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SEM examination of clinkers containing foreign elements

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Abstract

In this paper, the structure of clinker, modified by the introduction of foreign elements in the raw mix, is examined. One reference mixture and 16 modified mixtures, prepared by mixing the reference sample with 2.5% w/w of chemical grade CuO, MoO_3, WO_3, ZnO, Nb_2O_5, Ta_2O_5, MnO_2, V_2O_5, Li_2O, Co_2O_3, NiO, SnO_2, SrO, CrO_3, TiO_2 and BaO_2 were studied. The samples, after sintering at 1450 °C, were examined using a scanning electron microscope. As it is concluded the incorporation of foreign elements in clinker considerably affects the texture of the silicates and the interstitial material. Nb, Mo, Ta, Ti, Co, Ni and Mn are preferentially incorporated in the melt. Cr and Sr are found mainly in the silicates while W and V seem to be equally distributed into the clinker compounds. Cu, Ni and Sn are mainly incorporated in solid solutions combining with CaO. Li and Sr modify considerably the texture of alite and belite indicating a strong effect on the growth of the calcium silicate crystals.

Keywords: Clinker; Mineralizers; Crystal structure; SEM

1. Introduction

The incorporation of foreign ions in the cement raw meal and their effect on the clinker formation and cement properties have been broadly discussed during the last years. Minor elements in clinker primarily come from the raw materials and fuel used in cement making, as well as the widely used auxiliary materials such as blast furnace slag, spent catalysts and industrial by-products. Additional sources of minor components could be the refractories, chains and grinding media such as liners and grinding balls [1].

Such compounds may modify the temperature of the first liquid phase formation and/or the amount of the melt, change the rate of the reactions occurring in the solid state within the liquid phase or at the liquid–solid interface, alter the viscosity and surface tension of the melt and affect both crystal growth and morphology [2]. In our previous work we studied the effect of numerous foreign elements on the reactivity of the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system and we found out that most of them exert a considerable effect especially during the last stage of the sintering process [3,4]. This stage involves the partial melt of the material and the formation and development of alite ($3CaO \cdot SiO_2$) crystals. Most of the foreign elements, present in the raw mix, are dissolved in the melt and affect its properties. In previous works, quaternary mixtures, having the typical composition of the melt, were studied and the correlation between the electronic configuration of the added ions (ionic radius, electronegativity, field intensity) and their effect on the properties of the melt was well established [5,6]. Since nucleation and growth of alite crystals take place in the melt, any modification of the melt properties is expected to be reflected on the morphology of the crystals. In addition, the incorporation of foreign elements in alite affects the growth of alite and the texture of its crystals.

Despite the extensive literature on the subject, results are often contradictory, due to the variety of the materials and techniques that have been applied [7–17]. There is a general agreement that foreign elements are preferentially concentrated in ferrite followed by calcium aluminate, with the exception of Cr and V which are selectively retained in belite.

In this paper, the structure of clinkers, modified by the introduction of W, Ta, Cu, Zn, Nb, Mo, Cr, Ti, Ba, Co, Ni, Li, Sn, V, Sr and Mn in the raw mix, is examined. This work is part of a research project concerning the effect of foreign elements on the reactivity of the raw

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mix and on the properties of the cement. The examination of the modified clinkers is expected to elucidate the way these elements affect the sintering process and their incorporation in the clinker compounds.

2. Experimental

One reference mixture, composed of chemical grade $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3 and having a composition very close to this of a typical cement raw meal, was prepared. Quartz and aluminum oxide were ground to a particle size less than 90 μm and then were intensively mixed with Fe_2O_3 and precipitated $CaCO_3$ in a laboratory swing mill for 1 h. Homogeneity was ascertained by measuring the loss of ignition (LOI) in three individual samples of the mixture. Table 1 shows the chemical and the mineral composition (according to Bogue) of the reference mixture, after sintering at 1450 °C.

Sixteen modified mixtures were prepared by mixing the reference sample with 2.5% w/w of chemical grade CuO, MoO_3, WO_3, ZnO, Nb_2O_5, Ta_2O_5, MnO_2, V_2O_5, Li_2O, Co_2O_3, NiO, SnO_2, SrO, CrO_3, TiO_2 and BaO_2. In our previous work we observed that the addition of 1% w/w of the above compounds has a strong effect on the reactivity of the mixture [4]. In this work the doping concentration was increased to 2.5%, in order to strengthen the effect of these elements on the structure of the clinker and facilitate their detection by SEM in the clinker compounds. The studied elements were introduced in the form of oxides, in order to avoid the effect of foreign anions on the structure of the clinker. When necessary, the added compounds were ground in order to have, approximately, the same fineness with the reference sample and sieved, prior to mixing, in order to avoid agglomeration. The homogeneity was ascertained by dosing the added elements in the mixture. All the samples were pressed to form pellets, then sintered at 1450 °C for 30 min in an electrical furnace and cooled rapidly in air. Mineralogical studies of the sintered samples were performed using a Siemens D-5000 X-ray diffractometer, with nickel-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å).

Selected clinker nodules of the burned samples were coated with Au and examined using a JEOL JSM-5600 scanning electron microscope equipped with an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDS), (accelerating voltage: 20 kV, beam current: 0.5 nA).

Table 1
Chemical and mineral composition (% w/w) of the reference clinker

Chemical composition	
CaO	68.08
SiO_2	22.81
Al_2O_3	5.84
Fe_2O_3	3.27
Mineral composition (according to Bogue)	
C_3S	65.0
C_2S	15.0
C_3A	10.0
C_4AF	10.0

3. Results and discussion

The examination of clinkers by SEM led to the photographs presented in Fig. 1. The photos were selected to be representative as far as the distribution, size and form of alite and belite crystals are concerned. An evaluation of size and shape of clinker silicate minerals is presented in Table 2. With the spot analysis of EDS, the composition of the principal phases was analyzed at five to eight points. In the case of Nb, Ta and Mo, interference from Au coating affected the accuracy of the results. Additional problems occurred in the sample containing Sr because of the overlapping of the Si and Sr characteristic peaks, while Li could not be detected by EDS. Although EDS analysis gives good results in the case of silicate grains, it cannot be restricted to very small volume, as it is the case of interstitial phases, because of the contributions from underlying or surrounding grains. We examined numerous points of interstitial phases on each sample and we took the results into account only in the cases that the ratio of the main elements (Ca, Al and Fe) was close to the expected one and Si was present in traces. In any case, the comparison of the spot analysis in each clinker phase can lead only to qualitative results about the distribution of the added elements in the individual clinker compounds.

In reference sample (Fig. 1a) belite grains were uniformly distributed as small roundish grains, having a size of approximately 10–20 μm, indicating rapid cooling [18]. Neither secondary belite (which is an indicator of slow cooling) nor belite nests (indication of coarse raw feed, particularly of siliceous component) were observed. Alite crystals dominated the sample's texture, with particle size ranging from 20 to 30 μm. Alite appeared as compact basal prismatic crystals of slightly rounded hexagonal outline. The interstitial material had a fine-crystalline structure and it was generally adequate.

The sample containing WO_3 (Fig. 1b) showed well-formed larger alite crystals (30–40 μm) having a more roundish shape at the rims. Belite crystals were also larger than in the reference sample. The interstitial matrix has a fine-crystalline structure and EDS analysis showed that the belite and the interstitial material contain almost the same amount of W. Traces of W were also detected in alite.

Fig. 1c presents the morphology of the clinker containing 2.5% w/w Nb_2O_5 in the raw meal. Alite crystals were bigger in size and more roundish in shape than in the reference clinker. EDS for Nb indicated an enhanced

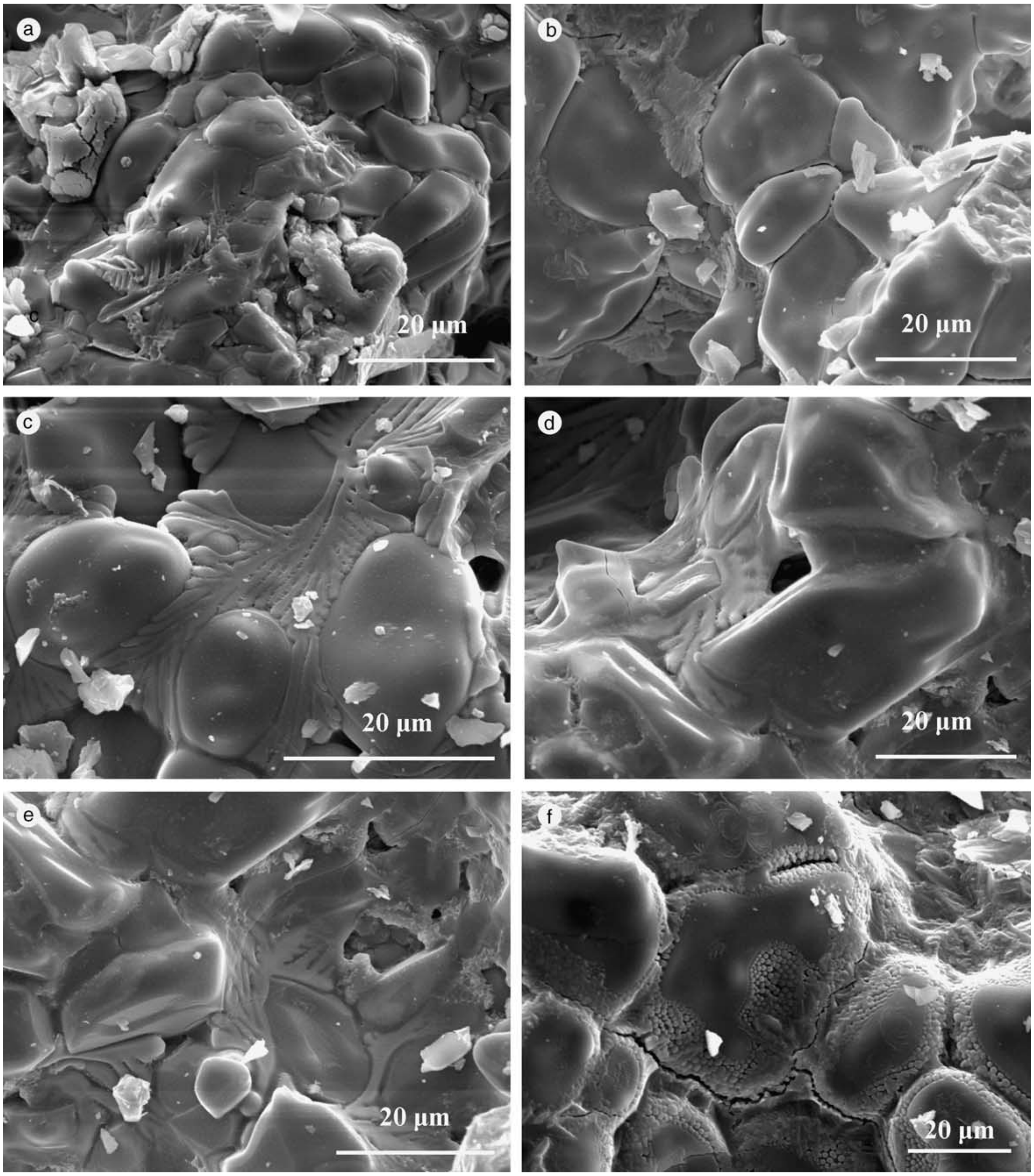

Fig. 1. SEM photos of clinker. (a) Reference, (b) WO_3, (c) Nb_2O_5, (d,e) Ta_2O_5, (f) MoO_3, (g) Co_2O_3, (h,i) CuO, (j,k) SrO, (l) SnO_2, (m) CrO_3, (n) TiO_2, (o) V_2O_5, (p) BaO_2, (q,r) LiO, (s) MnO_2, (t,u) NiO and (v) ZnO.

accumulation of Nb in the interstitial matrix, which presented a characteristic fishbone texture and appeared to be less crystalline than in the reference clinker. No significant quantities of Nb in C_3S and C_2S were found.

Images of sample containing Ta_2O_5 are given in Fig. 1d and e. Alite (Fig. 1d) appeared in profuse as characteristically angular, rather elongated, big prismatic crystals. Belite grains are also roundish and small in size. Two kinds of interstitial matrix can be distinguished: one having the common crystalline structure (Fig. 1d) and another that seems to be amorphous (Fig. 1e). Both kinds were well developed and equally distributed in the sample. EDS analysis performed in alite and belite suggested that Ta is not incorporated in these phases. On the contrary, both kinds of interstitial matrix exhibited high concentrations of Ta. Though interference problems for Ta detection existed, as it was previously mentioned, it can be suggested that Ta is mostly incorporated in the amorphous matrix. The XRD pattern of this sample did not show any indications of a new phase. Therefore it is concluded that the presence of Ta affects mainly the crystallization process and specifically the solidification

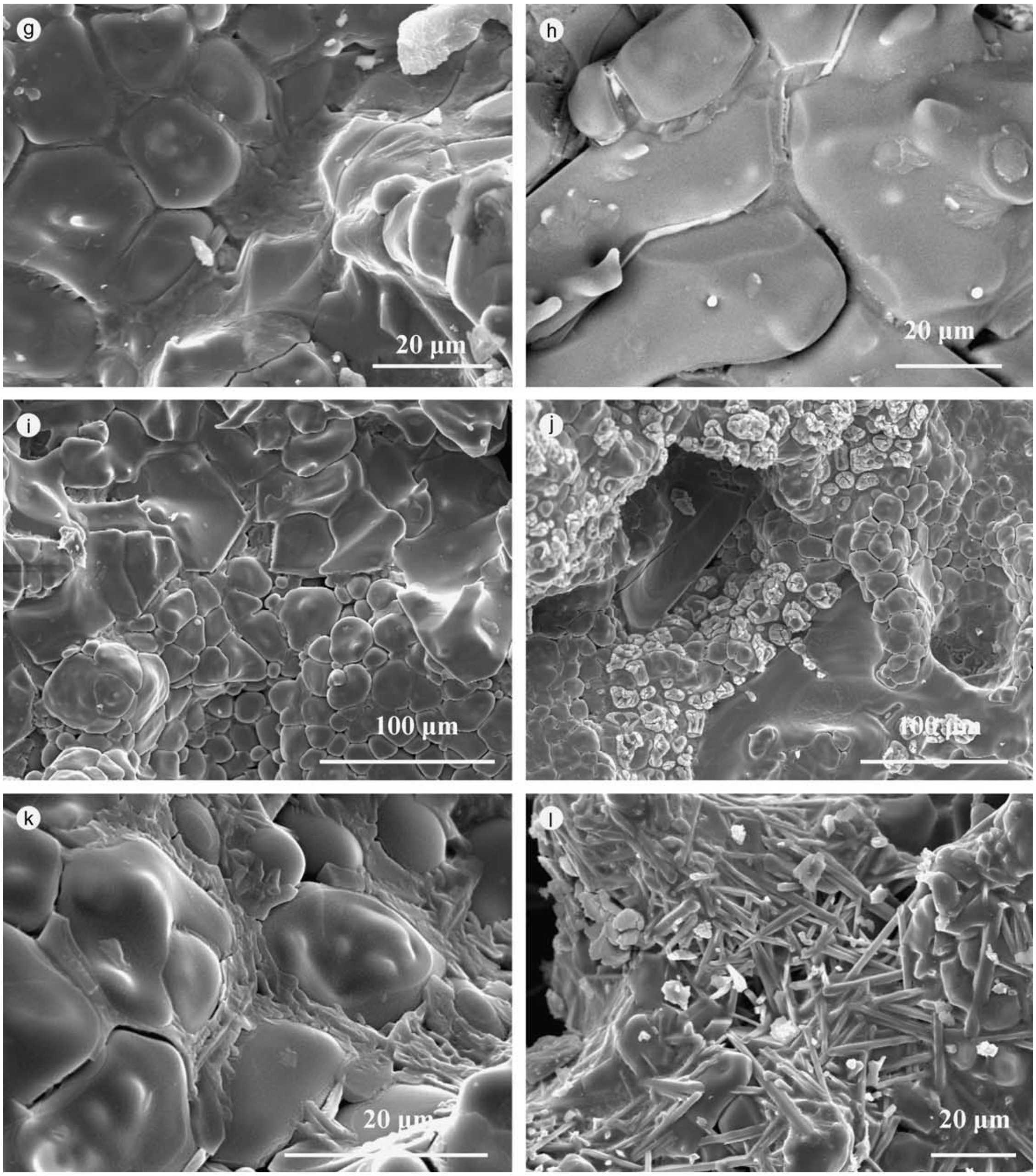

Fig. 1 (*continued*)

of the ferrite solid solution (the amorphous portion of the interstitial material is also rich in Fe).

The sample containing MoO_3 had well-formed large alite crystals rounded at the contours. Belite crystals were also round in shape and smaller in size, embedded in the crystalline interstitial material. The presence of Mo oxide in the raw mix caused, in a small extend, dendritic secondary crystallization of belite (Fig. 1f). This form of belite is usually crystallized from the melt as a result of excess SiO_2 [18], caused probably by the partial replacement of Si^{4+} by Mo^{6+}. The EDS analysis on these fine grains on the surface of larger belite crystals indicated a CaO:SiO_2 ratio very close to 2:1 and an average content of Mo (≈2–3% w/w as an oxide). Traces of Mo ware also detected in alite but considerable amount was found in the interstitial phase.

The sample containing Co oxide (Fig. 1g) is quite similar with the sample containing Mo as far as the size and shape of the calcium silicate crystals are concerned. Small amounts of Co were detected in the alite and belite but considerable amount was found in the interstitial phase. Since the radii of Mo, Co and Fe ions are relatively close, Mo and Co ions may replace Fe ions in the aluminoferrite phase.

In the sample containing CuO, a different morphology can be observed (Fig. 1h and i). Belite grains

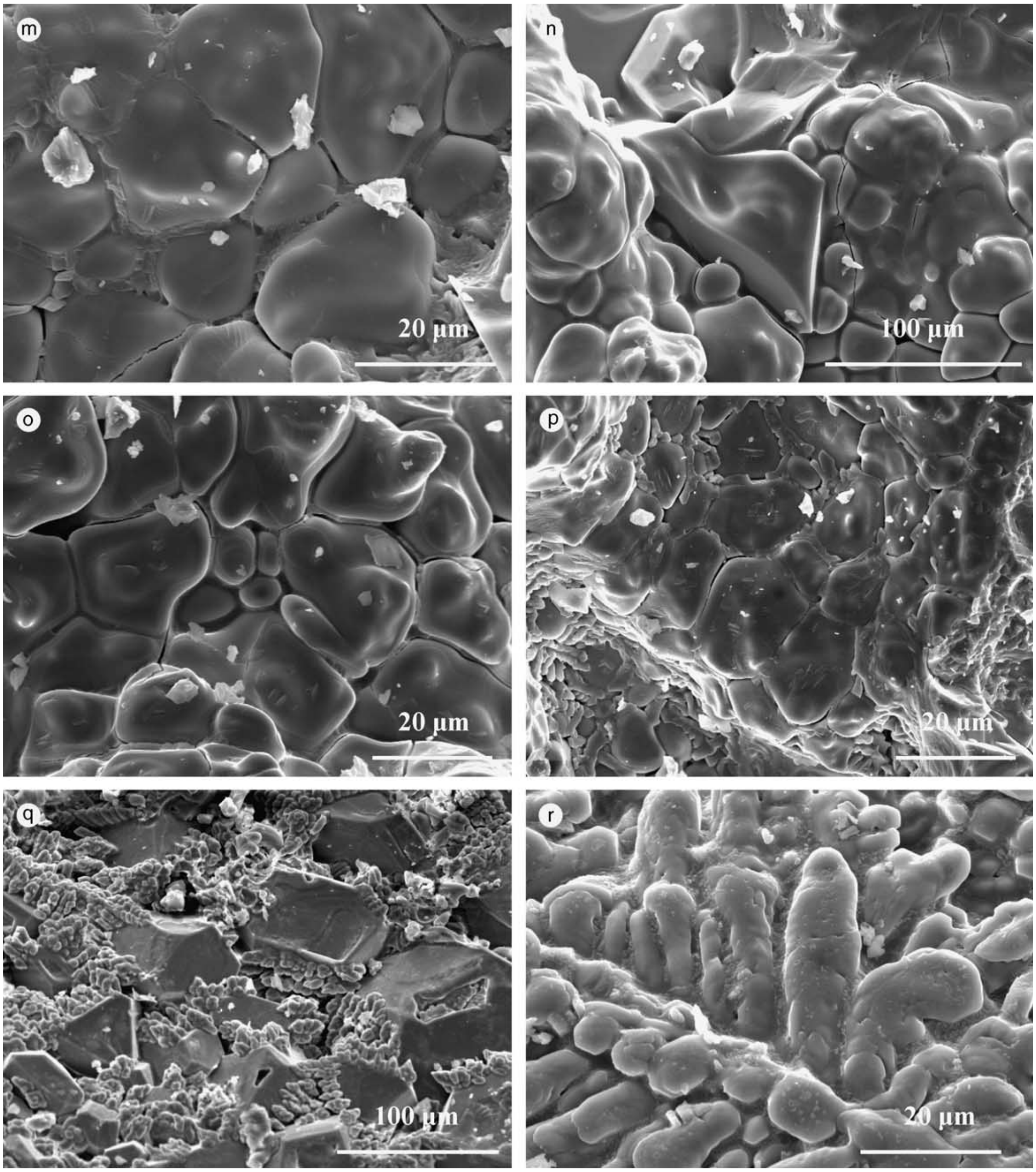

Fig. 1 (*continued*)

formed nests while alite was developed in large compact, prismatic, angular, crystals. In comparison to the previous samples, packing of silicate grains is so dense that little interstitial phase exists between them. EDS analysis indicates that little Cu is dissolved at the various phases. However a new phase, appeared as thin white rims around alite crystals (Fig. 1h), was detected in this sample. EDS analysis on these spots indicated a high Cu and Ca content (CaO:CuO approximately equals 1:2). XRD pattern showed some indications of this compound but the low content of this phase and the overlapping of the clinker peaks do not permit a safe identification.

Fig. 1j and k presents the morphology of the clinker doped with SrO. C_3S crystals are strongly differentiated from the other samples in terms of their dimensions, since they have a particle size of about 100–200 μm. C_3S crystals show euhedral hexagonal-shaped elongated plate or short prismatic outline with distinct pyramidal faces and embedded in belite clusters (Fig. 1j). Belite forms clusters of rather rounded grains uniformly distributed in the sample. Free CaO grains are also evident as light white spherical crystals having a leaflet configuration. The coexistence of free lime with belite crystals indicates the decomposition of alite into belite and free lime. Phase equilibrium studies

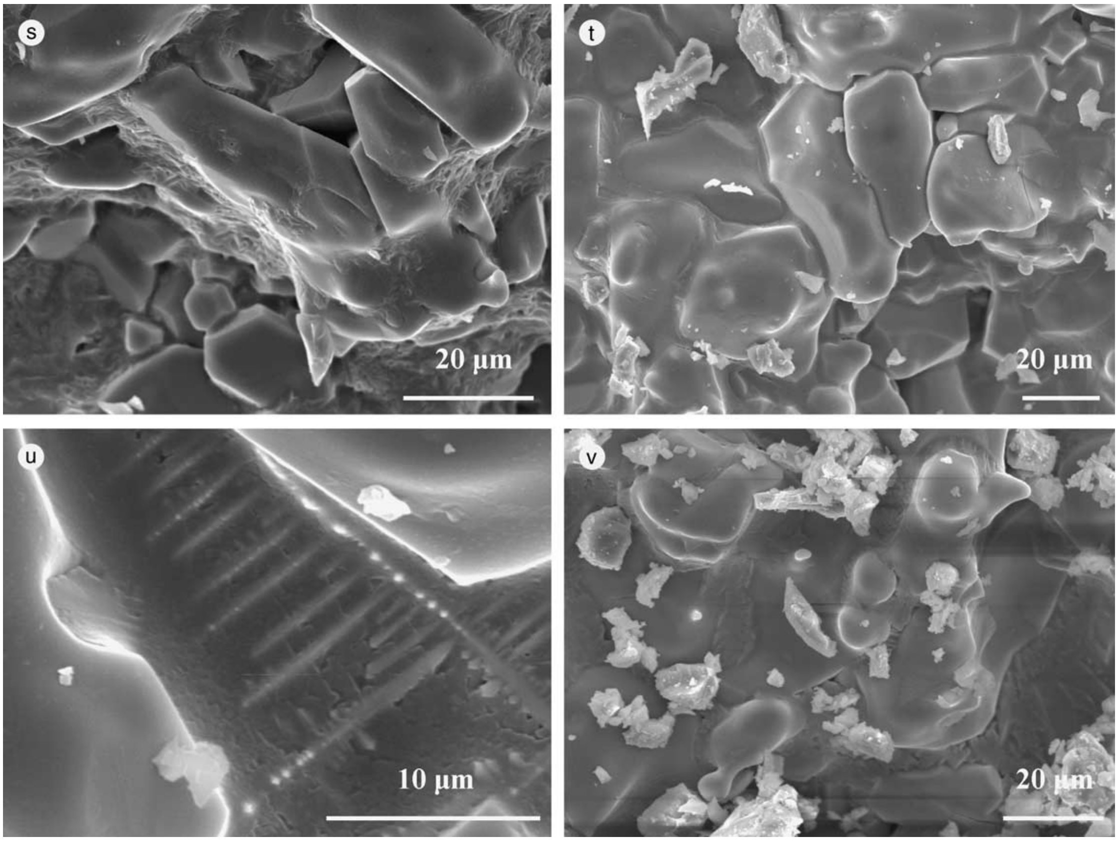

Fig. 1 (*continued*)

Table 2
Size and shape of alite and belite phases for samples burnt at 1450 °C

Sample	Alite		Belite	
	Size (µm)	Shape	Size (µm)	Shape
Reference	20–30	Compact, prismatic, with slightly rounded hexagonal outline	10–20	Small, roundish
Ta	30–50	Angular, rather elongated, prismatic	10–20	Small, roundish
Ti	30–60	Angular, rather elongated, prismatic	10–20	Round compact grains
Sr	100–200	Large compact, prismatic, angular	20–30	Roundish
Li	80–200	Large, compact, prismatic, angular	5–30	Small, roundish (fish-bone growth)
Mn	20–50	Large, compact, prismatic, angular	5–10	Small polygonal
Cu	40–60	Large compact, prismatic, angular	10–30	Roundish
Ni	20–50	Large, compact, prismatic, angular	10–15	Round, compact
Zn	20–40	Large, rounded at the rims	10–20	Round
W	30–40	Compact, rounded at the rims	20–30	Large, round, compact
V	20–30	Compact, prismatic, with slightly rounded hexagonal outline	10–20	Small, roundish
Nb	30–40	Large, round	10–20	Round
Mo	30–40	Large, rounded at the rims	10–20	Small, round
Co	30–40	Large, rounded at the rims	10–20	Small, round
Cr	20–40	Large, rounded at the rims	10–20	Small, round
Sn	20–30	Large, rounded at the rims	10–20	Small, roundish
Ba	30–40	Large, rounded at the rims	20–30	Large, round, compact

suggest that Sr favors free lime formation by going into solid solutions and displacing CaO from other compounds [1,19]. The XRD studies and the chemical test confirmed a high content of belite and free lime in this sample. The interstitial matrix is adequate and appears to be semi-crystalline (Fig. 1k). EDS analysis resulted that Sr is distributed in all clinker phases, especially in belite.

In the sample doped with SnO_2 a unique morphology is observed (Fig. 1l). Belite nodules were round, smaller in size, while alite were developed as large rounded crystals. EDS analysis indicated that very little Sn is incorporated in C_3S and no Sn was detected in C_2S. The interstitial matrix has a fine-crystalline structure and up to 5% w/w of Sn (as oxide) was detected. Remarkable configurations of needle-like crystals are observed in adequate amount in this sample. EDS on selected spots of the needles indicated a high Sn and Ca content (CaO:SnO_2 equals approximately to 1:1) but it was not possible to identify a specific CaO–SnO_2 compound in the XRD pattern.

Fig. 1m presents the morphology of the sample containing CrO_3 in the raw mix. C_3S crystals are large and rounded at the rims. Belites are small and rounded in shape, embedded in a fine-crystalline interstitial material. EDS analysis implies that Cr is preferentially found in the silicate phases, especially in belite. The content of belite and free lime seems to be higher than in the other samples as it was also confirmed by XRD and fCaO determination. This is in accordance with previously published works reporting high content of belite and low content of alite in sample doped with Cr oxide. It seems that either alite is decomposed in the presence of Cr, or belite is stabilized in a way that further reaction with lime is inhibited [7,11,16,17].

The sample containing TiO_2 is shown in Fig. 1n. Alite crystals were bigger in size, having a polygonal, elongated prismatic shape. Belite grains are round and compact. The packing of the silicate grains is so dense that little interstitial material, rather glassy in appearance, exists between them. EDS analysis showed that Ti concentrates in the interstitial phase.

In sample containing V_2O_5 (Fig. 1o), belite crystals were uniformly distributed as small roundish grains having a size of approximately 10–20 μm. Alite nodules dominate the sample's texture, appearing as compact prismatic crystals of slightly rounded hexagonal outline. The interstitial material had a fine-crystalline structure. EDS analysis showed that V is preferentially concentrated in the silicates, especially in C_3S, followed by C_2S. It is, however, also found in the interstitial matrix. In previous work, however, V was reported to affect the size of alite and to be incorporated, preferentially, in belite [1,8].

Fig. 1p presents the morphology of the clinker containing 2.5% BaO_2. Well-formed large alites rounded at the contours and big spherical belites are embedded in an amorphous interstitial material that tends to create needle-like structure. EDS suggested a uniform distribution of Ba in both silicate and interstitial matrix.

Distinct differences in clinker containing Li_2O were observed, concerning specifically the size and shape of belite grains (Fig. 1q and r). The alite crystals are coarse (80–200 μm in size), prismatic with distinct pyramidal phases and deposited in an idiomorphic underlay of belite (Fig. 1q). A magnification of the belite grains is presented in Fig. 1r. Belite distribution around the alite crystal has a fish bone-shaped dendritic configuration of mixed elongated and roundish grains. As it is known, Li oxide easily forms eutectic mixtures with silica. The unique configuration of belite can be attributed to the effect of Li ions on the crystallization and development of silicates in the clinker.

The microscopic study of the sample doped with MnO_2 (Fig. 1s) showed prismatic alite crystals with hexagonal outline and small roundish belite crystals. Mn is preferentially found in the matrix, although small but detectable equal amounts of Mn were detected in alite and belite.

Fig. 1t and u presents representative areas in the sample containing Ni oxide. Alite is well-developed in big polygonal crystals while belite grains appear rounded at the rims, densely packed in the fine-crystalline interstitial matrix (Fig. 1t). However the morphology of the interstitial phase is not uniform. Grains having a dendritic configuration and enriched in Ni and Ca are clearly seen in the interstitial matrix (Fig 1u). Aluminates with similar configuration were also detected in white cement clinker doped with NiO [7]. Only a little of Ni was found in C_2S and C_3S but intakes of up to 10% were detected in the fine-crystalline interstitial matrix.

Finally in Fig. 1v a photo of the clinker containing Zn is given. Alite as well as belite were formed as large rounded crystals. The interstitial material appeared to be crystalline. EDS for Zn showed a rather uniform distribution of Zn in all phases.

As it is concluded the incorporation of foreign elements in clinker considerably affects the texture of the silicates and the interstitial material. Since burning and cooling conditions were kept strictly constant for all samples, these changes can only be attributed to the influence of the added oxides on the properties of the melt and their effect on the growth environment of alite crystals. Alite crystals are formed and developed in the melt. Therefore, the properties of the melt (viscosity, surface tension on the solid–liquid interface) exert a considerable effect on the shape and the size of these crystals. Besides, any incorporation of foreign elements in the lattice of the silicate minerals, may also, affect the configuration of alite and belite crystals.

An attempt to summarize the above remarks, is presented below:

- The 16 studied elements showed a non-uniform distribution in the clinker minerals. Most of them (Nb, Mo, Ta, Ti, Co, Ni and Mn) are preferentially incorporated in the melt. In samples containing Nb, Ta and Ni a modified configuration of the solidified melt is observed. Cr and Sr are found mainly in the silicates while W and V seem to be equally distributed among

the silicates and the melt. Cu, Ni and Sn are mainly incorporated in solid solutions combining with CaO.
- Li and Sr cause the greatest modifications as far as the texture of silicates is concerned. Much larger alite crystals are formed in both cases. In addition, a unique configuration of belite is found in the sample containing Li. As it is mentioned, the modifications of the silicates' texture can be attributed either with the effect of the added elements on the properties of the melt or with their incorporation in the lattice of the silicate minerals. Li and Sr seem to fulfill both requirements. Their oxides form eutectic mixtures with silica and it is reasonable to assume that these elements are extensively dissolved in the melt. Besides, according to the families of isomorphous elements [12], Sr shows a relatively high capability of replacing Ca in solid solutions. This was previously reported by other researchers [1,15], and it is also confirmed by the EDS analysis in this work. Li cannot be detected by EDS, but the small size of this element favors the formation of interstitial solid solutions.
- The elements Mo, W, Cr and V, that according to Timashev [5] are the most effective reducers of the melt viscosity, seem to favor the formation of big rounded alite crystals.

4. Conclusions

From the present study the following conclusions can be drawn concerning the effect of CuO, MoO_3, WO_3, ZnO, Nb_2O_5, Ta_2O_5, MnO_2, V_2O_5, Li_2O, Co_2O_3, NiO, SnO_2, SrO, CrO_3, TiO_2 and BaO_2 on the texture of the clinker minerals:

- The incorporation of foreign elements in clinker considerably affects the texture of the silicates and the interstitial material.
- Nb, Mo, Ta, Ti, Co, Ni and Mn are preferentially incorporated in the melt. Cr and Sr are found mainly in the silicates while W and V seem to be equally distributed into the clinker compounds. Cu, Ni and Sn are mainly incorporated in solid solutions combining with CaO.
- Li and Sr modify considerably the texture of alite and belite indicating a strong effect on the growth of the calcium silicate crystals.

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