1

CEMENT AGING: SOMETHING OF THE PAST!

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ABSTRACT
The aging behaviour of calcium aluminate cement packed in plastic bags was investigated by storing in a warehouse for 40 months. The cement was tested periodically in a castable for mixing behaviour (wet out time), self-flow behaviour, setting and strength.

Introduction
Calcium aluminate cement, well established as a binder in the refractory industry, shows hygroscopic behaviour and needs to be protected against moisture pick up during the storage period to prevent the cement from aging. The use of aged cement has an impact on the workability and setting behaviour of refractory castables.
Multilayer paper bags are commonly used as standard packaging for cement, often in combination with additional pallet protection, e.g. stretch hood or shrink wrap.
Nevertheless cement packed in paper bags has a limited shelf life. The guaranteed shelf life provided by the suppliers is typically between six and twelve 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, a shelf life of 12 months is guaranteed in the Almatis calcium aluminate cements datasheets [1], if material is stored under adequate dry conditions.
Offenbecher [2] 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 pallet had 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. This shows the impact of moisture on the product properties, e.g. 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.
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 which are 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.
Almatis has alumina production facilities in the different regions but cement production is concentrated at the Rotterdam plant. Cement is shipped from Rotterdam to all regions of the world. For this reason 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 which could cause formation of lumps in the middle of the pallet despite the additional protection (figure 1).

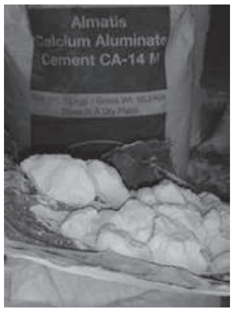

Fig. 1: Lump formation during intercontinental transport

Several options have been considered to further improve the moisture protection for cement packaging for all shipments, and intercontinental shipments in particular. Moisture absorption bags added to the containers are a simple approach but whilst providing protection during shipment, do not provide protection during later warehouse storage. Special refrigerated containers are said to be very effective, but are expensive and also only limit the protection during transportation. Plastic bagging of cement was considered the best approach as it provides full protection from bagging in the plant until the time when the product is finally used. It was expected that the general shelf life problem with cement could be overcome using this solution.
This study presents the results of long term aging testing of calcium aluminate cement, packed in plastic bags (figure 2), which has been stored in a warehouse for up to 40 months. A series of tests were performed using Almatis cement grade CA-470 TI which is the most critical of all Almatis cements when considering moisture absorption.

Fig. 2: Test plastic bag for Almatis cement

Test castable

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

Tab. 1: Composition and properties of self flowing test castable at start status

Component / Castable			Norcast 5
Coarse fraction T60/T64	3 - 6 mm	%	30
	1 - 3 mm	%	15
	0,5 - 1 mm	%	10
	0,2 - 0,6 mm	%	5
	0 - 0,3 mm	%	10
Fine fraction T60/T64	- 45 MY Li	%	8
	- 20 MY	%	7
Reactive Alumina	CL 370	%	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 / 24 h	MPa	6
	110°C / 24 h	MPa	15
	1000°C / 5 h	MPa	9
	1500°C / 5 h	MPa	41
CCS	20°C / 24 h	MPa	22
	110°C / 24 h	MPa	82
	1000°C / 5 h	MPa	41
	1500°C / 5 h	MPa	130
Density	110°C / 24 h	g/cm³	3,10
	1000°C / 5 h	g/cm³	3,08
	1500°C / 5 h	g/cm³	3,07
Shrinkage	110°C / 24 h	%	-0,02
	1000°C / 5 h	%	-0,08
	1500°C / 5 h	%	+0,02

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

Test conditions

Calcium aluminate cement CA-470 TI, produced at the Almatis plant in Rotterdam, was packed in 25 kg sealed plastic bags (figure 2). A pallet of two metric tons from the same batch was shipped to the plant in Ludwigshafen 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.
In addition one plastic bag was stored outdoors at the Rotterdam plant for 12 months after 20 months storage in the warehouse.
Before testing the cement, the particular 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 prefiring temperatures (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.
The castable was wet mixed in batches of 5 kg using a Hobart A 200 planetary mixer at speed 1 for 4 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 100 mm, upper diameter 70 mm, height 80 mm). The setting behaviour was measured by both exothermic and ultrasonic equipment as described in a previous paper (figure 3) [4].

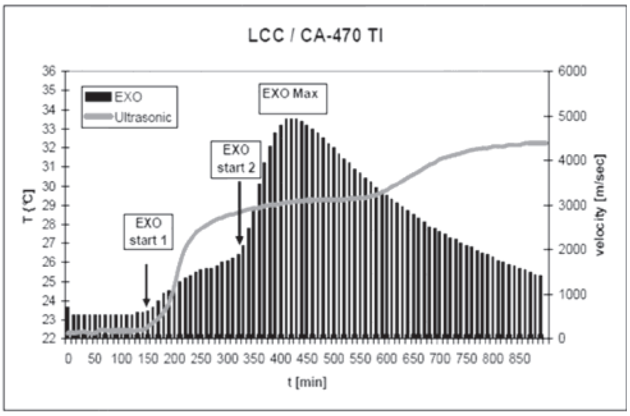

Fig. 3: Measurement of setting by exothermic reaction and ultrasonic equipment

The test period of 40 months can be split into two phases: for the first 21 months the setting occurred in the air conditioned lab at 20 °C, whereas for the second phase (22 – 40 months) the samples were put in a temperature cabinet at 20 °C. Experience showed that the lab air conditioning was not able to keep the room temperature constant at 20 °C, and therefore the change was made.
The test series will continue until the cement becomes unusable or is consumed.

Results and discussion

In general, the test castable can show some variation in results during the testing period. These are not considered to be due to aging unless the specific values are 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.

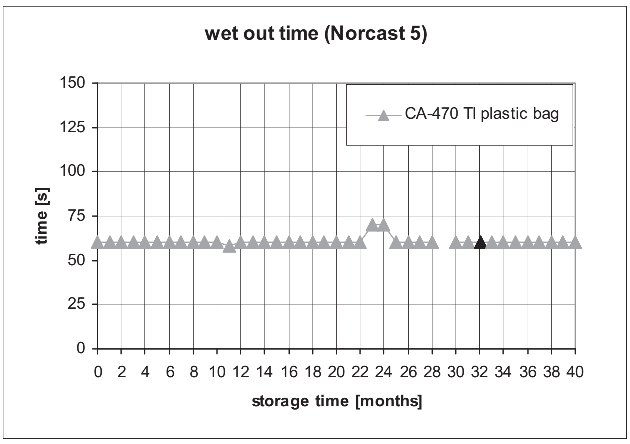

Fig. 4: Impact of warehouse aging of plastic bagged CA-470 TI on wet out time. Data point at 32 months see text.

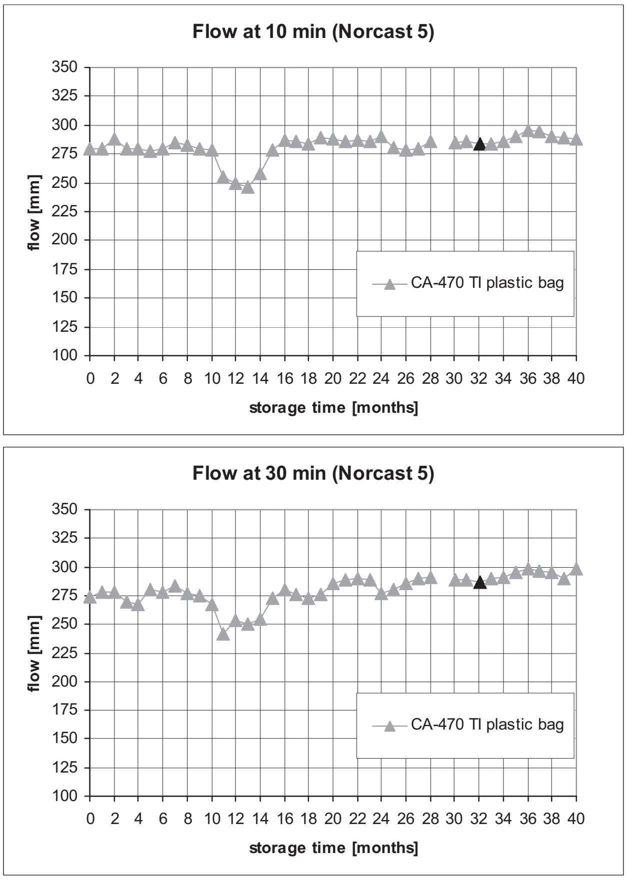

Fig. 5: Impact of warehouse aging of plastic bagged CA-470 TI on flow at 10 and 30 minutes. Data point at 32 months see text.

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

The wet out time is about 60 seconds and the flow values at 10 and 30 minutes are on average 280 mm. For cement in plastic bags these values remain stable over the entire test period. This is shown in 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 shows a narrower range of ultrasonic setting

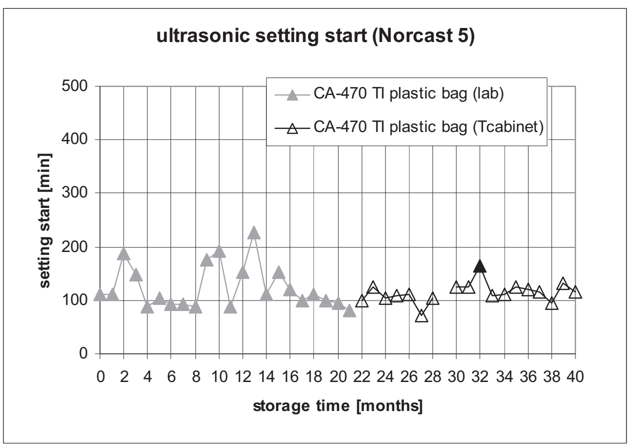

Fig. 6: Impact of warehouse aging of plastic bagged CA-470 TI on ultrasonic setting start. Measurement phase 1 (0 – 21 months) in the lab and phase 2 (22 – 40 months) in a temperature cabinet at 20°C. Data point at 32 months see text.

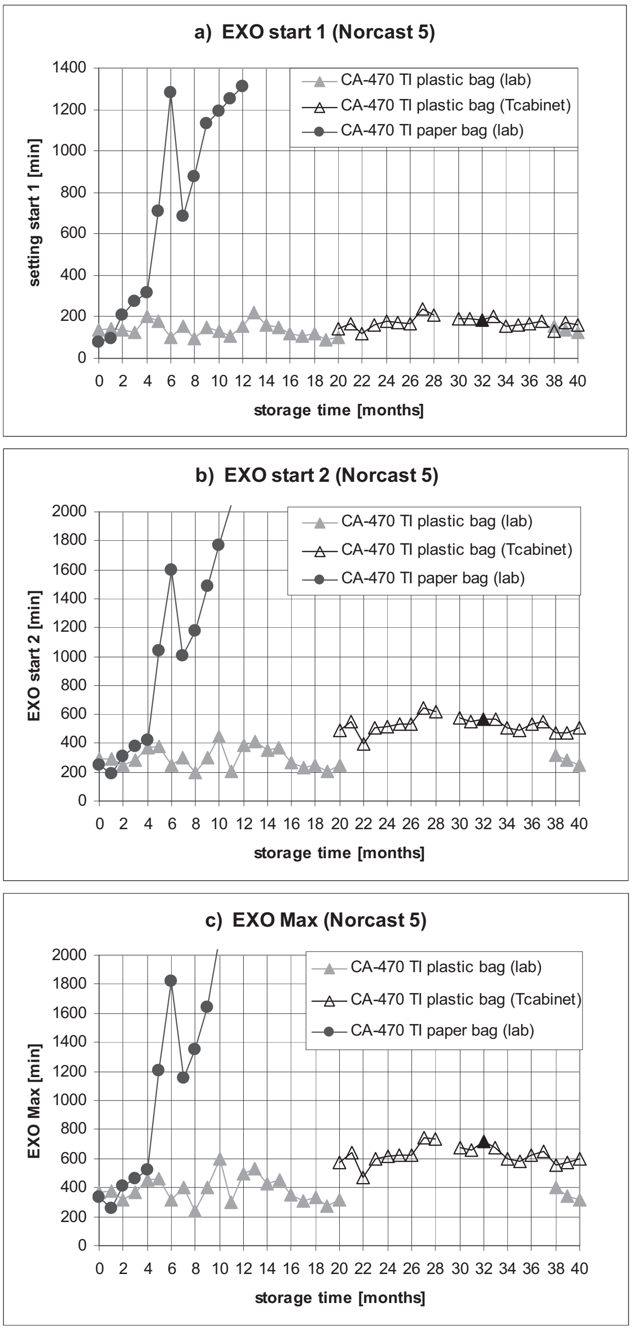

Fig. 7a-c: Impact of warehouse aging of CA-470 TI on setting (EXO start 1, start 2, and Max); plastic vs. paper bag. Measurement for CA-470 TI in plastic bags: phase 1 (0 – 21 months) in the lab and phase 2 (22 – 40 months) in a temperature cabinet at 20°C. Data point at 32 months see text.

start. These results show that even slight temperature differences of a few degrees only can have an impact on the setting start of low cement castables.

The EXO results given in figure 7 a-c also show the effect of tighter temperature control in the temperature cabinet. Here, the variation range of setting start also becomes a bit narrower, and the overall levels of EXO start 2 and EXO MAX show a difference between phases 1 and 2. The setting times increase considerably when setting occurs in the temperature cabinet. Obviously the cabinet is reacting quickly to the temperature increase of the castable during the exothermic cement hydration and can quickly cool the sample back down. This retards 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 to 40 months which were tested under the same conditions as in phase 1 still show the same setting times as the samples tested after aging in the period up to 21 months (figure 7 b and c).

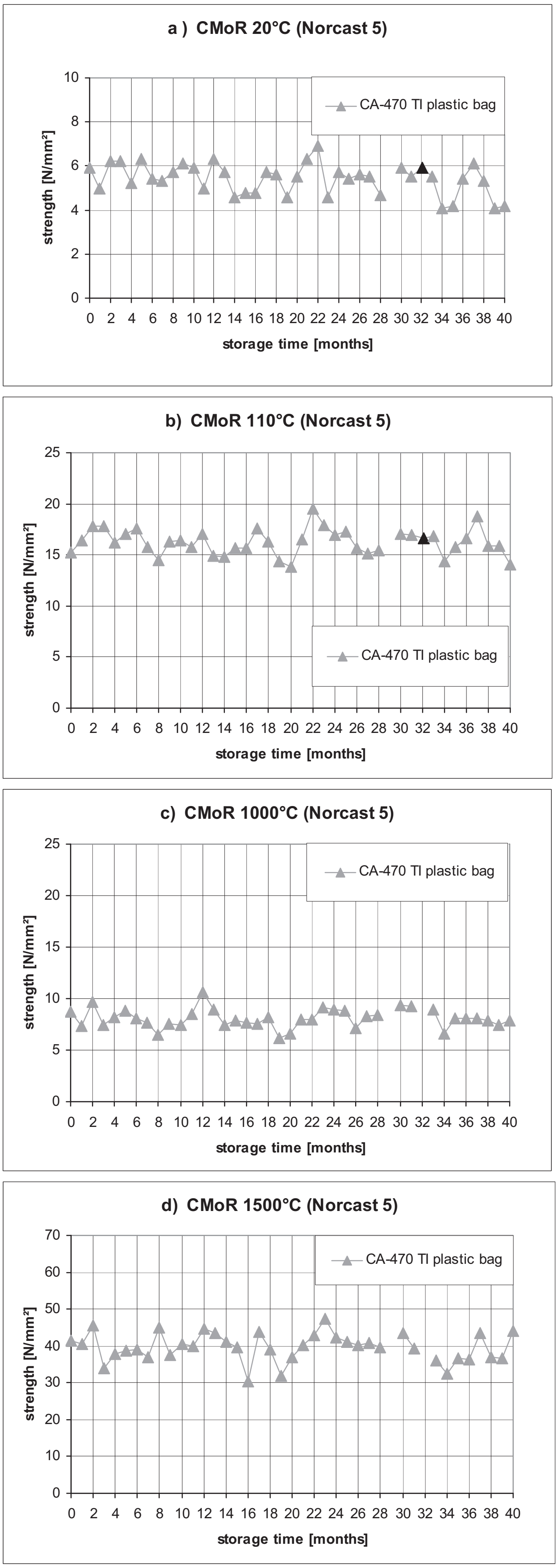

Fig. 8: Impact of warehouse aging of plastic bagged CA-470 TI on strength of test castable (CMoR 20 – 1500 °C). Data point at 32 months see text

It is unclear as yet 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. This is currently being investigated and will be reported later.

The strength data given in figures 8 a-d 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.

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. In comparison CA-470 TI packed in paper bags shows a clear aging trend with regard to setting behaviour. The exothermal measurement already shows an increase in setting times after two to three months, and a steep rise after five months storage. Then EXO Max is at 1200 minutes when compared to 366 minutes for the fresh cement.

Even the one plastic bag which was stored outside for one year shows no aging trend neither for wet out and flow nor for setting times. The data points for this sample are highlighted in figures 4 – 7. The overall age was 32 months (20 months warehouse plus 12 months outside). Wet out of 60 seconds is achieved and a flow of 287 mm 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.

PRACTICAL ASPECTS

In addition to the moisture protection, other features are important for proper cement packaging. The de-aired 25 kg plastic bags are compact and easy to handle. An anti-slip coating on the bag surface prevents the bag from sliding off the pallet during fork lift transportation. The disposal of the plastic bags is not considered as a problem as plastic bagging has in recent years become common practice. In Germany a system called WEPA is in place for returning empty bags.

A new plastic packaging line has been installed in the Rotterdam plant for all Almatis cement grades.

Summary

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 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. Plastic bags can overcome potential moisture and lump formation problems in overseas shipments and provide a long shelf life even after the pallet shrink wrapping has been removed. Plastic bags are also advantageous when for some reason a pallet is stored outside, or the “first in – first out“ principle is not applied and cement is stored for a longer period than usual.

Plastic bagging smoothes the way for packed cement with greatly extended shelf life. **Cement aging: something of the past!**

REFERENCES

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

[2] Offenbecher M. Influence of bag design and storage conditions on shelf life of cement. Mondi Packaging Bag Division GmbH, 2007, also published as: Research Study: Bag Design and Storage, World Cement, March 2007, 77-82.

[3] Kockegey-Lorenz R, Büchel G, Buhr A, Aroni JM, Racher RP. Improved Workability of Calcia free Alumina binder Alphabond for Non-Cement Castables. 47th International Colloquium on Refractories, Aachen: 2004. p. 67-71.
[4] Gierisch D, Buhr A, Dutton J, Hösler M, Franz B. Aging behaviour of Alphabond and Calcium Aluminate Cement bonded castables. 49th International Colloquium on Refractories, Aachen; 2006. p. 137–142.