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Prehydration of calcium sulfoaluminate (CSA) clinker at different relative humidities

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Abstract:

The use of CSA cement in practice has been hindered by its unstable performance and short shelf-life caused by the prehydration of CSA clinker. In this study, the effect of ambient humidity on the prehydration rate and process of CSA clinker was investigated. The prehydration degree, ageing progress, and the dynamic change of mineral composition of CSA clinker exposed to five different relative humidities (ranging from 23% to 98%) for up to 180 days were studied. Experiments revealed that the ambient humidity of 60% RH can be considered a threshold value for storage of CSA clinker. Exposure of CSA clinker to RH higher than 60% will not only result in a significant decrease of hydraulic reactivity, but also in agglomeration of the clinker. Although the exposure of CSA clinker to RH lower than 60% has little effect on the hydraulic reactivity, the main hydration peak was found to be slightly delayed with the increase of RH.

Keywords:

CSA cement; prehydration; ye'elimite; Anhydrite; phase assemblage

1. Introduction

The production of ordinary Portland cement (OPC) has increased more than 30-fold since 1950, and almost 4-fold since 1990. Especially in developing countries, such as China, the cement production has grown by a factor of almost 12 since 1990. Consequently, 73 % of global growth in Portland cement production during this period occurred in China [1]. A recent study estimated that the total emissions from the cement industry are responsible for up to 5.6 % of global CO_2 emissions [2]. Clearly, current trends in cement production are not sustainable. Therefore, the cement industry is looking for new options to reduce its CO_2 emissions.

Calcium sulfoaluminate (CSA) cement seems to be a promising and eco-friendly alternative to OPC [3, 4]. CSA cement is mainly based on the mineral substance ye'elimite ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, $C_4A_3\hat{S}$ in cement notation). The production of ye'elimite releases 66% less CO_2 compared to the production of alite (the dominant phase of OPC [5]), due to the lower consumption of calcium carbonate in production. In addition, the production of CSA cement requires a sintering temperature of only 1250 ℃, which is about 200 ℃ lower than the sintering temperature of OPC. Moreover, the grinding process of CSA consumes less energy compared to OPC as the hardness of CSA clinker is relatively low [6]. The combination of these factors makes CSA cement an ideal option for reducing CO2 emissions of the cement industry. Recent data shows that CSA cement releases only 0.56 g CO_2 per mL cementing phase during production, while alite releases 1.80 g [5]. Apart from environmental advantages, CSA cement also has technical advantages compared to OPC: it has comparable early and late strength with lower shrinkage [7]. Furthermore, the relatively short setting and hardening time can of CSA cement can, to a large extent, promote construction efficiency. Although lower strength and durability issues due to e.g. carbonation are a big concern hindering CSA application in large-scale construction, in-depth studies that can push the application of CSA cement further are of great value.

It has been demonstrated that the exposure to water vapour pressure of a certain intensity will lead to prehydration of cement clinker. Moisture is present in the process of cement production, transportation, and storage. Although improved packaging may help, the prehydration of cement cannot be fully prevented. Silica-based clinker minerals, such as tricalcium silicate (C_3S) and dicalcium silicate (C_2S), start to prehydrate at ambient humidity above 85% and 90% RH, respectively [8]. Some hydration products of OPC, such as ettringite, monosulfate and calcium aluminate hydrate, may also undergo a phase deformation or transformation due to the change of ambient climate [9, 10]. Recent work suggests that prehydration of OPC not only results in a decrease in the hydraulic reactivity and prolongation of the setting time [11], but also causes a reduction in the rate of strength development [12, 13]. Dubina et al. [14] attributed the occurrence of prehydration to the surface adsorption of water vapor on the cement grains, which results in a reduction in surface area and changes in surface charge. Thermodynamic analyses were performed to understand the reason C_3S hydration stops below 80% RH on the basis of the change in water activity [15]. Compared to silica-based clinker minerals, aluminate-based clinker minerals such as ye'elimite (the main constituent of CSA cement) and tricalcium aluminate (C_3A) are more susceptible to moisture. C_3A was found to hydrate at ambient humidity of 60% RH [8]. A recent study [13] shows that the exposure of commercial CSA cement to RH above 60% (ranging from 67%-78%) has negative effects on the hydration and strength development of both CSA and CSA-OPC cement pastes. In fact, fast and unpredictable prehydration of CSA cement resulting from accidental moisture exposure has long been a problem in practical applications, especially in tropical and subtropical coastal regions. Although the negative effect of the exposure of CSA cement to ambient humidity has been explored in lab conditions, a quantitative relation between the prehydration degree and the exposure condition has not been established. There is a lack of in-depth knowledge about the degradation of ye'elimite at various RH and how this is linked to the dynamic change of the mineral phases. In addition, it has been reported that the properties of CSA cement depend largely on the calcium sulfate ($CaSO_4$) content [5, 16]. By changing the molar ratio of gypsum/ye'elimite, the hydration products, setting time, strength development and volume stability of CSA cement can be controlled [5, 17]. However, the influence of calcium sulfate addition on the prehydration of CSA clinker is not clear.

The aim of this work is to investigate the influence of relative humidity on the prehydration of ye'elimite. This should allow defining a relationship between the ambient humidity and shelf-life of CSA cement. To this end, phase pure ye'elimite was produced using a stoichiometric mixture of calcium carbonate, aluminium oxides and gypsum. The synthetic ye'elimite, with and without addition of anhydrite ($CaSO_4$), was exposed to five different RH, ranging from 23 to 98%, for a maximum 180 days. The RH was controlled by the saturated salt solution method in sealed conditions at 23 °C. The hydration degree was determined using thermogravimetric analysis (TGA) by calculating the weight loss of chemically bound water. X-ray diffraction (XRD) coupled with Rietveld method was used to investigate the dynamic changes of mineral composition of ye'elimite exposed to various RH. The morphology and the microstructure of mineral grains were observed by using an environmental scanning electron microscope (ESEM). The hydration kinetics of prehydrated ye'elimite was monitored by means of isothermal calorimetry. In the end, based on the result of hydration heat, the influence of prehydration of ye'elimite on its final hydration products was further analysed with the help of TGA and XRD. The findings reported herein do not only contribute to understanding of CSA cement prehydration, but may also provide guidance to the cement industry for better storage and application of CSA clinker in practice.

2. Materials and Methods

2.1 Materials

Phase pure calcium sulfoaluminate (ye'elimite) clinker mineral was synthesized from a stoichiometric mixture of calcium carbonate ($CaCO_3$), aluminum hydroxide ($Al(OH)_3$) and calcium sulfate dihydrate ($CaSO_4{\cdot}H_2O$). Potassium acetate, potassium carbonate, sodium bromide, sodium chloride, potassium chloride and potassium sulphate were used to maintain a constant RH value of 23%, 43%, 60%, 85% and 98%, respectively, at 23 °C. Organic solvents, isopropanol and diethyl ether, were used to stop the process of cement hydration, as recommended by RILEM TC-238 SCM [18]. Anhydrite was obtained by burning calcium sulfate dihydrate at 700 °C for 2h. All chemicals used were analytical grade without further purification.

2.2 Sample preparation

2.2.1 Preparation of ye'elimite

Ye’elimite was prepared using reagent grade materials. According to the molecular formula of $C_4A_3\hat{S}$, the molar ratio of $CaCO_3$, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ should be 3:6:1. For synthesizing 100 g of ye’elimite, the stoichiometric amounts of $CaCO_3$, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ are 49.20, 76.67, 28.20 g, respectively. However, due to the volatilization of sulfur in the sintering process, the weight calculation based on the molar ratio is not accurate. Furthermore, the decomposition of $CaSO_4$ will also result in an excess of CaO. To obtain relatively pure $C_4A_3\hat{S}$, the amount of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ has to be recalculated. Zhang et al. [19] concluded that the volatile content of $CaSO_4$ accounts for around 7% of the total mass of $C_4A_3\hat{S}$. This means that for producing every 100 g $C_4A_3\hat{S}$, 8.85 g extra of $CaSO_4 \cdot 2H_2O$ and 5.15 g less of $CaCO_3$ has to be added to the mixture. The recalculated masses of raw materials, $CaSO_4 \cdot 2H_2O$, $CaCO_3$, $Al(OH)_3$, are 37.06, 44.05, and 76.7 g, respectively.

The raw materials were first homogenized in a ceramic bowl with deionized water using a mechanical stirrer for 2 h and then dried at 105 °C for 24 h. The obtained mixture was compacted by hand using a flat pestle in a corundum crucible. The crucible was then placed in a muffle furnace and then sintered. The mix was heated from 20 °C to 900 °C with a heating rate of 5 °C/min, and kept for 1 h at 900 °C. Afterwards, the mix was heated up to 1250 °C applying a heating rate of 10 °C/min. The mix was sintered in the furnace for 3 h at 1250 °C followed by fast cooling（quenching process）in air at lab temperature. The final product was dry-ground manually in a grinding bowl. The grinding process was performed in a glovebox with nitrogen gas protection. Anhydrite was prepared by burning calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) in a furnace at 700 °C for 2 h. To study the influence of calcium sulfate on the prehydration of ye’elimite, besides the pure ye’elimite (henceforth referred to as PY) clinker mineral, ye’elimite was finely blended with anhydrite with a ye’elimite to anhydrite ratio of 7:3 (henceforth referred to as 7Y3A). Both clinker types reached the desired fineness of $D_{90} < 40\ \mu m$. Purity of the achieved mineral was identified by X-Ray Diffraction (XRD) coupled with Rietveld refinement method. The achieved composition for the two clinkers was: PY - 97.2% ye'elimite and (hard burnt) 2.8% anhydrite; 7Y3A - 67.5% ye'elimite, 32.5% anhydrite.

2.2.2 Prehydration procedure

The clinker minerals were aged at 23%, 43%, 60%, 85% and 98% RH, respectively, for a maximum 180 days. The corresponding RHs were maintained in separate sealed glass drying jars using the saturated salt solution method [20]. Ambient temperature, saturated salt solution type, the target RH, and the standard RH which summarized by National Institute of Standards and Technology (NIST) [21] are shown in Table 1. To reach equilibrium, the saturated salt solutions were premixed (heated up to 90°C followed by cooling down to lab temperature) and left in a glass drying jar for 3 days. Before the exposure of clinker to water vapour, the samples were dried using a silica gel desiccant at the exposure temperature for 1 day. To make sure that the clinker was sufficiently exposed to water vapour, the mineral powder was evenly spread on glass dishes with a layer thickness of 3 mm. The schematic diagram of the clinker prehydration setup is shown in Fig. 1.

Table 1. Prehydration conditions of PY and 7Y3A clinkers for different exposures.

Environment temperature	Saturated salt solution	Target RH (%)	Standard RH (%)
23 ± 2 °C	Potassium acetate	23	22.51±0.32
	Potassium carbonate	43	43.16±0.39
	Sodium bromide	60	57.57±0.40
	Potassium chloride	85	84.34±0.26
	Potassium sulfate	98	97.3±0.45

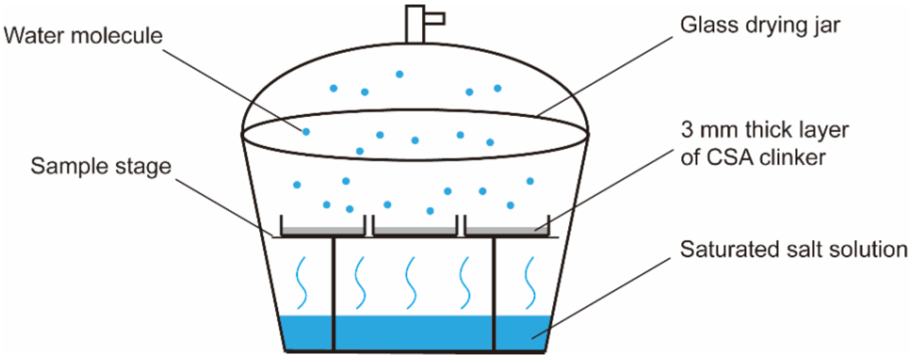


Fig.1 Schematic diagram of CSA the clinker prehydration setup.

2.2.3 Stoppage of hydration

After the samples were aged at different RH for a certain period of time, the aged clinker mineral was taken out from the glass jar and the hydration was stopped by the solvent exchange method. To do this, the clinker mineral was immersed in isopropanol and ground in a corundum mill for 15 minutes. The ground clinker was filtered by vacuum to extract the organic solution. The filtrate was dried in an aerated oven at 40°C for 10 min and then vacuum sealed in a plastic sample bag. Since long-term storage could possibly result in an instable mineral composition, analytical measurements such as thermogravimetric analysis (TGA), X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM) were performed immediately after stopping the clinker hydration.

2.4 Characterization methods

The experiments carried out to characterize the prehydration process are summarised in Table 2.

Table 2. Summary of conducted tests.

Test	Exposure time (Day)

	0	7	14	28	90	180
Water sorption	√	√	√	√	√	√
TGA	√	√	√	√	√	√
XRD	√	√	√	√	√	√
SEM						√
Calorimetry						√

The water sorption kinetics of clinker minerals at different RHs was measured by monitoring the dynamic change of clinker mass. Before the test, the clinker was vacuum dried at 20 ℃ for 24 hours. An average of 3 g clinker was weighted, spread evenly on glass sheet, and then stored in the glass jar with corresponding RH. The water sorption kinetics was reflected by the weight increment ratio (%) of clinker exposed to water vapour compared to the initial weight of the dry sample. To minimize the experimental error, the samples were weighted immediately as they were taken out from the drying jar.

The thermogravimetric analysis was carried out on each 30 ± 2 mg ground sample using a TGA analyzer (Q50, TA Instruments, USA) under flowing nitrogen (40 ml/min). The temperature was increased from 30 to 1000 ℃ at a heating rate of 10℃ /min. The degree of hydration, α, was calculated based on the thermogravimetric analysis using the following equation [8, 22]:

$$\alpha = \frac{W_{chem.w.}}{W_{max.chem.w.}} - LOI \tag{1}$$

All weights in this formula are relative to the ignited clinker weight: g/g ignited clinker. $W_{max.chem.w.}$ is the mass proportion of chemically bound water of the fully hydrated clinker. In this study, the fully hydrated clinker was defined as PY or 7Y3A clinker hydrated at 23℃ for 28 days with a water to cement ratio of 1. The calculated $W_{max.chem.w.}$ of PY is 0.56 g/g and 7Y3A is 0.65 g/g, respectively. LOI (Loss On Ignition) is the normalized weight loss of the unhydrated cement, and $W_{chem.w.}$ is the normalized weight loss of the hydrated sample [23], determined as:

$$W_{chem.w.} = \frac{W_{50℃} - W_{550℃}}{W_{550℃}} \tag{2}$$

Finally, the physically adsorbed water on the surface of the crystal was calculated by subtracting the chemically bound water from the overall weight increment after water absorption.

XRD was performed on the CSA clinker (after stopping the hydration) using a Bruker D8 in a θ - 2θ configuration with a monochromatic CuKα radiation and equipped with the LYNXEYE detector. The voltage and the current of the generator were set to 40 kV and 40 mA, respectively. The measurement 2θ range was 5° to 70° with a step-size of approximately 0.02°. The quantitative phase assemblages of the anhydrous and aged clinker, as well as the hydrated paste, were analyzed using the Rietveld method. Aluminium oxide (Al_2O_3) was applied as an external standard, and was always measured on the same day and under the same measurement conditions as the other samples. The quantitative phase content was recalculated to a anhydrous statue by taking into account the amount of chemically bound water. The mineral phases used in the quantitative phase analysis and their corresponding abbreviations are given in Table 3.

Table 3 Mineral phases used in the quantitative phase analysis and its corresponding abbreviation.

Mineral phase	Abbreviation	Ref.
Ye'elimite	Y	[24]
Anhydrite	A	[25]
Ettringite	Et	[26]
Monosulfate	Ms	[27]
Gibbsite	AH	[28]
Hannebachite	CS	[29]

The morphology of clinker mineral particles exposed to various RHs was observed with ESEM (Quanta TM 250 FEG, FEI, United States). To obtain homogeneous dispersion of clinker particles, the clinker powder was first dispersed in isopropanol, and then droplets of the suspension were deposited on a conductive tape glued to a sample holder. Upon complete evaporation of isopropanol, the dried samples were coated with a gold film and subjected to ESEM observations.

The hydration heat of samples aged at different RHs during the first 48 h was measured with an 8-channel isothermal calorimeter (Thermometric TAM Air). The ambient temperature was set to 23 °C. 3.2 g of aged CSA clinker and 3.2 g of deionized water were poured into a glass vial and mixed (outside of the calorimeter) using a laboratory mixer for 30 s to obtain a water/binder ratio of 1. The glass vial was then sealed with a cap and placed into the calorimeter. Since the initial peak was found not to be significantly influenced by the composition of the minerals [5], the hydration heat obtained immediately after the addition of water to the cement was not taken into consideration in the measurement. In this test, the measurements were only carried out on samples prehydrated at 23, 43, 60, 85 and 98 RH for 180 days. The hydration heat of the sample prehydrated for 0 days was taken as a reference. The measured heat flow and the cumulative heat were normalized to the clinker mass.

Finally, the hydration stopped CSA clinker powder that was prehydrated for 180 days was used to link the prehydration effect with the clinker hydration products. The obtained powder was mixed with water to have a water/binder ratio of 1. At the stage of the dormant period (2h), the main hydration period (10h for PY sample and 12h for 7Y3A sample), and the final period (24h) of clinker hydration, the hydrated clinker was subjected to hydration stoppage and ground. The mineral composition of the hydrated clinker was characterized by XRD and TGA. The phase assemblage was analysed by QXRD using an external standard.

3. Result and discussion

3.1 Prehydration mechanism of CSA clinker

3.1.1 Water sorption kinetics

Fig. 2 shows results from the water adsorption test carried out on PY (a) and 7Y3A (b) samples exposed to different RH. The weight increase of the clinker powder was recorded for a maximum of 180 days. It is apparent that only clinker samples exposed to 85% and 98% RH show an increase of absorbed water, irrespective of whether the anhydrite was added or not. Contrary to the OPC cement in which the free CaO in the clinker starts to hydrate at 55%RH [12], no water adsorption was found in CSA clinker aged at 23, 43 and 60% RH; a slight desorption was even observed on 7Y3A sample exposed to 23% RH. For the PY sample aged at 98% RH, the amount of adsorbed water increased almost linearly for the first 28 days, from 0 to about 0.22 g per gram of ignited clinker. Afterwards, it increased steadily up to 0.6 g/g. When the ambient RH decreased from 98 to 85%, the water sorption kinetics decreased correspondingly. Only 0.2 g/g water adsorption was found after 180 days of exposure. In case of anhydrite blended with ye'elimite clinker (7Y3A), the water adsorption was obviously different. The water adsorption rate increased sharply for 7Y3A samples aged under 85 and 98% RH during the first 28 days. Afterwards, however, the exposure of 7Y3A clinker to 85 and 98% RH for additional 152 days led to an increase of bound water of only about 0.03 and 0.06 g, respectively.

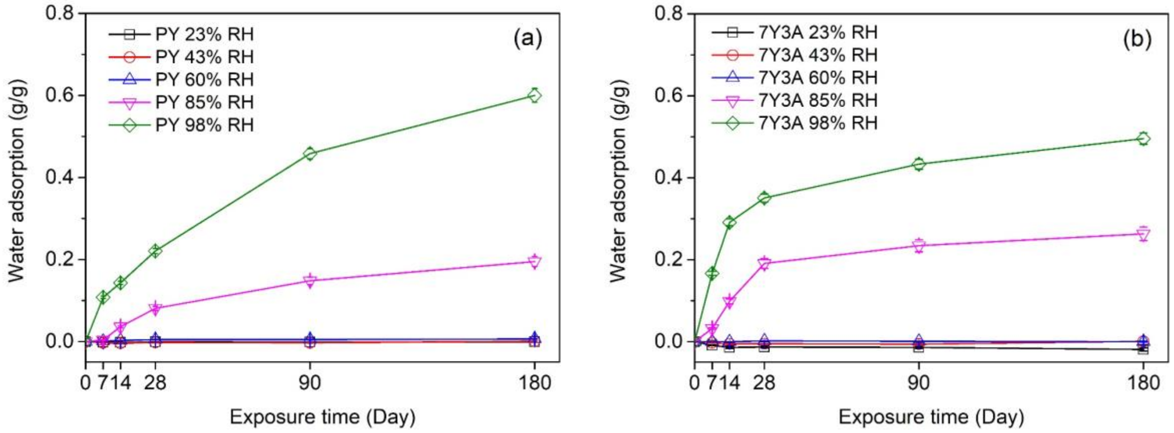


Fig. 2 The amount of water held by (a) PY and (b) 7Y3A clinker exposed to water vapor of different RHs for a maximum 180 days.

Although the results of water adsorption tests clearly suggest that the ambient water starts to be adsorbed on the PY and 7Y3A clinker materials when the ambient RH is higher than 85%, it is unfortunately not possible to differentiate between the water that is physically adsorbed on the surface of the clinker powder and the water that is chemically bound in the inter-channel of the hydrates. To have a better understanding of these differences at various conditions, the amount of chemically bound water was calculated using Eq. 2, based on the TGA data. The results are shown in Fig. 3. In general, for both the

PY and the 7Y3A samples, the chemically bound water exhibits a very similar growth pattern as the overall result of water adsorption: only samples exposed to ambient RH higher than 85% showed an increase in the amount of chemically bound water. It is noteworthy that there is a 7-day induction period for the onset of chemical water adsorption, observed for both the PY and the 7Y3A samples exposed to 85% RH. This may be caused by the exposure conditions - when a porous material is exposed to water vapour, an adsorption equilibrium is not established immediately due to the limited water activity. A similar phenomenon has been observed previously for tricalcium aluminate (C_3A): less than 1% degree of hydration of C_3A was achieved after the samples were exposed to 75% RH for 7 days whereas the degree of hydration surged up to 6% after 14 days [8]. A possible reason for the existence of this induction period can be the instability in exposure conditions. When the clinker is first placed in the drying jar, the target water vapour pressure cannot be established immediately. It takes time for the evaporation of water molecules from the saturated salt solution to reach an equilibrium vapour pressure in the sealed environment. Moreover, even if the vapour pressure reached an equilibrium in the drying jar, it is believed that the diffusion of water molecules from the ambient to the solid surface of the clinker, which finally results in the hydration of the clinker, will also delay the formation of chemically bound water. This assumption can be proven by the immediate growth of the chemically bond water when samples are exposed to an environment with higher RH (98%). Under high RH, the concentration of water molecules is much denser in the environment. There are more sites for the water molecules to react with the clinker. In that case, diffusion of water molecules from the environment to the clinker surface becomes easier.

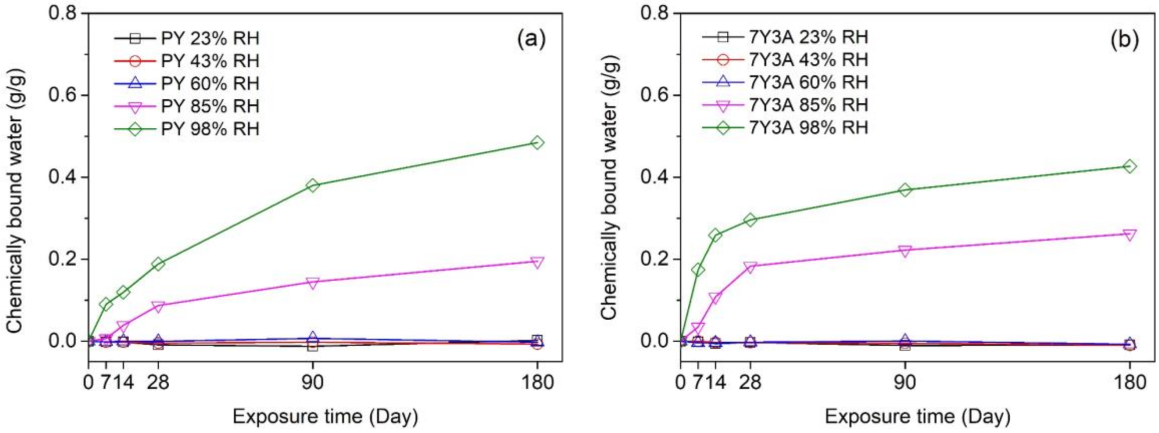


Fig. 3 The amount of chemically bound water held by (a) PY and (b) 7Y3A clinker exposed to water vapor of different RHs for a maximum 180 days.

Finally, the amount of physically bound water was calculated by subtracting the weight of chemically bound water from the total sample weight after water adsorption (Fig. 4). It was found that only samples exposed to 98% RH show a significant increase in the amount of physically bound water. The PY clinker seems to have more physically bound water than the 7Y3A clinker. The reason for this difference is not clear. It may be due to the difference in porosity and water adsorption between ye’elimite and anhydrite.

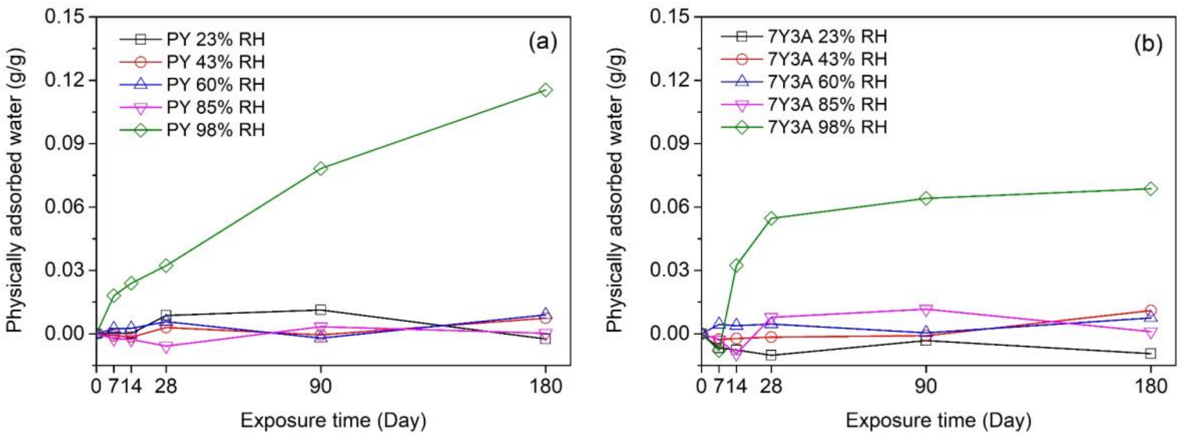


Fig. 4 The amount of physically bound water held by (a) PY and (b) 7Y3A clinker exposed to water vapor of different RHs for a maximum 180 days.

3.1.2 Degree of hydration

It has been proposed [30, 31] that the loss of chemically bound water of OPC can be defined as the weight loss between the weight after solvent exchange and the weight exposure to 550 °C. For CSA clinker, the main hydration products (ettringite, monosulfate and aluminum hydroxide) are believed to dehydrate above 50 °C at low RH [10], while no mass loss occurs after the clinker is heated up to 550 °C. Therefore, the weight loss between 50°C (after the solvent exchange) and 550°C can be attributed to the dehydration of chemically bound water. Based on the TGA results, the degree of hydration is calculated using Eq. 1, and the results are summarized in Table 4. As can be seen from the table, both the PY and the 7Y3A clinker remained unhydrated after exposure at 23%, 43% and 60% RH up to 180 days. With the increase of RH from 60% to 85%, the onset of prehydration is observed. Both clinker minerals, PY and 7Y3A, show an increase of hydration degree during the prehydration exposure at 85% and 98% RH. However, the growth trend is different. The prehydration rate of ye'elimite blended with anhydrite (7Y3A) seems to be faster than prehydration of pure ye'elimite (PY) during the initial period of 28 days. The degree of hydration increased from 5.4% to 28.3% at 85% RH and from 27% to 45.8% at 98% RH for the 7Y3A sample. This is significantly higher than prehydration of the PY sample, in which the hydration degree increased from 1.1 to 15.6% and from 16 to 33.9% under the same conditions. The prehydration of ye'elimite is promoted by the addition of the sulfate phase. However, after the initial period of 28 days, the prehydration rate of the PY samples increased. This is more prominent for the PY sample exposed to 98% RH, as the degree of hydration of the PY sample at 90 days is more than double than that at 28 days. The degree of hydration steadily increased further, reaching 87.3% at 180 days, which is 20% higher compared with 7Y3A sample. Overall, based on the degree of hydration, the safety threshold RH for CSA clinker storage can be identified as 60% RH.

Table 4 Degree of hydration of PY and 7Y3A clinker exposed to various RH.

	Time (Days)	Exposure RH (%)				
		23	43	60	85	98
7Y3A	7	0	0	0	5.4	27
	14	0	0	0	16.7	40
	28	0	0	0	28.3	45.8
	90	0	0	0	34.4	57.1
	180	0	0	0	40.6	66.1
PY	7	0	0	0	1.1	16
	14	0	0	0	6.9	21.5
	28	0	0	0	15.6	33.9
	90	0	0	0	26	68.4
	180	0	0	0	35	87.3

3.1.3 Assemblages of mineral phases

To further investigate the prehydration mechanism, XRD and TGA were used to characterize the dynamic evolution of phase assemblages in the prehydrated clinker. As no significant differences of phase assemblages were found among samples exposed to 23%, 43% and 60% RH, only the results of PY and 7Y3A samples exposed to 60% RH are reported here. The term in the figure “Ref” refers to the result of freshly sintered clinker powder. Figure 6 shows the results of XRD and TG analysis.

60% RH

From Fig. 5(a1) it can be seen that, compared with the Ref sample, no visible intensity changes or shifts of XRD peaks can be observed from PY and 7Y3A samples. Ye’elimite is the dominant phase for the PY sample with a trace of hard burnt anhydrite. When anhydrite was added into pure ye’elimite, the characteristic peak of anhydrite could be clearly observed (Fig. 5 (b1)). This suggests that no new crystal mineral has formed in PY and 7Y3A samples, even after 180 days exposure at 60% RH. TGA measurements were performed to supplement the XRD analysis. It is clear that no significant mass loss for both the PY (Fig. 5 (a2)) and the 7Y3A (Fig. 5 (b2)) samples can be detected from the TG measurements when heating the clinker from 50 to 600°C, which indicates that no main hydration products were formed during the prehydration exposure, neither in crystal nor in XRD-amorphous form.

85% RH

At prehydration condition of 85% RH, obvious changes of mineral assemblages can be observed from the XRD patterns. For PY-85% RH sample, the formation of ettringite was identified after it was exposed to 85% RH for 28 days, accompanied with decreased peak intensities of ye’elimite (Fig. 5(c1)). Meanwhile, microcrystalline aluminium hydroxide (Gibbsite) occurs in an XRD broad peak form from

14 days. The characteristic peak of monosulfate (Ms) was hardly visible until the clinker was prehydrated for 90 days, probably due to the poor crystallinity of monosulfate when it forms at air exposure. Similar information can be obtained from the TGA analysis (Fig. 5 (c2)), from which monosulfate with multiple broad characteristic peaks at around 70-150 and 150-200 °C can be identified. Ettringite cannot be clearly distinguished from the DTG curve after the first 28 days, as it is only present in minor amounts and its dehydration peak overlaps with the one of monosulfate. With the increase of exposure time to 90 days, more intense peaks were observed at around 100-120 and 250-290°C, representing the steady formation of ettringite and gibbsite, respectively. For the 7Y3A sample exposed to 85% RH, when anhydrite is added to ye'elimite, ettringite occurs as the main hydration product of the prehydrated clinker, accompanied with gibbsite (Fig. 5 (d1)). In the meantime, the amounts of anhydrite and ye'elimite decreased correspondingly. This is further supported by the DTG curves, where only peaks assigned to ettringite and gibbsite are present (Fig. 5 (d2)). A relatively weak characteristic signal of microcrystalline aluminium hydroxide was detected via DTG compared to pure ye'elimite clinker, which can be explained by the dilution of the ye'elimite with sulfate, leading to the formation of less amorphous aluminate phase and more microcrystalline aluminium hydroxide in the clinker. Similar findings have been previously reported [5].

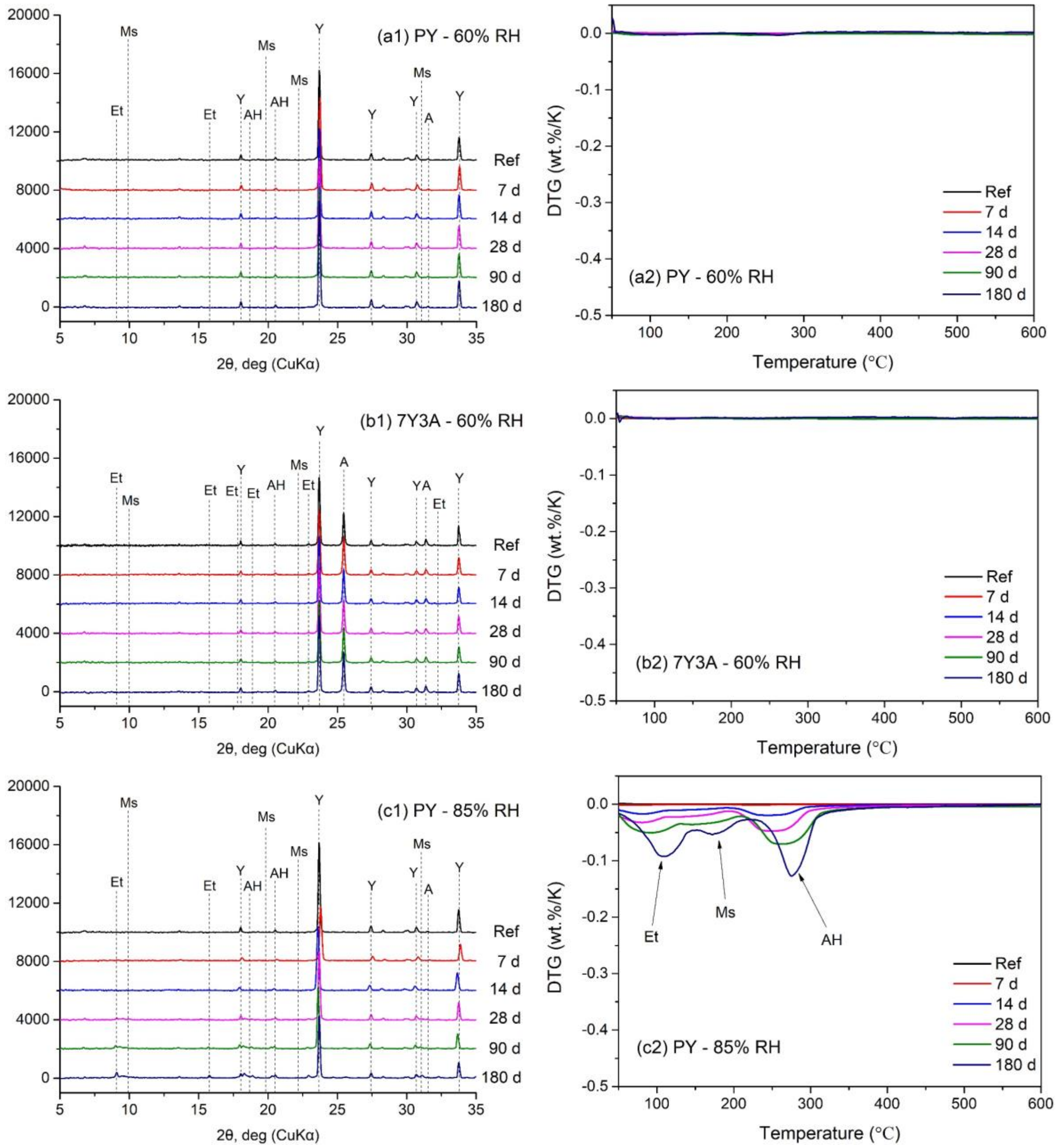
98% RH

The prehydration behaviour of PY and 7Y3A samples at elevated RH of 98% is similar to that observed at 85% RH, while the changes in mineral composition become more intense. As it was hydrated in higher moisture condition, monosulfate and aluminium hydroxide formed in the PY sample with depletion of ye'elimite according to Eq. 3 [3].

$$C_4A_3\hat{S} + 18H \rightarrow C_4A\hat{S}H_{12} + 2AH_{3\,microcrystalline} \qquad (3)$$

After exposure at 98% RH for 90 days, almost all ye'elimite presented in the PY sample has been consumed and ettringite occurs as a minor hydration product (Fig. 5 (e1)). In the DTG diagram (Fig. 5 (e2)), aluminium hydroxide with the mass loss between 250 - 300°C appears to be the most predominant prehydration product after long term exposure to higher RH, apart from monosulfate. The main hydration product of 7Y3A that formed at 98% RH is recognized as ettringite, while traces of monosulfate could also be identified after 90 days of exposure (Fig. 5 (f1)). Unlike the PY sample, ye'elimite and anhydrite were not fully consumed even after being exposed to 98% RH for 180 days since the pertinent characteristic peak can be observed clearly in the XRD pattern.

Moreover, a shift is observed in the characteristic peaks of DTG with increased exposure duration, from lower dehydration temperature to higher dehydration temperature. Longer exposure leads to a higher amount of chemically bound water. Therefore, this shift can be attributed to the dehydration of a larger amount of chemically bound water, resulting in higher vapour pressure in the environment of the solid, thus higher temperatures are needed to dehydrate the clinker. A similar phenomenon has been reported when a larger amount of gypsum was present in the sample [32].



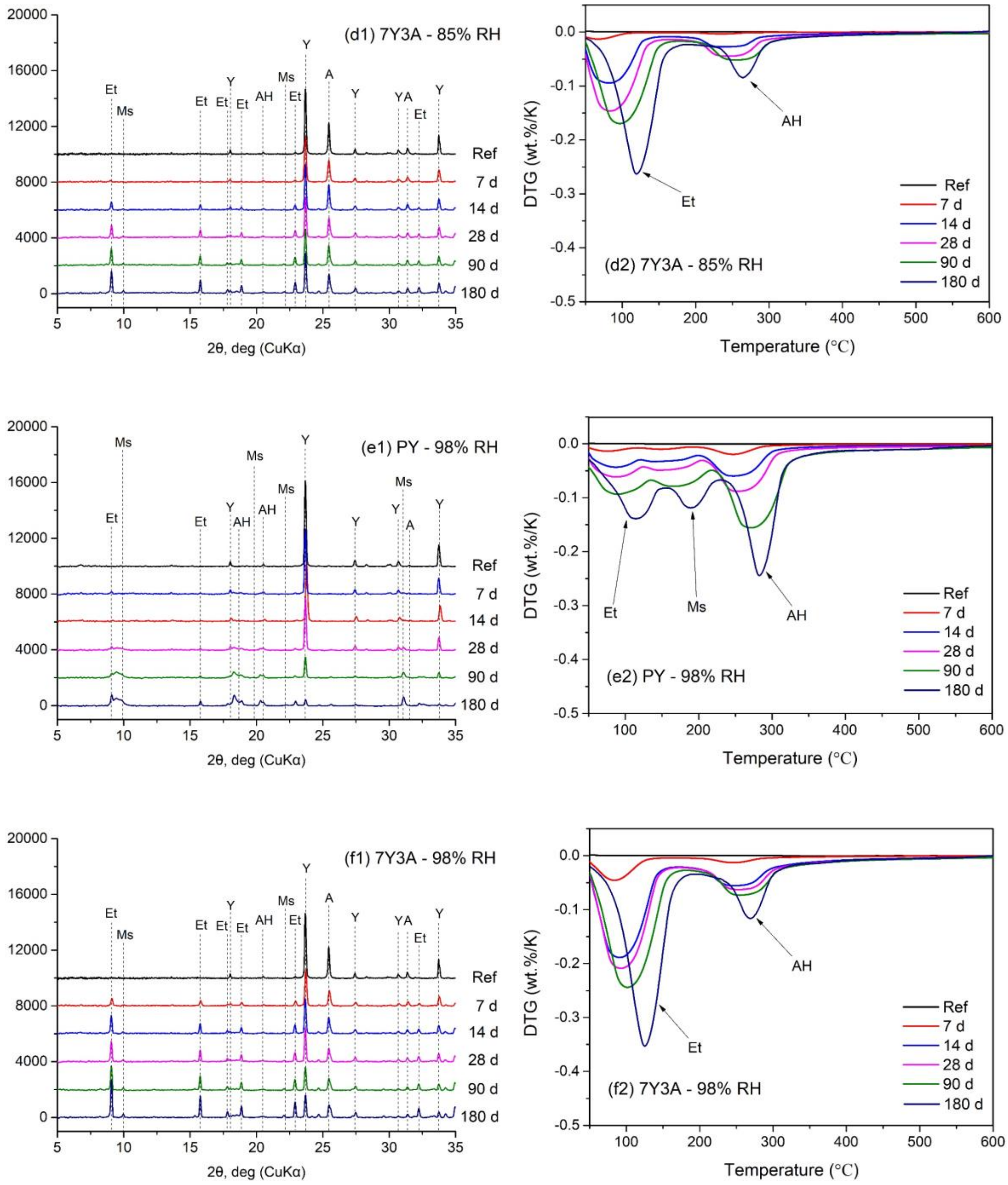


Fig.5 Comparative study of XRD (left) and DTG (right) results of PY and 7Y3A clinker aged at (a, b) 60%, (c, d) 85% and (e, f) 98% RH for 0 (Ref), 7, 14, 28, 90 and 180 days.

3.1.4 QXRD analysis of phase assemblage

Since amorphous mineral phases such as aluminium hydroxide cannot be characterized from the XRD pattern, additional information of the phase assemblage of the prehydrated clinkers were obtained using Rietveld refinement coupled with an external standard method. The results are shown in Fig. 6.

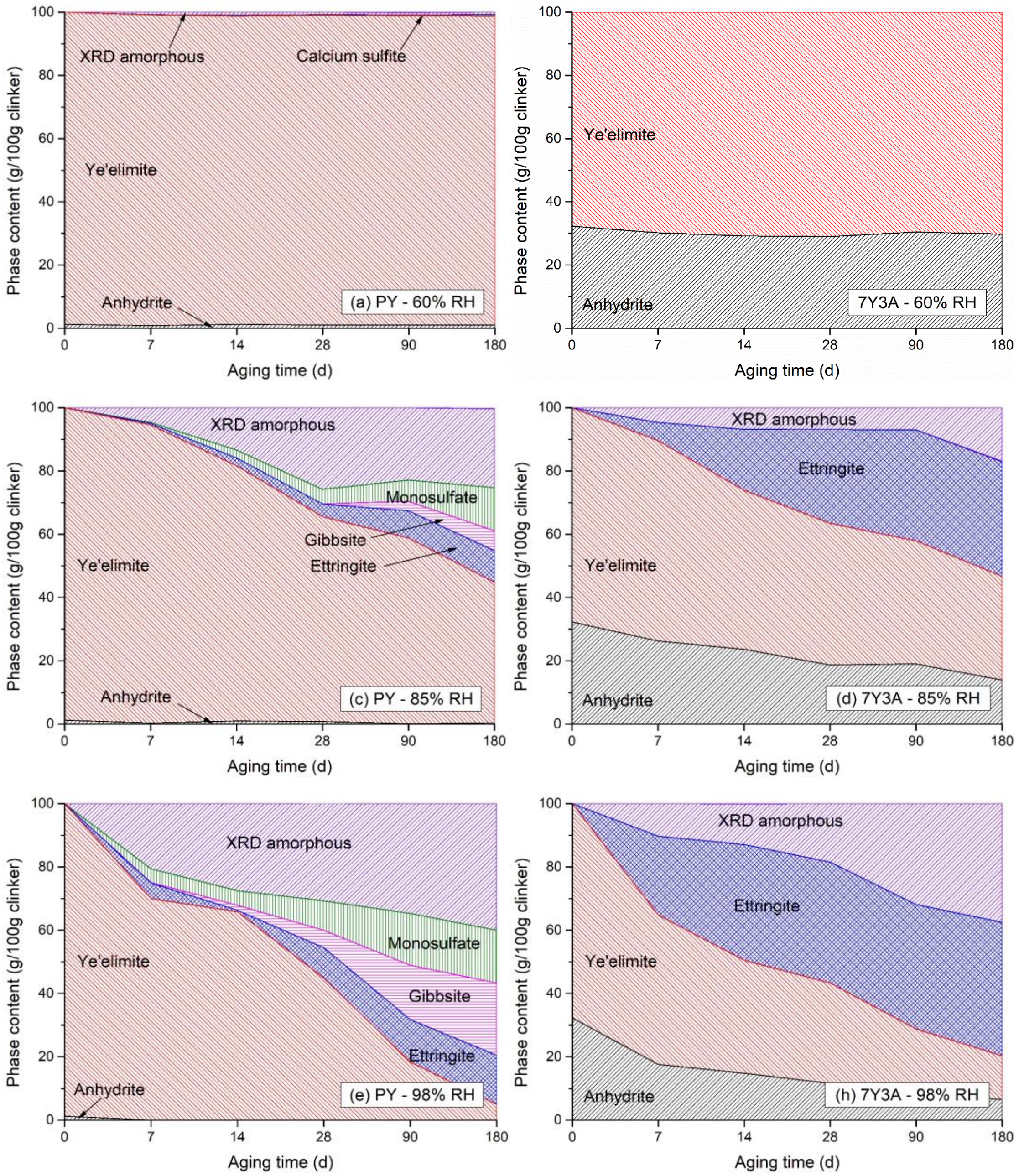


Fig.6 The dynamic of phase assemblage of PY (left) and 7Y3A (right) clinker exposed to (a, b) 60%, (c, d) 85% and (e, f) 98% RH for up to 180 days.

No obvious phases change was observed in neither the PY (Fig. 6a) and the 7Y3A (Fig. 6b) samples exposed to 60% RH after the 180 days of prehydration. However, despite the existence of the hard-burnt anhydrite originally coming from the sintered clinker, trace amounts (less than 0.5%) of XRD amorphous and calcium sulfite ($CaSO_3 \cdot (H_2O)_{0.5}$) were found in the PY sample after 7 days of exposure at 60% RH. It has been reported that low RH favours formation of solid products with low water content [8]. The formation of these two phases with low water content can be attributed to the dissolution of ye'elimite and hard-burn anhydrite under low RH. With prolongation of the prehydration time from 7 days to 180 days, the amount of XRD amorphous phases and calcium sulfite remained stable, without further increase.

When the storage humidity is increased to 85% RH, amorphous aluminium hydroxide (XRD amorphous) is the first prehydration product formed in the PY clinker during the initial 7 days of prehydration (Fig. 6c). This is similar to the case previously reported for CSA initially hydrated in water [33], where amorphous aluminium hydroxide, instead of monosulfate and microcrystalline aluminium hydroxide, was considered to form as a result of dissolution of ye'elimite. With longer prehydration time, the amount of ye'elimite decreases, which leads to the formation of ettringite and monosulfate, followed by gibbsite at 28 days. Unlike the PY sample, no gibbsite and monosulfate were observed from the XRD result for the 7Y3A sample even after 180 days of exposure (Fig. 6d). Ettringite, accompanied with XRD-amorphous phases, is the main prehydration product due to the sufficient supply of sulfate.

The tendency of both PY and 7Y3A samples at 98% RH is similar to that found at 85% RH. New phases did not form with the increase of RH. Ye'elimite in the PY sample was almost depleted after 180 days exposure at 98% RH (Fig. 6e). Moreover, it is interesting to note that the phase content of XRD amorphous, monosulfate, gibbsite and ettringite of PY sample exposed to 85% RH for 180 days are 25%, 13.6%, 6.3% and 10% respectively, values which are almost equivalent to those of the PY sample exposed to 98% for 28 days. The phase assemblages of the PY and the 7Y3A samples exposed to 85% and 98% for 180 days are in good agreement with the literature [33].

3.1.5 ESEM

ESEM was employed to study the morphology of ye'elimite dissolution and the precipitation of hydration products. Fig. 7 shows SEM micrographs of clinkers prehydrated at different RH for 180 days. Similar to the results obtained from XRD and TGA, no obvious differences can be seen between the PY and the 7Y3A samples exposed to 23% and 43% RH, and the Ref sample. Grains of anhydrous particles are closely attached together, and no dissolution or precipitation occurs under this condition. For the PY sample exposed to 60% RH, it is interesting to observe that globule-like particles have formed on the surface of the clinker (Fig. 7e). A similar feature was described by Bullerjahn et. al. [34], where the globule-like particles occurred when ye'elimite hydrated at 23 ^{o}C with a w/b ratio 100 for 420 seconds. The difference is that the globule-like particles observed by Bullerjahn et al. [34] are much denser than those observed in the current study. This may result from the much more water molecules being available when the clinker hydrates in liquid water compared to being exposed to gaseous water vapour. According to the QXRD result in Fig. 6a, the globule-like particles observed on the PY - 60% RH sample can be considered to be the trace amounts of XRD amorphous or calcium sulfite hydrates. The formation of these globule-like particles can be regarded as onset of clinker hydration. From the reaction kinetics point of view, the kinetic barrier of the hydration of clinker minerals is going to be overcame at this water activity (RH). No globule-like particles were observed in the 7Y3A sample (Fig.7f).

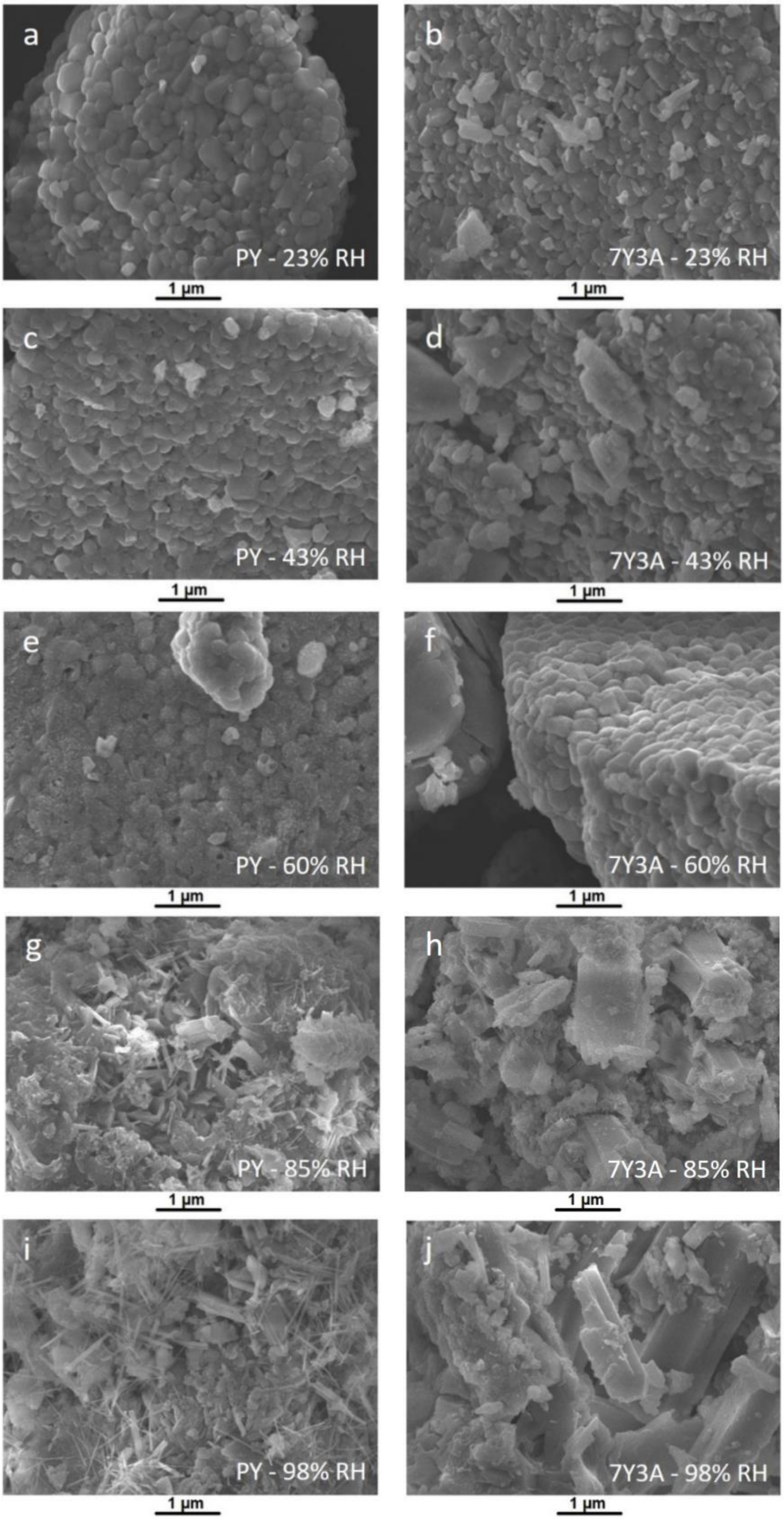


Fig.7 SEM images of PY (left) and 7Y3A (right) clinker exposed to (a, b) 23%, (c, d) 43%, (e, f) 60%, (g, h) 85% and (i, j) 98% RH for 180 days.

At 85% RH, prehydration causes obvious changes in the anhydrous CSA clinker morphology, while the hydration products of PY and 7Y3A seems to be different. For the PY sample (Fig. 7g), needle-like ettringite intermixed with amorphous or microcrystalline aluminium hydroxide has formed. Meanwhile, flake-like monosulfate can also be clearly identified. When anhydrite was added (Fig. 7h), the hexagonal ettringite crystals in the 7Y3A sample became more obvious and the volume of such needle-like crystals is much higher than that observed in the PY sample. No monosulfate can be observed in the images of the 7Y3A sample, which agrees well with the XRD analysis. With increase of RH from 85% to 98% RH, more hydration products can be observed. Ettringite needles in the PY sample at 98% RH (Fig. 7i) seem longer than those observed at 85% RH. A lower amount of amorphous or microcrystalline aluminium hydroxide with more hexagonal ettringite crystals was found in the 7Y3A sample (Fig. 7j). It should be noted that the clinker powder has already coagulated and became a solid block after 28 days of exposure at 85% RH. Therefore, it can be considered unsuitable for practical applications.

3.2 Influence of clinker prehydration on the hydration products

3.2.1 Isothermal calorimetry

To further investigate the influence of prehydration humidity on the hydration of CSA clinker, 8-channel isothermal calorimetry was used to measure the hydration reactivity of the CSA clinker prehydrated at different RHs for 180 days. The results are shown in Fig. 8.

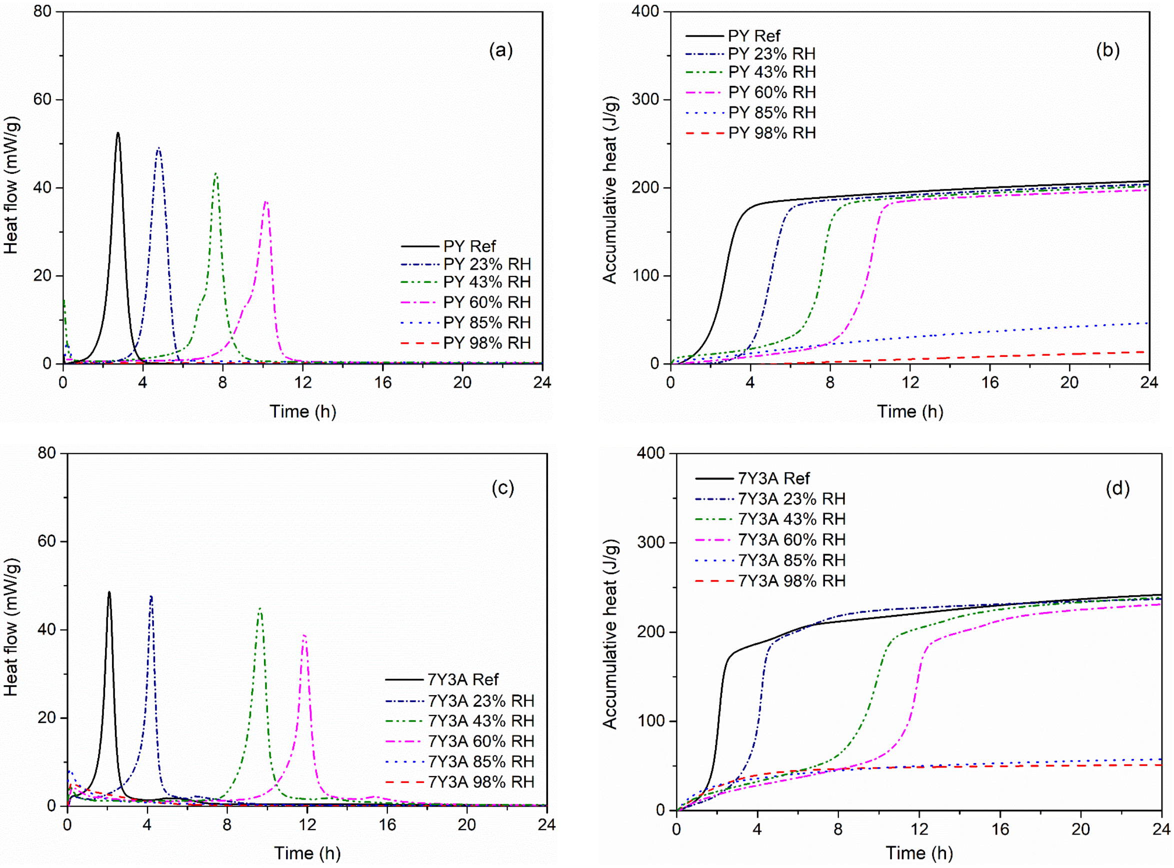


Fig.8 Heat flow (left) and accumulate heat (right) of (a, b) PY and (c, d) 7Y3A clinker aged at different RHs for 180 days.

In general, for both the PY and the 7Y3A sample, the increase of prehydration humidity causes a deceleration of the hydration activity, as shown by the delayed occurrence of the main hydration peak. Compared with the Ref sample, a broader but a less intensive main hydration peak occurs with increasing the prehydration humidity from 23 to 60% RH. This may be linked to the very slow process of surface relaxation/reconstruction of clinker grains at ascending RH. A less active layer of dissolved ye'elimite, which is difficult to observe in SEM micrographs, might have formed on the surface of clinker grains. Some evidence for such an effect has been put forward for OPC systems by Dubina et al. [35], who noted that C_3S hydration is retarded by extending the exposure duration of C_3S. The formation of this passivation layer could slow down the migration of water molecules from the environment to the interior of clinker grains and therefore delay the occurrence of main hydration peak. With the increase of the storage relative humidity, the passivation layer became denser which could result in delaying the occurrence of the main hydration peak of the PY sample from 2.7 h (PY-Ref) to 10.1 h (PY 60% RH). As for the 7Y3A sample, the calcium sulfate addition accelerated the hydration of ye'elimite [5]. Compared with the PY Ref and the PY 23% RH sample, the hydration peak of 7Y3A Ref and 7Y3A 23% RH occurred earlier: from 2.7 and 4.8 h to 2.1 and 4.1 h, respectively. A further increase of ambient humidity from 23 to 60% RH significantly delayed the occurrence of the main prehydration peak to 9.7 h (7Y3A 43% RH) and 11.9 h (7Y3A 60% RH). Although the main hydration peak was clearly delayed, the cumulative heat for both PY and 7Y3A specimens is more or less the same, showing that the overall reactivity was less affected by increasing RH until 60%. Similar values (approximately 200 J/g clinker) have been reported elsewhere for fresh CSA cement [13].

As soon as the ambient RH was increased to 85% RH, the balance between the dissolution of clinker grains and the ambient humidity is be broken and the passivation layer that covered the clinker grains is penetrated by the larger number of water molecules. No significant hydration peak for neither the PY nor the 7Y3A sample exposed to 85% and 98% RH could be detected in the later stage, and only a rapid exothermic peak occurred directly when the sample is mixed with water. This peak can be attributed to the heat of wetting and the very limited hydration reaction of ye'elimite clinker [5]. The PY sample exposed to 98% RH showed the lowest cumulative hydration heat after 180 days of exposure, which is consistent with the result of the degree of hydration and QXRD test as shown in table 1 and Fig. 6e, respectively.

3.2.2 Hydration of CSA paste aged at various RH

In the previous section, it has been shown that the ambient humidity has a great influence on the mineral composition of CSA clinker and the hydration of CSA cement paste [13]. However, the mineral composition of the aged CSA clinker hydrated at different hydration stage is still not clear. In order to have a deeper insight into the dynamic change of the mineral phase composition of hydrated CSA clinker, PY and 7Y3A sample aged at 60, 85 and 98% RH for 180 days were mixed with water with a water to cement ratio of 1:1. The mineral composition of aged CSA clinker hydrated during the dormant period (2h), the main hydration period (10h for PY sample and 12h for 7Y3A sample), and fthe inal period (24h) was characterized by XRD and TGA, respectively, and the QXRD results are shown in Fig. 9. For PY and 7Y3A clinker exposed to 60% RH, a significant decrease of the anhydrous phase can be found with longer elapsed hydration time (from 2 to 24 h). Ettringite and amorphous phases are the two main hydration products observed after two hours of hydration. After that, a considerable proportion of gibbsite and monosulfate forms during hydration of the PY sample (Fig. 9a). On the other hand, for the 7Y3A sample, ettringite is the most predominant phase after 24 h of hydration, and accounts for almost 60% of the total (Fig. 9d). For the PY - 85%RH sample (Fig. 9b), the phase assemblage is constant throughout the 24 hours of hydration, which indicates that the hydration has finished. The amorphous phase is believed to originate from the prehydration process. In addition, a portion of unhydrated ye’elimite was still present in the hydrated clinker. It is not clear why ye’elimite has not hydrated, as no hydration heat could be detected by isothermal calorimetry after 12 hours of hydration (Fig. 8a). Only a slight change of phases was observed for the 7Y3A - 85%RH sample. A small portion of unhydrated ye’elimite was converted to ettringite and gibbsite (Fig.9e). Finally, for PY- 98%RH (Fig. 9c) and 7Y3A - 98%RH (Fig. 9f), no significant difference in phase assemblage was observed, despite that the amount of XRD amorphous phase was found to slightly decrease with longer hydration. This suggests that the hydraulic reactivity of CSA clinker has been almost exhausted by the prehydration process at 98% RH after 180 days. The decrease of amorphous phases can be attributed to the recrystallization of XRD-amorphous phases such as aluminate hydroxide.

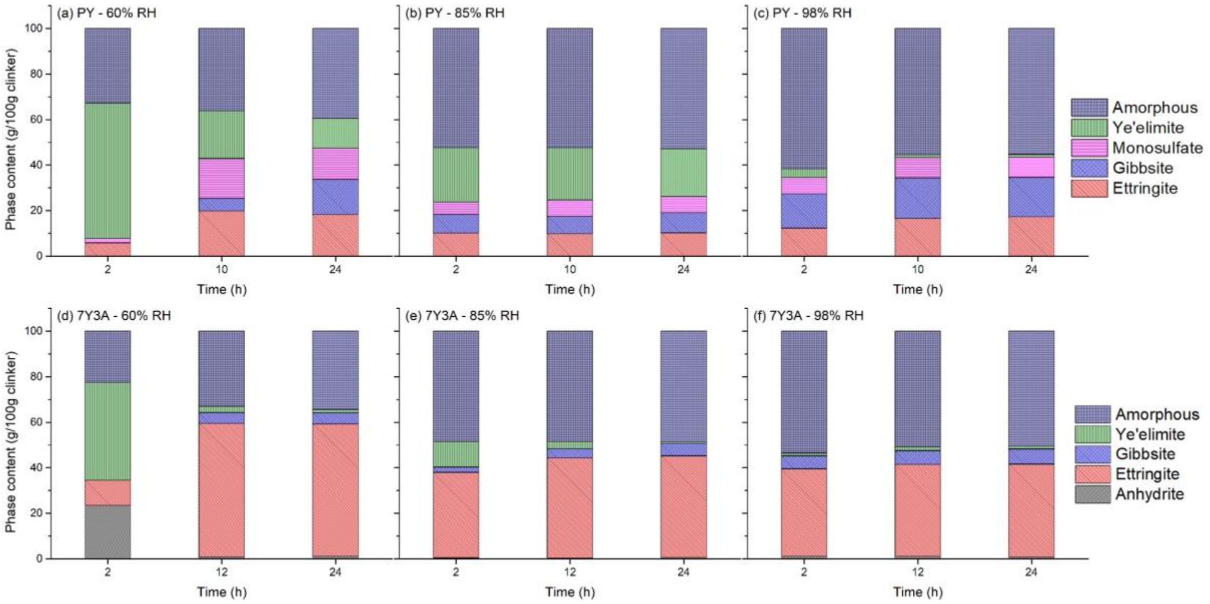


Fig.9 Phase assemblage of aged PY clinker (a, b, c) and aged 7Y3A clinker (d, e, f) hydrated in water at different stages.

3.3 Mechanisms of RH affecting the hydraulic activity of CSA clinker

Based on the results presented above and the protective layer theory proposed by Dubina et al. on C_3S and C_3A [35], the prehydration mechanism of CSA clinker composed mainly of ye'elimite can be divided into two stages. A hypothesis for explaining the observed behavior is based on the passivation layer theory, as schematically shown in in Fig. 10.

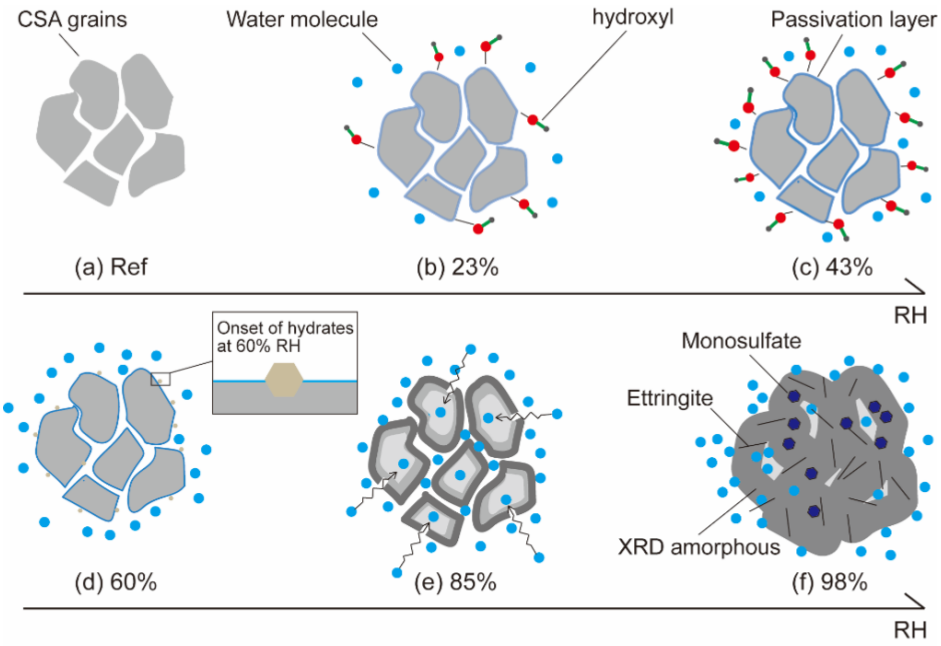


Fig.10 Schematic diagram of prehydration mechanism of CSA clinker exposed to various RH.

The first stage is ranging from the freshly sinter clinker to clinker exposed to 43% RH (Fig. 10a - Fig. 10c). In this RH range, no sign of hydration was observed. Note that this does not mean that the hydration of clinker will not happen at RH lower than 60%. However, a very long induction time must precede this reaction. In a previous study, it was calculated that the induction time for C_3A can be 30000 years at 43% RH and 20°C [8]. With the increase of RH, more water molecules will be available in the ambient air. According to the molecular diffusion theory, there is a higher chance of water molecules to attack and be adsorbed on the clinker surface at high RH compared to lower RH. Theoretically, when a porous material is exposed to water vapour, an equlibrium is not extablished immediately. Jensen [8] calculated that the equilibirum between clinker and various mineral phases can only established at extremely low RH (e.g., RH less than 1%). However, the fact is that no hydrates were found for neither PY nor 7Y3A clinkers exposed to RH lower than 60%. A possible reason is that there ia very thin passivation layer forms due to the adsorption and condension of water molecules at the exposed suface of clinker grains. Although the measuring techniques used cannot directly confirm this hypothesis, it can be proven by the delayed occurrence of the exothermic peak of PY and 7Y3A after 180 days exposure (see Fig. 8). As this passivation layer stops the water molecules from further penetrating into the porous clinker, no further hydrates can form from the unhydrated clinker. Previously, Bullerjahn et al. [5] attributed the long dormant period in the hydration heat of ye'elimite to a surface coverage of the clinker grain by early hydration products. In an OPC system, the formation of this layer was termed “surface hydrxylation” for tricalcium silicate hydrated in water at the very initial period [36]. It was found in previous studies that the solubility of this passivation layer formed on the surface of tricalcium silicate is 17 orders of magnitude lower than the one obtained from bulk thermodynaics [37, 38]. For C_3A polymorphs, the formation of this liquid water film condenses on the surface of the phases was regarded as a consequence of capillary condensation between the particles [39].

Consequently, 60% RH can be regarded as the threshold value for CSA clinker exposed to the ambient humidity. At this turning point, although there are still no detectable hydrates formed, the onset of initial hydrates such as globule-like XRD amorphous or calcium sulfite can be observed on the surface of CSA clinker with the ESEM (Fig. 10 d). As the RH rises from 60% to 85%, the intensity of water molecular diffusion increases further. The prehydration progress is significantly promoted by the increased water activity. If the hypothesis that the exisitance of passivation layer is correct, the passive layer is supposed to be pierced by the formation of initial hydrates. These spots where the initial hydrates form provide pathways for the water molecules to get inside the porous clinker grains through capillary (Fig. 10 e). Under this exposure, prehydration of clinker occurred as the hydration products such as ettringite and monosulfate were observed after only 7 days of exposure at 85% RH. At 98% RH, the equlibirum of the passivation layer between the clinker grain and the environmental water vapour pressure is broken more rapidly. The hydration reaction starts immediately once the clinker is exposed to such water vapour pressure. In that case, the CSA clinker is almost depleted after 180 days of exposure (Fig. 10 f).

It should be pointed out that the current measurements performed in this study cannot directly confirm and/or disprove the passivation layer theory described above. In fact, there is some controversy in the literature related to wether the passivation layers can have an important effect on the water transport. For example, Scrivener et al. [40] did not agree with the existence of any inhibiting layer formed by dissolution and precipitation of a type of C-S-H on the surface. They suggested that dissolution controlled by undersaturation is a better explanation for the induction period. Other authors do not necessarily agree. For example, Galan and Andrade [40] showed, by direct observation, that passivation layer of Portlandite does indeed occur when exposed to CO_2 at high RH. Therefore, further investigations are needed to fully understand (and confirm or disprove) the mechanism. Advanced instruments such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) might be helpful in chracterizing the formation of the passivation layer directly.

Conclusions

In this investigation, the prehydration mechanism of CSA clinker stored under various RH conditions has been experimentally studied. The hydration degree, phase assemblage, and hydration reactivity of PY and 7Y3A samples after prehydration were characterized by means of TGA, XRD coupled with

Rietveld method, and isothermal calorimetry. The influence of anhydrite on the prehydration process and products was investigated. The experiments revealed that:

1. Prehydration humidity plays an important role on the reactivity and usablilty of CSA cement. CSA clinker must be stored in RH equal to or lower than 60% at atmospheric pressure. Exporsure of CSA clinker to RH above 85% will not only result in a significant decrease of hydraulic reactivity, but also in agglomeration of clinker.
2. Similar to the clinker hydrated in water, the prehydration products of pure ye'elimite exposed to RH at 85% or higher are ettringite, gibbsite, monosulfate and XRD amorphous, in which XRD-amorphous is an important component at the intial peroid of prehydration. The addition of 30% anhydrite results in significant changes to the hydration assemblage: only ettringite was found formed besides XRD amorphous.
3. Although no apparent hydration products were found on neither the PY nor the 7Y3A sample exposed to 60% RH, globule-like particles have formed on the surface of PY clinker, which can be considered as a signal of the onset of prehydration.
4. Although increasing the RH from 23 to 60% RH has little effect on the clinker activity, a gradual delay of the main hydration peak was observed with the increase of RH (from freshly sintered clinker to clinker exposed to 60% RH). It is assumed that this is caused peak by the formation of passivation layer.
5. After the clinker has been exposed to 85% and 98% RH for 180 days, hydraulic reactivity of both PY and 7Y3A samples has almost been exhausted. The main hydration peak did no longer exist when the aged CSA clinker was hydrated in water. Only slight changes in the phase assemblage were observed.

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