A robot applies the colloidal silica bonded shotcrete material to a blast furnace.

Better Refractories through NANOTECHNOLOGY

by **Michael Anderson**, Senior Research Engineer, Magneco/Metrel, Inc., Addison, Ill.

New cement-free refractories capitalize on advances in nanotechnology to provide higher strength, improved permeability and porosity, and better oxidation and acid resistance than their cement-bonded counterparts.

Most castables and gun mixes use calcium aluminate cement (CAC) to bond the refractory aggregate together. The amount of CAC in the mix can vary from relatively low quantities to 10% or more, depending on the manufacturer and the mix. The presence of CAC is evident by CaO in the chemical composition of the material. For most CAC products, the CaO content will be in the range of 0.8 to 3.0%. These castables and gun mixes are blended with water to a proper consistency and installed in place. The added water reacts with the CAC, forming hydrated phases that provide low-temperature bonding of the refractory material. These phases depend on the curing temperature and are indicated in Table 1.

At low temperatures, the CAC materials are very dense and have very low permeabilities. As the refractory is heated, the physical water is first driven off, followed by the chemically bonded hydrated water. Because several hydration phases are present, the complete dehydration process occurs over a broad temperature range (410 to 1148°F). As each of these phases gives up its chemically bonded water, bonding strength decreases, and permeability and porosity increase until all water has been removed.

Recently, new pumpable refractory products have been developed based on a patented sol-gel bonding nanotechnology containing no CAC. The pumpable products use a colloidal silica binder (not water) that is mixed with the dry powder

Reprinted with permission from the October 2005 issue of *Ceramic Industry* magazine.

component at the jobsite prior to installation. Special setting additives in the dry component cause the pumpable material to gel and set at a controlled rate. This gellation is due to a condensation reaction that involves the release of water. Unlike CAC bonding, which produces chemically bonded water, the colloidal silica bonded material liberates chemically attached water and creates a chemical bond that does not break down through dehydration as the material is heated. Since the water is not chemically bonded, the majority of the water in the gel structure is free to be released at very low temperatures (212°F). However, a very small quantity of water in the form of attached hydroxyl groups can still be released at much higher temperatures. This release of water, although nearly undetectable, results in the formation of additional Si-O-Si bonds that further enhance strength development.

Colloidal silica bonded material liberates chemically attached water and creates a chemical bond that does not break down through dehydration.

Permeability and Porosity

Figure 1 shows the porosity as a function of temperature for two similar cement and colloidal silica bonded castables. The porosity of the cement bonded castable increases as chemically bonded water is released over a broad temperature range. At high temperatures, the porosity can become very high and leave the refractory more prone to gas and slag attack. With colloidal silica bonded refractories, once the physical water has been removed, the porosity remains relatively constant to much higher temperatures. The lower porosity at intermediate temperatures leaves the colloidal silica bonded refractory more resistant to oxidation, gas attack and slag attack.

The permeability of colloidal silica and cement bonded refractories also depends on the type of bonds produced. Figure 2 shows the permeability of a colloidal silica bonded material and a similar cement bonded composition as a function of heating

Table 1. Hydration reaction products of calcium aluminate cements.

Curing Temperature (°F)	Hydration Products
< 70	$CAH_10 + Al_2O_3$ gel
70 - 95	$C_2AH_8 + AH_3$ (gel)*
95	$C_3AH_6 + AH_3$ (crystalline)
Hydrothermal pressures	$C_4A3H_3 + AH$

*Gel crystallizes between 81 and 90°F

Source: MacZura, G., "Refractory Cements," Ceramic Proceedings, February 1983.

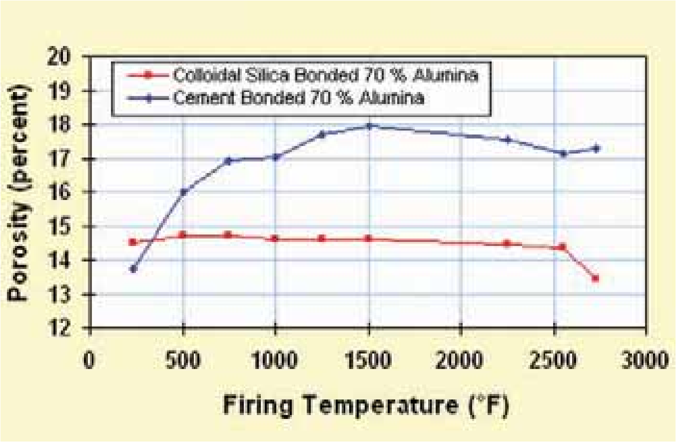

Figure 1. A comparison of porosity for cement bonded and colloidal silica bonded refractories.

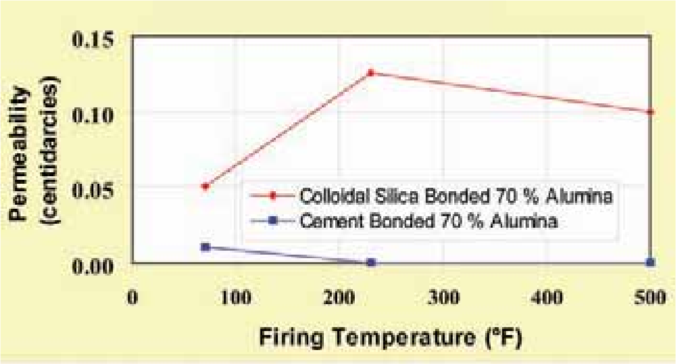

Figure 2. Permeability as a function of heat treatment.

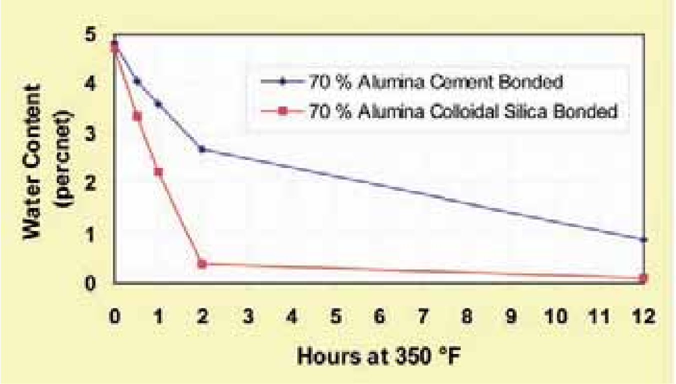

Figure 3. Drying rate of cement bonded and colloidal silica bonded refractory castables.

Castables, Pumpables and Shotcreting

Precast Shape and Castable Refractories

The new pumpable refractory materials can also be used as castables for shape production. The liquid colloidal silica binder is added to the dry aggregate, and setting agent additions in the dry aggregate cause the castable to set at a controlled rate. Because of the materials' self-leveling properties, minimal vibration is usually applied in casting into molds. No hydrated cement phases are involved, so complete drying of shapes can be accomplished at much lower temperatures than cement based shapes and without the risk of explosive spalling. Shapes can range from a few pounds to several tons.

Pumpable Refractories

The colloidal silica bonded pumpable materials can be easily placed via concrete pumping equipment. The self-leveling characteristics of these materials allow placement without the aid of vibration. The ability to pump and the easy dryout characteristics allow for very short turnaround times, reducing costly losses in production and equipment availability.

Shotcrete Refractories

Shotcrete or "spray gunned" materials were developed to remove some of the inconsistencies of dry gunned materials. The expected advantages include:

- Minimal or no dust
- Minimal rebound
- Homogeneously mixed materials
- Reduction of laminations
- Significantly improved properties
- Castable properties without the need of a form

Figure A. High alumina colloidal silica bonded kiln furniture.

Figure B. An electric arc furnace delta.

Shotcrete materials are wet mixed like normal pumpables and pushed through a hose or pipe using a pump. At the hose end a set accelerant is injected via a high-pressure air stream, and the air stream forces the material out through a nozzle and at a target. The accelerant causes the material to thicken, losing flowability in a matter of seconds rather than hours, as in the case of normal pumpables. The key to a good shotcrete material is to have the proper accelerant. The accelerant needs to:

- Cause a fast thickening of the pumpable material
- Have low sensitivity to concentration variations
- Retain a high plasticity of the pumpable material
- Be adaptable to various compositions
- Preserve the properties of the pumpable material

The ideal situation is of a fast flocculation so that the pumpable material exhibits a plastic consistency over a broad accelerant concentration range. This allows for good packing and densification of the shotcrete material. The primary advantage is the ability to install a castable product in areas otherwise restricted to gun mixes, such as hot inaccessible areas or areas that are difficult or too time consuming to form. The photo on p. 29 illustrates a robotic application of the colloidal silica bonded shotcrete material.

temperature. The presence of chemically bonded hydration phases in cement bonded materials results in very low permeability up to 500°F. The low initial permeability values for the cement bonded castables make it very difficult for gases and liquids to exit. In the case of colloidal silica bonded materials, the lack of hydration phases results in higher permeabilities and easier gas and liquid passage at drying temperatures.

Water Release

The distinctly different bond nature of cement and colloidal silica bonded refractories also produces a significantly different drying behavior. Due to the numerous hydration phases present in cement bonded castables, the water is released in stages at various temperatures. Since the water in the colloidal silica bonded refractory is not chemically bonded, it is free to be released at low temperatures. In a comparison of the water release from both a cement and a colloidal silica bonded matrix paste, more than 95% of the water was removed from the colloidal silica bonded material at only 230°F. Additional firings to higher temperatures were required to remove a comparable amount of water from the cement bonded material.

Likewise, Figure 3 illustrates the drying rates of two similar cement and col-

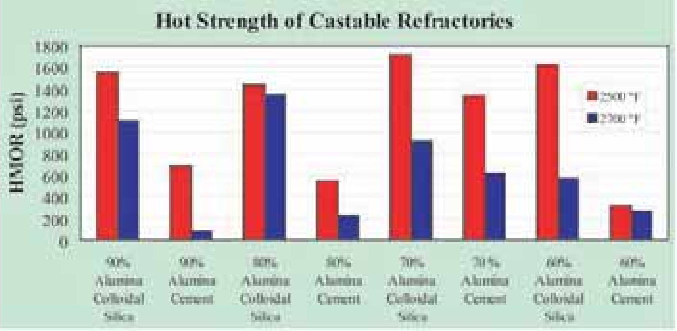

Figure 4. Hot strengths of colloidal silica and similar cement bonded alumino-silica castables.

loidal silica bonded castables. At moderate temperatures, the colloidal silica bonded material releases nearly all of its contained water in only a couple of hours, whereas the cement bonded material releases less than 50% of its water in the same amount of time. Even after longer time periods, significant water remains in the cement bonded material, and it must be heated to much higher temperatures to remove this contained water. This is due to both the presence of hydrated water phases as well as low permeability values.

> **Studies have shown that the colloidal silica bonded materials stand up well to acids under all firing conditions.**

For colloidal silica bonded refractories, the high drying rates and initial permeabilities result in linings that are much less susceptible to steam spalling problems. The resulting dryout schedules tend to be much quicker, allowing for faster vessel turnaround. In some cases, the drying times can be cut in half or more using colloidal silica bonded refractories.

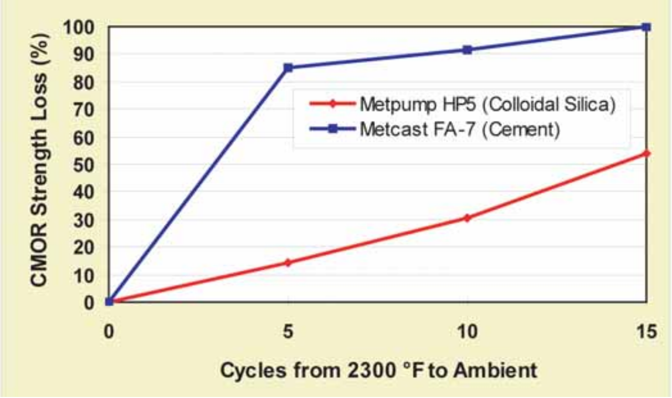

Figure 5. Thermal shock resistance of cement and colloidal silica bonded refractories.

Strength

Cement bonded materials often have greater initial strengths than colloidal silica bonded materials due to the hydraulic bond. However, CAC materials lose this strength as dehydration takes place. A cold modulus of rupture test showed a dip in the strength curve at about 1000°F for a cement bonded material due to a hydration phase loss and the associated bonding loss. Although the colloidal silica bonded product showed a lower initial strength, it showed a good progression in strength development and quickly equaled the cement bonded material at moderate temperatures (<1000°F).

At elevated temperatures, the strength differences become more dramatic. Figure 4 shows the hot strength values of colloidal silica bonded and similar cement bonded castables. Low-melting-temperature $CaO\text{-}Al_2O_3\text{-}SiO_2$ phases associated with CAC castables are responsible for liquid phase formation at the indicated temperatures and the resulting lower hot strengths. Because the colloidal silica bonded materials are CaO-free, they do not generate these low melting phases and typically exhibit higher hot strengths—which results in better in-service erosion resistance for these materials.

Thermal Shock Resistance

Glassy phase formation and volume instability associated with CAC castables often cause degradation of properties upon thermal cycling. In most systems, colloidal silica bonded products have been shown to be superior in cycling applications. Figure 5 shows the strength loss of a CAC castable and a similar colloidal silica bonded pumpable material. After only a few cycles, the CAC material shows a loss of over 85% of its initial strength, while the colloidal silica bonded material loses strength much more slowly and at a steady, predictable rate.

Dependence on Installation Parameters

Colloidal silica bonded materials have proven to be much less

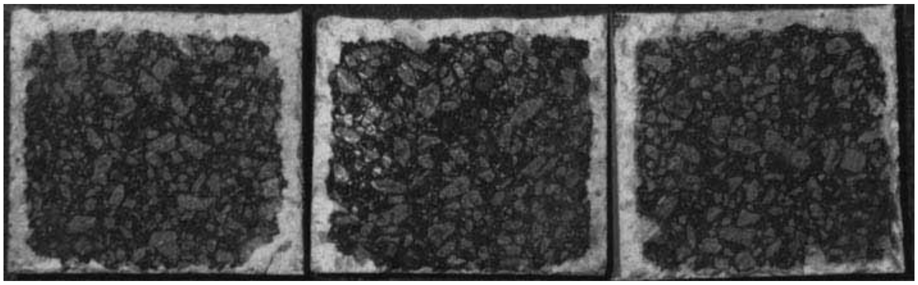

Figure 6. A colloidal silica bonded refractory (Magneco/Metrel's Metpump AGSX) with antioxidants after 5, 10 and 96 hours at 2500°F.

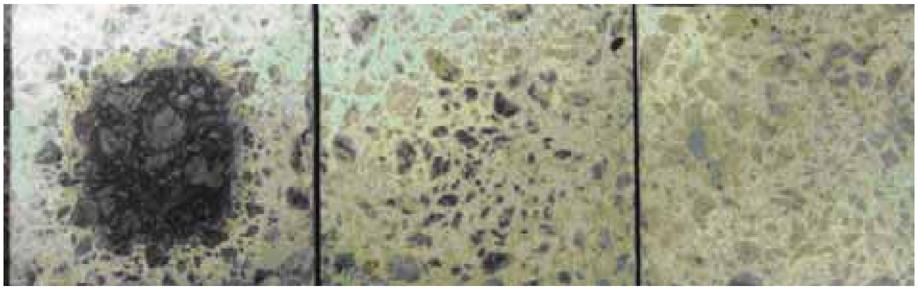

Figure 7. A colloidal silica bonded refractory (Magneco/Metrel's Metpump AGSX) without antioxidants after 5, 10 and 96 hours at 2500°F.

Pumping of a glass furnace crown.

dependent on installation variables than CAC refractories. In a test to determine the relative effects of increasing the moisture content in both a CAC castable and a colloidal silica bonded pumpable refractory, the CAC material exhibited a significant drop in strength when the moisture added was increased by even just small amounts. The colloidal silica bonded material was less affected by changes in moisture addition, and only changed slightly in strength with a higher liquid content.

Oxidation Resistance

Carbon additions to refractories can significantly reduce the wettability of slags and metals to the refractory and result in reduced corrosive attack. For this reason, many companies add extra carbon to the refractory material. However, carbon has a tendency to oxidize in certain environments. In the short term, the retained carbon may be greater, but in the long term the refractory body will become more and more porous because of the large amounts of carbon that are oxidized. Higher porosity allows oxygen to reach the refractory carbon at a much higher rate than in a low porosity material, and eventually the refractory will lose its integrity due to complete oxidation.

The colloidal silica bonded material contains less carbon and is therefore much less susceptible to oxidation. Furthermore, the binder system allows the use of effective antioxidants that are incompatible with cement bonded systems. Figure 6 shows a colloidal silica bonded refractory with these antioxidants heated to elevated temperatures in an oxygen environment. Visual inspection indicates reasonable carbon retention. Without the antioxidants (Figure 7), the material becomes completely oxidized.

Acid Resistance

Magneco/Metrel studies have shown that cement bonded castables show significant attack and degradation in the

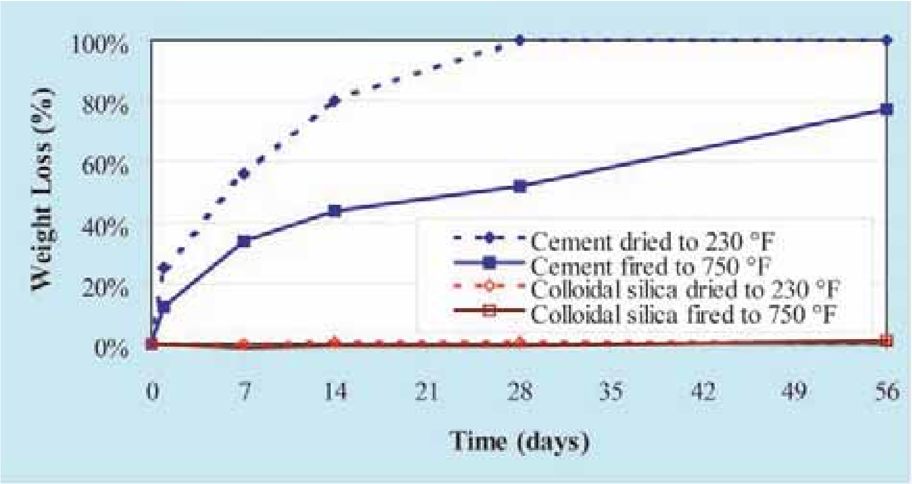

Figure 8. Weight loss of 90% alumina refractories exposed to a sulfuric acid solution.

Figure 9. Cut surface of a 60% alumina colloidal silica material cast onto a 75% alumina-15% SiC product and fired to 1500°F.

presence of hydrochloric acid and sulfuric acid unless they are adequately heat treated. Unfortunately, some applications cannot withstand such temperatures. For instance, in certain pickling tank applications, a rubber lining is used at the refractory cold face. Firing the refractory to high temperatures would result in melting and breakdown of the rubber lining. These studies have also shown that colloidal silica bonded pumpable materials stand up well to acids under all firing conditions. When both cement bonded and colloidal silica bonded refractories were exposed to sulfuric acid, degradation in the cement bonded refractories was rapid, whereas the colloidal silica bonded material showed no attack.

Measurements of weight loss as a function of acid exposure indicate the resilience of colloidal silica bonded materials to acid. Figure 8 indicates that although 90% alumina cement bonded castables show rapid weight losses in the presence of sulfuric acid, colloidal silica bonded materials show minimal losses.

Bonding to Existing Material

The ultra-fine nature of the colloidal silica binder and the nature of the siloxane bond formation allows for excellent bonding to existing refractory linings. The nanometer-sized (10^{-9} meter) particles are much finer than the typical micron-sized (10^{-6} meter) cement particles and more easily penetrate the surface of existing linings. Siloxane bonds can then form and penetrate into the surface material of the lining. Cement bonds do not extend into the refractory lining, but only allow for a physical interlocking with voids or cracks in the surface. Figure 9 illustrates the excellent bond of a colloidal silica bonded castable to another refractory material.

Enhanced Performance

Colloidal silica bonded refractories have exhibited excellent flow behavior, hot strength, thermal shock resistance, oxidation and acid resistance, and bond strength in a variety of applications. With these new materials, manufacturers in the ceramic, glass and related industries have a new alternative for enhancing the performance of their thermal processing operation. ⊕

For more information about colloidal silica bonded refractories, contact Magneco/Metrel, Inc., 223 Interstate Rd., Addison, IL 60101; (630) 543-6660; fax (630) 543-1479; or visit www.magnecometrel.com.