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Journal of Hazardous Materials 145 (2007) 511–514

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Short communication

Electrothermal atomic absorption spectrometric determination of Cr(VI) during ferrochrome production

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Received 24 November 2006; received in revised form 17 January 2007; accepted 17 January 2007

Abstract

The level of the generation of hexavalent chromium during ferrochrome production was checked. The concentration of Cr(VI) increases with each stage of ferrochrome production, 7070 $\mu g\, g^{-1}$ being the highest concentration encountered in the last stage of production (dust). This concentration exceeds the maximum acceptable total Cr concentration per 8 h by a factor of more than 1000.

It was further observed that there is a higher contamination of soil by this pollutant closer to the plant than further away. The highest concentrations of Cr(VI) in soil and grass were found to be 12.7 and 4.2 $\mu g\, g^{-1}$, respectively. The results of the investigation indicate that the consumption of such grass by animals do not pose any health hazard, for concentrations of the toxic Cr species are very low. Therefore, the release of emissions, including dust, during ferrochrome production, is a major contributor to occupational diseases and death to people working in ferrochrome production plant or mine.

Keywords: Ferrochrome; Hexavalent chromium; Ore; Electhrothermal atomic absorption spectrometry

1. Introduction

Ferrochromium, the master alloy of iron and chromium, contains 45–80% Cr with various amounts of Fe. It is produced by carbothermic reduction of chromite ore ($FeO{\cdot}Cr_2O_3$). The ferrochromium slags consist mainly of SiO_2, Al_2O_3 and MgO in different phases and smaller amounts of CaO, chromium and iron oxides and metal fragments. The slag/metal amount ratio in smelting varies from 1.0 to 1.8, depending on raw materials [1].

Ferrochrome production results in the discard of slag as a waste material in enormous quantities. Slags normally contain high levels of extractable toxic Cr(VI) which could pose environmental problem. In a study dealing with the process water of metal recovery from slag, it has been reported that Cr has been detected as chromate in the processing water, which may create chromium pollution [2]. On the other hand, it has been indicated that other solid wastes such as bag filter dust or its sludge produced during the ferrochromium production contain high levels of soluble hexavalent chromium [3–6]. The production of ferrochromium and stainless steel has been mentioned among the greatest contributors to atmospheric emission of chromium [7]. These facts show that ferrochromium production is a source of Cr(VI) pollution which can threat the environment.

Chromium is a redox active metal that persists as either Cr(III) or Cr(VI) in the environment. These two oxidation states have opposing toxicity and mobility. The trivalent Cr is an essential nutrient at low amounts and a little-toxic element at higher content and is mostly insoluble in water, while hexavalent Cr is very toxic and readily transported [8,9]. The occupational exposure to Cr(VI) compounds can leads to a variety of clinical problems such as asthma, bronchitis, pneuminitis, inflammation of the liver and kidney [10,11]. Skin contact with Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion [12,13].

Chromium contamination of soil and water is a significant problem since hexavalent form of chromium is highly toxic, mutagenic and potentially carcinogenic to living organisms [14,15]. Because of the benign character of Cr(III), detoxification and immobilisation processes of Cr(VI) is based on its reduction to Cr(III). Conventionally, the reduction of Cr(VI) is performed by using SO_2 and sulphite salts and ferrous sulphate in the treatment processes practiced [16–19].

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doi:10.1016/j.jhazmat.2007.01.077

This paper describes the determination of Cr(VI) in samples from different stages of ferrochrome production and the level of Cr(VI) in the surrounding grass and soil.

2. Experimental

2.1. Apparatus

A Perkin-Elmer AAnalyst 600 atomic absorption spectrometer with Zeeman-effect background correction equipped with Cr hollow cathode lamp operating at 25 mA was used for all measurements. The wavelength and spectral band pass were set at 357.9 and 0.7 nm, respectively. Transversely heated graphite tubes (THGA) with integrated L'vov platforms (Perkin-Elmer, part N B050-4033) were used as atomizers with argon as the sheath gas throughout.

2.2. Reagents and standard solutions

Standard stock solutions containing 1000 mg L^{-1} Cr(VI) as K_2CrO_4(Merck) was used for the preparation of working standards for chromium. Ultra-pure water (resistivity, 18.2 MΩ cm), obtained from a Milli-Q water purification system (Millipore Corp., USA), was used for all dilutions and sample preparation. Ultra-pure $HClO_4$(Merck), HF(Merck) and HCl(Merck) were used during the digestion for the total chromium determination. Hydrophilic PVDF 0.45 μm filters (Millipore Millex, USA) were used for the filtration of all solutions. Certified Reference Materials: PACS-2, MESS-3 (marine sediments for trace metals obtained from the National Research Council of Canada) and CRM 545 [atmospheric dust that contains only Cr(VI), Brussels] were used as quality control samples for the evaluation of analytical results of total and Cr(VI) determinations.

2.3. Collection of samples

Several samples collected during different stages of ferrochromium production have been analyzed, viz., chromium ore: the raw material from underground; lumpy ore: the crushed ore that has been removed of all junks; slag: the product of the lumpy slag that has undergone thermal decomposition; Pellets: the product of fused slag and dust: the emissions from the last stage of ferrochromium production. These samples were accompanied by soil and grass (*Chloris gayana*) samples collected within 15 km from the ferrochrome plant. The samples were air-dried and homogenized by grinding in a IKA A11 milling system to a grain size less than 200 μm.

2.3.1. Sample preparation for the determination of Cr(VI)

Approximately 0.25 g of the sample was weighed and transferred into a 100 mL glass beaker. Twenty-five millilitres of 0.1 M Na_2CO_3 was added and the content of the beaker was boiled on a hot-plate for 10 min [20,21]. After cooling, the sample was filtered through Whatman no. 1 filter paper and diluted to a final volume of 25.0 mL with deionized water. Before the determination of Cr(VI) the solution was filtered through Hydrophilic Millipore PVDF 0.45 μm filter to remove Cr(III) species that may be trapped within the colloidal suspension.

2.3.2. Sample preparation for the determination of total Cr in ore and soil

For the determination of total concentration of Cr in the respective samples, 10 mL of concentrated HF and 2 mL of concentrated $HClO_4$ were added to 0.25 g of the sample in a platinum crucible. The mixture was heated till evaporation of the excess acid. To eliminate the remaining organic matrix, 2 mL of concentrated $HClO_4$ was added and heated to dryness. The residue was dissolved in 5 mL of 6 M HCl and diluted to 50.0 mL with deionized water.

2.3.3. Sample preparation for the determination of total concentration of Cr in plants

A nominal mass of 0.25 g of grass was accurately weighed into a Teflon digestion vessel (CEM type) and 5.0 mL of concentrated HNO_3, 3.0 mL concentrated HF and 1.0 mL concentrated HCl were added. The vessels were capped and the samples were digested in microwave at a pressure 120 psi for 20 min. After cooling, the cap was removed and the open vessel was heated on a hot plate to evaporate the excess acid. The final volume of each sample solutions was adjusted to 25.0 mL with deionized water.

3. Results and discussions

3.1. Analytical determination of Cr

The samples were analyzed to determine Cr(VI) concentrations by electrothermal atomic absorption spectrometry (ETAAS), as a method of detection, using recommended temperature program summarized in Table 1 [20,21]. The pyrolysis temperature used ensured the complete removal of the matrix prior atomization, thereby eliminating any influence that the matrix could have during atomization.

The mechanism behind the leaching of Cr(VI) in solid samples with 0.1 M Na_2CO_3 involves the transformation of insoluble Cr(VI) compounds into soluble form, while Cr(III) species form insoluble hydroxides or carbonates [22], thereby separating the two chromium species.

The validation for the total determination of chromium and hexavalent chromium concentrations were evaluated by analyzing certified reference materials (CRMs), viz. MESS-3, PACS-2 and CRM 545. Table 2 gives a summary of the determination of Cr(VI) and total Cr in CRMs. The results of the analysis

Table 1
Temperature program for the determination of Cr

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar (mL min^{-1})
1	110	1	10	250
2	250	5	20	250
3	1400	5	30	250
4	2450	0	5	0
5	2450	1	3	250

Table 2
The results of the determination of Cr(VI) and total Cr in CRMs ($\mu g\ g^{-1}$)

CRM	Total Cr		Cr(VI)	
	Certified	Found[a]	Certified	Found[a]
CRM 281, rye grass	1.68 ± 0.41	1.78 ± 0.25	–	–
CRM 545, atmospheric dust	–	–	39.5 ± 1.3	38.9 ± 1.2
PACS-2, marine sediments	90.7 ± 4.6	92.1 ± 3.8	–	–
MESS-3, marine sediments	135 ± 5	133 ± 6	–	–

[a] Average of six determinations at 95% level of confidence: Mean $\pm\, t_{0.05} \times \frac{s}{\sqrt{n}}$.

Table 3
The average concentrations of Cr(VI) in ferrochrome samples ($n = 6$)

Type of sample	Concentration range ($\mu g\ g^{-1}$)
Chromium ore	0.38–0.44
Lumpy ore	0.62–0.76
Slag	3.0–4.2
Pellets	8.8–10.40
Dust (kiln1)	2270–2860
Dust (kiln2)	6570–7070

show good agreement between found and certified values, thus validating the whole analytical procedure.

3.2. Results of Cr(VI) determination in ferrochrome production samples

The results in Table 3 and the absorbance-time signals of Cr(VI) of samples (Fig. 1) indicate that the concentrations of Cr(VI) in different stages of ferrochrome production increase with each level of ferrochrome purification, the lowest being 0.38 $\mu g\ g^{-1}$ (chromium ore) and the highest being 7070 $\mu g\ g^{-1}$ (dust). It therefore follows that, during the last stage of ferrochrome production, Cr(VI) concentration increases tremendously. Its formation is caused by the oxidation of Cr(III) by atmospheric oxygen at high temperatures [19]. The dust samples have concentrations of Cr(VI) that are way above the defined acceptable levels for total Cr in solid samples, and which exceeded the maximum acceptable Cr(VI) levels by a factor of more than 1000 [23], thus implying that people exposed to such high toxic levels may suffer from symptoms of Cr poisoning in the long term.

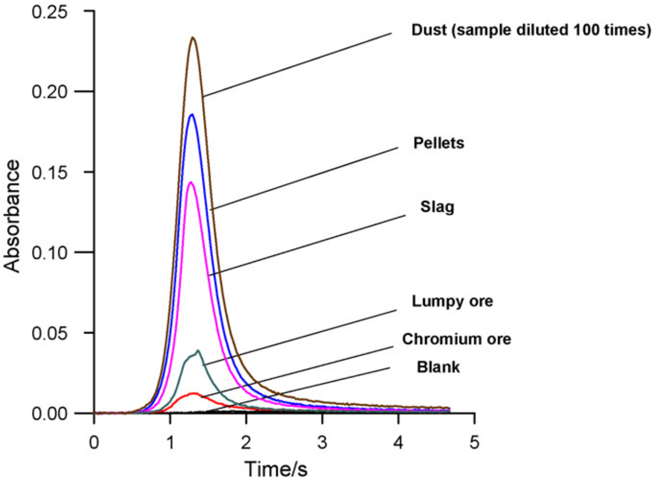

Fig. 1. Cr(VI) at different stages of ferrochrome production.

Table 4
The correlation of Cr(VI) in soil with the distance from the ferrochrome plant

	Samples of soil	
	[Cr(VI)][a] ($\mu g\ g^{-1}$)	Total [Cr][a] ($\mu g\ g^{-1}$)
1 km	12.7 ± 1.3	356 ± 15
2 km	6.3 ± 1.2	196 ± 6
3 km	4.2 ± 2.1	150 ± 15
12–15 km	0.29 ± 0.2	79 ± 6

[a] Average of six determinations at 95% level of confidence: Mean $\pm\, t_{0.05} \times \frac{s}{\sqrt{n}}$.

3.3. Analyses of soil and grass around the ferrochrome production plant

Soil samples around the ferrochrome plant were checked for potential contamination by Cr(VI). The soil samples were taken over a radius of 0–15 km from the ferrochrome plant. The results of the investigation given in Table 4 indicate that the soil samples closer to the plant are more contaminated with Cr(VI) than the samples from soil further away. Therefore, this means that the effects of ferrochrome pollution on the environment are inversely proportional to the distance of such pollution from the ferrochrome plant. The lower levels of Cr(VI) in soil sam-

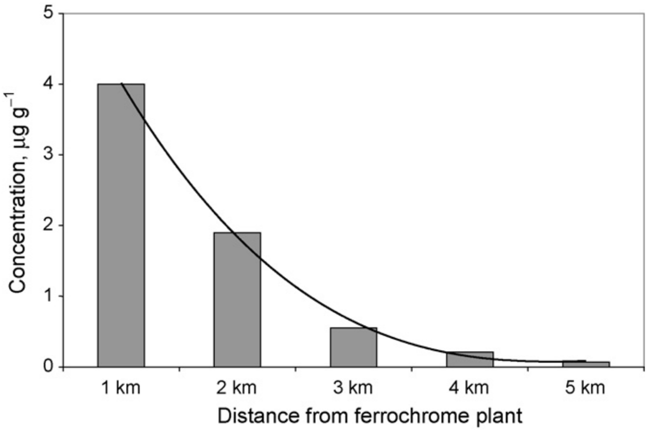

Fig. 2. Concentration of Cr(VI) in grass as a function of distance from ferrochrome plant.

ples may be attributed to the leaching of Cr(VI) to underground waters, since the samples were taken in April, which the month is in the South African rainy season.

The same observation was made in respect of grass samples, where the amount of Cr(VI) decreases as the distance from the source of pollution increases. The highest concentration of hexavalent chromium in grass was found to be 4.2 $\mu g\,g^{-1}$ at a distance of approximately 1 km from the plant.

The results obtained indicate that grass has low accumulative ability of Cr(VI) as shown by the low concentrations. Therefore, there is lower probability that animals, which consume grass in this area, will show symptoms of chromium poisoning (Fig. 2).

4. Conclusions

The results of the investigation bring one to the conclusion that ferrochrome production is a major sources of Cr(VI) in the local environment. The level of Cr(VI) increases in line with each level of purification during ferrochrome production. The last stage of ferrochrome production generates most Cr(VI) species, highest being 7070 $\mu g\,g^{-1}$ (dust). This concentration exceeds the maximum acceptable levels and therefore poses health hazard to animals and men. Overexposure to such levels could probably result in animals and humans showing symptoms of Cr poisoning.

The concentration of Cr(VI) in both soil and grass increases as the distance from the ferrochrome plant increases, but overall, they are not high enough to be of concern, therefore, airborne dust from the plant remains the major source of poisoning by chromium.

Acknowledgements

This study was supported by the National Research Foundation of South Africa (grant no. 2053116). We are grateful to Ralph Sturgeon (NRC, Canada) for the supply of PACS-2 and MESS-3.

References

[1] M. Riekkola-Vanhanen, Finnish expert report on best available techniques in ferrochromium production, The Finnish Environment 314, Finnish Environment Institute, Helsinki 1999. pp. 49–51.

[2] G. Coetzer, E.W. Giesekke, R.N. Guest, Hexavalent chromium in the recovery of ferrochromium from slag, Can. Metall. Quart. 36 (1997) 261–268.

[3] J.P. Beukes, J.J. Pienaar, G. Lachmann, E.W. Giesekke, The reduction of hexavalent chromium by sulphite in wastewater, Water SA 25 (1999) 363–370.

[4] W.A. Gericke, Environmental solutions to waste products from ferrochrome production, in: Proceedings of the Eighth International Ferroalloys Congress (INFACON 8), Beijing, China, 1998, pp. 51–58.

[5] B. Cohen, J.G. Petrie, Containment of chromium and zinc in ferrochromium flue dusts by cement-based solidification, Can. Metall. Quart. 36 (1997) 251–260.

[6] W.A. Gericke, Environmental aspects of ferrochromium production, in: Proceedings of the INFACON 7, Trondheim, Norway, 1995, pp. 131–140.

[7] A.B. Mukherjee, Chromium in the environment of Finland, Sci. Total Environ. 217 (1998) 9–19.

[8] S.E. Fendorf, Surface reactions of chromium in soils and waters, Geoderma 67 (1995) 55–71.

[9] D. Rai, E.A. Eary, J.M. Zachara, Environmental chemistry of chromium, Sci. Total Environ. 86 (1989) 15–23.

[10] A.K. Shanker, C. Cervantes, H. Loza-Tavera, S. Avudainayagam, Chromium toxicity in plants, Environ. Int. 31 (2005) 739–753.

[11] N. Koleli, Speciation of chromium in 12 agricultural soils from Turkey, Chemosphere 57 (2004) 1473–1478.

[12] C.S. Gad, Acute and chronic systematic chromium toxicity, Sci. Total Environ. 86 (1989) 149–157.

[13] K.P. Lee, C.E. Ulrich, R.G. Geil, H.J. Trochimowicz, Inhalation toxicity of chromium dioxide dust to rats after two years exposure, Sci. Total Environ. 86 (1989) 83–108.

[14] A. Leonard, R.R. Lauwerys, Carcinogenicity and mutagenicity of chromium, Mutat. Res./Rev. Genet. Toxicol. 76 (1980) 227–239.

[15] J.W. Moore, S. Ramamoorthy, Heavy Metals in Natural Waters, Springer-Verlag, New York, 1983.

[16] M. Sittig, Pollution Removal Handbook, Noyes Data Corp, UK, 1973.

[17] J.W. Patterson, Industrial Wastewater Treatment Technology, Butterworths Publishers, Stoneham, MA, 1975.

[18] W.W. Eckenfelder, Industrial Water Pollution Control, McGraw-Hill Book Co., New York, 1984.

[19] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 10 (2000) 263–283.

[20] N. Panichev, K. Mandiwana, M. Kataeva, S. Sibert, Determination of Cr(VI) in plants by electrothermal atomic absorption spectrometry after leaching with sodium carbonate, Spectrochim. Acta B 60 (2005) 699–703.

[21] N. Panichev, K. Mandiwana, G. Foukaridis, Electrothermal atomic absorption spectrometric determination of Cr(VI) in soil after leaching of Cr(VI) species with carbon dioxide, Anal. Chim. Acta 491 (2003) 81–89.

[22] G.S. Svehla, Vogel's Qualitative Inorganic Analysis, 7th ed., Longman Publishers, 1996.

[23] ACGIH: American Conference of Governmental Industrial Hygienists Documentation of the threshold limit values and biological exposure indices, 7th ed., Cincinnati, Ohio, USA, 2001.