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IMPROVED FURNACE EFFICIENCY THROUGH THE USE OF REFRACTORY MATERIALS

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Abstract

This paper describes efforts performed at Oak Ridge National Laboratory (ORNL), in collaboration with industrial refractory manufacturers, refractory users, and academic institutions, to improve energy efficiency of U.S. industry through increased furnace efficiency brought about by the employment of novel refractory systems and techniques. Work in furnace applications related to aluminum, gasification, and lime are discussed. The energy savings strategies discussed are achieved through reduction of chemical reactions, elimination of mechanical degradation caused by the service environment, reduction of temperature limitations of materials, and elimination of costly installation and repair needs. Key results of several case studies resulting from a US Department of Energy (DOE) funded research program are discussed with emphasis on applicability of these results to high temperature furnace applications.

Introduction

Refractory materials are called upon to function throughout industrial applications as insulation and/or containment vessel linings in high-temperature and corrosive environments. Therefore, they must possess properties suitable for exposure to extreme environments for extended periods of time. Indeed, it would be difficult to identify an industrial process that does not use refractory materials in one aspect or another. In a furnace application, these materials must not only be capable of performing these tasks at elevated temperatures, but may also be called upon to bear mechanical loads and transfer heat. As such, refractories are a vital class of materials for the sustaining of the world industrial economy related to the manufacturing of the products that we rely on in our modern world.

Many factors can affect the applicability and performance of refractory materials in a furnace environment. These can include chemical reactions (corrosion) between the service environment and the refractory material which may lead to depletion of the material or formation of other compounds on the refractory surface, mechanical degradation (wear and erosion) of the refractory material by the service environment, penetration of molten material into cracks or pores present, limitations on temperature at which a material can be safely used, and the ability or inability to install and/or repair a particular refractory material in a cost effective manner or while the vessel is in service (i.e. at temperature).

All of the above mechanisms of attack will lead to drastic reductions in the energy efficiency of the furnace and can ultimately lead to complete failure of the refractory lining as described in further detail elsewhere [1]. The decrease in energy efficiency is further compounded by associated environmental impacts and related reductions in the economic viability of the associated processes through such impediments as necessitated process shut downs, impurities created in the metal or glass being processed, need for the implementation of filtering or purification of the furnace bath, the need for additional melting, and greater heat losses through the furnace walls, floor and roof as the lining deteriorates or forms less insulating phases.

Therefore, there is a need to develop innovative refractory compositions to address these issues. The work described in this paper intended to develop improved refractory compositions based on novel compositions, new aggregate materials, alternative bond systems, protective coatings, novel phase formation techniques (in-situ phase formation, altered conversion temperatures, accelerated reactions, etc.), and alternative application techniques, (castables, gunnables, shotcretes, etc). The developed materials were tailored for use in specific industrial environments such as those found in the aluminum, cement, chemical, and forest products industries.

The intent of the work described in this paper was to improve energy efficiency in the targeted applications and industries through three approaches. The first was through the identification of materials capable of operating at higher temperatures (goal of increasing operating temperature by 100-200°C over current operating temperatures depending on the process). The second was through identification of materials capable of operating for longer periods of time (goal of twice the life span of current materials or next process determined service increment). The third was through alternative refractory application techniques that could lead to less expensive or faster installation of refractory linings. Such materials and techniques could lead to less process down time, greater energy efficiency through more heat kept in the process, and materials that could be installed/repaired in a more efficient manner. The overall goal of the project was a 5% improvement in energy efficiency (brought about through a 20% improvement in thermal efficiency) resulting in a savings of 3.7 TBtu/yr (7.2 billion ft^3 natural gas) by the year 2030 as predicted through an analysis performed using DOE Government Performance and Reporting Act (GPRA) analysis software.

Material Development

Five process vessels from the targeted industries were selected for improvement through implementation of newly developed refractory material systems. These were rotary and reverberatory aluminum furnaces (aluminum industry), black liquor gasifiers (forest products), coal gasifiers (chemical industry), and lime kilns (forest products with possible extension to cement). Additionally, refractory systems were developed for two specific purposes. Initial efforts focused on materials designed for new (original) lining installations. These compositions were formulated with the intention of being direct replacements for currently available castable and brick formulations traditionally used in these furnace applications. Subsequent efforts focused on refractories which were designed and specifically tailored for on-line (hot) maintenance or repair installations where the material could serve as a "patch" to extend the service life of a furnace between relines. A separate part of the project also focused on pursuing alternative application techniques and systems for the optimized installation of the newly developed refractory materials in an effort to maximize the properties of installed linings and to facilitate hot installation and repair.

Several alumino-silicate, magnesia and spinel forming castable refractory systems were developed as shown in Table I. These materials were designed to either possess favorable phases (alumino-silicates 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. Additionally, the specific spinel composition chosen (alumina-rich verses magnesia-rich) was selected based on the operating environment being acidic such as in aluminium furnaces and coal gasifiers (alumina-rich required) or basic such as in black liquor gasifiers and lime kilns (magnesia-rich needed) [2].

Table I. Materials Developed for Specific Industrial Furnace Applications

Industry	**Material**	**Application**
Aluminum	AS (A) AS (B) SF (A)*	Primary lining Repair material Repair material
Black Liquor	SF (B)[+] PBC	Primary lining Repair material
Coal Gasification	SF (C)*	Repair Material
Insulation	LWC	Back-up lining
Lime Kiln	SF (B)[+]	Primary lining

AS = alumino-silicate material
SF = spinel forming system
PBC = phosphate bonded magnesia castable
LWC = light weight castable
A, B, and C in parenthesis designate sequential compositional designations
*alumina-rich spinel
[+] magnesia-rich spinel

Although spinel-based materials were initially sought for all of these applications, it was found that in several cases they were not the best choice. Therefore alumino-silicate or magnesia-based systems were selected instead. Additionally, a light-weight back-up refractory system was developed for use with the spinel forming systems to help offset the high thermal conductivity inherent in the spinel materials, as compared to traditional alumina-based or alumino-silicate materials.

Shotcreting of monolithic refractory materials was selected as an alternative application method to traditional brick or castable linings that are often used for these applications. Thus, materials developed under this project were designed and tested for application by such a method. 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, elimination of joints, and elimination of geometric constraints.

Aluminum

Through physical, chemical, and mechanical characterization of salvaged refractory materials from the aluminum industry a number of sources of refractory failure were previously identified [1, 3]. In summary these are poorly performing anti-wetting additives, degradation of the aggregates used in refractory castables, reaction of micro-silica in the refractory matrix with cement binder systems, and poor furnace maintenance practices leading to mechanical damage of refractory linings. The effectiveness of anti-wetting additives and the choice of aggregate and dispersant systems were investigated in this work.

Three candidate materials were developed for aluminum applications (as shown in Table I). Two of these were alumino-silicate materials based on previous formulations produced by MinTeq, with one developed as a primary lining material and one developed with the intent of serving as a high-temperature repair material. Both materials are 70% alumina content pumpable formulas designed for shotcreting. The anti-wetting additive systems in these materials were redesigned to provide superior resistance to corrosion and the refractory matrix was modified to improve hot modulus of rupture (HMOR) at higher temperatures and to provide enhanced high temperature corrosion resistance. An alumina-rich spinel material which showed improved corrosion and erosion resistance was also developed for repair applications, but was not further pursued due to the substantially higher cost of this material compared to the developed alumino-silicate material which performed equally as well.

Examples of cup testing results from the alumino-silicate materials developed for aluminum contact applications are shown in Figure 1. Both cast and shotcrete versions of the material were evaluated after being pre-fired at 871 and 1260°C (1600 and 2300°F) through testing at 815°C (1500°F) for 72 hours in aluminum alloy 7075 aluminum (magnesium-rich aluminum alloy).

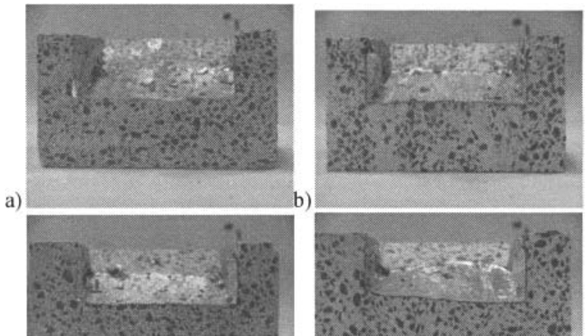

Figure 1. Refractory cup testing results for alumino-silicate materials develop for aluminum applications. Testing performed in 7075 aluminum alloy for (a) shotcrete sample pre-fired at 871°C, (b) shotcrete sample pre-fired at 1260°C, (c) cast sample pre-fired at 871°C, and (d) cast sample pre-fired at 1260°C.

Such testing is qualitative and usually results in either a pass/fail or a ranking (excellent, satisfactory, poor) evaluation. The samples shown above were all rated as possessing "excellent" corrosion resistance due to the fact that the original cored geometry was maintained (sharp corners still present and no metal penetration was found). It was also determined that firing temperature did not seem to affect the corrosion behavior, nor was there a difference seen between cast and shotcrete samples (often a problem when quoting properties of a shotcrete material based on cast sample testing).

To further evaluate the performance of these materials, before moving to a full industrial trial, a rotary furnace simulation was conducted at the MinTeq research facilities in Easton, PA. Pictures of the constructed unit are shown in Figure 2. The furnace was lined with shotcrete panels which were exposed to molten aluminum metal heated by a gas burner. Pictures of installed panels of the alumino-silicate formulation before and after testing are shown in Figure 3. Based on the successful performance of these materials in this test, full industrial trials are currently being initiated.

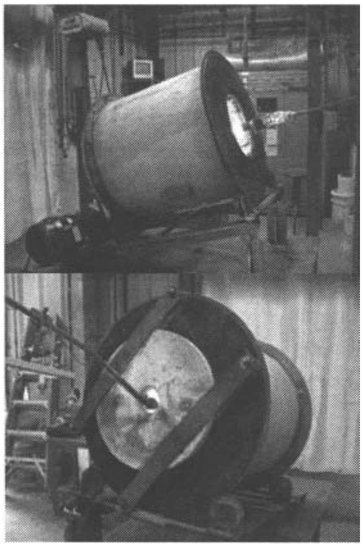

Figure 2. Rotary furnace simulation test system built at MinTeq in Easton, PA shown with gas burner assembly.

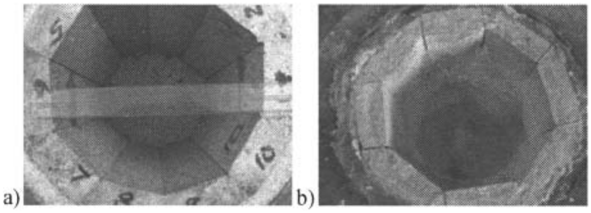

Figure 3. Installed refractory panels exposed to molten aluminum in rotary furnace simulation test (a) before and (b) after testing showing the relatively unchanged refractory surfaces after testing.

To further assess the performance of the repair material, a test was performed to evaluate the adhesion of this material on a candidate refractory wall consisting of degraded refractory material (alumino-silicate castable) and solidified aluminum. A spent crucible containing aluminum metal, dross, and flux was heated to 538°C (1000°F) in a laboratory furnace. Upon heating, the hot surface of the crucible bathed in the aluminum/dross/flux mixture was veneered with the developed maintenance material. The temperature of the furnace was then raised to 927°C (1700°F) and held for four hours. After the hold, the crucible was cooled and sectioned to evaluate the adhesion of the repair material on the crucible wall. Results of this test are shown in Figure 4.

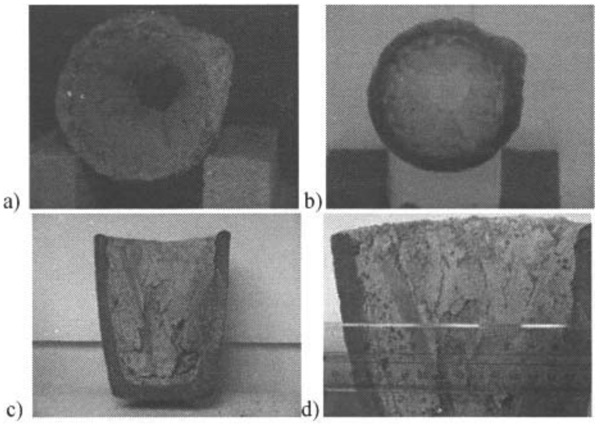

Figure 4. Evaluation of alumino-silicate repair material through high-temperature adhesion test. A crucible containing solidified aluminum/dross/flux (a) was heated and vennered with repair material (b) before being cooled and sectioned (c). Evaulation of the coating after cooling showed good adhesion of repair material to the degraded crucible wall.

Black Liquor Gasification

Black liquor gasification provides the pulp and paper industry with a technology which could potentially replace recovery boilers with equipment that could reduce emissions and, if used in a combined cycle system, increase the power production of the mill allowing it to be a net exporter of electrical power. In addition, rather than burning the syngas produced in a gasifier, this syngas could be used to produce higher value chemicals or fuels. However, problems with structural materials, and particularly the refractory lining of the reactor vessel, have caused unplanned shutdowns and resulted in component replacement much sooner than originally planned.

Previous work at ORNL resulted in the identification of fusion-cast spinel brick materials which extended the lifetime of the hot face refractory lining of these vessels from months to years [4, 5]. Although these lining materials were highly successful, a lower cost option is still sought. It was thought that a non-brick material may offer such an alternative if the corrosion and wear resistance of the brick material could be maintained. With this in mind, two magnesia-containing materials were developed as shown in Table I. The first material was a magnesium-rich spinel forming shotcrete material designed for primary linings. The second material was a phosphate bonded magnesia castable designed as a hot repair material.

Both formulations were tested through laboratory immersion testing as described elsewhere [4, 5]. Testing was conducted for 100 hours at 1000°C (1832°F) using an in-house constructed laboratory immersion test system. This system has been demonstrated to successfully reproduce the corrosion products observed to form on refractories exposed in operating gasifiers using commercially generated smelt (nominal composition: 60-

75% Na_2CO_3, 20-38% Na_2SO_4, 1-4% Na_2S, and 1-4% $Na_2S_2O_3$) [6].

Results of previous testing for the currently used fusion-cast spinel material were compared to the corresponding results obtained for the spinel shotcrete and magnesia castable materials as shown in Figure 5.

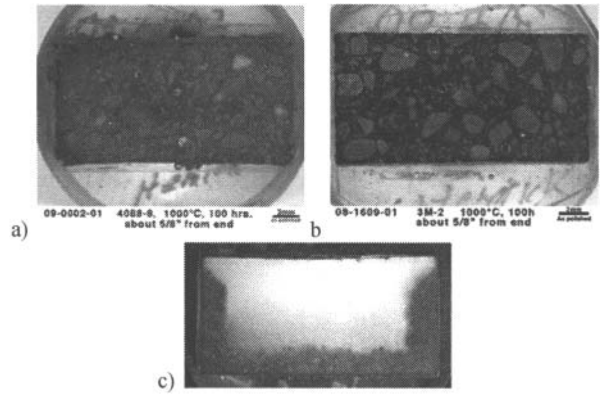

Figure 5. Refractory test samples after exposure to molten smelt immersion test. Samples shown are (a) phosphate bonded magnesia castable repair material, (b) magnesium-rich spinel schotcrete for primary lining, and (c) currently used fusion-cast alumina.

It was found that the spinel shotcrete material performed well when exposed to molten smelt for 100 hours at 1000°C (1832°F). Similar to the currently used fusion-cast spinel material, the spinel shotcrete sample retained its sharp edges and integrity even though it did show some signs of smelt penetration. A color change (darkening of the sample matrix) was seen in both materials, which was confirmed to be a chemical change due to penetration of sulfur and alkali. Yet, this chemical change did not result in the expansion of the sample structure as seen in previous high-alumina containing refractories used for this application, which led to spalling and failure of the hot face lining due to the formation of beta-alumina.

The phosphate bonded magnesia castable did not perform as well as the other two materials when subjected to the same conditions, but still maintained its integrity and only had slight dissolution of the exposed refractory surfaces. Less penetration of the smelt was evident in this sample as well. Based on these results it is still believed that this material would serve well as a repair material since it would not need to survive as long in the hostile molten smelt environment. Adhesion studies, similar to those performed for the candidate aluminum furnace repair material discussed previously, are still needed for this material. Additionally, industrial validation of both the spinel shotcrete primary lining material and the phosphate bonded magnesia castable repair material are desired.

Coal Gasification

Similar to the black liquor gasifer, coal gasification systems involve high temperatures (≈1300-1600°C), aggressive chemical species (including sulfur, alkali salts, and heavy metals), and erosion/corrosion effects. Additionally, issues such as thermal cycling, variable environments, and elevated pressures (≥400 psi) may be present. Therefore, there is a need for longer life refractory materials for this application that could improve gasifier reliability, availability, and affordability.

Current state-of-the-art refractories for this application are high-chrome containing alumina based refractories (60-95% Cr_2O_3). Typical lifetimes of these materials in this environment are four to eighteen months with replacement costs often being on the order of $1M and down time during replacement lasting as long as two to three weeks [7]. Improved materials are of interest which are longer lasting, less expensive, and non-chrome containing due to environmental and disposal issues associated with Chrome VI compounds.

One approach to producing improved materials has been through the use of surface coatings [8]. These are low cost coatings using a colloidal approach for protection against corrosion attack of the refractory brick. This has been shown to be both valid in the laboratory and commercially successful through industrial trials.

The approach taken in this project was to try and apply the spinel shotcrete technology developed for the black liquor application to this environment. Spinel-based materials were thought to be suitable for this application due to the high temperature and high alkali contents of the service environment. Yet, since this is an acidic environment, an alumina-rich as opposed to magenesia-rich spinel formulation was considered as shown in Table I. These materials would offer the advantages of being non-chrome containing and less expensive to produce and install.

Evaluation of this material was performed through refractory cup testing of samples supplied by MinTeq. A reservoir was core drilled in a refractory block and filled with 35 grams of commercial slag. The sample was then heated to 1600°C (2912°F) at 5°C/min (41°F/min) under Argon and held for four hours before being cooled naturally back to room temperature. Upon cooling, the sample was sectioned for analysis.

Results from the first round of samples tested are shown in Figure 6.

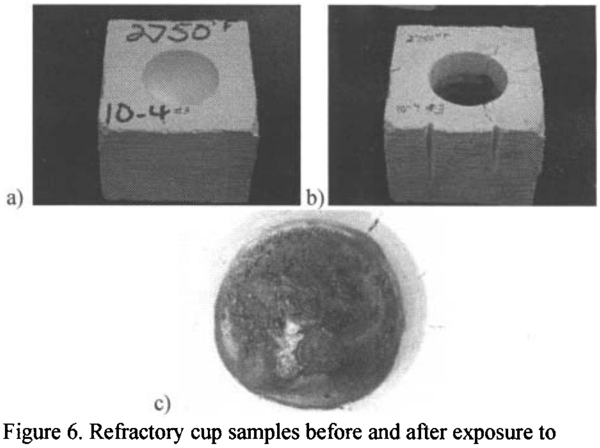

Figure 6. Refractory cup samples before and after exposure to molten coal slag. Alumina-rich spinel material before testing (a), after testing (b), and showing the interaction of molten smelt with the exposed refractory surface (c).

Cracking was seen in this material due to shrinkage issues during heating to 1600°C which are being investigated in future optimized compositions. Otherwise, these materials appeared to perform well with only minimum interaction between the molten slag and the refractory material. Visual observations were substantiated through X-ray diffraction data. At the sample interface between the melted smelt and the refractory, significant iron from the smelt (in the form of free magnetite – Fe_3O_4) and the formation of forsterite – $(Mg,Fe)_2SiO_4$ were seen where it appears free magnesia is combining with iron at this interface. Yet, when the analysis was moved away from this area to the middle of the brick no free iron (magnetite) was seen and the amount of fosterite was greatly reduced. At the back side of the brick, low levels of iron and high levels of spinel ($Mg_2Al_2O_4$) were seen. This would seem to indicate that although there is some interaction of the smelt with the brick at the interface, it is relatively confined to there.

To improve the performance of the spinel-based material, modifications are being made by MinTeq in the composition of this material. Additionally, surface coating technology similar to that currently used for this application, as discussed above, is being developed at ORNL for the spinel-based material system utilizing a unique ORNL coating process. A slurry coating process (as shown pictorially in Figure 7) is being considered since it is non-line-of-sight, can be used for complex shapes, will fill open porosity, requires no unique equipment, and can be automated. Once the coating has been developed and successfully applied to the current spinel-based refractory system, testing will be carried out through exposure to molten slag in refractory cup testing. Additionally, abrasion testing will be carried out on coated and uncoated spinel-based shotcrete materials. If successful, it is hoped to then pursue industrial testing of this material in actual gasifier applications.

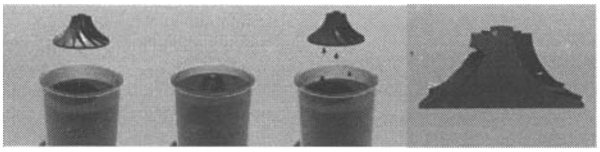

Figure 7. Schematic representation of slurry based coating process. (used courtesy of Beth Armstrong, ORNL).

Lime

Lime kilns are also high temperature and high alkali environments operating at temperatures as high as 1500-1600°C. In the various zones of the kilns high strength castables, high duty fireclay bricks, magnesia-based bricks and high-alumina bricks are utilized. This work focused on the burning zone of the kiln which is the hottest zone and where high-alumina or magnesia-based brick is traditionally used. Due to the rotating nature of the kiln, materials are subjected to both high temperature corrosion and mechanical abuse. Therefore, materials used for this application are desired to be resistant to chemical attack, abrasion resistant, spall resistant, thermally insulating, mechanically strong, and low cost.

Based on the above list of desired properties and the use of lime kilns in the pulp and paper industry, the magnesia-rich spinel material developed for black liquor gasification applications was pursued as a candidate material for this application as well (as shown in Table I). This in-situ spinel forming shotcrete material was tested as developed through laboratory refractory cup testing. Refractory cubes (50 x 50 x 50 mm) were drilled using a 20 mm carbide tip masonry bit to a depth of 25 mm. The cups were filled with 6 grams of dried mud (nominal composition: 55-60% $Na_2S * 9H_2O$, 4-5% K_2CO_3, 0.5-1% NaCl, 35-37% Na_2CO_3) before being heated to 1500°C (2732°F) in four hours. Samples were held for six hours at temperature, and then cooled over a twelve hour period before being sectioned for analysis. Samples were rated based on the cross-sectional area of penetration as shown in Figure 8. Previously tested materials exhibited large areas of penetration as shown in Figure 9.

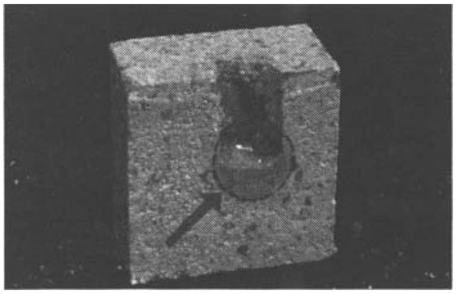

Figure 8. Cross-sectional area of penetration used for evaluation of candidate lime kiln refractories.

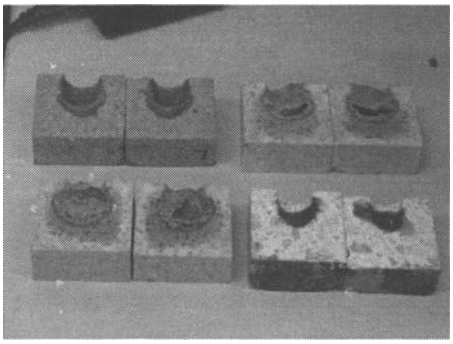

Figure 9. Picture showing large cross-sectional areas of penetration for previously tested candidate lime kiln refractory materials.

Static cup testing of the magnesia-rich spinel formulation in contact with industrially obtained lime mud is shown in Figure 10. This testing showed it to be highly resistant to attack at processing temperatures characteristic of those provided by industrial partners with no adherence of the mud to the refractory cup.

Additionally, preliminary energy analyses have been performed that predict significant projected energy and economic savings can be achieved (as compared to use of current state-of-the-art materials) when materials such as these are used in lime kilns in conjunction with an insulating refractory back-up material like the one shown in Table I. This alumino-silicate material was developed under this project since the conductivity of the spinel-based material is substantially higher (≈5-8 W/mK) than that of a traditional alumino-silicate refractory (≈2-5 W/mK). Therefore, a traditional composite lining strategy can be used consisting of a more corrosion/erosion resistant and mechanically sound hot face lining teamed with a highly insulating back-up lining material. The advantage that the newly developed back-up lining material offers though is it still exhibits good mechanical properties (shown in Table II) despite having very low thermal conductivity (≈0.5 W/mK).

Figure 10. Magnesia-rich spinel material after exposure to industrial lime mud in refractory cup test. Slug of lime solidified and fell out of cup after testing leaving a clean, unaltered refractory surfacewhere the lime mud was in contact with the refractory.

Table II. Mechanical Properties of Insulation Back-Up Lining Material

Firing Temperature (°C)	Bulk Density (g/cm^3)	Modulus of Rupture (MPa)	Cold Crushing Strength (MPa)	Apparent Porosity (%)
110	1.15	3.03	6.89	37
815	1.09	1.45	7.58	45
1093	1.11	2.28	7.58	48
1260	1.11	3.10	6.21	55

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