Journal of Cleaner Production 165 (2017) 874–889

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Review of Cr(VI) environmental practices in the chromite mining and smelting industry – Relevance to development of the Ring of Fire, Canada

J.P. Beukes [a, *], S.P. du Preez [a], P.G. van Zyl [a], D. Paktunc [b], T. Fabritius [c], M. Päätalo [d], M. Cramer [e]

[a] Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa
[b] CanmetMINING, Natural Resources Canada, 555 Booth St., Ottawa, Canada
[c] University of Oulu, Laboratory of Process Metallurgy, PO Box 4300, Oulu, Finland
[d] Outokumpu Chrome Oy, 95490 Tornio, Finland
[e] Ferroalloy Smelting Technologies, Hatch, Ontario, L5K 2R7, Canada

ARTICLE INFO

Article history:
Received 28 April 2017
Received in revised form
21 July 2017
Accepted 21 July 2017
Available online 22 July 2017

Handling Editor: Cecilia Maria Villas Bôas de Almeida

Keywords:
Hexavalent chrome
Cr(VI)
Chromite
Ferrochrome
Ring of Fire
Canada

ABSTRACT

During stainless steel production, new chromium units are obtained from ferrochrome, a relatively crude alloy produced from chromite ore. Large chromite reserves have recently been discovered in the so-called Ring of Fire, Canada. Due to the strategic importance of uninterrupted stainless steel production in North America, it is highly likely that these reserves will be exploited in the foreseeable future. However, the Ring of Fire is located in an area that forms part of the largest peatland in the world, as well as the traditional territories of several First Nations (indigenous American communities), which highlights the environmental and social sensitive nature of the intended developments. In this review, relevant mining and/or smelting processes were considered within the context of possible prevention and mitigation of hexavalent chromium, Cr(VI), formation, and the treatment of possible Cr(VI) containing waste materials. Cr(VI) is classified as a carcinogen and it has several negative environmental impacts.

Prior to commencing chromite mining in the Ring of Fire, baseline studies should be undertaken to determine the possible natural occurrence of Cr(VI) in soils, untreated chromite ore and surface/groundwater, as well as sources thereof. During mining and ore processing, dry milling was identified as the only process step with the potential to generate Cr(VI); therefore, it should be avoided. Instead, wet milling should be used.

Assessments of all process steps associated with conventional ferrochrome production indicated that smelting will lead to the formation of unintended small amounts of Cr(VI) ($mg.kg^{-1}$ concentration range), irrespective of the technology applied. However, this review proved that it will be possible to produce ferrochrome without causing occupational/community health issues related to Cr(VI), as well as environmental pollution, if appropriate preventative and mitigation measures are applied. Apart from Cr(VI) related considerations, it is acknowledged that factors such as physical and chemical characteristics of the ore, capital and operational costs, specific electricity consumption, carbon footprint, and availability of expertise will determine what process options will be implemented.

Crown Copyright © 2017 Published by Elsevier Ltd. All rights reserved.

Contents

* Corresponding author.
E-mail address: paul.beukes@nwu.ac.za (J.P. Beukes).

http://dx.doi.org/10.1016/j.jclepro.2017.07.176
0959-6526/Crown Copyright © 2017 Published by Elsevier Ltd. All rights reserved.

1. Introduction

1.1. The Ring of Fire deposit

Various chromium (Cr) compounds, Cr metal and/or Cr-containing alloys are used in modern society. By volume the largest application for Cr is in the production of stainless steel (Murthy et al., 2011), which owes its corrosion resistance mainly to the inclusion of Cr. Cr can occur in 82 different ore types (Motzer and Engineers, 2004), but the only type that is mined in commercial volumes that can supply the required new units for the production of stainless steel is chromite (Motzer and Engineers, 2004). Chromite ($FeCr_2O_4$) is a mineral belonging to the spinel group of minerals characterized by the following formula $[(Mg,Fe^{2+})(Al,Cr,Fe^{3+})_2O_4]$ (Haggerty, 1991). The largest exploitable deposits of chromite occur in South Africa and Zimbabwe, with significant deposits in several other countries such as Finland, Kazakhstan and Turkey. Only 31,250 tons of chromite was produced in North America during 2012, which represented less than 0.13% of the more than 24.5 million tons of chromite produced internationally (ICDA, 2013). Fairly recently very large chromite reserves were discovered in the so-called Ring of Fire in Canada. Due to the strategic importance of uninterrupted stainless steel production in North America, it is highly likely that these deposits will be exploited in the foreseeable future.

The Ring of Fire is located in the relatively remote far north of Ontario in the James Bay Lowlands (Fig. 1a). It is approximately 1000 and 500 km from Toronto and Thunder Bay, respectively. Although the Ring of Fire has an approximate surface area of 5000 km^2, most of the mineral deposits discovered to date are located within a 20 km long strip (Fig. 1b).

The first commercially viable quantities of chromite in the Ring of Fire were discovered in 2008 (Chong, 2014). It has been estimated that the chromite reserves in the Ring of Fire could meet North American needs for several centuries. However, the Ring of Fire is located in an area that forms part of the largest peatland (a type of wetland) in the world (Warner and Rubec, 1997), which makes it environmentally and logistically challenging for mining operations. Developing chromite mining and/or processing, as well as building infrastructure in this sensitive ecosystem will require careful planning to mitigate environmental impacts. The Ring of Fire is also located within the traditional territories of several First Nations (Chong, 2014). Exploitation of the mineral deposits will therefore require adequate consultations with the First Nations.

1.2. Relevance of hexavalent chromium

Chromium can occur in several oxidation states, but only trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), are common in near surface environments, while metallic chromium, Cr(0), is mainly produced by human intervention (Motzer and Engineers, 2004; Bartlett, 1991).

Cr(VI) compounds are generally classified as carcinogenic, with specific ailments of the respiratory system being implicated (Beaver et al., 2009; IARC, 2012). Cr(VI) is also on the List of Toxic Substances under Schedule 1 of the Canadian Environmental Protection Act, 1999 (Environment Canada, 2014). Furthermore, Cr(VI) has been shown to have several negative environmental impacts, e.g. reduced germination and growth of some plants (Peralta et al., 2001), increased mortality and reproduction rates in earthworms (Abbasi and Soni, 1983), organ damage in crayfish (Bollinger et al., 1997), detrimental effects on survivability, growth and post-exposure reproduction of marine fish larvae and copepods (Hutchinson et al., 1994), toxic effects on gill, kidney and liver cells of fresh water fish (Mishra and Mohanty, 2008), and possible diatom demise (Loock-Hattingh et al., 2015). Therefore, it is important to prevent or at least mitigate the formation of such compounds, and to apply proper treatment strategies to Cr(VI) containing wastes. This is of particular importance within the context of the possible development of the Ring of Fire chromite ore deposits, considering the sensitive nature of the area.

Cr(III) and Cr(0) are not classified as carcinogenic. Cr(III) is in fact an important trace element in a balanced nutritional diet and is in certain circumstances specifically included as a dietary supplement (Hininger et al., 2007).

1.3. Methods

Considering the significant differences in the impact of Cr(VI) on human health and the environment, as opposed to Cr(III) and Cr(0),

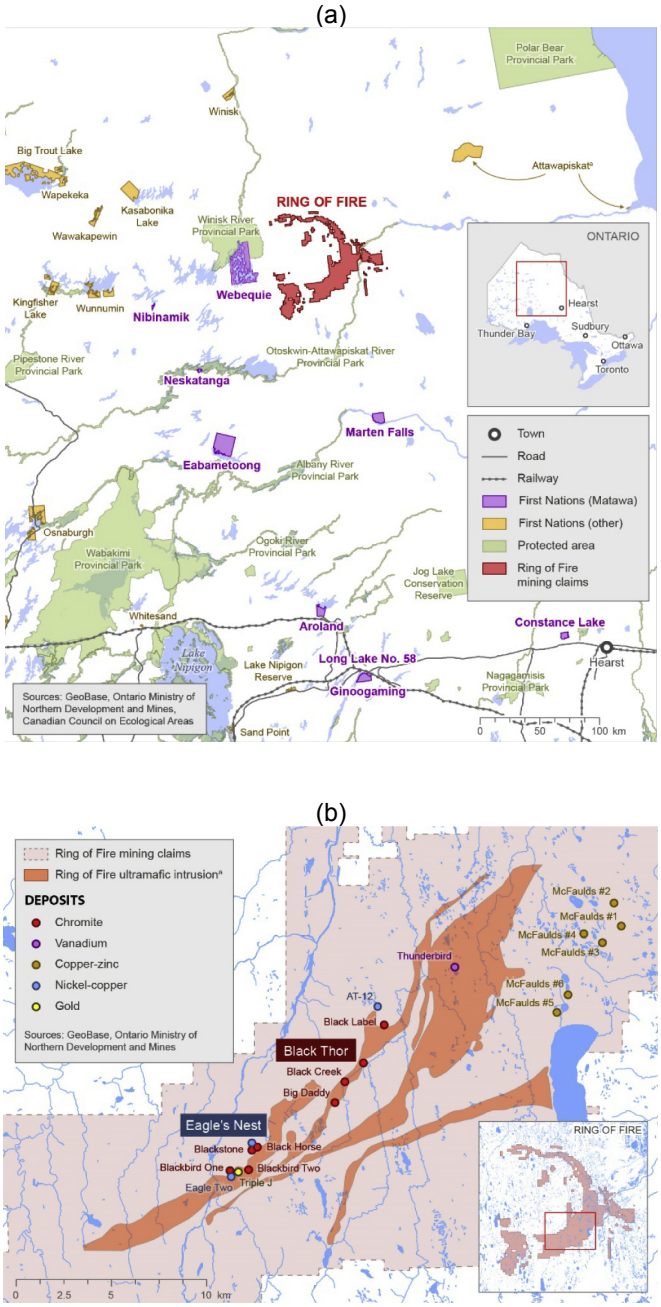

Fig. 1. Location of the Ring of Fire within a regional perspective (a), as well as an enlarged area showing the mineral deposits (b) (Chong, 2014).

it is important to consider the current knowledge base and the gaps therein, as well as best practices related to mining and smelting of chromite to produce ferrochrome (FeCr) within the context of the possible development of the chromite deposits in the Ring of Fire. Several aspects have to be considered: (1) the possible natural occurrence and/or natural formation of Cr(VI), (2) prevention and mitigation of Cr(VI) formation during mineral and metallurgical processing leading to the production of FeCr, and (3) treatment of possible Cr(VI)-containing waste materials originating from the afore-mentioned processes.

Although information (literature) and experience available internationally was considered in this review, where possible specific reference will be made to the Finnish mining, beneficiation and pyrometallurgical conversion of chromite, since the environment in which these operations occur is somewhat similar to the Canadian conditions. The Finnish chromite/ferrochrome operations are also regarded as leaders in environmental practices (e.g. Riekkola-Vanhanen, 1999; Päätalo and Raiskio, 2015).

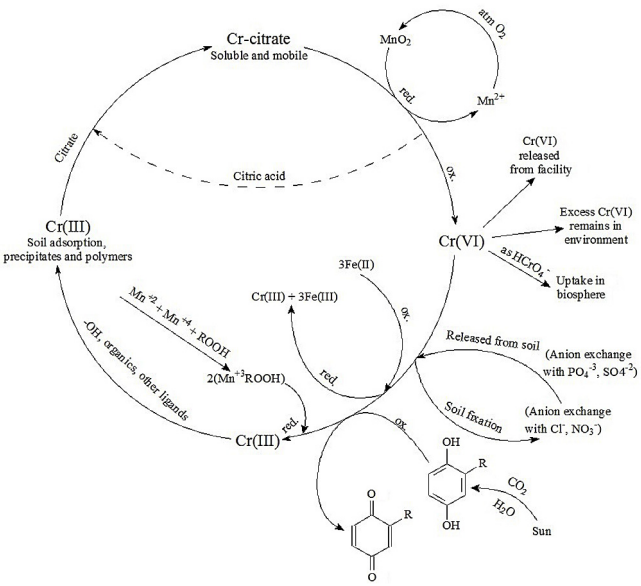

Fig. 2. The Cr cycle, adapted from Testa (2004) and Bartlett (1991).

2. Natural occurrence and/or natural formation of Cr(VI)

In order to contextualize the possible natural occurrence and/or formation of Cr(VI), the basic Cr cycle in soil and water, as presented in Fig. 2 (Bartlett, 1991; Testa, 2004), needs to be considered first. Only a synopsis of this Cr cycle will be considered here, with detailed information available in the original text and references therein (Bartlett, 1991; Testa, 2004).

In essence, the soil/water Cr cycle (Fig. 2) indicates that Cr(III) is the dominant species under most near-surface environmental conditions. However, Cr(III) can be oxidized under ambient environmental conditions in the presence of MnO_2, which serves as a catalyst for the atmospheric oxidation of Cr(III) in surface or ground water. However, for this to take place Cr(III) must be in a soluble form (Bartlett, 1991). Cr(III) hydroxides are relatively insoluble over a wide pH range (see Fig. 3; Rai et al., 1987) and therefore usually do not contribute significantly to such oxidation. Cr(VI) can be reduced by various inorganic species, including aqueous Fe(II) (Eary and Rai, 1988), magnetite (Peterson et al., 1996), green rust (Williams and Scherer, 2001) and zero valent iron (Chang et al., 2014). Additionally, Cr(VI) can be reduced by numerous organic compounds (both synthetic and natural) and microorganisms (March, 1992; Dong et al., 2014; Miller et al., 2016; Jin et al., 2017; Gupta et al., 2017; Wang et al., 2017). However, some organic compounds could complex Cr(III) and in so doing solubilize it, which could facilitate the formation of Cr(VI) due to natural oxidation in the presence of MnO_2. Cr(VI) species primarily occur under oxidizing (Eh > 0) and alkaline (pH > 6) conditions (Motzer and Engineers, 2004 and references therein).

In the ambient atmosphere, Cr(VI) is associated exclusively with particulate matter and/or atmospheric water, since the vapor pressure of all Cr compounds at ambient conditions is negligible (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). All atmospheric inter-conversion reactions leading to possible Cr(VI) formation and reduction to Cr(III) are therefore water-phase

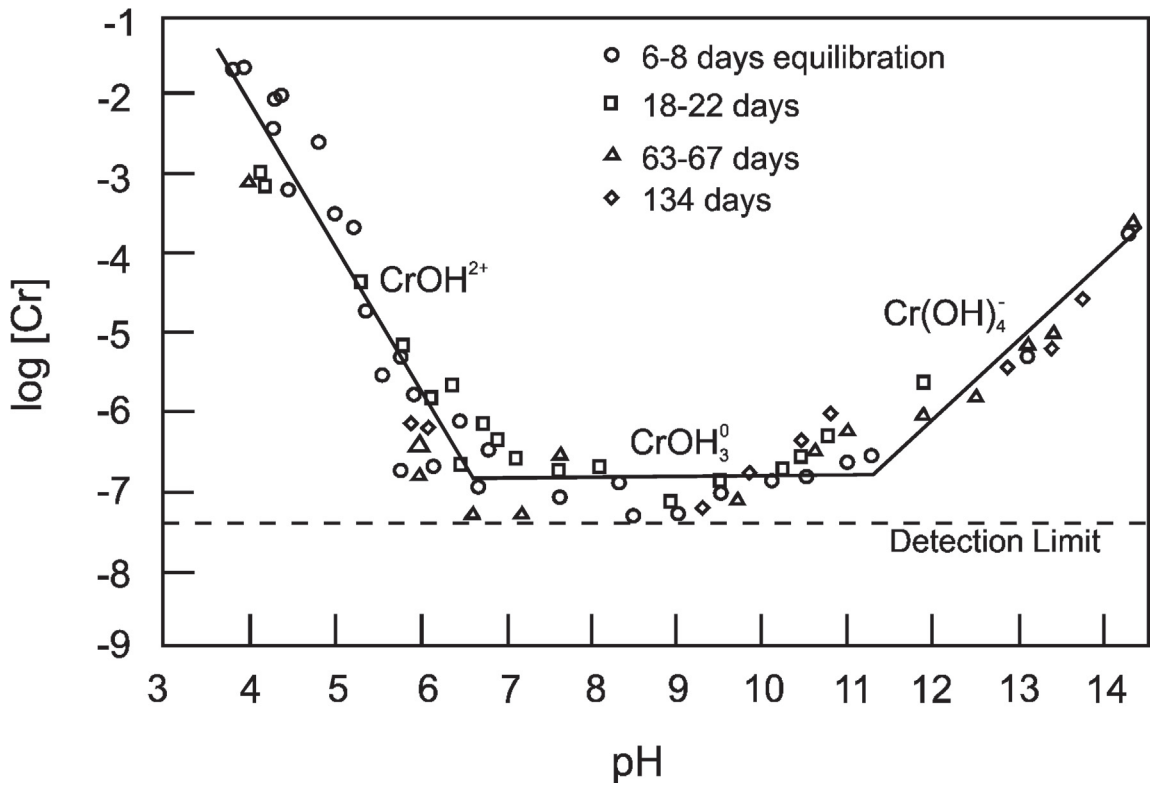

Fig. 3. The solubility of $Cr(OH)_3$ (s), adapted from Rai et al. (1987).

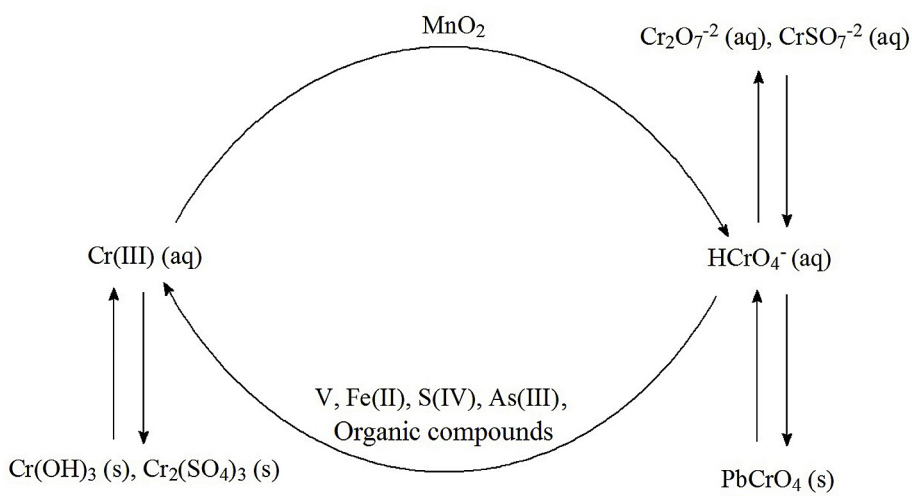

Fig. 4. The basic atmospheric cycle of Cr, adapted from Seigneur and Constantinou (1995).

reactions (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). The basic atmospheric cycle of Cr, as presented in Fig. 4, has some similarities to the soil/water cycle previously presented (Fig. 2). Again, Cr(III) is the dominant species, with many compounds able to reduce Cr(VI) to Cr(III). In the atmosphere S(IV) is a relatively important species that can reduce Cr(VI) to Cr(III). S(IV) is basically SO_2, which is a common atmospheric anthropogenic pollutant, dissolved in water (Seigneur and Constantinou, 1995; Beukes et al., 1999, 2000). Cr(VI) formation is usually associated with the presence of MnO_2 (Kimbrough et al., 1999; Seigneur and Constantinou, 1995).

Notwithstanding the likely dominance of insoluble Cr(III) in natural environments, naturally occurring Cr(VI) and/or natural formation thereof have been reported for various locations. At least 24 known Cr(VI)-bearing minerals occur (Motzer and Engineers, 2004 and references therein), which could serve as a natural sources of Cr(VI). This includes minerals such as crocoite ($PbCrO_4$) that form in the oxidized zones of lead (Pb) deposits and Cr(VI) minerals in nitrate-rich evaporite deposits in arid environments such as the Chilean nitrate deposits in the Atacama Desert. Motzer and Engineers (2004) and references therein, also described Cr(VI) as occurring in groundwater due to natural formation/processes at various locations in the USA, including Paradise Valley (Arizona), the Presidio in San Francisco, Davis (California), the western Mojave

Desert (California) and Soquel Water District south of Santa Cruz (California). In general, it is believed that most of these natural occurrences of Cr(VI) in groundwater are linked to the hydrolysis of feldspar, some common mafic minerals such as Cr-bearing pyroxenes and chromite, together with calcite, which cause alkaline groundwater conditions. This, coupled with the absence of natural reducing agents, e.g. Fe(II), organic matter and reducing organisms (see Fig. 2), may have allowed oxidation of Cr(III) to Cr(VI).

Chromite is a stable non-soluble mineral, in which Cr occurs in the Cr(III) oxidation state. However, Cr(VI) contamination of ground and/or surface water has been reported as a direct result of chromite mining in India. Godgul and Sahu (1995) postulated that serpentinization and magnesium (Mg) ion release during deuteric alteration of ultramafic rocks (peridotites) and associated oxidation (laterization) created alkaline pore water in the chromite deposits of the Sukinda belt of Orissa (India), which resulted in conditions favorable for natural Cr(VI) formation. Dubey et al. (2001), Tiwary et al. (2005) and Dhal et al. (2010) subsequently reported on several aspects related to the Cr(VI) leaching from these deposits and/or mine dumps in the same area.

As far as the authors could ascertain, Cr(VI) has not been reported in surface and/or ground-waters in Finland as a result of natural occurrence/formation, or chromite mining. Pöykiö et al. (2005) did, however, show that Scots pine (Pinus sylvestris L.) bark used as a passive bio-indicator in the immediate vicinity of the FeCr and stainless steel works at Tornio and near the open-cast chromite mine at Kemi (both in northern Finland) indicated Cr pollution factors (PF i.e. ratio of heavy metal concentrations in the bio-indicators to those in the background area) of 81 and 5.3, respectively. However, this data does not imply that the Cr occurred as Cr(VI).

Considering that Cr(VI) has been reported to occur/form naturally in some environments, it is vital to properly assess the possible occurrences of natural Cr(VI) in surface and ground-waters, and soils before large-scale chromite mining commences in the Ring of Fire. Failure to do so will result in industry carrying the total burden if Cr(VI) contamination were to be reported later, even if natural processes are responsible in part, or wholly. Additionally, since chromite mining has been implicated in Cr(VI) pollution in India, the susceptibility of all Cr-bearing minerals (not only chromite) that will be exposed during chromite mining in the Ring of Fire to form Cr(VI) needs to be established in the presence of natural oxidants and/or catalysts for such oxidation. Preliminary results by Paktunc (2016) indicated that apart from chromite that would be the targeted mineral, various other Cr-bearing minerals occur in the Ring of Fire, e.g. clinochlore, phlogopite, amphibole and clinopyroxene, with traces of minor Cr content also occurring in orthopyroxene, olivine, serpentine and carbonates. Preliminary leach tests by the same authors indicated that Cr(VI) can be generated from these minerals in the presence of birnessite, a Mn-containing mineral. Although the afore-mentioned leach conditions were not necessarily realistic for chromite tailings disposal, it does indicate the need to evaluate the possible formation of Cr(VI) from chromite mining and/or process residue for the Ring of Fire deposits.

3. Cr(VI) formation, prevention and mitigation in various process options

Cr(VI) formation and mitigation need to be considered within the context of process options that are likely to be considered for the development of the Ring of Fire. As far as the authors could ascertain, a relatively detailed mineral processing strategy was developed for the chromite ore mining and processing activities that Cliffs was planning for their Ring of Fire development, by the research and development company Mintek (2016). However, Cliffs abandoned this development and the report was not available in the public domain by the time that this paper was prepared. Therefore, techniques generally associated with mining, beneficiation and conversion of chromite ore are considered further. Within the context of this paper, two categories will be considered: (1) mining and beneficiation of chromite ore and (2) pyrometallurgical conversion of chromite into FeCr.

3.1. Mining and beneficiation of chromite ore

Run-of-mine (ROM) chromite (mined ore, prior to beneficiation) is usually beneficiated with relatively simple processes. The most commonly applied processes include primary and secondary crushing, screening, milling, dense media separation and gravity separation methods (Murthy et al., 2011). More sophisticated processes such as flotation can also be used (Wesseldijk et al., 1999), but are usually not economically feasible.

In order to generate beneficiated lumpy, chip and/or pebble chromite ore (the coarser fractions, typically 6–150 mm) crushing, screening and dense media separation would be applied. The finer fraction (typically < 6 mm) of ROM chromite would normally be milled to approximately < 1 mm and then upgraded with a series of hydrocyclones and spiral concentrators to generate metallurgical and/or chemical grade chromite concentrate (Murthy et al., 2011). Fig. 5 presents a process flow diagram for the beneficiation of

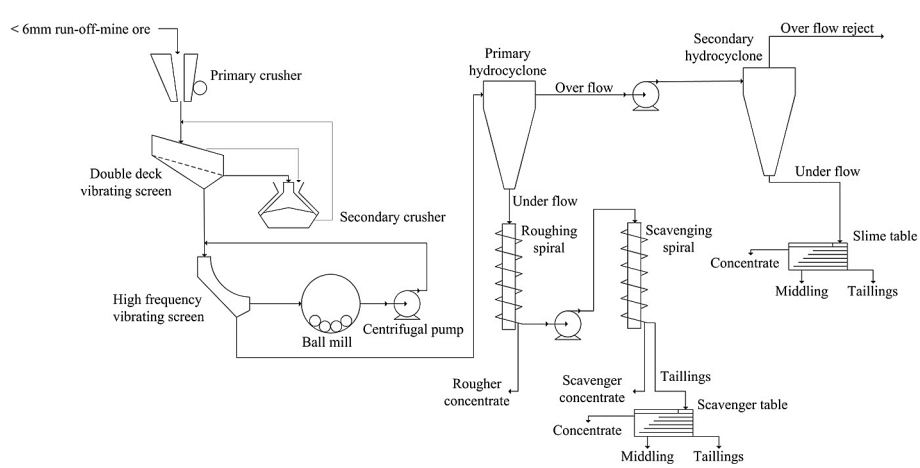

Fig. 5. General process flow diagram of a beneficiation circuit for chromite concentrate (typically < 1 mm), adapted from Murthy et al. (2011).

chromite concentrate (<1 mm) adapted from Murthy et al. (2011), who reviewed chromite beneficiation. The shaking tables (slime and scavenger tables) in this diagram would probably not be used in large-scale operations and the single spiral concentrators would probably consist of numerous banks of spiral concentrators operating in parallel.

Milling is the only process step applied during chromite beneficiation that has been implicated in the possible generation of Cr(VI). However, only dry milling of chromite has been proven to generate Cr(VI) (Beukes and Guest, 2001; Glastonbury et al., 2010). Extreme grinding (i.e. pulverization), which is not a typical comminution technique, was applied in both the afore-mentioned referenced studies and it could therefore be argued that Cr(VI) is less likely to be formed by industrial dry milling. However, Beukes and Guest (2001) also report relatively high levels of Cr(VI) in samples gathered from a dry ball mill circuit at a FeCr producer. In contrast, wet milling does not seem to generate Cr(VI) (Beukes and Guest, 2001). Wet milling would also be the obvious choice during chromite concentrate beneficiation, since hydrocyclones and spiral concentrators are wet processes. Also, during chromite concentrate beneficiation the milling step would be aimed only at liberating the chromite crystals from the gangue minerals. This is in contrast to the dry milling tests conducted by Beukes and Guest (2001) and Glastonbury et al. (2010), during which Cr(VI) was generated, where the intent was to obtain particle sizes fine enough for pelletization (which will be discussed in Section 3.2.2 and 3.2.3).

3.2. Ferrochrome production

There are four grades of FeCr that are produced commercially, i.e. High Carbon FeCr (typically > 60% Cr and 6–9% carbon, C), Charge Grade FeCr (typically 50–60% Cr and 6–9% C), Medium Carbon FeCr (typically 56–70% Cr and 1–4% C) and Low Carbon FeCr (typically 56–70% Cr and 0.015–1.0% C) (Goel, 1997). Due to the similarities of High Carbon FeCr and Charge Grade FeCr, it is common to refer to these two grades combined as High Carbon Charge

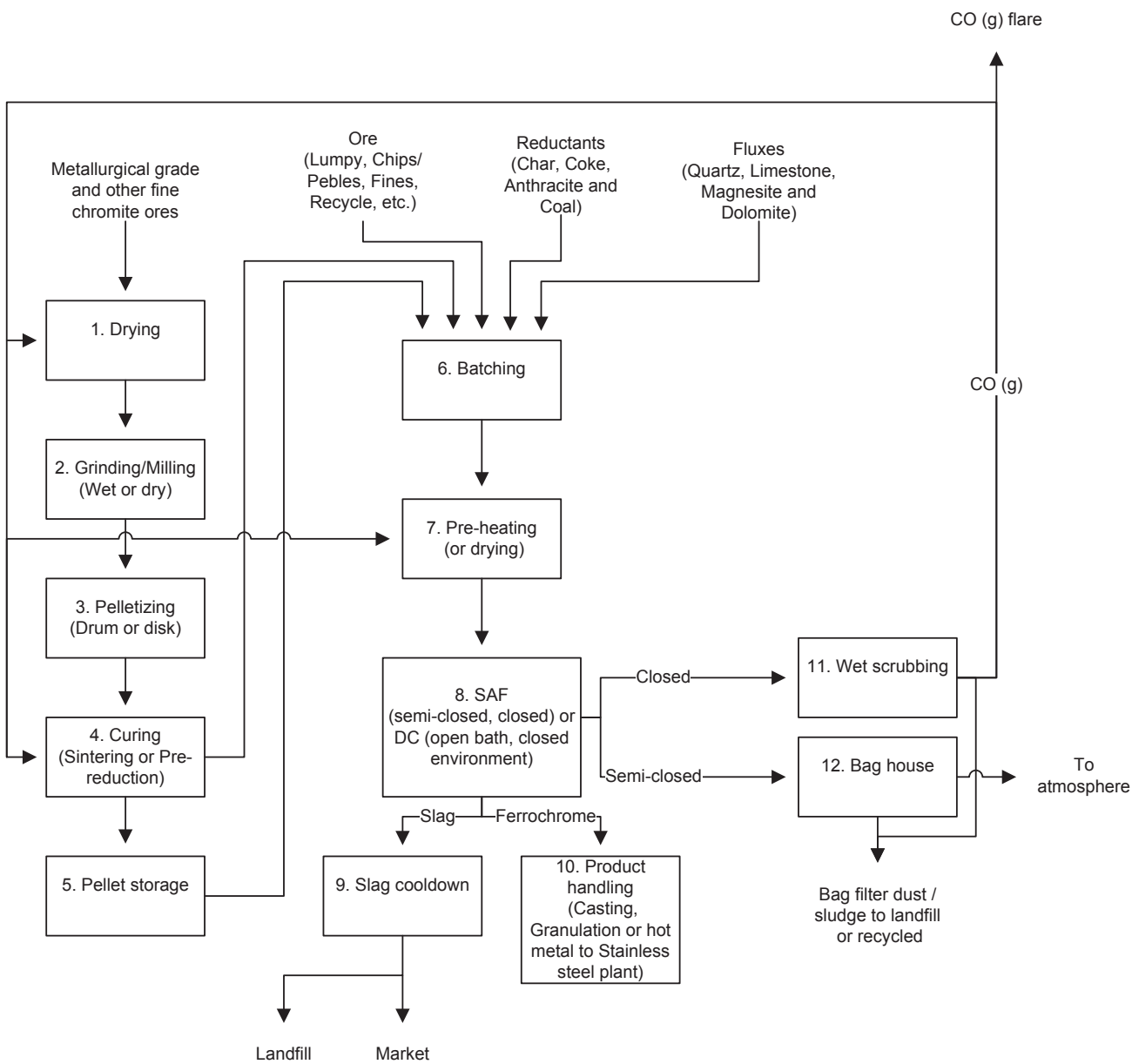

Fig. 6. A flow diagram adapted from Riekkola-Vanhanen (1999) and Beukes et al. (2010) indicating the most common process steps used for High Carbon Charge Grade FeCr production.

Grade FeCr (ICDA, 2013). The demand for low and medium grade carbon FeCr has decreased dramatically due to the development of processes such as argon oxygen decarburization (AOD) and vacuum oxygen decarburization (VOD), which allow for the removal of C from stainless steel with acceptable losses of Cr. In 2012, medium and low carbon FeCr accounted for less than 8.5% of the global annual FeCr production (ICDA, 2013). Therefore, in this paper the focus will be on Cr(VI) aspects related to High Carbon Charge Grade FeCr production, although certain aspects of other process options will also be explored.

High Carbon Charge Grade FeCr is produced with carbo-thermic reduction of chromite. Fig. 6 presents a generalized flow diagram indicating the individual process steps most commonly applied during High Carbon Charge Grade FeCr production.

Four relatively well-defined process combinations are used by most High Carbon Charge Grade FeCr producers (Beukes et al., 2010 and references therein). A brief description of each is presented below, within the context of Fig. 6.

A) Conventional open/semi-closed submerged arc furnace (SAF) operation. As the name implies, the roofs of these SAFs do not fit with a gas tight seal on the furnace sidewalls, with the subsequent unavoidable combustion of process-rich CO gas on top of the furnace bed. This is the oldest technology being applied, but internationally it still accounts for a substantial fraction of overall production (Gediga and Russ, 2007). In this type of operation, coarse (typically 6–150 mm) chromite is smelted in the presence of coarse carbonaceous reductants and coarse fluxes. The coarse nature of the feed material allows processed gas that emanates from the smelting process to permeate to the top of the bed and prevent the bed surface from sintering, which could cause dangerous blow-outs or bed turnovers (Riekkola-Vanhanen, 1999). A small fraction of fines (typically $\leq$ 6 mm) can be fed into an open/semi-closed SAF, but this increases the afore-mentioned risk. Due to the lack of sophisticated feed material pre-treatment, this process option requires the lowest capital investment. With reference to the process flow diagram (Fig. 6), the process steps followed are 6, 8, 9, 10 and 12. Some open/semi-closed SAFs do consume pelletized feed (it can also be other agglomerates such as briquettes), in which case all, or some of process steps 1–5 would also be included. Most open/semi-closed SAFs are operated on an acid slag, with a basicity factor (BF, defined in Equation (1)) smaller than 1.

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

Some open/semi-closed SAFs operate with BF > 1. Such operations are sometimes only temporarily undertaken to either compensate for refractory linings being in poor condition (basic slag has a higher liquidus temperature than acidic slag), or if enhanced sulfur-removing capacity (through formation of sulfides in the slag) is required. Bag filter off-gas cleaning is typically applied with open/semi-closed SAF operation.

B) Closed furnace operation, using oxidative sintered pelletized feed together with coarse reductants and fluxes – commercially known as the Outotec process, which is applied at the Outokumpu smelter at Tornio in Finland (Outokumpu, 2016). This technology has been commonly applied in many countries, including South Africa where the majority of green and brown field expansions during the last two decades have utilized it. Process steps usually include steps 2, 3, 4, 5, 6, 8, 9, 10 and 11, with or without 7. In most green field FeCr developments, the pelletizing and sintering sections (steps 3 and 4) are combined with closed SAFs, in which case off-gas cleaning is achieved with wet venturi scrubbing. However, pelletizing and sintering sections have also been constructed to feed conventional open/semi-closed furnaces. SAFs consuming oxidative sintered pelletized feed are usually operated on an acid slag (BF < 1).

C) Closed furnace operation with pre-reduced pelletized feed, together with coarse reductants and fluxes – commercially known as the Premus Process, as applied by Glencore Alloys (previously Xstrata Alloys) in South Africa (Naiker, 2007). FeCr smelters applying this process are also being developed in China, but this information is not yet available in the public domain. The process steps include steps 1, 2, 3, 4, 6, 8, 9, 10 and 11, with or without 5. The pelletized feed differs substantially from the oxidative sintered type (Process Option B) since the pellets are pre-reduced and mostly fed hot, directly after pre-reduction, into the SAFs. The SAFs are closed and operate on a basic slag (BF > 1), with off-gas cleaning achieved with wet venturi scrubbing. A basic slag (which is conductive) is required, since not enough lumpy carbonaceous reductants can be added during the smelting process to facilitate burden conductivity, as a result of the chromite being pre-reduced. This process option is likely to have the highest capital requirement, but the lowest specific electricity consumption (SEC) (Kleynhans et al., 2016).

D) Direct current arc furnace (DCF) operation (Jones, 2014) – currently applied at several smelters in Kazakhstan and South Africa. For this type of operation, the feed (chromite, carbonaceous reductants and fluxes) can consist exclusively of fine material. Process steps include 6, 8, 9, 10 and 11, with or without step 7. The DCF typically utilizes a basic slag (BF > 1), with off-gas cleaning achieved with wet venturi scrubbing. Of all the process options, this process has the highest SEC. In order to reduce the SEC pre-reduction of the fine chromite ore prior to DCF smelting has been attempted (McCullough et al., 2010), but has not yet been implemented commercially.

In the subsequent sections, the individual process steps presented in Fig. 6 are discussed.

3.2.1. Drying of fine feed material prior to dry milling (Fig. 6, process step 1)

Process Option C requires that the chromite concentrate, as well as other fine feed materials, be dried prior to milling and pelletization. As far as could ascertained, no studies considering the formation of Cr(VI) during this process step have been published in the public domain. However, temperatures required to drive off moisture would typically not be high enough to facilitate oxidation of chromite to generate Cr(VI).

3.2.2. Milling (Fig. 6, process step 2)

The friability of many chromite ores, e.g. the Bushveld Complex in South Africa, necessitated the implementation of agglomeration processes prior to SAF smelting to ensure a permeable bed. This applies to Process Options B and C. The most commonly applied agglomeration technique is pelletization (both with drum and disk), although briquetting is also used. Pelletization of chromite requires milling prior to agglomeration. Milling and subsequent pelletization also increase the effective surface area for reduction during smelting, which have been linked with improved SEC (Zhao and Hayes, 2010).

Currently dry milling is applied in the pre-reduced pelletized feed process (Process Option C), with a targeted particle size of d_{90}

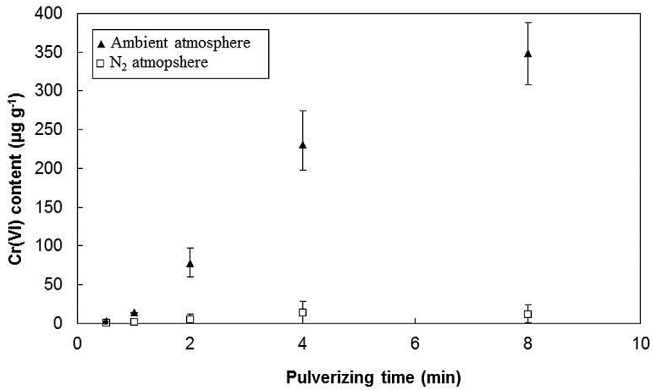

Fig. 7. Cr(VI) formation during dry milling with a Siebtechnik pulverizer under ambient and inert atmospheric conditions (adapted from Glastonbury et al., 2010).

equal to 75 μm (90% of the particles smaller than 75 μm) prior to pelletization (Kleynhans et al., 2012). Previously it was proven that dry milling of chromite ore (and other Cr containing materials) leads to Cr(VI) formation (Beukes and Guest, 2001; Glastonbury et al., 2010). Although not common, some chromite ores, e.g. chromite of the Sukinda belt of Orissa (India) might contain Cr(VI) that occurs naturally (Section 2) (Godgul and Sahu, 1995; Dubey et al., 2001; Tiwary et al., 2005; Dhal et al., 2010). However, as indicated in Fig. 7 (Glastonbury et al., 2010), Cr(VI) is formed during dry milling and not merely liberated from the mineral matrix, since no Cr(VI) was formed with dry milling under a nitrogen (N_2) atmosphere. The generation of Cr(VI) during dry milling was also acknowledged in the health, safety and environmental guidelines document compiled by the International Chromium Development Organization (ICDA) (ICDA, 2007).

No previously published data (Beukes and Guest, 2001; Glastonbury et al., 2010) can be used to quantify the generation of Cr(VI) by dry milling, since Cr(VI) generation is likely to depend on various factors, e.g. chromite composition, initial ore particle size, targeted particle size, milling equipment design, milling intensity and retention time.

Wet milling does not seem to generate Cr(VI) (Beukes and Guest, 2001). Therefore, ignoring all other aspects (e.g. capital investment, operational costs, integration with other process steps), it can be stated that wet milling has an advantage with regard to Cr(VI) formation. Currently wet milling is used in conjunction with the oxidative sintered pelletized process (Process Option B), with a targeted d_{80} of 74 μm.

Presently there seems to be conflicting views with regard to the human health hazards associated with Cr(VI) ingestion. Numerous studies (e.g. Proctor et al., 2002; Guertin, 2004) have indicated that ingested Cr(VI) is not problematic. However, all literature agrees that airborne Cr(VI) is hazardous. Therefore, if dry milling of chromite cannot be prevented, dust prevention, extraction and suppression must be applied. Captured dust must be contacted with water to immediately reduce the risk of human respiratory exposure and such captured dust must be recycled, since it consists of fine feed material. Process water utilized for contacting/capturing milling dust must be treated to reduce Cr(VI), which will be discussed later (Section 4). The wearing of appropriate dust masks must also be made compulsory for operational personnel in the dry-milling section(s).

3.2.3. Pelletization (Fig. 6, process step 3)

The formation of green (uncured/newly-formed) pellets and briquettes are not known to generate Cr(VI) in any manner, since the materials usually contain moisture (for enhanced green pellet strength) and the processes typically take place at ambient temperatures. However, curing of these green agglomerates, which will be discussed in the next section, could lead to Cr(VI) formation.

3.2.4. Curing of green pellets (Fig. 6, process step 4)

Curing of green pellets takes place in Process Options B and C. Since both these curing steps are high-temperature processes in which oxygen is not totally excluded, Cr(VI) could be generated. These two process options are therefore discussed separately.

As previously stated, the oxidative sintered pelletized process (Process Option B) is commonly applied, since it is a proven technology. It also originated from Finland, which is internationally regarded as a leader in FeCr technology and environmental aspects (Riekkola-Vanhanen, 1999). In this process, chromite concentrate (<1 mm) together with 1–2 wt % carbonaceous reductant (e.g. coke), is wet milled and thereafter de-watered. Fine refined clay (e.g. activated bentonite) is then mixed into the moist milled ore-carbon blend. The mixture is then pelletized with a pelletizing drum. The over- and undersized green pellets are recycled, while the appropriate-sized green pellets are layered on a stainless steel sintering belt, which is protected by a layer of already sintered pellets. The green pellets are then heated in a furnace, while air is pulled through the pellet bed to sinter the pellets. The amount of carbon in the green pellets is limited to supply just enough exothermic energy to sinter the pellets to the correct hardness. This process produces evenly-sized, hard and porous furnace pelletized feed material, which result in reduced furnace instabilities, lower SEC and improved Cr recovery efficiencies, if compared to the conventional open/semi-closed SAF operation (Process Option A). However, the sintering step is in essence an oxidizing process and a small amount of Cr(VI) might therefore form. The levels of Cr(VI) that form will depend on the raw material composition, particle size, plant layout, green pellet carbon content, reaction temperature, residence times, etc. Mandiwana et al. (2007) reported Cr(VI) concentrations of 2270–7070 $\mu g\ g^{-1}$ in dust collected in the proximity of such sintering furnaces. However, these values are likely to be over-estimations, since Glastonbury et al. (2010) proved that the sample preparation techniques applied by the aforementioned authors were prone to *in situ* generation of Cr(VI). It should therefore be an important future research objective to quantify Cr(VI) in off-gas particulates originating from such a sintering plant.

In the pre-reduced pelletized process (Process Option C) the chromite concentrate (<1 mm) is dry-milled together with 12–16 wt % carbonaceous reductant (fine coke, char or anthracite) and a clay binder (bentonite, or attapulgite). As is evident, substantially more carbon is added to the mixture than in the oxidative sintered process (Process Option B). Water is then added during the mixing step to obtain the desired moisture content, after which the moist material is pelletized on a pelletizing disk. The green pellets are then dried and pre-heated in a grate, after which they are cured in a counter-current rotary kiln. Such kilns are usually fired with pulverized coal, although CO-rich off-gas from closed SAFs (Du Preez et al., 2015) and crude oil can also be used. 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 pellet carbon content also results in a partial positive CO gas pressure inside the pellets. This partial positive pressure prevents oxygen from entering the core of the pellets. Due to its reductive nature, less Cr(VI) is expected to be generated during the pre-reduced pellet curing process than is generated during an oxidizing pellet-curing process (Process Options B). However, since firing of these counter-current rotary kilns takes place from within the kiln, oxygen must be available for the combustion of the pulverized coal, CO

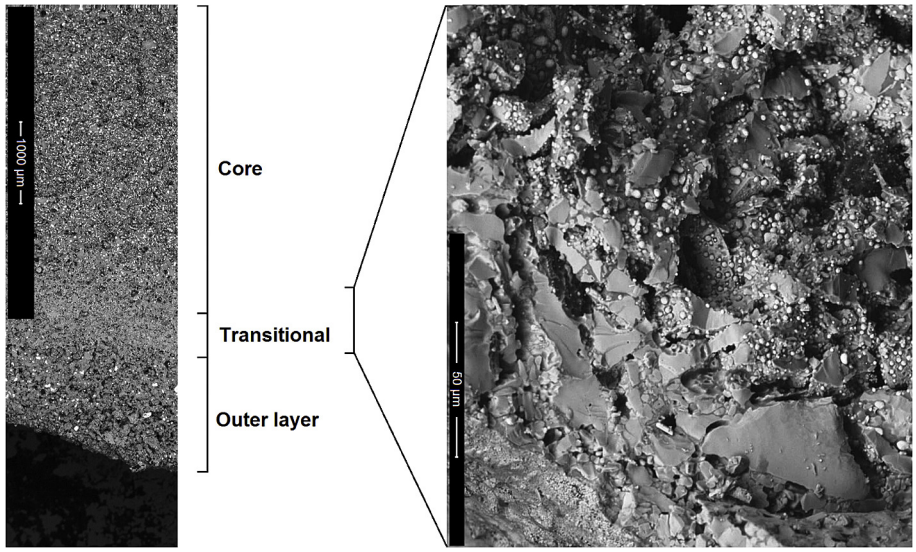

Fig. 8. SEM micrograph of a polished section of a pre-reduced pellet (left), as well as a micrograph of an unpolished section zoomed-in on the transitional zone and a portion of the pre-reduced core, with metallized droplets clearly visible (right) (Kleynhans et al., 2012).

gas or the crude oil. This results in the cured pellets usually having a thin oxidized outer layer (as indicated in Fig. 8, Kleynhans et al., 2012) in addition to the reduced core, suggesting that small amounts of Cr(VI) might also be formed.

As far as the authors could assess, a direct comparison of Cr(VI) generation between the curing steps of Process Options B and C has yet to be undertaken and it can therefore not be stated with confidence which process option generates less Cr(VI). This comparison should therefore be an important future research objective. However, both these processes represent a huge improvement in terms of the overall Cr(VI) footprint, if compared to conventional open/semi-closed FeCr production (Process Option A).

3.2.5. *Pellet storage (Fig. 6, process step 5)*

Assessments of possible Cr(VI) leaching from cured pellets produced by Process Options B and C have not yet been published. Therefore, leaching tests performed on such pellets should be considered as an important study aspect prior to selecting smelting process options for the Ring of Fire. Such results will indicate whether any preventative measures should be taken during pellet storage, e.g. storing of cured pellets on a lined surface.

As previously mentioned (Section 2), the possible natural occurrence and/or formation of Cr(VI) under ambient conditions for the Canadian ores needs to be assessed. In the unlikely event that liberation and/or formation of Cr(VI) from such ores is/are possible, the area where the lumpy chromite ore stockpiles are located prior to batching would also need to be lined to prevent possible surface and ground water pollution. This would also apply to chromite concentrate consumed by the pelletization section of the plant (i.e. storage prior to process step 1).

3.2.6. *Batching (Fig. 6, process step 6)*

The action of batching (i.e. weight proportioning of pellets, as well as lumpy chromite, reductants and fluxes according to a predetermined metallurgical recipe) does not hold any dangers of Cr(VI) generation. However, spillages of possible Cr(VI) containing materials during batching and conveying should be avoided with appropriate engineering solutions and subsequent maintenance procedures.

3.2.7. *Pre-heating (Fig. 6, process step 7)*

As far as the authors could ascertain, the possible Cr(VI) formation during pre-heating of batched material mixtures, prior to smelting of these materials in a furnace has not yet been evaluated and presented in the public domain. The pre-heating temperatures would be considerably lower than the temperatures required during pellet curing (process step 4), and the likelihood of Cr(VI) formation is therefore substantially lower. Typical pre-heating temperature achieved at the Outokumpu smelter in Finland is 500 °C.

3.2.8. *Furnace smelting (Fig. 6, process step 8)*

Many factors will affect the possible formation of Cr(VI) during smelting, of which the most important are likely to be the availability of oxygen, slag composition, presence of very fine ore and the temperature above the material bed (i.e. area above material bed and below furnace roof). These factors are therefore discussed separately.

Since oxygen is required for the oxidation of Cr(III) to Cr(VI), the availability of oxygen during smelting will influence the formation of Cr(VI). In practice, this implies that a closed furnaces (SAF or DCF) will generate less Cr(VI) than an open/semi-closed SAF, with all other factors being equal (e.g. production capacity, bed temperature, composition of feed material, slag basicity). Although both open/semi-closed and closed furnaces have a reducing environment below the burden material, a closed furnace also has a reducing CO-rich atmosphere above the burden material, while an open/semi-closed furnace has a partially oxidizing environment due to ambient air entering below the furnace roof. These basic principles are demonstrated by the simple pictorial representations of an open/semi-closed SAF and a closed SAF presented in Fig. 9.

During smelting, Cr(VI) is likely to form in the area above the bed material, since the feed material bed itself contain carbonaceous reductants (e.g. coke, char and anthracite) that reduce Cr(III) in the ore to Cr(0) in the FeCr product. Table 1 presents data from Gericke (1995), who indicated the differences in water soluble Cr(VI) contents (not total Cr(VI)) of particulate matter obtained from the off-gas from semi-closed and closed FeCr SAFs. The significance of the slag regimes (acid or basic) will be discussed later in this section, while the relevance of the water soluble contents referred to in this data (Table 1) will be discussed in Section 4.

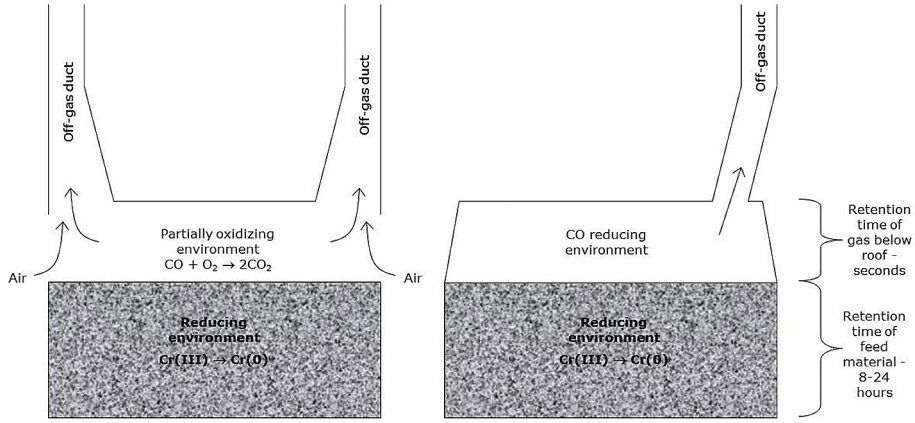

Fig. 9. Simplified representation of an open/semi-closed SAF (left) and a closed SAF (right) to demonstrate the availability of oxygen and the effect on Cr(VI) formation.

Table 1
Water soluble Cr(VI) contents of off-gas particulate matter from various types of FeCr SAFs fed with South African chromite ore (Gericke, 1995).

Furnace and slag description	Cr(VI) ($\mu g.g^{-1}$)
Closed furnace, with acid slag operation	5
Closed furnace, with basic slag operation	100
Semi-closed furnace, with acid slag operation	1000
Semi-closed furnace, with basic slag operation	7000

Considering all the afore-mentioned, and assuming comparative operating characteristics (furnace capacities, bed temperature, composition of feed material, slag basicity, etc.), it is strongly recommended that only closed furnace designs, which generates less Cr(VI) than open/semi-closed furnaces, should be considered for the Ring of Fire developments.

From the data presented in Table 1 it is also evident that a FeCr smelting furnace operated on a basic slag regime will generate more Cr(VI) than a similar furnace operated on an acid slag regime. This is due to the presence of higher concentrations of alkali and/or alkaline earth metal containing compounds in basic slag, which is achieved by the addition of fluxes such as limestone, magnesite and dolomite, in addition to the acid flux component (quartz). In contrast to FeCr production, Cr(VI) chemicals are produced *via* alkali roasting of chromite ore, by purposefully oxidizing the Cr(III) in the ore to Cr(VI) in the presence of soda ash (e.g. Antony et al., 2001). The alkali and/or alkaline earth content of FeCr feed materials is obviously only a fraction of that encountered during alkali roasting of chromite, but fundamental aspects that stimulate oxidation of Cr(III) to Cr(VI) are the same. Therefore, with all other factors being equal, a FeCr furnace operated on an acid slag generates less Cr(VI) than a comparable furnace operated on a basic slag. In a similar manner, the use of binders, catalysts, accelerants and any other compounds containing alkali and/or alkaline earth containing compounds should be avoided or minimized in all high temperature process steps applied during FeCr production. For instance it is known that several alkali and/or alkaline earth containing compounds enhance the degree of pellet pre-reduction obtained during Process Option C (e.g. Neizel et al., 2013 and references therein).

As previously stated, it is not preferred to feed fine materials directly into a FeCr SAF, since it makes the furnace bed impermeable that could result in so-called bed turnovers and blowing of the furnace. Apart from the obvious safety risks associated with the afore-mentioned instabilities, bed material disruptions also result in more fine material being suspended off the bed. Such suspended fines could be extracted with the furnace off-gas. Fig. 10 presents a

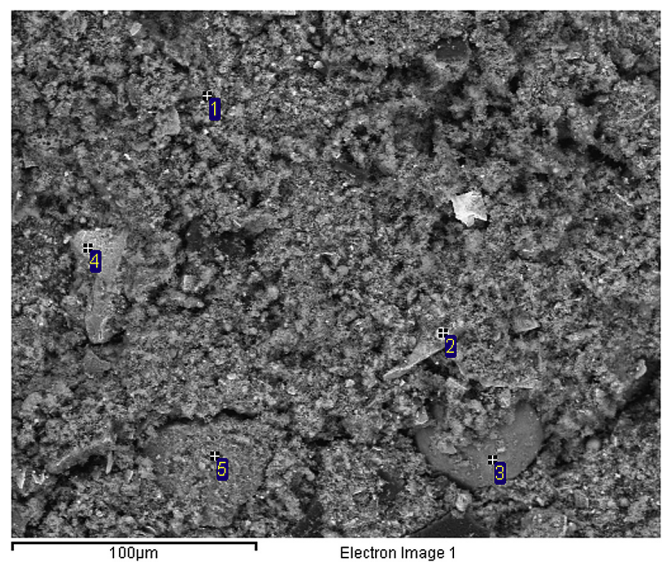

Fig. 10. A SEM micrograph of a typical bag filter dust sample originating from a semi-closed FeCr SAF.

SEM micrograph of a typical bag filter dust sample from a semi-closed FeCr SAF. The larger unevenly shaped particles that can be seen (numbers 2 to 5 in the figure) are un-reacted feed materials (chromite, fluxes and reductants). During the process of suspension and extraction, the fine Cr-containing particles will be exposed to partially oxidizing conditions above the bed material (see Fig. 9, with the associated text) in open/semi-closed furnaces (Process Option A), leading to a possible increase in Cr(VI) generation. Data to quantify the correlation between increased fines content of the feed material and possible Cr(VI) generation have not been presented in the public domain, but as a general rule of thumb it can be recommended that the content of Cr-bearing material that is fine enough to be ejected off the furnace bed must be kept as low as possible. In practice this can be achieved by screening feed materials before it is consumed in a FeCr SAF. Currently, Outokumpu in Finland (applying Process Option B) screens the FeCr smelter feed to remove the < 4 mm material.

The stability of a SAF bed, as referred to in the previous paragraph, depends on various factors. The fine material content has already been discussed. However, electrode length also plays a significant role. The oxidation of Cr(III) to Cr(VI) is dependent on temperature and oxygen partial pressure. Under normal operating

conditions on a particular SAF, the carbon content of the feed is adjusted in accordance with the metallurgical balance, 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/semi-closed FeCr SAF, a hotter partially oxidizing environment above the furnace bed will increase Cr(VI) generation. These deductions were made by Glastonbury et al. (2010) based only on logical assumptions and practical experience. As far as could be ascertained, no data quantifying the possible increased Cr(VI) formation during short electrode periods have been published. Short electrodes are not a design issue, but more an indication of operational stability.

3.2.9. Tapping, slag cool down and product handling (Fig. 6, process steps 9, 10)

As far as the authors could assess, there is no data available in the public domain that quantify the formation of Cr(VI) during tapping. However, it stands to reason that Cr-containing slag and metal that are tapped at > 1600 °C in ambient atmospheric conditions (with oxygen available) could result in some Cr(VI) formation. This notion is supported by the Health Safety and Environment Guidelines for Chromium report of the ICDA (2007), which states that "*hexavalent chromium compounds are found in small amounts in the highly oxidizing fumes from the melting/smelting processes, particularly the tapping process*". The key to reducing the potential Cr(VI) occupational health effects during this process step is to minimize splashing of liquid slag (decreased reaction area between the atmosphere and melt) and to have an effective taphole and runner fume extraction system, which will limit the exposure of operational personnel to possible Cr(VI) containing fumes. Additionally, fumes/dust captured by the extraction system must be contacted with water (e.g. in a wet scrubber), since this will immediately reduce the occupational health risk. Contact with water also eliminates the possible risk of wind dispersal. Maintaining operational availability of the taphole fume extraction system should be one of the highest priorities. Therefore, the design of the taphole fume extraction system should receive significant attention for any Ring of Fire developments. Cleaning of the runner, i.e. the furrow in which metal and slag are tapped from the furnace is usually a mechanized action. This is typically achieved with a front-end-loader/excavator, or with an overhead crane, during which the taphole fume extraction system can easily be damaged.

After solidification of the FeCr metal, it is unlikely that it could serve as a source of Cr(VI). However, slag is by volume the largest waste product produced during chromite smelting (Beukes et al., 2010) and it therefore requires additional attention. According to Beukes et al. (2010) in early period FeCr production, mono-product type disposal of FeCr slag was not rigorously applied and it was common to encounter the co-disposal of Cr(VI) containing bag filter dusts, together with FeCr slag. Within the context of possible future Ring of Fire FeCr developments, historic slag issues are irrelevant since new operations in Canada could prevent such mistakes. With regard to the tapping practice associated with hot current arising slag, two main hot slag handling practices are usually applied, i.e. (1) air cooling with limited water addition to enhance the cooling rate and (2) water granulation of the liquid slag.

Most of the South African FeCr smelters allow liquid slag to run into a designated slag bay, where it is air-cooled and spayed with a limited amount of water to accelerate the cooling process. However, this method is prone to the formation of additional Cr(VI), since the liquidus temperature of acid slag is in the order of > 1600 °C, while that of basic slag is > 1700 °C. According to Riekkola-Vanhanen (1999), FeCr slag contains 3–15% Cr_2O_3, mainly as unreduced, or partly reduced ore. Exposure of Cr-containing materials at the afore-mentioned temperatures to ambient atmospheric conditions will result in some Cr(VI) formation. Although data do not exist to quantify the Cr(VI) formation in this slag cooling process, preventative measures such as including a reducing agent, e.g. Fe(II), in the water that is used during slag cooling and capturing of aqueous drainage from slag bay areas should be considered. Additionally, any remaining FeCr metal in the slag can be recovered with physical separation techniques such as water-borne jigging, which can facilitate the effective treatment of Cr(VI) (Shen and Forssberg, 2003; Mashanyare and Guest, 1997; Coetzer et al., 1997). Properly treated air-cooled slag can be used as a replacement for building agglomerate (stone) in various applications, including cement bricks, concrete and road construction.

In contrast to the above-mentioned, 80% of the hot liquid slag at the Outokumpu FeCr smelter in Finland is granulated (Riekkola-Vanhanen, 1999). This process entails that the liquid slag is directed down a runner with water jets into a larger water pool. There are two advantages to this process, if compared to the above-mentioned air cooling of slag: (1) the exposure time of hot slag to the ambient atmosphere is substantially reduced, since granulation takes place within seconds after the liquid slag exits the tap hole, (2) the crystalline structure of the granulated slag consists of glassy-like phases (Riekkola-Vanhanen, 1999), which will limit/prevent leaching of compounds from it. The granulated slag is used in various applications, including road-building, under-building filling, paving, as a sand blasting grit and for the production of refractory castables (Riekkola-Vanhanen, 1999), with under-building filling and road-building being the most common in Finland (Niemelä and Kauppi, 2007). However, during slag granulation extreme caution should be taken to avoid liquid FeCr metal accidentally entering the slag runner, since this could results in an explosion. Therefore, plant design should prevent run-away taps from entering this area.

3.2.10. Wet scrubbing and flaring of CO-rich off-gas (Fig. 6, process step 11)

The volume and composition of the off-gas formed by a closed FeCr furnace (SAF or DCF) depend on various factors such as the feed materials, feed pre-treatment methods, design of the furnace, furnace operating philosophy and metallurgical condition of the process (Beukes et al., 2010). Gas volumes generated by closed SAF FeCr have been reported to be 220 to 250 $Nm^3 . h^{-1}$ per MW or 650 to 750 $Nm^3 . ton^{-1}$ FeCr, consisting of 75–90% CO, 2–15% H_2, 2–10% CO_2 and 2–7% N_2 (Niemelä et al., 2004). The solid content of the uncleaned furnace off-gas is typically 35–45 g. Nm^{-3} and depends on the operational conditions and the production technology (Niemelä et al., 2004). Cleaning of this off-gas is usually achieved with wet venturi scrubbing. The cleaning efficiency of wet scrubbers can be as high as 99.9%, after which the cleaned off-gas typically contains less than 50 mg. Nm^{-3} particulates (Niemelä et al., 2004). The particles remaining in the cleaned off-gas are very fine, with particles smaller than 1 μm being very difficult to remove with a wet venturi scrubber. At the Outokumpu FeCr operations in Finland, the cleaned off-gas is cleaned further by filtering the gas with a sintered plate filter to reduce particulate levels to <5 mg. Nm^{-3} (Niemelä et al., 2004; Päätalo and Raiskio, 2015). As far as the authors could assess, the sintered plate filters after wet venturi scrubbers are not used by the South African FeCr producers that apply Process Option B, C and D, and it is unlikely that it is used in other FeCr producing countries such as China, India and Kazakhstan. However, application thereof should be compulsory for the Ring of Fire developments, in order to ensure application of best practice.

The first study available in the peer-reviewed public domain to quantified the possible formation of Cr(VI) in the flaring of CO-rich off-gas from closed FeCr furnaces, was recently published (Du Preez

et al., 2015). These authors found that Cr(VI) formation during flaring was dependent on flaring temperature, size of the particles passing through the flare, and retention time within the flame. However, if no Cr-containing particles pass through the flare, no Cr(VI) can be formed. Therefore, the importance of implementing additional measures, such as the above-mentioned filtering of the off-gas after the wet venturi scrubbers with a sintered plate filter, is obvious. Burning of un-cleaned off-gas in the raw gas stack should be avoided as far as possible, since this will result in a significant amount of Cr-containing particles passing through the flare. Cleaned CO-rich off-gas should be utilized as an energy source at the plant, keeping the toxicity and explosive nature of CO gas in mind (Niemelä et al., 2004). Excess CO-rich off-gas could be combusted to generate hot water for the workforce/community, generating electricity to minimize the carbon footprint of the plant, or as fuel in rolling mills for reheating slabs in integrated stainless steel plants.

Du Preez et al. (2015) formulated an empirical model that can be used to predict Cr(VI) generation during flaring, which is indicated in Equation (2).

$$\%\ \mathrm{Cr(VI)}\ \mathrm{conversion} = -3.78\mathrm{x}10^{-3} + (1.51\mathrm{x}10^{-6}\ \mathrm{x\ Temp}) + (1.07\ \mathrm{x}\ 10^{-2}\ \mathrm{x}\ d_{90}^{-0.3203}) + (0.94\ \mathrm{x}\ 1.08\ \mathrm{x}\ 10^{-3}\exp^{(2.75475)(\mathrm{Retention\ time})}) \quad (2)$$

In Equation (2), "Temp" is the flaring temperature (K), "d_{90}" the d_{90} particle size (μm) of the particulate matter passing through flare and "Retention time" the retention time (seconds) of particles within the flare. The afore-mentioned equation was used to predict formation of Cr(VI), which compared relatively well with laboratory results (Fig. 11).

3.2.11. Bag filter dust (Fig. 6, process step 12)

As was indicated in Table 1, bag filter dust from open/semi-closed FeCr SAFs is likely to be the FeCr waste material with the highest Cr(VI) content. As with dry milling dust, captured bag filter dust must be contacted with water to immediately reduce the risk of human respiratory exposure and environmental dispersion.

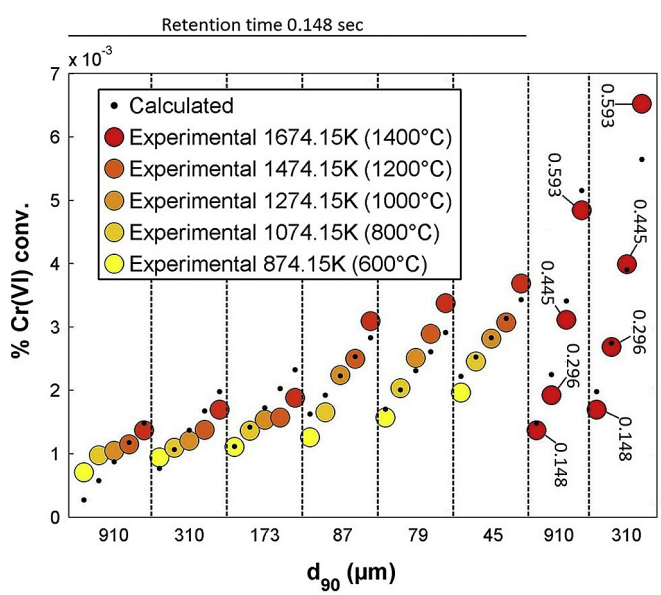

Fig. 11. Calculated % Cr(VI) conversion values using Equation (2) compared to experimental values for metallurgical grade South African ore chromite. All data presented in the figure were for particles spending 0.148 s in the heated area of a furnace to simulate a flare, except for the last two columns which also indicate retention times of up to 0.593 s (Du Preez et al., 2015).

Process water utilized for contacting bag filter dust must be treated to reduce Cr(VI) (discussed in Section 4). The wearing of appropriate dust masks must also be compulsory for operational personnel in the bag filter section.

Quantifying the atmospheric lifetimes of Cr(VI) containing particles that might be emitted (e.g. bag filter particles or particles passing through CO-rich off-gas flare) by future Canadian FeCr developments should be an important future research objective, since such values must be considered in atmospheric modeling studies to evaluate the wider regional impact. As far as could assess, there is currently no such assessment available in the public domain for the Finnish conditions. As was indicated in Section 2 (Fig. 4 and associated text), all atmospheric inter-conversion reactions leading to the possible Cr(VI) formation and reduction to Cr(III) are water-phase reactions (Kimbrough et al., 1999; Seigneur and Constantinou, 1995). During the humid Canadian summer conditions, Cr(VI) reduction will dominate and result in likely shorter atmospheric lifetimes, while in winter when moisture is frozen out of the atmosphere the situation might be different. Current estimates of the atmospheric half-life of Cr(VI) range from 16 h to 4.8 days (Kimbrough et al., 1999 and references therein), but this might not be valid for Canadian conditions. Recently Venter et al. (2016) detected Cr(VI) in ambient particulate matter that was sampled 105 km downwind of the nearest pyro-metallurgical smelter in the western Bushveld Complex, South Africa.

3.2.12. Disposal of bag filter dust and scrubber sludge (Fig. 6, process step 11 and 12)

According to the authors, bag filter dust originating from open/semi-closed SAFs and scrubber sludge originating from wet venturi scrubber cleaning the off-gas of closed SAFs or DCFs should be treated to reduce Cr(VI) and thereafter be disposed of in hazardous waste storage facilities (e.g. lined slimes dams). The reason for this recommendation will become evident in Section 4, where Cr(VI) treatment is discussed.

3.3. Additional processes

Hot liquid High Carbon Charge Grade FeCr can be refined in a converter to produce Medium and/or Low Carbon FeCr. In essence, this process is somewhat similar to stainless steel processes, during which argon oxygen decarburization (AOD) and vacuum oxygen decarburization (VOD) are used to remove C from stainless steel; however, in this case the objective would be to remove C from FeCr. Outokumpu's operations in Finland currently use such a conversion process (i.e. CRC, to remove silicon and some C from the liquid FeCr). During the CRC process, oxygen is blown into the liquid metal, which reduces the silicon content from 4–5 to less than 0.5 wt %, and the C content from approximately 7 to 3 wt % (Heikkinen, 2013). The heat released during the process is used for scrap melting. Since FeCr in all the afore-mentioned converter processes is in the hot liquid form and some oxidation has to take place to remove C (and silicon), small amounts of Cr(VI) might form. Also, limestone is typically added as a flux on top of the liquid FeCr in some of these processes, which as explained in Section 3.2.8 can enhance Cr(VI) formation. As far as could be ascertained, Cr(VI) formation and content of the lime-rich slag of such convertors have not yet been presented in the public domain. Therefore, if any Canadian development want to adopt such processes, it must assess Cr(VI) formation and develop appropriate preventative measures.

Within the Canadian context, the possible production of a FeCr-like alloy by direct solid state reduction without smelting, has received significant attention (Winter, 2014). It is not the intention of the current paper to evaluate the operability of this process, therefore only Cr(VI) related aspects are considered. Also, since no

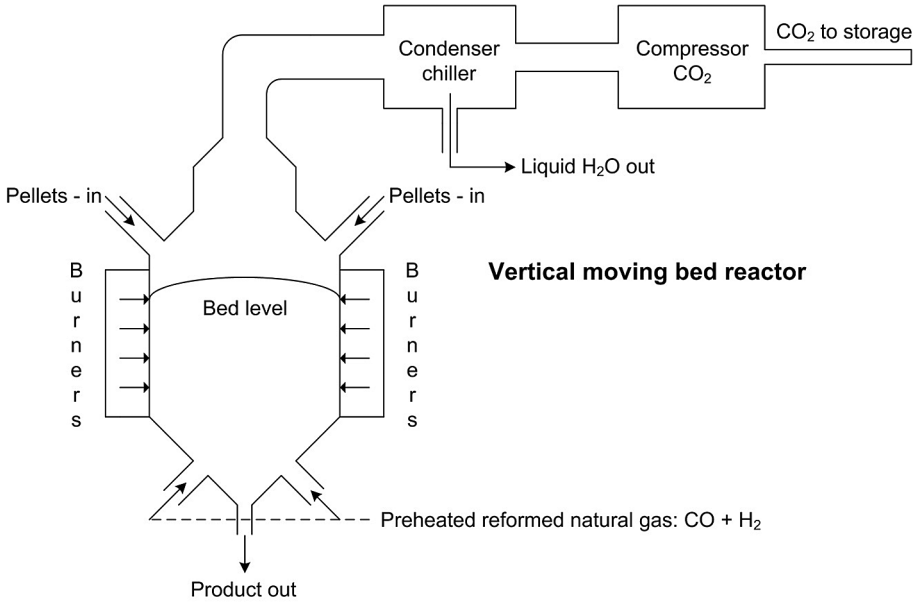

Fig. 12. Schematic outline indicating the proposed new process to produce Cr-containing alloy without smelting (adapted from Winter, 2014).

such operations exist, the evaluation is based solely on documentation available in the public domain (Winter, 2014). Fig. 12 presents the schematic outline of the proposed process. In essence, the process entails that chromite agglomerates (e.g. pellets) containing a carbonaceous reductant and an alkaline accelerant are reduced in a reaction vessel to such an extent that Cr-containing alloy can be recovered with physical separation after being liberated with milling, without the need for smelting. The most significant aspect of this proposed process is that firing of the process (indicated as "Burners" in Fig. 12) is proposed to be external to the reaction vessel. This is in contrast to the curing of green pellets produced during the pre-reduced pelletization process (Process Option C, Section 3.2.4) where pellets are cured within the same reaction vessel in which firing occurs (counter-current rotary kiln). External firing, as proposed in this new process, will reduce the tendency of the cured chromite agglomerates to form an oxidized outer layer as previously indicated (Fig. 8 and associated text). Based on this, the Cr(VI) formation potential of this process seems to be lower than the currently applied pre-reduction process (Process Option C). However, the use of an alkaline accelerant may have detrimental consequences, as previously indicated (Section 3.2.8).

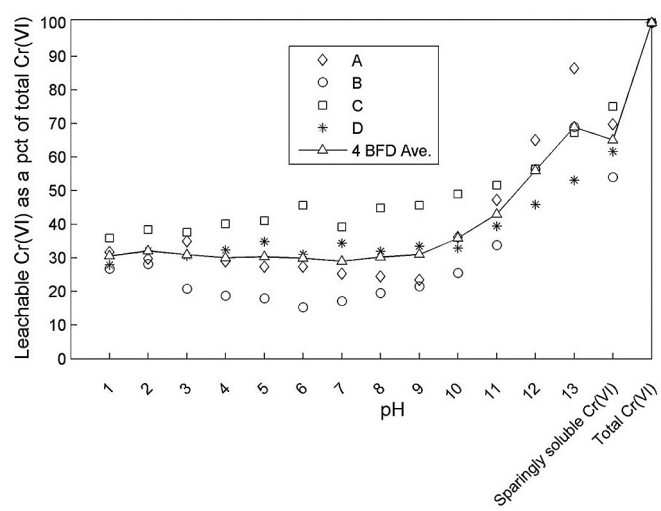

Fig. 13. Percentage leachable Cr(VI) as a function of solution pH (adapted from Du Preez et al., 2017).

4. Treatment of Cr(VI) containing waste

Prevention and waste minimization are obvious waste management options for Cr(VI). However, if Cr(VI) containing wastes are produced, recycling or treatment of such wastes must be applied. Treatment would involve capturing of the Cr(VI)-bearing materials, their leaching, and reduction in the aqueous phase. Beukes et al. (2012) reviewed the use of chemical reduction of Cr(VI) containing waste of the FeCr industry and this review is therefore not repeated here. The most important aspects that Beukes et al. (2012) pointed out were that an appropriate inorganic reducing agent should be used to reduce Cr(VI), so that insoluble Cr(III) hydroxide species form (Fig. 3 and associated text). Currently in South Africa, most FeCr producers use Fe(II) containing reducing agents to treat Cr(VI) containing process water (Beukes et al. 2012 and references therein). Some organic compounds can form water-soluble Cr(III)-complexes that are undesirable (Figs. 2 and 4 and associated text) and should therefore be avoided. Although soluble Cr(III) species may not be toxic or carcinogenic, potential exists for the soluble Cr(III) coming into contact with MnO_2 that is a naturally occurring oxidant for Cr(III) (Figs. 2 and 4).

From the above-mentioned discussion, it is evident that Cr(VI)-containing waste water can be dealt with in an acceptable manner. However, Maine et al. (2005) reported Cr(VI) leaching from FeCr wastes for days. Additionally, the authors also know from personal experience that properly treated Cr(VI) containing waste that has been stored in a purposefully designed waste facility (e.g. slimes dams) could leach small amounts of Cr(VI) over a prolonged period. Initially, it was thought that this slow leaching was due to some Cr(VI) containing waste (e.g. bag filter dust) containing glassy phases, which prevented the Cr(VI) in the core of such particles from leaching out quickly (Beukes et al., 1999). However, recent results by Du Preez et al. (2017) proved that the leachability of Cr(VI) from typical FeCr bag filter dust is dependent on pH. Even more significant is that within the pH range in which most FeCr waste waters occur (up to pH 9) only approximately 31% of total

Cr(VI) is released (Fig. 13). The reason for this is because Cr(VI) compounds can be classified as water-soluble (e.g. K_2CrO_4, Na_2CrO_4, $Na_2Cr_2O_7$), sparingly water-soluble (e.g. $SrCrO_4$) and water-insoluble (e.g. $BaCrO_4$ and $PbCrO_4$) (Ashley et al., 2003). By using appropriate buffer solutions Du Preez et al. (2017) proved that the afore-mentioned bag filter dusts contained approximately 34% sparingly water-soluble Cr(VI) compounds. The possible occurrences of sparingly-soluble Cr(VI) compounds in FeCr wastes are very problematic and new methods to dissolve both the water-soluble and sparingly water-soluble Cr(VI) fractions from such wastes should be a priority for researchers and FeCr producer alike. Ideally, to address this, the cation associations of the anion (chromate) in which the Cr(VI) occurs should be established for all Cr(VI)-containing wastes, since this directly determines the solubility characteristics. The inability to leach the Cr(VI) sparingly water-soluble fraction from FeCr wastes currently prevents optimal Cr(VI) treatment. The possible occurrence of water-insoluble Cr(VI) compounds are less problematic, since the solubilization of these compounds under conditions likely to occur during storage of waste material is unlikely.

From the literature review and discussions in this paper the authors believe that Cr(VI) containing wastes generated by chromite mining and FeCr production can be classified into three broad categories, i.e. wastes that should be i) recycled within the process (e.g. captured dust that mainly contain feed materials), ii) repurposed or re-used in other applications (e.g. granulated slag, or air cooled slag that has been treated to effect Cr(VI) reduction) and iii) considered as hazardous (e.g. open/semi-closed SAF bag filter dust that has been treated to reduce Cr(VI), closed SAF/DCF scrubber sludge that has been treated to reduce Cr(VI), mining tailings/wastes that are prone to Cr(VI) formation through atmospheric oxidation). The latter group, i.e. hazardous wastes, should be stored in appropriately designed lined waste facilities (e.g. lined slimes dam) that comply with the country specific legislation and international best practice. Such waste facilities should also be monitored to detect possible failure (e.g. leakage detection system indicating that liner have failed). However, metallurgical process performance, as well as occupational health and environmental practices should also be monitored, and continuous improvements undertaken to address shortcomings that are observed.

5. Conclusions

The conclusions and recommendations from this paper are summarized in Fig. 14. Prior to the development of the Ring of Fire reserves, baseline studies (Step 1, Fig. 14) needs to be conducted. The possible natural occurrences of Cr(VI) and the potential natural oxidation of Cr-containing minerals should be investigated. Additionally, existing anthropogenic sources that emit/release Cr(VI) and/or environmentally mobile Cr(III) species, should be identified. Failure to conduct the afore-mentioned baseline studies will result in the chromite and FeCr industries carrying the total burden if Cr(VI) contamination were to be reported later, even if natural or existing anthropogenic processes are responsible in part, or wholly.

The only process options that is known to generate Cr(VI) during mining and ore beneficiation is dry milling, which should therefore be avoided if possible (Step 2, Fig. 14).

The literature review proved that FeCr production, using recognized processes, will lead to the formation of small amounts of Cr(VI). The Cr(VI) quantities formed are usually in the $mg.kg^{-1}$ concentration range (or lower) and cannot be compared to the manufacturing of Cr(VI) chemicals (e.g. chromate or dichromate). From the assessment of the various process steps, an overall process can be chosen to minimize the formation of Cr(VI) (Step 3, Fig. 14). However, even the most ideal process will still lead to some Cr(VI) being generated. Although the operability of process option was not discussed in this review, it is important to state that individual process steps cannot merely be strung together to find the best overall process to limit Cr(VI) formation, since certain processing steps are not compatible with others. Therefore, a holistic view should be applied, which recognizes that many factors (e.g. physical and chemical characteristics of the ore, capital and operational costs, SEC, carbon footprint, availability of expertise) and not only Cr(VI) will dictate what process options will be chosen.

Since Cr(VI) formation cannot be totally eliminated, some Cr(VI) containing waste will be generated. Therefore, optimum waste treatment (e.g. chemical reduction to effect Cr(VI) reduction), re-use (e.g. slag that has been treated or verified as safe for use) and hazardous waste storage (e.g. slimes dams containing treated bag filter dust and/or scrubber sludge) should be applied (Step 4, Fig. 14).

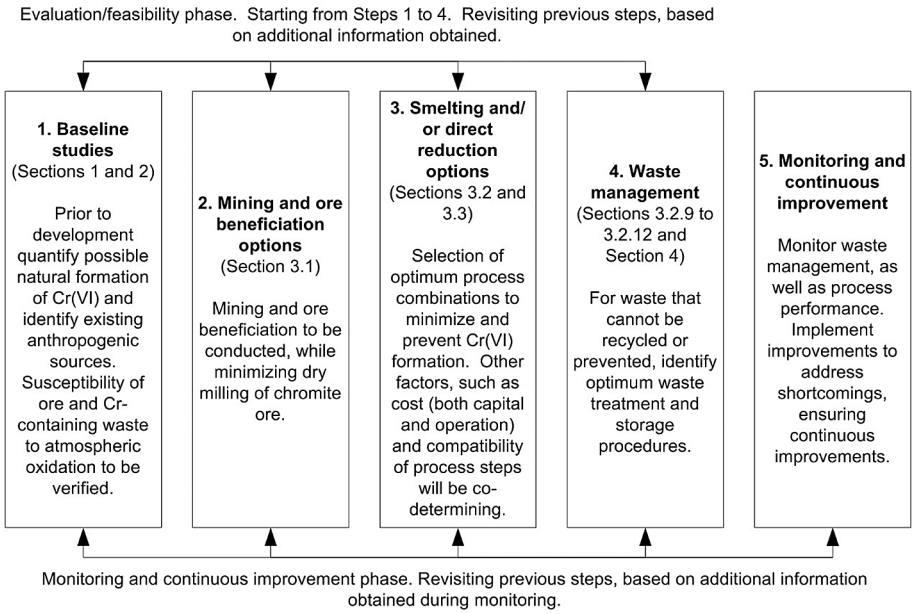

Fig. 14. Iterative steps that need to be considered for the possible development of the ROF to prevent and mitigate Cr(VI) impacts.

During the evaluation/feasibility phase, Step 1 to 4 (Fig. 14) should be considered in an iterative manner. For instance results obtained during the baseline studies (Step 1, Fig. 14) might influence the selection of process options (Step 2 to 3, Fig. 14), or waste management strategies (Step 4, Fig. 14). Alternatively, evaluation of different process options or waste management strategies, might give new insight into additional baseline studies that need to be undertaken. This iterative evaluation should be repeated until a satisfactory overall approach to the development of the ROF is obtained.

Ultimately if the chromite and FeCr industries are established, the effectiveness of preventative and mitigation measures identified during the evaluation/feasibility phase (Steps 1 to 4, Fig. 14) should be monitored (Step 5, Fig. 14). If shortcomings are observed, improvements to selected process options and/or waste management strategies should be applied as required. This again leads to an iterative approach, which results in continuous improvement.

Overall it can be stated that it is possible to produce FeCr without causing Cr(VI) occupational and community health issues, as well as environmental pollution. For instance, Huvinen and Pukkala (2013, 2016) conducted a cohort study of personnel employed by the Finnish FeCr and stainless steel industries during the period 1967–2004 and found that these workers did not have an increased mortality or cancer risk, when compared with the general population. Also, no significant Cr(VI) environmental pollution have been reported for the Finnish chromite mining and smelting industries.

Acknowledgements

The financial assistance of the National Research Foundation (NRF, South Africa, grant number: 101345) towards this PhD bursary of S.P. du Preez is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the NRF. The financial assistance and support of Natural Resources Canada under contract Number 3000603956 as part of the Canadian Rare Earth Elements and Chromite R&D Program is hereby acknowledged. All copyrights to this paper are held by the Government of Canada.

References

Abbasi, S., Soni, R., 1983. Stress-induced enhancement of reproduction in earthworm octochaetus pattoni exposed to chromium (vi) and mercury (ii) – implications in environmental management. Int. J. Environ. Stud. 22, 43–47. http://dx.doi.org/10.1080/00207238308710100.

Antony, M., Tathavadkar, V., Calvert, C., Jha, A., 2001. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium. Metall. Mater. Trans. B 32, 987–995. http://dx.doi.org/10.1007/s1166300100876.

Ashley, K., Howe, A.M., Demange, M., Nygren, O., 2003. Sampling and analysis considerations for the determination of hexavalent chromium in workplace air. J. Environ. Monit. 5, 707–716. http://dx.doi.org/10.1039/b306105c.

Bartlett, R.J., 1991. Chromium cycling in soils and water: links, gaps, and methods. Environ. Health Perspect. 92, 17–24.

Beaver, L.M., Stemmy, E.J., Constant, S.L., Schwartz, A., Little, L.G., Gigley, J.P., Chun, G., Sugden, K.D., Ceryak, S.M., Patierno, S.R., 2009. Lung injury, inflammation and Akt signaling following inhalation of particulate hexavalent chromium. Toxicol. Appl. Pharm. 235, 47–56. http://dx.doi.org/10.1016/j.taap.2008.11.018.

Beukes, J.P., Dawson, N.F., Van Zyl, P.G., 2010. Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry. J. South. Afr. Inst. Min. Metall. 110, 743–750.

Beukes, J.P., Guest, R.N., 2001. Cr(VI) generation during milling. Min. Eng. 14, 423–426. http://dx.doi.org/10.1016/S0892-6875(01)00022-X.

Beukes, J.P., Pienaar, J.J., Lachmann, G., 2000. The reduction of hexavalent chromium by sulphite in wastewater - an explanation of the observed reactivity pattern. Water SA 26, 393–396.

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

Beukes, J.P., Van Zyl, P.G., Ras, M., 2012. Treatment of Cr(VI)-containing wastes in the South African ferrochrome industry – a review of currently applied methods. J. South. Afr. Inst. Min. Metall. 112, 347–352.

Bollinger, J.E., Bundy, K., Anderson, M.B., Millet, L., Preslan, J.E., Jolibois, L., Chen, H.-L., Kamath, B., George, W.J., 1997. Bioaccumulation of chromium in red swamp crayfish (Procambarus clarkii). J. Hazard. Mater 54, 1–13.

Chang, D., Chen, T., Liu, H., Xi, Y., Qing, C., Xie, Q., Frost, R.L., 2014. A new approach to prepare ZVI and its application in removal of Cr (VI) from aqueous solution. Chem. Eng. J. 244, 264–272. http://dx.doi.org/10.1016/j.cej.2014.01.095.

Chong, J., 2014. Resource Development in Canada: a Case Study on the Ring of Fire. http://www.lop.parl.gc.ca/content/lop/ResearchPublications/2014-17-e.htm#a3. (Accessed 22 March 2016).

Coetzer, G., Giesekke, E., Guest, R., 1997. Hexavalent chromium in the recovery of ferrochromium from slag. Can. Metall. Q. 36, 261–268.

Dhal, B., Thatoi, H.N., Das, N.N., Pandey, B.D., 2010. Reduction of hexavalent chromium by Bacillus sp. isolated from chromite mine soils and characterization of reduced product. J. Chem. Technol. Biotechnol. 85, 1471–1479. http://dx.doi.org/10.1002/jctb.2451.

Dong, X., Ma, L.Q., Gress, J., Harris, W., Li, Y., 2014. Enhanced Cr(VI) reduction and As(III) oxidation in ice phase: important role of dissolved organic matter from biochar. J. Hazard. Mater 267, 62–70.

Du Preez, S.P., Beukes, J.P., Van Dalen, W.P.J., Van Zyl, P.G., Paktunc, D., Loock-Hatting, M.M., 2017. Aqueous solubility of Cr(VI) compounds in ferrochrome bag filter dust and the implications thereof. Water SA 43, 298–309. http://dx.doi.org/10.4314/wsa.v43i2.13.

Du Preez, S.P., Beukes, J.P., Van Zyl, P.G., 2015. Cr (VI) generation during flaring of CO-rich off-gas from closed ferrochromium Submerged Arc furnaces. Metall. Mater. Trans. B 46, 1002–1010. http://dx.doi.org/10.1007/s11663-014-0244-3.

Dubey, C., Sahoo, B., Nayak, N., 2001. Chromium (VI) in waters in parts of Sukinda chromite valley and health hazards, Orissa. India. B. Environ. Contam. Toxicol. 67, 541–548. http://dx.doi.org/10.1007/s00128-001-0157-0.

Eary, L., Rai, D., 1988. Chromate removal from aqueous wastes by reduction with ferrous ion. Environ. Sci. Technol. 22, 972–977. http://dx.doi.org/10.1021/es00173a018.

Environment Canada, 2014. Proposed Amendments to the Chromium Electroplating, Chromium Anodizing and Reverse Etching Regulations. https://www.ec.gc.ca/lcpe-cepa/208517F9-6423-4E9F-86FC-F74D6E0F4E71/Modifications_R%E8glement_Amendments_Regulations-eng.pdf. (Accessed 10 May 2016).

Gediga, J., Russ, M., 2007. Life Cycle Inventory (LCI) Update of Primary Ferrochrome Production. ICDA (International Chromium Development Association).

Gericke, W.A., 1995. Environmental aspects of ferrochrome production. In: Proceedings of 7th International Ferroalloys Congress, Trondheim, Norway, pp. 131–140.

Glastonbury, R.I., Van Der Merwe, W., Beukes, J.P., Van Zyl, P.G., Lachmann, G., Steenkamp, C.J.H., Dawson, N.F., Steward, H.M., 2010. Cr(VI) generation during sample preparation of solid samples – a chromite ore case study. Water SA 36, 105–110.

Godgul, G., Sahu, K., 1995. Chromium contamination from chromite mine. Environ. Geol. 25, 251–257.

Goel, R.P., 1997. Smelting technologies for ferrochromium production - recent trends. In: Vaish, A.K., Singh, S.D., Goswami, N.G., Ramachandraroa, P. (Eds.), Ferro Alloy Industries in the Liberalized Economy. NML Jamshedpur, pp. 37–50.

Guertin, J., 2004. Toxicity and Health Effects of Chromium (All Oxidation States). In: Guetin, J., Jacobs, J.A., Avakian, C.P. (Eds.), Chromium(VI) Handbook. CRC Press, USA, pp. 215–234. ISBN 1-56670-608-4.

Gupta, S., Yadav, A., Verma, N., 2017. Simultaneous Cr(VI) reduction and bioelectricity generation using microbial fuel cell based on alumina-nickel nanoparticles-dispersed carbon nanofiber electrode. Chem. Eng. J. 307, 729–738.

Haggerty, S.E., 1991. Oxide mineralogy of the upper mantle. Rev. Mineral. Geochem 25, 355–416.

Heikkinen, E.P., 2013. On the Role of Computational Thermodynamics in Research and Development of AOD and CRC Processes. PhD. University of Oulu, Finland, p. 106.

Hininger, I., Benaraba, R., Osman, M., Faure, H., Roussel, A.M., Anderson, R.A., 2007. Safety of trivalent chromium complexes: no evidence for DNA damage in human HaCaT keratinocytes. Free Radic. Biol. Med. 42, 1759–1765. http://dx.doi.org/10.1016/j.freeradbiomed.2007.02.034.

Hutchinson, T.H., Williams, T.D., Eales, G.J., 1994. Toxicity of cadmium, hexavalent chromium and copper to marine fish larvae (Cyprinodon variegatus) and copepods (Tisbe battagliai). Mar. Environ. Res. 38, 275–290.

Huvinen, M., Pukkala, E., 2013. Cancer incidence among Finnish ferrochromium and stainless steel production workers in 1967–2011: a cohort study. BMJ open 3, e003819. http://dx.doi.org/10.1136/bmjopen-2013-003819.

Huvinen, M., Pukkala, E., 2016. Cause-specific mortality in Finnish ferrochromium and stainless steel production workers. Occup. Med. 66, 241–246. http://dx.doi.org/10.1093/occmed/kqv197.

IARC (International Agency for Research on Cancer), World Health Organization, 2012. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Arsenic, Metals, Fibers and Dust, Vol. 100C, Chromium(VI) Compounds. International Agency for Research on Cancer, Lyon, France, pp. 147–167. ISBN 978 92 832 1320 8.

ICDA, 2007. International Chromium Development Association, Health Safety and Environment Guidelines for Chromium Edition, Paris, France.

ICDA, 2013. International Chromium Development Association, Statistical Bulletin 2013 Edition, Paris, France.

Jin, R., Liu, Y., Liu, G., Tian, T., Qiao, S., Zhou, J., 2017. Characterization of product and potential mechanism of Cr(VI) reduction by anaerobic activated sludge in a

sequencing batch reactor. Sci. Rep. 7, 1681.
Jones, R.T., 2014. DC arc furnaces–Past, present, and future. In: Mackey, P.J., Grimsey, E.J., Jones, R.T., Brooks, G.A. (Eds.), Celebrating the Megascale, Proceedings of the Extraction and Processing Division Symposium on Pyrometallurgy in Honor of David GC Robertson. Wiley, TMS, California, pp. 16–20. http://dx.doi.org/10.1002/9781118889657.ch10.
Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L., Mabuni, C., 1999. A critical assessment of chromium in the environment. Crit. Rev. Env. Sci. Tec. 29, 1–46. http://dx.doi.org/10.1080/10643389991259164.
Kleynhans, E.L.J., Neizel, B.W., Beukes, J.P., Van Zyl, P.G., 2016. Utilisation of pre-oxidised ore in the pelletised chromite pre-reduction process. Min. Eng. 92, 114–124. http://dx.doi.org/10.1016/j.mineng.2016.03.005.
Kleynhans, E.L.J., Beukes, J.P., Van Zyl, P.G., Kestens, P.H.I., Langa, J.M., 2012. Unique challenges of clay binders in a pelletised chromite pre-reduction process. Min. Eng. 34, 55–62. http://dx.doi.org/10.1016/j.mineng.2012.03.021.
Loock-Hattingh, M.M., Beukes, J.P., Van Zyl, P.G., Tiedt, L.R., 2015. Cr(VI) and conductivity as indicators of surface water pollution from ferrochrome production in South Africa: four case studies. Metall. Mater. Trans. B 46, 2315–2325. http://dx.doi.org/10.1007/s11663-015-0395-x.
Maine, C.F., Smit, J.P., Giesekke, E.W., 2005. The Solid Stabilization of Soluble Wastes Generated in the South African Ferrochrome Industry. Final report to the Water Research Commission (of South Africa), WRC Report no 942/1/05.
Mandiwana, K.L., Panichev, N., Ngobeni, P., 2007. Electrothermal atomic absorption spectrometric determination of Cr(VI) during ferrochrome production. J. Hazard. Mater 145, 511–514. http://dx.doi.org/10.1016/j.jhazmat.2007.01.077.
March, J., 1992. March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, sixth ed. John Wiley & Sons, New Jersey.
Mashanyare, H., Guest, R., 1997. The recovery of ferrochrome from slag at Zimasco. Min. Eng. 10, 1253–1258.
McCullough, S., Barcza, N., Hockaday, S., Johnson, C., 2010. Pre-reduction and Smelting Characteristics of Kazakhstan Ore Samples. Mintek.
Miller, R.B., Giai, C., Iannuzzi, M., Monty, C.N., Senko, J.M., 2016. Microbial reduction of Cr (VI) in the presence of chromate conversion coating constituents. Bioremed. J. 20, 174–182.
Mintek, 2016. http://www.mintek.co.za/. (Accessed 23 March 2016).
Mishra, A.K., Mohanty, B., 2008. Acute toxicity impacts of hexavalent chromium on behavior and histopathology of gill, kidney and liver of the freshwater fish, Channa punctatus (Bloch). Toxicol. Pharmacol. 26, 136–141.
Motzer, W.E., Engineers, T., 2004. Chemistry, geochemistry, and geology of chromium and chromium compounds. In: Guetin, J., Jacobs, J.A., Avakian, C.P. (Eds.), Chromium(VI) Handbook. CRC Press, USA, pp. 23–91. ISBN 1-56670-608-4.
Murthy, Y.R., Tripathy, S.K., Kumar, C.R., 2011. Chrome ore beneficiation challenges and opportunities – a review. Min. Eng. 24, 375–380. http://dx.doi.org/10.1016/j.mineng.2010.12.001.
Naiker, O., 2007. The development and advantages of Xstrata's Premus Process. In: Proceedings Ferroalloys 11th International Congress, pp. 112–119.
Neizel, B.W., Beukes, J.P., Van Zyl, P.G., Dawson, N.F., 2013. Why is $CaCO_3$ not used as an additive in the pelletised chromite pre-reduction process? Min. Eng. 45, 115–120. http://dx.doi.org/10.1016/j.mineng.2013.02.015.
Niemelä, P., Kauppi, M., 2007. Production, characteristics and use of ferrochromium slags. In: Proceedings of 11th International Ferroalloys Congress, New Delhi, India, pp. 171–179.
Niemelä, P., Krogerus, H., Oikarinen, P., 2004. Formation, Characterization and Utilization of CO-gas Formed in Ferrochrome Smelting. In: Proceedings of 10th International Ferroalloys Congress, Cape Town, South Africa, pp. 68–77.
Outokumpu, 2016. http://www.outokumpu.com/en/company/outokumpu-in-europe-middle-east-and-africa/production-sites/Tornio/Pages/Outokumpu-production-site-Tornio-Works-Finland.aspx (accessed 23 March 2016).
Päätalo, M., Raiskio, J., 2015. Dust Emission Minimizing, Measuring and Monitoring in FeCr-production in Tornio Works. In: Proceedings of 14th International Ferroalloys Congress, Kiev, Ukraine, pp. 703–708.
Paktunc, D., 2016. Chromite: Update on Progress. Presentation Presented at the Chromite Processing and Environment Technical Committee.
Peralta, R.J., Gardea-Torresdey, L.J., Tiemann, J.K., Gomez, E., Arteaga, S., Rascon, E., Parsons, G.J., 2001. Uptake and effects of five heavy metals on seed germination and plant growth in alfalfa (Medicago sativa L.). B. Environ. Contam. Toxicol. 66, 727–734.
Peterson, M.L., Brown, G.E., Parks, G.A., 1996. Direct XAFS evidence for heterogeneous redox reaction at the aqueous chromium/magnetite interface. Colloids Surf. A Physicochem. Eng. Asp. 107, 77–88. http://dx.doi.org/10.1016/0927-7757(95)03345-9.
Pöykiö, R., Perämäki, P., Niemelä, M., 2005. The use of Scots pine (Pinus sylvestris L.) bark as a bioindicator for environmental pollution monitoring along two industrial gradients in the Kemi–Tornio area, northern Finland. Int. J. Environ. An. Ch 85, 127–139.
Proctor, D.M., Otani, J.M., Finley, B.L., Paustenbach, D.J., Bland, J.A., Speizer, N., Sargent, E.V., 2002. Is hexavalent chromium carcinogenic via ingestion? A weight-of-evidence review. J. Toxicol. Environ. Health A 65, 701–746. http://dx.doi.org/10.1080/00984100290071018.
Rai, D., Sass, B.M., Moore, D.A., 1987. Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. Inorg. Chem. 26, 345–349.
Riekkola-Vanhanen, M., 1999. Finnish Expert Report on Best Available Techniques in Ferrochromium Production. Helsinki.
Seigneur, C., Constantinou, E., 1995. Chemical kinetic mechanism for atmospheric chromium. Environ. Sci. Technol. 29, 222–231.
Shen, H., Forssberg, E., 2003. An overview of recovery of metals from slags. Waste Manag. 23, 933–949.
Testa, S.M., 2004. Sources of chromium contamination in soils and groundwater. In: Guetin, J., Jacobs, J.A., Avakian, C.P. (Eds.), Chromium(VI) Handbook. CRC Press, USA, pp. 143–163. ISBN 1-56670-608-4.
Tiwary, R., Dhakate, R., Rao, V.A., Singh, V., 2005. Assessment and prediction of contaminant migration in ground water from chromite waste dump. Environ. Geol. 48, 420–429. http://dx.doi.org/10.1007/s00254-005-1233-2.
Venter, A.D., Beukes, J.P., Van Zyl, P.G., Josipovic, M., Jaars, K., Vakkari, V., 2016. Regional atmospheric Cr (VI) pollution from the Bushveld complex, South Africa. Atmos. Pollut. Res. 7, 762–767. http://dx.doi.org/10.1016/j.apr.2016.03.009.
Wang, G., Zhang, B., Li, S., Yang, M., Yin, C., 2017. Simultaneous microbial reduction of vanadium (V) and chromium (VI) by Shewanella loihica PV-4. Bioresour. Technol. 227, 353–358.
Warner, B.G., Rubec, C.D.A., 1997. The Canadian Wetland Classification System, second ed. Wetlands Research Centre, University of Waterloo, Waterloo, Ontario. ISBN: 0-662-25857-6.
Wesseldijk, Q., Reuter, M., Bradshaw, D., Harris, P., 1999. The flotation behavior of chromite with respect to the beneficiation of UG2 ore. Min. Eng. 12, 1177–1184.
Williams, A.G., Scherer, M.M., 2001. Kinetics of Cr (VI) reduction by carbonate green rust. Mar. Environ. Res. 35, 3488–3494. http://dx.doi.org/10.1021/es010579g.
Winter, F. 2014. Production of chromium iron alloys directly from chromite ore. PCT patent number PCT/US2014/054644, International filing date: 9 September 2014, Priority date: 21 October 2013.
Zhao, B., Hayes, P., 2010. Effects of Oxidation on the Microstructure and Reduction of Chromite Pellets. In: Proceedings of 12th International Ferroalloys Congress, Helsinki, Finland, pp. 263–273.