

Wet-Shotcrete for Refractory Castables

A systematic investigation has been conducted involving parameters that control the wet-shotcrete technique for refractory castables.

During recent years, the refractory industry has focused on discovering novel techniques for castable installation that combine high placing rate and low cost, while maintaining final material properties. Versatile and automated placing methods, such as pumping¹ of self-flowing castables and shotcrete,²⁻⁴ have been promoted to replace traditional vibration-molding techniques. Therefore, wet-shotcrete²⁻⁴ is of technical interest, particularly for the lining of large areas and for the repair of damaged surfaces.

The wet-shotcrete technique consists of pumping the castable from the mixer to the pipeline nozzle, where high-pressure compressed air is injected so as to project the pumped castable onto the surface to be covered. This promotes a spray flow that ensures a high installation rate and the formation of a thick layer.

One of the difficulties of the shotcrete technique is the bonding of the material to the area to be lined. The primary condition for a successful operation is that the projected material does not flow over the back lining of the refractory surface. This requires a sudden loss of castable fluidity. Traditionally, this effect is achieved by the controlled use of cement-setting accelerators,²⁻⁴ which also are injected into the nozzle.

Although they ensure cohesion of the material, conventional accelerators, such as sodium silicate and aluminum sulfate, usually deteriorate the mechanical properties of the castables at high temperatures.^{2,3} Therefore, proposals have been made for novel additives³ based on distinct concepts to promote the rapid decrease of castable fluidity.

In most cases, material waste is generated during shotcrete application because of the rebound effect. This waste occurs when a portion of the sprayed castable, which may amount to as much as 30%,^{2,4} fails to adhere to the applied surface. The rebound effect, which is enhanced by the use of accelerators, can be minimized by selecting additives that simultaneously impart adhesive and plastic characteristics to the castable, resulting in homogeneous and cohesive linings, even when successive layers are applied.

In addition to the intrinsically complex pumping operation, wet-shotcrete applications must take into account⁴ an abrupt increase in the castable shearing rate and injection of additives, which are controlled by the air rate supplied in the nozzle, as well as material adhesion and consolidation on the surface.

Conventional testing techniques, however, do not properly evaluate shotcrete castables, because the rheological behavior of these castables under similar shearing conditions during their installation has not been analyzed. The traditional approaches⁴ focus mainly on the influence of additives on castable consistency (fluidity measurements) and on postsetting properties.

**R.G. Pileggi, Y.A. Marques, D. Vasques Filho,
A.R. Studart and V.C. Pandolfelli**

Dept. of Materials Engineering, Federal University of
São Carlos, São Carlos, Brazil

Novel Characterization Technique

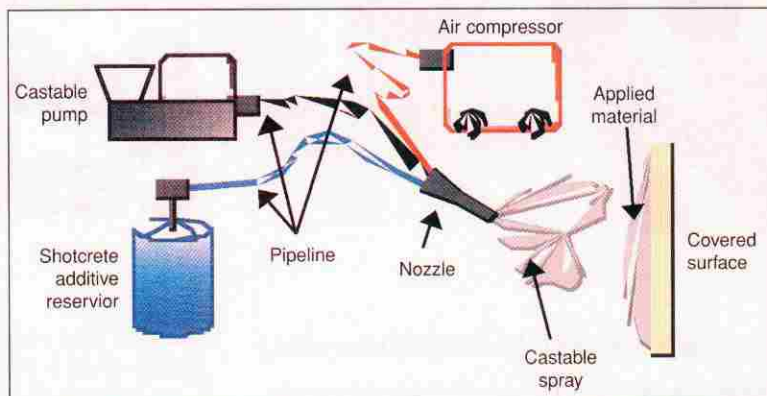
The innovative concept introduced by the new shotcrete characterization technique is the use of a refractory castable rheometer⁵ to simulate the various stages involved in material application. The new testing method consists of two consecutive steps.

- Castable mixing at a constant speed (33 rpm) with the continuous addition of water. In this step, the maximum torque applied should be limited to 20 N·m to avoid excessive heating. After the mixing process, the material is homogenized for another 120 sec at 33 rpm.

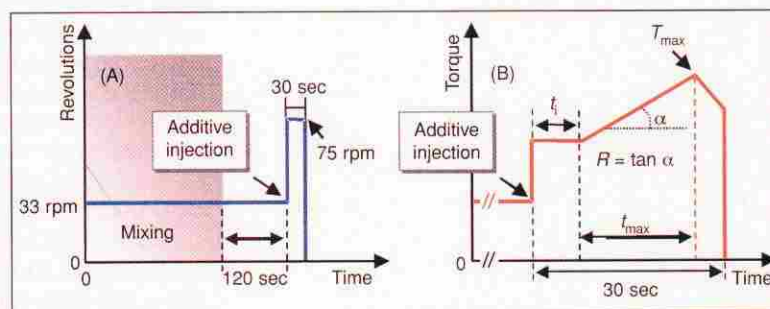
- Injection of shotcrete additives at the end of the homogenization step. In this step, the revolution speed is suddenly increased to 75 rpm, held there for 30 sec, and subsequently decreased to zero. The shotcrete parameters evaluated using this procedure are the time for onset of the stiffening mechanism (t_i), reaction rate (R), maximum torque (T_{\max}) and time to reach maximum torque (t_{\max}) after the onset of stiffening.

Considering that castables for shotcrete applications are pumped before they are sprayed, a high-alumina, ultra-low-cement refractory composition having pumpable characteristics was first formulated. The composition was based on a $q = 0.26$ Andreasen particle-size distribution, with particles ranging from 0.1 to 4750 μm , as suggested by Pileggi and Pandolfelli.¹ The water content was set at 15 vol%, and citric acid (0.26 mg/m²) was used as dispersant.

Two amounts (0.2 and 0.4 wt%) of six distinct shotcrete additives were tested based on the experimental procedures described. Some of these additives (sodium silicate and aluminum sulfate; Synth, Brazil) have been used conventionally,^{2,3} and some of these additives (gluconic acid lactone, hydroxy-aluminum diacetate and alginic acid salt, Fluka Chemie AG, Switzerland, and hydroxyethyl cellulose, Dow Chemical, Brazil) never have been reported as being used.⁶⁻⁸ The results were compared to an additive-free



Schematic drawing of the wet-shotcrete method, illustrating the accessories and devices used and the castable-covered surface.



Schematic drawing of the experimental setup, using a rheometer to simulate the various shotcrete stages: (A) revolution speed program, indicating the instant of additive injection, and (B) typical torque response after additive injection, highlighting the selected shotcrete parameters.

composition (pure castable). Castable matrix suspensions (68 vol% of solid) were prepared to evaluate the pH changes induced by the distinct additives.

Stiffening Mechanisms

In the high-speed step of the experimental setup (75 rpm for 30 sec), the torque profile was strongly influenced by the shotcrete additives, as evidenced by the rheological curves obtained when compared with the reference composition (pure castable). Some of the additions resulted in nonplastic structures, whereas others led to plastic structures. Therefore, two distinct groups of additives were easily identified.

The first group was composed of additives that caused an abrupt increase in torque at high speed, followed by a structural breakdown at the maximum torque. Castables containing such additives failed to small and stable cohesionless agglomerates.

This behavior, attributed to the rigid and fragile nature of the formed structures, was induced by the conventional additives aluminum sulfate and sodium silicate and by the additive hydroxyaluminum diacetate, which was used in this study based on the suggestion of Studart et al.⁶

All these additives dissociate in water, changing the system pH and/or increasing the ionic strength of the liquid medium. Such increases in ionic strength and change in the pH toward the system isoelectric point (IEP) compress the double electric layer around particles, causing the suspension to coagulate because of van der Waals attractive forces.⁹

However, it was not possible to associate the increased torque only with the shift in pH, because the amounts of the additives (0.2 and 0.4 wt%) used were insufficient to change the suspension pH to the expected IEP of alumina particles containing 0.26 mg/m² of citric acid (pH of ~5; Ref. 9). Thus, the increase in ionic strength probably exerted a major effect on particle coagulation.

The castable breakdown observed reflected strong particle coagulation around the primary minimum of the potential energy curve, because rigid structures with low capacity for plastic deformation at high speed (75 rpm) were formed under this condition.

Although it led to particle coagulation,⁶ the addition of gluconic acid lactone did not cause the rigid behavior previously observed.

Before inducing coagulation, lactone ($M_w = 178$ g/mol) produced an unexpected decrease in the initial torque in comparison with the reference composition. The lubricant effect created by low-molecular-weight molecules among solid particles,

known as depletion stabilization,¹⁰ possibly explains this behavior.

The coagulation that followed this preliminary dispersing stage was not as intense as that induced by the other additives, and it was influenced by the extent of the initial torque decrease. No rupture occurred in the composition containing 0.2 wt% of lactone, whereas the castable with 0.4 wt% failed after 30 sec at 75 rpm at a torque level lower than the pure castable.

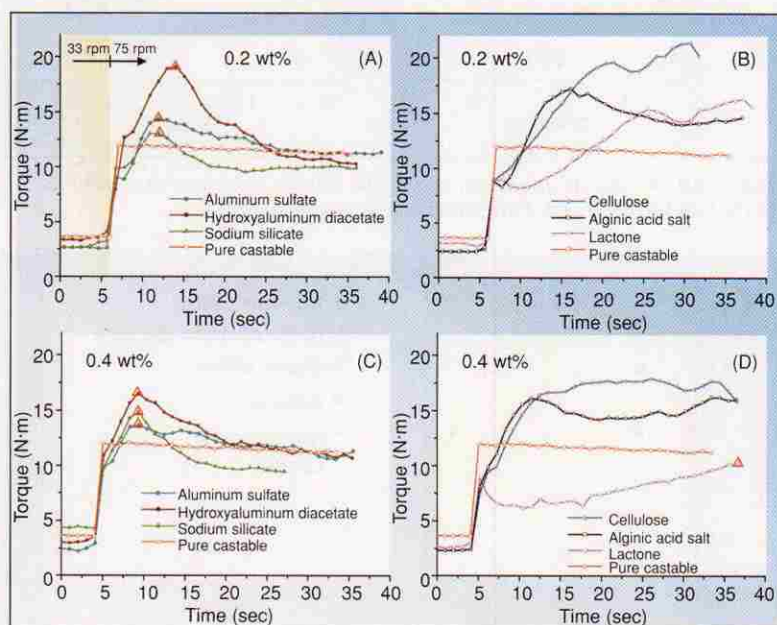
The best probable reason for this abnormal behavior is that the lactone initially coagulated particles around the secondary minimum of the potential energy curve, because the depletion stabilization mechanism led to an additional repulsive barrier against coagulation around the primary minimum. At the secondary minimum, particles could move to some extent around the equilibrium position, which favored castable cohesion.

Coagulation around the primary minimum was achieved only after 30 sec at 75 rpm with the addition of 0.4 wt% of lactone. Secondary minimum coagulation also was expected when the other additives were used (aluminum sulfate, sodium silicate and hydroxyaluminum diacetate), if lower contents were added to the castables.

The desired positive combination between high flow resistance and plasticity was achieved only when additives classified as liquid-medium modifiers (hydroxyethyl cellulose and alginic acid salt) were used.

Hydroxyethyl cellulose (HEC) is a water-soluble, nonionic, semisynthetic⁸ organic polymer that increases liquid viscosity and yield stress by generating a thixotropic lubricant gel without affecting system pH and/or ionic strength. The rheological characteristics of this gel confer plasticity on the system and decrease particle mobility. Therefore, this additive increases the flow resistance without causing castable failure.

Alginic acid salt is a high-molecular-weight polymer ($M_w = 48$ –186 kg/mol) derived from brown marine



Influence of shotcrete additives on the rheological behavior of castables. Effect of these additives is evidenced by comparing the curves obtained with that recorded for the additive-free reference composition, which was affected only by increased revolution speed. Additives that induced a rigid behavior are grouped on charts (A) and (C), whereas charts (B) and (D) show the compounds that conferred plastic characteristics on the castable. (Red triangles (Δ) indicate the instant of castable failure.)

High-Alumina Refractory Castable Composition†

Component	Raw material‡	Composition (vol%)
Matrix (<100 μ m)	Calcined alumina	22.0
	CA 14	2.0
	BFA 200/F	14.5
Aggregate (>100 μ m)	BFA	61.5

†($q = 0.26$) ‡Calcined alumina is A1000 SG and A3000 FL, CA 14 is calcium aluminate cement and BFA is brown-fused alumina. Raw materials were supplied by Alcoa-Brazil and Alcoa-USA. Formulation was calculated using the PSDESIGNER® software program.

algae.^{7,8} This additive produces a gel in water by cross-linking its molecules with the calcium ions provided by the cement. The influence of alginic acid salt on castable behavior and matrix pH is similar to that observed with the HEC.

Selection Criteria

Several technological parameters are suggested to aid in the selection of additives for shotcrete applications.

The first parameter is the time elapsed between the injection of additives and the beginning of the increase in torque, which must be short but greater than zero ($0 < t_i < 5$ sec). This narrow interval for the onset of stiffening is expected to minimize castable sliding on the installed surface (if $t_i > 5$ sec), nozzle obstruction (if $t_i \approx 0$ sec) and castable setting before the target is reached.

All the additives, except lactone (0.4 wt%), resulted in $t_i < 5$ sec, which confirmed their high dissociation and reaction rates. However, hydroxyaluminum diacetate (0.2 and 0.4 wt%), sodium silicate (0.4 wt%), HEC (0.2 and 0.4 wt%) and alginic acid salt (0.4 wt%) led to undesirable instantaneous stiffening ($t_i = 0$ sec).

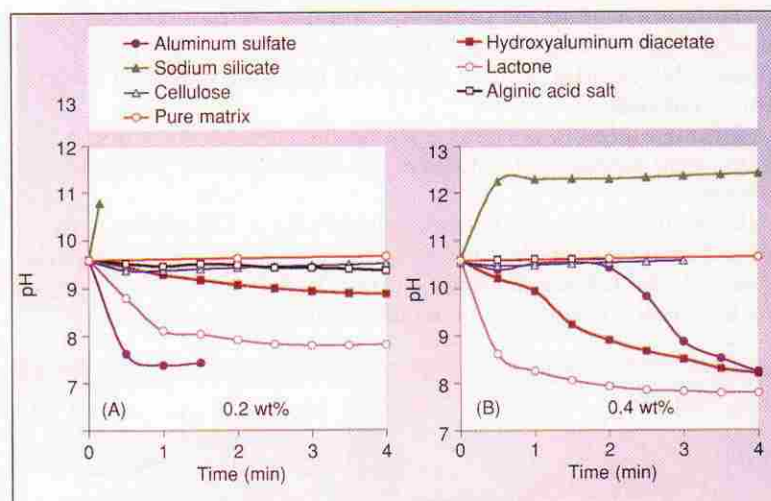
The second parameter suggested for the selection of shotcrete additives is the reaction rate (R). This measurement indicates the stiffening velocity. In practice, the low R values produced by lactone do not favor the formation of cohesive castable layers because of a probable sliding effect on the applied region. Excessively high rates, which have not been observed in this study, may cause the material to set before it hits the surface, enhancing rebound.

The parameters t_i and R must be evaluated simultaneously to determine the effective coagulation rate of a system. A combination of low t_i values and high R values probably causes nozzle obstruction or increased rebound, while high t_i values and low R values probably cause castable sliding on the projected surface.

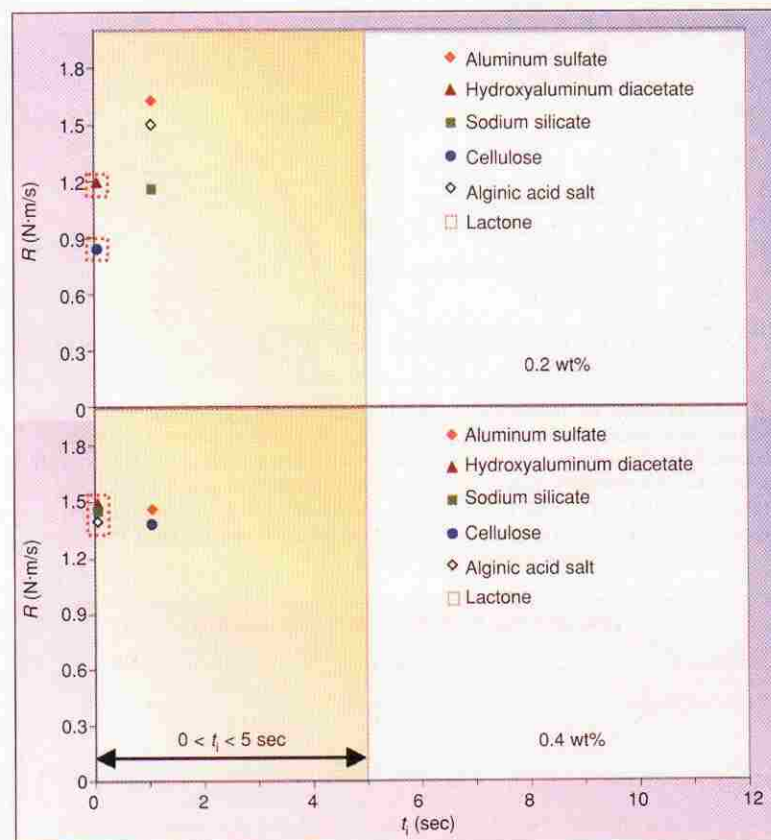
The third parameter is T_{max} at high

speed, which describes the actual flow resistance of the castables. This measure reflects the strength and cohesiveness of the material. Thicker castable layers can be applied when T_{max} is enhanced.

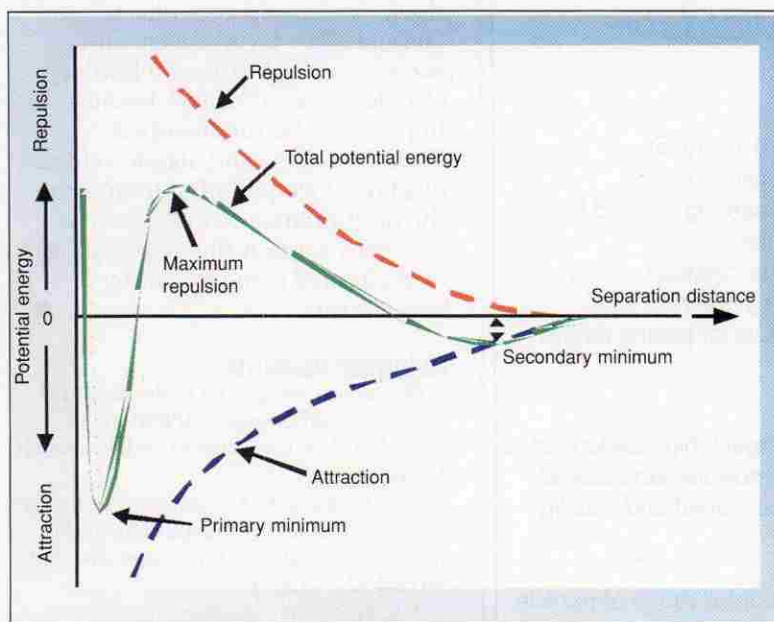
HEC and alginic acid salt produced high T_{max} levels because of the plasticity and cohesion of their resulting gels. These compounds did not cause castable failure, as observed with the



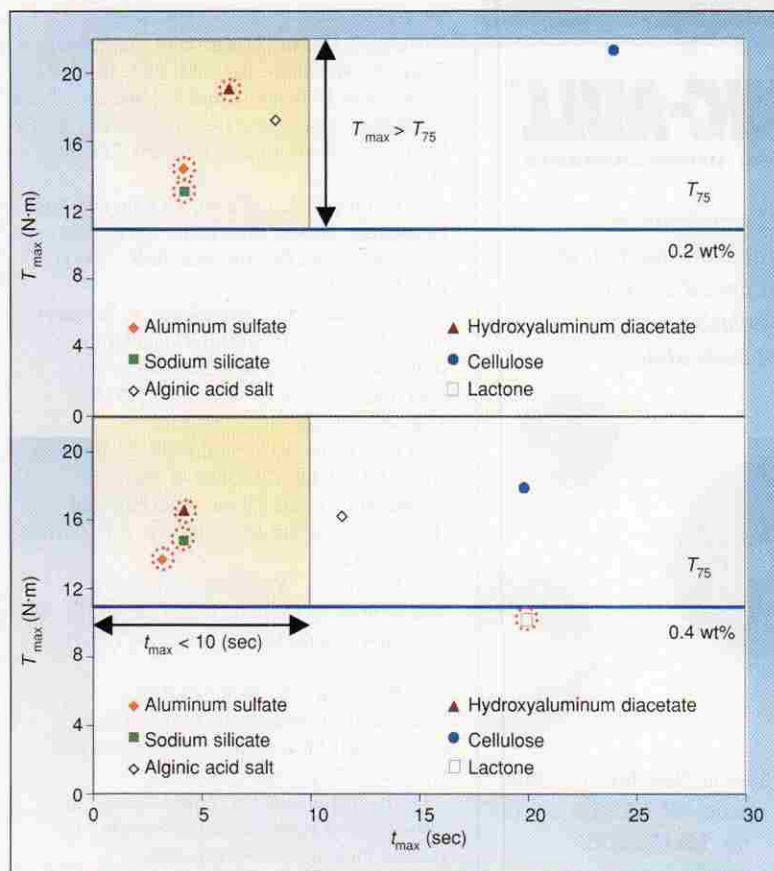
Matrix pH changes as a function of time for distinct wet-shotcrete additives: (A) 0.2 and (B) 0.4 wt%. Pure matrix contained no additives.



R vs. t_i for wet-shotcrete additives. (Yellow areas specify the most suitable range for t_i values. Dotted squares identify the systems with $t_i = 0$).



Interaction potential energy as a function of the distance separating two charged particles in an aqueous medium, according to the DLVO theory.



T_{max} vs. t_{max} for wet-shotcrete additives. (Yellow areas specify the most suitable range for T_{max} and t_{max} values, blue line indicates the torque at 75 rpm of the pure castable and dotted red circles identify the systems that failed during high-speed shearing.)

additives that induced coagulation by a pH shift and/or increased ionic strength.

Among the nonplastic additives, only hydroxyaluminum diacetate resulted in high T_{max} values. The sharp initial decrease in torque induced by the addition of 0.4 wt% of lactone decreased T_{max} to below the torque response of the pure castable (T_{75}) in the high-speed shearing step (75 rpm).

The fourth parameter—when thick layers are required through successive shotcrete applications—is T_{max} . The sprayed material must rapidly develop a minimum resistance level ($>T_{75}$) before receiving the next layer of sprayed castable; hence, t_{max} should not exceed 10 sec.

An appropriate selection of shotcrete additives should always take into account the complete set of parameters proposed. Castables coagulated by pH shifts and/or ionic strength increases show a combination of low t_i and t_{max} values and high R values, but the fragile rupture at high-speed shearing is the most probable reason for their decreased T_{max} , based on the applied testing technique.

Additives that produce nonplastic systems probably enhance the rebound effect, because each newly sprayed layer may strike a rigid surface. This behavior associated with the high coagulation rate (low t_i and high R) also prevents homogenization between successive layers and results in laminated structures. The severe shearing that occurs during shotcrete application may break the previously applied rigid and fragile material, which has not yet totally consolidated.

These negative points are not expected in the case of liquid-medium modifiers, such as HEC and alginic acid salt. Their greater t_{max} (in most cases >10 sec) is compensated by a positive combination of high T_{max} and plastic behavior. High torque levels are obtained with such additives 10 sec after onset of the stiffening reaction.

The association of a plastic nature and high flow resistance assures

HORIBA LA-300 Particle Size Analyzer

Powerful, Portable, Affordable



- Range: 0.1-600 μm
- High resolution
- Light scattering method for fast analysis
- Complete compact, portable system
- Contact us for pricing details

Horiba's LA-300 particle size analyzer is a compact, high performance instrument that takes up little space in today's crowded laboratories while providing the same powerful performance, speed and stability of our full-range instruments.

Contact us today for details on the LA-300 or our full range of particle characterization equipment.

"World's 5th Largest Analytical Instrument Company."

Phone: 800-446-7422

email: labinfo@horiba.com

www.horibalab.com

Wet-Shotcrete for Refractory Castables

thick, homogeneous, cohesive and laminate-free layers, even with successive applications. Plasticity also decreases rebound, because impacts are better absorbed. Therefore, HEC and alginic acid salt display a high potential to improve the performance of wet-shotcrete castables without the disadvantages of traditional cement-setting accelerators. ■

Acknowledgments

The authors are grateful to the Brazilian research-funding agency FAPESP and to Alcoa-Brazil for their support of this research.

References

- ¹R.G. Pileggi and V.C. Pandolfelli, "Rheology and Particle-Size Distribution of Pumpable Refractory Castables," *Am. Ceram. Soc. Bull.*, **80** [10] 52-57 (2001).
- ²L.R. Prudêncio, "Accelerating Admixtures for Shotcrete," *Cem. Concr. Res.*, **20**, 213-19 (1998).
- ³C. Paglia, F. Wombacher and H. Böhm, "The Influence of Alkali-Free and Alkaline Shotcrete Accelerators within Cement Systems: I. Characterization of the Setting Time," *Cem. Concr. Res.*, **31**, 913-18 (2001).
- ⁴M. Jolin, D. Beaupré and S. Mindess, "Tests to Characterize Properties of Fresh Dry-Mix Shotcrete," *Cem. Concr. Res.*, **29**, 753-60 (1999).
- ⁵R.G. Pileggi, A. E. Paiva, J. Gallo and V.C. Pandolfelli, "Novel Rheometer for Refractory Castables," *Am. Ceram. Soc. Bull.*, **79** [1] 54-58 (2000).
- ⁶A.R. Studart, V.C. Pandolfelli, E. Tervoort and L.J. Gauckler, "In Situ Coagulation of High-Alumina Zero-Cement Refractory Castables," *J. Am. Ceram. Soc.*, **85** [8] 1947-53 (2002).
- ⁷A.R. Studart, V.C. Pandolfelli, E. Tervoort and L.J. Gauckler, "Gelling of Alumina Suspensions Using Alginic Acid Salt and Hydroxyaluminum Diacetate," *J. Am. Ceram. Soc.*, in press.
- ⁸K.H. Khayat, "Viscosity-Enhancing Admixtures for Cement-Based Materials: An Overview," *Cem. Concr. Res.*, **20**, 171-88 (1998).
- ⁹A.R. Studart, W. Zhong and V.C. Pandolfelli, "Rheological Design of Zero-Cement Self-Flow Castables," *Am. Ceram. Soc. Bull.*, **78** [5] 65-72 (1999).
- ¹⁰A.L. Ogden and J.A. Lewis, "Effect of Nonadsorbed Polymer on the Stability of Weakly Flocculated Nonaqueous Suspensions," *Langmuir*, **12** [14] 3413-24 (1996).

SONIC-MILL®

MACHINING THE UNMACHINABLE

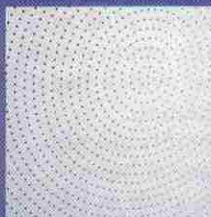
Specializing in the precision-machining of technical ceramics and glass—to your specifications.



Silicon
Quartz
Glass
Sapphire
Alumina



Alumina Nitride
Silicon Carbide
Various Composites
Fiber-Optic Materials



Boron Carbide
Ferrite
Graphite
Ruby
Boron Nitride
Zirconia



Albuquerque, New Mexico, USA
phone: 505.839.3535
fax: 505.839.3525
contact@sonicmill.com
www.sonicmill.com

source code: ADCEB

