Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry

by J.P. Beukes*, N.F. Dawson†, and P.G. van Zyl*

Introduction

Relevance of Cr(VI)

Only two oxidation states of chromium are commonly found in the natural environment, i.e. Cr(III) and Cr(VI). Metallic chromium, i.e. Cr(0), is produced by human intervention. According to Yassi and Nieboer and references therein, a linkage between exposure to 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 in 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.

Keywords

Hexavalent chromium, Cr(VI), ferrochrome production, South Africa.

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 per cent of the world’s viable chromite ore reserves5,6,7. Based on 2007 statistics, the South African ferrochrome smelting industry produces approximately 46 per cent of the global production volume of ferrochrome (FeCr), in the form of charge chrome (typically containing 48–54 per cent Cr). The balance of virgin Cr units are 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/year9.

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:

➤ Give researchers insight into practical problems that might still require further investigation.

Synopsis

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 in 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.

Keywords

Hexavalent chromium, Cr(VI), ferrochrome production, South Africa.

* Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, Potchefstroom, South Africa.
† Xstrata Alloys, Rustenburg, South Africa.
© The Southern African Institute of Mining and Metallurgy, 2010. SA ISSN 0038–223X/3.00 + 0.00. This paper was first presented at the, Infacon 2010 Congress, 6–9 June 2010, Helsinki, Finland.
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome

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.

Processes utilized 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 generalized process flow diagram, which indicates the most common process steps utilized by the SA FeCr producers, is shown in Figure 1.

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

- 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. 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, 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 pelletized 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):

\[ BF = \frac{\%CaO + \%MgO}{\%SiO_2} \]  

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.

- Closed furnace operation, usually utilizing oxidative sintered pelletized feed. 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 pelletizing and sintering (steps 2 and 3) sections were combined with closed furnaces. However, pelletizing and sintering sections have also been constructed at plants where the pelletized feed is utilized by conventional semi-closed furnaces. These furnaces are usually operated on an acid slag (BF<1).

- Closed furnace operation with pre-reduced pelletized feed. The process steps include steps 1, 2, 3, 4, 5, 7, 8, 9, 11. The pelletized feed differs substantially from the oxidative sintered type due to the fact that the
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome 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.

- DC arc furnace operation\(^4\)\(^,\)\(^5\). For this type of operation, the feed can consist exclusively of fine material. Currently three such furnaces are in routine commercial operation for FeCr production in SA and typically utilize a basic slag regime (BF>1). Process steps include 5, 7 (with a DC, instead of a submerged arc furnace), 8, 9 and 11. Drying (process step 6) might also be included.

Cr(VI) generation

The production of FeCr alloy from chromium containing ore can be conducted only 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.

Cr(VI) formation during milling

Due to the friability of SA chromite\(^6\), it is common to recover in the region of only 10–15 per cent of the ore as lumpy ore (6–150 mm) and 8–12 per cent chip/pebble ores (6–25 mm) during the mining and beneficiation processes employed\(^7\). The remainder of the processed ore would be <1 mm, which would typically be resized to <1 mm (crushed or lightly milled where required) and upgraded with physical separation techniques to contain >45 per cent Cr\(_2\)O\(_3\) 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\(^8\). PGM mineralization in certain ore horizons in SA is strongly associated with chromite ores\(^9\) 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\(^9\). After the extraction of the PGMs, the fine, upgraded UG2 ore (typically to >40 per cent Cr\(_2\)O\(_3\)) 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 pretreatment 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 pelletization, 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\(^23\) 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 compares dry and wet milling, wet milling has an advantage with 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 prerequisites. Firstly a large storage surge capacity of already milled material must be possible, which is difficult with moist material. Secondly, the reduced material included during pelleting must be intimately admixed with the chromite. Such combination of fine sizing and thorough mixing (given the relative large volume of reduce) 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 pre-reduction and pellet strength. Moisture removal of such fine material generated by wet milling, prior to pelleting, would be difficult.

Each individual process may well have its own particular challenges and benefits including the aggregated impact on health, safety, environmental and community (HSEC) issues. The following are recommended specifically for FeCr plants utilizing dry milling:

- Cr(VI) health hazards are particularly associated with airborne Cr(VI). 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\(^22\). Process water utilized 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.

Cr(VI) formation during agglomeration processes

Due to the availability of mostly fine chromite ores in South Africa, an agglomeration step prior to furnace feeding is required. Pelletization 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 pelletization technologies are applied, but by far the most common is the oxidative sintered pelleted feed process (combination B). Most of the SA brown and greenfield projects during the last decade, have adopted this technology, with at least seven different FeCr plants utilizing 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 pelleted in a pelleting process.
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome

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, whereafter 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 pelletized feed material, which results in reduced furnace instabilities, lower electrical energy consumption and improved efficiencies, if compared to conventional processes (combination A). However, the process is oxidizing 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 pelletization technology in the SA FeCr industry. Two FeCr plants utilize 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, whereafter the moist material is pelletized on a pelleting 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 per cent 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 oxidizing pellet curing process. However, the pellets generated by the pre-reduction process usually have an thin oxidized 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 of overall Cr(VI) footprint, if compared to conventional semi-closed FeCr production (combination A).

Cr(VI) formation during furnace operation

Many factors affect the formation of Cr(VI) during the smelting process step24, 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.

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, whereas an open/semi-closed furnace has a partially oxidizing environment due to ambient air entering below the furnace roof. Gerickc28 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 I.

The following recommendations can be made about the availability of oxygen:

- With all other factors being equal (e.g. slag basicity, the presence of fines in the feed material and temperature, etc.), 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.

The presence of alkaline compounds

Cr(VI) chemicals are produced via alkali roasting of chromite ore, by purposefully oxidizing the Cr and Fe species in the ore, in the presence of soda ash26. 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 elements27. Thus, the addition of materials containing alkali compounds could increase the Cr(VI) generation of a FeCr furnace. Some processes utilized 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 I are used as a guideline, the off-gas dust of furnaces with basic slag regime generates a smaller Cr(VI) footprint than the off-gas dust of furnaces with acid slags. The following recommendations are therefore made about 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, etc.), a furnace operating with an acid slag regime generates a smaller Cr(VI) footprint than an equivalent furnace operating with a basic slag regime.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical water solube Cr(VI) content of SA FeCr furnace dusts25</td>
</tr>
<tr>
<td>Process description</td>
</tr>
<tr>
<td>Closed furnace, with acid slag operation</td>
</tr>
<tr>
<td>Closed furnace, with basic slag operation</td>
</tr>
<tr>
<td>Semi-closed furnace, with acid slag operation</td>
</tr>
<tr>
<td>Semi-closed furnace, with basic slag operation</td>
</tr>
</tbody>
</table>

The Journal of The Southern African Institute of Mining and Metallurgy
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome

- The use of binders and other compounds containing alkaline compounds should be avoided if possible.

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, SA FeCr producers have large quantities of fine chromite available. It is not preferred to feed these fine ores directly into a submerged arc FeCr 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 a semi-closed FeCr furnace. The larger unevenly shaped particles that can be seen are in fact unreacted feed material. The SEM EDS analyses of the light grey particle indicated as area 4 contained 30.74 per cent Cr and 20.78 per cent 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 oxidizing conditions expected in conventional semi-closed furnaces (process combination A), leading to a partially oxidizing environment above the furnace bed material. The presence of fines in 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.

Practical perspective on the influence of temperature

Since the oxidation of Cr(III) to Cr(VI) is dependent on temperature and oxygen partial pressure, 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, but long electrodes will result in a cooler surface layer. In a semi-closed FeCr furnace, a hotter surface layer will result in a hotter partially oxidizing environment above the furnace bed, hence increased Cr(VI) generation potential. These deductions can be made based only on logical assumptions and practical experience. No such data, quantifying the increased Cr(VI) formation during short electrode periods, have been published.

In addition to increasing the temperature of the partially oxidizing 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 earlier, additional suspension of fine chromium containing particulate matter could increase the Cr(VI) generation potential of a furnace.

The use of binders and other compounds containing alkaline compounds should be avoided if possible.

Temperature and composition of the off-gas

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 pretreatment 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 Nm³/h per MW or 650 to 750 Nm³/ton FeCr, consisting of 75 to 90 per cent CO, 2 to 15 per cent H₂, 2 to 10 per cent CO₂ and 2 to 7 per cent N₂. The solid content of the uncleaned furnace off-gas is typically 35 to 45 g/Nm³ and depends on the operational conditions and the production technology employed. The cleaning efficiency of wet scrubbers can be as high as 99.9 per cent, after which the cleaned off-gas usually contains less than 50 mg/Nm³ particulates.

The cleaned off-gas could be cleaned further by filtering the gas with a sintered plate filter to reduce particulate levels to 1mg/Nm³. 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
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome

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.20 Beukes24 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 per cent of the total chromium content of the particulate matter in the cleaned off-gas of a closed FeCr furnace could be oxidized to Cr(VI) during flaring of the cleaned off-gas.29 However, the basis for this figure was not given. Visser20 presented modelling scenarios for a plant with both semi-closed and closed furnaces and used a 10 per cent 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 II. Although 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.

The following recommendation can be made about the possible generation of Cr(VI) during the flaring of cleaned off-gas, originating from closed FeCr 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 emphasized.

➢ 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.

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’. In 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 mechanized 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.

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. If one takes the production volumes for SA FeCr into consideration8 and use a slag-to-metal ratio of 1.5 as an average, it can be calculated that approximately 8.3 million tons of slag were produced in 2007 alone. As far as the discussion of Cr(VI) in 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 led to the reclamation of virtually all of these early FeCr slag dumps across South Africa.20,31,32,33 These FeCr reclamation processes have mainly been based on waterborne physical separation techniques, facilitating Cr(VI) extraction and successful treatment.28,36 Cr(VI) reduction in such instances has mainly been achieved via chemical reduction techniques.28,36

Baldwin and Chettle37 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 at the time, i.e. Minimum Requirements for Waste38,39,40. However, the straightforward use of acid leach procedures, are likely to mobilize heavy metals and are therefore prone to be biased in that regard. Baldwin and Chettle37 also did load/dose calculations according to the SA Minimum Requirements for Waste Act, which revealed that SA FeCr slags could be disposed at only 144 to 585 tons/ha/month on specifially 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.

Gericke37 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

| Table II |
| Characteristics of CO gas, adapted from Niemelä et al.28 |

| Density | 1.19 to 1.26 kg/Nm³ |
| Ignition temperature with air | >552°C |
| Ignition temperature with oxygen | >520°C |
| Heating value | 12636 KJ/Nm³ |
| Theoretical burning temperature with air | 2250°C |
| Explosiveness with air | 12 to 75% CO |

748 DECEMBER 2010 VOLUME 110 The Journal of The Southern African Institute of Mining and Metallurgy
Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome

Swedish), are extensively used in road building, paving and landfill applications. The authors therefore 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 utilized by first-world countries.

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 processes. 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 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 properly treated 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 utilization 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 utilized internationally.

Acknowledgements

The authors wish to thank Xstrata Alloys SA for their support of chrome-related research activities at the North-West University, South Africa.

References

Theoretical and practical aspects of Cr(VI) in the Southern African ferrochrome


Book Review

Diccionario de Mineria*

by: M.I. Silano and J.P. Rojas

In today’s global mining world, this Spanish-English-Spanish dictionary of mining will be of value to anyone involved in the mining industry in South and Central America. The dictionary has been authored by María Isabel Silano and Jorge Pérez of Intérpretes Asociados in Santiago, Chile. Intérpretes Asociados provides specialist simultaneous translation services to the mining industry. The dictionary is the outcome of the knowledge and terminology that they have captured during their translating experience. The book was launched in Santiago, Chile in November 2010.

The dictionary is arranged conventionally in two sections—Spanish-English and English-Spanish. These occupy the major portion of the book. However, it is in the last 40 pages of the book that this dictionary is different from others. This part includes fifteen illustrative sections: geology; deposit assessment; geomechanics and geotechnics; drilling and blasting; open pit; underground methods; crushing and grinding; concentration; pyrometallurgy; hydrometallurgy; electrometallurgy; mining equipment; water and environment; mining economy; and management and administration. These sections provide illustrations to enhance understanding of the terms. For example, in the underground method section, the block caving mining method is illustrated diagrammatically, with the various components such as drawpoint, undercut level, ventilation level, and orepass indicated in English and Spanish. Many of the mining terms are specific to South America, and particularly to Chile, and this last part of the dictionary will be of help in searching for, and understanding, particular terms.

This is a recommended book for those dealing in ‘Spanish’ mining. ◆

* Reviewed by: T.R. Stacey, School of Mining Engineering, University of the Witwatersrand