

# CHROMIUM IN CONTAMINATED SOILS: BOUND FORMS AND CHROMIUM IMMOBILIZATION BY FERROUS IRON

J. Gerth<sup>1</sup>, R. Wienberg<sup>2</sup>, U. Förstner<sup>1</sup>.

## ABSTRACT

In a contaminated soil containing up to 7000 mg/kg chromium this element was mainly present (>90%) as Cr(III) and bound to organic matter and hydrous ferric oxide. Although being difficult to extract even after prolonged extraction by 1M HCl, Cr(III) was, to some extent, water soluble and mobile. Chromium can partly be removed by separating the finer grain size fraction (<63  $\mu\text{m}$ ). Treatment of contaminated soil material with ferrous iron and subsequent oxidation results in an immobilization of chromium in a matrix of hydrous ferric oxide.

## INTRODUCTION

The average concentration of chromium in non-polluted soils is around 100 mg/kg. Much higher contents of several thousand mg/kg can be found in soils of old sites of chrome plating plants and sewage farms of leather industry. In order to assess the potential hazards emanating from such contaminations it is essential to determine the speciation of chromium. In the environment, this metal exists as Cr(III) and Cr(VI) with both forms being chemically completely different. Trivalent Cr forms hydrolysis products and co-precipitates with ferric iron [ref 1]. It also forms stable complexes with amino groups in organic material and is therefore used for leather tanning [ref 2]. In soils, Cr(III) is relatively immobile. Cr(VI) exists as the chromate anion which as a strong oxidizing agent is considered to be 100 to 1000 times more toxic than Cr(III) [ref 2]. Chromate is much more mobile in soils because it is only weakly bound by sorption reactions [ref 3]. Both forms, Cr(III) and Cr(VI), interact with soil constituents and can co-exist depending on the soil Eh-pH conditions. Chromate is reduced to Cr(III) by soil organic matter and ferrous iron. Cr(III) can be oxidized to Cr(VI) by Mn(IV) oxides [ref 4] or even by oxygen at neutral to alkaline conditions [ref 2]. In the present study, we attempted to determine the speciation of chromium in a highly contaminated soil and to devise procedures for removing and immobilizing the contamination.

## OUTLINE OF STUDY AND METHODS

On an old site of a chrome plating plant in the city area of Hamburg, two soil profiles (B4 and B5) were investigated for texture, pH, Eh, weight loss on ignition (560°C), and total content of Cr and Mn by extraction with aqua regia and analysis by atomic absorption spectrophotometry. Cr(VI) was determined

---

<sup>1</sup> Technical University of Hamburg-Harburg, Eißendorfer Str. 40, 2100 Hamburg 90

<sup>2</sup> Büro Dr. R. Wienberg, Gotenstr. 4, 2000 Hamburg 1

photometrically after a threefold 24-hour extraction with water. Pedogenic iron was extracted by oxalate [ref 5] ("amorphous" fraction) and citrate dithionite (total pedogenic Fe).

Different procedures were tested to remove or immobilize Cr in contaminated soil samples:

1. Chemical extraction using water, dilute KCl and HCl.
2. Separation of the highly polluted finer grain size fraction (<63  $\mu\text{m}$ ) by dry sieving.
3. Application of ferrous iron and subsequent oxidation to immobilize Cr in a matrix of hydrous ferric oxide.

These experiments were performed with model soil material (sand, clay and peat) contaminated in vitro. Samples were mixed with solutions of Cr(III) as  $\text{CrCl}_3$  and Cr(VI) as  $\text{K}_2\text{Cr}_2\text{O}_7$ , respectively, and then air-dried to give a final concentration of 1000 mg/kg. The dried material was suspended in a solution of ferrous sulphate at an Fe-to-Cr ratio of 10. During aeration and ferric hydroxide precipitation the pH was kept at around 7 by addition of dilute NaOH. Completion of the oxidation process was indicated by constant pH values. After drying the mobility of bound Cr in iron treated and also in non-treated samples was characterized by a sequential extraction procedure consisting of the following steps:

a) water, b) 0.5M  $(\text{NH}_4)_2\text{SO}_4$ , c) 0.3M  $\text{NH}_4$ -oxalate and d) hot  $\text{NH}_4$ -oxalate (modified sequence after ref 6).

## RESULTS

In both profiles the original soil was covered by a layer of non-contaminated sand (ca. 160 cm) which had been filled in during a previous amelioration measure. The Cr content is

Table 1 Summary of soil analytical data

Spl.	Depth cm	Texture	pH	Eh mV	WLI <sup>1</sup> %	Cr <sub>t</sub> <sup>2</sup> mg/kg	Cr(VI) <sup>3</sup> mg/kg	Mn <sub>t</sub> <sup>2</sup> mg/kg	Fe <sub>o</sub> <sup>4</sup> mg/kg	Fe <sub>d</sub> <sup>4</sup> mg/kg
	170									
B4/1	-300	sand	6.8	340	3.4	7002	6	<1	0	3790
B4/2	-360	l.sand	6.8	310	1.0	2344		10	0	400
B4/3	-410	s.loam	7.0	300	0.9	1439	47	29	30	590
B4/4*	-450	clay	7.6	280	1.6	1311		115	620	870
B4/5*	-500	clay	7.6	300	2.3	2047	83	180	480	
B4/6*	-600	s.clay	7.7	320	1.4	1757	221	90	390	1540
	160									
B5/1	-310	sand	6.7	370	0.6	313	8	<1	0	370
B5/2	-350	s.loam	6.2	370	0.6	316	7	80	290	1530
B5/3	-410	s.clay	7.4	170	1.4	59	10	75	510	3810
B5/4	-430	sand	7.3	350	0.9	336	20	68	140	5550
B5/5	-450	s.clay	7.6	320	2.5	343	-	141	310	3080
B5/6	-460	s.clay	7.7	370	2.8	325	27	153	140	1580

\*sample contains carbonate

<sup>1</sup>weight loss on ignition

<sup>2</sup>total metal content as extracted by aqua regia

<sup>3</sup>water extractable Cr(VI) during three times 24 hours

<sup>4</sup>oxalate ( $\text{Fe}_o$ ) and citrate dithionite extractable iron ( $\text{Fe}_d$ )

highest in B4/1 and can be related to the WLI values (Table 1). The high weight loss on ignition of this sample is due to a high content of small wood particles which act as a strong sink not only for Cr but also for Fe. To some extent, Cr is also bound as a stable Fe/Cr co-precipitate as is suggested by the oxalate extractable Fe being zero. In both profiles, the Cr(VI) values increase with depth and pH. Carbonate stabilizes chromate which under these reaction conditions is not adsorbed and completely mobile. Manganese is probably present as MnCO<sub>3</sub> and not as a Mn(IV) oxide. An oxidation of Cr(III) can therefore only occur by O<sub>2</sub> which is present in low concentrations only as indicated by the E<sub>n</sub> values.

A cleaning of Cr-contaminated soils by extraction procedures is nearly impossible because even with 1M HCl and long shaking periods the extraction is far from being complete (Table 2). A total mobilization was only found with the carbonate containing sample B4/6 due to a complete dissolution of the carbonate. Weak extractants like water and KCl mobilized clearly detectable concentrations of Cr(III) which, in consequence, should not be neglected when considering Cr transport in soil.

Table 2 Percent chromium removed by a 24-hour extraction

Extractant	Sample			
	B4/1	B4/3	B4/6	B5/1
water (3x24 hours)	0.2	5.5	11.8	3.0
1M KCl	0.1	2.6	10.8	2.3
0.1M HCl	2.7	6.9	9.2	44.0
1M HCl	-	53.0	100.0	-

Grain size separation to remove the highly contaminated high surface area particles can be a useful technique to ameliorate contaminated soils as can be seen from the Cr contents of the <63µm and the >63µm fraction of selected samples (Table 3). This method, however, can only be applied to sandy soils with a small <63µm fraction and a high specific Cr load like samples B4/1 and B5/1.

Table 3 Chromium removal by grain size separation

Spl.	%<63µm	mg/kg Cr in		%Cr removed with <63µm	%Cr removed / %<63µm
		<63µm	>63µm		
B4/1	2.7	51500	4250	25	9.3
B4/3	22.6	2800	970	46	2.0
B4/6	52.0	3100	2030	62	1.2
B5/1	2.3	4900	180	39	17.0

Because of its high affinity to ferric hydroxide Cr can easily be incorporated and immobilized in a matrix of hydrous ferric oxide. This demonstrated by the results given in Table 4. Sand contaminated with Cr(III) or Cr(VI) can be cleaned by washing with water. If Cr is, however, occluded in a ferric iron hydroxide matrix it can only be recovered by a strong

Table 4 Sequential extraction of soil samples after in-vitro contamination with Cr (1000 mg/kg) as Cr(III) (A) and Cr(IV) (B) with and without Fe(II) treatment

Spl.	Extractant	Without Fe(II)		With Fe(II)	
		Cr (mg/kg)			
		A	B	A	B
Sand	H <sub>2</sub> O	1140	1130	<2	<2
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (3X)	14	28	<2	<2
	NH <sub>4</sub> -oxalate	5	3	40	20
	hot oxalate	150	8	800	830
Clay	H <sub>2</sub> O	<2	590	<2	7
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (3X)	20	170	20	<2
	NH <sub>4</sub> -oxalate	40	50	20	20
	hot oxalate	890	300	790	810
Peat	H <sub>2</sub> O	4	4	<2	<2
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (3X)	20	10	<2	<2
	NH <sub>4</sub> -oxalate	130	100	110	30
	hot oxalate	790	720	870	240

extracting agent like hot oxalate. Cr(III) added to the clay sample is immobilized even without Fe(II) treatment. This is due to a fixation by hydrous ferric oxide associated with this material. Additions of chromate are highly water extractable and only become immobilized after treatment with Fe(II). Peat is a strong fixation medium for both oxidation states of Cr alike. Cr(VI) is instantly reduced to Cr(III) and is then also bound by complexation. A strong fixation of Cr added as Cr(VI) occurs in connection with an Fe(II) treatment. Even hot oxalate is not strong enough to dissolve the precipitate. The mechanism of this effect which was not observed with Cr added as Cr(III) is not yet understood.

#### REFERENCES

1. U Schwertman, U Gasser, H Sticher, Geochim. Cosmochim. Acta 53, 1293 (1989)
2. J Gauglhofer, V Bianchi in E Merian (ed.) Metals and their compounds in the environment (VCH Weinheim, 1991) p 853.
3. D Rai, L.E. Eary, J.M. Zachara, Sci. Total Environ. 86, 15 (1989)
4. A Manceau, L. Charlet, Geochemistry of the earth's surface and of mineral formation, 2nd internat. symposium (Aix en Provence, 1990) p 275.
5. U Schwertmann, Z. Pflanzenern., Düng., Bodenk. 105, 194 (1964)
6. J H Grove, B G Ellis, Soil Sci. Soc. Am. J. 44, 238 (1980)