journal

J. Am. Ceram. Soc., **93** [4] 987–992 (2010)
DOI: 10.1111/j.1551-2916.2009.03536.x

A Combustion Method to Synthesize a Belite Cement Clinker

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The calcination method is the usual method to synthesize cement clinkers. The production of ordinary Portland cement requires temperatures as high as 1450°C. High amounts of energy are used and huge flows of carbon dioxide are liberated to the atmosphere. In the literature, the combustion method has been often reported as a fast and effective method to prepare ceramics. The precursor solutions are metal nitrates and organic combustibles such as urea or glycine. The oxidation–reduction exothermic reaction is very fast. In this work, the effect of H_2O_2 addition to the combustion preparation of clinker is discussed. A conventional clinker prepared by calcinations at 1200°C is used for comparison purposes. The combustion preparation with H_2O_2 as an additive reduces calcination time and temperature.

I. Introduction

Among the various methods to prepare ceramics, the combustion synthesis has been introduced to synthesize advanced ceramics, intermetallic compounds, or nanomaterials. It is an alternative method whose main advantage is the fast synthesis of the compounds as it is an auto-maintained process. The energy required for the reaction is provided by the heat liberated by the reacting compounds through an oxidation–reduction reaction. In some cases, the process has to be activated as the reaction enthalpy may not be enough to autopropagate the process. Often, a compound that can be oxidized has to be added to the synthesis reactants.

Urea, in the combustion synthesis, is the most frequently used fuel as it is economical and it produces less gases

$$\mathrm{CO(NH_2)_2}(s) + 1.5\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2O}(g) + \mathrm{N_2}(g) \quad (1)$$

The combustion enthalpy ΔH_r/mol of urea with air is −129.9 kcal/mol of urea at 25°C, Table I.[1,2] Often, hydrated nitrates are proposed as fuels due to their oxidizing character. They are, then, useful to surpass the activation energy barrier. Furthermore, they melt at lower temperatures than the decomposition temperature of the fuel.[3–7]

However, if silicates and aluminates such as belite or tricalcium aluminate are prepared, no nitrates can be used. Then, the reactants have to be mixed with urea and a second compound, such as NH_4NO_3, HNO_3, NH_4Cl, or H_2O_2, which are assumed to work as an additional oxidizer.[4] If urea is used in excess, with NH_4NO_3 as a combustion aid, the temperature may reach 1176°C and, if the combustion aid is H_2O_2, temperature may reach 1249°C. Still, large amounts of gases are produced.[5] The oxidation–reduction reaction between urea and H_2O_2 is:

$$\mathrm{CO(NH_2)_2}(s) + 3\mathrm{H_2O_2}(l) \rightarrow \mathrm{CO_2}(g) + 5\mathrm{H_2O}(g) + \mathrm{N_2}(g) \quad (2)$$

with a $\Delta H = -168.621$ kcal at 25°C. Note that, in such a reaction, no nitrogen oxides are obtained. Indeed, the amount of fuel to react completely with the oxidizer depends on the final oxidation state of nitrogen, carbon, and hydrogen. Nitrogen can have a valence of +2 (as NO), $2x$ (as NO_x), or +4 (as NO_2) after the combustion reaction. Therefore, calculations of the stoichiometric composition are based on the assumption that the nitrogen species in the product has a valence of 0. However, some authors suggest that this may not be the case, making the calculation of stoichiometric amounts difficult.[8] To optimize the process, the reaction can be performed in a preheated muffle (500°C) so that the temperature remains constant all around.[4,6] Although, in the literature, mullite and aluminum titanate have been prepared through this procedure,[5,6] no reports are found on the preparation of cement clinker.

Cement clinker is a ceramic. Cements are a mixture of clinker and gypsum (3%–4%), and some additives that reduce hydration time, enhance hardness, etc. Clinker is obtained from the calcination of clays or fly ashes and limestone at temperatures from 1260° to 1450°C, depending on the type of clinker required. Portland clinker obtained at 1450°C presents a high content of alite, which provides cements with a fast setting and a rapid strength development. Instead, belite clinker composed mainly by belite has the advantage to produce cements with low hydration heat and long-time strength.

In the present work, the synthesis of a belite clinker through a modified combustion process is discussed. The aluminum and silicon sources are Mexican minerals: on the one hand, a zeolite from San Luis Potosí and on the other, a calcite from Yucatán. First, we study the synthesis using only urea and, then the effect of H_2O_2 addition is presented.

In a previous paper,[9] we reported on clinker synthesis using urea and ammonium nitrate, and in this work we report on the use of hydrogen peroxide as a combustion additive. The relative amount of each mineral reactant was estimated from the following global reaction:

$$\begin{aligned}78\mathrm{CaCO_3} + \mathrm{Ca_4Al_8Si_{28}O_{72}\cdot 24H_2O} &\rightarrow 14\mathrm{(CaO)_3SiO_2}\\ &+ 14\mathrm{(CaO)_2SiO_2} + 4\mathrm{(CaO)_3Al_2O_3} + 24\mathrm{H_2O} + 78\mathrm{CO_2}\end{aligned} \quad (3)$$

where the zeolite is calcium clinoptilolite (molar ratio Si/Al = 3.5 and Ca/Si = 0.14) as clinoptilolite is the main compound present in the San Luis Potosí mineral. At 25°C, the reaction between zeolite and calcite requires a reaction enthalpy of $\Delta H_r =$ 2,955.48 kcal/mol of zeolite. The ratio Si/Al = 3.5 of the zeolite is close to the required ratio to synthesize Portland clinker; therefore, no aluminum compound had to be added. The amount of calcite was adjusted to reach a value of Ca/Si = 2.93, i.e., close to 3. Note that in the zeolite a high amount of calcium is already present (zeolite Ca/Si = 0.14). Therefore, 0.0143 mol of calcite corresponds to 0.000183 mol of zeolite.

L. Struble—contributing editor

Manuscript No. 26434. Received June 22, 2009; approved November 13, 2009.
This work was financially supported by the Dirección General de Estudios de Posgrado.
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Table I. Relevant Thermodynamical Data 1

Compound	ΔH_f° at 25°C (kcal/mol)
$Ca_4Al_8Si_{28}O_{72} \cdot 24H_2O(s)$	−10147.32
$CaCO_3(s)$	−288.45
$CO(NH_2)_2(c)$	−79.71
$H_2O_2(l)$	−44.90
$Ca_3SiO_5(s)$	−700.57
$Ca_2SiO_4(s)$	−551.87
$Ca_3Al_2O_6(s)$	−858.34
$CaO(s)$	−151.90
$Al_2O_3(s)$	−400.90
$SiO_2(s)$	−217.90
$CO_2(g)$	−94.05
$H_2O(g)$	−57.80

Thus, the corresponding clinker composition would be 48.2% $(CaO)_3SiO_2$, 35.5% $(CaO)_2SiO_2$, and 16.3% $(CaO)_3Al_2O_3$ obtained using the Bogue method.

The parameter Φ_e, defined as the elemental stoichiometric coefficient, correctly predicts whether a mixture is fuel lean, fuel rich, or stoichiometrically balanced.[10] Φ_e is the ratio between the composition of oxidizing and reducing elements, calculated by multiplying the corresponding coefficients by the valences of each element.[5] In our experiments, $\Phi_e = 0.598$ was maintained constant, i.e., 200% of urea in excess from the stoichiometrical value. Then, the process will have a thermal efficiency of 50%. Modern cement plants reach efficiencies of 60%. Using the energy content values presented above and a theoretical clinker energy penalty of 1.76 MJ/kg,[11] the urea method requires 3.4 MJ of fuel releasing 225 g of CO_2 while conventional clinker using coal requires 2.9 MJ of fuel releasing 225–320 g of CO_2. Depending on the type of coal, the lower efficiency may result in similar emission profiles for the urea method.

II. Experimental Procedure

(1) Materials

The calcium, silicon, and aluminum sources used for the synthesis of belite cement clinker were two minerals from Mexico: a high purity calcite from Yucatán (close to Mérida, South of the country) and a natural zeolite (mainly clinoptilolite) from San Luis Potosí, Tadeo Concession (North of the country). For the combustion reaction, urea 99.5% (Merck, J.T.BAKER, D.F. Mexico) and hydrogen peroxide aqueous solution (30%) provided by J. T. Baker, were used.

Two series of experiments were performed depending on the particle size of the zeolite and calcite mixture. The first group was constituted by a particle size of 300 μm in an aqueous suspension (3 mL of distilled water), the (calcite: zeolite: urea) molar ratio was (0.0143: 0.000183: U) where $U = 0.0125$, 0.0333, or 0.0515 mol. To study the mineral particle size effect, the sample with $U = 0.0515$ mol was also prepared varying the mineral particle size (150, 75, or 32 μm).

Then, the second group of samples, was constituted by samples prepared at 1200°C and from a mineral particle size either of 75 or 32 μm. In this second group of samples the amount of urea was the stoichiometrical amount: 0.00416 mols. The molar ratio H_2O_2/CON_2H_4 has to be 6:2 as proposed by Jain and Adiga.[10] For comparison purposes, two samples were prepared, from mineral particle sizes of 75 or 32 μm, with the same conditions but without urea, with a calcination time of 20 min at 1200°C, samples SII-1 and SII-5, respectively.

(2) Procedure

(A) Series I Samples: Zeolite and calcite mixed with urea were suspended in water. The slurry was heated in a stove at 70°C until it was viscous. Then, it was transferred to a preheated muffle where it was maintained for 15 min. Four muffle temperatures were chosen: 500°, 1000°, 1100°, and 1200°C. Ignition was observed during this step. The sample holder was a platinium crucible; therefore, the conditions were static and different from industrial cement production, which uses a rotary kiln to provide mixing. The corresponding samples constitute the "Series I" and are described in Tables II and III.

(B) Series II Samples: The samples were prepared using urea and a liquid additive (0.0125 mol of H_2O_2 solution) was added. The preheating on the stove was initially 70°C for only 3 min and then 250°C for 2 min. The sample was, then, transferred to a preheated muffle at 1200°C for 15 min. After this thermal treatment, the sample was immediately extracted from the muffle. The corresponding samples constitute the "Series II" and are described in Table IV.

(3) Characterization Techniques

The samples were characterized by X-ray diffraction using a Bruker-AXS D8-advance diffractometer (Bruker AXS, Karlsruhe, Germany) coupled to a copper anode X-ray tube. A diffracted beam monochromator selected the $K\alpha$ radiation. The compounds present in the powdered samples were identified in the conventional way using the JCPDS files. The usual labelling for cement compounds is adopted: $C = CaO$, $S = SiO_2$, and $A = Al_2O_3$.[12,13]

The morphology of three clinkers (SII-5, SII-6, and SII-8) was studied by scanning electron microscopy using a Leica Cambridge (Leica Cambridge Ltd., Cambridge, U.K.) Stereoscan 440. The samples were coated with gold to avoid charge problems.

Table II. Samples Prepared in Aqueous Suspension (Series SI)

					Synthesis temperature (°C)		
Samples	Particle size (μm)	$CaCO_3$ (mol)	$Ca_4Al_8Si_{28}O_{72} \cdot 24H_2O$ (mol)	$CO(NH_2)_2$ (mol)	Hot stove		Muffle
SI-1	300	0.0143	0.000183	0.0125	70	250	500
SI-2				0.0333			
SI-3				0.0515			
SI-4	300	0.0143	0.000183	0.0125	70	250	1000
SI-5				0.0333			
SI-6				0.0515			
SI-7	300	0.0143	0.000183	0.0125	70	250	1100
SI-8				0.0333			
SI-9				0.0515			
SI-10	300	0.0143	0.000183	0.0125	70	250	1200
SI-11				0.0333			
SI-12				0.0515			

Table III. Samples Prepared in Aqueous Suspension (Series SI) Varying the Mineral Particle Size

					Synthesis temperature (°C)		
Samples	Particle size (μm)	$CaCO_3$ (mol)	$Ca_4Al_8Si_{28}O_{72} \cdot 24H_2O$ (mol)	$CO(NH_2)_2$ (mol)	Hot stove		Muffle
SI-12	300	0.0143	0.000183	0.0515	70	250	1200
SI-13	150	0.0143	0.000183	0.0515	70	250	1200
SI-14	75	0.0143	0.000183	0.0515	70	250	1200
SI-15	32	0.0143	0.000183	0.0515	70	250	1200

III. Results

(1) Samples of Series I (SI)

Figure 1 compares the X-ray diffraction patterns of samples SI synthesized varying the oven temperature: 500°, 1000°, 1100°, and 1200°C. For an oven temperature of 500°C, only some zeolite, calcite, and an amorphous compound (whose contribution is found in the angular interval $5<2\theta<20$ not shown in the figure) are present, although urea has reacted. Still, to identify a compound by X-ray diffraction it has to be crystalline, the crystallite size has to be >3 nm, and the amount of the compound higher than 3%. Thus, as the heat increase is instantaneous and as the temperature is maintained for a short time, the amount of CaO formed must be very small, and CaO must be only on the surface of the very large reactant particles. CaO appears at a temperature of 700°C. The reaction is fast, short, and local. If the oven temperature is $\geq$ 1000°C, the main compound turns out to be CaO. Still, in the 1100°- and 1200°C-treated samples, some calcium silicate is already formed, $CaOSiO_2$ (CS); however, belite is not obtained. Hence, the higher the temperature, the highest the amount of CS.

If the amount of urea is varied, 0.0125, 0.033, or 0.0515 mol for an oven temperature of 1200°C, Fig. 2, the X-ray diffraction patterns are rather similar. Only a small increase in CaO crystallinity is observed as the urea concentration is higher and the X-ray diffraction peaks of CS and β-C_2S also seem to be more defined. Thus, the higher the amount of urea, the better is the crystallinity.

A well-known parameter that affects clinker preparation is the particle size of the departure mineral materials. Namely, the use of nonsoluble reactants (such as carbonates) in the combustion synthesis has obvious implications on particle sizes and reaction temperature. Smaller particles should lead to better synthesis results. Higher temperatures have to be reached to decompose the larger particles of carbonate; hence, excess urea and combustion aids have to be used. This observation explains the chosen calcium carbonate amount that corresponds to a Portland clinker. Indeed, as the temperature reached is limited, the core of the calcium carbonate particles, depending on the particle size, could not react. Our purpose was to dispose of enough calcium carbonate even if the core did not react in the large particles. Then, for a constant temperature 1200°C and the same amount of urea, we diminished the particle size of the zeolite and calcite mixture from 300 to 32 μm, Table III. Although the X-ray diffraction pattern corresponding to the 300 μm mineral particles shows a very high amount of CaO, as the particle size is decreased the amount of β-C_2S increases. The CaO and CS concentrations become rather low in the 32 μm sample; belite (β-C_2S) is now the main compound, Fig. 3.

(2) Samples of Series II (SII)

If, as in this work, nitrates of the reactants are not available, a combustion aid is recommended such that an oxidation–reduction reaction increases the temperature. In this work, we have mixed H_2O_2 to urea Table IV. Excess urea and combustion aids have to be used to reach the high temperatures required to decompose calcium carbonate. If urea is added to this formula in an aqueous suspension, and in 200% excess, the belite cement clinker compounds, β-C_2S, C_3S, and $C_{12}A_7$ (mayenite), appear. Instead, if H_2O_2 is added but the amount of urea is not enough (just stoichiometrical), the main compound is CaO. The best composition is reached with a high amount of urea (200% in excess) and H_2O_2, as shown by Burgos-Montes *et al.*[4,5] Note that in this sample the amount of CaO is very low. Two particle sizes were tried (75 and 32 μm), the oven temperature was always 1200°C, and the urea amounts were 0.0125 and 0.00416 mol. Figures 4 and 5 show that the additive effect is crucial to obtain belite. The comparison of both figures shows, again, that a small particle size favors belite production.

Let us focus on the samples prepared from the 75 μm mineral particles, Fig. 4. The first diffractogram corresponds to a sample prepared for comparison purposes (SII-1), i.e., without urea or H_2O_2. As expected, only CaO is obtained.

If the same samples are prepared starting from a smaller mineral particle size of 32 μm, the corresponding diffractograms, Fig. 5, follow the same trend but the reactions go further, i.e., the amount of belite obtained in the last preparation (200% of urea in excess, 32 μm, 1200°C, and addition of H_2O_2) is the highest, and actually it is the main compound. Some alite (C_3S), gehlenite (C_2AS), and mayenite ($C_{12}A_7$) are also found. Note that the reference sample SII-5, in this case, although it contains a high amount of CaO, it also shows belite and some alite. The series II samples all show an amorphous percentage, X-ray diffraction background line enhanced in the angular interval of 5–20° (2θ), which is higher in the SII-5 sample than in the combustion prepared materials.

The morphology of the calcined sample (SII-5) is rather homogeneous as the globular particles are all *ca.* 1 μm, Fig. 6. From the X-ray diffraction patterns, we know that the sample is

Table IV. Samples Prepared with Urea and H_2O_2 as Combustion Aids (Series SII)

Samples	Particle size (μm)	Φe	$CaCO_3$ (mol)	$Ca_4Al_8Si_{28}O_{72} \cdot 24H_2O$ (mol)	$CO(NH_2)_2$ (mol)	H_2O_2 (mol)	T. synthesis muffle (°C)
SII-1	75	—	0.0143	0.000183	—	—	1200
SII-5	32	—					
SII-2	75	—	0.0143	0.000183	0.0125	—	1200
SII-6	32	—					
SII-3	75	1	0.0143	0.000183	0.0041	0.0125	1200
SII-7	32	1					
SII-4	75	0.59	0.0143	0.000183	0.0125	0.0125	1200
SII-8	32	0.59					

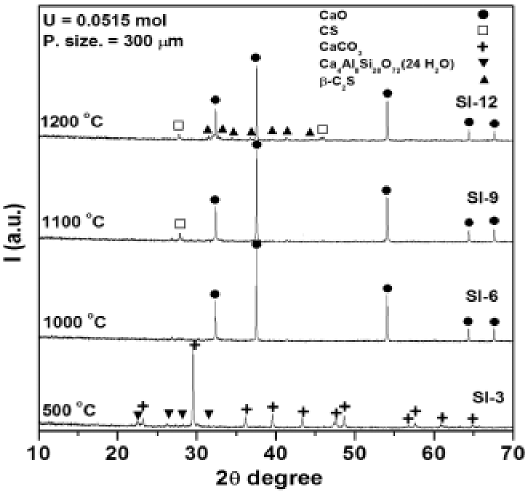

Fig. 1. X-ray diffraction patterns of the samples obtained at different muffle temperatures using a constant amount of urea (0. 0515 mol).

mainly constituted by CaO; thus, the observed particles should correspond to that composition. Instead, the combustion sample (SII-6) is heterogeneous. It is constituted by a smooth surface partially covered by small particles *ca.* 0.5 µm, similar to those observed in the SII-5 sample. Therefore, these small particles are most probably CaO and the smooth surfaces can be compared with those reported by Kacimi *et al.*[14] Large craters around 3.0–7.0 µm probably due to gas bubbles are observed. If H_2O_2 is added to the combustion mixture (sample SII-8), again the surface is covered by agglomerates of small particles of 0.5–1.5 µm, and no craters are observed, only cracks, Fig. 6. The comparison with the belite clinkers reported by Kacimi *et al.*[14] shows the same size of belite agglomerates.

IV. Discussion

In samples of Series I, the heat has to diffuse to the core of the particle, then the smaller the particle the higher is the area exposed to temperature and the thermal diffusion phenomena are reduced. The results obtained with urea only, were very encouraging as with a muffle temperature of 1200°C for 15 min and a cooling time of 25 min the reaction of minerals was obtained. Other authors report thermal treatments of 900°C for 30 min followed by 15 min at 1325°C.[13] In the cement industry, minerals are treated at 1260°–1330°C to obtain a ferrobelite clinker.[15] The heating rate is usually 10°C/min up to 1450°C, and this temperature is maintained for 1 h.[16]

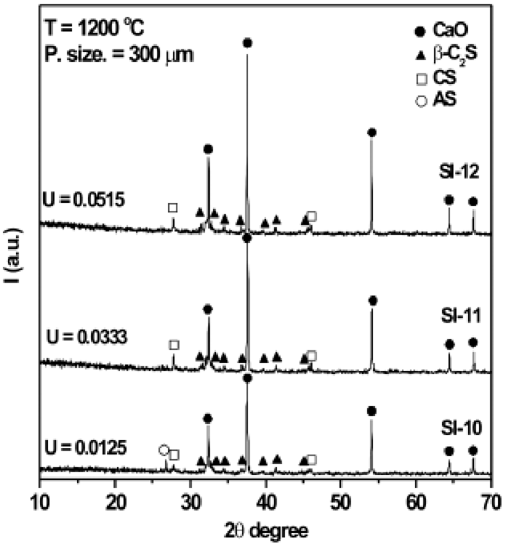

Fig. 2. X-ray diffraction patterns of the samples obtained with different amounts of urea maintaining a constant muffle temperature (1200°C).

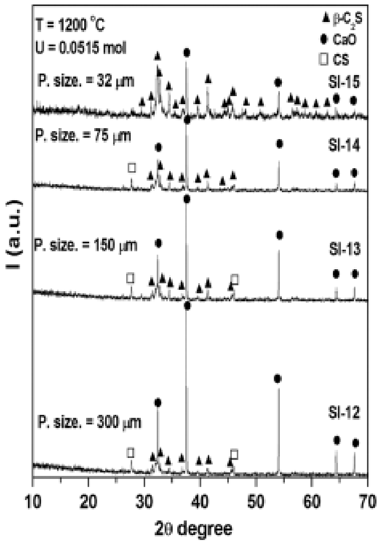

Fig. 3. X-ray diffraction patterns of the samples obtained varying the mineral particle size for 1200°C and 0.0515 mol of urea.

It has to be emphasized that the best cement clinker obtained in this work was from the 32 µm mineral particles mixed with urea (200% in excess) and H_2O_2 (stoichiometric amount) at 1200°C (Series II). Note that this sample contains mayenite ($C_{12}A_7$) and gehlenite (C_2AS). The first compound has been reported by Taylor,[12] Tas,[17] and Fumo *et al.*[7] This compound is highly recommended at low percentages as it provides a fast setting; mayenite is, indeed, hydrated easily. Gehlenite contributes to enhance the mechanical properties of cement mixtures.[18,19] Therefore, the method proposed in this work to synthesize belite cement clinker through a modified combustion method, using urea and H_2O_2, provides a temperature close to 1300°C due to the compounds formed; the resulting cement clinker contains belite, alite, mayenite, and gehlenite. Although some CaO is still observed, most probably this amount can be reduced diminishing the mineral particle size; the temperature

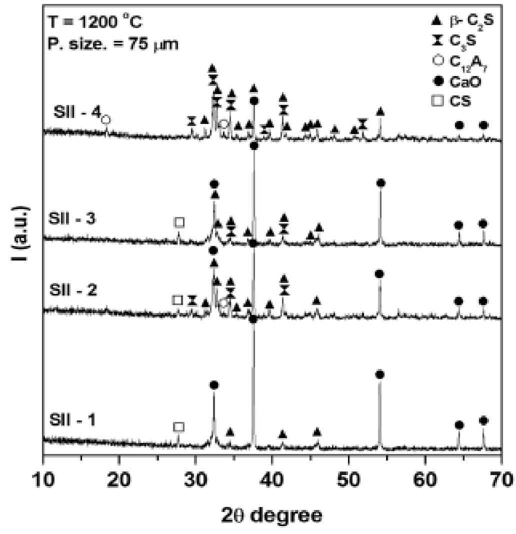

Fig. 4. X-ray diffraction patterns of the samples prepared with H_2O_2 (series SII) for a mineral particle size of 75 µm. SII-1: Sample prepared without urea. SII-2: Sample prepared with urea (200% in excess). SII-3: Sample prepared with urea and H_2O_2 (stoichiometrical amount). SII-4: Sample prepared with urea (200% in excess) and H_2O_2 (stoichiometrical amount). SII, Series II.

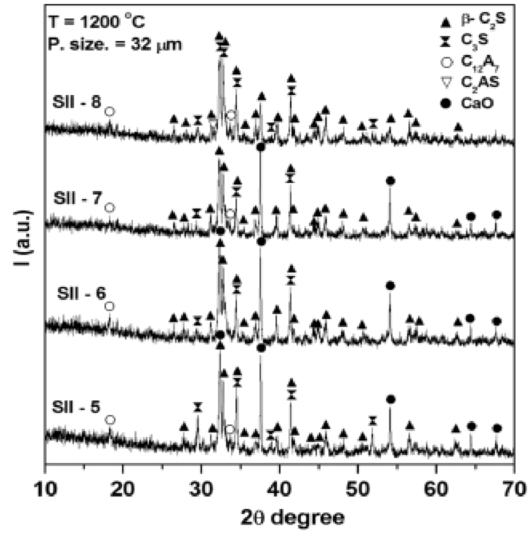

Fig. 5. X-ray diffraction patterns of the samples prepared with H_2O_2 (SII) for a mineral particle size of 32μm. SII-5: Sample prepared without urea. SII-6: Sample prepared with urea (200% in excess). SII-7: Sample prepared with urea and H_2O_2 (stoichiometrical amount). SII-8: Sample prepared with urea (200% in excess) and H_2O_2 (stoichiometrical amount). SII, Series II.

reached instantaneously seems to be high enough to synthesize a belite clinker.

The lime saturation factor (LSF) can be estimated[12] and it turns out to be 88%, which is close to the 84% usually reported for belite clinkers. Note that, in our case, no Fe_2O_3 was obtained as the zeolite did not contain iron. In a Portland cement, the LSF is 96%. Two features have to be emphasized, on the one hand, the level (16.3%) of $(CaO)_3Al_2O_3$ is high, the normal value being 10% and, on the other, no calcium aluminoferrite can be reported.

The morphology and the particle size, in the combustion prepared clinker, vary depending on the addition of H_2O_2. The compound obtained with urea and H_2O_2 shows the crucial effect of the additive. No more CaO is observed and, therefore H_2O_2 acts with urea and increases temperature. Particles of belite, alite, calcium aluminate, or gehlenite are, then, formed.[20]

In our previous work,[9] ammonium nitrate was the additive used. The clinker obtained contained slightly more C_3S and C_2S, whereas the clinker synthesized with H_2O_2 in the present work contained more $C_{12}A_7$ and C_2AS. Strength should be better in the ammonium nitrate prepared clinker but the second clinker should be more reactive due to the composition obtained. The differences in composition may be attributed to the standard reduction potential of additives as shown by Burgos-Montes *et al.*,[4,5] who report that for NH_4NO_3 and H_2O_2, it is 0.957 and 1.776 eV, respectively. Therefore, the addition of NH_4NO_3 provides an oxidizer almost twice as powerful as H_2O_2. If the enthalpies are compared, the NH_4NO_3 enthalpy ($\Delta H_{\mathrm{UN}} = -214.320$ kcal) is 20% lower than the H_2O_2 enthalpy ($\Delta H_{\mathrm{UH}} = -168.64$ kcal).

V. Conclusion

The synthesis method of belite cement clinker through a combustion-modified procedure proposed in the present work is new. The clinker obtained fulfills the composition of a belite clinker. The reactants have to be heated 5 min in a stove (70°C for 3 min and 250°C for 2 min) and in an oven at 1200°C for 15 min. These thermal treatments, compared with those found in the literature,[21] correspond to the lowest reported temperatures, 100°C lower,[15] to obtain belite cement clinker. The heating time is the shortest ever experimented for such temperature. Another advantages of the method are the simplicity and the use of Mexican natural resources. Still, the reported method has only been tested at a laboratory level.

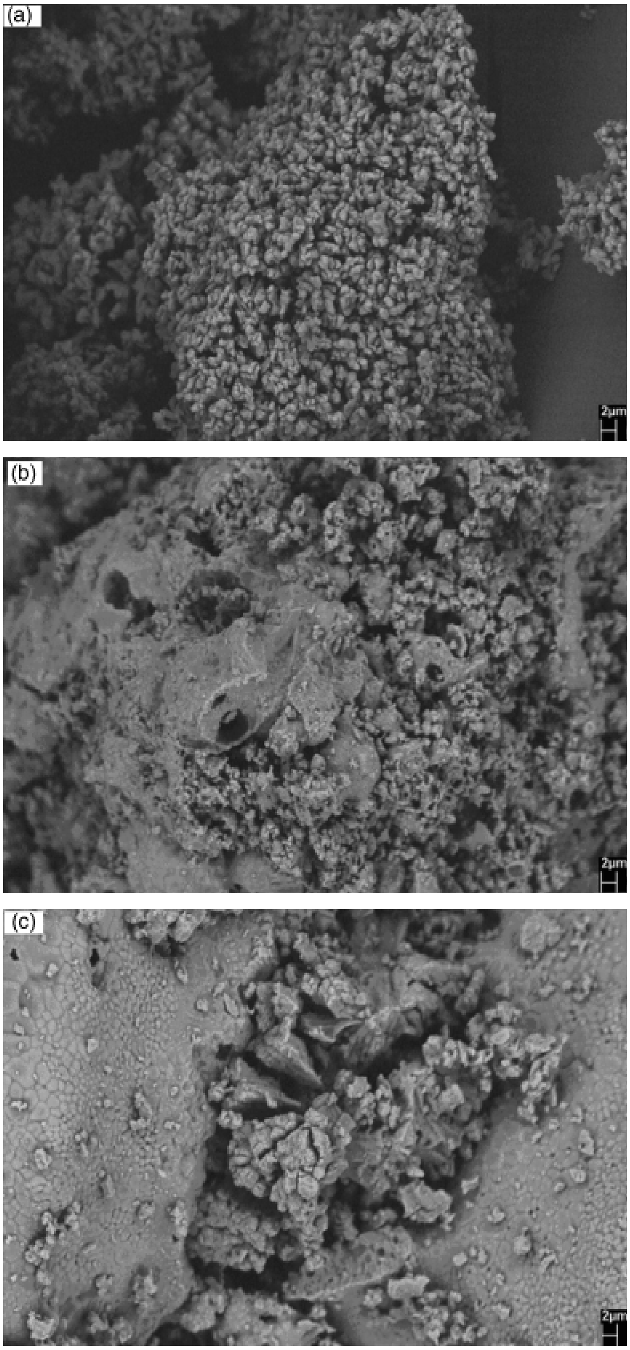

Fig. 6. Scanning electron microscopic images of the samples: (a) SII-5, (b) SII-6, (c) SII-8. SII, Series II.

Acknowledgments

The helpful discussions with Heriberto Pfeiffer, Cristina Piña, Enrique Lima, Silvia Bulbulian, and Marilú Chávez and the technical work of Lety Baños and Omar Novelo are gratefully acknowledged.

A. Zapata is grateful to Adriana Camino, Julio García Bautista, José Luis Bahena, and Guillermo Herrera Pérez for their help.

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