Micro-Porous Refractory Castable for Molten Aluminum Contact

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Abstract

A micro-porous refractory aggregate was investigated for use as a thermally insulating material in aluminum contact applications. The aggregate was characterized to determine the optimum physical and chemical properties which make it suitable as a base aggregate in a refractory castable product for molten aluminum contact applications. A reduction in steady state heat flux for a typical lining configuration was predicted using thermal conductivity measurements and a corresponding reduction in energy consumption was expected. Empirical measurements made on a 'standard' furnace lining and a furnace lined with the experimental castable material confirmed the predicted results. Reaction and behavior of the material in contact with molten aluminum was characterized by laboratory testing. Wear and reaction were also measured and observed empirically in service trials that exposed the castable material to specific wear mechanisms and aluminum contact conditions in commercial vessels. Improved wear and non-wetting behavior for many commercial applications was demonstrated.

Identification of Aluminum Industry Problems and Production Issues

Industry Problems

The aluminum industry is the second largest producer of metal in the United States, behind the iron and steel industry, and the largest consumer of energy on a per-weight basis. Smelting, which utilizes an electrolytic reduction process known as the Hall-Héroult process, is the largest energy consuming operation[1] Process heating is required to melt, hold, purify, alloy, and heat treat the metal, and accounts for 25% of the energy consumed to manufacture aluminum.

Refractories are used to contain thermal processes and to provide protection for personnel and furnace structures. In order to be successful, the refractory must possess several beneficial properties, including resistance to the various wear mechanisms inherent to the process, and thermal conductivity that suits the energy needs of the process. Historically, dense, high thermal conductivity refractories have been used as working linings to provide wear resistance and process containment, and secondary layers of less dense, more thermally insulating materials have been used to reduce heat flux through the lining.

The energy efficiency of secondary aluminum production is affected greatly by the properties of refractories used. This is true not only at installation but throughout the refractory's working life. This energy efficiency, or lack of it, translates directly to process cost for aluminum producers. Using annual production tonnages, the cost per BTU of various energy sources, and estimates of energy consumption by the industry, it can be calculated that the aluminum industry spent over $500 million on fuel for production operations in 2000[2]. Every 1% improvement in energy efficiency would result in over $5,000,000 in savings annually.

In addition to the actual production costs it is also important to consider the decrease in greenhouse emissions that will result from burning less of these fossil fuels. Over 3.75

million metric tons of CO_2 were produced by aluminum production processes in the year 2000[3]. The same 1% improvement in efficiency would result in a reduction of more than 96,500 MT of CO_2 produced.

In February of 2003 the aluminum industry released their technology roadmap[4]. Among the things this document highlights are the process areas where the need for technological improvement is recognized and listed by the aluminum industry. One of the biggest recognized short falls listed as a priority problem is "Low fuel efficiency in melting and holding furnaces; furnaces are not optimized for scrap heating and waste heat recovery." Six R&D needs were identified. One of these is Energy-Efficient Technologies. Within this need, the top priority listed includes the development and design of a furnace that improves cost effectiveness and improves fuel/energy efficiency.

Production Issues

Undesirable reactions sometimes occur within the furnace, either within the refractory lining or adjacent to it within the vessel. These reactions can reduce the service life of the refractory lining, impede the desired production process or can be the cause of unscheduled maintenance outages.

Corundum formation - Corundum is a naturally occurring form of aluminum oxide (Al_2O_3) also known as alpha alumina or a-Al_2O_3. This material forms as a result of oxidation of the liquid aluminum metal in a vessel. Once the corundum crystals reach a certain size and volume, they interfere with the physical operations of the furnace. They can impede the charging process, cause doors and ports to close improperly or incompletely, deflect burner flame, and insulate the metal from desired heat transfer. Manufacturers will remove the corundum by physically scraping the walls of the vessel with a mechanical arm or other device. In this process, the refractory can be damaged in several ways. First, the corundum is strongly bonded to the refractory surface. Removing the corundum typically removes the surface of the refractory, thereby damaging the lining. Second, penetration into, and formation within the lining will cause stress fractures in the refractory. This causes the lining to become susceptible to thermal cycling or thermal shock and increases the likelihood that mechanical cleaning will damage the lining.

Air is the most readily available source of oxygen for the formation of corundum. Because of constantly opening these vessels for charging, and poor sealing around doors and ports, it is difficult to completely eliminate available oxygen. A second source of oxygen is attributed to the reduction of SiO_2 (silica), which is often a component of the refractory lining material. Aluminum that penetrates the porosity of the refractory can reduce the silica, making oxygen available for the formation of corundum within the pore structure of the refractory. Physical damage to the refractory, in the form of cracks, and the continued reduction of the refractory thickness allows aluminum to penetrate further into the lining, continuing the process. Because this penetration increases the thermal conductivity of the refractory, more waste heat is produced by the process. The shear stress of the differential expansion causes the material to fracture. These fractures exacerbate the problem by allowing further penetration. Repetition of this process will cause the refractory lining to wear to the point of having to be replaced.

Spinel formation - A spinel mineral phase can be formed by the reaction of aluminum and magnesium in the presence of oxygen (O_2) or of alumina (Al_2O_3) with periclase

(MgO). It occurs naturally as $MgAl_2O_4$, ($MgO-Al_2O_3$). Certain alloys of aluminum, such as 7075, contain magnesium metal. When these alloys are exposed to free oxygen, spinel can form. This crystal expands on formation and if this reaction occurs within the porosity of a refractory, the ceramic can fracture. It is more commonly present near door seals and ports where free oxygen is available due to atmospheric leakage. Formation of spinel can cause the same operational problems as corundum formation.

Development of Refractory Castable to Address Issues

The development of a new type of refractory castable was undertaken. Specific objectives were set and development was focused on thermal efficiency and suitability for molten aluminum contact. Ease of installation was also called out as a secondary objective. In addition to laboratory work, the development process also involved service trials of the product in aluminum contact application at cooperating manufacturing facilities.

The aggregate was chosen based on its specific form and mineralogy. Once characterized to determine chemistry, mineralogy, and porosity, the aggregate was used to create a model refractory castable product. The aggregate was screened into specific size distributions and additional fractions were utilized to form bond phases and enhance the inherent aluminum penetration resistance. Several iterations of product formulation were evaluated, and one formulation best met the goals set out for the development work. That formulation was designated "D-1" and the results for that mix are presented here.

In summary, the castable formulation D-1 has a unique combination of characteristics:

- 60% porosity, with an average effective pore diameter of less than 5 microns, creating a surface tension differential with aluminum that prohibits penetration and providing excellent insulating capacity.
- Less than 0.30% silica (SiO_2), eliminating one source of oxygen that can contribute to corundum formation.
- Coefficient of Thermal Conductivity of less than 5 BTU-in/hr-ft^2-°F at normal operating temperatures, allowing for significant reductions in energy consumption.
- Homogenous mineralogy resulting in uniform resistance to aluminum penetration and thermal shock resistance comparable to amorphous silica compositions.
- Strengths approaching those of low cement castables, and exceeding the strengths of most ceramic fiber boards, limiting degradation of the lining because of mechanical cleaning operations.
- Conventional castable style installation requiring only blending with water, vibration casting and a linear temperature increase for dry out.

<u>Physical Properties Compared to Industry Standards</u>

Table 1 compares certain key properties of the formulation D-1 to industry standard products, as discussed below:

Coefficient of Thermal Conductivity: An independent testing organization used the Hot Wire method for testing the Coefficient of Thermal Conductivity (K Factor) of formulation D-1. That data was compared to typical data for a low cement castable composed of 65% alumina (Al_2O_3) with aluminum penetration inhibitors added and to a low cement amorphous silica (SiO_2) based castable. The K Factor relates directly to the predicted heat flux calculated for any particular lining configuration relative to operating conditions. A lower K Factor indicates better insulating capacity, and a reduction in heat flux through the refractory lining. Table 2 details the thermal conductivity measurements for formulation D-1.

Silica (SiO_2) Content: Since silica (SiO_2) is considered a source of oxygen and can contribute to the formation of corundum, lower silica content will result in a reduced likelihood of corundum formation within the refractory. Although corundum can form on the refractory surface from other oxygen sources, a working lining refractory with virtually no silica will not develop internal corundum, and surface corundum will be easily removed during the cleaning process.

Density: Comparison of the quantity of refractory needed to line a molten aluminum vessel can be calculated if the volume of the lining and the density of the refractory are known. Although strength and thermal conductivity properties are often correlated to density for standard refractory materials, the same correlation cannot be made for refractories based on micro-porous aggregate. Formulation D-1 is approximately 60% porous, resulting in a very low K Factor compared to products of similar density, but has a high strength bond phase making it much stronger than refractories with similar levels of porosity.

Table 1: Comparison of Key Characteristics

	WAM® Formulation D-1	65% AL_2O_3 LCC	75% SiO_2 LCC
Thermal Conductivity @ 1450 °F (800 °C)	4.7 BTU/Hr-Ft^2-In (0.69 W/m-C)	13.3 BTU/Hr-Ft^2-In (1.9 W/m-C)	9.9 BTU/Hr-Ft^2-In (1.4 W/m-C)
Silica Content	0.28%	29.3%	72.0%
Density	130 pcf (2.08 g/cm3)	155 pcf (2.48 g/cm3)	127 pcf (2.03 g/cm3)
Maximum Use Temp	2500 °F (1370 °C)	2600 °F* (1425 °C)	2000 °F (1095 °C)

*with aluminum penetration inhibitors added

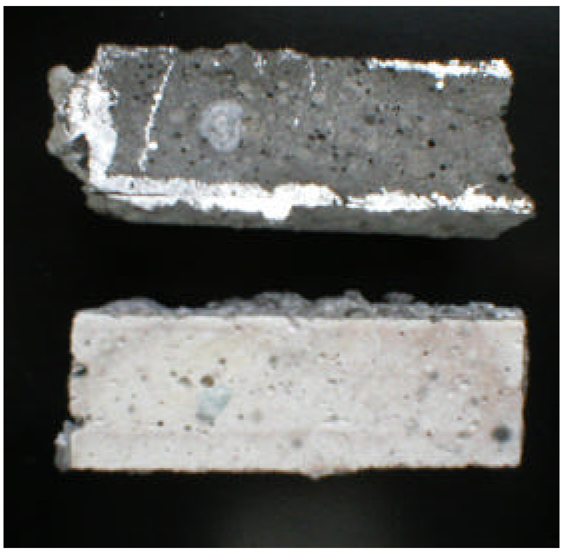
Maximum Use Temperature: The additives typically blended with alumina-silica based refractories to enhance their resistance to aluminum penetration and adhesion limit the recommended service temperature to around 2600 °F. Amorphous silica based products will undergo crystallization if cycle to temperatures over 2000 °F. Formulation D-1 is comparable to the alumina-silica based products in terms of service temperature, but compares favorably to silica based systems in terms of thermal cycling resistance and density.

Molten Aluminum Contact

Laboratory Testing

A preliminary iteration of Formulation D-1 was subjected to a preliminary aluminum immersion test. In this test a sample bar of material is submersed for 72 hours in 7075 alloy at 850 ^oC. The sample is then removed from the molten aluminum and is cross sectioned to allow visual examination for any reaction of penetration into the sample bar. Figure 1 shows the cross section of formulation D on the bottom and the cross section of a typical 60% alumina composition containing no penetration inhibiting additives on the top.

Figure 1. Comparative Results of Immersion Test



The standard sample shown in the top image shows discoloration as a result of the material being exposed to a reducing environment. This gives a black coloration but does not affect the refractoriness of the material. However, penetration of aluminum into the sample is evident around the edges. In addition, penetration into forming cracks can also be observed. The bottom image shows that formulation D-1 is not penetrated nor is there a reduction reaction. The aluminum that is on the surface of the material does not adhere and is easily removed. This represents a very good result for this test and allowed for confident progression to field testing service applications.

Field Trial Testing

Based on review of the lab testing results, several customers agreed to field trials of the material at their manufacturing facilities. Because formulation D-1 offered the best combination of properties as tested, the field trials were run with this mix.

Trials were run in three different application areas:

- Aluminum holders for die cast operations (two trials at different customers).
- Over-the-road crucibles at a recycling operation providing molten metal to another production facility.
- High temperature reaction vessel used to create specialized aluminum alloys.

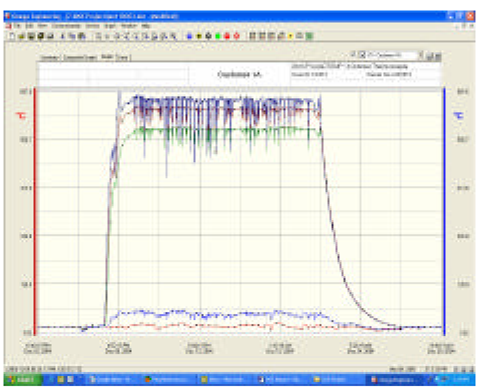
Two separate customers agreed to trial formulation D-1 in aluminum holding furnaces at their manufacturing facilities. Both used electrically heated holding furnaces of slightly varying geometry.

Customer 1 – Holding Furnace Engineering for Efficiency

Customer 1 agreed to design and cast a single furnace of a design focused on energy efficiency in both the choice of lining materials and in the electrical heating system used. The design and fabrication of this furnace was contracted out to a refractory installer. This installer utilized proprietary heating elements in combination with formulation D-1 as the 'working' or 'hot face' lining for the vessel. The formulation D-1 lining was approximately 4" thick. Thermocouples were placed at several different depths within the cast lining in order to monitor in service temperature performance. This furnace was designated DOE3. Because this furnace was an atypical design, there was no means of comparing the temperature performance to a 'typical' furnace at their facility on an 'apples to apples' basis. Furnace shell temperatures were taken to evaluate the overall performance of the lining, and to confirm steady state heat flux calculations made during the engineering process. Figure 2 shows a picture of the data collection device mounted on the furnace. Figure 3 shows the temperature profile of the lining during temperature ramp up to service conditions and subsequent performance with aluminum in the vessel. The observed spikes are a result of varying metal levels as metal was removed from the furnace to feed the die casting machine, and subsequently replenished from a transfer ladle.

Figure 2. Thermocouples and Data Recorder

Figure 3. In-Service Temperature Profile of Furnace



Heat Loss Efficiency Evaluation – DOE3

The shell temperature of the test furnace was measured at an average of 38.5 ^{o}C while in operation. This is compared to this customers typical furnace shell temperatures which range from 93.3 – 204.4 ^{o}C. This represents a 58.7 – 81.1 % improvement. However, not all of this improvement can be attributed to formulation D-1 since the design optimization of this furnace uses a different backup lining configuration compared to a standard furnace. Unfortunately, the furnace was taken off line only after a few weeks in service due to a malfunction in the heating elements. This did provide a unique opportunity to examine the inside of the furnace at the contractors shop. Figures 4 and 4A show the interior of the furnace with aluminum on the formulation D-1 wall and how easily the aluminum is removed. For standard refractory linings, removal of the aluminum often damages the refractory.

Figure 4. Cold Cleaning

Figure 4A. Aluminum Peels Off

After the repair was made to the heating element system, this furnace was placed back into service. In the short term, observed shell temperatures show an improvement in efficiency but no quantitative conclusions can be drawn on the specific contribution of formulation D-1.

Customer 2 – Comparison of Two Holding Furnaces

Customer 2 agreed to line a holding furnace with formulation D-1. This furnace is approximately twice the size of furnace operated by Customer 1. In addition, Customer 2 also agreed to line another furnace with their 'standard' material with exactly the same configuration as the test vessel. A direct comparison between two vessels was made. The vessels are identified as DOE1 and DOE2. Thermocouples were embedded in each furnace at identical points within the lining and data was recorded over several months of operation.

DOE1 is the furnace lined with Formulation D-1 and DOE2 is the furnace lined with the standard refractory material. Metal temperature in each furnace averaged 1133 °F. Both hot face thermocouples reported an average temperature of 1130 °F. The shell temperature of DOE1 Formulation D-1 was 113 °F on average, while DOE2 was 138 °F on average. Overall, DOE1 caused more heat to be retained in the furnace. This fact was also confirmed by monitoring the kilowatt usage of each furnace. This experiment was performed by Customer 2 and the results were shared with us. For DOE1 the one week kilowatt usage average was 2,920 kWh. For DOE2 the kilowatt usage for the same period was 3,460 kWh. Therefore, the standard furnace (DOE2) used 18.5% more electrical energy than the furnace lined with formulation D1 over a 7 day period holding the same alloy at the same target metal temperature. If the 540 kWh per week savings is annualized 28,080 kWh will be saved over one year. At a current kWh price of $0.0463 the furnace lined with Formulation D-1 customer 2 about $1,300 annually. This customer has over 40 similar furnaces on site as well as several larger melting furnaces.

This experiment also demonstrated the much improved performance of formulation D-1 compared to the standard lining after 9 months of service. Figure 5 shows the formulation D-1 furnace after cold cleaning. All material buildup was easily removed from the walls with very little effort. As a result, there was no appreciable damage to the refractory. In addition, no penetration of the refractory is observed. The conclusion is that while a furnace lined with a standard refractory material will degrade both physically and thermally, a furnace lined with formulation D1 will maintain its physical integrity, even though bench testing exhibits lower overall strength, and will retain its optimum thermal efficiency over a longer period of time.

Customer 3 – Over-the-Road Crucibles

Customer 3 trialed Formulation D-1 in over-the-road-crucibles. This application was to improve the wear rate of the vessel and therefore improve the vessel's lifetime and average efficiency. The trial is of interest because in this application, heat is supplied by a gas burner. It was desired to see how the material performed in this environment compared to the holding furnaces which were heated electrically. Gas heat is less controllable compared to its electric counterpart, but the reaction time need to make temperature adjustments is quicker. As a result, head space temperatures tend to be higher and thermal shock becomes a concern. The head space and metal line in these vessels represent the highest wear area.

Commonly, the crucibles are filled with metal and kept at an appropriate temperature by the use of a lid that contains a burner. When ready to transport, the burner is removed, the lid is sealed and the crucible is placed on the transport vehicle. Because the crucible needs to retain as much heat a possible, they are typically lined with an insulating material. Initially, the current material is more insulating than Formulation D-1. However, this is achieved by the use of porous aggregate with a large pore size. In time the refractory develops buildup, becomes penetrated and the insulating capability is significantly reduced. The current refractory is relatively weak and is easily damaged during cleaning efforts to remove buildup. The current refractory must be replaced often. Customer 3 wanted to find a material that would maintain an average insulating character over the lifetime of the crucible, which was an improvement over the current refractory.

Figure 6. Over the Road Crucible

Initially only burner/transport lids were cast of Formulation D-1. These were put into service along with lids comprised of the current material. Both were monitored for wear and average lifetime. One lid was run with a combination of the two materials which allowed for a side by side comparison. The standard material wore greatly while the surrounding material, Formulation D1, wore much better. Unfortunately, the company running this trial would not permit a picture of this particular hardware, so no photo is available.

After successfully demonstrating its capability in the lids, Formulation D-1 was installed in the most difficult section of the crucible body, which is the top 18". This is a difficult application because it is at the metal line. There is a great temperature differential between the area above and below the metal line when the burner is on. Furthermore, this area is susceptible to corundum buildup because of the availability of atmospheric oxygen. Excessive wear in this area typically takes the vessel out of service. Figure 6 shows the crucible body lying on its side. The division between the two materials is apparent with formulation D1 comprising the top 18”. This photo was taken after a few runs and the vessel was turned down to observe any differences and to clean buildup that typically occurs (photo taken by customer). Customer 3 reported that the 18” band cleaned very easily while the current material required more drastic measures to remove the buildup. The more drastic method used a mechanical device to scrape off the buildup. Scrape marks can be observed in the current material. As mentioned, this causes premature wear. Shell temperatures were periodically measured between the portion of the crucible lined with the standard material and that portion lined with Formulation D-1. As stated earlier, the standard lining started with a better insulating capability than Formulation D-1 however, over time, this advantage is lost due to penetration and loss of the standard lining. Formulation D-1 retains its structural integrity by resisting penetration and cleaning much easier. As a result, after 11 months of service in the sidewall of the crucible the area lined with the standard material is reading an average 8.4% higher in shell temperature compared to Formulation D-1. This difference can be expected to continue to increase with time.

Customer 4 – Special Alloy Production

Customer 4’s application was solicited because it operates at a higher than typical temperature, approximately 1204 ^oC. Their alloy is atypical and their experience is that the alloy is very aggressive to refractories.

The process of Customer 4 is considered highly confidential and as such we were not permitted to monitor the performance of the furnace in which Formulation D-1 was installed. However, Customer 4 did monitor energy efficiency and shell temperatures as part of their evaluation process. They shared this information, as well as some pictures of the particularly bad buildup they generate, and how easy Formulation D-1 seems to clean. Customer 4’s normal lining lasted only six months. By six months, the furnace is so penetrated that the lining and backup up are disrupted and most thermal efficiency is gone.

Table 2. Customer 4 Energy Records

Furnace Lining Material		Steady State Energy Consumption	
Formulation D-1		29.7%	
Standard Lining		35.6%	
Lining Material	Front of Furnace	Left Side Furnace	Right Side Furnace
Formulation D-1	88 ^oC	82 ^oC	88 ^oC
Standard Lining	121 ^oC	109 ^oC	118 ^oC
Temp Diff	33 ^oC	27 ^oC	30 ^oC
Improvement	27.3 %	24.7 %	25.4 %

Table 2 tabulates the measured energy usage values for each lining. Reported results indicate that the furnace lined with the standard material uses 19.9% more energy compared to a lining of Formulation D-1. Selected temperature readings are shown in the bottom portion of the table. Actual and relative differences are shown for comparison.

Customer 2- Expansion of Service Trial to Reverberatory Furnace

Customer 2 was impressed with the demonstrated performance of Formulation D-1 in their holders. They solicited us to trial this material in a hot wall of a 100,000 pound melting furnace at another location. Since they agreed to cover the costs of the trial we agreed to the test. The trial required us to provide 11,000 lbs of Formulation D-1 for installation in the hot wall. A picture of the wall after stripping the forms is shown in Figure 7. This view is from the inside of the furnace. Aluminum can be seen sticking to the roof. The only portion that was cast in Formulation D-1 was the wall, with doorways. The discoloration is a result of the grease that is used as a release for the wooden forms. This particular application is difficult and as a result this wall typically fails before any other part of the furnace, for two main reasons. One, the molten aluminum level comes close to the top of the doors. As a result, you have the bottom of the wall immersed in molten aluminum at the bath temperature. The area on the outside of the wall and above the metal in the well is exposed to atmosphere at another temperature. Finally, the inside of the wall above the aluminum is exposed to the furnace atmosphere and more importantly is impinged by the flame from two gas burners which are mounted on the opposite wall, exposing the hot wall to a third temperature. So, the overall temperature profile would look something like Figure 8. This puts tremendous thermal stress on the wall at area depicted by the red lines. The current refractory composition used for the wall lasts approximately 2 years before it finally breaks apart and has to be replaced. After 8 months service the hot wall installation is holding up as well as the prior lining and showing no signs of thermal stress cracking. Although no heat transfer benefits occur for this

Figure 7. Hot wall installation with forms stripped

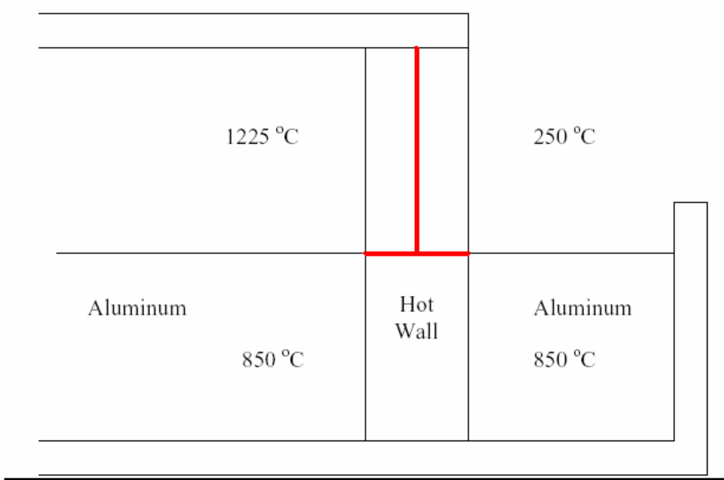


Figure 8: Hot Wall Temperature Profile

installation, the overall performance in the toughest area of this furnace will prove Formulation D-1 is suitable for future use in the bellyband and sidewall areas.

Conclusion

This research has been successful in creating a product for aluminum applications that will improve the thermal efficiency of aluminum manufacturing operations. A unique refractory castable has been developed. The composition is such that aluminum will not adhere or penetrate the lining, corundum will not form internally, and any external corundum that forms due to availability of other oxygen sources will not strongly adhere. The micro-porous nature of the castable provides significant insulating capability and resultant reduction in energy consumption. The customers who have trialed the castable have also found that cleaning operations take less time and result in less wear on the refractory lining.

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Formulation D-1 and variants are protected under United States Patent Application US20050049138A1 Dated March 3, 2005, and in the European Union under appropriate filings
Additional photos and information available at http://mysite.verizon.net/vze4dq68/

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[1] U.S. Energy Requirements for Aluminum Production, (Washington, D.C.:U.S. Department of Energy, February 2003 v 1.1). The report was prepared for the Energy Efficiency and Renewable Energy Industrial Technologies Program

[2] U.S. Department of Energy Grant Number DE-FG02-04ER84118, Westmoreland Advanced Materials, LLC pages 3,4 April, 2005.

[3] Ibid, page 4

[4] Aluminum Industry Technology Roadmap (Washington D.C.: The Aluminum Association, February 2003) Listed priority research areas for primary and secondary aluminum.