Chromite — A Cost-Effective Refractory Raw Material for Refractories in various Metallurgical Applications

N McEwan, T Courtney, RA Parry, 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, now known as Anglocoal, a division of the Anglo American corporation. 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 divisionalised 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 1.
Verref employs about 700 people in its mining and refractory operations. Verref 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.

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.

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.

In 1998, after Gencor’s unbundling exercise, Billiton established a joint venture with Anglo American Corporation 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 with the effective date of sale on 1 June 2005.

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

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.

The Marico Chromite Deposit

The Marico deposit is part of the far western limb of the Bushveld igneous complex. See figure I. 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 through to associated thermal metamorphism. It was formed approximately between 2040 and 2060 million years ago.

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 2mm to 50µm 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.

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 steepening towards the centre.
Exploration and mining activities have revealed 5 chromite layers which whilst different in nature have stratigraphically been linked with the LG layers of the main western Bushveld complex.

Figure 2: The Groot-Marico Chromite Deposit.

Whilst part of the Bushveld igneous complex, the Marico deposit do 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 Cr$_2$O$_3$ content
   - Up to 49% for the refractory-grade product
2. Lower in SiO$_2$
   - Typically below 1%
3. Higher Cr: Fe ratio
   - Typically 2:1 compared with 1.6:1 in LG1.
4. Lower magnetite content
   - This results in more refractory MgO.Cr$_2$O$_3$ in the spinel phases and associated higher refractoriness.

The combination of these characteristics makes the Marico chromites suitable for refractory applications because of the low impurities (SiO$_2$ & Fe$_2$O$_3$) and high relative content of chromium compared with iron which reduces the
potential for iron oxide bursting and volume expansion at high temperatures and results in higher refractoriness.

**Chromite as a refractory material**

**Refractory materials**

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. Refractories are a branch of ceramics, which is mankind’s oldest art.

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 in about 2000 BC higher temperatures were required and the use of refractories probably became increasingly conscious.

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 brick 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 lead, steel, ferroalloys and copper, cobalt, nickel and pgm’s. 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.

Table I: Compounds with melting point > 1500 °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borides</td>
<td>13</td>
</tr>
<tr>
<td>Carbides</td>
<td>19</td>
</tr>
<tr>
<td>Nitriles</td>
<td>10</td>
</tr>
<tr>
<td>Silicides</td>
<td>7</td>
</tr>
<tr>
<td>Oxides</td>
<td>11</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>60</strong></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting Point (°C)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>1728 Acid Refractory</td>
</tr>
<tr>
<td>Alumina</td>
<td>Al₂O₃</td>
<td>2010 Neutral Refractory</td>
</tr>
<tr>
<td>Chrome</td>
<td>Cr₂O₃</td>
<td>2265 Neutral Refractory</td>
</tr>
<tr>
<td>Zirconia</td>
<td>ZrO₂</td>
<td>2670 Basic Refractory</td>
</tr>
<tr>
<td>Lime</td>
<td>CaO</td>
<td>2614 Basic Refractory</td>
</tr>
<tr>
<td>Magnesia</td>
<td>MgO</td>
<td>2800 Basic Refractory</td>
</tr>
</tbody>
</table>

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.

Refractories are also classified according to their form.

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

Both of these categories can then 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 its unique properties the Marico chromites with a higher proportion of Mg than Fe in the spinel phase is postulated to have an even higher liquidus temperature than other chromites. See table III.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Molecular (%)</th>
<th>Melting Point (°C)</th>
<th>Calculated Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO.Al₂O₃</td>
<td>30.58</td>
<td>2105</td>
<td>643.7</td>
</tr>
<tr>
<td>MgO.Cr₂O₃</td>
<td>25.89</td>
<td>2400</td>
<td>621.0</td>
</tr>
<tr>
<td>FeO.Cr₂O₃</td>
<td>36.26</td>
<td>2160</td>
<td>783.0</td>
</tr>
<tr>
<td>FeO.Fe₂O₃</td>
<td>7.27</td>
<td>1600</td>
<td>116.3</td>
</tr>
</tbody>
</table>

   **Estimated liquidus temperature of Marico Chromite = 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>
<thead>
<tr>
<th>Brick quality</th>
<th>Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesia brick</td>
<td>1.4%</td>
</tr>
<tr>
<td>Magnesite-Chrome brick</td>
<td>1.1%</td>
</tr>
<tr>
<td>Chrome-Magnesite brick</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

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/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 again 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 and hence are silica-rich fayalite (2FeO.SiO₂), rapidly attack and deeply penetrate aluminosilicate refractories. This resistance is exceptional against these iron silicate-rich slags (fayalitic slags) which are common in many non-ferrous metallic smelting processes.

Figure 4 is a photomicrograph of the working face of a magnesia chrome brick and demonstrates resistance of chromite to silicate slag attack. The chromite grain in the centre of the field is standing proud of the surrounding and altered magnesia grains.

Figure 3: Refractory use as a function of slag Lime/Silica ratio
**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.

The addition of magnesia “solved” many of these problems and this lead to the development of the magnesia-chromite, chrome-magnesite series of refractories during the 1930s.

The effect of the silicate melt on brick properties was established in the 1950s and 60s and particularly in the steel industry the demand increased for lower SiO₂ brick for OH and electric arc furnaces. Magnesia chrome brick become the preferred quality based on their superior slag resistance and stability at higher temperatures.

In the firing process FeO in the chromite oxidises to Fe₂O₃ and diffuses at high temperature into the MgO. Magnesio-ferrite (MgO.Fe₂O₃) - a refractory spinel - is formed. The chromite is “stabilised” reducing the risk of 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 brick with high hot strength and good spalling resistance. High Cr₂O₃ contents give rise to low wettability by fayalite (2FeO.SiO₂) slags and high chromite spinel content give rise to low slag solubilities.

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):

<table>
<thead>
<tr>
<th>Brick quality</th>
<th>Cr₂O₃ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite–Chrome brick</td>
<td>&lt;30%</td>
</tr>
<tr>
<td>Chrome-Magnesite brick</td>
<td>&gt;30%</td>
</tr>
<tr>
<td>Picrochromite</td>
<td>&gt;75%</td>
</tr>
</tbody>
</table>

Five types of these brick are manufactured:

1. **Silicate bonded**
   The magnesia crystallites and the chromite grains are bonded together by silicates. These bricks are limited in refractoriness, but can have good thermal shock resistance and high pressure flexibility.
2. Direct bonded
By lowering the impurity content and high-temperature firing a direct bonded brick is produced in which the chromite reacts with the MgO to form a highly refractory spinel \( \text{MgO}_2(\text{Al}, \text{Cr}, \text{Fe})_2\text{O}_3 \).

3. Chemically bonded – generally with magnesium salts and unburned.

4. Co-burned
Magnesia clinker and chromite grains being sintered before brickmaking

5. Fusion cast
Magnesia clinker and chromite grains being fused before brickmaking

Applications for chrome-bearing refractories are—
1. It is the preferred refractory for all pyrometallurgical Cu, Ni and Pt extraction processes.
2. In the steel industry quantities of fused grain brick are still used in vacuum degassers.
3. Ferroalloys CLU converter
4. Foundries EAF

**Environmental issues associated with chrome-containing refractories**

Chromium exists in a number of different oxidation states which gives 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\(^{10}\) —

1. **Cr(III) - Trivalent Chrome**
   Trivalent chromium is the most stable oxidation state of chromium and trivalent chromium compounds are stable, generally have low solubility in water and do not present a significant environmental problem. 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 Chrome**
   The most common example of hexavalent chromium compounds are sodium and potassium dichromates and chromic acid, 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 be formed. 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 are 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 the environment and circumstances favour it.

The \( \text{Cr}^{6+} \) content, following the CaO-Cr\(_2\)O\(_3\) phase diagram, increases with exposure to temperatures below 1022°C and with an increase in CaO (from 0 to 42% CaO). In the case of magnesia chrome refractories temperature, basicity (CaO/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.

Because of the likely formation of \( \text{Cr}^{6+} \) when exposed to alkali/CaO environments there has been an increasing trend away from chromium-containing refractories in those applications where such chemical and physical conditions exist—a prime example of this being the cement industry and the glass industry. This trend has also been seen in other industries and applications even where the formation of \( \text{Cr}^{6+} \) is not at all likely but a view has been taken that chromium-based refractories are not environmentally acceptable and could be harmful to health.

The trend to substitute chrome-containing materials has seen development of many other possible replacements in refractories. These include magnesium-alumina spinels, spinel-bonded magnesia, very high alumina materials, zirconia-containing materials and various fused cast products.

**Exposure limits to \( \text{Cr}^{6+} \)**

Occupational exposure limits to hexavalent chrome range from 1.0 to 0.01 mg/m\(^3\) on an 8 hour TWA, depending on the country. The exposure limit soon to be adopted by the European Community will probably be 0.01 mg/m\(^3\). The South African limit is 0.05 mg/m\(^3\).

If the maximum nuisance dust level of 10 mg/m\(^3\) is assumed, of a material at a hexavalent chrome level of 450 ppm (unused chrome-bearing refractories vary between 20 to 200 ppm) exposure to hexavalent chrome would be 0.005 mg/m\(^3\), which is well below the TWA maximum.
Limits for landfill disposal are typically:
1. Germany — Chromium (VI) = 0.5 mg/l in the leachate
2. Japan — Chromium (VI) = 1.5 mg/l in the leachate
3. South Africa — Chromium (VI) = 30g/ha/m. The leachable Cr$_6^+$ is determined according to the USEPA TCLP or the acid rain test $^{12}$.

**Exposure limits and analytical techniques**

One of the problems with comparing exposure limits is that environmental and occupational organizations limits are based on different extraction and analytical test methods that yield different results. In addition, there is disagreement in the results from different laboratories.

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 $^{13}$.

**CONCLUSIONS**

Chromium plays an essential role in a wide range of industrial processes. In refractories, chromite is a very cost-effective material that has properties ideal for a number of metallurgical applications ranging from lead, steel, ferroalloys, copper, cobalt, nickel and platinum. The specific properties of the 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 indications are that in the remaining user industries, hexavalent chrome 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 refractories producer and the refractories user, through product development or recycling of used lining materials will be the most cost effective solution.

**ACKNOWLEDGEMENTS**

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


---

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 and Project Manager and Technical Manager.

Niell has also completed a MBA (Heriot Watt University UK, 2002) and also a Masters of Engineering in Project Management (MPM), University of Pretoria, 2010.