

# INTERACTIONS BETWEEN SILICA FUME AND CAC AND METHODS TO OPTIMIZE CASTABLE PLACING PROPERTIES

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## 1. ABSTRACT

Low cement castables (LCCs) have become standard products in the portfolio of most refractory monolithic producers. However, the ability to achieve consistent rheological behavior with a repeatable hardening profile for these systems remains a subject of research. The hydration of calcium aluminate cement (CAC) in LCCs depends not only on the quality and regularity of the CAC itself but also on silica fume (SF) employed. The present study addresses the interaction between cement and silica fume. This understanding, once achieved, may be used to control the observed variability in placement behavior of LLCs containing silica fume. This approach could then be used to develop a new binder system.

## 2. INTRODUCTION

High performance low cement castables are formulated with well-controlled calcium aluminate cements like Secar<sup>®</sup>71 containing about 70% Al<sub>2</sub>O<sub>3</sub> and 30% CaO. While the hydration course of CAC responsible for strength development has been described previously [1, 2], the additional LCC components can influence the performance and the regularity of the castable system. Silica fumes are widely used in LCCs and when combined with admixtures a system with low water demand can be achieved. Decreased water demand generally translates to lower porosity levels and improved strength development.

Silica fume influences CAC dissolution and hydration and generally has a retarding effect when used in combination with additives (phosphates) that rely on electrostatic dispersion. In practical terms this means that satisfactory working time can be achieved with one single additive like tripolyphosphate (TPP). However, impurity variability across and within fume silica sources can perturb the hydration reactions and lead to variable working and hardening times.

Impurities present in fume silica as well as the basic physical properties can have a marked effect on castable placement via interactions with the hydration process. In order to achieve optimized and controlled placing behavior, it is necessary to assure the control of the silica fume employed.

## 3. CAC HYDRATION

Calcium aluminate cement hydration depends largely on its initial phase assemblage. Phase development in a CAC depends on parameters like chemistry and surface area. **Table 1** shows the anhydrous phases that are present in a number of commercially available cements.

The cement mineralogy was determined by a quantitative X-ray diffraction method using Rietveld refinement [3]. The dominant phase in all cases was calcium monoaluminate (CA). Reactivity of CAC hydration is influenced by its phase assemblage. A general comparison of the reactivity of the anhydrous phases is shown in **Table 2**. In general, phase reactivity increase with the ratio of lime to alumina.

**Table 2. Reactivity of calcium aluminate phases at 20°C [4]**

	C <sub>1</sub> A	C <sub>12</sub> A <sub>7</sub>	CA	CA <sub>2</sub>	CA <sub>6</sub>
C:A Ratio	3	1.7	1	0.5	0.2
Reactivity	Very rapid	fast	slow	Very slow	none

In contrast to Portland cement where the hydrates formed remain broadly similar with time and temperature the hydration of CAC is strongly temperature dependent [5]. The reactions shown in **Table 3** illustrate the temperature sensitivity of CAC hydration products.

**Table 1. Anhydrous phases in a number of commercial CAC**

Phase (wt%)	CAC/CF <sup>®</sup> 40% alumina	CAC/Secar 51 <sup>®</sup> 50% alumina	CAC/Secar 71 <sup>®</sup> 70% alumina	CAC/Secar 80 <sup>®</sup> 80% alumina
Al <sub>2</sub> O <sub>3</sub>	37.5-41.5	50.8-54.2	68.7-70.5	79.5-82.0
CaO	36.5-39.5	35.9-38.9	28.5-30.5	16.2-17.8
SiO <sub>2</sub>	2.5-5.0	4.0-5.5	0.2-0.6	<0.35
FeO+Fe <sub>2</sub> O <sub>3</sub>	14.0-18.0	1.0-2.2	<0.4	0.2
TiO <sub>2</sub>	<4.0	<4.0	<0.5	<0.3
CA	47-57	64-74	54-64	35-45
CA <sub>2</sub>			+++	++
A			+	++
C <sub>12</sub> A <sub>7</sub>	1-5%	trace	trace	trace
C <sub>2</sub> AS	++	++		
C <sub>4</sub> AF	++			
C <sub>2</sub> S	trace			

**Table 3. Calcium Aluminate Cement Hydration**

Temperature	Hydration reaction
<10°C	CA+10H → CAH <sub>10</sub>
10-27°C	2CA+11H → C <sub>2</sub> AH <sub>8</sub> +AH <sub>3</sub> CA+10H → CAH <sub>10</sub>
>27°C	3CA+12H → C <sub>3</sub> AH <sub>6</sub> +2AH <sub>3</sub>
Conversion f (temp, time)	2CAH <sub>10</sub> → C <sub>2</sub> AH <sub>8</sub> +AH <sub>3</sub> +9H 3C <sub>2</sub> AH <sub>8</sub> → 2C <sub>3</sub> AH <sub>6</sub> +AH <sub>3</sub> +9H

At temperatures below 10°C the formation of CAH<sub>10</sub> is favored initially. Between 10°C and 27°C, CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub> are the primary hydration products. At higher temperatures, above 27°C, C<sub>3</sub>AH<sub>6</sub> formation occurs early in the hydration process; although, it is believed that the formation of C<sub>3</sub>AH<sub>6</sub> often passes through a transient C<sub>2</sub>AH<sub>8</sub> phase. The other important (and detrimental) reactions are associated with conversion of the metastable hydrates, CAH<sub>10</sub> and C<sub>2</sub>AH<sub>8</sub>, to the thermodynamically stable C<sub>3</sub>AH<sub>6</sub> hydrates over time.

In addition to the C-A-H hydrates, AH<sub>3</sub> is a reaction product of hydration. The morphology of the AH<sub>3</sub> formed is influenced by temperature. At lower temperatures it exists as a gel and becomes increasingly crystalline as temperature increases.

Analogous hydration reactions can be written for CA<sub>2</sub> and C<sub>12</sub>A<sub>7</sub>. Other hydrates including C<sub>4</sub>AH<sub>13</sub> and C<sub>4</sub>A<sub>3</sub>H<sub>3</sub> have also been reported to exist [6, 7]. All of the reactions discussed are temperature, time, and humidity dependent.

#### 4. SILICA FUME

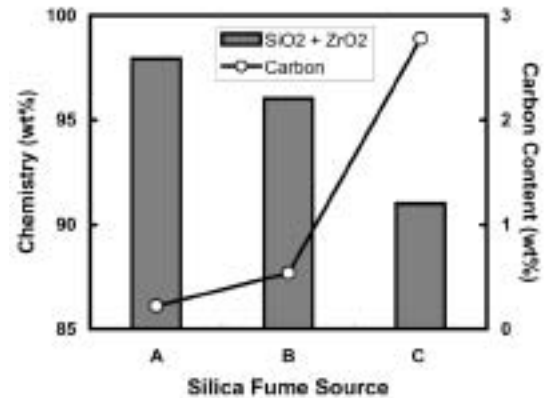
When producing silicon metal, ferro-silicon metal, or zirconium, large quantities of fine, spherical, non-crystalline SiO<sub>2</sub> dust particles are generated as a by-product (sub 1 μm, nominally 0.1-0.2 μm). The fume or dust is collected directly or after further processing steps via bag filters. Depending on the origin and the processing method, various qualities of silica fume result. Variability in silica fume characteristics in LCCs results in variability in rheological behavior and the hardening process as shown in **Table 4**. This study investigates the impact of silica fume quality on the early placement behavior of LCCs.

#### 5. EXPERIMENTAL PROCEDURES AND DISCUSSION

A low cement castable (**Table 5**) designed to contain silica fume was formulated. The characteristics of the three silica fume sources studied are shown in **Figure 1**. Three aspects of the fumes were characterized and shown to vary; the SiO<sub>2</sub>+ZrO<sub>2</sub> content, the C (carbon) content, and the concentration of water-soluble elements.

**Table 5. Model castable formulation**

Raw Material	Particle Size	Composition (wt%)
Tabular alumina	6-14 mesh	29
Tabular alumina	14-28 mesh	22
Tabular alumina	-48 mesh	29
Calcined alumina	D50 = 4 μm	10
CAC Secar <sup>®</sup> 71		5
Silica fume		5
Na-TPP		0.15
Mixing water		5.5

**Figure 1.** SiO<sub>2</sub>+ZrO<sub>2</sub> and C content of the three silica fumes used in this study.

Low cement castables prepared with the three silica fume sources were characterized for initial flow, flow decay after 30 minutes, and working time. Flow value was determined using a cone with 100 mm base diameter, 50 mm high and 70 mm top diameter. The cone was placed on a vibrating table (according to the ASTM norm 230C) filled with the castable, then removed and subjected to 20 seconds of vibration at 0.5 mm amplitude. The flow was taken as the ultimate diameter of the “cake” measured in millimeters. Flow decay was determined as the difference between the initial flow value and the flow value 30 minutes after water addition. Working time was determined to be the time after mixing at which the castable no longer flowed under vibration. The results are included as **Figure 2**. Castables prepared with fumes A and B displayed good flow behavior and reasonable working time. Silica Fume C contained a high carbon content and low SiO<sub>2</sub>+ZrO<sub>2</sub> content. It would be expected that this fume would show

**Table 4. Effect of Fume Silica properties on CAC hydration**

Element /Property % increasing	Effect on CAC hydration	Impact on LC castable properties and characteristics
Na <sub>2</sub> O, K <sub>2</sub> O, MgO, SO <sub>3</sub>	Provoke creation of gels and flocculation	Reduced flow and rapid flow decay
SO <sub>3</sub>	Retards hydration kinetics	Increased hardening time
pH	Accelerates precipitation	Decreased hardening time
BET	Accelerates precipitation	Reduced flow and rapid flow decay
LOI/moisture content	Retards dissolution via hydroxylation of the surface of the cement grains	Increases ageing and decrease shelf life of dry mix
	Promotes presence of early hydrates which affect rheology	Reduces flow
Carbon	Delays precipitation reactions	Reduces mechanical strength

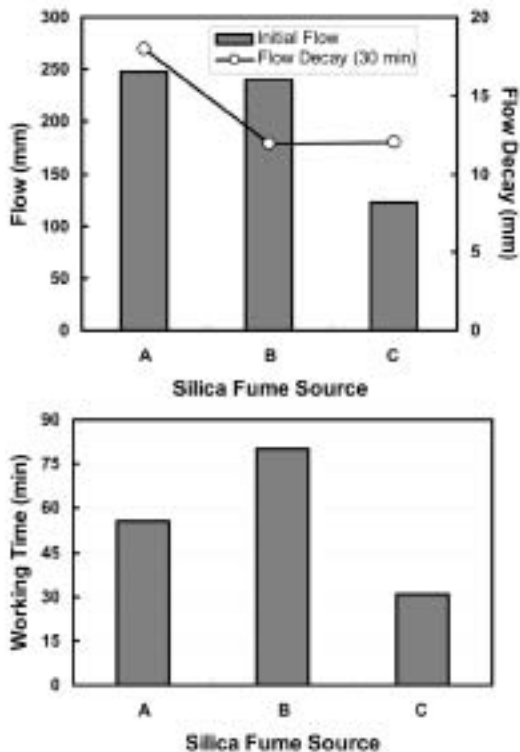


Figure 2. Flow, flow decay and working time for a low cement castable prepared using three silica fume sources.

poor placing properties relative to types A and B based upon the general observations cited in Table 4. In fact, a shorter working time and a low and inadequate flow value resulted when silica fume C was utilized.

The relationship between working time and the  $\text{SiO}_2 + \text{ZrO}_2$  and C contents were not found to have a direct correlation. Consequently, the silica fume chemistry was examined in terms of the concentration of water-soluble elements with the realization that CAC dissolution and hydration may be influenced by their presence. Figure 3 indicates the amount of soluble elements released into the mixing water for the three silica fumes. The sum of the water-soluble elements is expressed as a normalized percentage of oxides in millimoles per kilogram of silica fume. Relative to the amount of soluble ions released by CAC alone (roughly 21 mmol  $\text{Al}_2\text{O}_3$  and CaO per kg

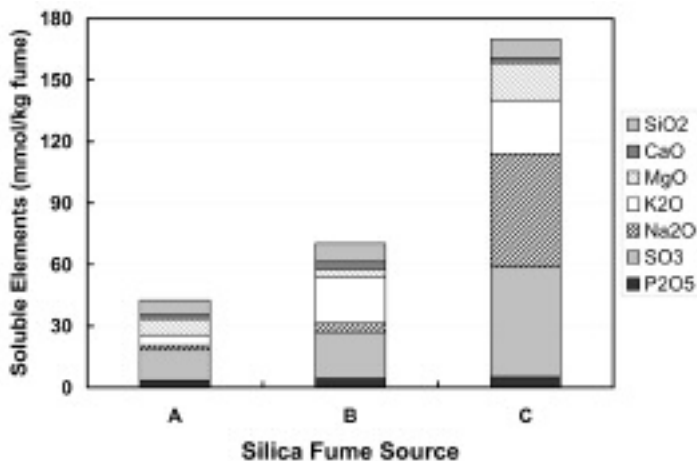


Figure 3. Water soluble elements in the three silica fumes.

CAC), the concentration of ions released by the silica fumes is significant. As a consequence, the solution chemistry during hydration is significantly modified leading to the observed variability in rheology and working time of the LCC-silica fume systems studied.

There is some correlation between the total amount of soluble elements and the initial flow value. As soluble elements in the silica fumes increase, the initial flow of the model formulation decreased. A similar tendency was observed for the carbon content.

Correlations between working time and ionic concentrations have been also been studied previously but the picture is less clear in that there are no evident simple, single correlations. These results are included as Figure 4. It seems that it is quite difficult to draw a simple picture and each silica fume has to be considered individually due to wide chemistry variations. These factors seem to impact the hydration process and, in general, it appears that low levels of impurity solubility and carbon contents are desirable.

It is necessary to continue work of this type to confirm and deepen the results of this study. It seems, however, that a detailed knowledge of the chemical nature of silica fumes is essential to understand their interactions with deflocculating admixtures and the hydraulic CAC binder. This understanding may be used to control the variability that is induced by silica fume sources into the castable in order to obtain more reliable monolithic products. This approach could then be used to develop a new binder system in the future.

## 6. SUMMARY

Low cement castables have become standard products in the portfolio of most refractory monolithic producers. The hydration of calci-

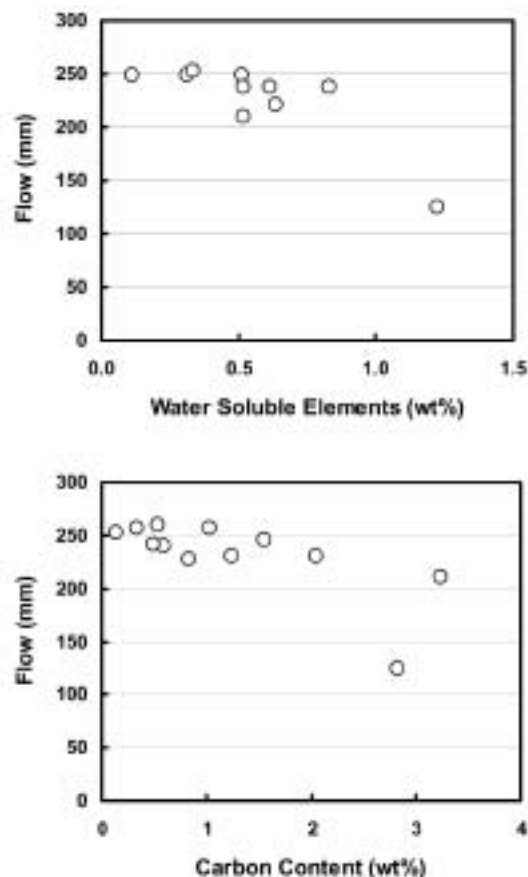



Figure 4. Vibration flow as a function of water soluble elements and C content.

um aluminate cement in LCCs depends not only on the quality and regularity of the CAC itself but also on the characteristics of the silica fume employed. Three silica fumes were characterized and tests regarding rheology and working time in a model system were conducted. The source of silica fume was found to influence CAC hydration and consequently the placement behavior of the LLCs. Although no absolute correlations could be established, in general terms, high-purity silica fumes, with low carbon and soluble foreign species levels, are desirable for LCC applications.

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## Obituary . . .

### EXPERT IN REFRACTORY TECHNOLOGY, CMU FACULTY MEMBER EDWIN RUH APRIL 22, 1924 - JAN. 28, 2007

By David Templeton Pittsburgh Post-Gazette, dtempleton@post-gazette.com or 412-263-1578.

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When it came to displaying the value of teamwork, Edwin Ruh pointed overhead to wild geese.

Flying in a V-formation meant going 71 percent farther than if a goose flew alone. Geese rotate the lead position, and those in the back honk encouragement to those in front.

As with geese, Dr. Ruh felt, a team could accomplish much more than the individual. He also believed encouragement worked better than criticism. His career as a noted expert in refractory technology, author, educator, builder, and restorer of antiques and antique automobiles proved that philosophy.

"He knew the collective could accomplish much more than the individual," his son, Edwin Ruh Jr. of Bay Head, N.J., said.

Dr. Ruh, of Mt. Lebanon, died Sunday from heart problems. He was 82.

The Westfield, N.J., native served with the 87<sup>th</sup> Infantry Division during World War II and fought in the Battle of the Bulge. He then earned bachelor's and master's degrees from Rutgers University,

where he proceeded to earn a doctoral degree with a thesis on thermo-conductivity. While at Rutgers, he married Bette Mundy.

Upon graduation, Dr. Ruh headed to Pittsburgh to become assistant director for research at Harbison-Walker Refractories Co., first in Hays, then at its Garber Research Center in West Mifflin, which he designed. The company produced refractory technology -- high-temperature material used to contain heat in furnace linings for the steel, aluminum and glass industries.

With Dr. Ruh's input, the company also built the first launchpad for the Saturn V rockets in the 1960s.

During the Nixon administration, he was appointed to serve on the Kissinger Science Commission and was one of the first to operate a business in China, primarily to import bauxite -- the ore used to make aluminum.

In 1974, he took a position with another refractory manufacturer, Vesuvius Crucible, now Vesuvius USA, based in Robinson.

"He definitely was the leader in refractory technology in the United States," said David Skelly, a Mt. Lebanon friend who worked 20 years with Dr. Ruh at Harbison-Walker.

Dr. Ruh left industry about 1976 to take a position in the metallurgical engineering and material science department at Carnegie Mellon University, where he edited Metallurgical Transactions. In 1984, he published his textbook, "Refractories for the Chemical Process Industry." He also published 55 journal articles on refractory technology and held a patent on a thermo-conductivity measuring apparatus.

In 1985, he took a teaching position at Rutgers and for eight years, commuted there weekly from Mt. Lebanon.

Another talent of Dr. Ruh was architecture. He produced a full set of blueprints in three days for his house at Virginia Manor in Mt. Lebanon. At Rutgers, he designed the McLaren Center for Ceramic Research and the fiber optics building.

About that time he also founded his own consulting company, Ruh International Inc., and helped develop ceramic tiles used as heat shields on spacecraft. He always corrected those who claimed the space shuttle disaster resulted from tile problems: "It was a glue problem," he would insist.

Over the years he restored antiques and old cars, including a 1966 Dodge Charger.

A brain-stem stroke in 1994 almost killed him and forced his retirement. Through persistence, he was able to walk without a cane and talk again and inspire other stroke victims to work to restore their health.

"He was a rock," his son said. "He did everything to perfection, set very high standards, but not in an overbearing way. He led by example."

Mr. Skelly said Dr. Ruh was interested in refractory technology until his final days. The week before he died, Mr. Skelly picked him up for lunch, but Dr. Ruh took considerable time getting to the door.

"He said he was engrossed in a journal from the Australian Ceramics Society," Mr. Skelly said.

Besides his wife and son, Dr. Ruh is survived by a daughter, Beth Ruh of Upper St. Clair, and his brother, Robert Ruh, of Dayton, Ohio.

He was buried yesterday in Bound Brook, N.J. 