THE PRODUCT DEVELOPMENT PROCESS FOR SMELTER REFRACTORIES  
A TEXT BOOK AND PRACTICLE PERSPECTIVE  

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ABSTRACT

The paper explores the practical experience that Verref has had with the development of smelter refractory products from Magnesia to Fused Magnesia Chrome and including Chrome enriched products. It includes the practical in house testing of raw materials and products (Rotary slag testing and subsequent microscope analysis of wear mechanisms) and how laboratory results have been borne out in refractory performance. It further describes the various products that were initially introduced and what results (in terms of lifetime) were obtained. It is concluded that the product development and product introduction process for smelter refractories can take between 5 – 7 years which fits with a typical text book model.

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1. INTRODUCTION

Refractories are predominantly based on six high melting point metal oxides together with carbon and some carbides and nitrides. The oxides used are those which are reasonably abundant, of reasonable price and alone or in combination give brick and monolithic products with the thermal, mechanical, physical and chemical properties required for a particular application. To meet the varied demands of the major metallurgical and heat containment industries the “big six oxides” expand to a range consisting of approximately 400 chemically or physically distinct brick and monolithic products. Taking brick shapes into account, individual items number in excess of 5 000.

Development of improved and new refractory products is an ongoing process critical to both manufacturer and user. The combined effect of developments in refractories and metallurgical processing is reflected in the specific consumption in the steel industry, which over the last four decades has fallen from 35 kg/t to 10 kg/t in the Western World [1]. When specific consumption was high, refractories were regarded as an auxiliary raw material rather than a component of the production equipment [2], which they now are.

A new product progresses through a sequence of stages from introduction to growth, maturity and decline. This sequence is known as the product life cycle and is a process involving both technical development and marketing strategy and decisions.

2. THE PRODUCT LIFE CYCLE

Product life-cycle stages and sales volume can be presented as the well known Life Cycle Curve, an example of which is shown in Figure 1.

![Figure 1 - Product life cycle curve](image-url)
2.1 Concept, R&D and Introduction Stage

Concepts for refractory development derive from in house ideas, examination of used materials, licence agreements, technical literature, customer requirements, consultants and existing commercially available products.

Preliminary work based on concepts frequently does not go ahead, but forms the springboard for successful development when an idea’s time arrives or associated process technology is introduced and often work that is started for one industry will find its main application in a totally different area. Surprisingly development is not always logical and occasionally there is sometimes a pleasant element of serendipity.

During the development and introduction stage, product quality standards are firmly established and product awareness is developed. Marketing targets innovators and early adopters and pricing may be low to rapidly increase production volume, or higher to recover research and development costs.

2.2 Growth Stage

In the growth stage, product preference is established, market share increases and the first competition from similar products is encountered.

2.3 Maturity Stage / Market Saturation

On product maturity, growth in sales starts to decrease due to competition from similar materials and marketing effort moves increasingly from promotion to defence. Long term proven performance and unique product features are emphasised and improved if possible. Pricing incentives may have to be introduced.

2.4 Decline Stage

Volumes continue to decline and the only options are to further decrease price or to discontinue the product.

The time scale from initial concept to decline and eventual discontinuation of the product differs widely with industry and application. For a steel plant ladle which is of relatively small capacity, is part of a multi-stream process and where life is measured in weeks, production and commercial losses associated with an unsuccessful trial are relatively low and market saturation can be reached in 18 to 24 months [3].

This paper examines the development and introduction of four generations of products for large, at times single stream smelters in the platinum, copper, nickel and cobalt industries where typical furnace lives are seven to ten years. Risks are high and procedures during the development and introduction stages are more rigorous, time consuming and costly. Simulative testing which is used as an indicator of service performance is an integral part of the development process.

3. DESTRUCTIVE SERVICE FACTORS IN SMELTERS

Destructive service factors include the following.

- **Thermal Shock Spalling**
  This is highly unlikely in a smelter where commissioning and cooling times are measured in weeks. The crack pattern is different for heating and cooling spalling.

- **Pinch Spalling**
  Associated with lack of expansion allowance or filling of open joints during cool down and heat up. It is difficult to differentiate between pinch spalling and thermal shock spalling.
- **Structural Spalling**
  Peeling on thermal cycling of a lining surface that has been penetrated by metal, slag or matte.

- **Chemical Attack**
  Hydration.
  Sulphur compounds.
  Carbon monoxide.

- **Slag Attack**
  In this paper slag attack only is examined.

  Slag compositions are silica rich fayalite (2FeO·SiO$_2$), which rapidly attacks and deeply penetrates aluminosilicate refractories. Basic materials, are also attacked as indicated by the simplified phase diagram FeO-MgO-SiO$_2$ shown as Figure 2.

![Figure 2 - FeO-MgO-SiO$_2$ phase diagram [4]](image-url)
Depending on the industry, slag compositions may lie either on the SiO₂ or MgO/FeO side of the Pyroxene field. The former slags are more aggressive as solution of magnesia reduces slag viscosity, increasing the volume of fresh slag in contact with the refractory surface.

4. DEVELOPMENT TEST METHODS

4.1 Physical and Chemical

The routine test methods for the quality control of normal production are used to define the bulk properties of new products. These are density, porosity, mechanical strength and chemical analysis. For high risk applications additional simulative testing is required.

4.2 Simulative - Pot Slag Tests

Slag pot test samples consists of a 75 mm cube which is core drilled, charged with crushed slag, fired and then cut as shown in Figure 3. Erosion and depth of penetration of the sample are quantified if possible.

Pot testing is a useful and simple technique for the rapid initial evaluation of a large number of samples, but the results must be carefully interpreted considering both the limitations of the test and the chemical composition of the refractory sample and slag. Limitations of the test are:

- No temperature gradient across the sample.
- No flow of slag in contact with the refractory surface.
- No fresh slag.
- The slag may quickly become saturated with refractory oxides.

Figure 3 - Pot slag test sample

4.3 Simulative - Rotary Slag Tests

The rotary slag test method is described in ASTM C 774 – 75. Refractory specimens are cut from a 230 x 114 x 76 mm sample, assembled as a hexagonal cartridge and installed in the test furnace as shown in Figures 4 and 5. To reduce possible interactions between adjacent samples the Verref test piece hot face dimension is 56 mm rather than the ASTM dimension of 44 mm.
As the test gives the relative resistance of refractory materials against slag erosion a reference sample must be included to allow comparison of different runs. If the materials being evaluated are likely to give very different wear rates, then two samples of each should be included to minimize the effect of a high wear sample on those adjacent to it.

![Figure 4 - Rotary slag test sample size](image1.png)

The rotating furnace is heated and charged with fresh slag at regular intervals to ensure that the chemical composition of the liquid slag is close to the original composition. The test is run until significant differential wear on the specimens can be easily seen.

![Figure 5 - Rotary slag furnace in operation](image2.png)
After removal from the furnace the samples are sectioned longitudinally as shown in Figure 6 and the erosion and depth of penetration measured. XRD and microscopy can be carried out. Compared with pot testing, rotary testing has the following advantages:

- There is a temperature gradient across the sample.
- Thermal cycling can be included.
- There is flow of slag across the face of the refractory.
- Slag composition remains close to original.
- The test can be run until there is significant differential wear.

A disadvantage is that atmosphere cannot be closely controlled.

![Figure 6 - Sectioned rotary slag test sample](image)

The test rig at Verref was originally constructed to evaluate materials for gasifiers and since then has been used in a wide range of development projects, including smelter refractories. In all cases the test results are a very good indicator of actual performance.

### 4.4 Simulative - Hydration Resistance

Magnesia reacts with water with an associated large volume expansion. Cracking and disintegration of the brick and damage to the furnace structure results.

![Figure 7 - Attack on magnesia by a silica rich fayalite slag](image)

Field width 1000 µm
Hydration resistance testing is a standard for basic (magnesia containing) lining materials for large smelters. Whole brick samples are placed in an autoclave and exposed to a steam atmosphere at a specified temperature and pressure. Visual appearance and residual physical properties are determined.

4.5 Mineralogical Examination

Mineralogical examination of raw materials, rotary slag test samples and field trial samples is an indispensable tool in the development of new raw materials or brick. The series of five photomicrographs below demonstrates the usefulness of the technique.

Figure 7 shows a magnesia grain on contact with a silica rich fayalite slag. At the bottom of the field unaltered hexagonal magnesia (periclase) crystallites are clearly visible. On the working face magnesia has been transformed to an iron rich phase, which is disrupted and is floating into the slag.

Figure 8 is 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. At top left a second large chromite grain is being dissolved out of the brick by silicate attack on the magnesia matrix.

Figure 8 - Resistance of chromite to silica rich fayalite slag
Field width 1000 μm

5. MAGNESIA CHROME BRICK AND CHROMITE STABILIZATION

Three approaches are employed for the manufacture of magchrome and chromag brick.

5.1 In Situ Reaction of Chromite and Magnesia

Magnesia chrome brick were first produced in Japan in 1925 and in the UK a decade later [2]. Initially brick batches were based on magnesia and raw chromite with reaction taking place during kiln firing. Although still produced today, redox reactions of unstabilized iron oxide from the chromite may give unpredictable expansions during manufacture and at times in service. Residual magnesia grains are susceptible to silicate slag attack.

5.2 Co-Sinter and Co-Clinker

Magnesia and chromite either as a blend of individual particles or briquettes are sintered in a rotary kiln at temperatures in excess of 1600°C. Iron oxide is stabilized, but there is still free magnesia
As energy prices rise the energy inefficiency of small rotary kilns is making co-clinker increasingly uncompetitive.

5.3 Fused Grain

Reconstituted fused magnesia chrome refractories were introduced in the mid 1960’s with Verref being one of the first manufacturers, following the installing of a fusion plant in 1967. Since then fused magnesia- chrome products have been increasingly used in metallurgical applications ranging through lead, steel, ferroalloys, copper, cobalt, nickel and platinum. Industries where their use was discontinued due to the high level of hexavalent chrome formed, are glass and cement.

6. FUSED GRAIN COMPOSITIONS

For historical reasons most of the fused grain produced initially contained approximately 60% MgO and 22% Cr₂O₃. Composition can however be varied to meet application requirements, with a dramatic effect on the microstructure.

![Figure 9 - Fused magnesia-chrome grain - 22% Cr₂O₃](image)

Figure 9 shows a 22% Cr₂O₃ fusion. Hexagonal crystallites of magnesia containing white recrystallized chromite are clearly visible with some white recrystallized spinel along the magnesia crystal boundaries. Silicates are present at triple points and on crystal boundaries.

Figure 10 demonstrates that although fused grain products are more resistant to attack by silica slag than magnesia/chromite blends the primary wear mechanism is still dissolution of magnesia. The lower part of the figure shows a particularly large crystal of fused magnesia-chrome with the flat uniform surface indicating rapid slag refractory reaction with solution of magnesia in a silica rich slag. No silicate penetration or reaction was apparent within the grain. Recrystallized chromite within the crystal, although resistant to the slag, is released into the slag layer and coalesces following solution of the magnesia component of the fused grain.
Figures 10 and 11 show the effect of increasing chrome content on the microstructure of fused magnesia-chrome. In Figure 10 the recrystallized spinels (2) are larger and better defined than in Figure 11, but still surrounded by periclase crystals. Silicates can be identified along crystal boundaries.

In Figure 12 at 37% Cr₂O₃ recrystallized spinel is the major phase, and periclase occurs as isolated pockets. Silicates are apparent. This composition would be expected to exhibit very much improved resistance to attack by silica rich fayalite slag.
7. SMELTER LINING MATERIAL DEVELOPMENT

Although the slags are acidic, magnesia brick were traditionally used in the working lining of the smelters due to their relatively high thermal conductivity. High thermal conductivity promotes the formation of a freeze lining, but in addition to poor resistance to acidic slags, magnesia is inherently prone to hydration and reaction with sulphur compounds. Increasing problems were experienced as the introduction of more efficient cooling systems prevented the removal of small quantities of moisture and elemental sulphur from the furnace lining.

Since 2000, magnesia-chrome brick have increasingly been used in place of magnesia brick. In a smelter application where performance could be easily quantified, lining life was increased by a factor of three, which confirmed the results of laboratory rotary slag testing.

Typical properties of the four generations of materials developed and introduced, together with two additional products still in development are given in Table 1.

7.1 **Product M1 – Magnesia** (Hydration resistant)

As magnesia is inherently hydration prone, raw materials, chemical composition and firing temperatures are chosen such that the hydration resistance of the product is maximized. A post firing chemical treatment is also employed. The finished product shows hydration resistance, but is not by any means hydration proof.

Verref developed a hydration resistant magnesia brick equivalent to the industry standard in the late 1970’s, but lacking references and a track record in smelters it was only in 1994 that the first lining was installed and five years later in 1999 that further lings were supplied. Production volumes increased until 2003.
Table 1 – Product Features, Properties and Performance Ratios

<table>
<thead>
<tr>
<th>Products</th>
<th>M1</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
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7.2 Product D1 (Magnesia-chrome - 100% fused grain, 21.7% Cr₂O₃)

As Verref had supplied materials for copper and nickel converters from the early 1960’s and manufactured fused magnesia-chrome grain and fused grain from 1967 the base technology was available in house. Rotary slag testing performed in 1998 and 1999 against a fayalitic slag type indicated one third of the wear of a magnesia brick. The product was first installed in 2001 in a ferrochrome furnace converted for the cleaning of platinum industry slags. As this was a limited period project no quantitative measure of performance was obtained, but the performance of D1 was shown to be superior to a magnesia brick in the high wear areas.

7.3 Product D2 (Magnesia-chrome - 100% fused grain, 21.7% Cr₂O₃, increased bulk density)

The bulk density of product D2 was increased to meet furnace design company specifications. The performance of D1 provided the confidence for D2 to be installed in a full scale slag cleaner and a new 68 MVA smelter in 2002. In 2004 D2 was installed in a high wear end wall, where magnesia brick had historically required replacement after six months. Life achieved was 18 months, which was close to the performance factor of 3.4 : 1 over magnesia brick indicated by the simulative rotary slag testing.
Production volumes of D2 continued to increase until 2009, at which point it was increasingly replaced by D3. A large trial quantity has also been supplied in the export market.

7.4 **Product D3** (Magnesia-chrome - 100% fused grain, 24.2% $\text{Cr}_2\text{O}_3$, enhanced matrix type 1)

The Cr$_2$O$_3$ content of D3 was raised in order to increase the proportion of the more refractory spinels in the matrix. Laboratory rotary slag testing indicated a slag resistance factor increase of 2.5 : 1 over product D2 (≈8 : 1 over magnesia). In early 2007 D3 was installed in the same high wear end wall in which D2 was proved. To date it has been in service for 27 months compared with 18 months for D2 and 6 months for M1.

7.5 **Product D4** (Magnesia-chrome - 100% fused grain, 33.5% Cr$_2$O$_3$, cost effective)

Compared with D1, D4 chrome oxide content is higher and production costs are lower. Laboratory and plant development has been completed and an initial field trial in an application other than an electric smelter is imminent. Slag resistance is indicated as intermediate between that of D2 and D3.

7.6 **Product D5** (Magnesia-chrome - 100% fused grain, 24.2% Cr$_2$O$_3$, enhanced matrix type 2)

D5 is in the early stage of development and destructive service factors in addition to slag attack are to be included in the development and evaluation programme. The objective is to reduce penetration by metal, slag and matte.

8. **CONCLUSION**

A 16 year period over which the introduction of an initial product equivalent to the then magnesia standard quality, followed by three magnesia-chrome qualities has been examined. The time period from concept through development was not discussed as some of the products were initially targeted at other industries, but typically this stage requires from one to five years.

From completion of development to introduction of magnesia brick M1 took 14 years and a further five years before significant growth occurred. Magnesia-chrome products D1/D2 and D3 gained more rapid acceptance and after introduction showed growth over eight and two years respectively.

Key factors in minimizing the acceptance period for a new product and showing early volume growth are a track record in the industry and a simulative laboratory test method that is a good indicator of service performance.

**References**


