

## **Chromite—A cost-effective refractory raw material for refractories in various metallurgical applications**

**N. McEwan, T. Courtney, R.A. Parry, and P. Knupfer**  
Vereeniging Refractories (Pty) Ltd

*Keywords:* refractories, chromite, Marico

**Abstract** – This paper examines the role of refractory-grade chromite in refractories. The chromite deposit at Verref's Marico Chrome mine is described. The refractory properties of chromite and their role in basic refractories are described. The properties and metallurgical applications of chrome-containing refractories are described and finally environmental issues associated with chrome-containing refractories are discussed.

### **INTRODUCTION**

Chrome-containing refractories have been around since 1879 and are critical for various metallurgical applications. Refractory-grade chromite is important as a source of chromite in these chrome containing-refractories.

The specific desirable properties of chromite that give chrome-containing refractories their specific properties are discussed in this paper. The properties and metallurgical applications of chrome-containing refractories are examined, and finally environmental issues associated with chrome containing refractories are discussed.

### **MARICO CHROME CORPORATION**

#### **Introduction to Marico Chrome Corporation**

Marico Chrome Corporation is a 50:50 joint venture between Vereeniging Refractories (Verref) and Samancor Chrome SA.

Vereeniging Refractories was established in 1882 and is the oldest and largest refractory company on the African continent. In 1946 the company was registered and listed on the Johannesburg and London stock exchanges. It was listed as a subsidiary of The Vereeniging Estates Limited, later known as Anglocoal, a division of Anglo American. The name of the company was changed in 1967 to Vereeniging Refractories Limited, to reflect its main line of business. In 1989 the business was split into Amcoal Colliery and Industrial

Operations Limited, under the name Verref. The last change of ownership was in 2001, when Verref became an independent and privately owned company.<sup>1</sup>

Verref employs about 700 people in its mining and refractory operations. It has the capacity to produce about 150,000 tonnes per annum of shaped and unshaped products in a wide range of qualities, including magnesia, magchrome, chromag, doloma, alumino-silicate, high-alumina, zircon and acid resistant materials. Basic and alumino-silicate castables, mortars, gunning and ramming materials are also produced by Verref.<sup>2</sup>

Vereeniging Refractories serves the industries of southern Africa and also exports to central Africa and to overseas markets.

Samancor was formed by the amalgamation of SA Manganese Ltd and African Metals Corporation Ltd (Amcor) in 1975. It was known as SA Manganese Amcor Ltd until 1985, when the name was changed to Samancor. In 1983, Gencor became the single biggest shareholder in Samancor, with about 40% of the shares, giving it effective control.<sup>3</sup>

By 1986, Samancor had a number of interests in the production of ferromanganese, chromium-alloys, ferrosilicon, graphite electrodes, and other carbon products, phosphate fertilizers, phosphoric acid and sodium tripolyphosphate, and interests in mineral deposits like chromium ores, dolomite, limestone, vanadium, serpentine and, of course, the huge manganese ore deposits.<sup>3</sup>

In 1998, after Gencor's unbundling exercise, Billiton established a joint venture with Anglo American to purchase and de-list Samancor Ltd. Billiton owned 60% of the shares. Billiton subsequently merged with BHP to form BHP Billiton (in 2001). The Samancor Chrome and Samancor Manganese divisions were split, with the Kermas group acquiring 100% of Samancor Chrome. The effective date of sale was 1 June 2005.<sup>3</sup>

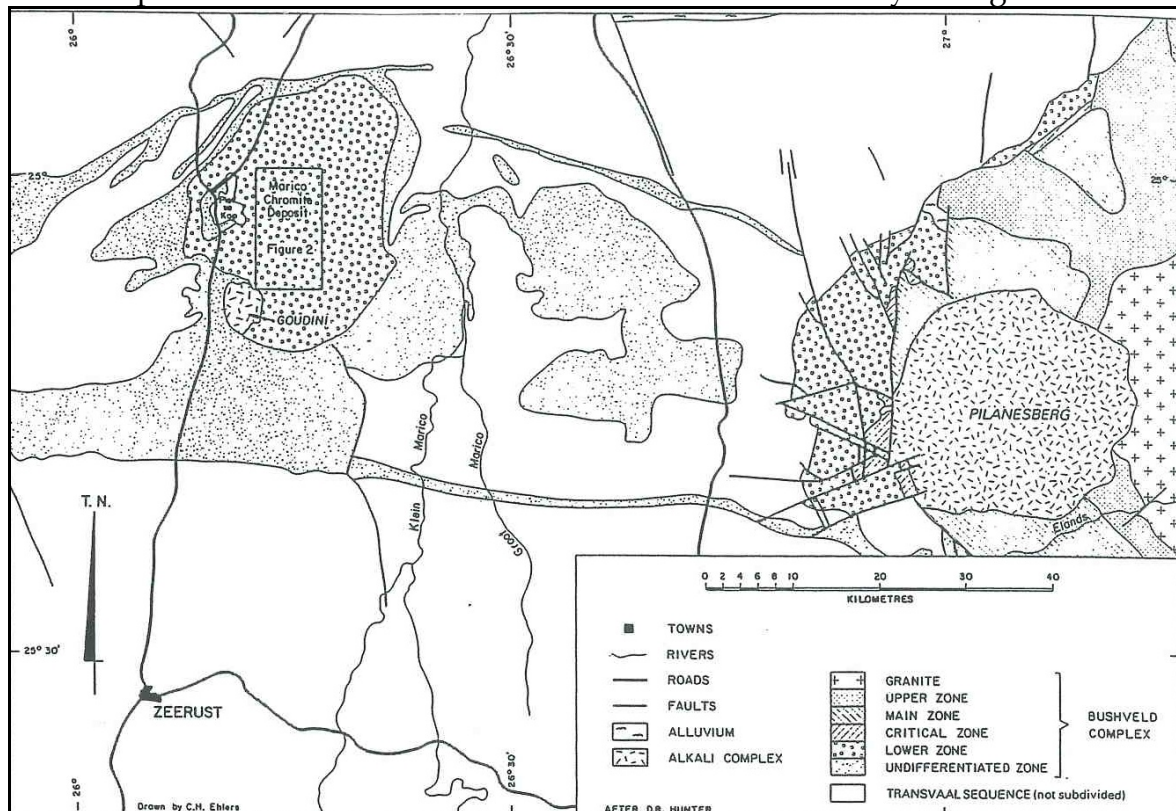
Samancor Chrome currently operates two sets of mines and three alloy producing plants in the North West and Mpumalanga provinces of South Africa.<sup>3</sup>

Marico Chrome Mine is a relatively small-scale producer located 60 km north of Zeerust and close to the Botswana border. The mine produces about 40,000 tonnes per annum of metallurgical and refractory-grade chromite for domestic and export markets. Mining at Marico Chrome Mine commenced in 1978 and the mine has an estimated 9 million tonnes of ROM reserves with a 40–50 year life of mine.<sup>2</sup>

### **The Marico Chromite Deposit**

The Marico deposit is part of the far western limb of the Bushveld igneous complex (see Figure 1). The Bushveld complex is approximately 460 km long and 245 km wide and is one of the most remarkable geological formations in the

world, comprising a suite of rock types from basal sedimentary layers, through intrusive and extrusive igneous formations, to associated thermal metamorphism. It was formed between 2040 and 2060 million years ago.



**Figure 1:** Geological setting of the Groot-Marico Chromite Deposit<sup>4</sup>

Throughout the main Bushveld complex one can recognise some general trends.

1. The chromium content of the layers decreases upwards:
  - LG6.....46–47%
  - MG layers.....44–46%
  - UG2.....43%
2. An associated upward decrease in Cr:Fe ratio:
  - LG 6.....1.56 to 1.60 :1
  - MG layers.....1.35 to 1.5 :1
  - UG2.....1.26 to 1.4 :1
3. The alumina content decreases upwards through the geological succession
4. Chromite grain size varies in size from 2 mm to 50 µm from lower to upper layers

There have been many theories as to the relationship between the Marico body and the western Bushveld complex. These vary from the suggestion that the Marico basin is entirely separate to its being regarded as an eruptive feeder to the main western area.<sup>4</sup>

The lenses, or kidney-shaped, deposit (figure 2) is composed of mafic rocks forming an elongated body along a north- south central synclinal axis. The body is shallow at the rim and steepens towards the centre.

Exploration and mining activities have revealed 5 chromite layers, which, while different in nature, have been linked stratigraphically with the LG layers of the main western Bushveld complex.<sup>4</sup>

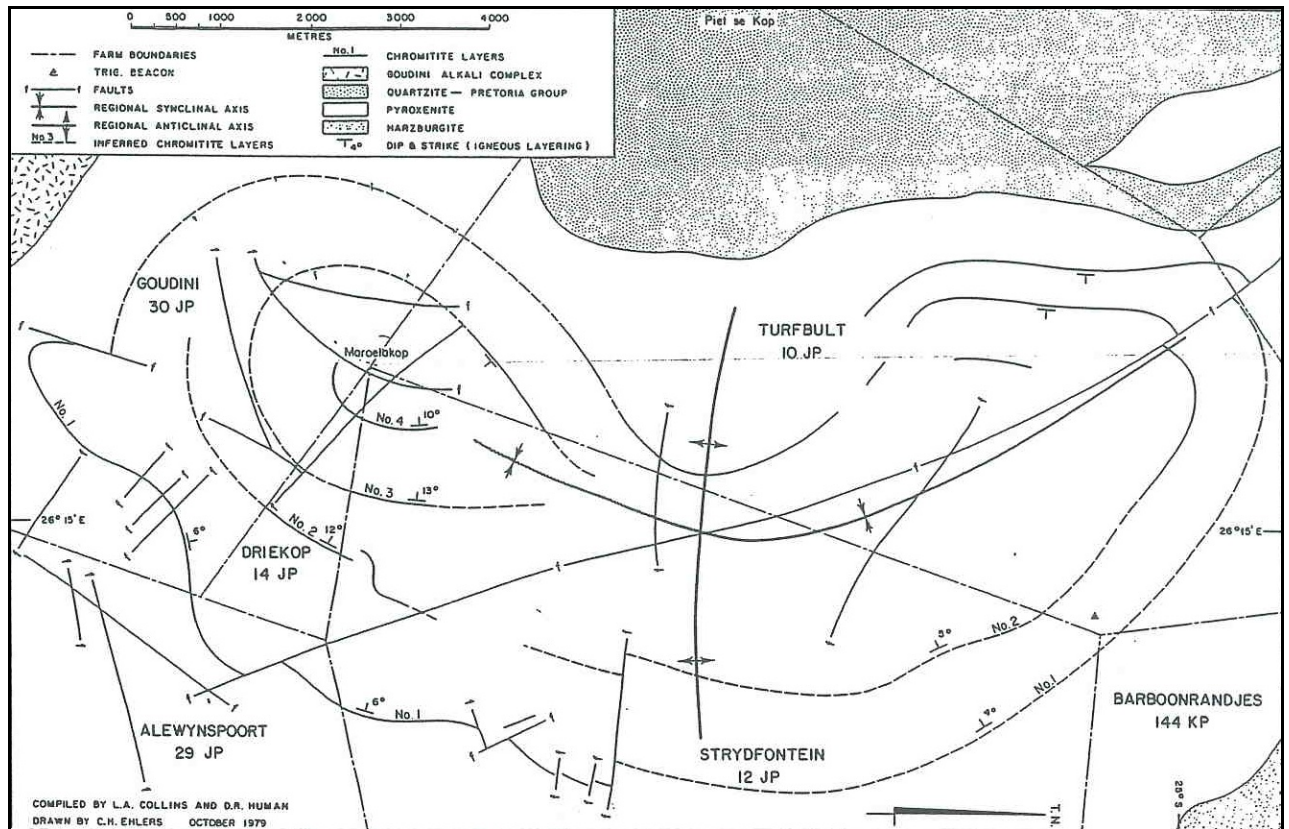


Figure 2: The Groot-Marico Chromite Deposit<sup>4</sup>

Although part of the Bushveld Complex, the Marico Deposit does show some significant differences from the chromites of the main Bushveld Complex, and it is some of these differences in the nature of the chromite that give Marico Chrome its superior properties with respect to refractory production.

Typically the Marico chromites are—

1. Higher in  $\text{Cr}_2\text{O}_3$  content
  - Up to 49% for the refractory-grade product
2. Lower in  $\text{SiO}_2$ 
  - Typically below 1%
3. Have higher Cr-Fe ratios
  - Typically 2:1 compared with 1.6:1 in LG1
4. Lower magnetite content
  - This results in more refractory  $\text{MgO} \cdot \text{Cr}_2\text{O}_3$  in the spinel phases and an associated higher refractoriness

The combination of these characteristics makes the Marico chromites suitable for refractory applications: the low levels of impurities ( $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ ) and the relatively higher proportions of chromium to iron reduce the potential for iron

oxide bursting and volume expansion at high temperatures and result in higher refractoriness.

## **CHROMITE AS A REFRACTORY MATERIAL**

### **Refractory materials**

Refractories are a branch of ceramics, which is mankind's oldest art. The word refractory is defined as resistant to change, and in the metallurgical industry refractories are materials that are resistant to change at elevated temperatures. Refractories are used in any application where a supporting furnace structure must be protected from the temperature required for the metallurgical process, or where heat loss must be limited.<sup>5</sup>

Refractory materials were probably inadvertently first used during the transition from the Stone Age to the Bronze Age during the chalcolithic (copper) period, with the earliest evidence in the Timna Valley between the southern tip of the Dead Sea and the Gulf of Aqabah in 6000 BC. These early smelting installations were simple bowl-shaped hearths in small pits, with above-ground stone enclosures. With the advent of the Iron Age at about 2000 BC higher temperatures were required and the use of refractories would probably have become a more conscious pursuit.<sup>6</sup>

Modern refractories technology began in the late 18th century with the growth of the iron industry and later the steel industry during the Industrial Revolution. The greater demands placed on refractories required materials other than alumino-silicates and silica; magnesite and chrome brick were all introduced in the late 1880s. It was only in 1931 that the superior hot strength of blends of chromite and magnesite was recognized and chrome-magnesite bricks were introduced with tonnage usage in open hearth and electric steel-making furnaces.

In the mid-1960s low-silica, magnesia-chrome and reconstituted fused-grain magnesia-chrome refractories were introduced worldwide, with Verref commissioning a fusion plant in 1967. Since then fused magnesia-chrome chrome-mag products have been increasingly used in extractive metallurgical applications ranging from ferroalloys and steel, to base metals (lead, copper, cobalt and nickel), to PGMs. Two industries where their use has been discontinued because of the high level of hexavalent chrome formed are glass and cement.

The principal refractory consuming manufacturing process that we can easily identify with would be –

1. Iron and steelmaking
2. Non-ferrous metal production
3. Cement production
4. Glass production
5. Petrochemical production

If a refractory material is defined as having a melting point of greater than 1500°C, then there are sixty compounds identified in the Handbook of Chemistry and Physics that meet this criteria.<sup>5</sup>

**Table I:** Compounds with melting point > 1500 °C

Compound	Number
Borides	13
Carbides	19
Nitrides	10
Silicides	7
Oxides	11
<i>Total</i>	<i>60</i>

If in addition to a high melting point, the limits of reasonable abundance and reasonable price are introduced, the list reduces to the six oxides on which, together with carbon, silicon carbide and silicon nitride, the vast range of refractory materials are based.

**Table II:** Refractory oxides

Oxide		Melting point (°C)	Classification
Silica	SiO <sub>2</sub>	1728	Acid refractory
Alumina	Al <sub>2</sub> O <sub>3</sub>	2010	Neutral refractory
Chrome	Cr <sub>2</sub> O <sub>3</sub>	2265	
Zirconia	ZrO <sub>2</sub>	2670	
Lime	CaO	2614	Basic refractory
Magnesia	MgO	2800	

Of these oxides, chrome in the form of chromite is the most cost effective. Depending on its chemical composition each type of refractory material will be more compatible with certain chemical and physical environments than with others

Refractories are also classified according to their form:

1. Shaped refractories—essentially bricks
2. Unshaped refractories—commonly called monolithics

Both of these categories can be sub-divided into further categories.

#### **Suitability of chromite as a refractory raw material**

The usefulness of chromite as a refractory is based on four factors:

1. It has a high melting point

Because of their unique properties the Marico chromites, with a higher proportion of Mg than Fe in the spinel phase, are postulated to have an even higher liquidus temperature than other chromites (see Table III).

**Table III:** Theoretical liquidus temperature of Marico chromite<sup>4</sup>

Spinel	Molecular mass (%)	Melting point (°C)	Calculated melting point (°C)
MgO · Al <sub>2</sub> O <sub>3</sub>	30.58	2105	643.7
MgO · Cr <sub>2</sub> O <sub>3</sub>	25.89	2400	621.0
FeO · Cr <sub>2</sub> O <sub>3</sub>	36.26	2160	783.0
FeO · Fe <sub>2</sub> O <sub>3</sub>	7.27	1600	116.3
<i>Estimated liquidus temperature of Marico chromite</i>			2164

## 2. Moderate thermal expansion

Refractory materials will expand when heated up and shrink when cooled down. If no permanent changes occur in the original dimensions this effect is known as reversible thermal expansion. Chromite has a linear expansion of about 1.3% at 1400°C, which is almost 50% of that of magnesia (MgO). As a consequence, when added to magnesia refractories, chromite will improve the thermal shock resistance of the refractory (see Table IV).

**Table IV:** Thermal expansion at 1000°C

Brick quality	Thermal expansion
Magnesia brick	1.4%
Magnesite-chrome brick	1.1%
Chrome-magnesite brick	1.0%

## 3. Neutral chemical behaviour

In addition to refractoriness, a lining material must be compatible with the process slag chemistry. Figure 3 shows the range of slag lime-to-silica ratios with which magnesia, mag-chrome and high-alumina refractories are compatible. Chromite-containing materials can tolerate slags ranging from slightly acid to basic, and can be used in place of tabular-alumina brick or magnesia brick in most applications.

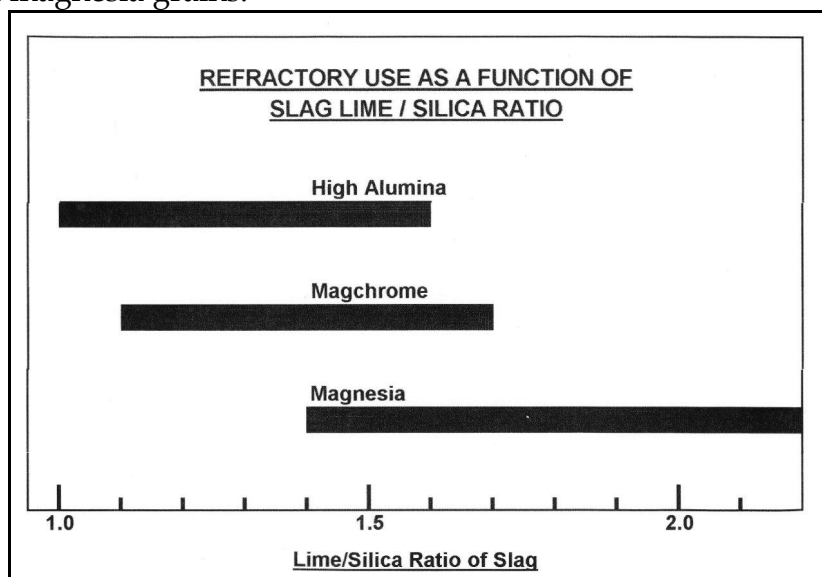
## 4. Relatively high corrosion resistance

Chromite has exceptionally good resistance to pyrometallurgical slags. Slags that are acidic and contain high levels of iron—in other words, are silica-rich fayalite (2FeO · SiO<sub>2</sub>)—rapidly attack and deeply penetrate alumino-silicate refractories. The resistance of chromite against fayalitic slags—which are common in many non-ferrous metallic smelting processes—is exceptional.

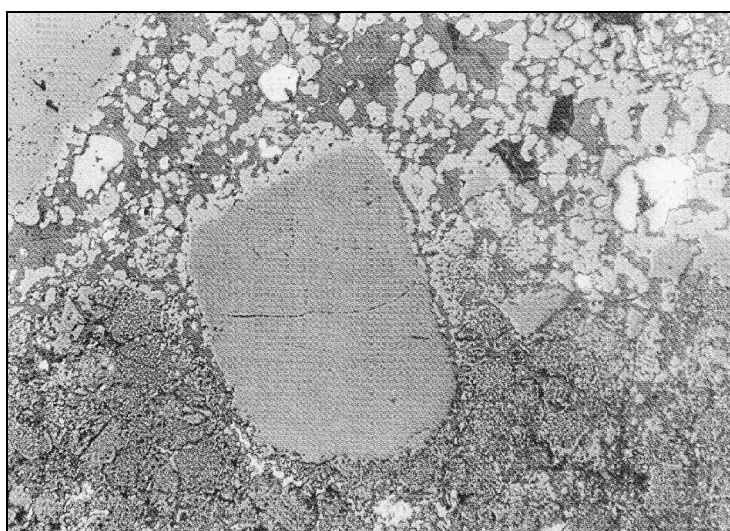
Figure 4 is a photomicrograph of the working face of a magnesia-chrome brick and demonstrates the resistance of chromite to silicate-slag attack. The



chromite grain in the centre of the field stands proud of the surrounding, altered magnesia grains.



**Figure 3:** Refractory use as a function of slag lime-to-silica ratio



**Figure 4:** Resistance of chromite to silica-rich fayalitic slag  
Field width, 1000  $\mu\text{m}$

### CHROMITE-CONTAINING REFRACTORIES

The early chrome refractories consisted of moulded and fired chromite. These refractories had several problems because of their bursting and crumbling as a result of alternative exposure to oxidising and reducing atmospheres. They also shrank and softened at high temperatures.<sup>8</sup> The addition of magnesia "solved" many of these problems, and this led to the development of the magnesia-chromite, chrome-magnesite series of refractories during the 1930s.<sup>8</sup>

The effect of a silicate melt on brick properties was established in the 1950s and '60s, and in the steel industry in particular the demand increased for lower-SiO<sub>2</sub> bricks for OH and electric-arc furnaces. Magnesia-chrome brick became the



preferred quality because of its superior slag resistance and stability at high temperatures.<sup>8</sup>

In the firing process FeO in the chromite oxidises to Fe<sub>2</sub>O<sub>3</sub> and diffuses at high temperature into the MgO. Magnesio-ferrite (MgO·Fe<sub>2</sub>O<sub>3</sub>)—a refractory spinel—is formed. The chromite is “stabilised”, thereby reducing the risk of undergoing subsequent redox reactions. There is also development of direct bonding between MgO crystals and MgO and chromite grains.

A combination of low silica and good bonding gives bricks a high hot strength and good spalling resistance. High Cr<sub>2</sub>O<sub>3</sub> contents give rise to low wettability by fayalitic slags and a high chromite-spinel content gives rise to low slag solubilities.<sup>7</sup>

By fusing (melting together) the chromite and magnesia the chromite spinel is completely stabilised and completely dispersed as small spinel crystals throughout the magnesia. Optimum performance is then obtained.

Chromite-containing refractories are divided into three main groups (according to the chrome oxide content (see Table V).

**Table V:** Chrome-containing refractories<sup>9</sup>

<b>Brick quality</b>	<b>Cr<sub>2</sub>O<sub>3</sub> (%)</b>
Magnesite-chrome brick	<30
Chrome-magnesite brick	>30
Picrochromite	>75

Five types of these brick are manufactured.<sup>9</sup>

1. Silicate bonded

The magnesia crystallites and the chromite grains are bonded together by silicates. These bricks have limited refractoriness, but can have good thermal shock resistance and high pressure flexibility.

2. Direct bonded

By lowering the impurity content and high-temperature firing, one can produce a direct-bonded brick in which the chromite reacts with the MgO to form a highly refractory spinel, MgO·(Al, Cr, Fe)<sub>2</sub>O<sub>3</sub>

3. Chemically bonded – generally with magnesium salts and unburned

4. Co-burned

Magnesia clinker and chromite grains being sintered before brick-making

5. Fusion cast

Magnesia clinker and chromite grains being fused before brick-making

Applications for chrome-bearing refractories include—

1. All pyrometallurgical extraction processes for Cu, Ni and Pt. They are the preferred refractory these applications
2. The steel industry, in which quantities of fused-grain brick are still used in vacuum degassers
3. CLU converters in the ferroalloy industry

#### 4. Foundry electric-arc furnaces

### **ENVIRONMENTAL ISSUES ASSOCIATED WITH CHROME-CONTAINING REFRACTORIES**

Chromium exists in a number of different oxidation states which give it the ability to modify other chemical compounds, or to act as a catalyst in promoting chemical reactions. Hence its wide use in the chemical industry. The most important oxidation states are –<sup>10</sup>

#### 1. Cr(III) – trivalent chromium

Trivalent chromium is the most stable oxidation state of chromium. Trivalent chromium compounds are stable, generally have low solubility in water, and do not present a significant environmental hazard. The most common example of trivalent chromium is green chrome oxide ( $\text{Cr}_2\text{O}_3$ ), which is widely used as a pigment in paints and as a component in alumino-silicate refractories. Chromium in chromite is also in the trivalent form.

#### 2. Cr(IV)

Cr(IV) oxide ( $\text{CrO}_2$ ) is a black, conducting, ferromagnetic compound used in the production of audio and video tapes.

#### 3. Cr(VI) – hexavalent chromium

The most common examples of hexavalent chromium compounds are chromic acid and the dichromates of sodium and potassium, which are used in the chemical industry and to surface-treat steels to improve corrosion resistance. Hexavalent chromium compounds are soluble, toxic, and are known to increase the risk of respiratory cancer.

When chrome-based refractory materials are exposed to high temperatures and pressures combined with certain chemical phases, a possibility exists that toxic by-products can form. In particular the transition in the oxidation state of the chrome from  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  is of particular concern, as hexavalent chromium compounds are classified as carcinogenic and harmful to health.

As chromite comes into contact with alkali and alkaline earth oxides the transition from  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  is accelerated. In particular it is clear that exposing chromium-containing materials to alkali or calcium oxide-rich environments will most likely result in the accelerated formation of  $\text{Cr}^{6+}$ . The reaction in chromium-containing refractories begins along the grain boundaries and can thus spread throughout the structure of the refractory at a fairly rapid rate where circumstances and the environment favour it.

The  $\text{Cr}^{6+}$  content, following the  $\text{CaO-Cr}_2\text{O}_3$  phase diagram, increases with exposure to temperatures below  $1022^\circ\text{C}$  and with an increase in CaO (from 0 to 42% CaO). In the case of magnesia-chrome refractories temperature, basicity (the CaO-to- $\text{SiO}_2$  ratio) and the chromite grain size all play a role in  $\text{Cr}^{6+}$  formation. Thus the formation of  $\text{Cr}^{6+}$  can be minimized by carefully controlling

the levels of CaO in the refractory and by avoiding the use of fine chromite during brick making. The use of fused magnesia-chrome or chrome-magnesia grains will also help minimise the potential to form  $\text{Cr}^{6+}$  within the refractory structure.<sup>8-11</sup>

Because of the likely formation of  $\text{Cr}^{6+}$  when exposed to alkali or CaO environments there has been a move away from chromium-containing refractories in those applications where these chemical and certain physical conditions exist—a prime example of this being the cement and glass industries. This move has also taken place in other industries and applications where the formation of  $\text{Cr}^{6+}$  is not at all likely, but a view has been taken that chromium-based refractories are environmentally damaging and could be harmful to health.

The move to replace chrome-containing refractories has seen development of several other possibilities. These include magnesia-alumina spinels, spinel-bonded magnesia, very high alumina materials, zirconia-containing materials, and various fused-cast products.<sup>9</sup>

#### **Exposure limits to $\text{Cr}^{6+}$**

Occupational exposure limits to hexavalent chromium range from 1.0 to 0.01 mg/m<sup>3</sup> on an 8 hour TWA. Values vary from one country to the next. The exposure limit soon to be adopted by the European Union will probably be 0.01 mg/m<sup>3</sup>. The limit in South Africa is 0.05 mg/m<sup>3</sup>.<sup>12</sup>

If the maximum nuisance dust level of 10 mg/m<sup>3</sup> is assumed, of a material at a hexavalent-chromium level of 450 ppm (unused chromium-bearing refractories vary between 20 and 200 ppm) exposure to hexavalent chromium would be 0.005 mg/m<sup>3</sup>, which is well below the TWA maximum.<sup>10</sup>

Limits for landfill disposal are typically —

1. 0.5 mg/L Cr(VI) in the leachate—Germany
2. 1.5 mg/L Cr(VI) in the leachate—Japan
3. 30g/ha/m Cr(VI)—South Africa. The leachable  $\text{Cr}^{6+}$  is determined according to the USEPA TCLP test or the acid-rain test.<sup>12</sup>

#### **Exposure limits and analytical techniques**

One of the problems with comparing exposure limits is that environmental limits and the limits of occupational organizations are based on different extraction and analytical-test methods, which all yield different results. In addition, the results from different laboratories do not always agree.

The Ceramic Research Association in Britain has carried out extensive work on the development of a reliable and significant test method for the determination of hexavalent chrome.<sup>13</sup>

## CONCLUSIONS

Chromium plays an essential role in a wide range of industrial processes. In refractories, chromite is a cost-effective material that has properties ideal for a number of metallurgical applications ranging from ferroalloys and steel, to base metals (lead, copper, cobalt and nickel), to PGMs. The specific properties of Marico chromite further improve the properties of refractories required for these industries.

Under certain operating conditions, however, toxic and hazardous hexavalent chromium is formed. The major industries in which this occurred have moved to alternative lining materials and the indications are that in other user industries hexavalent chromium will not present an occupational or environmental disposal hazard.

In areas where hexavalent chromium may be identified as a problem, a joint approach by the refractory producer and the refractory user, through product development or recycling of used lining materials, will be the most cost-effective solution.

## ACKNOWLEDGMENTS

This paper is published with the permission of Vereeniging Refractories and Samancor Chrome. The contributions of colleagues are gratefully acknowledged.

## REFERENCES

1. W. Ebersohn (Editor), Verref, a company rich in history, A Succeed/ESSENTIAL Special Publication, 2007.
2. T. Courtney, Presentation, "Trusting in Experience and Innovation", Vereeniging Refractories (Pty) Ltd, 2009.
3. M. Visser, An Overview of the History and Current Operational Facilities of Samancor Chrome, *Southern African Pyrometallurgy 2006*, Edited by R.T. Jones, South African Institute of Mining and Metallurgy, Johannesburg, 5-8 March 2006, pp. 286-288.
4. L.A. Collins and D.R. Human, The Groot-Marico Chromite Deposit, Western Transvaal, *Mineral Deposits of Southern Africa*, Vol I & II, 1986, pp.1299-1235.
5. R.A. Parry, What are refractories?, VTS Module 02 Rev 04, Vereeniging Refractories (Pty) Ltd, 2005.
6. K. Sugita, "Historical Overview of Refractory Technology in the Steel Industry", Nippon Steel Technical Report 98, July 2008.
7. P. Knufer, Presentation, VTS Module 05 Rev 00 Basic BBR 716 Basic Rm & Ref., Vereeniging Refractories (Pty) Ltd, 2005.
8. R Engel, Chrome Bearing Refractories: Is There a Future?, *The Refractory Engineer*, May 2010, pp 12-14.
9. P. Hloben, *Refractory Materials – Major Industrial Applications*, Rexxon Corporation, Bryanston, South Africa, 2000.
10. R.A. Parry, Alternatives to chrome-containing refractories, presented at the Institute of Refractory Engineers, Vereeniging Refractories (Pty) Ltd, 22 June 2000.
11. T. Courtney, personal communication, Vereeniging Refractories (Pty) Ltd, 5 Sep. 2010.
12. International Chromium Development Association: Health Safety and Environment Guidelines for Chromium (2007 edition), pp.29-31.
13. P. Hodsinn, Hexavalent Chromium in Refractories in the UK., Report of CERAM Research Working Group, October 1998.

**Niell McEwan***Technical Manager, Vereeniging Refractories*

Niell completed his schooling at Carletonville High School in 1987, and studied Metallurgical Engineering at the University of Potchefstroom (now North West University).

He started his working career at Samancor in the Chrome division in 1993 and fulfilled the positions of Metallurgist, Production Engineer, and Production Superintendent at Middelburg Ferrochrome and Ferrometals. Achievements included commissioning and operating the first charge chrome furnace with Outokumpu pelletising and preheating technology in South Africa.

In 2002 Niell joined Vereeniging Refractories and fulfilled the positions of Operations Manager, Business Development; Project Manager; and Technical Manager.

Niell has also completed an MBA from Herriot Watt University in the UK (2002) and a Masters of Engineering in Project Management (MPM) from the University of Pretoria (2010).

---

