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Preparation of Economic Belite Cement from Saudi Raw Materials

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ABSTRACT

This research investigates the preparation of economic belite cement from the marble of Gabal Al-Qaren Al-Abyad (Gabal Almarmr) and white sand from Riyadh. Lime was produced from the marble after calcination at 950˚C for 2 hours. A mixture of lime and white sand (CaO/SiO_2=2) in 2 M NaOH solution with the solution/solid ratio 5 was hydrothermally treated in a stainless steel capsule at 135˚C for 3 hours and calcined at 1000˚C for 3 hours. FTIR, XRD, and SEM-EDX confirmed the formation belite in addition to calcium and sodium silicate phases. A semi-quantitative phase analysis derived from XRD results estimated that the obtained economic belite cement contains 73.9% β-C_2S.

1. Introduction

Alite (tricalcium silicate) is considered as the main calcium silicate phase in the ordinary Portland cement that contribute to the hardening and strength gain of cement paste after hydration. The formation of alite needs a high temperature (i.e. 1450^{o}C), whereas, belite (dicalcium silicate) can be formed at a much lower temperature (i.e. 800-1000^{o}C) [1]. Belite cement can be produced by the hydrothermal treatment of a mixture of lime and a siliceous raw material with the mole ratio CaO/SiO_2=2 followed by calcination of the product at 700-1000^{o}C. Decreasing the clinkering temperature during production of belite cement results in an energy saving up to 16% [2] as well as a reduction of CO_2 emissions up to 8% [3]. The main disadvantages of the belite cement are the slow hydration process and low strength gain after 28 days. These disadvantages can be overcome by adjusting the method of the preparation of belite cement by preparing the active belite phases such as The α'_L, α'_H, and β-C_2S, that have a reactivity similar to that of alite [4]. Hence, such a kind of belite cement may be suitable for long-term sustainable materials [5].

Accordingly, great efforts are always being made around the world for developing of production of active and economic belite cement. β-C_2S was prepared from different siliceous raw materials such as silica fume, white sand, rice husk ash, metakaolin, and dealuminated kaolin under various hydrothermal conditions with lime in presence in stabilizer such as $BaCl_2$ followed by calcination of the product at 650˚C-1000˚C [6]. The aim of this research paper is to prepare the belite cement from local Saudi raw materials.

2. Materials and Methods

The Saudi raw materials that are used in this study are marble powder from Gabal Al-Qaren Al-Abyad (Gabal Almarmr, 140 km northern Mecca) and white sand from Riyadh. Marble powder was calcined in a muffle furnace at 950˚C and cooled to room temperature to lime. Sand was milled to a fine powder. Figure 1 illustrates the procedure for the synthesis of belite. The mixture of lime and sand with a mole ratio (CaO/SiO_2 = 2) in 2 M NaOH solution with the liquid to solid ratio 5.

The mixture was hydrothermally treated in a stainless steel capsule keeping the occupied volume equals 67% of total volume capacity at 135˚C for 3 hours in an electric oven. After cooling down to the room temperature, the hydrated product was filtered, washed with distilled water, and dried in an electric oven overnight at 80^{o}C. The calcination of the hydrated product was done in the muffle furnace at 1000˚C for 3 hours followed by cooling down to the room temperature. The raw materials, hydrated product, and calcined product were analyzed by FTIR, XRD, and SEM-EDX techniques. XRF was measured by Philips PW1606 X-ray fluorescence spectrometer. XRD was measured by Philips X-ray diffractometer PW 1370, Co. with Ni-filtered CuK_α radiation (1.5406 Å). A semi-quantitative phase analysis was calculated using the Bruker AXS configuration program. FTIR was measured by spectrometer Perkin Elmer FTIR System Spectrum X in the range 400-4000 cm^{-1}. TGA/DrTGA/DSC was measured by Netzsch STA 409 C/CD analyzer with 2^{o}C/min heating rate from room temperature up to 1000^{o}C, under air atmosphere at 50 ml/min flow rate, the hold time at the appropriate temperature is zero. SEM-EDX was measured by Jeol-Dsm 5400 LG apparatus. Table 1 represents the chemical composition of different phases that appear in this study.

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Table 1 The chemical composition of different phases.

Phase	Formula
Afwillite	$Ca_3Si_2O_8(OH)_2(H_2O)_2$
Alite, C_3S	Ca_3SiO_5
Belite (β-C_2S)	Ca_2SiO_4
Calcite	$CaCO_3$
Combeite	$Na_4Ca_4(Si_6O_{18})$
Hillebrandite	$Ca_2(SiO_3)(OH)_2$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Lime	CaO
Portlandite	$Ca(OH)_2$
Quartz	SiO_2
Rankinite	$Ca_3Si_2O_7$
Sodium calcium silicate	$Na_2Ca_3(Si_3O_{10})$
Sodium hydrogen silicate hydrate	$Na_2(H_2SiO_4).7H_2O$
Xonotlite	$Ca_6Si_6O_{17}(OH)_2$

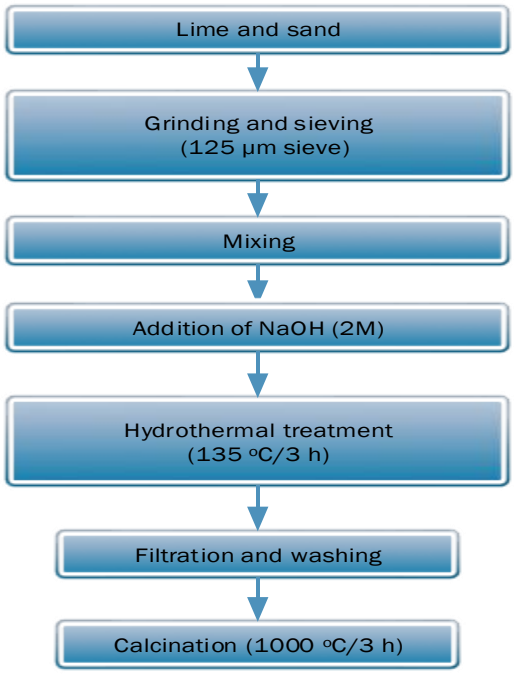

Fig. 1 Procedure of synthesis of belite.

3. Results and Discussion

Table 2 illustrates the chemical composition of lime and sand determined by XRF analysis. The lime composes of 86.64% CaO and the sand composes of 98.27% SiO_2.

Figure 2 illustrates the FTIR spectra of raw materials as well as the hydrothermally treated and calcined products. Table 3 illustrates the interpretation of the main absorption bands. The results illustrate that lime is partially carbonated whereas sand contains residual kaolinite. The hydrothermally treated product composes of calcium silicate hydrate, afwillite, xonotlite, quartz, portlandite, and calcite. Figure 3 illustrates the XRD diffraction patterns of raw materials, hydrothermally treated, and calcined products. Lime composes of CaO and sand composes of quartz. The main crystalline phases that were detected in the hydrothermally treated product are afwillite, xonotlite portlandite, and quartz. The main crystalline phases that were detected in the calcined product are rankinite, β-C_2S, combeite, sodium hydrogen silicate hydrate, sodium calcium silicate, calcite, portlandite, lime, and quartz. Table 4 illustrates the semi-quantitative phase analysis of the calcined product derived from XRD results illustrates that the calcined product composes of 73.9% β-C_2S, 14.8% combeite, and 11.3% lime. Figure 4 illustrates DSC/TGA/DrTGA thermograms of the hydrothermally treated product. The first endothermic peak at 408°C is attributed to the dehydration of Portlandite [7]. The second endothermic peak at 643°C is attributed to the formation of β-C_2S by dehydration of the calcium silicate hydrate [8].

Table 2 Chemical composition of lime and sand determined by XRF.

Oxide	Lime	Sand
SiO_2	1.92	98.27
Al_2O_3	0.65	0.90
CaO	86.64	0.20
Fe_2O_3	0.34	0.03
MgO	0.69	0.14
SO_3	0.48	0.05
Na_2O	0.20	0.13
K_2O	0.04	0.01
P_2O_5	0.20	0.03
TiO_2	0.06	0.08
ZnO	0.01	-
SrO	0.03	0.01
Cl^-	0.05	-
LOI	7.27	0.03
Total	98.58	99.88

Table 3 The interpretation of the FTIR results.

Wavenumber, cm^{-1}	Interpretation
Lime	
3644	Vibration of OH-associated with hydrated lime present as a partial hydration of lime [6]
876 and 1468	v^2 and v^3 vibration of carbonate (CO_3^{2-}) present as a result of the partial carbonation of lime [9]
458	The Ca-O stretching vibration [10]
1630 and 3425	Stretching and bending vibrations of structural hydroxyl groups and water [11]
1420	Ca-OH vibration band of lime [12]
Sand	
1087, 787, 472	Si-O-Si asymmetric stretching vibration, Si-O-Si symmetric stretching vibration and O-Si-O bending vibration of quartz [13]
689, 540	Si-O vibration of kaolinite
1032	Si-O stretching (in-plane) vibration of kaolinite
918	AlAlOH vibration of kaolinite [14]
3694, 3623	Stretching vibrations of surface OH groups and stretching vibrations of inner hydroxyl groups [15]
Hydrothermally treated product	
965	Vibration of calcium silicate hydrate
796, 1070	Absorption bands are attributed to the residual quartz
3642	Absorption band is attributed to residual portlandite
1424	Absorption band is attributed to calcite formed due to partial carbonation of portlandite
3382	Absorption band is attributed to the vibration band of water molecules
480, 875, 965	Absorption bands of afwillite
449, 480, 668, 965	Absorption bands of xonotlite
Calcined product	
1006, 876, 520	Vibration bands of β-C_2S [16]
917	Absorption band of combeite
846, 998	Absorption bands of rankinite
796, 1070	Absorption bands of quartz
877	Absorption band of lime

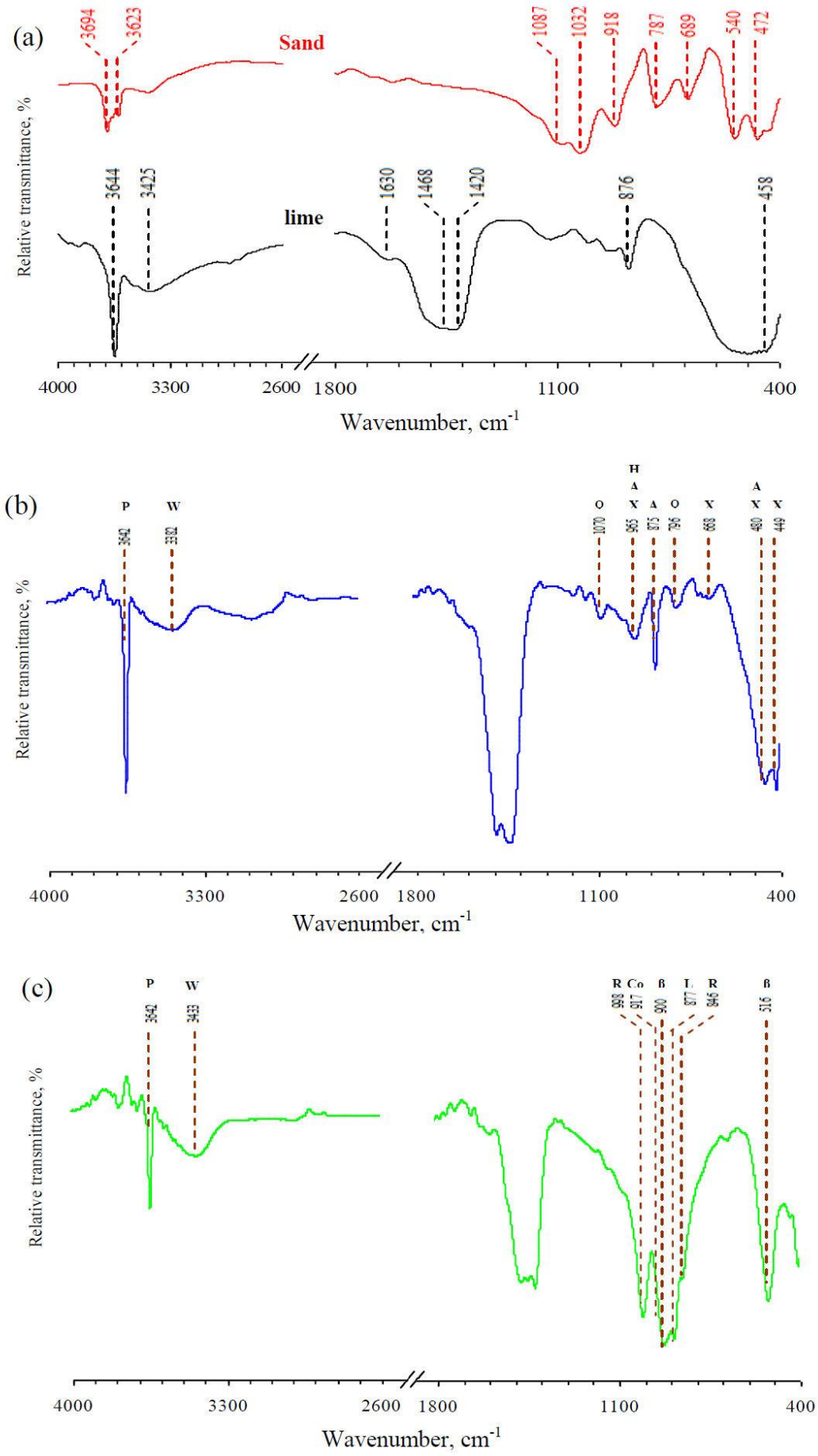

Fig. 2 FTIR spectra of (a) lime and sand, (b) hydrothermally treated and (c) calcined products (***A*** afwillite, ***β*** β-C_2S, ***C*** calcite, ***Co*** combeite, ***H*** calcium silicate hydrate, ***L*** lime, ***P*** portlandite, ***Q*** quartz, ***R*** rankinite, ***W*** water and ***X*** xonotlite).

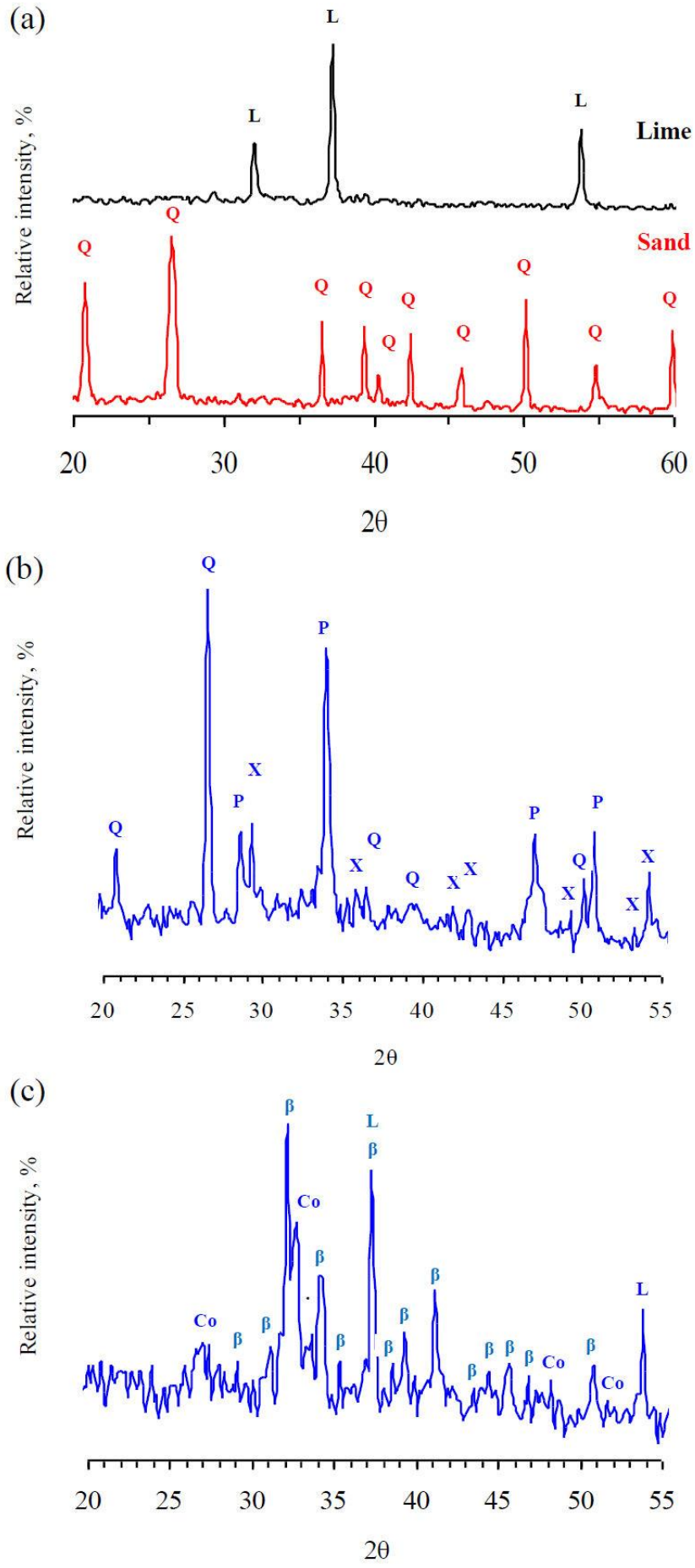

Fig. 3 XRD diffraction patterns of (a) lime and sand, (b) hydrothermally treated and (c) calcined products (***A*** afwillite, ***β*** β-C_2S, ***C*** calcite, ***Co*** combeite, ***L*** lime, ***P*** portlandite, ***Q*** quartz, ***R*** rankinite, ***S*** sodium hydrogen silicate hydrate, ***Sc*** sodium calcium silicate and ***X*** xonotlite).

Table 4 The semi-quantitative phase analysis of belite cement.

Phases	Wt %
β-C_2S	73.9
Lime	11.3
Combeite	14.8
Total	100

Figures 5-7 illustrate the SEM-EDX analysis of raw materials as well as the hydrothermally treated and calcined products. The empirical formulae of different phases that were pointed out were calculated using the EDX data expressed in normalized atom%. Taking into consideration that the calculated formulae are approximate due to the presence of variable contents of foreign ions depending on the proximity of the EDX point analysis to the underlying other phases [17, 18]. SEM results of raw materials show the morphology of fine lime grains as well as that of large quartz grains with the existence of hexagonal platelets of kaolinite crystals [19, 20] laying on its surface. The hydrothermally treated product composes of calcium silicate hydrate (hillebrandite) gel. The calcined product composes of fine β-C_2S aggregates.

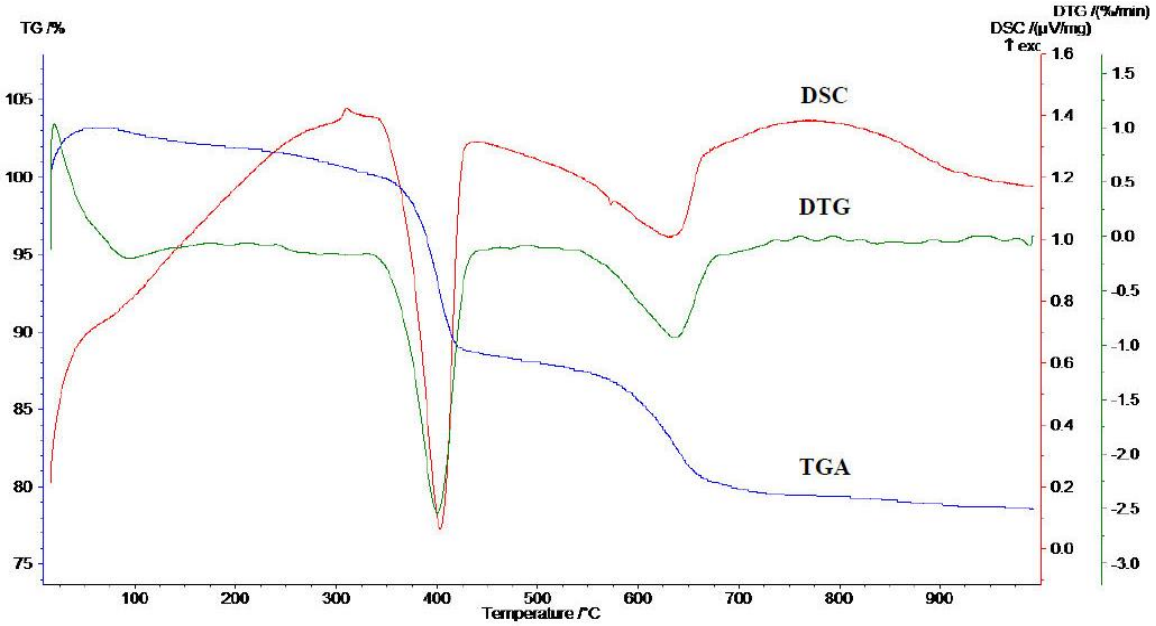

Fig. 4 DSC/TGA/DTG of the hydrothermally treated product.

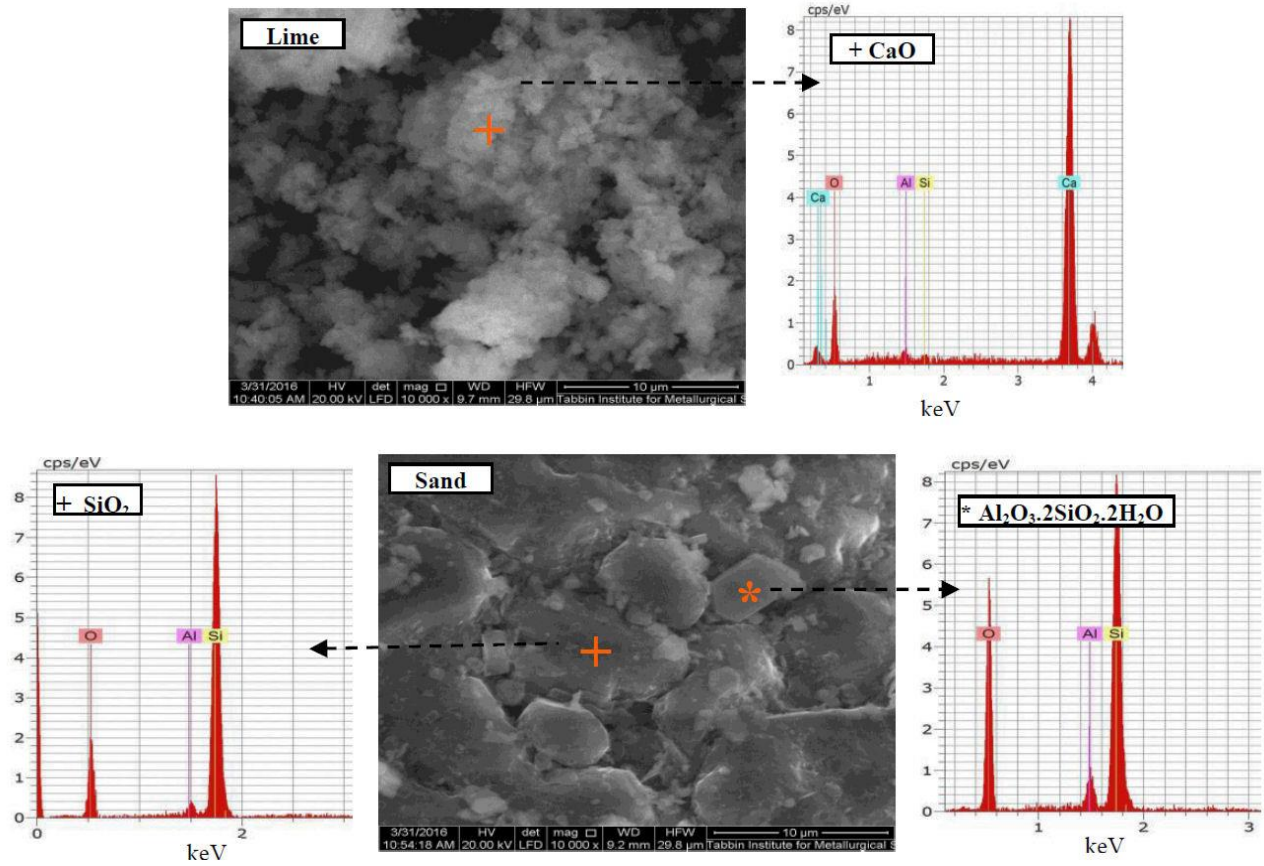

Fig. 5 SEM-EDX of lime and sand.

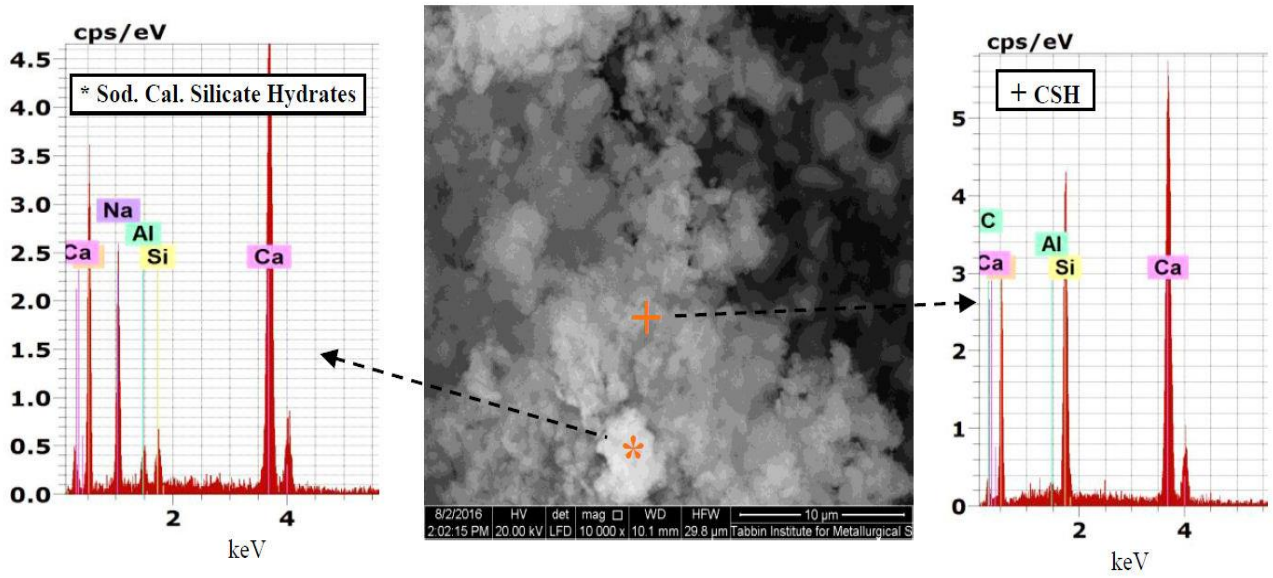

Fig. 6 SEM-EDX of the hydrothermally treated product.

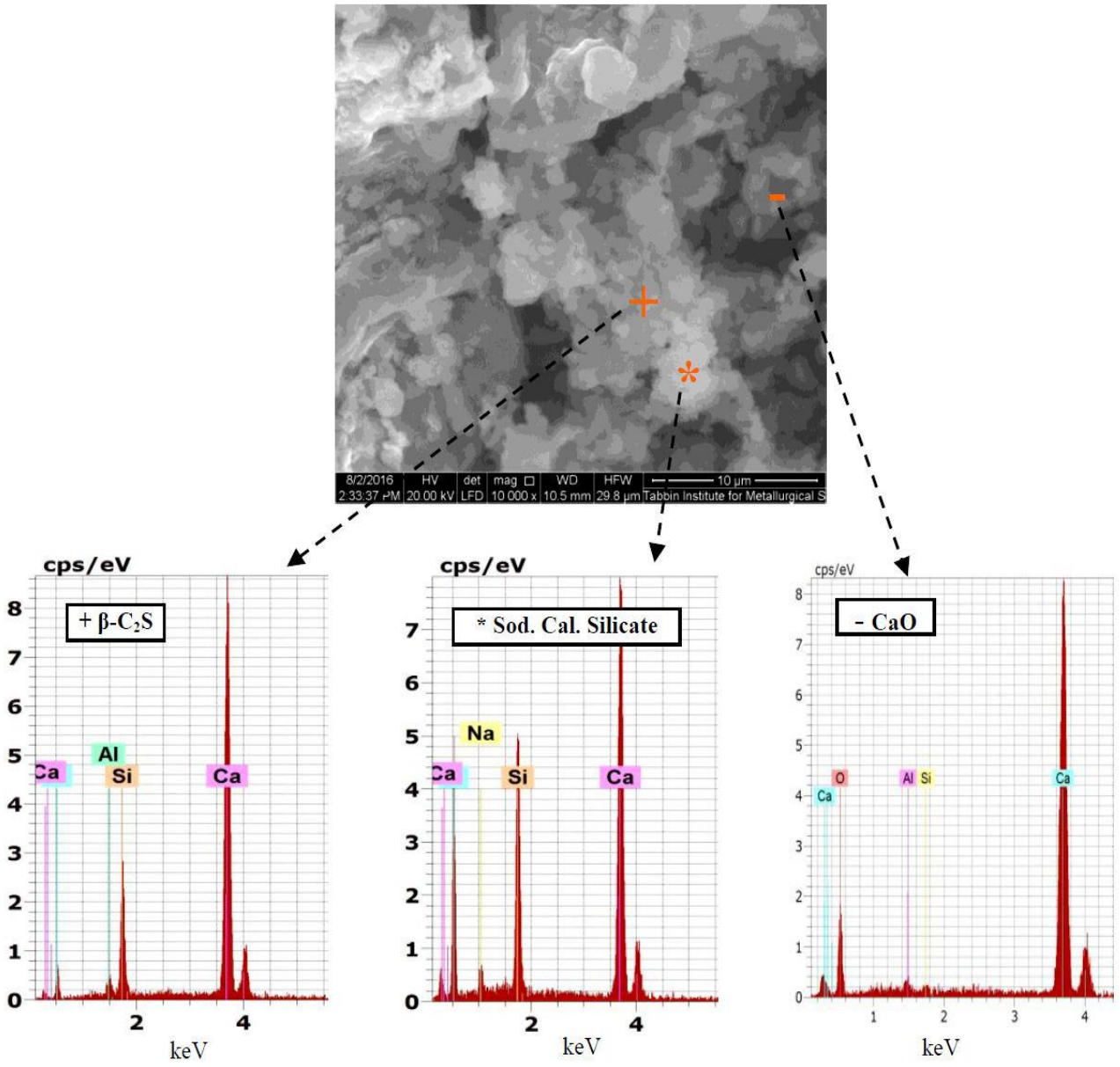

Fig. 7 SEM-EDX of the calcined product.

4. Conclusion

Belite cement was successfully prepared from the Saudi raw materials (marble powder from Gabal Al-Qaren Al-Abyad and white sand from Al Riyadh). An economic belite cement was prepared from a mixture of lime and sand (Ca/Si=2) in 2 M NaOH solution with liquid to solid (l/s) ratio 5. The mixture was hydrothermally treated in a stainless steel capsule at 135˚C for 3 hours and calcined at 1000˚C for 3 hours. The prepared belite cement composes of 73.9% of β-C_2S. Future studies must be conducted to investigate the cementitious properties of the belite cement that was prepared by applying the experimental procedure illustrated in this study.

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