

Chromium and its forms in soils in the proximity of the old tannery waste lagoon

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Received October 16, 2000; accepted November 21, 2000

A b s t r a c t. Chromium is a heavy metal whose presence in soil, water and atmosphere can cause hazard to the natural environment. The valences of chromium are sharply related to the redox potential. Precise Eh-pH conditions determine the valence of chromium. Present under adequate Eh-pH conditions, one form of chromium can change into another. The purpose of this paper is to determine chromium concentration and the possible changes of its forms in soil samples from the proximity of old tannery waste lagoon. The relationship between the presence in soils of tri- and hexavalent chromium in water and acidic extracts and Eh and pH in soil paste was examined. In the investigated area total chromium concentration in soil samples reaches value as high as 24 340 mg kg⁻¹. For different soil samples Eh values in soil paste changed from 0.38 to 0.55 V and pH from 3.7 to 6.25 which is characteristic for trivalent Cr.

K e y w o r d s: chromium, soil, tannery wastes, Eh, pH

INTRODUCTION

Chromium can exist in oxidation levels varying from -2 to +6, but in the environment chromium is mainly present with values: +3 and +6 (Barnhart, 1997a). Trivalent chromium is naturally present in the soil. The origin of chromium in the environment is connected with its presence of chromite spinels FeO·Cr₂O₃. Chromium as a chromite (FeCr₂O₄) and magnesiochromite (MgCr₂O₄) is a constituent of peridotite rocks and the derived serpentines (Hesse, 1971). Other sources of chromium in soils are from industrial waste originating from the tanning, chemical, metallurgy, cement and asbestos industries (Barnhart, 1997b), in which chromium exists under hexavalent forms: chromate (VI) and dichromate (VI) ions, as well as in trivalent forms.

Hexavalent chromium is very toxic. When inhaled it is carcinogenic. In general it is poisonous to humans and other mammals (Barlett and James, 1998; Burrows, 1983; James, 1996) whereas trivalent chromium is an essential component as a mineral supplement (Saner, 1980).

Values of chromium are related to pH and Eh conditions. Cr(VI) is stable in the more oxidising environment with Eh higher than 0.6 V and pH above 6.0 (Pao-Kuo F. Chin, 1994), whereas Cr(III) is thermodynamically stable at pH from 2 to 8 and Eh from +0.295 to -1.0 V (Fig. 1).

Eh-pH conditions directly effect the solubility of chromium compounds. Chromium solubility increases with acidity (Hekstra, 1995). In appropriate pH and Eh conditions and in the presence of reducing or oxidising agents one form of chromium can transform into another.

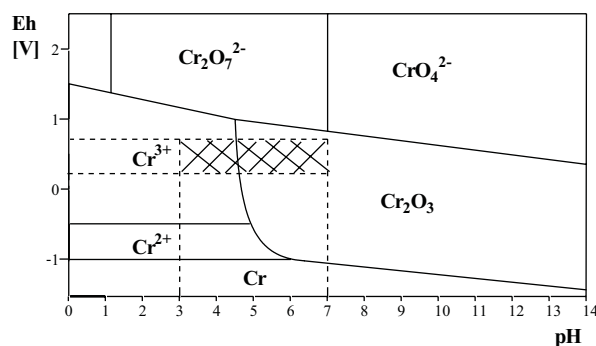


Fig. 1. Eh-pH diagram for chromium compounds (Barnhart, 1997). Lined area shows the area of the occurrence of appropriate Eh and pH in investigated soils.

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In environmental conditions, Cr(VI) can be reduced to Cr(III) which is the most stable form of chromium in these conditions. By measuring Eh and pH of the soil, one can estimate the dominant form of chromium present.

The purpose of this paper was to determine chromium concentration and possible changes in its forms III and VI in soil samples from the proximity of old tannery waste lagoon depending on their Eh and pH.

MATERIALS

The investigated site is the tannery waste lagoon of the Lubartów tannery (eastern Poland), where over 24 years, more than 200 000 Mg of waste containing 5-10% of Cr₂O₃ were dumped. The storage yard is situated in a basin where sand was excavated over an area of 6 ha. This area was not appropriately secured and was situated among cultivated fields in the vicinity of the Wieprz River. In this area sandy soils predominate. The precipitation in this region is about 600 mm y⁻¹.

The soil samples representing different sides inside and outside the lagoon (Fig. 2) were taken from:

- 1 - the bottom of the lagoon (depth 0-10 cm);
- 2 - the bottom of the lagoon (depth 10-20 cm);
- 3 - shallow layer (0-5 cm) covering shavings gathered inside the lagoon;
- 4 - patch covered with iron oxides inside the lagoon (surface layer 0-5 cm);
- 5 - surface layer (depth 0-15 cm) of the cultivated field close to the waste lagoon wall (to the East);
- 6 - surface layer (depth 0-15 cm) of the cultivated field situated 10 m from the point 5;
- 7 - 10 m from the wall of the lagoon to the West point in the cultivated field 5 meters from the sampled side 7;
- 8 - 50 m from the storage lagoon in the cultivated field (surface layer 0-15 cm).

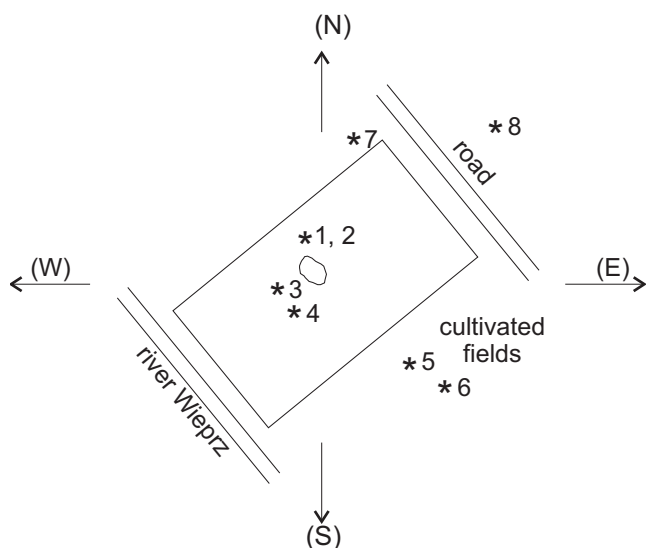


Fig. 2. Scheme of tannery waste lagoon with tested points.

METHODS

Total chromium content (in acidic extracts) and water soluble chromium forms were determined.

To make a water extracts of soils, moist soil samples (40 g) were placed in plastic vessels, to which 400 ml of distilled water was added. Then the vessels were shaken for 8 h. After filtration through a paper filter, all water extracts were analysed for chromium contents (the sum of III and VI valents) by FAAS (HITACHI Z-2800) technique.

Determination of the concentration of Cr(VI) in water extracts was preceded by separation of two species of chromium (III and VI). Separation was carried out by precipitation of Cr(III) in form of Cr(OH)₃. After separation samples were analysed for Cr(VI) content colorimetrically with the use of colour reaction of Cr(VI) with diphenylcarbazide and detection of the colour complex was performed by spectrophotometer UV- VIS (HITACHI) (Official gazette announcing current legislation, 1990; Fodor and Fischer, 1995; Zawadzka and Baryłkiewicz, 1987).

To make acidic extracts, mineralization of soils with nitric (V) and hydrochloric acids were made.

Air-dried soils were ground in a ball mill made of zirconium (IV) oxide. These samples (0.5 g) were digested using a mixture of concentrated HNO₃ and concentrated HCl and performed in open microwave system (Maxidigest MX 4350, Prolabo). Then after filtration the extracts were diluted with distilled water to 50 ml and analysed for chromium contents by FAAS (Z-8200, HITACHI).

The pH and Eh of soils were measured in paste at room temperature, pH - by silver-silver chloride electrode, type ESA g PT-304 and Eh with the use of platinum electrode as an indicator electrode and a calomel electrode as a reference electrode after Eh was established.

RESULTS AND DISCUSSION

Chromium concentration determined in water and acidic extracts are presented in Table 1 and these concentrations are calculated as chromium content in dry mass of the soil (mg Cr×kg⁻¹).

The results showed the presence of Cr (VI) in samples 5-8 outside the lagoon. The presence of highly oxidised form of chromium in these samples is connected with optimal Eh-pH conditions and the presence of the compounds such as manganese oxides and hydroxides, which are electron acceptors in oxidation reaction of Cr (III) to Cr (VI).

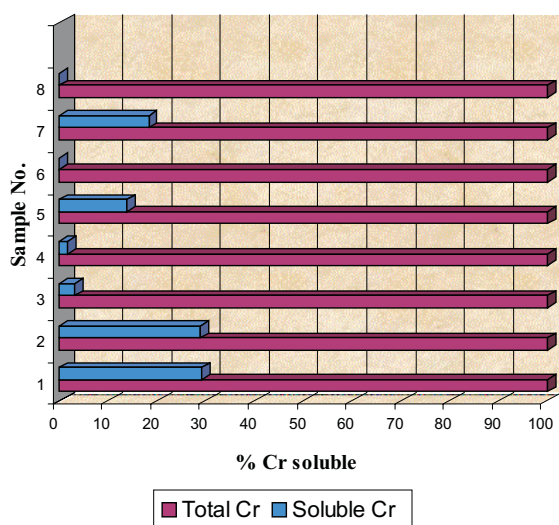
The sum (III and VI) of chromium concentration in water and total in acidic extracts of soil are showed appropriately in Table 1. The total chromium concentration exceeded the acceptable level of chromium in soil, which is 100 mg kg⁻¹ in every sample except 6. Lower concentrations of the sum (III and VI) chromium in water extracts show the domination of insoluble forms of chromium, which is trivalent chromium in majority. Soluble chromium

Table 1. Chromium form concentrations in water and acidic extracts of soil samples (mg kg^{-1})

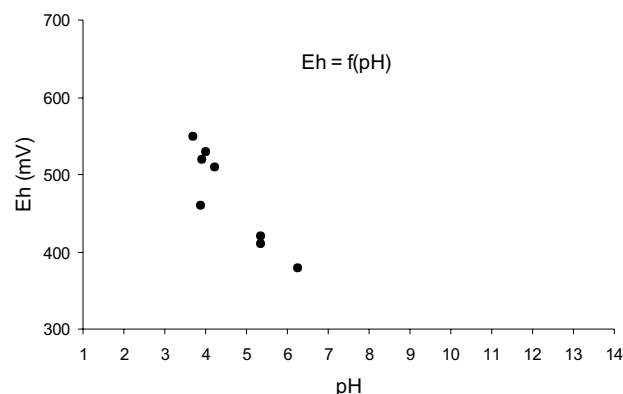
Sample No.	Depth (cm)	Water extracts		Acidic extract
		Cr (III and VI)	Cr (VI)	Total Cr
1	10-20	59.5	0	204
2	20-30	85.9	0	297
3	0-5	769.4	0	24340
4	0-5	253.8	0	14830
5	0-15	343.4	0.306	2495
6	0-15	0	0.275	44.5
7	0-5	123.2	0.277	675
8	0-5	0	0.410	282.5

content in relation to total chromium concentration in soil samples is shown in Fig. 3.

Table 2 presents values of Eh and pH measured in soil paste. The typical relationships Eh vs pH is shown in Fig. 4. Eh values range from 0.38 to 0.55 V, and pH from 3.7 to 6.25. pH is characteristic for sandy soils with small CEC and

**Fig. 3.** The percentage of soluble in water sum (III and VI) forms and total chromium in soils.

big cations H^+ saturation. Such a reaction favours chromium leaching from the soil. The lowest Eh value was registered in sample 5, situated in cultivated field, and the biggest value in sample 3, situated in the central point of the lagoon. In the majority of soil, conditions typical for good oxygenation with O_2 , as a main form, which is submitted to reduction, were recorded. Only in sample 5, did the value of Eh indicate poorly reduced conditions, where beside oxygen couple, NO_3^- and Mn (IV) are subjected to reduction. In these Eh values and pH below 4.5 Cr^{3+} can become mobile and can penetrate to the ground water. Taking as a base pH-Eh diagram, one can note that such a possibility exists in samples 1, 3, 4 and 6.

**Fig. 4.** Eh-pH relation for examined soils.**Table 2.** Values of Eh, pH and temperature in soil paste

Sample No.	Depth (cm)	Eh (mV)	pH	Temperature ($^{\circ}\text{C}$)
1	10-20	510	4.23	18.2
2	20-30	530	4.00	18.2
3	0-5	550	3.70	18.2
4	0-5	520	3.91	18.2
5	0-15	380	6.25	18.1
6	0-15	460	3.89	18.2
7	0-5	410	5.33	18.2
8	0-5	420	5.33	18.4

CONCLUSIONS

1. Total Cr concentration in soil samples from the vicinity of tannery waste lagoon near Lubartów ranged from 44.5 to 24340 mg kg⁻¹ and exceeded in most samples its acceptable level (100 mg kg⁻¹).

2. Chromium in soil water extracts showed the domination of Cr(III) form in them.

3. Eh values from 0.38 to 0.55 V and pH from 3.7 to 6.25 in soils reflects the ranges characteristic for Cr(III).

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