



Treatment of Cr(VI)-containing wastes in the South African ferrochrome industry—a review of currently applied methods

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Synopsis

South Africa holds approximately three-quarters of the world's viable chromite ore resources and dominates the global production of ferrochrome. Albeit completely unintended, small amounts of Cr(VI) are formed during ferrochrome production. Certain Cr(VI) species are regarded as carcinogenic, hence making the treatment of some ferrochrome waste materials necessary. In this paper, the Cr(VI) treatment strategies currently employed by the South African ferrochrome producers are investigated by means of a literature review and a questionnaire survey. From the discussion, it is evident that various treatment strategies are available to deal with Cr(VI)-containing waste in the ferrochrome industry. However, by far the most commonly applied treatment strategy remains the aqueous reduction of Cr(VI) with ferrous iron. The advantages and the correct application of this strategy, together with the disadvantages and pitfalls, are argued. Innovative improvements on historic practices are also discussed

Keywords

hexavalent chromium treatment, Cr(VI) treatment, ferrochrome production, Cr(VI) containing waste, South Africa

Introduction

South Africa holds approximately three-quarters of the world's viable chromite ore resources^{1,2,3} and dominates the global production of ferrochrome (FeCr)⁴. FeCr is a relatively crude alloy of predominantly iron and chromium, used mainly in the production of stainless steel. There are currently fourteen separate FeCr smelters in South Africa, with a combined production capacity⁵ in excess of 4.7 Mt/a. Table I provides an overview of the production capacities of these facilities and also indicates recent capacity increases. Although the current electricity shortage in South Africa and the rising cost of power have partially stunted growth in this electricity-intensive industry, it is foreseen that South Africa will remain the leading producer of FeCr in the foreseeable future.

Hexavalent chromium, Cr(VI), is formed in small quantities as an unintended by-product during ferrochrome production⁶. Certain Cr(VI) species are regarded as carcinogenic, with specifically airborne exposure to these Cr(VI)

species being associated with cancer of the respiratory system^{7,8}. In a recent paper, the generation of Cr(VI) in the various production processes utilized by the South African FeCr industry was reviewed and possible mitigating steps were discussed⁶. In the present paper, Cr(VI) treatment strategies currently employed by the South African FeCr producers in dealing with waste products, possibly containing Cr(VI), are reviewed.

Questionnaire survey

This paper is primarily a review and not an empirical study. However, the knowledge of the authors and the information in the public domain were augmented by a survey questionnaire pertaining to Cr(VI) treatment strategies. This survey was circulated to individual South African FeCr smelters in 2011. The questionnaire was kept simple to enhance participation—mostly requiring the respondent to tick the most appropriate answer box, with space for additional comments or notes. The questionnaire consisted of seven questions, which are summarized as follow:

- Q1: Assessing whether any Cr(VI) treatment took place onsite
- Q2: Determining the process origin(s) of the possible Cr(VI) containing material that is treated on site
- Q3: Whether aqueous or direct treatment(s) of dry materials, possibly containing Cr(VI), were used
- Q4: If aqueous Cr(VI) treatment took place, which reducing agent(s) was/were used

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Table 1

Production capacity of South African FeCr producers (adapted from Jones⁵)

Plant	Locality	Production capacity (t/a)
ASA Metals Dilokong	Burgersfort	360 000#
Assmang Chrome	Machadodorp	300 000
Ferrometals	Witbank	550 000
Hemic Ferrochrome	Brits	420 000#
International Ferro-Metals	Rustenburg-Brits	267 000
Middelburg Ferrochrome	Middelburg	285 000
Mogale Alloys	Krugersdorp	130 000
Tata Ferrochrome	Richardsbay	135 000
Tubatse Ferrochrome	Steelpoort	360 000
Xstrata Lydenburg	Lydenburg	400 000
Xstrata-Merafe Boshhoek	Rustenburg-Sun City	240 000
Xstrata-Merafe Lion	Steelpoort	364 000*
Xstrata Rustenburg	Rustenburg	430 000
Xstrata Wonderkop	Rustenburg-Brits	545 000
TOTAL		4 786 000

#Production capacities of these facilities in the original reference⁵ were updated, since it did not consider relatively recent capacity enlargement projects

*An expansion project for this facility is currently under way and will double its current capacity

- Q5: If aqueous Cr(VI) treatment took place, why the specific reducing agent(s) was/were chosen.
- Q6: If aqueous Cr(VI) treatment took place, what was the pH range of the process or waste water
- Q7: What analytical technique(s) was/were used to assess Cr(VI) levels.

Of the fourteen FeCr smelters mentioned previously⁵, thirteen are full-time FeCr smelters and one is a part-time FeCr smelter. Nine of the full-time FeCr smelters (~70%) completed the survey. The results from this survey are included in the discussions that follow.

Cr(VI) treatment

Ma *et al.*⁹ reported on the formation, treatment, and stabilization of certain South African metallurgical wastes and pointed out that there are a number of different methods to deal with these wastes:

- Minimization of the wastes at the source by optimizing the operational parameters
- Direct recycling of certain materials to the furnace
- Recovery processes, which include hydrometallurgical methods and pyrometallurgical methods
- Solidification/stabilization methods, for instance cementation and vitrification (glassification) processes
- Use as a raw material in an appropriate product, such as fertilizer
- Treatment and land filling.

According to the authors, most of the above-mentioned treatment options are used at least to some degree in the South African FeCr industry on possible Cr(VI)-containing wastes. Minimization of the wastes at the source by optimized operational parameters is a prime objective of all South African FeCr producers, since minimized waste implies higher profitability. Direct recycling is also applied. However, direct recycling of furnace off-gas wastes (e.g. bag filter dust and scrubber sludge) to a FeCr smelting furnace could lead to the build-up of more volatile species, such as sodium and zinc⁹, resulting in lower production capacity and even possibly the risk of explosions. Recovery processes used by

South African FeCr producers to recover valuable Cr units from wastes are currently limited mainly to coarser materials, such as FeCr slag¹⁰⁻¹⁴. Solidification/stabilization of FeCr wastes is also currently mostly limited to slag, since some South African FeCr slags have recently been declassified, making it possible to utilize these slags as agglomerate material in commercial cementation applications. Bag filter dust and scrubber sludge are still classified as hazardous wastes, therefore very little of these materials are treated in this manner, although in theory it is possible to achieve solid stabilization of Cr(VI)-containing wastes¹⁵⁻¹⁷. Apart from FeCr slag, the only other FeCr-related waste that is utilized as a commercial product is relatively small quantities of a calcium-rich waste produced by a specific smelter. This is utilized as a soil additive or fertilizer. However, by far the most common process for dealing with possible Cr(VI)-containing waste in the South African FeCr industry is aqueous chemical Cr(VI) reduction, with subsequent precipitation of the Cr(III) hydroxides and land filling in specially designed waste facilities. In the survey conducted, all the respondents indicated that aqueous Cr(VI) treatment is performed on site. Materials most commonly treated include bag filter dusts, scrubber sludge, and certain process waters.

As indicated by Beukes *et al.*⁶, Cr(VI) can be generated during various FeCr production processes. By volume, slag is the main waste material generated⁶. However, with regard to Cr(VI) content, fine particulate matter originating from the off-gas of high-temperature processes can be regarded as the most significant Cr(VI)-containing waste material generated by the FeCr industry^{6,18}. Exposure to airborne Cr(VI) by inhalation is also much more hazardous than other exposure routes⁷, which further emphasises the importance of these fine, potentially airborne materials.

In order to treat Cr(VI) wastes effectively, several basic process steps have to be followed. These include capturing materials that potentially contain Cr(VI) (if the waste originated from an off-gas), contacting such materials with water, reducing Cr(VI) to Cr(III) (e.g. in the aqueous phase) and storing the treated material. These treatment steps are illustrated in Figure 1, as applicable to possible Cr(VI)-

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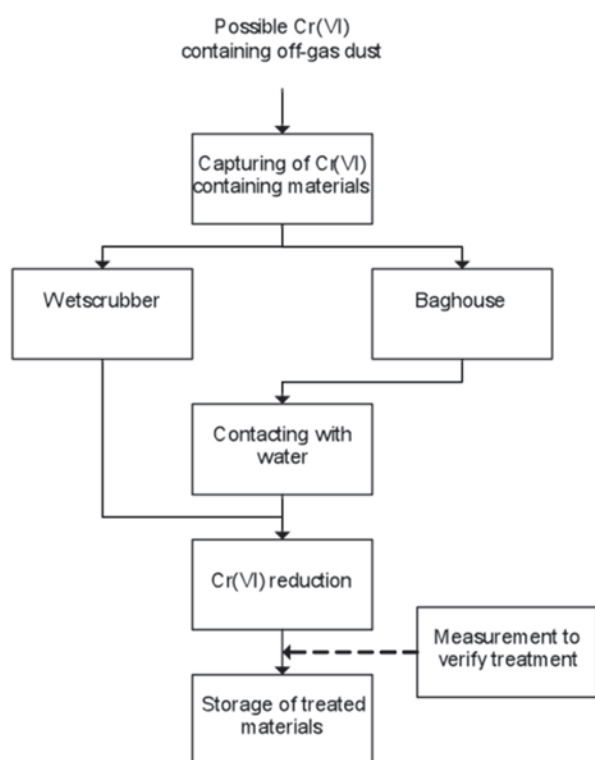


Figure 1—Flow diagram indicating the basic steps required for the containment and treatment of fine material potentially containing Cr(VI) originating from hot process off-gas during FeCr production

containing wastes originating from process off-gas streams. These steps seem very elementary; however, there are certain pitfalls that must be avoided. The first three steps, i.e. i) capturing of fine materials from off-gases, ii) contacting the contained materials with water, and iii) Cr(VI) reduction to Cr(III), are therefore discussed in more detail. Analytical verification of the effectiveness of the treatment and storage of the treated materials are not considered in this paper.

Capturing fine materials potentially containing Cr(VI) from off-gas streams

Gas cleaning equipment currently used by the South African FeCr industry for processes generating fine particulate matter are typically wet venturi scrubbers and bag filters. Bag filters are associated mainly with semi-closed furnaces and certain other processes, such as milling, agglomeration and curing of the agglomerates, while wet scrubbers are associated mainly with closed furnaces^{6,18}.

In general, it can be stated that wet venturi scrubbers should be regarded as a better control mechanism for removing Cr(VI)-containing particulate matter from off-gas than bag filter systems. This belief stems from the fact that wet scrubbers immediately contact the particulate matter possibly containing Cr(VI) with water during the capturing mechanism. This is in contrast to bag filter systems, which capture the particulates as dry matter. As mentioned previously, airborne Cr(VI) is more hazardous than aqueous Cr(VI)⁷. However, it is not that straightforward to recommend the use of wet scrubbers for all FeCr production processes in the South African FeCr industry. South Africa has a relatively

low and unpredictable rainfall. On average, South Africa only receives approximately 480 mm/a, which is about half of the 860 mm/a world average¹⁹. The Bushveld Igneous Complex, where all the chromite reserves in South Africa are located, lies within a semi-arid region. According to a 37-year rainfall record from the South African Weather Service²⁰, Burgersfort, a town situated on the eastern limb of the Bushveld Igneous Complex, has an annual average rainfall of 493 mm/a. During this period, it had a minimum annual rainfall of 163 mm/a, while a maximum of 1005 mm/a was measured. For Brits and Rustenburg, towns situated on the western side of the Complex, rainfall averages of 627 mm/a (50-year average) and 538 mm/a (17-year average) were reported, respectively. The minimum rainfall values for Brits and Rustenburg were 255 and 274 mm/a, respectively, while the respective maximum values reported were 1362 and 954 mm/a. Therefore, it is clear that rainfall, which has a direct effect on the availability of surface water, is relatively low and unpredictable in the Bushveld Igneous Complex. Although process water is usually clarified and re-used in a typical wet venturi scrubbing process, large quantities of water are lost due to the unavoidable evaporation by the hot off-gas that is cleaned. As a result, the use of wet scrubbing as a process technique is sometimes unpractical and could in some cases even be prohibited by South African environmental legislation (e.g. through overall environmental considerations during an Environmental Impact Assessment). The water requirements of communities, agriculture, and livestock will always take preference. In industry, the use of wet venturi scrubbers is usually limited to applications where carbon monoxide (CO) rich off-gas can be obtained and latent energy recovered from the subsequent combustion of such off-gas²¹. Other technical process-related aspects, as well as the capital and operational costs of the different off-gas cleaning technologies, are obviously also taken into consideration when off-gas cleaning technologies are chosen for a particular application.

Contacting the captured materials with water

Since the relative health risk associated with exposure to airborne Cr(VI) is much higher than the risk associated with exposure to aqueous Cr(VI)⁷, it is essential to contact the captured particulate matter with water as soon as possible. This simple action is extremely effective in mitigating possible occupational health impacts of Cr(VI).

Wet scrubbers immediately contact captured off-gas particulates with water; however, bag filter units do not. When considering a generic bag filter at a FeCr smelter, the following procedure is recommended. The closed hoppers into which the dust from the bag filters falls should be sealed off at the bottom with a rotary or double flap valve. These valves should release the dry dust from the hopper at a controlled rate. The discharge from each valve should fall into a sealed chute leading to a furrow of running process water directly below. This furrow should also be covered with removable cover plates to prevent any possible wind dispersal. The abovementioned procedure (or a similar procedure) will ensure that dry captured dust is contacted with water as soon as possible, preventing dry dust spillages or wind dispersal. The Cr(VI) present in this process water or sludge can then be reduced as described below.

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Cr(VI) reduction

There are numerous reducing agents that can be utilized to convert Cr(VI) to Cr(III) in the aqueous phase. However, within the context of this paper, the reduction of Cr(VI) with Fe(II) in the aqueous phase warrants an in-depth discussion, since all respondents indicated in the survey that they used aqueous ferrous treatment to reduce Cr(VI) to Cr(III). The reasons why ferrous chemicals, such as ferrous chloride or ferrous sulphate, have been the reducing agents of choice for South African FeCr producers are:

- Ferrous iron is an inorganic reducing agent that leads to the formation of insoluble Cr(III) hydroxide species in the pH range that is applicable to the FeCr production process and waste waters. This might seem inconsequential, but it is well known that most organic compounds can reduce Cr(VI)²². However, some organic compounds can form water-soluble Cr(III)-complexes that are undesirable. Although soluble Cr(III) species are not toxic or carcinogenic, soluble Cr(III) could be transported by ground or surface water and come into contact with manganese dioxide—a naturally occurring oxidant for Cr(III)^{23,24,25}. Therefore, Cr(VI) might be formed far from the original source if an inappropriate organic reducing agent is used
- Ferrous reduction of Cr(VI) has received much research attention²⁶⁻³⁴ and the theory of reduction is therefore well understood
- In the survey, numerous South African FeCr producers indicated that this treatment strategy is used since it is considered a proven technology
- Ferrous iron reduction is effective over the entire pH range applicable to FeCr process or waste waters (pH values between 6.2 and 9.0 were reported in the survey). This is in contrast to other industrially utilized inorganic Cr(VI) reducing species, such as S(IV) (dissolved SO₂, sulphite, or bisulphite), which can be used effectively only at pH ≤ 5^{35,36}. Dissolved O₂ can oxidize Fe(II), especially under alkaline conditions^{29,32,34}. This competing reaction can reduce the effective pH range of ferrous iron reduction of Cr(VI). However, the oxidation of Fe(II) by dissolved O₂ will not affect the efficiency of Cr(VI) reduction, or result in unnecessary losses of Fe(II), if the conditions are turbulent enough at the Fe(II) dosing point. Buerge and Hug³² compared the rate of reduction of Cr(VI) by Fe(II) to the rate of oxidation of Fe(II) by dissolved O₂. They reported that Cr(VI) reduction by Fe(II) was faster than Fe(II) oxidation of dissolved O₂ by the factors of 3×10⁴, 6×10³ and 1×10³, measured at pH 4, 6, and 8 respectively. He *et al.*²⁹ proved that Fe(II) is an effective reducing agent for Cr(VI), even at hyper-alkaline conditions, if enough turbulence is achieved to ensure almost instantaneous mixing. However, if Fe(II) is added to relatively stagnant process or waste water, only the Cr(VI) immediately contacted with the Fe(II) will be reduced and the rest of the Fe(II) will be oxidized to Fe(III) without coming into contact with Cr(VI). Typically, a furrow with running process water, a turbulent pump sump, or an agitated mixing tank could be considered as suitable localities to dose

ferrous iron for Cr(VI) reduction, while dams, clarifiers/thickeners, and other relatively stagnant water bodies would be inappropriate dosing points

- Ferrous chemicals are readily available in South Africa. More than half of the survey respondents indicated that availability of ferrous reducing agents has been a key factor when selecting a reducing agent for aqueous Cr(VI).

Although highly effective in reducing Cr(VI) to Cr(III), the use of ferrous chemicals has numerous disadvantages. These include:

- Their use increases the total dissolved solids (TDS) content of the process and waste water. Fe(II) is removed by oxidation to Fe(III), which consequently forms an Fe(III) hydroxide. This hydroxide precipitates from solution at the pH levels relevant to the FeCr process and waste waters. However, the chloride or sulphate remains in solution, causing the increase in TDS
- The abovementioned increase in TDS could result in increased scale build-up in pipes, spray nozzles of wet scrubber systems, and other equipment. This ultimately results in increased downtime and therefore production losses
- Although the 'major' environmental and health risk, i.e. Cr(VI), is effectively dealt with during the reduction of Cr(VI) to Cr(III) by Fe(II), the increased TDS and chloride or sulphate load could result in increased salination of surface and ground water, due to potential process and waste water leakages. Although salination of surface and ground water is not regarded as serious as Cr(VI) contamination, it is certainly not acceptable
- Since aqueous Fe(II) is oxidized by dissolved O₂ at elevated pH levels^{29,32,34}, ferrous chemicals have to be stored prior to use as strong acid solutions (e.g. ferrous chloride) or as solid powders (e.g. ferrous sulphate). Acid solutions of ferrous chloride are regarded as hazardous chemicals. FeCr producers therefore usually store ferrous chloride solutions in special tanks in bunded areas. These bund walls should be able to contain spillages that might occur and thereby prevent pollution of the environment and/or prevent injuries to personnel. Notwithstanding these safety measures, ferrous chemicals are considered occupational health risks for the operational personnel at FeCr smelters
- Ferrous chemicals have to be transported by road from the manufacturers to the user, i.e. the FeCr producer. This results in additional traffic on the South African roads, which are already regarded as relatively overloaded and dangerous.

Theoretically, the electrochemical reduction of Cr(VI) is a feasible solution to the abovementioned problems, since the ferrous ions are generated *in situ* and are not associated with chloride or sulphate anions. The electrochemical process occurs through redox reactions taking place at the surface of conductive iron electrodes immersed in water, leading to the subsequent reduction of Cr(VI) by Fe(II)³⁷:

Oxidation reaction at the anode:

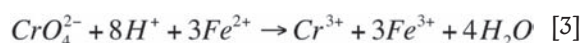


Reduction reaction at the cathode:

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Reaction stoichiometry with Cr(VI):



Although the electrochemical reduction of Cr(VI) has received considerable research attention³⁷⁻⁵⁴, the needs of the FeCr industry have until recently not really been addressed. The reason for this is that FeCr process and waste water have not been the intended treatment objective of most of these studies. However, the development of proprietary electrochemical Cr(VI) treatment technology in South Africa⁵⁵ has recently resulted in the full-scale implementation of electrochemical reduction of Cr(VI) in process and waste water at several local ferrochrome producers. Approximately 45 per cent of the survey respondents indicated that this specific electrochemical reduction technology was already being used on site, while additional respondents indicated that they were considering this treatment option. However, it is of concern that no peer-reviewed public domain information on the effectiveness and environmental soundness of this treatment process is available, and it can therefore not be compared to the currently applied chemical Fe(II) reducing process.

This absence of public domain information on the abovementioned technique is indicative of the reduced interest in the research and development field over the last decade by the South African FeCr industry at large. Previously, some South African ferroalloy companies had separate research and development (R&D) departments, which supported research initiatives. However, an increasing focus on only the core business activities has led to most of these in-house R&D initiatives being terminated or substantially reduced. Additionally, the R&D efforts have not been transferred to external/contract-based R&D organizations. This has in part led to other, potentially more environmentally friendly Cr(VI) treatment options being ignored. One such option is the bacterial reduction of Cr(VI), which was piloted by the South African ferrochrome industry⁵⁶, but never fully implemented. The implementation of such alternative Cr(VI) treatment options might require more precise control of process parameters (e.g. water temperature, nutrient levels, etc.) and possible support from R&D personnel.

Conclusions

From the literature review, it would seem that a number of treatment options for Cr(VI)-containing waste are feasible. However, all the survey respondents indicated that the aqueous reduction of Cr(VI) with ferrous iron was currently the preferred method. This treatment option is a proven technology that is well researched, and the reducing agents (e.g. ferrous chloride or sulphate) are readily available in South Africa. However, this treatment strategy has some disadvantages, which should be considered by FeCr producers. The actual Cr(VI) reduction step should also not be considered in isolation, since the capturing of possible Cr(VI)-containing materials (e.g. capturing of fine particulate matter with bag filters or scrubber systems) and contacting these materials with water as soon as possible are equally

important within the overall Cr(VI) treatment strategy. Waterborne Cr(VI) is much less hazardous than airborne Cr(VI), and consequently the correct application of these simple steps will result in a significant decrease in the overall occupational health and environmental risks associated with Cr(VI) at a FeCr smelter.

It also seems that the ever-growing environmental consciousness of the South African FeCr producers has resulted in the implementation of *in situ* electrochemically-generated ferrous reduction of Cr(VI). Almost half of the South African FeCr producers have already implemented this technology. Theoretically, electrochemically-generated ferrous reduction of Cr(VI) has the potential to negate most of the negative aspects associated with the traditional chemical reduction of Cr(VI). However, no public domain information on the effectiveness and environmental soundness of this technology is currently available, making comparison with more traditional chemical Fe(II) reduction impossible.

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