

# Sequential Extraction of Chromium from Galvanic Wastewater Sludge

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## Abstract

The sequential extraction of chromium from galvanic wastewater sludge was studied. A five-step sequential fractionation scheme was used to partition the chromium into exchangeable (F I), acid-soluble (F II), reducible (F III), organic matter (F IV) and residual (F V) fractions. The results of investigations indicate that 59.5% of chromium occurred in residual fraction, which is permanently immobilized, whereas 40.5% of chromium in galvanic wastewater sludge can be released to ecosystems under changing natural conditions.

**Keywords:** sequential extraction, chromium, galvanic sludge

## Introduction

Two oxidation steps of chromium, Cr(III) and Cr(VI), are present in various forms in soil, water and in biota. Chromium and its compounds originate in the environment mainly from anthropogenic sources (industry emissions, combustion processes). Furthermore, in plants, soil and in aquatic systems chemical equilibrium between chromium species can exist [1-8].

Environmental concentration of chromium is known to increase due to industrial development. The use of chromium compounds in many industries is a source of a large quantity of waste, e.g. leather waste after chrome tanning and solid waste containing chromium hydroxide after chromic wastewater treatment as well as a large amount of liquid waste [8-10].

Aqueous solutions of NaOH, HCl, H<sub>2</sub>SO<sub>4</sub>, Cr(III) and Cr(VI), iron and other metal ions are the main components in chromium industry wastewater. Acidity and significant concentration of chromium compounds in the

wastewater makes the chromium industry of high environmental concern [8,9].

Technology of chromium wastewater neutralization is based on detoxification of waste, in most cases, by reducing chromium(VI) to chromium(III) and then using sodium or calcium hydroxide to precipitate insoluble chromium(III) hydroxide. Other metal hydroxides are coprecipitated. Very often dewatered sludges are stored at landfills in specially prepared vats [8,9].

Proper evaluation of the effect of heavy metals on the natural environment is possible by knowing their chemical forms and bindings with soil, sediment, sludge or solid waste components. Sequential extraction could be a source of the above-mentioned information, enabling identification and quantitative determination of operatively defined forms of the same chemical element. It is therefore widely used as a tool for the study of fate of metals in the environment [11-13].

The aim of this work was to identify different chromium fractions in galvanic wastewater sludge determined by the sequential extraction method according to the procedure of Tessier et al. [15].

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## Methods and Materials

### Sludge Preparation

In experiments, dewatered galvanic sludge from an electroplating plant was used. It was air-dried and ground in mortar to grain diameters of appropriately of 2, 1, 0.75, 0.5, 0.25, 0.2, 0.1, 0.075, 0.05 mm. The studied industry sludges contained  $1024 \pm 22$  mgCr/kg d.m. and 22% d.m. of organic substances on average.

Investigations were performed with air-dry weight sludge samples having mass  $m=0.2$  g and grain diameter  $0.1 \text{ mm} < \varphi < 0.5 \text{ mm}$ .

### Sequential Extraction

A five-step sequential fractionation scheme was used to partition the chromium into exchangeable (F I), acid-soluble (F II), reducible (F III), organic matter (F IV) and residual (F V) fractions. The sequential extraction of chromium was carried out according to the schematic diagram presented in Fig. 1 [14-19]. In this diagram the optimum experimental ratio of the mass of sludge sample to the volume of extractants is also presented.

Between each successive extraction, separation was affected by centrifuging at 8,000 rpm for 15 min. The supernatant was removed with a pipette and analyzed for chromium quantity, whereas the residue was washed with pure water and subjected to the next extraction step.

## Chromium Determination

Total chromium concentration was determined spectrophotometrically (HACH DR 2000) using HACH reagents, according to the application notes and using the Atomic Absorption Spectroscopy Method (AAS model 300 of the Karl Zeis Jena company).

Total chromium content was analyzed spectrophotometrically at wave length 540 nm. Trivalent chromium in the samples was oxidized to the hexavalent form by hypobromite under alkaline conditions. The samples were acidified. The total chromium content was determined as a complex of chromium(VI) with 1,5-diphenylcarbohydrazide.

The sequential extraction of the studied sludge was carried out on seven parallel samples. The determined chromium concentration in sludge eluates was recalculated to Cr concentration in appropriate fractions (Table 1).

## Results

The range of the chromium content and mean value with standard deviation in particular fractions are presented in Table 1.

The quantities of chromium extracted with different extractants, with each chromium fraction expressed as a percentage of the sum of Cr contents in F I - F V fractions are given in Fig. 2.

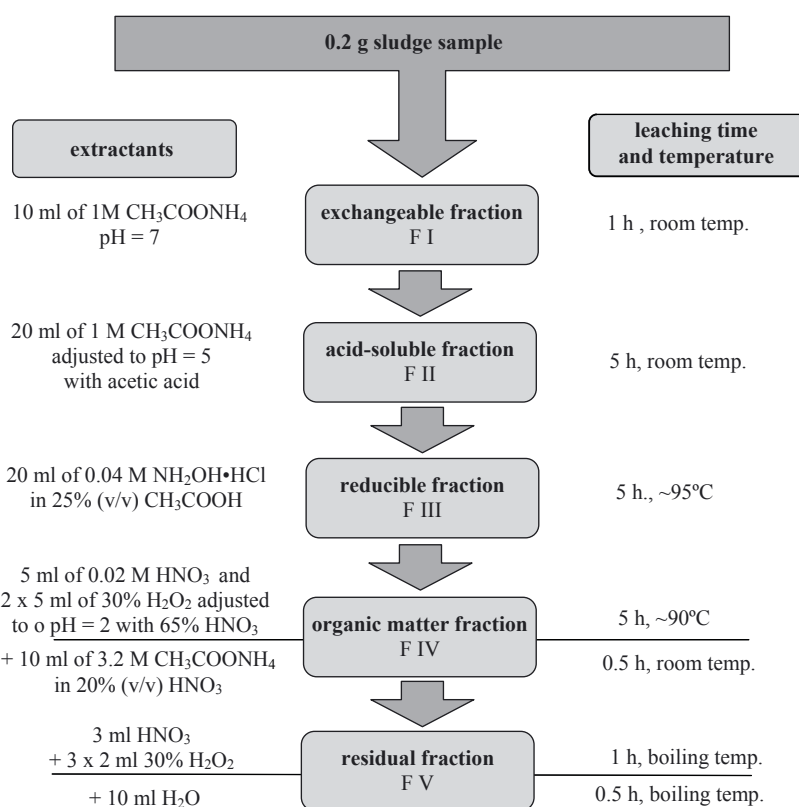


Fig. 1. Schematic diagram of the sequential extraction of chromium from galvanic wastewater sludge.

Table 1. Chromium content in particular fractions in galvanic wastewater sludge determined by sequential extraction.

Fraction		Chromium content [mg Cr/kg of dry weight of the sludge]	
		range	mean $\pm$ S.D., n= 7
F I	exchangeable	3.75 - 5.65	4.7 $\pm$ 0.62
F II	acid-soluble	23.25 - 34.55	28.9 $\pm$ 3.23
F III	reducible	93.60 - 119.20	107.5 $\pm$ 6.95
F IV	organic matter	218.70 - 243.60	237.5 $\pm$ 8.11
F V	residual	540.80 - 577.50	556.3 $\pm$ 14.44

Analysis of contribution of particular fractions of chromium present in the sludge samples from galvanizing plant has shown the predominant contribution of residual fraction F V – 59.5% and the fraction bound to organic matter F IV – 25.4%. Its smaller amounts were determined in reducible (F III – 11.5%) and acid-soluble (F II – 3.1%) forms. The exchangeable fraction contained only 0.5% of total chromium content in the galvanic wastewater sludge.

### Conclusions

The results obtained show that 40.5% of chromium in galvanic wastewater sludge occurred in fractions F I - F IV. That chromium forms are potentially bioavailable and under changing natural conditions can be included in the biogeochemical cycle of chromium.

The results of our study indicate that 59.5% of chromium occurred in a residual fraction which is permanently immobilized. The chromium forms occurring in this fraction in natural conditions cannot be released to the environment so they are practically unavailable for biota and excluded from biocirculation.

### Acknowledgments

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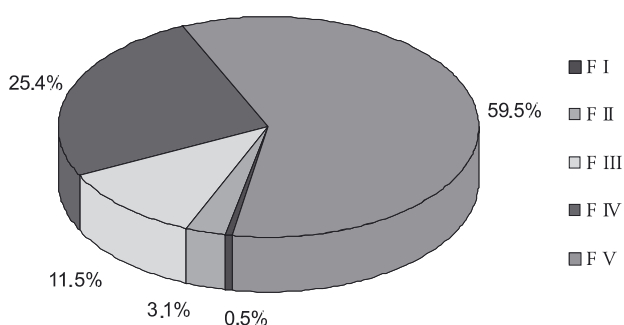


Fig. 2. Percent contribution of chromium in particular fractions in the sum of chromium contents in appropriate chromium fractions.

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