



Improved additives for high purity low cement castable systems

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Abstract

Many types of organic molecules that are used as deflocculants in refractory castables are derivatives from developments for the building industry with either Portland cement or mixed binder systems consisting, e.g., of Portland cement, Calcium Aluminate cement and Calcium Sulphate. Only few products have been developed which fit specifically to pure Calcium Aluminate cements. Two new Polycarboxylate Ethers, Peramin® AL200 and Peramin® AL300 will be presented in this paper which are molecules tailor-made to deflocculate high purity alumina / alumina spinel castables. Peramin® AL deflocculants provide the desired placing properties of these castable systems. Mixing water can be reduced to a minimum to provide castables with an excellent self-flowing and vibratable consistency. The rapid wet-out during mixing, predictable and sustained flow during placing, and effective de-airing during consolidation will be demonstrated. In addition, by using these additives either singly or in combination, depending on the ambient conditions, it is possible to achieve the required hardening profile without the addition of classical accelerators. Peramin® AL additives tailor-made for refractory castables that contain high quality 70 % Calcium Aluminate cements like Secar® 71 and Secar® 712 bring improved quality to the installed castable, and ultimately, improve the in-situ performance of the final lining.

Keywords: Low cement castable, Deflocculant

ULEPSZONE DODATKI DO BETONÓW NISKOCEMENTOWYCH O WYSOKIEJ CZYSTOŚCI

Wiele rodzajów cząsteczek organicznych, które wykorzystywane są jako deflokulanty w betonach ogniotrwałych, pochodzą z opracowań dla przemysłu budowlanego na bazie cementu portlandzkiego albo mieszanych systemów spoiwa składających się np. z cementu portlandzkiego, cementu wapieniowo-glinowego i siarczanu wapieniowego. Opracowano niewiele produktów, które są dostosowane specjalnie do czystych cementów glinowo-wapieniowych. W niniejszej pracy zostaną przedstawione dwa nowe etery polikarboxylowe, Peramin® AL200 i Peramin® AL300, dostosowane do deflokulacji wysokiej czystości betonów glinowo-spinelowych. Deflokulanty Peramin® AL zapewniają pożądane własności instalowania tych systemów betonów. Wodę zarobową można ograniczyć do minimum w celu zapewnienia betonowi doskonałej samolejności i konsystencji w procesie wibrowania. Pokazane zostanie szybkie nawilżanie betonu w trakcie mieszania, przewidywalny i zrównoważony przepływ w trakcie instalacji oraz efektywne odpowietrzenie w czasie zestalania. Ponadto, używając tych dodatków albo pojedynczo, albo w połączeniu, w zależności od warunków otoczenia, można uzyskać wymagany profil utwardzania bez pomocy klasycznych przyspieszaczy. Dodatki Peramin® AL, dostosowane do potrzeb betonów ogniotrwałych zawierających wysokiej jakości 70 % cementy glinowo-wapieniowe takie jak Secar® 71 i Secar® 712, polepszają jakość zainstalowanego betonu, a w konsekwencji jakość wyłożenia *in-situ*.

Słowa kluczowe: beton niskocementowy, deflokulant

1. Introduction

Low cement (LC) or deflocculated castable technology has been widely adopted in recent years due to the improved thermo-mechanical properties and corrosion resistance that these castables display in service. These improvements in performance have been made possible by the increased sophistication of refractory formulations and improvements in installation methods.

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. In the case of high purity systems that do not contain fume silica as the

matrix filler but rely on fine calcined and reactive aluminas instead, there is a tendency to exhibit shear stiffening rather than fluid behaviour. This often leads to rapid flow decay and a short working time. However, the key formulation parameter for a LC castable is to ensure satisfactory placing properties at low water demand. Minimising the water addition maintains the dense, low porosity cast structure that improves the thermo-mechanical properties, and minimises corrosion and abrasion of the self-flow castable. Deflocculants are essential in fluidifying the fine particles to give the required flow despite the low water addition and in maximising the rheological characteristics to optimise the installation.

However, the deflocculant addition 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 casts *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 [1] 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 minimising the nucleation period it is possible to improve hardening and the rate of strength development.

In the past, inorganic additives (e.g., Sodium Tripolyphosphate) were used extensively to modify the rheology of LCC systems. More recently, organic additives (more commonly known as super-plasticisers) 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 (PA), due to their structure and mechanism of attachment to the surface of the various particles. PA work simply through electrostatic stabilisation, but the long side chains on PCE are believed to provide both steric stabilisation and an electrostatic repulsion [1]. 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 [1]. This obviously delays the setting time, hardening and strength development of the castable.

Peramin AL200 and AL300 are commercially available polycarboxylate ether based additives that have been tailor-made for alumina and alumina-spinel refractory formulations containing CAC. Using the Peramin AL system, 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.

The key development parameter for the Peramin AL additives was to maintain the initial fluidity above 100 % (ASTM tap flow) at a range of water levels, whilst simultaneously maintaining a suitable hardening profile and avoiding the necessity to add classical additives to correct the setting time. The "dual additive" approach provides the flexibility to adapt the formulation to meet the required placing and setting characteristics under a wide range of environmental conditions. The two additives can be used singularly (at a recommended dosage of 0.1 %) or in combination (with

the total additive dosage remaining at 0.1 %) to provide:

- a means of optimising the rheology so that the product can be placed using vibration or self flow techniques, depending on the water addition,
- a way to modulate the workability and the hardening profiles,
- a control mechanism to accommodate variances in ambient temperature.

2. Experimental details

Generic low cement castables based on tabular and alumina spinel was used in conjunction with a 70 % alumina calcium aluminate cement to provide the reference systems for testing the Peramin AL additives. These reference systems are described in Table 1.

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 and 0.2 - 0.25 for the self-flow formulation.

3. Analytical methods

The vibration flow (amplitude 0.5 mm, 50 Hz, 20 sec) using a standard ASTM C230 cone was measured at periodic intervals after casting, to determine the flow profile as a function of time [1, 3]. Vibration flow data is presented here rather than ASTM tap flow data since this is more representative of installation techniques in the field. Self-flow values were determined using the same cone (no vibration) and flow values were recorded at specified time intervals. In all cases, flow values were presented as a % 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: peak time to temperature). These were backed up by the measurement of MOR and CCS at 6 hours after casting and 24 hours after casting. In both cases, samples were conserved at > 90 % r.h. and 20°C. Samples were dried at 110°C for 24 hours and then fired at different temperatures for 3 hours before determining the density, performance strength and porosity measurements.

4. Placing and hardening properties

The first objective was to develop additives to provide adequate and sustainable flow for a high purity alumina system 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. 1 shows results obtained using Peramin AL200 and AL300 singularly and in combination in the vibration castable formulation LCC1 (outlined in Table 1). The flow profile of Peramin AL200 (which provides a longer working time and

Table 1. Composition of LCC reference formulations.

[%]	LCC1 Vibration	LCC2 Self flow
Tabular Alumina: 0 - 7 mm	60	56
Al Spinel: AR 78 0 - 1 mm	13	13
Al Spinel: AR 78 -0.05 mm	10	10
Alumina: CTC 30	11	15
Cement: Secar® 71	6	6
Additive: Peramin® AL 200	0.0 - 0.1	-
Additive: Peramin® AL 300	-	0.0 - 0.1
Water	3.5 - 4.5	4.5 - 5.0

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.

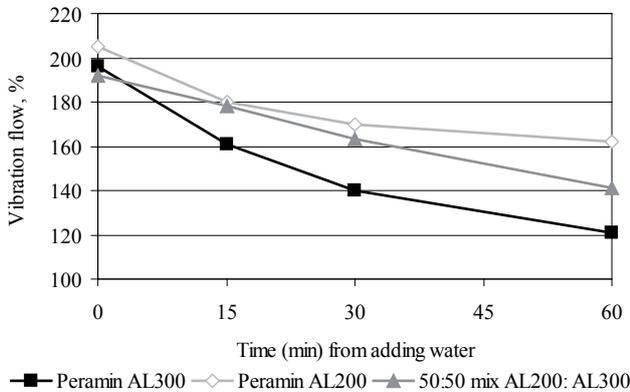


Fig. 1. Vibration flow vs time at 4.5 % water and 20°C.

Figs. 2, 3 and 4 illustrate the predictable results obtained using combinations of Peramin AL200 and AL300 more clearly, despite dramatic variations of the ambient working temperature. As to be expected, at low ambient temperatures, the addition of the Peramin additives, either individually or in combination, show good flow retention (the flow values shown are taken at 60 minutes after water was added to the castable). The time taken to reach the peak hydration temperature is, however, very different depending on which additive has been used. With Peramin AL200 alone, the castable takes more than 2000 min to reach initial set, whereas the addition of Peramin AL300 at 0.1 %, without any additional additives decreases the setting time by more than 50 % to around 1000 min. Even more importantly, we see that the blends of Peramin AL200 and AL300 behave in a progressive and linear way that would be easy to predict and work with.

At 20°C, we see a very similar trend with respect to flow, with minimal flow decay at 60 minutes across the full range of combinations of AL200 and AL300. The setting profile also shows the same predictable trend seen at low ambient temperature – a progressive and predictable shortening of the setting times with increasing additions of Peramin AL300 to the formulation. The difference in the setting time between the two individual additions alone is, however, larger than before – 1015 min for 0.1 % AL200 compared to only 330 min for 0.1 % AL300.

At 35°C (Fig. 4) though, the high ambient temperature initiates a very rapid flow decay in the formulations containing more than 0.05 % Peramin AL300. In addition, for these three formulations, the peak temperature on the exotherm is reached in less than 100 min making these mixes extremely difficult to install within a comfortable working period. In this case, using Peramin AL200 alone (or in combination with only a very small amount of AL300) provides adequate working time and good flow throughout the working period.

Thus, it is possible to meet both the required rheology and hardening profiles over a wide range of ambient temperatures

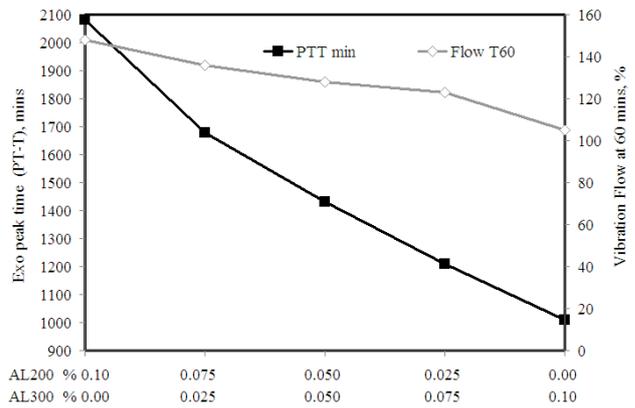


Fig. 2. Castable properties with Peramin AL200 : AL300 blend at 10°C.

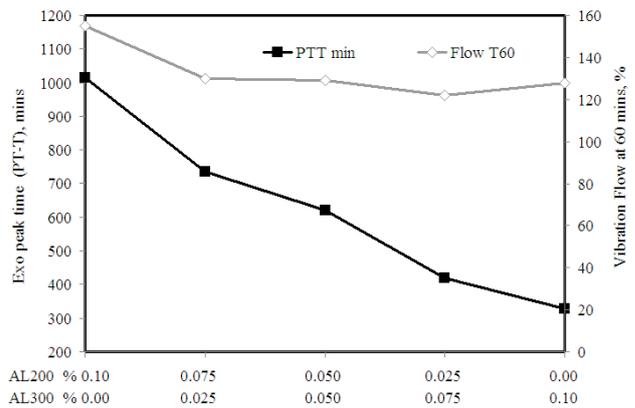


Fig. 3. Castable properties with Peramin AL200 : AL300 blended at 20°C.

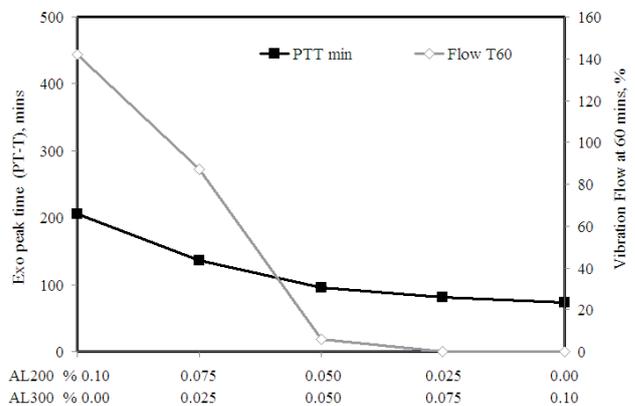


Fig. 4. Castable properties with Peramin AL200 : AL300 blend at 35°C.

through the combination of the two Peramin additives.

The rheological characteristics of any given LCC formulation, whether designed to be placed by vibration, pumping or self flow techniques, are determined by the type and amount of deflocculant, the amount of water added and the mixing energy provided. During the development the Peramin AL additives, special focus was placed on minimising the wet out time of the castable during mixing. 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 formulations given in Table 1 we typically see wet out times of 15 – 20 seconds.

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 on site 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. This also reduces the final porosity of the castable further improving the final *in-situ* performance. Peramin AL 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.

5. Vibration and self flow castables

Through an adjustment of the aggregate sizes and proportions, it is possible to optimise the particle size distribution to change the flow characteristics of the castable. Table 1 gives the formulation details (LCC1) for the vibration castable (*i.e.*, >100 % initial flow on a vibration table) and the adjusted formulation, LCC2 that meets the self-flow criteria (*i.e.*, >100 % initial flow after 3 minutes of flow time using a standard ASTM C230 cone with a height of 50 mm). Fig. 5 shows the self flow measured in LCC2 at various Peramin AL additions at 1, 3 and 5 minutes after the completion of mixing. Although the minimum flow criteria are met in all three cases, there is a significant difference in the flow rates between 1 and 3 minutes between the three systems. It is interesting to note, that Peramin AL200 at 0.1 % has the lowest flow value at 1 min but shows a dramatic flow rate between 1 and 3 minutes, and is still flowing 5 min after mixing. Peramin AL200 alone flows for much longer than any combination containing AL300 and a 50:50 blend of AL200:AL300 attains more than 90 % of the final flow value within 1 min after mixing.

Fig. 6 shows the difference in the flow decay between the self-flow and vibration castables at various water additions for 0.1 % Peramin AL200 addition. All the flow profiles are very similar over the first 60 minutes and as expected, the higher water addition, very markedly in the case of the vibration castable, provides better flow.

The effect of the optimised particle size distribution can be seen very clearly in the small spread between the curves in the case of the different water levels for the self-flow formulation in Fig. 4. The large spread between the curves for the vibration castable at the various water additions suggests that water can easily be used as an effective lever to manipulate flow in this castable. This reinforces the idea of being able to predictably modify the fluidity of the system by varying the water addition only and appeals as a simplistic tool that could be particularly beneficial to casting on site.

The comparison in the flow decay between the addition of only Peramin AL200 and the blended system in the self-flow formulation is shown in Fig. 6. Once again, the higher water addition is seen to improve the initial flow and enhance the flow retention within the system. The addition of the Peramin AL300 in this system has a very marked affect and flow decay is very rapid. This can easily be further elaborated

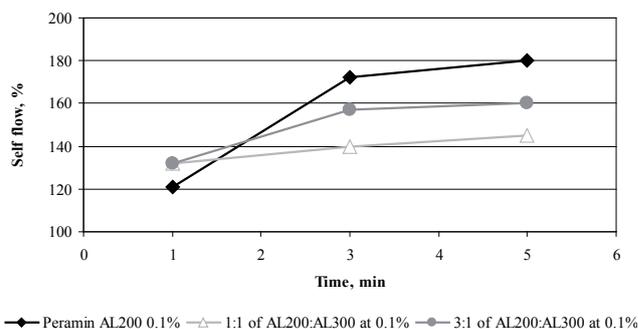


Fig. 5. Early flow vs. time for self flow castables with 0.1 % additive addition, at 4.5 % water and at 20°C.

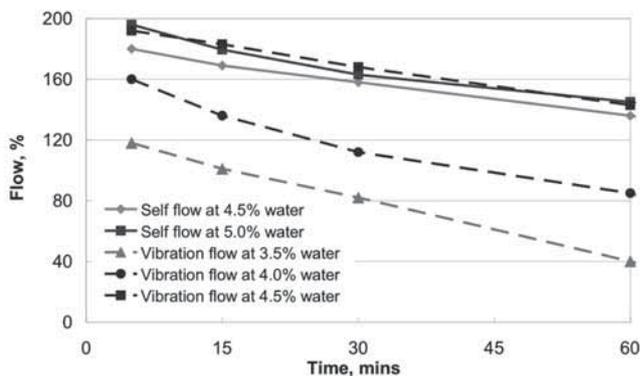


Fig. 6. Flow vs. time for self flow (LCC2) and vibration consistency (LCC1) castables with 0.1 % Peramin AL200 at various water additions and at 20°C.

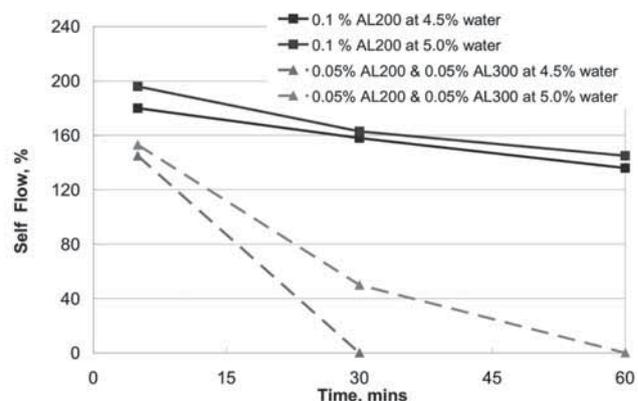


Fig. 7. Flow vs. time for self flow castables with 0.1 % additive addition, at various water additions and at 20°C.

by considering the hardening profile and the early strength development (Table 2) in conjunction with the flow data.

There is a very strong agreement between the time to the exothermic peak temperature and the flow decay for these mixes. In particular, the 50:50 blend at 4.5 % water addition has a markedly rapid flow decay, the shortest PT-T time and is correspondingly the only castable in the example that shows significant early strength development. It should also be noted that the strength development is a much stronger function of the water addition than the additive addition. The strengths achieved with 5 % water addition are markedly lower than those for the same formulation made with only 4.5 % water.

In contrast, there is very little difference between the respective 24 h and 110°C dried strengths with the different

Table 2. Strength development of LCC2 with different additive combinations.

AL200 [%]	+0.1	+0.1	+0.05	+0.05
AL300 [%]			+0.05	+0.05
Water [%]	4.5	5.0	4.5	5.0
6 h CCS [MPa]	0.0	0.0	9.1	0.0
10 h CCS [MPa]	29.2	20.4	32.1	25.9
24 h CCS [MPa]	51.3	44.7	45.0	37.9
110°C CCS [MPa]	156.2	118.5	142.0	124.5
Time of peak temp .(PT-T) [min.]	664	610	350	416

additive additions but at the same water addition. Table 2 also provides a level of confidence wet green strength development in that the system could easily be adapted to ensure enhanced demoulding performance and rapid mould turn around times in precast applications.

6. Conclusions

Peramin AL200 and Peramin AL300 are PCE molecules tailor-made for deflocculating high purity alumina / alumina spinel castables. Peramin AL deflocculants provide the desired placing properties of these castable systems – rapid wet-out during mixing, predictable and sustained flow during placing, and effective de-airing during consolidation. In addition, by using these additives either singly or in combination, depending on the ambient conditions, it is possible to achieve the required hardening profile without the addition of classical accelerators.

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. This will improve the ease and quality of the installation of the castable, and ultimately, improve the in-situ performance of the final lining.

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