



## Scanning electron microscopic studies on tricalcium aluminate hydrate pastes after hydration in presence of inorganic admixtures

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### Abstract

Tricalcium aluminate is considered as one of the most important main inorganic compounds that constitute cement. It plays an important role in controlling hydraulic characteristics of cement and strength development of concrete. Although its percent do not exceed (7-12%), of the total essential compounds constituting cement, but it acquired special importance through its capability of reserving cement in a form of a paste, since can be handled easily during construction when water is added to cement. It is responsible of setting time in cement mixture so can be adjusted according to different whether conditions. To adjust setting time, organic or inorganic compounds must be added to cement mix in the presence of water to accelerate or retard hydration process according to the type of added admixture. The object of this work is to study the change in morphology and microstructure of tricalcium aluminate pastes after hydration in presence of different inorganic admixtures (Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, CaSO<sub>4</sub> hydrate and CaCl<sub>2</sub>) at different periods of hydration (1 hr, 3 hr, 7 hr, 1 day, 7days, 14 days and 28 days) using scanning electron microscopy (SEM) measurements .

*Abbreviations:* C=CaO, S=SiO<sub>2</sub>, A=Al<sub>2</sub>O<sub>3</sub>, H=H<sub>2</sub>O, F=Fe<sub>2</sub>O<sub>3</sub>,

*Keywords:* Calcium aluminate, Hydration, Admixtures.

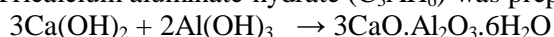
### 1. Introduction:

Scanning electron microscopy is a powerful technique for analyzing cement-based materials [1], and has been applied successfully to cement clinkers [2], cement powders [3,4] and hydrated cement pastes and concretes[5]. The SEM provides high contrast images that can be segmented to identify the component phases comprising the complex microstructure. Tricalcium aluminate, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C<sub>3</sub>A) is one of the main crystalline phases of cements [1]. It plays a fundamental role in the early stages of hydration process of Ordinary Portland Cements and Calcium Aluminate Cements. The reaction of C<sub>3</sub>A with water produces calcium aluminate hydrate, Afm-type phases according to the cement nomenclature, and the more thermodynamically stable hydrogarnet [1,6] . The hydration of C<sub>3</sub>A is a strongly exothermic reaction and if the kinetics is not controlled, the so called "flash-setting" of cement may occur with undesirable effect on the rheological properties of the hydrating paste [1]. In order to prevent this reaction in cements, Ca-sulphate is usually added to the clinker [7]. When sulphates are present, ettringite is the phase crystallizing during the hydration of C<sub>3</sub>A and the reaction is less exothermic. It is known from XRD analyses that crystalline ettringite is present since the early stages of hydration of the C<sub>3</sub>A paste [8]. Moreover observations performed by scanning electron microscopy show that at the beginning of the process ettringite appears with a gel-like morphology. The characteristics of the ettringite gel are thought to play a fundamental role in controlling both the dissolution kinetics of the clinker phases and the formation of hydrates. Ettringite, also called Aft-type phase, C<sub>3</sub>A·3CaSO<sub>4</sub>·32H<sub>2</sub>O, is triagonal and the crystal structure is composed of columns of alternately Ca-(O,OH) and Al-(O,OH) octahedra along the c direction [9]. The columns are connected by SO<sub>4</sub> groups and water molecules, located in fairly large channels running parallel to the columns. The frequent morphology of synthetic and natural ettringite crystals

is that of a prismatic fine needles elongated along *c*. Ettringite is present in the first hours of OPC hydration indicating that  $C_3A$  and  $C_4AF$  ( $Ca_2AlFeO_5$ ) are the most reactive phases in the early stages of the hydration process [1]. Ettringite is also the main hydrate phase (at least in the first hours) in many other cementitious materials, such as shrinkage compensating OPC/CAC based formulates, expansive cements, sulphoaluminate cements, etc. There is a close relationship between ettringite characteristics (i.e. morphology) and the physical properties (rheology, mechanical strengths) of the hydrating cement paste. In our opinion the knowledge of the crystallographic details of ettringite and of the kinetics of its formation in cementitious system is crucial to understand the physical behavior of cement materials [10]. Calcium chloride ( $CaCl_2$ ) is one of the most effective accelerators of hydration and setting in tricalcium silicate ( $C_3S$ ) and portland cement pastes. The accelerative power of this salt increases with increasing concentration, with a practical dosage being 1–2% by weight of cement. It has often been observed that  $CaCl_2$  increases the rate of formation of hydration products, thereby increasing the rate of heat evolution during hydration. This acceleration is thought to occur by direct acceleration of the growth rate of calcium silicate hydrate (C-S-H), but the mechanism is not understood at the molecular level [11]. It is to be expected that accelerating the hydration reaction would affect the microstructure of the hydration products. Calcium chloride is known to increase the nitrogen surface area and pore volume of Portland cement and  $C_3S$  pastes [12–14]. The investigated using a variety of microscopy effects of  $CaCl_2$  on microstructure have been techniques. Early work using transmission electron microscopy (TEM) for samples less than 1 day old showed fibrous growths in the presence of  $CaCl_2$  [15], forming in a cross-linked network in one case [16]. In contrast, further electron microscope work on samples with ages of 10–30 days described  $C_3S$  hydration products as small needles in the absence of  $CaCl_2$ , and “crumpled foils” or plates in its presence [12,17]. The use of scanning electron microscopy (SEM) allows a greater depth of focus; using this technique, researchers saw “honeycomblike” morphologies of hydration products in the presence of  $CaCl_2$  at ages of 3 h to 7 days [18–20], agreeing with the previous cross-linked observations. Ramachandran and Feldman [21] noticed that the morphology of hydration products (older than 1 day) varied depending on the amount of  $CaCl_2$  added to cement pastes. In the absence of  $CaCl_2$ , needles of C-S-H and ettringite were the primary morphology observed. At a dosage of 1%  $CaCl_2$ , thin sheets of C-S-H appeared. Increasing the dosage to 2% consolidated the structure, and plates were observed. Addition of 3.5%  $CaCl_2$  resulted in a “spongy mass.” TEM on pastes older than 1 year showed similar results to the SEM studies—less fibrillar hydration products when  $CaCl_2$  was present [22].

## 2. Materials and methods

Tricalcium aluminate hydrate ( $C_3AH_6$ ) was prepared according to the following equation :



$C_3AH_6$  was prepared using the following procedure [23]: Starting powder of  $Ca(OH)_2$  (99%+ Merck, Darmstadt) was weighed in appropriate amount (3moles) and then dissolved in distilled water with continuous stirring in water bath at 30°C to produce a suspension solution of  $Ca(OH)_2$ . Also, appropriate amount of  $Al(OH)_3$  (2moles) ( 99% + Merck, Darmstadt, Germany) was weighed and dissolved in distilled water with continuous stirring in water bath at 30°C to produce a suspension solution of  $Al(OH)_3$ .  $Ca(OH)_2$  suspension solution was added carefully to  $Al(OH)_3$  suspension solution with continuous stirring in water bath at 30°C, then the produced suspension solution left one hour in water bath and measuring the pH value. Finally, the produced suspension solution left for 24 hours up to the pH value equal 13, where as there is complete formation of  $C_3AH_6$ . The suspension was filtrated with suction through a Schott 1G4 sintered glass filter directly from the suspension vessel. The produced precipitate ( $C_3AH_6$ ) was washed with ether to get rid of excess water. In our study, we prepared  $C_3AH_6$  as mention before but with different cases as follows:

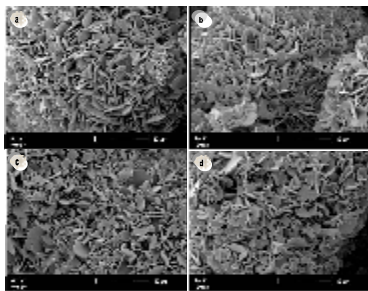
- i-  $C_3AH_6$  in excess  $Ca(OH)_2$  ( 4 moles  $Ca(OH)_2$  + 2moles  $Al(OH)_3$  ).
- ii-  $C_3AH_6$  in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$  ( 4moles  $Ca(OH)_2$  + 2moles  $Al(OH)_3$  + 1 mole  $CaSO_4 \cdot 2H_2O$  ) .
- iii-  $C_3AH_6$  in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$  and  $Al(OH)_3$  ( 4moles  $Ca(OH)_2$  + 3 moles  $Al(OH)_3$  + 1mole  $CaSO_4 \cdot 2H_2O$  ) .
- iv-  $C_3AH_6$  in presence of  $CaCl_2$  and excess  $Ca(OH)_2$  ( 4 moles  $Ca(OH)_2$  + 2 moles  $Al(OH)_3$  + 1 mole  $CaCl_2$ ).
- v-  $C_3AH_6$  in presence of  $CaCl_2$  and excess  $Al(OH)_3$  ( 3moles  $Ca(OH)_2$  + 3moles  $Al(OH)_3$  + 1 mole  $CaCl_2$ ).

For each case, first there is preparation of  $C_3AH_6$  as mentioned before then addition of admixtures ( $CaSO_4 \cdot 2H_2O$  or  $CaCl_2$ ) to the prepared  $C_3AH_6$  for studying the hydration process after different periods (1hr, 3hr, 7 hr, 1day, 7days, 14 days and 28 days) and the produced precipitate was washed with mixture of ethyl alcohol and ether to stopping the reaction and the precipitate was kept in desiccators to study the change in morphology and microstructure of  $C_3AH_6$  at different conditions using SEM technique.

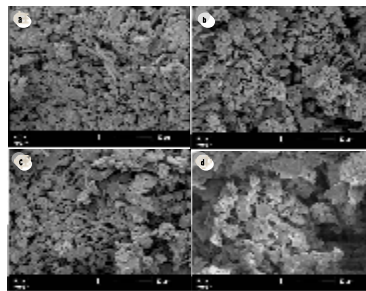
### 3. Results and discussion:

Figure 1(a,b,c,d), Figure 2(a,b,c,d) and Figure 3(a,b,c,d) show the SEM micrographs of  $C_3AH_6$  pastes after 3hrs, 7days and 14 days hydration, respectively, in presence of excess  $Ca(OH)_2$ . It is clear that, there is no formation of amorphous or crystalline products after after 3 hrs hydration (Figure 1), but irregular shapes of ettringite. After 7days and 14 days hydration (Fig.2 and 3), the structure was closed, but still with formation of poor gel- like crystal structure which means low hydraulic properties of  $C_3AH_6$  pastes[24]. Accordingly, presence of excess  $Ca(OH)_2$  retards the hydraulic properties of  $C_3AH_6$  due to the increasing in formation of ettringite.

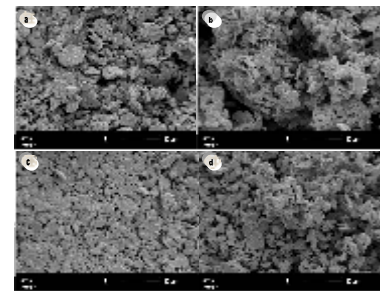
The SEM micrographs of  $C_3AH_6$  pastes after 7hrs, 1 day and 14 days hydration in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$  was illustrated in Figure 4(a,b,c,d), Figure 5(a,b,c,d) and Figure 6(a,b,c,d), respectively. It is clear that there formation of ill crystalline and amorphous layer after 7 hours due to initial hydraulic activation and formation of ettringite as monosulphate phase ( $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ ) AFm in presence of low concentration of  $CaSO_4 \cdot 2H_2O$  which disappear after 1 day forming poor amorphous phase with increasing the crystalline phase after 14 days due to the formation of ettringite as trisulphate phase ( $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ ) AFt which causes deceasing in the hydraulic properties of  $C_3AH_6$ [25].



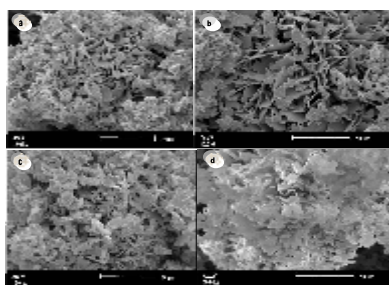
**Figure 1:** SEM micrographs of  $C_3AH_6$  pastes after 3 hrs hydration in presence of excess  $Ca(OH)_2$ .



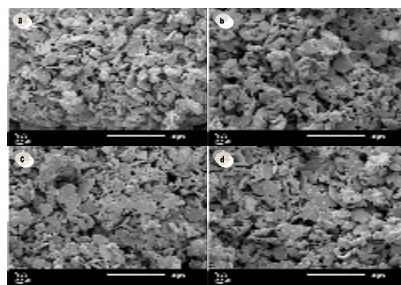
**Figure 2:** SEM micrographs of  $C_3AH_6$  pastes after 7 days hydration in presence of excess  $Ca(OH)_2$ .



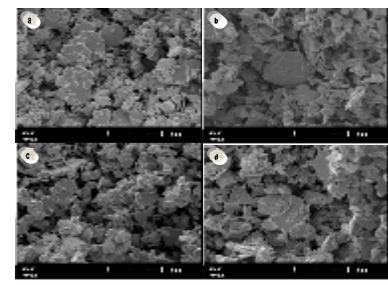
**Figure 3:** SEM micrographs of  $C_3AH_6$  pastes after 14 days hydration in presence of Excess  $Ca(OH)_2$ .



**Figure 4:** SEM micrographs of  $C_3AH_6$  pastes after 7 hrs hydration in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$ .



**Figure 5:** SEM micrographs of  $C_3AH_6$  pastes after 1 day hydration in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$ .

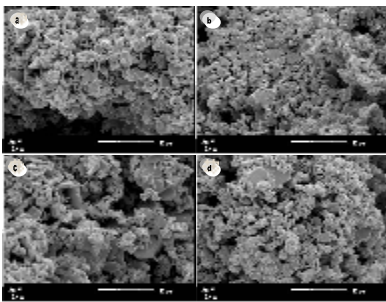


**Figure 6:** SEM micrographs of  $C_3AH_6$  pastes after 7 days hydration in presence of  $CaSO_4 \cdot 2H_2O$  and excess  $Ca(OH)_2$ .

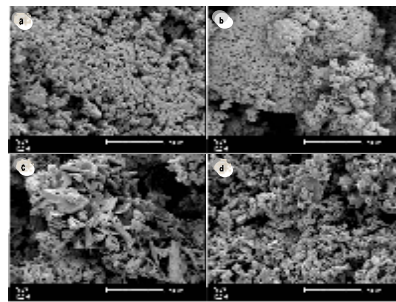
The SEM micrographs of  $C_3AH_6$  pastes after 1hr, 7 hrs and 1 day hydration in presence of  $CaSO_4 \cdot 2H_2O$  and excess of  $Ca(OH)_2$  and  $Al(OH)_3$  are shown in Figure 7(a,b,c,d), Figure 8(a,b,c,d) and Figure 9 (a,b,c,d),

respectively. There is formation of mix of amorphous and ill-crystalline phase after 1 hr and formation of closed texture after 1 day hydration due to presence of excess  $\text{Al}(\text{OH})_3$  which causes increasing in the hydraulic properties of  $\text{C}_3\text{AH}_6$  pastes. Accordingly, presence of excess  $\text{Al}(\text{OH})_3$  decrease the formation ettringite which has high crystalline properties.

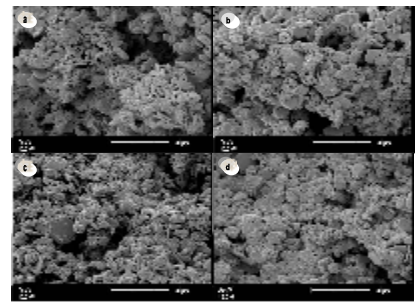
Figure 10(a,b,c,d), Figure 11(a,b,c,d), Figure 12(a,b,c,d) and Figure 12(a,b,c,d) show the SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 1hr, 7hrs and 1 day hydration in presence of  $\text{CaCl}_2$  and excess  $\text{Ca}(\text{OH})_2$ , respectively. The micrographs indicated formation of uncombined particles after 1 hr with high crystalline properties producing low hydraulic properties [26]. After 7 hours of hydration there is decreasing in the porosity and formation of amorphous and ill-crystalline phase indicated high hydraulic properties of the pastes. After 1 day hydration, there is increasing in the amorphous and ill-crystalline phase with formation of closed texture phase indicating increasing in the hydraulic properties of  $\text{C}_3\text{AH}_6$  pastes. Accordingly, addition of  $\text{CaCl}_2$  in presence of  $\text{Ca}(\text{OH})_2$  accelerate the hydration of  $\text{C}_3\text{AH}_6$  and increase the hardening process.



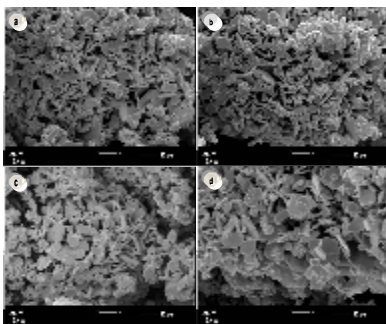
**Figure 7:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 1 hr hydration in presence of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and excess  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$



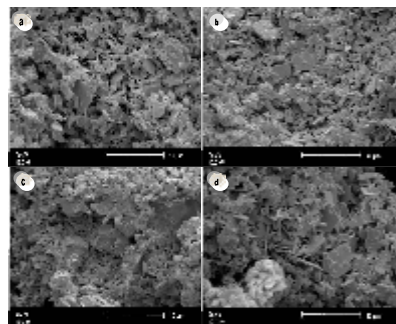
**Figure 8:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 7 hrs hydration in presence of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and excess  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$



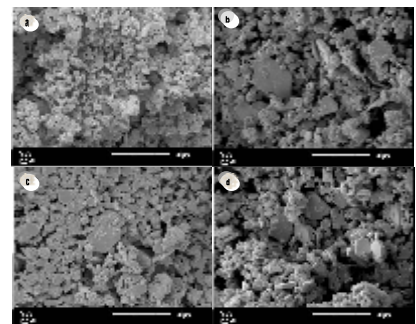
**Figure 9:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 1 day hydration in presence of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and excess  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .



**Figure 10:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 1 hr hydration in presence of  $\text{CaCl}_2$  and excess  $\text{Ca}(\text{OH})_2$



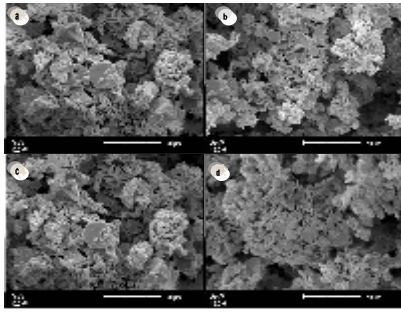
**Figure 11:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 7 hrs hydration in presence of  $\text{CaCl}_2$  and excess  $\text{Ca}(\text{OH})_2$



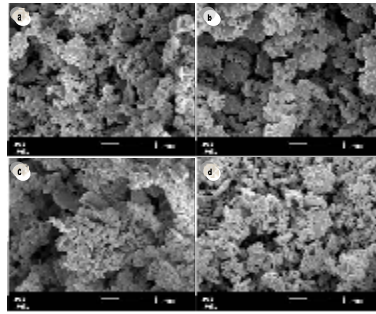
**Figure 12:** SEM micrographs of  $\text{C}_3\text{AH}_6$  pastes after 1 day hydration in presence of  $\text{CaCl}_2$  and excess  $\text{Ca}(\text{OH})_2$

The change in morphology and microstructure of  $\text{C}_3\text{AH}_6$  pastes after 7 hrs, 7days and 14 days hydration in presence of  $\text{CaCl}_2$  and excess  $\text{Al}(\text{OH})_3$  are shown in SEM micrographs of Figure 13(a,b,c,d), Figure 14(a,b,c,d) and Figure 15(a,b,c,d), respectively. It is clear that, presence of  $\text{Al}(\text{OH})_3$  increase the amorphous layers of the pastes which causes increasing in the bonding between crystalline layers and formation of amorphous and ill- crystalline phase after 7 hrs of hydration . After 7 days, there is increasing in the condensed structure of the amorphous and ill-crystalline phase with high coagulation of the layers which increase sharply after 14 days forming closed–textured structure having high hydraulic properties and high hardening process of  $\text{C}_3\text{AH}_6$  [27].

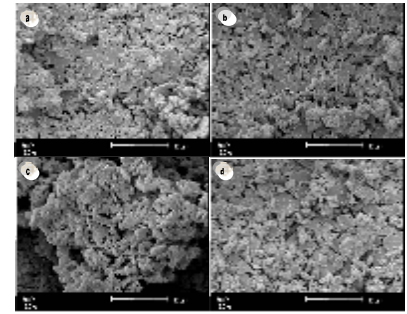




**Figure 13:** SEM micrographs of  $C_3AH_6$  pastes after 7 hrs hydration in presence of  $CaCl_2$  and excess  $Al(OH)_3$



**Figure 14:** SEM micrographs of  $C_3AH_6$  pastes after 7 days hydration in presence of  $CaCl_2$  and excess  $Al(OH)_3$



**Figure 15:** SEM micrographs of  $C_3AH_6$  pastes after 14 days hydration in presence of  $CaCl_2$  and excess  $Al(OH)_3$

## Conclusion

From this investigation we concluded that:

- 1- Presence of excess  $Ca(OH)_2$  retards the hydration of  $C_3AH_6$  at the earlier ages of hydration, but this retardation disappeared at later ages ( after 7 days).
- 2- Presence of excess  $Al(OH)_3$  accelerates the hydration of  $C_3AH_6$  at all ages of hydration.
- 3- Presence of excess  $Ca(OH)_2$  in the hydration process of  $C_3AH_6$  in presence of  $CaSO_4 \cdot 2H_2O$  causes an increasing in the formation of ettringite (AFt) , accordingly, the hydraulic properties of  $C_3AH_6$  will be decrease.
- 4- Presence of excess  $Al(OH)_3$  in the hydration process of  $C_3AH_6$  in presence of  $CaSO_4 \cdot 2H_2O$  and excess of  $Ca(OH)_2$  causes a decreasing in the formation of ettringite , accordingly, the hydraulic properties of  $C_3AH_6$  will be increased and the bad effect of formation of high amount of ettringite on the hydraulic properties of  $C_3AH_6$  will be disappeared.
- 5- Presence of excess  $Al(OH)_3$  in the hydration process of  $C_3AH_6$  in presence of  $CaCl_2$  accelerates the hydration process and increases the hydraulic properties of  $C_3AH_6$  at all ages of hydration.

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