HIGH PURITY CALCIUM ALUMINATE CEMENTS, PRODUCTION AND PROPERTIES

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ABSTRACT

The manufacture and use of high purity calcium aluminate cements is reviewed. Particular attention is given to the influence of these cements on the set and flow behavior of refractory castables. The use of dispersing aluminas together with careful selection of cement properties can be shown to overcome variability in typical low-cement castable raw materials such as microsilica.

KEYWORDS: Calcium aluminate cements, dispersants, dispersing aluminas, microsilica, refractory castables, monolithics

INTRODUCTION

The history of the development of calcium aluminate cements is long and well documented, covering over 150 years. Kopanda and MacZura (Ref 1) give a good summary of these developments. Calcium aluminate cement was originally developed for its chemical resistance, but found rapid growth because of its high early strength development. There were several early instances of these new cements being used for refractory applications (e.g. crucibles) but extensive use of calcium aluminate cements as binders for refractory castables did not occur until the 1920's. As calcium aluminate cements became more popular for refractory applications, the refractory performance of traditional 40-50% alumina cements quickly became a limiting factor and, to overcome these deficiencies, high purity calcium aluminate cements were developed in the mid-1950's. The availability of these high purity calcium aluminate cements significantly increased the rate at which refractory monolithics were adopted for use in severe wear applications. The primary application for high purity cements is still refractory monolithics, although there are significant applications in construction.

Both 70% and 80% alumina calcium aluminate cements have been factors in the growth of monolithic technology worldwide. However, it was the 70% calcium aluminate cements which became the dominant cements used in the development of low-cement castables in the early 1970's. New castable technologies for low moisture, self-leveling, vibratable and wet gunning (shotcreting) installations required increasingly sophisticated formulations, which often contain a wide variety of components. Since that time, the use of high-purity 70% alumina cement has increased, as the demands of these castables on the cement properties have become more severe. The overall amount of cement has continued to be reduced for the most severe refractory applications, in order to lower the total level of CaO in the formulation, which can lead to development of low-melting point phases in combination with silica containing refractory aggregates.

The availability of another critical raw material, microsilica (silica fume), was also a major factor in the development of high-performance low-cement castables. However, the presence of these raw materials in the fine fraction of the castable will lead to matrix interaction, as the hydration of the calcium aluminate cement is affected by such factors as pH and presence of organic contaminants. The hydration of the calcium aluminate cement can be significantly affected by the quality of the microsilica. As the type and amount of available microsilica grades has increased, interaction between the microsilica and cement has been shown to cause problems in the control of monolithic set and flow.

MANUFACTURING

High purity calcium aluminate cements are manufactured by sintering (Figure 1), usually in rotary kilns. This is in contrast to the fusion route generally used to manufacture lower purity calcium aluminates. Alcoa World Chemicals manufactures high purity calcium aluminate cement in its Rotterdam (The Netherlands) plant. In 2001, the decision was taken to concentrate worldwide cement production in this plant to optimize the availability of consistent calcium aluminate cement for the global cement market. The Rotterdam plant has state-of-theart production controls, and utilizes the Alcoa Production System (APS) to ensure consistent product, delivered to the customer when it is needed, at the lowest cost. APS utilizes dedicated materials flow paths, based on pull signals from the downstream process, with intermediate stores for management of production to meet customer demand (Ref 2).

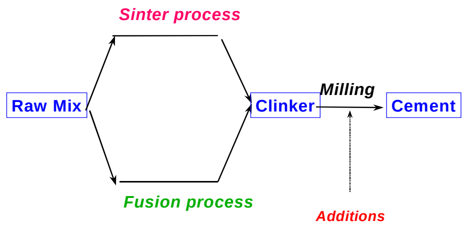

Figure 1 - Cement Production Process Type

70% calcium aluminate cements are usually manufactured from high-purity raw materials, such as low-silica lime-bearing compounds and reactive aluminas. It is certainly possible to manufacture 70% calcium aluminate cement from lower purity raw materials, but the inconsistency of the feedstocks will lead to variability in finished product properties which will, in turn, make the manufacture of consistent refractory monolithics more difficult.

The production process for making 70% alumina calcium aluminate cements is, on the surface, very simple. High purity raw materials are blended and ground together and fed to a rotary kiln. The raw materials sinter very readily to yield a cement clinker. The lime and alumina compounds react to form a variety of cement phases (Figure 2), predominantly CA (calcium mono-aluminate) and CA2 (calcium di-aluminate). The effect of impurities, particularly SiO_2, TiO_2 and Fe_2O_3 (S, T, F) can have a marked influence on the amount and ratio of these phases that can, in turn, lead to inconsistency in cement properties. This is because these impurities react preferentially with the calcia and alumina, producing (generally) non -hydratable compounds such as calcium titanate, calcium alumino-ferrites and calcium alumino-silicates and thus reducing the amount of available calcium aluminate for proper cement hydration and affecting setting time and strength development.

QUALITY

Alcoa manufactures four grades of 70% cement, targeted at different applications. CA-14 cements are traditional 70% cements, whereas CA-270 is a 70% cement with different mineralogy and particle size distribution, developed to give low water demand and high hot strength. The development of CA-270 required the ability to precisely control clinker production under conditions of great stability. Transferring the knowledge gained, Alcoa could improve the clinker process to be able to precisely control CA-14 cement properties with regard to working and setting times. CA-14 is now offered in three tightly controlled grades, differentiated by working time (Figure 3). These grades are designated as CA-14S (S = summer grade, cement is relatively slow-setting), CA-14M (M = Medium) and CA-14W (W = Winter grade, relatively fast setting). The ranges of the tested properties are tighter than previously offered, giving good consistency between lots of cement. CA-14 properties are controlled without the use of any chemical additives, only by consistent but different relative ratios of the cement phases (Ref 3).

<u>Sintering:</u> Lime + alumina react to hydratable clinker phases

$$C + A \Rightarrow C_{12}A_7 > CA > CA_2$$

- Setting behavior of Clinker Phases

↳ Fast Setting:	$C_{12}A_7$
↳ Moderate Setting:	CA
↳ Slow Setting:	CA_2, C_4AF
↳ Minimal or Non-Setting:	CA_6, α-Al_2O_3, C_2AS, CT, C_2F

●with C=CaO, A=Al_2O_3 , S=SiO_2 , F=Fe_2O_3 , T=TiO_2

Figure 2 - Calcium Aluminate Cement Phases

Product		CA-14 W		CA-14 M		CA-14 S		old CA-14 M		old CA-14 S	
		min	max	min	max	min	max	min	max	min	max
Vicat Setting Time		10% H2O						12% H2O			
Initial Setting	[min]	150		230		320		150		290	
Final Setting	[min]	170	250	250	350	350	480		350		450
Vibration Flow											
F10	[cm]	15		15		15		15		16	
F30	[cm]	>13		14		14		12		14	
F60	[cm]	>12		13		13		11		12	

Figure 3 – CA-14 Setting Time Comparison

To illustrate the differences between grades, CA-14 has been tested in three separate standard refractory formulations; Alcoa’s Nortab test grog, an alumino-silicate low-cement vibration castable, and a tabular alumina self-flow castable.

Test Mix			NORTAB		
CAC			CA-14 W	CA-14 M	CA-14 S
Testing temperature			20°C	20°C	20°C
+Mixing Water	% H2O	%	10	10	10
Vicat setting	Initial set	min	220	280	330
	Final set	min	230	300	350
Vibration flow	F 10	cm	15.7	16.6	17.2
	F 30	cm	15.5	16.6	17.4
	F 60	cm	15.4	16.2	17.4
Exoth. Reaction	Exo start	min	227	289	313
	Exo +5°C	min	278	337	357
	Exo max	min	367	416	432
Flex. Strength	20°C/24h	N/mm²	8.9	9.1	8.0
	110°C/24h	N/mm²	12.5	13.5	11.9
	1000°C/5h	N/mm²	6.4	5.6	6.1
Crush. Strength	20°C/24h	N/mm²	49.1	43.8	46.3
	110°C/24h	N/mm²	63.1	70.0	60.4
	1000°C/5h	N/mm²	38.4	36.9	36.8

Figure 4 – CA-14, Nortab Test Mix

Test Mix			SFL-204		
CAC			CA-14 W	CA-14 M	CA-14 S
+ Additives	ADS-3	%	0.5	0.5	0.5
	ADW-1	%	0.5	0.5	0.5
+Mixing Water	% H2O	%	4.5	4.5	4.5
	F 10	cm	23.8	23.0	24.2
	F 30	cm	20.3	23.0	24.4
	F 60	cm	No flow	No flow	18.3
Exoth. Reaction	Exo start	min	36	54	59
	Exo start 2	min	156	197	209
	Exo Max	min	257	306	311
Crush. Strength	20°C/24h	N/mm²	19	19	18
	110°C/24h	N/mm²	91	89	74
	1000°C/5h	N/mm²	44	46	44
	1500°C/5h	N/mm²	293	301	292

Figure 5 – CA-14, Tabular Self-flow Test Mix

Test Mix			Mulcoa		
CAC			CA-14 W	CA-14 M	CA-14 S
+Mixing Water	% H2O	%	6.0	6.0	6.0
Vibration Flow	F 10	cm	18.8	18.4	18.5
	F 30	cm	18.6	17.5	18.3
	F 60	cm	16.3	17.1	17.7
	F 90	cm	No flow	13.7	17.5
	F 120	cm		No flow	No flow
Exoth. Reaction	Exo start	min	51	74	76
	Exo start 2	min	211	236	227
	Exo Max	min	301	334	328
Flex. Strength	20°C/24h	N/mm	4.1	4.0	4.0
	110°C/24h	N/mm	9.6	9.8	8.9
Crush. Strength	20°C/24h	N/mm	25.0	23.8	23.1
	110°C/24h	N/mm	60	59.4	60.6

Figure 6 – CA-14, Mulcoa Vibration Test Mix

As standardized test methods are often used to compare types and grades of ordinary Portland cements, our Nortab test grog was developed to standardize test methods between Alcoa laboratories and our customers for evaluation of quality of calcium aluminate cements. Alcoa also utilizes the measurement of castable heat development (exotherm) to study the evolution of heat from the reactions of the cement during setting and hardening. Two points on the curve of heat evolution vs. time are particularly important. Exo Start is the time at which the temperature of the test castable begins to rise, and corresponds to the end of workability, Exo Max is the time of maximum temperature rise, and corresponds with hardening, to the point of developing sufficient strength for demolding (Ref 4).
In order to demonstrate specific raw material concepts, Alcoa has developed test mixes that more closely match formulations common in the refractories industry. The two formulations used here (Mulcoa VIB and SFL 204) are typical of these test mixes and are utilized in Alcoa's Applications Laboratories worldwide.

Figures 4-6 show that the type of cement used controls the properties of the individual mixes. In general, the properties of the mixes follow the properties of the individual cements – i.e., as the cement addition changes from CA-14W (fast) to CA-14S (slow) the properties of the mixes change similarly. The importance of this control can not be underestimated when refractories manufacturers have to produce mixes intended for widely varying environmental conditions (high summer heat vs. cold winters).

Purity of raw materials is extremely important in controlling properties, particularly hot properties (creep, hot MoR). CA-14 and CA-270 are designed with the highest purity raw materials consistent with maintaining realistic cost. A comparison of CA-14 and CA-270 with other available 70% cements shows the dramatic effect of just small amounts (even for a LCC mix with only 5% CA cement) of impurities on the hot MoR and, by extension, all high temperature properties (Figure 7). Hot MoR drops by about 80% with increase of impurities by about 1%.

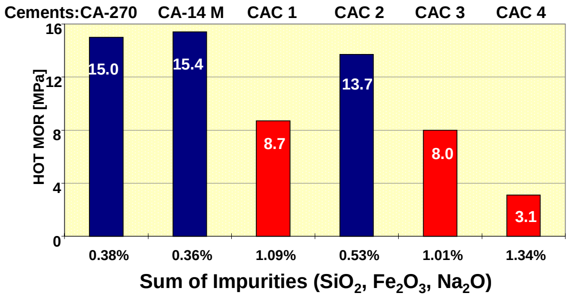

Figure 7 – Effect of Impurities on Hot MoR (1500C) of Tabular vibration castable castable, 5% cement

CASTABLE FORMULATION

Another aspect of the interactions present in low-cement castable materials is the presence of strong dispersant systems, which are required for modern low cement castables containing reactive aluminas or microsilica (silica fume). Alcoa has developed dispersing aluminas designed to optimize flow and setting behavior under conditions of widely differing ambient temperature (Figure 8). It is well known that the reduction of water content improves physical properties of the refractory castable, as the material components become more tightly packed and porosity is minimized. However, under normal conditions, there is a lower limit of water requirement, below which the castable will not flow. Alcoa's dispersing aluminas decrease water requirements when compared to "traditional" dispersant packages, as well as allowing superior control over flow and setting behavior at varying temperatures.

Short/long workability at different temperature conditions

Temperature Range:	**< 15 °C**	**15 - 25°C**	**> 25°C**
Dispersant Combinations:	ADW 1 and ADS 1	ADW 1 and ADS 1 ADW 1 and ADS 3	ADW 1 and ADS 3
Workability -> SHORT	0,9 % ADW 1 0,1 % ADS 1	0,5 % ADW 1 0,5% ADS 1 or 0,8 % ADW 1 0,2 % ADS 3	0,1 % ADW 1 0,9 % ADS 1 or 0,5 % ADW 1 0,5 % ADS 3
Workability -> LONG	0,5 % ADW 1 0,5 % ADS 1	0,4 % ADW 1 0,6 % ADS 3	0,1 % ADW 1 0,9 % ADS 3

Figure 8 – Dispersing Aluminas

Figure 9 shows the control of setting and hardening, as measured by Exo, of a tabular alumina based self-flowing castable with a varying ratio of retarding and accelerating dispersing aluminas. ADS 3 is stronger retarding than ADS 1, ADW 1 is accelerating. Pure ADS 3 may result in never setting.

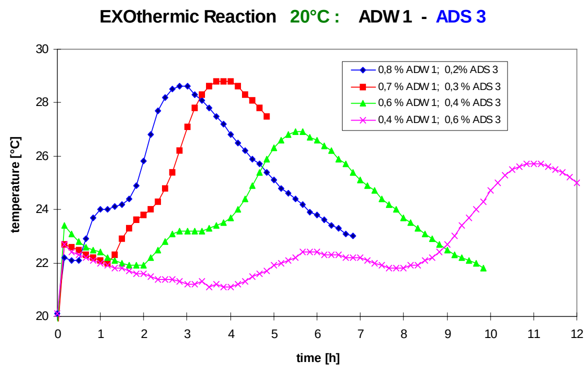

Figure 9 – Effect of Dispersing Aluminas on Exo

The traditional additive packages for low-cement castable have, for many years, been based on a very small variety of chemicals – phosphates for deflocculation, typically sodium hexa-metaphosphate or sodium tri-poly phosphate, water-reducing agents such as citric acid or sodium citrate, and (occasionally) an accelerator such as lithium salts to overcome the retarding effects of the other additives. A review of the effects of various additives on castable performance was given by Banerjee (Ref 5). Such an additive cocktail has the advantage of being well proven. However, the drawback is the very small amounts of these materials required. Only a few tenths of one percent in total are usually needed to significantly affect the set and flow of castables. The primary concern then becomes the physical dispersion of these additives throughout the dry castable during batching. Because the dispersing aluminas are primarily fine reactive alumina with blended organic ingredients, the alumina thus acts as a carrier, allowing more thorough mixing of the dispersant into the castable. The dispersing alumina system requires the addition of a higher amount of overall additive and thereby the improved mixing will yield significant improvement in consistency.

There is a further difference in the efficiency of dispersing aluminas when used in conjunction with 70% calcium aluminate cement. A dispersing alumina system is capable of significant reduction in water demand over an equivalent traditional phosphate/citrate system. Figure 10 shows the reduction in water demand capable when switching between these two systems. Consequently, a considerable improvement in physical properties is gained. One concern of such a dense castable would be the thermal shock resistance. However, TSR tests show that such a formulation is quite capable of surviving 20 cycles without deterioration.

	7/1	VB 173 (7/1)
T-60 up to 6 mm [%]	83	83
CL 370 C [%] CT 4000 SG-R [%]	4.5 6.5	4.5 6.5
CA-14 S [%]	6	6
Additives [%]	Phosphate 0.05 Citric acid 0.03	ADS 3 0.4 ADW 1 0.6
H2O [%]	5.5	4.6
VIB Flow 10 min [cm]	18.8	18.5
20 °C / 24 hrs CCS [MPa]	8	31

Figure 10 – Comparison of dispersing aluminas to traditional additives in a Tabular vibration test mix

The original dispersing aluminas ADS 1, ADS 3, ADW 1 did not work well in systems containing microsilica. As these systems are important formulations for low-, and ultra-low-cement castables, new dispersing aluminas were developed to be compatible in microsilica containing systems. The M-ADS 1 and M-ADW 1 dispersants were tested in a tabular alumina based self-flow castable containing 3% microsilica (Fig. 11). A plot of the exotherm curves for the mix with varying ratios of accelerating and retarding dispersing aluminas shows that a similar control of setting and hardening time is available with these silica compatible products as with the other dispersing aluminas products.

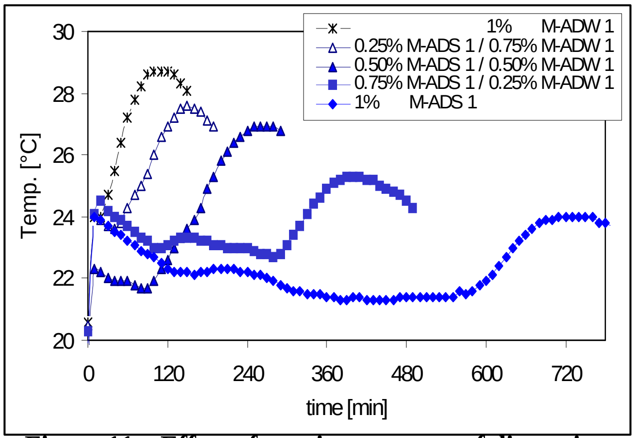

Figure 11 – Effect of varying amounts of dispersing aluminas on exotherm of a microsilica-containing tabular self-flow castable

EFFECT OF MICROSILICA PURITY

It has been clear for some time that the precise setting characteristics required by the current generation of low-cement castables is significantly influenced by the chemical purity of the microsilica added (Ref 6). The purity of microsilica, and its effect on the control of low-cement castable systems, is also of critical importance in the development of robust castables. The effect of low-purity fumes are primarily seen in flow and set control, as seen in the following figures. Three microsilicas were incorporated into mullite-based formulations (Figure

- **Formulation of Mulcoa test-castable:**

M-60 88%
Microsilica* 5% *)SiO2 = 98%, 97%, 94%
CAC-cement 7% **) CA-14 W, CA-14 S**

H2O: 6%
M-ADS 1/ M-ADW 1 addition: 1% in total
Test temperature condition: 20 °C

Figure 12 – test castable components

Castable test No.	1	2	3	4	5	6
Microsilica 98%	5			5		
Microsilica 97%		5			5	
Microsilica 94%			5			5
Cement CA-14 S [%]	7	7	7	7	7	7
Dispersing Alumina M-ADS 1 [%]	0.5	0.5	0.5	0	0	0
Dispersing Alumina M-ADW 1 [%]	0.5	0.5	0.5	1	1	1
Mixing Water [%]	6	6	6	6	6	6
Flow Diameter F10 [mm]	194	186	180	140	186	168
Flow Diameter F30 [mm]	185	181	177	no flow	102	161
Flow Diameter F60 [mm]	183	180	172	no flow	no flow	146
Exo start [min]	77	199	254	17	35	115
Exo max [min]	261	382	1354	131	151	270

Figure 13 - Flow and exo in Mulcoa test-castable with CA-14 S cement

Castable test No.	7	8	9	10	11	12
Microsilica 98% SiO2	5			5		
Microsilica 97% SiO2		5			5	
Microsilica 94% SiO2			5			5
Cement CA-14 W [%]	7	7	7	7	7	7
Dispersing Alumina M-ADS 1 [%]	0.5	0.5	0.5	1	1	1
Dispersing Alumina M-ADW 1 [%]	0.5	0.5	0.5	0	0	0
Mixing Water [%]	6	6	6	6	6	6
Flow Diameter F10 [mm]	193	186	169	191	183	175
Flow Diameter F30 [mm]	134	169	165	191	180	170
Flow Diameter F60 [mm]	no flow	100	160	128	178	169
Exo start [min]	49	77	187	115	238	428
Exo max [min]	216	244	435	544	638	1514

Figure 14 Flow and exo in Mulcoa test-castable with CA-14 W cement

12) using both fast setting (CA-14W) and slow setting (CA-14S) cements. The significant difference between the three grades of microsilica is in the overall chemical purity, with the total silica content, ranging from relatively low (94% SiO_2) to high (>98%). It is important to note that dispersing aluminas can be adjusted to overcome the deleterious effects on set and flow of low-purity microsilicas, as seen in Figures 13-14. Note that even though the decreasing purity of the microsilica can have a significant effect on the setting and flow characteristics of the mix, this can be overcome with the correct choice of cement and use of dispersing aluminas.

SUMMARY

The production of 70% calcium aluminate cements has been improved to allow close control over the cement clinker phases developed. This allows close control of cement properties, which is critically important to the use of these cements in current high-performance refractory castables. In particular, the control of set and flow characteristics has allowed the development of high-flow castables. The combination of consistent cement together with dispersing aluminas allows considerable flexibility in castable formulation, and may be able to overcome inconsistencies introduced by other raw materials such as low-purity microsilicas.

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