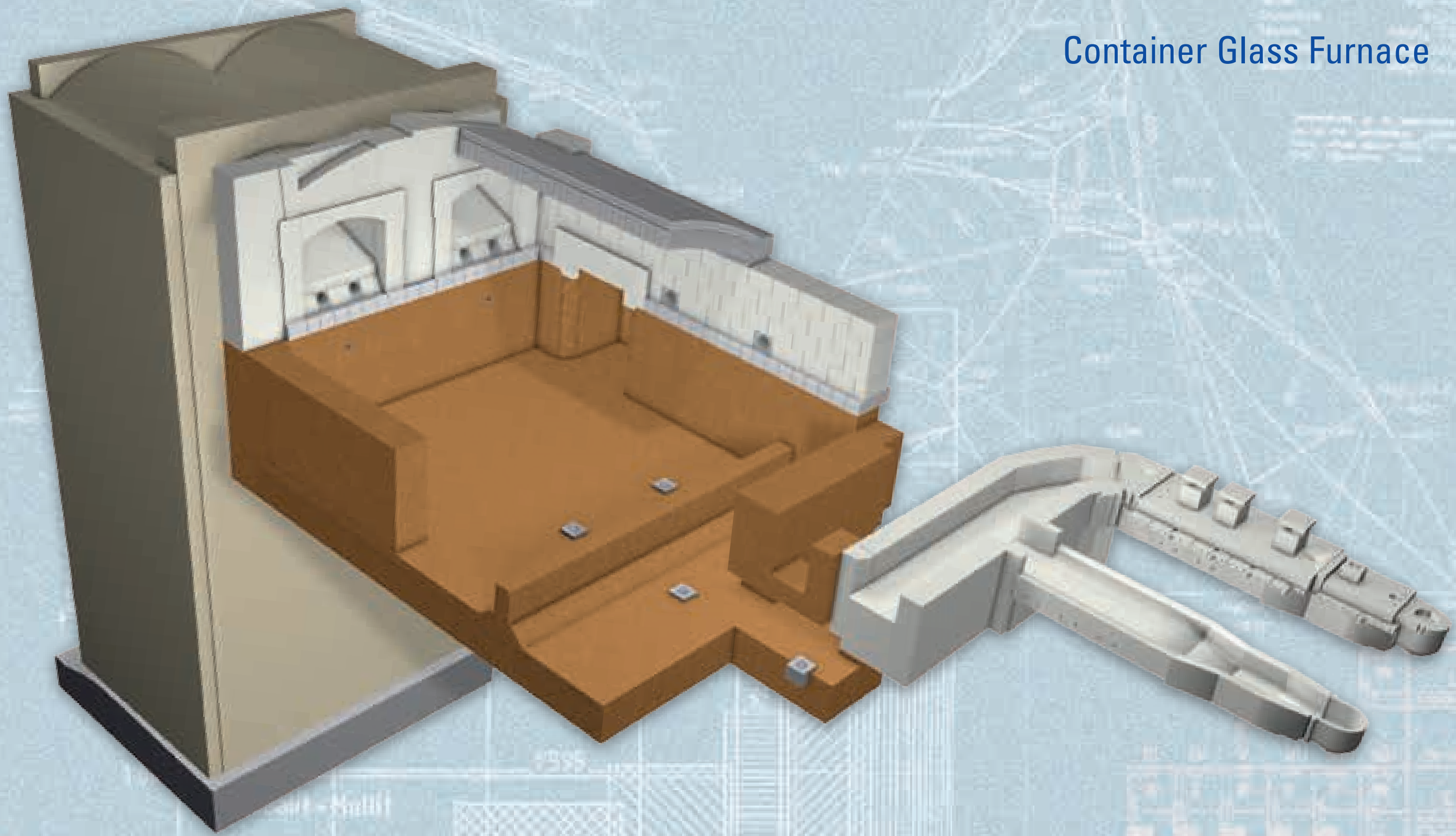
Industrial Edition

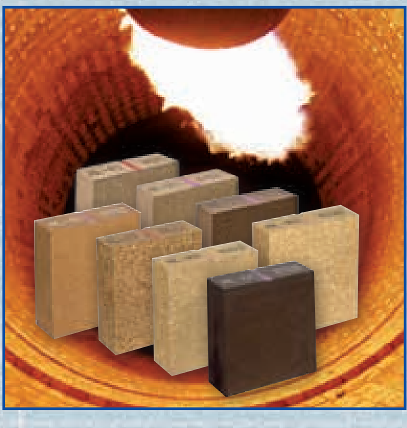
RHI Bulletin >2>2014

The Journal of Refractory Innovations

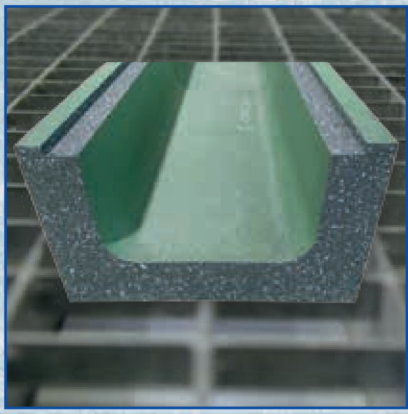
Container Glass Furnace



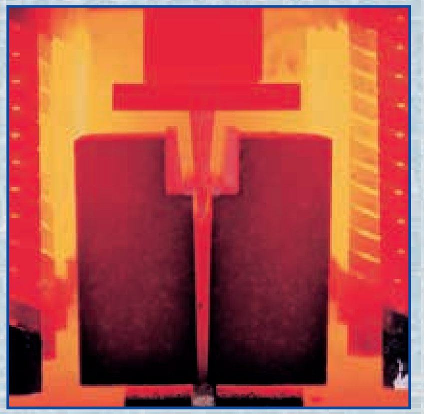
Extended Facilities at RHI's Training Center Cement



Vibrocast DIDURITAL RK55 Feeder Channel



High-Temperature Mechanical Fracture Characterization



RHI Bulletin >2>2014
The Journal of Refractory Innovations

RHI Bulletin 2/2014
Industrial Edition

Published by: RHI AG, Vienna, Austria
Chief Editor: Christian Majcenovic
Executive Editors: Markus Dietrich, Roland Krischanitz, Alfred Spanring
Raw Materials Expert: Gerald Gelbmann
Technical Writer: Clare McFarlane
Proofreader: Clare McFarlane
Project Manager: Ulla Kuttner
Photography, Graphics and Production: Markus Kohlbacher, Christoph Brandner
Design and Typesetting: Universal Druckerei GmbH, Leoben, Austria
Printers: Universal Druckerei GmbH, Leoben, Austria

Contact: Ulla Kuttner
RHI AG, Technology Center
Magnesitstrasse 2
8700 Leoben, Austria
E-mail: ulla.kuttner@rhi-ag.com
Tel: +43 50213-5323
Fax: +43 50213-5237
www.rhi-ag.com

RHI worldwide

Austrian Industrial Ceramics Apprenticeship Programme Established by RHI

Austria >> In September 2014, the first Austrian industrial ceramics apprentices successfully completed their 3-year training programme, which had principally taken place at RHI's Trieben and Leoben sites in combination with a vocational college in Graz.

The training to become an industrial ceramics technician at RHI comprises the selection, evaluation, and preparation of raw materials as well as the subsequent production of refractories using processes such as pressing and casting. The comprehensive knowledge of an industrial ceramics technician also includes heat treatment processes (e.g., tempering and firing), the operation of relevant production equipment (e.g., mixers and presses), and the subsequent characterization of refractory products.

During their training the apprentices also had the opportunity to participate in exchange programmes and work at other RHI sites. Due to the success of this programme, three additional apprentices are currently training at RHI.

RHI India Receives the 2014 Best Supplier Award From Tata Steel

India >> Recently, RHI India received Tata Steel's 2014 Best Supplier Relationship Management Implementation Award. It was presented in recognition of the numerous developments and successful work performed not only by the local RHI Indian organization (Sales and Marketing) but also for the technical support from Europe.

The Head of RHI's Indian Sales Offices together with the Tata Group Sales Manager received the award from Mr T.V. Narendran, Managing Director of Tata Steel. This award is a very prestigious achievement since it encompassed all Tata suppliers, not just refractory companies.

Successful Commissioning of the New RHI/INTERSTOP Converter Gas Purging Technology at ArcelorMittal Poland

Poland >> On September 28, 2014, the first INTERSTOP converter gas control unit was successfully commissioned at ArcelorMittal Poland in Krakow. Gas purging and its availability have a significant influence on efficient converter process management. An efficient system is characterized by short control times, individual flow control units, and a broad flow rate spectrum.

The gas flow control unit was developed in a close collaboration between RHI and INTERSTOP. It is a central component of the RHI converter gas purging technology, which is marketed under the name Converter Inert Purging (CIP). The new gas flow control unit distinguishes itself significantly from systems existing in the market through its high flexibility, extremely short regulation times, large control ranges, and fine-tuning of the purging programs. In order to ensure maintenance friendliness and process safety of the system, a modular design, which allows maintaining the system rapidly and independent of processes, was chosen.

A signal test and cold test were performed on site prior to commissioning the system. The system was switched on during hot operation and worked excellently. The compact design and simple operation were additional benefits appreciated by the customer.

10th Anniversary of RHI's Isostatic Pressing Plant in Saybrook

USA >> On October 1, 2014, a celebratory event took place at the Saybrook plant in Ohio (USA) to mark the site's 10th anniversary. About 65 employees, local business partners, together with RHI's Chief Operations Officer, Mr Franz Buxbaum, took part.

The Saybrook plant produces isostatically pressed products for the steel continuous casting process. It is RHI's most modern ISO plant and has the capability to provide the highest quality products for the most demanding applications. A high level of specialist knowledge exists in Saybrook and the site has a proven capability to develop tailored, value-adding solutions for customers located principally in North America.

The event was opened by Mr Franz Buxbaum and the plant manager, who described a favourable business situation both currently and for the future. The teamwork, determination, and passion of the employees were highlighted as critical reasons it has been possible to establish a new ISO facility under demanding market conditions.

RHI Participates at Aluminium China

China >> Aluminium China is Asia's leading aluminium industry platform, held annually in Shanghai (China). From July 9–11, 2014, over 460 international exhibitors from 30 countries represented the entire aluminium value chain. There were more than 16000 attendees this year, an increase of 8% compared to 2013. RHI was represented with a 60 m² booth that was visited by numerous renowned customers. The next Aluminium China will take place from July 8–10, 2015.

RHI worldwide

First Ferrochrome Produced at Kazchrome JSC's Aktobe Plant

Kazakhstan >> On August 23, 2014, the first tapping was performed with Kazchrome's DC electric arc furnace No. 1 after a 3-week heat-up schedule that had been concluded and supervised by RHI service technicians. Following an installation period of more than a year with four RHI supervisors at ENRC's Aktobe site in Kazakhstan, this event marked the start of the company's huge expansion project, comprising four new 72 MW DC SMS Siemag electric arc furnaces, which will provide an annual production capacity of more than 400000 tonnes of high-carbon ferrochrome.

RHI delivered four complete refractory lining sets for this important project, including all the materials as well as the design, engineering, and simulation work.

RHI Presents at the European Continuous Casting Conference

Austria >> From June 23–26, 2014, the 8th European Continuous Casting Conference was held in Graz (Austria). The ECCC is one of the most important conferences in the field of continuous casting and serves as a forum to discuss present and future developments in the continuous casting processes. The programme included lectures on the newest developments in control and automation, advanced continuous casting technologies, and the continuing improvement of product quality.

RHI was not only represented with a booth and life-size 3D model of the MNC-RSP Metering Nozzle Changer, but also with various lectures on the experimental verification of a three-phase continuous casting simulation using water modelling, optimization of submerged entry nozzles to improve steel cleanliness and productivity, argon control systems for the steel industry, as well as technical advances in ladle gate design.

RHI's Niederdollendorf Plant is Fit for the Future

Germany >> The Niederdollendorf plant produces nonbasic, ceramic-bonded special products for glass applications. Market developments in recent years indicate that there has been a continuous rise in the demand for high-quality products. In light of this, RHI has made major investments in the plant, totalling €8 million since 2011, in order to increase its production capacities and further improve production reliability while also ensuring the use of environmentally friendly and resource-efficient technologies.

One aspect of the project was the expansion of the mixing plant, which has enabled separate allocation of the mixers depending on the raw material base. As a result of purchasing a new 2000-tonne LAEIS press, large-format products such as bottom pavers and cover tiles (up to 700 mm x 500 mm) can be pressed. An additional shuttle kiln with a 75 m^3 furnace chamber led to a capacity increase for special silica and chrome corundum bricks as well as for tank blocks and large-format fired vibrocast products. Over the course of the project existing presses were refurbished, new drying capacities were created, and firing units were relined. Optimizations in the grinding workshop area have also resulted in a significant productivity increase in the final process step.

The investment in a fluorine filter system ensures that the plant will meet the required emission limit values in the coming years, and modernization efforts in the grinding water cleaning system also provide process security for water treatment. Furthermore, a modern heat recovery system in the firing units provides sustainable energy management.

The continuous optimization of production facilities with regard to safety, quality standards, and the use of resources is an important priority for RHI. All of these measures ensure that the Niederdollendorf plant will continue to supply high-quality products in the future and enable RHI to successfully continue its role as a full-range provider for the glass industry.

10-Year Anniversary of Production and Product Development at the Technology Center ISO

Austria >> On September 20, 2014, the isostatically pressed product competence centre in Trieben (Austria) celebrated its 10-year anniversary. Following the startup phase in 2004, production processes were initially established for the commercial supply of ladle shrouds and prototype products for customer trials. Subsequently, the facilities were extended in 2008 to enable additional manufacturing routes to be introduced and production of the complete isostatically pressed product range.

The tooling and design expertise available at the Technology Center ISO (TCI) as well as its close proximity to RHI's Technology Center Leoben enable material and product developments to be rapidly achieved for steel customers worldwide. The manufacture of various flow control advances, including the SHP-Stopper, GYRO Nozzle, and COUNTER HELIX, was initiated at TCI in addition to the production of numerous material grades tailored to specific continuous casting requirements.

Many of the leading-edge manufacturing techniques and innovative product developments are subsequently transferred to RHI's isostatically pressed production plants located in Scotland, China, and the USA.

RHI Celebrates a 10-Year Collaboration With the Vietnam Steel Corporation and an Agreement Extension

Vietnam >> A ceremony was held at the beginning of October in Hanoi to celebrate the long-term relationship between RHI and the Vietnam Steel Corporation.

The event was attended by Deputy Minister of Industry and Trade, Mr Cao Quoc Hung, Austrian Ambassador to Vietnam, Dr Thomas Loidl, General Director of Vietnam Steel Corporation, Mr Nghiem Xuan Da, and many other guests and customers.

The official speeches where followed by festivities and the entire event was covered by local Vietnamese television and press. The event also outlined the benefits of entering into a long-term relationship with RHI to all Vietnamese customers.

RHI Awarded Cement Project Orders

As a continuation of the successful business relations with ThyssenKrupp Industrial Solutions, RHI's Cement Department has secured further orders for three projects in Guatemala, Saudi Arabia, and Algeria. The decisive advantage over competitors is tailor-made concepts that incorporate economical and logistical aspects through a combination of RHI's production plants in Europe, Mexico, India, and China, while maintaining high-quality standards. The orders include supply of the entire refractory lining, as well as engineering and supervision. In the case of the Guatemalan customer installation is also included.

ORL Receives the IRMA Award for Excellent Performance

India >> For the ninth consecutive time, Orient Refractories Ltd., (ORL) received an award for "Excellent Overall Performance 2013–2014", in the large company category, from the Indian Refractory Makers Association (IRMA).

At the 53rd annual general meeting held in Calcutta, on September 20, 2014, the prize was officially presented to Mr Parmod Sagar, Managing Director of ORL.

The IRMA was founded in 1958 and is the national organization for refractory producers in India.

RHI Recieves Second Place in the Austrian Sustainability Reporting Awards

Austria >> Fourteen Austrian companies, among them RHI, were awarded the Austrian Sustainability Reporting Award (ASRA) for the balanced and transparent presentation of their sustainability activities at the Federation of Austrian Industries' Small Ballroom on October 22, 2014.

RHI submitted its sustainability report for the first time and immediately succeeded in obtaining second place in the "Large Companies" category. In particular, the jury praised the illustration of the value-added chain as well as the process description to define the main sustainability topics.

The specified sustainability topics are in line with the expectations and demands of RHI's stakeholders (Management Board, employees, shareholders, clients, suppliers, politicians and public authorities, as well as civic groups). As part of an open, international employee survey in September 2013, RHI employees were invited to list the sustainability issues that they believe are most important for RHI. At the stakeholder forum in October, customers, suppliers, non-government organizations, and other interested parties evaluated the issues developed internally from their own perspectives and thus provided a valuable external view of the company. Based on all the statements from this dialog process, an internal working group developed the RHI Materiality Matrix, which shows the most important sustainability issues for RHI. This will enable RHI to guide its future efforts in the area of sustainability in an even more targeted manner.

The ASRA is awarded by the Austrian Chamber of Public Accountants together with its cooperative partner the Institute of Austrian Certified Public Accountants, and in collaboration with the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management; the Environment Agency Austria; the Federation of Austrian Industries; respACT – austrian business council for sustainable development; the Austrian Economic Chambers; the Austrian Society for Environment and Technology; and Mensalia. The objective of the ASRA is to promote sustainability reporting in Austria in compliance with international standards and to draw attention to innovative reports. This year the ASRA was awarded for the fifteenth time.

Development of EAF Slide Gate Plates at RHI Clasil

India >> For the first time RHI Clasil Ltd., recently developed EAF slide gate plates, which are used to tap liquid steel from the electric arc furnace to the ladle.

The development process comprised a customer visit, sample analysis, generating product drawings, steel can development, grade selection, standardizing the manufacturing process, a cold trial, and then actual trials at the customer. Each plate weighs 101 kg and consists of an insert ring and insert plate, both manufactured from an Al_2O_3–ZrO_2–C grade (GRASANIT AC100 T4). The surround is filled with SANIT 180 MAWF 0-6 V castable. In addition, both the fixed and sliding nozzle are attached to the plates.

The manufacturing process is very complicated and involves two casting steps. Very precise assembly of the ring, insert plate, and steel can is important, as well as the type of fixture used to secure them during casting, since no gap between the insert ring and plate is allowed. Similarly, heat treatment and grinding the working surface is very challenging. Currently, the developed plate is being used at two Indian companies and performance is 30% better than the competitor product.

RHI worldwide

RHI's Tlalnepantla Plant Celebrates 70 Years

Mexico >> On August 11, 2014, approximately 160 employees, union representatives, suppliers, and subcontractors celebrated the 70th anniversary of RHI's Tlalnepantla production site, located north of Mexico City.

The plant director officially welcomed all the guests and in his speech emphasized the outstanding success and performance of the entire team, in addition to highlighting upcoming challenges that will characterize future actions.

The Tlalnepantla plant produces nonbasic bricks and mixes as well as special products like exchangeable nozzles and heavy delta parts for the steel sector. It principally serves the Mexican market, with a diverse customer base from the steel, cement, lime, glass, nonferrous metal, and petrochemical sectors. Additionally, products are delivered to customers in Central and South America as well as the Caribbean.

RHI Services for the Glass Industry

Recently, RHI launched SMART SOLUTIONS, a comprehensive range of services for the glass industry. In the last years RHI listened carefully to customers worldwide and has enhanced the portfolio of services it can provide relating to glass production beyond refractories. Designed to simplify glass producers' day-to-day processes, the new SMART SOLUTIONS concept offers expert services to add value to glass production processes.

Currently the areas include glass defect characterization, where not only basic and advanced analyses are performed in RHI's modern laboratories, but support can be given for customers to establish their own in-house expertise through classes and workshops. Refractory training courses are also available, providing state of the art knowledge relating to the selection and installation of refractories in the glass industry. Offered in multiple languages, the training modules range from standard classes covering the basic and advanced aspects of refractories to special topics regarding areas such as hot repair materials, recycling, and diagnostics. Full and partial furnace inspection is another service that RHI can supply to help reduce production losses and improve furnace yield and having teamed up with Franke IndustrieOfen - Service (Germany), one of the industry leaders for advanced thermal and endoscopic inspections, extended inspections are also available. A further SMART SOLUTION is the customized design of preassembled spout lips to improve glass quality as well as full spout lip management and exchange.

RHI Participates at the 57th International Colloquium on Refractories

Germany >> From September 24–25, 2014, the 57th International Colloquium on Refractories was held in Aaachen (Germany). The colloquium is one of the most widely respected refractory conferences worldwide and provides a unique opportunity to exchange experience and know-how during the lectures, discussions, and at the exhibition.

RHI had a booth in the trade fair and presented papers at the conference on several topics including the benefit of gas purging in basic oxygen furnaces and electric arc furnaces with the focus on material efficiency and CO_2 emission reduction, the interplay between product development and technical marketing within RHI's nonferrous refractory environment, as well as supply security though backwards integration.

The 58th International Colloquium on Refractories will take place next year in conjunction with UNITECR 2015 in Vienna (Austria) on September 15–18, 2015.

RHI's New Cement-Free Sol-Bonded Mixes Generate Record-Setting Results at Solnhofen Portland Cement Works

Germany >> In order to save fuel costs, companies in the energy-intensive cement industry are increasingly relying on alternative fuels. However, the use of such fuels puts refractory materials under much more intensive loads than conventional fossil fuels.

The Portland Cement Works in Solnhofen (Germany) had been using RHI refractory materials in various areas. Then at the beginning of 2013, RHI started testing the newly developed sol-bonded mixes together with the customer. The special bonding process gives the chemically bonded, cement-free mixes excellent characteristics, which were demonstrated in the field trials.

Sensational service lives were achieved even in the most critical plant areas, for example the bull nose, clinker bed, and burner, which are exposed to intense chemothermal attack. Previously, the maximum service life in the bull nose was 7 months; however, the CARSIT SOL M10G-6 lining showed hardly any signs of wear even after 15 months.

The record-setting service lives seen in Solnhofen and other German cement works prove that sol-bonded mixes from RHI withstand the toughest requirements. In addition, the mixes do not require predrying, making them a particularly cost-effective solution for customers.

RHI Attends glasstec 2014

Germany >> glasstec 2014 took place in Düsseldorf from October 21–24. It is the largest and world's most important trade fair for the glass sector, and no other specialist event presents the entire spectrum relating to glass—from production to processing, application, and recycling—in an equally comprehensive form. Approximately 1200 exhibitors from 54 countries and about 43000 trade visitors from 86 countries attended this year's biennial trade fair.

An international team of RHI employees welcomed visitors at the 150 m^2 booth. Despite the currently difficult market environment, the number of customer contacts, meetings, and intensive technical discussions exceeded expectations. The excellently designed trade fair stand with two meeting rooms, a lounge, and bar provided an ideal setting for these talks. In addition, new folders were available describing RHI's SMART SOLUTIONS concept for the industry to simplify glass producers' day-to-day working requirements.

The next glasstec will take place in Düsseldorf from September 20–23, 2016.

DIPLASTIT 259 0-3 Achieves Excellent Field Results

RHI's high-duty DIPLASTIT 259 0-3 mix, designed for extremely erosive conditions (see RHI Bulletin 2 > 2008) achieved excellent results in two different refineries after approximately 6 years in operation.

In June 2008, the product was installed in a 1 m^2 test field in the regenerator riser of a fluid catalytic cracking unit (FCCU) at the TOTAL Mitteldeutschland GmbH refinery in Leuna (Germany). Now 6 years later when the riser was inspected, the test field showed no difference compared to the standard product used for this type of application.

This very positive result was also confirmed at another location. In April 2009 a second, larger test field was installed in the primary cyclone of a FCCU at the Esso Augusta refinery in Sicily (Italy). Recently, after more than 5 years in operation, the inspected area showed a much better overall result compared to the competitor mix that had been used, which itself is often installed as an alternative to the standard product mentioned in the reference above. Of decisive significance is the fact that DIPLASTIT 259 caused no corrosion of the used hex metal, compared to the alternatives available from other companies.

Both results were so convincing that TOTAL have included the DIPLASTIT 259 0-3 on their specifications. In September 2014 the material was used for the installation of two entire regenerator cyclones of another FCCU at the TOTAL Donges refinery near Nantes (France). In addition, repair of a regenerator cyclone and the plenum chamber at the TOTAL La Mede refinery (France) is already scheduled.

RHI Extends Sales of ORL Flow Control Products in Turkey

Turkey >> Following the 2013 acquisition of a 69.6% stake in Indian Orient Refractories Ltd., (ORL), RHI has been expanding sales of the wide-ranging shaped and monolithic product portfolio for the iron and steel industry.

After successful trials at Koç Çelik Sanayi A.Ş and Ekinciler Demir ve Çelik Sanayi A.Ş., both customers awarded 3-year refractory contracts to RHI for the CS 60 ladle gate system as well as other ORL refractory products. In addition, RHI has secured LS 70 ladle gate business at former customers including Kroman Çelik Sanayii A.Ş and Kaptan Demir Çelik End., ve Ticaret A.Ş.

The first order of ORL isostatically pressed products has been delivered to Kroman and enlarging the customer-base for these products in Turkey is envisaged as a result of successful operations.

Customer trials are also underway with purging plugs in the region.

Nondestructive Physical Testing Introduced at the RHI Dalian Plant

China >> Recently, physical testing equipment that can perform measurements on bricks in a nondestructive manner was installed at the Dalian plant (China). As a result the bulk density distribution can be determined instantly after pressing the bricks, enabling immediate adjustment of the press settings. In addition, measurements can be performed on the end product, thereby providing an examination of the bulk density distribution, porosity as well as the cold crushing strength via ultrasound.

Previously, in order to examine bulk density distribution, porosity, and cold crushing strength, cylinders had to be drilled and cut out of bricks. Not only did this require several hours' processing time, but it also caused material loss as well as contaminated sewage due to wet drilling and cutting, resulting in high recycling and disposal costs.

The new method enables a higher testing frequency and continuous quality control, with only every 50^{th} brick that is tested nondestructively needing to be examined via classical methods. As a result, material loss and damage to the environment are reduced.

The system is a RHI internal development that was implemented for the fourth time in collaboration with Seibersdorf Laboratories (Austria). The successful and rapid launch in Dalian was due to excellent cooperation within the project team, located in China and at multiple Austrian locations.


RHI—A World Market Leader
in Refractory Technology

Editorial

RHI offers a vast range of refractories for the glass industry, manufactured at plants in Austria, Germany, Italy, the US, and Russia. These products enable complete packages to be provided from a single source and include for example fused cast blocks for melting tanks, ceramically bonded checkers installed in regenerators, hot repair materials, as well as castables. Developed by a team of technical experts, they comprise specific raw materials carefully selected to achieve the required performance. A guaranteed top product quality is complemented by the worldwide sales and service network, which ensures the best and most reliable customer service. Furthermore, in 2014 RHI launched SMART SOLUTIONS, an enhanced portfolio of services relating to glass production beyond refractories. The aim is to simplify glass producers' day-to-day activities and provide added value to the glass production process.

The first five papers in this Industrial Edition focus on various innovative products and services for our glass customers. They were also published as part of a special glasstec 2014 RHI Bulletin, to coincide with the globally renowned glasstec trade fair that took place in October. The additional three papers in this issue pertain to the cement and nonferrous industries.

The extensive vibrocast product range produced at the Niederdollendorf plant (Germany) is introduced in the first article. It consists of high-quality vibrocastable grades, based on different raw materials, which can be used to manufacture large complex shapes for various application areas such as the superstructure. The next paper describes REFEL 1616ULX, a unique fused cast product with a low zirconia content. Although originally invented to lower exposure to this highly volatile raw material, the grade has almost no glassy phase exudation while retaining the benefits of standard fused cast AZS.

Glass defect analysis and refractory postmortem investigations are two important services that RHI offers the industry and are frequently requested by customers. Two papers provide examples of both and describe various analytical approaches to improve final glass quality as well as examine the performance of specific grades under in-service conditions.

Since the integrity of glass melting tank components has a significant impact on furnace lifetimes, nondestructive testing methods are used for the quality assurance of glass tank blocks. A feasibility study described in the fourth paper compares the use of radar and ultrasound for quality control of fused cast products and highlights the sensitivity, spatial accuracy, and simplicity of a hand-held radar device that allows preassembled blocks and complete glass tanks to be examined.

The subject of the sixth paper is a case study regarding the new RHI Thrust Lock System for cement rotary kilns. It focuses on the specific installation procedure and various design options to eliminate axial lining thrust at the outlet zone. This is followed by an update of the extended facilities at the Training Center Cement (Austria), which now include successful burner lance monolithic lining.

In the final paper, characterization of magnesia-chromite and magnesia bricks using nondestructive and destructive testing at operating temperatures is described, which provides an understanding of thermomechanical behaviour and enables the most appropriate lining concept to be selected for specific applications.

In closing I would like to express my thanks to all the authors and editorial team for their considerable commitment to this edition.

Yours sincerely

Christian Majcenovic
Corporate Research and Development
RHI AG

Contents

Subscription Service and Contributions

We encourage you, our customers and interested readers, to relay your comments, feedback, and suggestions to improve the publication quality using the contact details below. Furthermore, to receive the RHI Bulletin free of charge please e-mail or fax your details to the Subscription Service using the form on the back page.

E-mail: ulla.kuttner@rhi-ag.com
Phone: +43 50213-5323
Fax: +43 50213-5237

RHI Bulletin > 2 > 2014, pp. 10–15

Viktoria Reiter, Markus Dietrich and Harald Noppinger

Extensive Vibrocast Product Range for the Glass Industry

For glass applications, several high-quality vibrocastable grades have been developed based on different raw materials such as zirconia mullite, tabular alumina, andalusite, fused silica, chrome corundum, and fireclay. Application areas in the glass industry (e.g., container glass, float glass, and fibreglass) include the tin bath, feeder superstructure, and feeder channels. The vibrocast shapes exhibit excellent characteristics for the different requirements and show a homogeneous structure as well as a high surface quality. With vibration casting it is possible to produce shapes with heights of up to 400 mm. Vibrocast materials complete RHI's product portfolio, following its goal to be a full-line supplier to the glass market.

Introduction

Vibrocasting enables high-quality glass furnace parts to be manufactured (e.g., burner block, doghouse arch, feeder channel, and feeder superstructure) and is therefore gaining ever more importance. For example, complex shapes with a height of up to 400 mm and a length of more than 3000 mm (or up to 2 tonnes) can be cast using this technology. Such block dimensions cannot be produced by hydraulic pressing, hand ramming, or impact impressing [1]. Compared to the alternative method of slip casting where the moulds must be dried after use, vibrocasting is faster, making it the most appropriate process to meet market requirements for production of large shapes. In addition, the more complicated the shape the higher the cost advantage of casting, as the costs for cutting, mechanical finishing, and material losses for pressed shapes increase rapidly with complexity. Due to these benefits a production line for vibrocast components was established at RHI's Niederdollendorf plant (Germany) in 2010 [1,2].

Vibrocasting is a sensitive production method and therefore all the process steps (Figure 1) must be accompanied by comprehensive quality assurance. The corresponding equipment, know-how, and experience are available at the Niederdollendorf plant, enabling the production of high-quality vibrocast products. With the introduction of vibrocast material, RHI can complete its portfolio, in line with the aim to offer complete packages and services from a single source and strengthen its position as a full-line supplier to the glass market.

Production of Vibrocast Shapes

Production is performed with compulsory pan mixers. To assure good surface quality, mainly wooden moulds are used with polyurethane inlets. The mould design and construction is performed by the Competence Center Moulds in Niederdollendorf. Standard vibrocast blocks can be produced with a thickness of 400 mm, width of 800–1000 mm, length of 2000 mm, and weight of 1 tonne. Additionally, large vibrocast blocks of up to 2 tonnes are possible (i.e., 3000 mm long, 1500 mm wide, and 600 mm thick). Flexible and complex temperature programs can be run in the shuttle kilns at Niederdollendorf. Therefore, the temperature curves can be adjusted according to the product's properties (e.g., large format and grade composition), enabling production of high-quality refractories without faults [2]. The vibrocast shapes are dried at 110 °C in a climate chamber and then fired at up to 1450 °C. If necessary vibrocast shapes can subsequently be treated and mechanically finished by cutting and grinding.

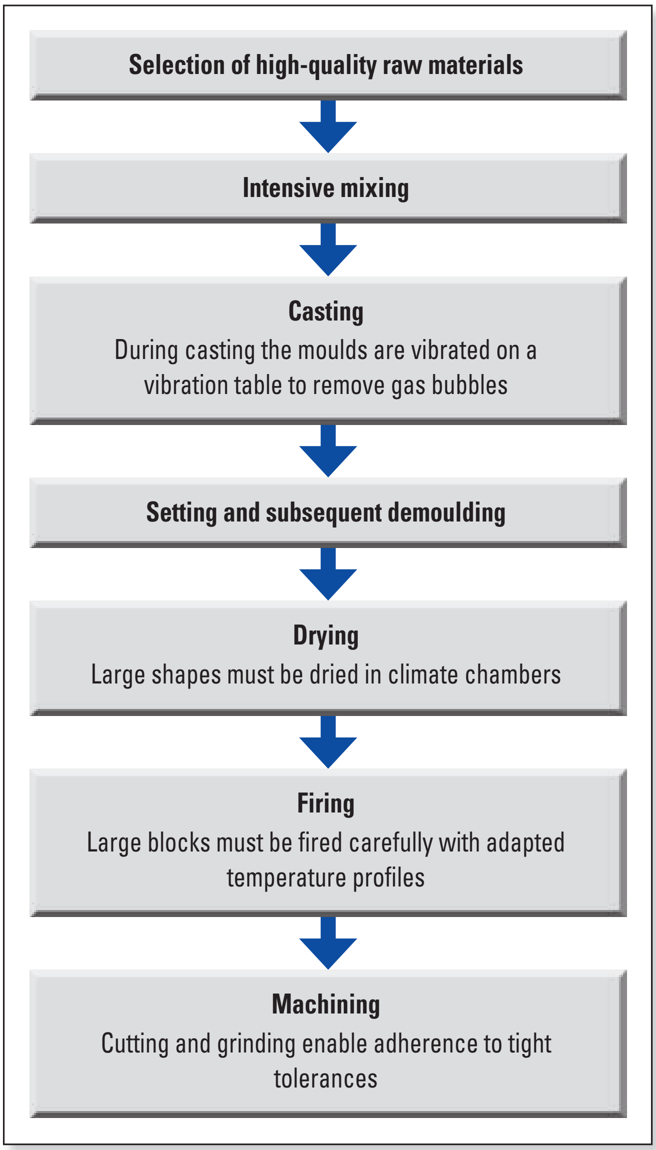


Figure 1. *Vibrocasting production process.*

Vibrocast Product Range for Glass Applications

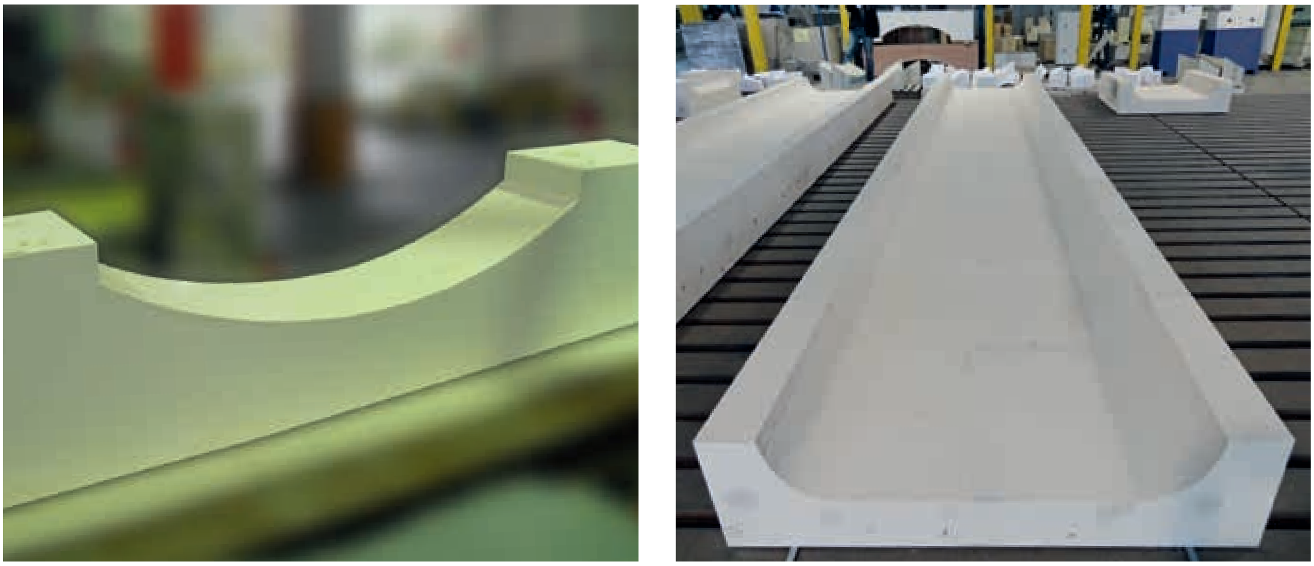
The use of vibrocast products is common practice in container glass, float glass, and fibreglass furnaces. The main application areas are the feeder channel, feeder superstructure, as well as hot and cold bays in the tin bath. For the various areas, alkali- and glass-resistant grades have been developed comprising different raw materials, namely zirconia mullite (DIDURITAL AZ52), tabular alumina (DIDURITAL A98), andalusite (DIDURITAL S67), chrome corundum (DIDURITAL RK30 and DIDURITAL RK55), fireclay (DIDURITAL F55), and fused silica (FONDAL SXW). The vibrocast grades are based on ultra-low-cement and low-cement castables. The typical chemical, physical, and thermomechanical properties (i.e., refractoriness under load and creep resistance) of the available product range are summarized in Tables I–III. Additionally, the results of corrosion and alkali vapour tests with the various grades are presented in the following sections. The corrosion mechanism strongly depends on the chemical composition, mineral phases, microstructure (e.g., texture and cracks), porosity, surface quality, and chemical impurities (e.g., carbon, iron oxide, and titanium oxide). As RHI focused on the development of refractory materials with low glass defect potential, high corrosion resistance, and low blister potential, carefully selected raw materials with high purity are used to increase the corrosion resistance and to avoid contamination. Additionally, the produced shapes, even in the case of very large formats, all show a homogenous microstructure and a high surface quality.

DIDURITAL AZ52

Due to their high corrosion resistance to soda-lime glass melts, zirconia mullite products with a ZrO_2 content of 20–30 wt.% have proved their effectiveness for feeder channels. DIDURITAL AZ52 (Figure 2) is based on fused raw materials and has a ZrO_2 content of 33 wt.% (see Table I). Synthetic zirconia mullite is used to avoid mullite formation during operation, which can result in expansion and stresses. Compared to classical fused cast AZS feeder material, DIDURITAL AZ52 has a good hot modulus of rupture and thermal shock resistance.

The corrosion resistance of zirconia mullite products was compared in the laboratory using static plate corrosion tests. At high temperatures refractory samples are corroded at the triple point where the refractory is in contact with both the glass melt and atmosphere. The notch depth at this triple point is an indication of the corrosion resistance. Figure 3 shows the results of a corrosion test examining the relative corrosion resistance of DIDURITAL AZ52 in soda-lime glass at 1400 °C for 96 hours. The vibrocast material exhibited a slightly better corrosion resistance than the equivalent pressed grade.

Nowadays, due to advances in furnace technology, the alkali concentration in the furnace atmosphere is rising. Therefore, resistance against these vapours has become more important. DIDURITAL AZ52 is also a suitable material solution for the superstructure of flint and coloured glass furnaces due to its good refractoriness ($T_{0.5}$ = 1650 °C) and



(a) (b)

Figure 2. *DIDURITAL AZ52: (a) arch with a 2.4 m span width and (b) feeder channel.*

Brand	Al_2O_3 (wt.%)	SiO_2 (wt.%)	ZrO_2 (wt.%)	Fe_2O_3 (wt.%)	CaO (wt.%)	BD (g/cm³)	AP (%)	CCS (MPa)	TSR H_2O (cycles)	RUL $T_{0.5}$ (°C)	TE 1000 °C (%)
DIDURITAL AZ52	51	15	33	0.1	0.5	3.10	18	100	> 30	1650	0.6
DIDURITAL S67	67	29	-	0.6	1.80	2.65	17	110	> 30	> 1700	0.6
DIDURITAL A98	98.8	0.1	-	0.1	0.7	3.00	18	100	> 30	1550	0.8

Table I. *Typical chemical composition and physical properties of DIDURITAL AZ52, DIDURITAL S67, and DIDURITAL A98. Abbreviations include bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), thermal shock resistance (TSR), refractoriness under load (RUL $T_{0.5}$), and thermal expansion (TE).*

high alkali resistance. The alkali vapour resistance of DIDURITAL AZ52 was evaluated at 1370 °C for 72 hours in sodium carbonate vapour (Figure 4). After the test the samples showed no cracks or bursting had occurred.

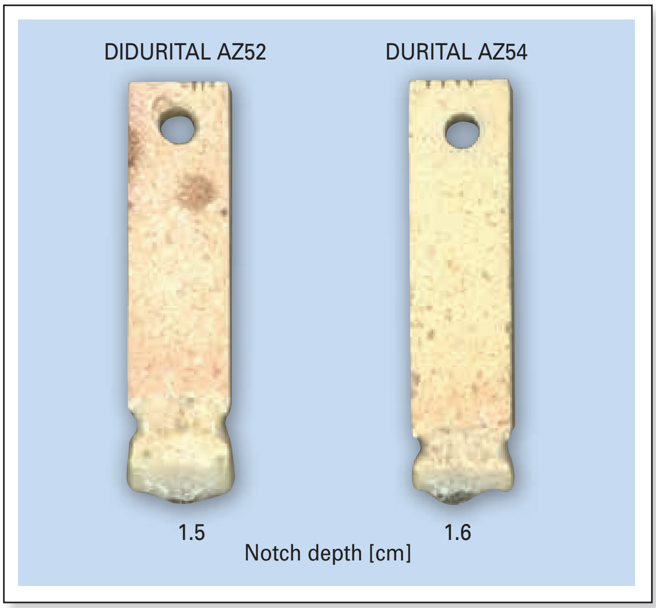


Figure 3. *Static plate corrosion test comparing DIDURITAL AZ52 with the equivalent pressed DURITAL AZ54 grade for 96 hours at 1400 °C in soda-lime glass.*

DIDURITAL A98

Most feeder channel material is based on zirconia mullite or tabular alumina [3]. While zirconia mullite has a high corrosion resistance, a disadvantage is the risk of glass defects, like cat scratches, due to ZrO_2 being corroded out of the channel. Therefore, high-alumina materials are used for the production of high-quality glass. DIDURITAL A98 (Figure 5) is based on tabular alumina and has only low impurity levels (see Table I), resulting in a low risk of glass defects.

DIDURITAL S67

The refractory material used for the feeder superstructure is dependent on both the glass composition and geometric shape. Grades based on andalusite and fused mullite are common for the superstructure of melting furnaces and feeders for flint and coloured glass production. The andalusite-based DIDURITAL S67 grade (Figure 6) shows excellent thermomechanical properties (Figure 7).

The long and intensive firing of the andalusite bricks assures complete mullitization, since the formation of mullite during use can lower the hot properties. Additionally, free silica bears the risk of reacting with alkalis and thereby forming low melting phases. Other possible application areas besides the superstructure are peepholes and burner bricks. The alkali vapour attack of DIDURITAL S67 was

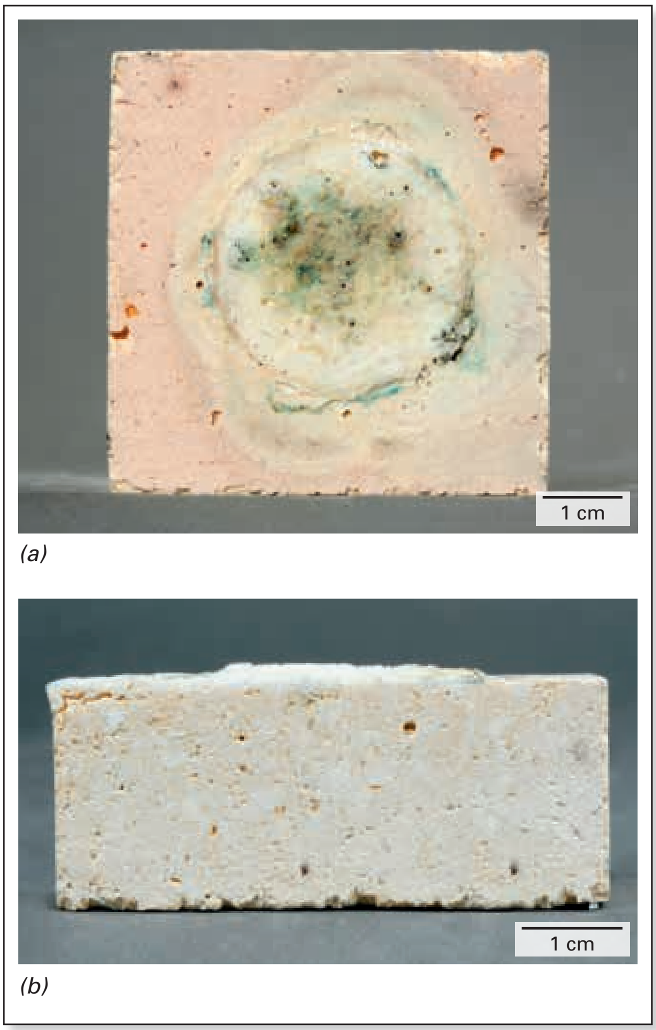


Figure 4. *DIDURITAL AZ52 test sample after alkali attack. The test was performed in sodium carbonate vapour at 1370 °C for 72 hours. (a) surface and (b) cut sample.*

Figure 5. *Feeder channel manufactured from DIDURITAL A98.*

Figure 6. *DIDURITAL S67 burner brick.*

evaluated at 1370 °C for 72 hours in sodium carbonate vapour (Figure 8) and the test samples showed a high alkali resistance.

An overview of the typical chemical composition and physical properties of alumina-based grades is provided in Table I and Figure 7.

Chrome Corundum Products

Today chrome-bearing refractory grades are used when excellent corrosion resistance is required, for example furnaces for the production of aggressive fibreglass and mineral wool. The main raw materials used in alumina-chromia products are fused or calcined alumina, chromium oxide, and prereacted $(Al,Cr)_2O_3$ solid solution materials. The $(Al,Cr)_2O_3$ solid solution is particularly favourable as it is more corrosion resistant than pure corundum and less susceptible to chromate formation than pure chromium oxide [4]. Prereacted $(Al,Cr)_2O_3$ solid solutions are produced in the electric arc furnace. The resulting fused chrome corundum raw materials (smelts) consist of a very homogeneous mixed crystal with a well-defined Al_2O_3/Cr_2O_3 ratio and uniform properties. Two different fused materials with a chromium oxide content of 30 wt.% and 60 wt.% are available [4]. The chemical analysis and physical properties of the chrome corundum vibrocast grades are shown in Table II.

DIDURITAL RK30 and DIDURITAL RK55

DIDURITAL RK30 consists of the prereacted fused chrome corundum with a Cr_2O_3 content of 30 wt.%, chromium oxide, fused corundum, and a zirconia-based material. Due to its very high corrosion resistance, the main application fields are feeder channels (Figure 9), feeder covers, and exhaust channels in contact with aggressive fibreglass and mineral wool melts. The excellent corrosion resistance was shown to be comparable to the established equivalent

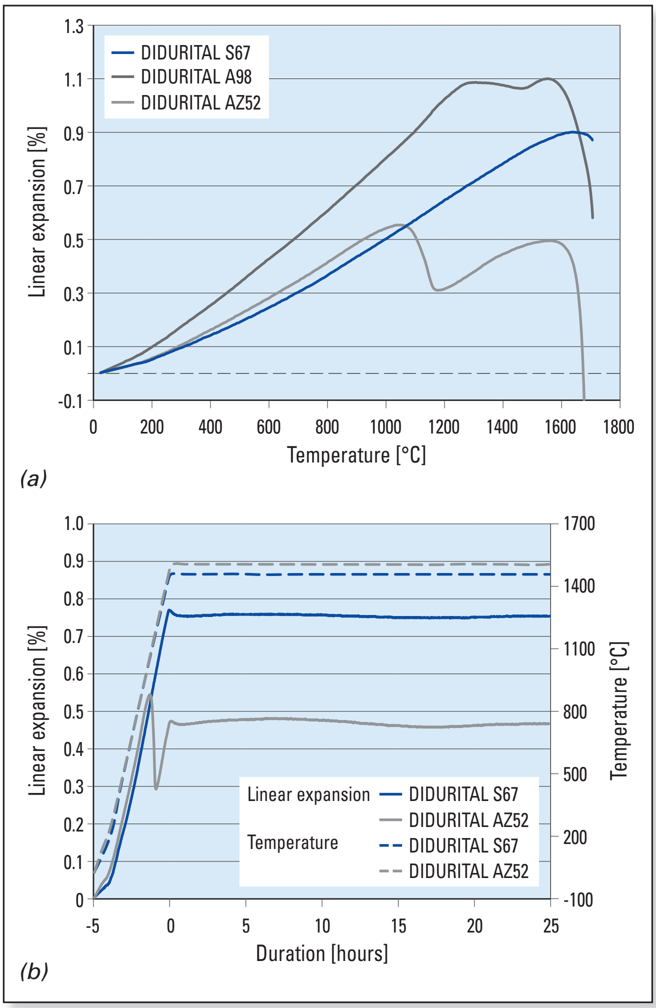


Figure 7. *Typical (a) refractoriness under load values and (b) creep data for DIDURITAL AZ52, DIDURITAL S67, and DIDURITAL A98.*

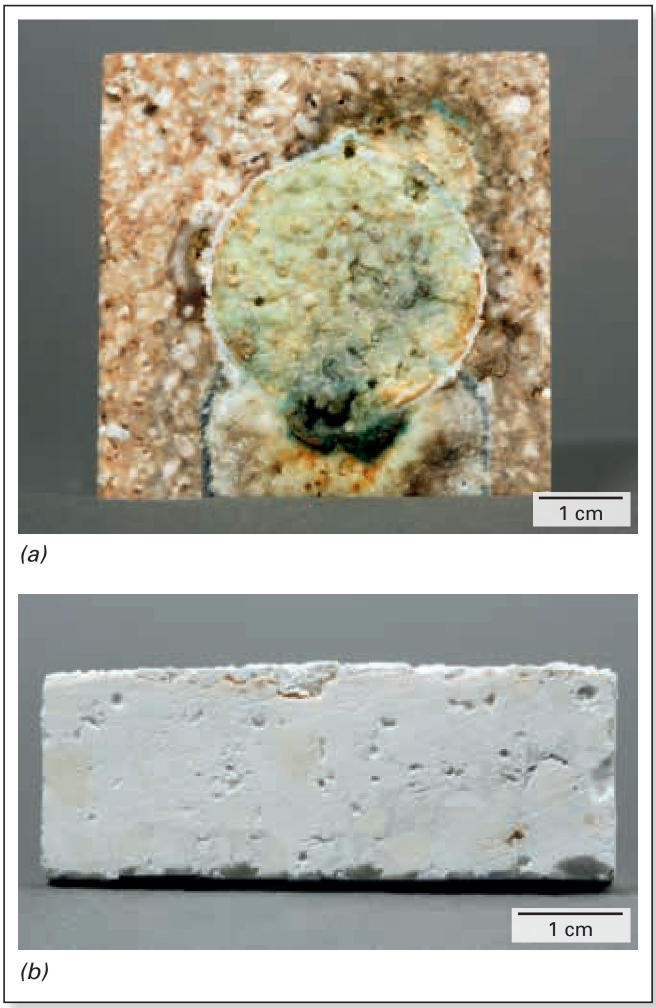


Figure 8. *DIDURITAL S67 test sample after alkali attack. The test was performed in sodium carbonate vapour at 1370 °C for 72 hours. (a) surface and (b) cut sample.*

Brand	Al_2O_3 (wt.%)	SiO_2 (wt.%)	ZrO_2 (wt.%)	Cr_2O_3 (wt.%)	CaO (wt.%)	BD (g/cm³)	AP (%)	CCS (MPa)	RUL $T_{0.5}$ (°C)	TE 1000 °C (%)
DIDURITAL RK30	62	3.4	1.7	30.5	0.8	3.32	19	160	> 1700	0.77
DIDURITAL RK55	31	4.5	5.0	55	1.1	3.44	21	150	> 1700	0.68

Table II. *Typical chemical composition and physical properties of DIDURITAL RK30 and DIDURITAL RK55. Abbreviations include bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), refractoriness under load (RUL $T_{0.5}$), and thermal expansion (TE).*

SUPRAL RK30S pressed material in static plate tests. The application field of DIDURITAL RK55 is similar to DIDURITAL RK30 (Figure 10a). However, because it is produced with a chromium oxide content of 55 wt.% it exhibits a higher corrosion resistance, which is again comparable to the pressed equivalent SUPRAL RK50S (Figure 10b).

Both grades also exhibit good hot properties (Figure 11). The addition of zirconia-based phases leads to a good thermal shock resistance by microcrack reinforcement [4], which is required at several positions in glass furnaces.

FONDAL SXW

Traditionally, the crowns of regeneratively heated container glass furnaces comprise silica-based refractories that have proved themselves through many years of successful use [3]. FONDAL SXW (Figure 12), based on a cement-free fused silica mix, was developed for hot repair of glass furnace crowns. The material has a SiO_2 content of 98.5 wt.% (see Table III). The CaO and Al_2O_3 levels are minimized to avoid a negative impact on the thermomechanical properties and corrosion resistance against alkalis. The thermal expansion

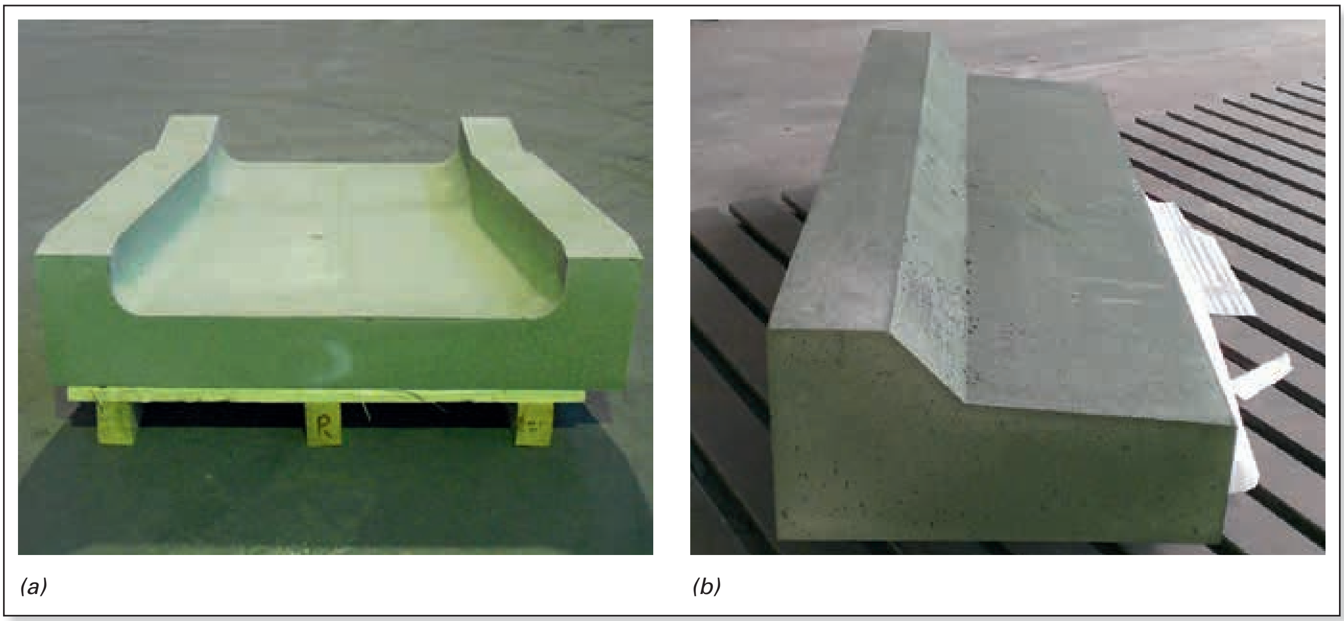


Figure 9. *DIDURITAL RK30: (a) feeder channel block and (b) very large 2.3-tonne bottom block.*

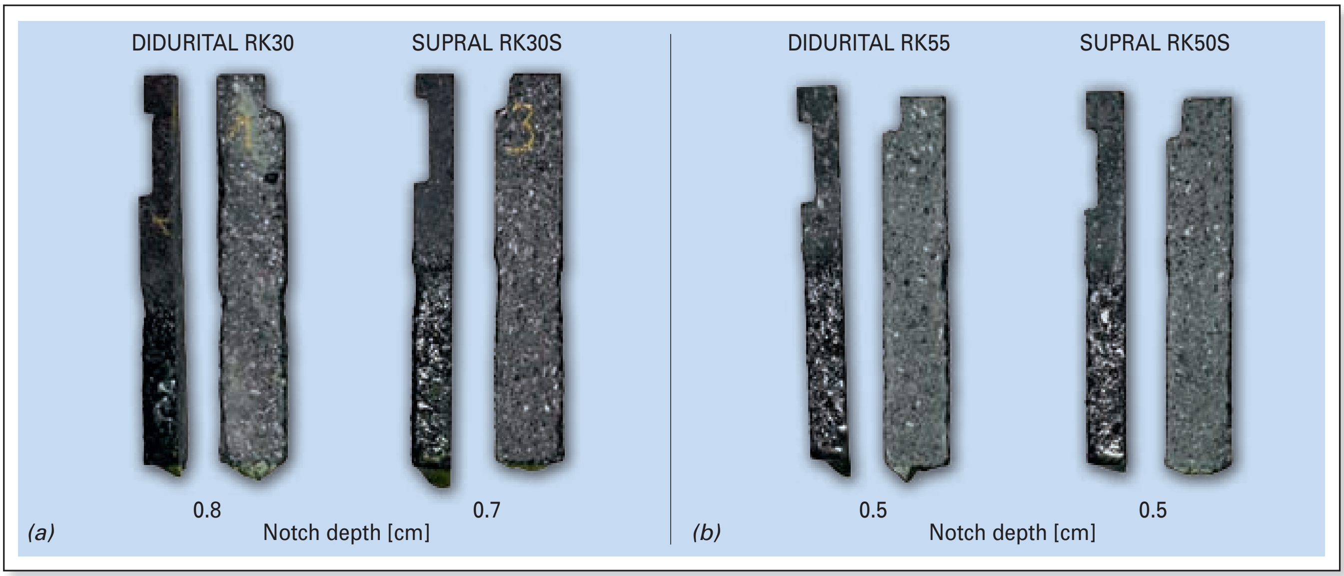


Figure 10. *Corrosion behaviour of (a) DIDURITAL RK30 and (b) DIDURITAL RK55 in C-glass. In the static plate corrosion tests DIDURITAL RK30 and DIDURITAL RK55 were compared to the analogous pressed SUPRAL RK30S and SUPRAL RK50S grades, respectively, for 96 hours at 1500 °C.*

Brand	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	BD (g/cm³)	AP (%)	CCS (MPa)	TSR H_2O (cycles)	RUL $T_{0.5}$ (°C)	TE 1000 °C (%)
FONDAL SXW	98.5	0.9	0.1	1.85	15	35	> 30	1600	0.1

Table III. *Typical chemical composition and physical properties of FONDAL SXW. Abbreviations include bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), thermal shock resistance (TSR), refractoriness under load (RUL $T_{0.5}$), and thermal expansion (TE).*

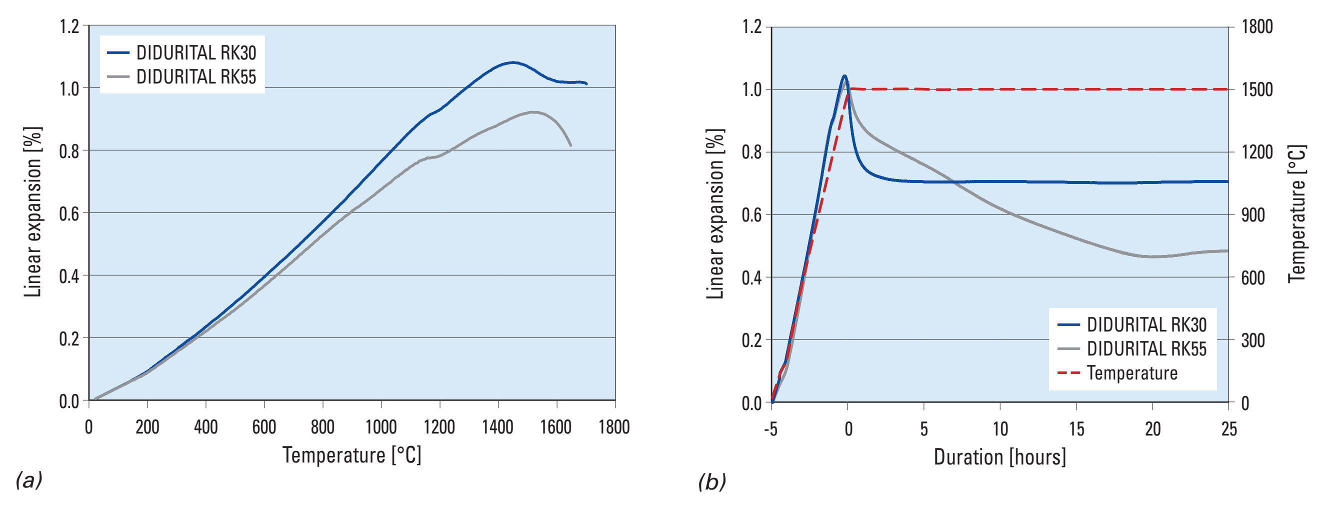


Figure 11. *Typical (a) refractoriness under load values and (b) creep data for DIDURITAL RK30 and DIDURITAL RK55.*

of FONDAL SXW is low resulting in very high thermal shock resistance. The refractoriness under load $T_{0.5}$ is 1600 °C. FONDAL SXW has a high corrosion resistance to gaseous components released from glass melt. Furthermore, FONDAL SXW dissolves without causing glass defects in the case where small pieces fall into the glass melt. The application areas are suspended blocks for hot repair and the doghouse outer arch of container glass tanks for flint and coloured glass.

Conclusion

A large portfolio of vibrocast fired products is produced at the Niederdollendorf plant. Using vibrocasting, complex geometries and large shapes can be produced at relatively reasonable cost. The vibrocast shapes show a homogeneous microstructure and a high surface quality. The product range covers the main product groups for glass applications, such as andalusite, alumina, zirconia mullite, chrome corundum, fireclay, and silica. Application areas of the developed grades in container glass and fibreglass furnaces are the feeder superstructure, feeder channels, burner bricks, and glass crowns. Products are also available for the hot and cold bays in the tin bath of float glass furnaces. The experience RHI has gained in manufacturing fired vibrocast shapes enables tailor-made solutions to be offered that meet customer requirements in multiple application areas (e.g., glass, iron and steel, nonferrous metals, and the environmental, energy, and chemical industries).

Figure 12. *Vibrocast tempered FONDAL SXW block.*

References

[1] Reiter, V., Noppinger, H., Santowski, K. and Dietrich, M. Vibrocast Shapes—Product Range for the Glass Industry. *RHI Bulletin*. 2011, No. 2, 29–33.

[2] Düpre, K. and Dietrich M. RHI Invests More Than €6.5 Million in the Niederdollendorf Plant. *RHI Bulletin*. 2012, No. 2, 39–40.

[3] Postrach, S. State-of-the-Art Refractory Linings for Container Glass Furnaces. *RHI Bulletin*. 2007, No. 2, 18–21.

[4] Dietrich, M. and Postrach, S. Chrome Corundum: An Alternative to Isostatically Pressed Products. *RHI Bulletin*. 2013, No. 2, 27–30.

Authors

Viktoria Reiter, RHI AG, Technology Center, Leoben, Austria.
Markus Dietrich, RHI AG, Industrial Division, Wiesbaden, Germany.
Harald Noppinger, RHI AG, Industrial Division, Königswinter, Germany.
Corresponding authors: Viktoria Reiter, viktoria.reiter@rhi-ag.com
Markus Dietrich, markus.dietrich@rhi-ag.com

Roland Heidrich, Amul Gupta, Stefan Postrach and Markus Dietrich

REFEL 1616ULX—An Ultra-Low Exudation Fused Cast Product for the Superstructure of Glass Melting Furnaces

Introduction

All fused cast alumia-zirconia-silica (AZS) products contain a significant quantity of glassy phase [1]. It is well known in the glass industry that a portion of this AZS glassy phase exudes onto the superstructure surface during furnace heat-up, until the furnace has achieved a stable temperature profile. The exuded glass—often containing small zirconia crystals—tends to run down into the glass bath. This is a major concern to glass producers since this glassy phase often causes defects, such as viscous knots and stones. In the last decade, some manufacturers have developed AZS with reduced levels of exudate, but until recently complete or near-complete elimination of exudation has not been achieved. This has now changed due to the development of RHI's new solution: REFEL 1616ULX.

In comparison to standard 33 wt.% ZrO_2 fused cast AZS, REFEL 1616ULX is an AZS refractory with reduced ZrO_2 content and an increased quantity of Al_2O_3 and glassy phase. This chemistry results in a very different microstructure than found in standard 33 wt.% ZrO_2 AZS products. However, the main innovation is the chemistry of the glassy phase in this product, which has been adjusted to augment its viscosity and thereby reduce viscous flow at the operating temperatures in glass melting furnaces. Consequently, in comparison to all available products on the market, REFEL 1616ULX shows almost no glassy phase exudation, even after several heat-up and cool-down cycles.

Exudation Behaviour

Several tests were conducted to demonstrate the particularly advantageous behaviour of this innovative brand. Figure 1 shows the excellent exudation behaviour of REFEL 1616ULX compared to a currently available standard fused cast AZS grade. The test was performed according to the International Commission on Glass TC11 recommended procedure.

Another test that is closer to real application conditions was developed in the RHI Falconer laboratory (USA). Samples with dimensions of 300 mm x 150 mm x 100 mm were placed in the door of a laboratory furnace so that a temperature gradient developed across the sample thickness. This type of test is more representative of the heat-up conditions in glass melting furnaces. Larger samples of standard AZS and REFEL 1616ULX following this exudation test at 1550 °C are shown in Figure 2. The standard AZS sample was tested just once for 72 hours, whereas the REFEL1616 ULX sample was tested for a total of 82 hours (the initial 72 hour cycle followed by 5 cycles of 2 hours each). The photograph clearly shows exudation on the standard AZS sample whereas the REFEL 1616ULX block was dry even after 6 heat-up and cool-down cycles.

In order to confirm the very positive laboratory test results, samples of REFEL 1616ULX have been installed in several glass furnaces during the last year in collaboration with

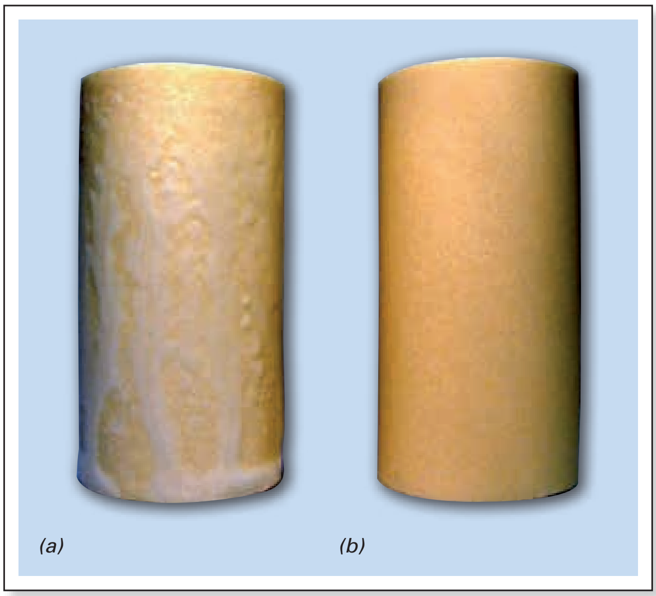


Figure 1. *Samples after TC11 exudation testing (10 cycles). (a) standard 33 wt.% ZrO_2 AZS showing exudation (b) and almost zero exudation of REFEL 1616ULX. The sample dimensions are 50 mm in diameter x 100 mm high.*

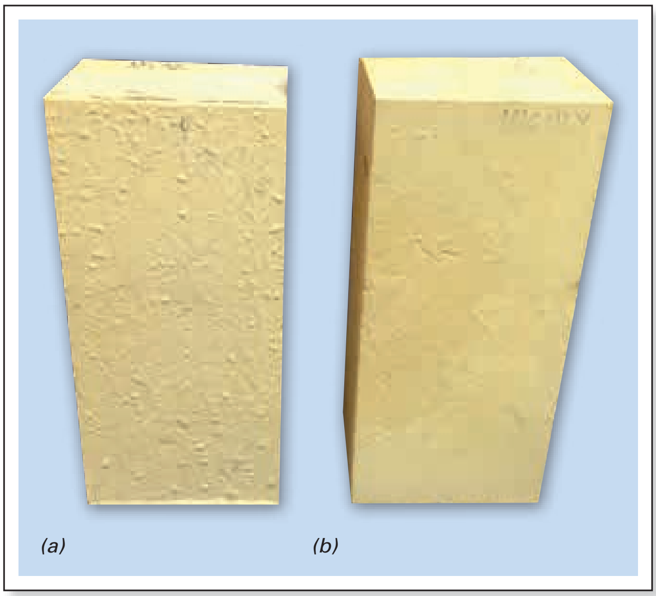


Figure 2. *(a) standard 33 wt.% ZrO_2 AZS block after the door test at 1550 °C for 72 hours and (b) REFEL 1616ULX after the door test at 1550 °C for 72 hours followed by a further 5 cycles of 2 hours each. Glassy phase is clearly visible on the standard material while the REFEL 1616ULX block surface is absolutely dry. The sample dimensions are 300 mm x 150 mm x 100 mm.*

glass producers. Some samples have already been removed and investigated. Thus far, the REFEL 1616ULX products have not shown any exudation and at the same time demonstrated very good vapour corrosion resistance.

Application Areas

The main applications for REFEL 1616ULX can be seen in the superstructure of all glass melting furnaces, such as:

>> Container glass tanks for flint glass and coloured glass.
>> Specialty glass tanks for borosilicate glass.
>> Fibreglass tanks.
>> Float glass tanks.

The first installation of several blocks in the superstructure of a container glass furnace was realized in the first quarter of 2014.

Composition and Properties

The typical chemical composition, mineralogy, and physical properties of REFEL 1616ULX are detailed in Table I. REFEL 1616ULX blocks have all the important advantages of fused cast products, such as high refractoriness under load ($T_{0.5}$ > 1720 °C) and low open porosity, which provides the high corrosion resistance confirmed by laboratory tests. Additionally, the thermal expansion hysteresis is less compared to standard AZS due to the lower zirconia content.

	REFEL 1616ULX
Chemical composition (wt.%)	
Al_2O_3	64.2
SiO_2	16.5
$ZrO_2 + HfO_2$	16.9
Na_2O	2.4
Crystallography	
Corundum	0.61
Zirconia	0.14
Glass phase	0.25
Physical properties	
Bulk density (FVB type)	3.55 g/cm³
Thermal expansion under load at 200–1300 °C	8.9 x 10^{-6}/°C
Maximum thermal expansion under load at 1645 °C	1.25%
Refractoriness under load $T_{0.5}$	> 1720 °C
Cold crushing strength	195 N/mm²

Table I. *Typical chemical composition, mineralogy, and physical characteristics of REFEL 1616ULX. Abbreviations include free-void special shaped blocks (FVB).*

The microstructure of REFEL 1616ULX (Figure 3) consists of corundum crystals (light grey), zirconia dendrites (white), and a sodium aluminosilicate glassy phase (dark grey). Unlike standard AZS, the corundum crystals do not contain fine crystals of ZrO_2.

REFEL 1616ULX is melted in an electric arc furnace using prime-grade raw materials under controlled oxidation conditions. The annealing process is optimized to achieve superior and overall homogeneous physical and chemical properties. This fused cast brand is available in various block sizes prepared using different casting techniques (i.e., normal cavity (N), cavity-free block (FVB), and cavity-free special shape (FVS). The production cycle is in accordance with ISO 9001.

Conclusion

A combination of excellent properties makes fused cast AZS products the standard superstructure material in glass furnaces worldwide. The only weakness of this material group, criticized by glass producers for years, is its tendency to exude a glassy phase, which can be the origin of some glass defects. The patented new REFEL 1616ULX fused cast AZS products retain most of the positive properties of other fused cast AZS materials while effectively dealing with this last disadvantage. This highly beneficial improvement has been confirmed in laboratory experiments and field test trials in glass furnaces. The near elimination of exudation will reduce glass defects such as viscous knots and stones. Consequently, the new material is an innovation that contributes to further improvements in glass quality.

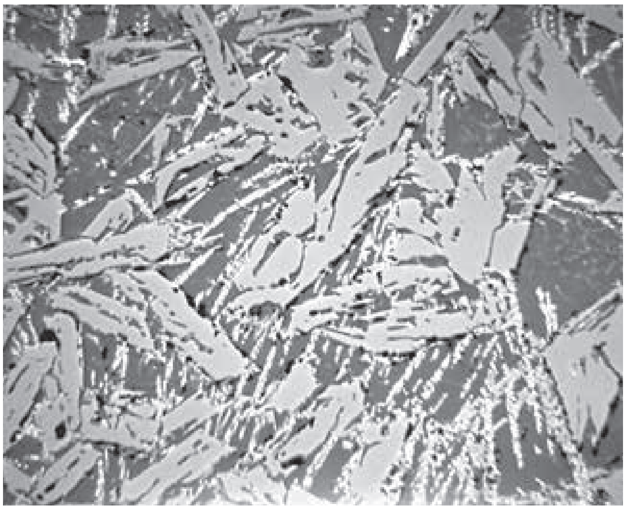


Figure 3. *Microstructure of REFEL 1616ULX. Corundum crystals (light grey), zirconia dendrites (white), and a sodium aluminosilicate glassy phase (dark grey) are clearly visible.*

Reference

[1] Heidrich, R. and Gupta, A. Fused Cast AZS Glassy Phase Exudation: Intrinsic or Pathological Property? *RHI Bulletin.* 2011, No. 2, 24–28.

Authors

Roland Heidrich, RHI Refel S.p.A., San Vito al Tagliamento, Italy.
Amul Gupta, RHI Monofrax Ltd., Falconer, USA.
Stefan Postrach, RHI AG, Industrial Division, Wiesbaden, Germany.
Markus Dietrich, RHI AG, Industrial Division, Wiesbaden, Germany.
Corresponding author: Roland Heidrich, roland.heidrich@rhi-ag.com

RHI Bulletin > 2 > 2014, pp. 19–26

Kevin Selkregg

Characterization of Glass Defects Arising in Today's Evolving Glass Technologies

Manufacturers in the glass industry are increasingly challenged to produce high-quality glass products with the ever-rising demand for meeting lower inclusion tolerance levels in the body of the glass article. Such inclusions in glass, termed defects, include stones (primary or secondary), vitreous inhomogeneities, and bubbles. The consumer often takes for granted the high quality of today's traditional glass products. Container bottles, plate glass for home and commercial buildings, as well as glass for the automotive industry are just some of the items produced in high-temperature furnace environments. The expanding new markets involving the impact-resistant glasses such as Corning's Gorilla Glass for cell phone touch displays, laptop computer screens, and millions of other portable electronic devices are adding a new challenge regarding identifying defects in the form of inclusions in glass.

Introduction

Glass defects can be in the form of stones, vitreous inhomogenities, and bubbles; all having been a scourge to the glassmaker for centuries [1]. The following discussion concentrates on stones and vitreous inhomogeneities. The stones observed in a final glass product may be a primary undissolved stone from the refractory lining or an unmelted batch stone. Secondary stones are those precipitated out of the tank glass and generally are due to reactions with the refractory lining leading to by-product phases or the result of a dissolved component in the glass reaching saturation limits. The glassy defect inclusion is typically the result of undissolved viscous liquid from the refractory lining, due to its corrosion by the glass tank environment. It can also be from liquid rundown formed from the reaction of batch carryover on the superstructure walls. These vitreous inclusions are manifested in the form of "swirly" viscous glass knots with clear visual boundaries or an internal viscous glass stream that ultimately presents itself as a surface defect called a "cat scratch". In each of these cases, the vitreous inclusion has a composition different from the bulk. A truly remarkable fact is that glass furnace linings have a large refractory surface area (up to 650 m^2 in a container tank and up to 3065 m^2 in a float tank) with the potential of generating millimetre-sized defects unacceptable to the final glass quality goals. Yet, in spite of this, manufacturers successfully produce quality glass items.

Glass product manufacturers must determine the acceptable glass defect control parameters to meet the customer quality requirements. Through their own experiences they can ascertain the cause of defects observed and modify their process appropriately. The Monofrax research and development laboratory in Falconer (USA) receives dozens of requests throughout the year from customers who are unable to characterize the defects and establish the reason for their formation. The steps adopted by Monofrax to respond to these requests are generally conducted as follows:

- Provide the customer with a questionnaire to complete regarding background information on the age of the affected furnace in question, lining type, glass type, defect frequency, and other details necessary for a better understanding of the defect problem.
- Upon receiving the samples analysis is started immediately with high priority because the customer is losing money and losses are continuing unless the defects have stopped.
- During the analyses, some preliminary results are often relayed to the customer, which may be helpful in their dealing with the current defect problem. Frequently the customer contact and the Monofrax research and development laboratory will be in continual discussions regarding the problem.
- The final results are provided in a report with the background, discussion of the data, and a summary/conclusion section with some thoughts regarding the cause and potential source of the defects.

Glass Defect Characterization

In early 2010, a Monofrax customer was experiencing an unusual and serious problem of losses due to defects in their rolled and patterned sheet glass [2]. These defects were white and swirly and found imbedded as stone-like inclusions within the glass. They were often clustered in groups, with significant porosity within the clusters, and appeared to be a breakdown of an odd spherical or round solid bead. This population of defects was not typical for glass inhomogenities such as viscous knots nor did it contain stones of a specific mineralogy (Figure 1).

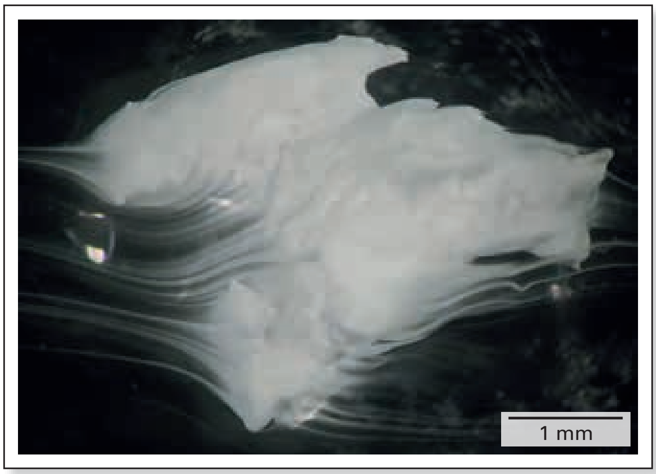


Figure 1. *Stereoscopic micrograph of the white defect.*

To begin the analyses, sample preparation involved cutting across the defect body with a wafer saw, grinding and polishing, followed by reflected light and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) analyses. The results revealed nearly spherical beads with internal "birdseye" pores along with a "trail" of fine zirconia crystals emanating from the beads (Figure 2). The EDS chemical analyses showed 34 wt.% Al_2O_3, 51 wt.% SiO_2, 14 wt.% ZrO_2, and < 1 wt.% Fe_2O_3 in the sphere centre, an unusual chemistry for a solid, foreign defect particularly when considering the absence of Na_2O. Any viscous foreign vitreous defect such as a knot or cord would typically not have this high zirconia level in solution within the defect glass nor would it not contain any alkalis such as sodium. In addition to this peculiar chemistry was the odd trend that all the individual spheres analysed were nearly identical in chemistry. The observation of this highly unusual feature strongly suggested the defect was neither refractory nor batch related, but still from a source of intentional furnace lining design.

The mystery of the defect source was solved by recalling the types of products made by a particular high-temperature ceramic fibres company, such as fibre mats, papers, and boards, for insulation applications in high-temperature furnaces. The majority of these fibre compositions were high alumina; however, there was one product line utilizing an alumina-zirconia-silica composition (AZS fibre). A fibre blanket for such high-temperature applications manufactured by this fibres group is shown in Figure 3. The appearance of a fibre blanket's internal fibre makeup at high magnification is shown in Figure 4.

An undesirable by-product of refractory ceramic fibre blankets, commonly referred to as "shot" particles, has the true fibre chemistry. These are round or nearly spherical glass pieces many times larger than the normal fibre diameter. Analyses of the shot particles by SEM-EDS methods showed, for all intents and purposes, an identical composition to the glass bead defects (Table I).

	Defect bead centre (wt.%)	Ceramic fibre shot (wt.%)
Na_2O	-	-
Al_2O_3	34.4	31.6
SiO_2	51.3	53.8
Fe_2O_3	0.3	-
ZrO_2	14.0	14.6
Total	100.0	100.0

Table I. *EDS analyses of the defect beads and the ceramic fibre shot samples, showing nearly identical alumina-zirconia-silica chemistries.*

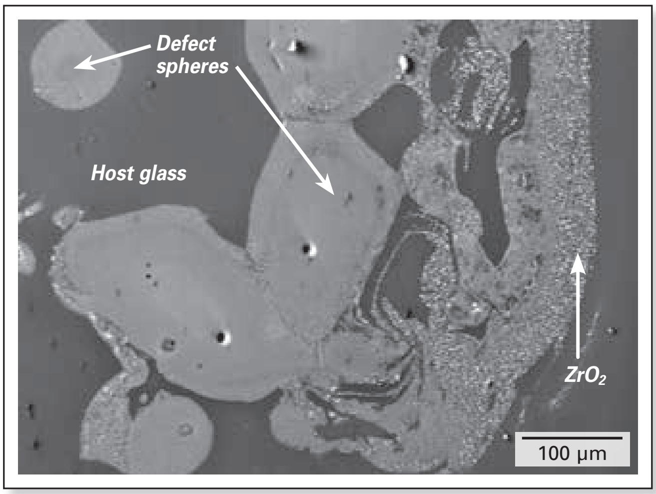


Figure 2. *SEM backscattered electron image of the round defects and secondary zirconia from these round defects.*

Figure 3. *Refractory ceramic fibre insulation blanket roll.*

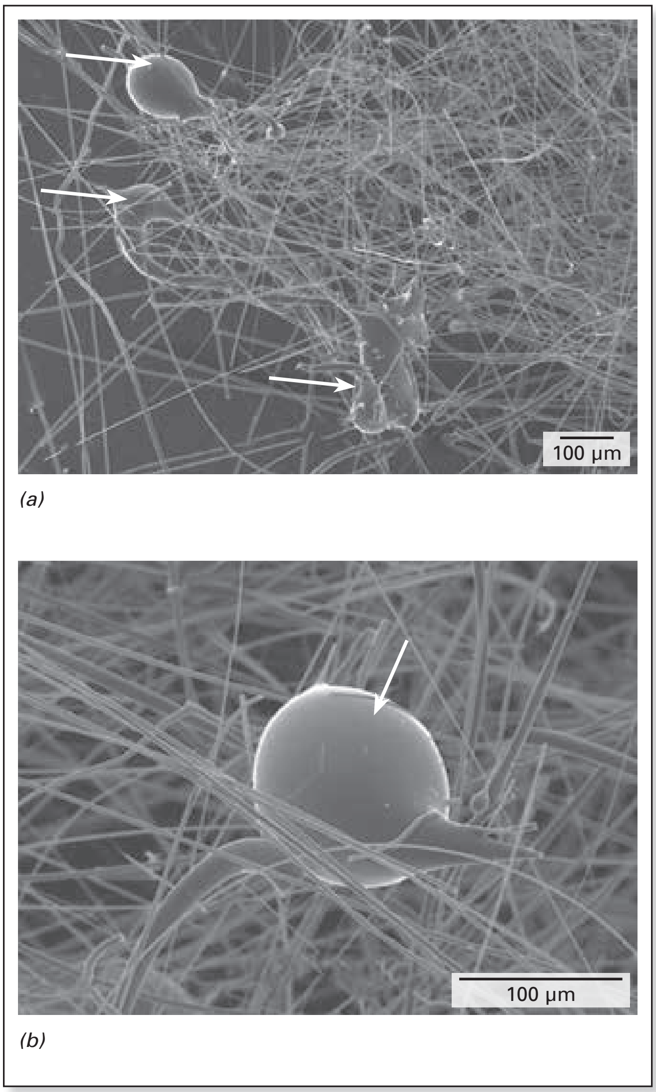


Figure 4. *SEM images of the blanket structure. (a, b) in addition to the thin fibres there are also round glass beads or masses, termed shot, indicated by the arrows.*

A final part of the analysis involved X-ray diffraction (XRD) analysis of these defects since there was a sufficient amount of the defect material to prepare a powdered sample. The results show a diffraction scan with a broad diffraction hump and some zirconia peaks superimposed upon it (Figure 5). This broad hump reflects the amorphous nature of the defects, showing them to be stones with a glassy not crystalline structure, an unusual feature for glass defects.

Further discussions with the engineers at this glass company revealed that they used this particular type of fibre blanket as an insulation cover over gaps in their feeder crown refractories. The fibre blanket was crumbling under high temperature and pieces were falling into the glass below. The smaller diameter and higher surface area fibres would dissolve quickly, probably forming the zirconia "swirls" found around the beads.

A number of lessons can be learned from this defect analysis investigation. The first is in regards to the analytical tools at the analyst's disposal. These can make a significant difference in obtaining all the chemical and microstructural facts necessary for arriving at conclusions in the defect investigations. Accurate chemical analyses of the defects are essential and establish a foundation to work towards identifying any potential sources. Accurate analyses by EDS methods with the SEM are obtained by referencing to standards of known compositions. This is particularly true for light elements such as sodium, which will have significant errors in EDS results if a "standardless semiquantitative" software routine is relied upon (i.e,. not referencing actual standards). Other tools such as the stereo microscope, reflected light microscope, and XRD methods are also essential. For example, in the previous discussion regarding the AZS fibre, the XRD results have a broad diffraction hump showing the sample to be mostly amorphous, a fact that was puzzling at first because a solid stone defect will generally be crystalline. However, this was additional evidence to confirm the ceramic fibre blanket was the defect source since the fibre shot is amorphous.

The second lesson relates to communication with the glass customer. It is essential for the customer to provide as much background information as possible regarding the furnace generating the defects. When defects are submitted for analyses, Monofrax utilizes a standard questionnaire for the customer to complete, answering basic questions such as furnace age, defect frequency, lining type, and batch makeup. This is a valuable tool to help in the correct identification of the defect type and source.

The third lesson relates to the quality of the final report. The reporting strategy at Monofrax is to present the background of the problem, clearly report the results, and provide reasons for the conclusions regarding the potential source of defects.

The fourth lesson is really a recommendation and relates to the ability to simulate defect formation by utilizing high-temperature laboratory furnaces. If the analyst is able to reproduce the defect chemistry and morphology in the laboratory by performing melting experiments with the customer glass and possible defect source features, it provides very strong confirmation of the defect cause and source. This fourth recommendation regarding the ability to simulate defect formation has been a critical tool for identifying defect sources. Often conclusions regarding defect sources and formation kinetics have been altered and corrected when laboratory furnace tests were run on samples using cullet from the glass manufacturer. In fact, a simulation laboratory furnace experiment was conducted with samples of the AZS ceramic fibre blanket mentioned above. The results duplicated the defect formation and further confirmed the source and cause of the defects observed in the furnace.

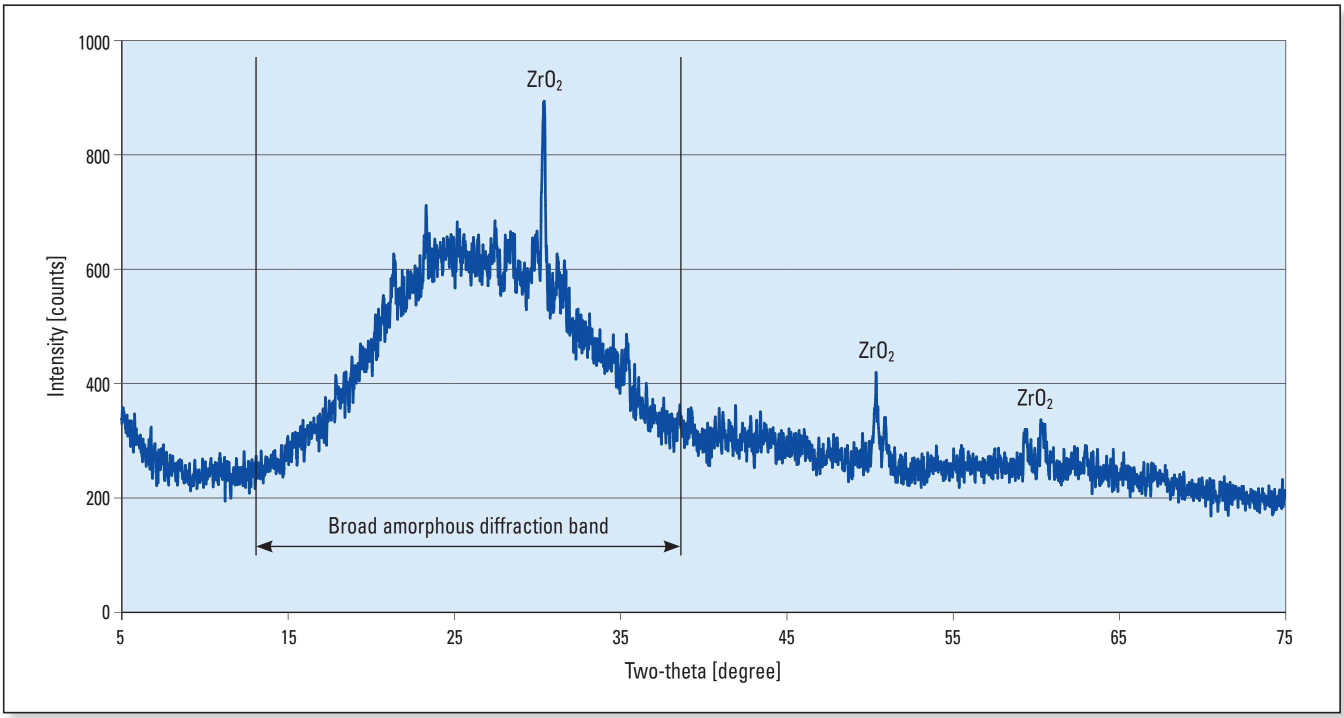


Figure 5. *XRD scan of the white defect solid inclusions.*

Glass Defect Simulation

Another example of one of many glass defect simulations Monofrax has performed in the laboratory involved a manufacturer of green glass containers who was having serious defect problems with large dark stones (Figure 6).

The defects were found to be a chrome oxide type, consisting of two chemically distinct populations: A chrome alumina solid solution phase and a pure chromium oxide phase. Stereoscopic images of both types are shown in Figure 7. The pure chrome oxide stone in Figure 7a has a well-formed crystalline nature. This is the feature of a crystal growing freely in glass and is unlikely to be from a refractory; however, there needed to be confirmation of this hypothesis suggesting a nonrefractory source. It was known (from the questionnaire) that the customer used chromite colourant, which is a magnesium aluminium chrome spinel.

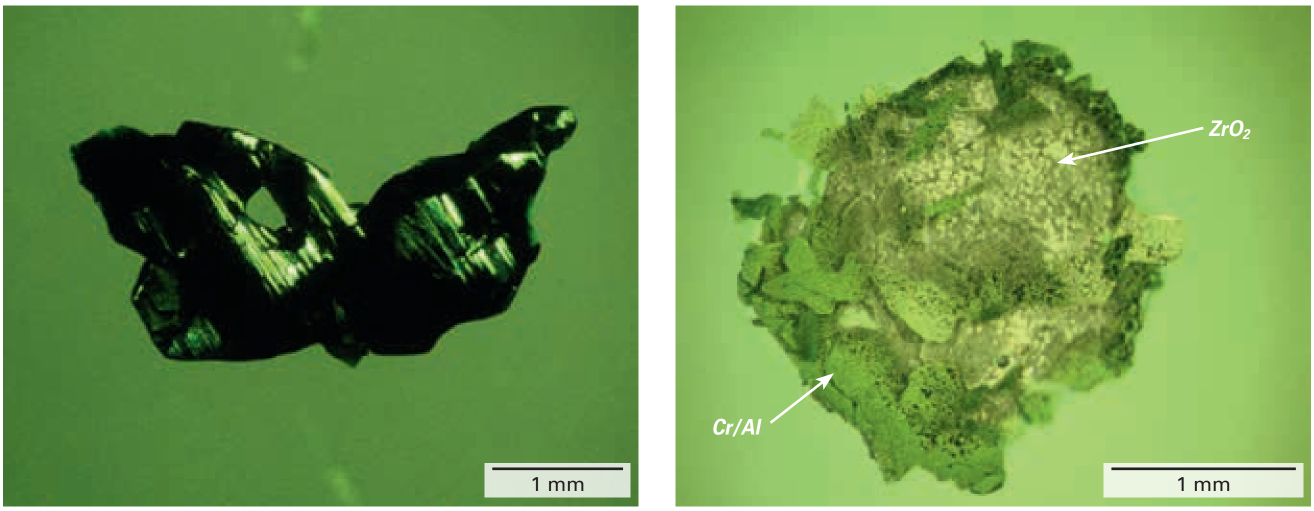
From experience it is known that chromite spinel can readily dissociate leaving a pure chromium oxide phase while the more soluble components go into the molten glass. A furnace experiment was planned using chromite colourant from the customer with the objective of observing if it dissociated to chromium oxide. A photograph of the fine colourant powder and the chemistry is provided in Figure 8. Besides Cr_2O_3, MgO, and Al_2O_3, the second major oxide is Fe_2O_3.

The sequential steps in the laboratory furnace experiment are shown in Figure 9. Samples of the powder were made damp, rolled into small beads, and immersed and covered with the soda-lime glass cullet in platinum crucibles. Once the furnace reached 1490 °C for 1.5 hours, a sufficient time to melt the glass and allow for dissolution of the colourant, the glass was poured into a graphite block mould to cool.

Figure 6. *Bottles containing dark stones.*

	Colourant (wt.%)
MgO	10.23
Cr_2O_3	44.30
SiO_2	3.16
Al_2O_3	14.22
TiO_2	0.71
Fe_2O_3	27.17
CaO	0.21
Total	100.0

Figure 8. *Colourant powder and its corresponding chemistry.*



(a) *(b)*

Figure 7. *Stereoscopic micrographs of (a) pure chrome oxide stone and (b) chrome alumina solid solution stone with zirconia.*

The reflected light micrograph of the colourant powder shows individual chromite grains having a maximum size of 20 microns or slightly less (Figure 10a). Following the laboratory test, new crystals formed with a much larger size than the original colourant powder they had dissociated from (Figure 10b). The defect stones in the green bottle glass showed a similar crystal morphology but they are much larger than those from the laboratory test (Figure 10c). The results of the laboratory furnace test conclusively showed the original powder dissociated to form new crystals of pure chromium oxide identical in shape and aspect ratio observed in the defect stones from the customer furnace. In addition, the rapid conversion rate from the colourant to chromium oxide crystals was informative.

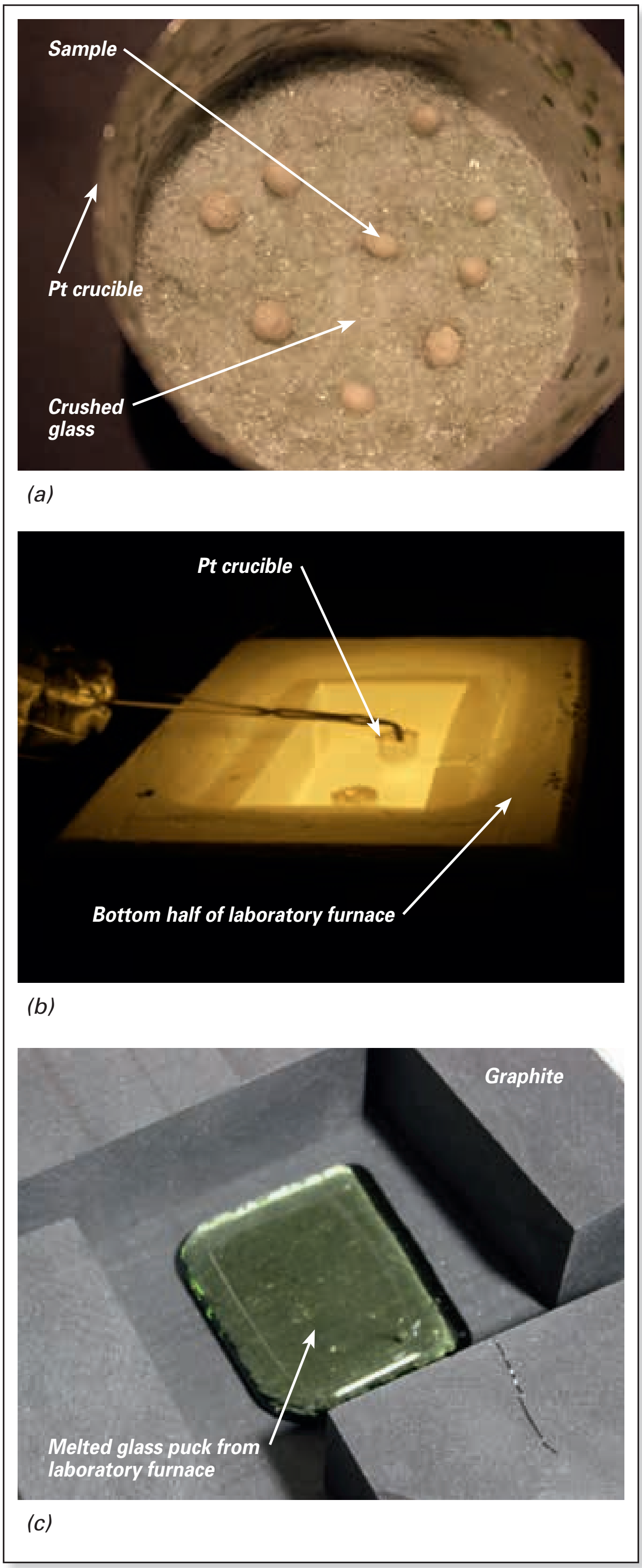


Figure 9. *Laboratory furnace experiment with the chromite spinel colourant. (a) balls of sample colourant in soda-lime glass cullet within a platinum crucible, (b) platinum crucible placed in the laboratory furnace underneath the raised furnace lid, and (c) after the colourant was melted in the glass cullet it was poured into a graphite block mould to contain the glass as it cooled.*

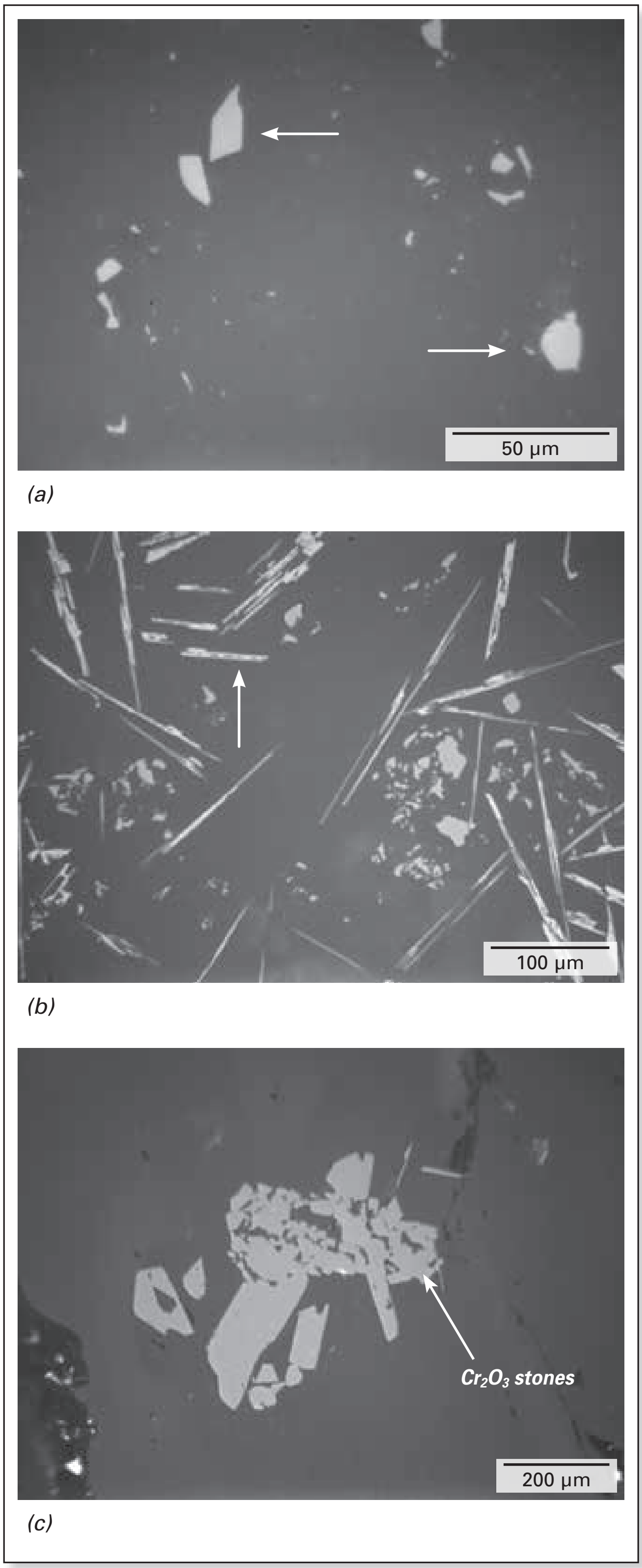


Figure 10. *Reflected light micrographs of the (a) colourant (arrows), (b) results of the laboratory furnace test showing chromium oxide blades (arrow), and (c) a stone defect from the green bottle glass.*

Two superimposed XRD scans to determine the crystal phase identities are shown in Figure 11. The red trace is the original colourant powder and the green line shows the results of a crushed sample of the molten soda-lime glass with the dissociated chrome iron spinel colourant within the glass. The red trace of the colourant powder confirms the chrome iron spinel form. The green trace of the laboratory tested colourant displays a broad diffraction hump in the low two-theta angle range that represents the amorphous melted glass cullet structure. However, superimposed on the glass hump are peaks of crystalline Cr_2O_3, which confirms dissociation of the colourant to Cr_2O_3 crystals not yet dissolved in the glass.

The results show that the chromium oxide stones observed in the green bottles are likely to be the result of unmelted colourant and not the corrosion of a chromium oxide refractory. The laboratory furnace experiment and subsequent microanalyses were critical in showing the actual source of the chrome-containing defect stones.

Future Glass Challenges

The cover glass for today's mobile electronic devices has a toughness requirement because of its application in touch displays. Smart phones with touchscreen technology currently utilize a new type of glass called Gorilla Glass, which now has an additional requirement in that the defects must be much smaller and fewer. Defects in these glasses, detected to 25 µm in size, can block out one or two pixels in the display. The additional no defect requirement is closely tied to the strength of this very thin glass as the marketing advertisement emphasizes in Figure 12 [3]. A small defect stone can easily be a source of breakage when stress is applied.

The photograph in Figure 13 shows some cover glass samples recently received for defect analyses. These pieces

Figure 12. *The strength and durability of thin Gorilla Glass provide high performance in cover glass applications [3].*

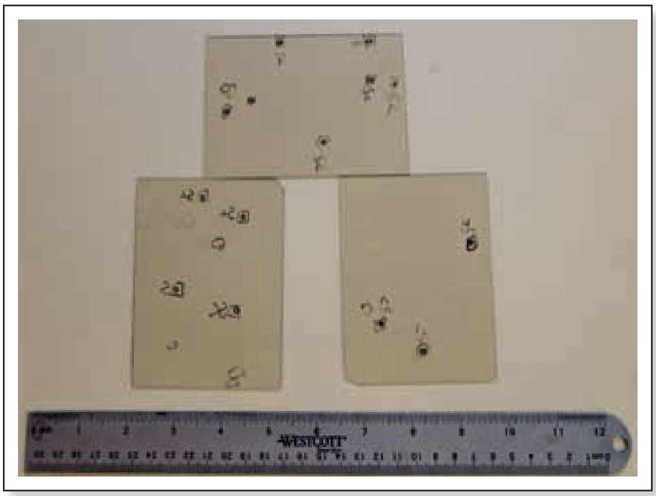


Figure 13. *Cover glass samples with stone defects circled on the pieces.*

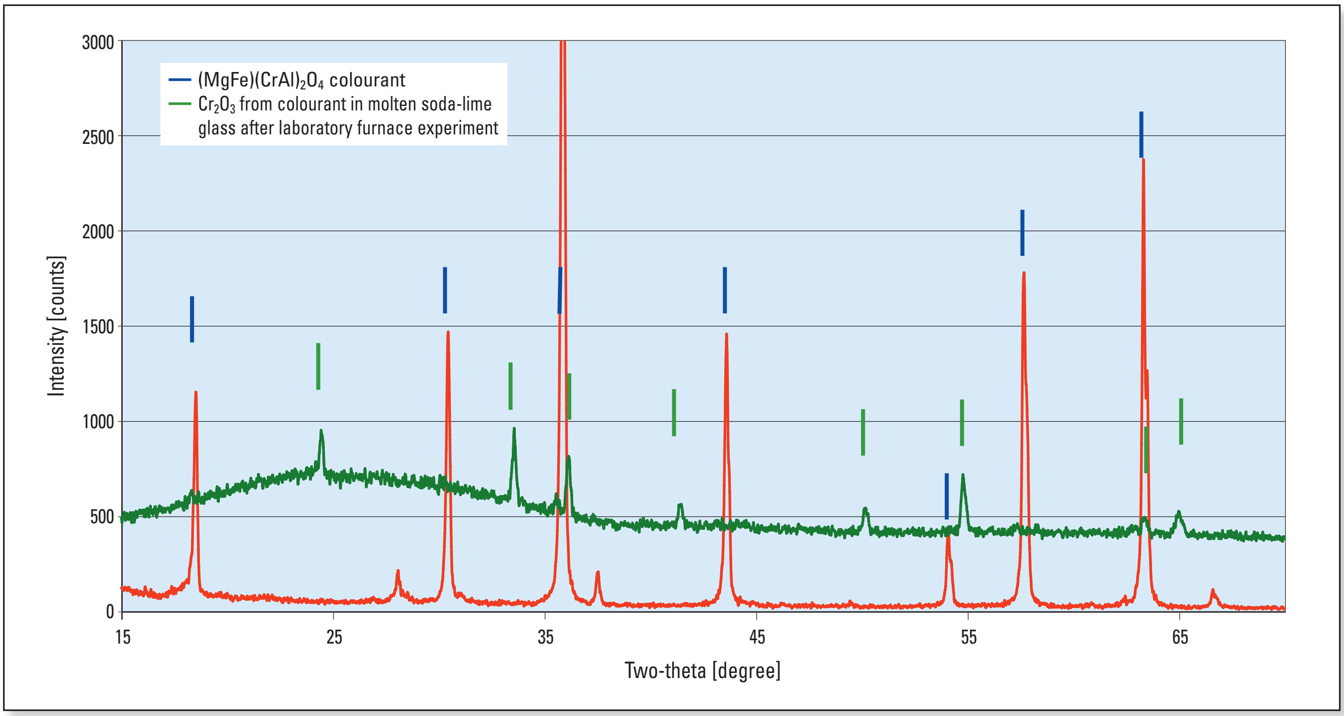


Figure 11. *Superimposed XRD traces of the original colourant powder (red trace) and a sample of the molten soda-lime glass with the dissociated chrome iron spinel colourant (green trace) showing the peaks associated with crystalline phases. The chromite colourant completely dissociated to chromium oxide in the soda-lime glass cullet after 1.5 hours at 1490 °C.*

were 1 mm thick, making sample preparation challenging. The EDS analyses of the glass identified as the "host" had a higher aluminium oxide and potassium oxide chemistry than normally seen in the soda-lime glass example (Table II). A stereoscopic micrograph and SEM images of the defects in Figures 14 and 15, respectively, reveal the small sizes the analyst must work with when examining these stone defects. Often it is important to obtain the glass chemistry immediately around or within a stone region to determine any other chemistry as a clue to the source.

	Host (wt.%)	Stone region (wt.%)
Na_2O	14.2	13.0
Al_2O_3	13.1	12.8
SiO_2	59.3	58.8
K_2O	5.8	5.9
MgO	4.4	3.7
ZrO_2	3.2	5.8
Total	**100.0**	**100.0**

Table II. *Cover glass EDS analyses of the main glass type (host) and glass adjacent to the stone defect (stone region).*

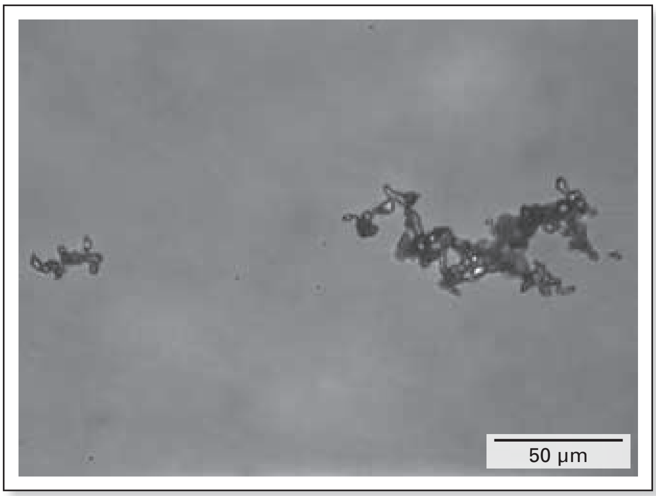


Figure 14. *Stereoscopic micrograph of a stone with branching patterns within the glass wall thickness.*

In this case, the adjacent chemistry was nearly identical to the host glass with the exception of increased zirconia in solution with the glass (see Table II and red asterisks in Figure 15). Since there was no increase in alumina, an AZS refractory source could be ruled out. High zirconia (~ 94 wt.%) fused cast refractories were known to be a major refractory lining in this furnace and consequently would be the likely source of these stone defects.

Concluding Comments

Glass tank melters with their harsh environments due to temperatures in the 1500 °C range, corrosive atmospheres with penetrating vapour species, as well as convection currents in the melt and atmosphere—all these operational aspects insure that unwanted, foreign defect inclusions will find their way into the final glass product. This is irrespective of any high-quality refractory lining with superior corrosion resistance. The irony is that a highly corrosion-resistant refractory lining will also produce defect stones that are very difficult to dissolve away.

As the glass industry progresses to new technologies using various glass types, the glass defect analyst will have to adapt with intuitive means, guided by experience and knowledge. The quality of the analyses must be one of accuracy and precision to the best of the analyst's skill—a fact that cannot be overemphasized. Good sampling procedures, accurate furnace background information, and high-quality sample preparation is already challenging enough. The analyst should not allow erroneous chemical analyses to creep into the investigation by presuming "standardless" EDS software programs will provide sufficiently accurate answers. However, even with a good EDS software program that utilizes reference standards, the operator of the SEM must be knowledgeable enough about electron microscopy theory to insure proper conditions are met for meaningful analyses.

With the glass industry moving onward to newer technologies, defects in the form of foreign solid inclusions and vitreous inhomogenieties will continue to plague manufacturers. The glass defect analyst will have the opportunity to

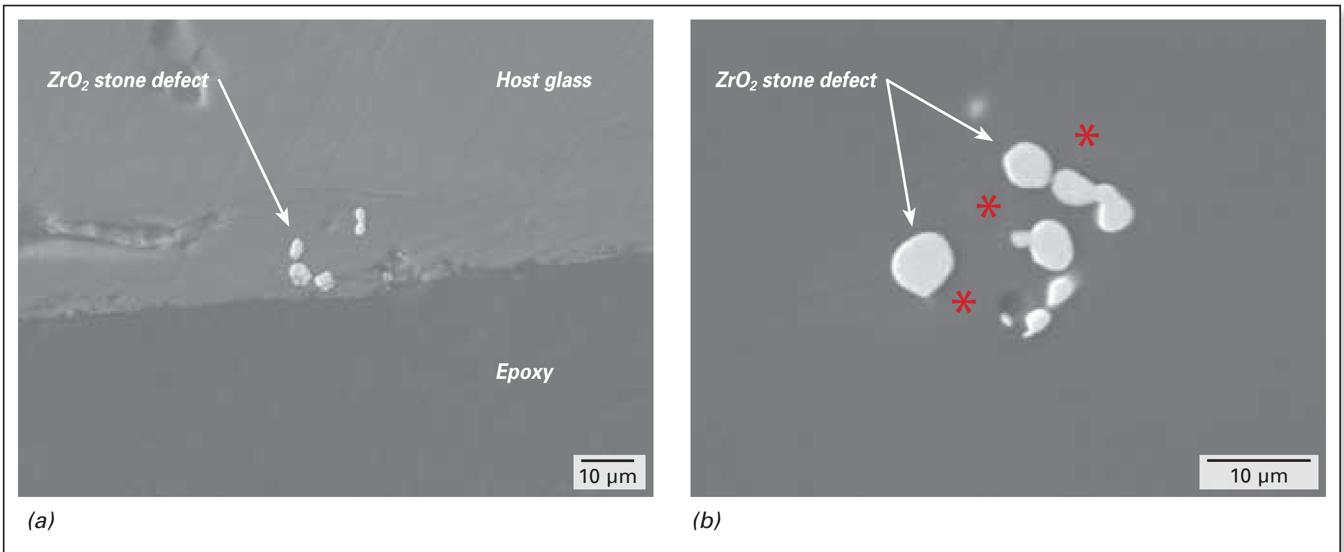


Figure 15. *SEM backscatter micrographs of polished sections across the stone body. The red asterisks are glass regions within the stone. EDS analyses confirmed the stones to be zirconia.*

provide a service second to none if he or she has the tools, knowledge, and experience to do so.

The RHI Monofrax research and development laboratory in Falconer has been investigating glass defects for over 50 years, having presented and published many papers on the subject. When defects occur in the product, the glass manufacturer could easily have lost hundreds of thousands of dollars by the time the samples reach Monofrax for analyses. Consequently, Monofrax understands the importance of immediate attention to the problem and makes it a priority to address the issue as quickly as possible.

RHI Monofrax research and development also conducts seminars at customer facilities involving discussions on the general understanding of defect identification and their potential sources in addition to discussions of results of any defect problems specific to that customer site. All of these services involving glass defect analyses, provided to our customers and potential customers, are viewed as an important support benefit.

References

[1] Clark-Monks, C and Parker. J.M. *Stones and Cord in Glasses;* Society of Glass Technology: Sheffield, 1980.

[2] Selkregg, K. and Gupta, A. Identifying Glass Defects: Minimizing Defects is an Integral Part of Producing High-Quality Glasses. *Ceram. Ind.* 2010, 160, No. 9, 31–33.

[3] http://www.corninggorillaglass.com

Author

Kevin Selkregg, RHI Monofrax Ltd., Falconer, USA.

Corresponding author: Kevin Selkregg, kevin.selkregg@rhi-ag.com

RHI Bulletin > 2 > 2014, pp. 27–30

Roland Heidrich

Nondestructive Testing of Fused Cast Refractory Blocks for Glass Melting Tanks Using Radar Technology

A feasibility study was performed with two different nondestructive testing methods—radar and ultrasound. The measuring techniques were evaluated on fused cast blocks with and without a cavity. The test procedure was significantly faster with radar technology since the device could be simply rolled across the block surface. In addition, the results were far more spatially accurate, enabling preassembled blocks and complete glass melting tanks to be tested. In contrast, the level of noninformative signal interference was comparatively high with ultrasound.

Introduction

The integrity of glass melting tank components like sidewall and throat blocks is of particular importance. These blocks are in permanent glass melt contact and exposed to accelerated corrosion caused by melt line attack and gas bubble drilling. Resistance of the sidewall and throat against corrosive attack has a significant impact on the glass tank service lifetime. Therefore, nondestructive test methods are used for quality assurance of glass tank blocks.

Voids, Cavities, and Porosity

The generation of voids is a characteristic of fused cast block production. After casting and melt solidification, voids occur inside the block (also termed cavities in the case of larger dimensions) due to the volumetric shrinkage on cooling (Figure 1). The formation of voids can be influenced by the manufacturing technology, melt chemical composition, as well as block size and shape. Furthermore, special casting techniques affect the location and size of voids or can even eliminate them. To produce void-free blocks additional casting headers of sufficient volume are required to supply extra melt and compensate the void.

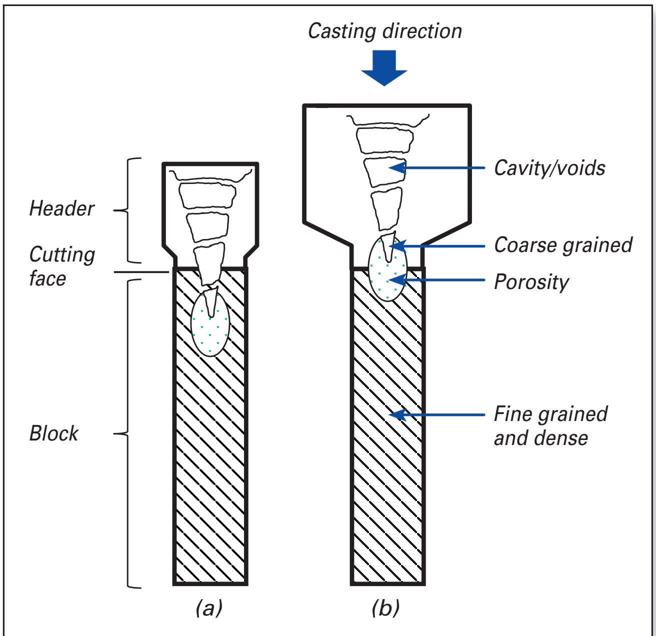


Figure 1. *Correlation between the cavity volume and casting header size. (a) the block contains a reduced size cavity and (b) the block is cavity-free because the larger header compensates the volume shrinkage.*

At the end of casting, the void is located at the top of the mould not in the centre of the fused cast block. This is due to the fact that while the void initially forms in the centre of the casting, it is successively filled with melt from the header and moves upwards. Since voids and the adjacent coarse crystalline zone with increased porosity are weak points in fused cast refractory blocks, avoiding or minimizing their presence is desired by the glass industry because this leads to significantly longer glass melting tank service lifetimes. Therefore, it is paramount to know the size and location of voids after the block has solidified. This evaluation can be performed with nondestructive testing methods.

Test Requirements

In brief, the nondestructive testing requirements are to detect block heterogeneities, such as the aforementioned voids, cavities, and porosity. The analysis should ascertain whether such flaws are present inside the block and—when indicated—their spatial extent.

Test Methods

Radar (Radio Detection and Ranging), operating in the microwave range, is well established in the field of aviation. For many years radar has also been applied for terrestrial purposes, termed ground penetrating radar (GPR), in areas such as geology and archaeology. Today, with the miniaturization of measurement devices, radar technology is also used in the construction sector to examine building materials. Inside the tested material the microwave transition losses, namely absorption, refraction, and reflection, depend on the dimensionless relative permittivity, which is ≈ 1 for air and ≈ 9 for a refractory [1–4].

For decades ultrasound imaging has also been used to detect flaws inside solid materials. Here the transition losses are a function of acoustic impedance. This is dependent on the test material density, which is ≈ 400 Ns/m^3 for air and in the case of refractories has the much higher value of $\approx 20 \times 10^6$ Ns/m^3 [4].

If the physical properties of mechanical ultrasound waves and electromagnetic microwaves are considered, there is no requirement for a coupling medium with radar technology when the measurement instrument is moved along the block surface for testing, as the change of material properties is significantly small at the air-refractory interface [4]. In contrast, ultrasound requires either dry contact, where the transducer is in direct contact with the sample, or noncontact coupling using a suitable medium between the transducer and sample surface that minimizes signal energy loss [5].

Feasibility Study

For the nondestructive testing feasibility study of fused cast refractory blocks a StructureScan Mini radar device with a 1.6 GHz antenna (Geophysical Survey Systems GSSI, Inc., Salem, USA) was evaluated (Figures 2 and 3). The portable unit is not restricted by any cables, working autonomously with a battery power source and memory card for data storage. During testing, the instrument is wheeled along the block surface.

For comparative reasons an ultrasound A1040 MIRA device operating at 20–100 kHz (Acoustic Control Systems, Moscow, Russia) was also tested. The idea of this latest ultrasound development is to overcome the aforementioned need for a coupling medium with multiple flexible transmitter-receiver probes (i.e., dry point contact). This instrument is connected to a portable computer by data cables and has to be placed forcefully and stepwise on the block surface during testing [6,7].

Both instruments work on the basis of a reflective technique (i.e., pulse-echo), whereby the transmitter (signal emitter) and receiver (return signal detector) are located on the same surface.

For calibration reasons, two different blocks were examined in the investigation: A free-void block (FVB) without any cavity and a cavity-reduced block (CRB) with a specified open cavity (Figures 4 and 5).

Results

The two-dimensional radar scans along the centre line of both the FVB and CRB are shown in Figures 6 and 7. The cut face between the header and block is located on the left-hand side (i.e., y-axis). The radar images show a dense and homogeneous, void-free structure for the FVB, while black-white wavy interferences clearly indicate the position and size of a shrinkage void and an adjacent zone of porosity in

Figure 2. *Tested fused cast blocks: The FVB with the radar measuring instrument (foreground) and the CRB.*

Figure 4. *Cut face between the block and casting header of the FVB without any cavity. Cross section 250 × 500 mm².*

Figure 3. *The radar measuring device in action.*

Figure 5. *Cut face between the block and casting header of a CRB. The residual cavity is visible, which is typical for CRBs. Cross section 250 × 460 mm².*

the CRB. After scanning the CRB was cut longitudinally using a diamond saw. The cut face showing a visible void and porosity (Figure 8) confirmed the radar image.

The radar results do not show the void or porosity as a direct image, but the microwave echo—reflections at boundaries with different permittivities—as grey-scale waves ranging from black to white. The overall smooth waviness along the complete cross section correlated with the interaction between the microwaves and microstructure. Furthermore, radar could differentiate between the more homogeneous and epitaxial crystallized block surface (i.e., casting skin) and the central block region, which relate to the different melt cooling and solidification rates.

Ultrasound interacts with macrostructural grains and pores as a function of wavelength. Therefore, the ultrasound equipment did not reveal the fine microstructural variances detected with radar (Figure 9). The indicated cavity position in the CRB depended on the cavity back wall echo, and did not correlate to the actual cavity location (Figure 10). All the other various colourations were signal interferences and not related to block flaws. In comparison to the radar results, the ultrasound images were less precise and required careful interpretation.

Summary

In the nondestructive test evaluation, the radar device was rapid and sensitive, as well as easier to handle than the ultrasonic equipment. Using the radar instrument a two-dimensional cross section (i.e., C-scan) along the centre line of a block can be performed in a few minutes. In addition, a more time consuming three-dimensional display is possible.

When the wave characteristics of ultrasound (working with a frequency in the kHz range) and microwaves (with a frequency in the GHz range) are compared, the latter provides better resolution, which is correlated to the higher frequency.

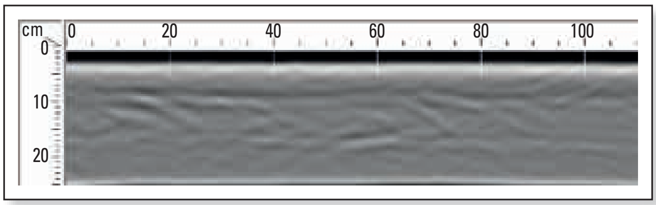


Figure 6. *Radar image of the FVB. A smooth image without signal interferences indicates the absence of any cavity.*

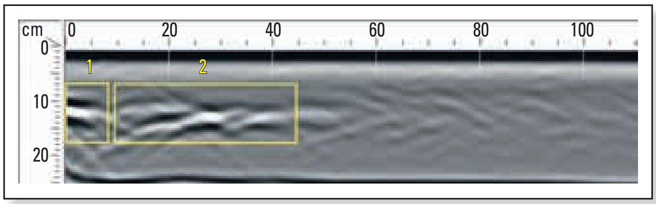


Figure 7. *Radar image of the CRB. Visible black-white interferences indicate the location of (1) a void and (2) porosity.*

Figure 8. *Longitudinal section of the cut CRB, with a clearly visible cavity followed by a porous region.*

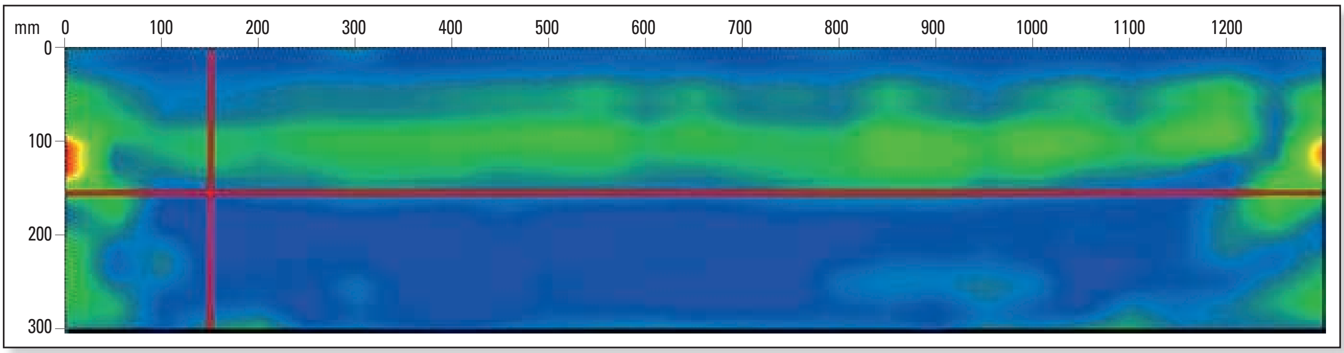


Figure 9. *Ultrasound image of the FVB. The various colourations are signal interferences and are not related to block flaws.*

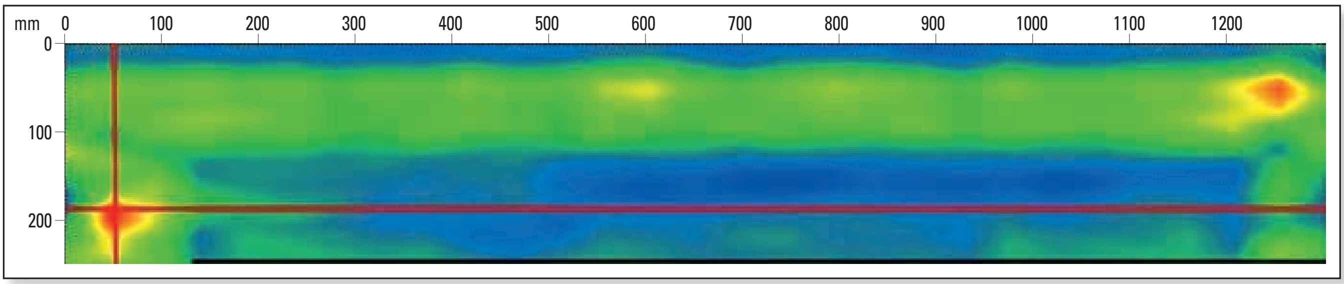


Figure 10. *Ultrasound image of the CRB. The red coloured area (close to the intersecting red lines) indicates the presence of a cavity. The various other colourations are signal interferences and are not related to block flaws.*

Taking all observations into consideration (i.e., no coupling medium necessary, time savings, testing of already preassembled blocks, and high resolution) the radar technology is state of the art for quality-relevant investigations. These initial results show the potential of nondestructively testing fused cast refractory blocks with radar technology. Further production-related tests are in progress.

References

[1] Daniels, J.J. Ground Penetrating Radar Fundamentals. Appendix to U.S.EPA, Region V Report. Department of Geological Sciences, Ohio State University, 2000.

[2] Reynolds, J.M. *An Introduction to Applied and Environmental Geophysics;* Wiley: Chichester, 1997.

[3] Boinet, M., Pires Franco, P., Crouzet, A., Massard, L., Gaubil, M. and Norgeot, C. Localization of Structural Heterogeneities in Refractory Blocks Using Ground Penetrating Radar. Presented at the 14th International Conference on Ground Penetrating Radar (GPR), Shanghai, China, June 4–8, 2012.

[4] Fleischmann, B. Non-Destructive Testing of Refractories, Especially AZS Materials, With Ultrasound, Microwaves and Gamma-Radiation. *Glastech. Ber. Glass Sci. Technol.* 1995, 68, No. 8, 259–265.

[5] Manhart, C., Schickert, M. and Urbanek, G. Ultrasonic Imaging of Refractories Using Different Coupling Techniques. *RHI Bulletin.* 2013, No. 1, 67–73.

[6] Bishko, A.V., Samokrutov, A.A. and Shevaldykin, V.G. Ultrasonic Echo-Pulse Tomography of Concrete Using Shear Waves Low-Frequency Phased Antenna Arrays. Presented at the 17th World Conference on Nondestructive Testing, Shanghai, China, Oct., 25–28, 2008.

[7] http://www.acsys.ru/eng/production/detail/a1040-mira/

Author

Roland Heidrich, RHI Refel S.p.A., San Vito al Tagliamento, Italy.

Corresponding author: Roland Heidrich, roland.heidrich@rhi-ag.com

RHI Bulletin > 2 > 2014, pp. 31–37

Rongxing Bei, Martin Geith, Christian Majcenovic, Barbara Krenzer and Ulrich Körner

Postmortem Analysis of Magnesia and Magnesia Zircon Checkers After One Campaign in a Soda-Lime Glass Melting Furnace

Checker bricks were examined after an 8-year campaign in a soda-lime glass furnace. The study confirmed the experience of a significant number of glass producers: In the hot zone of the regenerator checker work (> 1100 °C) the waste gas is relatively clean and ANKER DG1 high-purity magnesia chimney blocks with openings in the brick walls (TL design) are a very good choice, since the brick shape induces turbulences and improves heat exchange. For the condensation zone (< 1100 °C) where sulphate condenses in the checker bricks, RUBINAL EZ magnesia zircon chimney blocks without openings in the brick walls (TG design) show excellent performance.

Introduction

Magnesia bricks were used for the first time in the glass industry during the 1940s because fireclay as well as silica bricks were unsatisfactory. Since this time basic bricks, namely magnesia bricks and bricks containing magnesia, have been widely applied in the glass industry, especially in glass melting furnace regenerators. In this article the performance of both high-purity magnesia and magnesia zircon checker bricks after an 8-year glass furnace campaign is reported.

Characteristics of High-Purity Magnesia Bricks

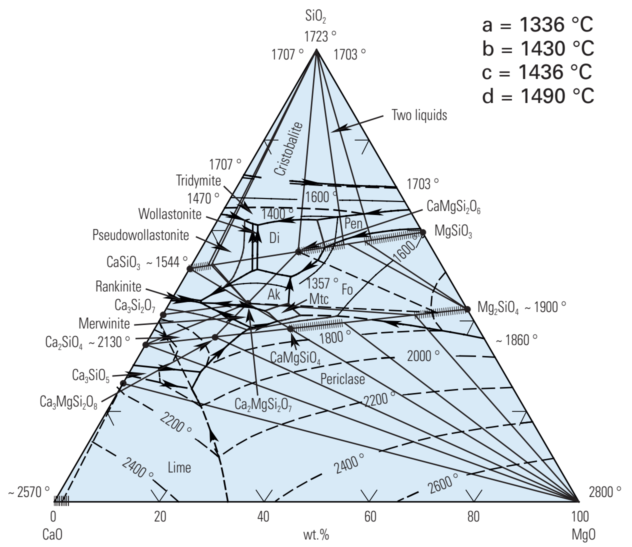
ANKER DG1, a high-purity magnesia brick, was developed by RHI in the 1980s (Table I). The main characteristics of this product are that it is manufactured from very pure raw materials and the CaO and SiO_2 molar ratio is > 2.

Magnesia brick performance is dependent on the production parameters such as pressing and firing intensity and is significantly influenced by the raw material purity. The importance of the raw material chemical composition can be seen in the MgO-CaO-SiO_2 phase diagram (Figure 1): Pure MgO (periclase = M) has a melting point of ~ 2800 °C.

Brand	ANKER DG1	RUBINAL EZ
Chemical composition (wt.%)		
MgO	97.0	73.7
Fe_2O_3	0.5	0.5
CaO	1.6	1.2
SiO_2	0.6	10.5
ZrO_2	-	14.0
Physical properties		
Bulk density (g/cm³)	2.96	3.10
Apparent porosity (vol.%)	15.9	14.5
Cold crushing strength (MPa)	70.0	90.0
Thermal expansion at 1400°C (%)	1.95	1.80
Refractoriness under load $T_{0.5}$ (°C)	> 1700	1570

***Table I.** Chemical composition and physical characteristics of ANKER DG1 and RUBINAL EZ.*

However, magnesia also contains small amounts of CaO (C) and SiO_2 (S). In this regard the C/S ratio and the amount of C + S are decisive because the C/S ratio determines the temperature at which the first melting phase forms and coexists with MgO. The total amount of C + S influences the amount of molten phase in the M-C-S system at a particular temperature (see Figure 1).



Crystalline phases

Notation	Oxide formula
Cristobalite, Tridymite	SiO_2
Pseudowollastonite	α = CaO·SiO_2
Wollastonite	β = (Ca,Mg)O·SiO_2
Rankinite	3CaO·2SiO_2
Lime	(Ca,Mg)O
Periclase	MgO
Forsterite	2(Mg,Ca)O·SiO_2
Protoenstatite	(Mg,Ca)O·SiO_2
Diopside	(Ca,Mg)O·MgO·2SiO_2
Akermanite	2CaO·MgO·2SiO_2
Merwinite	3CaO·MgO·2SiO_2
Monticellite	(Ca,Mg)O·MgO·SiO_2

***Figure 1.** Phase diagram of MgO-CaO-SiO_2 [1].*

Besides CaO and SiO_2, Fe_2O_3 is another common impurity in magnesite ($MgCO_3$), the raw material used to produce magnesia (MgO). Together with CaO, Fe_2O_3 can form dicalcium ferrite ($2CaO{\cdot}Fe_2O_3$), which has a single low melting point phase (1449 °C) [2]. In addition, Fe can change its valence between +2 and +3 to form magnesiowüstite ($Mg_{1-x}Fe_xO$) or magnesioferrite ($MgO{\cdot}Fe_2O_3$) in magnesia bricks. This can negatively influence the brick stability. Therefore, only MgO raw materials with a low iron content (< 0.7 wt.%) are used for ANKER DG1.

The C/S ratio in magnesia bricks significantly influences the formation of secondary mineral phases (Table II). The typical C-S containing phases in a magnesia brick are dicalcium silicate (Ca_2SiO_4 = C_2S), merwinite ($Ca_3Mg(SiO_4)_2$ = C_3MS_2), monticellite ($CaMgSiO_4$ = CMS), and forsterite (Mg_2SiO_4 = M_2S).

If the C/S ratio in a magnesia brick is higher than 1.87 the calcia can react with silica and form C_2S, which has a high melting point (1800 °C) in paragenesis with MgO. If the C/S ratio is lower than 1.87, the main calcia-containing secondary mineral phases formed are merwinite (C_3MS_2) and monticellite (CMS). Both these phases have relatively low melting points and the resulting brick hot properties are insufficient for regenerator applications.

This characteristic can be seen in the results of a laboratory test where the C/S ratio was varied in magnesia (Figure 2). While the cold crushing strength did not significantly change as the C/S ratio became greater, the hot modulus of rupture increased dramatically [3].

C/S ratio	Mineral formation in paragenesis with MgO (M) in the C-M-S system	Formation of first melts (invariant point)
< 0.93	M, M_2S M, M_2S, CMS	1860 °C 1502 °C
0.93–1.4	M, CMS, C_3MS_2	1490 °C
1.4–1.87	M, C_3MS_2, C_2S	1575 °C
1.87–2.8	M, C_2S M, C_2S, C_3S	1800 °C 1790 °C

Table II. *Relationship between the C/S ratio and the formation of different minerals in typical magnesia brick compositions. Data obtained from Figure 1. Abbreviations include CaO (C), SiO_2 (S), MgO (M), and CaO/SiO_2 (C/S) ratio.*

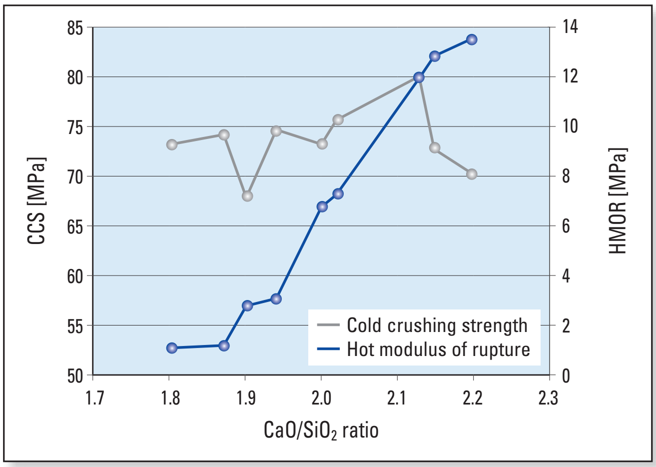


Figure 2. *Variation in cold crushing strength (CCS) and hot modulus of rupture (HMOR) of magnesia bricks containing an increasing C/S ratio.*

Production parameters are very important for achieving the final magnesia brick properties. For example high-temperature firing is necessary to generate direct bonding between the MgO-MgO grains (Figure 3). This direct bonding leads to good performance at high temperatures due to the higher refractoriness under load and lower creep in compression values (Figure 4). The creep in compression of ANKER DG1 at 1500 °C between 5 and 25 hours is much lower than 0.2%. As a result of the direct bonding between the MgO-MgO grains, ANKER DG1 also shows high corrosion resistance against the alkaline components in the waste gas flowing through the glass furnace regenerator.

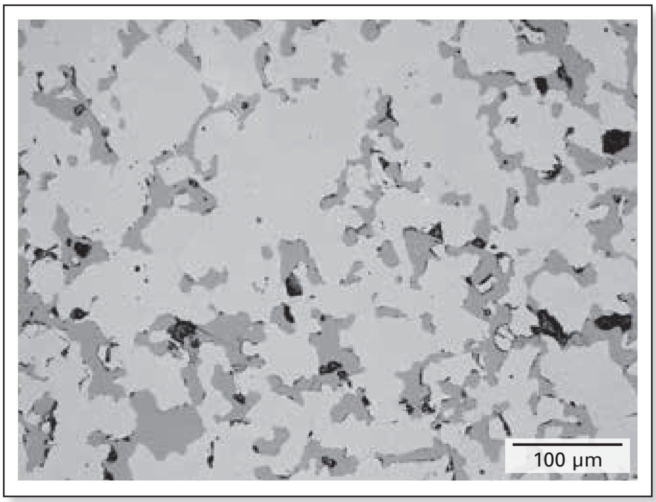


Figure 3. *Direct bonding between MgO-MgO in ANKER DG1.*

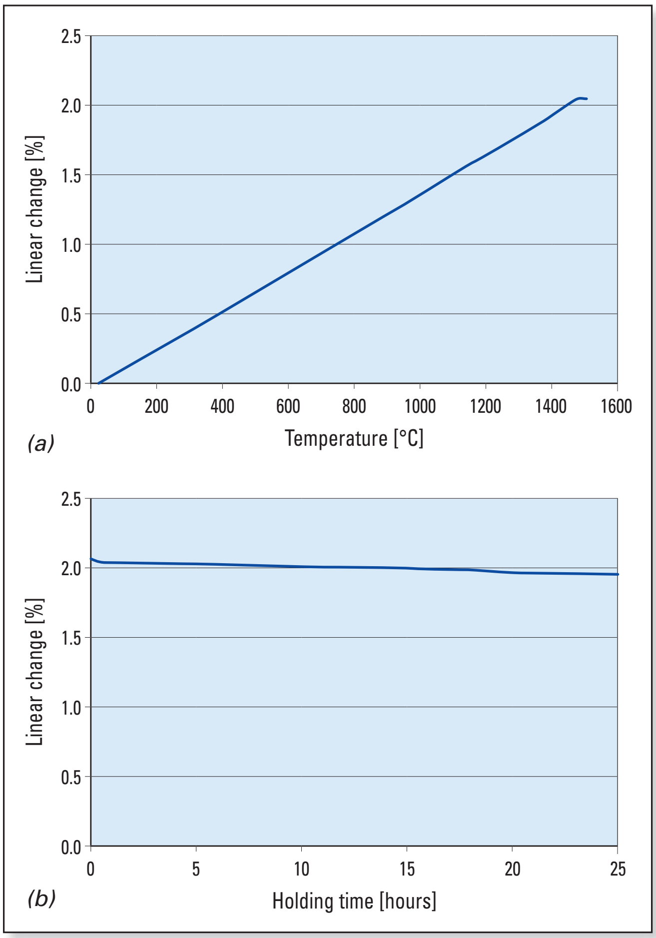


Figure 4. *ANKER DG1. (a) linear change from room temperature up to 1500 °C and (b) creep in compression at 1500 °C over 25 hours.*

Characteristics of Magnesia Zircon Bricks

The RUBINAL EZ magnesia zircon brand was developed in the 1980s for checker bricks used in the condensation zone of glass melting furnaces [4]. Since this time, magnesia zircon has replaced chrome-magnesia as a chrome-free solution, which previously was widely used for the condensation zone.

Zircon ($ZrSiO_4$) is one of the raw material components in RUBINAL EZ and decomposes during firing to SiO_2 and zirconia (ZrO_2). In reaction with MgO, SiO_2 forms the bonding phase forsterite ($2MgO{\cdot}SiO_2$) in the matrix, which can be clearly seen using scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analyses (Figure 5 and Table III). Forsterite (point 2) and ZrO_2 (points 1 and 3) could be clearly detected in the matrix. Furthermore, in the area analysis (F) a mixture of forsterite and ZrO_2 was identified. The ZrO_2 was stabilized by 3-4 wt.% CaO and 3–4 wt.% MgO. Approximately 2 wt.% CaO was dissolved in the forsterite. Interestingly, the rim around the MgO grains (periclase) was forsterite containing tiny ZrO_2 crystals, which protects the magnesia against corrosive agents such as acidic sulphate.

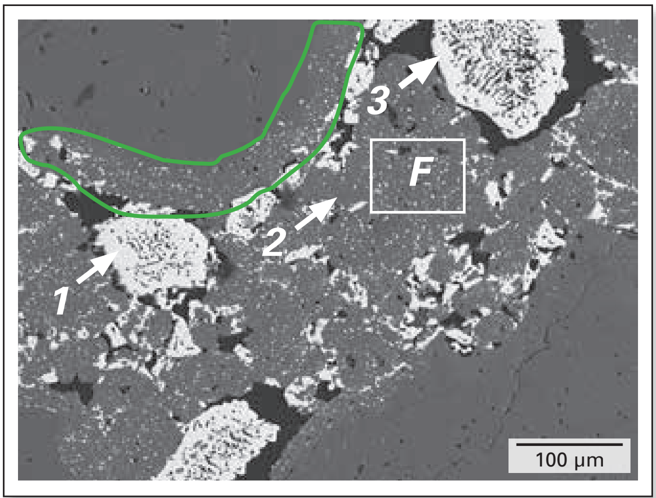


Figure 5. *Scanning electron micrograph of unused RUBINAL EZ. ZrO_2 (points 1 and 3), forsterite (point 2), and a mixture of forsterite and ZrO_2 (area F) are indicated. A rim of forsterite containing tiny ZrO_2 crystals was detected around the MgO grains (green line).*

Area/ Spot	MgO (wt.%)	SiO_2 (wt.%)	CaO (wt.%)	ZrO_2 (wt.%)	HfO_2 (wt.%)	Mineral phase
1	3.6		3.3	90.7	2.5	Zirconium oxide
2	55.7	42.4	2.0			Forsterite
3	3.3		3.6	90.6	2.5	Zirconium oxide
F	50.0	35.4	2.3	12.4		Forsterite, Zirconium oxide

Table III. *SEM-EDX microanalyses of the spots (1–3) and area (F) in Figure 5 (unused RUBINAL EZ) and principal mineral phases.*

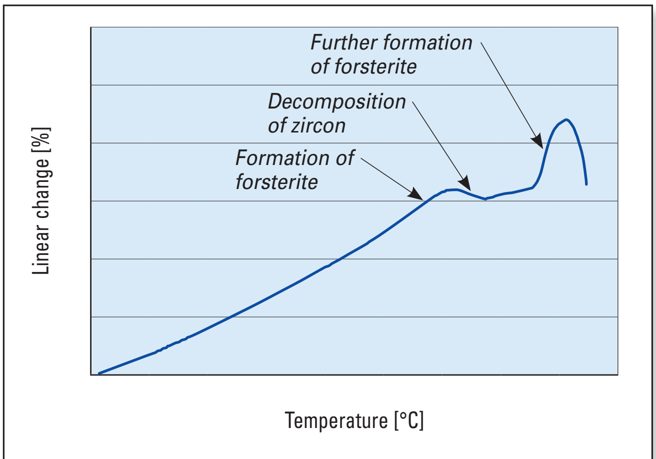


Figure 6. *Firing behaviour of magnesia zircon.*

The firing behaviour of magnesia zircon bricks is shown in Figure 6. The RUBINAL EZ production process is optimized accordingly, to ensure that all the zircon raw material components form forsterite ($2MgO{\cdot}SiO_2$) and zirconia (ZrO_2) in the bonding matrix. The firing parameters are selected so that decomposition of zircon is ensured and forsterite formation completely occurs but does not result in a too high volume expansion.

The typical temperature range in the condensation zone of a glass melting furnace regenerator is 800–1100 °C. Therefore, it is important the bricks have low creep values in this temperature range. An important quality control for RUBINAL EZ is determining the creep values at 1300 °C, which is higher than the application temperature of 1100 °C. Figure 7 shows the typical creep values of RUBINAL EZ at 1300 °C. The creep in compression at 1300 °C between 5 and 25 hours is much lower than 0.2%.

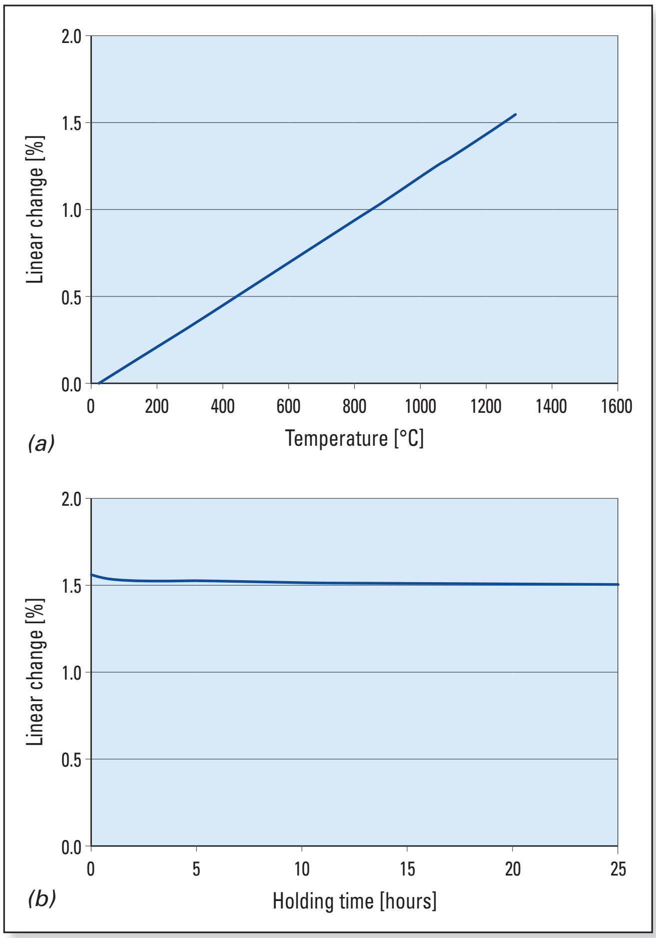


Figure 7. *RUBINAL EZ. (a) linear change from room temperature up to 1300 °C and (b) creep in compression at 1300 °C over 25 hours.*

Postmortem Analyses of Magnesia und Magnesia Zircon Checker Bricks

The soda-lime glass melting furnace at Glaswerk Ernstthal GmbH (Germany) is an end-port design with a melting area of ~ 50 m^2. It is fired with natural gas and has additional electric boosting. The furnace went into production in 2005 and was producing white glass at a daily pull of 120 tonnes. The furnace was shut for general repairs in 2013 after 8 years in operation. The typical temperature of the waste gas was ~ 1400 °C at the top of the regenerator and ~ 600 °C underneath the rider arches.

ANKER DG1 had been installed in the high-temperature (> 1100 °C) regenerator zone and RUBINAL EZ was used for the condensation zone (< 1100 °C). Both checker brick brands had a flue size of 140 mm, a height of 175 mm, and a wall thickness of 38 mm. The ANKER DG1 bricks in the high-temperature zone had openings in each of the four brick walls (TL design) to improve the flue gas turbulence and achieve high thermal efficiency. The RUBINAL EZ bricks had no openings in the walls (TG design) to avoid strong condensation of sulphate from the waste gas on the brick surface.

No clogging in the checker work channels was observed during the furnace operation. This was subsequently confirmed during an inspection after the furnace and regenerator had cooled down. Visually, both the ANKER DG1 (Figure 8a) and RUBINAL EZ (Figure 8b) brands demonstrated good performance when the used bricks were demolished.

Representative samples were taken to examine the brick properties after one furnace campaign (Figure 9). The specific ANKER DG1 checkers had been installed ~ 6 m above the rider arches (the flue gas had a temperature of

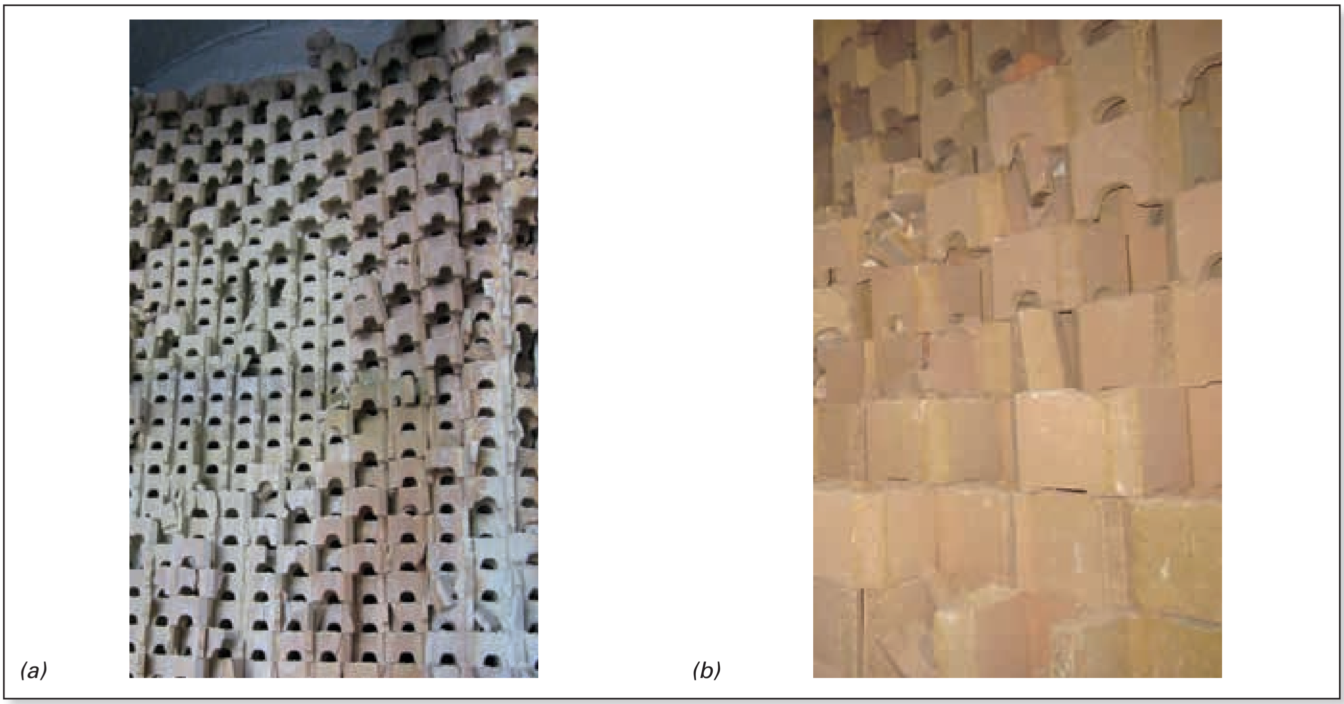


Figure 8. *Checker work after 8 years in operation. (a) ANKER DG1 in the regenerator upper region and (b) RUBINAL EZ in the condensation zone.*

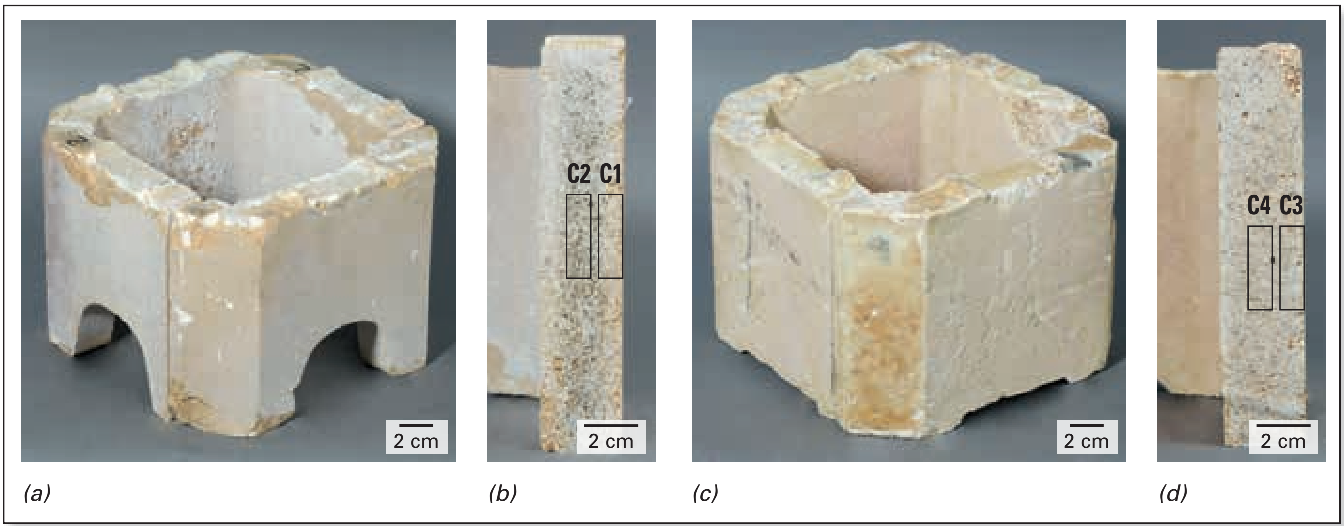


Figure 9. *Postmortem samples for testing and analysis. (a,b) ANKER DG1 and (c,d) RUBINAL EZ. The analysis positions at the hot face and mid-brick region are indicated by the rectangles.*

~ 1200 °C at this position), while the RUBINAL EZ bricks were taken out 3.5 m above the rider arches (the flue gas had a temperature of ~ 900–1000 °C at this position). Not only the surface but also the cross section of the bricks was in good condition.

The chemical analysis and physical properties of postmortem and unused samples of ANKER DG1 and RUBINAL EZ are detailed in Table IV. In addition to X-ray fluorescence, carbon-sulphur element analysis and inductively coupled plasma optical emission spectroscopy were used to increase the alkali and sulphur detection accuracy. The bulk density and porosity were measured to determine the degree to which pores in the bricks were filled with condensed sulphate and dust from the waste gas. The hot modulus of rupture was tested to assess the mechanical condition of the bricks.

In comparison to an unused brick, the chemical composition of the installed ANKER DG1 was nearly unchanged except for a slight increase in SiO_2 at the hot face, which was most probably due to sand from the batch. This indicated that the waste gas was relative clean. For such conditions, the choice of checkers with openings in the brick walls was correct. In cases where the waste gas is not so clean, condensate and dust destroy the bricks more easily if the specific heat transfer area is higher and there is greater waste gas turbulence. Therefore, bricks with openings in the walls are not appropriate for such conditions.

In line with the chemical analysis, the porosity of the used ANKER DG1 had practically the same value as a new brick (15 vol.%). In addition, the hot modulus of rupture value confirmed the used ANKER DG1 brick was in good condition.

The chemical analysis revealed the used RUBINAL EZ contained Na_2O and SO_3 not present in the new brick sample. The sum of Na_2O and SO_3 equated to 4–6 wt.% depending on the sample location, with higher levels of both Na_2O and SO_3 present at the hot face compared to the brick centre. Consequently, the porosity decreased from the original value of 14.5 vol.% to ~ 11 vol.%. This fact hardly influenced the good brick performance in the regenerator. The hot modulus of rupture value of used RUBINAL EZ was still high and indicated a stable brick structure.

General information						
Sample	ANKER DG1			RUBINAL EZ		
	Hot face C1	Centre C2	Unused	Hot face C3	Centre C4	Unused
Sample distance from the hot face (mm)	0–5	10–20		0–5	10–20	
Chemical analysis (wt.%) Determination by XRF[1]						
Na_2O	0.02	0.00		2.85	2.24	
MgO	95.9	97.2	97.0	69.1	71.2	73.7
Al_2O_3	0.13	0.04		0.15	0.27	
SiO_2	1.23	0.75	0.6	10.71	10.50	10.5
SO_3	0.02	0.00		2.86	2.13	
K_2O	0.02	0.01		0.40	0.48	
CaO	2.12	1.77	1.6	0.26	0.27	1.2
Fe_2O_3	0.18	0.18	0.5	0.54	0.48	0.5
ZrO_2	0.02	0.05		12.71	12.06	14.0
HfO_2	0.00	0.00		0.27	0.26	
C-S element analysis[2]						
Sulphur	0.032	0.029		1.38	1.20	
SO_3	0.08	0.07		3.45	2.99	
ICP-OES[2]						
Na_2O	0.09	0.02		2.22	1.79	
K_2O				0.18	0.15	
Physical properties						
Bulk density (g/cm³)	2.98		2.96	3.15		3.10
Apparent porosity (vol.%)	14.91		15.9	11.17		14.5
Hot modulus of rupture at 1400°C (MPa)	14.1			8.5		
[1] Sample after ignition at 1050 °C [2] Original sample						

Table IV. *Chemical analysis and physical properties of postmortem and unused samples of ANKER DG1 and RUBINAL EZ. Sample after ignition at 1050 °C (1) and original sample (2) are indicated. Abbreviations include X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES).*

Scanning electron microscopy of the used ANKER DG1 and RUBINAL EZ samples showed that up to 0.5 mm from the hot face, the ANKER DG1 had become densified (Figure 10a). In addition, some deposits were observed on the surface and strong bonding was evident between the magnesia grains. In the mid-thickness of the ANKER DG1 (Figure 10b) C_2S was found at a few positions and strong MgO-MgO bonding between magnesia grains could be clearly seen.

Alkali sulphates had infiltrated the hot face of RUBINAL EZ (Figure 10c) and magnesia grains directly at the hot face were corroded. Directly below the hot face, magnesia grains were also partly corroded in regions facing the hot face. A strong forsterite bonding matrix was detected that protected the magnesia and zirconia reinforced this fosterite matrix. In the mid-thickness of the RUBINAL EZ (Figure 10d), alkali sulphate infiltration was also observed, but the magnesia was hardly corroded. A strong forsterite bonding matrix containing zirconia was also evident, which ensured the very good brick performance.

Thermogravimetric analysis and differential thermogravimetric analysis were performed on used RUBINAL EZ samples (Figure 11). At 1100 °C the sample started to lose weight, indicating alkali sulphate evaporation. The results confirmed that the condensation zone in the regenerator checker work started at 1100 °C.

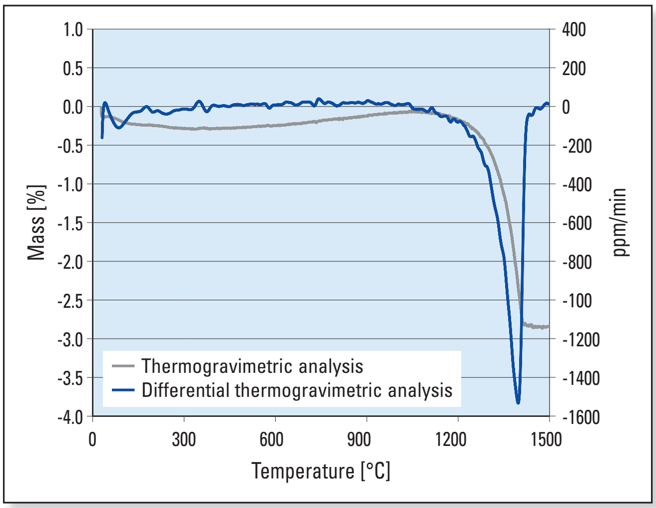


Figure 11. *Thermogravimetric and differential thermogravimetric analyses of RUBINAL EZ.*

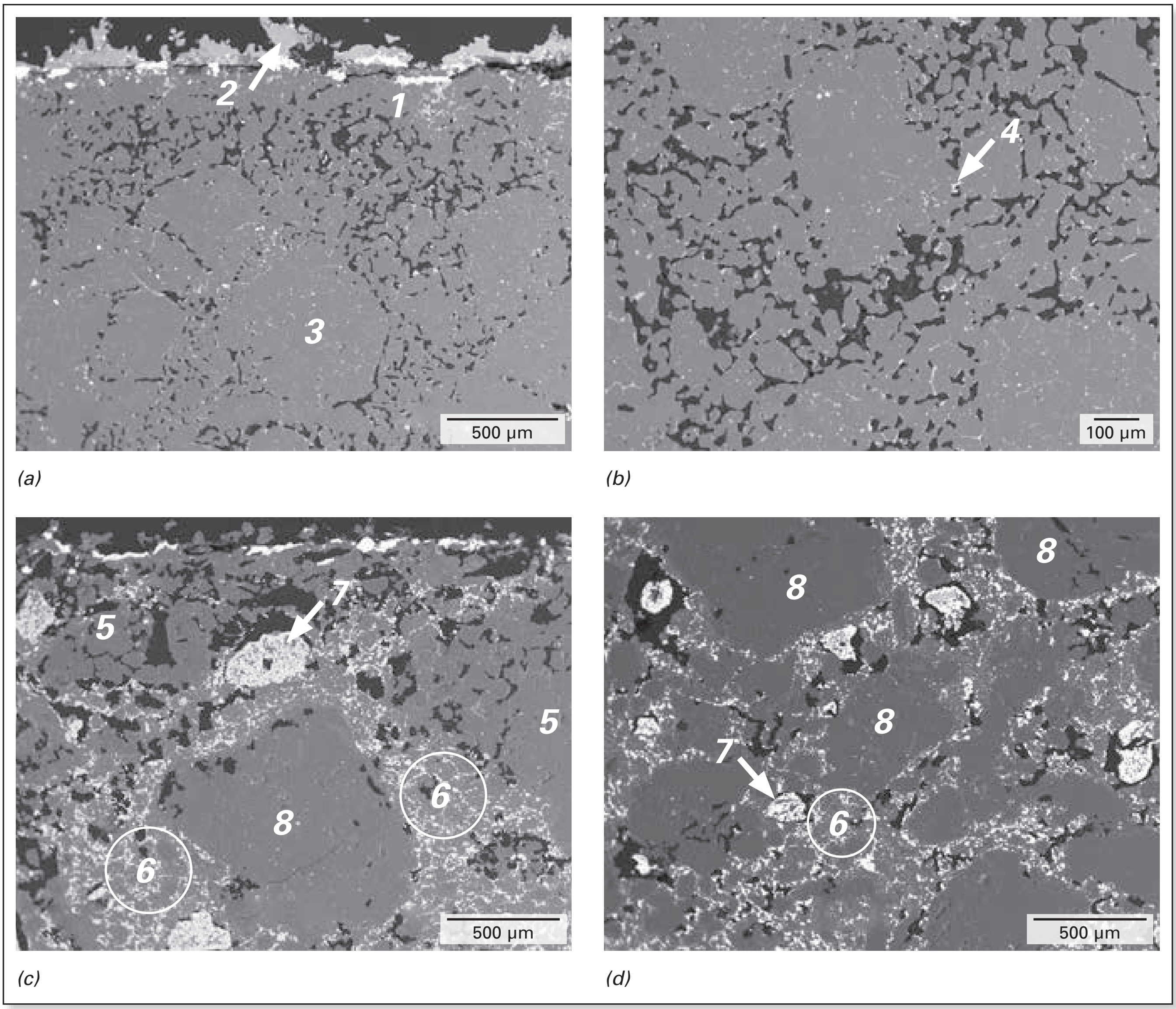


Figure 10. *Scanning electron micrographs of used ANKER DG1 and RUBINAL EZ (a,c) at the hot face and (b,d) 20 mm from the hot face, respectively. Densification (1), surface deposits (2), strong bonding between the magnesia grains (3), dicalcium silicate (4), corroded magnesia (5), forsterite bonding matrix (6), zirconia (7), and intact magnesia grains (8) are indicated.*

Conclusion

The postmortem study of two checker brick brands after an 8-year furnace campaign confirmed the experience of a great number of glass producers:

- >> ANKER DG1 checker bricks with openings in the brick walls are a very good choice for the checker work in the regenerator hot zone (> 1100 °C) where the waste gas is relatively clean.
- >> RUBINAL EZ checker bricks without openings in the brick walls show excellent performance in the regenerator condensation zone (< 1100 °C) where sulphate condenses on the checker bricks.

References

[1] Osborn, E.F. and Muan, A. Phase Equilibrium Diagrams of Oxide Systems, Plate 2; American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

[2] Phillips, B. and Muan, A. Phase Equilibria in the System CaO-Iron Oxide in Air and at 1 Atm. O_2 Pressure. *J. Am. Ceram. Soc.* 1958, 41, No. 11. 445–454.

[3] Guo, Z. Influence of Lime/Silica-Ratio on Properties of RADEX VS-CN With limestone Addition, 2007. Internal Report D20070016. RHI AG, Dalian, China.

[4] Weichert, T. Verfahren zur Herstellung eines gebrannten, feuerfesten Magnesiasteins auf der Grundlage von Sintermagnesia und feinverteiltem Zirkonsilikat. German Patent DE 3720460 A1, 1987.

Authors

Rongxing Bei, RHI AG, Industrial Division, Wiesbaden, Germany.
Martin Geith, RHI AG, Technology Center, Leoben, Austria.
Christian Majcenovic, RHI AG, Technology Center, Leoben, Austria.
Barbara Krenzer, RHI AG, Industrial Division, Wiesbaden, Germany.
Ulrich Körner, Glaswerk Ernstthal GmbH, Lauscha-Ernstthal, Germany.
Corresponding author: Rongxing Bei, rongxing.bei@rhi-ag.com

PARTNERSHIP IN MATERIALS AND TECHNOLOGY

Picture credits: © WienTourismus – Claudio Alessandri (1)/Peter Rigaud (2)/Lois Lammerhuber (3)/Claudio Alessandri (4)

14th Biennial Worldwide Congress

UNITECR 2015

Unified International Technical Conference on Refractories

VIENNA · AUSTRIA
SEPTEMBER 15–18

www.unitecr2015.org

CALL FOR PAPERS

Topics

- Industrial Refractory Applications
- Raw Materials and Recycling
- Advances in Manufacturing, Control and Installation
- Tests, Testing Equipment and Standardization
- Innovation in Materials and Technology
- Basic Science in Refractories
- Refractory Engineering – Design, Modeling and Simulation
- Environment and Sustainability
- Education
- Economic and Political Challenges

DFFI Verband der Deutschen Feuerfest-Industrie e.V.

– in conjunction with the 58th International Colloquium on Refractories –
Contact: unitecr@ecref.eu

European Centre ECREF for Refractories

RHI Bulletin > 2 > 2014, pp. 40–41

Andreas Wiry

RHI Thrust Lock System—Case Study

Introduction

The operating principle and unique features of the new RHI Thrust Lock System were previously described in the 2013 Industrial RHI Bulletin [1]. By means of this Thrust Lock System (Figure 1) the axial lining thrust, which causes most refractory lining failures at the kiln outlet, can be stopped due to the special skew brick set. Based on a case study, various design options were developed with the novel system, which are highlighted in this paper. The specific installation procedure is also described in a stepwise manner.

Kiln Lining Damage

Over the last years, frequent lining failures have occurred at the nose ring and retaining ring of the Zementwerk Leube GmbH (Austria) precalciner kiln (3.5 m diameter). In spite of several different designs and lining concepts, the achieved service life was only 6 months and in the worst case the lining had to be replaced after 3 months (Figure 2).

Failure Analysis and Lining Concepts

After a detailed analysis of the mechanical kiln conditions (e.g., shell test measurements), process conditions, wear mechanisms, and postmortem investigation of brick samples the following lining concepts were developed (Figure 3):

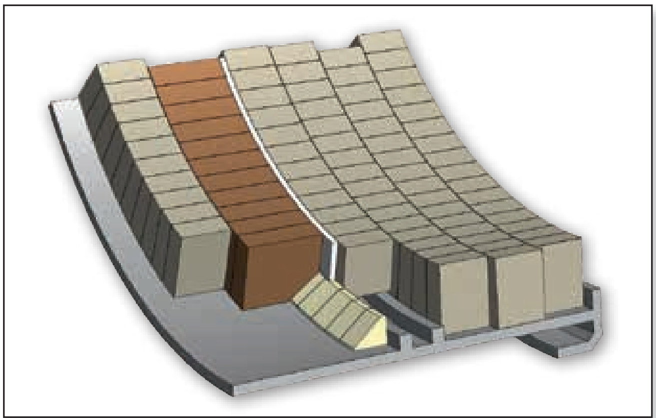


Figure 1. New RHI Thrust Lock System installed at a retaining ring, comprising special skew brick sets (cream and brown) and an expansion joint (white).

Figure 2. Lining damage after 3 months in operation.

>> Thrust Lock System and brick lining at the outlet (staggered lining of ANKRAL Q1) (Figure 3a).
>> Thrust Lock System and monolithic outlet using CARSIT SOL M10-6 (Figure 3b).
>> Thrust Lock System and extended monolithic outlet—for the case where existing retaining ring conditions do not enable correct installation of the skew bricks (Figure 3c).
>> Thrust Lock System and a second Thrust Lock System step (TL System 2) in front of the nose ring (Figure 3d).

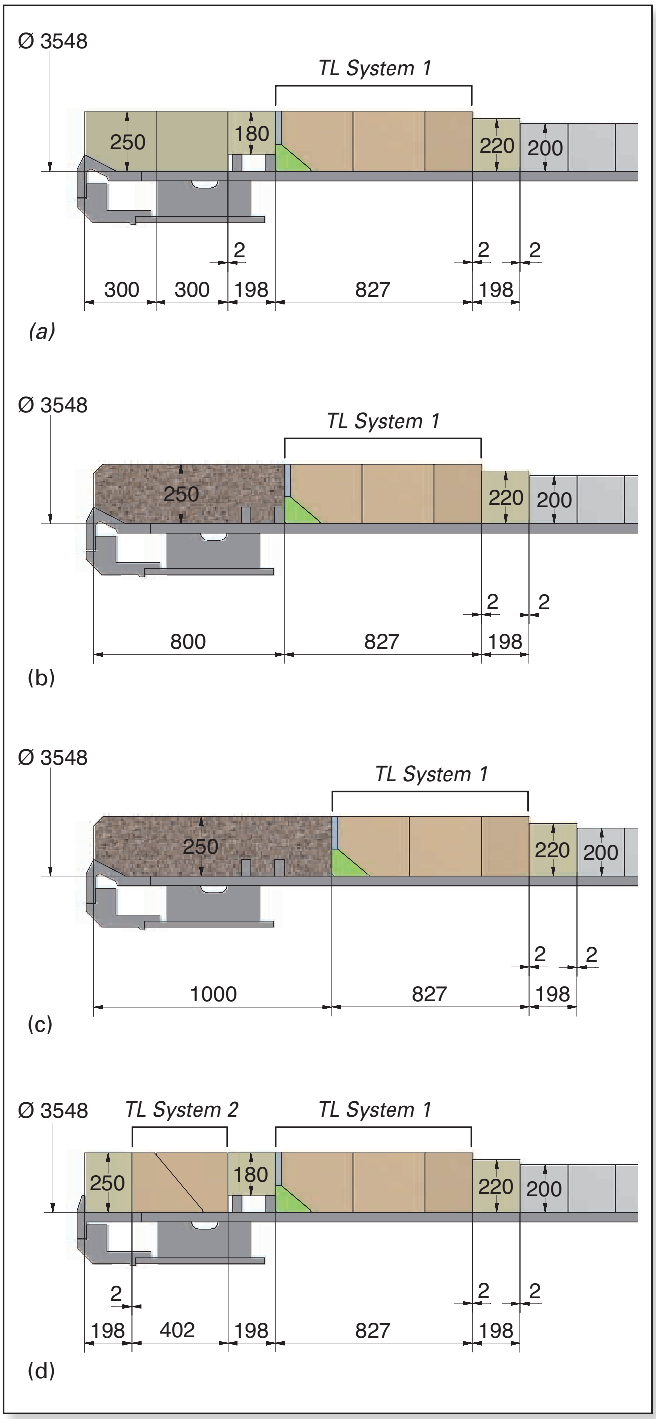


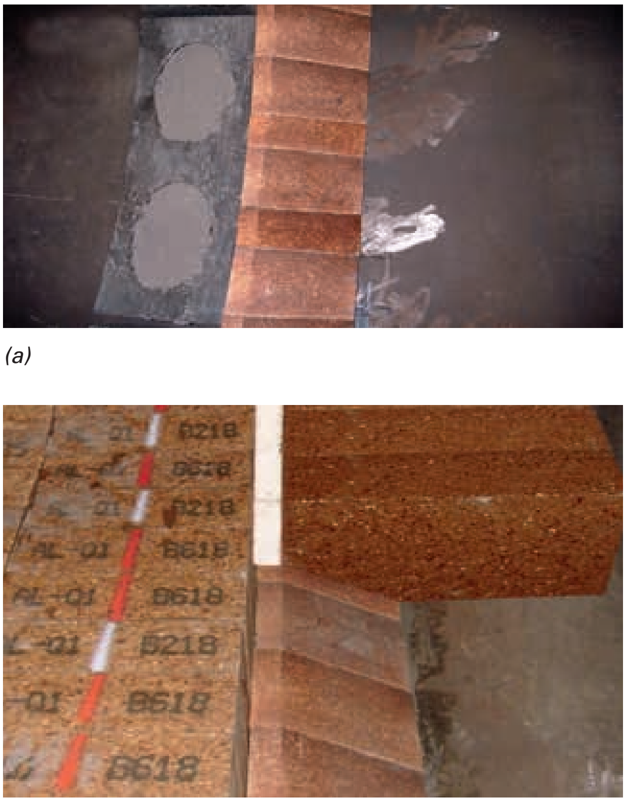
Figure 3. Different lining concepts: Thrust Lock (TL) System and (a) brick lining at the outlet, (b) monolithic outlet, (c) extended monolithic outlet, and (d) second TL System step. Dimensions are in mm.

As a result of previous poor results when using a monolithic lining at the outlet and a short distance between the retaining and nose ring, the design in Figure 3a—Thrust Lock System and brick lining at the outlet—was selected for the customer.

A staggered lining at the outlet (600 mm long) was installed to avoid brick twisting in this section. Due to the established high thermomechanical stress and positive experiences previously gained with ANKRAL Q1 in the lower transition zone, this brand was chosen for the outlet. ANKRAL TLS used for the Thrust Lock System is characterized by excellent fracture mechanical properties and high thermochemical resistance.

Installation of the Thrust Lock System and Outlet Lining

During the winter shutdown period 2013/2014, the entire outlet zone (running metre 0–2.4) was newly installed. After overhauling the retaining ring and performing necessary grinding of any kiln shell imperfections, the first ring of skew bricks (Figure 4a) was installed using a two-component adhesive. Subsequently, the second shape of the Thrust Lock System skew brick set was installed (Figure 4b).



(a)

(b)

__Figure 4.__ Installation of the (a) first ring of skew bricks and (b) second Thrust Lock System shape.

In order to achieve a uniform load distribution on the entire skew brick ring and to counteract spiralling of adjacent rings, a staggered lining (500 mm) is part of the Thrust Lock System. This design helps divert the axial lining thrust into radial and circumferential forces, consequently reducing the mechanical load on the bricks and retaining elements.

While the outlet (ANKRAL Q1) was installed using the gluing method, the Thrust Lock System and upper part of the outlet zone were installed by means of a bricking rig (DAT rig). The Thrust Lock System rings were closed using special key bricks and shims. Ceramic felt (PYROSTOP SUPERFELT 1400) was inserted in the defined expansion gap between the Thrust Lock System and the brick ring at the retaining ring (Figures 4 and 5).

Conclusion

This first Thrust Lock System installation provided evidence that it can be easily performed and managed by a skilled installation company, in the common way, within a typical time frame. However, special attention needed to be paid to the condition and appropriate maintenance of the retaining ring, especially a precise right angle of the retainer. However, in order to ensure trouble-free and correct installation, RHI provided a supervisory service. After successfully achieving a service life of 8 months, the Thrust Lock System is still in operation.

Due to the various design options and combination possibilities with the Thrust Lock System, tailor-made concepts for every individual case can be developed. To select the most appropriate concept, prevailing operating conditions, existing design, lining history, gained experiences, and wear patterns need to be jointly evaluated with the customer.

__Figure 5.__ Thrust Lock System installed at the outlet zone.

Reference

[1] Wiry, A. and Marschall, H.U. RHI Thrust Lock System for Cement Rotary Kilns. *RHI Bulletin.* 2013, No. 2, 17–19.

Author

Andreas Wiry, RHI AG, Industrial Division, Vienna, Austria.
Corresponding author: Andreas Wiry, andreas.wiry@rhi-ag.com

Roland Krischanitz and René von der Heyde

RHI Extends the Training Center Cement Programme

In October 2011 the Training Center Cement, located close to RHI's Technology Center Leoben (Austria), started offering refractory installation training courses (bricks and monolithics) for the cement industry. Since this time more than 20 internal and external workshops have been conducted. The well-balanced mix of theory and practical application has proved an excellent approach to developing in-depth know-how regarding refractory materials, and this has been confirmed by the extremely positive feedback from course participants. To further optimize the training programme, RHI has been extending the facilities and monolithic installation can now also be practiced on a burner lance model.

Introduction

Correct monolithic installation is an essential prerequisite in order to achieve the product properties detailed in the data sheet. In contrast to fired bricks, a castable achieves its final properties during installation. Consequently, incorrect handling will result in poor product properties, for example high porosity or low cold crushing strength. Under the critical operating conditions associated with the burner pipe this significantly reduces product performance. Accordingly, lining lifetimes differ dramatically ranging from as low as only several weeks in the worst case scenario up to more than one year.

To highlight the types of mistake that can occur, especially during burner pipe lining installation, and to sharpen awareness regarding the importance of correct application, RHI has integrated burner lance lining into the existing, extensive Training Center Cement programme [1]. A burner pipe tip model enables practical training under realistic conditions (Figure 1). For demonstration purposes one section of the burner is already lined, while the rest can be lined during the training. Unlike the usual procedure that involves welding anchors to the shell, in the case of this model anchors are just screwed to the burner lance tube from inside. This allows easy and fast removal of the castable without compromising the training goals. The sessions convey useful tips regarding how to successfully prepare the moulding and perform the installation, providing the basis for satisfactory product performance. Furthermore, the newest generation of RHI monolithics can be used for the installation (Figures 2 and 3). For example cement-free castables,

Figure 2. *Preparation of a mould for castable installation.*

Figure 1. *Burner lance model for monolithic installation training.*

Figure 3. *Casting and vibrating the sol-bonded CARSIT SOL M10-6 castable.*

the so-called sol-bonded castables, feature unique properties that specifically match the refractory requirements for burner lance applications.

Drying and Heating Up Monolithics

A more theoretical topic that is also discussed encompasses correct drying and heating up of monolithics, since it is often difficult to conduct these procedures correctly as appropriate predrying furnaces are rarely available. Under ideal conditions, hydraulically bonded castables should be heated up to at least 400 °C in order to remove the majority of free and chemically bonded water and thereby reduce the risk of vapour pressure damage when heating up to process conditions.

If drying and heating up is not correctly performed with conventional monolithics, the lining is predamaged from the beginning when the burner lance is abruptly exposed to high temperatures. However, due to the special properties of sol-bonded castables [2], predrying is not required. In addition, heating up can be performed very rapidly, making these types of cement-free castable the ideal basis for burner lance applications.

Product Initiatives

RHI not only provides the know-how for correct castable installation in order to optimize burner lance lifetime but is also intensively developing novel material solutions. With the new extended product range of burner refractories, RHI can improve performance in this critical area. In particular, the lower part of the burner tip is exposed to severe high temperature loads (Figure 4), thermal shocks (especially during start up), chemical attack, as well as abrasion from the dust loaded, hot secondary air coming from high-efficiency grate coolers.

Based on preexisting, successful sol-castables like CARSIT SOL M10-6 and CARSIT SOL M10-5 V (Figure 5), developments have continued resulting in a further generation of sol-bonded castables with the highest thermal resistance that are optimally suited for burner lance applications.

The so-called mullite-bonded castables [3], which are also cement-free castables, represent a further advance in the sol-bonded mixes. The unique matrix design enables outstanding material properties to be realized. First applications of this new generation such as COMPAC SOL MB A100-15 and CARSIT SOL MB A10-15, based on corundum as the main raw material, have already proven very successful for burner tips in the cement industry. Mullitic-bonded sol products based on fireclay have shown extremely promising laboratory results and it is likely that even more products will be based on this concept in the near future. The special matrix design of this latest castable generation is intended for applications where the highest refractoriness, abrasion resistance, and outstanding strength properties are required at high temperatures (Table I).

In additional to the beneficial properties determined for sol-bonded castables, the new mullite-bonded castables feature the following characteristics [3]:

Figure 4. *Burner lance after 5 months in operation demonstrating castable overheating at the burner tip. The burner tip was lined with a conventional low-cement castable. The adjacent segment was lined with a sol-bonded high-alumina castable and clearly shows less wear.*

(a)

(b)

Figure 5. *Burner tip lined with CARSIT SOL M10-5 V in perfect condition after 7 months in operation. Traditional low-cement castables resulted in a lifetime of only 4 months.*

Brand	Al_2O_3 (wt.%)	SiO_2 (wt.%)	Fe_2O_3 (wt.%)	SiC (wt.%)	MR (t/m³)	Mixing liquid (l/100 kg)	CCS (N/mm²) 110 °C	CCS (N/mm²) 1000 °C	TL (°C)	TE 1000 °C (%)	Raw materials
Sol-bonded (casting)											
CARSIT SOL M10-6	58.0	28.0	0.8	10.0	2.53	6.5–7.5	70	100	1650	0.55	Mullite/SiC
CARSIT SOL M10-5 V	57.0	29.0	1.2	10.0	2.45	8.0–9.0	50	80	1650	0.55	Mullite/SiC
Mullite-bonded (casting)											
COMPAC SOL MB A100-15	98.5	1.0	0.1	-	3.05	5.7–6.5	80	180	1850	0.75	Tabular alumina
CARSIT SOL MB A10-15	89.0	1.3	0.1	10.0	2.95	5.5–6.5	45	200	1650	0.68	Tabular alumina/SiC
COMPAC ROX A97-15	97.0	2.2	0.1	-	2.95	5.5–6.5	40	110	1900		Sintered alumina
Cement-bonded (casting)											
CARSIT M10-6	55.0	30.5	0.8	10.0	2.50	5.3–5.9	70	120	1650	0.55	Mullite/SiC
CARSIT S30-6	41.0	26.5	0.4	29.0	2.60	4.5–5.0	70	105	1580	0.55	Andalusite/SiC
COMPRIT A95-6	95.2	0.2	0.1	-	2.74	8.0–9.0	85	85	1800	0.75	Sintered alumina

Table I. *Overview of the product range for burner lances. Abbreviations include material requirement (MR), cold crushing strength (CCS), application temperature limit (TL), and linear thermal expansion (TE).*

- >> Very high maximum application temperatures due to the use of a high-alumina raw material (i.e., sintered alumina) as the main component in combination with the special matrix design.
- >> In service formation of a mullite matrix at higher temperatures.
- >> The matrix structure comprises designed micropores with an average pore size distribution approximately one-tenth that of traditional cement-bonded systems. This enables rapid and simple drying procedures.
- >> A cement-free refractory castable with extremely low brittleness despite the very high refractoriness and extremely high strength (> 150 MPa) over a broad temperature range.

Conclusion

The available product range detailed in Table I now offers tailor-made solutions for various wear scenarios such as chemical attack, thermal load, as well as a combination of both. The easy drying and heating up properties also provide major application benefits. Nevertheless lining at the burner tip remains a critical application area where flawless refractory material processing is essential in order to achieve optimal product properties.

References

[1] Schachenhofer, E. Brick by Brick: Customers and Employees Mortar and Cast in the RHI Training Center. *RHI Bulletin.* 2012, No. 2, 17–18.

[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.

[3] Hochegger, M., Blajs, M., Nonnen, B. and Zottler, P. First Practical Results With COMPAC SOL A100S-15—A High-End Sol-Bonded Castable Designed for EAF Deltas. *RHI Bulletin.* 2013, No. 1, 14–19.

Authors

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

René von der Heyde, RHI AG, Industrial Division, Mülheim-Kärlich, Germany.

Corresponding author: Roland Krischanitz, roland.krischanitz@rhi-ag.com

Angelika Ofner-Ressler, Christian Manhart and Rainer Neuboeck

Characterization of Magnesia-Chromite and Magnesia Bricks Using Different Nondestructive and Destructive Testing Methods

Magnesia-chromite and magnesia refractory bricks have a wide field of application in the nonferrous metal industry. Due to their use in the highest wear areas, they are characterized by high refractoriness and good resistance to slag corrosion. For quality management purposes, physical properties (e.g., bulk density, open porosity, and cold crushing strength) are routinely determined at room temperature. However, brick behaviour at application temperatures (i.e., 1200 °C up to 1750 °C) cannot be precisely extrapolated from these measurements and characterization under operating temperatures is necessary to provide a better understanding of the thermomechanical behaviour. Therefore, properties that have a high impact on in-service performance, for example modulus of elasticity, modulus of rupture, and thermal shock resistance, were comprehensively investigated at room temperature, 1250 °C, and 1400 °C for six different magnesia-chromite and magnesia brick grades. In this paper the different analytical methods employed are described and the results examined. Comparing the various brick properties tested nondestructively and destructively at room temperature and different application temperatures enables the most appropriate lining concept for specific applications to be selected.

Introduction

RHI offers a vast range of high-fired direct-bonded magnesia-chromite (MCr) and magnesia (M) bricks for the nonferrous metal industry. The function and final properties of these basic bricks are significantly influenced by both the raw material content and manufacturing technology. For example, the principal raw materials (i.e., magnesia and chrome ore) are processed in different ways and this affects characteristics such as the corrosion resistance, thermal shock resistance, and price-performance ratio of the final product.

In the case of prereacted fused grain MCr bricks, calcined MgO and chrome ore are fused in an electric arc furnace. The subsequent slow cooling generates a relatively large crystal size and because the atmosphere is oxygen-free any iron present is predominantly in the bivalent form. For prereacted co-clinker MCr bricks, calcined MgO and chrome ore are heated in a shaft kiln up to 2000 °C. The resulting OXICROM is one of RHI's unique raw material developments produced at the Trieben plant (Austria). Since the material cools in an oxygen-containing atmosphere any iron present principally forms Fe^{3+}. Direct-bonded MCr bricks are manufactured from sintered MgO and chrome ore, and magnesia bricks are produced from sintered and/or fused magnesia. The typical microstructures of these different brick types are shown in Figure 1.

To compare the properties of different magnesia-chromite and magnesia bricks at room temperature and service conditions, six basic brands were selected from the broad RHI product range (Table I). The test bricks were based on magnesia and chrome ore raw materials. The brick brands were classified in accordance with ISO 10081-2. In addition, a further categorization was performed based on the raw material composition.

Testing Methods

Prior to the destructive testing methods, ultrasonic and resonance frequency measurements were performed. Measuring the ultrasonic velocity is a well-established nondestructive testing method that can be used to determine material properties [1] at both room temperature and elevated temperatures. Direct transmission was used to measure the ultrasonic transit time and enabled the ultrasonic velocity, v, and Young's modulus, E, to be calculated in accordance with ASTM C1419 – 99a.

The resonant frequency is determined by the impulse excitation of vibration measurement technique [2] and was performed in accordance with ASTM C1259 – 08 at room temperature. The Young's modulus can also be calculated using this nondestructive technique and the values obtained are comparable to the Young's modulus determined by the ultrasonic method [3].

The three different destructive methods subsequently carried out were the wedge splitting test, modulus of rupture, and a thermal shock resistance test.

Raw material characteristics	Type
Prereacted fused grain	MCr 40FG
	MCr 50FG
	MCr 60FG
Prereacted co-clinker grain	MCr 50OX
Direct-bonded	MCr 50DB
Magnesia	M 95

__Table I.__ Magnesia-chromite and magnesia brick types examined using different testing methods. Abbreviations include magnesia (M), chrome ore (Cr), fused grain (FG), OXICROM co-clinker grain (OX), and direct-bonded (DB).

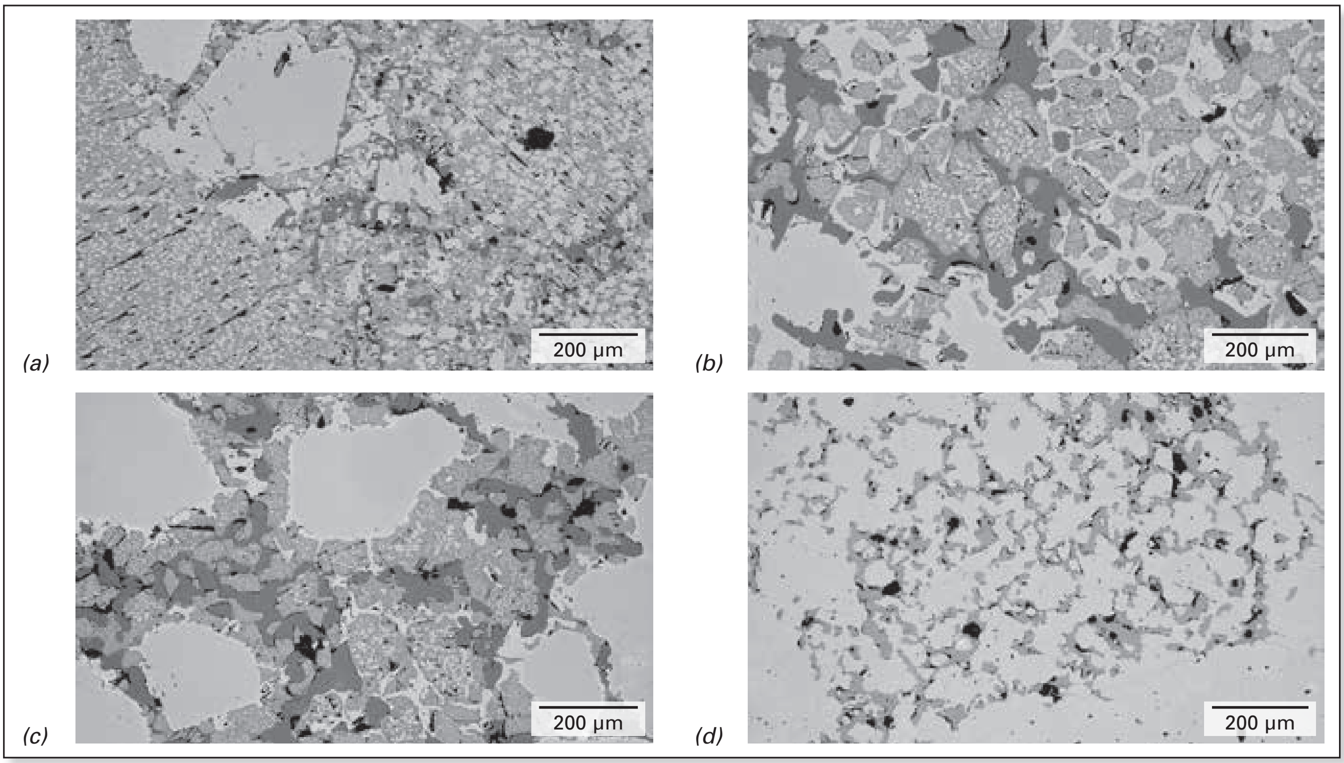


Figure 1. *Microstructures of the different magnesia-chromite and magnesia brick types comprising (a) prereacted fused grain magnesia-chromite and chrome ore, (b) prereacted co-clinker magnesia-chromite (OXICROM) and chrome ore, (c) direct-bonded magnesia-chromite and chrome ore, and (d) pure magnesia.*

The wedge splitting test according to Tschegg [4] can be conducted from room temperature up to 1500 °C, in a controlled atmosphere (Figure 2). The load displacement graph in Figure 3 illustrates the typical fracture behaviour of refractory materials determined using this method [5]. The results can be used to calculate various mechanical fracture properties including the specific fracture energy, G_F, the nominal notch tensile strength, σ_{NTS}, the characteristic length, l_{ch}, and the critical energy release rate at crack initiation, G_c. Where:

$$l_{ch} = \frac{G_F \cdot E}{\sigma_{NTS}^{\ 2}} \qquad (1)$$

A lower l_{ch} describes a more brittle material behaviour [6].

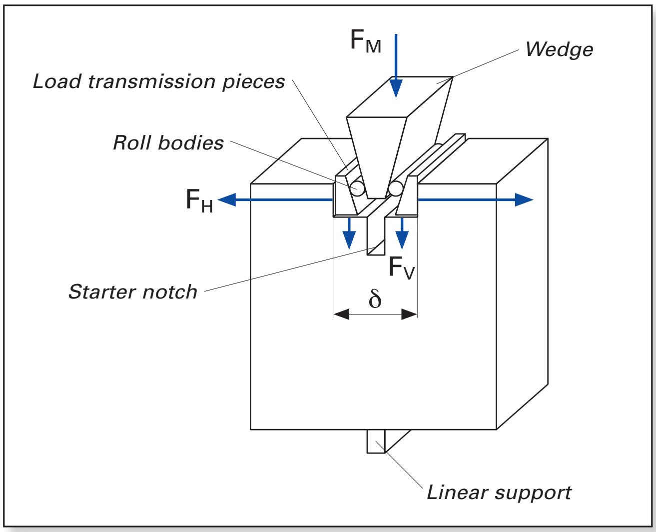


Figure 2. *Principle of the wedge splitting test according to Tschegg under uniaxial loading [5].*

G_c shows an inverse trend to l_{ch} [7] (Figure 4) and:

$$G_c \propto \frac{\sigma_{NTS}^{\ 2}}{E} \qquad (2)$$

The thermal shock parameter R'''', proposed by Hasselman [8] to compare the thermal shock damage resistance of various materials, is analogous to l_{ch} [5]:

$$R'''' = \frac{\gamma \cdot E}{\sigma_f^{\ 2}} \qquad (3)$$

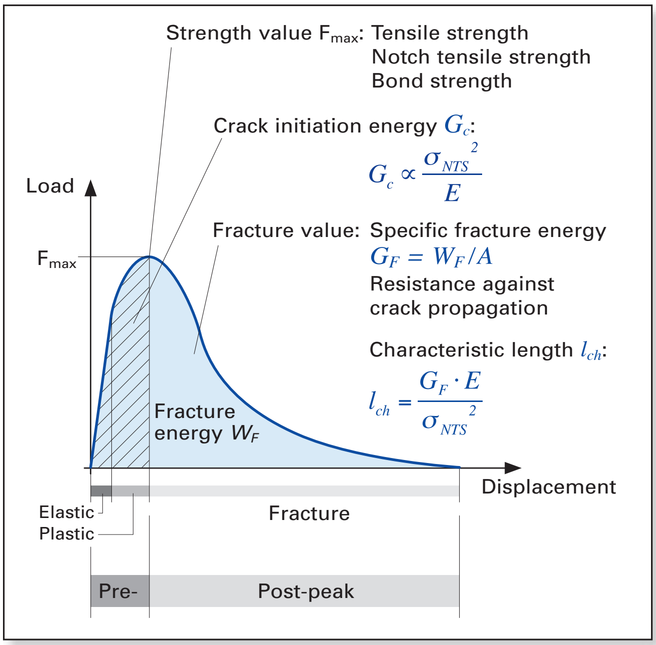


Figure 3. *Typical load-displacement graph of a refractory material generated using the wedge splitting test according to Tschegg [5].*

Where γ is the specific fracture surface energy and σ_f is the strength. R'''' is directly proportional to the ratio of the specific fracture energy, G_F, to the critical energy release rate at crack initiation, G_c [6].

$$R'''' \propto \frac{G_F}{G_c} \tag{4}$$

The modulus of rupture (MOR) is defined as the maximum stress a material can withstand before it breaks. It was tested at room temperature in accordance with DIN EN 993-6 and at 1250 °C and 1400 °C in accordance with DIN EN 993-7.

A direct thermal shock resistance investigation based on ENV 993-11 was also performed. It involved repeatedly heating the samples to 950 °C and quenching them in air. After 5 cycles the MOR was measured at room temperature and the relative decrease in flexural strength was calculated.

Results and Discussion

Nondestructive Testing

The nondestructive evaluation of Young's modulus, using both the ultrasonic and resonant frequency methods, showed clear differences between the various brick types at room temperature (Figure 5). Typically, materials with a higher brittleness are described by a higher Young's modulus. As expected, M type bricks, which are known for their brittle behaviour, showed a significantly higher Young's modulus than all the MCr type bricks. Among the magnesia-chomite bricks, the direct-bonded type had the lowest Young's modulus values and only minor variations were observed between the two prereacted brick types.

Mechanical Fracture Characterization

The relationship between σ_{NTS}^2/E and l_{ch} values calculated from the wedge splitting tests and ultrasonic determination of Young's modulus performed at room temperature, 1250 °C, and 1400 °C is shown in Figure 6. The data for all the tested brands at the various temperatures correlated well with the graph in Figure 4. The materials tested at room temperature (black ellipse) had a range of σ_{NTS}^2/E levels and the lowest l_{ch} values. The measurements performed at 1250 °C (grey ellipse) showed a trend towards slightly decreased σ_{NTS}^2/E levels and increased l_{ch} values compared to the results at room temperature. At 1400 °C (light grey ellipse) the l_{ch} values were higher for all the brick types, and all the σ_{NTS}^2/E levels were lower, describing a high resistance to crack propagation but a reduced crack initiation energy. This analysis of the temperature influence on mechanical fracture properties indicates a decrease in brittleness for all the materials with increasing temperature, typically a result of the first ductile phases forming.

The relationship between σ_{NTS}^2/E and l_{ch} for the three different MCr 50 brick types was examined in more detail (Figure 7). As already shown in Figure 5, the prereacted MCr types are characterized by a higher Young's modulus, and therefore a more brittle behaviour at room temperature, than the direct-bonded type. Analysis of the fracture mechanical parameters showed that the prereacted brand based on co-clinker displayed a higher σ_{NTS}^2/E, and therefore a more brittle behaviour than the prereacted brand based on fused grain, and both exhibited a decrease in σ_{NTS}^2/E with increased temperature. The direct-bonded material showed an increase of σ_{NTS}^2/E up to 1250 °C and then a decrease at 1400 °C. This apparent strength increase is due to the higher reactivity of the raw materials. All three MCr 50 brick types showed an increase in l_{ch} with temperature.

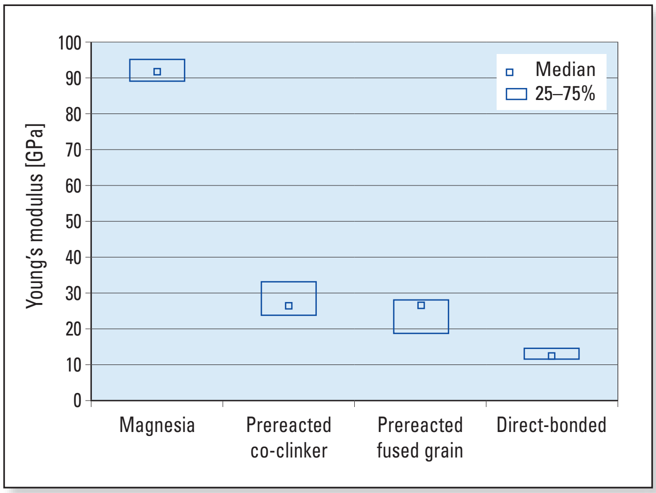


Figure 5. *Box plot of the Young's modulus results determined nondestructively using the ultrasonic and resonant frequency test methods at room temperature.*

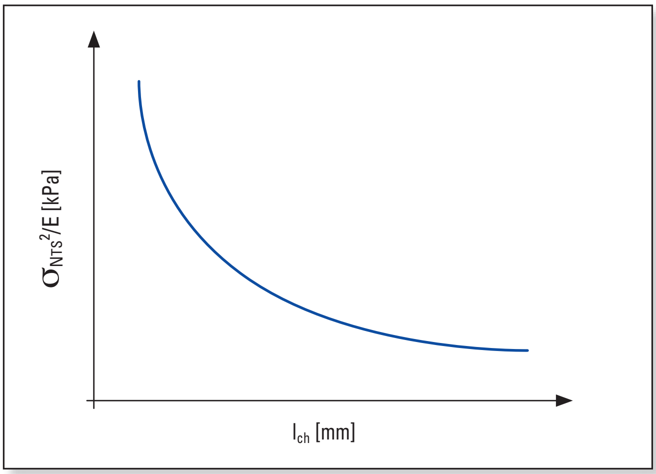


Figure 4. *Inverse trend between σ_{NTS}^2/E and the characteristic length, l_{ch}. A lower l_{ch} indicates a more brittle behaviour.*

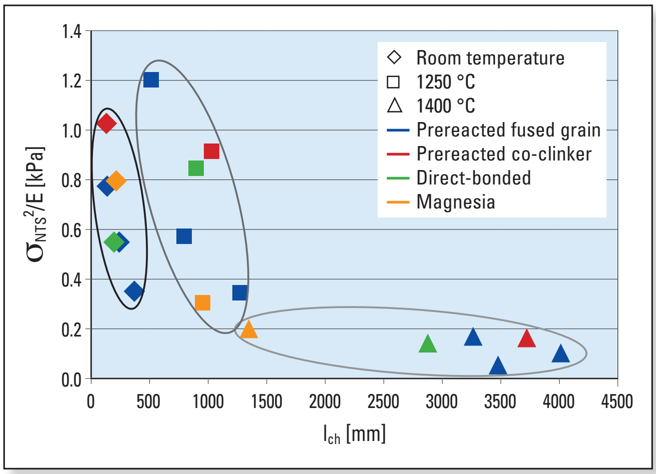


Figure 6. *Relationship between σ_{NTS}^2/E and the characteristic length, l_{ch}, for all the brick types examined at room temperature, 1250 °C, and 1400 °C.*

Thermomechanical Properties

The relationship between the l_{ch} values, derived from the wedge splitting test and ultrasonic determination of Young's modulus, and the MOR is shown in Figure 8. The MCr 50 type bricks showed the lowest MOR values of all the brick types at room temperature (black ellipse) and low l_{ch} values, indicating the most brittle material behaviour. An increase in both the l_{ch} and MOR was observed for all the MCr 50 types at 1250 °C (Figure 9). At 1400 °C the l_{ch} of all the MCr 50 brands increased approximately three times or more compared to the values at 1250 °C but only the MOR value for the co-clinker increased; the other two MCr 50 brick types showed a decrease in MOR at 1400 °C. All the bricks based on prereacted fused grain raw materials had high l_{ch} values of between 3000–4000 mm at 1400 °C. This increase in l_{ch} represents a more ductile behaviour.

Thermal Shock Behaviour

Results of the thermal shock investigations are shown in Figure 10. R'''', calculated from the wedge splitting test results, was compared to the relative decrease in MOR (ΔMOR) after thermal shock testing.

A low R'''' value and a high ΔMOR describe a less thermal shock resistant material. According to the R'''' value, the different brands can be subdivided into three groups. The thermal shock sensitive group is based on magnesia. This brand also showed very brittle material properties in the other analyses. The second group comprises the prereacted brands, which demonstrated a slightly higher resistance against thermal shock stress than the magnesia brand. The highest thermal shock resistance was observed for the direct-bonded brand. This characteristic was also evident from the other test results, for example the low Young's modulus determined by nondestructive methods (see Figure 5).

The group comprising the prereacted brands showed considerable variation in the ΔMOR values, with MCr 50OX having the lowest ΔMOR value and good thermal shock resistance. These results correlate with the analysis of l_{ch} versus MOR (see Figure 8), since this brand had the highest strength at 1400 °C and a more ductile behaviour shown by the high l_{ch}.

Conclusion

The results of various nondestructive and destructive testing methods performed at room temperature, 1250 °C, and 1400 °C have provided a more detailed description of magnesia-chromite and magnesia brick behaviours at

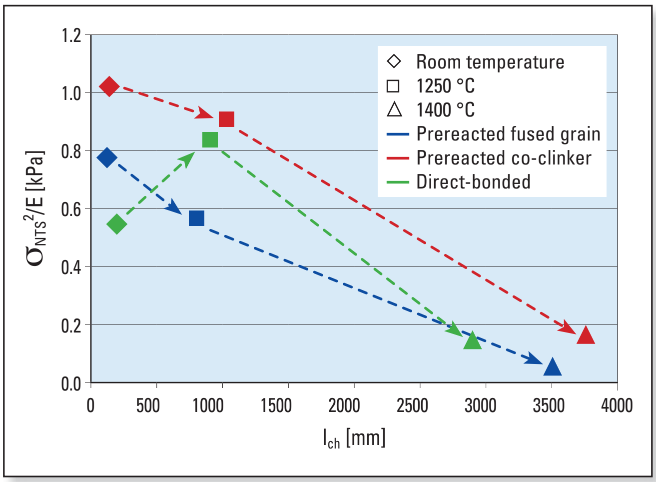


__Figure 7.__ Comparison of the relationship between σ_{NTS}^2/E and the characteristic length, l_{ch}, for the MCr 50 types examined at room temperature, 1250 °C, and 1400 °C.

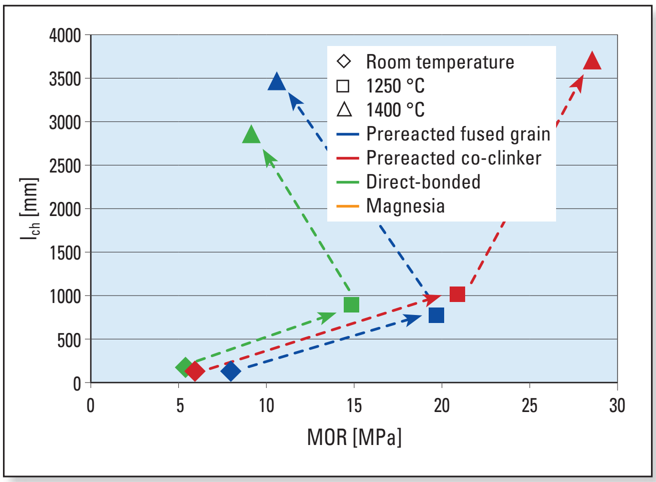


__Figure 9.__ Comparison of the relationship between the characteristic length, l_{ch}, and MOR for the MCr 50 types examined at room temperature, 1250 °C, and 1400 °C.

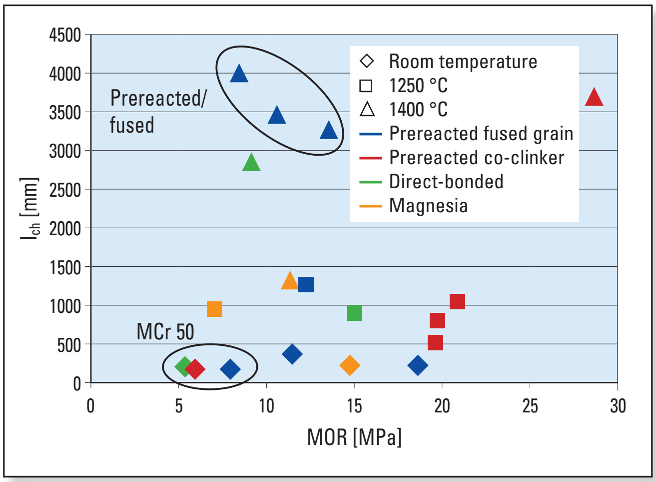


__Figure 8.__ Relationship between the characteristic length, l_{ch}, and MOR for all the brick types examined at room temperature, 1250 °C, and 1400 °C.

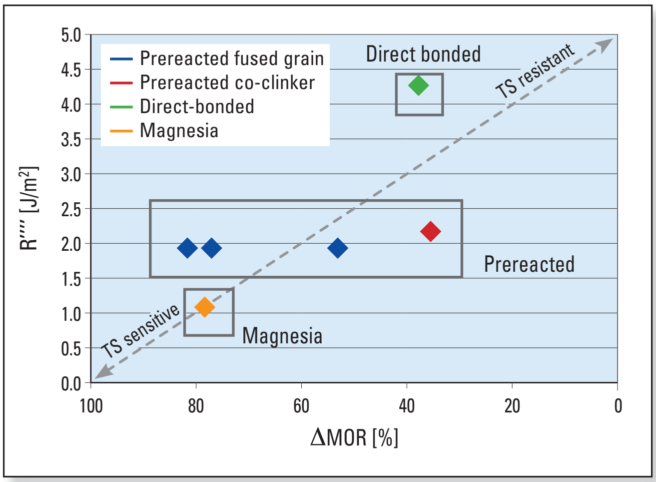


__Figure 10.__ Relationship between the thermal shock resistance parameter R'''' and the ΔMOR, an indicator of thermal shock damage.

application temperatures. This type of analysis enables the most appropriate brands to be selected for the different application fields in nonferrous pyrometallurgical furnaces. For example, the results indicate that prereacted brands are a good choice for areas subject to high corrosion and stress in copper producing vessels as a result of slag contact, while the direct-bonded type is appropriate for gas-contact zones like the freeboard and tuyere areas. The brands based on prereacted co-clinker grain are suitable for bottom working linings whereas magnesia brands show good results for highly stressed areas. With this detailed knowledge, RHI is able to provide tailored lining solutions for the nonferrous metal industry.

References

[1] Manhart, C., Schickert, M. and Urbanek, G. Ultrasonic Imaging of Refractories Using Different Coupling Techniques. *RHI Bulletin*. 2013, No. 1, 67–73.

[2] Manhart, C. and Harmuth, H. Resonant Frequency and Damping Analysis of Refractories With and Without Reduced Brittleness. Presented at UNITECR '09, Salvador, Brazil, Oct., 13–16, 2009.

[3] Manhart, C., Urbanek, G. and Stieblaichinger, M. Investigation and Verification of the Ultrasonic- and Resonant-Frequency-Measurement Method for Burned Refractory Products With Original Geometry and a Application Example. Presented at 56th International Colloquium on Refractories, Aachen, Germany, Sept., 25–26, 2013.

[4] Tschegg, E.K. Prüfeinrichtung zur Ermittlung von bruchmechanischen Kennwerten sowie hiefür geeignete Prüfkörper, Austrian Patent 390 328, 1986.

[5] Tschegg, E., Fendt, K., Manhart, C. and Harmuth, H. Fracture Properties of Refractory Materials Under Uniaxial and Biaxial Loading. *RHI Bulletin*. 2010*, No. 1, 40–47.*

[6] Harmuth, H. and Tschegg, E.K. A Fracture Mechanics Approach for the Development of Refractory Materials With Reduced Brittleness. *Fatigue and Fracture of Eng. Materials and Structures*. 1997, 20, No. 11, 1585–1603.

[7] Harmuth, H. and Bradt, R.C. Investigation of Refractory Brittleness by Fracture Mechanical and Fractographic Methods. *Refractories Manual*. 2010, 6–10.

[8] Hasselman, D.P.H. Unified Theory of Thermal Shock Fracture Initiation and Crack Propagation in Brittle Ceramics. *J. Am. Ceram. Soc.* 1969, 52, No. 11, 600–604.

Reprinted with permission from ACerS and the UNITECR Proceedings. http://www.wiley.com/WileyCDA/WileyTitle/productCd-1118837037.html

Authors

Angelika Ofner-Ressler, RHI AG, Technology Center, Leoben, Austria.
Christian Manhart, RHI AG, Technology Center, Leoben, Austria.
Rainer Neuboeck, RHI AG, Technology Center, Leoben, Austria.
Corresponding author: Angelika Ofner-Ressler, angelika.ofner-ressler@rhi-ag.com

RHI Bulletin

The Journal of Refractory Innovations

To facilitate efficient distribution of the RHI Bulletin, we would be grateful if all recipients could check their delivery details are correct and select the preferred format. Please use the form below to fax any amendments or e-mail the required alterations. In addition, if you would like to register and receive the RHI Bulletin on a biannual basis, please complete the form below and return it to us by fax or e-mail.

New registrant	☐	Yes	☐	No		
Preferred format	☐	Print	☐	E-mail	☐	Print & e-mail

Title	
First name	
Surname	
Company	
Department	
Street / no.	
Postbox	
City (town)	
Area code	
Country	
Phone	
Fax	
E-mail	

Phone: +43 50213-5323, Fax: +43 50213-5237, E-mail: ulla.kuttner@rhi-ag.com

RHI Bulletin >2>2014
The Journal of Refractory Innovations