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Refractories Applications *Transactions*

INVESTIGATIONS INTO THE INTERACTIONS OF DEFLOCCULATED CASTABLES WHICH CONTROL PLACING AND HARDENING PROPERTIES, PART 1: PLACING PROPERTIES

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ABSTRACT

This paper presents a novel approach to investigate the chemical reactions that take place during the placing phase of deflocculated castables and the underpinning mechanisms that explain the visible placing properties. An experimental procedure has been developed to study reactions within the matrix binder phase (calcium aluminate, alumina, fume silica, and additives) in a concentrated suspension similar to that used in complete deflocculated castables. This has provided new evidence of the interactions that occur during the placing phase of deflocculated castables.

A low cement castable (LCC) containing calcium aluminate, alumina, fume silica and a sodium phosphate based additive has been studied. Experiments are conducted using wet mixed model systems through the different placing phases of initial flow, flow decay and stiffening. Newly developed measurement techniques of concentrated suspension conductimetric analysis, in parallel with existing techniques of ultrasonic velocity and thermal analysis are performed. During the placing and stiffening phase periodic extractions of the pore solution are made using a new approach to determine the various ionic concentrations. Conclusions show that the working time is controlled by two mechanisms: the progressive formation of calcium polyphosphate by ionic exchange with sodium and the presence of silica ions derived from the fume silica, which regulate the formation of calcium polyphosphate. Together they govern the workable period and flow decay of deflocculated castables.

INTRODUCTION

Castables, based on calcium aluminate binders have evolved from high cement conventional formulations to the era of reduced cement castable systems that can be placed using a variety of techniques such as casting, gunning, self flow, pumping and shotcreting. The usage chain of monolithics containing calcium aluminates contains several steps such as mixing, placing and consolidation, commissioning and dry out and finally use in service. Each of these steps within the castable placing chain is intimately linked to the hydration process of the calcium aluminate binders. In order to understand the role of calcium aluminates it is first necessary to consider the reactions that take place during the hydration process and to then link these reactions to the physical aspects of the castable properties. The mechanisms within the deflocculated family of castables are intrinsically complicated to understand due to composition of the matrix components, which usually contain sub micron fillers and additives. The flow decay, stiffening and setting behavior of deflocculated castables depends on these matrix components and their influence can be considered in terms of three main concepts; the particle packing, the forces which develop between surfaces of particles and thirdly the reactions of calcium aluminate

binders which give rise to changes in ionic concentrations and the subsequent formation of hydrates which influences the inter-particle forces. This paper will focus on the chemical interactions which control the placing properties of deflocculated castables and in particular the mechanisms, which control the working time.

Previous analyses^{1,2,3} have relied upon studying matrix phase interactions of ionic concentrations and activities in dilute suspensions with a water/binder ratio up to 10. A typical curve of conductimetry (Fig. 1) as a function of time, using a matrix phase of model low cement castable is produced at a water to cement (w/c) ratio of 7. The curve reveals three distinct periods which have been attributed to firstly 'delayed' calcium aluminate dissolution to achieve saturation then an induction or nucleation period and thirdly the period with precipitation of hydrates. However, the fact that this analysis is done at a w/c of 7 or more can distort the results relative to the real situation where the w/c is often less than 1. For example, dilution may retard reactions, which may or may not be overcome by the accelerating effect of stirring, which increases ionic mobility. In addition, the eternal question of whether to dose additives as a function of the cement or water content is raised. This can lead to differences between the model systems and the real behavior of the castable and induce errors with respect to interpretation of the results.

Therefore the development of a new experimental approach was commenced with the objective of being able to analyze matrix phase interactions at a w/c close to that which is used in actual castables. The aim was to develop a conductimetry technique at w/c levels around 1 and to allow extraction of the pore solution during the entire hydration process which would cover the time frame of placing and stiffening of reduced cement castables. This would provide the means to perform mechanistic studies of the chemical interactions, which control placing and set-

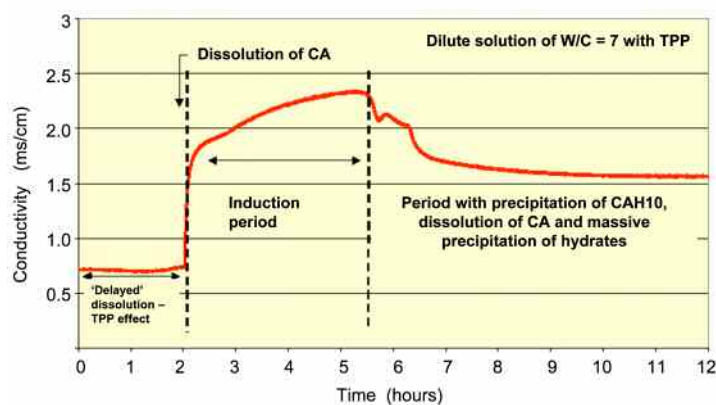


Fig. 1. Dilute solution conductimetry analysis of a LCC binder phase at W/C=7.

ting properties as well as yielding a new insight into the hydration kinetics of the calcium aluminate binder. A mortar was proposed rather than simply a mix of the binder phase components, as this would allow an easier transposition of result to the actual concrete.

EXPERIMENTAL DETAILS

Model Systems

A model deflocculated castable and more specifically a low cement castable (LCC) has been used for the experimental study (**Table 1**). A 'binder phase' mortar comprising of the fine part of a model (LCC) has been derived from the full sized LCC. The particle size distribution has been re-calculated from a maximum size of 10 mm to 3 mm in the case of the mortar.

The relative proportions of the matrix components have been held constant in the mortar and the additions re-calculated to 100%. Different water additions were studied with a water to cement ration (w/c) of the mortar ranging from 0.72 to 1.44. The recalculated particle size distribution allowed a higher w/c ratio to be used whilst at the same time conserving the workability close to the complete concrete and avoiding problems with segregation.

The water content was determined on the basis of achieving at least 100% initial vibration flow (vibration 30 sec at 0.5 mm amplitude with initial cone diameter of a lower diameter of 100 mm and an upper diameter of 70 mm. The height of the cone measures 50 mm). The working time was measured as defined by the time at which the concrete, when subjected to vibration, displays zero flow. It was measured for the whole castable system (WT=120 min). This is sometimes referred to as the "setting time" which is a somewhat ambiguous term as it can lead to confusion with a "setting" associated with hydrate formation in classical or conventional refractory concrete.

Conductimetry Analysis

The basic apparatus is described elsewhere⁴. The circular electrodes are around the circumference of the conductimetry cell. A modified cell is used here, which allows the safe removal of stiffened/hardened mortars without damaging the cell at low w/c ratios. The data acquisition and processing is as in previous studies and publications^{3,4}.

Exothermic Profiles

Hardening kinetics were followed by exothermic profile. Exothermic profiles were determined at 20°C with castable samples placed in an insulated chamber. A thermocouple, imbedded in the cast sample, is linked to a data capture system and the temperature recorded as a function of time⁵.

Ultrasonic Profiles

A special ultrasonic cell has been used to follow the wave propagation during the first hours after mixing of the concrete with water. A detailed description of the test method is presented by Simonin, e al⁶. The results are expressed as speed vs. time. These graphs allow the

observation of structuring during the early phase after mixing and of the subsequent hydration process of the concrete.

Pore Solution Extraction and Analysis

The mortar is wet mixed for a total of 8 min and the resulting wet mixed mortar is used to fill test tubes, which are placed in a centrifuge. Samples are subsequently centrifuged at 4500 rpm for 3 min after a pre-determined time interval. The liquid is recovered, filtered, diluted and acidified to precipitate the fume silica residue. These extractions are analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES – Perkin-Elmer). It is possible that the extracted pore solution contains some colloidal particles that are not visible during the analysis. Similarly other residues (such as AH_x , $A=Al_2O_3$, $H=H_2O$) may also be dissolved. The technique requires further refinement to eliminate these potential effects. Therefore a certain caution is needed when analyzing the results.

Hydrate Characterization and Analysis

Hydration is stopped by acetone-ether treatment⁷. At pre-determined intervals by washing/filtration of the mortar with acetone-ether, drying and screening out the +80 micron residue. The resulting samples are analyzed by x-ray diffraction (XRD, Bruker AXS Model S4) carbon and water content and via Differential Thermal Analysis (DTA-Perkin Elmer Thermogravimeter).

EXPERIMENTAL RESULTS

Optimization of Mortar and w/c Ratio

The first requirement was to find a water/cement (w/c) ratio that would permit extraction of the pore solution whilst at the same time preserving the intrinsic hydration kinetics relative to the complete LC castable. As a starting point, a w/c ratio of 0.72 was chosen and the results compared with the previously used dilute solution with a w/c of 7 (**Fig. 2**).

As with the dilute solution, the initial conductivity shows a period of stable conductivity values with a similar duration to that of the dilute solution but with a higher initial value. After approximately 2 hrs there is a divergence of the two curves and it is difficult to discern the induction period and the start of the massive precipitation in the case of the concentrated solution. The curve then decreases to almost zero, which indicates insufficient free water to provide an electrical continuity. At this w/c, it was not possible to extract pore solutions in a sufficient quantity that could be analyzed. Therefore, it became necessary to increase the w/c ratio.

The w/c was increased up to 1.44 and the interval 1.08 to 1.44 studied (**Fig. 3**). At 1.08 and 1.26 w/c ratio the curves appear to be similar

Table 1. Composition of Model Low Cement (LCC)

	Castable	Mortar
BFA : 10-1 mm	56	-
BFA : 3-1 mm	-	27.9
BFA : -1 mm	27	44.2
FS : Elkem 971U	5	8.2
Alumina/Alcan P152SB	7	11.5
CA: Secar [®] 71	5	8.2
Sod. Tripolyphosphate (TPP)	+0.07	+0.11
Water	3.6	5.9-11.8
w/c	0.72	0.72-1.44

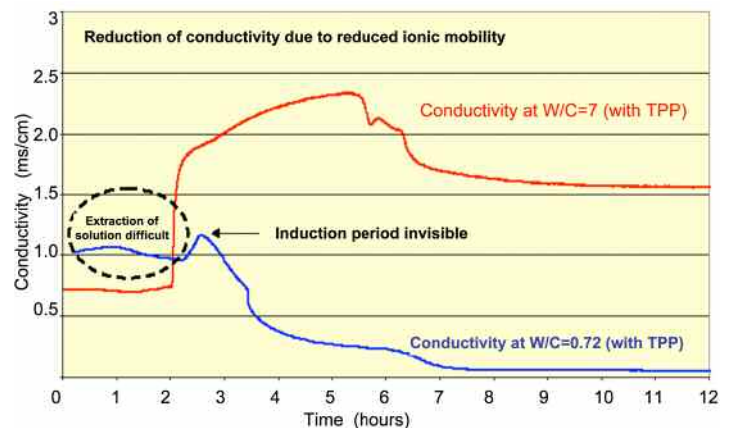


Fig. 2. Comparison of dilute and concentrated conductivity analysis.

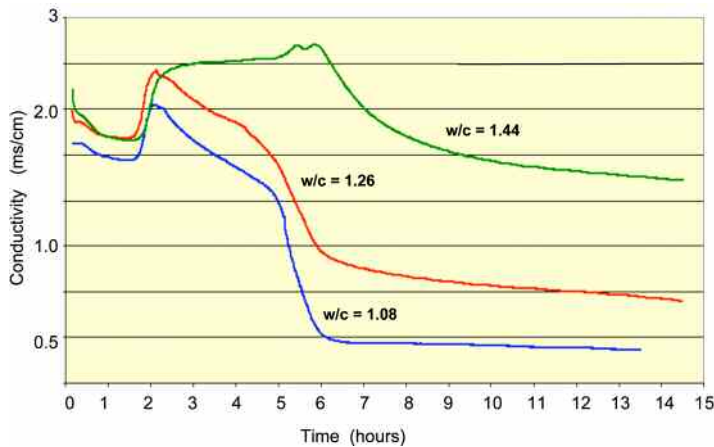


Fig. 3. Influence of W/C ratio on the conductivity profile of the LCC mortar.

to the case of w/c at 0.72 with the main difference being the final conductivity value, which does not decrease to zero. In addition the conductimetry values during the first 2 hrs tend to decrease compared to a stable value at w/c at 0.72. At 1.44 the curve resembles that of the dilute solution, except for the initial period up to 2 hrs but the different 'events' seem to occur in the same time interval. The choice of 1.44 w/c was preferred for subsequent analysis as it was possible to extract sufficient pore solution at this w/c . Given that the solution is more dilute than the complete LCC a validation compared to the reference LCC is required. Shear effects on the hydration kinetics should not be ruled out.

Validation of the Mortar and w/c Ratio

Three methods, conductimetry, ultrasonic profile and the exothermic profile have been compared simultaneously using the same mortar (Fig. 4). During the first 2 hrs a 'pseudo plateau' is observed which reveals a slightly decreasing conductivity. The temperature increases slightly during this period and the ultrasonic propagation speed remains stable.

At around 2 hrs the measured values of the three techniques increased rapidly indicating an increased ionic activity, chemical activity and the start of stiffening. At about 5 hrs, the conductivity can be seen to increase to a maximum prior to a rapid decrease. There is also a rise in the propagation speed and at the same time the temperature rises to a maximum (28-29°C) during the period 5 to 8 hrs. Thus, it can be seen that the different events as measured by the three techniques are simultaneously linked to the developing structure. The event at 2 hrs corresponds with the working time of the complete LCC. The initial flow decreases during the period up to 120 min. A further validation was performed by comparing the ultrasonic curves of the complete LCC and the corresponding mortar. The results showed that the different events occurred at the same time but the final propagation speeds were higher in the case of the complete LCC.

It was concluded that although the w/c at 1.44 is higher than the real system and that the ratio of additive to water is two times more dilute there is no significant effect upon the kinetics of the different observed events.

Analysis of Pore Solution

The extraction and analysis of the pore solution was a major experimental objective, as conductimetry alone does not provide enough information to understand different phenomena. Periodic extractions

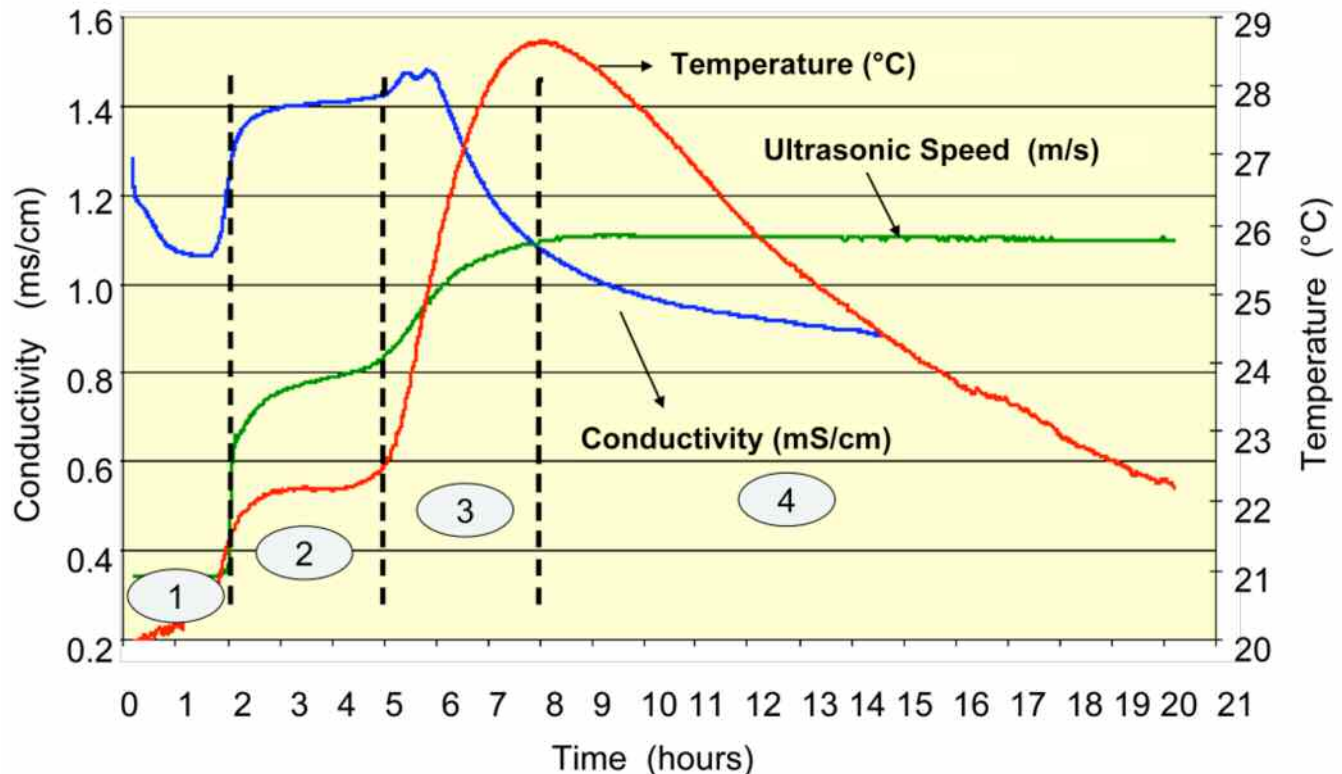


Fig. 4. Comparison of ultrasonic, exothermic and conductivity curves for the LCC mortar at 1.44 w/c .

were made of the pore solution of the LC mortar during the workable period and prior to the rapid loss of flow and stiffening associated with the arrival of the end of the working time. The first extractions were made 10 to 15 min after the water addition. Due to mixing effects it was not possible run extractions earlier. Progressive extractions were made between 15 and 120 min from mixing and the change in ionic concentration of each species (Fig. 5) was measured via ICP-AES.

During this period significant change in ionic concentrations was observed which is somewhat contrary to the picture from the conductivity analysis where an initial 'pseudo plateau' is seen. A number of observations can be made:

1. Alumina passes progressively into solution with an accelerated dissolution between 60 and 80 min.
2. Calcium is present in an initially higher concentration than alumina. The calcium concentration increases up to 110 min then decreases.
3. Phosphate (from the TPP) has a high initial value, which decreases progressively. After about 80 min, it decreases more rapidly than the calcium.
4. Magnesia and silica in relatively low concentrations follow the same trend as the calcium and phosphate.
5. The concentration of the alkalis remains relatively stable albeit at a high level in the case of sodium (from TPP).

After the period of rapid stiffening it is no longer possible to extract pore solution by centrifugal forces and another technique would have to be developed to study this period.

Analysis of Hydrates

The analysis of the hydrates is the only technique available to study this period after the end of working time. Samples were taken at 5, 8 and 24 hrs after the hydration stopped and the residue was analyzed by CO₂/H₂O, XRD and DTA. XRD did not identify any crystalline hydrates despite an increase in the amount of combined water as a function of time. Only DTA was able to identify the presence of hydrate species (Fig. 6) as evidenced by a series of peaks associated with the different calcium aluminate hydrates.

- At 5 hrs the first signs of a peak (120°C) attributed to CAH₁₀ (where C=CaO, A=Al₂O₃, H=H₂O, S= SiO₂).
- At 8 hrs an additional peak around 190°C was attributed to either C₂AH₈ or C₂ASH₈. A third peak can also be discerned around 290°C and is believed to be AH₃ and C₃AH₆.
- At 24 hrs there was an increase in all peak sizes.

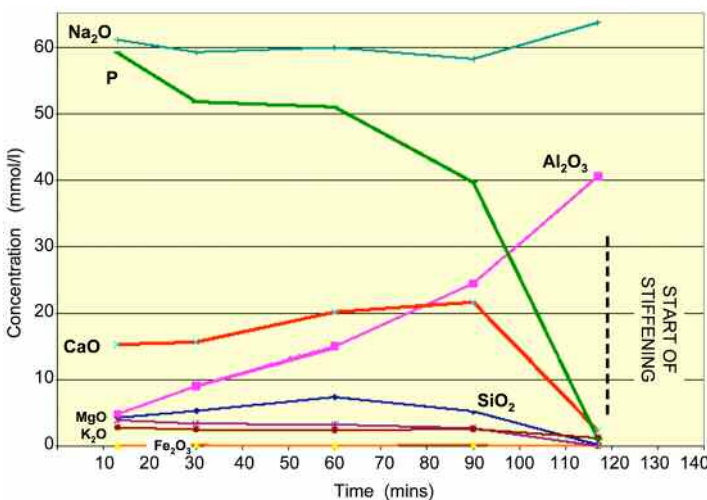


Fig. 5. Ionic concentration as a function of time after mixing for the LCC mortar.

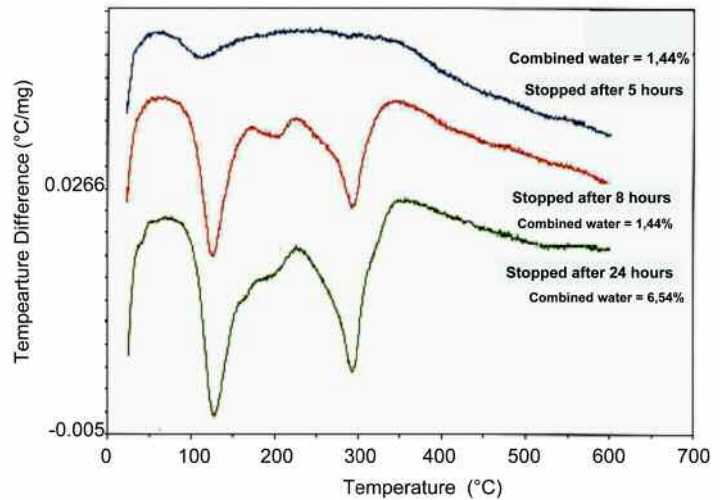


Fig. 6. DTA curves of the LCC mortar during the hardening phase.

The attribution of hydrates remains a hypothesis, because no technique for independent verification has been devised.

Effect of Fume Silica and pH

The change in pH with time has been measured simultaneously with the conductivity measurements during the first 180 min (Fig. 7).

The pH drops initially to a minimum of 9.4 at 15 min. It subsequently rises with time until a value of 10.9 is reached at 110 min. At this moment there is an inflection in the rise of pH and this happens at the same point the conductivity suddenly increases.

In order to better understand the nature of the TPP interactions the base mortar was modified to substitute the fume silica for more reactive alumina. The conductivity curves for the standard and the modified mortar (Fig. 8) are similar after 2 hrs.

In the case of the modified mortar there is no initial 'pseudo' plateau. At the same time the mortar was very stiff and corresponded to previous experience with such fume silica free systems⁹.

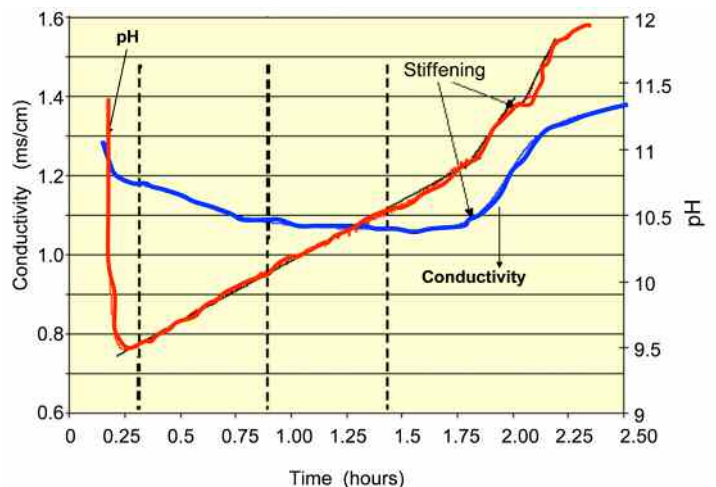


Fig. 7. Comparison of the change in pH and the conductivity curve.

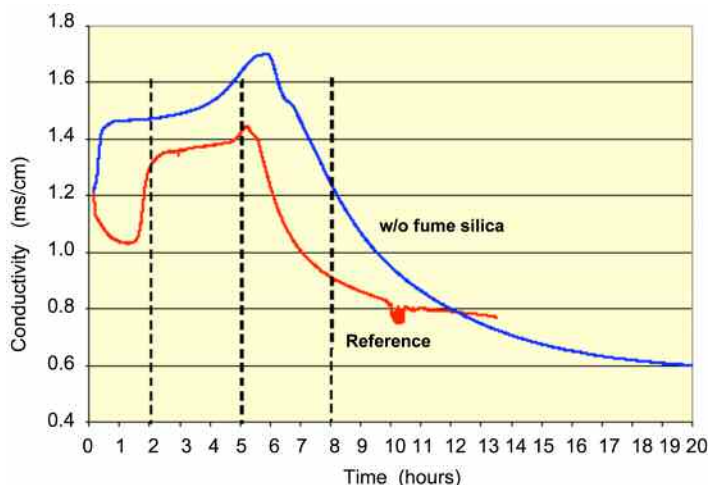


Fig. 8. Effect of fume silica on the conductimetry profile of the LCC mortar.

DISCUSSION

The study of interactions of binder phase systems has been the subject of numerous previous publications and in particular the previously established view that TPP is effective as a single additive as it ensures sufficient fluidity and working time for a base system without recourse to retarders and other fluidifiers⁸. This is fundamentally different from the systems without fume silica, which often need to have a fluidifying additive coupled with a retarder⁹. This leads to the supposition that there is an interaction between the calcium aluminates, the phosphate and the fume silica. Diagnostic studies^{1,2} dating back to 1989, using calorimetry and conductivity, proposed a mechanism whereby the TPP formed an insoluble precipitate with the calcium and the fume silica adsorbed calcium on to its surface. The initial 'pseudo plateau' (see Fig. 1 for an example) was interpreted as a 'blocking' of the calcium aluminate dissolution. The mechanism was postulated that the insoluble phosphate was precipitated on the surface of the cement as an impermeable or semi-impermeable layer of calcium phosphate and/or C-S-H gel. The TPP is slowly consumed via the formation of this layer. Once the TPP had been consumed the end of working time occurs. At the same time there is a rapid dissolution of the calcium aluminates due to the disappearance of this layer.

The current experiments and analysis conducted in a more concentrated solution than previous work clearly raises questions about the validity of this hypothesis. This will be shown through a discussion of the role of TPP, fume silica and the calcium aluminates. More recent studies^{10,11,12} have also cast new light on the role of fume silica, and the nature of the interactions between CA-TPP-FS.

Role of Sodium Tripolyphosphate

Reference is made to Fig. 5 and the change in ionic concentration with time. The concentration of TPP added to the mortar equates to 26.4 mM/l of $\text{Na}_5\text{P}_3\text{O}_{10}$. This corresponds to a theoretical maximum value of 66 mM/l of Na_2O and 71 mM/l of P.

- An initial concentration of 63 mM/l of Na_2O is measured.
- The initial concentration of P is measured at 60 mM/l this decreases to 40 mM/l at 90 min and only 1 mM/l at 117 min, which is the end of the workability period. Thus, the phosphate is removed from solution at the same time as the workability decreases to zero. Both the initially measured concentration of sodium and phosphate would suggest that effectively all of the TPP has passed into solution. The difference between the ini-

tially measured value 60 mM/l and the theoretical maximum of 71 mM/l is presumed to be principally linked to the quantity of phosphate adsorbed on to the surfaces.

- The calcium ion concentration is initially 15 mM/l and rises to a maximum of 21.6 mM/l before dropping to a minimum value of 2.25 mM/l. It appears as if the precipitations of calcium and phosphate are intimately linked. It should be noted that during the time the TPP is in solution the calcium is complexed by the NaTPP and does not necessarily exist in the form of a free ionic species.
- The concentration of alumina (which is a major constituent of the calcium aluminate cement) is only 4.8 mM/l at 13 min and increases slowly to a value of 40.6 at 117 min.
- Silica increases to 7.4 mM/l, decreases slowly then drops rapidly at the same time as the calcium and the phosphate.

The concentrations of calcium and alumina that are found are clearly very different from the situation of a calcium aluminate binder by itself where the lime and alumina concentrations increase simultaneously. If the measured alumina is assumed to come from the mono calcium aluminate phase then the following observations can be made:

1. The initial concentration of alumina should be equivalent to that of the calcium and more than 10 mM/l. It is possible that some of the alumina has already passed into solution and been precipitated as AH_3 in a gel form. This being promoted by the drop in pH that is observed which reduces the alumina solubility. It cannot be said, as previously imagined that there is a 'blockage' of dissolution of the calcium aluminate phases.
2. At the end of the working time the alumina concentration reaches 40 mM/l whereas the calcium drops to effectively zero. Logically, the calcium concentration should be of a similar value. If this 40 mM/l is considered plus the additional 10 mM/l (corresponding to the part of alumina precipitated as AH_3) then a total of 50 mM/l of calcium has been precipitated.

Thus, at the end of this working time it is logical to suggest that the calcium has precipitated as a form of phosphate with a concentration of 50 mM/l of calcium and 70 mM/l of phosphate. Considering different forms of calcium phosphates the most likely is calcium tripolyphosphate ($\text{Ca}_5(\text{P}_3\text{O}_{10})_2$). This can exist in several forms of a gel and as a crystallized species. Based on the change of concentration it is presumed that the formation of calcium tripolyphosphate (TPP-Ca) is progressive, and there is an ionic exchange between the sodium and the calcium. In summary, the TPP-Na is believed to adsorb on the particle surfaces to ensure a deflocculation. The TPP, which is not absorbed, forms complexes with calcium and magnesium, which helps to stabilize the solution rich in alumina and silica. The phosphate forms calcium tripolyphosphate by ionic exchange which results in the removal of phosphate from solution and this provokes the rapid stiffening of the castable at the end of the working time. Therefore the dissolution of the calcium aluminate is not "blocked" but regulated by the formation of the tripoly phosphate complexes, which are then precipitated. Unfortunately there is no experimental protocol available today to confirm the formation of TPP-Ca and this hypothesis.

Role of the Fume Silica

It is clear from Fig. 8 that there is some form of interaction with the fume silica, which prolongs the workability period compared to a system without fume silica. The presence of fume silica gives rise to a relatively high concentration of silica in solution with values rising to 8 mM/l, which equates to 300 mg/l. This is only possible as the calcium is complexed with the phosphate, otherwise the silica would normally precipitate as a C-S-H species when calcium ion concentrations are present up to 20 mM/l. In the same manner a high concentration of silica would precipitate very rapidly any calcium ions coming from a dis-

sociation of the TPP complexes or further dissolution of calcium aluminates. It can be imagined that the soluble silica plays a role of 'regulator and retarder' with respect to calcium that is 'free' in solution. It also delays the formation of TPP-Ca, which as a consequence lengthens the working period. From the concentrations measured (Fig. 5) it appears as if the alumina does not precipitate. It is not unreasonable to imagine the formation of C-S-H species as a result of soluble silica reacting with calcium. The calcium comes either from reversing the Ca complex or that which is not consumed by the precipitation of calcium triphosphate.

Comparison of Dilute vs Concentration Solutions

As a comparison the ionic concentrations and conductimetry of the binder phase have been followed in a dilute solution of w/c 7 (Fig. 9). The binder phase was comprised of the fume silica, CAC, alumina and additives only in the same ratio as the mortar. It is immediately obvious that the curves and solution chemistry are quite different from the measurements in concentrated solution, however a number of similarities can be noted;

- A similar 'pseudo' plateau of stable values is noted during the first hour. The conductivity values then increase to a maximum.
- The phosphate concentration decreases to zero at the end of the plateau.

The main differences between dilute and concentrated solution are observed for the calcium and alumina concentrations which are seen to:

- Alumina increases progressively to a maximum of 19.2 mM/L and thereafter a decrease is noted parallel with the drop in conductimetry.
- Calcium initially decreases then increases to a maximum of 16.6 mM/L in a parallel manner to the alumina.

It should be noted that the conductivity values rest higher for the concentrated solution and a low w/c (1.44) due to the fact that the concentration of sodium (from NaTPP) is higher. If the measurements in concentrated and dilute solution are compared, a number of important differences can be noted; the first being the concentration scale which is 0 to 20 mM/L for the dilute solution and 0 to 60 mM/L for the concentrated solution. During the workable period the conductimetry shows a 'pseudo' plateau and a flat profile for measurements in concentrated and dilute solution, however the values are higher in the case of the concentrated solution due to the higher concentration of sodium ions. The conductivity of the solid phase is negligible for the systems studied. So the conductivity of a dilute suspension is practically identical to the conductivity of the solution itself and is proportional to the ionic concentrations as seen in the Fig. 9. This is also true for the concentrated mortar (Fig. 2) during the first period where the volume of interstitial solution remains sufficient to form a continuous network and the conductivity follows the ionic concentrations.

A demonstration of the 'pseudo' plateau can be seen through an estimate calculation of the conductimetry from the ionic concentration. The calculation estimates the equivalent conductivity of a solution by taking the product of the concentration of the elements as a function of time and the equivalent conductivity of each ion [13]. The value for [OH] has been estimated from the measured pH as a function of time.

A number of assumptions were made including: silica and iron are not considered as only weakly ionized and poor conductors, phosphate based on the assumption that it exists in solution as polyphosphate and therefore a poor conductor, calcium and magnesium which are complexed by the TPP and therefore present only a low level of free ions able to act as conductors. The results in Table 2 show that the equivalent conductivity values are relatively stable during this period. Hence,

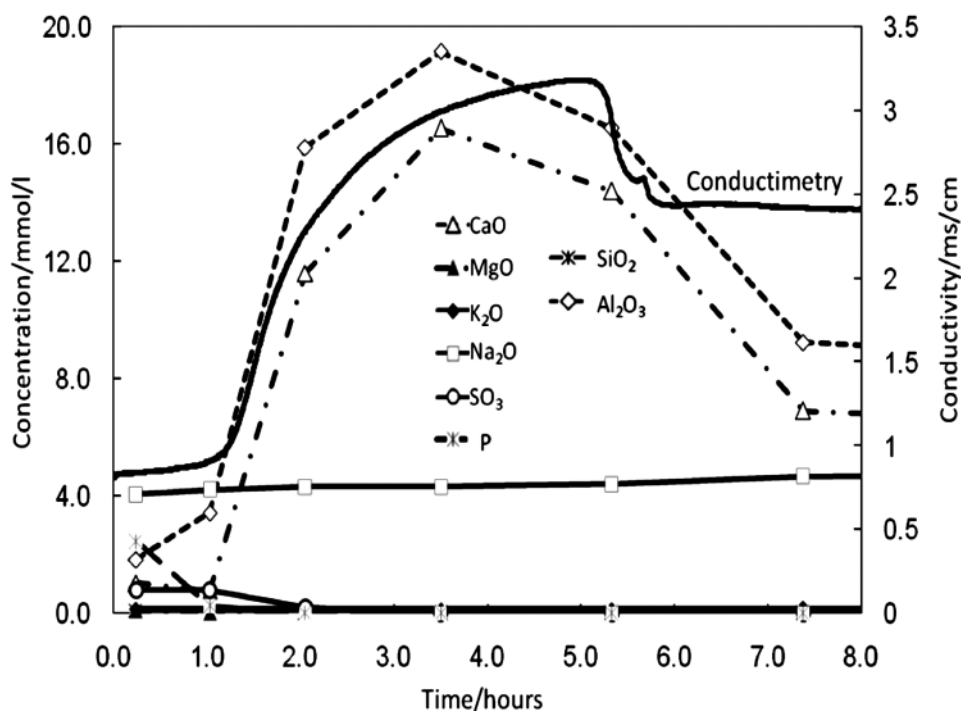


Fig. 9. Concentration and conductimetry in dilute solution (w/c=7) as a function of time.

Table 2. Estimated equivalent conductimetry conductivity values during the working time

Time Min	mmol/l K ₂ O	mmol/l Na ₂ O	mmol/l SO ₃	pH	OH	Equiv. Conductimetry
13	0.42	6.22	2.07	9.55	0.01	8.72
30	0.37	6.03	1.87	9.70	0.01	8.28
60	0.36	6.10	2.10	10.18	0.03	8.59
90	0.38	5.92	2.01	10.58	0.07	8.39
117	0.18	6.48	2.17	11.25	0.34	9.18

the idea of a 'pseudo' plateau which indicates stable conductivity values but in reality the ionic concentrations are changing and the stable conductivity values are in fact an illusion of the reality.

CONCLUSIONS

These new techniques have allowed the study of chemical interactions during the initial stages of castable placing. This provides new information on the different matrix interactions and in particular provides a much clearer explanation of the mechanism of action between the phosphates, fume silica and calcium aluminate phases, which control the period of flow decay and initial stiffening:

- The sodium tripolyphosphate absorbs on the surface of the particles in order to deflocculate them. Residual phosphate in solution forms calcium and magnesium complexes and is able to stabilize the solution in the presence of high ionic concentrations of alumina and silica, which come from the fume silica and calcium aluminates. The progressive formation of calcium polyphosphate by ionic exchange with the sodium results in a reduction of phosphate concentration and eventually the end of working is reached when no more phosphate is in solution.
- A portion of the fume silica is transformed into soluble silica in solution and this limits the quantity of non complexed calcium and slows down the formation of calcium tripolyphosphate hence it can be considered to play a part in the regulation of working time. Non-complexed calcium is hypothesized to result in the formation of C-S-H type gels.

Furthermore, the analysis has shown that the 'pseudo' plateau seen during conductimetry analysis, which had previously been attributed to the 'blockage' of the calcium aluminate phases, is in fact a coincidence. There are significant changes in ionic concentration during this period but the total conductance remains relatively constant. Unfortunately no techniques are available to characterize and confirm the existence of the calcium polyphosphate and the C-S-H hydrates. Therefore the hypothesis established to explain the mechanisms remains unconfirmed. One of the limits of this approach is that it is not possible to extract pore solutions by centrifugation after stiffening has occurred. In addition, the technique needs to be further developed to ensure that there is no carry over of colloidal particles or dissolved residues after filtering. The technique requires further refinement to eliminate these potential effects.

Another new technique has been developed which allows the extraction of pore solutions after stiffening and during the hardening phase. It is expected that this will give complementary information relating to the hydration kinetics during the precipitation of hydrates. Thus, it is hoped that by coupling this approach with the newly developed centrifugation technique it will be possible to gain a greater understanding of the whole castable placing chain. Part II of this paper will examine the hardening sequence.

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