

Liquid phase sintering of CMCs based on clinker Portland

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Abstract

Portland clinker is normally used as the main component in cement manufacturing. It is a mix of different oxides and silicates suitable for the production of low cost structural ceramics. In this work, it is used as raw material in making ceramic matrix composites fit for use as structural ceramic. The sinterability of Portland clinker with different oxides (Al_2O_3 , MgO and SiO_2) and other ceramic enhancers (CaF_2) is evaluated by dilatometry and density in response to temperature. The manufacturing process includes mixing, followed by cold isostatic pressing at 180 MPa and sintering in air at temperatures between 1100 and 1420°C. At these temperatures the sintering is carried out with liquid phase, demonstrated by optical and scanning electronic microscopy (SEM). There are indications of reactivity between the base material and the additives. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In general, the sintering of ceramic materials and CMCs implies the formation of a liquid phase, only special aluminas, zirconas and SiC are sintered in solid state.¹ Liquid phase sintering (LPS) is an old technology,² used in ceramic consolidation for thousands of years, although from the engineering point of view it is considered an advanced technique. The first liquid phase sintered products were bricks. Most ceramics (traditional or advanced) are manufactured by this process: china, porcelain, abrasives, insulating, electric substrates and refractories.³

Liquid phase sintering (LPS) produces densification at temperatures lower than those of solid state sintering,³ which leads to better mechanical properties. The sintering of ceramics forms a vitreous liquid phase at the grain boundaries.^{4,5} The liquid phase can be eutectic, or by melting of some of the components, and usually it

accelerates the densification process.^{6,7} Some advantages of this process are the elimination of porosity and the high diffusion rates through the liquid phase.⁸ However, deformations of the sintered parts and differential densifications may be produced,⁹ so an extreme control of the conditions is required. Sintering maps analyse the kinetic process and predict the most adequate sintering conditions.^{10,11}

Portland clinker is defined¹² as an artificial material obtained from crudes with an appropriate chemical composition through a process called clinkering (calcinating + sintering). After the clinkering process, clinker should be milled till the appropriate particulate size and its composition is balanced to reach the standard chemical composition. Clinker is composed (by weight) of two-third parts of calcium silicates.¹³ The balance is of calcium aluminates and iron containing calcium aluminates.

The clinkering behaviour of the clinker relies on the initial raw materials, their mineralogy and particle size. The formation of the liquid phase produces an important shrinkage and microstructural changes. The formation of liquid marking the beginning of the sintering occurs between 1260 and 1310°C. At temperatures near 1450°C, the liquid phase is about 20–30% by weight, depending on the material composition (less when the

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Chemical formulas: 3 $\text{CaO}\cdot\text{SiO}_2 = \text{C}_3\text{S}$ = alite; 2 $\text{CaO}\cdot\text{SiO}_2 = \text{C}_2\text{S}$ = belite; 3 $\text{CaO}\cdot\text{Al}_2\text{O}_3 = \text{C}_3\text{A}$ = tricalcium aluminate; 4 $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 = \text{C}_4\text{AF}$ = tetracalcium ferroaluminate

silica content is higher). At the beginning of the clinking process, non-combined CaO reacts with belite (C_2S) through liquid phase to form the alite (C_3S) phase by intermediate compounds,¹⁴ which is the main objective. Concerning the reactions produced through the liquid, the diffusion mechanisms between CaO and C_2S in the melt and the extension of the liquid phase are of great importance.¹⁵

The reactions may be accelerated as the amount of liquid phase increases and its viscosity decreases. The chemical composition, particle size and homogeneity of the raw materials all affect the process.^{16,17} Components such as Al_2O_3 and Fe_2O_3 are in liquid phase at about 1400°C, while C_2S and C_3S phases are solid at this stage.

The addition of different enhancers or mineralizers has an important influence on the sintering behaviour of clinker. Rumyantsev et al.¹⁸ studied clinking using eutectics or near eutectics of low melting point. The effect of fluoride on clinking temperature^{19–21} and liquid viscosity¹⁶ has been investigated. Other additions such as Mo and W oxides, CuO,²² MgO,²³ ZnO^{21,24} or MnO₂²⁵ have influence on the microstructure of clinker phases.

A few studies of non-hydrated Portland clinker and its possible use as structural material,^{26–29} have demonstrated the presence of liquid phase during the sintering of the CMCs based on Portland clinker with Al_2O_3 and SiC, which activate the densification and therefore the mechanical properties associated to the microstructure. The ceramic behaviour of this material is excellent. It is sintered at temperatures between 1300 and 1400°C, to produce high densities near to the theoretical one.

2. Experimental procedure

The sintering behaviour of sintered clinker Portland mixed with ceramic particles is investigated by dilatometric study and sinterability curves. The composite materials are processed by powder technology methods. The Portland clinker used as base material was supplied by Portland Valderrivas, S.A. (Spain). The chemical and mineralogical compositions are as in Table 1. The average size of the Portland clinker is 27 μm with 99% of particles < 45 μm . Table 2 shows materials used as additions/enhancers: alumina, silica, magnesia and calcium fluoride.

The compositions were dry mixed in a laboratory ball mill during 30 min. In all cases three different amounts of additions (3, 6 and 9% by weight) were chosen. The different mixes were pressed by cold isostatic pressing (in wet bag) at 180 MPa.

The sintering was carried out in air at different temperatures to 1420°C during 30 min at a heating/cooling rate of 10°C/min to plot the sintering curves (sintering

Table 1
Chemical composition of Portland clinker

Chemical composition	Clinker (in weight)	Mineralogical composition	
% SiO ₂ (S)	20.24		
% Al ₂ O ₃ (A)	6.09		
% Fe ₂ O ₃ (F)	3.51	Tricalcic silicate (C ₃ S) %	63.18
% MgO	1.11	Bicalcic silicate (C ₂ S) %	12.13
% Sulphates	1.34	Tricalcic aluminate (C ₃ A) %	10.20
% CaO (total)	65.72	Tetracalcic ferrite-aluminate (C ₄ AF) %	10.68
% CaO (free)	1.21		
Fire losses (%)	0.14		
A/F rate (flux modulus)	1.47		
S/A rate (siliceous modulus)	2.17		
Standard of cal	96.90		

Table 2
Characteristics of the additives

Additives	Powder characteristics
α -Al ₂ O ₃	Purity: 99.9%; size: 99% < 2 μm ; density: 3.9 g/cm ³ ; Alcoa (Brazil)
SiO ₂	Amorphous: purity, 99%; density, 2.65 g/cm ³ ; Crosfield Chemicals (UK)
MgO	Purity: 90.0%; size 95% < 5 μm ; density: 3.6 g/cm ³ ; Panreac (Spain)
CaF ₂	Industrial grade (purity: 65.0%)

density versus temperature). Sintering densities were measured by Archimedes' method (MPIF Standard 42). Differential dilatometric studies (using alumina as reference) were made in a Bähr dilatometer (in vacuum up to 1300°C with heating and cooling rates of 10°C/mm). The dilatometric curves indicate the temperatures at which the main thermal phenomena occur: the beginning of the shrinkage, the highest shrinkage rate and the phase transformations. These data determine the sintering window.

A study by optical microscopy and SEM was made to determine the reactions between additions and base material and illustrate the sintering behaviour of the materials.

3. Results

Figs. 1–4 present the sintering behaviour of the studied materials. In all the materials, except those with CaF₂ additions, the beginning of the densification process is between 1290 and 1320°C, and maximal density around 1400°C. In materials with CaF₂ (Fig. 4), the beginning of sintering is advanced to 1310–1380°C.

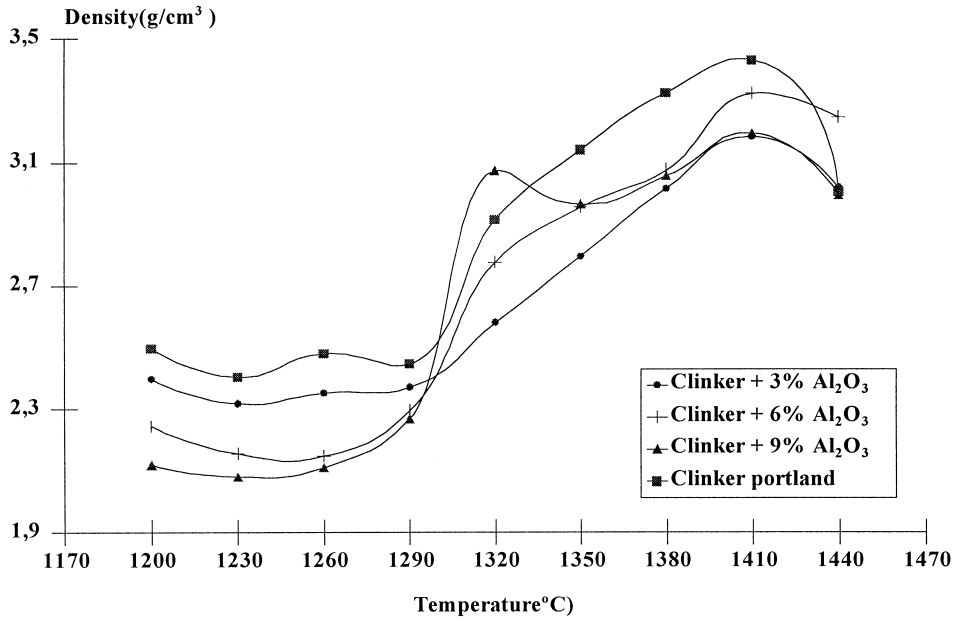


Fig. 1. Evolution of sintering density with temperature of materials with Al₂O₃ as compared with plain clinker.

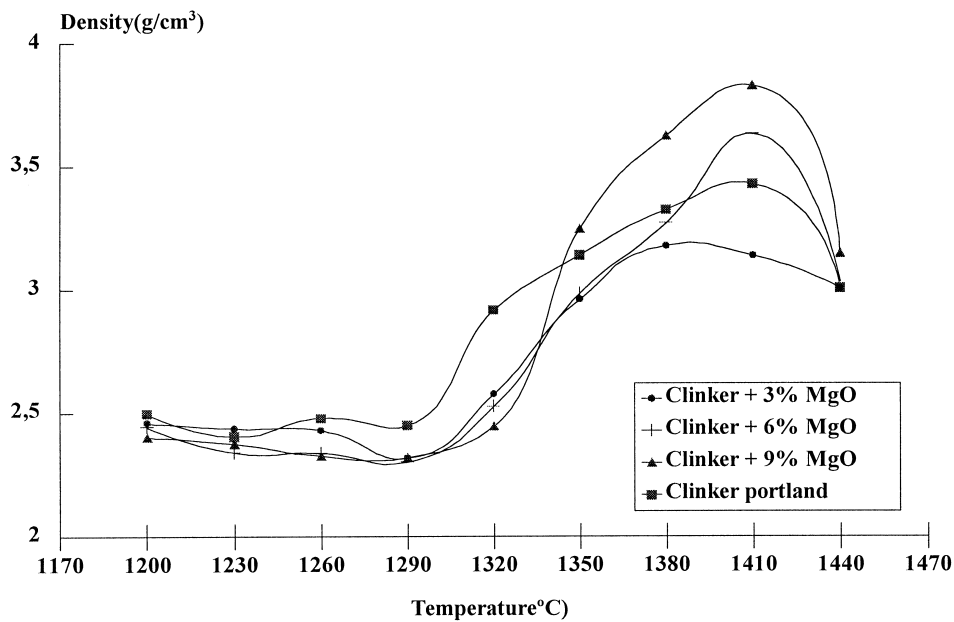


Fig. 2. Sintering density versus temperature of plain clinker compared with Portland clinker with MgO.

Fig. 5 shows the dilatometric curves obtained, with the time and the relative changes in length versus temperature. Main results are shown in Table 3.

Fig. 6 shows the microstructural evolution of materials with alumina addition, and Fig. 7 illustrates the reaction between alumina and clinker (by the results of mapping of the elements Si, Fe, Ca and Al). Fig. 8 presents the porosity evolution for materials with magnesia and Fig. 9 the reaction of this oxide with the base material. Microstructural changes in CMCs with silica are shown in Fig. 10. Fig. 11 presents the reactivity

between silica and clinker base. Fig. 12 presents microstructural evolution for materials with fluorite and Fig. 13 shows an example of acicular phases in pores in MgO composites, phenomenon that appears in all the materials.

4. Discussion

The sintering process of clinker with different additives is explained by its thermal behaviour. Densification

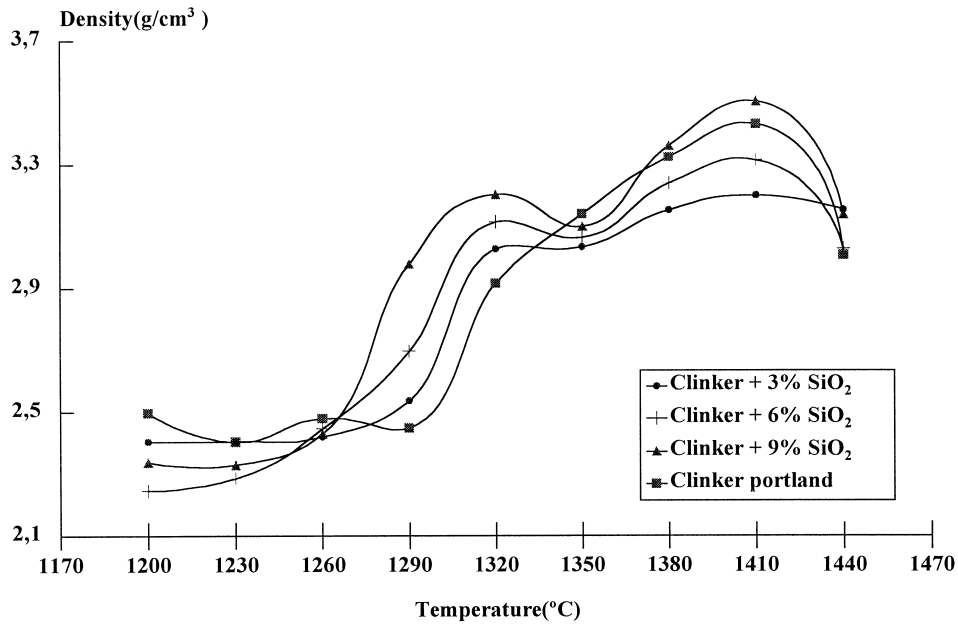


Fig. 3. Sintering density obtained for materials with SiO₂ compared with plain Portland clinker.

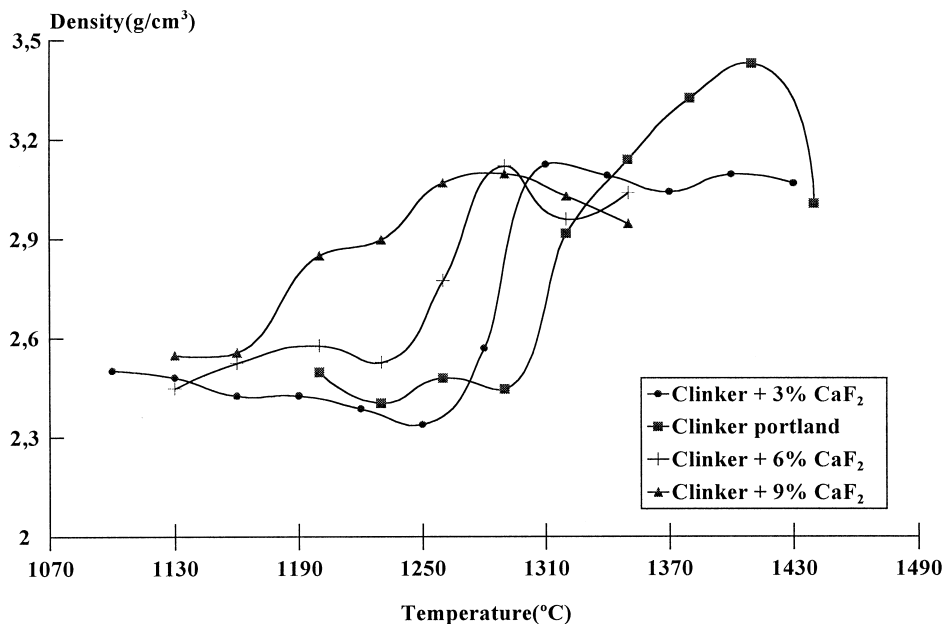


Fig. 4. Sinterability curve of materials with CaF₂ compared with plain Portland clinker.

begins (Fig. 1) about 1290°C and increases up to 1410°C, where maximum density is reached. Solid state sintering occurs till 1290°C as also seen in the dilatometry test (Fig. 5). Liquid phase sintering is produced at higher temperatures, as shown by the microstructure (Fig. 6a) which also shows the main phases of clinker (alite, belite, aluminoferritic and vitreous phases).

In the case of alumina addition, all the materials begin to densify at 1290°C with a liquid phase at 1350°C (according with liquid phase appearance during clinking),¹⁴ that produces high-density values, the max-

imum at 1410°C (Fig. 1). These values are similar to those obtained in a previous work.²⁹ The addition of alumina produce no improvement in the density as compared with plain clinker. The sintering window is between 1370 and 1410°C.

The dilatometry carried out at 1300°C demonstrates that materials with alumina present a lower shrinkage than plain clinker due to a reaction with Al₂O₃ which delays shrinkage (Fig. 5a). This is consistent with the sinterability curve (Fig. 1), where the plain clinker offers the highest density and maximum shrinkage. The reaction

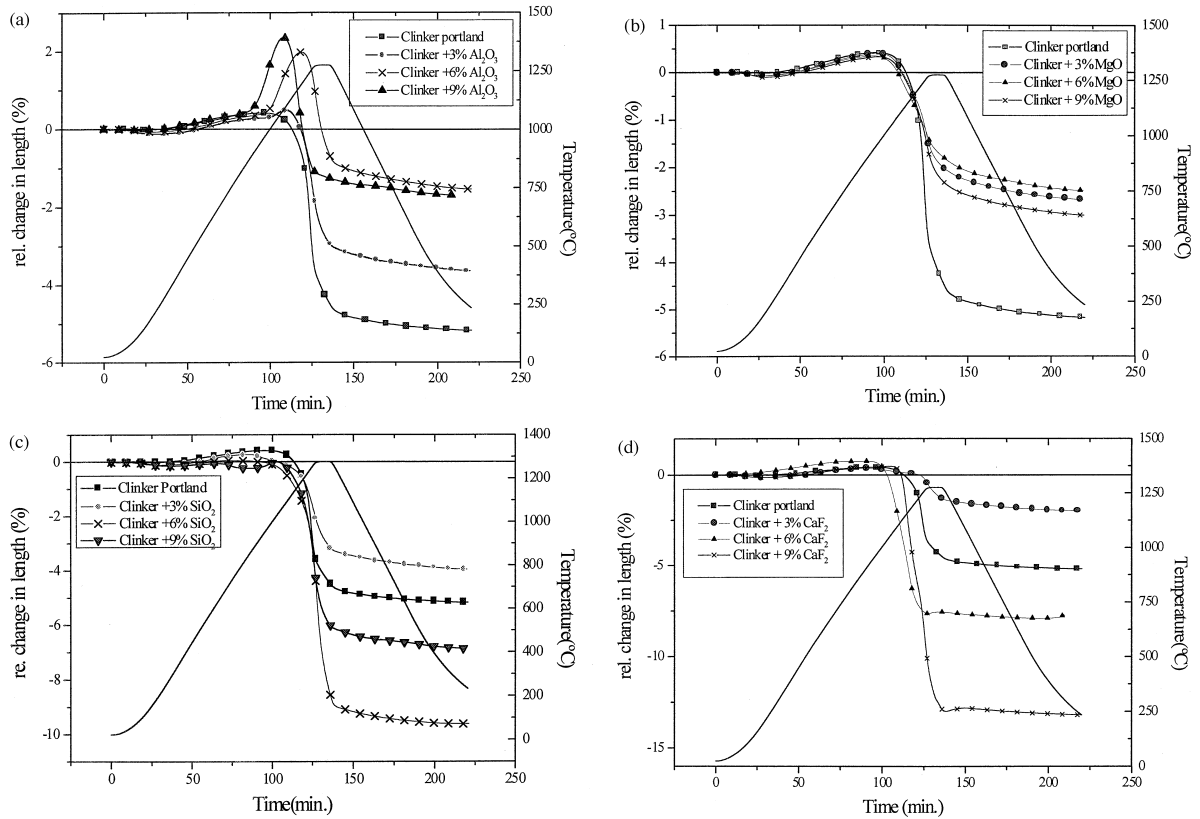


Fig. 5. Dilatometric curve (time versus relative change in length and temperature) for plain Portland clinker with several compositions of Al_2O_3 , MgO, SiO_2 and CaF_2 .

Table 3
Main values in the dilatometric study up to 1300°C

Portland clinker	T_1^a (°C)	T_2^b (°C)	C_3^c (%)
Al_2O_3	1136	1244	-5.20
+ 3%	1194	1260	-3.75
+ 6%	1279	1278	-1.50
+ 9%	1278	1273	-1.75
MgO			
+ 3%	1122	1260	-2.68
+ 6%	1092	1253	-2.50
+ 9%	1112	1258	-3.00
SiO_2			
+ 3%	1023	1262	-3.88
+ 6%	751	1112	-9.52
+ 9%	1023	1273	-6.82
CaF_2			
+ 3%	1222	1269	-2.00
+ 6%	1129	1247	-8.20
+ 9%	1129	1147–1267	-13.20

^a T_1 , temperature when the materials begin to shrink.

^b T_2 temperature where the shrinkage rate is maximum.

^c C_3 maximum shrinkage after sintering cycle (%).

between alumina and clinker is also shown in dilatometry by an abrupt dilation at 1200°C, that increases with the alumina content. This strong reaction does not reduce the sintering temperature.

The sintering activation for materials with alumina is due to reactions with the base material to form C_3A (Fig. 6), producing a decrease of the CaO in the base clinker due to the basic reaction:



Optical microscopy shows a greater number of white zones indicating the formation of C_3A phases (Fig. 6), CaO disappearing from the base material to form silica rich zones (light grey). Analyse by SEM were realised and it is possible to differentiate zones with a higher content of Fe (C_4AF) from those with a higher content of Al (C_3A) (Fig. 7). A view of the clinker with 9% Al_2O_3 (by BSE) reveals slightly darker zones near the white phase. A mapping of the area shows that the darkest zones are rich in Al and with a small Fe content; these grey phases are tricalcic aluminate and correspond to the added sintered alumina. Mapping of Ca in this area indicates a total diffusion to form tricalcic aluminate, disappearing as alumina, but silica does not diffuse to zones rich in aluminium.

In materials with MgO addition, the sintering process begins at 1300°C and the liquid phase at about 1350°C. This delay is due to the reduction of free CaO which reacts in the liquid phase.²³ The addition of magnesia increases density over that of plain clinker, reaching a

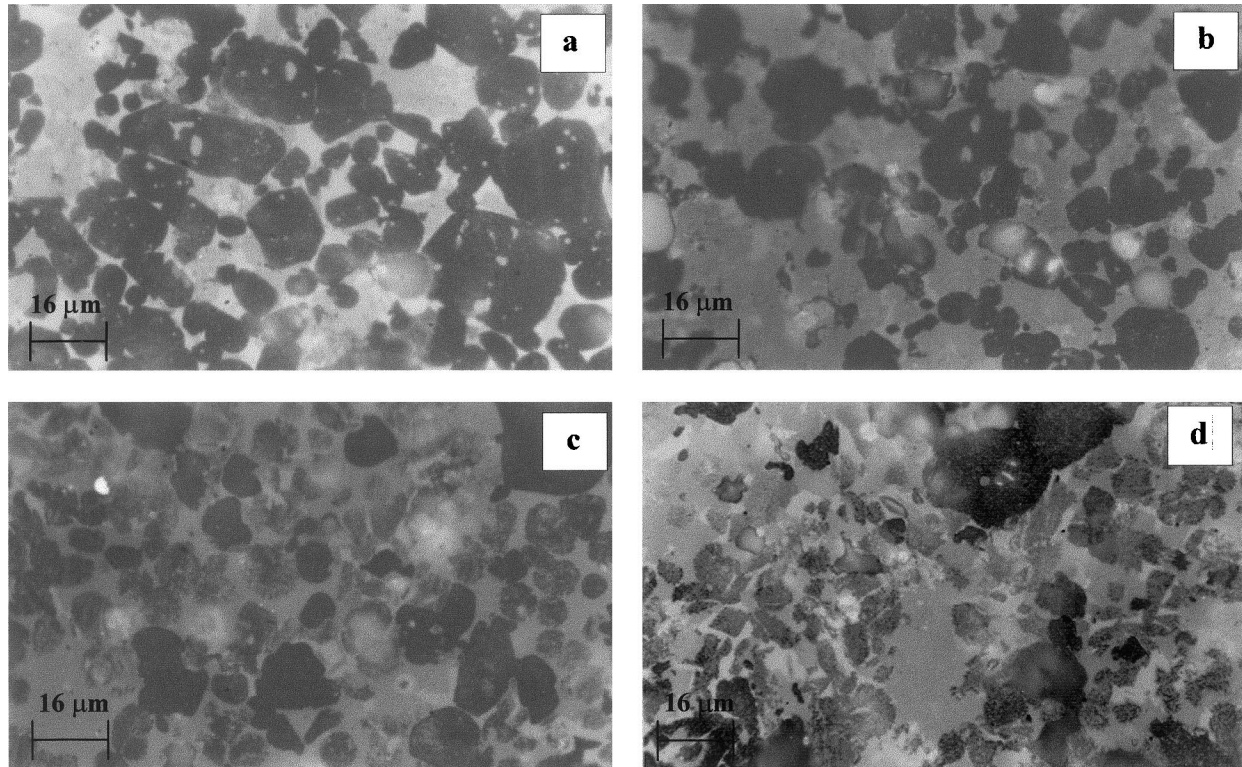


Fig. 6. Morphological evolution of phases with increasing alumina content. Increment in belitic phase to form calcium aluminates: (a) plain Portland clinker; (b) with 3% alumina; (c) with 6% alumina; (d) with 9% alumina. Etching with 13% vol acetic acid/ethanol.

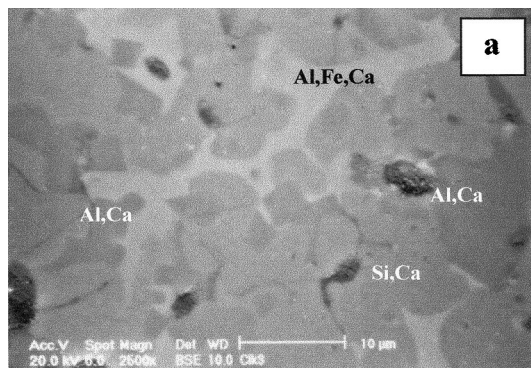


Fig. 7. Detail of clinker + 9% of Al_2O_3 , where clearer zones have CaO , Fe_2O_3 and Al_2O_3 (C_4AF), while the darkest zones correspond only to CaO and Al_2O_3 .

maximum in the material with 9% (Fig. 2). The sintering window for these materials is in the temperature range 1350–1420°C. From the point of view of density, the optimal sintering temperature is about 1400°C. Sinterability studies show an important change in the densities, probably due to reactions between the magnesia and C_4AF or C_3A phases. However, the reaction between the liquid phase (produced by the aluminoferritic phase) and the adjacent magnesia is possible in these conditions.³⁰ The porosity of these composite materials is slightly higher than that of plane clinker (Fig. 8).

The dilatometric study (1300°C) does not indicate any important reactions between MgO and base clinker (Fig. 5b) and there are no significant differences between the different compositions. In all cases, the shrinkage (Table 3) is lower in the composite materials than in plain clinker and the sintering is not activated by magnesia in this range of temperatures.

In the semiquantitative analysis by SEM of materials with magnesia, MgO is presented as darker zones (Fig. 9). There is no an important diffusion phenomenon. Different analysis reveals that Si and Ca appear in all the structures and less in the darkest zone (Figs. 9a and b). The two main phases (alite and belite) do not dissolve Mg from magnesia, as demonstrated by optical microscopy where the magnesia was predominantly associated with aluminate phases (C_3A or C_4AF), indicating reactions with these phases. In the first line scanning (Fig. 9b) the particle of MgO is enclosed by the aluminate phase and Mg is diffused.

The silica addition lowers the sintering temperature and promotes shrinkage (Figs. 3 and 5c). Silica does not produce density improvement when increase silica amount. The final density is lower than or similar to that of plain clinker, but at 1300°C (when the densification begins) it rises above plain clinker due to the appearance of new areas of rich silica phase of flake shape (Fig. 10). The same occurs with SiC additions due to their oxidation.²⁹ The liquid phase appears at about

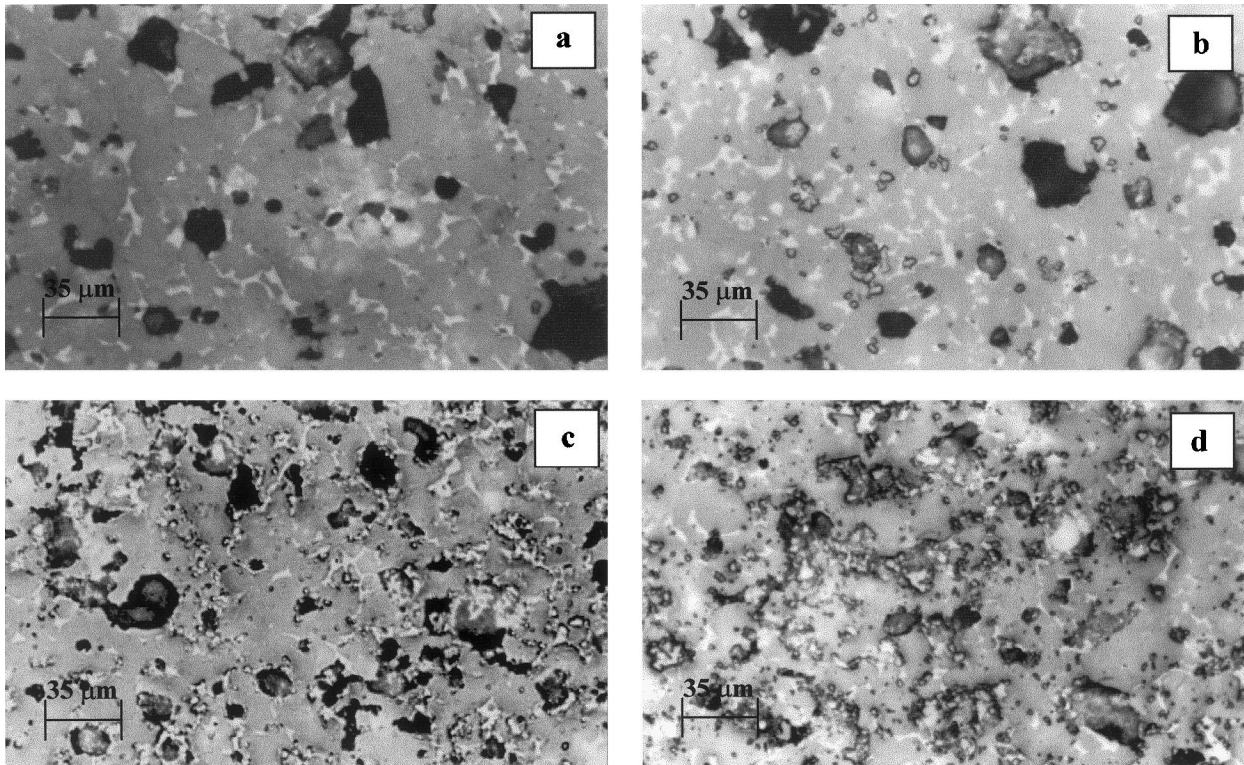


Fig. 8. Porosity evolution of composite materials based on clinker with magnesia: (a) plain clinker Portland; (b) with 3% MgO; (c) with 6% MgO; (d) with 9% MgO. Without etching.

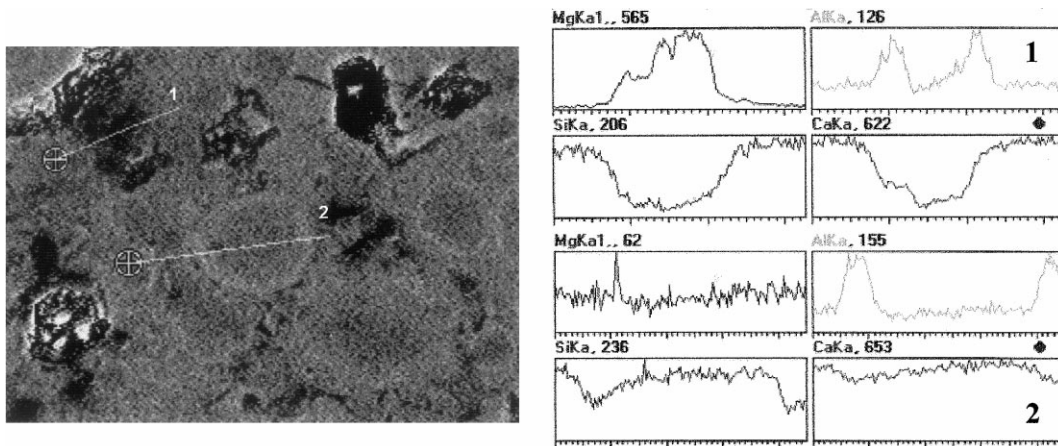


Fig. 9. Microstructure of material with 6% of MgO: (a) line scanning for a MgO particle, (b) line scanning for base material.

1350°C (from aluminoferritic phases). The sintering window is 1350–1420°C. The maximum sintering density is about 1400°C. The pore size increases with the amount of silica due to belitic phase segregations (C₂S) produced during solid state sintering (Fig. 10d) and increasing with silica content, although these materials present the lowest porosity.

The dilatometric study also shows reactions between silica and base clinker to form C₂S (Fig. 5c) that can be found through maximum and minimum points. The

maximal shrinkage rate is at 6% of silica. The most remarkable fact is that shrinkage begins at a lower temperature than for pure clinker, and a high silica content enhances sintering, improving the sintering in two ways: (1) increasing the shrinkage rate, and (2) advancing the onset of shrinkage. Silica does not produce any increase in liquid phase content during sintering.

Fig. 11a shows the main phases of the clinker without additives, and their semiquantitative analyses by SEM.

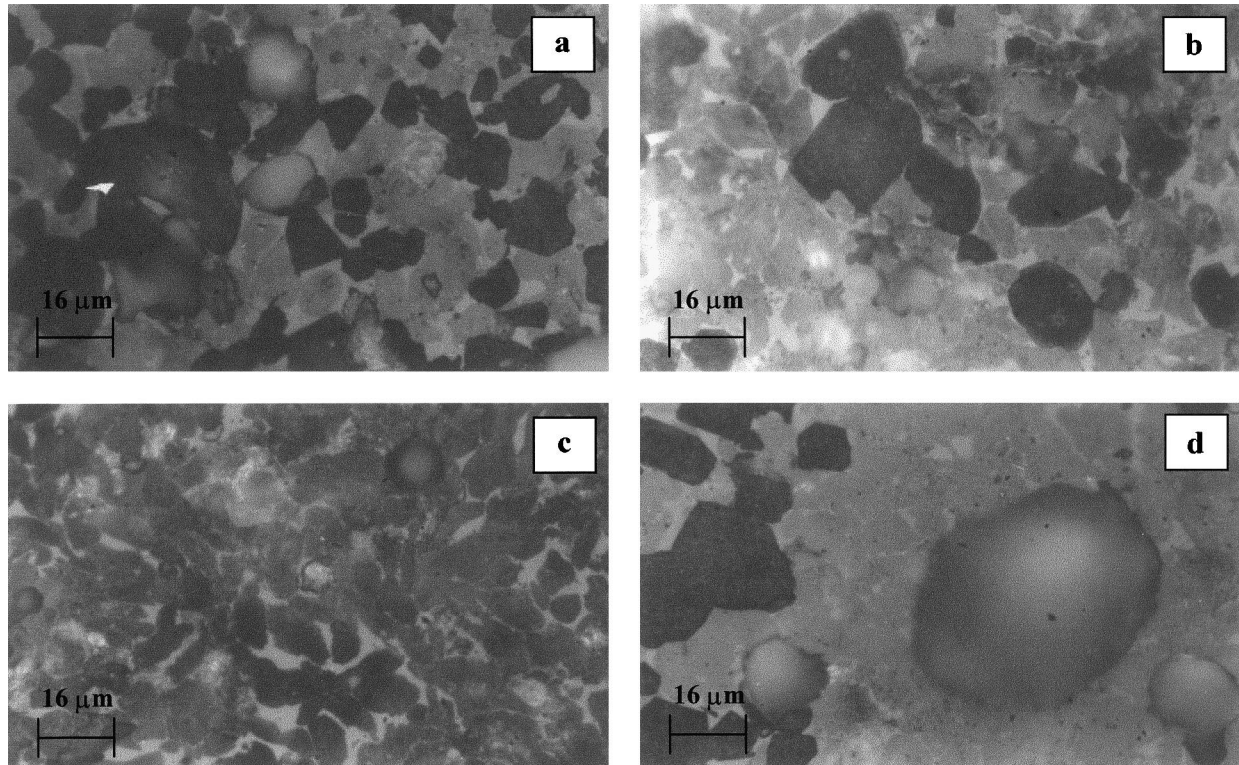


Fig. 10. Morphological evolution of phases with increment of silica: (a) clinker with 3% silica; (b) with 6% silica; (c) with 9% silica; (d) detail of a pore surrounded by a zone of rich-phases silica. Etching with 13% vol acetic acid/ethanol.

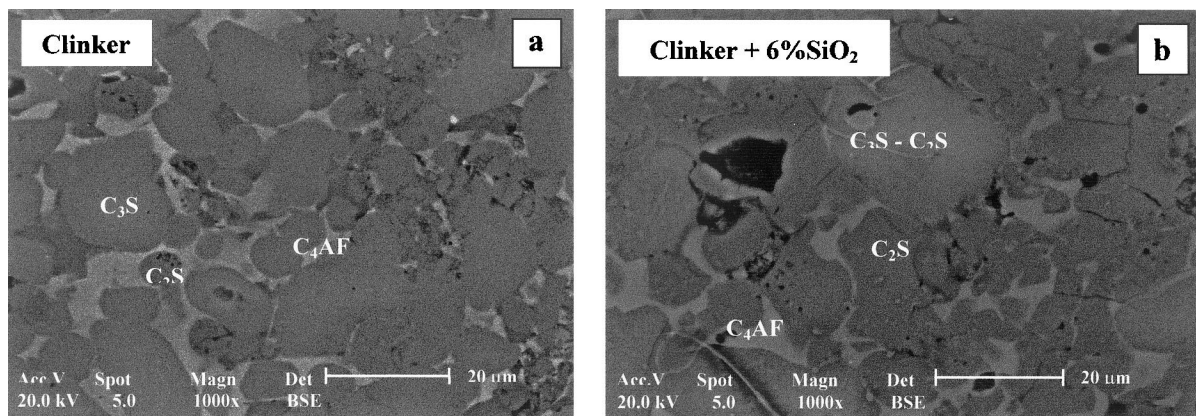


Fig. 11. (a) Main phases of Portland clinker; (b) main phases of Portland clinker reinforced with 6% SiO_2 . Photographs: phases localisation.

Fig. 11b gives the results of material with 6% SiO_2 , with an increase in silica rich phases and morphological changes (illustrates in the optic microscopy; Fig. 10). This corroborates the dilatometry and sinterability results obtained which confirm the reactions between base material and silica.

The most important effect of fluorite on the sinterability of base clinker is a lowering of the sintering temperature, and sintering with liquid phase is advanced with a higher fluorite content (Fig. 4). The temperature at which sintering begins is the lowest of all the studied

materials: 1200°C (for 9%) and 1280°C (for 6%). This improvement of the sintering temperature was expected because the effect of the CaF_2 in the clinkering process was well known.²¹ This is due to the appearance of liquid phase at lower temperatures and the interaction with the aluminoferritic phase and eutectic formation. The maximum sintering density for 9 and 6% of fluorite is about 1310°C, and 1370°C for 3%. The density of materials decreases with a higher fluorite content. Porosity in these materials is high as compared with that of plain clinker and of the other composite materials, due

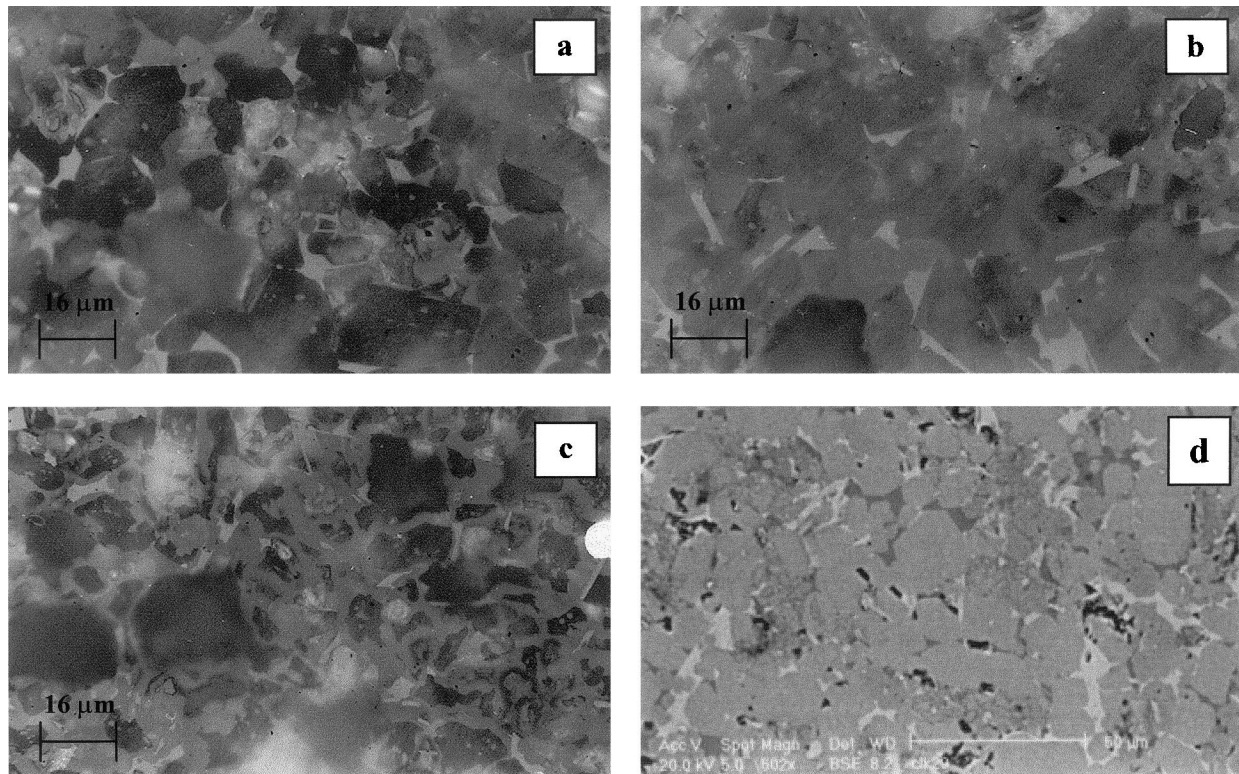


Fig. 12. Microstructural evolution of materials base clinker with fluorite; (a) with 3% CaF_2 ; (b) 6% CaF_2 (c) 9% CaF_2 (d). Changes in morphology of liquid phase formed at lower temperatures can be observed. Etching with 13% vol. acetic acid/ethanol.

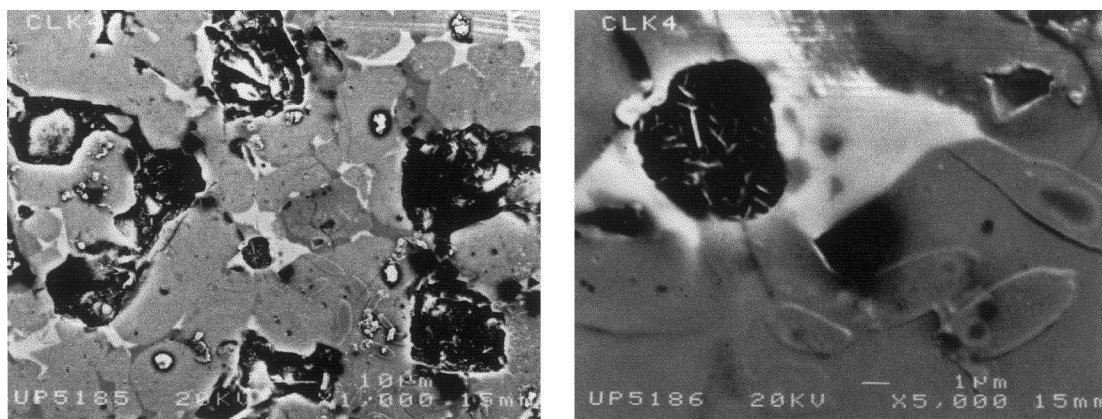


Fig. 13. Scanning electron microscopy of material with 3% MgO: (a) general morphology; (b) detail of zones with acicular morphology with a high content in Fe, S, Ca, Si, due to residual porosity as a result of solidification of adjacent liquid phase (C_3A and C_4AF).

to the great amount of liquid phase formed. These results are consistent with the dilatometric study (Fig. 5d). As the amount of fluorite increases so does the shrinkage level (Table 3).

Fig. 12 shows the effect of the liquid phase formed at low temperature by the fluorite. This addition is mainly associated with the liquid phase, as well as with the impurity in alite and belite phases. Porosity was always seen near a previously liquid phase. Inside the pores (Fig. 13) are concentrated most of the impurities (Fe, S, K, Ba, P, etc.) as acicular formations, and appears gen-

erally associated to C_4AF or C_3A , which form the liquid phase during sintering. These acicular zones were observed in all the compositions.

This study confirms the good sinterability of plain clinker and its composites, demonstrated in previous works.^{26,27,29} Different behaviours of the different additives in the sintering process are also confirmed. Additives such as magnesia has small interactions with the aluminoferritic phase of clinker. Alumina reacts with the base material and decreasing Ca content to form belitic phase, but without activating the sintering process.

Silica and fluorite propitiate modifications and enhance the sintering process.

5. Conclusions

- During the process of sintering or clinkering a liquid phase is generated. The additions studied modify this process.
- Alumina reacts with the clinker, increasing the quantity of liquid phase and reducing the sintering temperature, increasing the C₄AF and C₃A phases.
- Magnesia contributes to densification and seem to react with the rich alumina phases.
- Silica reacts with the base clinker without contributing to liquid phase. Densification at lower temperatures is due to the reaction of the silica with the initial components of the clinker, especially through the appearance of the belite phase.
- Fluorite diminishes the temperature of sintering (by increase of liquid phase) without an important densification.
- The density level obtained is evidence of good mechanical behaviour and reliability. The Portland clinker is an excellent raw material for the fabrication of structural ceramics, from the sinterability point of view. These materials can be consolidated by powder technology.

References

1. Lee, W. E and Rainford, W. M., *Ceramics Microstructures: Property Control by Processing*. Chapman & Hall, London, 1994.
2. Kingery, W. D., Sintering from prehistoric times to the present. *Solid State Phenomena*, 1992, **35–36**, 1–10.
3. German, R. M., *Liquid Phase Sintering*. Plenum Press, New York, 1985.
4. Cawley, J. D. and Lee, W. E., Oxide ceramics. In *Materials Science and Technology*, ed. R.W. Cahn et al. VCH, New York, 1994.
5. Nowok, J. W., A model of diffusion viscous mass transport in silicates during liquid phase sintering. *Journal of Materials Research*, 1995, **10**, 401–404.
6. Chae, K. W., Kim, D. Y. and Niihara, K., Sintering of Al₂O₃–TiC composite in the presence of liquid phase. *Journal of the American Ceramic Society*, 1995, **78**, 257–259.
7. Reed, J. S., *Principles of Ceramics Processing*. John Wiley & Sons, New York, 1995.
8. Sands, R. L. and Shakespeare, C. R., *Powder Metallurgy. Practice and Applications*. W. Clowes, London, 1966.
9. Handwerker, C. A., Blendell, J. E. and Coble, R. L., Sintering of ceramics. In *Science of Sintering*, ed. D. P. Uskokovic et al. Plenum Press, New York, 1990, pp. 3–37.
10. Skorokod, V. V., The main trends in study and quantitative description of the sintering process. In *Science of Sintering*, ed. D. P. Uskokovic et al. Plenum Press, New York, 1990, pp. 39–54.
11. Nikolic, Z. S., Ristic, M. M. and Huppman, W. J., A simple method for computer simulation of liquid phase sintering. *Modern Developments in Powder Metallurgy*, 1981, **12**, 497–502.
12. Spanish Standard UNE 80-301-88, Cements. Definitions, Classification and Specifications.
13. Spanish Standard UNE 80-302-85, Cements. Chemical Specifications for its Constituents.
14. Chatterjee, T. K., Burnability and clinkerization of cement raw materials. In *Advances in Cement Technology*, ed. S. N. Ghosh. Pergamon Press, Oxford, 1983.
15. Viggli, O. E., Estimation of grindability of Portland cement clinker. *World Cement*, 1994, **25**, 44–48.
16. Wang, S. B. and Chen, Y., Negative effect of alkali on burning and properties of Portland cement clinker and its improving measures. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 29–35.
17. Ahluwalia, S. C., Goswami, R. K. and Kouznetsova, T. V., Role of clinker liquid in promoting the clinkerization and its impact on the clinker morphology and microstructure. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 56–61.
18. Rumyantsev, P. F. and Erofeeva, N. T., Acceleration of the clinker formation process. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 62–66.
19. Zhang, H. and Odler, I., The texture of SO₃-rich Portland cement clinkers. *World Cement*, 1992, **23**, 30–33.
20. Ye, Q., Jianmin, K. and Baoyuan, L., Effect of fluorite–gypsum composite mineralizer on the microstructure and properties of Portland cement clinker phase. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 342–350.
21. Zhongyuan, L., Wenxi, H. and Guangliang, X., The effect of the composite mineralizers of CaF₂, CaSO₄, and ZnO on the formation of the Portland cement clinker in a rapid heating-up burning. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 386–392.
22. Kakali, G., Kasselouris, V. and Parissakis, G., Effect of Mo, Nb, W, and Zr oxides on the formation of Portland cement clinker. *Cement Concrete Research*, 1990, **20**, 131–138.
23. Christensen, N. H., Magnesia effects on combinable lime in the clinker. *Revista de Materiales de Construcción*, 1979, **174**, 73–75.
24. Xinrong, W., Jiaoqun, Z., Yafang, X. and Shanba, W., Sintering mechanism of Portland cement clinker with energy saving and early strength. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 294–300.
25. Prakash, R., Ahluwalia, S. C., Katyal, N. K. and Mathur, V. K., Role of manganese on the kinetics of formation and hydration of C₃S phase. In *Proceedings of 9th International Congress on Chemistry of Cements*, Vol. II, Paris, 1992, pp. 420–426.
26. Torralba, J. M., Cambronero, L. E. G. and Ruiz Prieto, J. M., Viability study of using clinker Portland as raw material in structural ceramics manufacturing. In *Third Euro-ceramics*, Vol. 3, Faenza Editrice, S.L., Firenze, 1993, pp. 1085–1090.
27. Torralba, J. M., Cambronero, L. E. G. and Ruiz-Prieto, J. M., Mechanical behaviour and reliability of sintered clinker Portland. *Journal of the European Ceramic Society*, 1994, **14**, 523–527.
28. Torralba, J. M., Cambronero, L. E. G. and Ruiz-Prieto, J. M., Using Portland clinker in structural ceramics. *The American Ceramic Society Bulletin*, 1995, **74**, 90–91.
29. Torralba, J. M., Cambronero, L. E. G., Velasco, F. and Ruiz-Prieto, J. M., Mechanical behaviour and reliability of sintered Portland clinker reinforced with Al₂O₃ and SiC. *International Ceramic Review: Inter-ceram*, 1996, **45**, 315–318.
30. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London, 1990.