Low Temperature Synthesis of Belite Cement from White Sand and Lime

M. A. Tantawy

Chemistry Department,
Faculty of Science, Minia University,
Minia, Egypt.

Abstract— **This paper studies the low temperature synthesis of β-C_2S from mixture of lime, $BaCl_2$ and white sand with the ratio (Ca+Ba)/Si = 2. The Mixture was hydrothermally treated in stainless steel capsule at 180°C for 5 hours, calcined at 600-900°C for 3 hours and analyzed by FTIR, XRD, TGA/DTA and SEM techniques. Dicalcium silicate hydrate was formed by hydrothermal treatment of lime/white sand mixture at 180°C for 5 hours. β-C_2S was produced when hydrothermally treated lime/white sand mixture was calcined at 750°C for 3 hours. In lime/white sand mixture, β-C_2S does not stabilized and transformed to γ-C_2S with raising temperature of calcination to 900°C. In contrast, β-C_2S was stabilized in lime/$BaCl_2$/white sand mixture that was calcined at 900°C. This due to that Ba^{2+} ions stabilizes β-C_2S and retards its transformation to γ-C_2S.**

Keywords— White sand, Lime, Hydrothermal treatment, Dicalcium silicate hydrate, Calcination, β-dicalcium silicate.

I. INTRODUCTION

Tricalcium silicate (alite, C_3S) and dicalcium silicate (belite, C_2S) are the major components of Portland cement and determine most of the adhesive properties, strength and durability of Portland cement. Belite hydrates much slower than that alite. Whatever, alite and belite show about the same physical and mechanical properties after complete hydration.[1] Production of Portland cement releases about 900-1000 kg of CO_2 per tonne of clinker due to calcination of $CaCO_3$ and fuel combustion.[2,3] Production of Portland cement also consumes about 3000-4000 MJ of thermal energy per tonne of clinker for dry process and about 324-540 MJ of electrical energy per tonne of cement for grinding of raw materials and cement.[4,5] Accordingly, the synthesis of low-energy reactive belite cement as an alternative to Portland cement is one of the most important challenges.

Belite have five polymorphs (β, γ, α, $α_L´$ and $α_H´$) and their thermal transformation relationship is illustrated in figure (1).[6] α-C_2S is stable at high temperature and transforms to α'-C_2S and finally to γ and β-C_2S at low temperature. β-C_2S is hydraulic whereas γ- C_2S is a non-hydraulic and does not account for the setting and hardening of cement.[7] γ-C_2S causes cracking of β-C_2S crystals forming dust (i.e dusting phenomenon) because γ-C_2S crystals are larger than β-C_2S crystals. Dusting phenomenon can be prevented if β-C_2S is stabilized by inclusion of stabilizing ions (Fe^{3+}, Al^{3+}, Mg^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, B^{3+}, Na^+ and K^+) which replace calcium and/or silicon atoms in the β-C_2S structure.[8,9] The reactivity and hydraulic properties of stabilized β-C_2S depends on the type and amount of the stabilizing ions.[10] Stabilizing ions modify charge density localization of the electronic structure of β-C_2S and enhance its reactivity.[11] Fast cooling may produce fine β-C_2S crystals affording transformation of β-C_2S to γ-C_2S, even without need to stabilizer.[12]
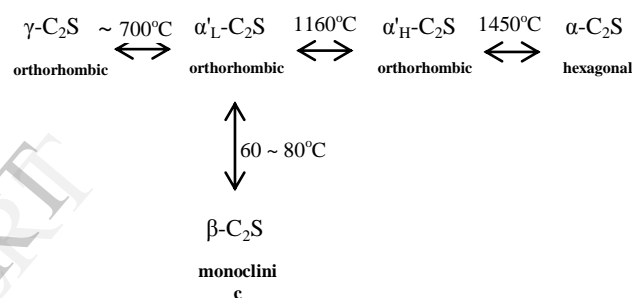

Figure (1): Thermal transformation relationship of belite Polymorphs

Dicalcium silicate hydrate (hillebrandite, $Ca_2(SiO_3)(OH)_2$) was prepared by hydrothermal treatment of lime/quartz mixture with Ca/Si = 2.0 at 200-250°C for 5-10 hours.[13] Hillebrandite was synthesized by mechanochemical treatment of amorphous precipitated lime/silica mixture at room temperature.[14] Hillebrandite decomposes at about 500°C producing low-crystalline β-C_2S.[15,16] The temperature at which β-C_2S begins to form decreases as the Ca/Si ratio and/or temperature of hydrothermal synthesis of hillebrandite becomes higher.[17,18] Dicalcium silicate hydrate dissociates at 390-490°C forming γ-C_2S plus an intermediate phase that subsequently transforms to $α'_L$ phase at 920-960°C and yields β-C_2S on cooling.[19] The aim of this work is preparation of belite cement from lime/white sand mixture hydrothermally treated and calcined at low temperature.

II. MATERIALS AND EXPERIMENTAL TECHNIQUES

Freshly prepared lime was produced by calcination of limestone powder (purity > 99%) in an electrical muffle furnace at 950°C for 3 hours. Lime was cooled to room temperature in desiccator, milled and stored in tightly closed plastic bag to avoid carbonation. White sand was provided from Royal Cement Company, Minia, Egypt. Distilled water and analytical grade barium chloride were used without further purification. Mixtures of white sand, lime, $BaCl_2$ (with the ratio Ca/Si or (Ca+Ba)/Si = 2) and

distilled water (water/solid ratio of 5/1 by weight) placed in stainless steel capsule keeping the occupied volume equals 0.67 of total volume capacity. The capsule was tightly closed to avoid sealing of water vapor, was shacked to obtain homogeneous suspension inside and was heated at 180°C for 5 hours in electric oven. The capsule was removed from oven and cooled to room temperature. The product of hydrothermal treatment was filtered, washed with distilled water, dried in microwave oven and calcined in an electric muffle furnace at 600-900°C for 3 hours. The calcined product was cooled to room temperature in desiccator, milled and stored in tightly closed plastic bottles. X-ray fluorescence XRF and X-ray diffraction XRD analyses were carried out by Philips x-ray diffractometer PW 1370, Co. with Ni filtered CuK_α radiation (1.5406 Å). The Fourier transform infrared FTIR analysis was measured by spectrometer Perkin Elmer FTIR System Spectrum X in the range 400-4000 cm^{-1} with spectral resolution of 1 cm^{-1}. Scanning electron microscopy SEM was investigated by Jeol-Dsm 5400 LG apparatus. The thermogravimetric TGA and differential thermogravimetric analyses DTG were carried out with the aid of Shimadzu Corporation thermo analyzer with DTG-60H detector with 10°C/min heating rate from room temperature up to 1000°C, under nitrogen atmosphere at 40 ml/min flow rate, the hold time at the appropriate temperature is zero.

III. RESULTS AND DISCUSSION

Table (1) illustrates the chemical composition of limestone and white sand determined by XRF. The chemical composition results confirm that limestone and white sand are mainly composed of $CaCO_3$ and SiO_2 respectively in presence of small amount of impurities. Figure (2) illustrates the XRD patterns of lime and white sand. Lime mainly composes of calcium oxide (CaO) in addition to small amount of portlandite (Ca(OH)$_2$) that may present due to partial hydration of lime. White sand mainly composes of quartz (SiO$_2$) in addition to small amount of kaolinite (Al$_2$O$_3$.2SiO$_2$.2H$_2$O). Figure (3) illustrates the FTIR spectra of lime and white sand. The absorption band that appear at 3640 cm^{-1} is due to OH- associated with portlandite (hydrated lime). The absorption band that appear at 875 and 1441 are due to the v^2 and v^3 of carbonate (CO$_3^{2-}$) present as a partial carbonation lime.[20,21] The absorption band that appear at 452 cm^{-1} is due to Ca-O stretching vibration.[22] The absorption bands of silica (Figure (3b)) appear at 1084, 795 and 464 cm^{-1} are corresponding to asymmetric stretching vibration of Si–O–Si, symmetric stretching vibration of Si–O–Si, and bending vibration of O–Si–O respectively.[23]

Figure (4) illustrates the FTIR spectra of hydrothermally treated lime/white sand and lime/BaCl$_2$/white sand mixtures. The absorption band of silica at 1084 cm^{-1} was shifted to lower wavenumber value 1029 cm^{-1}. This is an indication for lowering of the degree of polymerization of silicate structure due to reaction between white sand and lime under the hydrothermal conditions. At the same time, the intensity of absorption

bands of silica that appear at 794 and 464 cm^{-1} were reduced significantly. Whereas, the absorption band of combined water appear at 3449 cm^{-1}. Also, there is a new absorption band appear at 2924 cm^{-1}. These observations indicate that the hydrothermal treatment initiates the reaction between lime and white sand leads to the formation of intermediate dicalcium silicate hydrates. The existence of unreacted lime and silica indicates that the hydrothermal treatment of the lime/silica mixture (Ca/Si=2/1) at 180°C for 5 hours does not drive the reaction to completion.

TABLE I.   THE CHEMICAL COMPOSITION OF LIMESTONE AND WHITE SAND DETERMINED BY XRF

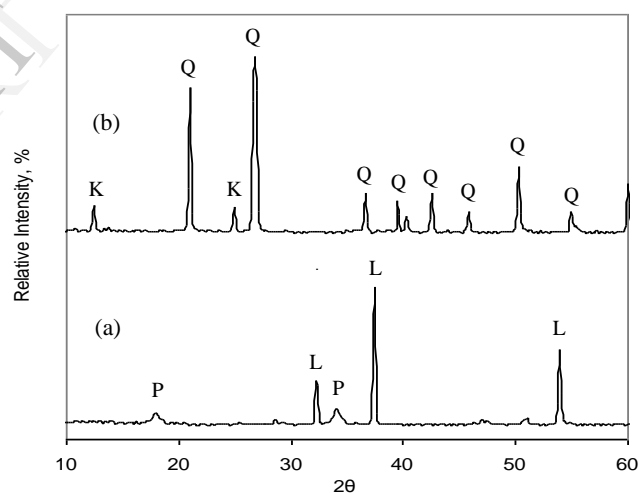| Oxide	Limestone	White sand
SiO$_2$	0.26	96.66
Al$_2$O$_3$	0.16	2.87
CaO	54.59	0.14
Fe$_2$O$_3$	-	0.08
MgO	0.29	0.02
SO$_3$	0.05	-
Na$_2$O	0.11	-
K$_2$O	0.03	-
Cl$^-$	-	-
LOI	43.72	1.20
TiO$_2$	-	-
Total	99.21	99.97

Figure (2): XRD patterns of (a) lime and (b) white sand
(K kaolinite, L lime, P portlandite, Q quartz)

Figures (5 and 6) illustrate TGA and DTA thermograms of hydrothermally treated lime/white sand and lime/BaCl$_2$/white sand mixtures. Result of thermal analysis was illustrated in table (2). TGA/DTA thermograms illustrates the in situ sequence of thermal reactions and phase transformations that occur when hydrothermally treated lime/white sand and lime/BaCl$_2$/white sand mixtures were calcined up to 900°C. Absorbed water was lost at 132°C.[24] Residual portlandite Ca(OH)$_2$ was dehydrated at 450°C.[25] Dicalcium silicate crystallizes into β-C$_2$S at 659°C. β-C$_2$S transforms to α'-C$_2$S at 832°C.

Figure (7) illustrates the SEM micrographs of hydrothermally treated lime/white sand and

lime/BaCl$_2$/white sand mixtures. Lime/white sand and lime/BaCl$_2$/white sand mixtures have different morphologies. The former is characterized by appearance of large grains with rough surfaces whereas the later show the presence of small cube-like grains. The change in morphological properties is accompanying presence of Ba^{2+} ions that replace calcium and/or silicon atoms and modify the structure of calcium silicate hydrates.

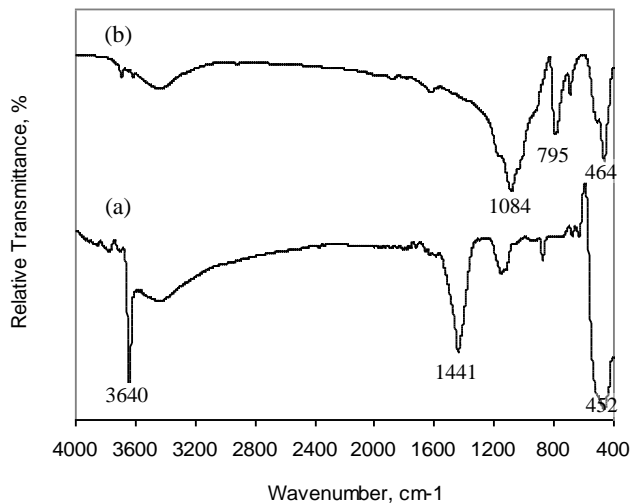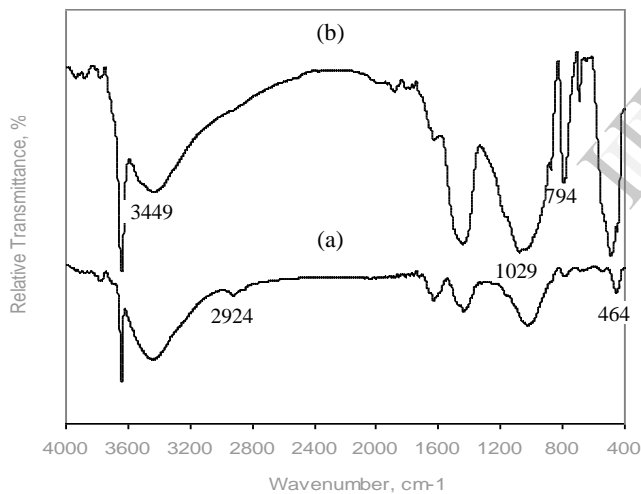Figure (3): FTIR spectra of (a) lime and (b) white sand

Figure (4): FTIR spectra of hydrothermally treated
(a) lime/white sand and (b) lime/ BaCl$_2$/white sand mixtures

Figure (8) illustrates the FTIR spectra of hydrothermally treated lime/white sand mixture calcined at 600-900°C. Calcination at 600°C was accompanied with the following observations; the absorption band of silica was shifted from 1029 cm^{-1} to lower wavenumber value (958 cm^{-1}) at the same time, new absorption band appears at 876 cm^{-1}. This is an indication for transformation of intermediate dicalcium silicates hydrate to β-C$_2$S.[26] Raising the temperature of calcination to 750°C was accompanied with appearance of absorption band at 520 cm^{-1}. This is an indication for transformation of β-C$_2$S to γ-C$_2$S.[27] At 900°C, the absorption bands located at 520 and 955 cm^{-1}

were sifted to lower wavenumber values (516 and 951cm^{-1} respectively). This is an indication for transformation of γ-C$_2$S to α'-C$_2$S.[28] Figure (9) illustrates the FTIR spectra of hydrothermally treated lime/BaCl$_2$/white sand mixture calcined at 600-900°C. Appearance of absorption band at 885 cm^{-1} even at 900°C indicates for existence of β-C$_2$S at higher temperatures. Ba^{2+} ions may stabilizes the β-C$_2$S and retards its transformation to γ-C$_2$S or α'-C$_2$S phases. Except formation of some of γ-C$_2$S as indicated from its characteristic absorption bands located at 520.
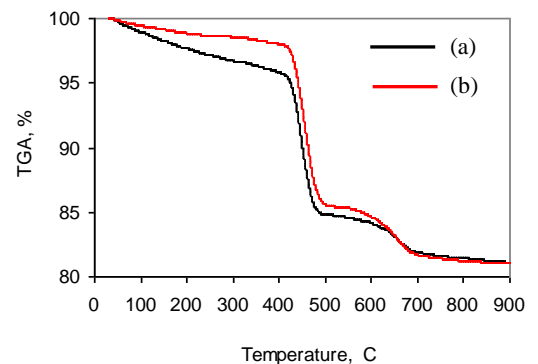

Figure (5): TGA thermograms of hydrothermally treated
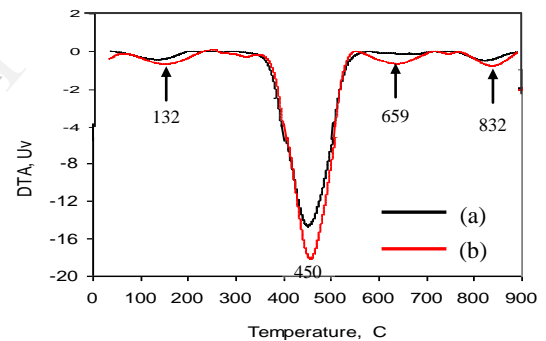(a) lime/white sand and (b) lime/BaCl$_2$/white sand mixtures

Figure (6): DTA thermograms of hydrothermally treated
(a) lime/white sand and (b) lime/BaCl$_2$/white sand mixtures

TABLE II.   RESULT OF THERMAL ANALYSIS

Phase	Temperature (°C)	Peak Temperature (°C)	Weigh Loss (%)	Weigh Loss (mg)
Loss of absorbed water	33-317	132	-3.37	-0.56
Dehydration of portlandite	317-590	450	-12.37	-2.06
Formation of β-C$_2$S	590-760	659	-3.17	-0.52
β-C$_2$S → α'-C$_2$S transformation	760-1000	832	-0.26	-0.03
			-19.17	-3.17

Figure (10) illustrates XRD patterns of hydrothermally treated lime/white sand mixture calcined at 600-900oC as well as lime/BaCl2/white sand mixture calcined at 900°C for 3 hours. Dicalcium silicate hydrates do not appear in the XRD analysis (figure 9a) because of its amorphous structure. β-C$_2$S appears in lime/white sand mixture that was calcined at 600°C (figure 9b) and its amount increases with raising calcination temperature to 750°C (figure 9c). β-C$_2$S transforms to γ-C$_2$S when lime/white sand mixture was calcined at 900°C (figure 9d).

This proves that β-C_2S was not stabilized in case of hydrothermally treated lime/white sand mixture that was calcined at higher temperature and when it was cooled it transforms to γ-C_2S.[8,9] In contrast, β-C_2S was stabilized in case of hydrothermally treated lime/$BaCl_2$/white sand mixture that was calcined at 900°C (figure 9e). This proves that Ba^{2+} ions stabilizes β-C_2S and retards its transformation to γ-C_2S. In other words, Ba^{2+} ions replace calcium and/or silicon atoms hence it stabilizes the structure of β-C_2S.[10]
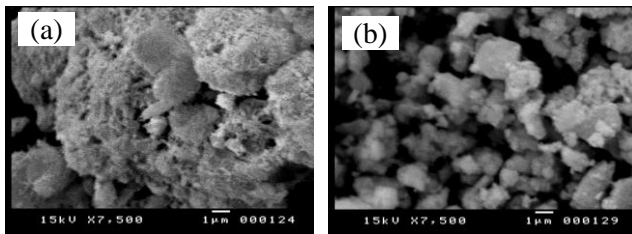

Figure (7): SEM micrographs of hydrothermally treated (a) lime/white sand and (b) lime/$BaCl_2$/white sand mixtures
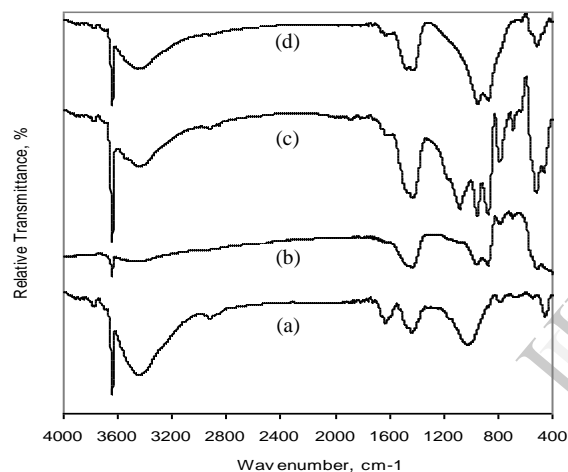

Figure (8): FTIR spectra of hydrothermally treated (a) lime/white sand mixture calcined at (b) 600, (c) 750 and (d) 900°C

CONCLUSIONS

A method for the low temperature synthesis of β-C_2S from lime/$BaCl_2$/white sand mixture (Ca/Si=2 and 2% Ba) was described. Dicalcium silicate hydrate was formed by hydrothermal treatment of lime/white sand mixture at 180°C for 5 hours. β-C_2S was produced when hydrothermally treated lime/white sand mixture was calcined at 750°C for 3 hours. In lime/white sand mixture, β-C_2S does not stabilized and transformed to γ-C_2S with raising temperature of calcination to 900°C. In contrast, β-C_2S was stabilized in lime/$BaCl_2$/white sand mixture that was calcined at 900°C. This due to that Ba^{2+} ions stabilizes β-C_2S and retards its transformation to γ-C_2S.
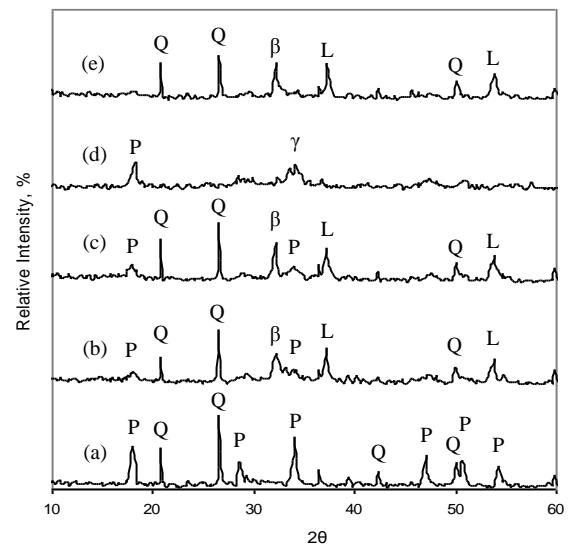

Figure (9): FTIR spectra of hydrothermally treated (a) lime/$BaCl_2$/white sand mixture calcined at (b) 600, (c) 750 and (d) 900°C
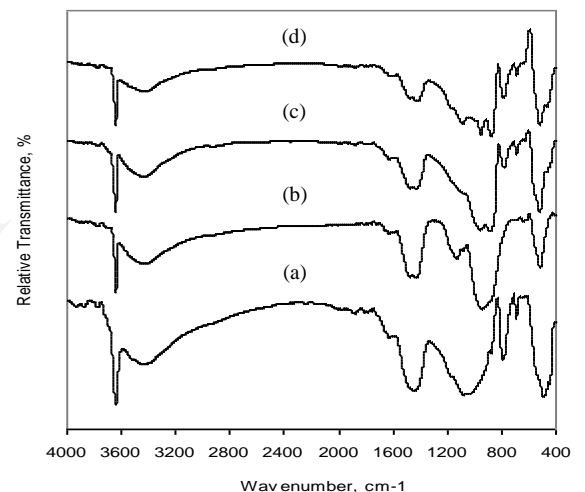

Figure (10): XRD patterns of hydrothermally treated (a) lime/white sand mixture calcined at (b) 600°C, (c) 750°C and (d) 900°C as well as lime/$BaCl_2$/white sand mixture calcined at (e) 900°C (P Portlandite, Q quartz, β β-C_2S, L lime and γ γ-C_2S)

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