Lessons on aging

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Calcium aluminate cement, well established as a binder in the refractory industry, shows hygroscopic behaviour and therefore needs to be protected against moisture during storage to prevent aging. While multilayer paper bags are commonly used as standard packaging, shelf life is typically limited to 6-12 months. Therefore, the aging behaviour of Almatis calcium aluminate cement packed in plastic bags was investigated by storing it in a warehouse for 40 months. The cement was tested periodically in a castable for mixing and self-flow behaviour, setting and strength, and the findings presented below.

Multilayer paper bags are commonly used as standard packaging for cement, often in combination with additional pallet protection (eg, stretch hood or shrink wrap). However, cement packed in paper bags has a limited shelf life, typically between 6-12 months.

In the 1990s extended tests were carried out to investigate the shelf life of Almatis calcium aluminate cements. This included Brazilian warehouse storage and even more severe testing under 'jungle room' conditions in a climate chamber. Based upon the results of these tests, Almatis guarantees a shelf life of 12 months,[1] provided the material is stored under adequate dry conditions.

Offenbecher[2] further investigated the influence of bag design and storage conditions on the shelf life of cement. Standard Portland cement originating from the same batch was packed in different types of paper bag, with and without a moisture barrier. For each bag design, one pallet was covered with an additional stretch hood and another with no pallet protection. Each was stored for six months in a dry warehouse.

For the evaluation of moisture protection standardised cement quality testing was performed. Such tests show the impact of moisture on the product properties, eg water demand, initial setting and soluble chromate concentration. All bag designs without additional pallet protection show aging effects during storage. Differences in cement properties become significant after two months for the chromate concentration, and after six months for standard consistency and setting time.

Almatis investigates the longer-term aging process in calcium aluminate cement when packed in plastic bags

Cement in bags without a moisture barrier and any pallet protection also show an increase in water demand. Water demand remains stable for cement packed in bags incorporating a moisture barrier. For pallets covered with a stretch hood, the type of bag is of minor importance and cement parameters such as initial setting and water demand remain stable over the entire storage period.

Further moisture protection

Almatis has alumina production facilities in different regions, but cement production is concentrated at the Rotterdam plant in The Netherlands. As a result, cement is shipped from Rotterdam to all parts of the world and proper packaging is mandatory.

Almatis cement is packed in paper bags with a plastic foil within the paper to act as a moisture barrier. All pallets are also shrink-wrapped. However, during intercontinental transport through different climate zones condensation can occur, causing the formation of lumps in the middle of the pallet despite the additional protection (see Figure 1).

Figure 1: lump formation during intercontinental transport

Several options have been considered to further improve the moisture protection for cement packaging for all shipments, particularly for intercontinental shipments. Moisture absorption bags added to the containers are a simple approach, but whilst providing protection during shipment, do not provide protection during subsequent storage in warehouses. Special refrigerated containers are also reported to be effective but can be expensive and limit protection during transportation. Plastic bags were therefore considered the best approach as they provide total protection: from bagging at the plant right through to when the product is used.

Tests procedure

A series of tests were undertaken to determine the long-term aging of calcium aluminate cement, packed in plastic bags which were stored in a warehouse for up to 40 months. The tests were performed using Almatis cement grade CA-470 TI – the most critical of all Almatis cements when considering moisture absorption.

For shelf life testing of CA-470 TI, a low-cement self-flow castable based on tabular alumina was used, which contains dispersing aluminas ADS/W as additives. The castable matrix was composed of T60/T64 -45MY LI and -20MY and reactive alumina CL 370. The water demand was adjusted to 4.9 per cent (see Table 1).

The 'Norcast '5 test castable is also used for the quality control of the CA-470 TI in Almatis' laboratory in Rotterdam.

Table 1: composition and properties of self-flowing test castable at start status

Component		*Castable Norcast 5*
Coarse fraction T60/T64	3-6mm(%)	30
	1-3mm (%)	15
	0.5-1mm (%)	10
	0.2-0.6mm (%)	5
	0-0.3mm (%)	10
Fine fraction T60/T64	-45MY Li (%)	8
	-20MY (%)	7
Reactive Alumina	CL370 (%)	10
Cement	CA-470 TI (%)	5
Dispersing Alumina	ADS 3 (%)	0.8
	ADW 1 (%)	0.2
Water	**(%)**	**4.9**
Wet out time	(sec)	60
Self-flow	10 min (mm)	279
	30 min (mm)	274
	60 min (mm)	261
EXO	Start 1	138'/24.1°C
	Start 2	4.8h/26.0°C
	Max.	6.1h/31.6°
C		
Ultrasonic setting start	(min)	112
CMoR	20°C/24hr (MPa)	6
	110°C/24h (MPa)	15
	1000°C/5h (MPa)	9
	1500°C/5h (MPa)	41
CCS	20°C/24h (MPa)	22
	110°C/24h (MPa)	82
	1000°C/5h (MPa)	41
	1500°C/5h (MPa)	130
Density	110°C/24h (g/cm3)	3.10
	1000°C/5h (g/cm3)	3.08
	1500°C/5h (g/cm3)	3.07
Shrinkage	110°C/24h (%)	-0.02
	1000°C/5h (%)	-0.08
	1500°C/5h (%)	+0.02

Test conditions

Calcium aluminate cement CA-470 TI, produced at the Almatis plant in Rotterdam, was packed in 25kg sealed plastic bags (see Figure 2). A 2t pallet from the same batch was shipped to the plant in Ludwigshafen, Germany, and stored in a warehouse tent for up to 40 months. The bags were protected from rain, but the cement was exposed to seasonal temperature and humidity variations. The pallet was stored without shrink wrap protection.

For comparison, a series of tests were also carried out with CA-470 TI packed in standard paper bags (multi-layer: paper-plastic foil-paper) and stored under the same conditions for up to 12 months.

Furthermore, one plastic bag was stored outdoors at the Rotterdam plant for 12 months after 20 months of storage inside the warehouse.

Figure 2: test plastic bag for Almatis cement

Before testing the cement, the bags were stored in the lab at 20°C for temperature acclimatisation. Within one week the cement was tested in the castable Norcast 5 for wet-out time, flow behaviour up to 60 minutes, setting and strength after various pre-firing temperatures (see Table 1). A new, unopened bag was always used each month and for the particular test period in the lab, the open cement bag was stored in a properly-closed vessel.

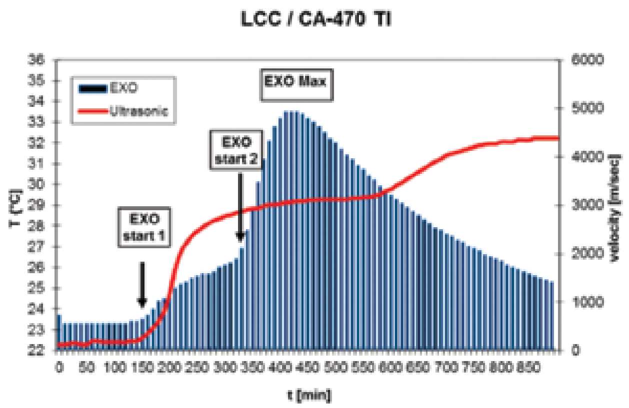

Figure 3: measurement of setting by exothermic reaction and ultrasonic equipment

The castable was wet mixed in 5kg batches using a Hobart A 200 planetary mixer at speed 1 for four minutes. The castable properties were tested at a constant water demand. The wet-out time was determined as described in a previous paper.[3] The flow properties after 10, 30 and 60 minutes (F10, F30, F60) were measured by the cone test (lower diameter 100mm, upper diameter 70mm, height 80mm). The setting behaviour was measured by both exothermic and ultrasonic equipment (see Figure 3).[4]

The test period of 40 months was split into two phases:

- During the first 21 months the setting occurred in the air-conditioned lab at 20˚C
- For the second phase (months 22-40) the samples were placed in a temperature cabinet at 20˚C. Experience showed that the air conditioning in the lab was unable to keep the room temperature at a constant 20˚C, and therefore the temperature cabinet was selected instead.

The test series continued until the cement became unusable or was consumed.

Results and discussion

In general, the test castable shows some variationS in results during the testing period. These are not considered to be due to aging unless the specific values would be confirmed by later results. For example, lower flow values were noted after 11-13 months, but from 14-40 months flow values comparable to the initial results were again achieved.

It has also been accepted that there can be some variation in measurement of the setting behaviour, both exothermal and ultrasonic, without attributing this to aging unless a clear trend occurs.

The wet-out time is about 60s and the flow values at 10 and 30 minutes are on average 280mm. For cement in plastic bags these values remain stable over the entire test period (see Figures 4 and 5).

The ultrasonic setting start ranges from 72 to 228 minutes without showing a trend towards longer setting (Figure 6). The variation range in phase 1 (up to 21 months) is higher when compared to phase 2 (22-40 months). The higher variation in phase 1 was the motivation for testing the setting in the temperature cabinet, and indeed, phase 2 demonstrates a narrower range of ultrasonic setting start. These results show that even temperature differences of just a few degrees only can have an impact on the setting start of low-cement castables.

The EXO results given in Figure 7 also show the effect of stricter temperature control in the temperature cabinet. Here, the variation range of setting start also becomes a bit narrower. The setting times increase considerably when setting occurs in the temperature cabinet. The cabinet is reacting quickly to the temperature increase of the castable during

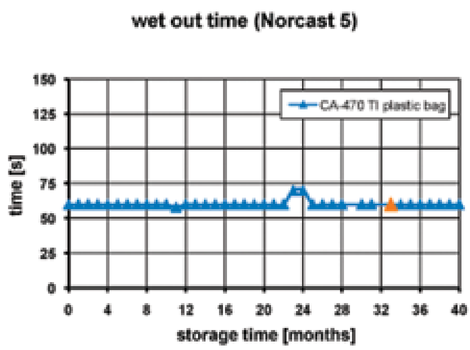

Figure 4: impact of warehouse aging of plastic bagged CA-470 TI on wet-out time (month 32 data point, see text)

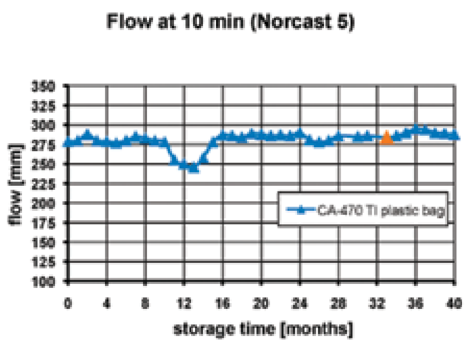

Figure 5: impact of warehouse aging of plastic bagged CA-470 TI on flow at 10 and 30 minutes (month 32 data point, see text)

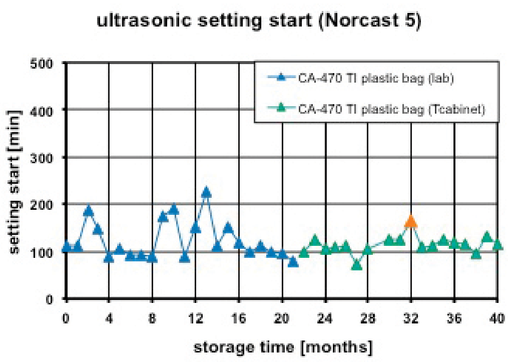

Figure 6: impact of warehouse aging of plastic bagged CA-470 TI on ultrasonic setting start. Measurement phase 1 (0 – 21 months) in the lab and phase 2 (22 – 40 months) in a temperature cabinet at 20°C (month 32 data point, see text)

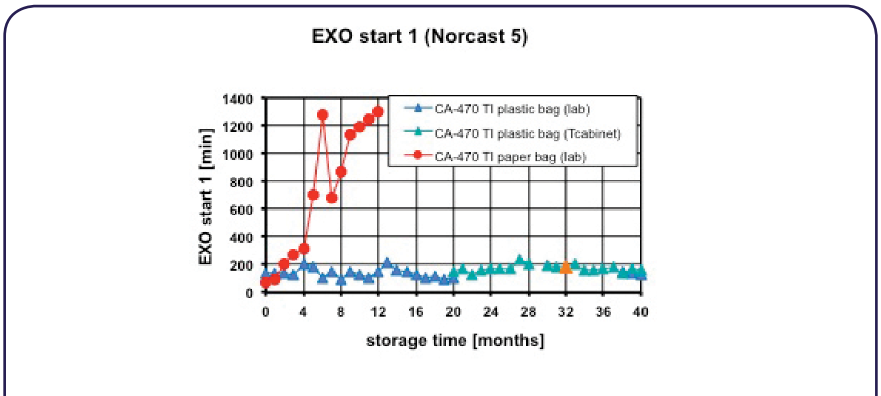

Figure 7: impact of warehouse aging of CA-470 TI on setting (EXO start 1), plastic versus paper bag. Measurement for CA-470 TI in plastic bags: phase 1 (0-21 months) in the lab and phase 2 (22-40 months) in a temperature cabinet at 20°C (month 32 data point)

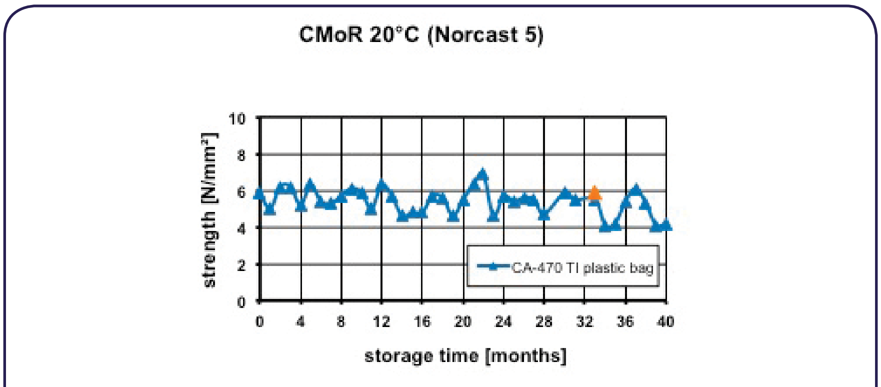

Figure 8: impact of warehouse aging of plastic bagged CA-470 TI on strength of test castable (CMoR 20°C) (Month 32 data point, see text)

the exothermic cement hydration and can quickly cool the sample back down. This slows the hydration reaction and results in longer times for setting start 2 and EXO Max.

The longer EXO setting times during phase 2 are not related to a cement aging but are only due to the change in testing conditions. Cement samples aged for 38-40 months, which were tested under the same conditions as phase 1, still show the same setting times as the samples tested after aging in the period up to 21 months.

It is unclear whether the use of a temperature cabinet has an impact on other castable properties. As the temperature development at EXO Max is much lower when the setting occurs in the temperature cabinet at 20°C in comparison to the laboratory at 20°C, it may result in lower strength properties and is currently being investigated.

The strength data given in Figure 8 show some variation but no trend which could be attributed to an aging effect. The strength testing was performed on two test bars but not multiple samples, at each temperature. This must be considered with regard to the statistical variation which is normal for castable strength testing. Density and permanent linear change values remain very stable over the entire test period.

The extended tests prove that plastic bags provide a much better moisture protection and preserve the guaranteed properties of the cement for much longer storage times when compared to paper bags.

Calcium aluminate cement CA-470 TI packed in plastic bags shows no aging trend over a storage period of 40 months when tested in test castable Norcast 5. However, CA-470 TI packed in paper bags demonstrates a clear aging trend with regard to setting behaviour. The exothermal measurement shows an increase in setting times after just 2-3 months and a steep rise after five months of storage. EXO Max is at 1200 minutes when compared to 366 minutes for the fresh cement.

Even the plastic bag that was stored outside for a year suffered no aging trend, either for wet-out and flow or for setting times (see Figures 4-7). The overall age was 32 months (comprising 20 months inside the warehouse plus 12 months outside). Wet-out of 60 seconds is achieved and a flow of 287mm after 30 minutes. Ultrasonic setting shows the start at 164 minutes whereas the first rise in the EXO graph occurs a little later at 186 minutes.

The case for plastic

Calcium aluminate cement CA-470 TI packed in plastic bags did not show any aging trend, even after a 40-month storage period. The extended tests proved that plastic bags provide much better moisture protection and preserve the guaranteed properties of the cement for much longer storage times compared to paper bags. Plastic bags can also overcome issues with potential moisture and the formation of lumps during overseas transportation and provide a long shelf life even after the pallet shrink wrapping has been removed. They are also beneficial for when a pallet must be stored outside, or when the first in/first out (FIFO) principle is not applied at a plant and cement must be stored for longer periods than usual. Consequently, Almatis introduced plastic packaging for all their cement grades. Shelf life is extended to 24 months and cement aging is a matter of the past.

References

1 *Almatis Calcium Aluminate Cements global product data sheet GP-RCP/005/R06/1207.*

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