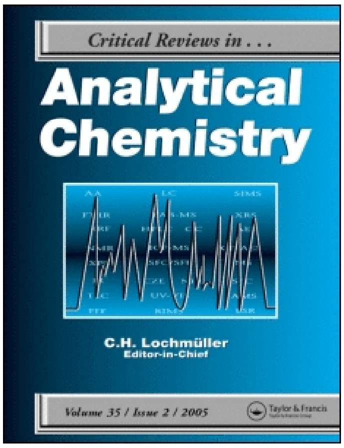

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Safe Disposal of Chromium-Rich Waste Materials

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ABSTRACT: Speciation analysis plays a crucial role in the investigations of transformation and mobility of Cr in the environment. In order to investigate the conditions for safe disposal of chromium-rich waste materials, appropriate speciation techniques regarding specific characteristics of sample matrix should be applied. Partitioning of Cr between various phases in waste materials, in soils, and in waste materials mixed with soils give useful data for the assessment of the environmental hazards. For this purpose, it is necessary to apply long-term experiments and to study possible oxidation-reduction processes of Cr after disposal of waste to various soils. On the basis of complex investigations estimation can be done on conditions for safe disposal of chromium-rich waste materials.

I. INTRODUCTION

In the environment Cr is present in ores and minerals, volcanic dust, and gases. Cr chemicals are frequently used in metallurgy, chemical industry, in leather tanning, and in wood protection. Cr is frequently present as a pollutant in the environment. The toxicity of Cr depends primarily on its chemical form. Trivalent Cr compounds are much less toxic than those of hexavalent Cr.[1,2] Under certain conditions, for example, the presence of Mn(IV) oxides, Cr(III) could be oxidized in soil to its toxic hexavalent form.[3,4] At high alkaline pH's slow oxidation with dissolved oxygen in buffered solutions of Cr(III) was also observed.[5] The prevailing oxidizing or reducing conditions in soils influence the equilibrate concentration of the particular Cr species.

The easily soluble chemical species of elements have the greatest influence on the terrestrial environment and ground water and are regularly uptaken by plants. Therefore, it is very important to optimize the procedures for the determination of total metal content in the water-soluble soil fraction as well as its particular chemical species.[6] In the studies of the metal impact on terrestrial environment, it is also very important to determine other moderately and sparingly soluble metal species in soil. Several fractionation procedures, so-called "operational speciation" applying a number of successive selective extractions have been developed for that purpose.[7,8]

In the present work the most important parameters that should be investigated in order to ensure safe conditions for disposal of some chromium-rich waste materials are represented.

II. THE ROLE OF SPECIATION IN THE INVESTIGATIONS OF TRANSFORMATION AND MOBILITY OF CR IN THE ENVIRONMENT

Speciation plays a crucial role in the investigations of transformation and mobility of Cr in the environment. In order to obtain reliable analytical data, it is very important to study the influence of sample matrix on speciation of Cr in soil samples

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and chromium-rich waste materials. Several analytical techniques were investigated in our group to develop reliable methods for the determination of Cr(VI) in various matrices.[6,9-15] Among them ion-pairing reversed phase HPLC-ETAAS was found to be a sensitive (LOD 0.3 ng cm^{-3} of Cr(VI)) and the appropriate procedure for the determination of Cr(VI) in most of natural soils.[9] Extraction of Cr(VI)-HCl complex ($HCr0_3C1$) into methylisobutyl ketone (MIBK) at 277 K, followed by determination of Cr in the organic phase by FAAS, was suitable for the determination of trace amounts of Cr(VI) in the large excess of Cr(III) in samples of waste materials,[10] waste-amended soils[13] and leather.[12] LOD for the technique in real samples was found to be 5.0 ng cm^{-3} of Cr(VI). Anion-exchange fast protein liquid chromatography (FPLC) - ETAAS enabled simultaneous separation of Cr(VI) from some negatively charged Cr(III) complexes (EDTA, oxalate) and from Cr^{3+} species. The technique was applied in the investigations of uptake and transformation of various Cr species in plants,[11] in determinations of Cr(VI) in soil extracts and in the investigation of oxidation-reduction processes of Cr in lime-treated and sawdust-amended sewage sludge.[15] LOD in real samples was 1.5 ng cm^{-3} of Cr(VI).

The choice of the technique employed in the determination of Cr(VI) in various samples depends on its concentration and on sample matrix.

Fractionation procedures based on Tessier's sequential extraction scheme were found to be suitable for study of the partitioning of Cr in natural soils,[13] waste materials,[10,13,15] and waste-amended soils.[13] This scheme was particularly applicable to highly alkaline samples,[16] since it reflects the real solubility of metals in the easily soluble fractions. The widely used BCR scheme was appropriate to the acidic samples and samples close to neutral pH.[8,17] This scheme was not applicable to highly alkaline samples, due to the tremendous change in the pH of sample (use of 0.11 mol dm^{-3} acetic acid for estimation of the easily soluble metal fraction).[18]

III. FRACTIONATION AND OXIDATION OF CR IN TANNERY WASTE AND SEWAGE SLUDGE-AMENDED SOILS

Cr(III) salts are used frequently as tanning agents in the leather industry, and it would be very difficult to replace them by other tanning agents for the time being. Tannery waste, rich in Cr(III), is under environmental scrutiny due to its high chromium content (25 to 35 mg g^{-1}). When tannery waste is disposed of on land, the risk of potential oxidation of some Cr(III) species to toxic Cr(VI) exists in the presence of Mn(IV) oxides. The investigation was performed on oxidation-reduction processes of Cr in tannery waste and sewage sludge-amended soils (clay, sandy and peat soil). The addition of waste material to soil was in the amount that covered the requirement for nitrogen in one season. The experiment was carried out for 2 years under atmospheric conditions. To study the oxidation-reduction processes of Cr in soils amended with waste materials, Cr(VI) was determined in the water-soluble soil fraction. For the estimation of the environmental hazards, partitioning of Cr was also performed by applying modified Tessier's sequential extraction procedure.[13]

The results of fractionation studies in tannery waste amended sand and clay soils (Figure 1) indicated two orders of magnitude enhancement of Cr in the water-soluble and exchangeable fractions in the first 5 months after the waste application. In peat soil this increase was moderate. After a 5-month period water-soluble and exchangeable chromium were partially eluted from topsoil with rainwaters. A part of the Cr was redistributed into the less soluble soil frac-

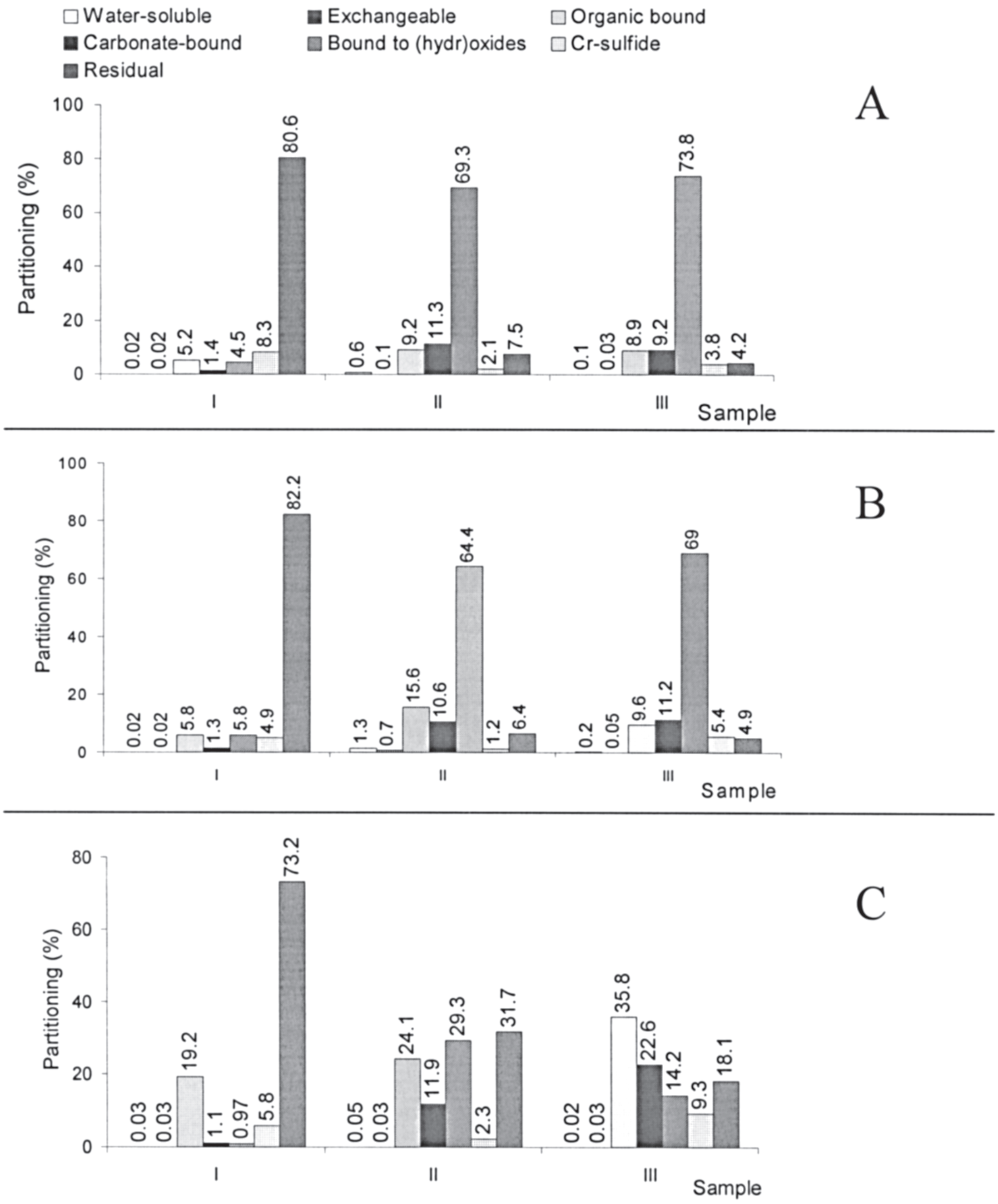

FIGURE 1. Partitioning of Cr in natural soils (I) and tannery waste amended soils (II — after 5 months, III — after 2 years). A — sand soil, B — clay soil, C — peat soil. The total concentration of Cr in natural soils ranged from 65 to 85 mg kg^{-1} and in tannery waste-amended soils from 1700 to 2300 mg kg^{-1}.

tions, which was responsible for its decrease in the water-soluble and exchangeable fractions (see data of fractionation study after 2 years). In sand and clay tannery waste-amended soils the prevailing fraction of Cr was bound to Fe and Mn oxides and hydroxides, while in peat soil Cr was distributed predominantly between organic, hydroxylamine hydrochloride extractable and mineral fractions. The oxidation of Cr(III) to Cr(VI) was found to be a slow process (Figure 2). The increase in Cr(VI) concentration was observed in the first 5 months after the tannery waste application followed by the decrease in the second period of the experiment. The degree of Cr oxidation was found to be proportional to the concentration of Mn(IV) oxides and water-soluble Cr in soils, but it also depended on the reducing capacity of the soil. Thus, the oxidation of Cr was found to be negligible in peat soil (high content of organic matter, high reducing capacity of peat soil). Reasonable amounts of tannery waste could be safely applied on such soils. Care should be taken with other soil types, because those low in organic matter and high in Mn(IV) oxides are able to oxidize Cr. Rates of application should be small and concentration of soluble Cr(VI) should be monitored in the top soil a few months after the application to prevent the potential contamination of ground water.

Data of fractionation of Cr in sewage sludge-amended soils indicated that Cr in the water-soluble and exchangeable fractions was only slightly increased in the first 5 months after sludge application. In the continuation of the experiment, a decrease of Cr concentrations in these fractions to almost the natural level in soils was observed. Due to the reducing characteristics of sewage sludge and low concentrations of total water-soluble Cr, the processes of oxidation of Cr(III) was not observed in sewage sludge-amended soils. Regarding Cr content, sewage sludge could be disposed on land without a hazardous effects on the terrestrial environment as far as total Cr is concerned and the rate of sludge application covers only the requirement for nitrogen in one season.

IV. OXIDATION-REDUCTION PROCESSES OF CR IN LIME-TREATED AND SAWDUST AMENDED LIME-TREATED SEWAGE SLUDGE

Tradtionally, liming has been used for abiotic remediation to increase the alkalinity and hence in general reduce the mobility of heavy metals. Sewage sludge containing pathogenic microorganisms was amended with quicklime (CaO) for disinfection and with sawdust for post-stabilization prior to disposal or reuse in the environment. The amount of quicklime added to the sludge or sludge mixed with sawdust was selected according to the criterion of raising the pH above 12. The mobility of Cr and other heavy metals in the sewage sludge and its mixtures with quicklime and sawdust by applying a modified Tessier's sequential extraction procedure was investigated.[16] The possible oxidation-reduction processes of Cr in highly alkaline lime-treated sludge samples were investigated in the time span of 6 months by determination of Cr(VI) in sludge extracts using anion-exchange FPLC–ETAAS procedure.[15] On the basis of the experimental data, an estimation was made whether lime treatment is environmentally acceptable for safe sludge disposal.

Data from the fractionation study (Figure 3) indicate that liming slightly decreased the total water-soluble Cr in dewatered and sawdust amended sludge 48 h and 3 months after the start of the experiment, but has no influence on the redistribution of Cr to other sludge phases. On the contrary liming significantly increased solubility of Ni and Cu and cannot be recommended for sludge stabilization if these two metals are present at elevated concentrations in the sludge.[16]

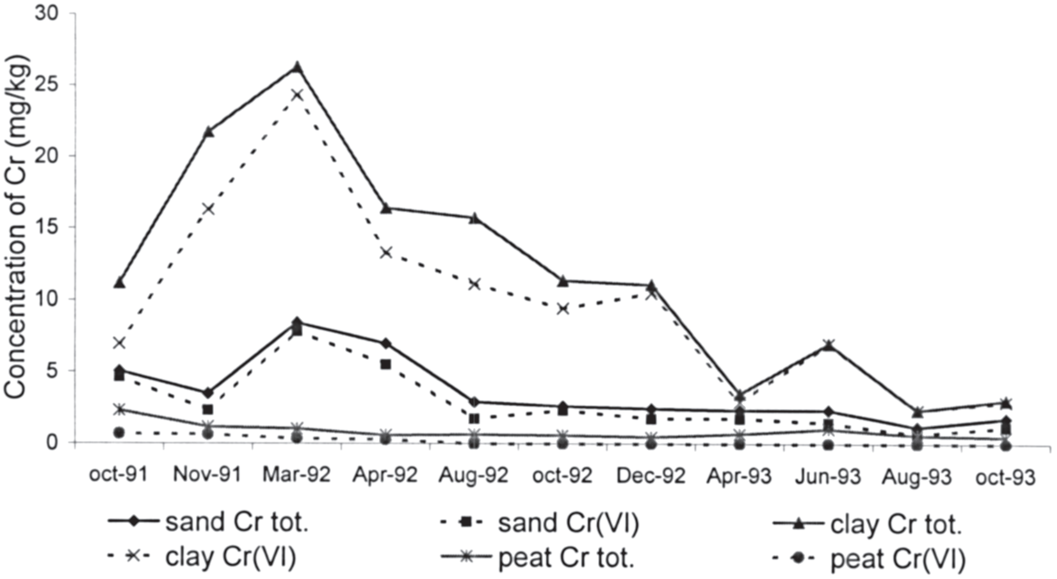

FIGURE 2. Variation of total water-soluble (KH_2PO_4, 0.015 mol dm^{-3}) Cr and Cr(VI) with time in various tannery waste-amended soils.

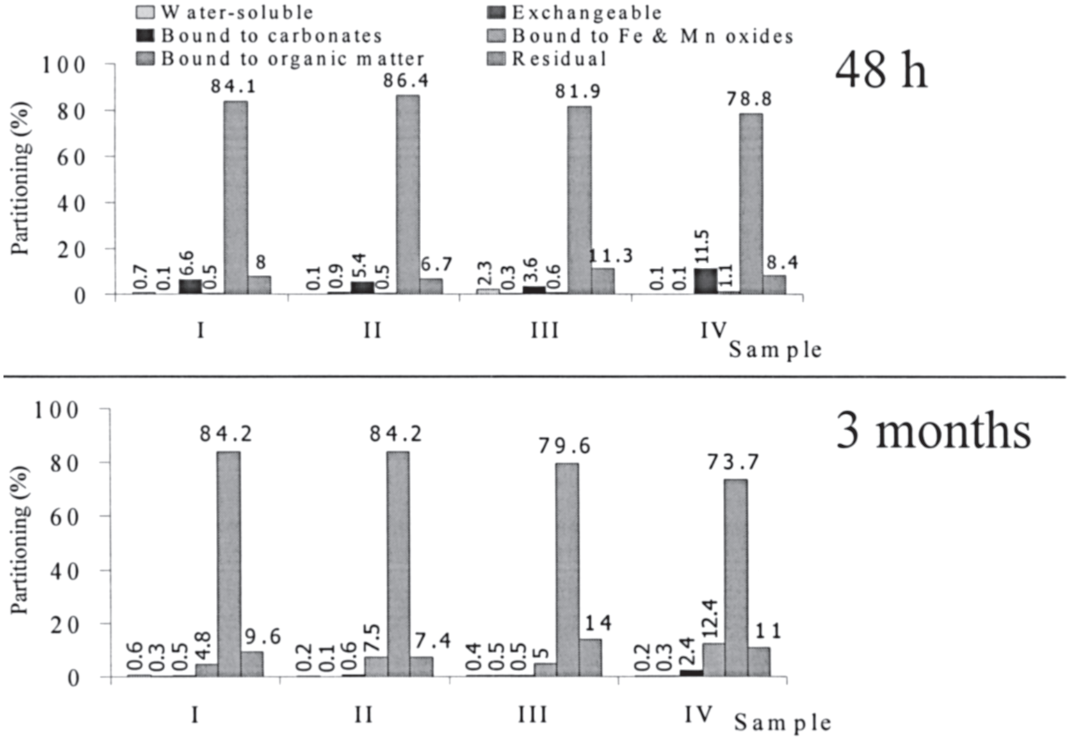

FIGURE 3. Partitioning of Cr in the dewatered sludge (I), lime-treated sludge (II), sludge mixed with sawdust (III) and in the lime-treated sludge mixed with sawdust (IV) 48 h and 3 months after the start of the experiment. The total concentration of Cr in the dewatered sludge was 945 mg kg^{-1}, in lime-treated sludge 695 mg kg^{-1}, in sludge mixed with sawdust 375 mg kg^{-1}, and in the lime-treated sludge mixed with sawdust 343 mg kg^{-1}.

An analysis of Cr(VI) in untreated and lime-treated sludge indicated that in aqueous extracts of dewatered and sawdust amended sewage sludge Cr(VI) was not detected. In aqueous extracts of lime-treated and sawdust amended lime-treated sewage sludge Cr(VI) was determined 48 h after liming (Figure 4). Despite the highly reducing characteristics of the sewage sludge, liming caused oxidation of Cr(III) to Cr(VI) at pH 12, probably through the action of $MnOOH_{(s)}$ and dissolved oxygen. The amount of Cr(VI) in lime-treated sludge slightly increased and after 3 months was almost constant (very low concentrations, about 300 ng g^{-1} Cr(VI)). During the course of the experiment no significant changes in pH of these sludge samples was observed. The concentration of Cr(VI) in the lime-treated sludge amended with sawdust increased in the first 3 weeks elapsed after lime treatment to about 300 ng g^{-1}, and appreciably decreased after one month to a concentration of about 50 ng g^{-1} Cr(VI). In the latter sludge samples a decrease of pH from 12.0 at the start of the experiment to 9.6 after 6 months was observed. The decrease in pH the and reduction of Cr(VI) to Cr(III) was presumably caused by the release of organic acids from decaying sawdust.

Taking into consideration possible environmental hazards and in particular formation of Cr(VI) at high pH, liming cannot be recommended for sludge disinfection prior its disposal on land. On the other hand, a beneficial effect was observed on sludge stabilization when sludge was amended with sawdust.

CONCLUSIONS

In order to ensure the safe disposal of chromium-rich waste materials complex long-term experiments need to be performed. Redistribution of Cr to easily and sparingly soluble soil fractions after the waste disposal should be followed. Cr(VI) must be monitored in the water-soluble fraction, applying appropriate and reliable analytical techniques. On the basis of the investigations presented, it was concluded that sewage sludge could be disposed on land without hazardous effects on the terrestrial environment concerning Cr concentration if the rate of sludge application covers the requirement for nitrogen in one season. The disposal of tannery

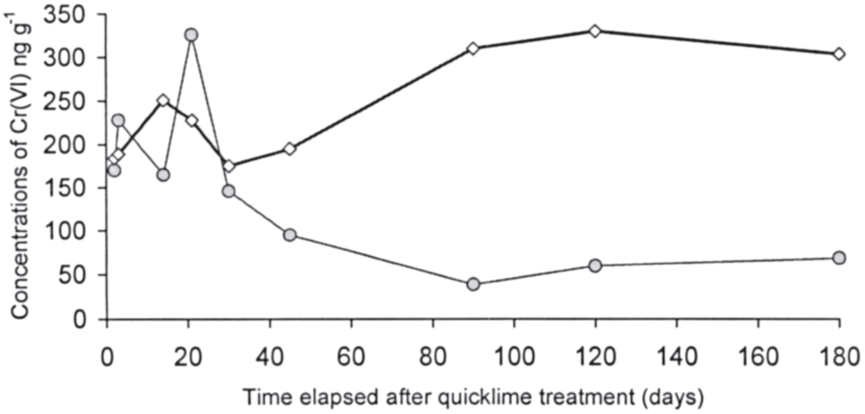

FIGURE 4. Variation of Cr(VI) concentrations (dry mass basis) with time elapsed after quicklime treatment in extracts of sludge samples treated with 5% of quicklime (bold curve) and sludge samples amended with sawdust and treated with 5% of quicklime (normal curve). Cr(VI) was determined by the FPLC-ETAAS technique.

waste to soils high in Mn(IV) oxides and low in organic matter may provoke oxidation of Cr(III) to its hazardous hexavalent form. Rates of application should be small and Cr(VI) should be monitored in the top soil to prevent pollution of groundwater. Reasonable amounts of tannery waste could be safely applied on soils low in Mn(IV) oxides and high in organic matter. Liming cannot be recommended for sewage sludge disinfection prior to its disposal on land due to possible environmental hazards caused by formation of Cr(VI) at high pH. Beneficial effects for sludge stabilization were observed when sludge was amended with sawdust.

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