

## **IMPROVED ADDITIVE SYSTEMS FOR LOW CEMENT, HIGH PURITY CASTABLES**

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## 1 Introduction

In recent years, there has been significant growth in the application of low cement (LC) or deflocculated castables due to the improved thermo-mechanical properties & corrosion resistance displayed in service. These improvements in performance have been made possible by the increased sophistication of refractory formulations & 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, a reduced calcium aluminate cement (CAC) content is possible 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 & 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, & minimises corrosion & abrasion of the self-flow castable. Deflocculants are essential in fluidifying the fine particles to give the required flow despite the low water addition & 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 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 [5] have shown how the 3 distinct steps of CAC hydration (namely, dissolution of the anhydrous phases, nucleation & precipitation of hydrates from solution) can be linked to the physical properties (rheology, flow, hardening & strength development, etc.) of the castable. By minimising the nucleation period it is possible to improve hardening & the rate of strength development.

In the past, inorganic additives (eg. Sodium Tripolyphosphate) were used extensively to modify the rheology of LCC systems. 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 (PCEs) 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's work simply through electrostatic stabilisation, but the long side chains on PCE's are believed to provide both steric stabilisation & 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 & precipitation phases [5]. This obviously delays the setting time, hardening and strength development of the castable.

It will be shown, however, that by coupling the latest generation of superplasticisers with classical accelerators, it is possible to meet the technical requirements of high fluidity, low water demand and a rapid gain in early strength in high purity alumina LCC systems.

## 2 Experimental details

A generic low cement castable based on tabular alumina and calcium aluminate cement (with a nominal alumina content of 70 %) was used in conjunction with a variety of additives. This reference system is described in table 1.

**Table 1. Composition of LCC reference formulation**

Component	Particle size	(%)
Tabular Alumina	3.35 - 6.7 mm	33
Tabular Alumina	1.18 - 2.36 mm	16
Tabular Alumina	0.3 - 0.6 mm	6
Tabular Alumina	0-0.3 mm	5
Spinel AR78	0.5-1 mm	9
Spinel AR78	0-0.5 mm	4
Spinel AR78	0-0.09 mm	10
Reactive Alumina	(CTC30)	11
Secar 71		6

Aggregate sizes and proportions were chosen to fit the Dinger & Funk particle size distribution model. It is well known that optimising the particle packing density maximises the flow properties of the castable and also optimises the final product properties of the LCC.

Four commercially available PCE's were investigated at two dosages and two water additions. Unfortunately, the data in the public domain is insufficient to be able to draw any conclusions with respect to quantifiable parameters or distinguishing characteristics for any of the PCE's tested. Despite the lack of clarity in this regard, the effects of these superplasticisers on the castable properties can be discussed although the mechanisms remain unsubstantiated.

The key parameter was to maintain the initial fluidity above 100% (ASTM shock or tap flow) at both water levels, whilst simultaneously monitoring the effect on the hardening characteristics. Thereafter, a number of classical additive additions were investigated to meet the required hardening profile.

### ▪ Analytical Methods

The vibration flow was measured at periodic intervals after casting, to determine the flow profile as a function of time [3, 5]. This data is presented here instead of the ASTM tap flow data since this is more representative of installation techniques in the field.

A variety of techniques were used to quantify strength development in the phase where the initial structure had been sufficiently developed to facilitate a measurement of mechanical strength. Exothermic profiles [5] were coupled with ultrasonic techniques [3] to measure the developing structure as this can be linked to the hydration steps of the calcium aluminate binder. Penetrometer measurements [6] were used to assess early mechanical strength in situ. In addition, MOR and CCS were measured at 6 & 24 hours, and 2 & 7 days from casting. The experimental details are as previously described [5].

## 3 Experimental results

### Placing properties

Figure 1 shows the flow profiles for all four PCE's at a dosage of 0.075 %, at 4.5 % & 5 % water addition. All the PCE's provide a similar flow profile over the first 60 minutes &, as expected, the higher water addition (i.e. 5 %) provides better initial flow.

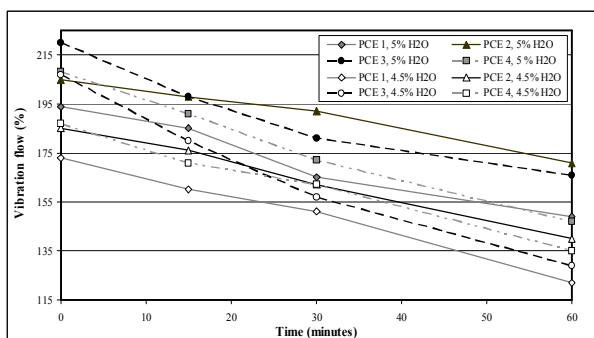


Fig. 1. Vibration flow profiles at 0.075 % PCE addition

Note that PCE 3 at only 4.5 % water addition provides the same initial flow (T0) as PCE 2 & 4 at 5 % water addition. Flow decay for PCE 3 (4.5 % H<sub>2</sub>O) is very rapid & very marked though. The ideal profile flow as flat as possible, with little loss of flow over the desired working period. In this respect, PCE 2 offers the more preferred flow profile.

At 0.15 % PCE addition (Fig 2) we see very similar trends, with a higher water addition generally leading to higher flow. However:

- In most cases the initial flow values (T0) with a 0.15 % PCE addition are LOWER than those seen at 0.075 % PCE addition.
- Very flat profiles can be achieved for PCE 2 & 4 at 5 % water addition.
- PCE 2 (4.5 % H<sub>2</sub>O), shows improved fluidisation at 15 min. This may suggest that at a high PCE 2 concentration there is a dissolution / activation barrier.

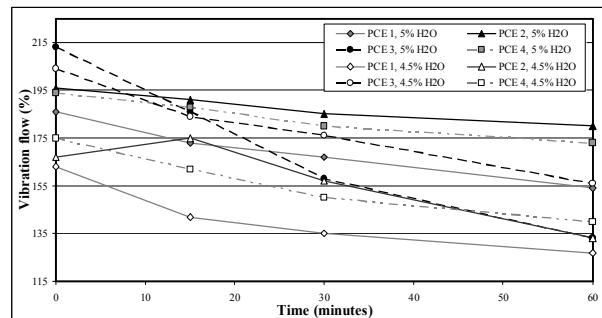


Fig. 2. Vibration flow profiles at 0.15 % PCE addition

The flow values obtained at both PCE dosages, despite the significant difference in the amounts, are very similar. A closer inspection of the effect of PCE dosage at constant water addition seems warranted.

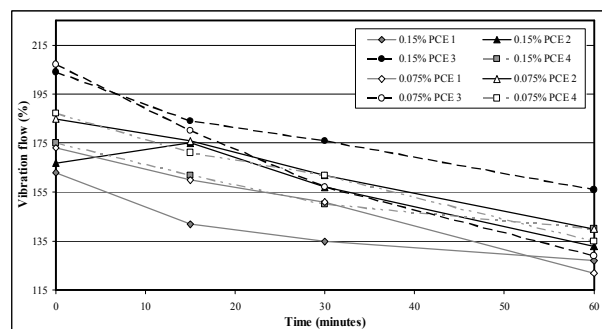


Fig. 3. Vibration flow profiles at 4.5 % water addition

For 4.5 % water addition:

- The PCE 3 formulation is the only one that displays higher flow values at the higher PCE dosage.
- The formulations containing PCE 2 & 4 give better flow at the low addition level, with a very marked difference at T0 & a diminishing difference at T60.
- PCE 1 formulation shows the same trend as the PCE 2 & 4 formulations until T60 when the higher dosage gives better flow.

At 5 % water addition:

- PCE 3 formulation now follows a similar trend as the other formulations & provides better flow at the lower PCE dose.

- Formulations containing PCE 1, 2 & 4 all show a similar trend to PCE 1 at 4.5 % water addition. There is a switching point at ~ 30 min, 45 min and 18 min respectively, where the high dosage gives better flow than the low dosage does.

There appears to be a maximum dosage beyond which flow is no longer improved. Each PCE addition would therefore need to be optimised with respect to the specific raw materials & formulation parameters. And finding the optimum water addition at the lowest practical PCE dosage will have positive effects on the desired hardening characteristics.

**Table 2. Castable properties for 4.5 % water and 0.075 % PCE dosages**

	Units	PCE 1	PCE 2	PCE 3	PCE 4
<b>Vibration flow</b>					
T0	(%)	173	185	207	187
T15	(%)	160	176	180	171
T30	(%)	151	162	157	162
T60	(%)	122	140	129	135
<b>T60 – T0</b>	(%)	51	45	78	52
<b>ASTM flow</b>					
T0	(%)	101	117	109	109
T60	(%)	84	69	45	70
<b>T60 – T0</b>	(%)	17	48	64	39
<b>Exotherm</b>					
Max peak T	°C	25.2	25	19.6	23.6
Time of peak	min	909	1164	1673	800
<b>Ultrasonic time - 1st peak</b>	min	732	1035	210	656
<b>Cold strength</b>					
6h MOR	MPa	0.00	0.00	0.00	0.00
24h MOR	MPa	5.60	6.66	0.00	8.88
2d MOR	MPa	7.61	8.27	0.00	10.56
7d MOR	MPa	12.87	12.75	11.57	13.31
6h CCS	MPa	0.00	0.00	0.00	0.00
24h CCS	MPa	39.01	49.73	0.00	78.95
2d CCS	MPa	51.78	64.35	0.00	92.58
7d CCS	MPa	93.98	102.38	109.28	117.68

## ▪ Hardening properties

Since high dosages of superplasticiser & water delay hardening, only the experimental conditions optimising rapid hardening for the formulations tested have been considered for this section & are presented in table 2.

Generally there is an agreement between the point of initial rise in the ultrasonic velocity & the first exothermic peak [3], indicating that the shortest flow decay results & the quickest development of structure. PCE 3, however, shows a different behaviour in that the initial exothermic peak occurs much later than the ultrasonic peak. Whilst the early ultrasonic peak accurately predicts the rapid flow decay for this system, the very late exothermic peak & slow evolution of strength are quite contradictory of the expected trend. This would suggest that PCE 3 may alter the hydration kinetics/mechanism.

Despite PCE 1, 2 & 4 showing very similar decay in vibration flow, PCE 4 shows the shortest exothermic peak time & correspondingly, the most rapid strength development.

It should, however, be noted that eventually all four systems reach comparable ultimate strengths (7 day results). The strength acquisition is only retarded in the initial period through manipulating the hydration kinetics i.e. prolonging the nucleation period [5]. In order to develop sufficient strength to facilitate demoulding in an acceptable time period, an accelerator must be added to prevent this lengthening of the nucleation period.

## ▪ Addition of conventional accelerators

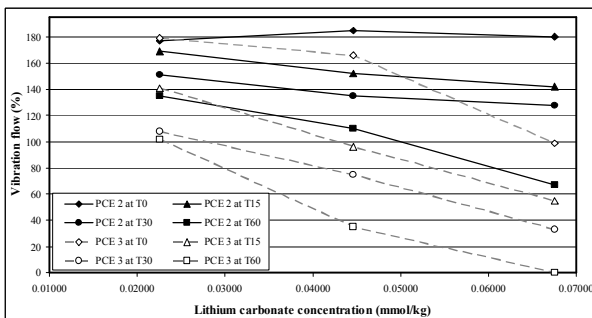
The most common, most effective accelerators for alumina cements are lithium salts. Li is effective in reducing the nucleation time without perturbing the dissolution period, and hence it has little affect on the rheological properties. However, addition levels need to be kept low (below 0.01%) in order to avoid any impact on long-term strength development [5, 7].

Lithium carbonate and lithium sulphate additions were made to the 0.075 % PCE 2 and 3 formulations with 4.5 % water addition, as described in Table 3.

**Table 3. Li salt additions to 0.075 % PCE 2 & 3 formulations at 4.5 % water addition**

		Low	Medium	High
Li <sub>2</sub> CO <sub>3</sub>	mmol/kg	0.02257	0.04459	0.06757
Li <sub>2</sub> SO <sub>4</sub>	mmol/kg	0.03000	0.04545	0.06064

Only the highest dosage of Li<sub>2</sub>SO<sub>4</sub> provided any appreciable strength in 6 hours, & this was only for PCE 2. Due to the poor initial results, the trials with Li<sub>2</sub>SO<sub>4</sub> were discontinued. Figure 4 shows the flow evolution over time as a function of Li<sub>2</sub>CO<sub>3</sub> addition.



**Fig. 4. Vibration flow profiles at 0.075 % PCE addition and 4.5 % water addition**

For the formulation containing PCE 2, the initial flow values (T0) are hardly affected by the increase in the Li<sub>2</sub>CO<sub>3</sub> dosage. However, the increasing spread of the data points as the Li<sub>2</sub>CO<sub>3</sub> addition increases shows that the flow decay of the PCE 2 formulation increases at high Li<sub>2</sub>CO<sub>3</sub> dosages. The PCE 3 formulation is affected much more by the Li<sub>2</sub>CO<sub>3</sub> additions, & the rapid flow decay is visible at all concentrations tested. Increasing the Li<sub>2</sub>CO<sub>3</sub> dosage also has a significant & negative impact on the initial flow values for the PCE 3 formulation.

The castable properties from a selection of suitable formulation results are presented in Table 4. The PCE 2 formulation with 0.0676 mmol/kg Li<sub>2</sub>CO<sub>3</sub> provides reasonable & sustained flow, a suitable working time & sufficient green strength to demould at 6 hours.

**Table 4. Castable properties for 4.5 % water and 0.075 % PCE dosages**

		PCE 2	PCE 2	PCE3	PCE 3
Li <sub>2</sub> CO <sub>3</sub>	mmol/kg	0.0446	0.0676	0.0446	0.0676
<b>Vibration flow</b>					
T0	(%)	185	180	166	99
T15	(%)	152	142	96	55
T30	(%)	135	128	75	33
T60	(%)	110	67	35	0
<b>ASTM flow T0</b>	(%)	108	115	97	54
<b>Durometer Setting time</b>	min	240	180	60	25
<b>Exotherm</b>					
Max peak T	°C	26.5	26.6	25.5	25.4
Time of peak	min	437	329	620	376
<b>Ultrasonic time - 1st peak</b>	min	171	93	12	12
<b>Cold strength</b>					
6h MOR	MPa	0.47	2.80	0.00	0.61
24h MOR	MPa	5.63	5.95	6.54	6.35
2d MOR	MPa	7.12	6.51	8.00	7.94
7d MOR	MPa	12.01	11.96	13.84	14.37
6h CCS	MPa	5.18	16.84	0.00	4.16
24h CCS	MPa	37.15	34.95	37.20	35.68
2d CCS	MPa	46.70	41.20	41.70	52.08
7d CCS	MPa	82.00	83.63	100.20	81.13

## 4 Conclusion

The use of PCE's that effectively fluidify high purity, LCC systems generally retard the onset of strength development. Whilst the reasons for this retardation are not fully understood, it would appear that the PCE addition prolongs the nucleation period of the CAC hydration process. This can be overcome through the use of lithium ions without any detrimental effect on the rheology. Thus, by coupling the latest generation of superplasticisers with classical additives, it is possible to maintain the fluidity & desired placing properties of the castable whilst simultaneously achieving the required hardening profile.

The use of multiple additive systems is thus necessary to control each step of the CAC hydration process in order to obtain the desired physical properties of the castable. Unfortunately, this implies the development of increasingly complicated and optimised formulations. A future challenge could be to offer the active binder phase to the refractory producer to provide a simplicity and robustness that doesn't exist today.

## 5 References

- [1] Y. Tanaka, A. Ohta, T. Sugiyama, "Poly-carboxylate based advanced superplasticisers for high performance concrete", *Cement & Concrete* Vol 52, 1998.
- [2] J. von Seyerl, "Use of Polycarboxylate ethers to improve workability of castables", *DKG*, Vol. 84, No. 9, pp E46 – E49, 2007.
- [3] C. Parr, M. Lievin, C. Wohrmeyer, C. Alt, "Optimisation of the hardening properties of refractory castables using non-destructive techniques to measure early age properties", *Int. J. Appl. Ceram. Technol.*, 4 [6], pp524-534, 2007.
- [4] C. Parr, T. Bier, "The design fundamentals of high technology castables: an understanding for steelmakers", *International Iron & Steel Conference*, Chicago, USA, 1999.
- [5] C. Parr, C. Wohrmeyer, B. Valdelievre, A. Namba, "Effect of Formulation Parameters upon the Strength Development of Calcium Aluminate Cement Containing Castables", *Taikabutsu Overseas*, Vol. 23, part 4, p231-238, 2003.
- [6] E. Maeda, "The Setting Behaviour of Low Cement Castables", *90th Technical Committee on Refractories for Casting TARJ*, 2008.
- [7] T. Bier, A. Mathieu, B. Espinosa, C. Marcelon, "Admixtures and their interactions with high range calcium aluminate cement", *UNITECR*, Japan, 1995.