High Performance Castable Refractories for Cupola Applications

INTRODUCTION:

Cupola melting is a desirable method of producing large quantities of consistent iron for high volume foundry casting operations. Minimizing downtime for these furnaces is key to optimal productivity. Erosion of refractories that are in contact with iron and slag limits the campaign duration and thus reduces the potential iron output of the cupola. These furnaces are available in a variety of configurations but operate on similar principles.

The modern cupola furnace dates to the late 18th century with some evidence of similar melting furnaces for centuries prior in China (American Foundrymen's Society, 1965). Lining materials help protect the structural components of the cupola and extend the campaign life. Refractory materials are used to provide protection against molten iron and slag attack, particularly in the well, siphon box and tap hole (Fig 1).

The demand on refractories in the cupola furnace is severe. Materials must withstand thermal, mechanical, and chemical attack. Since cupola downtime is costly, repairs are made in very short windows of time which requires that refractory maintenance materials can be installed, dried, and sintered very quickly to allow for production to resume.

With the high production volumes, the demand on refractories used in these furnaces have continuously increased. Typical lining materials used are based on combinations of aluminum oxide, silicon carbide and carbon. A variety of additives are typically employed to enhance the corrosion and oxidation resistance.

While shaped refractories or bricks historically have been used in many applications, the need to repair and maintain the slag and iron contact portions of the furnaces quickly has led to the use of monolithic products that can be placed, cured, and returned into service during the relatively short window of time allotted for furnace maintenance. Minimizing the downtime for these repairs is essential to keeping the foundry in operation. To the foundry using a cupola for melting, the furnace is the "heart of the foundry" providing molten iron to the rest of the operation.

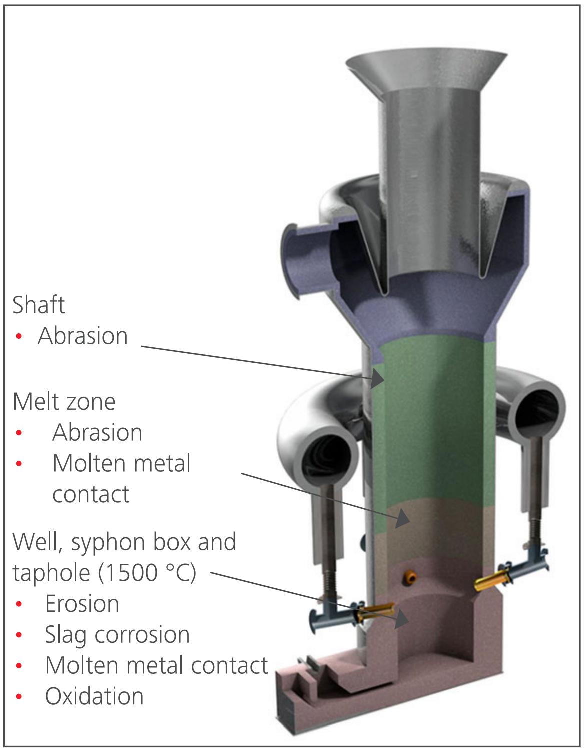

Figure 1 Typical Lined Cupola (atmospheric front slagging)

PRODUCT DESIGN:

The trend in refractory monolithic design has long been aimed toward reducing the cement content of the compositions. Concurrently, refinement of the particle size distribution, additives, and dispersants used have been optimized over the years. As a result, excellent properties of ultra-low cement castables have been achieved.

Elimination of the cement bond system is a concept that has been in practice for several decades and is used in a variety of applications. There are numerous advantages to eliminating the cement bond phase including: fast wetting in the mixing operation, excellent flow characteristics, and rapid dry-out capability for the application. The elimination of the $CaO\text{-}Al_2O_3$ cement phase should also provide a bonding matrix that is mullite based and therefore more refractory.

Additionally, the elimination of metallic additions that can lead to the evolution of hydrogen gas during curing is an important consideration reduce/eliminate these risks associated with these additives.

Colloidal silica is a colloidal dispersion of nanometer sized particles. These particles are stabilized with a surface charge. The particles are amorphous (non-crystalline) and spherical and are homogeneously distributed in the liquid. Commercially available colloidal suspensions can vary in particle size from 10 nm to 50 nm, surface area from 80 to 250 m^2/g and concentration (typically 30-50%).

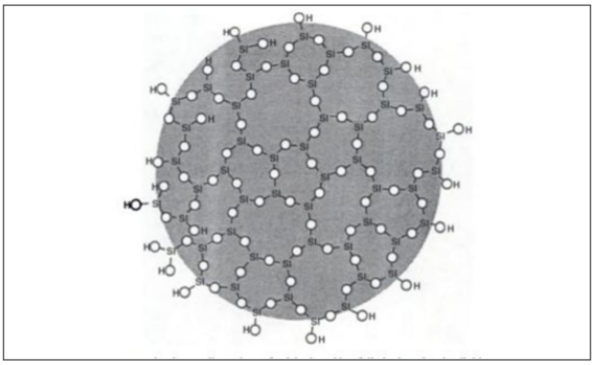

Figure 2 Representation of colloidal particle

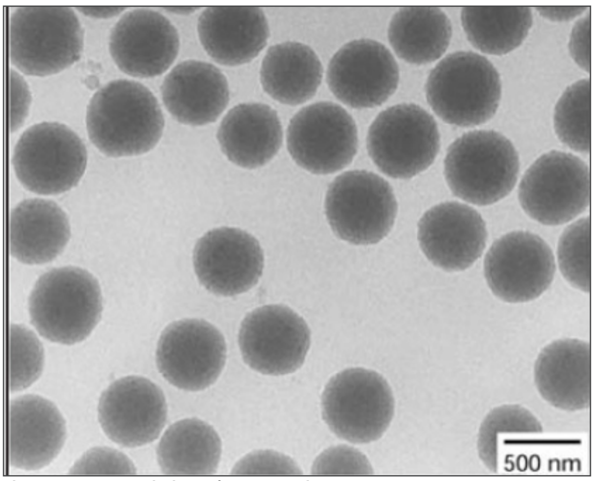

Figure 3 Transmission Electron Microscope Image

The benefits of the use of colloidal silica in place of traditional microsilica additives include improved sinterability due to the small particle size, high surface area and well distributed silica particles within the composition. The improved sintering behavior can result in increased densification, lower porosity, higher strength and abrasion resistance along with improved corrosion and oxidation resistance.

EXPERIMENTAL PROCEDURE:

Multiple compositions were developed using a variety of aggregates and additives. These materials were cast in the laboratory and given different thermal treatments. After firing, they were evaluated for physical and chemical properties. Testing was performed in accordance with Vesuvius UK R&D standard procedures.

RESULTS AND DISCUSSION:

For the development of high performance sol bonded products, several compositions were evaluated to determine which provided the optimum properties for iron and slag resistance. In addition to improving the bonding system, it is important to also consider the large aggregates. The inherent oxidation resistance of the sol bonding allows for an additional benefit of eliminating the metallic additives regularly used to reduce oxidation of the carbon in the systems was employed.

	Traditional LCC	Sol Bond 1	Sol Bond 2	Competitive Sol Bond
Aggre-gate type	A	A	B	A
SiC + C	27%	21%	21%	19%
Bond	CAC	CS	CS	CS

Table 1

General Composition of Materials Evaluated

PHYSICAL PROPERTY TESTING:

Key physical properties of refractory materials used in high-temperature corrosive applications include density, porosity, and strength. More appropriately, the strength at temperature is one of the key indicators of performance in service. The data in Table 2 below shows a comparison of various castables with newly developed sol bonded products. A competitive sol bonded product previously analyzed is shown for comparative purposes. For the characterization, the samples were treated at different temperatures and atmospheres up to 1500 °C which is close to the expected application temperature.

Bulk Density (g/cc)		Standard Low Cement Castable	Sol Bonded Castable 1	Sol Bonded Castable 2	Competitive Sol Bond
Dried	110°C oxidizing	2.93	3.22	3.14	3.01
Fired	1000°C oxidizing	2.87	3.17	3.1	2.96
Fired	1500°C oxidizing	2.86	3.06	3.04	2.95
PLC	(%)				
Fired	1000°C oxidizing	0.0	-0.1	0.0	0.0
Fired	1500°C/oxidizing	1.5	1.5	0.8	1.2
Fired	1500°C/reducing	0.1	0.5	0.0	2.0
Apparent Porosity (%)					
Fired	1000°C oxidizing	18.1	13.7	15.1	19.8
Fired	1500°C/oxidizing	16.5	12.9	14.3	19.2
Fired	1500°C reducing	17.5	12.3	13.6	20.4
Cold Crushing Strength (N/mm2)					
Dried	110°C oxidizing	45	47	64	26
Fired	1000°C oxidizing	55	93	124	45.5
Fired	1500°C/oxidizing	55	147	118	48
Hot MOR (N/mm2)					
Fired	1500°C/reducing	2.5	2.5	9.9	2.0

High quality low cement castables (LCC) typically exhibit excellent density due to the very low water required to cast. The chart below (Figure 4) highlights the significant improvement in density obtained with sol bonded castables. Up to 10% improvement in density was noted for the sol bonded mixes when dried and fired. Improved density can be attributed to reduced water content used in casting as well as the elimination of chemically bound water in the LCC.

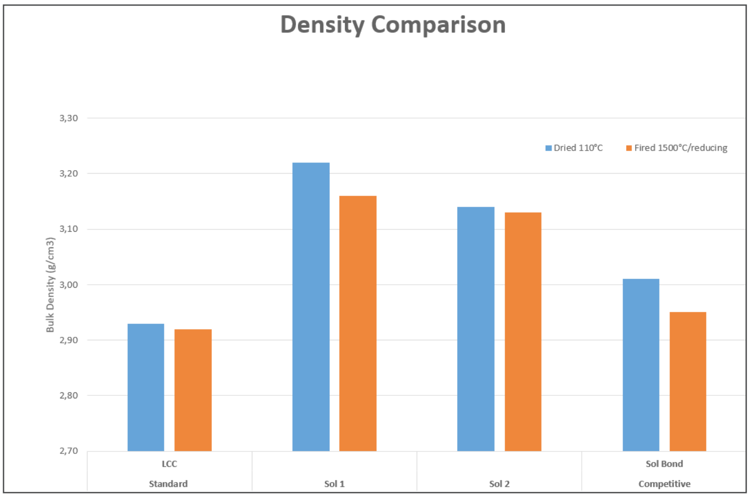

Figure 4 Density Comparison

Porosity of the sol bonded mixes follows the opposite trend exhibiting a 25% reduction was found for the sol bonded castable as compared with the LCC analogue.

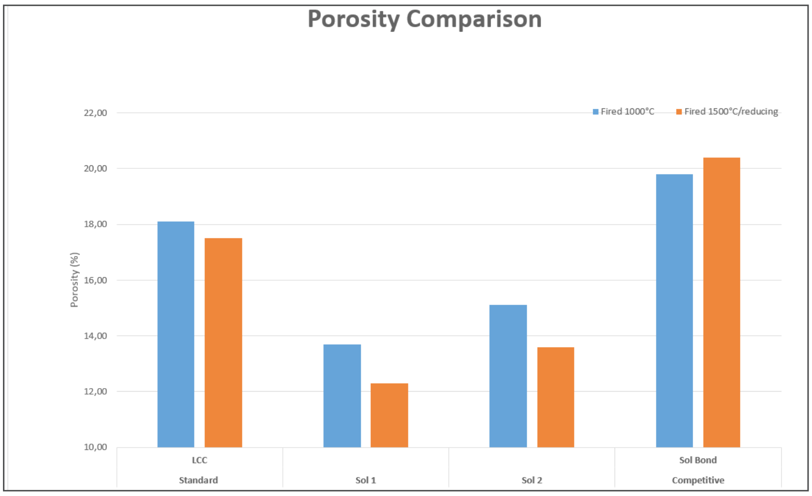

Figure 5 Porosity Comparison.

One of the most important properties measured in this test is modulus of rupture at high temperature. The second sol bonded castable composition (Sol 2) showed almost a four-fold increase in strength measured at 1500 °C.

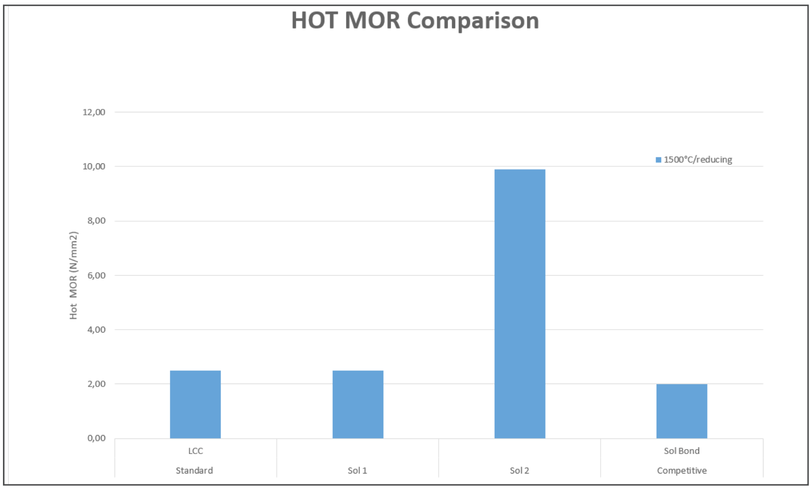

Figure 6 Hot MOR of Castables

SLAG CORROSION TESTING:

A variety of slag corrosion tests are employed to evaluate refractory resistance to slag corrosion. These tests vary from static cup tests where a relatively small amount of slag is placed in to a refractory "cup" to dynamic tests where slag is replenished over the duration of the test. In all cases, the results give some relative indication of the resistance to slag corrosion of the refractories being tested.

SLAG CUP TESTING:

Slag cup testing is a static test procedure whereby the materials are exposed to slag and iron for a prescribed period. The test provides a good indicator of relative resistance to corrosion by iron and slag and the ease of the test makes it a very good protocol for comparing a large amount of materials, quickly.

Typical testing conditions include preparation of the slag cups by casting, curing and drying to 110 °C. The cups are charged with either 10g of iron filings or 10g of slag followed by testing at 1500 °C for 5 hours. The atmosphere can be either oxidizing or reducing. Once the testing is complete, the cups are sectioned for direct comparison of the materials under identical testing conditions. Results are typically evaluated subjectively but may be further analyzed via SEM to study the reactions that take place in the test.

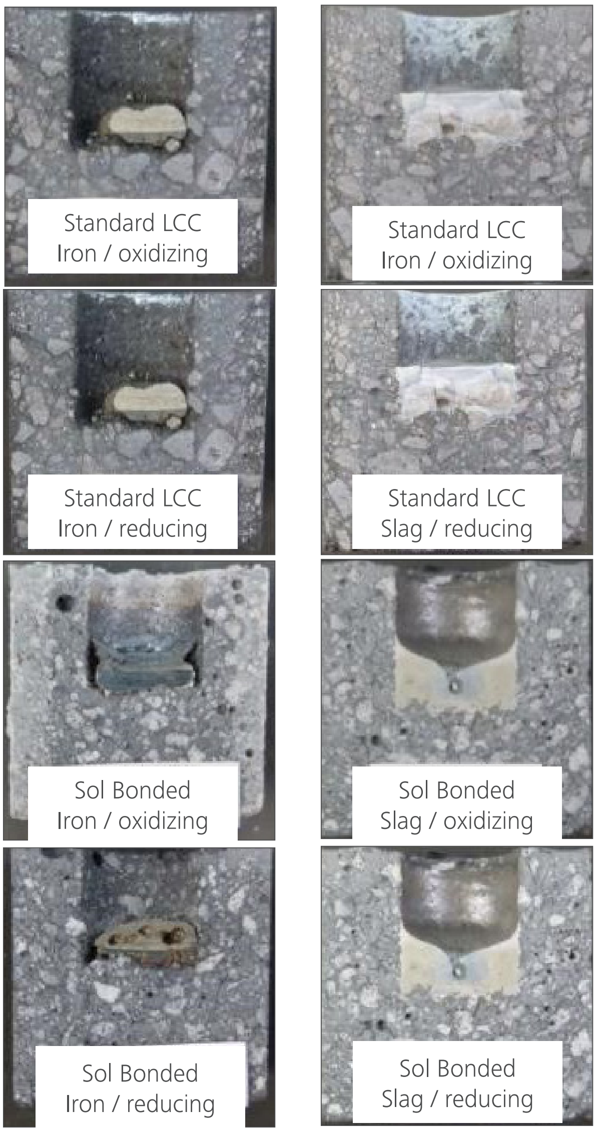

Figure 7. Images of slag cups sectioned after testing.

ROTARY SLAG TESTING:

A more rigorous testing method for castables is the rotary slag test (BS 1902: Section 5.13: 1984). In this test, the samples are exposed to high temperature slag that is continuously replenished for a pre-determined period (typically 6 or 12 hours). The samples for this test are cast into specimens that can be arranged around a hexagonal mandrel to form a lining for a small rotary furnace. The furnace is heated with a gas burner to the desired temperature.

Test specimens in this case were pre-fired to 1000 °C prior to testing at 1550 °C. A typical cupola slag was synthesized in the laboratory and used for the test. This slag was replenished at 30 minute intervals to avoid saturation with reaction products and to maintain the aggressiveness. Testing was continued for a total of six hours. The chemical analysis of the slag used for this testing is shown in Table 3 below.

	Wt %
SiO_2	41.23
Al_2O_3	12.77
TiO_2	0.52
Fe_2O_3	0.24
Mn_3O_4	0.69
CaO	39.68
MgO	1.31
Cr_2O_3	0.01
ZrO_2	0.02
P_2O_5	0.01
K_2O	0.12
Na_2O	1.61
SO_3	1.48
BaO	0.32
$CaO:SiO_2$ ratio	0.96

Table 3 Chemical Analysis of Slag used for Testing

After cooling, the furnace is disassembled and samples are removed. The samples are then sectioned down the center of the corroded face. Corrosion is measured by the average wear (loss in thickness) relative to the initial thickness. The test results are typically normalized to a standard, with a rating index of 100. In the case of this test, the standard material was the traditional low cement castable.

Figure 8 Rotary Slag Testing Configuration

Rotary slag test data is shown in Table 4 below. Slag resistance was measured in millimeters of wear with measurements taken at 25mm intervals along the length. Results are shown in Table 3 below with both the average wear and results normalized to the LCC at 100. The results show that the sol bonded castable based on aggregate B had superior resistance to corrosion compared to all the other samples evaluated. Images of the samples are shown in Figure 9 below.

	Average Wear	Normalized Wear
	(mm)	(LCC-100)
Sol Bonded 2	9.55	72
Sol Bonded 1	14.56	109
Low Cement Castable	13.35	100
Competitive Sol Bond	26.48	198

Table 4. Rotary Slag Testing Data

Reducing the area of the filter print in this fashion to slightly increase yield (0.9kg, 2lbs saved) has significant adverse effects on the flow characteristics in the filter print inlet, the filter inlet face, the filter outlet face, the filter print outlet, and in the downstream runner bar. This type of alteration is not recommended for best practice filter print design.

Figure 11 shows a configuration with the area of the filter print outlet modified to match the standard print shown in Figure 1, but the reduced filter print inlet area is unchanged.

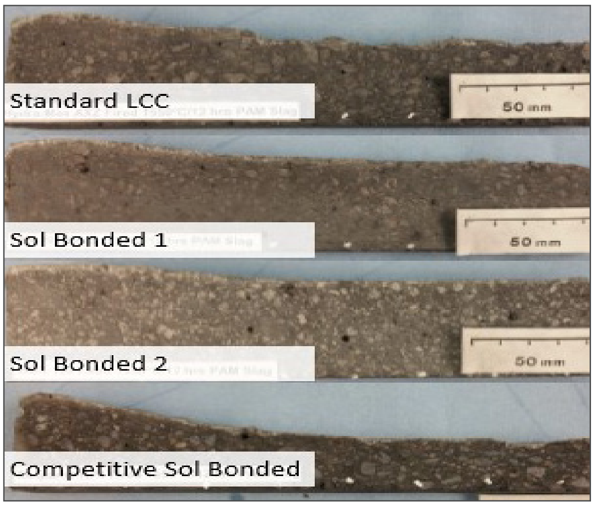

Figure 9 Rotary Slag Test Samples

INDUCTION FURNACE TESTING:

Induction furnace testing provides a means of testing the samples under a dynamic condition. In this test, bars that are 25mm x 25mm x 150mm long are attached to a steel spindle and allowed to rotate in the bath of molten iron and slag at a specified rotational speed. Slag can be replenished at regular intervals to ensure the chemistry remains aggressive. Images of this test are shown in Figure

Iron temperature was maintained at the 1575 °C (average) with a typical cupola slag added in 500g charges every 30 minutes until the testing was complete. A test time of 60 minutes was adequate to show some erosion with a rotational speed of 12-15 rpm. After testing, the samples are re-measured and compared to the original dimensions and an erosion rate is calculated.

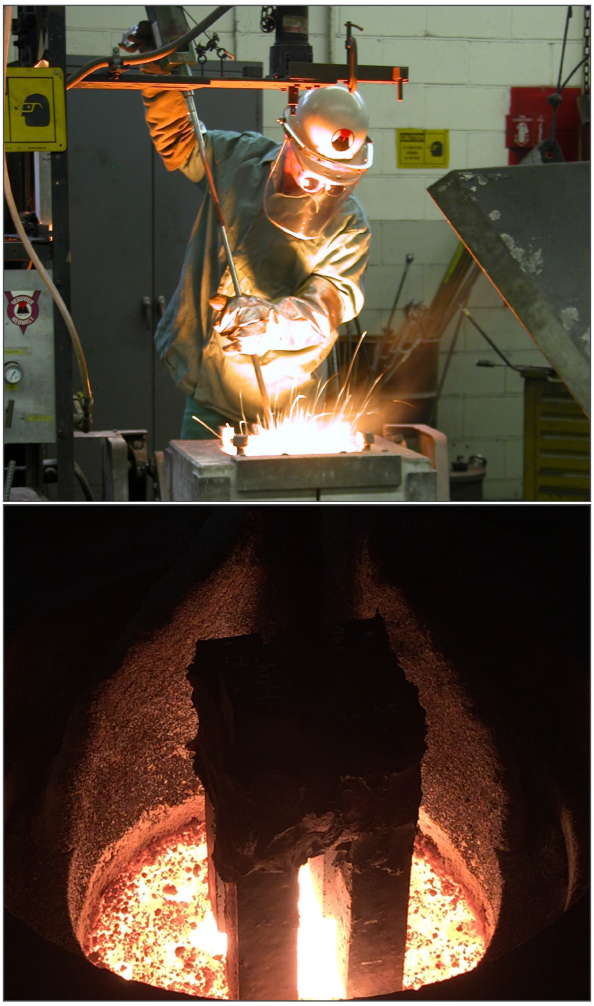

Figure 10 Induction Furnace Testing

Erosion test results are shown in Table 5 below. Slag line results follow a similar trend to the rotary slag testing with the SOL BOND 2 mix exhibiting the best slag resistance. Corrosion below the slag line, in contact with the metal favored the SOL BOND 1 composition.

Material	Slag Line	Metal Line
	(mm/hr)	(mm/hr)
STANDARD LCC	2.01	0.63
SOL BOND 1	1.28	0.37
SOL BOND 2	0.98	0.85
COMPETITIVE SOL BOND	3.14	1.25

Images of the corrosion test bars after testing are shown in Figure 11 below. Bars of Sol Bond 2 show the least material loss in the immersed area.

Figure 11 Induction Furnace Test Samples after testing.

FIELD VALIDATION:

The optimized sol bonded castable composition was evaluated in a high-volume iron foundry in the USA. The evaluation process followed a progression of stages of increasing scope. First, a precast block was cast into place along with the incumbent material in the slag separator in the slagline. This area is typically the location with the highest wear during a campaign.

Corrosion following exposure to 12 days of iron/slag within this area typically sees about 100-120 mm of material loss within the slagline. There is very little wear below the slag where there is only iron contact. The precast shape trial exhibited a favorable comparison in terms of material loss with the incumbent material. (See figs 12 and 13 below). While results were taken somewhat subjectively, the reduction in thickness after this campaign was approximately 90mm with normal slag corrosion of the cast material measured at approximately 100mm.

Figure 12 Slag Separator after 12-day campaign

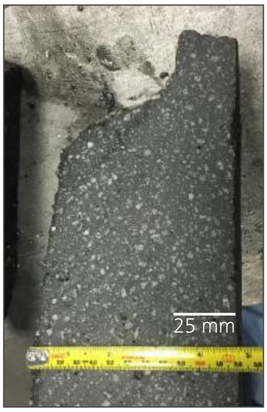

Figure 13 Precast Shape after trial

Following success in this application, the castable was evaluated in a small launder used to divert iron from the cupola to the desulfurization ladle. This application was prone to high thermal stress and corrosion from the $CaCO_3$ and CaF_2 added to the ladle. The launder or drawbridge was previously cast with a high alumina, ultra-low cement castable containing SiC. Life was limited to about 3 days of use with failure due to erosion near the exit end of the launder.

When this launder was cast with the Sol bonded castable, the life was initially extended to a full week (six days). Subsequent launders have been used for 2 weeks with periodic cleaning. At the time of the initial trial the foundry was casting both ductile and grey iron requiring the launder to be used intermittently. The current production has been changed to 100% ductile iron which requires that the launder can withstand continuous use without interrupting production. Images of the launder during dryout and in service are shown in figures 14 and 15 respectively.

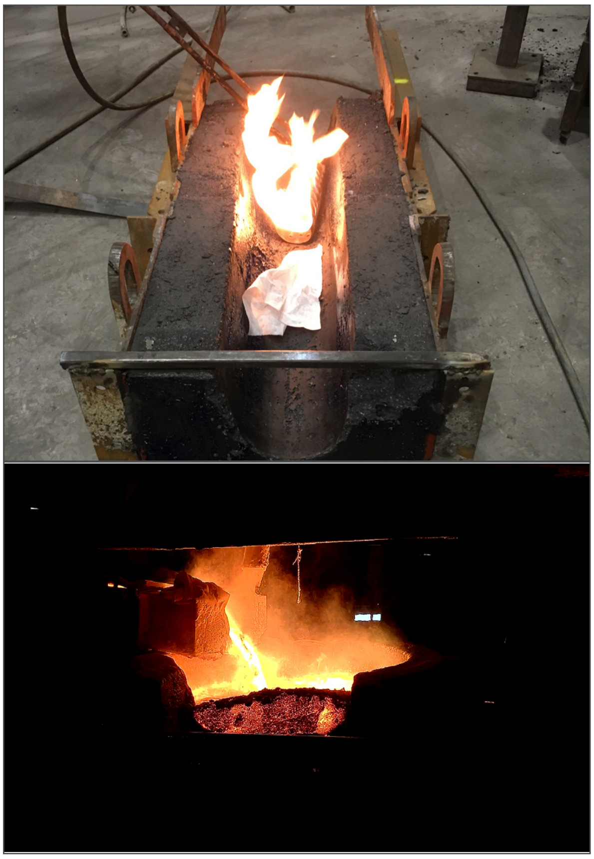

Figure 10 Induction Furnace Testing

SLAG SEPARATOR:

The slag separator originally used for the precast shape was also cast with the sol bonded castable in a veneer repair. This repair involves shaving back the worn refractory in a tapered fashion widening toward the top to facilitate installation. Once cleaned, a consumable form is added to create the shape of the iron and slag channels formed in the slag separator. The castable was vibrated into this cavity. Once cast, the material set and subsequently dried out with a burner over the next 30 hours.

Figure 16 Schematic of veneer repair in slag separator

Figure 17 Schematic of veneer repair in slag separator

The slag separator was used for the campaign without incident. Wear was measured at approximately 75mm which is favorable compared to the incumbent low cement castable. Additional benefits were ease of installation and the lack of spalling that can occur when the standard LCC is dried out rapidly. The sol bonded castable is more suitable for the demands of this application.

SHOTCRETE:

Sol bonded castables are excellent candidates for shotcrete repairs. The setting mechanism for the sol bond is conducive to shotcreting and provides a long working time until an activator is added at the shotcrete nozzle. The castables are also able to be mixed quickly and pumped through relatively small diameter hoses. Application rates of several tons per hour can be achieved. The set characteristics once the activator is added allow for relatively thick sections to be shot. Subsequently, the material can be dried and preheated quickly to resume production.

In the cupola, the melting zone and well where lining materials experience contact with molten iron and slag, shotcrete is a good repair technique to repair the worn lining. Application rates of between 3 to 10 tons per hour are achievable depending on installation equipment capability making repairs to large cupolas relatively fast.

A shotcrete repair was completed in December 2016 in a high capacity cupola capable of melting 1000 tons per day. An area approximately 200mm thick was repaired using shotcrete of the sol bonded material used in other areas of the foundry. Twelve (12) MT of sol bonded material was applied in approximately 4-hours. The furnace could be pre-heated immediately. Inspections were carried out every two weeks and performance has exceeded that of previously used materials with a successful 5-week campaign. Include example of previous campaign life using competitive material

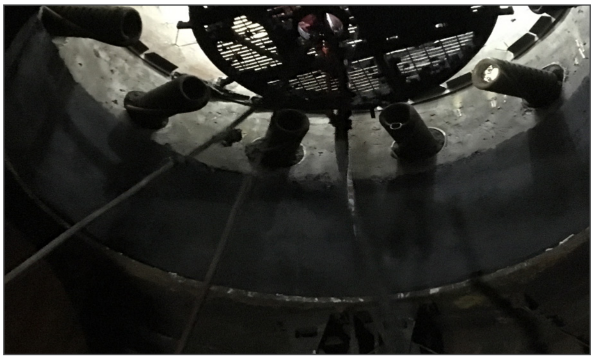

Figure 18 Cupola prior to shotcrete

Figure 19 Shotcrete being applied

BIBLIOGRAPHY

American Foundrymen's Society. (1965). The Cupola and its Operation. Des Plaines, IL: American Foundrymen's Society.

BS 1902: Section 5.13: 1984 - Methods of testing refractory materials. Refractory and thermal properties. Determination of resistance to attack by slag (Method 1902-513)