Additives for High Purity Reduced Cement Castables

C. Parr, G. Assis, H. Fryda, S. Li

This paper presents a study into new, cost effective additive systems that yield high fluidity, low water demand and a rapid gain in early strength in high purity alumina LCC systems. Placing properties can be modulated between vibration, tamping and self-flow consistencies through small adjustments in water addition and without the need for specific formulation optimisations. The effect of different dosages of these new additives together with various types of reactive alumina is investigated in conjunction with the optimization of the water demand, flow and hardening properties. Results are compared with other additive systems.

1 Introduction

Formulations for deflocculated or self-flow castables rely on the use of fine, reactive matrix fillers to optimise the packing density in the cast mass. At the same time, it is possible to reduce the calcium aluminate cement (CAC) content due to the higher inter-granular contact of the system. Electrical surface charges are created when the ultra fine fillers and water come into contact with each other and this creates flocculation. It is thus necessary to add dispersing/fluidifying additives to disperse the system. If dispersion cannot be effectively achieved, the installer will need to increase the water addition to place the castable and all the in-situ benefits of using a deflocculated LCC will be lost. And this is precisely why additives a such critical components in LCC systems [1, 2].

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In the case of high purity systems that do not contain fume silica as the matrix filler but rely on fine calcined and reactive alumina instead, there is a tendency to exhibit shear stiffening and this often leads to rapid flow decay and a short working time. Previous studies [3], have shown the impact on placing properties of fine reactive alumina fillers and the problems of short and rapid flow decay. In these systems with classical fluidifying additives such as phosphates and acrylates there is the need to use retarders in combination with the principal additives to ensure sufficient working time to allow placing of the castable.

However, this has the drawback that the additive combination of fluidifiers and retarders not only influences the rheology of the wet castable but also affects the setting time, the hardening characteristics and the final strength of the product. In particular, flow is often achieved at the expense of early strength development which, for many cast in-situ applications, is important to facilitate early demoulding. But the physical properties of the castable are intimately linked to the hydration of the CAC. Previous studies [4] have shown how the 3 distinct steps of CAC hydration (namely, dissolution of the anhydrous phases, nucleation and precipitation of hydrates from solution) can be linked to the physical properties (rheology, flow, hardening and strength development, etc.) of the castable. By shorting any

of these steps it is possible to improve hardening and the rate of strength development. More recently, organic additives (more commonly known as superplasticisers) have been used because of their superior performance in dispersing the fine particles in LCC systems at very low water additions. Polycarboxylate ethers (PCE) have been shown to be more effective deflocculants than polyacrylates (SPA), due to their structure and mechanism of attachment to the surface of the various particles. SPA work simply through electrostatic stabilisation, but the long side chains on PCE are believed to provide both steric stabilisation and an electrostatic repulsion [5, 6]. This results in a reduction of the internal friction of the system which significantly enhances the flow properties.

However, and more particularly in the case of additives using electrosteric dispersion, there is a strong impact on the hydration of the CAC, often retarding the nucleation and precipitation phases [7]. This obviously delays the setting time, hardening and strength development of the castable.

Relying on in-house super-plasticizer know-how, new polycarboxylate-ether-based additives have been developed that have been tailor-made for alumina and alumina-spinel refractory formulations containing CAC. Through their use, it is possible to meet the technical requirements of high fluidity at a low water demand, whilst maintaining a rapid gain in early strength in high purity alumina LCC systems. Specific objectives for the additives included a means of optimising the rheology so that castables can be placed using vibration or self-flow techniques, depending on the water addition, a way to modulate the workability/hardening profiles and ensure a control mechanism to accommodate variances in ambient temperature. The basic formulation levers in terms of the type and dosage of additives and reactive alumina type will be reviewed. The paper will show how the trade-off between fluidity as a function of time and hardening can be managed whilst offering a simple approach

Tab. 1 Composition of LCC reference formulations.

Percentage [%]	LCC 1 vibration	LCC 2 vibration
Tabular alumina 0 – 7 mm	60	60
Al spinel AR 78 0 – 1 mm	13	13
Al spinel AR 78 −0,05 mm	10	10
Reactive alumina (RA1, RA2, RA3)	11	11
Secar® 71	6	6
Additive AL200		+0,0 – 0,1
Additive AL300		+0,0 – 0,1
Additive D7S	+0,05	
Water	4,5 – 5,5	3,5 – 4,5

Tab. 2 Characteristics of reactive alumina

	RA1	RA2	RA3
Particle size distribution	multimodal	multimodal	monomodal
BET [m²/g]	3,9	2,6	2,2
D_{50} [µm]	1,8	2,7	3,5
Na_2O [%]	< 0,1	< 0,1	< 0,2

Fig. 1 Vibration flow at 5 % water addition for 2 additives

Fig. 2 Vibration flow at 4,5 % water addition for 2 additives

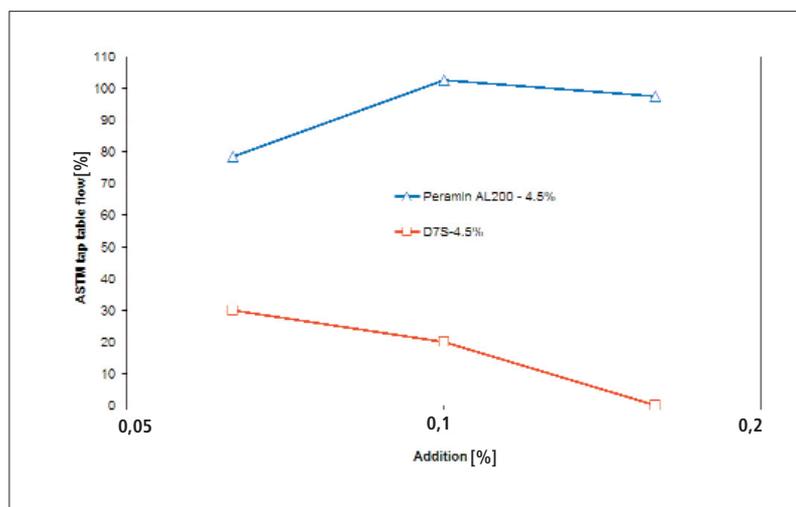to control fluidity through the water addition.

2 Experimental procedure

A generic-model low cement castable based on tabular and alumina spinel was used in conjunction with a 70 % alumina calcium aluminate cement to provide the reference systems for testing different additives. Aggregate sizes and proportions were chosen to fit the *Dinger & Funk* particle size distribution model at a q value of 0,3 for the vibration system.

Two new additives, Peramin AL200 and AL300 are evaluated. These additives are based on polycarboxylate ethers and present fluidifying profiles. AL300 will give a more rapid flow decay and quicker hardening than AL200. The reference systems are described in Tab. 1. They are compared with a sodium methacrylate, Darvan 7S (SPA). In addition, a number of classical retarders have been used, such as citric acid (AC) and sodium carbonate (NC). Three different reactive alumina were used and their basic characteristics are described in Tab. 2.

2.1 Analytical methods

The vibration flow (amplitude 0,5 mm, 50 Hz, 20 s) using a standard ASTM C230 cone was measured at periodic intervals after casting, to determine the flow profile as a function of time. Vibration flow data is presented, as well as ASTM tap flow data. This will give a comparison between field installation techniques and the minimum water demand to achieve vibration flow. In all cases, flow values were presented as a percentage of the initial diameter of the ASTM cone (100 mm). Working time is taken at the point when there is no more flow under vibration and the castable is stiff, although not set in the sense that it does not possess any intrinsic strength at that time. The same samples were then used to measure the exothermic [8] profiles through the measurement of the time to peak temperature (PT–T). These were backed up by the measurement of MOR and CCS at 6 h after casting and 24 h after casting. In both cases, samples were conserved at > 90 % r.h. and 20 °C. Samples were dried at 110 °C for 24 h before determining the density, performance strength and porosity measurements.

3 Experimental results
3.1 Placing and hardening properties

A first evaluation of the fluidifying effect of AL200 compared with D7S was run at different additive additions and a constant water addition. The results are shown in Fig. 1

and 2, which compare the impact of additive dose on initial vibration flow at 5 % and 4,5 % water respectively. Flow has been determined using the ASTM shock table (25 taps). The optimum additive addition for AL200 to maximise flow is around 0,1 mass-%, where flow of more than 130 % is recorded at 5 % water addition. At 4,5 % water addition the maximum flow is also found at 0,1 % addition with more than 100 % flow. In the case of D7S, the optimum addition is around 0,05 mass-% but the flow is much lower at an equivalent water addition than the AL200. At 4,5 % water addition the flow can be barely registered.

From the data in Figs. 1 and 2, 0,1 mass-% and 0,05 mass-% additive additions were chosen for the AL200 and D7S respectively. The flow profile was recorded using the same ASTM shock table. D7S showed a very rapid flow decay (Fig. 3) with a working time of less than 30 min. In order to extend the working time and enhance the flow profile, citric acid (AC) and sodium carbonate (NC) were used as retarders. They are successful in extending the working time to around 40 – 45 min but the flow decay still remains rapid. However, in contrast AL200 showed a gradual decrease in flow over 60 min and remained fluid at 60 min with more than 60 % flow. This was also achieved with 0,5 % less water addition than in the case of the D7S addition.

The impact of using vibration to measure the flow was evaluated via a vibration table (20 s). This allows significantly lower water additions to be recorded than the case of flow measurement via a tapping flow table. At all water additions the AL200 gives a much higher flow value and vibration flow can be measured at water additions as low as 3,5 %. In contrast D7S requires 4,5 % water to achieve the same flow. This difference of around 1 % point in water addition is mirrored at different levels of water addition/flow. The differences in flow properties between D7S and AL200 are as marked with the vibration table as with the shock table. The AL200 additive allows a significant reduction in water demand for an equivalent flow compared to the polyacrylate-based system.

From these results, it was decided to maintain vibration flow as the means to characterise flow properties. Using the flow table with such systems risks overdosing water
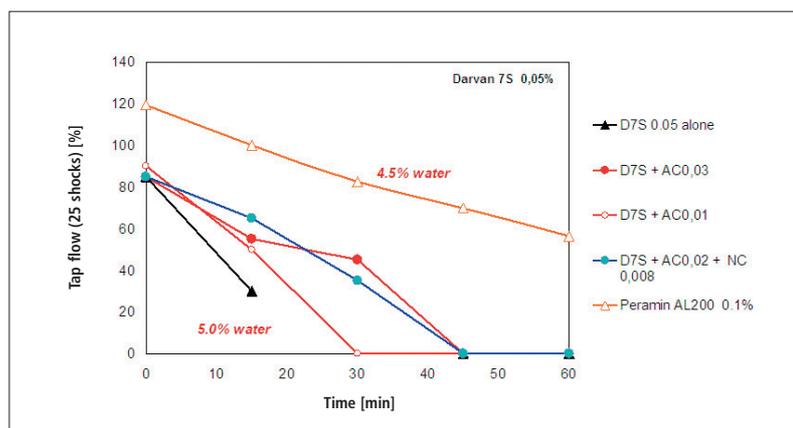

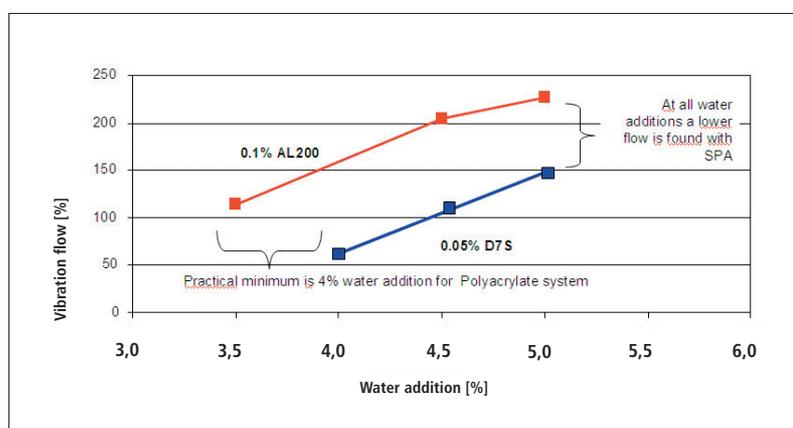**Fig. 3** Vibration flow profile for different additives

Fig. 4 Vibration flow for different additives as a function of water addition
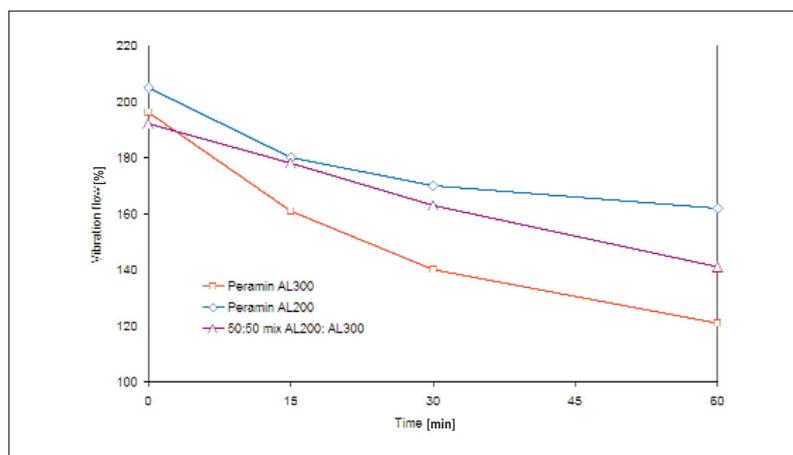

Fig. 5 Vibration flow vs. time at 4,5 % water and 20 °C

relative to minimum placing properties necessary for vibration casting.

AL200 additive gives a high fluidity to alumina castables at a low water addition. Furthermore, adequate and sustainable flow for a high purity alumina system is provided throughout the working period. Bearing in mind that the ideal flow profile is flat over

time (i.e. little loss of flow over the desired working period), there is, in practice, the additional and conflicting requirement of meeting the desired hardening profile. In order to achieve a suitable system, compromises need to be made between these conflicting requirements. Fig. 5 shows results obtained using Peramin AL200 & AL300 sin-
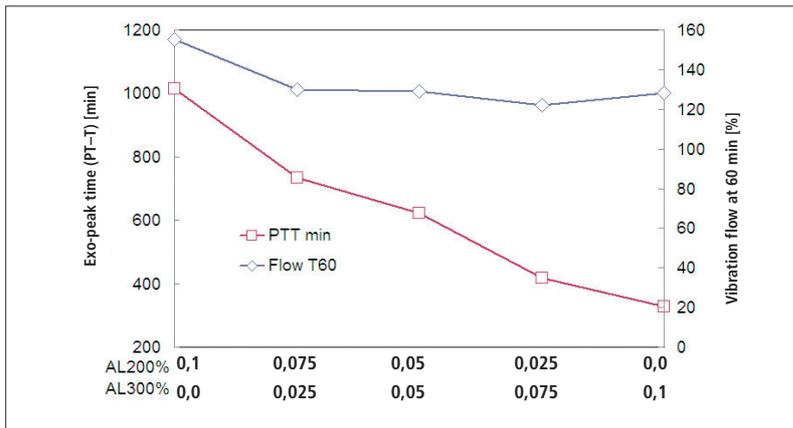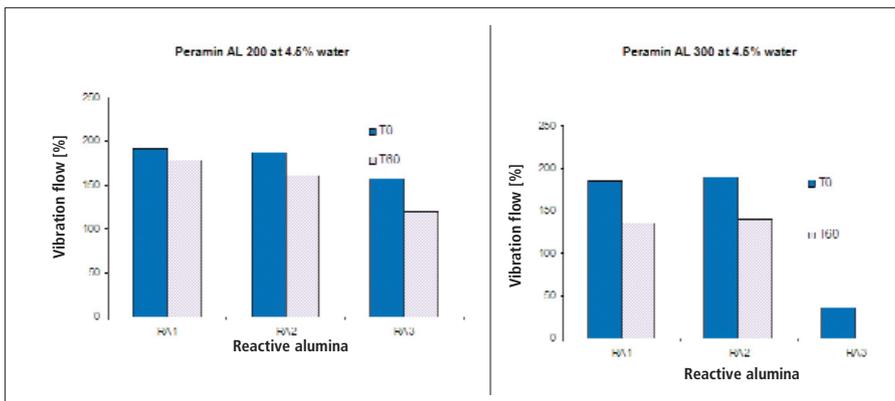
Fig. 6 Castable properties with Peramin AL200/AL300 blend at 20 °C

gularly and in combination in the vibration castable formulation LCC1 (outlined in Tab. 1). The flow profile of Peramin AL200 (which provides a longer working time and has a longer hardening profile) displays a very flat flow profile over the first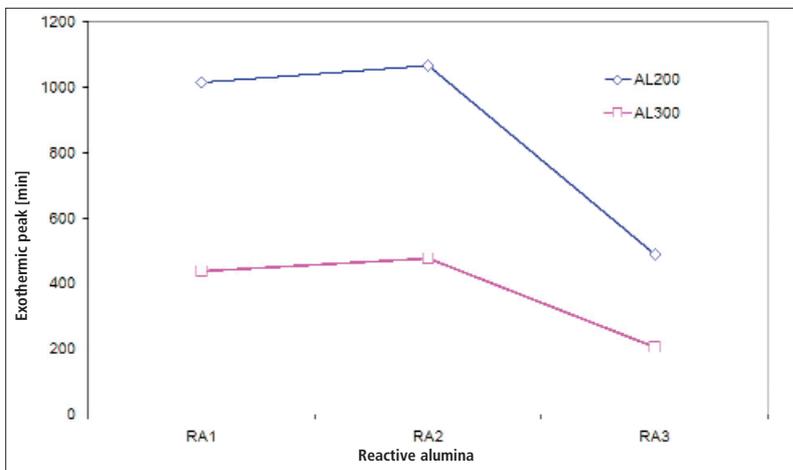 60 min. Peramin AL300 which displays a much more rapid hardening profile, shows a more pronounced loss of flow after 60 min, although the final flow is still more than double the original cone diameter and would provide adequate workability. And importantly, blending the two additives provides predictable results and a progressive and linear

Fig. 7 Variation of vibration flow as a function of reactive alumina type

Fig. 8 Variation of Exothermic peak times (PTT) as a function of reactive alumina type

behaviour that would be easy to predict and work with.

Fig. 6 illustrates the predictable results obtained using combinations of Peramin AL200 & AL300. At 20 °C a very similar trend with respect to flow, with minimal flow decay at 60 min across the full range of combinations of AL200 and AL300 is observed. The setting profile also shows a predictable trend, progressive and predictable shortening of the setting times with increasing additions of Peramin AL300 to the formulation. Thus, it is possible to meet both the required rheology and hardening profiles through the combination of the two Peramin additives. It is important to have a quick wet out time to limit water dosing on site, achieve constant mix consistency with successive batches, and ultimately provide a better final product performance. With Peramin AL additives in the LCC model formulations given in Tab. 1 typical wet out times of 15 – 20 s are noted. In addition, the de-airing ability of the concrete during consolidation is another important practical consideration that is often overlooked. This characteristic is especially important for field casting where the length of the cast section has a much larger dimension than the thickness (e.g. ladle walls). In this case, in order to avoid casting flaws, it is important that all the air trapped in the castable during mixing and placing can be removed easily under vibration. The additives were specifically designed to reduce the viscosity of the pore solution of CAC based castables in order to better facilitate the release of air bubbles during placing.
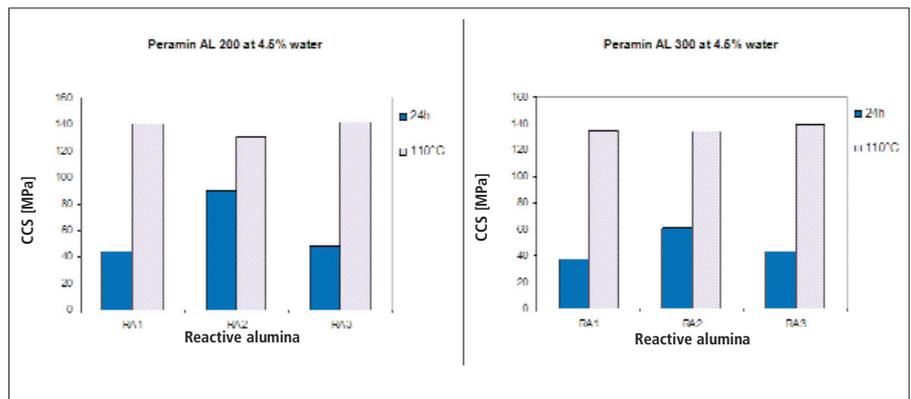
The effect of alumina type upon castable flow with two different PCE additives is shown in Fig. 7. Initial flow and flow after 60 min is shown. In most cases satisfactory flow over the 60-min period is observed, with AL300 showing more rapid flow decay than AL200. The one exception is the reactive alumina RA3, which had a very low initial flow and no 60-min flow. This can probably be linked to the differences in sodium, surface and particle size with this alumina. The difference in exothermic peak time between AL200 and AL300 is clearly visible (Fig. 8) for the high alumina model formulation. The impact of alumina on exothermic peak time is particularly marked in the case of RA3 which shows a much shorter PTT for both AL200 and AL300. The biggest difference in exothermic peak time (PT–T) with the different alumina is

observed with the AL200 additive. The combination of AL200 and RA3 gives an exothermic peak time similar to that observed with RA1 or RA2 in combination with AL300. Therefore, another formulation optimisation route would be to modify the alumina type with a fixed additive. This option could be used to change the flow profile and adjust castable hardening. Therefore simple substitution of one alumina for another can lead to significant changes in placing properties and castable hardening depending on which additive system is employed.

Mechanical strengths measured after 24 h curing and a further drying at 110 °C (Fig. 9) do not show major differences between the different combinations of reactive alumina and additive. The biggest differences in mechanical properties are found after 24 h curing. This is presumably linked to a kinetic effect induced by the different alumina types. Based on available data it is somewhat difficult to explain the high green strengths of the AL200/ RA2 alumina combination after 24 h curing.

4 Conclusions

Peramin AL200 and Peramin AL300, in combination or separately, provide the fluidity and desired placing properties of the castable whilst simultaneously achieving the required hardening profiles. Properties can be further optimised through the selection of reactive alumina. The building block approach of coupling these tailor-made additives with calcium aluminate cements in refractory applications allows the levers of formulation to meet a specific function to be simplified. It is possible to achieve the required hardening profile without the addition of classical accelerators. This will improve the ease and quality of the installation of the castable, and ultimately, improve the in situ performance of the final lining.

Fig. 9 Variation of installed compressive strengths as a function of reactive alumina type

Acknowledgements

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