and organic complexation, and microbially mediated species transformations such as biomethylation. Four different ways can be envisaged for the assessment of metal mobility in typical environmental compartments (Förstner *et al.*, 1990): (i) The most comprehensive approach involves evaluation of all species changes along the pathway of the element through the system ("full-system speciation"). (ii) For many objectives, e.g. for studying effects on biota, determination of the elemental species distribution at a critical section within the system or at its efflux may be sufficient ("part-system speciation"). (iii) Model considerations, which are aimed to generalize typical distribution or transformation processes, need data on dominant species combined with typical mobilizing/inhibiting parameters such as pH, and pH_2S in the dissolved phase and surface properties of the solid phase ("model species/mobility approach"). (iv) Long-term prognosis of the behavior of metals at critical sites requires both the knowledge of interactions of element species in solid matter and solution, and an estimation of the future borderline conditions in a dynamically evolving medium ("prognostic mobility/species approach"). In the present contribution we will discuss the latter approach, which is based mainly on characteristic changes of total metal fluxes, i.e. on mobility variations derived from laboratory experiments.

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2. METHODS AND MATERIALS

2.1 Revies of Leaching Procedures

Various laboratory techniques have been reported for the characterization of reactivity and mobility of pollutants generating leachates from hazardous waste, and are generally grouped into batch and column extraction methods. The batch extraction method offers advantages through its greater reproducibility and simplistic design, while the column method is more realistic in simulating leaching processes which occur under field conditions. It has been noted by Jackson *et al.* (1984) that relative standard deviation of experimental data was over twice as great for the column method as for the batch method; this result was attributed to varying degrees of "channeling" that may have occurred during leaching of waste constituents using the column method. Initial estimation of potential release of metal from contaminated solids is mostly based on elutriate tests, which - apart from the characterization of the reactivity of specific metals - can provide information on the behavior of metal pollutants under typical environmental conditions. Common single reagent leachate tests, e.g. U.S. EPA, ASTM, IAEA, ICES, and DIN use either distilled water or acetic acid (Theis and Padgett, 1983). A "mobility test" procedure for soils based on variations of pH-values has been proposed by Kiekens and Cottenie (1985). Application to a large number of polluted and non-polluted soils indicate that typical mobilisation patterns are obtained for the different heavy metals. Beside the nature of the element, the pH-curves reveal typical textural features of different soil substrates. Best results with respect to the estimation of middle-term effects can be attained by "cascade" test procedures at variable solid/solution ratios: A procedure of the U.S. EPA (Ham *et al.*, 1979) designed for studies on the leachability of waste products consists of a mixture of sodium acetate, acetic acid, glycine, pyrogallol, and iron sulfate. For the study of combustion residues a standard leaching test has been developed by the Netherland Energy Research Centre (Van der Sloot *et al.*, 1984). In the column test the material under investigation is percolated by acidified demineralized water (pH = 4; for evaluating most relevant effects of acid precipitation) to assess short-term leaching (< 50 yr). In the cascade test the same quantity of material is extracted several times with fresh demineralized water (pH = 4) to get an impression of medium-term leaching behavior (50-500 yr). As a time scale the liquid/-solid ratio (L/S) is used (De Groot *et al.*, 1987). Single reagent leaching tests, in particular short-term batch procedures, can be used for easily soluble components such as halides or sulfates, but in most cases are not adequate for assessing mobility of trace metals. For example, cascade test procedures demonstrated much high increases in the percent elution of elements such as As than can be expected from the increase of the solution/solid ratio (Van der Sloot *et al.*, 1984). Another example, from the time-dependent leachability of Cd and Pb in filter-dust samples, indicated much greater percentages of released metals after short-time treatment (0.5 and 5 hr) than after longer contact (50 hr) between dissolved and solid metal species; a reverse time-dependency was observed for Pb in dust samples solidified with cement;

both developments can be interpreted as resulting from pH changes (Brunner and Baccini, 1987).

In connection with the problems arising from the disposal of solid wastes, particularly of dredged materials, chemical extraction sequences have been applied which are designed to differentiate between the exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual fractions. The undisputed advantage of this approach with respect to the estimation of long-term effects on metal mobilities lies in the possibilty, that rearrangements of specific solid "phases" can be evaluated prior to the actual remobilisation of certain proportions of an element into the dissolved phase (Förstner, 1985).

The widely used extraction sequence of Tessier and collaborators (1979) consists of five steps. Applications of these methods have been given for atmospheric particulates (e.g., Lum *et al.*, 1982), street dust and roadside soils (Harrison *et al.*, 1981), sewage sludge (Rudd *et al.*, 1986), sediments (review by Kersten and Förstner, 1989), incinerated sludge ash (Fraser *et al.* 1982), and coal and waste incineration ashes (Wadge and Hutton, 1987). The latter study indicated, for example, that about 20% of total Cd and 1% of total Pb in coal fly ash was in exchangeable fraction; in contrast, the single largest fractions of Cd and Pb in refuse ash, at 72% and 41%, respectively, were present in the exchangeable form.

2.2 Procedure for Long-Term Predictions

Because these approaches involve neither reaction-mechanistic nor kinetic considerations, they are of limited value with regard to prediction of long-term effects in waste-deposits. This lack can be avoided by an experimental approach, originally been used by Patrick *et al.* (1973) and Herms and Brümmer (1978). Metal mobility can be estimated by comparing sequential extraction results before and after treatment of waste material by controlled intensification of significant release parameters such as pH-value, redox-potential and temperature using an ion-exchanger system for extracting and analysing the released metals at a adequate frequency (Figure 1).

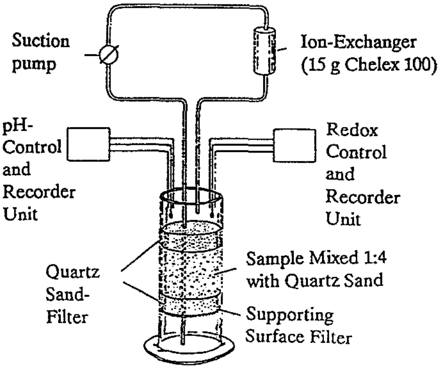

Figure 1 Experimental design for long-term prognosis of metal release (Schoer and Förstner, 1987)

This system was used in an initial series of experiments for the evaluation of the long-term behavior of metal contaminants (including As, Cd, Tl, and V) in metal oxide residues from different waste materials, including heat processing wastes, which had been deposited into borrow pits from sand removal along the river Rhine. We simulated the interaction between the water and the deposit - flow-through at high and flow-by at low permeability of the deposit as it takes place in the surrounding groundwater aquifers. Simulation of extreme conditions between water and critical components - which may result from erosion of waste materials - was also reproduced by the experimental design. With respect to the release of most elements, acidity was more effective than changes in redox potential. The experimental data indicated more reduced mobilization of metals in the flow-by experiments compared to flow-through conditions. For Cd, Pb and Zn, maximum release during the flow-by experiment was less than 1 % of the flow-through experiment under the same chemical conditions.

3. RESULTS AND DISCUSSION

Using the previously described experimental design a second series of investigations was undertaken with various types of industrial waste materials, which were intended for co-disposal in borrow pits. In these experiments special attention should be given to the efficiency of individual components with respect to long-term behavior of critical trace elements in such mixed deposits.

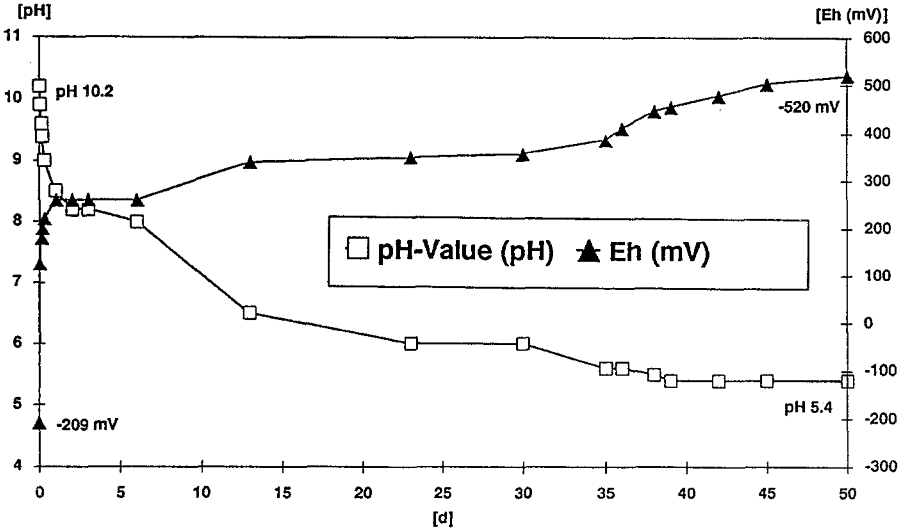

Figure 2. Changes of pH- and redox values in a suspension of industrial waste material (20 g dw l^{-1} distilled water) under continuous aeration during 50 d.

3.1 Results

The mixture of industrial waste studied here contains higher percentages of components such as silicates and oxides from high-temperature incineration processes, and these materials can be expected to behave essentially inert subsequent to deposition. For other components, e.g. sulfates and halides, short-term dissolution and metal-release has been observed from simple elutriate tests as mentioned above (section 2.1). A third group of components is particularly interesting with respect to their middle- and long-term behavior, since these materials exhibit characteristic temporal changes of pH- and redox conditions upon aeration, and may affect the properties of the whole mixture. Figure 2 represents the example of a typical component, which has been proposed as a potential additive for solidification/stabilisation of metals in large-volume waste materials, mainly due to its high initial pH-value. It is demonstrated, that within a short time after aeration the redox potential in the suspension of this material is increasing while the pH-value is lowered, respectively. Total decrease of pH is approximately five orders of magnitude; the reaction is not fully completed with the experimental period of 50 d.

From these data, it should be argued that the long-term effect of the initial high-pH additive on the stability of trace elements in the disposal mixture is less advantageous that previously assumed. Figure 3 presents the cumulative mobilization of three typical elements from different waste compositions, which were studied in experiments with pH 5 solutions during 10 weeks. Addition of the high-pH component is reducing release of all three elements in the initial stage of the experiment. Mobilization of As is reduced by a factor three to four; for both untreated and mixed waste the cumulative release curves are levelling towards the end of the experimental period. For Tl, rates of release are significantly reduced was well; here, however, mobilization is still active at the end of the experiment. Cumulative mobilization of Zn from the treated waste is very low during the initial phase of the experiment. From the 6th week on, however, the release of Zn from the suspended material is distinctly increasing and is finally surpassing the rates from the untreated industrial waste.

Kinetic of element's release from "conditioned" waste material, i.e., treated with high-pH additives, is shown in Figure 4 for As, Tl, and Zn. By treatment with pH 5 solutions, mobilization of As is essentially completed after the initial five weeks of the experiment. Rate of Tl release is not significantly varied within the experimental period of time. Mobilization of Zn is strongly enhanced towards the end of the study period.

Cumulative percent release of the before-mentioned elements within the 10 weeks experiment time has been calculated as approximately 25% for As, 27% for Tl, and 2% for Zn in the waste materials treated with high-pH additives; for untreated material the cumulative percentage over 10 weeks are 61% (As), 33% (Tl) and approximately 2% (Zn). Regarding the latter element, it can be expected that the cumulative percentage of release from the treated material would significantly be enhanced after continuation of the experiment.

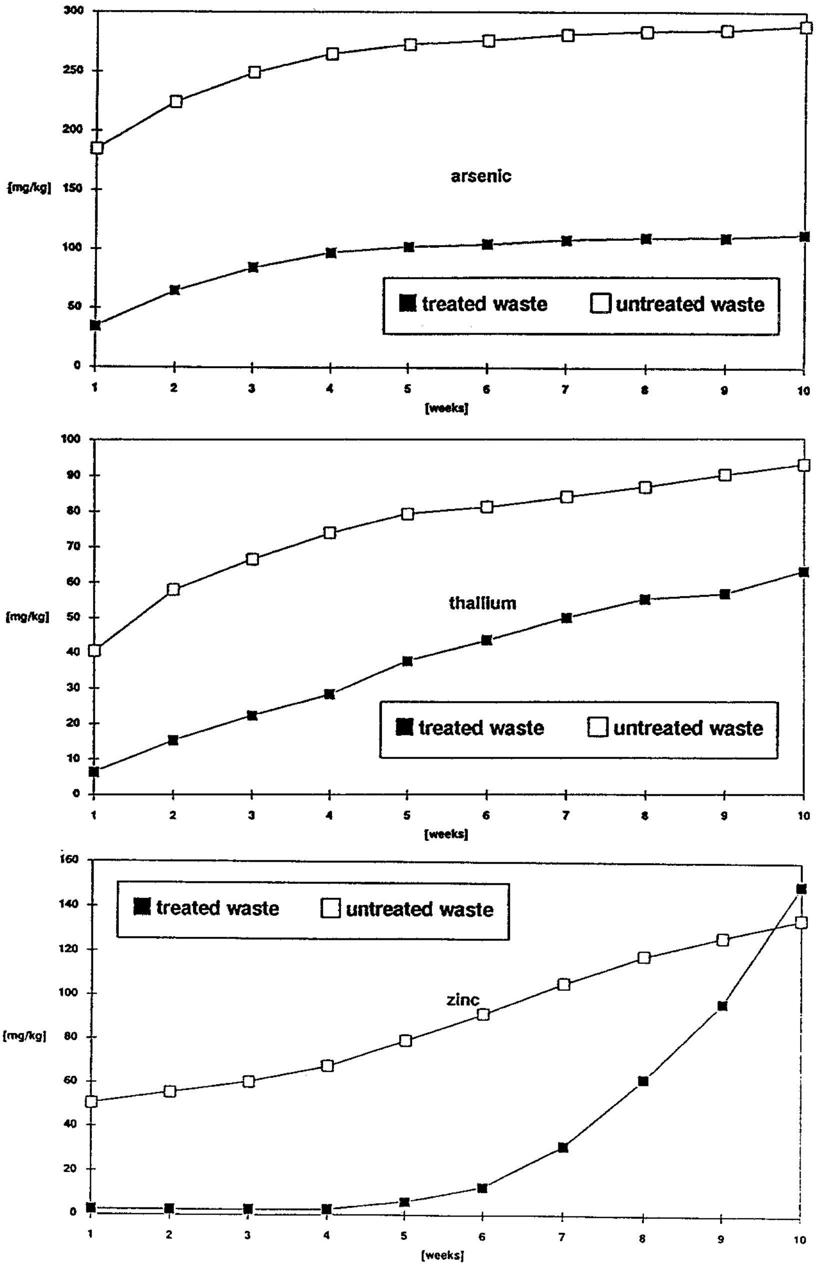

Figure 3. Cumulative mobilization of As (above), Tl (middle) and Zn (below) from untreated and treated industrial waste

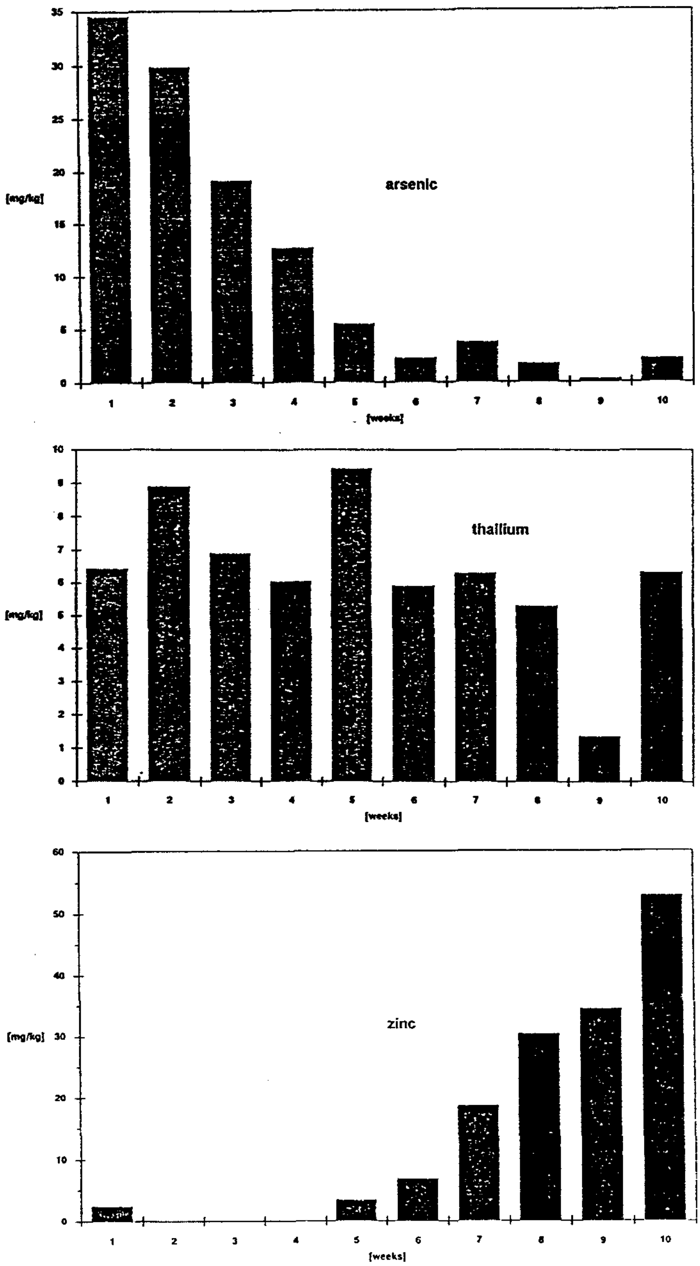

Figure 4. Kinetic of release of As (above), Tl (middle), and Zn (below) from industrial waste treated with a high-pH additive. Experiments were conducted with pH 5 solution.

In particular for the elements, of which the end-point of release cannot be estimated from the respective cumulative curves - e.g. Tl and Zn in the present study - extrapolation with respect to total mobilizable "pools" can be performed by comparing data from circulation experiments with results from sequential extraction procedures. Taking the example of Tl in Figure 5, where the column experiment data (pH 7 of the circulating solution) were compared with the operational fractions from a four-step leaching sequence applied to treated waste material before and after the circulation experiment, it is suggested, that in particular the more labile "exchangeable" (ammonium acetate at pH 7; solid/solution ratio: 1 : 20) Tl should be released under "normal" conditions in the waste deposit. The potential of easily mobilizable Tl, according to the present extrapolation, would correspond to approximately one third of the total Tl content on the sample. Remedial measures, should be aimed to a significant reduction of this proportion of the Tl content.

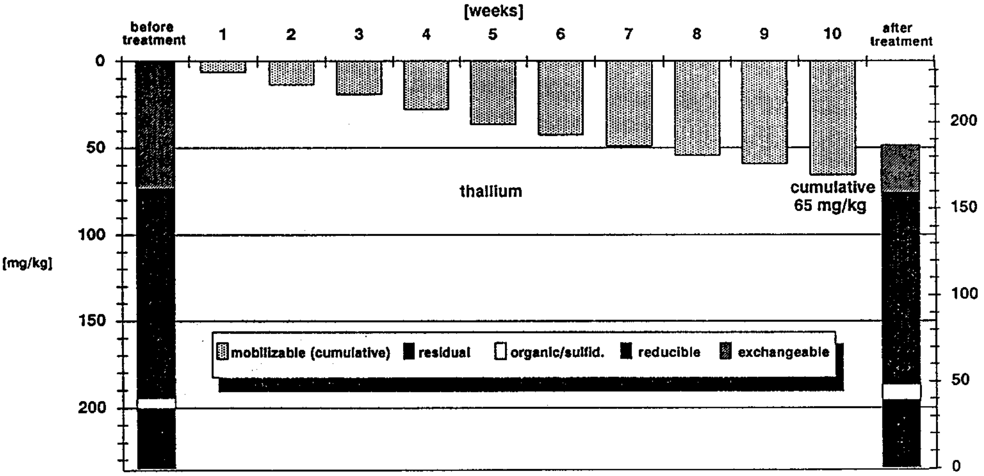

Figure 5. Comparison of Tl "pools" in a sample of industrial waste material before and after treatment with distilled water.

3.2 Discussion

Changes from reducing to oxidizing conditions in waste materials, which involve transformations of sulfides and organic matter, followed by a shift to more acid conditions, increase the mobility of critical metals. This has important consequences both for domestic and industrial landfilling. It has been inferred that oxidation of sulfidic minerals by intruding rainwater may mobilize trace metals from landfills subsequent to the methanogenic phase, and the impact on the underlying groundwater could be even higher, if a chromatographic-like process, involving continuous dissolution and reprecipitation during passage of oxidized water through the deposit, would preconcentrate critical elements prior to final release with the leachate (Förstner *et al.*, 1989). It has been shown by Peiffer (1989) from laboratory experiments on sewage sludge, that due to slow oxidation kinetics of the sparingly soluble metal sulfides ZnS, CdS, PbS, and CuS, ion exchange will become the rate-determining mechanism in this system. From the current pH-decrease it can be expected that Zn and Cd are being exchanged for H^+, whereas Pb and Cu do not, because of their stronger bonding to the solid substrate. Similar effects have been postulated for residual organic carbon in municipal solid waste incinerator slag as a potential H^+-producer due to microbial degradation to CO_2 (Krebs *et al.*, 1988).

With regard to industrial waste materials, typical mobilization processes of transition elements can be expected in particular from the oxidation of S-containing components. At low buffer capacity, mostly in connection with low carbonate contents, even relatively small concentrations of sulfide and thiosulfate may effect long-term release of elements such as Zn and Cd. Special attention should be given to As, which - according to calculations based on laboratory experiments by Blakey (1984) - shows least attenuation and greatest mobility under mildly reducing conditions in the pH range of 5 to 9. These conditions are typical for the transition stage of aerobic and acetic anaerobic phases in municipal solid wastes, and As is typically mobilized from such materials during initial change of redox conditions subsequent to waste disposal. On the other hand, not much is known about the mechanisms, which affect the release of elements such as Tl. The present study indicates, that relative high percentage of Tl is mobilized even at intermediate pH-values, which can be expected for most low-organic waste deposits. It seems that a significant proportion of Tl is behaving like alkali ions, i.e. is easily released into the percolating water. For this proportion, pretreatment of the waste material prior to deposition - e.g. by washing with water in a circulation process - would be more efficient than stabilization by high-pH-additives.

4. CONCLUSIONS

Four major conclusions can be drawn from the present experiments:

(i) Simple "standard" leaching tests can be used for easily soluble components such as halides or sulfates, but in most cases are not adequate for assessing mobility of many trace elements in waste material both from domestic and industrial origin. metals.

{ii) With respect to long-term prognosis of metal mobility in solid materials, test procedures combining data from column experiments with extrapolations from sequential extraction methods seem to provide reliable values.

(iii) At this stage, no remedial measures are known for stabilizing the full spectrum of potentially problematic elements, i.e. both transition metals and elements, which are mobile at intermediate pH-values, such as arsenic and thallium.

(iv) Addition of high-pH solid material for stabilization/solidification of large-volume wastes should carefully examined using longterm assessment methods. In particular, organic matter and sulfidic minerals, apart from their own content of toxic elements, may induce reactants for long-term mobilization effects.

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