

The Impact of Different Additive Systems upon the Properties of a High Purity Low Cement Castable

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Modern dense refractory castables can be built around a variety of matrix compositions depending on the final usage characteristics required. These matrix compositions use a variety of fine reactive fillers such as alumina, spinel and fume silica in conjunction with calcium aluminate cement and additives. Each of these components presents a different series of formulation challenges for the refractory producer, not least of which is the optimisation of placing properties whilst achieving the target installed properties. Additives play an important role in determining the rheological behaviour and setting characteristics of these systems. This paper will review additives used in three castable systems, namely alumina-silica, alumina-spinel and alumina-alumina and the mechanisms that determine their effectiveness.

1 Introduction

Formulating deflocculated or low cement castables is not particularly difficult. However,

formulating to ensure repeatable performance of a castable within a targeted quality range over an extended period of time can be quite challenging – particularly when considering the rapidly changing international raw material market. Dense, deflocculated refractory castables have complex compositions despite being formulated from essentially generic components, namely: aggregates, fine reactive fillers (e.g. alumina and fume silica), additives and calcium aluminate cement (CAC). And it is precisely the complexity of the number of components that leads to inconsistencies in the placing behaviour and final properties of the castable. It is thus very important to consider the entire system to be interdependent since the interactions that occur between the soluble elements from all of the raw material components will affect the behaviour of the castable.

Deflocculated castables rely on the use of fine reactive fillers (silica, alumina, chrome etc.) to more effectively pack particles in the cast mass. At the same time, the calcium aluminate cement content is often reduced in these systems (hence, 'low cement castables') due to the higher inter-granular contact between the increased fine particles coming from the addition of the reactive fillers. Dispersing additives are, however, needed to fluidify the fine particles so that the castable can be placed at low water additions. Incorporating these fillers, reducing the cement content and using additives results in:

- Lower CaO in the castable which reduces the amount of low melting CAS2 and C2AS phases.
- Reduced water demand reduces porosity and increases the matrix density.
- Increased particle packing density.

And these physical factors dramatically improve the high temperature mechanical properties and corrosion and abrasion resistance of the castable.

However, the key formulation parameter is to ensure satisfactory placing characteristics at low water demand in order to provide a dense, low porosity matrix structure, otherwise all the benefits of using a deflocculated castable will be lost. And this is precisely why the additives are such critical components of these systems. The type of additive used is largely dependent on the specific choice of fillers. Two broad families of deflocculated castables can be identified – those that contain fume silica (commonly referred to as "alumina-silica" systems) and that using other reactive fillers (e.g. alumina-alumina and alumina-spinel systems). Previous studies [3, 4] have shown the impact and the role of additives and fillers in a variety of castable systems. The use and effect of additives within each of these systems will be reviewed below.

2 Alumina-silica systems

The most commonly used fine fillers are fume silica and fine alumina in conjunction with high purity calcium aluminate cement (typically, with a 70 % alumina content). The fine alumina and fume silica react at high temperature to form mullite (providing CaO percentage is kept low) which enhances the high temperature thermo-mechanical behaviour of the castable.

The concentration of the soluble compounds in fume silica produced as by-products of ferrosilicon, silicon or the zirconium production can vary from one lot to another and significantly from one product to the next. The most typical soluble species in fume silica are sulphates, phosphates and chlorides of magnesium, calcium, potassium and sodium. Using silica fume that contains a small but, with respect to calcium aluminate cement dissolution and precipitation, significant amount of soluble species [5] can cause the setting time of a castable to become unpredictable. Minimising

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Tab. 1 The effect of fume silica type on the placing properties of a castable

LCC formulation [mass-%]			
Alumina aggregate	80		
Reactive alumina 1	10		
Fume silica	5		
70 % CAC	5		
	FS1	FS2	FS3
Analysis of fume silica			
SiO ₂ [%]	97,5	85,5	91,2
Carbon [%]	< 0,5	4,1	2,0
BET [m ² /g]	20	17	21
pH	06. Sep	09. Apr	08. Jul
	LCC1 with FS1	LCC2 with FS2	LCC3 with FS3
Castable flow [%]			
T = 0 min	158	80	112
T = 30 min	144	0	115
T = 60 min	140	0	105
Working time [min]	95	30	135

the variability of the soluble salts greatly improves the consistency of the rheological behaviour of the castable.

Tab. 1 shows the effect that changing the fume silica source can have on the placing properties of the castable. The formulation used is a typical high purity alumina low cement castable with a 5 % addition of a 70 % alumina cement together with 10 % of a fine reactive alumina and 5 % fume silica. The water addition was kept constant at 5 %.

The effect on castable workability, as measured by flow under vibration, is extremely noticeable. In addition, the castable working time is also clearly affected by the quality of fume silica used. It is possible to minimise the effects of the different fume silica types on the system by adjusting the additive additions. Fig. 1 shows the effect that sodium triphosphate (STPP), in this case, has on the setting time when two different fume silica types are used.

The choice of fine alumina is also important in determining castable placing properties. However, it also has an effect on the degree of mullitisation at high temperature which is important since the amount of mullitisation will govern the hot strength development of the castable. Using the same base castable system as that outlined in Tab. 1, different fine reactive alumina powders were assessed to identify the effects on the castable placing properties.

Two key parameters were found to strongly affect the castable fluidity, namely the BET surface area and the soluble soda (Na₂O) level in the alumina [6]. Increasing the BET and in-

creasing the soda level were both found independently to reduce the flow, accelerate the CAC hydration and shorten the working time. Fig. 2 shows the relationship between the soluble soda level in the various reactive aluminas tested and the castable working time. It should be noted that the other properties of fine aluminas such as particle size and crystal size can also have a significant impact upon castable properties. In many instances, it may be necessary to add a number of additives in order to accurately control the placing characteristics of the formulation. By using several additives, each with a different function, it is possible to optimise the castable rheology and obtain more consistent behaviour between batches. For example, the use of a multiple additive system allows an optimisation of the initial castable flow as well as the flow decay. The example in Tab. 2 shows the effect of a multiple additive system on castable properties. In this example, the use of four additives in LCC 5 allows the water demand to be reduced by 20 % whilst maintaining the placing properties of the castable. The lower water content significantly reduces the porosity of the castable and dramatically improves the mechanical properties and the wear performance. Two dispersing additives are used to disperse the fine fillers, i.e. the phosphate is used for the fume silica whilst the polyacrylate is used to disperse the reactive alumina. Two types of retarders / stabilizers are added to ensure a working time of 60 min even at the lower water demand of 4 %.

Optimising such complex systems is time consuming. In the case of deflocculated alumina-

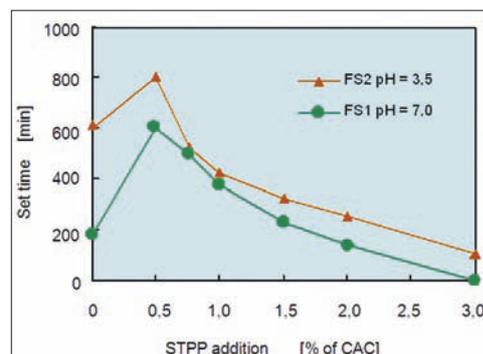


Fig. 1 The effect of STPP additions in combination with different fume silica types on the setting time of a low cement castable

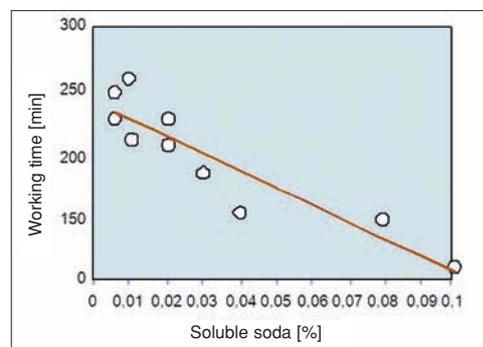


Fig. 2 The effect of soluble soda in fine reactive alumina fillers on the working time of a low cement castable

silica systems where lot to lot variations in fume silica quality (essentially due to this raw material being a by-product rather than being produced to meet strict chemical specifications) can be considered the norm, adjusting the additive additions to provide consistency in the placing qualities of the castable was generally considered to be a continuous process.

However, to make deflocculated microsilica castables more robust, a new calcium aluminate binder with ~ 84 % Al₂O₃ has been developed and introduced as Secar Xeniom™. It contains a buffering system to reduce the inconsistencies in castable performance caused by the variability in the soluble components of fume silica types and other types of aggregate fines (like fireclay, andalusite and bauxite). At the same time, the use of Secar Xeniom reduces ambient temperature sensitivity so that even andalusite based LCCs, well known to exhibit delayed setting at low temperatures, have a homogeneous and fast set. The new binder with its integrated and rapid deflocculating system is also more robust with different kinds of industrial intensive wet mixing

Tab. 2 The effect of additive type on a low cement castable

	LCC 4	LCC 5
	Single additive	Multiple additive
Formulation		
Alumina aggregate	80	80
Reactive alumina 1	10	10
Fume silica	5	5
70 % CAC	5	5
Additives [% of castable]		
Sodium tripolyphosphate	0,12	0,03
Sodium polyacrylate		0,03
Sodium bicarbonate		0,015
Citric acid		0,015
Water addition [%]	5	4
Vibration flow [%]		
T = 0	123	109
T = 30	80	80
Working time [min]	50	60
Cold crushing strength [MPa]		
110 °C	54	165
800 °C	166	165
1100 °C	210	245

equipment compared to a reference system based on a 70 % CAC with TPP as the deflocculant.

The basic characteristics of this new binder system, Secar Xeniom are shown in Tab. 3 in comparison to the reference calcium aluminate cement, Secar® 71, with 70 % Al₂O₃. The new binder Secar Xeniom allows deflocculated castables to be formulated:

- Without addition of further deflocculants
- With a higher robustness to lot-to-lot variations in fume silica
- With a large range of microsilicas with more than 92 % SiO₂ (+ ZrO₂)
- That are easy to switch from one aggregate to another (e.g. bauxite vs. andalusite or fireclay etc.) without significant changes in hardening characteristics
- With a homogeneous hardening of the full monolithic body even at low ambient temperatures and with andalusite in the mix
- That they are easy and quick to mix with water so that a wide range of concrete mixers can be used.

The model formulation LCC 6 (Tab. 4) is based on this new binder system and will be compared with a classical LCC system (LCC 7) which is based on calcium aluminate cement with 70 % Al₂O₃, Secar 71. In the latter case, sodium tripolyphosphate has been chosen as deflocculant (LCC 7).

Tab. 3 Characteristics of the calcium aluminate binders Secar Xeniom and Secar 71

		Secar Xeniom	Secar 71
Main fields of application	Unit	Fume silica containing ULCC, LCC, MCC	All types of deflocculated and non-deflocculated castables
Al ₂ O ₃	%	82 – 85	68,7 – 70,5
CaO	%	14 – 16	28,5 – 30,5
Blaine	cm ² /g	> 10 000	3800 – 4400
BET	m ² /g	5 – 8	1
Main mineral phases		CA, CA2, A	CA, CA2
Castable deflocculation system		integrated	not integrated
Buffering system against raw material and ambient temperature variability		integrated	not integrated

In order to be able to compare the two formulations at constant castable chemistry, 5 % Secar 71 and 5 % calcined alumina have been replaced by 10 % Secar Xeniom. Since Secar Xeniom already contains a deflocculation system it was not necessary to add TPP in the case of LCC 6. In order to evaluate the robustness of this new binder system different aggregates and fume silicas have been tested in the two model recipes. The amount of fume silica has been fixed at 5 % in all cases and the amount of aggregates at 85 %. The aggregates comprise the fractions 0 – 0,09 mm, 0 – 1 mm, 1 – 3 mm and 3 – 6 mm with similar overall grain size distributions for the formulations with different aggregate types. Rheology, castable setting and strength development have been measured using the classical methods as described by [7]. The water addition has been adapted to reach similar initial flow values on a vibration table for the different mixes.

Testing three different lots of 95 % silica fume in LCC 7 with Secar 71 and TPP gives three castables with very variable working times (~ 50 min to ~ 115 min). The buffering system employed in Secar Xeniom, however, limits the impact of the lot-to-lot variation in the microsilicas and provides three castables (LCC 6) with very similar working times.

Further, Secar Xeniom is also very effective in masking the effects of impurities in fume silicas from different sources. Fig. 4 shows the effects of substituting undensified fume silicas of different purities in the bauxite based LCC 6 and LCC 7. In addition, the reference system, LCC 7 with Secar 71 has been formulated in one case with Na-TPP (0,08 %) and in the second case with a combination of 0,1 % polyacrylate (PA) and 0,02 % citric acid (CA) instead of the Na-TPP. Both reference systems

show a high sensitivity to the different silica fume products and the PA/CA system seems to be even more sensitive than the Na-TPP system. Contrary to this behaviour, LCC 6 with Secar Xeniom, and its integrated buffering and deflocculating system, shows very stable behaviour in combination with all 5 fume silica products.

Fig. 5 summarizes the effect of the aggregate type on the working time. A high purity (97 % silica) microsilica has been used in this case for all the mixes. The concretes with tabular alumina and bauxite give similar working times in the reference LCC 7. The working time becomes extended when andalusite is used and shortens for 60 % and 45 % fireclays. When the castables are formulated with the Secar Xeniom integrated binder (LCC 6), they show very similar working times irrespective of the aggregate type. This makes switching a castable between bauxite and andalusite or combinations of both much easier, and facilitates a modular formulation and production concept.

3 Alumina-spinel and alumina-alumina systems

The fundamental deflocculated castables, namely standard low cement castables are somewhat handicapped in terms of high temperature performance. This is due to the formation of CAS2 and C2AS (where C = CaO, A = Al₂O₃, S = SiO₂) phases which are liquid at relatively low temperatures. Thus, once these phases form in any quantity the hot mechanical properties of the castable deteriorate rapidly.

Improvements in low cement castables can only be made through a change in the basic mineral system. In the case of deflocculated castables there are two options but both op-

Tab. 4 Model formulations with equal castable chemistry but 2 different binder systems

		LCC 6	LCC 7
Aggregates	0 – 6 mm	85	85
Silica fume	≥ 93 % (SiO ₂ + ZrO ₂)	5	5
New binder Secar Xeniom	84 % Al ₂ O ₃	10	-
Reference LCC binder Secar 71	70 % Al ₂ O ₃	-	5
Calcined alumina AC44B4	d ₅₀ = 4 μm	-	5
Na-TPP powder		-	0,08
		100	100,08

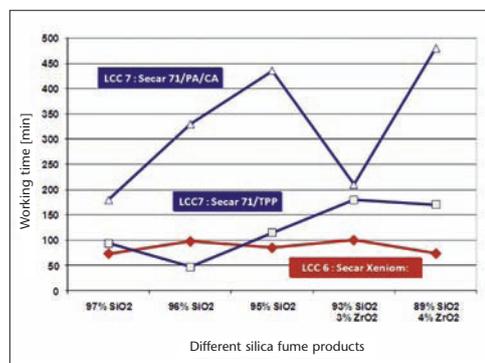


Fig. 4 Working time of the bauxite based LCC 6 and LCC 7 with fume silicas of different purity

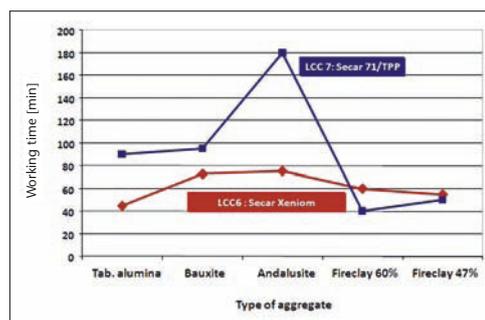


Fig. 5 Working time of LCC 6 and LCC 7 with different types of aggregates

tions involve moving the mineral system from a ternary C-A-S system to a binary system based on either alumina-silica or alumina-lime. The objective is to reduce the formation of liquids at relatively low temperatures within the castable matrix. The first option relies on reducing the CaO level (i.e. the cement content) down to trace levels of < 1 %. When CaO levels are reduced to ultra low levels then mullite is readily formed at high temperature

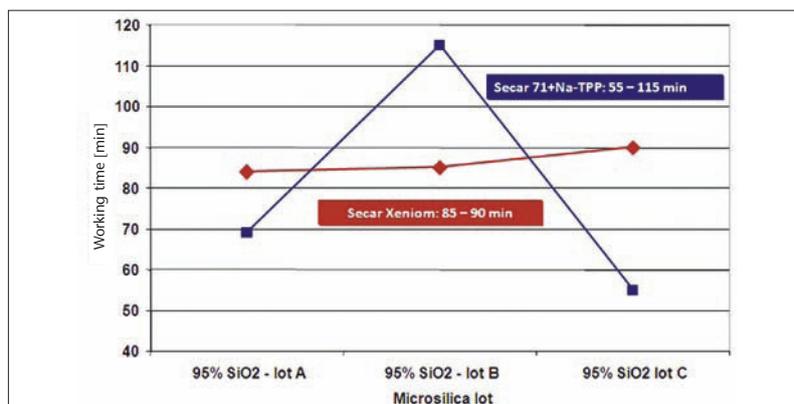


Fig. 3 Working time of LCC 6 and LCC 7 with different lots of a 95 % fume silica using bauxite aggregates

through the reaction of silica and fine alumina. This controls the high temperature mechanical properties. These ultra low cement castables exhibit greater mechanical strengths at high temperatures. The second option is to reduce the silica level and formulate deflocculated castables in the alumina-lime system. This binary system relies on the formation of CA6 as the high temperature bonding phase. This is formed through the solid phase sintering of fine alumina and calcium aluminate cement during castable use.

However, removing the fume silica from the deflocculated castable poses several problems in terms of maintaining the placing characteristics of the castable. Generally, more rapid flow decay profiles and shorter working times are seen with low cement castables containing alumina only. This is due to the different interactions within the castable bond system [8]. Essentially, when fine silica is present it provides a natural retarding effect which extends the castable working time. When the fume silica is removed and replaced with alumina this effect is lost and must be compensated by a change of additive system. This, once again reinforces the notion of an interdependent system based upon calcium aluminate cement, reactive fillers and additives.

The base model formulation used for alumina-spinel castables can be found in Tab. 5. The type of fine spinel used was chosen to be inactive as far as the castable placing properties are concerned but thermally reactive at high temperature. In fact, the presence of spinel was not found to have any marked effect upon the castable rheology. This type of formulation is most commonly used in ladle casting applications where a high initial flow followed by a stable flow decay and a working time of at

least 45 to 60 min was considered to be critical rheological properties.

In order to achieve these rheological properties, the binder phase (i.e. the CAC, additives and reactive alumina) must be optimised. Tab. 6 shows three basic additive systems which allow the system to meet the basic placing property criteria. The three systems use fundamentally different dispersants with correspondingly different active mechanisms. Additive pack 1 is a pure electrostatic dispersing system that uses boric acid as a retarder. Additive pack 2 uses a polyacrylate dispersant with two retarders, whilst additive pack 3 uses a polymer system with an electrosteric type of dispersing mechanism. In the latter case the dispersing and retarding effect of the PCE is so strong that a small addition of an accelerator (lithium carbonate) is necessary. The resulting castable flow for each of these additive types is shown in Fig. 6. The minimum flow considered to provide acceptable placing properties for this system was 160 mm. It can be seen that with additive packs 2 and 3, sufficient flow properties can be maintained even at very low water additions (less than 4 %). Furthermore, the working times of these casta-

Tab. 5 Model formulation for an alumina spinel system (LCC 8)

Raw materials [%]	LCC 8
Sintered alumina -7 mm	58
Alumina-spinel -1 mm	25
Silica fume	-
Reactive alumina (BET: 3,3 m ² /g)	11
70 % calcium aluminate cement	6

bles were maintained in line with the target values.

Whilst optimising the placing properties to ensure suitable fluidity at low water demand, steps must be taken simultaneously to ensure that the strength development, de-moulding times and final thermomechanical properties are not compromised by an optimisation of the placing properties. This can be seen in Tab. 7 where the short term mechanical strengths (24 h after casting) are quoted for systems based on different reactive aluminas. This table clearly shows that additive pack 3, despite having the optimum flow properties, does not yield the best results in terms of mechanical strength development. This would probably have implications for de-moulding times.

An analysis of the underlying mechanisms [2] shows that two types of interactions exist which explain the working time/flow and the acquisition of mechanical strength.

The first interaction is related to the dissolution of the calcium aluminate cement into solution and it therefore controls the working time.

The other is the massive precipitation of the cement hydrates which governs the mechanical strength development of the cast structure. Due to the interactive nature of the binder phase, the type of additive system and the alumina can and does impact upon these reactions, thus affecting the flow/working time and mechanical strength development.

4 Conclusions

The placing characteristics of a castable can be altered by modifying the binder phase components including calcium aluminate cement, reactive fine fillers and additives. Due to the interdependence of these components they must, however, be optimised simultaneously

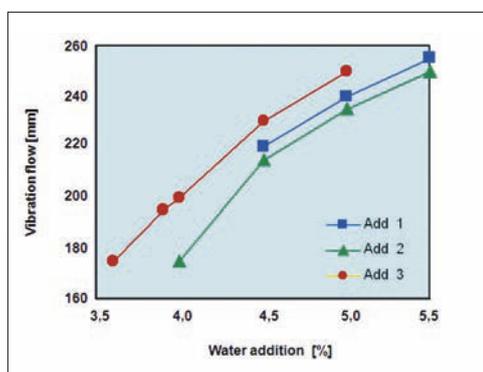


Fig. 6 The flow properties of different additive systems for an alumina-spinel castable

Tab. 6 Different additive packs / systems for alumina-spinel castables

	Add 1 [%]	Add 2 [%]	Add 3 [%]
Sodium hexametaphosphate Boric acid	0,06 0,01		
Sodium polyacrylate Boric acid Sodium carbonate		0,05 0,022 0,001	
PCE Lithium carbonate			0,3 0,002

Tab. 7 Mechanical strength development of LCC 8 using different reactive alumina sources

Reactive alumina (RA)	RA1	RA2	RA3	RA4
Alumina, BET [m ² /g] Na ₂ O [%]	7,0 0,08	3,3 0,02	3,0 0,26	0,8 0,27
CCS [MPa]				
Additive pack 2				
24 h	44	44	33	10
110 °C	112	116	109	52
Additive pack 3				
24 h	25	23	23	24
110 °C	98	90	113	92

and within the context of each specific castable type. Since the choice of calcium aluminate cement and fillers will eventually govern the properties of the in-situ castable, due consideration must be given to these parameters as well. Although compromises between placement characteristics and the final thermo-mechanical properties may have to be made, it has been shown that the selection of 70 % or 80 % alumina calcium aluminate cements available today provide a wide range of options that will fulfill these requirements.

LCC formulations containing fume silica rely on the microsilica to achieve good flow properties and can sometimes effectively be used with only one additive. Using the new calcium aluminate binder, Secar Xeniom, designed specifically for fume silica containing systems can dramatically improve the consistent behaviour of a deflocculated alumina-silica castable. In addition, this integrated buffering and deflocculation system enables reformulation with a wide range of refractory aggregates such as bauxite, andalusite or fireclay without having a negative impact on the cement hydration when switching from one aggregate to another.

LCC formulations based on alumina-spinel or alumina-alumina systems are more difficult and often require a complex additive pack comprising 2 or more additives.

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