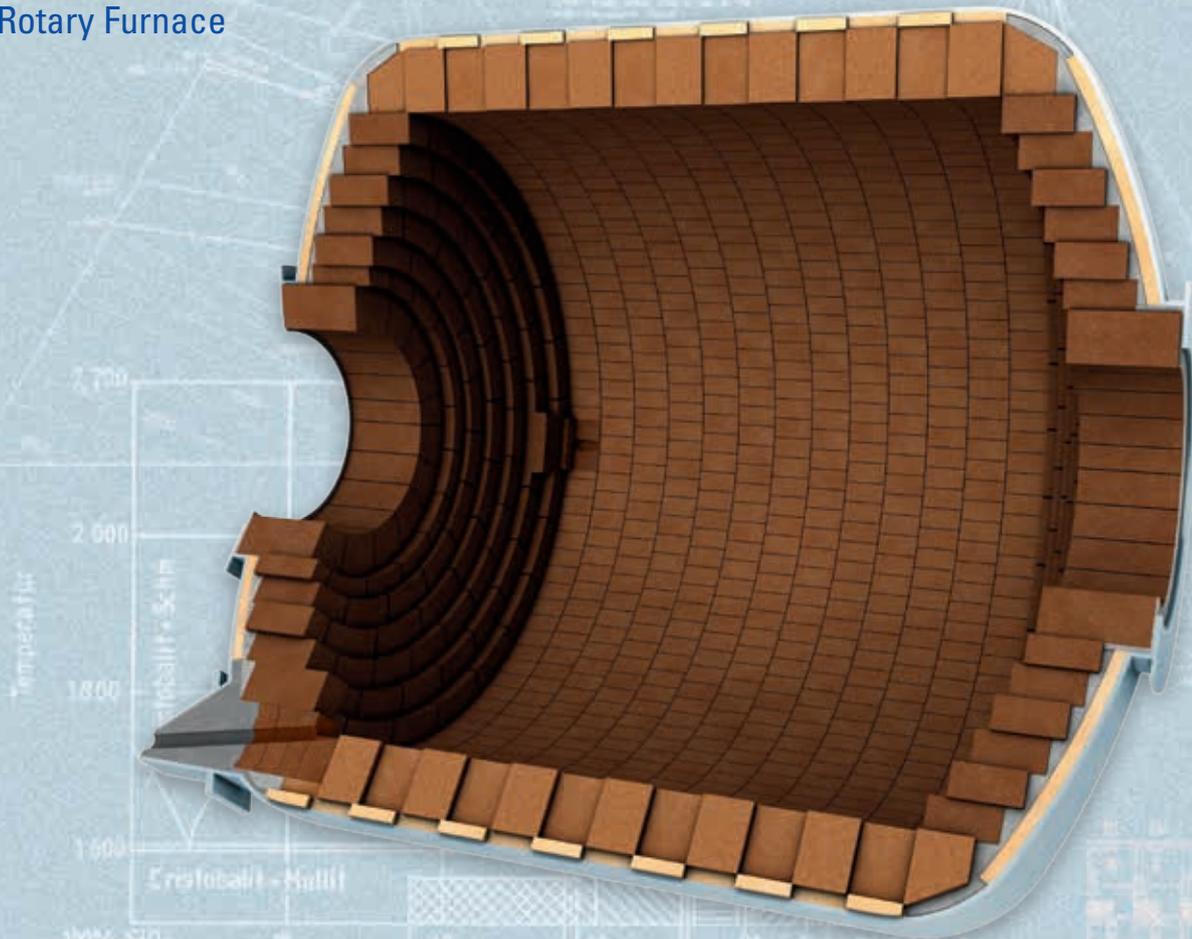


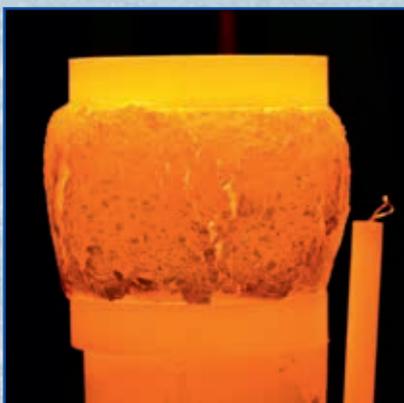
# RHI Bulletin >2>2015

The Journal of Refractory Innovations

## Rotary Furnace



Alumina Mullite Bricks for Sulphur Recovery Applications



New Innovative Lightweight Castable and Guniting Concepts



No-Cement Sol Mixes Achieve Service Life Records



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RHI Bulletin 2/2015  
Industrial Edition

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Lingual Proofreader: Janine Pink  
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Contact: Ulla Kuttner  
RHI AG, Technology Center  
Magnesitstrasse 2  
8700 Leoben, Austria  
E-mail: [ulla.kuttner@rhi-ag.com](mailto:ulla.kuttner@rhi-ag.com)  
Tel: +43 50213-5323  
Fax: +43 50213-5270  
[www.rhi-ag.com](http://www.rhi-ag.com)

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# RHI worldwide

## RHI Impresses at UNITECR 2015

**Austria >>** This year's UNITECR, the most important international refractory conference, was held at the historic Hofburg palace in Vienna from the 15–18<sup>th</sup> September. More than 900 international visitors, including refractory producers, raw material suppliers, numerous customers from different industries, and scientists from many different institutions discussed the latest trends and developments in the sector of high temperature materials.

RHI was represented with ten presentations and the extremely positive feedback and numerous questions asked of the expert technical speakers, showed once again that RHI leads in setting the standards within the refractories industry. As a gold sponsor RHI was also pleased to host the traditional gala dinner further adding to the event's social program.

## Best Raw Material Supplier Award for RHI Clasil

**India >>** Sagar Cements Limited, based in Telangana, India, is a leading producer of different types of cements for over 30 years. Recently, they honoured their best suppliers. RHI Clasil Limited, Visakhapatnam, was pleased to be awarded a memento for "Continuous Supplies of Refractory Material to their plant without any quality problems and commitment delays".

## Significant New Supply Contracts for the Glass Industry in China

**China >>** In 2015 RHI's China Glass sales team successfully signed package contracts for two local projects, Chongqing "Aureavia" and Fujian "Longthai". The Chongqing "Aurevia" project has opened the market for RHI SUPRAL CA products and shows the potential for high alumina project in China.

Within the the Fujian "Longthai" project, RHI will supply over 5000 tonnes of material for two furnaces. The key to success for these projects was the RHI quality standard and the tailor-made Regenerator Refractory Design.

## RHI Awarded "Bronze Resource Efficiency Pledge" (REP) Certificate

**UK >>** Launched by the Scottish Government in April 2013, the "Resource Efficient Scotland" initiative's aim is to not only reduce costs in the public and private sectors, but to also support and encourage sustainability and resource efficiency in businesses. Up to now, over 33000 companies in Scotland have participated in this program including the RHI sites in Clydebank and Bonnybridge.

The effort has paid off, upon completion of this 12-month initiative, RHI was presented with the "Bronze Resource Efficiency Pledge (REP) certificate". In order to be awarded this certificate, RHI had to identify a resource efficiency action plan and meet all its targets within one year. Following the bronze certificate, companies may progress on to achieve silver, gold and finally platinum certification over subsequent years.

## ISO9001 Certification of the RHI Dashiqiao Plant

**China >>** After the efforts and preparation of nearly one and a half years, the Dashiqiao Plant has been audited and confirmed to be certified within RHI's corporate ISO 9001 certification by LRQA (Lloyd's Register Quality Assurance). This represents an additional step forward in the development of the plant.

As part of the preparations, a series of training and implementation of procedures were carried out, in which awareness of quality orientation, continuous improvement, customer satisfaction was established and strengthened. Compliance with the standard provided the plant not only with a certificate but also, more importantly, with an opportunity to use a systematic management tool to improve the future of the plant.

This success was achieved based on the contributions and support of all employees from the top management to the front line workers of the plant.

## Full Line Supply Contract Between OMK Steel and RHI WOSTOCK SERVICE

**Russia >>** On 17<sup>th</sup> July, 2015, a 2-year full line supply contract was signed between OMK Steel and RHI WOSTOCK SERVICE. The groundwork for this contract began in April 2013 with an agreement between OMK Steel and RHI WOSTOK SERVICE for the comprehensive service of steel casting ladles and slide gate systems. This agreement was made despite doubts within the Russian market on the effectiveness of technical outsourcing.

The plant has a capacity of 1.2 million tonnes of rolled coil per year including the specialized production of rolled tubular products such as high strength and corrosion resistant pipes. A difficult transition period was expected with the initial agreement, but due to a clear distribution of responsibilities for each party these fears were unfounded. RHI initiated a step-by-step lifetime improvement process and reduced the consumption of specific refractories.

The quality, accident free, and efficient cooperation in the initial agreement resulted in the signing of the 2 year full line supply contract despite the difficult economic situation. This contract is the result of the professional support by many divisions of RHI, and the experience and energy of RHI WOSTOCK SERVICE.

# RHI worldwide

## Full Line Supply Contract Awarded to RHI Steel Poland

**Poland** >> After an intensive period of negotiations, RHI has succeeded in signing a full line supply contract with CMC Poland. CMC Poland is a 100% subsidiary of the CMC Group based in Irving, Texas (USA). The CMC Zawiercie plant produces approximately 1.2 million tonnes of steel per year.

The scope of the newly signed supply contract includes complete refractory materials with machinery and services. This agreement is the result of a long standing partnership between CMC Zawiercie and RHI.

## IRMA Award to ORL for Overall Excellence in Performance for the Year 2014–15 in Large Scale Sector

**India** >> The Indian Refractory Makers Association (IRMA) has conferred the Overall Excellence in Performance for the year 2014–15 in Large Scale Sector to Orient Refractories Ltd. at the annual general body meeting of IRMA held in Kolkata on the 9<sup>th</sup> of September 2015. This is the 10<sup>th</sup> consecutive time that ORL has received this award.

## JSW Salem Works Awards RHI “Award for Excellence”

**India** >> JSW Steel Limited is India’s leading private steel producer, with steel plants in Karnataka, Tamil Nadu and Maharashtra and a combined capacity of 14.6 million tonnes per year. RHI is the largest refractory supplier to the Tamil Nadu plant.

In August JSW Salem Works organized a supply chain stake holders meeting called “Collate 2015”, where vendors were classified into 8 categories. RHI was honoured with the “Award of Excellence” the highest in the category “Refractories & Consumables”.

## RHI’s R&D Center Dalian Officially Opened

**China** >> To meet the increasing demands of the Chinese refractories market it was necessary to redefine the tasks and organizational structures of the R&D Center Dalian (China), and to adapt them to the needs of internal customers.

As part of this reorientation, the official opening ceremony of the R&D Center Dalian was held on July 14 in the presence of high ranking representatives of local and regional politics.

The R&D Center Dalian represents a link between customers, production, sales, and raw material procurement with full technical support. It acts as a local service center and is therefore able to meet local customer requirements more rapidly.

The establishment of R&D China opens up the opportunity for further independent innovations and the expansion of the industrial value chain for RHI (Dalian) in order to play a greater role in the global layout of the RHI Group.

## 3D Printing—New Direction for Prefabricated Products

**Austria** >> 3D printing is a leading market development affecting many different industries. Since 2014 3D printing has been used in the modelling and simulation department of the TCL. Recently new potential fields of application for 3D printing were analysed in cooperation with the RHI production plants Veitsch and Urmitz. This analysis identified the early stages of the internal mould production for prefabricated products as an ideal target, due to their complex geometry, which leads to long production times and high costs.

The economic feasibility was analyzed and evaluated by Innovation Management in cooperation with TCL and the mould production team in Urmitz. The results were extremely positive and have led to the order for an industrial 3D printer with the capability of producing moulds for prefabricated products with dimension of 600 mm x 400 mm x 290 mm in one pass. It is expected that this investment will lead to savings in production times (up to 50%) and cost (90%) for special sections of the moulds. The positive results from this project will lead to further investigations into the application of 3D printing in other fields. This project has demonstrated what can be achieved if resources and know-how are focused on a common target.

## RHI Clasil’s Third Tunnel Kiln Dedicated

**India** >> In July, the third tunnel kiln at RHI Clasil, India, was dedicated in the presence of COO Franz Buxbaum, Heinz Schretter, Head of CF Tech. & Investment Projects and Miguel-Angel Cano, Head of Operations West. The new kiln is part of a €3 million development project to meet growing demand for shaped refractory products in the Asia/Pacific region. Also included in the project is the purchase and installation of an additional grinding circuit, extra storage silos and mixers and a new 1600 tonne press.

Construction of this project began in February 2015 and is scheduled to be completed by February 2016 with the purchase of the press. Once completed the RHI Clasil plant will have an annual capacity of approximately 42000 tonnes of non basic, high fired bricks, resulting in a total capacity of 54000 tonnes of mixes and shaped product per annum.

## Editorial

In September, I was one of more than 900 delegates at UNITECR 2015, the 14<sup>th</sup> Biennial Unified International Technical Conference on Refractories. Hosted in Vienna, it provided an opportunity for the global refractory community to meet and present cutting-edge science and technology in the field of high-temperature ceramics. An enthusiastic atmosphere dominated the event and the importance of research to realize innovative steps for the industry was a constant theme throughout the three days.

This Industrial edition of the RHI Bulletin covers a diverse array of topics, ranging from the evaluation of material properties to tailored refractory lining designs for multiple customer applications. The first article describes four different methods available at RHI's Technology Center Leoben to measure the thermal conductivity of various refractory materials. Heat transfer is frequently a paramount selection criterion and the overview not only highlights the advantages of each technique but also provides a comparison of data obtained using the various experimental procedures. In the second paper, two ferronickel rotary kiln lining strategies are detailed along with the governing factors that influenced the overall concept. The first example comprised monolithic materials for the repair while the second complete relining was a combination of bricks and castables. In the next article the development of alumina mullite brick grades for the demanding conditions in sulphur recovery units is described that meet the stringent licensor requirements.

To provide a comprehensive understanding of refractory wear, used refractory materials are frequently analysed in detail by RHI. In the fourth article, postmortem results of a magnesia chromite brick from a lead recycling furnace are reported in addition to the FactSage calculations that supported the mineralogical findings. This is followed by a paper detailing two economical alternatives to fused cast material for the superstructure of glass melting furnaces.

Vertical shaft furnaces used for copper cathode melting must be lined with appropriate materials that meet the challenging pyrometallurgical requirements. In the sixth paper, the properties of nitride and oxide bonded silicon carbide refractories are presented as well as the positive results achieved in field tests. This is followed by a report detailing the excellent performance of no-cement sol-bonded mixes in the challenging environment of a cement rotary kiln fired with alternative fuels. In a case study described in the eighth article, not only the impact of alternative fuels on mullite bricks containing silicon carbide installed in a cement rotary is discussed, but also the benefits of brick impregnation and sol-bonded mixes for such severe operating conditions. The final article describes innovative, easy-to-use lightweight castables and gunite concepts for the petrochemical industry. These seven newly developed products fulfil the highest customer specifications and quality standards.

In closing I would like to express my gratitude to all the authors and the entire editorial team for their work in creating this edition.

Yours sincerely

Stefan Schriebl  
Corporate Research and Development  
RHI AG

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E-mail: [ulla.kuttner@rhi-ag.com](mailto:ulla.kuttner@rhi-ag.com)  
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Fax: +43 50213-5270

Bernd Lorenzoni

# Comparison of Different Measuring Methods for Thermal Conductivity

Thermal conductivity is an often discussed physical property of refractory materials. It can even be a deciding criterion for a certain application. There are many methods available to measure thermal conductivity, however material testing with various methods based on different physical principles can provide more reliable values. This paper describes the most commonly used measuring methods for thermal conductivity at the RHI Technology Center in Leoben, Austria. These are the ASTM C201, the laser flash analysis, the Dr. Klasse, and the hot wire methods. Each method has certain advantages with regards to the material that can be tested and there is no single method that can test every refractory product. In order to compare methods, two materials were selected that could be tested without drawbacks in at least three devices.

## ASTM C201

The ASTM C201 method belongs to the steady state group of methods for determining thermal conductivity. The heating chamber is placed above the test sample and can be heated electrically over a temperature range from 205–1540 °C [400–2800 °F]. A silicon carbide slab is positioned between the test sample and the heating chamber to provide uniform heat distribution. The copper calorimeter assembly that is used for measuring the quantity of heat flowing through the test specimen is located below the test sample. The water circulation through the calorimeter is such that adjacent passages contain incoming and outgoing streams of water to maintain a uniform heat distribution at the lower side of the sample. Additionally, the four independent sections of the calorimeter assembly have an individually adjustable rate of water flow. The test sample consists of three straight bricks and six soap bricks and must be free of broken corners or edges. This is important for a precise measurement. This test method has the largest sample size of all the methods covered in this article. The material must cover the whole calorimeter assembly (approximately 456x342 mm or [18x13.5 in]).

When measuring the thermal conductivity at a specific temperature the whole system has to fulfil certain equilibrium conditions that are specified in the ASTM standard [1]. As a result after every temperature change of the furnace it can take more than twelve hours to reach those conditions. In the original setup of the device this was controlled by the operator and was very time consuming and technically not up to date. A decision was made to upgrade the RHI device. Now the equilibrium conditions are electronically monitored and the measured data is recorded by a computer. These changes have resulted in a halving of the measurement time and improved accuracy. Due to the large sample size and the small area in the centre of the sample where data for the calculation is collected, radial losses of heat do not play a role in the precision of the evaluated values with this experimental setup. The duration of a complete measurement is dependent on the number of temperature levels to be tested. Usually it takes between three days to one week. This method is best suited for insulating refractory materials.

## Dr. Klasse

The Dr. Klasse method is also a steady state method for thermal conductivity measurements. Again the whole system must reach a thermodynamic equilibrium state at each temperature step to obtain a valid result. At the bottom of a Dr. Klasse device a disk shaped electrical heating plate is positioned. For a homogenous heat distribution an aluminium nitride slab is placed onto the heating plate and the sample is placed directly above this slab. The sample is also disk shaped with a diameter of 100 mm [4 in] and a height of 25 mm [1 in]. Two grooves are cut in the test sample for the thermocouples. To be able to calculate the thermal conductivity of the sample a reference disk of the same dimensions and with a confirmed thermal conductivity is placed on top of the disk pile. To minimize radial heat loss the area around the pile is filled with granular insulating refractory material [2]. With the Dr. Klasse devices measurements can be carried out in air (oxidizing conditions) or can be executed in an inert gas atmosphere. The inert gas atmosphere is commonly used for magnesia-carbon refractories as they are usually too coarse grained for laser flash.

As the sample size is significantly smaller than for the ASTM C201 method the equilibrium condition is usually achieved faster and as a result complete measurement is normally completed within two days.

## Laser Flash

Unlike the ASTM C201 and the Dr. Klasse method, the laser flash analysis belongs to the transient type of methods for measuring thermal conductivity. Transient type methods utilise change in temperature relative to time for the calculation of thermal conductivity. The test sample is located in the middle of the furnace which can be heated electrically from room temperature up to 1400 °C [2550 °F]. Measurements are always executed in an inert gas atmosphere. The sample size is the smallest of the methods described in this article. A disc with approximately 20 mm [0.8 in] in diameter and a height of several millimetres is usually used for the test. The upper and lower surfaces of a sample material with a naturally bright colour have to be

blackened with graphite, to prevent the laser light being reflected at the surface and significantly reducing the precision of the measurement [3]. When the furnace and the test sample have reached the desired measuring temperature a laser beam heats the lower surface of the sample for a few milliseconds. A detector measures the time dependant temperature rise at the upper surface of the sample and a computer program calculates the thermal diffusivity. There are several mathematically models which can be used for the calculation. At each temperature level of the furnace, the laser heats the test sample several times and a mean value is determined for the thermal diffusivity. Between each "shot" the sample needs to cool to the furnace temperature. In order to calculate the thermal conductivity the density and the specific heat capacity of the tested material must be known.

The laser flash analysis is best suited to fine grained carbon containing refractory materials, for example many isostatically pressed products fulfill these criterions. Due to the transient measuring method and the small sample size, this is the fastest method described in this paper. A complete measurement is usually carried out within a day.

### Hot Wire Methods

All variations of the hot wire methods belong to the transient type of methods for measuring thermal conductivity. They can only be used for noncarbonaceous, dielectric refractories and it is difficult to make accurate measurements of anisotropic materials, but they have the advantage of being applicable not only to bricks but also granular or powdered specimens. The duration of a complete measurement is dependent on the number of temperature levels to be tested. Usually it requires three days up to one week.

#### ASTM C1113

The test sample consists of two 228 mm [9 in] straight brick or equivalent which are heated in a furnace to specific temperature levels (up to 1500 °C). When equilibrium conditions are fulfilled a constant electrical current is applied to a pure platinum wire (the hot wire) placed between the two bricks. The rate at which the wire heats is dependent upon how rapidly heat flows from the wire into the constant temperature mass of the refractory brick. The rate of temperature increase of the platinum wire is accurately determined by measuring its increase in resistance in the same way a platinum resistance thermometer does. A Fourier equation is used to calculate the thermal conductivity based on the rate of temperature increase of the wire and power input. This method is applicable to refractories with a thermal conductivity up to 15 W/mK. [4].

#### DIN EN ISO 8894-1:2010-10 (cross array)

In addition to the setup described above a thermocouple is welded to the center of the hot wire. The limbs of the thermocouple are perpendicular to the hot wire.

The thermal conductivity is calculated from the known power input to the hot wire and the temperature at two specific intervals of time after the heating current is applied. The variation in temperature of the hot wire is a function of the thermal conductivity of the sample material. This method is applicable to materials with a thermal conductivity up to 1.5 W/mK and the minimum sample size

is two bricks of 200x100x50 mm or equivalent, ideally 230x114x64 mm. Measurements can be executed up to 1250 °C [5].

#### DIN EN 993-15 (parallel)

The difference in this method to the aforementioned hot wire methods is the location of the thermocouple to measure the temperature increase after application of the current to the heating wire. In this case the thermocouple is placed with the limbs parallel to the hot wire at a distance of 15 mm.

The method is applicable to materials with a thermal conductivity up to 25 W/mK and the minimum sample size is again two bricks of 200x100x50 mm or equivalent, ideally 230x114x64 mm. Measurements can be executed up to 1250 °C [6].

### Comparison of Results

There are ongoing discussions about the different measuring methods regarding their precision and the comparability of the results [7]. A simple comparison of measured thermal conductivity values from RHI devices with literature values (e.g., [8]) cannot be done purely on the knowledge of the main chemical components as the density/porosity and other structural parameters obviously have a significant influence on the results. It is clear that not all refractory materials can be tested accurately in all of described devices. For example many insulating materials often have a high porosity and quite large pores that negatively affect the precision when tested with laser flash. Alternatively it is impossible to cut samples that are big enough for the ASTM C201 device out of standard isostatically pressed products. For this article two different materials were selected that can in principle be measured in all devices. The first was a high alumina material with approximately 10% chromium oxide and the second contains about 93% chromium oxide. The tested samples of each material were cut from the same brick to exclude effects due to production variations.

The results are shown in Figure 1 and 2. It can be seen that in Figure 1 the Dr. Klasse and laser flash results

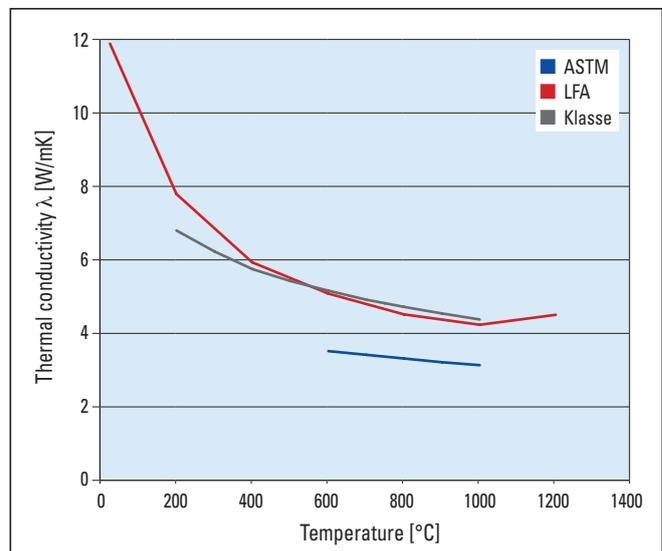
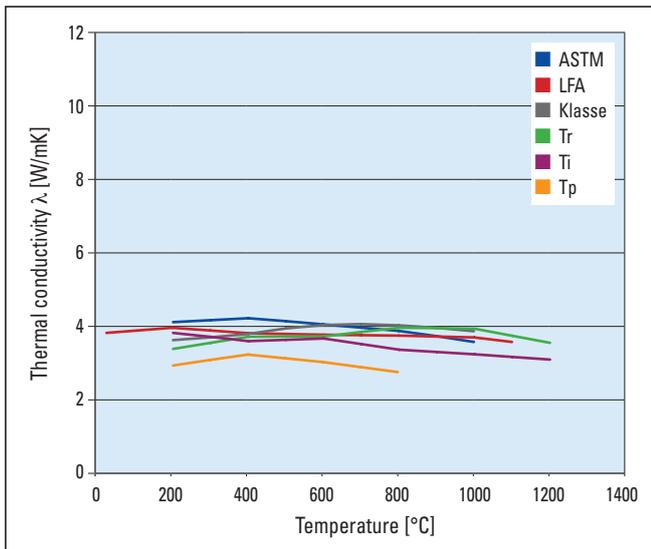


Figure 1. Thermal conductivity measured with three different methods of high alumina material.



**Figure 2.** Thermal conductivity measured with six different methods of chromium oxide material.

are almost identical over a wide temperature range and that the ASTM result is clearly a bit lower. This material has not yet been tested with the hot wire methods. In Figure 2 there is almost no difference between the methods except for the hot wire parallel result which was a bit lower.

## Conclusion

The test results of other materials that could not be included in this article often show the same behaviour as the materials above. The lower values sometimes generated from the ASTM C201 method are part of ongoing investigations. The variations in results appear to be influenced more by the quality and positioning of the thermocouples than the choice of method itself, provided that the test material is appropriate for the specific method. The selection of test samples and their preparation is of significant importance for consistent results and in particular the comparison of results between different methods.

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## Author

Bernd Lorenzoni, RHI AG, Technology Center, Leoben, Austria.

**Corresponding author:** Bernd Lorenzoni, [bernd.lorenzoni@rhi-ag.com](mailto:bernd.lorenzoni@rhi-ag.com)

Christine Wenzl, Bernhard Handle, Daniel Meza and Nestor Garcia

# Technical Aspects for the Proper Design of Refractory Concepts Applied to Ferronickel Rotary Kilns

The productivity of rotary kilns in the ferronickel (FeNi) industry depends on a set of process parameters tightly intertwined with refractory-related design criteria. The analysis of rotary kiln refractory designs, currently operated by the world's leading FeNi producers, revealed substantial differences in the refractory design. It is worthwhile to examine and explain the governing factors using a holistic approach, thereby triggering a search for optimised refractory concepts and finally paving the way for new and innovative ideas. This paper describes two FeNi rotary kiln repair projects recently carried out by RHI and the factors considered in such repair work, including refractory selection, lining design, installation, and heat-up.

## Introduction

Crude nickel laterite oxide ores contain substantial amounts of physically and chemically bound water, thus a drying and calcination step is carried out in a rotary kiln prior to smelting operations in the electric arc furnace (Table I). The kilns used in lateritic processing are fired counter-currently allowing the ore temperature to increase progressively as the ore moves towards the discharge end of the kiln. In the lowest temperature area, the feed section, the remaining free moisture is driven off. Crystalline water is then gradually eliminated as the solid temperature increases while moving through the kiln. The remaining function of the kiln is the reduction of about 30% of the nickel oxide to metal, as well as the iron oxides (mainly  $\text{Fe}_2\text{O}_3$ ) to FeO and Fe by means of the addition of carbon, thereby minimising the energy consumption in the following smelting stage (Table II) [1].

Pyrometallurgical processes are energy intensive and require substantial amounts of hydrocarbon fuels and electric power [1]. In addition, a worldwide increase of FeNi capacity forces FeNi producers to lower energy consumption and to cut capital and operational costs in order to remain competitive and profitable in a globalized world. RHI continuously strives to optimize not only the refractory concept and design of FeNi rotary kilns, but also creates alliances with customers to adopt improved techniques related to the refractory installation and heat-up process.

## Basic Engineering Stage

A proper design of the refractory concept assuring maximum equipment availability and productivity requires a detailed analysis of numerous factors stipulated in the specifications issued by the original equipment manufacturer (OEM) of rotary kilns as well as the FeNi producer. Process related topics such as the chemical composition of the kiln input and output materials, gas phases, and gas temperature profiles are of special interest with regard to the selection of appropriate refractory materials and to determine the steel shell temperature at any time and distance from the kiln discharge section. RHI's general approach to assess the refractory lifetime as a function

of the chemical constituents formed during the calcination process is based on thermodynamic simulations in combination with expansion and heat transfer calculations [2, 3]. Special attention is centered on the reduction and discharge areas where maximum temperatures may reach up to  $\sim 1250$  °C, whereas the temperature in the kiln inlet (drying zone) barely exceeds 400 °C. This in turn may lead to shortcomings when it comes down to achieving a sufficiently high strength of the refractory castable installed in this area. The number and position of secondary air inlet pipes, feed pipes, lifters, and retention rings located along the rotary kiln axis may also impact the design of the refractory concept.

Component	Upgraded laterite (%)
Ni	1.5–3
Co	0.04–0.08
Fe	15
O	5 (bonded to Ni, Co, and Fe)
$\text{SiO}_2$	40
$\text{MgO}$	25
$\text{Al}_2\text{O}_3$	1
Chemically bonded $\text{H}_2\text{O}$	11

**Table I.** Typical composition of laterite oxide ore [1].

Component	Calcine (%)
Ni	1.5–3 (25% as metal 75% as oxide)
Co	0.04–0.08 (20% as metal 80% as oxide)
Fe	15 (5% as metal 95% as FeO)
Coal	2
$\text{SiO}_2$	40
$\text{MgO}$	25
$\text{Al}_2\text{O}_3$	1

**Table II.** Typical composition of calcine [1].

Further aspects recommended to be taken into consideration throughout the initial design phase are:

- >> Synchronised refractory performance targets in conjunction with annual maintenance schedules.
- >> Evaluation of equipment (e.g., kiln tyre positions) and process parameters which may have caused premature refractory wear in previous campaigns (e.g., definition of high-frequency repair zones).
- >> Examination of the refractory lining thickness as well as number and geometry of refractory dams.
- >> Preliminary heat transfer calculations based on a pre-selected set of refractory materials.
- >> Estimation of required refractory materials, metallic anchors, manpower, and equipment to accomplish the installation and heat-up procedure according to the defined chronogram.
- >> Design, number, and location of lifters (welded and/or removable), secondary air inlet pipes, feed pipes, girth gear drive, kiln tyre position, and auxiliary gear drive.
- >> Type of burner fuel.
- >> Installation technique (for working areas).
- >> Design and fabrication of scaffolding and templates (wood or metal).
- >> Metallic anchor design and welding specifications.
- >> Cooling and heat-up schedule for total and partial repairs (e.g., energy input, rotation, and thermocouples).

### Project 1—Partial Repair of the Discharge Area in a FeNi Rotary Kiln

This section explains the interaction of numerous process and refractory parameters taken into consideration during the design stage of a refractory concept applied in the so-called discharge area in a rotary kiln 135 m long and 5.4 m in diameter. The kiln section depicted in Figure 1 suffers from severe thermo-mechanical loads and industrial experience has shown that cement bonded castables were not performing satisfactorily under the process conditions. Due to lost time, excessive cost, and intense maintenance interventions, RHI was invited by the customer to closely examine the prevailing chemical, thermal, and mechanical conditions and to design a solid refractory concept aiming to increase refractory lifetime (> 6 months of continuous operation), reduce installation time (< 6 days), and propose an optimized dry-out and heat-up schedule (up to 900 °C within 50 hours).

### Refractory Design Parameters

Compared to shaped refractory bricks, castables may offer superior chemical resistance, mechanical strength, and thermo-shock resistance, provided that attention is paid to specific criteria throughout the preparation, installation, and heat-up phase. For critical applications the castable's characteristics and properties call for a fine-tuning process at laboratory scale prior to launching the production process on an industrial scale. Thus, for the choice of a suitable refractory castable in the kiln discharge area, three different brands of castable were closely examined and evaluated at the RHI Technology Center prior to decision making. Additionally, representative samples from production lots were analyzed prior to shipment in order to validate and further support the obtained results from laboratory scale trials. Cement-bonded materials have proven performance in other FeNi rotary kiln applications, however it was decided to include sol-bonded materials in this investigation, based on experience with these materials in other industrial applications. The standard properties of the considered materials are summarized in Table III.

Conventional and low cement bonded castables have one significant disadvantage tied to the fact that they require a precise control of liquid addition and temperature monitoring during the dry-out and heat-up process, otherwise physical and mechanical properties are adversely affected (Figure 2). It should be noted that a higher liquid addition than recommended not only deteriorates strength properties, but also leads to increased setting time [4, 5]. As a general guideline, the stipulated amount of mixing liquid should be between the minimum and maximum value of liquid addition provided by the refractory producer.

Figure 3 illustrates the temperature evolution during setting of a conventional castable (CC) and a low cement castables (LCC). As both materials contain different amounts of cement, the curves differ in temperature evolution over time. The temperature increase is mainly caused by the exothermic formation of Ca hydrate phases (i.e., reaction of cement). Note the absence of any temperature increase for the LCC (DIDURIT M60-15) is due to its low cement content.

Eventually, intense mixing translates into excessive energy input and may bring the castable's temperature above 30 °C thereby considerably affecting its final properties (Figure 4).

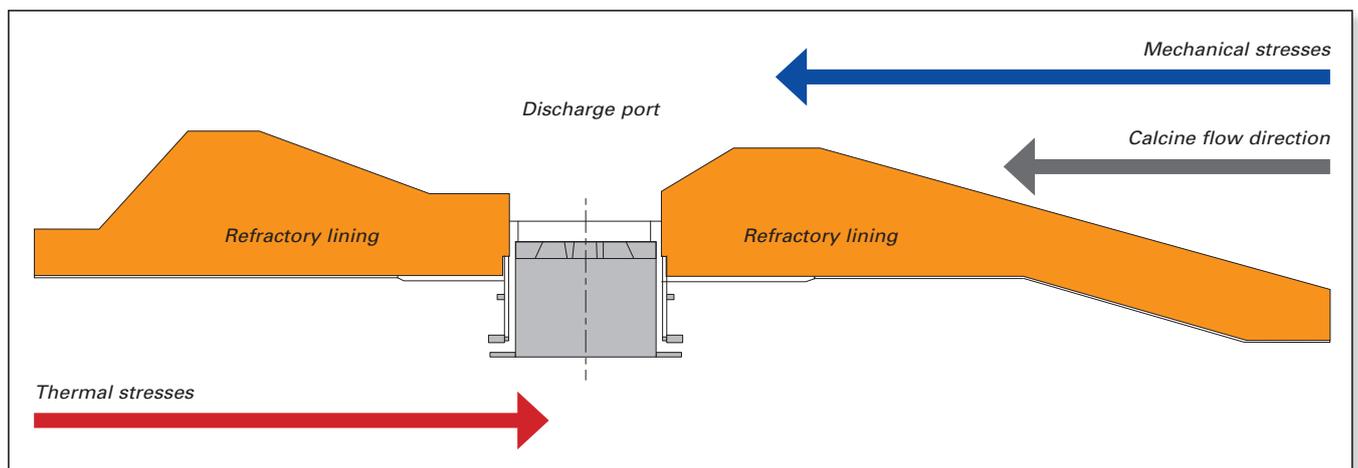


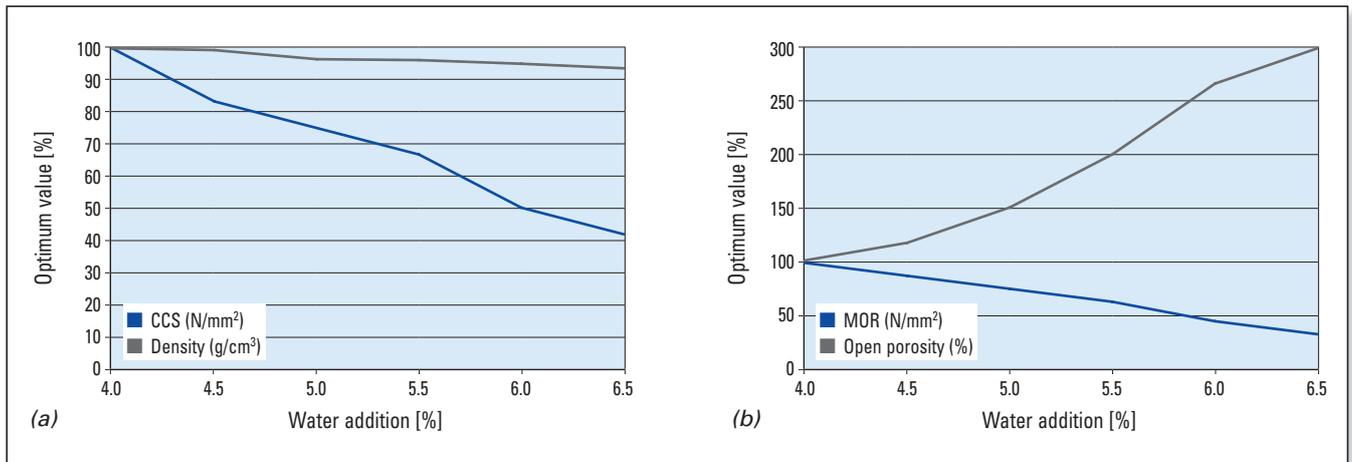
Figure 1. Discharge area of the rotary kiln (6900 mm long), comprising 130 tonnes of refractory castable.

From Table III it can be concluded that conventional cement bonded castables (CC) are less suitable for applications afflicted by severe thermo-mechanical stresses. Consequently these are considered to be an economically viable

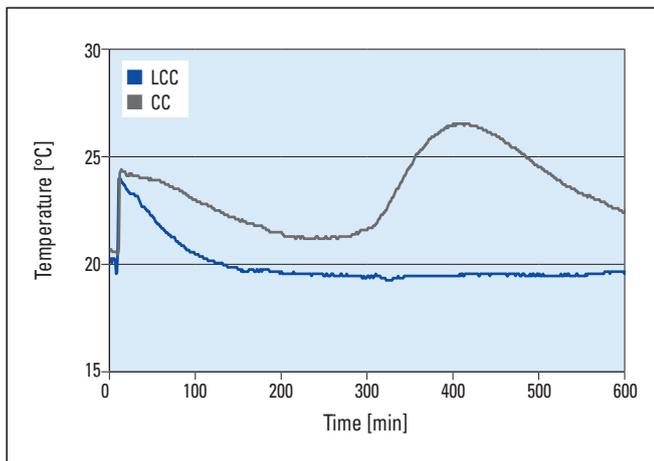
alternative when restricted to areas of less demanding performance. Finally, sol bonded castables were given priority over LCC mainly because of excellent flexibility in combination with reduced crack formation, low porosity, and

Type	COMPRIT F60-15 Conventional cement bonded castable (CC) with > 2.5% CaO	DIDURIT M60-15 Low cement bonded castable (LCC) with < 2.5% CaO	COMPAC SOL B88-6 Cement free sol bonded alumina castable (NC)
Liquid addition	H <sub>2</sub> O (8.4 l/100 kg)	H <sub>2</sub> O (5.6 l/100 kg)	DIVASIL (7.5-8.5 l/100 kg)
Application temperature	~1500 °C	~1650 °C	1700 °C
Raw material basis	Fireclay	Mullite rich material	Bauxite
Bulk density at 1000 °C (g/cm <sup>3</sup> )	2.38	2.51	2.85
Porosity at 1000 °C (%)	18	17	15
Cold crushing strength (CCS) at 1000 °C (N/mm <sup>2</sup> ) – EN ISO 1927-6	70	110	140
Thermal conductivity at 1200 °C (W/mK)	1.45	1.75	2.40
Permanent linear change (PLC) at 1000 °C (%)	-0.20	-0.20	-0.10
Thermal expansion at 1000 °C (%)	0.55	0.55	0.6
Abrasion (cm <sup>3</sup> )	10.0	8.0	6.0
CO resistance	Class A	Class A	Class A-B
Shelf life	12 months	8 months	18 months

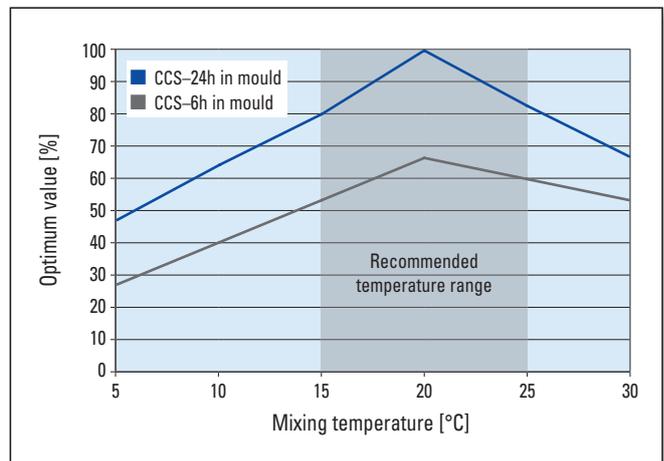
**Table III.** Comparison of castable properties, properties mentioned are inferred from test specimens and may differ significantly depending on the norms and testing standard procedures applied. CO resistance depends primarily on the Fe content and the raw material basis of the refractory castable.



**Figure 2.** Mechanical and physical properties of cement-bonded castables versus mixing liquid amount (in wt.% related to castable amount). Showing (a) CCS and density, and (b) MOR and open porosity [5].



**Figure 3.** Exothermic behaviour of LCC and CC during setting.



**Figure 4.** CCS of cement bonded castables versus mixing temperature [5].

superior abrasion resistance, as already confirmed by other industrial installations (Figure 5a). Additionally sol-bonded castables enable significant time and energy savings because of extremely fast dry-out and heat-up schedules that do not jeopardize the quality of the monolithic lining [6, 7, 8, and 9]. However, the advantage of straightforward dry-out and heat-up schedules can only be exploited to its maximum if no other CC or LCC are installed in the same kiln, otherwise the heat-up schedule will be forced to follow the requirements of the “slowest” material (Figure 5b).

Based on the criteria and outcomes described above, COMPAC SOL B88-6 was determined to be the ideal choice of castable for use in the discharge area.

### Refractory Installation and Heat-Up Schedule

The discharge area extends over a length of 6900 mm with a varying longitudinal lining thickness (Figure 6). Circumferentially the lining was divided into 12 segments. The total amount of COMPAC SOL B88-6 applied was approximately 140 tonnes. The installation sequence of each segment consisted of the following steps:

- >> Segment identification (pair/impair segments).
- >> Metallic anchor fixation.
- >> Installation of lateral templates.

- >> Installation of cover template.
- >> Casting and vibrating (4 hours/segment).
- >> Setting (2 hours/segment).

### Metallic Anchor Design

Expansions of metallic anchors at process temperatures largely exceed those of a monolithic body (Figure 7) [10]. Currently a large number of rigid and flexible anchor fixation systems are available on the market. However, to gain a better understanding of the interactions between metallic anchors and monolithic bodies at given process conditions, simulations using finite element analysis (FEA) were carried out at the RHI Technology Center.

Based on the results obtained from the modelling, a flexible anchor design (Figure 8) delivered convincing arguments for significantly reducing thermo-mechanical stresses thereby substantially minimizing the risk of a destabilized monolithic structure. Encapsulating the anchors’ fixation bolt with a plastic casing creates a barrier between the movable connection of the anchor and clip and the castable; the zone where highest flexibility is required. Further stress reduction is achieved by ensuring initial clearance between the contact area of the anchors and castable (e.g., bitumen painting and plastic caps). It is a prerequisite that the metallic anchor specification, steel

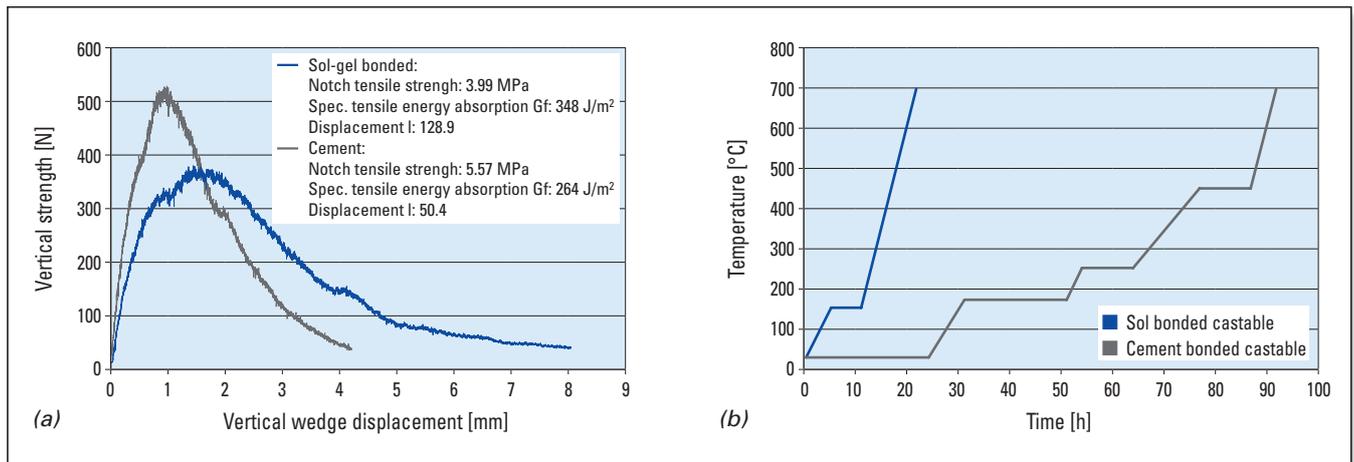


Figure 5. Comparison of sol-bonded materials (blue lines) and cement bonded materials (grey lines) [5]. (a) Crack propagation (wedge-splitting test) and (b) heat-up process.

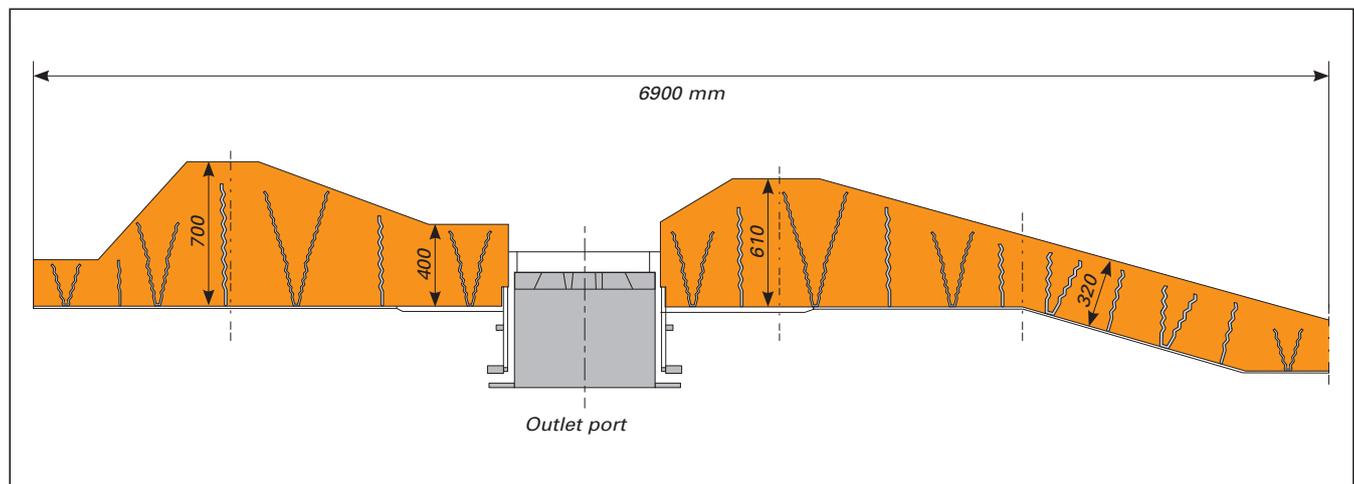


Figure 6. Schematic of the kiln outlet showing the metallic anchors.

shell quality, and welding electrodes are compatible with each other. Additionally, it is recommended to check the welding quality with a dye penetrant to guarantee good anchor fixation.

### Design and Installation of Templates

A highly effective installation method had to be adopted for the 12 segments, (Figure 9) to meet the tight maintenance schedule.

In the longitudinal direction the joints between each of the 12 segments were designed according to the principle of “tongue and groove” using special wooden templates. Each of the 12 segments is divided into 4 casting sections. Openings in the cover templates (2 openings per casting section, i.e., 8 openings per segment) serve as castable feed port and vibrator access (Figure 10). The type of vibrators, their size and power must be selected for each particular case.

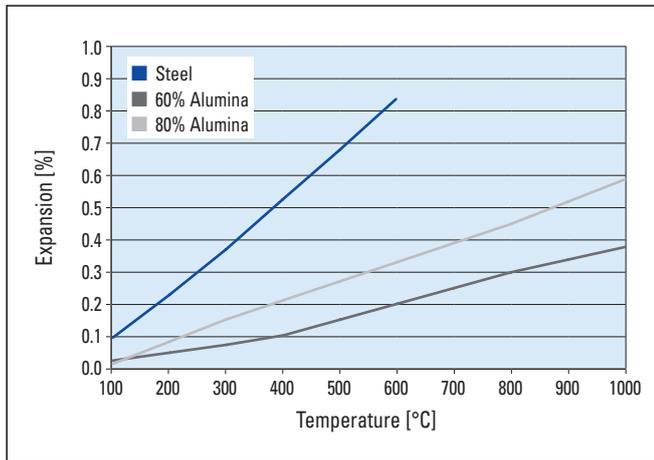


Figure 7. Thermal expansion of steel and refractory materials [10].

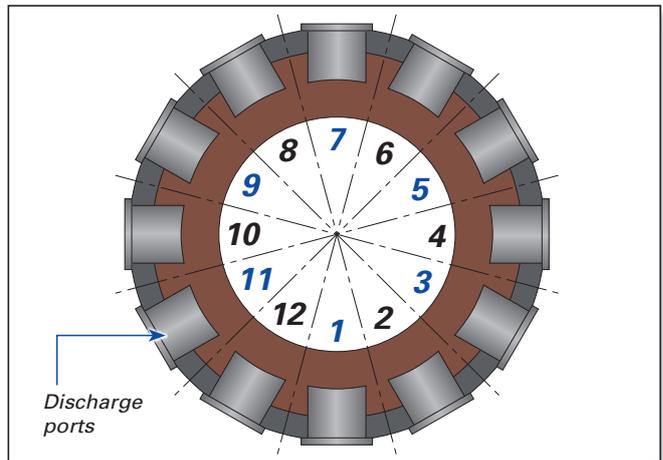


Figure 9. Cross-sectional view of discharge area (5.1 m diameter) showing the 12 segments of the repair area with discharge ports.

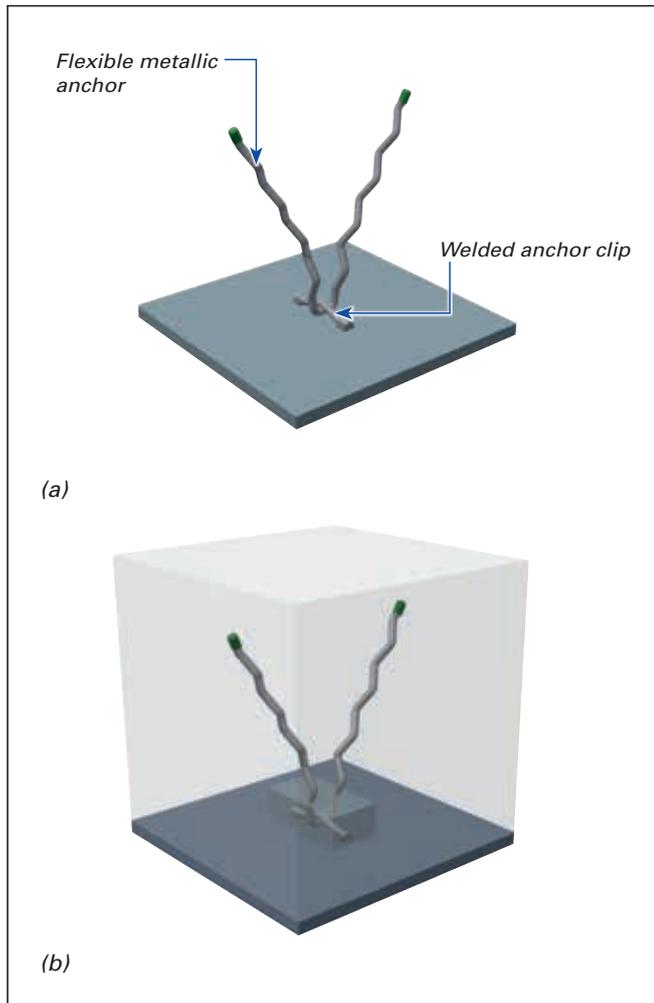


Figure 8. Flexible anchor design. (a) Anchor design (including plastic caps) and (b) anchoring system used in FEA modelling (anchor surrounded by cubic section of refractory castable).

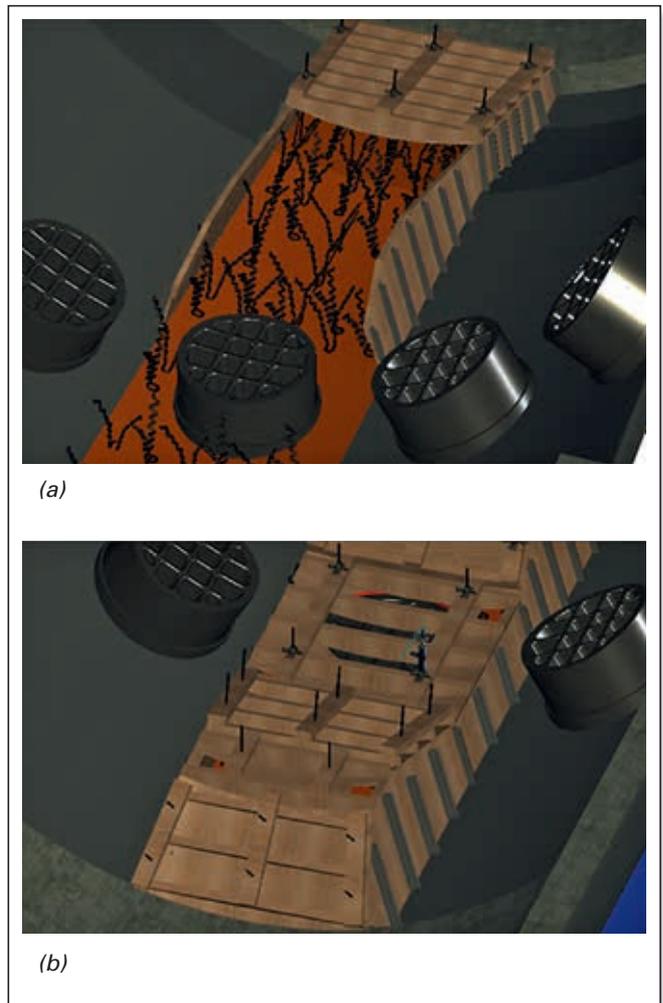


Figure 10. Wooden template of one segment with cover and openings. (a) Showing open template and anchors, (b) showing closed template with openings for feeding and vibrator access.

Parallel to the casting and vibrating operation of the first segment, the adjacent segments were prepared for anchor and template fixing. When the casting of the first segment was complete, the openings are shut, the kiln was prepared for turning to begin installation of the next impar segment. Once all the uneven numbered segments were installed, cast and vibrated, the templates are completely removed. The now mechanically stable castable of the uneven segments act as the template for the even segments. As such the even number segments were cast between the uneven numbered segments.

### Setting—Dry-Out—Heat-Up Schedule

Depending on the ambient temperature and the type of castable applied, the minimum setting time will be approximately 6 hours. The templates can be removed 10 to 12 hours after the installation has been completed. Afterwards, the monolithic body is exposed to air for a minimum of 24 hours. Once the setting process has terminated, the dry-out and heat-up process is initiated. The use of auxiliary burners and a series of thermocouples are recommended to check the temperature evolution during the heat-up procedure to make sure that the heat-up curve is respected at all times. For precise monitoring of the temperature curve, it is recommended to use thermocouples in several areas (hot and cold side) supported by optical pyrometers and thermographic cameras.

The dry-out and heat-up schedule illustrated in Figure 11 corresponds to a partial repair based on a COMPAC SOL

B88-6 lining thickness of 230 mm. Indicated temperatures refer to the kiln atmosphere measured in the discharge area. Although sol-bonded mixes can be heated quickly, the extended holding period at 150 °C was established in order to achieve a homogeneous temperature distribution to ensure no damage to the existing refractory lining composed of LCC, which was not the subject of this specific repair. It is not recommended to rotate the kiln at temperatures below 150 °C. As soon as temperatures approach 550 °C the heat-up cycle proceeds according to the customer’s best practice and OEM instructions.

As an integral part of the design phase of the refractory concept for the discharge area, heat transfer calculations were performed for varying lining thicknesses and temperatures, in an attempt to match theoretical calculations with practical experience and to provide a solid basis for future optimizations. Continuous onsite measurements seen in Figure 12 impressively confirmed the accuracy of theoretical heat transfer calculations. Considering an average lining thickness of 400 mm in the discharge area and a hot face temperature of 1200 °C, the theoretical steel shell temperature was determined to be 266 °C corresponding exactly to real-time measurements, suggesting that the refractory lining is in optimal condition. Thus, the combination of continuous monitoring of the steel shell supported by theoretical heat transfer simulations, are an effective way to detect in time any sort of deficiencies in refractory wear thereby contributing considerably to a safe and reliable kiln operation.

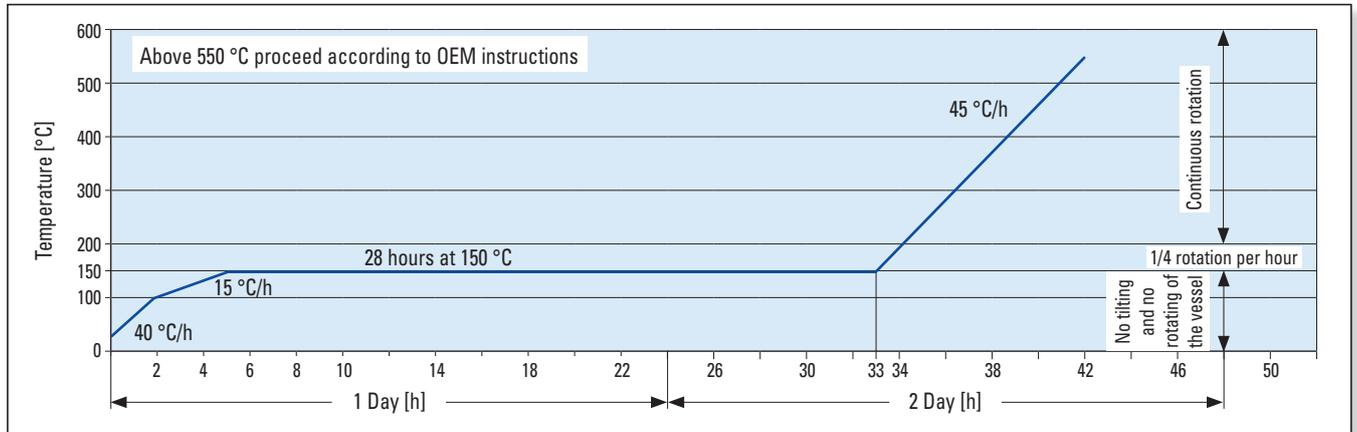


Figure 11. Applied dry-out and heat-up diagram based on COMPAC SOL B88-6.

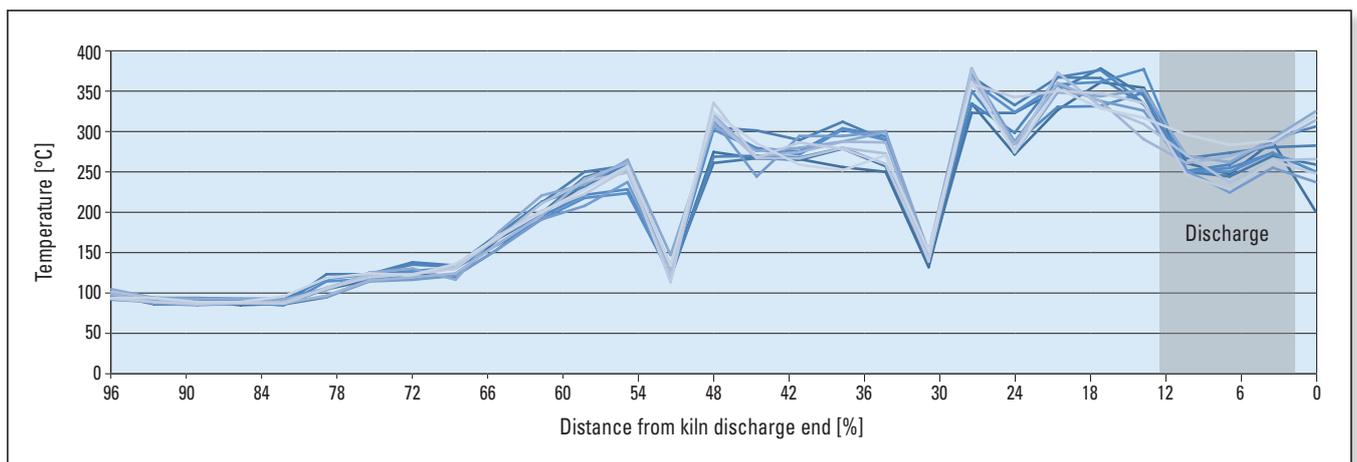


Figure 12. Onsite shell temperature monitoring resulting with an average 250 °C in the discharge zone.

## Industrial Experience

Earlier predictions about the favourable performance of COMPAC SOL B88-6 in the discharge zone were confirmed by the customer. After 7 months of continuous operation the refractory lining is still in an optimal and stable condition (Figure 13).

### Project 2—Complete Relining of a FeNi Rotary Kiln Based on a Combined Refractory Concept

This section outlines some major technical aspects encountered within the scope of completely relining a FeNi rotary kiln with a refractory concept composed of castables as well as bricks. The decision whether to use bricks, castables or a combined lining depends mainly on the kiln design, including the distance between the discharge area and last kiln tyre. The kiln dimensions were 115 m long and 5.5 m in diameter. Table IV shows the different kiln zones

	Drying zone	Heating zone	Reduction zone
Refractory type	Low cement castable	Low cement castable	High alumina brick
Refractory grade	DIDURIT F50-6	DIDURIT F50-6	RESISTAL SK65
Lining thickness (mm)	230	230	230

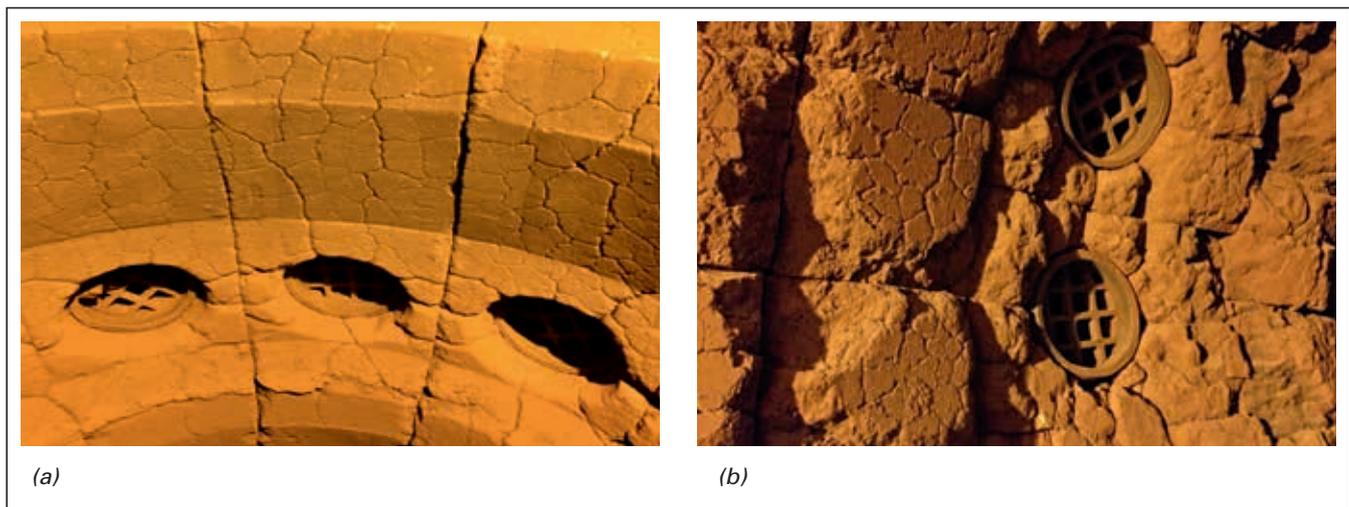
**Table IV.** Kiln zones and refractory lining.

and the refractory lining. The kiln is supported by five roller pairs with the drive gear located in the vicinity of the kiln inlet. Permanently fixed lifters are evenly distributed along the drying and heating zone. Additionally, the kiln is equipped with secondary air injectors positioned in the drying and heating zones. Calcine overflows the outlet dam and is subsequently collected in the kiln surge bin.

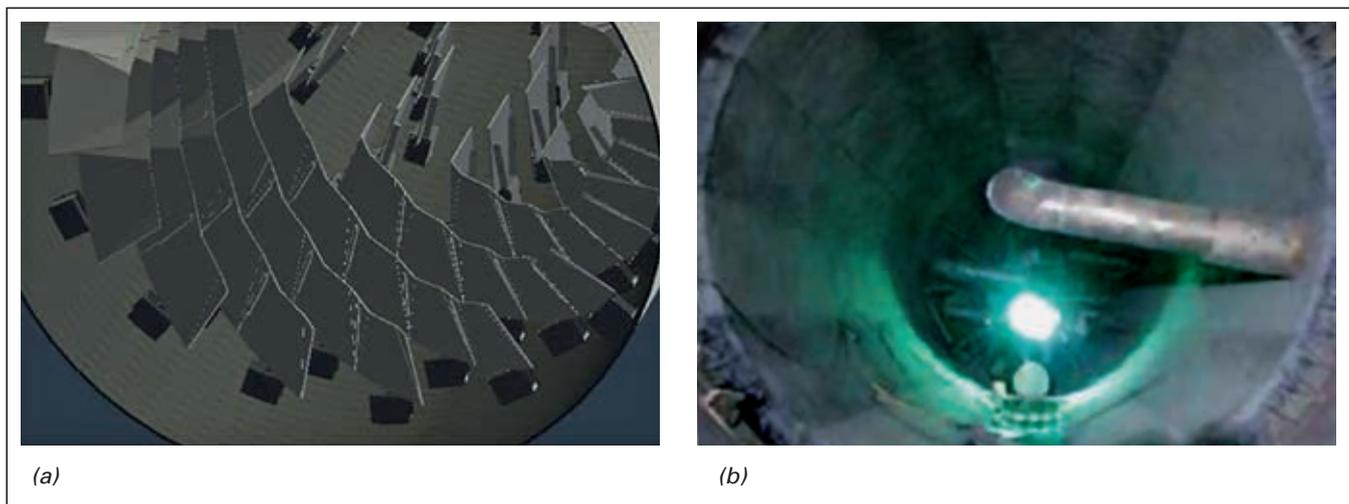
The inlet and outlet dams are both of monolithic nature. Due to the vast volume of the dam located near the kiln outlet, a brick design was considered to be more robust as it is less susceptible to premature damage induced by unforeseen events during the heat-up procedure especially in cases where the lining thickness exceeds 500 mm as it does in the dam area.

### Drying and Heating Zone—Installation of Low Cement Castables

Nowadays either monolithics or bricks are installed in the drying and heating zone, depending primarily on the kiln design and process parameters. However, bricks are not recommended for the inlet and outlet dam, and in areas of secondary air inlets and lifters as this would require excessive brick cutting efforts (Figure 14). Therefore, a monolithic lining was the preferred option in this case.



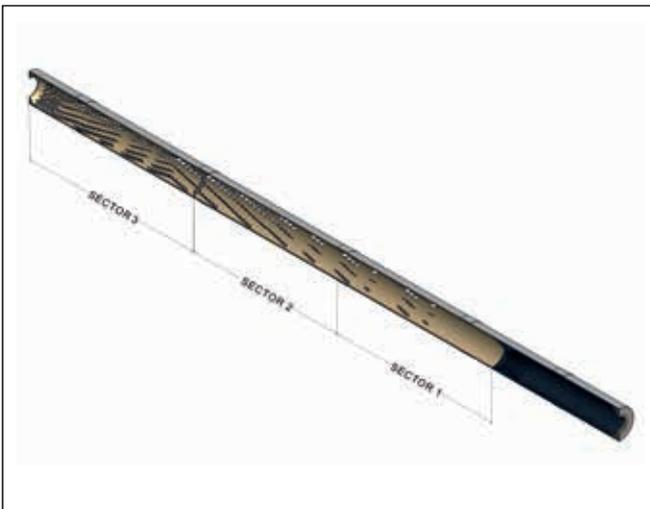
**Figure 13.** Comparison after 7 months of continuous operation showing (a) COMPAC SOL B88-6 and (b) low-cement castable.



**Figure 14.** Drying and heating section of the rotary kiln, showing (a) lifters and (b) secondary air inlet.

Prior to brick installation in the reduction zone, the casting process was launched in sector 1 (Figure 15) and proceeded towards the kiln inlet (sector 3). As soon as the castable installation in sector 3 was completed, refractory installation continued with bricking the reduction zone and concluded with casting the joint (0.8 m) between the monolithic and brick lining. Ideally, the overall time required for the complete relining should not be more than 22 days (dry-out and heat-up procedure not included).

Generally speaking, technical and economical trade-offs are fixed parameters in projects where large quantities of refractory materials are involved. Refractory castables are designed for high-temperature applications and develop their optimum mechanical properties at temperatures above 1000 °C. Consequently, kiln regions of lower temperatures (kiln inlet and drying zone) require special attention. For example, while conventional castables applied in low temperature zones do develop a certain strength, even at low-temperatures, when they contain a sufficiently high cement content, the higher cement content lowers the overall mechanical properties, in particular porosity resulting in a lower resistance to abrasion. Finally, based on technical and economical facts the preferred choice of refractory material in the drying and heating section was a low cement bonded castable.



**Figure 15.** Various rotary kiln sectors for monolithic installation.

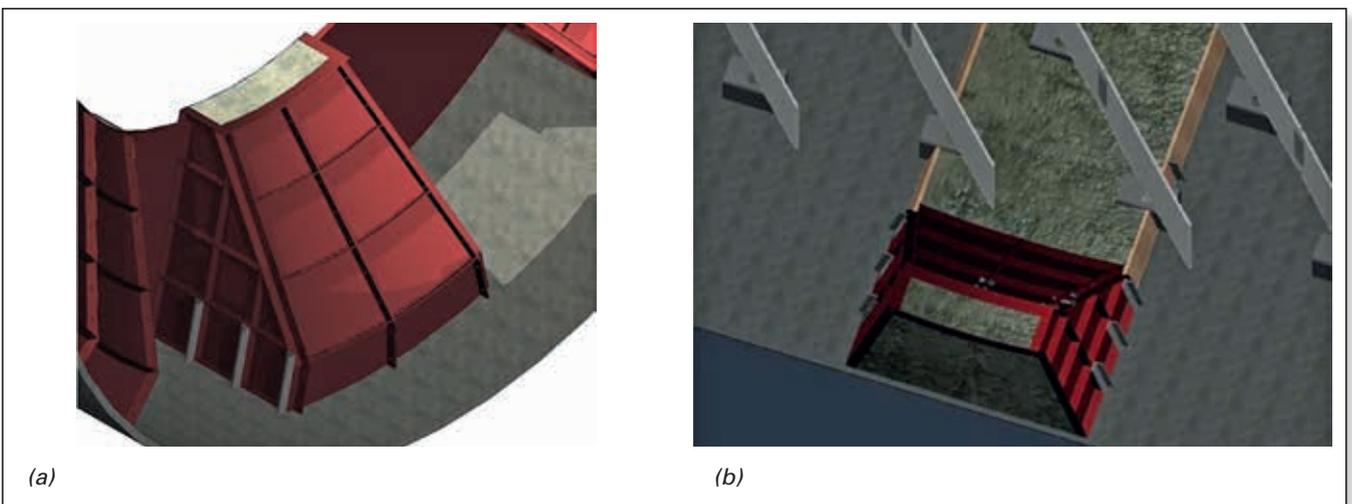
Using the installation procedure described in Project 1, the drying and heating zone was divided into 14 segments in the circumferential direction and each segment was further split into 20 sections in the longitudinal direction. This was partly determined by the high number and arrangement of lifters which, remained in place during the castable installation. The longitudinal and radial joints between each segment were of tongue and groove design and no additional expansion inserts were required. For the installation of the inlet and outlet dam, metal templates were designed according to Figure 16.

### Reduction Zone—Installation of High Alumina Bricks

Process temperatures towards the end of the reduction zone may reach up to 1250 °C, exposing the refractory material to severe thermo-mechanical stresses. Furthermore, substantial heat losses due to radiation from the kiln shell were found in the described zone. Therefore, importance needed to be placed on the insulating properties and lining thickness in order to optimize energy conservation while simultaneously ensuring kiln integrity for steel shell temperatures limited to 350 °C. Previously, high alumina bricks with a dense microstructure were used in the reduction zone but low-cement bonded and sol-based castables in conjunction with time-efficient installation techniques may supersede high-alumina bricks in the future.

Refractory bricks designed for the rotary kiln application are available in a large number of shapes and compositions. In general, their properties depend primarily on raw material grades, chemical and mineralogical composition, and manufacturing parameters. The type of refractory grade finally selected depends on the specific kiln and process parameters. In the design stage of the discussed project the suitability of three brick grades, shown in Table V, were closely examined from a technical and economical perspective. In principle, a suitable nonbasic brick (i.e., based on  $Al_2O_3$ ) for application in the reduction zone should exhibit the following characteristics:

- >> Excellent abrasion resistance.
- >> High temperature and thermal shock resistance.
- >> Adequate chemical resistance.
- >> Relatively low thermal conductivity.



**Figure 16.** Templates for the inlet and outlet dam (approximately 1.2 m dam height). Due to the dimensions of the dam a metal template was used.

	RESISTAL B50	RESISTAL SK65	RESISTAL B80
Raw material basis	Fireclay, bauxite	Andalusite, fused alumina	Bauxite
Al <sub>2</sub> O <sub>3</sub> (wt.%)	57	69	81
SiO <sub>2</sub> (wt.%)	39	29	13.0
Application temperature (°C)	1250	1450	1550
Bulk density at 1000 °C (g/cm <sup>3</sup> )	2.40	2.69	2.75
Porosity at 1000 °C (%)	18.0	13.0	20.5
Cold crushing strength (CCS) at 1000 °C (N/mm <sup>2</sup> )	40	110	70
Thermal conductivity at 1000 °C (W/mK)	3.0	2.2	2.5
Permanent linear change (PLC) at 1500 °C (%)	0.06	0.16	1.0
Thermal expansion at 1000 °C (%)	0.65	0.5	0.70
Abrasion (cm <sup>3</sup> )	30.0	9.0	16.0
CO resistance	D	A	B-C

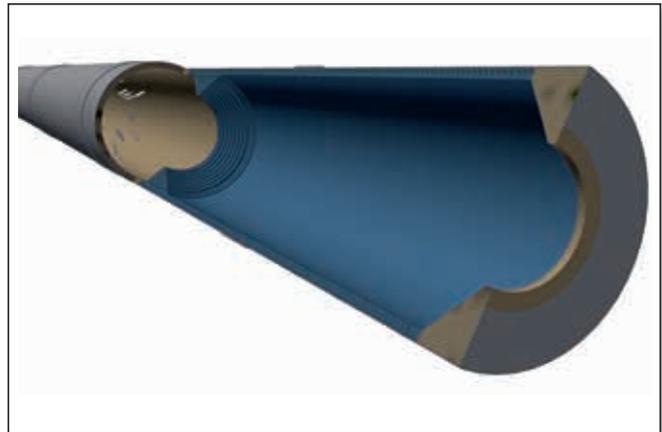
**Table V.** Comparison of brick properties showing the application temperature of nonbasic bricks rises with increasing Al<sub>2</sub>O<sub>3</sub> content.

In the reduction zone the temperature difference on the brick's hot face may fluctuate by more than 200 °C per revolution. The hot side temperature of the brick increases when exposed to the heat radiation of the burner flame and rapidly decreases when submerged below the calcine.

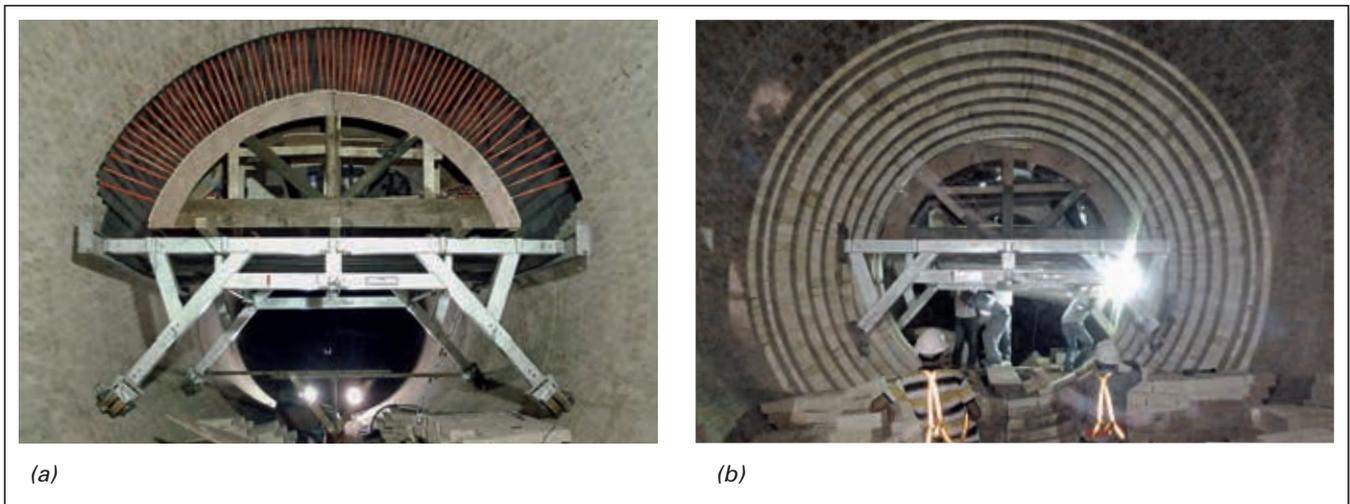
Where refractory lining and kiln shell are exposed to chemical attack, the permeability of the refractory brick becomes of great importance. The permeability is dependent on the porosity, such that the higher the porosity, the higher its permeability. Aggressive vapours and carbon monoxide containing kiln off-gases penetrate through the open pores of the refractory brick, resulting in a degenerated microstructure and eventually lead to partial brick fracture along the reaction zone. The phenomena also known as "brick spalling" will repeat at a reduced lining thickness in accordance with the new temperature gradient. Thus, to minimize lining degradation of this nature, the brick must be dense and exhibit low permeability in the kiln zone where aggressive process gases and liquid phases are present. Precautions also have to be taken with regard to the expansion/contraction of a brick lining, assuring that the stability of the lining is preserved throughout the kiln campaign. Moreover, the bricks must have insulating properties to keep the kiln shell temperature within acceptable limits and to reduce the overall heat loss of the kiln system.

Theoretical studies, practical experience, and economical considerations led to the conclusion that the brick grade RESISTAL SK65 would meet the required criteria.

The installation technique of RESISTAL SK65 bricks in the reduction zone, including the dam located near the kiln outlet, followed the pogo-stick/pneumatic jack method in combination with appropriate scaffoldings (Figures 17 and 18).



**Figure 17.** Kiln reduction zone including the dam entirely lined with high-alumina bricks.



**Figure 18.** Pogo-stick installation method as installed in (a) reduction zone, and (b) dam installation located near the kiln outlet.

For the present case, the pogo-stick method has two major advantages in comparison to other installation methods. On the one hand, the complete brick lining process can be achieved without the necessity to rotate the kiln, thereby protecting the castable lining from potential damage and on the other hand, the same set of sticks can be used for different ring diameters, thus becoming highly effective for the installation of the dam composed of several rings of varying diameters (Figure 18b). The brick section is entirely laid in independent rings, using only small amounts of mortar and steel sheets for a proper closure of each ring. With the participation of 30 skilled bricklayers the total installation was achieved in 9 days (2 shifts of 12 hours per day).

### Setting—Dry-Out—Heat-Up Schedule

The setting, dry-out, and heat-up schedule for combined refractory concepts composed of castables and bricks require a thorough evaluation of the core factors which determine a successful commissioning of the kiln. For a complete relining of the rotary kiln it is suggested to heat-up the kiln system by means of the main burner. Auxiliary burners may be used in specific areas which are difficult to access through the main burner, (i.e., the inlet and outlet hood). During the heat-up process the refractory lining as well as the steel shell must be inspected at regular intervals to ensure that the temperature profile strictly follows the supplier's recommendations and to detect local hot-spots in a timely manner. In cases where excessive kiln temperature is registered (especially in the reduction zone), the heat must be drawn upstream by increasing the draught.

The total amount of refractory castables and mortars installed contain large quantities of water that must be cautiously eliminated (Figure 19). Upon completion of the refractory installation (castables and bricks) the lining is maintained at ambient temperature for 24 hours to achieve acceptable castable strength determined by the bonding effect of hydrates. Free water starts to evaporate as soon as the temperature rises and the maximum evaporation rate is reached in the range of 100–150 °C. The initial temperature increase should be at the lowest possible rate to avoid the formation of a dense layer at the lining hot face and to promote maximum evaporation rate. After maintaining the temperature at 150 °C for 24 hours there is

still 20–25% of the initial water remaining in the monolithic lining. During the heat-up cycle, the remaining physical and chemically bonded water vaporises between 250–600 °C, depending on the types of hydrates formed during setting. Only a minor release of water takes place above 600 °C, allowing for a sharp increase in the heating rate until the average process temperature is reached. Any rotation of the kiln must be minimized during the first phases of setting and dry-out. As a general guideline, the refractory supplier provides a comprehensive heat-up manual but details need to be agreed with the OEM and FeNi producer especially in regards to kiln rotation intervals. In case of any interruptions to the heat-up process, the kiln must be cooled down in a controlled way, following a defined cool down curve.

Figure 19 illustrates a diagram of a properly designed dry-out and heat-up process for a combined refractory concept composed of castables and bricks. It should be noted, that in such a scenario the heat-up behaviour of the castable always prevails over the refractory brick and hence, castables are the governing factor with regard to the holding temperature/time and heating rate.

### Industrial Experience

A reliable performance of the refractory lining in each of the three sections had been reported by the customer and onsite temperature monitoring of the steel shell accurately agrees with predicted values. In the medium term, sol-bonded castables will be promoted for application in the reduction zone with the intention of shortening installation time and significantly reducing maintenance interventions.

### Engineering and Technical Services for FeNi Rotary Kilns

RHI provides a wide range of engineering and technical services to achieve optimised comprehensive solutions for its customers:

- >> Bill of materials (e.g., refractory materials, auxiliaries).
- >> Installation drawings and template design (3D).
- >> Metallic anchor design and positioning sketch.
- >> Thermodynamic modelling.
- >> Heat transfer calculations (energy conservation).

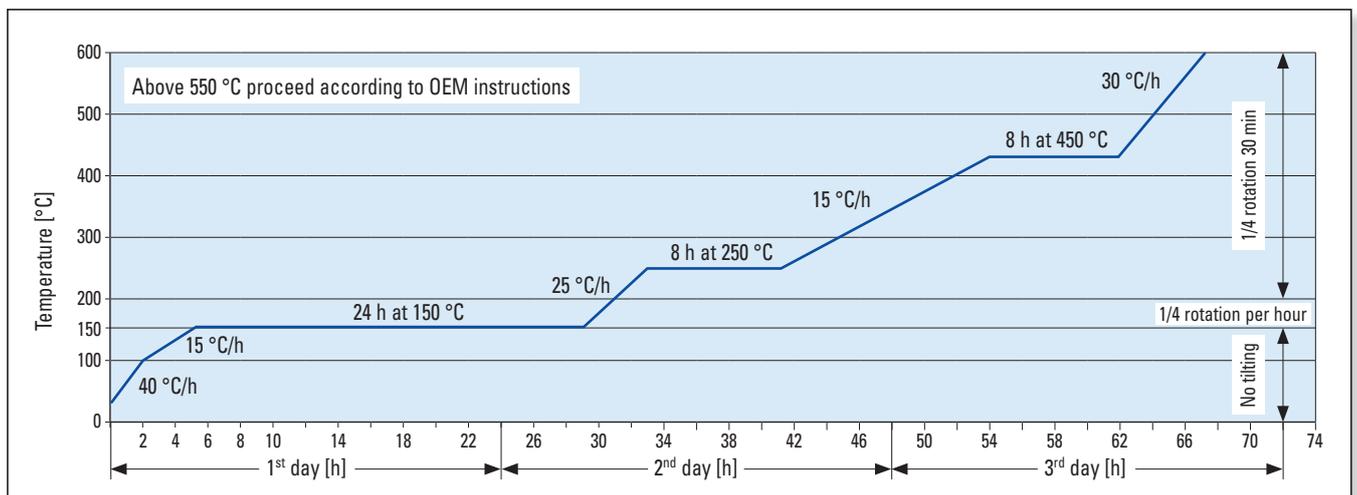


Figure 19. Combined dry-out and heat-up diagram for a complete relining composed of refractory castables and bricks.

- >> Expansion calculations.
- >> FEA simulations.
- >> Heat-up and cooling schedules for major and minor refractory maintenance.
- >> Installation manuals and chronograms (cooling–demolition–installation–heat-up).
- >> Onsite supervision.
- >> Project support (planning and execution) for minimizing installation time.
- >> RHI Training Center—kiln installation.
- >> Onsite ovality measurements of the kiln tyres.
- >> Qualitative measurements of the kiln distortion, determining the degree of deviation from the optimum alignment of the kiln end.
- >> Examination of the contact surfaces of the roller and tyre pairs.
- >> Examination of the roller pairs' behaviour, supporting the kiln tyres.
- >> Examination of the axial kiln movement.
- >> Analysis and presentation of the measurements supported by extensive reporting and data logs.

## Outlook

Based on the experience from industrial projects, further points for optimization of FeNi rotary kiln refractory linings were defined and will be pursued in the upcoming projects:

- >> Novel and innovative installation techniques for refractory castables.
- >> Steel shell expansion behaviour in conjunction with the monolithic lining.
- >> Time-saving potentials of the dry-out and heat-up schedule.
- >> Energy conservation (refractory insulation).

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## Authors

Christine Wenzl, RHI AG, Industrial Division, Vienna, Austria  
 Bernhard Handle, RHI AG, Industrial Division, Vienna, Austria  
 Daniel Meza, RHI AG, Industrial Division, Belo Horizonte, Brazil  
 Nestor Garcia, Technical Support RHI, Venezuela

**Corresponding author:** Christine Wenzl, christine.wenzl@rhi-ag.com

Johannes Brueck and Christina Stimpfl

# Alumina Mullite Bricks for Sulphur Recovery Applications

RHI decided to expand the product portfolio of the plus 90% mullite bonded alumina bricks in order to fulfil some of the most strict licenser requirements for hot face lining in the combustion chambers of sulphur recovery units. Typical failure modes of refractories, deformation behaviour, and especially the licensers requirements were the basis for further developments of the existing brand DURITAL E90. During product development, various tests, according to ASTM and EN standards, were used to compare and characterise the required hot properties. The results and conclusions of which brands fulfil specific requirements are summarised in the article below.

Sulphur recovery units are crucial process units in refinery operations as well as in gas plants for treatment of natural gas. In refineries the desulfurization of liquid fuels is done in the so called hydrotreating process. Middle distillates are treated with hydrogen in the presence of a catalyst to convert the sulphur in the sulphur containing hydrocarbons into hydrogen sulphide ( $H_2S$ ) at moderate temperatures of less than 400 °C. As  $H_2S$  is a highly poisonous gas it needs further processing.

In gas fields  $H_2S$  is naturally associated with methane. The  $H_2S$  is usually separated from the natural gas by adsorption or absorption technologies. The separated  $H_2S$  requires further treatment.

The most commonly used process to treat  $H_2S$  is the so called Claus process that allows the conversion of  $H_2S$  to elementary sulphur [1]. The modern Claus process utilizes a thermal reactor where the  $H_2S$  is substoichiometrically oxidized to  $SO_2$  (Equation 1) and leaving 2/3 of the  $H_2S$  non reacted. After cooling down the flue gases these two sulphur containing compounds are catalytically converted in a multi stage reactor system to elementary sulphur (Equation 2) with the resulting elementary sulphur being an easy manageable and sellable product.



Depending on the desired degree of  $H_2S$  conversion the off-gases from the catalytic reactors are either sent to an incinerator or are further processed in a tail gas treatment unit providing a higher overall yield of sulphur recovery.

With regard to refractories the thermal reactor is the key equipment in a sulphur recovery unit (Figure 1). These horizontal combustion chambers are operated at temperatures between 1150–1450 °C with the units in the gas fields typically operating at lower temperatures and the units in refinery service at higher temperatures. The higher temperatures in refineries are due to additional compounds with caloric content that are fed into the thermal reactor.

In some cases the refineries also switched to oxygen enriched air as oxidizing medium to increase the capacity by reducing the nitrogen ballast in the system. This leads to higher operation temperatures, which can, depending on the oxygen enrichment, be even higher than the temperatures indicated before.

Even though these design operating temperatures can still be regarded as moderate, refractory damages can be observed in such thermal reactors quite frequently. Typical damages seen are deformation, excessive thermal expansion or even melting of the hot face surfaces caused by exposure to elevated temperatures.

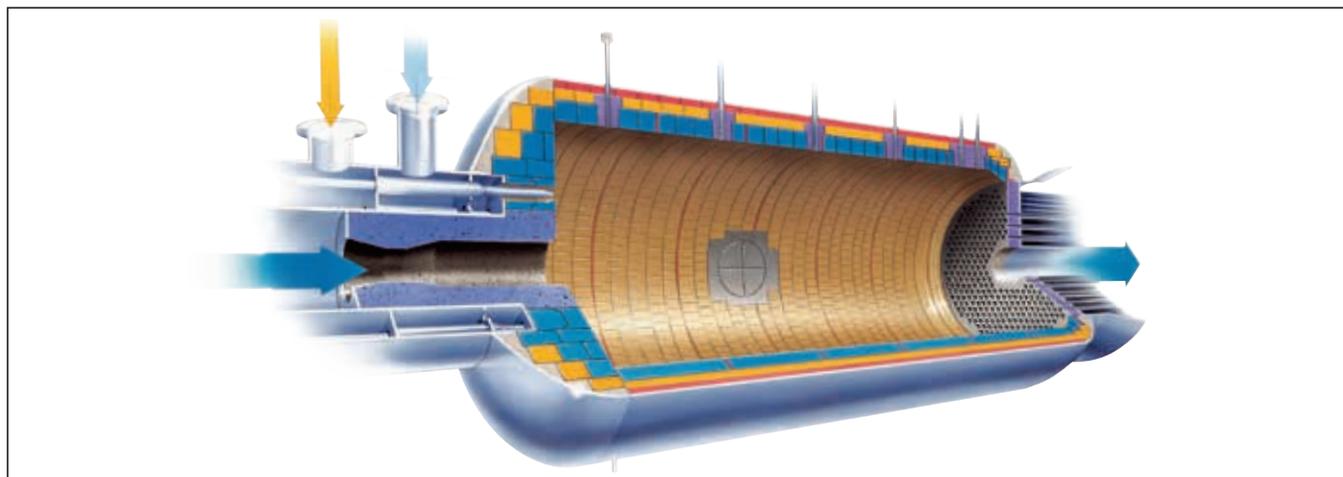


Figure 1. Typical thermal reactor design.

To avoid such “temperature phenomenon” the ratio of oxygen and fuel has to be controlled carefully. When the air flow approaches stoichiometric combustion conditions the flame temperature will increase to extreme high temperatures. Such a deviation from the design oxygen/fuel ratio mainly occurs during heat up, in hot standby or during cofiring when the unit is operated partly or fully with other high caloric fuels available in the refinery/gas field.

For this reason refractory materials not only need to withstand chemical attack of sulphur containing compounds, they also must be resistant to thermal shock. In particular the hot face material has to be adapted to withstand high temperatures and provide excellent hot properties thereby also providing long term durability when operated at lower temperatures [2].

This results in the requirement for an accurate investigation of the hot properties, in particular the deformation behaviour and the melting behaviour of bricks. The melting of bricks has to be considered to occur in a certain temperature range, because a heterogeneous multicomponent system never has a distinct single melting temperature [2]. This means that in this temperature range the microstructure of the brick gradually breaks up and viscosity decreases [2]. Bricks begin to melt, to deform, and change their geometry when entering into this temperature range (Figure 2). Therefore the softening temperature of bricks is determined via measuring its deformation. The deformation of the ceramic material in this temperature range of softening is particularly dependent on temperature, applied load, exposed time, and the atmosphere (e.g., oxidizing, neutral or reducing).

The deformation is further dependent on the volume and structure of pores, the amount of glassy phases in the

refractory, sizes of crystallites and the formation of crystals. At room temperature refractories show a brittle-elastic behaviour, at elevated temperatures plastic deformation and viscous flow occurs under constant load [2].

For characterization of the plastic deformation the method of creep under load (according to either ASTM C832 or DIN EN 993-9) can be applied [3, 4]. With these standard methods the deformation behaviour of refractory materials at a constant pressure load and constant temperature is observed over a specified period of time. Thus the operational demands can be simulated in the test. A cylindrical or cubic specimen is heated to a specified test temperature according to defined heating conditions and under constant load. The temperature is kept constant for a defined period of time. During the test run the change in height of the specimen as a function of time is recorded [3].

Another test method for describing hot properties and deformation behaviour of refractories is the ASTM C 16-03 “Standard Test Method for Load Testing Refractory Shapes at High Temperatures” or often simply referred to as hot load testing. The test describes the measurement of the deformation of rectangular bricks in direction of the applied constant load at an elevated temperature for a defined soak time [5]. The standard requires soak time of 90 min at test temperature. The applied load is defined to be 0.172 MPa. The result is reported as the average deformation of two samples derived from dimensional measurements taken on the “cold” specimen before and after testing [5].

Deviating from the ASTM C16-03 standard some modified licensor requirements are requesting extended soak times as long as 25 hours, 50 hours, or 100 hours at the highest scheduled temperature of 1650 °C (Table I).

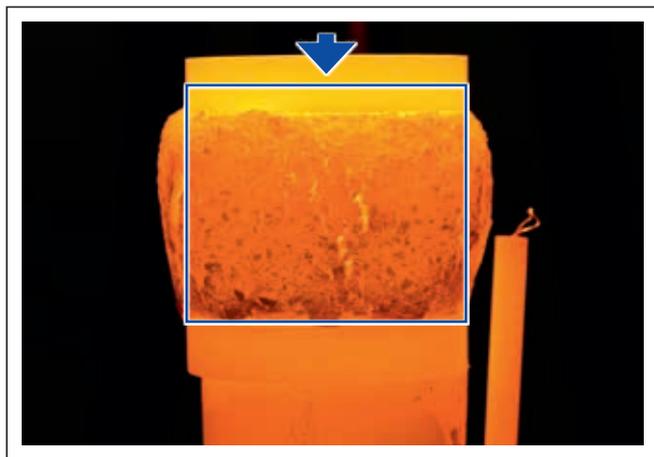


Figure 2. Plastic deformation of a specimen under load at elevated temperature.

In order to minimize the risk of potential damages of the hot face lining due to overheating the process licensors require high alumina bricks with typically more than 90% alumina content and with excellent hot properties. The lining design temperature is usually specified to be in the order of 1700 °C even if the normal operation temperature is well below. For the definition of the hot properties, the hot load deformation according to ASTM C16-03 hot load testing is referred to in most of the American licensor specifications. The ASTM C16-03 standard is assumed to be preferably used by the licensors as the definition of acceptance of the criterion is defined as single value of a maximum allowable deformation. While the creep test results in a graph showing the deformation as a function of time the ASTM C16-03 hot load test provides just one figure as a result. The licensor specifications obviously prefer to deal with such a singular, easy to be defined, criterion.

Licensor/engineering/user criteria	Testing after ASTM C16 schedule:	Testing after ASTM C16 soak time:	Maximal required deformation:	RHI Brands recommendation:
Licensor 1	Schedule 7	90 min	-/+ 0.5%	DURITAL E90
Licensor 2	Schedule 7	25 h	-0.5%	DURITAL E92
Licensor 3	Schedule 7	50 h	-0.5%	DURITAL E92
Licensor 4	Schedule 7	100 h	-0.4%	DURITAL E92 EXTRA

Table I. Licensor requirements for hot load test results for hot face bricks.

These specifications with the strict acceptance criteria for the hot face bricks is also driven by another remarkable trend seen over last couple of years, the thermal reactor vessels are getting much larger. In gas fields the internal diameter of some units have already exceeded five meters. The required long term stability and integrity of the lining is to be ensured by the selection of refractory material with superior hot properties.

In order to fulfil these strict criteria for the hot properties with various side requirements for example chemical composition, RHI decided to extend the product portfolio in the plus 90% alumina brick range for sulphur recovery unit (SRU) applications. While the RHI standard product DURITAL E90 provides extraordinary thermal shock resistance, the results of the hot load testing showed compliance with the requirement defined by licensor one only (Table I). Despite excellent records and many references for Claus burner systems and the large scale thermal reactors lined with DURITAL E90 the more strict hot load criteria of licensors 2, 3, and 4 can only be fulfilled by new developed bricks with higher Al<sub>2</sub>O<sub>3</sub> content—DURITAL E92 and DURITAL E92 EXTRA.

Starting the development based on the DURITAL E90 brick system the alumina content was increased to 92% to better fit into specifications of various licensors. Adaption of the recipes and the processing parameters resulted in the

development of DURITAL E92. Many external laboratory ASTM C16-03 tests would have been required to compare the improved hot properties with the specification requirements during development. As RHI possesses several apparatus for measuring creep under load the focus was set on testing creep under load according ASTM C832 and EN 993-9 standards (Figure 3). Investigations according the ASTM C16-03 hot load testing were outsourced to third parties and only used for benchmarking during the development phase.

As a first result the newly developed DURITAL E92 fulfilled the criteria for the ASTM hot load test of licensor 2 and 3 in a well reproducible manner. However, a reliable compliance with the strictest criteria of licensor 4 required some further improvements on the DURITAL E92 brick and finally resulted in the decision to have it included into the RHI product portfolio as a separate high end grade—DURITAL E92 EXTRA.

In Table II the results of the creep under load tests are summarized for Z<sub>50</sub> (period 0 to 50 hours) and the creep Z<sub>20-50</sub> (between hour 20 and hour 50 of the test run).

Table III shows the results of the ASTM C16-03 hot load tests at 1650 °C performed on the grades DURITAL E90, DURITAL E92, and DURITAL E92 EXTRA.

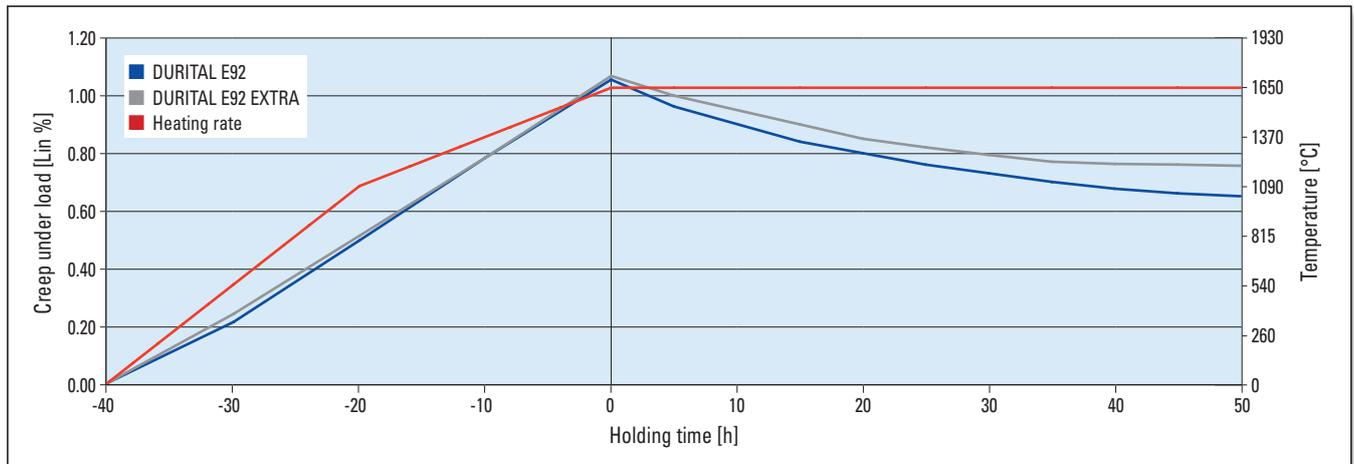


Figure 3. Shows the typical creep under load curves as derived on DURITAL E92 and DURITAL E92 EXTRA during creep testing according to ASTM C832 performed at 1650 °C.

RHI Brand	Temperature	Pressure	T <sub>0</sub>	Z <sub>50</sub>	Z <sub>20-50</sub>	Standard
DURITAL E92	1650 °C	0.172 MPa	1632 °C	-0.40%	-0.15%	ASTM C832
DURITAL E92 EXTRA	1650 °C	0.172 MPa	1638 °C	-0.30%	-0.10%	ASTM C832

Table II. Technical data of alumina silica bricks tested according to ASTM C832-00 standard.

RHI Brand	Standard	Soak time at test temperature:	Temperature schedules for heat up:	Testing temperature	Pressure	Change in length after testing:
DURITAL E90	ASTM C16-03	90 min	Schedule 7	1650 °C	0.172 MPa	-0.50%
DURITAL E92	ASTM C16-03	50 h	Schedule 7	1650 °C	0.172 MPa	-0.32%
DURITAL E92 EXTRA	ASTM C16-03	50 h	Schedule 7	1650 °C	0.172 MPa	-0.26%
DURITAL E92 EXTRA	ASTM C16-03	100 h	Schedule 7	1650 °C	0.172 MPa	-0.32%

Table III. Technical data of alumina silica bricks tested according to ASTM C16-03 standard.

The comparison of the results of hot load testing according to ASTM C16-03 and the creep under load testing according to ASTM C832 shows that the results are qualitatively consistent even though there is no quantitative correlation possible between creep under load and hot load testing. However the measurement of creep under load can be regarded as a useful tool for the development and improvement of alumina mullite based bricks aiming also to fulfil the strict criteria for ASTM C16-03.

It should be noted that to achieve the reproducibility in the hot property criteria a very narrow control of various production parameters in the plant is required. As such the production of DURITAL E92 and DURITAL E92 EXTRA is limited to a single production facility in Germany. In addition to the strict control of production parameters, frequent creep tests are utilised in the production quality control plan to ensure compliance with licensor specifications.

## Summary

In order to provide an adequate solution to the large variety of licensor specification and customer requirements for high alumina bricks for sulphur recovery units, RHI expanded the product portfolio of alumina mullite bricks to total three different grades. The focus was to achieve the

hot properties specified by the licensors and to fulfil further requirements regarding the chemical composition and other physical properties such as strength.

All three RHI grades of the DURITAL alumina mullite bricks (DURITAL E90, DURITAL E92 and DURITAL E92 EXTRA) are characterized by good to excellent thermal shock resistance and low thermal expansion. All three brands combine typical properties of mullite and corundum bricks such as high mechanical strength and high volume stability. Typical for these bricks is the quantitative formation of mullite from alumina and silica containing raw materials by firing the bricks at temperatures significantly higher than 1600 °C.

DURITAL E90 is a standard product with excellent thermal shock resistance and long term successful application in thermal reactors and Claus burners. DURITAL E92 and DURITAL E92 EXTRA are further developments with focus on hot properties and are fulfilling even the most strict acceptance criteria in a reproducible manner. Both grades can be regarded as being among the very few brands available on the market which comply with the most strict licensor requirements in the world. Several installations of DURITAL E92 made during the last two years are still successfully in service.

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## Authors

Johannes Brueck, RHI AG, Industrial Division, Wiesbaden, Germany  
Christina Stimpfl, RHI AG, Technology Center, Leoben, Austria

**Corresponding author:** Johannes Brueck, [johannes.brueck@rhi-ag.com](mailto:johannes.brueck@rhi-ag.com)

Dean Gregurek, Christian Majcenovic, Katja Reinharter, Viktoria Reiter, Christine Wenzl, Alfred Spanring, and Harald Harmuth

# Investigation of Magnesia Chromite Brick Wear Phenomena—Post Mortem Analysis From a Lead Recycling Furnace

The present work describes a detailed post mortem analysis of a used silicate-bonded magnesia chromite brick from a lead recycling furnace. It was carried out to evaluate wear parameters influencing the refractory performance in the respective furnace. The main wear factor was chemical attack by process slag, namely silicate slag containing CaO, BaO, and sulphur, as well as high amounts of Na<sub>2</sub>O from soda addition. This slag caused not only a deep infiltration of the brick microstructure, but also severe corrosion of the brick components, namely magnesia and chromite. FactSage™ calculations showed the formation of various Na-Ca-Al-silicates and high amounts of liquid phase in the infiltrated microstructure. The obtained information and insights serve as a basis for optimization of refractory materials (i.e., refractory selection for individual processes and new developments) and consequently furnace operations (i.e., prolonged furnace campaigns).

## Introduction

Post mortem studies provide a precise understanding of the wear parameters influencing refractory performance in pyrometallurgical furnaces [1].

In the nonferrous metals industry, particularly in secondary lead smelting furnaces, the refractory lining is mainly based on magnesia chromite bricks, which are exposed to complex wear caused by combined chemical, thermal, and mechanical stresses [2–4].

An overview of wear phenomena in lead processing furnaces and corresponding refractory corrosion testing is given in several papers [5–8]. The present study describes a detailed refractory wear analysis of a used magnesia chromite brick from a lead recycling furnace. The mineralogical findings and chemical analyses were supported by thermodynamic calculations using the software FactSage™.

Lead is one of the metals with the highest recycling rate worldwide, therefore, the importance of secondary lead production, namely recycling, has increased in the previous years [9]. The amount of secondary production has already surpassed that of primary production. Various furnace types can be used for lead recycling, for example the short rotary furnace (SRF), reverberatory furnace, top submerged lance reactor (TSL), and top blown rotary converter (TBRC). Despite the different furnace types, the metallurgical process of lead recycling is basically identical. The most important recycling material and hence input material for secondary lead smelters are lead batteries. In preparation for lead recovery, the used batteries undergo separation and pre-treatment steps to separate the battery components into the different material fractions. Lead recycling therefore deals not only with metallic lead (battery grids), but also with lead components (e.g., sulfates and oxides) that require correct metallurgical processing. Additionally, other lead-containing residues (e.g., slags from other metal production processes)

may be used in the recycling process, leading to varying input compositions that may require process adaptations. The slags used in secondary lead production are generally based on the system FeO<sub>x</sub>-SiO<sub>2</sub>-CaO, also the use of soda as slag additive is common practice. Many smelters also use a combination of different slag types, namely FeO<sub>x</sub>-SiO<sub>2</sub>-slag and soda slag in separate process stages [10–13].

As the lead processes are carried out at temperatures far higher than the lead melting temperature (327 °C), namely around 1000 °C and higher to achieve a liquid slag, the overheated metallic lead and resulting low viscosity causes deep-reaching infiltration into the refractory lining. This causes changes in thermal properties, which are of special importance in batch processes that comprise repeated heating and cooling cycles of the furnace. Additionally, the slags cause chemical attack on the basic magnesia chromite bricks, especially in the case of high SiO<sub>2</sub> loads, namely more acidic slags. Although soda slags are very efficient from a metallurgical point of view, they lead to refractory wear by both alkali and sulphur attack. Furthermore, the mechanical wear factors play an important role in refractory life, especially in rotating furnace types, but also due to liquid flows, for example during tapping operations. Generally, lead recyclers are (and need to be) flexible when it comes to varying input and adjusting the process, however as it is not possible to change the furnace lining with every input material variation, the refractory must deal with these process variations. Therefore, metallurgical process knowledge is a vital factor for initial refractory selection and, if required, lining adjustments.

## Results and Discussion

### *Macroscopical Appearance*

The investigated refractory product represents a silicate bonded magnesia chromite brick of type MCr60 (ISO 10081-2), which is based on magnesia and chromite. The residual brick thickness was 200 mm after six months (Figure 1). The original brick thickness was 390 mm. The immediate brick hot face

is covered with a thin slag coating. The macroscopic observation of the cross section shows that visible infiltration (pore infiltration predominantly by slag, but also metal) extends to the brick cold face. At varying distances from the hot face, cracks propagating parallel to the hot face and partly filled with metallic lead and slag can be observed.

### Chemical Analysis

Generally, in lead recycling furnaces the low-melting, partly alkali-rich silicatic slag is able to penetrate deeply into the brick microstructure [8]. The silica-rich slag and the reaction products formed by the corrosion of the brick structure extend up to the cold face. This is significant compared to slag attack and infiltration in copper furnaces, where the infiltration depth is just a few mm from the hot face [8].

Table I shows the chemical composition of a deeply infiltrated magnesia chromite brick. According to the chemical analysis, in the first 110 mm from the hot face a high sodium and silica content was determined. Nevertheless, the highest concentrations of  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{BaO}$ , in some areas also  $\text{CaO}$ , were confirmed to be located in the first 20 mm from the hot face. Sulphur could be detected over the entire

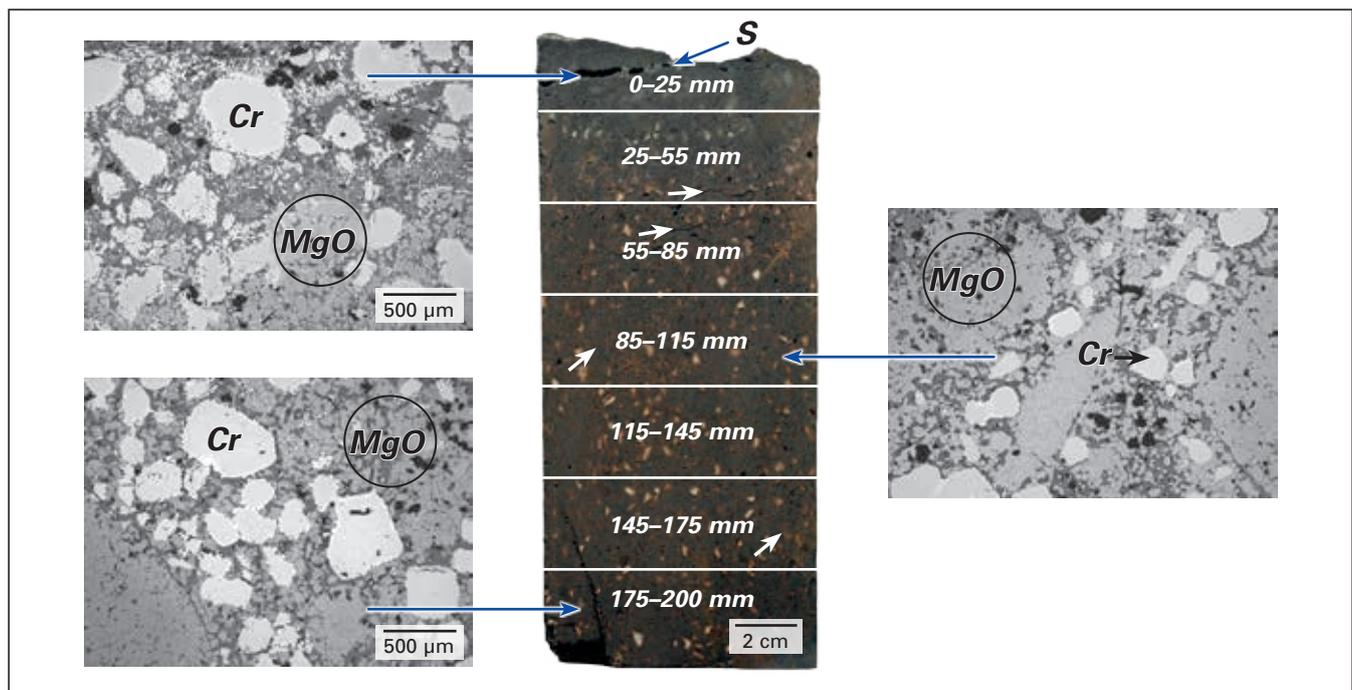
sample with a maximum in the middle section. Some minor phosphorous and lead content could also be identified.

### Mineralogical Investigation

For mineralogical investigation several polished sections were prepared (marked areas in Figure 1). On microscopic scale, some significant microstructural changes were detected and can be summarized as follows:

The immediate brick hot face shows a 2 mm thin reaction zone consisting of different Na-Ca-Mg-Fe-silicates with varying contents of barium, aluminium, phosphorous, and lead. The magnesia component is completely dissolved leaving relics of primary and secondary chromite precipitations (Figure 2a).

Below the reaction zone and across the whole polished section there is a pore-filling infiltration and corrosion of the brick microstructure (Figure 2 b). At least for the first slag/refractory contact, the kinetics of slag infiltration depends on several parameters such as viscosity, pore size distribution, and wetting angle [8]. Slag percolates into the refractory microstructure filling the pore space. In a standard situation the wear rate is lower than the possible rate of slag



**Figure 1.** Cross sectional view. Magnesia chromite brick from a lead secondary recycling furnace. The residual brick thickness is 200 mm. The immediate brick hot face is covered with a thin slag coating (S). Crack formation (arrows). Enlarged images are polished sections for mineralogical investigation of segments over the brick thickness. These show the microstructural overview of degenerated and corroded brick microstructure (enlarged images). Magnesia (MgO) and chromite (Cr).

Sample	$\text{Na}_2\text{O}$ (wt.%)	$\text{MgO}$ (wt.%)	$\text{Al}_2\text{O}_3$ (wt.%)	$\text{SiO}_2$ (wt.%)	$\text{P}_2\text{O}_5$ (wt.%)	$\text{SO}_3^{1)}$ (wt.%)	$\text{CaO}$ (wt.%)	$\text{TiO}_2$ (wt.%)	$\text{Cr}_2\text{O}_3$ (wt.%)	$\text{MnO}$ (wt.%)	$\text{Fe}_2\text{O}_3^{2)}$ (wt.%)	$\text{BaO}$ (wt.%)	$\text{PbO}$ (wt.%)
Hot face (0–25 mm) <sup>3)</sup>	9.0	47.0	5.0	10.0	0.8	2.0	2.0	0.3	11.0		9.0	2.0	0.8
Middle section (90–110 mm) <sup>3)</sup>	9.0	55.0	4.0	3.0	0.5	7.0	1.0	0.2	12.0		8.0	0.4	
Cold face (180–200 mm) <sup>3)</sup>	0.9	55.0	6.0	2.0	0.1	0.3	1.0	0.3	21.0	0.1	13.0	0.2	
Unused brick <sup>4)</sup>		60.4	6.3	1.8			1.1		19.0		12.0		

1) Sulfur analyzed as  $\text{SO}_3$

2) Total iron analyzed as  $\text{Fe}_2\text{O}_3$

3) Standardless semi quantitative X-Ray Fluorescence analysis

4) On ignited sample (1050 °C) by X-Ray Fluorescence Analysis

**Table I.** Chemical analysis of the magnesia chromite brick from the lead secondary recycling furnace (wt.%).

infiltration. Therefore, for a wetting angle of less than  $90^\circ$ , the infiltration depth proceeds to the lowest invariant point. This means that it is limited by the temperature gradient. Due to the temperature gradient slag will crystallize during percolation, the melt will reach regions of lower temperature until it solidifies totally at the lowest invariant point. Due to the partial crystallisation and the percolation of the residual melt to regions of lower temperature slag will not be in equilibrium. With proceeding wear of the brick, the temperature profile and therefore also the final invariant point will further shift outwards (towards the cold face). Diffusion may occur due to three reasons: one is due to the disequilibrium already mentioned. Another, more critical criteria is the particle size dependence of solubility. While the infiltrate is mainly saturated in the refractory components, this saturation limit depends on particle size and is governed by the Gibbs Thomson equation:

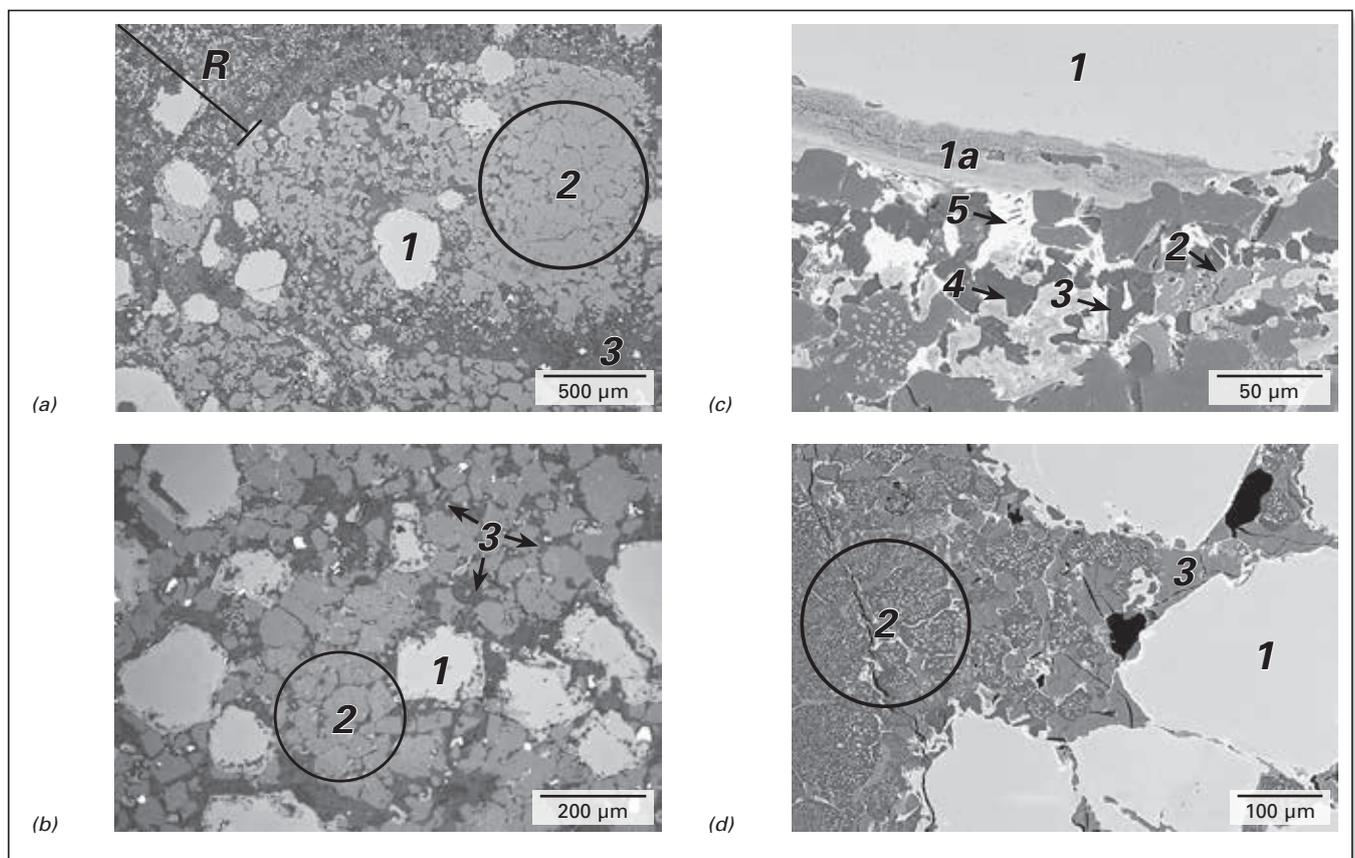
$$\frac{c - c_0}{c_0} = \frac{2\gamma_{s,l} \cdot V_M}{R \cdot T \cdot r} \quad (1)$$

Here  $c$  and  $c_0$  are the concentrations in equilibrium with a spherical surface of radius  $r$  and with a flat surface, respectively. Further  $\gamma_{s,l}$  is the solid/liquid interface energy,  $V_M$  is the molar volume of the dissolved species,  $T$  is the kelvin temperature and  $R$  the universal gas constant. The numerator on the left side of above equation gives the concentration difference which acts as the driving force of diffusion according to Fick's first law [14]. This corrodes the refractory bond which is composed of the fines. Unfortunately

this process never stops. Thirdly diffusion is caused by equilibration of the infiltrate with the liquid slag. This is only relevant close to the hot face, where diffusion paths are short enough. This means that corrosion is not limited to the very hot face only, or in other words, the hot face prone to corrosion is not an exact surface but rather a zone close to the refractory hot face. According to Figures 1 and 2, taking into account the profiles of silica and magnesia, diffusion between the infiltrate and the slag shows a significant contribution to the mass transfer in the of the first 20 to 30 mm only.

Due to the corrosion of the magnesia, the main reaction products are the Mg-silicate forsterite ( $\text{Mg}_2\text{SiO}_4$ ) slightly enriched with CaO, the Ca-Mg-silicate monticellite ( $\text{CaMgSiO}_4$ ) and a Na-Ca-Mg-Fe-Al-silicate (Figure 2c). A phosphorous and lead rich Na-Mg-Ca-Ba-silicate could be identified with the scanning electron microscope. Corrosion of magnesia and of the interstitial phases between the MgO grains can be detected up to a depth of approximately 90–100 mm from the hot face. Additionally, primary and secondary chromite precipitations which are typical for this brick brand, are not present close to the hot face. At some distance, as shown in Figure 2d, secondary spinel precipitations are observed.

As can be seen in Figure 3, in the infiltrated brick microstructure (e.g., 30–200 mm from the hot face) the chromite rims are strongly depleted in  $\text{Cr}_2\text{O}_3$ . The corrosion of chromite was obviously caused by high sodium supply, namely



**Figure 2.** Photomicrographs at varying distances from the hot face. Showing (a) 2 mm thin reaction zone ( $R$ ) at the immediate brick hot face. Chromite (1), corroded magnesia (2), infiltrate (3). (b) Infiltrated and corroded brick microstructure. Approximately 5 mm from hot face. Corroded chromite (1) and magnesia (2), infiltrate (3). (c) Infiltrated and corroded brick microstructure. Approximately 30 mm from hot face. Corroded chromite (1) with rims strongly depleted in Cr-oxide (1a). Main reaction products are monticellite (2), Na-Ca-Mg-Fe-Al-silicate (3), forsterite enriched with CaO (4) and phosphorous and lead rich Na-Mg-Ca-Ba-silicate (5). (d) Infiltrated brick microstructure. Approximately 150 mm from hot face. Chromite (1), corroded sintered magnesia (2), pores filled with barium-enriched Na-Ca-Cr-sulfate (3).

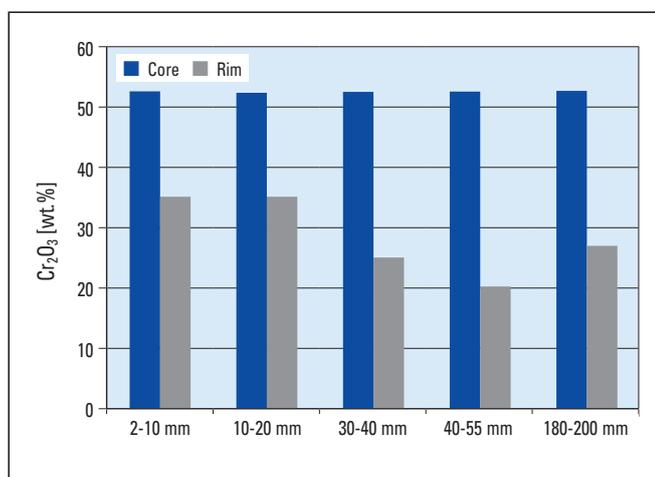
a surplus of sodium not saturated by sulphur. The dissolved chromium was then transported by a Na-Ca-Cr-sulphate phase towards the brick cold face (Figure 2d).

### FactSage™ Calculations

Thermochemical calculations were performed for the slag penetrated brick, with a focus on the phase composition and the amount of liquid phase at both the hot face and within the infiltrated brick microstructure (0–25, 25–55 and 175–200 mm, Figure 4). The software package FactSage™ 6.3 with the databases FactPS, FToxide, and FTmisc were used for these calculations. The calculations were performed with the average chemical analysis determined by SEM-EDX analysis. The following oxides were incorporated in the calculations: Na<sub>2</sub>O, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, CaO, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. Phosphorus and barium oxide were neglected. The phase composition was described for a temperature range of 700–1200 °C.

The calculated main phases of the unused brick are monoxide (Mg,Ca,Fe)O and spinel (Mg,Fe)(Fe,Al,Cr)<sub>2</sub>O<sub>4</sub>, additional olivine ((Mg,Ca,Fe)<sub>2</sub>SiO<sub>4</sub>) appears in minor amounts. The phase composition as a function of the temperature based on the chemical composition of the hot face and zones 25–55 and 175–200 mm from the hot face, respectively, are shown in Figure 4. The thermodynamically stable reaction phases are a sodium-calcium silicate named N<sub>2</sub>CS<sub>3</sub> [(Na<sub>2</sub>,Ca)Na<sub>2</sub>CaSi<sub>3</sub>O<sub>9</sub>], a phase named NAS (solid solution of NaAlO<sub>2</sub>–NaAlSiO<sub>4</sub>) and Na<sub>2</sub>SiO<sub>3</sub> (0–25 and 25–55 mm from hot face). At an infiltration depth of 25–55 and 175–200 mm Na<sub>2</sub>SO<sub>4</sub> is also stable. At the hot face a high amount of liquid phase (70 wt.%) is present at 1000 °C. With increasing infiltration depth the amount of liquid phase decreases and the solidus temperature increases. At 1000 °C, the amount of liquid phase is 25 wt.% at an infiltration depth of 0–25 mm and decreases to 6 wt.% at an infiltration depth of 175–200 mm.

The thermodynamic calculations show a good correlation with the mineralogical investigations, namely that olivine (forsterite) and different types of Na-silicates (Na-Al-silicate, Na-silicate, Na-Ca-silicates) are the stable phases near the

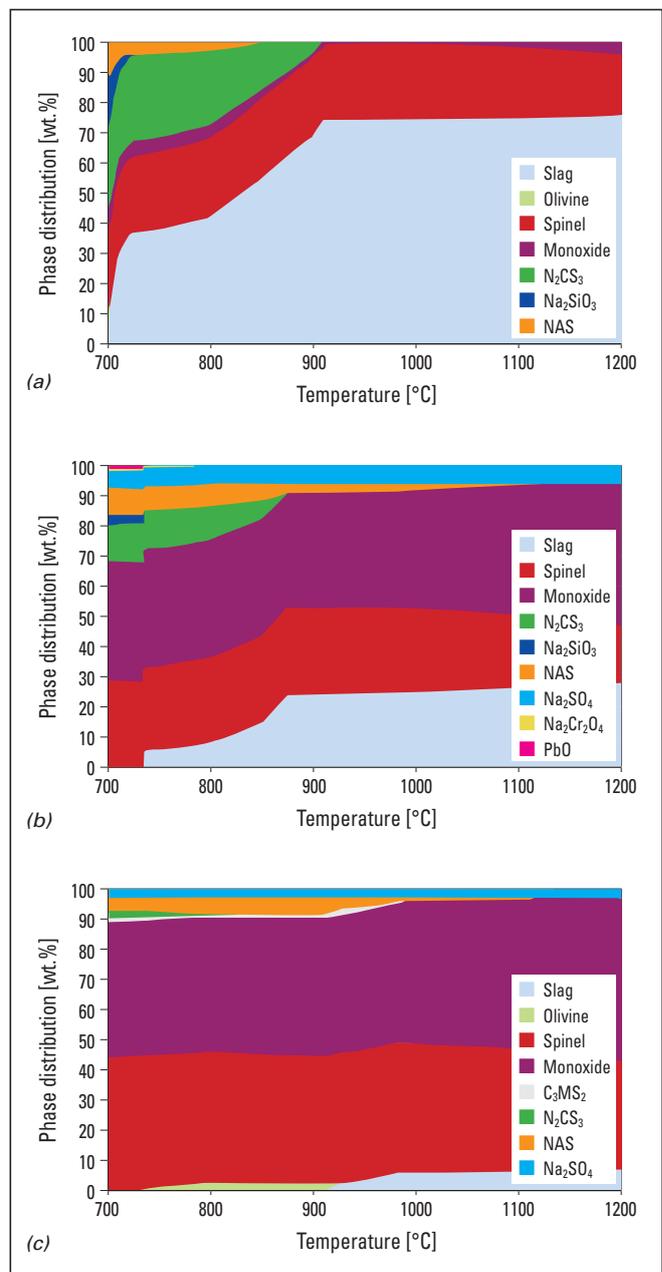


**Figure 3.** Chemical composition of Cr<sub>2</sub>O<sub>3</sub> in chromite core and rims. Towards the brick cold face the chromite rims are strongly depleted in Cr<sub>2</sub>O<sub>3</sub>.

hot face. At an infiltration depth of 25–55 mm and 175–200 mm additionally sodium sulphate is stable. Further incorporation of chromium and calcium in the sodium sulphate melt, that was found in the mineralogical investigations cannot be described due to the lack of thermodynamic data. The spinel volume in the infiltrated brick areas conforms to the mineralogical investigation of the magnesia and chromite corrosion in the previous section.

### Conclusions

The post mortem study showed that the main wear factor of the investigated silicate bonded magnesia chromite brick from the lead recycling furnace is chemical attack due to the process slag (i.e., silicatic slag with high content of Na<sub>2</sub>O supplied by soda, as well as CaO, BaO, and sulphur, as further constituents).



**Figure 4.** Phase distribution according to temperature as calculated with FactSage for reducing conditions. (a) Hot face. 0–25 mm depth. (b) Hot face. 25–55 mm depth. (c) Cold face. 175–200 mm depth. Meaning of abbreviations [(Na<sub>2</sub>,Ca)Na<sub>2</sub>CaSi<sub>3</sub>O<sub>9</sub>] N<sub>2</sub>CS<sub>3</sub>, [NaAlO<sub>2</sub>–NaAlSiO<sub>4</sub>] NAS, [Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>] C<sub>3</sub>MS<sub>2</sub>, [(Mg,Fe,Ca)O] monoxide, [(Mg,Ca,Fe)<sub>2</sub>SiO<sub>4</sub>] olivine, [(Mg,Fe)(Al,Fe,Cr)<sub>2</sub>O<sub>4</sub>] spinel.

The following two main phenomena were observed:

- >> Deep-reaching infiltration and corrosion of the brick microstructure, namely both the magnesia and the chromite.
- >> Corrosion of the chromite and interstitial phase both within and between the magnesia grains occurred, due to a high soda supply and a surplus of sodium (sodium is not saturated by sulphur).

Dissolution of the ceramic bonds, leading to later erosion, is not limited to the hot face due to the high infiltration depth of the slag. All above mentioned processes contribute to this. Additionally even in an apparently saturated infiltrate dissolution proceeds according to Equation (1). Corrosion also is observed for chromite and spinel precipitations contributing to the ceramic bond break down close to the hot face. It is assumed that erosion is the main dominating wear phenomenon. However, corrosion by dissolution close to the hot face, which is usually diffusion controlled, also contributes.

The thermodynamic calculations are in good agreement with the mineralogical investigations and also show the formation of different types of Na-silicates and Na-sulphates due to slag infiltration, as well as high amounts of liquid phase in the infiltrated microstructure corresponding to deep-reaching infiltration.

Furthermore slag infiltration also impacts the mechanical behaviour: such a deeply infiltrated and corroded brick microstructure is highly susceptible to crack formation and spalling especially in the case of discontinuous (i.e., batch-wise) furnace operation, when a part of the infiltrated region solidifies. As a result brittleness is increased and crack formation is expected with thermomechanical loading.

For all metallurgical processes and vessels, adequate refractory linings have to be chosen in order to guarantee safe furnace operation and satisfactory furnace lifetime with short downtimes for repairs. In order to consider all these aspects, holistic refractory solutions are required: starting with proper material selection, functional lining concepts for the individual process and refractory engineering, and also taking into account time-saving and safe installation methods. Furthermore, to guarantee further improvement of the refractory products and therefore production processes, post-mortem investigations of used refractory materials from production vessels help to understand the wear mechanisms and process challenges. RHI is constantly working on improving its products and product range, taking advantage of its own research and development specialists (RHI Technology Center) and close collaboration with customers.

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## Authors

Dean Gregurek, RHI AG, Technology Center, Leoben, Austria.  
 Christian Majcenovic, RHI AG, Technology Center, Leoben, Austria.  
 Katja Reinharter, RHI AG, Technology Center, Leoben, Austria.  
 Viktoria Reiter, RHI AG, Technology Center, Leoben, Austria.  
 Christine Wenzl, RHI AG, Industrial Division, Vienna, Austria.  
 Alfred Spanring, RHI AG, Industrial Division, Vienna, Austria.  
 Harald Harmuth, University of Leoben, Austria.

**Corresponding author:** Dean Gregurek, dean.gregurek@rhi-ag.com

Rongxing Bei, Bernard Schmalenbach, Stefan Postrach, Klaus Santowski, Stefanie Redik

# Zirconia Mullite and Bonded Alumina for the Superstructure of a Glass Melting Furnace

For the superstructure walls fused cast alumina zirconia silica (AZS) has been frequently used. Because of the exudation of fused cast AZS and price pressure, the glass industry searches for alternatives. Two bonded refractories, zirconia mullite and alumina were tested in both the laboratory and as field test in the superstructure. The good performance of these two materials is reported in this article.

## Introduction

The superstructure of glass melting furnaces includes all walls of the combustion chamber of the melting tank. While in most cases the furnace crown can be built with silica bricks, for the superstructure walls, fused cast materials play a more important role, because of the high stress on refractories such as strong carryover, direct flame contact, and high temperature in the combustion chamber [1, 2]. However the exudation of a glassy phase from the fused cast AZS can cause glass defects like “knots” and “stones” [3]. Additionally price pressure forces glass producers to find more economical solutions for furnace building. For these reasons the glass industry is searching for alternatives to fused cast AZS. Bonded refractories without glassy phase, and therefore without exudation, could be alternatives. In this article results of test installations of two ceramic bonded refractories, zirconia mullite and alumina, for the application in the superstructure are reported.

## Bonded Zirconia Mullite

DURITAL AZ58 is a ceramic bonded AZS materials consisting of fused zirconia mullite and alumina, and fired at a very high temperature. The characteristics of DURITAL AZ58 are shown in Table I.

DURITAL AZ58 consists of baddeleyite (~28%), corundum (~34%) and fused mullite (~36%) and has the following advantages:

- >> High corrosion resistance against SiO<sub>2</sub> attack because of the high amount of mullite.

	DURITAL AZ58
<b>Chemical properties</b>	
Al <sub>2</sub> O <sub>3</sub> (wt.%)	58.0
Fe <sub>2</sub> O <sub>3</sub> (wt.%)	0.1
SiO <sub>2</sub> (wt.%)	13.0
ZrO <sub>2</sub> (wt.%)	28.0
Determination on fired substance (1025 °C) acc. to EN 12677	
<b>Physical properties</b>	
Bulk density (g/cm <sup>3</sup> )	3.20
Apparent porosity (vol.%)	13.5
Cold crushing strength (CCS) (N/mm <sup>2</sup> )	125.0

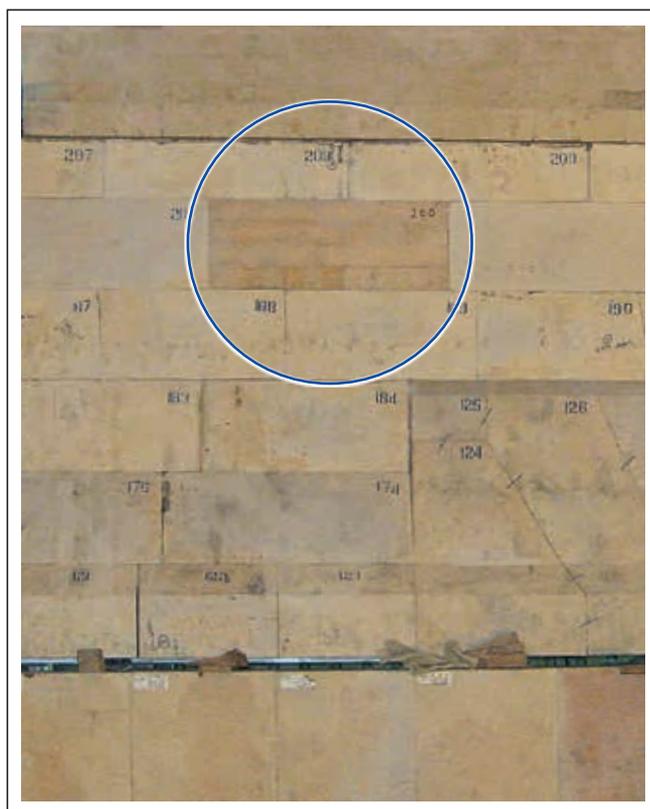
**Table I.** The chemical and physical properties of DURITAL AZ58.

- >> Insignificant glassy phase, and consequently no exudation.
- >> High refractoriness under load (T<sub>0.5</sub> = 1690 °C, in the same range as fused cast AZS).

These properties make DURITAL AZ58 the ideal material for the installation in the superstructure of glass furnaces.

To prove the performance of DURITAL AZ58 in glass furnaces a test field was lined in the superstructure of a soda lime container glass furnace. This field was the equivalent size of one fused cast AZS block in the superstructure, and was placed near the doghouse (Figure 1).

After 2 years in operation a DURITAL AZ58 sample was drilled from this position. On the hot face of the sample, no spalling or significant corrosion was observed. The hot face appeared dry and showed, when compared to the fused cast AZS, no exudation. The sample had the same thickness as an unused one (Figure 2).



**Figure 1.** Test field in the superstructure of a container glass furnace partly lined with DURITAL AZ58.

Table II shows the chemical and mineralogical analysis for the sample after 2 years in operation. On the cold face the main components ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{ZrO}_2$ ) are comparable with an unused material. On the hot face and in the transition zone (50 mm beneath the hot face), some components from the carryover ( $\text{CaO}$ ,  $\text{MgO}$ ) and from evaporation ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ) are enriched in a minimal range ( $\leq 0.3\%$ ).  $\text{Na}_2\text{O}$  infiltrated into the brick as well. However the  $\text{Na}_2\text{O}$  content at the hot face (0.7%) is lower than in the transition zone (2.9%). Further the  $\text{SiO}_2$  content at the hot face decreased compared to the other components of the sample. The reason could be that  $\text{Na}_2\text{O}$  decomposes mullite into  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and builds a glassy phase with  $\text{SiO}_2$ . This glassy phase on the hot face (only a few cm in depth) was removed from the brick structure during the application (Table II and Figure 3). Additionally the colouring agent for green glass,  $\text{Cr}_2\text{O}_3$ , is enriched on the hot face.

The main brick components corundum, mullite, and baddeleyite are unchanged on the cold face of the sample (Table II). The secondary  $\text{ZrO}_2$  remains on the hot face together with corundum as phases showing the strongest corrosion resistance in the system (Figure 3).

In the transition zone the mullite decomposed to corundum and silica, the silica then reacted with infiltrated  $\text{Na}_2\text{O}$  to form glassy phase, as it did on the hot face (Table II). However this glassy phase was not removed, but acted as a sealing agent. Consequently the structure in the transition zone is much denser compared to the hot face. This is clearly visible macroscopically (Figure 2) and microscopically (Figure 3). This dense structure in the transition zone prevents further infiltration and corrosion of the brick which is the main reason for a good performance of DURITAL AZ58.

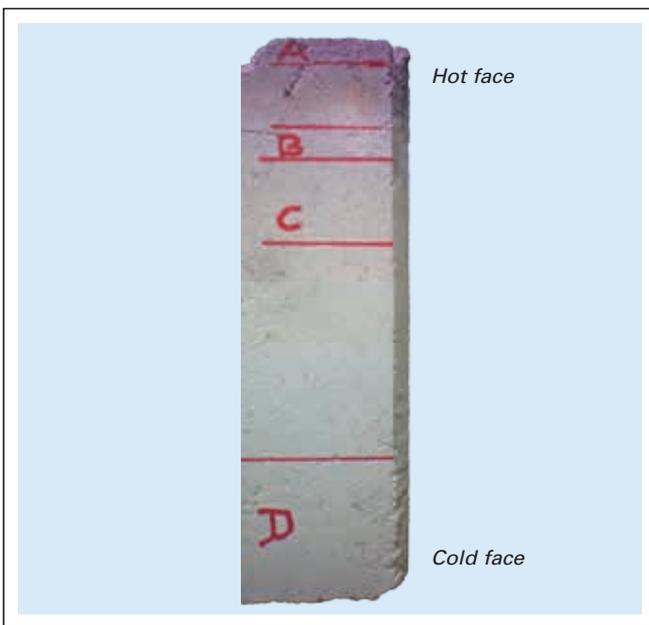


Figure 2. Drilled core sample of DURITAL AZ58 after 2 years in operation.

	Hot face	Transition zone	Cold face	Unused
Distance to hot face (mm)	0.0	50.0	280.0	
<b>Chemical analysis</b>				
$\text{Al}_2\text{O}_3$ (wt.%)	64.1	57.9	57.4	58.0
$\text{SiO}_2$ (wt.%)	2.7	12.0	13.6	13.0
$\text{CaO}$ (wt.%)	0.3	0.3	0.1	
$\text{MgO}$ (wt.%)	0.2	0.1	0.0	
$\text{K}_2\text{O}$ (wt.%)	0.1	0.3	0.0	
$\text{Na}_2\text{O}$ (wt.%)	0.7	2.9	0.2	
$\text{Cr}_2\text{O}_3$ (wt.%)	0.5	0.0	0.0	
$\text{ZrO}_2 + \text{HfO}_2$ (wt.%)	31.3	26.2	27.2	28.0
<b>Mineralogical analysis</b>				
Corundum	X	X	X	X
Mullite			X	X
Baddeleyite	X	X	X	X

Table II. Chemical and mineralogical analysis of the drilled core sample of DURITAL AZ58 after 2 years in operation.

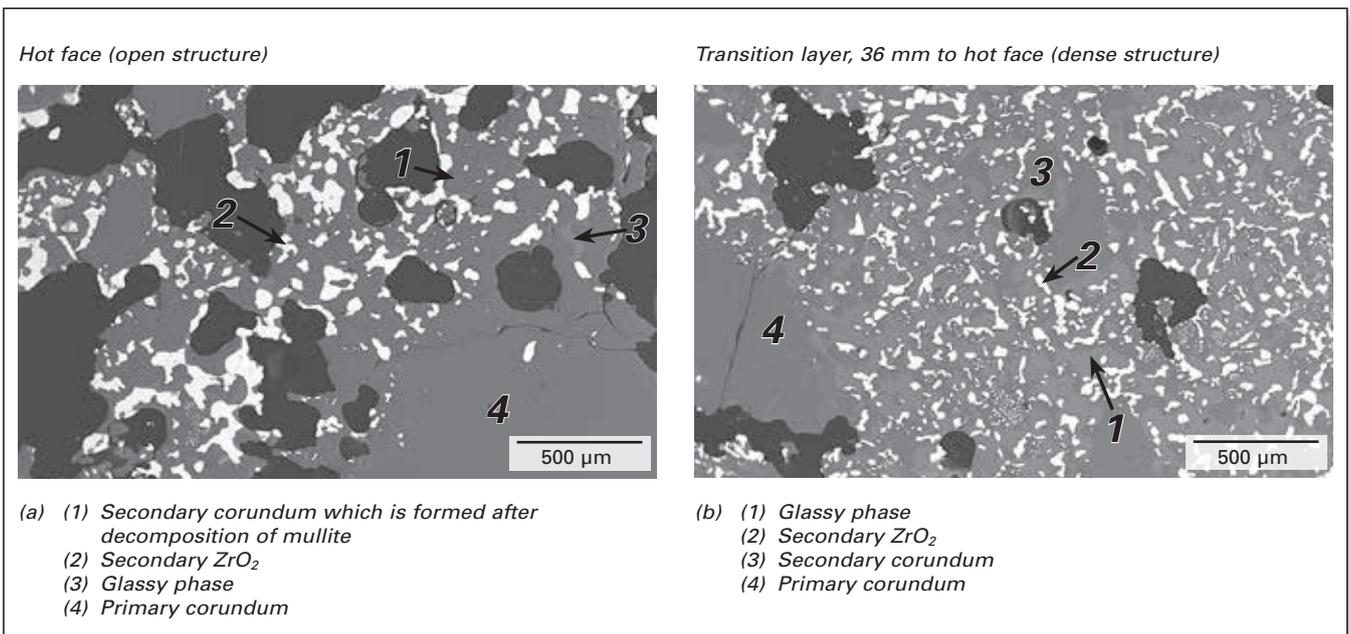


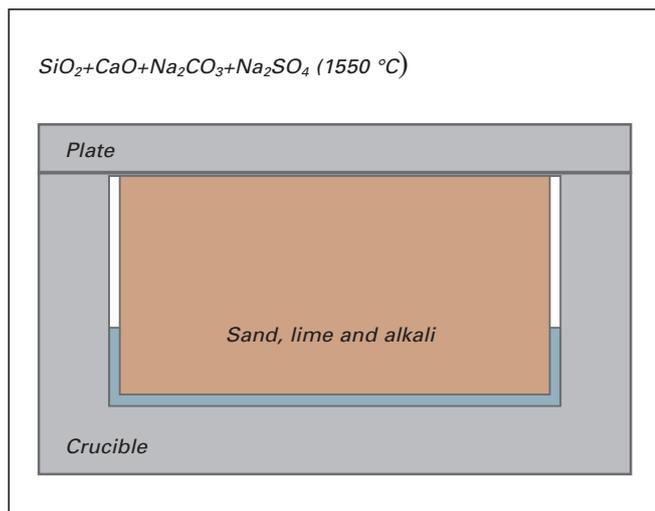
Figure 3. Photomicrographs of DURITAL AZ58 after 2 years operation. Showing the mineralogical analysis of (a) the hot face and (b) the transition layer.

## Bonded Zirconia Mullite With Silica Sol Impregnation

For further improvement of the corrosion resistance, DURITAL AZ58 can be impregnated with silica sol after firing. The impregnation results in the silica sol filling a large part of the pore spaces and results in improved brick properties (Table III). The impregnated bricks show an increase in density and mechanical strength while porosity and gas permeability decrease. Despite the dense structure, the brick doesn't lose its thermal shock resistance after impregnation.

	DURITAL AZ58	Impregnated DURITAL AZ58
<b>Physical properties</b>		
Cold crushing strength (CCS) (N/mm <sup>2</sup> )	125.0	223.0
Gas permeability (nPm)	3.4	0.0
Bulk density (g/cm <sup>3</sup> )	3.2	3.3
Apparent porosity (vol.%)	13.5	5.0
Thermal shock resistance (cycles)	> 30.0	> 30.0

**Table III.** Physical properties of DURITAL AZ58 with and without silica sol impregnation.



**Figure 4.** Schematic of the crucible test.

In order to evaluate the corrosion resistance of DURITAL AZ58 with and without silica sol impregnation a laboratory test was performed to examine the combined attack caused by alkalis and carryover. In this test, a crucible is manufactured directly from the refractory material to be tested. The crucible was filled with sand, lime, and alkali (i.e.,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$ ) and tested at 1550 °C (Figure 4).

The results of the crucible test show that the impregnated DURITAL AZ58 crucible suffered significantly less corrosion than the crucible without impregnation (Figure 5).

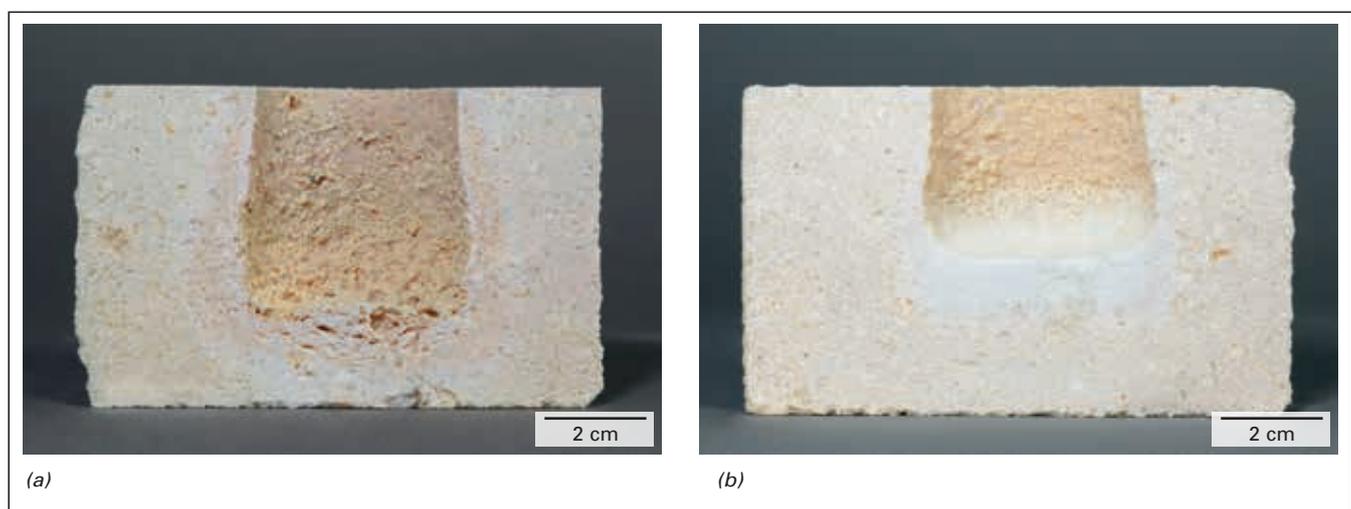
On the basis of these results further field trials are being conducted in the superstructure of industrial furnaces. Upon completion the samples will undergo further post mortem analysis.

## Bonded Alumina

The possible installation of bonded alumina, DURITAL K99EXTRA in the superstructure has been discussed in the past. The grade is based on fused  $\alpha$ -alumina. As the grade DURITAL AZ58, is fired at very high temperatures and has very good creep resistance. The creep behaviour is measured at 1600 °C. The typical creep under load between 5 and 25 hours is 0.2% or less. In comparison to fused cast AZS this grade has nearly no glassy phase and hence no exudation during application in the superstructure. The characteristics of DURITAL K99EXTRA are shown in Table IV.

	DURITAL K99EXTRA.
<b>Chemical properties</b>	
$\text{Al}_2\text{O}_3$ (wt.%)	99.3
$\text{Fe}_2\text{O}_3$ (wt.%)	0.1
$\text{SiO}_2$ (wt.%)	0.2
Determination on fired substance (1025 °C) acc. to EN 12677	
<b>Physical properties</b>	
Bulk density (g/cm <sup>3</sup> )	3.23
Apparent porosity (vol.%)	18.0
Cold crushing strength (CCS) (N/mm <sup>2</sup> )	75.0

**Table IV.** Showing the chemical and physical properties of DURITAL K99EXTRA.



**Figure 5.** Cross section of crucibles after testing at 1550 °C showing (a) the DURITAL AZ58 crucible and (b) the impregnated DURITAL AZ58 crucible.

To prove the performance of DURITAL K99EXTRA a test field was installed in the superstructure of a container glass furnace. This field is situated in the breast wall and near the throat. This area shows a temperature level of nearly 1600 °C. After 2 years in operation the sample was removed (Figure 6). The original length was unaltered and a material loss could not be observed. Additionally, no spalling or significant corrosion was found on the hot face of the sample. The hot face showed no indication of melting and, as expected, did not show any exudation.

The chemical and mineralogical analysis for this used sample is shown in Table V. The  $\text{Al}_2\text{O}_3$  content was decreased from original 99% to approximately 94%, not only on the hot face, but also through the whole sample to the cold face. Some components from carryover ( $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ) and from evaporation ( $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ )

	Hot face	Transition zone	Cold face	Unused
Distance to hot face (mm)		10–25	230–250	
<b>Chemical analysis</b>				
$\text{Al}_2\text{O}_3$ (wt.%)	93.4	94.2	94.0	99.3
$\text{SiO}_2$ (wt.%)	3.9	3.8	3.9	0.2
$\text{CaO}$ (wt.%)	0.3	0.2	0.2	
$\text{MgO}$ (wt.%)	0.2	0.2	0.5	
$\text{K}_2\text{O}$ (wt.%)	0.1	0.1	0.0	
$\text{Na}_2\text{O}$ (wt.%)	0.8	0.8	0.6	
$\text{Cr}_2\text{O}_3$ (wt.%)	0.6	0.1	0.0	
<b>Physical properties</b>				
Apparent porosity (vol.%)	8.6	6.5	5.7	16.5
<b>Mineralogical analysis</b>				
Corundum	X	X	X	X

**Table V** Chemical and mineralogical analysis for DURITAL K99EXTRA after 2 years in operation.

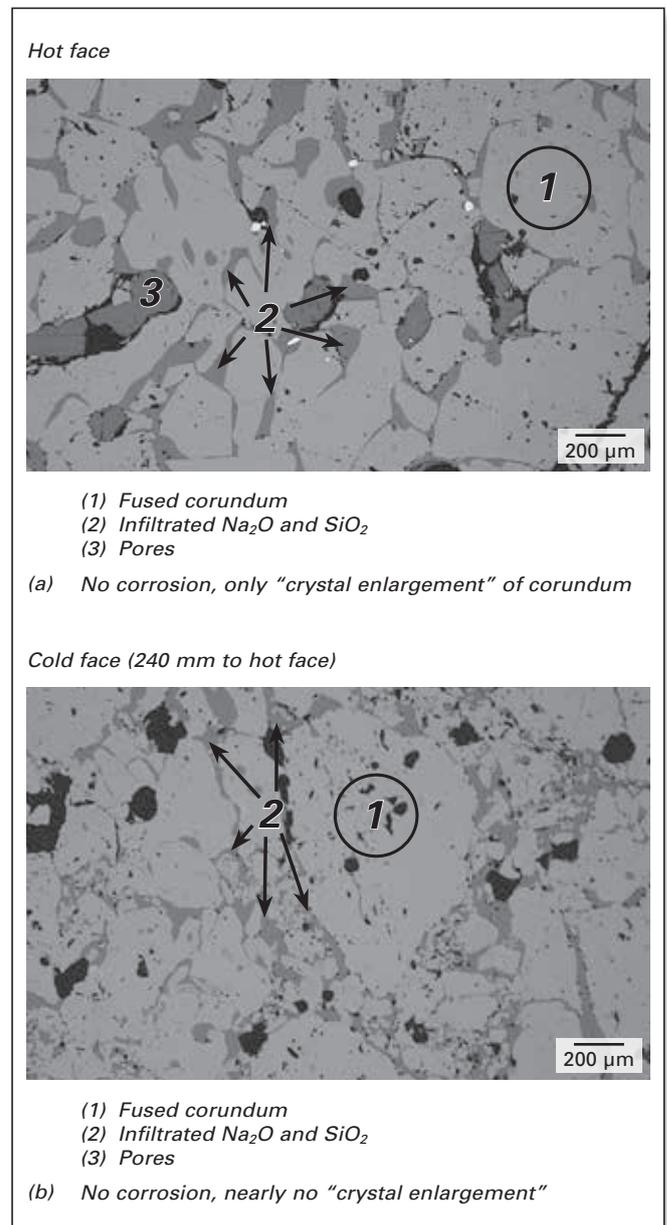


**Figure 6.** Sample of DURITAL K99EXTRA after 2 years in operation.

infiltrated into the whole brick. In addition the colouring agent for the green glass,  $\text{Cr}_2\text{O}_3$ , was enriched on hot face and can be observed in the red colour, which is caused by the formation of  $(\text{Al,Cr})_2\text{O}_3$  solid solution on the hot face.

The enrichment of  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  in the brick (together approximately 4.5%) caused a densification of the brick structure. Consequently the porosity decreased from 16.5% down to 6–9%.

The photomicrographs of the samples show strong crystal enlargement of corundum on the hot face of the brick (Figure 7). This formed a dense layer on the hot face and protected the brick against further attack. The crystal enlargement is a crystal growth under temperature by means of attacking components which react with the origin material. This process can be accelerated in the presence of liquid phases which allow the crystals to grow free in a viscous matrix. On the cold face there was infiltration from the waste gas as well, however neither strong crystal enlargement nor corrosion can be observed.



**Figure 7.** Photomicrograph and analysis of DURITAL K99EXTRA after 2 years operation. Showing (a) the hot face and (b) the cold face.

It is well known that  $\alpha$ -alumina can react with sodium from the furnace atmosphere to form so called  $\beta$ -alumina. This reaction can occur theoretically at temperatures lower than 2000 °C according to  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  phase diagram [4]. However according to thermodynamic calculations [5] the temperature stability range for  $\beta$ -alumina is much lower (< 1300 °C). The reason is that in this calculation a NaOH content is considered which has been measured in waste gas from an industrial glass furnaces. In the sample DURITAL K99EXTRA which was tested at 1600 °C only corundum exists and there is no formation of  $\beta$ -alumina (Table V).

## Conclusion

DURITAL AZ58 showed a good performance in a field test in the superstructure in the doghouse area after 2 years in operation. The direct hot face was corroded and has a loose structure with  $\text{Zr}_2\text{O}$  and corundum remaining. However the original brick thickness did not change. Furthermore, a few centimeters underneath the hot face a dense structure was formed with corundum,  $\text{Zr}_2\text{O}$ , and a small amount of glassy phase. This dense structure acts as barrier against further infiltration and corrosion.

A further development of DURITAL AZ58 with silica impregnation can increase the corrosion resistance significantly. Field tests have been initiated and further post mortem studies will be carried out.

The excellent performance of DURITAL K99EXTRA can also be reported after a field test in the superstructure at the hot end of the furnace after 2 years service. A strong crystal enlargement and re-arrangement of corundum crystals formed a dense layer on the hot face and protected the brick against the further attack.

Based on these results the following recommendation can be given to replace fused cast AZS and to overcome problems with exudation and glass defects:

- >> Installation of DURITAL AZ58 in the cooler end of the glass tank, where high carry over is the prevailing corrosion agent.
- >> Installation of DURITAL K99 EXTRA in the hot end of the glass tank, where evaporating  $\text{Na}_2\text{O}$  is the prevailing corrosion agent.

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## Authors

Rongxing Bei, RHI AG, Industrial Division, Wiesbaden, Germany.  
 Bernard Schmalenbach, RHI AG, Industrial Division, Wiesbaden, Germany.  
 Stefan Postrach, RHI AG, Industrial Division, Wiesbaden, Germany.  
 Klaus Santowski, RHI AG, Technology Center, Leoben, Austria.  
 Stefanie Redik, RHI AG, Technology Center, Leoben, Austria.

**Corresponding author:** Rongxing Bei, rongxing.bei@rhi-ag.com

Sonja Breyner and Anna Franzkowiak

# Insights Into Copper Wire Production With a Focus on Oxidic and Nitride Bonded Silicon Carbide Refractory Materials

RHI is striving for appropriate materials to meet the challenging pyrometallurgical requirements of its customers in the copper and particularly copper wire producing industry. This article gives a brief insight into copper wire production and identifies the material properties of oxidic and nitride bonded silicon carbide (SiC) refractory ceramics including cup test and field test results. According to the preliminary findings SiC refractory materials with oxidic bonds are a well suited and an efficient alternative to nitride bonded products for the application in shaft melting furnaces or holding furnaces. RHI offers both types of bonded materials and is in the position to offer tailor-made solutions for lining concepts, especially due to the long-standing manual manufacturing know-how and experience.

## Introduction

According to U.S. Geological Survey [1] the primary copper market is still increasing, entailing a growing secondary copper production due to resources and environmental aspects (Figure 1).

Economic considerations such as steadily increasing energy and resource costs have resulted in companies investing in recycling processes and optimizing process efficiency in general. This adversely affects the performance of standard linings and drives refractory producers to search for material innovations and product solutions with a longer service life in order to reduce repairs and idle times. Therefore, a special focus is placed on keeping the specific refractory consumption as low as possible. However the extractive metallurgy of copper has a high complexity in metallurgical processes, combined with an extensive variety of metal processing furnaces, precise knowledge of the system is indispensable for the appropriate selection of refractory products [2, 3]. As these aspects

are also important for copper wire production, research activities were focused on shaft melting furnaces, in particular silicon carbide (SiC) based refractory materials and their bonding systems.

Copper rods, tubes, and wires serve especially the biggest consumption fields of copper: electrical engineering, construction industry, telecommunications, and automotive (Figure 2).

## Shaft Melting Furnaces, Lining Concepts, and Product Development

Both in the primary and secondary copper production route, cathodes are melted in vertical shaft furnaces before the casting of cathode copper. In the three existing shaft furnace types (Asarco, Southwire, and Properzi/Luxi), descending cathode sheets are melted by ascending hot combustion gases produced by reducing flames. The latter and silicon carbide based refractories protect the copper from excessive oxygen pickup [3].

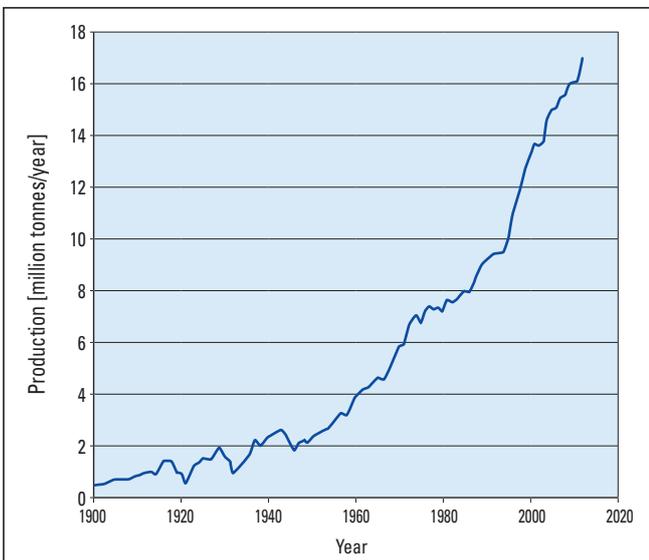


Figure 1. Trend of the copper world production [1].

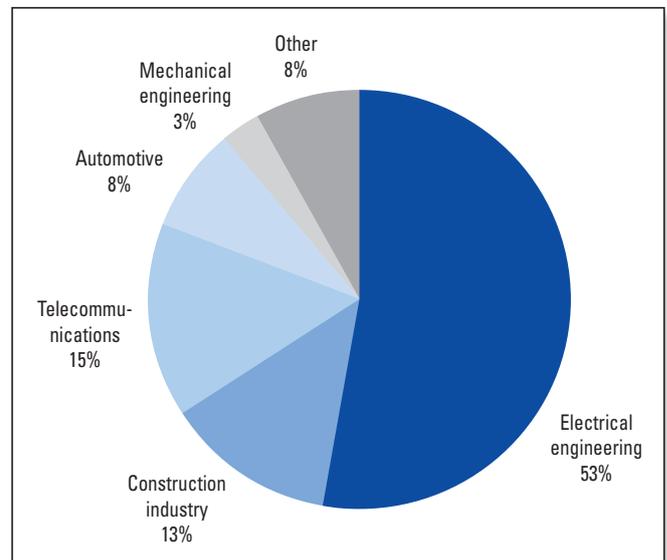


Figure 2. Annual copper consumption divided into use. Source: www.aurbis.com.de

A long-standing knowledge of customers' industries is incorporated into the extensive cycle of support, optimizing, development and testing of in RHI products (Figure 3).

The furnace lining is the heart of a vessel and has critical influences on its performance, the standard shaft melting lining is based on silicon carbide materials due to the prevailing reducing atmospheric conditions. Therefore, the addition of carbon to the six basic oxides on which refractories are based, results in further material combinations including the important silicon carbide (Figure 4).

Silicon carbide as a raw material is characterized by high strength, high abrasion resistance, high thermal conductivity, high oxidation resistance, and high corrosion resistance to nonoxidizing slags and acids, particularly in the

nonferrous industries. It can be sensitive to hydrogen and starts to disintegrate at ~1000 °C.

The common method used to produce refractory grade SiC is the Acheson method, where a mixture of quartzite and carbon are synthesized according to the following equation:



SiC refractories are produced in the same way as conventional refractories. The material properties are extended in a refractory brick based on SiC, especially in regards to temperature. The high thermal conductivity combined with a good spalling resistance make it the ideal material for cathode melting shaft furnaces [2, 4].

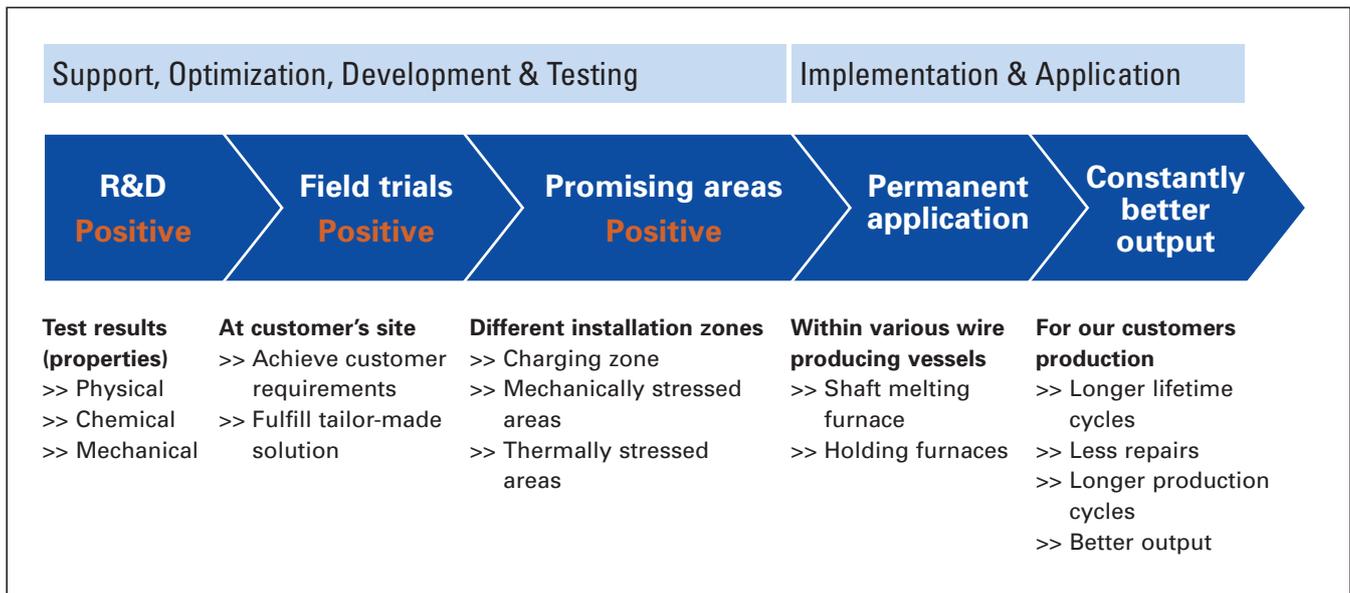


Figure 3. Product development work process of technical marketing and R&D.

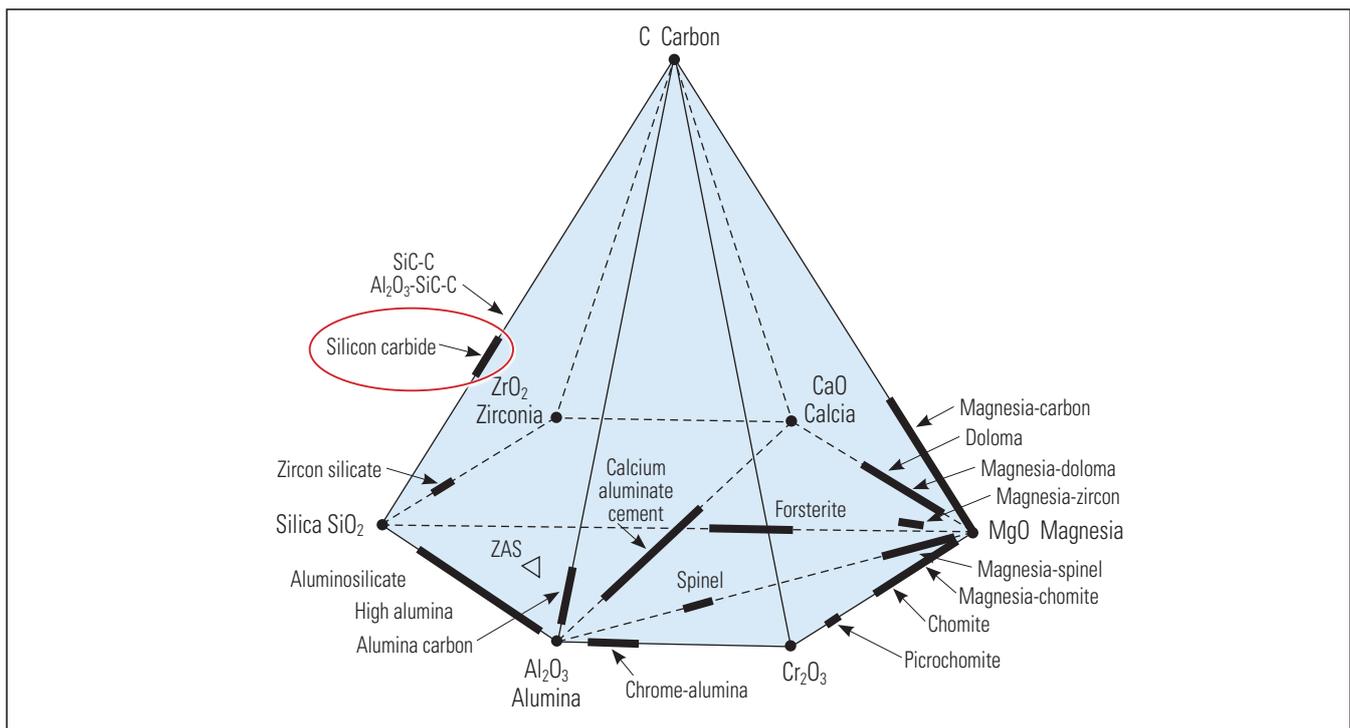


Figure 4. Base material pyramid with location of silicon carbide (marked in red) within the refractory materials [2].

## Comparability Study of SiC Products With Oxidic and Nitride Bond

Refractory bricks based on silicon carbide may be bonded either by N<sub>2</sub> containing phases (Si<sub>3</sub>N<sub>4</sub>, SiAlON, Si<sub>2</sub>ON<sub>2</sub>), native SiC ( $\alpha, \beta$  type) or siliceous oxides (ceramic). The diverse bonding types are formed by adjusting atmospheric conditions during firing. Table I gives an overview of the physical properties of differently bonded SiC refractory types [2].

### Physical Test Results

In this study one RHI brick grade with nitride bond and one grade with oxidic bond were investigated. The tests comprised the standard physical properties including cup corrosion tests with copper at 1150 °C under reducing conditions and subsequent mineralogical analysis. Both the nitride and oxidic bonded brick samples are composed of > 90% SiC. The results of the physical testing can be seen in Table II.

The values (Table II) of bulk density, apparent porosity, cold crushing strength and abrasive grit volume, and the resulting abrasion resistance, are better for the oxidic bonded type O. The cold as well as the hot modulus of rupture are on a very high level for both bonding types, especially for type N. The refractoriness under load of both brands is

General information			
Type of bond	Oxidic	N <sub>2</sub> containing bond	
		Si <sub>3</sub> N <sub>4</sub>	SiAlON
Physical test results			
Bulk density (g/cm <sup>3</sup> )	2.4–2.7	2.5–2.7	2.6–2.8
Apparent porosity (vol.%)	17–23	12–18	
Cold crushing strength (MPa)	50–150	150–300	
Cold modulus of rupture (MPa)	15–30	30–140	40–60
Hot modulus of rupture at 1400 °C (MPa)	15–25	35–160	40–60
Refractoriness under load T <sub>0.5</sub> (°C)	~ 1550	> 1700	

**Table I.** Literature data of oxidic and nitride bonded SiC materials [2].

General information		
Sample name	O	N
Type of bond	Oxidic	N <sub>2</sub> containing bond
Physical test results		
Bulk density (g/cm <sup>3</sup> )	2.72	2.65
Apparent porosity (vol.%)	12.7	15.3
Cold crushing strength (MPa)	150	140
Cold modulus of rupture (MPa)	33.1	47.5
Hot modulus of rupture at 1370 °C (MPa)	18.3	45.1
Refractoriness under load T <sub>0</sub> (°C)	1480	1475
Refractoriness under load T <sub>0.5</sub> (°C)	1475	> 1700
Abrasive wear resistance		
Grit volume (cm <sup>3</sup> )	3.7	5.2

**Table II.** Physical test results for RHI SiC brick types with oxidic bond (O) and nitride bond (N).

comparable as far as the temperature of the highest expansion is concerned (T<sub>0</sub>). In contrast, the temperature of 0.5% deformation (T<sub>0.5</sub>), is increased for the nitride bonded type N.

### Cup Tests and Mineralogical Investigation

The test cups were made from standard shaped bricks, the dimensions of which can be seen in Figure 5. A hole was drilled into the refractory and filled to two thirds with copper. The cups were covered with a refractory plate of the same material. In order to create a reducing atmosphere the cups were placed within a box and embedded with coke gravel. The test was run for 48 hours at 1150 °C.

After the test, the cups were cut in half in order to evaluate the cross sections and to take samples for mineralogical analysis. The results of the mineralogical investigations are documented in Figures 6–11.

#### Mineralogical Analysis of SiC Brick Grade O

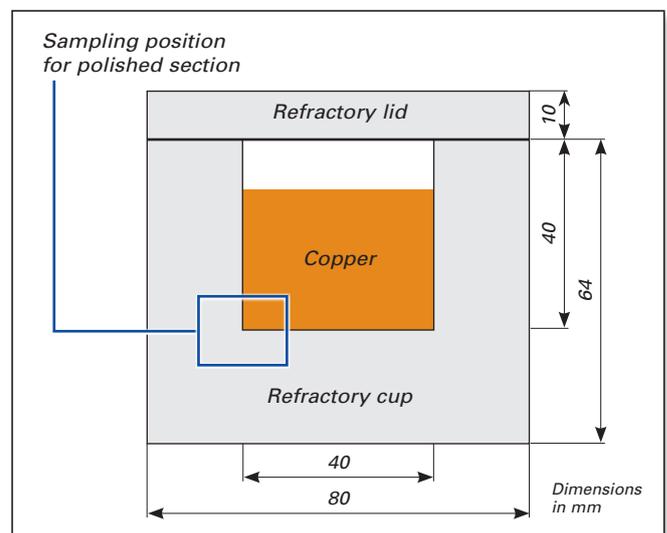
The analysis shows that there is no pore-filling copper (Cu) infiltration. The SiC grains (circle in Figure 6) are partly attacked by Cu and result in formation of CuSi (Figure 7). After this reaction the carbon remains in the pore space retaining the original SiC grain shape (Figure 8).

The SEM EDX analysis results of decomposed SiC grains (Figure 8) are listed in Table III. The results show that SiC grains near the reaction zone absorb ~ 1% Cu and that the newly formed CuSi alloy contains ~ 2% Si.

#### Mineralogical Analysis of SiC Brick Grade N

Brick N shows no pore-filling copper infiltration and the same reaction mechanisms as brick O were observed. Additionally there is corrosion of SiC grains (circle in Figure 10) and formation of CuSi.

The SEM EDX analysis results of decomposed SiC grains (Figure 11) are listed in Table IV. The results show a slightly lower Cu pickup of ~ 1% in the SiC grains. The newly formed CuSi alloy contain significantly more Si with a value up to ~ 4% Si.



**Figure 5.** Cup test assembly and sampling position for polished section.

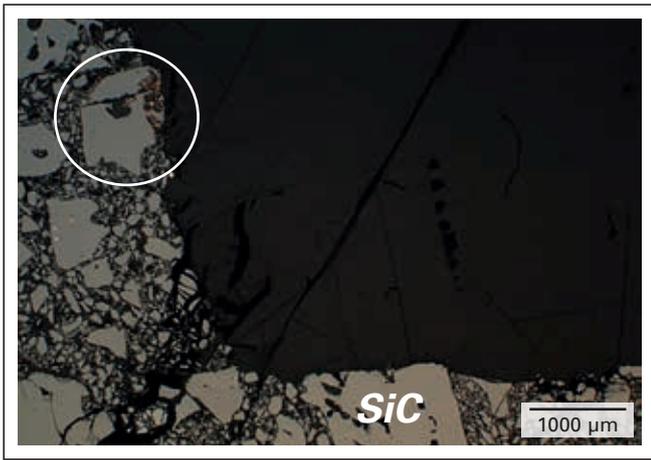


Figure 6. Photomicrograph (20x, reflected light, dry) of cup test polished section showing the inner cup edge area of grade O.

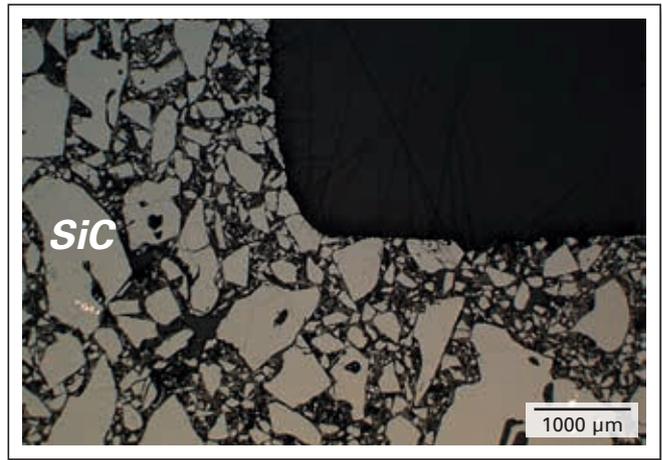


Figure 9. Photomicrograph (20x, reflected light, dry) of cup test polished section, showing inner cup edge area of grade N.

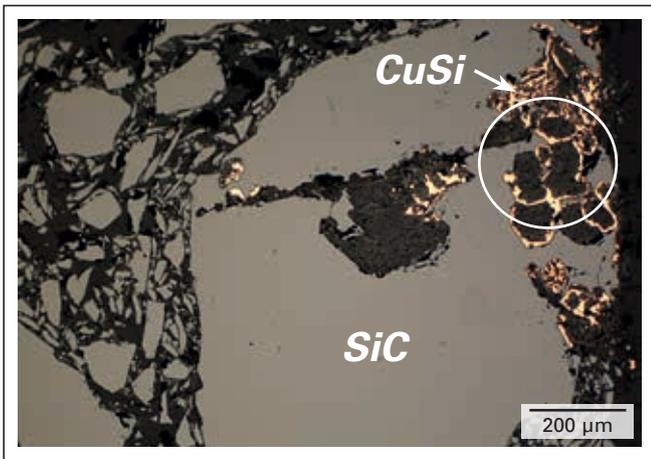


Figure 7. Photomicrograph (100x, reflected, light, dry) of cup test polished section of grade O, detail from Figure 6.

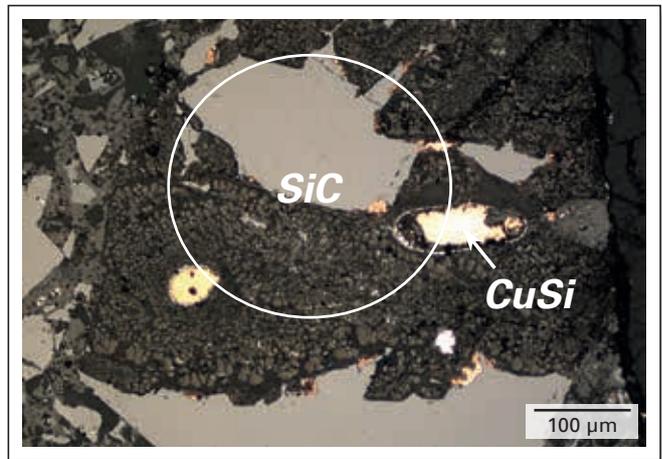


Figure 10. Photomicrograph (200x, reflected light, dry) of cup test polished section of grade N.

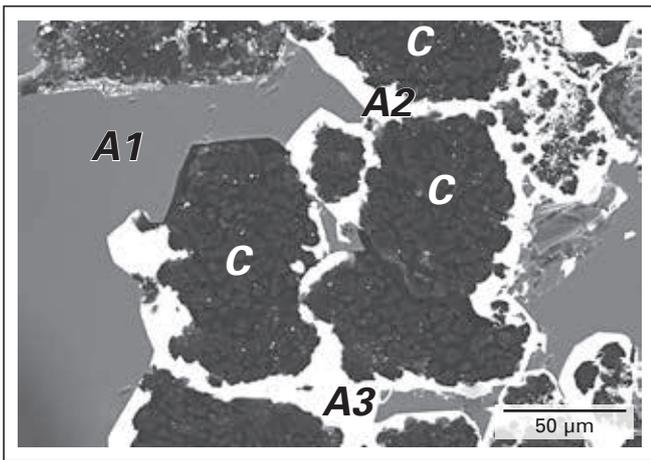


Figure 8. Photomicrograph (500x, SEM BSE) of cup test polished section of grade O, detail Figure 7, showing the residual carbon (C) and the SEM analysis points.

Brick O (from Figure 8, grade O)				
Spot	O [%]	Si [%]	Ni [%]	Cu [%]
A1	0.8	98.0		1.2
A2	1.1	2.1	0.6	96.2
A3	1.2	2.0		96.8

Table III. SEM EDX energy dispersive analysis from Figure 8.

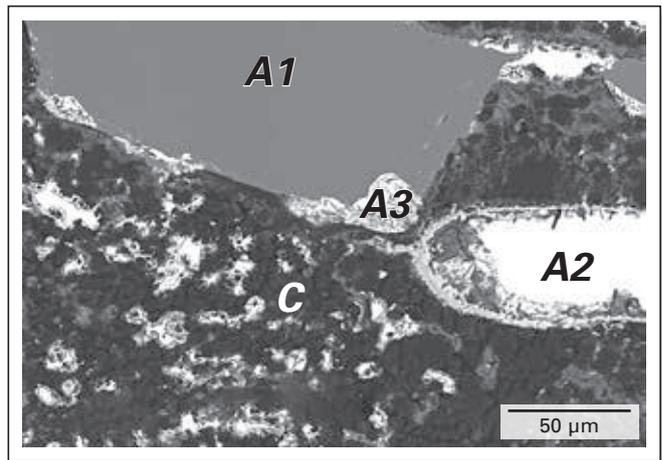


Figure 11. Photomicrograph (500x, SEM BSE) of cup test polished section of grade N, detail of Figure 10, showing the corroded SiC (C) and the SEM analysis points.

Brick N (from Figure 11, grade N)				
Spot	O [%]	Si [%]	Ni [%]	Cu [%]
A1		99.3		0.7
A2	1.1	4.2		94.7
A3	1.2	3.7		95.1

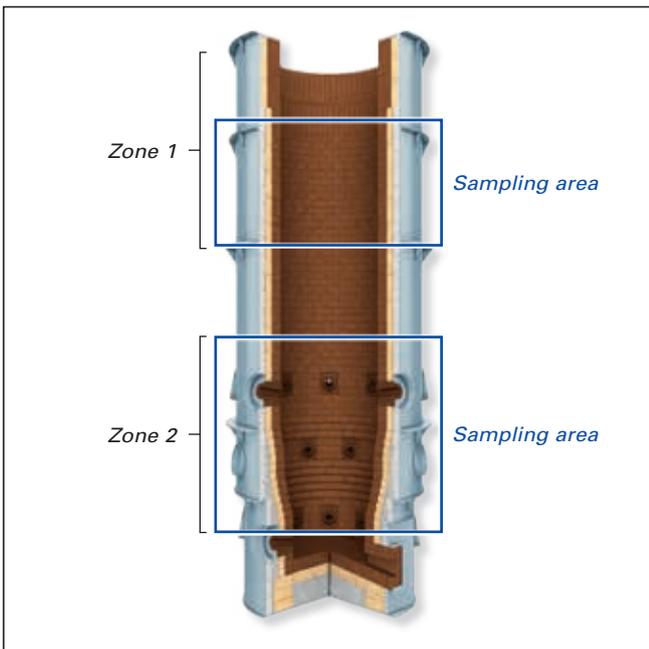
Table IV. SEM EDX energy dispersive analysis from Figure 11.

Identical wear mechanisms due to decomposition of SiC were found in both types of bricks, independent of their bonding system. No pore infiltration of copper takes place, however a copper alloy containing up to 4% Si is formed by copper attack on coarse grains. The carbon remains in the microstructure as relic of corroded SiC grains.

## Application Study

A field test was carried out in a copper cathode melting shaft furnace (Figure 12) with an oxidic bonded SiC brand [5].

The main specific requirement for the hot face lining can be described as follows: resistance to reducing conditions to avoid oxygen as well as hydrogen pickup in the molten copper [3]. Furthermore, sufficiently high wear resistance is important for the upper furnace (Figure 12, Zone 1) since the main stresses are induced by the charging of the cathodes, sliding downwards to the bottom section of the furnace during the continuous process. Reduced wear is very important to minimize inclusions in the final product, as this would be detrimental during the subsequent casting process. Additionally, the material must withstand the prevailing thermal stresses due to the induced heat of the burner flames in the lower part of the furnace (Figure 12, Zone 2).



**Figure 12.** Cathode melting shaft furnace with sampling and exposed furnace area positions.

With the existing temperature gradient from top to bottom, the oxidic bonded SiC refractory material is a versatile product for cathode melting as a first step of casting rods or billets.

Several samples were taken from the upper and lower sections of the furnace (sampling areas in blue, Figure 12) for further examination. An example of the post mortem field test results from Zone 1 can be summarized as follows:

- >> exhibited a residual thickness of 135 mm which represents a material loss of 11% during application.
- >> Chemically the hot side of the sample (0–8 mm) was enriched with SiO<sub>2</sub>.
- >> There was no infiltration of copper into the brick microstructure, but a Na- and Cu-rich silicate coating up to 1 mm thick was formed on the sample surface.
- >> In the infiltrated area SiO<sub>2</sub> precipitations were detected in the infiltrate.
- >> The noninfiltrated sample area corresponds to the original brick microstructure.

The samples from zone 2 showed identical results. The unique thermal stresses of this area did not interfere with the product performance.

The residual brick lengths of all samples were in a range of  $\geq 50\%$  after an average operation time lifespan of two years and a production capacity above 100000 tonnes per annum. Which represents the upper level of typical shaft furnace operations.

## Summary and Conclusions

The investigations establish that both bonding types, oxidic and nitride, exhibit excellent physical properties and high corrosion resistance under reducing conditions at laboratory scale. An upscaling test of oxidic bonded SiC bricks in a cathode melting shaft furnace at customer's site resulted in high performance and increased service life. Resulting in a minimization of the specific refractory consumption and increased overall operational efficiency for the customer. Despite nitride bonded SiC brick types often being installed, this study has confirmed that the application of oxidic bonded SiC bricks in vessels such as the cathode melting shaft furnace and adjacent holding furnace is more efficient and can therefore be strongly recommended.

Further specific field studies with selected products are currently ongoing. The results will be published in a subsequent RHI Bulletin issue.

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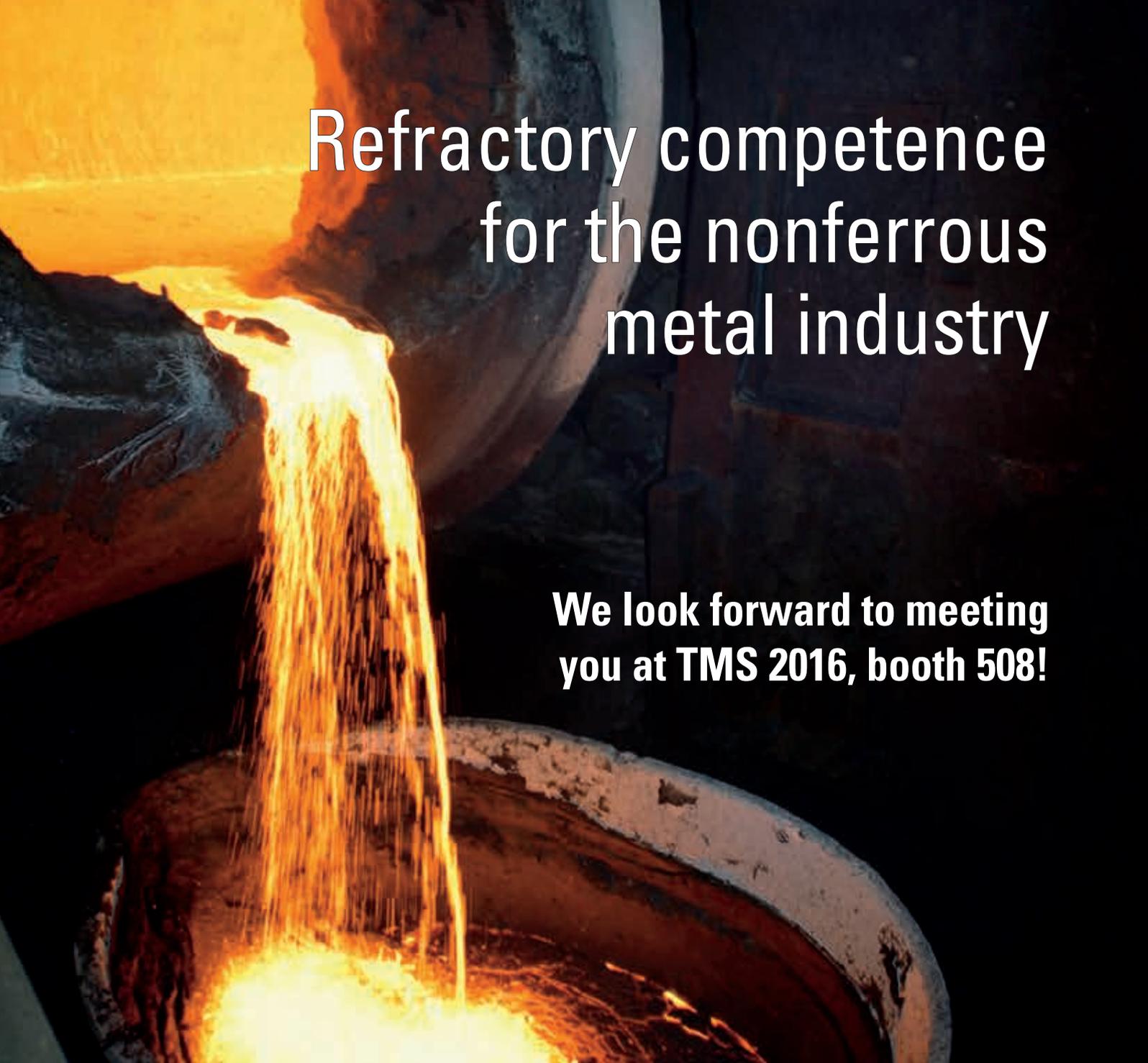
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## Authors

Sonja Breyner, RHI AG, Technology Center, Leoben, Austria.

Anna Franzkowiak, RHI AG, Industrial Division, Vienna, Austria.

**Corresponding author:** Anna Franzkowiak, [anna.franzkowiak@rhi-ag.com](mailto:anna.franzkowiak@rhi-ag.com)



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# No-Cement Sol Mixes Achieve Service Life Records at Solnhofer Portland-Zementwerke

The cement industry is one of the most energy intensive industries therefore the use of alternative fuels has a long tradition, especially in Central Europe. Solnhofer Portland-Zementwerke (SPZ) relies on fuel cost savings by burning alternative fuels, thereby making an important contribution to an ecologically and economically sensible utilization of waste materials. Modern kiln technologies and highest grade lining concepts enable the use of a wide range of alternative fuels. In comparison with the use of conventional fossil fuels, refractories are subject to significantly higher stress when alternative fuels are used. Consequently, a considerably shorter useful life of the refractory lining, in many cases has to be accepted. In cooperation with RHI AG, the cement plant successfully developed solutions for the most critical areas of the kiln. The following article reports on operational experiences with new refractory mixes technology.

## Solnhofer Portland-Zementwerke

Solnhofer Portland-Zementwerke (SPZ) was founded by the brothers Bucker-Flürenbrock on May 13, 1933. Known worldwide for spectacular fossil findings, the Jurassic Solnhofen Limestone provides the raw material for the production of premium cements. SPZ operates a modern 4 stage heat exchanger with a daily capacity of roughly 1200 tonnes (Figure 1).

Their product range comprises Portland cement, Portland composite cement, furnace cement, and binding agents. Furthermore, this medium sized family business operates in the areas of natural stones, ready-mix concrete, precast concrete components, and track construction.

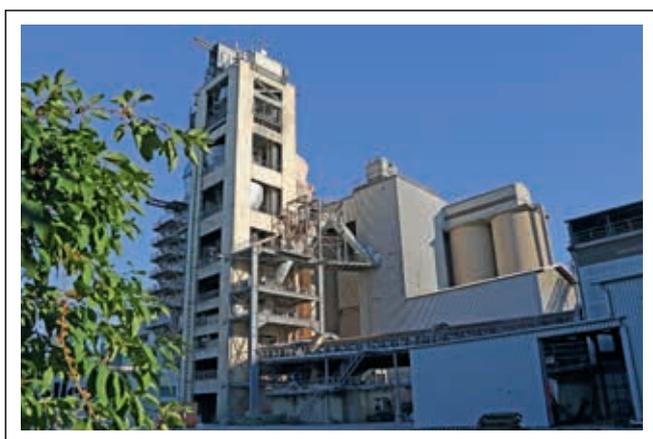
## Alternative Fuels as a Challenge

The high proportion of alternative fuels presents production with a considerable challenge. In addition to the conventional coal fuel, a mix of refuse derived fuels containing plastics (RDF), animal meal, and fly ash is currently used. The share of refuse derived fuels is up to 60% and thus corresponds to the German average. According to the German Cement Works Association (Verein Deutscher Zementwerke, VDZ), 62.5% of the fuels for clinker

production were provided by alternative fuels in German cement plants in the year 2013 [1]. The related introduction of volatile components such as chlorine, sulphur, and alkalis is not unproblematic for the stable operations of the plant. Over time, they accumulate in the kiln atmosphere and can severely disrupt operations by forming coatings, by causing premature wear of the refractory lining, and by corrosion of the kiln shell and anchors. One of the procedural measures taken to counteract this is the use of a bypass, which reduces the chlorine content in hot meal to a controllable level.

Nonetheless, some areas of the refractory lining are exposed to significant chemical attack due to the high concentration of alkali salts. Particularly critical areas in the cooler include the bullnose and the clinker bed as well as the inlet chamber and the riser duct. Moreover, the rotary kiln burner also caused significant problems for the cement plant as the monolithic lining had to be replaced every 6 to 10 weeks in the past.

The areas described are generally lined with monolithics. Despite numerous tests with various products made by different and reputable manufacturers, lifetimes of only 7-15 months were achieved in the critical areas.



**Figure 1.** View of the heat exchanger and the rotary kiln of the Solnhofer cement plant.

In some areas of the rotary kiln, SPZ already utilises refractory materials from RHI. ANKRAL QF, for example, is successfully used in the highly stressed and critical sintering zone in the area of the middle tyre. However, RHI, which is perceived as a specialist for basic refractory products, also offers a comprehensive product portfolio of alumina silica mixes, including the newly developed no-cement refractory castables. After numerous successful applications of sol mixes in the German cement industry, which uses the highest proportion of alternative fuels worldwide, the new mixes technology was also utilized in the critical areas at SPZ. This new development consists of chemically bonded no-cement mixes, which display outstanding properties due to their novel type of bond. As these mixes are only chemically bonded and not hydraulically bonded, they do not have to be predried and can consequently be heated quickly without the risk of a steam explosion. The firing

schedule of 36 hours, which is usually recommended for rotary kilns, is more than sufficient to bring sol mixes to operating temperature safely without prior drying. Moreover, the absence of cement leads to an increase in hot strength and chemical resistance. With their ease of handling, physical and chemical properties when compared to hydraulically bonded mixes, the use of this technology can increase kiln availability significantly, due to both faster kiln start up (no pre-drying, faster heat up compared with cement bonded mixes) and significantly longer service lives.

## Bullnose

The high proportion of alternative fuels alone is a challenge for the refractory material due to the increased chemical stress and the properties of the fuels, which naturally fluctuate more strongly. In addition, the clinker produced shows a silica modulus between 2.9 and 3.2 and an alumina modulus of 2.11 to 2.18, with a lime standard of 97–99. Accordingly, the melting phase content in the clinker is low, with values of 22–24% at 1450 °C. The clinker is therefore considered hard burnable, which results in higher thermal stress on the refractory material. As the volatility of alkali salts also depends heavily on temperature, this means not only higher thermal stress for the refractory lining, but also increased chemical stress.

One of the particularly critical areas was the bullnose. Here, maximum lifetimes of 7 months were realized with various refractory concepts. The mixes were dried and heated according to the manufacturers' specifications and the drying schedule applied for the kiln hood and the cooler took at least 88 hours including a 24 hour setting time. The lining was gradually heated up to 400 °C, and this temperature was maintained for 12 hours. The material was dried using gas fired auxiliary burners. After 7 months of operation, the low cement hydraulically bonded gunning mixes based on bauxite and additives of zirconium oxide containing raw materials and SiC showed severe damage to such an extent that repair was required (Figure 2).

In January 2013, the entire bullnose was lined with CARSIT SOL M10G-6. This chemically bonded mix developed by RHI is a no-cement sol-bonded gunning mix



**Figure 2.** Bullnose with severe damage after 7 months in operation. Lining with a hydraulically bonded low cement high alumina gunning mix with additives of zirconium oxide and SiC.

comprising mullite-rich raw material, with an additive of 10% SiC. This newly developed sol gunning mix was applied by the company Möller Feuerfesttechnik. The project manager, confirmed that the workability of both the sol gunning and casting mixes was outstanding.

During this process, the equipment normally used for the application of cement-bonded dry gunning mixes was employed and only for pumping the binder was a commercially available pump required. The area was put into operation without predrying in February 2013. Due to the special chemical bonding and the different pore structure in comparison with hydraulically bonded mixes, no separate pre-drying was necessary. Moreover, it was possible to start up the rotary kiln in 36 hours.

Figure 3 shows the bullnose during a shutdown in September 2013 after 7 months of operation. While the area usually had to be fully renewed after 7 months, no wear was identified in the sol-bonded mix.

The kiln was finally shut down for major repair in June 2014. The inspection of the bullnose again showed a very positive picture. After a further 8 months in operation, no significant difference was identified compared with the previous kiln shut down (Figure 4).



**Figure 3.** Bullnose lined with CARSIT SOL M10G-6 after joint maintenance. After 7 months no wear was identified.



**Figure 4.** Bullnose after joint maintenance showing the same area as in Figure 3 after a further 8 months of operation, no significant change can be identified. After 15 months in operation, the mix remains in the cooler without any further repair required.

This is an excellent result, especially considering that the conventional gunning method was applied. As it is still in operation after more than 2 years, the service life has now been at least tripled. A forecast for the definitive service life is not yet possible.

Despite the slightly higher, upfront cost of sol-bonded mixes, they offer considerable economic and operational advantages for cement plants. The benefits result from the extended operating time (currently already tripled), which saves not only material costs, but also installation costs. Moreover, the use of sol-bonded mixes does not require any predrying of the monolithic lining, so shutdown times and fuel costs can be reduced. An additional firing schedule which prolongs the shutdown is not required either, thus leading to further savings of time and costs.

### Clinker Bed

Due to the direct contact with the clinker that is still hot, the clinker bed is subject to high, especially hot, abrasive stress. In addition, the components, some of which are massive, are difficult to dry and heat. Previously, a maximum service life of 12–15 months could be attained using different high-grade low-cement castables and severe damage was identified after 7 months (Figure 5). Both the

clinker bed and the components represent an ideal application for sol mixes. With CARSIT SOL S30-6, an andalusite mix with 30% SiC based on sol bonding, the lifetime was increased significantly.

The installation was done in January 2013 and after an operating life of 7 months (Figure 6) and 15 months respectively (Figure 7), no significant wear was identified. Currently the clinker bed lining is still in operation and thus has already clearly outperformed previous installations. Consequently, this material also lends itself as a substitute for prefabricated components, which are often used in this area.

### Rotary Kiln Burner

Despite professional installation and exemplary pre-drying of the previous monolithic linings, during which the burner lance is heated to 450 °C in 72 hours, lifetimes of only 6 to 10 weeks maximum were obtained. Most recently, low-cement high alumina castables based on corundum were applied. In this area the refractory lining is exposed to a complex combination of different wear mechanisms. The hot, dust-loaded secondary air leads to thermal and hot abrasive wear. Moreover, deposits of alkali salts are formed, causing additional hot chemical



(a)



(b)

**Figure 5.** Clinker bed lined with a low-cement castable. Showing considerable damage after 7 months in operation. (a) exposed anchors and (b) broken structure.



**Figure 6.** Clinker bed with CARSIT SOL S30-6 after 7 months in operation.



**Figure 7.** Clinker bed with CARSIT SOL S30-6 after 15 months in operation.

attacks. As thermal wear was assumed to be the main problem, COMPAC SOL MB A100-15 was used in the first trial. This is a highly refractory high alumina no-cement mix. The castable displays excellent refractoriness and at the same time improved chemical resistance when compared to the low-cement castable used previously. Finally, the unique cold crushing strength of 180 N/mm<sup>2</sup> after firing at 1000 °C was also convincing.

The burner tip was initially put into operation in December 2013 and was not renewed until June 2014 as part of a scheduled major repair (Figure 8). Hence, a service life of 7 months was achieved immediately.



**Figure 8.** COMPAC SOL MB A100-15 after 7 months in operation.

## Conclusion

With the use of alternative fuels, waste materials can be utilized in an ecologically and economically sensible way. Although the use of these materials sometimes present the operators with challenges, kiln technologies and refractory concepts provide manageable solutions. On the refractories side, RHI, with its sol-bonded mixes, now offers products which successfully meet the increased requirements. This has been impressively demonstrated with service life records in the most critical areas at SPZ (bullnose, clinker bed, burner) and at many other cement plants in Germany. RHI's no-cement mix concept provides not only superior lifetimes, but also excellent workability and easy drying behaviour.

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## Authors

Uwe Schneider, Technical Plant Manager, Solnhofer Portland-Zementwerke GmbH & Co KG.

Roland Krischanitz, RHI AG, Industrial Division, Vienna, Austria.

Peter Fritsch, RHI AG, Industrial Division, Vienna, Austria.

**Corresponding author:** Roland Krischanitz, [roland.krischanitz@rhi-ag.com](mailto:roland.krischanitz@rhi-ag.com)

# RHI SOL Castables – The New Generation of Monolithics



RHI's sol-bonded monolithics offer a wide range of advantages. In addition to fast drying and heating-up, superior physical and chemical properties, easy application casting, gunning, and shotcreting, and 18 months shelf life

the top performance of these mixes, proven in numerous applications, is the main benefit. The pictures above show sol-bonded castables and gunning mixes installed in the bullnose, horse shoe and clinker bed wear lining after 15 months in service. The lifetime was increased from 7–15 months to more than 2 years.

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Roland Krischanitz, Susanne Jörg and Monika Fellner

# Silicon Carbide Refractories—Not Always a Magic Bullet

It is well known that the addition of silicon carbide (SiC) to alumina and fireclay bricks significantly improves different product properties which make their use beneficial in many cases where alternative fuels are applied. In addition to the improved resistance against alkalis, abrasion resistance can also be increased significantly. Furthermore it is possible to avoid or at least reduce the formation of undesired built ups. However under specific conditions the use of SiC can prove adverse. The following case study highlights the impact of alternative fuels with high water content on bricks containing SiC and discusses alternative solutions.

The use of alternative fuels (AFs) has been steadily increasing within the last years and has reached, in the German cement industry, a mean substitution rate of 62.5% in 2013 [1]. The commonly used AFs are fractions of industrial, and commercial waste, plastics, mixed fractions of municipal waste, waste tyres, meat and bone meal, animal fat as well as sewage sludge. Sewage sludge can be applied as mechanically dehydrated sewage sludge (MEKS) and dried sewage sludge (TKS). The first has a water content of about 75%, the latter only 8%. Within the German cement industry, approximately 80% of the sewage sludge utilised is in the MEKS (high water content) form.

## Case Study

In the present case study the cement plant fires MEKS with a water content of 70%. The material is fed in the inlet chamber. The kiln is a suspension preheater kiln. It has a 5.2 meter diameter, is 80 meters long, and has a daily capacity of 3000 tonnes. The below investigated brick sample was taken from meter 7, when measured from kiln inlet, where unusually high wear was observed in this lining area after only one year of operation (Figures 1, 2).

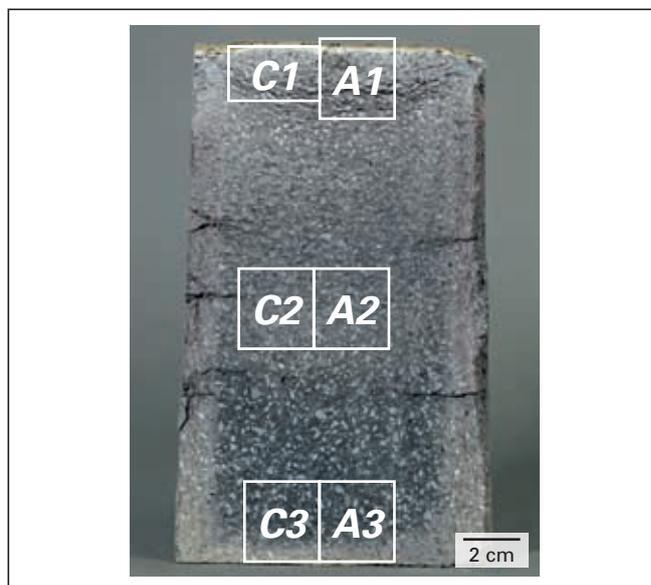
The respective area is lined with mullite bricks with an addition of 10% SiC. The observed wear was most severe at the kiln inlet with a residual thicknesses of 150 mm (from original 220 mm). The wear became less significant with increased distance from the inlet and reached about 190 mm residual thickness in the area 15 meters from the inlet.

The sample taken from meter 7 (measured from kiln inlet) had a residual thickness of 170 mm and showed clear structural changes up to 110 mm from hot face. The complete area appeared brightened. At depths of 55 mm, 80 mm, and 115 mm from the hot face there were short cracks reaching up to approximately 20 mm into the brick center. Most severely affected was the hot face up to approximately 20 mm depth. In this area there were numerous cracks parallel to the hot face.

The chemical analysis in the hot face area shows an increase of more than 3% potassium oxide, which reacted with brick components and formed feldspathoid minerals, such as leucite (Table I). This phase transformation resulted in a volume increase of up to 36%. Furthermore the



**Figure 1.** Brick sample received for post mortem analysis. The sample location was 7 meters from the kiln inlet.



**Figure 2.** Cross section of the used brick sample. The sample shows a residual thickness of 170mm. C1, C2, and C3 indicate samples for chemical analyses and A1, A2, and A3 indicate samples for mineralogical investigation.

formation of high amounts of alkali alumina silicates resulted in a reduction of refractoriness and softening of the brick structure. The newly formed phases have a higher thermal expansion compared to the original components. This can lead to crack formation and spalling of the hot face brick parts through thermal shock.

The mineralogical investigation showed a severe and deep reaching degeneration of the brick structure. At the immediate hot face there was no original SiC present (Figures 3, 4), it was been converted to carbon, SiO<sub>2</sub>, and fluorine containing potassium aluminium silicate. In the area 75–100 mm from hot face (polished section A2) there was no significant densification of the brick structure or formation of potassium aluminium silica compounds

observed. However, corrosion of the SiC was visible. The cold face brick part (polished section A3) was unchanged, showing original SiC (Figure 6). Accordingly the brightening of the brick structure up to about 110 mm from hot face could be attributed to the decomposition of SiC.

## Results

The dominant wear mechanism of the used mullite SiC brick was the corrosion of SiC. The input of sewage sludge obviously had a serious impact on the steadily increasing wear observed towards the inlet of the kiln. The high residual moisture (approximately 70%) of the sewage sludge fed at the kiln inlet chamber led to a severe corrosion of the brick inherent SiC. The corrosion of SiC in the presence of

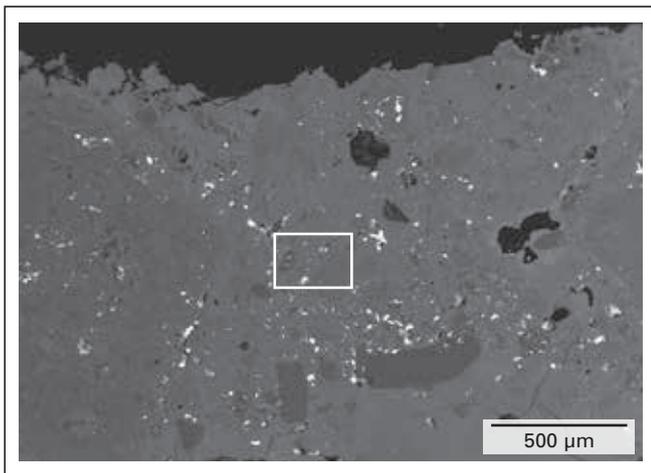
General information				
Aggregate	Cement rotary kiln			
Installation area	Inlet zone			
Brick type	Mullite based with 10% SiC			
Position	7 meters from kiln inlet			
Sampling	5–20 mm from hot face	75–100 mm from hot face	145–170 mm from hot face	Data sheet
Chemical analysis				
Loss on ignition (1050 °C) <sup>2)</sup> (DIN 51081)	0.23	0.00	-0.16	
Determination by XRF <sup>1)</sup> (ISO 12677)				
MgO (wt.%)	0.50	0.30	0.29	
Al <sub>2</sub> O <sub>3</sub> (wt.%)	51.91	54.53	54.38	57.00
SiO <sub>2</sub> (wt.%)	37.69 <sup>3)</sup>	40.14 <sup>3)</sup>	40.08 <sup>3)</sup>	28.50
P <sub>2</sub> O <sub>5</sub> (wt.%)	0.15	0.16	0.16	
CaO (wt.%)	0.44	0.46	0.48	
TiO <sub>2</sub> (wt.%)	2.11	2.20	2.22	2.50
Fe <sub>2</sub> O <sub>3</sub> (wt.%)	1.33	1.43	1.42	1.80
Determination by gas-volumetric analysis <sup>2)</sup>				
SiC (wt.%)	3.00	4.91	6.38	10.00
Determination by element-analysis <sup>2)</sup> (DIN 51085)				
SO <sub>3</sub> (wt.%)	0.05	0.05	0.37	
Total carbon content (wt.%)	1.09	1.92	2.10	
Residual carbon content (wt.%)	0.19	0.45	0.19	
Determination by ICP-OES <sup>2) 4)</sup> (DIN 26845)				
Na <sub>2</sub> O (wt.%)	0.06	0.07	0.08	
K <sub>2</sub> O (wt.%)	3.21	0.02	0.00	
Determination by titration <sup>2)</sup> (DIN 26845)				
Chloride (wt.%)	0.00	0.00	0.00	
Phase analysis by x-ray diffraction <sup>2)</sup>				
Mineral phase	Formula			
Mullite (wt.%)	Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	> 50.0	> 50.0	> 50.0
Corundum (wt.%)	Al <sub>2</sub> O <sub>3</sub>	10.0–50.0	10.0–50.0	5.0–10.0
Silicon carbide (wt.%)	SiC	2.0–5.0	2.0–5.0	5.0–10.0
Amorphous (wt.%)		5.0–10.0	5.0–10.0	5.0–10.0
Cristobalite (wt.%)	SiO <sub>2</sub>	0.5–2.0	5.0–10.0	2.0–5.0
Rutile (wt.%)	TiO <sub>2</sub>		0.5–2.0	0.5–2.0
Sillimanite (wt.%)	Al <sub>2</sub> SiO <sub>5</sub>	0.5–2.0	0.5–2.0	0.5–2.0
Quarz (wt.%)	SiO <sub>2</sub>		0.5–2.0	0.5–2.0
Leucite (wt.%)	KAlSi <sub>2</sub> O <sub>6</sub>	10.0–50.0		

**Table I.** Results of chemical and phase analysis of samples C1, C2, C3, and data sheet analysis of unused brick. <sup>1)</sup> On ignited sample (1050 °C) by X-ray fluorescence analysis. <sup>2)</sup> On original sample. <sup>3)</sup> Total silicon content originating from SiO<sub>2</sub> and SiC, given as SiO<sub>2</sub>. <sup>4)</sup> ICP-OES optical emission spectroscopy by inductively coupled plasma.

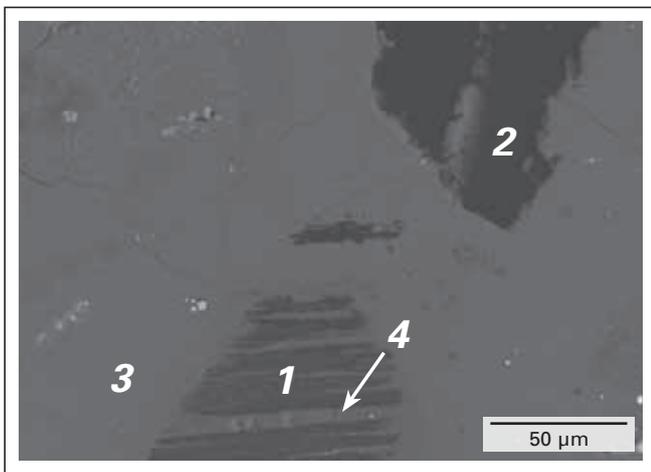
water vapour takes place predominantly in the range of 1000–1200 °C, leading to the formation of  $\text{SiO}_2$ . In the simultaneous presence of alkalis, a glassy phase can develop and orthoclase can form. In addition to this phase transformation the brick structure and bonding was softened, resulting in an increased hot abrasion. A higher residual thickness of the lining could be observed with increasing distance from the kiln inlet, the result of a continuous reduction in the humidity of the kiln atmosphere.

In addition to the observed degeneration of the brick structure by water vapour, the high load of potassium oxide led to the formation of potassium aluminium silicates, especially leucite. This caused the so called alkali spalling, the sudden shell-like spalling of hot face brick sections.

In comparison RESISTAL SK60CIS bricks located approximately 24 meters from the kiln inlet reached a satisfactory lifetime of 3 years despite being severely chemo-thermally loaded ( $\text{K}_2\text{O}$  content up to 8.7% at the hot face). The wear of the bricks installed towards the kiln outlet can be explained on the one hand by the different brick concept and on the other hand by the more favourable operation conditions in terms of vapour exposure in the respective lining area.



**Figure 3.** SEM—BSI of polished section A1. Overview of the strongly densified and severely degenerated microstructure at the hot face of the brick.



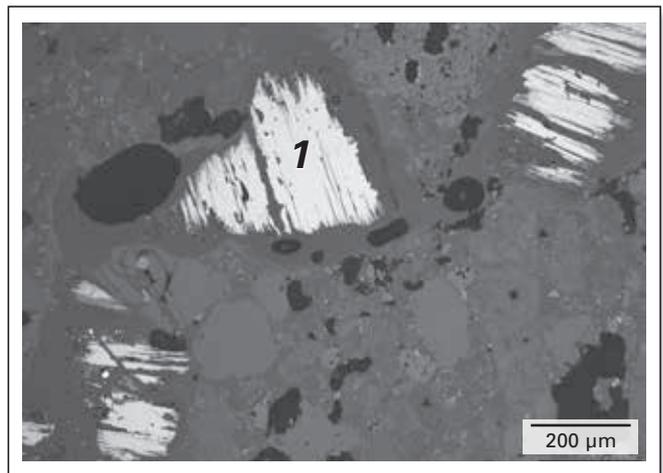
**Figure 4.** SEM—BSI of detail of Figure 3 (rectangular) SiC is nearly completely decomposed at the immediate hot face. In addition to small SiC relics (1), carbon (2) and fluorine containing potassium aluminium silicate phases, such as orthoclase (3) and leucite (4) can be observed.

## IS Impregnation—Performing Even in Water Vapour Rich Environments

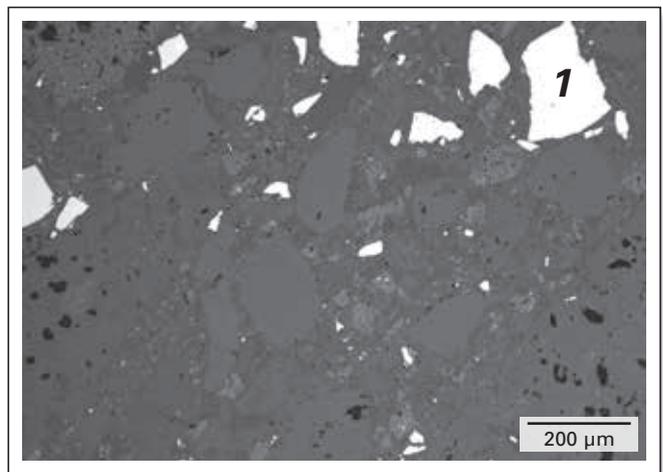
In this context especially the so called impregnation treatment of IS bricks needs to be mentioned, which increases the resistance to alkali attack and coating formation, entirely without the use of SiC.

This is of particular advantage where a steam rich environment leads to severe damages of the brick structure of SiC containing refractories. RHI offers this technology in addition to RESISTAL SK60CIS in selected products, based on fireclay and/or bauxite as well as andalusite, as shown in Table II.

The impregnation treatment deposits refractory oxidic substances in the pores and significantly increases the alkali resistance. The impregnation media consists of nanosized silica particles which homogeneously fill the pores spaces during the impregnation process. After the impregnation process, a heat treatment takes place during which all volatile substances (e.g., the carrier medium) are removed from the pores leaving only the refractory oxidic material in the pore spaces.



**Figure 5.** Photomicrograph (reflected light, dry) of polished section A1 at a distance of approximately 5 mm from the hot face, showing the strongly corroded SiC and only present as relics (1).



**Figure 6.** Photomicrograph (reflected light, dry) of polished section A3 at the cold face, showing the unchanged microstructure with original SiC grains (1).

The influence of the impregnation on the physical test values is shown in Table II. As expected, the bulk density has slightly increased while the open porosity has decreased correspondingly. Additionally a distinct increase of the cold crushing strength can be observed. The thermo-mechanical behaviour (refractoriness under load) is influenced only marginally.

The protection mechanism is based on two effects. Firstly the impregnation treatment leads not only to a significant reduction of the porosity but also to a major reduction of the permeability, thereby reducing the possibility for alkali salts to infiltrate the structure. The second effect is based on the ability of silica to bind alkalis without having a negative effect on the brick structure due to formation of new phases like leucite or nepheline.

When compared to products with SiC addition this technology allows an increase of alkali resistance without suffering an increased thermal conductivity, which is a disadvantage in applications without an insulation layer, such as the rotary kiln. To assess the alkali resistance, a crucible infiltration test was carried out. The crucibles were fed with alkalis at 1050 °C during each cycle. The decisive criterion was the number of cycles reached when the first formation of cracks could be observed.

Figure 7 shows the crucible with RESISTAL B50ZIS and RESISTAL B50Z after 7 temperature cycles, Figure 8 shows the corresponding crucibles in cross section where infiltration depth of the alkalis after the test is visible. Not only was the formation of cracks prevented by the impregnation treatment but the infiltration depth was reduced significantly.

## Solution for Monolithics

The newly developed so called sol bonded castables now offer a similar technology for monolithic castables. In this case the silica was introduced not via an impregnation treatment but is part of the special binder which is added to the mix instead of water. The binder, DIVASIL, is based on colloidal nano particle silica. This binder system replaces the complex system of calcium aluminate phases in cement bonded mixes.

The main advantages of sol bonded mixes in general result from the absence of any kind of cement phases, resulting in:

- >> Easy drying, no specific pre-drying required.
- >> Fast and easy heat up procedure.
- >> Reduced ambient temperature impact on final product properties.
- >> Reduced sensitivity to incorrect dosing of the mixing fluid.
- >> Easily adjusted to the desired setting time.
- >> Higher refractoriness compared to equivalent cement bonded products.
- >> Extremely good thermal shock resistance and internal flexibility.
- >> Workability is not significantly influenced by ambient air temperature. Customers can rely on very good workability under difficult conditions (e.g., winter repair period).
- >> Improved chemical resistance (e.g., alkali as well as sulphur) compared to equivalent cement bonded products.
- >> Longer shelf life than low cement castables (LCC), minimum of 18 months.

Sol bonded castables have a significantly improved resistance to chemical attack, from alkalis, sulphur and also chlorine [2]. The sensitive component to sulphur and chlorine

	Fireclay		Fireclay/bauxite		Andalusite		Bauxite		Mullite/SiC	
	MAX 334	MAX 334IS	RES B50Z	RES B50ZIS	RE SK60C	RE SK60CIS	RES B75Z	RES B75ZIS	RES M45SIC	RES M45SICIS
BD (g/cm <sup>3</sup> )	2.15	2.24	2.36	2.43	2.53	2.62	2.74	2.79	2.50	2.56
OP (vol.%)	15.00	9.00	18.00	14.50	15.00	11.00	18.00	14.00	14.00	11.00
CCS (N/mm <sup>2</sup> )	60	100	55	80	80	120	90	135	105	140
RUL (°C)	1350	1300	1400	1450	1500	1520	1500	1500	1490	1500

**Table II.** Comparison of the physical properties of conventional and impregnated fireclay and alumina bricks.



**Figure 7.** Crucible after 7 cycles of the crucible infiltration test, RESISTAL B50ZIS (impregnated, left) and RESISTAL B50Z (not impregnated, right).



**Figure 8.** Cross section of crucible after 7 cycles of the crucible infiltration test, infiltration depth, RESISTAL B50ZIS (impregnated, left) and RESISTAL B50Z (not impregnated, right).

attack is the calcium aluminate cement. The replacement of the cement by a chemical liquid binder in these castables improves resistance to sulphur and chlorine. Additionally the silica contained in the binder, causes an increase in alkali resistance without the addition of SiC. This is well confirmed by alkali cup tests, as shown in Figure 9, two equivalent castables based on mullite with an alumina content of approximately 60% were investigated. The alkali attack takes place via the gas phase using 20 g  $K_2CO_3$  as a corrosive phase, creating similar conditions to the cement industry. The test was carried out at 1100 °C and with a holding time of 5 hours.

One sample represents a conventionally cement bonded low cement castable, the second, a sol bonded equivalent. While the cement bonded castable showed severe crack formation after 7 cycles, the sol bonded material reached 18 cycles without any crack formation or damage. This impressively documents the superior properties of sol bonded mixes in terms of alkali resistance.

Especially due to the improved alkali resistance, sol bonded mixes are an alternative to SiC based monolithics in applications where high vapour contents in the kiln atmosphere are to be expected.

## Conclusions

The addition of SiC to shaped and unshaped refractories is a common method to increase the alkali resistance of refractories. Although still successful, the application of SiC enriched refractories has undergone some changes in recent years, in particular in areas with severe chemical load caused by alkali salt infiltration at high temperatures. In this case the high contents of SiC have proved adverse, due to the formation of a high amount of melt phase, which may lead to increased material loss by erosion. While previously quite high amounts of SiC, up to 60%, were implemented, currently the recommendation is to significantly reduce SiC addition in areas with high temperature levels.

The present case study furthermore shows that SiC containing refractories are not in general suitable for the severe operation conditions caused by the application of certain alternative fuels. Although improving operating lifetime in many cases where alkali attack is the predominant wear factor, special care needs to be taken when applying fuels with high water content. Especially in such cases, detailed knowledge of operation conditions and the fuels applied are required prior to selection of the most suitable refractory material. So called IS impregnated bricks and sol bonded monolithics are suitable solutions to counteract alkali salt attack on alumina based refractories not only, but particularly in the operating conditions described above.

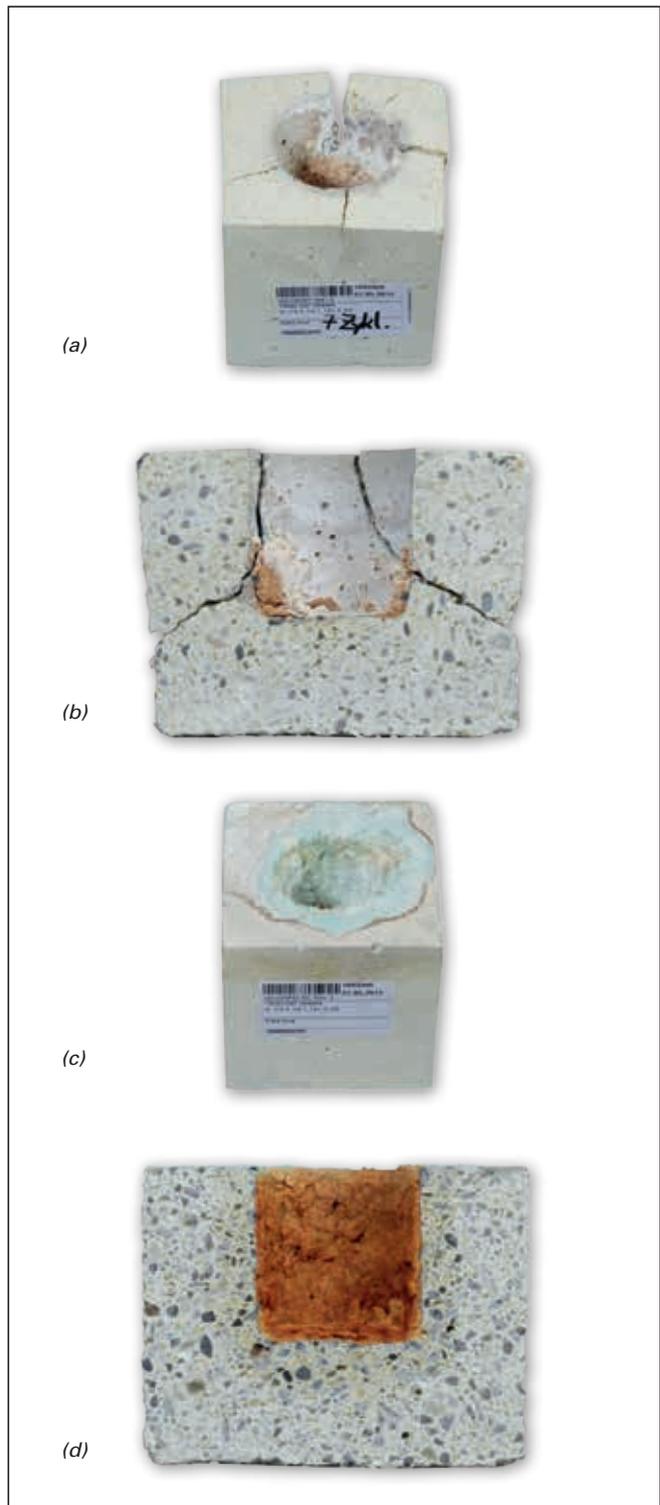
## References

- [1] [www.vdz-online.de/uploads/media/VDZ\\_Umweltdaten\\_2013\\_DE\\_GB.pdf](http://www.vdz-online.de/uploads/media/VDZ_Umweltdaten_2013_DE_GB.pdf)  
 [2] Blajs, M., von der Heyde, R., Fritsch, P. and Krischanitz, R. COMPAC SOL—The New Generation of Easy, Safe, and Fast Heat-Up No Cement Castables. RHI Bulletin. 2010, No. 1, 13–17.

## Authors:

Roland Krischanitz, RHI AG, Industrial Division, Vienna, Austria.  
 Susanne Jörg, RHI AG, Technology Center, Leoben, Austria.  
 Monika Fellner, RHI AG, Technology Center, Leoben, Austria.

**Corresponding author:** Roland Krischanitz, [roland.krischanitz@rhi-ag.com](mailto:roland.krischanitz@rhi-ag.com)



**Figure 9.** Crucible test and resulting cross sections, comparing low cement mullite based castable 60%  $Al_2O_3$  after 7 cycles (a and b) and equivalent sol bonded castable COMPAC SOL M64-6 after 18 cycles (c and d).

Dieter Pirkner, Milos Blajs and Viktoria Reiter

# New Innovative Lightweight Castable and Guniting Concepts for the Petrochemical Industry

Increasing time and cost pressure require refractory products that refractory installers, original equipment manufacturer (OEMs), and refinery owners can rely on, to keep the project schedules of necessary downtime or the installation of new process equipment. RHI has increased and reengineered its product portfolio to meet demand for easy to use high-end products.

## Introduction

When it comes to the discussion of maintenance and repair of equipment, customers don't have an easy life, because the downtime of a unit causes a partial or complete interruption to production. Therefore it is mandatory that downtime be reduced to a minimum to preserve productivity. This means that the refractory products must be easy to handle and be applied quickly. A good, reliable, and easy to use refractory concrete is therefore of utmost importance. However most of the time this is only half of the story. Due to the complexity of the different refinery units, the experience of a reliable partner who is qualified to install this refractory material is also absolutely mandatory. Particularly with growing time and cost pressure such an installer is indispensable, because only a person who knows the products they are working with can achieve the best possible results and observe all the various specifications and regulations of the different refinery owners or OEMs. This poses a big challenge to the refractory producers and installers. To this end RHI has in conjunction with the proprietary refractory installers RHI MARVO, LLC RHI WOSTOK, and RHI Canada Inc. developed a new product concept.

## Special Medium and Light Weight Heat Insulating Castables

As mentioned above, refinery products need to fulfil highest requirements and comply to some extent with opposing physical product properties. Often these specifications approach the limit on what is technically feasible. One of those requirements is high strength, while maintaining the best possible insulating properties. Additionally the transportation of the castable onsite to the mixing, and to the installation area, should be carried out as quickly as possible. This is managed by pumping.

Conveying and pumping of refractory concretes is not a new technology for RHI. Mixes based on high alumina can be pumped by pneumatic pumps and some castables based on fireclay or bauxite are pumped with double piston pumps in various wet gunning processes. However, concretes based on such raw materials are normally very dense. The maximum density for pneumatic pumpable mixes is roughly 3.0 g/cm<sup>3</sup> [187 lb/ft<sup>3</sup>] for fused alumina and 2.7 g/cm<sup>3</sup> [169 lb/ft<sup>3</sup>] for mixes based on alumina rich fireclay. The pumping of insulating castables is more difficult, because of the risk that the light weight insulating raw material separates from the heavier components of the mix.

The requirements on such a pump-cast mix and the used pumps are:

- >> Consistent conveyance of the material.
- >> Homogenous distribution of the density and all other physical properties across the whole fill level (no segregation of the light weight raw material).
- >> Sufficiently long processing time (late initial setting of the mix to prevent plugged hoses).
- >> Preferably low wear of the pump (screw).
- >> Lowest possible influence of the transportation on the material properties of the light weight concrete.

With regards to the physical requirements, there are two different approaches that affect the specifications available. In some cases a more rigid, therefore denser "medium" weight concrete is preferred, while in other situations the insulating properties are of greater importance. The situation becomes more complicated, when the better insulating "light" weight concrete results in a slight reduction in the strength properties.

The "medium" weight castable requirements are:

- >> Lowest possible density (e.g., < 1.32 g/cm<sup>3</sup> [82 lb/ft<sup>3</sup>] after drying at 110 °C [230 °F]).
- >> Preferably low thermal conductivity (e.g., a maximum of 0.45 W/mK [3.1 Btu in/h ft<sup>2</sup> °F]) generally good insulating properties.
- >> Lowest possible shrinkage.
- >> Preferably high strength (e.g., > 7.6 N/mm<sup>2</sup> [1100 psi]).

Special "light" weight heat insulating mixes have basically to meet the same requirements, however for this castable type a lower density < 1.12 g/cm<sup>3</sup> [70 lb/ft<sup>3</sup>] after drying and a thermal conductivity of 0.3 W/mK [2.1 Btu in/h ft<sup>2</sup> °F] is required at the cost of a slightly lower strength > 4.8 N/mm<sup>2</sup> [700 psi].

Of highest importance for practically all monolithic refractory applications in refineries is low shrinkage. The large dimensions, particularly the wide diameters of refinery equipment allow for only a very small shrinkage of the mixes to avoid the formation of cracks. Typically the shrinkage values are reported as the permanent linear change (PLC) values for green to dried (110 °C [230 °F]) and dried to fired (815 °C [1500 °F]) and are limited with -0.1% for the PLC green to dried and a maximum of -0.3% for the PLC dried to fired.

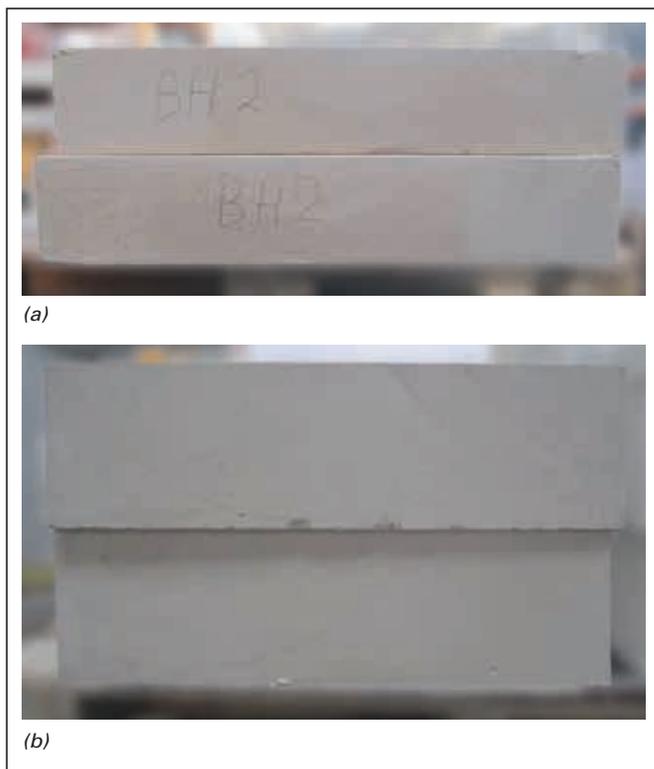
RHI's new products LEGRIT 132-1, 1PC 0-1 and LEGRIT 143-1, 2PC 0-1 fulfil all these specifications and allow a quick and easy installation with screw pumps. (Our references are Putzmeister S5 and SP11 screw pumps)

LEGRIT 132-1,1PC 0-1 is a special lightweight castable for oxidizing and alternately oxidizing and reducing atmospheres. LEGRIT 143-1,2PC 0-1 is a special medium weight castable which can be used for both, exclusively oxidizing or exclusively reducing atmospheres. Due to the high alumina content this mix is especially resistant to hydrogen atmospheres.

The chemical and physical properties of both mixes are shown in Table I.

	LEGRIT 132-1,1PC 0-1		LEGRIT 143-1,2PC 0-1	
<b>Chemical properties</b>				
Al <sub>2</sub> O <sub>3</sub> (wt.%)	41.2		51.9	
SiO <sub>2</sub> (wt.%)	41.1		35.8	
CaO (wt.%)	13.8		10.4	
Fe <sub>2</sub> O <sub>3</sub> (wt.%)	1.5		0.6	
TiO <sub>2</sub> (wt.%)	1.7		0.8	
Na <sub>2</sub> O (wt.%)	0.1		0.2	
K <sub>2</sub> O (wt.%)	0.3		0.1	
<b>Physical composition</b>				
Water demand (%)	40–42		28–32	
PLC green-dried at 110 °C [230 °F] (%)	-0.03		-0.04	
PLC dried-fired at 815 °C [1500 °F] (%)	-0.19		-0.09	
Dried density at 110 °C [230 °F] (g/cm <sup>3</sup> [lb/ft <sup>3</sup> ])	1.10	68.7	1.35	84.3
Fired density at 815 °C [1500 °F] (g/cm <sup>3</sup> [lb/ft <sup>3</sup> ])	0.98	61.2	1.18	73.7
CCS after firing at 815 °C [1500 °F] (N/mm <sup>2</sup> [lb/in <sup>2</sup> ])	5.0	725	10.0	1450

**Table I.** Chemical and physical properties of the new pump-cast mixes LEGRIT 132-1,1PC 0-1 and LEGRIT 143-1,2PC 0-1. All values were determined on pumped samples.



**Figure 1.** Cross section of the pump-cast mixes. Showing (a) LEGRIT 132-1,1PC 0-1 and (b) LEGRIT 143-1,2PC 0-1.

Figure 1 shows the completely homogenous cross section of both mixes. Homogeneity and consistent values across the whole filling level was of particular importance throughout the entire product development.

To evaluate the homogeneity the castable was pumped into an 80 cm [2.6 ft] high wooden mould and specimens were cut out from the top, middle, and bottom section of the monolithic block for testing. Figure 2 shows the casting procedure using a flat mould.

The test results shown in Table II confirm the consistency that can be observed in the cross sections, namely that the mix was spread homogeneously in the mould and that independent of the filling level no variations in the physical properties could be observed.

Theoretically the addition of steel fibers is possible, (mixing needs to be done in a separate mixer). Steel fibers cause a weakening of the fine matrix of the light weight castable, a contrary effect compared to dense castables and therefore the fibres diminish strength instead of enhancing it. The lower the density of the light weight mix, the greater is the impact of this effect. The use of 3% of steel fibers lowers the cold crushing strength of LEGRIT 143-1,2PC 0-1 by up to 20% and for LEGRIT 132-1,1PC 0-1 the loss of strength is more than 30%. This fact needs to be considered prior to

		LEGRIT 132-1,1PC 0-1		LEGRIT 143-1,2PC 0-1	
<b>Filling height</b>		<b>Dried density at 110 °C [230 °F]</b>			
(cm)	[in]	(g/cm <sup>3</sup> )	[lb/ft <sup>3</sup> ]	(g/cm <sup>3</sup> )	[lb/ft <sup>3</sup> ]
0–15	0–6	1.12	69.9	1.38	86.2
35–45	14–18	1.12	69.9	1.33	83.0
65–80	26–32	1.11	69.3	1.35	84.3
<b>Filling height</b>		<b>Fired density at 815 °C [1500 °F]</b>			
(cm)	[in]	(g/cm <sup>3</sup> )	[lb/ft <sup>3</sup> ]	(g/cm <sup>3</sup> )	[lb/ft <sup>3</sup> ]
0–15	0–6	0.99	61.8	1.20	74.9
35–45	14–18	1.00	62.4	1.16	72.4
65–80	26–32	1.00	62.4	1.17	73.0

**Table II.** Distribution of the dried and fired density across the entire mould filling height of 80 cm [2.6 ft].



**Figure 2.** LEGRIT 143-1,2PC 0-1 pumped with 29% water into a flat mould. The consistency is very “creamy”. The mix can easily be densified by poking.

the installation of this product type and the amount of steel fibers should be minimized or even deliberately omitted.

Particularly impressive is the low shrinkage of both light weight mixes. The overall PLC average value green to fired (815 °C [1500 °F]) is only -0.2%. These consistent results represent the stable product properties that are demanded especially for the lining of large scale areas in different vessels and heaters.

### Completely New Insulating Gunite Concept

Almost all of the trials showed decisively, that a single mix cannot fulfil the same criteria for different lining methods, which means, that it is impossible to achieve the same properties with different methods, (e.g., casting, gunning, ramming, or handpacking) even if the same mix is used. One of the reasons is, that the water demand of different lining methods results in varying physical values and that factors such as conveying capacity, gunning pressure or nozzle operator cause significant variances in the product properties, to the extent that the required specifications are no longer met.

Therefore the concept of an all-in-one product, which can fulfil the demands of each kind of installation method or application, was dismissed and RHI focused on the development of application-specific specialties.

### Special Medium and Light Weight Heat Insulating Gunning Mixes

Gunning mixes are basically covered by the same specifications and requirements as the related castables, but slightly wider tolerances for the physical properties are accepted, because the equipment used, the experience of the nozzle man, and gunning operators have considerable influence on the quality of the lining and of course also on the installed test results.

For medium weight insulating gunning mixes therefore a slightly higher density up to 1.44 g/cm<sup>3</sup> [90 lb/ft<sup>3</sup>] after

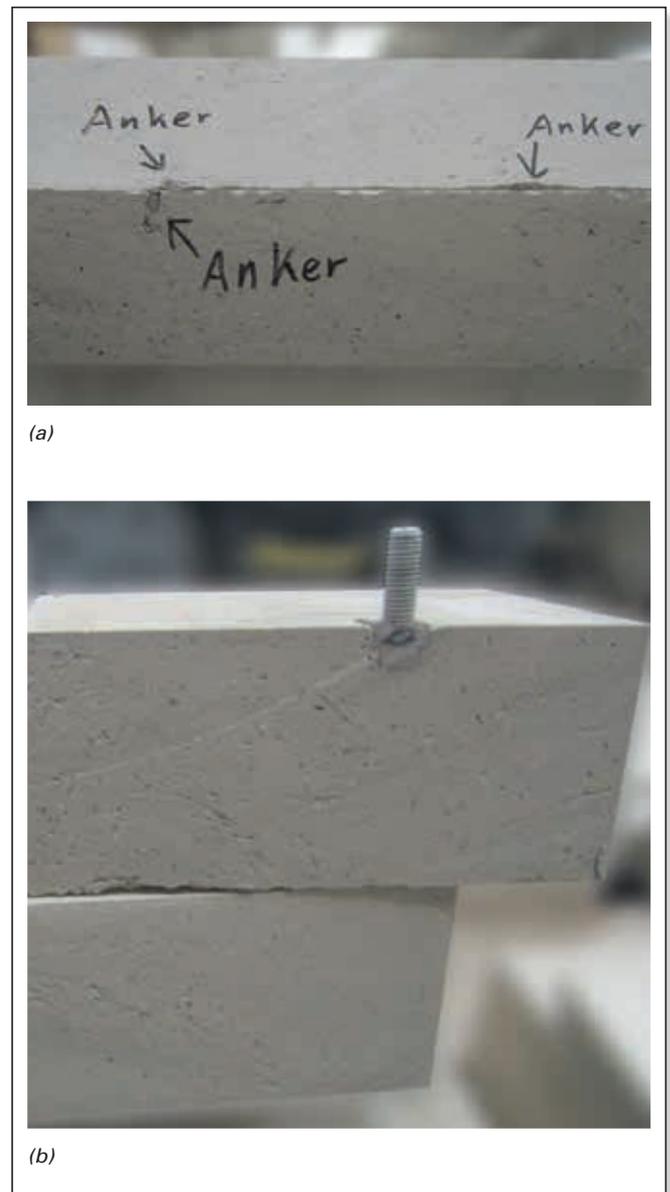
	LEGRIT 143-1,3G 0-1		LEGRIT 143-1,1G 0-3	
<b>Chemical properties</b>				
Al <sub>2</sub> O <sub>3</sub> (wt.%)	49.7		46.8	
SiO <sub>2</sub> (wt.%)	36.6		40.9	
CaO (wt.%)	11.7		9.9	
Fe <sub>2</sub> O <sub>3</sub> (wt.%)	0.6		0.9	
TiO <sub>2</sub> (wt.%)	0.8		0.9	
Na <sub>2</sub> O (wt.%)	0.2		0.2	
K <sub>2</sub> O (wt.%)	0.2		0.2	
<b>Physical composition</b>				
	Metric	Imperial	Metric	Imperial
PLC green-dried at 110 °C [230 °F] (%)	-0.02		-0.03	
PLC dried-fired at 815 °C [1500 °F] (%)	-0.04		-0.03	
Dried density at 110 °C [230 °F] (g/cm <sup>3</sup> [lb/ft <sup>3</sup> ])	1.42	88.6	1.17	73.0
Fired density at 815 °C [1500 °F] (g/cm <sup>3</sup> [lb/ft <sup>3</sup> ])	1.20	74.9	1.02	63.7
CCS after firing at 815 °C [1500 °F] (N/mm <sup>2</sup> [lb/in <sup>2</sup> ])	14.0	2030	8.0	1160

**Table III.** Chemical and physical properties of the new insulating gunning mixes LEGRIT 143-1,3G 0-3 and LEGRIT 143-1,1G 0-3. All values were determined on gunned samples.

drying is acceptable and also for the light weight version, density values of up to 1.28 g/cm<sup>3</sup> [80 lb/ft<sup>3</sup>] are accepted. However the strength requirements are identical to the specifications of the related castable.

With the development of LEGRIT 143-1,3G 0-3 and LEGRIT 143-1,1G 0-3 RHI has products which meet the required values, which have all been determined exclusively on gunned panels so far. Advantages are the high strength and the low shrinkage of the new products. Table III shows the chemical and physical properties of the two gunning mixes.

In addition to the required strength and shrinkage properties, an excellent gunning behaviour could also be realized. With a recommended pressure of 0.08–0.12 MPa and the use of a small rotor, almost no quantifiable rebound could be measured and even during overhead gunning the losses remain minimal. Figure 3 shows the cross-section of both gunning mixes after cutting the overhead panel along the metal anchors. The material is evenly distributed throughout the whole panel and free of any laminations or inclusions.



**Figure 3.** Cross section of the gunning mixes (a) LEGRIT 143-1,3G 0-3 and (b) LEGRIT 143-1,1G 0-3. The structure of the gunned panels is homogeneous, even directly behind the metallic anchors.

## Conclusion

The extensive development by RHI of mixes for the petrochemical industry addressed significant client issues, in particular the structure and physical properties of these state of the art products. The result of this development is four new high quality products. The collaboration with refinery experts from RHI MARVO in Nürnberg demonstrated the importance of existing installation know-how in product development and that high quality refractory products particularly require skilled installation. RHI now offers a range of products that fulfils the highest customer specifications and quality standards.

## Authors

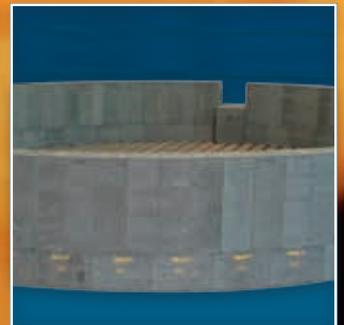
Dieter Pirkner, RHI AG, Industrial Division, Wiesbaden, Germany.

Milos Blajs, RHI AG, Technology Center, Leoben, Austria.

Viktoria Reiter, RHI AG, Technology Center, Leoben, Austria.

**Corresponding author:** Dieter Pirkner, [dieter.pirkner@rhi-ag.com](mailto:dieter.pirkner@rhi-ag.com)

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Phone: +43 50213-5323, Fax: +43 50213-5270, E-mail: [ulla.kuttner@rhi-ag.com](mailto:ulla.kuttner@rhi-ag.com)

