
MORPHOLOGY AND MICROSTRUCTURE OF TRICALCIUM ALUMINATE HYDRATE PASTES AFTER HYDRATION IN PRESENCE OF INORGANIC ADMIXTURES

M.A.TAHER^a AND A.I.AL-SULAMI^b^a*Chemistry Dept., Faculty of Science, Al Azhar University, Assiut, Egypt.*^b*Sciences Faculty for Girls, King Abdul Aziz University, Saudi Arabia*

Abstract

Tricalcium aluminate is considered as one of the most important material in the main inorganic compounds that constitute the cement. It plays an important role in controlling hydraulic characteristics for cement and leads to strength of concrete. Although its percent do not exceed (7-12%), of the total essential compounds constituting cement material, but it acquired special importance through its capability of reserving cement in a form paste, it 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 weather 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. In this study, the effect of inorganic admixtures ($\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, CaCl_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on the hydration of tricalcium aluminate hydrate pastes after different periods was investigated using scanning electron microscope (SEM). The results indicated that $\text{Al}(\text{OH})_3$ accelerate the hydration process while mixture of $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ retard this process. Presence of $\text{Al}(\text{OH})_3$ with CaCl_2 accelerate the hydration process. Presence of $\text{Al}(\text{OH})_3$ with mixture of $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ decreased the retarding effect of this mixture on hydration process.

Abbreviations: C=CaO, S=SiO₂, A=Al₂O₃, H=H₂O, F=Fe₂O₃,

Keywords: tricalcium aluminate, hydration, inorganic admixture, improvement of the cement.

Corresponding Author : M.A.Taher

E.mail: mahmoudtaher51@hotmail.com

Introduction:

Scanning electron microscopy (SEM) 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 (C_3A) 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_3A with water produces calcium aluminate hydrate, Afm-

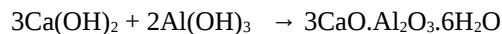
type phases ($C_3A \cdot CaSO_4 \cdot 12H_2O$) according to the cement nomenclature, and the more thermodynamically stable hydrogarnet (C_3AH_6) [1,6]. The hydration of C_3A is a strongly exothermic reaction and if the kinetics is not controlled, the so called “flash-setting” of cement may occur with undesirable effect on the rheological properties of the hydrating paste [1]. In order to prevent this reaction in cements, Calcium sulphate is usually added to the clinker [7]. When sulphates are present, ettringite is the phase crystallizing during the hydration of C_3A 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_3A 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, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, is trigonal 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_4 groups and water molecules, located in fairly large channels running parallel to the columns. Ettringite is present in the first hours of OPC hydration indicating that C_3A and C_4AF are the most reactive phases in the early stages of the hydration process [10]. Calcium chloride ($CaCl_2$) is one of most of hydration effective material for accelerate 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 [6]. 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 [11–13]. 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 $CaCl_2$ [14], forming in a cross-linked network in one case [15]. 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 [11,16]. 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 [17–19], agreeing with the previous cross-linked observations. Ramachandran and Feldman [20] 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 [21].

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 ($Ca(OH)_2$, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ and $CaCl_2$) at different periods of hydration (1 hr, 3 hr, 7 hr, 1 day, 7 days, 14 days and 28 days) using scanning electron microscopy (SEM) measurements.

Experimental:

Tricalcium aluminate hydrate (C_3AH_6) was prepared according to the following equation [22]:



Starting powder of $Ca(OH)_2$ (99%+ Merck, Darmstadt) was weighed in appropriate amount (3 moles) and then dissolved in distilled water with continuous stirring in water-bath at $30^\circ C$ to produce a suspended solution of $Ca(OH)_2$. Appropriate amount of $Al(OH)_3$ (2 moles) (99% + Merck, Darmstadt, Germany) was weighed and dissolved in distilled water with continuous stirring in water bath at $30^\circ C$ to produce a suspended white solution of $Al(OH)_3$. $Ca(OH)_2$ suspended solution was added carefully to $Al(OH)_3$ suspended solution with continuous stirring in water bath at $30^\circ C$, then the produced suspended solution and left one hour in water bath then 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 suspended solution was filtrated with suction through a Schott 1G4 sintered glass filter. The produced precipitate (C_3AH_6) was washed with ether. In our study, we prepared C_3AH_6 as mentioned above 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 $CaSO_4.2H_2O$ and excess $Ca(OH)_2$ (4moles $Ca(OH)_2$ + 2moles $Al(OH)_3$ + 1 moles $CaSO_4.2H_2O$) .
- iii- C_3AH_6 in presence of $CaSO_4.2H_2O$ and excess $Ca(OH)_2$ and $Al(OH)_3$ (4moles $Ca(OH)_2$ + 3 moles $Al(OH)_3$ + 1mole $CaSO_4.2H_2O$) .
- 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 above then addition of admixtures ($CaSO_4.2H_2O$ or $CaCl_2$) to the prepared C_3AH_6 for studying the hydration process after different periods (1hr, 3hr, 7 hr ; and 1day, 7days, 14 days and 28 days). The precipitate was washed with mixture of ethyl alcohol and ether (1:1) to stopping of further precipitation and kept in desiccators to dry the products. The change in morphology and microstructure of C_3AH_6 at different conditions (1,3 and 7 hr ; and 1,7,14 and 28 days) was studied using SEM technique.

Results and discussion:

Fig.1(a,b,c,d) , Fig.2(a,b,c,d) and Fig.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 at 3 hrs hydration (Fig.1), but there are irregular shapes of ettringite. After 7days and 14 days of hydration (Figs.2 and 3), the structure was closed, but still with formation of poor gel- like crystal structure. This mean that low hydraulic properties of C_3AH_6 pastes [23]. The presence of excess $Ca(OH)_2$ retards the hydraulic properties of C_3AH_6 due to the increasing in formation of ettringite [24]. .

The SEM micrographs of C_3AH_6 pastes after 7hrs , 1 day and 14 days hydration in presence of $CaSO_4.2H_2O$ and excess $Ca(OH)_2$ was illustrated in Fig.4(a,b,c,d), Fig.5(a,b,c,d) and Fig.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 (AFm, $3CaO.Al_2O_3.CaSO_4.12H_2O$) in presence of low concentration of $CaSO_4.2H_2O$ 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 (AFt, $3CaO.Al_2O_3.3CaSO_4.32H_2O$) which causes decreasing in the hydraulic properties of C_3AH_6 [25].

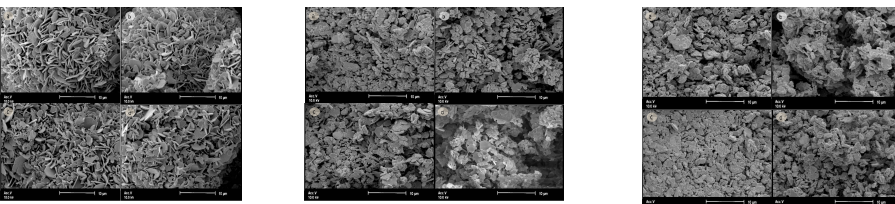


Fig 1.: SEM micrographs pastes after 3 hrs hydration in presence of excess $\text{Ca}(\text{OH})_2$

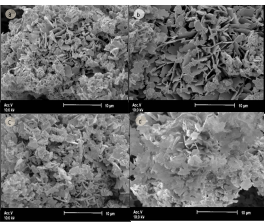


Fig 2.: SEM micrographs of C_3AH_6 pastes after 7 hydration days in presence of excess $\text{Ca}(\text{OH})_2$.

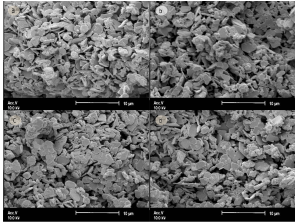


Fig.3: SEM micrographs of C_3AH_6 pastes after 14 days hydration in presence of excess $\text{Ca}(\text{OH})_2$.

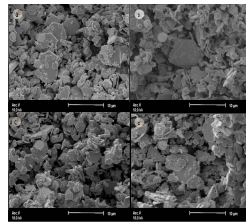


Fig 4.: SEM micrographs of C_3AH_6 pastes after 7 hrs hydration in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and excess $\text{Ca}(\text{OH})_2$

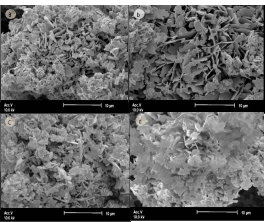


Fig.5.: SEM micrographs of C_3AH_6 pastes after 1 day hydration in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and excess $\text{Ca}(\text{OH})_2$

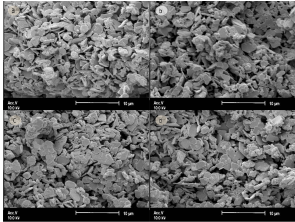
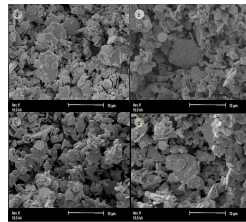


Fig.6: SEM micrographs of C_3AH_6 pastes after 7 days hydration in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



The SEM micrographs of C_3AH_6 pastes after 1hr, 7 hrs and 1 day hydration in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and excess of $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ are shown in Fig.7(a,b,c,d), Fig.8(a,b,c,d) and Fig.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 at 1 day hydration due to the presence excess of $\text{Al}(\text{OH})_3$ which leads to an increasing in the hydraulic properties of C_3AH_6 pastes. The presence of excess $\text{Al}(\text{OH})_3$ decrease the formation ettringite which has high crystalline properties [26].

Fig.10(a,b,c,d), Fig.11(a,b,c,d), and Fig.12(a,b,c,d) show the SEM micrographs of C_3AH_6 pastes after 1 hr, 7hr and one day hydration in presence of CaCl_2 and excess $\text{Ca}(\text{OH})_2$, respectively. The micrographs indicated a formation of uncombined particles after 1 hr with high crystalline properties producing a low of hydraulic properties [27]. Moreover, after 7 hours of hydration there is a decreasing in the porosity and formation of amorphous and ill-crystalline phase indicated high hydraulic properties of the pastes. At 1 day hydration, there is an increasing in the amorphous and ill-crystalline phase with formation of closed texture phase indicating increasing in the hydraulic properties of C_3AH_6 pastes. Therefore the addition of CaCl_2 in presence of $\text{Ca}(\text{OH})_2$ accelerate the hydration of C_3AH_6 and increase the hardening process [28].

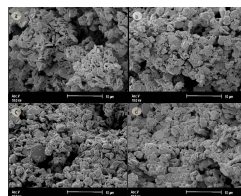
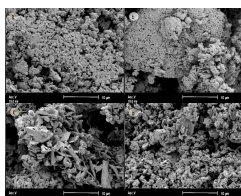
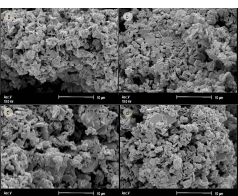


Fig.7: SEM micrographs of C_3AH_6 pastes after 1 hr hydration in presence of $CaSO_4 \cdot 2H_2O$ and excess $Ca(OH)_2$ and $Al(OH)_3$

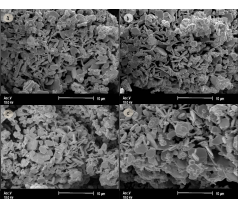


Fig.8: SEM micrographs of C_3AH_6 pastes after 7 hrs hydration in presence of $CaSO_4 \cdot 2H_2O$ and excess $Ca(OH)_2$ and $Al(OH)_3$

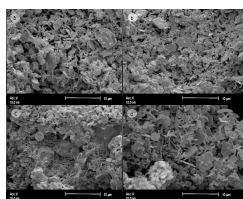


Fig.9: SEM micrographs of C_3AH_6 pastes after 1 day hydration in presence of $CaSO_4 \cdot 2H_2O$ and excess $Ca(OH)_2$ and $Al(OH)_3$.

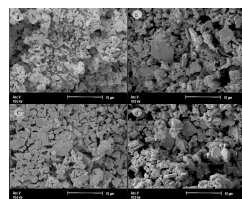


Fig.10: SEM micrographs of C_3AH_6 pastes after 1 hr hydration in presence of $CaCl_2$ and excess $Ca(OH)_2$



Fig.11: SEM micrographs of C_3AH_6 pastes after 7 hrs hydration in presence of $CaCl_2$ and excess $Ca(OH)_2$

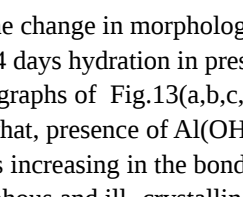
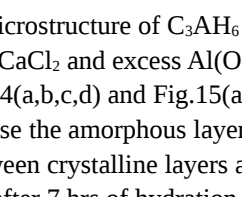


Fig.12: SEM micrographs of C_3AH_6 pastes after 1 day hydration in presence of $CaCl_2$ and excess $Ca(OH)_2$



The change in morphology and microstructure of C_3AH_6 pastes after 7 hrs, 7 days and 14 days hydration in presence of $CaCl_2$ and excess $Al(OH)_3$ are shown in SEM micrographs of Fig.13(a,b,c,d), Fig.14(a,b,c,d) and Fig.15(a,b,c,d), respectively. It is clear that, presence of $Al(OH)_3$ 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 C_3AH_6 [29].

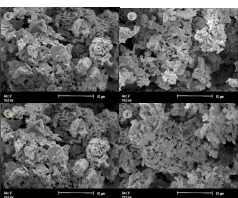


Fig.13: SEM micrographs of C_3AH_6 pastes after 7 hrs hydration in presence of $CaCl_2$ and excess $Al(OH)_3$

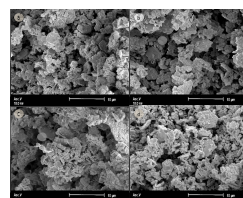


Fig.14: SEM micrographs of C_3AH_6 pastes after 7 days hydration in presence of $CaCl_2$ and excess $Al(OH)_3$

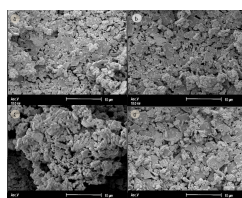


Fig.15: SEM micrographs of C_3AH_6 pastes after 14 days hydration in presence of $CaCl_2$ and excess $Al(OH)_3$

Conclusion

From this investigation we concluded that:

- 1- Presence of excess $\text{Ca}(\text{OH})_2$ 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 $\text{Al}(\text{OH})_3$ accelerates the hydration of C_3AH_6 at all ages of hydration.
- 3- Presence of excess $\text{Ca}(\text{OH})_2$ in the hydration process of C_3AH_6 in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ causes an increasing in the formation of ettringite (AFt), accordingly, the hydraulic properties of C_3AH_6 will be decrease.
- 4- Presence of excess $\text{Al}(\text{OH})_3$ in the hydration process of C_3AH_6 in presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and excess of $\text{Ca}(\text{OH})_2$ 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 $\text{Al}(\text{OH})_3$ 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.

References

1. H.F.W. Taylor, Cement Chemistry (2nd ed.), Thomas Telford, Publishing London, (1997).
2. P.E.Stutzman., "Cement clinker characterization by scanning electron microscopy", Cem.Concr.Aggregates, Vol.2, 109-114(1991).
3. D.P. Bentz and P.E. Stuzman, " SEM analysis and computer modeling of hydration of Portland cement particles". In Petrography of Cementitious Materials Ed.S.M.Dehayes and D.Stark(American Society for Testing and Materials, Philadelphia., pp.60-73,(1994)..
4. K.L.Scrivener, "The microstructure of anhydrous cement and its effect on hydration.", Proc.Mat.Res.Soc.Symp., Vol.85, 39-46(1987).
5. K.L.Scrivener and P.L.Scrivener, "The microstructure of concrete", In. Materials Science of Concrete I ED.J.P.Skalny(American Ceramic Society, Westerville, OH, pp.127-161(1987).
6. E.M. Gartner, J.F. Young, D.A. Damidot and I. Jawed, "Hydration of Portland Cement.", In: J. Bensted and P. Barnes (Eds), "The Structure and Performance of Cements, 2nd ed., Spon Press, London 2002. Chapter 3.
7. J. Bensted, "Gypsum in Cements", In: J. Bensted and P. Barnes, Editors, "Structure and Performance of Cements", Spon Press, London (2002).
8. P. Barnes et al., " The Use of Synchrotron Sources in the Study of Cement Materials". In: J. Bensted and P. Barnes, Editors, Structure and Performance of Cements, Spon Press, London (2002).
9. A.E. Moore and H.F.W. Taylor, "Crystal structure of ettringite", Acta Crystallogr. , B26 , pp. 386–393(1970).
10. M.Merlini ,G.Artiloli , T.Cerulli, F.Cella, A.Bravo, , "Tricalcium aluminate hydration in additivated systems. A crystallographic study by SR-XRPD ", Cement and Concrete Research , 38,477–486(2008).
11. M. Collepardi, and B. Marchese, " Morphology and surface properties of hydrated tricalcium silicate pastes ", Cem. Concr. Res., 2, 57–65(1972).

12. J. Skalny, I. Odler, and J. Hagymassy, "Pore structure of hydrated calcium silicates": I. Influence of calcium chloride on the pore structure of hydrated tricalcium silicate", *J. Colloid Interface Sci.* 35 (3) ,434– 441(1971).
13. M.C.G. Juenger, and H.M. Jennings, "The use of nitrogen adsorption to assess the microstructure of cement pastes", *Cem. Concr. Res.*, 31, 883–892(2001).
14. A.M. Rosenberg, "Study of the mechanism through which calcium chloride accelerates the set of Portland cement", *J. Am. Concr. Inst.*,61,1261– 1269(1964).
15. K. Murakami, and H. Tanaka, "Contribution of calcium thiosulphate to the acceleration of the hydration of Portland cement and comparison with other soluble salts", *Proceedings of the 5th International Congress on the Chemistry of Cement, Tokyo, vol. 2, The Cement Association of Japan, Tokyo, Japan, 1969, pp. 422– 436.*
16. V.S. Ramachandran, "Possible states of chloride in the hydration of tricalcium silicate in the presence of calcium chloride", *Mater. Constr.* ,4, 3 –12(1971).
17. J.F. Young, R.L. Berger, and F.V. Lawrence , "Studies on the hydration of tricalcium silicate pastes: III.Influence of admixtures on hydration and strength development", *Cem. Concr. Res.*, 3,689– 700(1973).
18. R.L. Berger, J.H. Kung, and J.F. Young, "Influence of calcium chloride on the drying shrinkage of alite paste", *J. Test. Eval.*, 4 ,85–93(1976).
19. P.J. LeSueur, D.D. Double, and G.W. Groves, " Chemical and morphological studies of the hydration of tricalcium silicate", *Br. Ceram. Proc.*, 35,177– 191(1984).
20. V.S. Ramachandran, and R.F. Feldman, "Time-dependent and intrinsic characteristics of Portland cement hydrated in the presence of calcium chloride", *Cemento*, 3,311– 322(1978).
21. G.W. Groves, P.J. LeSueur, and W. Sinclair, "Transmission electron microscopy and micro analytical studies of ion-beam-thinned sections of tricalcium silicate paste", *J. Am. Ceram. Soc.*, 69, 353–356(1986).
22. Q.Zhang, and F.Saito, " Sonochemical synthesis of ettringite from a powder mixture suspended in water", *Powder Technology* ,107, 43-47(2000).
23. P. Garces , E.G. Alcocel, S.Chinchon , C.G. Andreu and J. Alcaide, " [Effect of curing temperature in some hydration characteristics of calcium aluminate cement compared with those of Portland cement](#)", *Cem.Concr.Res.* , 27(9), 1343-1355(1997).
24. S. Pourchet , L. Regnaud, J.P. Perez, and A. Nonat , "Early C3A hydration in the presence of different kinds of calcium sulfate" , *Cem. Concr. Res.*, 39, 989–996(2009).
25. A.M.Cody, H.Lee, R.D.Cody and P.G.Spry," Reduction of concrete expansion " , *Cem.Concr.Res.*,34(8), 869-881(2004).
26. M.Merlini, G.Artioli, T.Cerulli, F.Cella and A.Bravo "Tricalcium aluminate hydration in additivated systems, A crystallographic study by SR- XRPD" , *Cem.Concr.Res.*, 38(4), 477-486 (2008).
27. P.Meredith , A.M.Donald, N.Meller and C.Hall," [The effects of chemical growth, and stability of ettringite". \$\[\text{Ca}_3\text{Al}\(\text{OH}\)_6\]_2\(\text{SO}_4\)_3 \cdot 26\text{H}_2\text{O}\$](#) ", *J.Materials Science*, 39, 997-1005(2004).
28. S. Ouellet, B. Bussière, M.Aubertin and M. Benzaazoua , "Microstructural evolution of cemented paste backfill: Mercury intrusion porosimetry test results" , *Cem.Concr.Res.*, 37, 1654 –1665 (2007).
29. M.A.Taher, "Influence of thermally treated phosphogypsum on the properties of Portland slag cement", *Resources, Conservation and Recycling Journal*, 52, 28-38 (2007).