

# THEORETICAL AND PRACTICAL ASPECTS OF Cr(VI) IN THE SOUTH AFRICAN FERROCHROME INDUSTRY

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## ABSTRACT

*The production of ferrochrome alloy from chromium bearing chromite ores is conducted at high temperature under highly reducing conditions. However, albeit completely unintended, it is impossible to completely exclude oxygen from all high temperature process steps, with the corresponding possibility arising for the generation of small amounts of Cr(VI) species. Certain Cr(VI) species are regarded as a carcinogenic, with specifically airborne exposure to these Cr(VI) species being associated with cancer of the respiratory system. With approximately three quarters of the world's viable chromite ore reserves located in South Africa, and annual ferrochrome production approaching almost half of total annual global output, aspects of Cr(VI) generation and control are of particular relevance and importance to the local industry, and naturally to the global industry at large. This paper seeks to examine theoretical and practical aspects associated with Cr(VI) generation (based largely on experience within the local South African industry, but considered to be generally encountered in the broader global industry context), together with mitigating measures that can be applied within the context of the production processes. From the discussions it is clear that significant improvements with regard to various Cr(VI)-related aspects have been made by the South African ferrochrome industry. However, it is also evident that several areas of uncertainty still exist, which require further research in order to better quantify risks and enhance the efficacy of mitigating steps.*

## 1 INTRODUCTION

### 1.1 Relevance of Cr(VI)

Only two oxidation states of chromium are commonly found in the natural environment, i.e. Cr(III) and Cr(VI)[1]. Metallic chromium, i.e. Cr(0), is produced by human intervention. According to Yassi and Nieboer[1] and references therein, a linkage between exposure to Cr(VI) and increased lung cancer was first made in 1932. Currently, Cr(VI) compounds are generally classified as carcinogenic, although there seems to be limited and even inadequate evidence to support the carcinogenicity of all Cr(VI) compounds[3]. In comparison, Cr(III) and Cr(O) are not classified as carcinogenic[3], in fact, Cr(III) is an important trace element in a balanced nutritional intake and is sometimes specifically included as a dietary supplement[4].

### 1.2 The importance of the South African ferrochrome industry

Mined chromite ore, containing chromium in classic spinel mineral form is the only commercially exploited source of virgin chromium units. South Africa (SA) holds 72 to 80% of the world's viable chromite ore reserves[5][6][7]. Based on 2007 statistics, the South African ferrochrome smelting industry produces approximately 46% of the global production volume of ferrochrome (FeCr), such being in the form of Charge chrome (typically containing 48-54%Cr)[8]. The balance of virgin Cr units being produced as mostly High Carbon FeCr, with far smaller amounts of low and medium carbon containing FeCr. There are currently fourteen separate FeCr smelter plants in SA, with a combined production capacity of some 4.4 million tons/year[9].

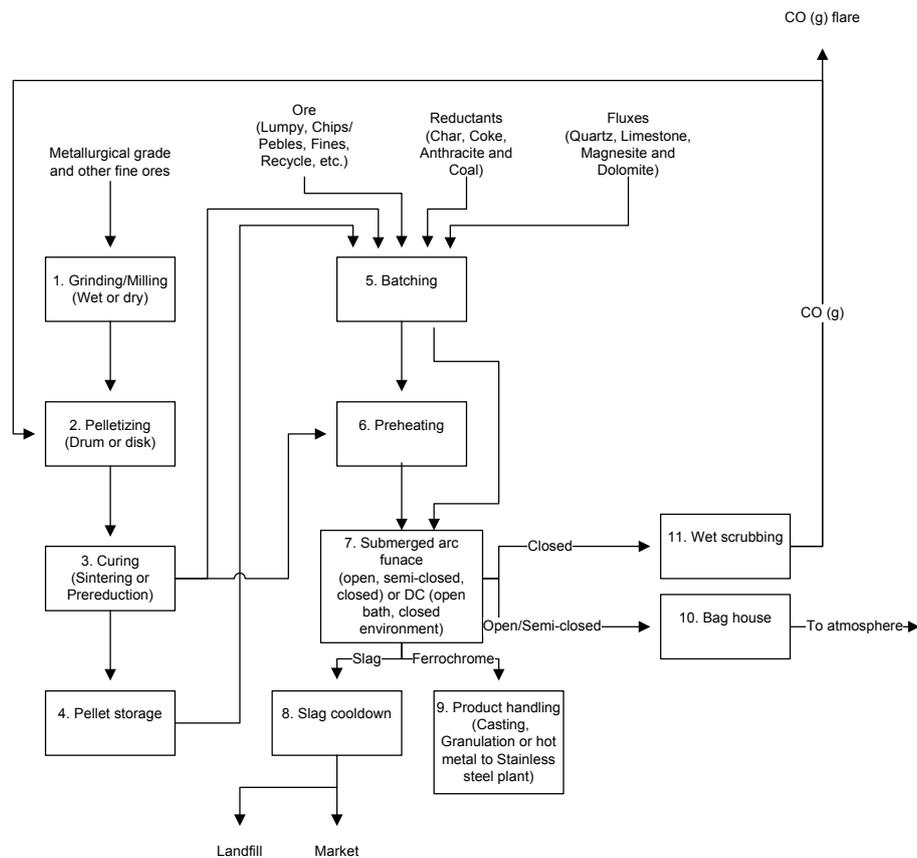
### 1.3 Objectives

Due to its size and relative importance in a global industry context, this paper was written with particular reference to Cr(VI) issues relating to the SA FeCr industry. However, most of the theoretical and practical aspects would also apply to FeCr producers worldwide. The main objectives of this paper are to:

- i) Give researchers insight into practical problems that might still require further investigation.
- ii) Empower operational personnel at FeCr producers to apply best practice for each application, which will help prevent possible occupational illnesses, negate possible health impacts on the broader community, as well as prevent or reduce environmental pollution.

## 2 PROCESSES UTILISED BY THE SA FeCr INDUSTRY

In order to facilitate discussions of Cr(VI)-related aspects within the SA FeCr industry, it is imperative to firstly understand the production processes employed. A generalised process flow diagram, which indicates the most common process steps utilised by the SA FeCr producers, is shown in Figure 1.



**Figure 1:** A flow diagram adapted from Riekkola-Vanhanen[7], indicating most common process steps utilised for FeCr production in SA

Four relatively well-defined process combinations are utilised by the SA FeCr producers:

- A) Conventional semi-closed furnace operation, with bag filter off-gas treatment. This is the oldest technology applied in SA, but still accounts for a substantial fraction of overall production[10]. In this type of operation, coarse (lumpy and chips/pebble ores) and fine ores can be smelted without an agglomeration process undertaken to increase the size of fine ores. Although it has been stated that fine ores cannot be fed directly into a submerged FeCr arc furnace without causing dangerous blow-outs or bed turnovers[7], a substantial amount of fine ores are in fact fed into some SA semi-closed furnaces. With reference to the process flow diagram indicated in Figure 1, the process steps followed are 5, 7, 8, 9 and 10. Some semi-closed furnaces do consume pelletised feed, in which case process steps 1-4 would also be included. Most of the SA semi-

closed furnaces are operated on an acid slag, with a basicity factor (BF) smaller than 1. Equation 1 defines the basicity factor (BF):

$$BF = \frac{\%CaO + \%MgO}{\%SiO_2} \quad (1)$$

Some semi-closed furnaces might operate on  $BF > 1$ , but these are less common and such operations are sometimes only temporarily undertaken to compensate for refractory linings being in poor condition, or if enhanced sulphur removing capacity by the slag is required.

- B) Closed furnace operation, usually utilising oxidative sintered pelletised feed[11]. This has been the technology most commonly employed in SA, with the majority of green and brown field expansions during the last decade utilizing it. Process steps usually include steps 1, 2, 3, 4, 5, 7, 8, 9 and 11, with or without 6. In all green field FeCr developments the pelletising and sintering (steps 2 and 3) sections were combined with closed furnaces. However, pelletising and sintering sections have also been constructed at plants where the pelletised feed is utilised by conventional semi-closed furnaces. These furnaces are usually operated on an acid slag ( $BF < 1$ ).
- C) Closed furnace operation with pre-reduced pelletised feed[12][13]. The process steps include steps 1, 2, 3, 4, 5, 7, 8, 9, 11. The pelletised feed differs substantially from the oxidative sintered type due to the fact that the pellets are pre-reduced and mostly fed hot, directly after pre-reduction, into the furnaces. The furnaces are closed and operate on a basic slag ( $BF > 1$ ). At present, two SA FeCr smelter plants use this process.
- D) DC arc furnace operation[14][15]. For this type of operation, the feed can consist exclusively of fine material. Currently 3 such furnaces are in routine commercial operation for FeCr production in SA and typically utilize a basic slag regime. Process steps include 5, 7 (with a DC, instead of a submerged arc furnace), 8, 9 and 11.

### 3 Cr(VI) GENERATION

As indicated previously, the production of FeCr alloy from chromium containing ore can only be conducted at high temperature under highly reducing conditions. However, it is impossible to exclude oxygen from all high temperature process steps and although completely unintended, small amounts of Cr(VI) bearing material might be formed. In this section, these process steps are discussed.

#### 3.1 Cr(VI) formation during milling

Due to the friability of SA chromite[16], it is common to only recover in the region of 10-15% of the ore as lumpy ore (6-150mm) and 8-12% chip/pebble ores (6-25mm) during the mining and beneficiation processes employed[17]. The remainder of the processed ore would be <6mm, which would typically be resized to <1mm (crushed or lightly milled where required) and upgraded with physical separation techniques to contain >45%  $Cr_2O_3$  content, i.e. metallurgical grade ore. The SA FeCr industry also receives a portion of its ore feed in the form of fine chromite ore gravity concentrate, produced as a by-product from the local platinum mining (PGM) industry, which is the largest in the world[18]. PGM mineralisation in certain ore horizons in SA is strongly associated with chromite ores[19] and mining of the PGM minerals and chromite therefore takes place in the same geographical regions. Specifically in the Bushveld Complex, one such chromite ore horizon targeted specifically for its PGM content is the UG2 ore seam[19]. After the extraction of the PGMs, the fine, upgraded UG2 ore (typically to >40%  $Cr_2O_3$ ) is made available to FeCr smelters for further treatment and smelting.

With the bulk of the chromite ore available as furnace feed being fine, an agglomeration step is typically required as a pre-treatment step prior to conventional AC submerged arc smelting. Agglomerated furnace feed ensures a permeable furnace bed, without gas eruptions and bed turnovers, as well as possible improved furnace efficiencies and decreased downtime[7][20]. The most widely used agglomeration technique is pelletisation, which requires particle size reduction via milling prior to agglomeration.

Beukes and Guest[21] were the first to publish evidence that dry milling (specifically under normal atmospheric conditions) can lead to the formation of Cr(VI). This fact was also recently mentioned in the health, safety and environmental guidelines document compiled by the International Chromium Development Organization (ICDA)[22]. The data reported by Beukes and Guest[21] cannot be used to quantify the generation of Cr(VI) by different industrial dry milling technologies, but serves as a useful primer to indicate the potential for oxidation of Cr(III) under milling conditions. Wet milling experiments

conducted suggested that Cr(VI) is not formed during such processes[21]. Although not published in the open scientific literature, it seems that the co-milling of carbon with the chromite ore also acts to significantly reduce the tendency for Cr(VI) generation during milling.

If one therefore compare dry and wet milling, wet milling has an advantage with regard to lower Cr(VI) formation. However, some FeCr production processes are not well suited to wet milling. The pre-reduction technology (combination C) is a typical example. This process has a number of pre-requisites. Firstly a large storage surge capacity of already milled material must be possible, which is difficult with moist material. Secondly, the reductant included during pelletising must be intimately admixed with the chromite. Such combination of fine sizing and thorough mixing (given the relative large volume of reductant) is best achieved in a dry milling operation (wet milling could introduce density segregation issues). Thirdly, a finer grind is required (if compared to the oxidative sintered process combination B) to ensure a high degree of reduction and pellet strength. Moisture removal of such fine material generated by wet milling, prior to pelletising, would be difficult.

Each individual process may well have its own particular challenges and benefits including the aggregated impact on HSEC issues. The following are recommended specifically for FeCr plants utilising dry milling:

- Cr(VI) health hazards are particularly associated with airborne Cr(VI)[23]. Dust prevention, extraction and suppression must therefore be considered, where practical, in the dry milling section of the plant. Captured dust must be recycled or contacted with water, which will eliminate almost all the airborne Cr(VI)-related health risks[23]. Process water utilised for this purpose must be treated to reduce Cr(VI).
- Co-milling of significant amounts of carbon with the chromite is likely to significantly reduce Cr(VI) generation.
- The wearing of appropriate personal protective equipment in the milling section of the plant must be made compulsory for operational personnel.

### 3.2 Cr(VI) formation during agglomeration processes

Due to the availability of mostly fine chromite ores in South Africa (Par 3.1), an agglomeration step prior to furnace feeding is required. Pelletisation is the most commonly applied agglomeration method in the SA FeCr industry, though multiple other techniques exist including briquetting and vibratory block pressing. Several different pelletisation technologies are applied, but by far the most common is the oxidative sintered pelletised feed process (combination B). Most of the SA brown and green field projects during the last decade, have adopted this technology, with at least seven different FeCr plants utilising this technology at present. In this process, chromite together with a small percentage of carbonaceous material, is wet milled and thereafter de-watered. Refined clay is then added and mixed into the moist milled ore-carbon blend. The mixture is then pelletised in a pelletising drum. The over- and undersized green pellets are recycled, while the appropriate sized green pellets are layered on a sintering belt, which is protected by a layer of already sintered pellets. The green pellets are then ignited in a furnace, where after air is pulled through the pellet bed to sinter the pellets. The amount of carbon present in the green pellets is limited to supply just enough exothermic energy to sinter the pellets properly. This process produces evenly-sized, hard and porous furnace pelletised feed material, which result in reduced furnace instabilities, lower electrical energy consumption and improved efficiencies, if compared to conventional processes (combination A)[20]. However, the process is oxidising and a small amount of Cr(VI) might form during high temperature sintering. The exact amount and concentration levels will depend on the raw materials, plant layout, green pellet carbon content, reaction temperature, residence times, etc.

The pre-reduction process (combination C) is the second most commonly employed pelletisation technology in the SA FeCr industry. Two FeCr plants utilise this process. Firstly, the chromite is dry milled together with a carbonaceous material and a clay binder. Substantially more carbon is added to the mixture than in the oxidative sintered process (combination B). Water is then added to the dry-milled material during mixing, to obtain the desired moisture content, where after the moist material is pelletised on a pelletising disk. The green pellets are then dried and pre-heated in a grate, after which they are cured in a contour current rotary kiln. In essence this is a reducing process. CO gas concentrations of 1-15% are common in the gas exiting the kiln and entering the grate. The high carbon content inside the pellets also results in a partial positive CO gas pressure inside the pellets themselves. This partial positive pressure prevents oxygen from entering the pellets. Due to its

reducing nature, less Cr(VI) is expected to be generated during the pre-reduced pellet curing process than what is generated during an oxidising pellet curing process. However, the pellets generated by the pre-reduction process usually have a thin oxidised outer layer, suggesting that small amount of Cr(VI) might also be formed. A direct comparison of Cr(VI) generation between these two process options have not yet been undertaken and it can therefore not be stated with confidence which generate less Cr(VI). However, both these processes signify a huge improvement in terms overall Cr(VI) footprint, if compared to conventional semi-open FeCr production (combination A).

### 3.3 Cr(VI) formation during furnace operation

Many factors affect the formation of Cr(VI) during the smelting process step[25], of which the four most important factors are the availability of oxygen (or absence of reductant in the immediate vicinity), the presence of alkaline compounds, the presence of ore in finely divided form and temperature. These factors are therefore discussed separately.

#### 3.3.1 Availability of oxygen

Since oxygen is required for the oxidation of Cr(III) to Cr(VI), it is logical that the availability of oxygen during the smelting step will influence the formation of Cr(VI). Therefore, the more reducing a process is, the less Cr(VI) would be formed. In practice, this implies that a closed furnaces will generate less Cr(VI) than an open or semi-closed furnace, with all other factors being equal. Although both open/semi-closed and closed furnaces have a reducing environment below the burden material, a closed furnace also has a CO-gas atmosphere (thus reducing) above the burden material, while an open/semi-closed furnace has a partially oxidising environment due to ambient air entering below the furnace roof. Gericke[24] gave an indication of the differences in Cr(VI) generation potential between semi-closed and closed FeCr furnaces in SA, as is indicated in Table 1.

**Table 1:** Typical water soluble Cr(VI) content of SA FeCr furnace dusts[24]

Process description	Cr(VI) / ppm
Closed furnace, with acid slag operation	5
Closed furnace, with basic slag operation	100
Semi-closed furnace, with acid slag operation	1 000
Semi-closed furnace, with basic slag operation	7 000

With regard to the availability of oxygen, the following recommendations can be made:

- With all other factors being equal (e.g. slag basicity, the presence of fines in the feed material and temperature), a closed FeCr furnace generates less Cr(VI) than an open or semi-closed furnace.
- Furnace design, i.e. open or closed furnace, should not be considered in isolation, since other factors also play an important role. These will be discussed in the following paragraphs.

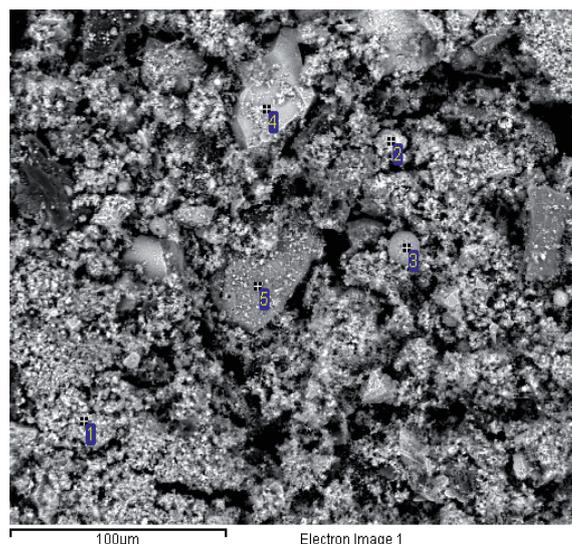
#### 3.3.2 The presence of alkaline compounds

Cr(VI) chemicals are produced *via* alkali roasting of chromite ore, by purposefully oxidising the Cr and Fe species in the ore, in the presence of soda ash[26]. The alkali content of FeCr feed materials is obviously only a tiny fraction of that encountered during alkali roasting of chromite, but fundamental aspects stimulating oxidation of Cr species might be concluded to be similar. Notwithstanding the lower concentration of alkali compounds in the FeCr feed materials, Cr(VI) in SA FeCr bag filter dusts seems to be associated primarily with alkali elements[27]. Thus, the addition of materials containing alkali compounds could increase the Cr(VI) generation of a FeCr furnace. Some processes utilised by the SA FeCr industry include the use of cement or sodium silicate as binders during agglomeration. Also, limestone, magnesite and dolomite are used as fluxes for basic slag operations. If the data in Table 1 is used as a guideline, the off gas dust of furnaces with basic slags contains 7 to 20 times more Cr(VI) than the off gas dust of furnaces with acid slags. The following recommendations are therefore made with regard to the alkaline content of FeCr furnace feed materials:

- With all other factors being equal (availability of oxygen, fine ore content of feed material and temperature), a furnace operating with an acid slag regime generates a smaller Cr(VI) footprint than an equivalent furnace operating with a basic slag regime.
- The use of binders and other compounds containing alkaline compounds should be avoided if possible.

### 3.3.3 The presence of fines in the feed material

The stability of the furnace bed, i.e. the surface of the raw materials in the furnace, depends on various factors, including electrode length and fine content of the feed material. The impact of electrode lengths will be discussed later. As was previously indicated (Par 3.1 and 3.2), SA FeCr producers have large quantities of fine chromite available. It is not preferred to feed these fine ores directly into a FeCr submerged arc furnace, since it makes the furnace material more impermeable and traps the gases generated during the reduction process. This could result in so-called bed turnovers and blowing of the furnace. These terms describe the instability of the surface layer of the furnace bed material. Bed turnover and blowing can vary from minimal disruption of the bed material, to catastrophic turnovers of a substantial amount of bed material. Apart from the obvious safety risks associated with such instability, bed material instability also results in more feed material fines being suspended into the furnace off gas. Figure 2 shows a Scanning Electron Microscope (SEM) photo of a typical SA bag filter dust sample from an semi-closed FeCr furnace. The larger unevenly shaped particles that can be seen are in fact un-reacted feed material. The SEM EDS analyses of the light grey particle indicated as area 4 contained 30.74% Cr and 20.78% Fe, which correlates well with chemical analyses of typical SA metallurgical grade ore. This is clear evidence that very fine chromite particles are suspended off the furnace bed and are extracted by the off gas system. During this process of suspension and extraction, the particle will be exposed to partially oxidising conditions expected in conventional open furnaces (process combination A), leading to a possible increase in Cr(VI) generation. Data to quantify the correlation between increased fines content of the feed material and Cr(VI) generation have not been published, but as a general rule of thumb it can be recommended that the content of chromium containing material, which is fine enough to be ejected off the furnace bed, must be kept as low as possible.



**Figure 2:** SEM photo of a bag filter dust sample originating from an open FeCr furnace in SA.

### 3.3.4 Practical perspective on the influence of temperature

Since the oxidation of Cr(III) to Cr(VI) is dependant on temperature and oxygen partial pressure[26], the nature of particularly the furnace freeboard environment needs to be considered in more detail. Under normal operating conditions on a particular given furnace, the carbon content of the feed is adjusted in accordance with classic metallurgical balance criteria, targeting specific alloy and slag chemistry. However, the length of the electrodes will determine the distribution of heat in the furnace bed material. Short electrodes will result in a hotter surface layer, while long electrodes will result in a cooler surface layer. In an open or semi-closed FeCr furnace, a hotter surface layer will result in a hotter partially oxidising environment above the furnace bed, hence increased Cr(VI) generation potential. These deductions can only be made based on logical assumptions and practical experience. No such data, quantifying the increased Cr(VI) formation during short electrode periods, have been published.

Additionally to increasing the temperature of the partially oxidising environment above the furnace bed of an open/semi-closed furnace, very short electrodes also result in substantially more fine feed

material being ejected from the furnace bed due to continuous bed blowing as a result of the tendency towards the partial exposure of the electrode arc. As indicated in Par 3.3.3, additional suspension of fine chromium containing particulate matter could increase the Cr(VI) generation potential of a furnace.

### 3.4 Flaring of cleaned off gas

The volume and composition of the off-gas formed by a closed FeCr furnace depend on the feed materials, the furnace feed pre-treatment methods (e.g. pre-reduced feed generates less gas than other feed materials), the design of the furnace, the furnace controls and metallurgical condition of the process. Gas volumes generated by closed furnaces have been reported to be 220 to 250 Nm<sup>3</sup>/h per MW or 650 to 750 Nm<sup>3</sup>/ton FeCr, consisting of 75 to 90% CO, 2 to 15% H<sub>2</sub>, 2 to 10% CO<sub>2</sub> and 2 to 7% N<sub>2</sub>[29]. The solid content of the uncleaned furnace off gas is typically 35 to 45 g/Nm<sup>3</sup>[29] and depends on the operational conditions and the production technology employed. The cleaning efficiency of wet scrubbers can be as high as 99.9%, after which the cleaned off gas usually contains less than 50mg/Nm<sup>3</sup> particulates[29]. The particles remaining in the cleaned off-gas are usually very fine. Particles smaller than 1µm are theoretically very difficult to remove from the gas with a wet venturi scrubber[29]. The cleaned off-gas could be cleaned further by filtering the gas with a sintered plate filter to reduce particulate levels to 1mg/Nm<sup>3</sup>[29]. However, as far as the authors know, the use of sintered plate filters are not yet applied by any of the SA FeCr producers.

As far as the authors could assess a study to quantify the possible oxidation of the very small amount of chromium containing particles remaining in the cleaned off-gas after wet scrubbing, during flaring of the excess off-gas, has not yet been published in the open scientific literature. In a recent ICDA update on the life cycle inventory of primary FeCr production, it was also mentioned that Cr(VI) emissions for closed furnaces are not yet validated by producers[10]. Beukes[25], did mention the possibility that Cr(VI) could be formed during combustion of closed furnace off-gas, but did not present any data to qualify or to quantify this statement. A personal communication cited in an environmental impact assessments for a new SA FeCr plant, indicated that 0.88 to 1% of the total chromium content of the particulate matter in the cleaned off gas of a closed FeCr furnace could be oxidised to Cr(VI) during flaring of the cleaned off-gas[28]. However, the basis for this figure was not given. Visser[20] presented modelling scenarios for a plant with both open and closed furnaces and used a 10% conversion factor, for total chromium to Cr(VI) conversion in total suspended particulate matter, during off-gas flaring. However, no reason for choosing this conversion factor was provided. The characteristics of CO gas are shown in Table 2. If the temperatures at which the cleaned CO-rich off-gas is flared are considered, it is clear that some conversion of Cr(III) to Cr(VI) could occur.

**Table 2:** Characteristics of CO gas, adapted from Niemelä et al.[29]

Density	1.19 to 1.26 kg/Nm <sup>3</sup>
Ignition temperature with air	>650°C
Ignition temperature with oxygen	>590°C
Heating value	12636 KJ/Nm <sup>3</sup>
Theoretical burning temperature with air	2250°C
Explosiveness with air	12 to 75% CO

The following recommendation can be made with regard to the possible generation of Cr(VI) during the flaring of cleaned off gas, originating from closed furnaces:

- The importance of a properly operating wet venturi scrubber system should be evident within the context of the above discussions, i.e. particulate matter content of cleaned off gas should be kept as low as possible. At plant level this implies that operational issues, such as water flow rates, gas flow rates and cleanliness/maintenance of the scrubbers system must be emphasised.
- Burning of uncleaned off-gas in the raw gas stack should be avoided as far as possible, since it will definitely increase the Cr(VI) generation potential of a closed furnace.

### 3.5 The tapping process

According to the Health Safety and Environment Guidelines for Chromium report of the ICDA[22], "hexavalent chromium compounds are found in small amounts in the highly oxidizing fumes from the melting/smelting processes, particularly the tapping process". With regard to occupational health, the

tapping process should therefore be an area of concern. The following recommendations can be made:

- The key to reducing the potential Cr(VI) occupational health effects during this process step is to have an effective taphole and runner fume extraction system, which will limit the exposure of the operational personnel to these fumes. However, the authors acknowledge that the installation of an effective extraction system for the taphole and runner area is not that simple, since runner cleaning is usually a mechanised action, during which large stationary fume extraction systems are easily damaged.
- Fumes/dust captured by the extraction system must be contacted with water (e.g. in a wet scrubber), since contacting with water immediately reduces the occupational risk[23]. It also eliminates the possible risk of wind dispersal of this particulate matter into the environment.

### 3.6 SA ferrochrome slag

According to the experience of the authors, the slag-to-metal production ratios of the SA FeCr producers vary from 1.1 up to 1.9. This spread is due to the wide range of production technologies applied (Par 2). If one takes the production volumes for SA FeCr into consideration[8] and use a slag-to-metal ratio of 1.5 as an average, it can be calculated that at least 5.3 million tons of slag was produced in 2007 alone. As far as the discussion of Cr(VI) with regard to SA FeCr slag is concerned, it is appropriate to make a distinction between historic slag dumps and current arising slags (newly produced slag).

In early period FeCr production, mono-product type disposal of slag was not rigorously applied across the South African industry and it was not uncommon to encounter the co-disposal of bag filter dusts and other wastes together with FeCr slag. However, the associated environmental risks, as well as financial incentives (recovery of FeCr metal), have lead to the reclamation of virtually all of these early FeCr slag dumps across South Africa[30][31][32][33]. These FeCr reclamation processes have mainly been based on waterborne physical separation techniques[34][35][36], facilitating Cr(VI) extraction and successful treatment [36]. Cr(VI) reduction in such instances has mainly been achieved via chemical reduction techniques[36].

Baldwin and Chettle[37] did comparative studies on current arising slags, as well as weathered slag from treated dumps, of almost all the SA FeCr producers. They concluded that most of the slags investigated would be classified as hazardous materials with specific ratings, mainly due to Fe and/or Mn leaching, not Cr(VI). These results were based on the use of TCLP and Acid Rain leach procedures, as specified by the appropriate SA legislation, i.e. Minimum Requirements for Waste[38][39][40]. However, the straight forward use of acid leach procedures, are likely to mobilise heavy metals and are therefore prone to be biased in that regard. Baldwin and Chettle[37] also did load/dose calculations according to the SA Minimum Requirements for Waste Act, which revealed that SA FeCr slags could only be disposed at 144 to 585 tons/ha/month on specially constructed hazardous landfill sites. Clearly, these figures are impractically low if the production volumes are considered, since it would result in disposal sites with huge surface areas.

Gericke[41] indicated that treated SA FeCr slags could safely be used as building agglomerates and in cement bricks. Also, treated FeCr slags produced with similar production technologies in first-world countries (e.g. Finland and Sweden), are extensively used in road building, paving and landfill applications[7][42]. The authors can therefore only conclude that the use of properly treated FeCr slags in SA has been over managed through legislation, resulting in the build-up of large FeCr slag stockpiles and the unnecessary use of natural resources. More research is definitely required to change the view that SA FeCr slags cannot be used in the type of application already utilised by first-world countries.

## 4 CONCLUSIONS

SA currently plays a dominant role in terms of international FeCr production and will in all likelihood continue to do so for the foreseeable future. Traditionally Cr(VI) generation issues in the SA FeCr industry have focused mainly on furnace design (e.g. closed vs. open furnaces). However, this paper clearly indicates that numerous other process production steps have to be considered in order to obtain a holistic view of Cr(VI) generation. Very limited, if any, data have been published for a number of these possible Cr(VI) formation process steps. Further investigation is certainly required in order to better quantify Cr(VI) generation and possible risks associated with them.

A previously published “weight of scientific evidence review” has clearly indicated that waterborne Cr(VI) is much less of a risk than airborne Cr(VI) at similar concentrations. By practical application of this phenomenon, i.e. contacting possible Cr(VI) containing material with water as soon as possible, a significant reduction in risks associated with Cr(VI) can be achieved at a FeCr plant. However, it seems as if some FeCr producers do not yet know or understand this fact, since dry material handling techniques are still applied for dusts possibly containing Cr(VI).

It is the opinion of the authors that slag, which is the largest FeCr waste by-product, has been over managed through legislation in South Africa. This has resulted in the build-up of slag stock piles instead of utilisation as already achieved in several first-world countries. Additional research is definitely required in this field.

Although this paper was written with specific reference to the SA FeCr industry, most of the principles can be applied to FeCr producers globally. This is due to the fact that most of the production technologies applied in South Africa are also utilised internationally.

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