A NEW INSIGHT INTO THE CHARACTERIZATION OF AGEING AND MECHANISMS THAT DETERMINE THE SHELF LIFE OF LOW CEMENT CASTABLES

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1 Introduction

Ageing is a generic name to describe interactions between a cement and the atmosphere and its impact on cement reactivity and castable properties. Ageing potentially occurs in all dry mixes but in the case of refractory monolithics its impact is much more evident in formulations containing lower amounts of binders like low or ultra-low cement castable. It often determines the effective shelf life of cement and low cements castables. The ageing process affects calcium alumina cement (CAC) from its production site to the point of use to produce the dry mix, and continues to affect the dry mixed castable itself once it is packed within its bag with all formulation components.

Ageing has been identified as an intrinsic difficulty of monolithic industry for many years and it is often the origin of on site problems linked to delayed hardening as well causing the scrapping and recycling of product due to internal quality control measures. It therefore remains a significant operational issue that incurs both quality and cost penalties. Progressing on this issue would need an understanding of the underlying mechanisms as well as measures and test. However this progress is made difficult for two main reasons (i) limits of usual analytical tools to better characterize the interaction because of the very low quantity of material that is involved and (ii) the numerous parameters involved in aging like humidity, temperature, nature and percentage of all dry mix components…

This paper presents results and analysis of different ageing experiments involving different conservation and climatic conditions, as well as different formulations. It will try to bring more understanding to the ageing mechanism and the impact of testing conditions.

2 Experimental procedure

Data from different studies run in different periods with different lots of cement will be presented. This is why the term “series 1”, “series 2” etc.. is sometime used. Data from the same series have been obtained with same raw materials. Ageing has been performed on cement alone or on total dry mix including all formula components. When cement is aged alone, castable properties are then measured including aged cement and non aged other raw materials.

Ageing has been performed as thin layer (5 mm) or in bags. All ageing test have been performed at 20°C. Most of ageing test have been performed in a laboratory climatised at 70% of relative humidity (RH). Ageing at 100% RH have been performed in a climatic chamber. Ageing at 100% CO_2 has been performed in sealed boxes with continuous gas flow of 100% CO_2.

Tab. 1 presents the different castable formula tested. Most of the data have been obtained with LCC TA1. Calcium alumina cement (CAC) is Secar®71, with 70% Al_2O_3, 29% CaO, 4000 cm^2/g of blaine surface, and its main mineral phases are CA and CA_2.

Tab. 1 : castable formulations

	LCC TA 1	LCC TA 2	LCC TA 3	LCC BA
Raw material	%	%	%	%
Tabular alumina	80	80	80	
Calcined Bauxite				85
Calcined alumina	10	10	10	5
Silica fume	5	5	5	5
CAC = Secar 71	5	5	5	5
TOTAL Dry	100	100	100	100
Na-TPP	0,03	0,08		0,08
PCE			0,15	
Water	5	5	5,5	5,5

Na-TPP = sodium tripolyphosphate / PCE = polycarboxylate ether

Characterisations

CAC powder after aging has been characterised by weight loss after heating at 950°C (% LOI) and X-ray diffraction to identify hydrates. Internal humidity within bags has been measured by inserting a remote sensor for humidity and temperature. Concrete flow is measured with an ASTM cone on a vibration table with amplitude of 0.5 mm and frequency of 50 hertz. The working time (WT) is the moment after which the concrete doesn't exhibit any flow under vibration anymore. The development of concrete structure has been measured using ultra-sonic speed as explained in [1]. Pore solution of the concrete has been analysed by ICP, after extraction of the matrix from the mixed concrete by screening at 1 mm, centrifugation and filtration.

3 Results

Typical impact of aging on LCC properties

Fig. 1 illustrates the typical impact of aging on the development of LCC structure followed by ultra-sonic velocity. The velocity curve with time is typical of LCC with silica fume and Na-TPP, and characterised by a two steps.. The first step is due to CAC dissolution / castable flocculation and corresponds to the working time with about 5 MPa in compression. The second step is the massive precipitation of hydrates leading to real hardening with compressive strength development above 10 MPa. Aging typically leads to a delay of the first step, the time between first and second step being constant. Other properties like water demand, 24h, 110°C or fired strength, porosity etc are not impacted by aging, as long as the water addition is the same.

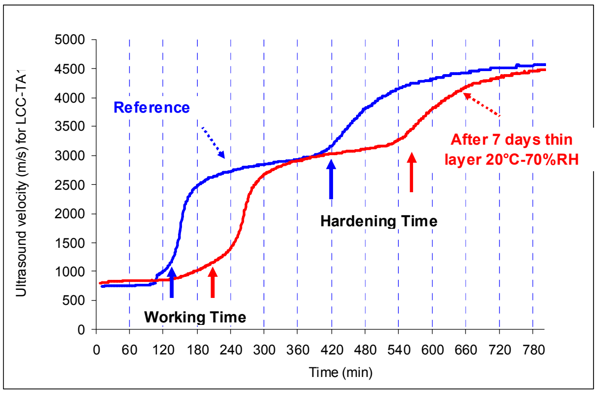

Fig. 1 : impact of aging of CAC (thin layer) on LCC-TA hardening kinetics (courbes US+ exo, visualiser WT et HT)

Impact of conservation conditions on aging of CAC

Fig. 2 compares aging at 70%RH-20°C of CAC alone as thin layer or within cement bags. For series 1, thin layer after 7 days leads to a WT increase of 200% and LOI of 0,3%. The same effect is observed after 2 months in a bag. Aging for 4 months in series 1 or series 2 is much more severe, WT can increase up to 800% with a LOI of 0,7% (4 months, series 2). It is interesting to note that WT at 8 and 10 months are shorter than working time at 4 months. However after 10 months centimetres agglomerates have been found in the bags. XRD analysis of these agglomerates revealed the noticeable presence of diffraction peaks for C_3AH_6 and AH_3.

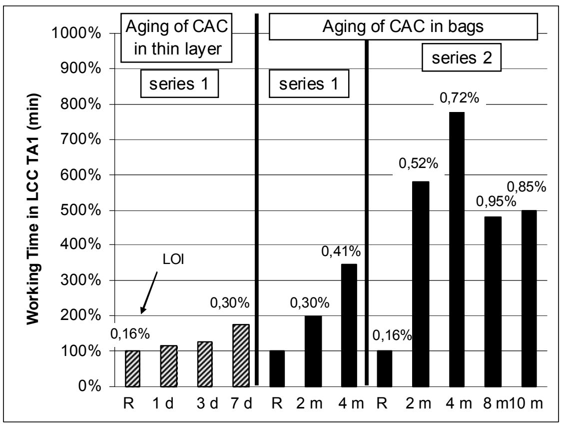

Fig. 2 : impact of aging of CAC alone in thin layer up to 7 days or in bags up to 10 months on working time in LCC TA1 and LOI %.

Fig. 3 shows aging of CAC as thin layer under extreme atmospheric conditions all at 20°C. Under 100% RH ageing is very quick. After 8 h LOI % and WT increase are similar to several months in bags under 70% RH-20°C. After 24h the LOI is very high at 2,54%, but WT is now very short at 40% of initial WT. This is the same phenomenon that is previously described in Fig. 2 : extreme ageing leads to formation of hydrates and reduction of WT. At 90% RH the rate is lower, the same level is obtained after 24 hours. Under 100% CO_2 and very low RH (< 15%) aging is observed only after 5 minutes at the same level as 2h under 100% RH ! This shows that aging is not only due to H_2O but also to CO_2 pick-up, as already shown [2]. However aging does not evolve between 5 min and 2 hours. Longer observation would be necessary to know if a steady state has been reached reflecting the amount of potential surface carbonation without humidity. Although very artificial, such test at high % RH and/or high % CO_2 could be useful as an accelerated test for aging, giving an answer in less than one day.

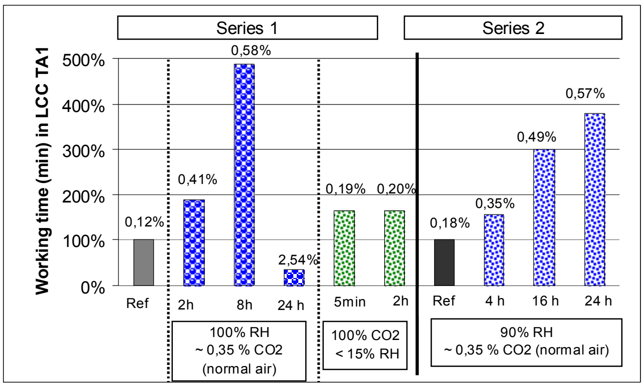

Fig. 3 : impact of aging on working time in LCC TA1 and LOI, aging of CAC alone as thin layer in different atmospheric conditions (all at 20°C).

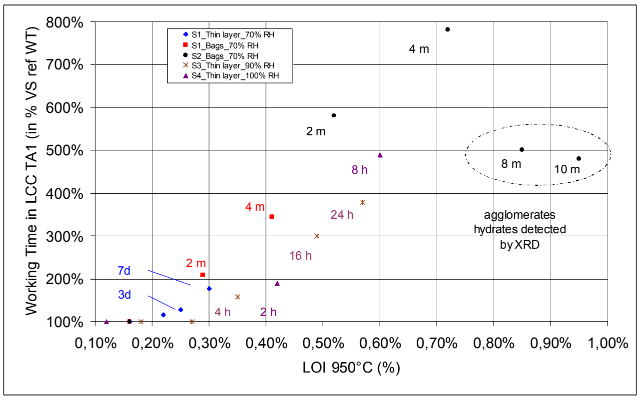

Fig. 4 : relation between working time in LCC TA1 and LOI of cement for different aging conditions of CAC.

Relation between reactivity and LOI

In Fig. 4 all available experimental data points for LCC TA1 have been plotted in a graph showing WT increase = f(% LOI). There is a continuous and almost linear relation up to about 0,70% LOI. The two points at higher LOI (>0,8%) fall outside out of this relationship, probably due to the precipitation of hydrates.

A prior publication [3] have shown that aging of CAC leads to a delay of conductimetry increase of a CAC suspension, assuming a delay in CAC dissolution. Fig. 5 shows calcium ion concentration of the pore solution of the LCC castable after 30 minutes. An increase of LOI from 0,12% to 0,58% leads to a decrease of Ca^{2+} concentration at 30 minutes 24 to 12 mmol/l which definitely confirms the delay of dissolution.

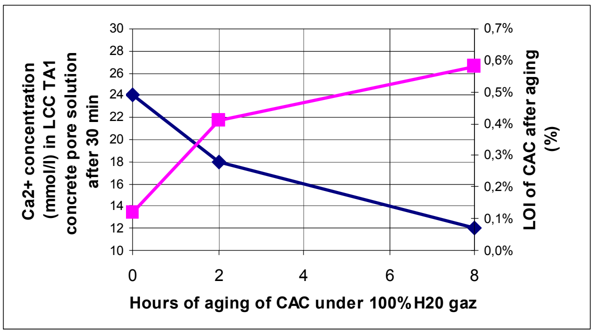

Fig. 5 : impact of aging of CAC on calcium content within the pore solution of LCC TA1.

Aging of total dry mix compared to CAC alone

Fig. 6 compares aging in bags of CAC alone and total dry LCC TA1 mix at 70% RH-20°C Total aging is similar, but it occurs more quickly for the total dry mix, where a decrease in WT is observed at 4 month.

The internal humidity within the bags hasbeen measured and compared with the humidity of the laboratory : Fig. 7. For the cement RH starts at 57% and gradually reaches an equilibrium with external atmosphere after 15 days. On the other hand for total dry mix RH is initially high high at 75% RHreaching the same level as cement after 45 days. This higher internal humidity explains the quicker ageing of the formula within the bag.

Comparison of different formulations

Fig. 8 compares aging of different formulas in bags. With TPP as additive, the switch from tabular alumina to bauxite aggregate increases aging, probably due to higher porosity, moisture content of bauxite.

Keeping tabular alumina as the aggregate, the switch from TPP to PCE increase aging. It is known that different admixtures don't all have the same hygroscopic behaviour, polymeric molecules like polyacrylate have a higher tendency to pick-up moisture [2].

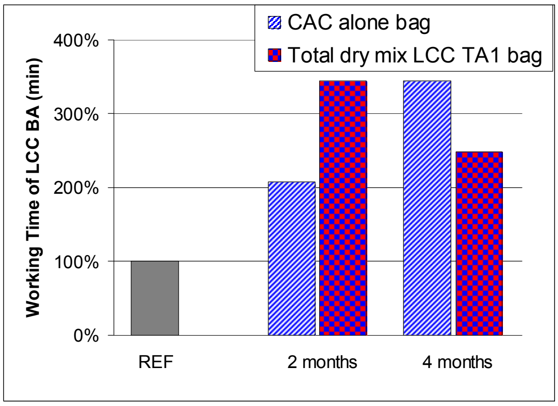

Fig. 6 : impact of aging on working time after aging (70% RH-20°C) as thin layer, either CAC alone or total dry mix LCC BA.

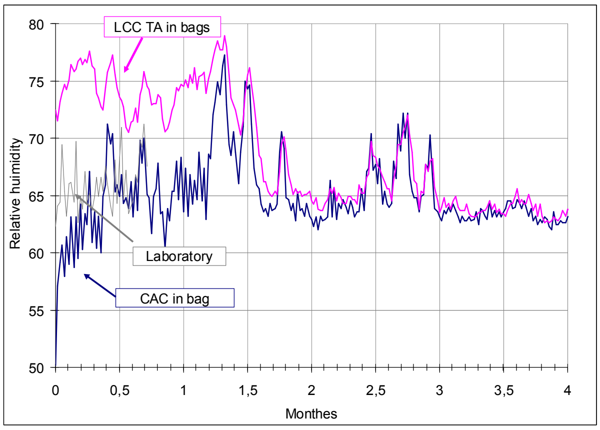

Fig. 7 : measure insitu of relavite humidity within the bags of CAC alone or total LCC TA 1 dry mix, and laboratory conditions.

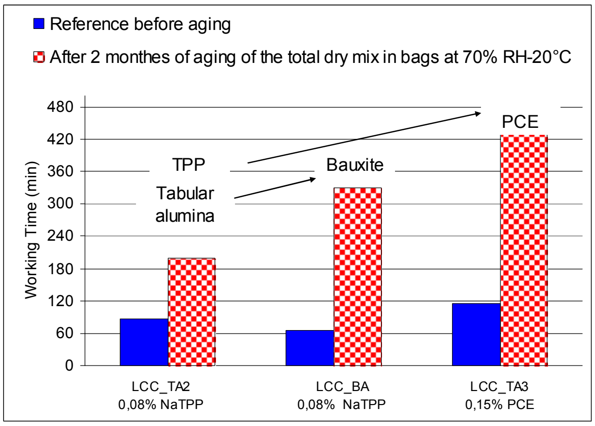

Fig. 8 : impact of aging of total dry mix in bags (70% RH 20°C), comparison of different formulas

4 Discussion

Ageing is initiated by H_2O and CO_2 pick up from the atmosphere, leading to a moderate weight increase of the CAC, an increase of working time and consequently the demoulding time. From a practical point of view it means variability and unpredictability on site depending on the freshness of the dry mix castable.

Fig. 4 shows an almost linear relation between WT increase and LOI of CAC as long as the LOI is inferior to 0,7%, at least for the formula tested, i.e. LCC containing silica fume and deflocculated by Na-TPP. No hydrates are detected at this stage. It can be assumed that

CAC surfaces are covered by hydroxyl and/or carbonate bonds, leading to a lower surface energy and delayed dissolution, as shown by Fig. 5. With a closer look at Fig. 4 it can be seen two set of points following two parallel trends. The points representing ageing at higher relative humidity (90% and 100%) exhibit lower WT increase for the same LOI. The relative split between H_2O and CO_2 molecules on the CAC surface and their relative impact on reactivity is not known. It is possible that they depend on relative humidity, which would explain these two sets of experimental points, dependant on % RH and that the impact of reactivity of H_20 pick up, are not the same as CO_2 pick up.
When ageing is pushed further LOI continues to increase and can reach very high values (> 2%). It is generally at this stage that lumps are observed. In extreme case like 24h_100% RH (Fig. 3), theWT after ageing is even shorter than before. In this situation it is probable that hydrates have been formed and are acting as nucleating agent for more hydration and/or are consuming admixture. The fact that hydrates have precipitated means that a liquid H_2O film have been formed since hydration always proceed by dissolution of anhydrous phases and precipitation of hydrates from ions dissolved within the liquid. Condensation of a liquid film from internal humidity can be due to condensation of water molecules in a meniscus within small pores of CAC or other powder particles. The liquid film can also be due to cooling, for example during the night, leading to temperature inferior to the dew temperature. For example, the atmosphere of a bag that would be packed at 20°C with internal relative humidity of 60% would have a dew temperature of 12°C.

Ageing of CAC alone is not equivalent to ageing of total dry mix including all components. In the case of LCC with Na-TPP it is assumed that the main impact of other components is to bring moisture, hence leading to a higher internal humidity within the bags and quicker ageing of CAC, as shown by Fig. 6 and Fig. 7. For this experiment LOI of silica fume and aggregates were 0,7% and 0,04% respectively, and this was enough to bring internal humidity of the bag from 58% to 72%. with quicker ageing. This effect should be enhanced when using more porous aggregate (Fig. 8). Other admixtures than Na-TPP are more hydroscopic, like for example hexametaphosphate (HMP) or PCE ether for example. This hydrophilic behavior can be the source of higher H_2O pickup, with a risk of a local liquid film formation. Hydrolysis of the molecule itself is also possible, with a modification of its effect, for example the generation of an acid group by hydrolysis of HMP [4] leading to a strong retarding effect.

Concerning a shelf-life and ageing test, on site testing of shelf-life is deemed to be necessary. But as ageing is dependant on so many parameters it would be useful to complement this type of test by other data. In situ measurement of temperature and internal humidity within bags during its shelf life would be very valuable. This can be easily done by special remote sensors.
Accelerated laboratory tests could be done within the day if humidity is high enough (typically 90%) for example to compare different formula or testing solution against ageing.

5 Conclusion

Ageing of CAC seems to proceed by two periods, each one leading to weight increase and characterised by increase of LOI, but having opposite impact on reactivity. The first period is a surface pick up of H_2O and CO_2 which leads to a delay of dissolution, working time and demoulding time. At this stage there is generally no visible sign of ageing like lumps. The second period is characterised by a decrease of working time and the precipitation of hydrates.

Other components of the formula also play a role in ageing, either because they bring moisture and increase internal humidity within the bag, or by hydroscopic behaviour of some admixtures.

In order to better understand ageing mechanisms and design rapid ageing test it is necessary to generate insitu internal humidity and temperature within bags during shelf life. Rapid ageing tests can be performed in the laboratory, for example at 90% RH the level of ageing after one day is equivalent to several months in bags.

6 References

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