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Short communication

Speciation of Cr(VI) in environmental samples in the vicinity of the ferrochrome smelter

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abstract

The impact of ferrochrome smelter on the contamination of its environment with toxic hexavalent chromium, Cr(VI), was assessed by analyzing smelter dusts, soil, grass and tree barks. For the separation of Cr(VI) from Cr(III), solid samples were treated with 0.1 M Na_2CO_3 and filtered through hydrophilic PDVF 0.45 μm filter prior to the determination of Cr(VI) by electrothermal atomic absorption spectrometry (ET–AAS). Ferrochrome smelter dust was found to contain significant levels of Cr(VI), viz. 43.5 $\mu g\,g^{-1}$ (cyclone dust), 2710 $\mu g\,g^{-1}$ (fine dust), and 7800 $\mu g\,g^{-1}$ (slimes dust) which exceeded the maximum acceptable risk concentration (20 $\mu g\,g^{-1}$). The concentration of Cr(VI) in environmental samples of grass (3.4 ± 0.2), soil (7.7 ± 0.2), and tree bark (11.8 ± 1.2) collected in the vicinity of the chrome smelter were higher as compared with the same kind of samples collected from uncontaminated area. The results of the investigation show that ferrochrome smelter is a source of environmental pollution with contamination factors of Cr(VI) ranging between 10 and 50.

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1. Introduction

The wide use of stainless steel products has made the mining of chromite ore and the production of ferrochrome prevalent in South Africa where 75% of the world's chromite ore occurs [1]. The structure of chromite is considered very stable, with chromium occurring entirely in the non-toxic oxidation state of Cr(III) [2,3].

Ferrochrome is manufactured on ferrochrome foundries in electric arc furnaces which are fed chromite ore [4]. Chromium and iron react with carbon, and reduced to form the metal products. The other metals fed to the furnace reactor, as part of the ore, are more volatile and certain fraction of these metals evaporate, to be condensed again when the off gas if cooled to form ferrochrome dust [5]. The dust generated by ferrochrome plants typically consists of coarse dust, which is collected by the cyclone separators, and fine dust that is captured by the bag house filters [6]. The dust captured by the cyclones is directed further where it is mixed with water to form slurry. The dry clay from the slurry is the slimes dust. These dusts are classified as hazardous wastes by the US Environmental Protection Agency [7], as they contain hexavalent chromium, Cr(VI), which is toxic and carcinogenic to humans [8].

Hexavalent chromium is capable of penetrating the biological membrane of humans and passes into the cytoplasm, where it is reduced to trivalent chromium and reacts with the intracellular materials [9]. Ferrochrome and charge-chrome industries emit tiny particles of dusts containing chromium through smoke, which upon settling down pollute the environmental compartments such as water, soil and plants, and can eventually enter the human bodies through food chains or direct ingestion, which will pose a threat to human health [10].

The objective of this study was to investigate the distribution of Cr(VI) in ferrochrome dusts as it is not well known and ultimately determine Cr(VI) in grass, soil and tree barks around a ferrochrome smelter to establish the level contamination of the environment with Cr(VI).

2. Experimental

2.1. Apparatus

A Perkin–Elmer AAnalyst 600 atomic absorption spectrometer was used for all measurements. The wavelength and spectral band pass were set at Cr 357.9 and 0.7 nm, respectively. Transversely heated graphite tubes with integrated L'vov platforms were used as atomizers. Ar was used as the sheath gas throughout.

A standard stock solution containing 1000 mg L^{-1} Cr(VI) as K_2CrO_4 was purchased from Sigma–Aldrich (Saint Louis, MO, USA). Working Cr(VI) standards were prepared daily by dilution of the stock standard solution with Milli-Q water (Direct-Q 5 Ultrapure water system, Millippore Watertown, MA, USA). The certified reference materials, CRM 281 (Rye grass), CRM 545 (atmospheric dust),

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SQC001 (metals in soil) and SQC012 (chromium(VI) in soil) were used to check the accuracy of the analytical procedures.

2.2. Samples and sample preparation

2.2.1. Samples

Ferrochrome dusts were supplied by Xstrata Wonderkop ferrochrome smelter, Rustenburg, South Africa. Samples of tree barks were collected from free-standing trees around the smelter. Outer rough, peeling of approximately 100 g was removed manually from Acacia Karoo Hyne, commonly known as sweet thorn tree at a height of 1.5–1.8 m above the ground. Soil and grass (Chloris gayana) were taken from the same area to check the level of Cr(VI) contamination from smelter emissions. Control grass and soil samples were collected in an uncontaminated area of Stone Ridge, Centurion, South Africa. The soil samples representing the upper soil layer with a thickness of 20 cm were taken. All samples were air-dried at room temperature and ground to a particle size less than 75 μm in a tungsten carbide milling vessel.

Dust samples were also analyzed by X-ray Diffraction (XRD) using a back loading preparation method. This was achieved by utilizing a PANalytical X'Pert Pro powder diffractometer equipped with X'Celerator and variable divergence and the fixed receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore plus software.

2.2.2. Leachability of chromium(VI) from samples

To estimate the leachability of chromium(VI) with water, 0.25 g sub-sample was transferred into plastic tubes and 25.0 mL deionized water was added to each tube. The contents of the tubes were shaken periodically for 24 h. The sample solution was filtered through Hydrophilic Millipore PVDF 0.45 μm filter to remove Cr(III) species that may be trapped in the colloidal suspension and transferred into 1 mL sampling cup of the AAS autosampler prior to determination of Cr(VI) by ET–AAS.

2.2.3. Determination of total chromium(VI) in samples

To approximately 0.25 g of the sample in a 100 mL glass beaker, 25 mL of 0.10 M Na_2CO_3 was added and the content of the beaker was boiled on a hot-plate for 10 min [11]. After cooling, the sample was diluted to a final volume of 25.0 mL with deionized water in plastic tubes. Before the determination of Cr(VI), the solution was filtered through hydrophilic PVDF 0.45 μm filter.

2.2.4. Determination of total chromium concentrations

Approximately 0.10 g of sample was accurately weighed into a Teflon digestion vessel (CEM type) and 5.0 mL conc. HNO_3, 3.0 mL conc. HF and 1.0 mL conc. HCl were added. The vessels were capped and the samples were digested at a pressure 120 psi for 20 min. After cooling, the content was diluted with 1% (v/v) HNO_3 and filtered through Whatman No. 540 filter paper and the final volumes of all sample solutions were adjusted to 25.0 mL with deionized water.

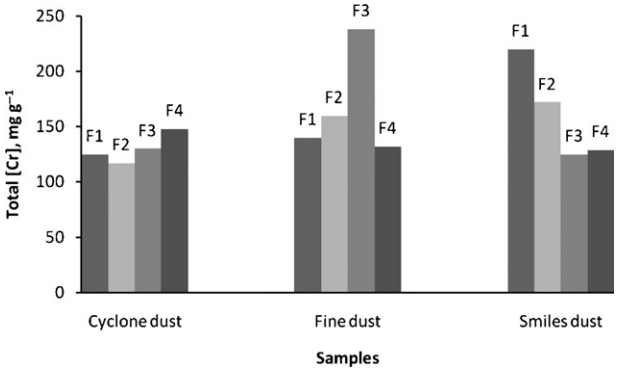

Fig. 1. Distribution of total chromium in ferrochrome dusts.

3. Results and discussion

3.1. Determination of chromium by ET–AAS

Chromium was determined in all samples by electrothermal atomic absorption spectrometry using the established temperature program [11]. The calibration curve of chromium standards was linear up to 70 μg L^{-1} as represented by $Y = 0.0061x + 0.0043$, with $R^2 = 0.9940$ as correlation coefficients. The limit of detection (LOD) for Cr(VI) determination in soil was found to be 0.07 μg g^{-1}.

3.2. Leachability of chromium(VI) with water

To estimate the amount of chromium(VI) that can be naturally leached with water, dust samples, viz., F1–F5 (representing samples collected from different arc furnaces) were allowed to stand in water for 24 h before being analyzed by ET–AAS. The results shown indicate that Cr(VI) in dust samples is significantly soluble in water where the content of Cr(VI) increases in the order of cyclone, fine dust and slimes dust (Table 1). The highest content of Cr(VI) leached was 2700 μg g^{-1} in slimes dust and this concentration exceeds the maximum acceptable environmental risk concentration of 20 μg g^{-1} allowed for the disposal of waste by a factor of 136 [12]. It means that after the settling of dust in the vicinity of chrome smelter could ultimately contaminate soil, grass and river waters.

3.3. Analytical results of total chromium(VI) determination in dusts

The determination of total chromium concentration in samples of dusts showed that the total concentrations of chromium in different dust types do not vary significantly at $p = 0.05$ (Fig. 1). The total Cr(VI) content in ferrochrome smelter dusts as leached by 1.1 M Na_2CO_3 was found to be rather very high (Table 1), ranging from 16.4 μg g^{-1} (cyclone) to 7800 μg g^{-1} (slimes dust). The highest concentration of Cr(VI) found in slimes dust is approximately 390

Table 1
Results of chromium(VI) determination (μg g^{-1}) in samples of ferrochrome dust.

Sample collected from furnace (F)	Cyclone dust		Normal dust		Slimes dust	
	[Cr(VI)][a]	[Cr(VI)][b]	[Cr(VI)][a]	[Cr(VI)][b]	[Cr(VI)][a]	[Cr(VI)][b]
F1	14.6 ± 1.20	16.4 ± 2.09	697 ± 40	2520 ± 140	1599 ± 145	5632 ± 237
F2	23.3 ± 2.10	29.9 ± 3.05	609 ± 31	1686 ± 132	1987 ± 149	6658 ± 300
F3	30.2 ± 1.50	43.5 ± 3.40	537 ± 29	2043 ± 160	2408 ± 128	7277 ± 327
F4	16.3 ± 1.10	24.8 ± 1.90	595 ± 35	2713 ± 139	2721 ± 141	7800 ± 290

Results represent the mean ± variation of two parallel samples.
[a] Water-soluble Cr(VI).
[b] Total concentration of Cr(VI) leached by 0.1 M Na_2CO_3.

Table 2
The results of complete ferrochrome dusts (wt%) analysis by XRD.

Analyte	F3 Cyclone dust	F3 Dust	F3 Slimes dust
Chromite, $FeO \cdot Cr_2O_3$	85.37 ± 2.07	78.89 ± 2.1	23.11 ± 1.02
Chromium, Cr	0.44 ± 0.24	0.91 ± 0.25	1.15 ± 0.19
Forsterite, Mg_2SiO_4	5.82 ± 1.89	9.54 ± 1.98	59.15 ± 1.35
Halite, NaCl	0	0.78 ± 0.45	2.13 ± 0.33
Periclase, MgO	2.02 ± 0.63	2.06 ± 0.66	11.02 ± 0.75
Quartz, SiO_2	5.34 ± 0.78	6.1 ± 0.75	0.7 ± 0.42
Thenardite, Na_2SO_4	0	1.25 ± 0.63	1.69 ± 0.9

times greater than the maximum environmental acceptable concentration of 20 $\mu g\,g^{-1}$ that is allowed on hazardous waste [12]. The Cr(VI) content found in normal dust (1680–2700 $\mu g\,g^{-1}$) is comparable to that obtained from a previous study (2270–2860 $\mu g\,g^{-1}$) in which Cr(VI) was determined at different stages of ferrochrome production in Hernic ferrochrome smelter [13].

XRD analysis of ferrochrome dusts (Table 2) showed that the major components of dusts are chromite ($FeO \cdot Cr_2O_3$), elemental chromium (Cr), forsterite (Mg_2SiO_4), halite (NaCl), periclase (MgO), quartz (SiO_2) and thenardite (Na_2SO_4). The concentration of chromite decreases with each level of purification whereas the concentration of elemental chromium increases. According to our results obtained by ETAAS (Table 1), the concentration of Cr(VI) also increases with each level of ferrochrome production due to the presence of NaCl and Na_2SO_4 generated during the formation of normal and slimes dusts.

3.4. Mechanism of the generation of Cr(VI) in an electric arc furnace

Hexavalent chromium is assumed to be formed during ferrochrome production since chromite only contain Cr(III). Since conditions in the submerged arc furnaces are reducing, with typical oxygen partial pressure of less than 10^{-8} atm [14], it is assumed that Cr(VI) is generated from Cr(III) when the dust is removed from the furnace of the cyclone separators and bag house filters, due to the increase in partial pressure of oxygen [15]. Therefore, Cr(VI) forms in the dust by either oxidation or through reaction with alkali oxides according to the following reactions:

$$2Cr_2O_3(s) + 3O_2 \rightarrow 4CrO_3(s) \quad (1)$$

$$2FeCr_2O_4 + 4Na_2CO_3 + 7O_2 \rightarrow 4Na_2CrO_4 + Fe_2O_3 + 4CO_2 \quad (2)$$

$$2FeCr_2O_4 + 4K_2CO_3 + 7O_2 \rightarrow 4K_2CrO_4 + Fe_2O_3 + 4CO_2 \quad (3)$$

$$4CaO(s) + 3O_2 + 2Cr_2O_3(s) \rightarrow 4CaCrO_4(s) \quad (4)$$

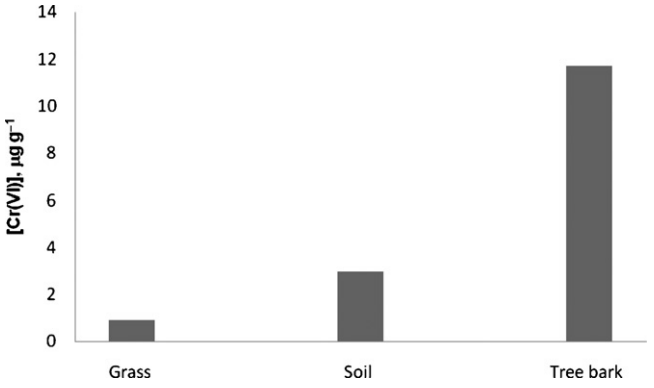

Fig. 2. Comparison of the distribution of Cr(VI) in grass, soil and tree bark.

3.5. Investigation of the environmental impact of ferrochrome emissions

In order to estimate the potential contamination of the environment with Cr, hexavalent chromium was determined in grass, soil and tree barks. The mean Cr(VI) concentrations found in different samples are shown in Table 3. As shown, all samples are contaminated with significant levels of Cr(VI) as compared with control samples taken from uncontaminated area. The contamination factor, defined as the ratio of the concentration of chromium in a given sample to that of the control sample, was found to be high ranging from 17 (soil) to 47 (tree bark) for Cr(VI) and 50 and 1710 for total Cr, respectively. The tree bark has the highest concentration of chromium due its high accumulation ability of metals over a long period of time due to its surface area (Fig. 2). The source of Cr(VI) in control samples could be the oxidation of Cr(III) to Cr(VI) in the environment by atmospheric O_2 during the bush fires [16].

To determine significance of washing the grass and tree bark, a paired t-test was performed, comparing chromium contents of washed and unwashed samples. The purpose of comparing Cr(VI) levels in washed and unwashed samples was to distinguish between airborne and soil borne contamination. The results of the determination of Cr(VI) in washed (6.95 $\mu g\,g^{-1}$) and unwashed (11.8 $\mu g\,g^{-1}$) tree bark shows that washing significantly reduces the concentrations of contaminants in grass and tree bark. This indicates that there was substantial aerial deposition of the hexavalent chromium thereby confirming that contamination with Cr(VI) originates from ferrochrome smelter dust emissions. It was further established that deposition and accumulation of Cr(VI) decreases as a function of the distance from the smelter (Fig. 3).

Table 3
Results of the determination of chromium in grass, soil and tree bark around a ferrochrome smelter.

Sample	Total [Cr(VI)][a], ($\mu g\,g^{-1}$)		Total [Cr][a], ($\mu g\,g^{-1}$)	
	Unwashed	Washed	Unwashed	Washed
Grass	3.39 ± 0.23	2.45 ± 0.19	139 ± 10	134 ± 14
Control	0.29 ± 0.02	0.14 ± 0.01	5.70 ± 0.15	4.90 ± 0.20
CF	12	18	24	27
Soil	7.70 ± 0.15	–	3723 ± 40	–
Control	0.45 ± 0.01	–	75 ± 4.0	–
CF	17	–	50	
Tree bark	11.8 ± 1.20	6.95 ± 0.60	6022 ± 220	5965 ± 195
Control	0.25 ± 0.02	0.16 ± 0.01	3.52 ± 0.24	3.49 ± 0.17
CF	47	43	1710	1709

Control, samples collected from uncontaminated area. CF: contamination factor.

[a] Average of six determinations at 95% level of confidence: mean ± $t_{0.05} \times (s/\sqrt{n})$.

Table 4
The results of the determination of chromium in certified reference materials (μg g^{-1}).

CRM	Cr(VI)		Total Cr	
	Found	Certified	Found	Certified
CRM 545, atmospheric dust	38.7 ± 1.3	39.5 ± 1.2	–	–
SQC012, soil	118 ± 20	117 ± 30	–	–
CRM 281, Rye grass	–	–	170 ± 0.50	168 ± 0.41
SQC001, soil	–	–	129 ± 25	131 ± 50

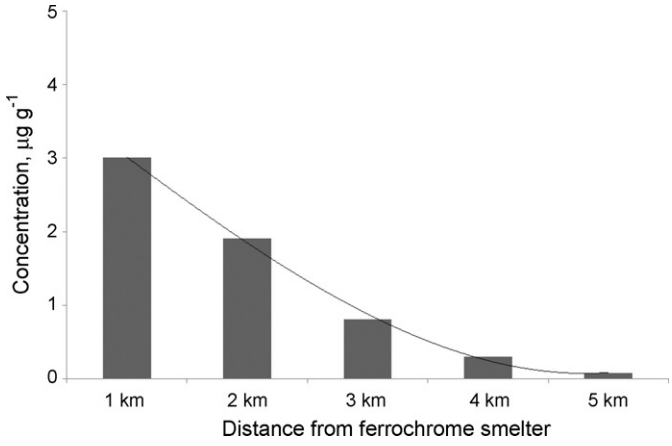

Fig. 3. Concentration of Cr(VI) in grass versus distance from the smelter.

3.6. Validation of the method

The accuracy of the methods applied in the leaching or/and digestions of chromium in samples was validated by the analysis of certified reference materials (CRMs). Good agreement of results was obtained between the determined and certified values, confirming accurate determination of Cr(VI) and total Cr by ET–AAS (Table 4).

4. Conclusions

It has been shown that ferrochrome smelter dusts contain significant higher levels of Cr(VI), up to 7800 μg g^{-1} that is significantly higher than the maximum acceptable risk concentration of 20 μg g^{-1} that is allowed for waste disposal. The emissions of ferrochrome smelter dusts to the environment has resulted in the elevation of Cr(VI) concentrations in grass, soil and tree bark. The mode of contamination of the environment was due to aerial deposition as there was significant difference in concentrations between unwashed and washed samples. On the basis of this investigation, it could be concluded that the area around the smelter is contaminated with Cr(VI) as contamination factor was found to range between 12 and 50.

Acknowledgement

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