INVESTIGATIONS ON THE REHYDRATION OF CALCIUM ALUMINATE CASTABLES

J. Angelkort *, M. Knoll, A. Reichert
Intocast AG, Westpreußenstr. 30, 47809 Krefeld, Germany

C. Wöhrmeyer
Kerneos GmbH, Centroallee 275, 46047 Oberhausen, Germany

M. Szepizdyn
Kerneos Research Center Europe, 1 rue le Chatelier, 38090 Vaulx-Milieu, France

ABSTRACT

In recent years the quality requirement for steel has increased significantly. The performance of steel can be penalized if for example the hydrogen content is higher than specified by the producer. In modern steel plants the tundish is the last vessel in which liquid steel is in direct contact with refractory materials. To investigate the rehydration process of a refractory material used in the production of tundish linings, different experiments were performed on samples of calcium aluminate-bonded low-cement castables and the pure cement constituting the binder of the castable. To achieve a high extent of rehydration, the samples were exposed to experimental conditions which were extremely humid and did not correspond to the conditions encountered by the refractory materials of the tundish in reality.

To determine the amount of chemically bound water present in samples of the low-cement castable after rehydration, the weights of non-rehydrated samples were compared with the weights of re-hydrated samples after drying. The water release was also investigated by conducting thermogravimetric analysis.

X-ray diffraction patterns were measured on a sample of pure calcium aluminate cement (CAC) to determine the phases composing the matrix of the castable. Changes of the phase composition caused by casting, heating and rehydration were studied.

Our experiments show that the extent of rehydration of samples of the low-cement castable is influenced by the relative humidity (RH) of the atmosphere in which the samples were rehydrated and the height of the temperature attained for pre-heating the samples. While samples rehydrated for two weeks in an artificial atmosphere possessing 70 %RH contained maximal 0.3 wt% bound water, samples exposed for two weeks to an atmosphere of 100 %RH or stored under water incorporated up to 1.9 wt% bound water. Castable samples that have been pre-heated at 1200°C didn't show any significant rehydration even after storage under water.

INTRODUCTION

In calcium aluminate cements (CACs) the phases $CaAl_2O_4$ (CA), $CaAl_4O_8$ (CA_2) and corundum (A) are frequently the main constituents and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) as well as possibly some other phases accessories. CA reacts under the influence of water to $CaAl_2O_4 \times 10H_2O$ (CAH_{10}) or $Ca_2Al_2O_5 \times 8H_2O$ (C_2AH_8), and to aluminium hydroxide gel at ambient conditions. At higher temperatures it hydrates to hydrogarnet (C_3AH_6) and aluminium hydroxide (AH_3) [1]. Depending on temperature, the CA_2 phase hydrates either to C_2AH_8 and AH_3 or to C_3AH_6. Compared to the CA phase the hydration of the CA_2 phase is slower and proceeds over a longer lapse of time [2].

As chemically bound water is generally released at higher temperatures than adsorbed water or pore water, the dehydration process of a sample can be spanned over a temperature range of several hundred degrees. Thermogravimetric measurements on AH_3, C_3AH_6 and hydrated CA show that most of the bound water is released at temperatures below 300-400 °C [1,3].
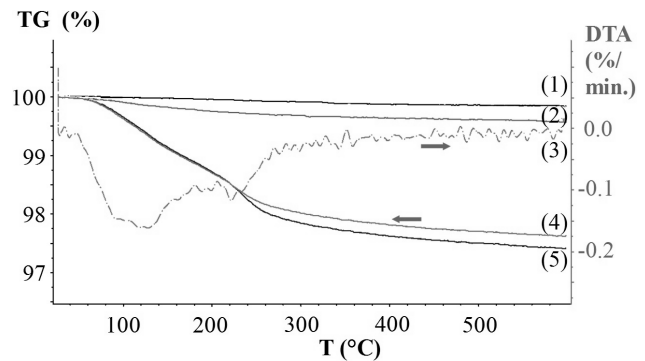

Fig. 1: TGA of samples pre-heated at 600 °C, for details see Tab. 1.

Another constituent of CACs, mayenite, ($C_{12}A_7$) can accommodate water molecules in pore holes of the crystal structure [4,5]. Water-containing minerals which can form as an alteration product of CACs are e.g. alkaline-free β-Al_2O_3 [6] and calcium carboaluminates [7].

EXPERIMENTAL

Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)

An andalusite-based low-cement castable was casted with 5 wt% tap water and dried at 110 °C. Samples of the dried castable were pre-heated to different temperatures and rehydrated for two weeks at room-temperature (~20 °C). After another drying, TGA/DTA measurements were carried out on the rehydrated samples within a temperature range of 30 to 600 °C using a Netzsch apparatus. During the measurements the samples were heated with a heating rate of 10 °C/min in a crucible of Al_2O_3 surrounded by an atmosphere composed of 20 vol.% O_2 and 80 vol.% N_2.

The pre-heating was accomplished by heating samples for 6 hours at temperatures of 300, 600 or 1200 °C. The samples were re-hydrated either through contact to an artificial atmosphere possessing a relative humidity (RH) of 70 % or 100 %, or by storing samples in a vessel filled with water. Fig. 1 shows curves of thermogravimetric measurements performed on samples pre-heated at 600 °C and treated in one of the different ways to accomplish rehydration (information about the depicted measurements are given in Tab. 1).

Tab. 1: Information about the measurements depicted in Fig. 1.

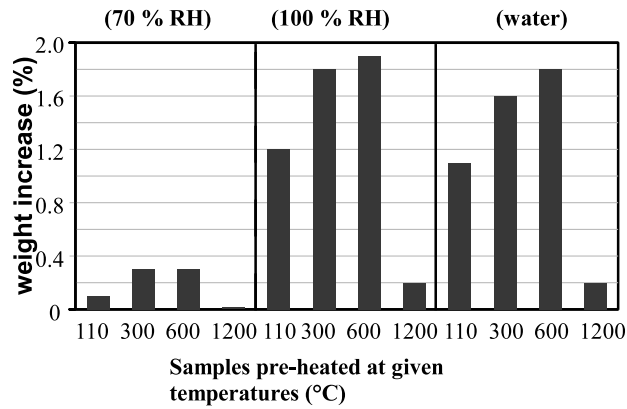| Measurement	Type of measurement	Sample hydration
(1)	TGA	Non-rehydrated sample
(2)	TGA	Rehydration at 70 %RH
(3)	DTA	Rehydration in water
(4)	TGA	Rehydration in water
(5)	TGA	Rehydration at 100 %RH

Fig. 2: Weight increase of samples after rehydration and drying.

The amount of chemically bound water in the sample was determined as weight increase $WI = ((m_{after} - m_{before})/m_{before}) \times 100$, where m_{before} is the mass of the pre-heated sample before its rehydration and m_{after} is the mass of the sample after rehydration and subsequent drying in a drying cabinet at 110 °C (Fig. 2).

X-ray diffraction investigations
Initial attempts to investigate the rehydration of the low-cement castable by performing X-ray diffraction experiments were affected by too large numbers of peaks present in the diffraction patterns. The rehydration process, however, can be studied using a model system containing phases of the CAH ternary system only, corresponding to the composition of the cement matrix in the andalusite-based low-cement castable. For this purpose two cements, possessing an alumina content of 70 and 80 wt%, respectively, were blended. The mixture was casted with about 20 wt% water to a mass weighing about 3 kg which was shaped in a mould to a cube with an edge length of about 10 cm. The cube was dried for one day at room-temperature and used for a series of experiments to survey the occurrence of mineral phases in the cement after subjecting the sample to different temperature and humidity conditions. To determine the phase composition at the different stages of the treatment of the sample, X-ray diffraction patterns were measured before casting the cement (A), after casting the cement and drying of the sample (B), after calcination of the sample in a furnace at 800 °C (C), after 24 hours of direct contact of the sample with water (D), after burning at 1160 °C (E) and after a three week long exposure of the sample to air (F) (Tab. 2, Fig. 3).

Tab. 2: Stages of the sample treatment before X-ray investigations.

A	Mixture of the two CACs
B	Casting with water, drying at 110°C
C	Calcination for 5 hours at 800 °C
D	Rehydration for 24 hours under water
E	Burning for 5 hours at 1160 °C
F	Exposure for three weeks to air

The diffraction patterns were measured in reflection mode (Bragg-Brentano geometry) employing an X'pert[3] diffractometer of PANalytical equipped with a copper X-ray tube and a position-sensitive X-ray detector. For the measurements the high voltage of the X-ray generator was adjusted to 40 kV and the electron beam current to 40 mA. The diffraction patterns measured after casting of the cement (Fig. 3, patterns B-F) were obtained by diffracting X-rays on the surface of the cube using a line-focus. As the diffractometer allows for measuring samples in q-q-scans,
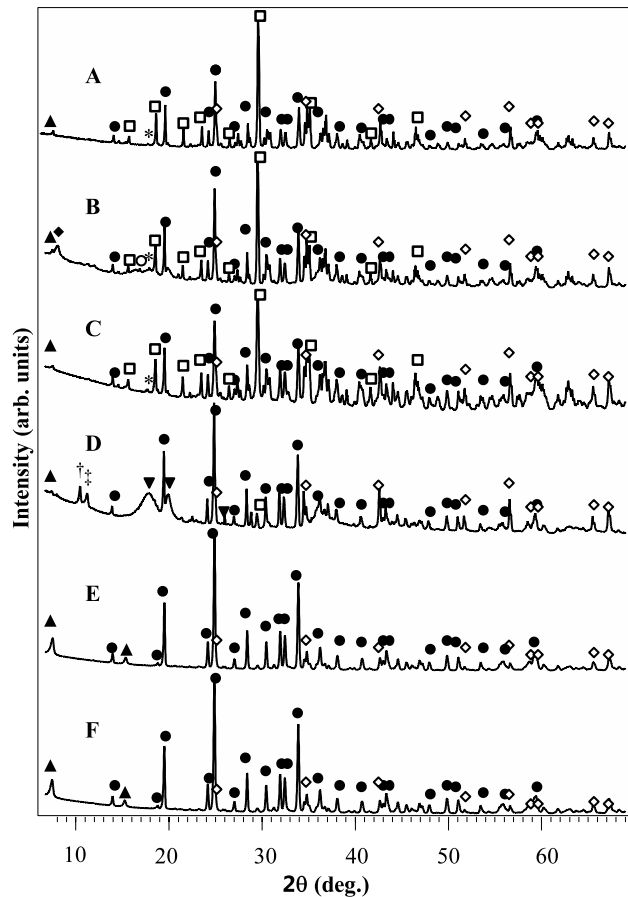

Fig. 3: Diffraction patterns measured on a sample of CAC.

during the measurement the cube rested motionless in respect to the coordinate system of the instrument. The X-ray diffraction patterns were measured for a scattering angle 2q ranging from 5 to 70° with a stepsize of 0.013° of the detector and a total measuring time of 15 minutes for each scan.

Peaks in the diffraction patterns were identified using the software program HighScore provided by PANalytical and database entries of the Crystallography Open Database (COD) and the International Center for Diffraction data (ICDD). Changes of the mineralogical composition of the sample were determined by quantitative phase analysis using HighScore. Standard uncertainties of the phase contents determined by quantitative phase analysis of measurements carried out on mixtures of known compositions were estimated to be of the order 5-10 %.

Tab. 3: Phase composition of the CAC (wt%), see text and Tab. 2.

		A	B	C	D	E	F
●	Grossite (CA$_2$)	31.4	33.1	35.5	36.8	89.6	89.3
□	Krotite (CA)	49.5	38.1	51.4	3.7	1.1	1.2
◊	Corundum (A)	18.3	11.0	12.0	13.6	6.6	6.6
*	Mayenite (C$_{12}$A$_7$)	0.4	-	0.8	0.0	0.0	0.0
○	Hydrogarnet (C$_3$AH$_6$)	0.0	1.0	0.0	0.0	0.0	0.0
▼	Gibbsite (AH$_3$)	0.0	16.8	0.0	45.6	0.0	0.0
▲	β-Al$_2$O$_3$ (NaAl$_{11}$O$_{17}$)	0.8	0.5	0.3	0.3	2.6	2.9

The phase compositions of the CAC determined by quantitative phase analysis of X-ray diffraction measurements performed at the different stages of the investigation are quoted in Tab. 3. Symbols used in Fig. 3 and Tab. 3 refer to the same phases.

Peaks of the diffraction pattern measured on the mixture of the non-rehydrated CACs were identified as intensity contributions of the mineral phases grossite (CA_2), krotite (CA) and corundum (A) (Fig. 3, pattern A, Tab. 3, col. A). Peak positions of some additionally measured weak peaks match the positions of peak maxima of mayenite ($C_{12}A_7$) and β-Al_2O_3 ($NaAl_{11}O_{17}$) and reveal the presence of both minerals as accessory phases. Due to an overlap with broad maxima of an amorphous phase the peaks of mayenite could not be observed in the diffractogram after casting of the sample (Tab. 3, col. B). The peaks assigned to intensity contributions of the strongest peaks of mayenite and β-Al_2O_3 are indicated in Fig. 3 by a filled triangle ($\blacktriangle$) and an asterisk, respectively.

RESULTS AND DISCUSSION

Thermogravimetric measurements on samples of the andalusite-based low-cement castable show that the amount of water released from the samples is strongly influenced by the extent of rehydration achieved during a rehydration process (Fig. 1). The amount of chemically bound water incorporated in the rehydrated samples depends mainly on the temperature at which the samples were heated during a pre-heating process and on the conditions of rehydration (Fig. 2). Samples rehydrated in an atmosphere of 70 %RH contained between 0 and 0.3 wt% bound water after drying (Fig. 2). By increasing the RH to 100 %, the amount of chemically bound water increased to more than five-fold (Fig.1 and Fig. 2). The rehydration of samples by placing the samples in water or by exposing them to an atmosphere possessing 100 %RH results in almost equally high amounts of bound water in the samples after a rehydration for two weeks. As can be seen from Fig. 2, the highest amounts of bound water were found after rehydration of samples pre-heated at 600 °C. A pre-heating at 1200 °C results in a content of maximal ~0.2 wt% bound water in the samples (Fig. 2).

The low amount of bound water in samples pre-heated at a temperature of 1200 °C is maybe related to changes of the mineralogical composition of the sample. Rehydration experiments carried out on samples of CAC exhibited that mayenite forms at temperatures of about 350 °C. After heating samples of CAC to 600 °C, the phase content of mayenite increased to ~25 wt% . Samples heated to higher temperatures possessed a lower content of mayenite and contained lower amounts of corundum and higher amounts of grossite in accordance with a transformation of mayenite and corundum into grossite [3]. As water molecules occupy cavities of the porous structure of mayenite, the amount of mayenite in a sample might be directly associated with the capability of the sample to chemically bind water.

From mineralogical point of view, the hydration reaction of CAC involves a reaction of krotite and grossite into gibbsite, hydrogarnet or other hydrated calcium aluminate phases [2]. This transformation process can, however, be slowed down through an incapsulation of not reacted material by a surrounding film of hydrated $Al(OH)_3$ gel, as observed for silica-free castables [2,8]. For a continuation of the hydration reaction the covering film has to undergo an aging process to become permeable for water [8].

By casting of our sample, the phase krotite only partially hydrated (Tab 4, col. B) consistent with the occurrence of an incomplete reaction of the pure binder. The reaction products of the setting were amorphous AH_3 as well as a small amount of hydrogarnet and $C_3A \times Ca(OH)_2 \times 18H$ ($3CaO \times Al_2O_3 \times Ca(OH)_2 \times 18H_2O$, PDF number: 00-042-0487). Because of a lack of structural data, the phase content of $C_3A \times Ca(OH)_2 \times 18H$ could not be determined by a quantitative phase analysis employing HighScore. Through a comparison of the intensities of the strongest peaks of hydrogarnet and $C_3A \times Ca(OH)_2 \times 18H$ (symbol ¨ in Fig. 3, pattern B), however, the phase content of $C_3A \times Ca(OH)_2 \times 18H$ was estimated to

have been about four times higher than the content of hydrogarnet in the sample.

A heating of the CAC to 800°C resulted in a decomposition of the hydrate phases and a pronounced increase of the phase content of krotite to about 51 wt%. An almost quantitative hydration of krotite was achieved subsequently by storing the sample for 24 hours under water (Tab. 4, col. D). The hydration resulted in a decrease of the amount of krotite to ~4 wt%, an increase of the amount of gibbsite to ~46 wt% and negligible small changes of the phase contents of grossite (~37 wt%) and corundum (~14 wt%). The occurrence of additional weak peaks in the diffraction pattern (symbols † and ‡ in Fig. 3, pattern D) can be attributed to a formation of $Ca_8Al_4O_{14}CO_2 \times 24H_2O$ (PDF number: 00-036-0129) and of a paragenetic mixture of the phases $Ca_4Al_2(OH)_{12}(CO_3)_{0.5} \times n$-$H_2O$ and $Ca_4Al_2(OH)_{12}CO_3 \times nH_2O$ (PDF number: 96-210-5252), respectively. A description of the carbonation of hydrated aluminates can be found in [7]. As also for $Ca_8Al_4O_{14}CO_2 \times 24H_2O$ no structural data were available, the amount of carbonate hydrate phases in the sample was estimated by a comparison of the peak shapes in the diffraction pattern. By this means, the total amount of carbonate hydrates of the sample was estimated to comprise about 5 wt% after rehydration of the sample.

By heating the sample to 1160 °C, the hydrate phases decompose and the phase content of grossite increased to about 90 wt% after firing. A three week long contact of the sample to air did not cause a remarkable change of the mineralogical composition. Throughout the experiments the sample contained a small amount of β-Al_2O_3 which increased to 2.6 wt% after heating the sample to 1160°C (Tab. 3, col. E). The formation of β-Al_2O_3 during the firing of the sample might result through a reaction of the aluminous phases and sodium-bearing additives at high temperatures.

As the material of the tundish only contains about 5-10 wt% CAC, the maximal amount of hydrate phases in the permanent lining of the tundish can, theoretically, adopt values of some percent. It should, however, be stressed, that the percentage of the hydrate phases relative to the total amount of calcium aluminate phases is obviously lower for the permanent lining than for the sample of the rehydrated castable from our experiments because of the comparably low humidity of the gunning mix and the short time the permanent lining is exposed to the moisture of the gunning mix. On heating, most hydrate phases CAH already decompose at temperatures below 300-400 °C. The presence of hydrate phases during the operation mode of the tundish can be excluded, as the tundish will usually at first be heated to a temperature of about 1160 °C after an exchange of the linings. Furthermore, at this temperature the CAC start to react with other components inside the castable matrix, especially silica fume, which results in the formation of anorthite or gehlenite which further reduces the amount of available calcium aluminate phases [9].

CONCLUSIONS

Rehydration experiments carried out on pre-heated samples of a low-cement castable were analyzed in respect to the amount of chemically bound water present in the sample and by thermogravimetric measurements. The extent of rehydration was strongly influenced by the relative humidity of the atmosphere in which the samples were rehydrated and the height of the temperature attained during the pre-heating of the samples.

Samples rehydrated for two weeks in an artificial atmosphere possessing 70 %RH contained maximal 0.3 wt% bound water. After the same time, in samples exposed to an atmosphere of 100 %RH or stored under water maximal 1.9 wt% bound water was incorporated. Among samples rehydrated under same conditions, the largest amount of bound water was found for samples which were pre-heated at a temperature of 600 °C. A pre-heating of the

samples at a lower or higher temperature resulted in an accommodation of lower amounts of bound water. TGA and DTA measurements exhibited that most of the bound water is released at temperatures below 300 °C.

Although several CAH phases are involved in the hydration and rehydration processes of CAC-containing castables, all of them decompose at temperatures far below the temperature attained during the preparation of the tundish for the use in the steel production. The heating of the tundish to a temperature of 1160 °C, low thermal stability of the hydrous phases and the high volatility of water vapor let it seem unlikely, that the lining could be an important source for the transfer of water (or its reaction products) into liquid steel.

REFERENCES

[1]   Cuesta A, Ichikawa RU, Londono-Zuluga D, De la Torre AG, Santacruz I, Turrillas X, Aranda MA. Aluminum hydroxide gel characterization within a calcium aluminate cement paste by combined Pair Distribution Function and Rietveld analyses. Cem. Concr. Res., 2017; 96:1-12.

[2]   Edmonds R N, Majumdar A J, The hydration of Secar 71 aluminous cement at different temperatures, Cem. Concr. Res., 1989;19: 289–294.

[3]   Wang Y, Li X, Zhu B, Chen P. Microstructure evolution during the heating process and its effect on the elastic properties of CAC-bonded alumina castables. Ceram. Int., 2016; 42:11355-62.

[4]   Boysen H, Lerch M, Stys A, Senyshyn A. Structure and oxygen mobility in mayenite ($Ca_{12}Al_{14}O_{33}$): a high-temperature neutron powder diffraction study. Acta Crystallogr., Sect. B, 2007; 63:675-682.

[5]   Maaroufi M, Lecomte A, Diliberto C,Francy O, Le Brun P. Thermo-hydrous behavior of hardened cement paste based on calcium aluminate cement. J. Eur. Ceram. Soc., 2015; 35:1637-46.

[6]   Kato K, Saalfeld H. Alkalifreies wasserhaltiges β-Al_2O_3. Acta Crystallogr., Sect. B, 1977; 33:1596-1598.

[7]   Runcevski T, Dinnebier RE, Magdysyuk OV, Pöllmann H. Crystal structures of calcium hemicarboaluminate and carbonated calcium hemicarboaluminate from synchrotron powder diffraction data. Acta Crystallogr., Sec. B, 2012; 68:493-500.

[8]   Tischer D, Krause O. The formation velocity of Ca hydrate phases in refractory castable after water addition. Conference paper: Unified International Technical Conference on Refractories, Vienna, Austria, 2015;Proceeding 342

[9]   Wöhrmeyer C, Parr C, Myhre B. The optimisations of deflocculated high cement castables (HCC). Conference paper: 49th International Colloquium on Refractories, Aachen Germany, 2006.