Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 29 (2009) 1879–1885

www.elsevier.com/locate/jeurceramsoc

Low temperature preparation of belitic cement clinker

Aída Zapata*, Pedro Bosch

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México, D.F., Mexico

Received 12 September 2008; received in revised form 3 November 2008; accepted 5 November 2008
Available online 18 December 2008

Abstract

Cement clinker production is a slow process as raw materials have to be treated at 1350–1450 °C. Several modifications to the conventional procedure have been proposed to improve the production process. In this work, we synthesize a Portland belitic clinker from calcite and natural zeolite. The preparation through the conventional thermal treatment is compared to the material synthesized by a modified combustion method. This procedure, using urea and ammonium nitrate, reduces drastically calcination time and temperature. The particle size effect of the initial minerals is discussed. The compounds were identified by X-ray diffraction and scanning electron microscopy.

Keywords: Cement; Mortar; Clinker; Urea; Combustion; Al_2O_3; Silicate; Calcite; Zeolite; Ammonium nitrate; Aluminate

1. Introduction

Portland cement is conventionally made by heating a mixture of limestone and clay, or other materials of similar bulk composition and sufficient reactivity, ultimately to a temperature of about 1450 °C.[1] Cement industry contributes about 5% to global anthropogenic CO_2 emissions, making the cement industry an important sector for CO_2-emission mitigation strategies. CO_2 is emitted from the thermal treatment of limestone, from combustion of fuels in the kiln, as well as from power generation.[2] Many methods to increase energy efficiency, such as optimization of the clinker cooler, a more efficient preheating, better burners as well as process control and management systems, have been suggested.[2] These improvements are only modifications of the conventional preparation method.

An original approach is to try to obtain the cement clinker applying the new synthesis methods for ceramics. In this sense, combustion synthesis seems to be very promising. Indeed, combustion synthesis[3] has emerged as an important technique for the preparation and processing of advanced ceramics, it is an attractive method to manufacture technologically useful materials rapidly and at lower costs if compared to the conventional ceramic synthesis processes. Another advantage of combustion synthesis is the use of relatively simple equipment.

This method, through a redox reaction, produces oxides in a very short reaction time, less than 5 min.[4] Aqueous solutions containing stoichiometric amounts of the respective metal nitrates (oxidizers) and fuels like urea are mixed and heated. Fuels as carbohydrazide, citric acid, glycine nitrate among others may be used in the synthesis of a variety of single and mixed ceramic oxides. Still, these fuels differ in their reducing power. Urea is the most convenient as it produces the smallest volume of gases (4 mol/mol of urea), it is readily available commercially, it is economical, and, of course, it generates a very high temperature.[5]

Still, the combustion synthesis may occur either not only in liquid phase, *i.e.* solution combustion (SC) but also in solid state phase, *i.e.* solid state combustion (SSC). In the SSC, initial reactants, intermediates, and final products are all in the solid state, and the solid reactant combustion follows a self-propagating high temperature synthesis. Fumo et al. have reported the combustion synthesis of calcium aluminates from the corresponding metal nitrates.[6] Chong Chen et al. have studied the low temperature combustion synthesis of alumina.[7]

However, it is not always easy to obtain the corresponding metal nitrates. Furthermore, the reaction is complex as the role of atmospheric oxygen cannot be neglected.[6–8] If no nitrates are available, as when silicon oxidizer nitrate is needed, oxygen from air can be considered as an external oxidant agent.[9]

---

* Corresponding author.
E-mail address: aidazapata@hotmail.com (A. Zapata).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.11.004

Thus, the very exothermic combustion of the fuel with air can be used to raise temperature and synthesize ceramics even from other compounds than nitrates.[10] To reach a higher temperature, ammonium nitrate or oxygenated water can be added.[11] These procedures should reduce, on the one hand, temperature as well as heating time in processes as important as the already mentioned clinker production in cement industry.

In this work, we present the synthesis of belite Portland clinker through the use of a modified combustion method inspired in the protocol reported in previous works.[9–13] Our purpose is to obtain the di- and tri-calcium silicates which are the main components of belitic cement clinker through the modified SSC method from natural zeolite and calcite.

2. Experimental procedure

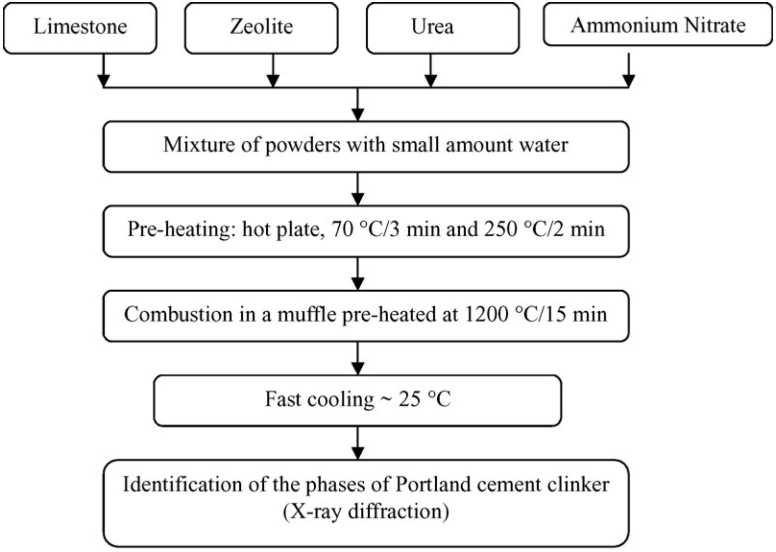
2.1. Materials

Two natural Mexican minerals were used as reactants. On the one hand, calcite, from a zone close to Mérida, Yucatán, was chosen as calcium source and, on the other, zeolite from San Luis Potosí as a source of silicon and aluminum.[14,15] The calcite is pure $CaCO_3$ as determined by X-ray diffraction. Zeolite from San Luis Potosí (Tadeo Concession), kindly supplied by Dr. Krason, is constituted mainly by clinoptilolite. Urea was provided by Merck, 99.5% purity $CO\ (NH_2)_2$.

As reference for the scanning electron microscopy study, two industrial samples of cement were chosen. They are Portland cements: *cemento Portland ordinario* and *cemento blanco*, both from CEMEX.

2.2. Procedure

Calcite and zeolite were ground. The minerals were mixed with urea and ground again. Ammonium nitrate was added at this step. A minimum amount of water was then added and the mixture was deposited in a platinum crucible, the mixture was heated in a plate for 3 min at 70 °C, then for 2 min at *ca.* 250 °C. The resulting compound was beige humid and homogeneous. It was, then, introduced in a preheated muffle at 1200 °C, the flame was small and depending on the amount of ammonium nitrate a high amount of gases was observed. After 15 min, the sample was cooled outside the muffle and powdered to be characterized, the following schema summarizes the procedure.



Schema summarizing the SS preparation of Portland Cement Clinker

The relative amount of each reactant was determined from the global reaction between calcite and zeolite:

$$\begin{aligned}&78CaCO_3 + Ca_4Al_8Si_{28}O_{72}\cdot 24H_2O\\&\quad \rightarrow 14(CaO)_3SiO_2 + 14(CaO)_2SiO_2 + 4(CaO)_3Al_2O_3\\&\qquad + 24H_2O + 78CO_2\end{aligned} \tag{1}$$

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. 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 close to Ca/Si = 3. Note that in the zeolite a high amount of calcium is already present (zeolite Ca/Si = 0.14). In this work, we prepared samples with a calcite:zeolite molar ratio of 78:1.

At 25 °C, the reaction between zeolite and calcite requires a reaction enthalpy of $\Delta H_r = 2955$ kcal/mol of zeolite. Instead, at 1450 °C the ΔH_r turns out to be 7593 kcal/mol.[16,17] As the ΔH_r/mol of urea combustion with air is −129.9 kcal/mol of urea at 25 °C, the required amounts of calcite, zeolite and urea can be calculated.

To increase temperature, we used urea mixed to ammonium nitrate, as it has been already reported, for the synthesis of mullite.[10] The redox reaction between urea and ammonium nitrate is:

$$CO(NH_2)_{2(s)} + 3NH_4NO_{3(s)} \rightarrow CO_{2(g)} + 8H_2O_{(g)} + 4N_{2(g)} \tag{2}$$

Table 1
Sample labeling and preparation conditions (mineral particle size of 32 μm).

Sample	Calcite (mol)	Zeolite (mol)	Urea (mol)	Ammonium nitrate (mol)	Φ_e	Muffle temperature (°C)
C78U68	0.00977	0.000125	0.0085	0.0085	0.66	1200
C78U176	0.00977	0.000125	0.0220	0.0220	0.66	1200
C78U68H	0.0143	0.000182	0.0125	0. 0125	0.66	1200
C78U176H	0.0143	0.000182	0.0320	0.0320	0.66	1200

Table 2
Samples prepared from a mineral particle size of 75 μm.

Sample	Calcite (mol)	Zeolite (mol)	Urea (mol)	Ammonium nitrate (mol)	Φ_e	Muffle temperature (°C)
C78U68L	0.0143	0.000182	0.0125	0.0125	0.66	1200
C78U176L	0.0143	0.000182	0.0321	0.0321	0.66	1200

with a $\Delta H_r = -214.461$ kcal at 25 °C. Note that, in such reaction, no nitrogen oxides are obtained.[6,7] 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 were based on the assumption that the nitrogen species in the product has a valence of 0. Still, some authors suggest that it may not be always the case, making the calculation of stoichiometric amounts difficult.[18]

In all samples, the molar ratio urea to ammonium nitrate was 1.00, an urea excess of 200% was used as suggested by Burgos-Montes et al.[19] The parameter Φ_e, defined as the elemental stoichiometric coefficient, correctly predicts whether a mixture is fuel lean, fuel rich, or stoichiometrically balanced.[20] In our experiments, $\Phi_e = 0.66$ was maintained constant. As in practice the thermodynamical conditions may be hard to obtain, the relative amounts of urea to zeolite were varied in order to optimize the clinker production.

Two samples were prepared with a ratio urea/zeolite equal to 68.68 and the other two with 176.00. The samples were labeled with the letter C indicating that the following number is the ratio calcite/zeolite (78.0) and U followed by the ratio urea/zeolite (either 68.7 or 176.0). Then the sample C78U68.7 was prepared with a calcite/zeolite ratio of 78 and a urea/zeolite ratio of 68.7. The resulting molar values used in the synthesis and sample labeling are presented in Table 1. The samples with the same relative amounts but prepared with higher amount of reactants (1.5 times) have the letter H at the end. For comparison purposes a sample (CONV) was conventionally prepared treating at 1200 °C for 15 min the mixture of 0.00977 mol of calcite and 0.000125 mol of zeolite, of course no fuel was added.

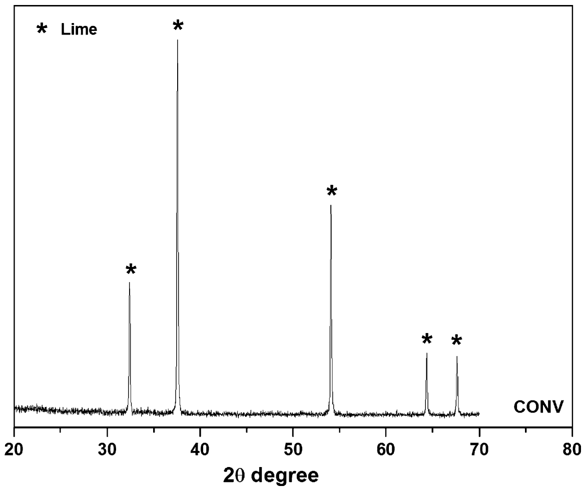


Fig. 1. X-ray diffraction pattern of the CONV sample.

All the previous samples were prepared grinding the initial minerals to reach a particle size of (32 μm). Two more samples were prepared from minerals with a larger particle size (75 μm). The labeling is the same used for the previous samples, only the letter L was added at the end to show that they were prepared from larger mineral particles. The synthesis conditions of these samples are presented in Table 2.

2.3. Characterization techniques

All samples were characterized by X-ray diffraction and scanning electron microscopy. A Bruker-axs D8-advance diffractometer coupled to a copper anode X-ray tube was used to identify the compounds present in the powdered samples. A diffracted beam monochromator selected the Kα radiation. The used electron scanning microscope was a Leica Cambrige modelo Stereoscan 440. The samples were covered with gold to avoid charge problems. To study the thermal behavior of calcite, zeolite and urea a thermal gravimetric analysis (TGA) was made in air atmosphere with a heating rate of 10 °C/min. A TA Instruments, model 2950 was utilized.

3. Results and discussion

Fig. 1 presents the X-ray diffraction pattern of the conventionally prepared sample, CONV, from a mineral particle size of 75 μm. Only lime (CaO) was obtained. The peaks are sharp and intense showing that the compound is highly crystalline. No other crystalline compounds of silicon or aluminum are found. Then, silicon and aluminum form amorphous compounds whose presence is revealed by the background line which, in the interval 6–30° (2θ), is not flat.

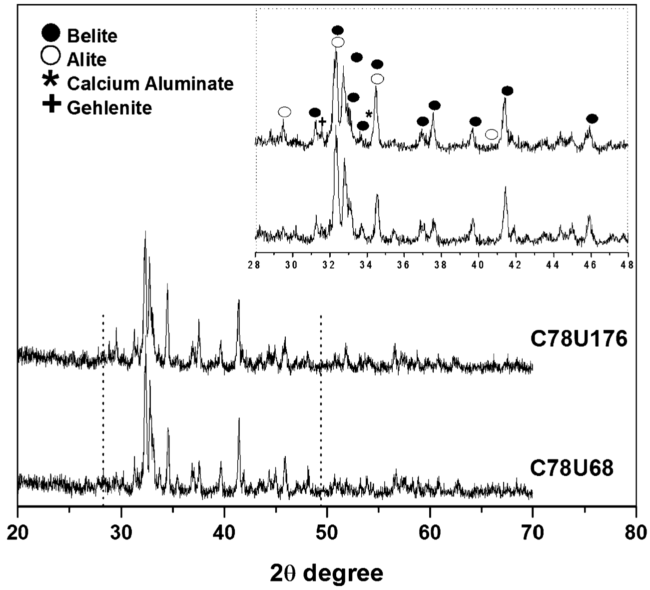


Fig. 2. Comparison between the X-ray diffraction patterns of samples C78U68 and C78U176.

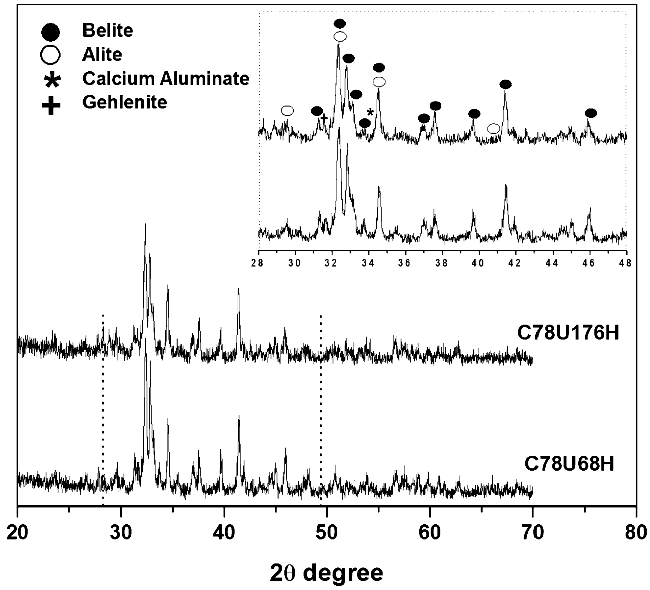


Fig. 3. Comparison between the X-ray diffraction patterns of samples C78U68H and C78U176H.

Sample C78U68 was prepared through the modified combustion method with urea and ammonium nitrate. The corresponding X-ray diffraction pattern shows that the obtained main compound is belite (Ca_2SiO_4), alite (Ca_3SiO_5), calcium aluminate ($Ca_{12}Al_{14}O_{33}$) and some gehlenite $Ca_2(Al(AlSi)O_7)$, are also present. It has to be emphasized that no lime was identified.

If the ratio urea to zeolite is increased, sample C78U176, the previous composition is almost reproduced, only the relative amount of alite has slightly decreased (Fig. 2).

These two samples were prepared again using large amounts of materials (1.5 times) but using the same relative amounts, samples C78U68H and C78U176H. The purpose was to determine if there were some differences due to new thermal gradients. In sample C78U68H the relative amount of alite is higher than in C78U176H, in agreement with the previous results, showing that an excess of carburant inhibits the alite formation (Fig. 3). Fig. 4 compares the X-ray diffraction patterns of samples C78U68L and C78U176L. These two preparations are very similar.

To study the particle size effect of the raw materials on the synthesized clinker, two more experiments were performed in the same conditions. The particle size was now 75 μm instead of 32 μm (Table 2). Again, the main compound was belite and some small amounts of alite and calcium aluminate but no gehlenite were found. The main difference due to particle size seems to be the amount of amorphous material, *i.e.* the shape of the background line and some CaO. These two samples contain more non crystallized material. Again the relative content of alite is higher in the sample prepared with a lower amount of fuel.

Scanning electron micrographs of the synthesized clinkers and reference Cemex cements are shown in Fig. 5. In the sample synthesized at 1200 °C with 200% urea excess and ammonium nitrate needle and platelet like particles, irregular particles and some bubbles due to gas escape are observed. Instead, the clinker synthesized without ammonium nitrate is mainly constituted by agglomerates of variable size. As expected, if neither urea nor ammonium nitrate were used, the morphology turns out to be definitely different, particles are globular and they associate to form large agglomerates. Two more micrographs are included they correspond to industrial Portland white cement produced by Cemex. These materials present larger particles and seem more homogeneous as they contain also gypsum, it is a finished product.

Fig. 6 compares the TGA curves of urea, zeolite and calcite. The decomposition of urea starts at 177 °C, whereas the zeolite looses weight continuously up to 300 °C, such losses are due to water elimination. Calcite disintegrates at 700 °C whereas

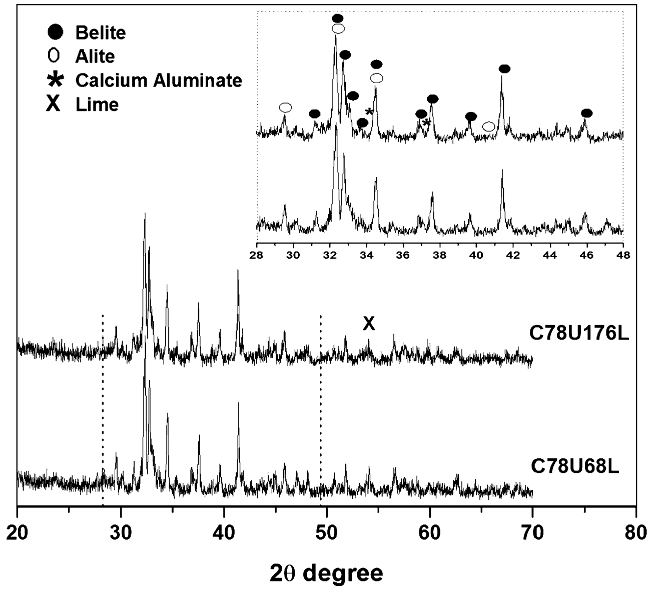


Fig. 4. Comparison between the X-ray diffraction patterns of samples C78U68L and C78U176L.

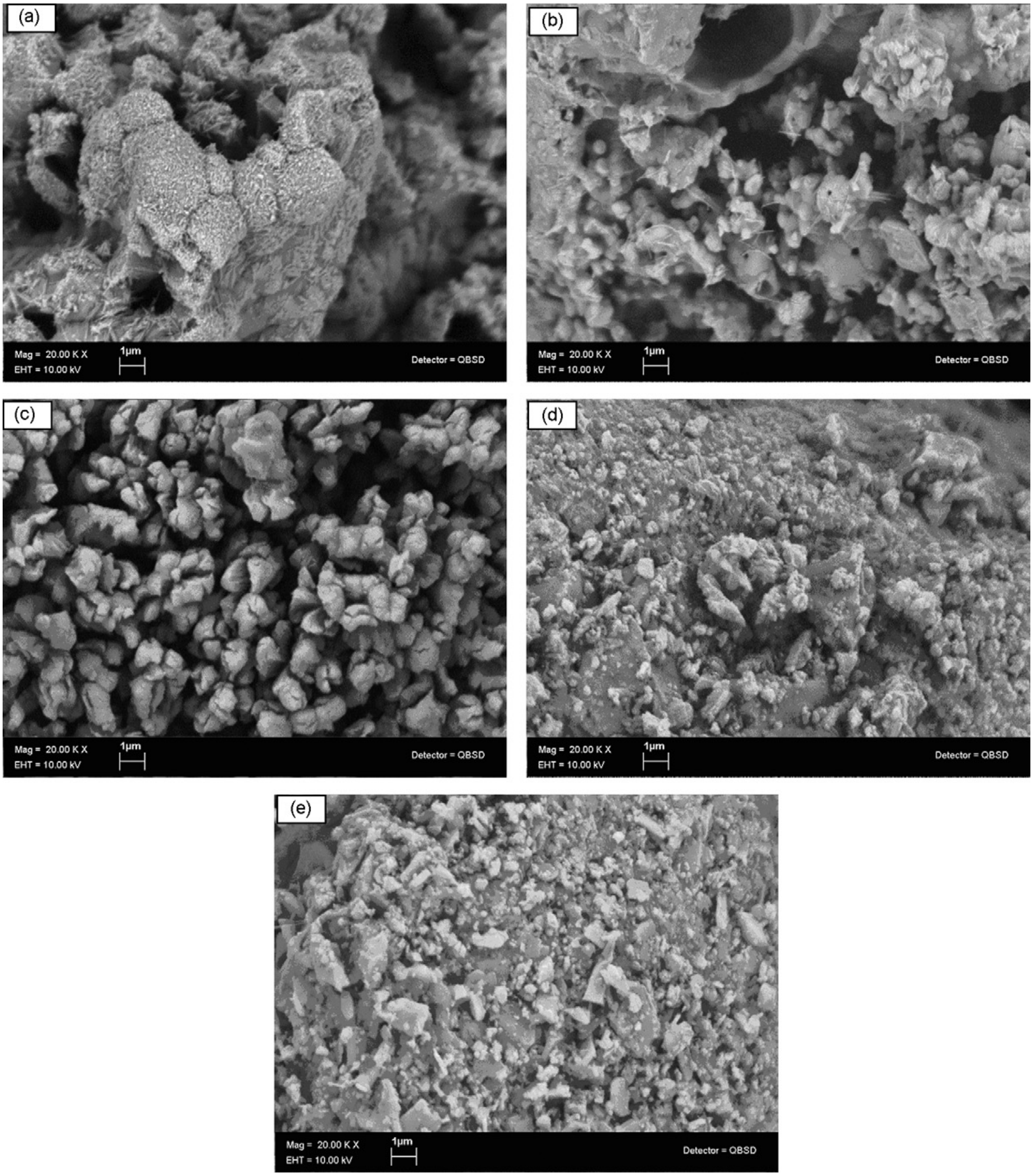


Fig. 5. SEM images of belitic cement clinker (a) synthesized employing urea 200 wt.% over the stoichiometric and ammonium nitrate as combustion aids, (b) synthesized using urea 200 wt.% over the stoichiometric, (c) synthesized without urea and without ammonium nitrate, (d) and (e) SEM images of two industrial cements.

ammonium nitrate at 210 °C.[21] Therefore, most probably, the reaction sequence is urea, ammonium nitrate, zeolite decomposition, and calcite decomposition to react and form other compounds.

Our results show that belite clinker may be prepared from a mixture of natural zeolite as aluminum and silicon source and calcite as calcium provider. If the clinker is prepared by the modified combustion method, the muffle preparation temperature is 1200 °C instead of the usually accepted 1360 °C.[22] With both particle sizes (32 and 75 μm) of the raw materials, the belitic clinker was obtained although the small amount of residual lime varied, if the particle size was 32 μm no lime was identified; still, in this sample some gehlenite was obtained. This method is simple and fast as only one preheating step is required (70 °C/3 min and *ca.* 250 °C/2 min on a plate) before introducing the sample into the muffle at 1200 °C.

It is interesting to note that although many works have reported the synthesis of some compounds present in cement as calcium aluminates,[6] the used combustion method requires nitrates which are not easily available. Our method is original

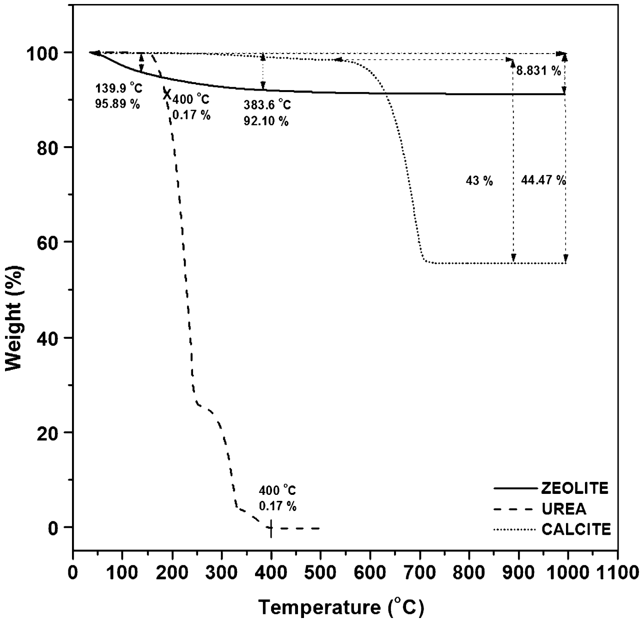


Fig. 6. TGA curves from zeolite, calcite and urea.

Table 3
Values of formation enthalpy of the involved compounds[1,16,17,29].

Compound	ΔH_f° at 25 °C (kcal mol^{-1})
$Ca_4Al_8Si_{28}O_{72}\cdot 24H_2O(s)$	−10147.32
$CaCO_3(s)$	−288.45
$CO(NH_2)_2(c)$	−79.71
$NH_4NO_3(s)$	−87.46
$(CaO)_3SiO_2(s)$	−700.57
$(CaO)_2SiO_2(s)$	−551.87
$(CaO)_3Al_2O_3(s)$	−858.34
$CO_2(g)$	−94.05
$H_2O(g)$	−57.80
$N_2(g)$	0
$O_2(g)$	0

and new as it proposes a modified combustion method which provides a clinker as good as the one prepared by De La Torre et al.[22], Trezza and Scian,[23] Popescu et al.[24] The lowest reported temperature is 1260–1300 °C with time treatments from 15 min to 1 h,[22,24] instead we obtained belitic clinker in one step at 1200 °C for 15 min. Other authors have proposed different methods to reduce treatment time and temperature. Hui Huang et al. have prepared nanocrystals of β-dicalcium silicate through a sol–gel and autocombustion method which reduced treatment time to 4 h and temperature to 650 and 1100 °C.[25] Rodriguez reports on cement synthesis of various chemical compositions adding rice hull ash at 600, 800 and 1000 °C under sonication with 2% and 3% of Ba.[26] The modified combustion method is, then, new and most promising as savings in external energy consumption should be significant. Furthermore, it provides a simple alternative to other elaborate and conventional methods.

The composition of the combustion prepared belitic clinker depends on the amount of fuel and on the raw material particle size. If the belitic clinker can accept some lime, the raw material particle size can be larger. The typical size for raw materials for the conventionally prepared clinkers is around 90 μm.[1] The comparison of the results obtained with the two particle sizes of the raw materials shows the presence of diffusion effects due, essentially, to temperature gradients. Lime begins to be formed at 800 °C and decomposes at 1350 °C.[1] Therefore, in the core of large particles, temperature reaches a value close to 1100 °C where lime is stable. Instead, if particles are small, no lime is observed and temperature seems to be the same in the core as in the particle surface. In small particle synthesis, no lime is found whereas some gehlenite seems to be present, showing that temperature reached at least 1350 °C in the whole particle.

If the amount of fuel is not enough or is too much the obtained clinker has a different composition, results not reported here. The use of a combustion aid is essential as it reduces the temperature of the reaction by *ca.* 150 °C although more gases are produced.[22]

Our experiments with higher amounts of raw materials show that the obtained clinker has a similar composition. Therefore, there is no diffusional effect or any other effect on the resulting compounds. Thus, fuel acts in the same way even if it is occluded into the high mass of the reactants; there are no hot points or no trapping of gases which diffuse easily.

Last but no least, some simple considerations on the energy required in this process can be made. The energy for the clinker production can be determined from the formation enthalpy at 25 °C (Table 3).[1,2] The energy to produce conventionally (calcination method) a kilogram of clinker is about 422 kcal. This estimation does not include energy losses due to radiation and convection, water evaporation, outgases and dust, losses in the cooler among others which may increase this value up to 3043 kcal if the process is dried with preheaters and precalciner.[27] Following the same procedure the energy to produce a kg of clinker through the combustion method turns out to be 433 kcal. Although the value obtained in the combustion synthesis is larger than the value obtained through the conventional method, it has to be emphasized that the synthesis temperature is diminished. Indeed, it is reduced 250 °C. The preparation time is only 25 min. The energy losses which increase enormously the conventional synthesis are very much reduced in the proposed combustion method. Lastly, the required equipment is much simpler and the industrial reactants are rather economical: ammonium nitrate price is 302.4 $ per ton and urea is 325 $ per ton in 2007.[28]

4. Conclusions

We have shown that belitic clinker can be obtained through a modified combustion method which reduces the temperature synthesis to *ca.* 1200 °C. In this way the preparation of the clinkers turns out to be 25 min starting from the grinded raw materials. Natural zeolite from San Luis Potosí and calcite from Yucatán are appropriate to synthesize belitic clinker. If the particle size is 75 μm a small amount of lime is observed, instead if the particle size is 32 μm no CaO is found.

The samples were prepared with urea and ammonium nitrate; 200% excess of urea and a very small amount of water provided the best clinker with a preheated muffle at 1200 °C. Only a pretreatment on a plate was necessary (70 °C for 3 min and *ca.* 250 °C for 2 min) and 15 min in the oven. Last but not least, the equipment was very simple.

Acknowledgements

The helpful discussions with H. Pfeiffer, C. Piña, E. Lima, S. Bulbulian and M. Chávez and the technical work of L. Baños, Esteban Fregoso and José Guzmán are gratefully acknowledged. This work would not have been possible without the financial support of the Dirección General de Estudios de Posgrado, UNAM. A. Zapata is grateful to A. Camino, J. García Bautista, J.L. Bahena, for their help.

References

1. Taylor, H. W., *Cement Chemistry*. Academic Press, London, 1990, pp. 1–32.
2. Worrell, E., Price, L., Martin, N., Hendriks, C. and Ozawa, L., Carbon dioxide emissions from the global cement industry. *Annu. Rev. Energy Environ.*, 2001, **26**, 303–329.
3. Patil, K. C., Aruna, S. T. and Mimani, T., Combustion synthesis: an update. *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 507–512.
4. Varma, H. K., Mukumdan, P., Warrier, K. G. and Damodaran, A. D., Synthesis of lithium silicate tritium breeder powders. *J. Mater. Sci. Lett.*, 1990, **9**, 377–379.
5. Fumo, D. A., Jurado, J. R. and Segadaes, A. M., Combustion synthesis of iron-substituted strontium titanate perovskites. *Mater. Res. Bull.*, 1997, **32**, 1459–1470.
6. Fumo, D. A., Morelli, M. R. and Segadaes, A. M., Combustion synthesis of calcium aluminates. *Mater. Res. Bull.*, 1996, **31**, 1243–1255.
7. Chong Chen, Ch. and Huang, K. T., Parametric effects of low-temperature combustion synthesis of alumina. *J. Mater. Res.*, 2005, **20**, 424–431.
8. Pederson, L. R., Maupin, G. D., Weber, W. J., McReady, D. J. and Stephens, R. W., Microstructure of Al_2O_3–ZrO_2 nanocomposites prepared by combustion process. *Mater. Lett.*, 1991, **10**, 437–443.
9. Cruz, D. and Bulbulian, S., Synthesis of lithium silicate tritium breeder powders by modified combustion method. *J. Nucl. Mater.*, 2003, **4**, 262–265.
10. Fei, L., Hu, K., Li, J., Zhang, D. and Chen, G., Combustion synthesis of γ-lithium aluminate by using various fuels. *J. Nucl. Mater.*, 2002, **300**, 82–88.
11. Burgos-Montes, O., Moreno, R., Colomer, M. T. and Fariñas, J. C., Synthesis of mullite powders through a suspension combustion process. *J. Am. Ceram. Soc.*, 2006, **89**, 484–489.
12. Chandran, R. G., Chandrashekar, B. K., Ganguly, C. and Patil, K. C., Sintering and microstructural investigations on combustion processed mullite. *J. Eur. Ceram. Soc.*, 1996, **16**(8), 843–849.
13. Burgos-Montes, O. and Moreno, R., Colloidal behaviour of mullite powders produced by combustion synthesis. *J. Eur. Ceram. Soc.*, 2007, **27**, 4751–4757.
14. Drag, E. B. and Krasón, J., Properties, and utilization of natural zeolites. In *Zeolite 06 – 7th International Conference on the Occurrence*, 2006, 16–21 July.
15. Drag, E. B., Kulazynski, M. and Krasón, J., Properties, and utilization of natural zeolites. In *Zeolite 06 – 7th International Conference on the Occurrence*, 2006, 16–21 July.
16. Dean, J. A., *Lange's Handbook of Chemistry*. McGraw-Hill, New York, 1979.
17. Perry, R. H. and Chilton, C. H., *Chemical Engineers Handbook*. McGraw-Hill, New York, 1975.
18. Collins, M. V. and Hirschfeld, D. A., Effects of processing parameters on properties of alumina formed by combustion synthesis of ceramics, and glasses, and composites IV. In *Ceramic Transactions*, *Vol. 115*, ed. N. P. Bansal and J. P. Singh, 2000, pp. 83–92.
19. Burgos-Montes, O., Moreno, R., Colomer, M. T. and Fariñas, J. C., Influence of combustion synthesis of mullite powders. *J. Eur. Ceram. Soc.*, 2006, **26**, 3365–3372.
20. Jain, S. R., Adiga, K. C. and Pai Verneker, V. R., A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures. *Combust. Flame*, 1981, **40**, 71–79.
21. http://www. hummelcroton.com/msds/amno3_m.html.
22. De La Torre, A. G., Aranda, M. A. G., De Aza, A. H., Pena, P. and De Aza, S., Bellite portland clinkers. Synthesis and mineralogical analysis. *Bol. Soc. Esp. Ceram.*, 2005, **44**, 185–191.
23. Trezza, M. A. and Scian, A. N., Estudio comparativo de clinkers producidos con diferentes reemplazos de combustibles residuales. *Mater. Res.*, 2003, **6**, 295–303.
24. Popescu, C. D., Muntean, M. and Sharp, J. H., Industrial trial production of low energy belite cement. *Cement Concrete Compos.*, 2003, **25**, 689–693.
25. Hui Huang, X. and Chang, J., Low-temperature synthesis of nanocrystalline β-dicalcium silicate with high specific surface area. *J. Nanoparticle Res.*, 2007, **9**, 1195–1200.
26. Rodriguez, F. A., Low-temperature synthesis of cements from rice hull ash. *Cement Concrete Res.*, 2003, **33**, 1525–1529.
27. Ozawa, L., Análisis del consumo de energía en el sector industrial Mexicano y comparaciones internacionales: industrias siderúrgica y cementera. *Tesis maestría. Universidad Nacional Autónoma de México*, 2000, **1**, 95–97.
28. Minag-Aduanas, Elaboración: AgroData-CEPES. *La revista agraria*, 2007, **82**.
29. Kiseleva, I., Navrotsky, A., Belitsky, I. and Fursenko, I., Thermochemical study of calcium zeolites – heulandite and stilbite. *Am. Mineralogist*, 2001, **86**, 448–455.