PROCEEDING O053

ROBUST CASTABLE BEHAVIOUR – HOW CAN IT BE ACHIEVED?

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ABSTRACT

The behaviour of refractory castables with regard to wet mixing, flow over time, and setting and strength development depends on the composition of the mix and external factors such as ambient temperature, water quality, intensity of mixing, etc. Variation of the castable behaviour in those properties mentioned above can challenge the whole installation, and bring into operation countermeasures on site. Sometimes these countermeasures are detrimental to the performance of the installation, e.g. through consequential increased water demand and higher porosity. The paper discusses the impact of raw materials and ambient conditions on castable properties and also considers solutions to improve the robustness of castables.

INTRODUCTION

In general, conventional castables can be considered more robust due to their higher cement content when compared to low and ultra-low cement mixes. The latter mixes provide higher performance in use but are more sensitive to changes in installation conditions. Their formulation is also more complex, including various fine matrix components and additives for dispersion and setting control. The raw materials, especially in the matrix fines can have a significant influence on the robustness of low and ultra-low cement castables. Trace contaminations and variations in homogeneity within raw materials, under- or over-dosage of small amounts of additive, aging behaviour in the ready dry-mix, and different wet out times depending on the mixing intensity are examples of these influences.

Ambient conditions such as temperature and humidity have a big impact on castable properties, in particular on the setting behaviour. Ambient conditions during storage and installation are not usually well controlled and due to the time lapse between castable production and usage, the adjusted setting times may not meet the requirements for on-site installation some months later. In order to overcome problems associated with too low or too high ambient temperatures during the installation, heated or cooled water is sometimes used, even if the effect might be questionable. Alternatively additives for retarding or accelerating the setting time are added to the mixer on-site. Schnabel et al. [1] and Kockegey-Lorenz et al. [2] reported on the adjustment of setting time with citric acid. Dosage levels were in the range of 0 – 0.08% and small increases of citric acid resulted in the desired extension of working time but also lead to undesired strong retardation of the main cement hydration and a weakening of the reaction. The papers also provided recommendations for a more robust way of setting time re-adjustment by using dispersing aluminas [3] as retarder and hydratable alumina Alphabond 300 as accelerator.

Today's trend in raw material and castable development focuses on both optimisation of the castable properties and on the robust behaviour and easy installation in order to achieve the best overall performance. This helps to make processes such as castable production, testing and installation smooth and less prone to error. The paper will present results from trials in the laboratory performed under defined conditions for systematic investigation of e.g. impact of water dosage and the influence of dry mix and mixing water temperature. The trials will also provide information on the robustness of additive systems at these different ambient temperatures. In addition, experiences and results with matrix compounds including cements are reported. This can contribute to higher robustness in shelf life and installation of more sophisticated low and ultra-low cement castables.

INTRODUCTION OF RAW MATERIALS FOR ROBUST CASTABLE BEHAVIOUR

CA-470 TI – temperature independent cement is an additive free 70% Al_2O_3 cement for use in low and ultra-low cement castables (LCC and ULCC) without or with silica fume. CA-470 TI has a fineness of 90% below 45µm and a d50 of 8µm (Cilas 1090). [4]

Dispersing Aluminas ADS/ADW for silica-free castables and M-ADS/M-ADW for silica-containing castables are a combination of modern organic additives with reactive alumina and other inorganic materials [2]. The ratio of the retarding "S" type to the accelerating "W" type is varied to achieve the control of setting time. The total amount of dispersing alumina is recommended to be about 1% by weight in low cement castables. [3]

Tab. 1: typical product data – dispersing aluminas.

	ADS 1	ADS 3	ADW 1	M-ADS 1	M-ADS 3	M-ADW 1
FOR USE IN CASTBLES	WITH SILICA FUME < 1%			WITH SILICA FUME > 1%		
Effect	Retarding	Strong Retarding	Accelerating	Retarding	Strong Retarding	Accelerating
Chemical Composition [%]						
Al_2O_3	80	76	80	91	95	96
Na_2O	0.10	0.10	0.10	1.40	1.40	0.10
B_2O_3	0.80	2.80	0.03	1.30	2.50	0.55
CaO	1.80	1.80	1.80	0.02	0.02	0.02

E-SY 1000 and E-SY 2000 (containing spinel) are bi-modal reactive aluminas with a typical d50 of 1.7µm and specific surface area (BET) of 2.0 m²/g (E-SY 1000) and 1.4µm and 2.3 m²/g (E-SY 2000). [5]

HOW CAN ROBUST CASTABLE BEHAVIOUR BE ACHIEVED?

Different aspects of castable behaviour are highlighted in the paper to demonstrate the effect of different influencing factors and actions which can be taken either by changing ambient conditions or by using less sensitive raw material concepts to improve the robustness and reliability of castables:

- Mixing and flow behaviour
- Impurities and inconsistency
- Temperature sensitivity
- Aging behaviour

Mixing and flow behaviour

On-site installations always start with the mixing of the dry mixed castables with water in order to achieve a good working consistency for proper placing, de-airing and densification without segregation occuring. Usually the water addition range required for the respective castable is given by the refractory supplier.

However, there are many factors why accurate water dosage can fail on-site, e.g.:

- Mixer type (low power)
- Mixing batch size (too small or too big)
- Improper dosage measuring equipment (low accuracy)
- Long castable wet out (excess water addition)
- Short working time (early flow decay)

Lab investigation with pure alumina low cement vibration castables and different water dosage levels shows the impact of water addition on the castable properties. An overview of the test castables and the water dosage ranges are given in table 2.

Tab. 2: Overview of test castables and water dosage ranges to investigate the impact of water addition on castable properties.

Castables	additive system	H_2O [%]
VIB-DA	1% ADS/W	4.0 - 6.0
VIB-PA	0.1% Polyacrylate 0.05% Citric Acid	4.75 - 6.5
VIB-STPP	0.08% Sodium tripolyphosphate 0.05% Citric Acid	5.0 - 7.0

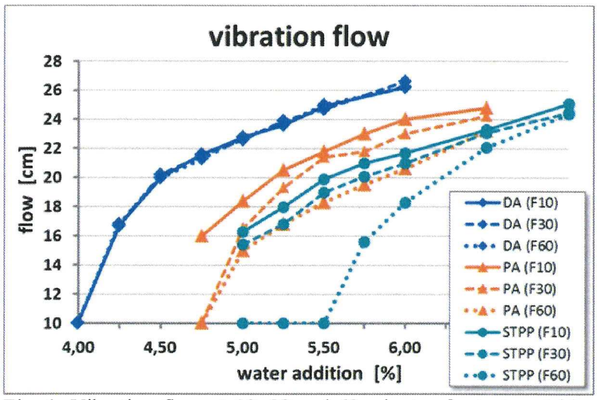

Fig. 1: Vibration flow at 10, 30 and 60 minutes for test castables mixed with different water additions.

Figure 1 shows the flow values for the different water dosages. A minimum amount of water is required to ensure good flow and placing properties. With increased water addition flow values increase. For the high water addition levels separation on the flow cones and the cast pieces was observed. The tendency for water separation was lowest for VIB-DA and stronger for VIB-STPP especially at a water dosage of 7%.

VIB-DA requires the lowest water addition to achieve good flowability when compared to VIB-PA and VIB-STPP. With 4.5% a vibration flow of 20 cm is achieved even after 60 minutes. For the other castables 5.25 – 5.5% is needed to achieve the same level after 10 minutes. However, these mixes still deteriorate in flow after 60 minutes with 17 cm for VIB-PA and no flow for VIB-STPP. An even higher water addition is needed to obtain a suitable flow at 60 minutes and then the risk of segregation is high.

In a second step the setting behaviour was investigated by measuring the temperature development of the exothermic reaction (EXO). VIB-DA shows a very stable EXO Max over the entire water dosage range with a variation range of less than two hours (figure 2). VIB-PA and VIB-STPP generally show very long setting times due to the use of citric acid as an additive. EXO Max for VIB-STPP increases further with higher water addition. For VIB-PA, EXO Max shows little variation and no trend with different water additions.

The cured and dried cold crushing strength results are shown in figure 3. A loss in strength with increasing water addition is observed for all test castables. Due to the lower water addition required and the earlier cement reaction for VIB-DA, a significantly higher strength level is achieved.

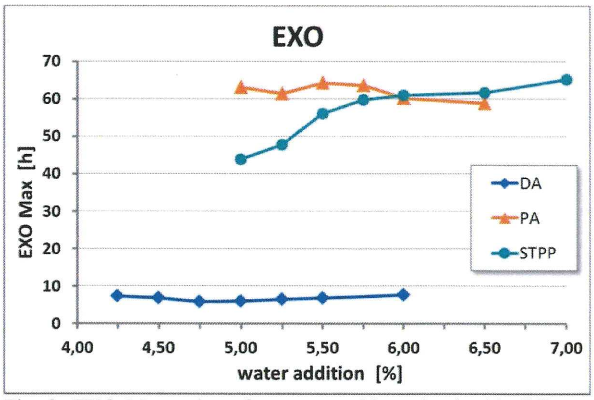

Fig. 2: EXO Max values for test castables mixed with different water additions.

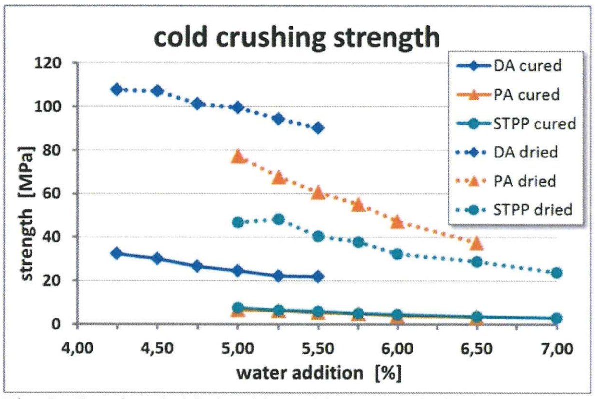

Fig. 3: Cured and dried cold crushing strength for test castables mixed with different water additions.

The risk of "overwatering" is high for castables which show a very long wet out behaviour after water addition. This is typical for modern castable concepts with an optimised matrix composition. Kockegey-Lorenz et al. [5] reported on the wet out and mixing behaviour of E-SY alumina containing castables. The mixing behaviour of different castable formulations has been tested with different mixers. All test castables with E-SY 1000/2000 as matrix alumina showed very short wet out times of one minute or less, regardless of the mixing equipment used. That excellent wetting behaviour eliminates the risk of overwatering a castable during on-site installations. Also fast wet out mixes with E-SY alumina guarantee smooth lining operations as they enable low energy mixing at very low water demand due to non-dilatant rheology and soft mixing consistency.

It is common practice in castable development and modification to use well established formulations as the basis and adjust the recipes to the requirements of a similar application. Small changes are often done without extended lab testing as the effort involved is time-consuming. However even small changes may influence placing properties such as wet out and flow. The modification of just the cement content was part of a lab test series. Low cement castables with and without silica fume were tested at cement contents of 2 – 10% (mix with silica fume) and 3 – 11% (mix without silica fume). Included in the test series was the modification of the dispersing alumina dosage in order to verify if the same additive dosage can be used for all cement contents or has to be adjusted to achieve the optimum dispersion and flow. The lab tests showed that in general a lower dispersing alumina dosage (0.7–1.1%) is required for lower cement contents (2-5%) and has to be increased (1.3–1.5%) for higher cement contents (10%) to achieve good flow properties. As an example wet out and flow results of a silica fume containing castable are shown in figure 4. For cement contents of 2% and 5%, good flow at 60 minutes is achieved with M-ADS/W additions of 0.7% and 1%. The mix with 10% cement suffers in flow if the additive dosage is 1% and below. Comparable flow to the LCC and ULCC castable types is achieved at a higher M-ADS/W addition of 1.3%. The dispersing agents are attaching to the surface of the cement particles. The more cement particles that are present the more additives that are required for good dispersion. The need to adjust the amount of dispersants may also be required if other fine matrix components are modified. The test series shows a trend towards higher M-ADS/W dosages for higher silica fume contents but more data is required to confirm that trend.

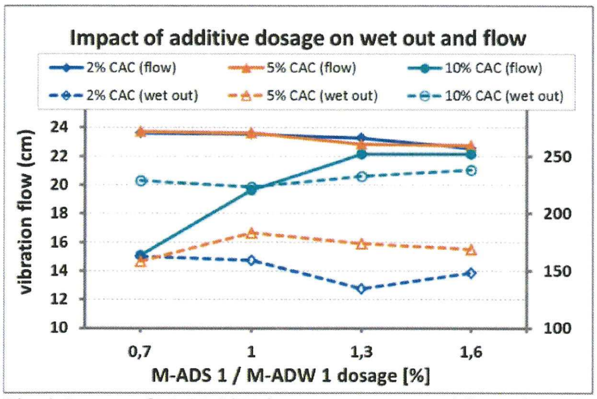

Fig. 4: Impact of M-ADS/W dosage on wet out and flow of a silica fume containing vibration castable with different calcium aluminate contents.

Impurities and inconsistency

Aggregate raw materials can contain trace impurities from their processing such as small residues from floatation or washing processes in Andalusite or other natural high alumina materials, or carbides and metallic inclusions in brown fused alumina. Synthetic alumina based raw materials usually do not have that problem, although white fused alumina fines may contain higher amounts of Na_2O, depending on material selection during crushing and sizing. These trace impurities are difficult to analyse but in many cases negatively influence the workability and setting properties of castables.

A low cement castable formulation containing 5% silica fume, 15% calcined alumina and 10% chamotte Mulcoa 60 in the matrix fines was tested both with Mulcoa 60 and Andalusite as coarse aggregates. Using dispersing aluminas M-ADS 1 and M-ADW 1 it is possible to adjust the formulation to obtain good flow properties and a reasonable setting time of 10.6 hours for EXO Max for the Mulcoa based castable at a water addition of 5.9%. The Andalusite mix requires only 5.3% water addition. However flow values are slightly worse when compared to the Mulcoa castable. The adjustment of setting is limited to EXO Max of 13 hours by adding 1% M-ADW 1 as an accelerator.

The replacement of CA-670 by CA-470 TI and use of M-ADS 3 and M-ADW 1 results in considerably improved flow properties, acceleration of setting to a range suitable for on-site installations and higher cured and dried strength at a constant water demand. Results are summarised in table 3.

Tab. 3: Mulcoa and Andalusite based test castables and properties.

coarse aggregate			Mulcoa	Andalusite	Andalusite
Cement	CA-670	%	5	5	
	CA-470 TI	%			5
Additives	M-ADS 1	%	0.3	0	
	M-ADS 3	%			**0.5**
	M-ADW 1	%	0.7	1.0	**0.5**
Water			5.9	5.3	5.3
VIB-Flow	10 min	cm	20.9	18.4	**20.9**
	30 min	cm	20.6	17.8	**20.9**
	60 min	cm	20.6	17.0	**19.9**
EXO	start	h	8.2	10.4	**4.4**
	Max	h	10.6	13.0	**7.3**
Strength	C MoR 20°C/24h	MPa	4	4	**5**
	C MoR 110°C/24h	MPa	13	11	**14**
	CCS 20°C/24h	MPa	25	18	**27**
	CCS 110°C/24h	MPa	97	81	**93**

Silica fume is known as a "troublemaker" in refractory castables. The quality of silica fume influences the castable properties, e.g. wet out, flow and setting. Myhre [6] reported on the impact of impurities such as carbon and potassium in 97% grade microsilica on flow and setting. Higher impurity levels deteriorated the flowability and significantly increased the working time of castables. Usually these quality variations or even batch to batch variations are often not possible to detect in simple quality control testing, but may have a negative impact on lining installations later. To increase the reliability of silica fume containing castables CA-470 TI can be used as cement binder. Repeated testing with eight different fume grades at 5°C ambient temperature showed a guaranteed setting start within 24 hours whereas the use of CA-14M resulted in unpredictable setting behaviour from fast to "never setting". [7]

Temperature sensitivity

The ambient conditions, such as temperature and humidity, have an influence on the setting behaviour of calcium aluminate bonded castables. This has taken into account for the installation of refractory castables especially in pre-cast shape production where often more than one casting sequence per day is scheduled and reliable setting behaviour is key.

The working and setting time of castables is adjusted and tested under lab conditions usually at 20°C. However, ambient conditions in practice are not as stable as in the lab due to seasonal temperature variations and varying temperature of the dry mixed material stored in the warehouse or outside. Higher temperatures will shorten the working time and low temperatures will retard the setting time and strength development. Schnabel et al. [8] reported about calorimetric measurements with an 80% tabular alumina and 20% cement mix performed at 23°C and 20°C. The reduction of ambient temperature of only 3°C retarded the main hydration peak by six hours.

To counterbalance the impact of ambient temperature on-site, cold, warm or hot water is sometimes added to the dry mixed castables. The effectiveness of this countermeasure has been systematically investigated in a test series in the laboratory. A low cement vibration castable with ADS 3/ADW 1 as additives and a water demand of 4.1% was used as a test castable. EXO Max at 20°C was adjusted to about 8 hours. Dry mix and water temperatures of 5, 20, 35 and 50°C were chosen for the test.

The flow properties over a time of 60 minutes remained stable independent from the dry mix and water temperature (figure 5). The impact of the mixing water temperature on the setting time is negligible. Only very small variations are observed. Conversely, the change in dry mix temperature has a strong influence on the castable setting as shown in figure 6. The comparison of 5°C vs. 50°C dry mix temperature results in a difference of about seven hours for EXO Max. In addition dry mix temperatures ≥ 35°C lead to slightly higher dried strength values compared to low dry mix temperatures.

The investigation showed that a long setting caused by usage of a cold castable mix cannot be counteracted with the addition of hot water. Instead it would be beneficial for low ambient temperatures to increase the dry mix temperature prior to an installation, e.g. by storage in a heated cabinet or warehouse, to reduce the tendency towards extended setting.

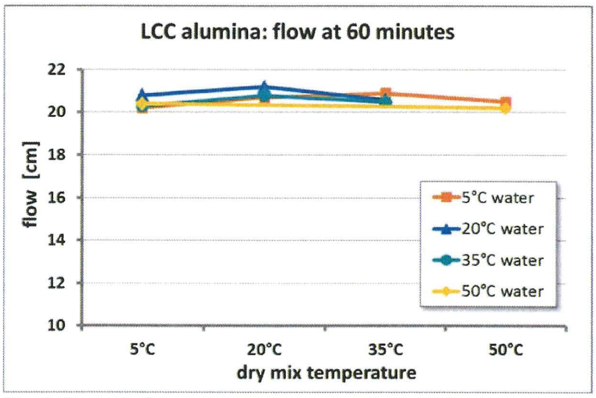

Fig. 5: Impact of dry mix temperature on flow at 60 minutes.

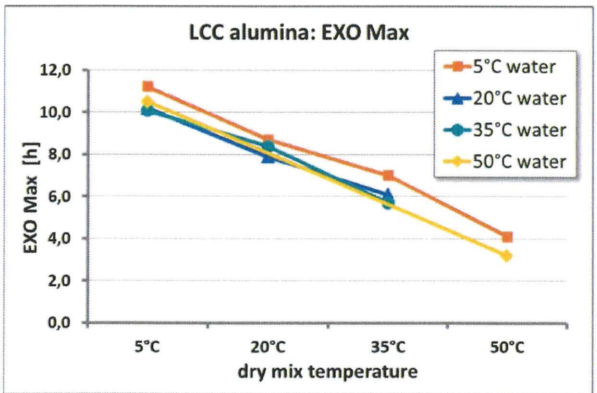

Fig. 6: Impact of dry mix temperature on exothermic reaction (EXO).

A guarantee for reliable setting, especially at low ambient temperatures, is the cement binder CA-470 TI as described by Buhr et al. [7; 9]. For CA-14M tested in three different low and ultra-low cement castables at 5°C ambient temperature a wide range of setting start times from 8 to 50 hours was observed in repeated testing. The replacement of the cement by CA-470 TI resulted in a reduction of the variation range to 6 to 20 hours. Although CA-14M may also occasionally show a reasonable setting start time at 5°C it often can become an extended setting start far longer than 24 hours. This unpredictable behaviour at low temperature is inherent for all regular 70% Al_2O_3 cements in the market. In comparison CA-470 TI demonstrated a setting guarantee even at low temperatures.

Aging behaviour

Castables are tailored to the individual on-site conditions by the determination of the additive system and the optimum dosage. Usually, after castable production, properties such as flow and setting behaviour are checked by quality control. However, castable material is not used immediately, but first transported and then stored for some weeks or even months. During storage aging can occur by interaction of castable components, e.g. between dispersion and setting control additives and calcium aluminate cement binders, or by ambient conditions. Such interaction can negatively influence workability, setting behaviour and also strength development.

Previous studies investigated the aging behaviour of warehouse-stored industrially packed castables. The paper of Gierisch et al. [10] included comparison between a low cement castable containing dispersing alumina ADS/W (LCC-ADS/W) and another one containing polyacrylate and citric acid as additives (LCC-PACA). The dispersing alumina system showed storage stability over a period of 9 months whereas LCC-PACA showed a decrease in flow after 7 months which resulted in no flow after 9 months. The castable was still usable but only at a 0.4% higher water demand. The test series was continued and subsequent measurements confirmed the storage stability over 23 months for the dispersing alumina containing castables. Figure 7 shows the flow properties for LCC with ADS/W and CA-14 M respectively CA-470 TI and LCC with polyacrylate/citric acid and CA-14 M.

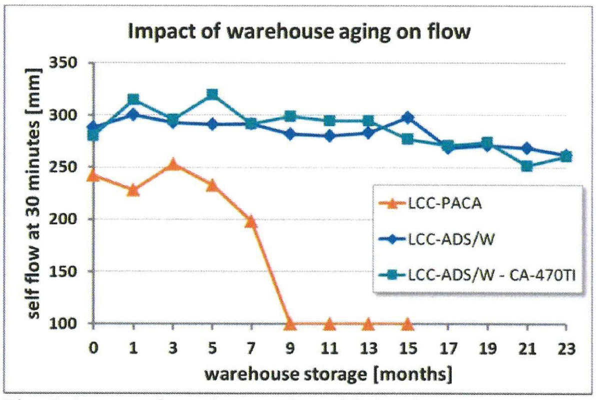

Fig. 7: Impact of warehouse aging of industrial packed castables on flow.

Aging behaviour of silica fume low cement castables in the warehouse has been tested over a period of one year by Schmidtmeier et al. [11]. As additive systems dispersing alumina M-ADS/W, sodium tripolyphosphate with and without citric acid and polyphosphate with and without citric acid were used. An aging trend was observed for all additive combinations tested. The aging of castable containing M-ADS/W remained within more narrow limits especially with regard to EXO Max which stayed well below 24 hours. The phosphate containing castables showed a short working time which can be retarded by small additions of citric acid, taking into account that the main reaction and the start of strength development were strongly retarded. In addition small additive dosages increase the risk of overdosage and insufficient

homogenisation which negatively affects the placing properties. When aged material is used for refractory installations problems during on-site installation or service life are inevitable, as castable properties have changed, and in the worst case scenario will no longer meet the requirements needed for the installation or the application.
Ambient conditions such as humidity also have an impact on aging. Some castable components, e.g. cement binders, show hygroscopic behaviour and need to be protected against moisture pick up. Schmidtmeier et al. [12] investigated the aging behaviour of calcium aluminate cement packed in plastic bags by storing them in a warehouse for 40 months. The cement was regularly tested in a castable application and the castable properties remained stable over the entire storage period. The test series was continued for up to 9 years without showing any aging effect. Figure 8 shows the EXO setting start of cement packed in plastic bags vs. paper bags tested in a test castable containing 5% cement.
This packaging concept could also be an option for refractory castables for better moisture protection during storage resulting in a longer shelf life.

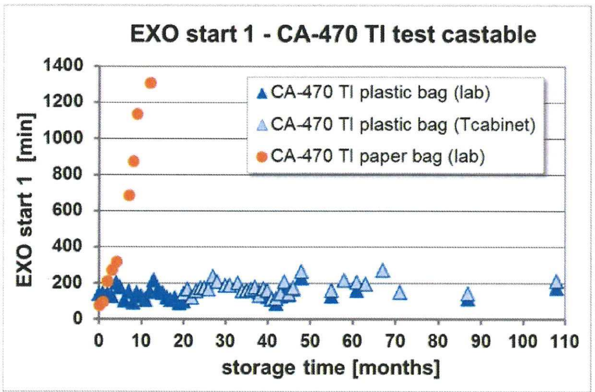

Fig. 8: Impact of warehouse aging of CA470 TI on setting (EXO start 1), plastic vs. paper bag. Measurement for CA-470 TI in plastic bags: phase 1 (0-21 and 40-108 months) cured in the lab and phase 2 (40-108 months) cured in a temperature cabinet at 20°C.

CONCLUSION

Castable producers and users have to deal with fluctuating ambient conditions and other uncertainties during on-site installations. Nevertheless lab investigations showed that different measures can be taken to increase the robustness of castable behaviour and therefore the reliability of castable installations.
Raw material selection is the one essential element to achieve that target. Dispersing Aluminas provide a tool to steer the castable set time in general, and in addition leads to more robust castble behaviour at different ambient temperatures and variations in water addition compared to conventional additive systems such as phosphate/citric acid. Dosage and homogenisation is easy and more reliable than for additives which have to be added in very small amounts. A series of tests with industrial mixed and packed castables showed a shelf life of at least one year for castables containing dispersing aluminas as additives. Reliable setting behaviour is guaranteed when using CA-470 TI as binder. The cement behaves less sensitively with regard to temperature variations, raw material inconsistencies and trace impurities. Furthermore improved flow is achieved in silica fume castables. The risk of castable overwatering can be eliminated by using E-SY alumina as a matrix component. It provides short wet-out times and enables low energy mixing at very low water demands.
As important as raw material selection are precautions taken prior to the installation. The lab trials showed that the temperature of the dry mixed castable is an important influencing factor for the setting behaviour. Therefore in winter time the storage of the castable in a pre-heated warehouse at a temperature above 15°C for at least two days prior to usage, is advisable to avoid very long setting times. An excellent moisture protection is provided by plastic bags which can be used not only for cement but also for pre-mixed castables. It would provide additional safety during storage even if material is unintentionally stored outdoors for a period of time.
For refractory installations, stable castable processing and product parameters are essential. Although robust raw material concepts, additional lab testing and on-site precautions are more costly, the risk of generating high unanticipated costs by installation delays or failures is much lower and justifies the efforts to improve the reliability and robustness of castable behaviour.

REFERENCES

[1] Schnabel M, Buhr A, Klaus S, Schmidtmeier D, Zacherl D, Zhongkai T. The value of additive systems in silica fume castables. UNITECR 2015, Vienna, Austria, proceeding 241.
[2] Kockegey-Lorenz R, Buhr A, Schmidtmeier D, Tian Z., Zacherl D, Chatterjee S. The value of additives in refractory castables, part 1: Castables without silica fume, refractories WORLDFORUM 6(2014) [3] 75-81.
[3] Almatis Refractory Brochure 2015.
[4] Almatis Calcium Aluminate Cements global product data sheet GP-RCP/005/R08/0516.
[5] Kockegey-Lorenz R, Schmidtmeier D, Buhr A, van Garsel D, Dutton J. E-SY alumina for easy to use high-performance castables. 52th International Colloquium on Refractories, Aachen, Germany, 2009, p. 86-88.
[6] Myhre B. Microsilica in refractory castables - how does microsilica quality influence performance?. UNITECR 2005, Orlando, USA.
[7] Buhr A, Schmidtmeier D, Wams G, Zacherl D, Dutton J. New results for CA-470 TI temperature independent cement – robustness against low temperature and impurities. Proceedings of UNITECR 2009, Salvador, Brazil, proceeding 051.
[8] Schnabel M, Schmidtmeier D, Buhr A, Wams G, Kuiper S. The influence of curing conditions on cement hydration and strength. 57th International Colloquium on Refractories, Aachen, Germany, 2014, p. 17-20.
[9] Buhr A, Gierisch D, Groß HL, Kraaijenbos F, Wams G, Dutton J. A new temperature independent cement for low and ultra low cement castables. Proceedings of UNITECR 2007, 2007 Sep 18-21, Dresden, Germany, 396-400.
[10] 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, Germany, 2006, p. 137-142.
[11] Schmidtmeier D, Buhr A, Schnabel M, Kockegey-Lorenz R, Vetsch E, Aust M. The value of additives in refractory castables – industrial castable aging trials. 59th International Colloquium on Refractories, Germany, Aachen, 2016, p. 134-138.
[12] Schmidtmeier D, Buhr A, Sadi R, Kraaijenbos F, Dutton J. Cement Aging: Something of the past!. 53rd International Colloquium on Refractories, Aachen, 2010, p. 22-26.