Development and Deployment of Shotcrete Refractories for Aluminium Rotary Furnace Application

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Work was performed by *Oak Ridge National Laboratory (ORNL)* in the United States, in collaboration with the industrial refractory manufacturer *Minteq International, Inc. (MINTEQ)*, academic research partner *Missouri University of Science and Technology (MS&T)* and end users to employ novel refractory systems and techniques to reduce energy consumption of refractory lined vessels found in the aluminum industry. The project aim was to address factors that limit the applicability of currently available refractory materials such as chemical attack, mechanical degradation, use temperature, and installation or repair issues. To this end, as part of the overall project, shotcretable refractory compositions were developed based on alumino-silicate based structures utilizing new aggregate materials, bond systems, protective coatings, and phase formation techniques for use in rotary dross furnaces. Additionally a shotcretable high strength insulating back-up lining material was also developed for use in this and other applications. Development efforts, materials validation, and results from industrial validation trials are discussed.

1 Introduction

The primary vessel for reprocessing of aluminum dross and scrap is the rotary furnace. Refractory ceramic lining materials for these units are called upon to not only serve as insulation to retain the process heat introduced to melt the aluminum dross and scrap, but also undergo extreme mechanical abuse. As such, typical rotary furnace refractory linings are subject to heat loss due to degradation and may require replacement in as little time as three to six months resulting in production outages, process down time and expense from lining replacement and lost product during shut down. Additionally, deterioration of refractory materials leads to decreased thermal efficiency of the aluminum processing unit. Also, large amounts of energy are lost during cooling of the furnace and are then required for reheating of the furnace.

The factors that can affect the performance of refractory materials include chemical reactions between the service environment and the refractory material leading to depletion of the material or formation of other compounds on the refractory surface, mechanical degradation (wear and erosion) of the refractory material, penetration of molten material into cracks or pores present or created in the refractory material during use, and limitations on temperature at which a material can be safely used as extensively discussed previously [1]. All of these attack mechanisms will lead to drastic reductions in the furnace's energy efficiency and can ultimately lead to complete failure of the refractory lining as has also been previously described [2, 3].

To address the need for improved refractory compositions and fabrication techniques for multiple applications, a project was initiated at *Oak Ridge National Laboratory* (*ORNL*)[1] to develop a family of unshaped refractory materials (castables, gunnables, shotcretes, etc.) based on combinations of magnesia and alumina. Such compositions were designed around the use of new aggregate materials, bond systems, protective coatings, and phase formation techniques (in-situ phase formation, altered conversion temperatures, accelerated reactions, etc.) and were specifically tailored for use in high-temperature, high-alkaline industrial environments like those found in the aluminum, chemical, forest products, glass, and steel industries. The project development team

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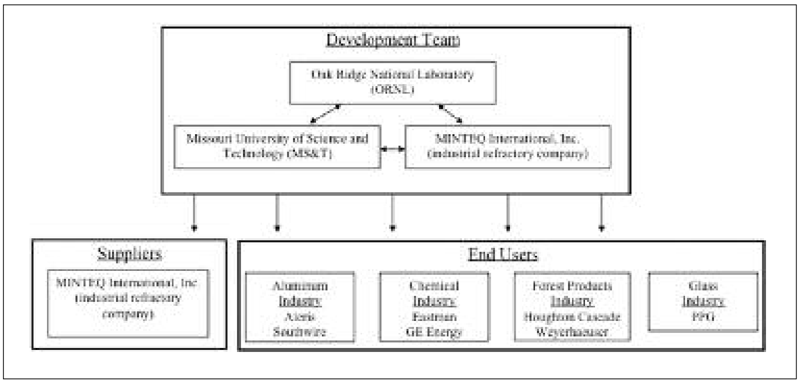

Fig. 1 **Organizational plan of project showing coordination and management**

(Fig. 1) was composed of ORNL, industrial research partner *Minteq International (MINTEQ, Easton, PA)* and academic research partner *Missouri University of Science and Technology (MS&T, Rolla, MO).* MINTEQ also served as the industrial refractory supplier for the project and initial industrial end user participation was provided by *Aleris International, Inc.* (aluminum), *Eastman Chemical* (chemical), *PPG Industries, Inc.* (glass), and *Weyerhaeuser, Inc.* (forest products). As the project continued additional industrial partners *Alcoa* (aluminium), *Al-Rec* (aluminium), *Electric Power Research Institute-EPRI* (coal gasification), *GE Energy* (coal gasification), *Houghton Cascade Holdings, LLC* (forest products), *Newco Metals* (aluminium), *Southwire Company* (aluminium), and *Tate and Lyle* (food processing) participated in various portions of the project.

2 Development of materials

Design of materials specifically for aluminium applications focused on identification of materials capable of operating for longer periods of time (through reduced wear and corrosion), identification of better insulating materials, and identification of alternative refractory application techniques for these materials that could lead to less expensive or faster installation of refractory linings. This strategy was based on analysis of salvaged refractory brick received from industrial partner Aleris Aluminum. These samples consisted of high alumina brick taken from rotary furnaces and samples of round melter brick taken from a reverberatory furnace. Core samples from these bricks were analyzed by various characterization techniques to identify chemical and mechanical failure mechanisms, which led to the degradation of these refractories. Macroscopic anomalies were characterized by optical microscopy and phase analysis of samples was conducted with X-ray diffraction (XRD). Chemical analysis was completed through scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

Core samples from varying brick depths and locations were studied to determine the impact of the metal/refractory interaction with respect to possible failure mechanisms. XRD analysis was performed on metal contact samples and compared to scans of core samples from deeper in the brick to verify phase changes as a result of elevated temperature and molten metal exposure. Extensive mechanical and corrosive damage were found for samples in contact with molten metal, resulting in grain structure and phase changes within these regions. In metal line regions, aluminum metal entering the bricks through porosity led to thermal shock and differing thermal expansions. Weakened aggregate in the material also appeared to have caused fractures throughout the samples leading to reduced mechanical properties. Finally, it was found that the chemistry and phase composition of the samples remained constant beyond the limited surface reaction zones above the metal line. As contact with the melt increased, microstructural and macroscopic changes occured to deeper core depths, increasing material failure from cracking.

SEM-EDS analysis was conducted on regions of interest based on the optical microscopy findings. It was confirmed through this analysis that significant mechanical and corrosive damage occured for samples in direct contact with molten metal, resulting in grain structure and phase changes within these regions as seen in the optical analysis. Additionally, it was found that formation of salts from reactions with alkali-based fluxes weakened aggregate in the material leading to fractures throughout the samples and reduced mechanical properties. Finally, it was found that although the chemistry and phase composition of the samples remain constant beyond the limited surface reaction zones above the metal line, at or below the metal line considerable microstructural and macroscopic changes are evident through the core depth.

Based on these findings, several alumino-silicate, magnesia and spinel forming castable refractory systems were developed for the targeted project applications. These materials were designed to either possess favorable phases (aluminosilicates or magnesia) when installed or to form favorable phases (spinel) during heating and drying as the furnace or process vessel was brought up to operating temperature. It should be noted that in several cases, as was the case for aluminium applications, spinel-based materials were not the best choice for the targeted applications, therefore aluminosilicate or magnesia-based systems were selected instead. Additionally, a lightweight back-up refractory system was developed which possessed high strength and a low thermal conductivity to help offset the high thermal conductivity inherent in the spinel materials and for use in increasing the thermal efficiency and mechanical performance of existing furnace configurations. Three materials were developed for aluminium

Tab. 1 **Materials developed for aluminium applications**

Application	Material	Use
Aluminum	alumino-silicate material (A) alumino-silicate material (B) spinel forming system*	primary lining repair material Repair Material
Insulation	light weight castable	back-up lining

A and B in parenthesis designate sequential compostional designations
* alumina-rich spinel

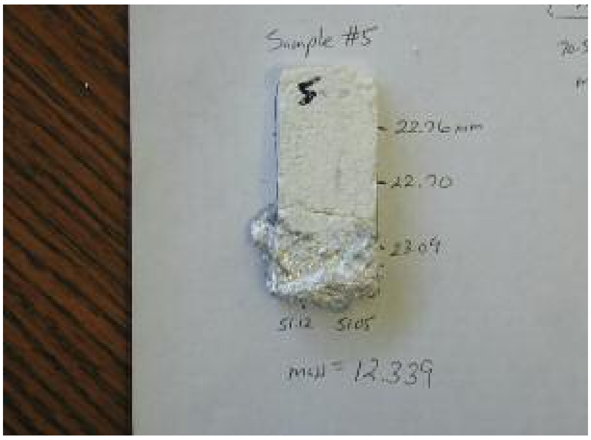

Fig. 2 Static immersion test sample of initially developed aluminum refractory

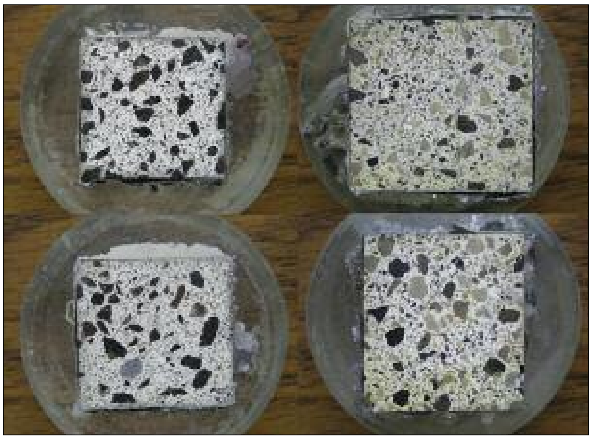

Fig. 3 Sectioned immersion test samples of developed refractories for aluminum

furnace applications and one lightweight composition was developed as shown in Tab. 1.

The first two materials were 70 % alumina aluminosilicate primary lining and high-temperature repair materials designed for shotcreting based on previous formulations produced by MINTEQ. The anti-wetting additives and matrix in these refractories were redesigned to provide superior corrosion resistance and improved hot modulus of rupture (HMOR) at higher temperatures. The third developed material was an alumina-rich spinel repair material designed with improved corrosion and erosion resistances. This material was not further pursued due to its substantially higher cost compared to the developed aluminosilicate material (which performed equally as well).

Shotcreting was selected as the fabrication method for the developed materials as opposed to traditional brick linings that are often used in many refractory applications. This method of applying refractory materials involves first mixing the refractory components with water and then adding an accelerator to the air supply of the nozzle system. Advantages of the method include rapid application, and elimination of joints and geometric constraints. To aid in the refractory development, work was undertaken at MS&T to further the fundamental understanding of the spinel microstructure and formation along with their effects on properties such as thermal diffusivity. Results of this work are discussed elsewhere [4–6]. Work was also focused on identifying appropriate additives to enhance the reaction kinetics for spinel formation.

3 Laboratory evaluation of developed materials

Initially developed materials were evaluated through static aluminum immersion testing as shown in Fig. 2. This testing consisted of submerging half of a rectangular refractory sample in a crucible of molten aluminum (alloy 7075 – Mg-rich aluminum alloy) and soaking the refractory in a static condition for 50–100 h. Upon completion of the soak, the refractory sample was sectioned and the cross section was analyzed for corrosion. Developed high alumina refractory materials were found to perform in a favorable fashion as shown in Fig. 3 and evident by the retention of sharp sample edges and corners and the apparent non-wetting of the refractory surface indicated by the peeling of the aluminum metal from the sample surface.

Additional corrosion testing of candidate refractory materials was conducted using a modified version of the *Alcoa* standardized cup test method which incorporates saturated steam and is believed to be a more extreme test. This test exposed deficiencies in these materials not previously seen in previous testing and led to down selection of candidate refractory compositions for aluminum applications. Pictures of exposed samples after sectioning are shown in Fig. 4.

As a final validation of materials developed for aluminum applications, both cast and shot versions of the developed materials were subjected to the same Alcoa standardized cup testing. Samples were evaluated after prefiring at 871 and 1260 °C (1600 and 2300 °F) through testing at 815 °C (1500 °F) for 72 h in alloy 7075 aluminum. Such testing is qualitative and usually results in either a pass/fail or a ranking (excellent, satisfactory, poor) evaluation. The samples shown below in Fig. 5 were rated as possessing "excellent" corrosion resistance due to the fact that their original cored geometry was maintained (sharp corners still present and no metal penetration found). It was also determined that firing temperature did not appear to affect the corrosion behaviour, nor was there a difference seen between cast and shot samples (often a problem when quoting properties of a shot material based on cast sample testing).

Additionally, an evaluation was carried out for the developed aluminosilicate repair material by assessing its adhesion on a simulated refractory wall consisting of degraded refractory material (aluminosilicate castable) and solidified aluminum as shown in Fig. 6. This test consisted of subjecting a

Fig. 4 Refractory samples following Alcoa standardized cup testing

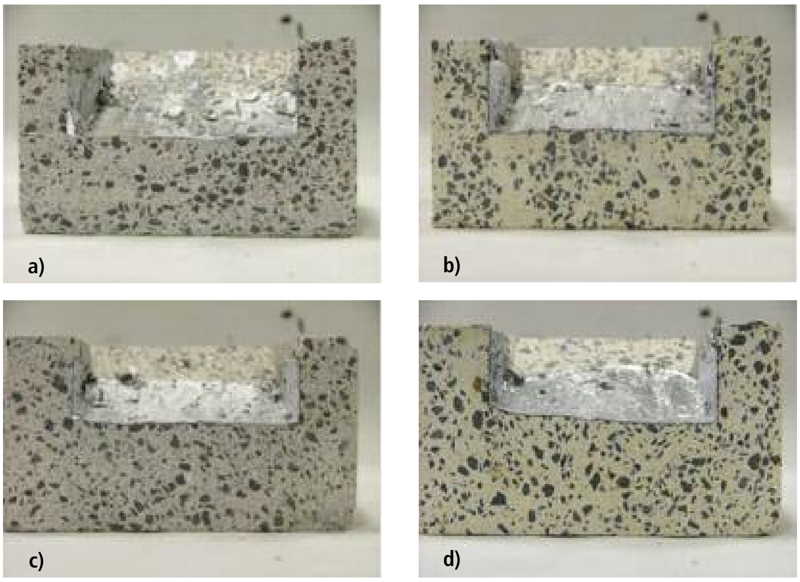

Fig. 5 **Aluminum cup penetration testing performed in 7075 aluminum alloy: a) shot sample pre-fired at 871 °C, b) shot sample pre-fired at 1260 °C, c) cast sample pre-fired at 871 °C, d) cast sample pre-fired at 1260 °C**

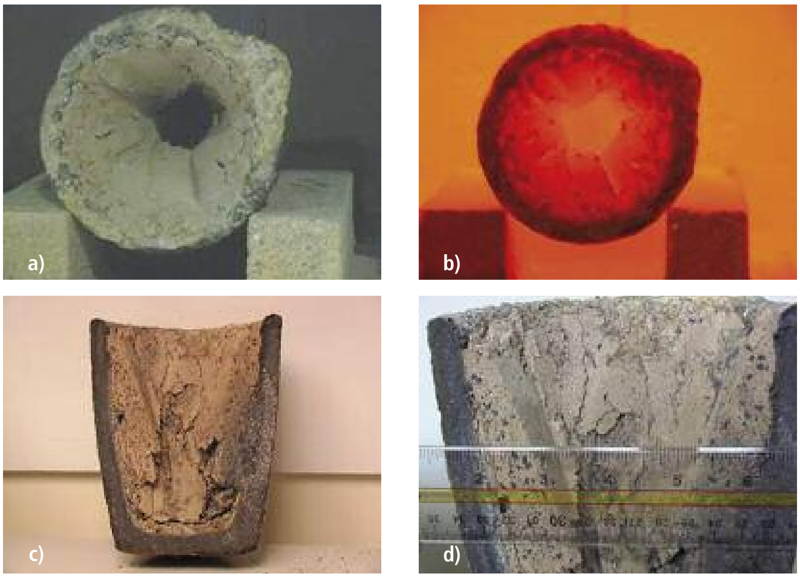

Fig. 6 **A crucible containing solidified aluminum/dross/flux: a) was heated and veneered with repair material, b) before being cooled and sectioned, c) evaluation of the coating after cooling showed good adhesion of repair material to the degraded crucible wall d)**

Fig. 7 **Rotary furnace simulation test system built at MINTEQ**

spent crucible containing aluminum metal, dross, and flux at 538 °C (1000 °F) in a laboratory furnace followed by application of a veneer of the developed maintenance material to the hot surface of the crucible. The temperature of the furnace was then raised to 927 °C (1700 °F) and held for 4 h after which the crucible was cooled and sectioned to evaluate the adhesion of the repair material on the crucible wall. Testing determined that the repair material could be successfully used to perform a hot repair of degraded refractory surfaces with adequate adhesion to a refractory wall covered with dross and flux.

4 Intermediate and industrial scale trails

As an intermediate scaled test between laboratory and full industrial scale testing, a rotary furnace simulation test system (Fig. 7) was built and operated by MINTEQ for evaluation of material performance in an aluminum environment. The furnace was lined with brick or cast test samples of both currently used and new materials developed under this project for a side by side comparison of material performance. Following testing the lining materials were removed and analyzed for relative performance. As an example, pictures of a sample lining before and after testing in contact with molten aluminum metal are shown in Fig. 8.

Developed refractories were also installed in actual commercial furnaces operated by project industrial partners. Industrial trials were monitored through the end of the project, with trials being continued by the respective industrial partner after the completion of the project as long as materials remained viable or until the associated processes where the materials were being tested was brought down for normal maintenance outages. In total, over one hundred and sixty tons of refractory for use in aluminum furnaces and sixty tons of the lightweight back-up refractory material were installed in commercial furnaces to validate the materials developed under this project and in all cases the materials exceeded the customer's expectations. Details of selected individual trials are given below.

The first full scale industrial trials consisted of two 14 t rotary furnace installations. The customer noted the easy/rapid installation of the installed product and was impressed by the durability of the product, which exceeded their expectation of a life time on the order of 6 months which was typical for previous linings in these furnaces. These trials were monitored in excess of 15 months and were still installed at the completion of the project, far exceeding material life time expectations.

A second industrial trial consisted of the installation of 70 t of material. This installation was monitored through thermal imaging for the remainder of the project and had been

Mark your calendars!

St. Louis Section/RCD 49th Annual Symposium: March 27-28, 2013

The St. Louis Section and the Refractory Ceramics Division of The American Ceramic Society will sponsor the 49th Annual Symposium on the theme "Refractory Challenges in the Chemical and Petro-Chemical Industries" on March 27-28, 2013 and the kickoff event to be held the evening of March 26,

The **Tabletop Expo** format is the same as previous years, with each vendor having a 6-foot table to display products and literature. The charge is $300, which will be used to cover the cost of the Expo Hall and provide an open two hour bar during the "Meet and Greet" for the attendees prior to dinner on Wednesday evening. If you are interested in participating in the Tabletop Expo, contact Patty Smith at (573) 341-6265 or psmith@mst.edu.

Please note that a meeting of the **ASTM International C-8 Committee on Refractories** will be held on March 26th, before this joint St. Louis Section/RCD conference. Contact Kate McClung at (610) 832-9717 for more information on this meeting.

A block of rooms has been set aside for the evenings of March 25-28, 2013 at the Hilton (314) 426-5500. The rate is $104.00 for a single or double. To receive the $104 rate mention the Group Name: St. Louis Section of The American Ceramic Society or Group Code: CER when making your reservation. The web address to make online reservations is: http://www.hilton.com/en/hi/groups/personalized/S/STLHIHF-CER-20130325/index.jhtml. All reservations must be received on or before **February 18, 2013.**

For further information please contact Patty Smith at tel: (573) 341-6265, Fax: (573) 341-2071 or email: psmith@mst.edu.

Fig. 8 Rotary furnace simulation test system lining (a) before and (b) after testing

operating successfully for over seven months when the project was completed, far exceeding the customer's expectations of 3–5 months. This lining was still installed at the completion of the project and based on current performance was scheduled to be run twelve to 18 months before being evaluated for repair or replacement.

A third rotary dross furnace refractory installation was performed using 46 t of primary lining material and 5 t of insulating back-up lining material developed under this project. At the completion of the project, this material had successfully performed for over three months meeting the customer's expectations. This lining was still installed at the completion of the project.

Additionally, 18 t of primary lining material was installed at two additional industrial aluminum producer sites and 52 t of insulating back-up material was installed by MINTEQ in other industrial aluminum producer sites.

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