EVALUATION OF THE EFFECT OF SOME MINERAL ADDITIONS ON THE BURNABILITY OF RAW MIX IN CEMENT PRODUCTION

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În această lucrare s-a apreciat prin analize termice (DTA şi TG) influenţa unor mineralizatori (oxizi, floruri şi amestecuri de oxizi şi florură), asupra proceselor care au loc la arderea amestecului brut la temperaturi joase,. Datele obţinute prin determinarea calcei libere au completat informaţiile referitoare la aptitudinea la clincherizare a amestecurilor brute. Clincherele obţinute prin arderea amestecurilor brute la temperaturi cuprinse între 1250-1450 ^oC au fost caracterizate prin analize difractometrice (XRD) şi de microscopie electronică (SEM).

The present paper deals with the influence of different types of mineralizer (oxides, fluorides and their mixtures) on the processes that take place at the burning of raw mix at temperatures below the eutectic temperature - assessed by thermal analysis (DTA, TG). Additional information about the burnability of the industrial raw mix with mineralizers content were obtained by free lime evaluation. The clinkers resulted by the burning of the raw mixes at temperatures between 1250-1450oC were also characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: Portland cement, clinker, mineralizers, burnability, microstructure

1. Introduction

The increase of the “greenhouse” gases levels in atmosphere and the related temperature increase of the environment are potentially able to alter the ability of the planet to support present life forms [1]. The cement industry has an important contribution to the release in the atmosphere of the greenhouse gases (especially CO_2) due to its important output - 2,3 Mt in 2006 [2] and to the specific processes which take place in cement production. According to calculations in the process of production of 1 ton of Portland cement clinker almost 1 ton of CO_2 is generated, 0.55 ton of CO_2 being generated in the

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formation process of clinker minerals and up to 0.4 tones by the fuel combustion [3].

The increase of the burnabilty of the cement raw mix, used for Portland clinker fabrication, may represent an attractive approach for energy preservation and reduction of the greenhouse gases emissions (especially CO_2); this may be achieved by introducing mineral additives in the raw mix. These materials may act as mineralizers, i.e. substances that added in small amounts in the raw meal promote the formation of a particular solid phase by affecting the equilibrium through incorporation in one or more of the solid phases or by promoting the formation of alite at lower temperatures [4]. Mineral additives may also act as fluxes assisting the development of liquid phase and improving its transport properties [1, 4].

Previous works pointed out that several substances such as fluorides or fluoride silicates may act as a fluxing and mineralizing additive [5,6]. Calcium sulfate and fluoride as so or combined are also known as efficient mineralizers [7,8]. An other important class of mineralizes are oxides, such as Fe_2O_3, Cr_2O_3, TiO_2, Mn_2O_3, MnO_2 and SnO_2 [7,9,10].

In practice, the burnability of the raw mix is assessed based on the unreacted lime content in samples burned at different temperatures. Thermal analysis can also provide useful information for the study of raw mix sintering process and the effect of mineral additions on clinker formation [11, 12] as well as on the processes involving hydration of resulted cements [11,13]. Teoreanu et. al. [5] used thermal analysis with good results to study the influence of fluoride compounds on the processes that takes place at the burning of limestone and cement raw mixes.

Despite the extensive literature on the subject, no information was found regarding the effect of mixing the two types of mineralizer – fluorides and oxides. Therefore, in this paper the influence of different types of mineralizer (oxides, fluorides and mixtures of the two materials) on lime decomposition – the main process that takes place at the burning of the raw mix at temperatures below the eutectic temperature - was assessed by thermal analysis (DTA, TG). Additional information about burnability of the industrial raw mix with mineralizers were obtained by free lime evaluation. The clinkers resulted by burning the raw mixes at temperatures between 1250-1450°C were also characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

Limestone, clay and pyrite ash with the chemical compositions presented in Table 1 and compounds such as NaF, KF, CuO and SnO_2 (chemical reagent grade) were used.

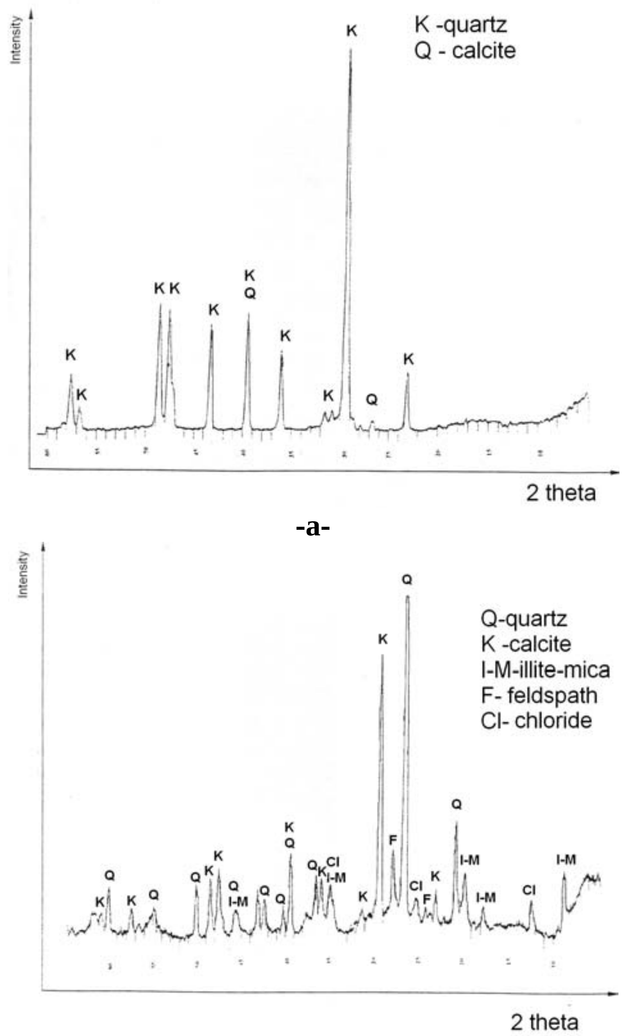
Table 1.

Chemical composition of raw materials (wt.%)

Raw material	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	L.O.I
Limestone	52.11	1.14	0.35	0.32	2.29	0.39	0.15	0.04	43.42
Clay	13.51	47.28	13.78	5.39	1.70	1.23	2.46	-	13.91
Pyrite ash	n.d. *	n.d.	n.d.	79.96	n.d.	0.44	0.25	4.89	n.d.

* not determined

The mineralogical composition of the limestone and clay was assesed by XRD (see fig. 1).



-a-

-b-

Fig. 1. XRD spectra of limestone (a) and clay (b)

As it can be seen, in fig.1, the main compound present in limestone is calcite along with a smaller amount of quartz. In clay, the mineralogical compounds detected by XRD are illite, calcite, quartz, feldspate and chloride. The high amount of quartz from the clay composition suggests a low burnability for this raw material.

The raw mix (F) obtained by the mixing of limestone, clay and pyrite ash has lime saturation factor - LSF[1]=0.96, alumina ratio[2]=1.2 and silica ratio[3]=1.87. The fineness of the raw mix corresponds to a residue of 2.3% on the 200 μm mesh sieve and 13.8% on the 90 μm mesh sieve.

The type and amount of mineralizers added to the raw mix are presented in Table 2.

Table 2.

Type of mineralizers' type and amount in the specimens

Specimen	Fluoride	Oxide
F0.3NaF	0.3%NaF	-
F0.5NaF	0.5%NaF	-
F0.8NaF	0.8%NaF	-
F0.3KF	0.3%KF	-
F0.5KF	0.5%KF	-
F0.8KF	0.8%KF	-
F0.5SnO_2	-	0.5 % SnO_2
F0.8 SnO_2	-	0.8 % SnO_2
F1SnO_2	-	1 % SnO_2
F0.5CuO	-	0.5% CuO
F0.8CuO	-	0.8% CuO
F1CuO	-	1% CuO
F0.5NaF0.5CuO	0.5%NaF	0.5% CuO
F0.5NaF0.5SnO_2	0.5%NaF	0.5 % SnO_2

The raw mixes were pressed to form pellets and then thermally treated in an electric furnace at temperatures between 1200 up to 1450°C, for 30 minutes and cooled rapidly in air. Free lime analysis (standard ethylene glycol method SR EN 196-2:2006) was performed on these specimens.

The decomposition of limestone (main component in the raw mix) was assessed by DTA and TG analysis, using a Shimadzu DTA-TG-50H instrument. The experiments were conducted in air at a constant heating rate of 10°C/min.

In order to investigate clinker formation, XRD analysis was performed on selected specimens thermally treated at 1250, 1350 and 1400°C, using a Shimadzu XRD 6000 difractometer.

[1] LSF= %CaO/ (2.8%SiO_2+1.1%Al_2O_3+0.7%Fe_2O_3)
[2] AR= % Al_2O_3/ %Fe_2O_3
[3] SR= % SiO_2/ (%Al_2O_3+%Fe_2O_3)

SEM analyses were performed on clinkers with/without mineralizer burned at 1430-1450°C for 30 minutes and cooled in air, using a HITACHI S2600N microscope.

4. Results and discussions

4.1. Thermal analysis of the raw mixes

The DTA curves of raw mixes without and with different mineralizers are presented in figs. 2-4.

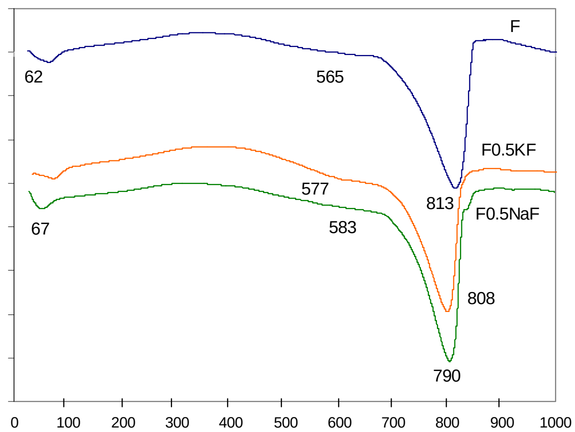


Fig. 2. DTA curves of the raw mix as so (F) and mineralized with 0.5% NaF and 0.5% KF

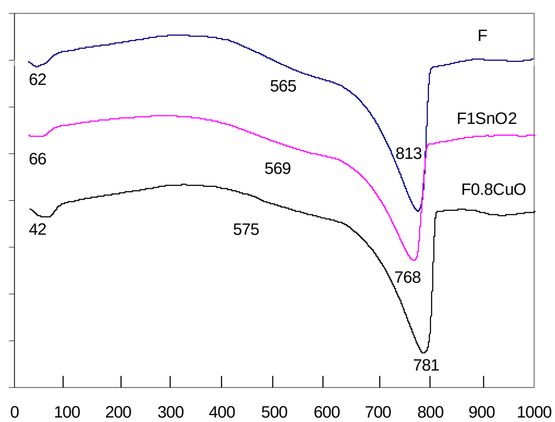


Fig. 3. DTA curves of the raw mix as so (F) and mineralized with 1% SnO_2 and 0.8% CuO

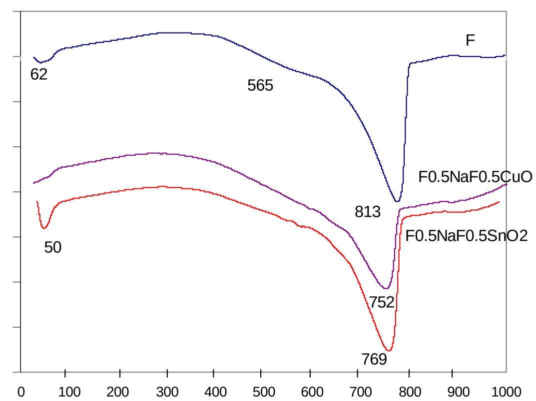


Fig. 4. DTA curves of the raw mix as so (F) and mineralized with mixture of 0.5%NaF+0.5% SnO_2 and 0.5%NaF+0.5% CuO

The DTA curves show the following endothermic effects [11,13]:

- the endothermic effect attributed to the water loss (humidity) – 30-100^{o}C;
- the broad endothermic effect attributed to the molecular water loss and dehydroxilation of the clay structure – 100-650^{o}C;
- the large endothermic effect attributed to the limestone dissociation – 650-1000^{o}C.

The information obtained from the DTA and TG curve processing are presented in Table 3.

Table 3.

Weight loss recorded on TG curves and the maximum temperature of limestone dissociation effect (assesed on DTA curve).

Weight loss (%) Specimen	Temperature (oC)		T max (oC) decarbonation effect
	100-650	650-1000	
F	1.879	32.950	813
F0.5KF	3.266	31.593	808
F0.5NaF	3.088	31.488	790
F1SnO_2	2.179	32.502	768
F0.8CuO	2.271	32.711	781
F0.5NaF0.5SnO_2	2.148	31.306	769
F0.5NaF0.5CuO	4.474	28.685	752

The temperatures at which the maximum of the endothermic effect attributed to limestone dissociation is recorded on the DTA curves are smaller (with 5 up to 60^{o}C) for the mineralized specimens as compared to reference (F). This behavior suggests an acceleration of decomposition process of the limestone existent in the raw mixes [5, 7]. It should be noted that for the mixture of sodium fluoride and CuO (F0.5NaF0.5CuO) the decrease of the temperature characteristic for the limestone dissociation effect is higher as compared with the raw mixes with one mineralizer (F0.8CuO or F0.5NaF) and this suggests a synergetic effect of these two substances.

The effect determined by mineralizers on the reactions that take place in solid phase consists mainly in the increase of weight loss at lower temperatures (see Table 3), suggesting a shifting of the clay and limestone dissociation process at lower temperatures. The important weight loss recorded for specimen F0.5NaF0.5CuO between 100-650^oC correlated with the important decrease of limestone dissociation temperature confirms the beginning of this important endothermic process at temperatures below 650^oC. Therefore, the increase of weight loss recorded for mineralised specimens suggests a higher rate of limestone dissociation process with positive influence on the Portland clinker formation.

This effect of oxides on the processes that take place below the eutectic temperature, such as limestone dissociation process, seems to be less important as compared with fluorides. Literature data suggest a more intense effect of the oxides on the processes specific to Portland clinker formation that take place in the presence of liquid phase [7, 9].

4.2. Mineralizers effect on the free lime content and burnability of the raw mix

The effect on the burnability of raw mix was evaluated based on the free lime content (f_{CaO}) in the specimens thermally treated at different temperatures. The burnabilty (BC) of the raw mix was calculated with the following formula [10]:

$$BC=3.75(f_{CaO,\,1350^oC}+f_{CaO,\,1400^oC}+f_{CaO,\,1450^oC})/(f_{CaO,\,1350^oC})^{1/4}.$$

Lower values of BC correspond to a higher burnability of the raw mix. Based on the data presented in fig. 5, it can be estimated a positive effect of all mineralizers used (florides, oxides and mixtures of NaF and oxides). The synergic effect of the mixture of sodium fluoride and oxides (SnO_2 and CuO) on the raw mixes burnability is also confirmed by the data presented in fig. 5.

The influence of the mineralizers amount on the free lime content is shown in figs 6 and 7. The optimum amount of mineralizers in the raw mix depends on the mineralizer type and burning temperature. For the samples with SnO_2 the lower values of free lime are recorded for 1% wt. mineralizer and for those with CuO for a smaller amount - 0.3-0.5%.

For the specimens with NaF the increase of the mineralizers amount decrease the free lime content in the burned clinkers, especially for lower temperatures (fig.6). As it can be seen the mineralizer effect of NaF is more intense as compared with KF; for the specimens mineralised with 0.5-0.8% florides is possible to decrease the clincher burning temperature up to 1400°C and to obtain a clinker with free lime content under 2%.

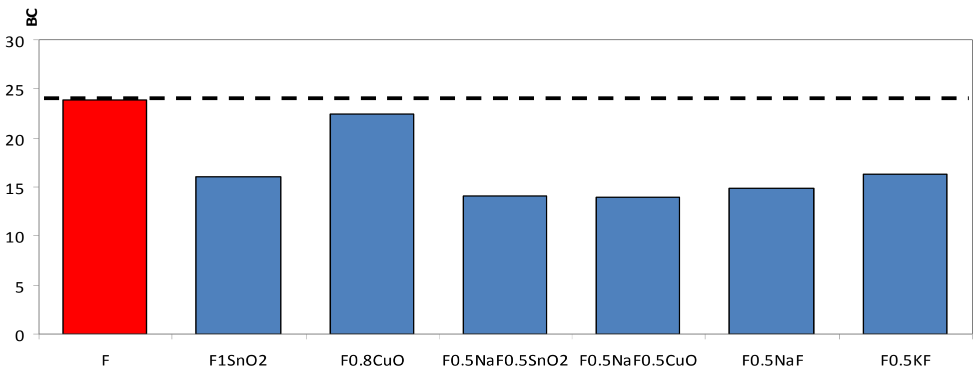
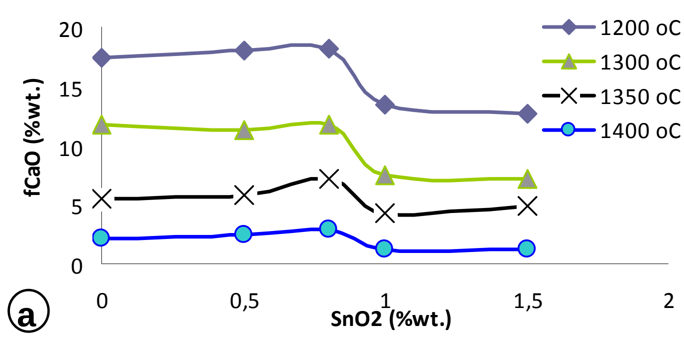


Fig. 5. The effect of mineralizers on the burnability of raw mix



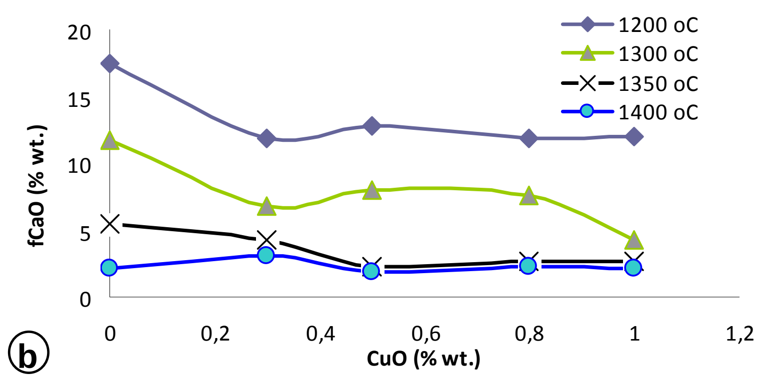


Fig. 6. The influence of oxides amount on free lime content of the raw mix burned at temperatures between 1200-1400°C: a) SnO_2; b) CuO.

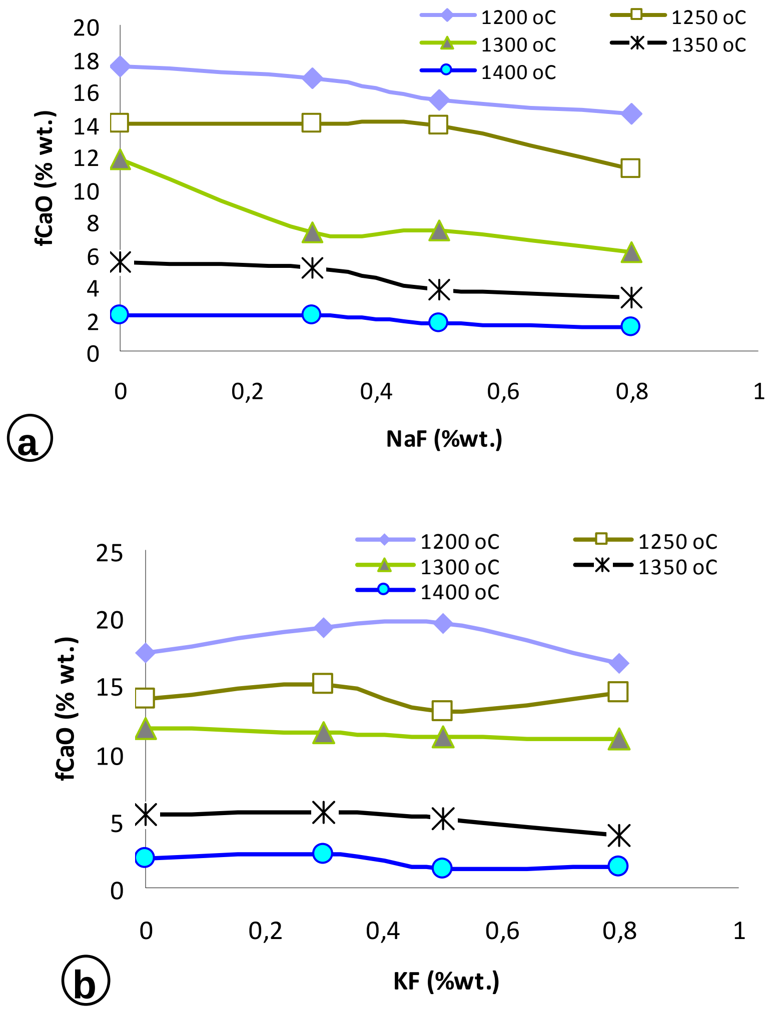


Fig. 7. The influence of fluorides amount on free lime content of the raw mix burned at temperatures between 1200-1400°C: a) NaF; b) KF.

4.3. XRD and SEM analysis of clinkers

In figures 8-10 are shown the XRD patterns of the clinkers with/without mineralizers burned at different temperatures. As it can be seen the XRD peaks specific for calcium silicates ($3CaO.SiO_2$ -C_3S and $2CaO.SiO_2$ - C_2S) are more intense for the specimens burned at higher temperatures and with mineralizer suggesting an intensification of the formation process of these clinker minerals.

The content of C_3S in burned clinkers assessed through the intensity of its specific peaks (d=1.76Å and 3.01Å) is presented in fig. 11; for the samples with mineralizer the C_3S formation seems to be more intense as compared to reference. This can be explained by the formation of liquid phase in the mineralized specimens at lower temperatures, phenomenon that promote the formation of this mineral [5, 9, 14].

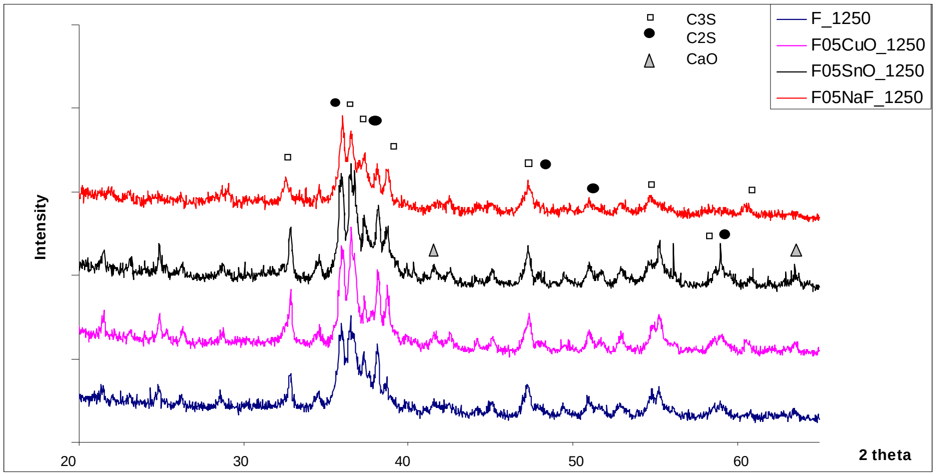


Fig.8. XRD spectra of the clinkers with/without mineralizers burned at 1250°C

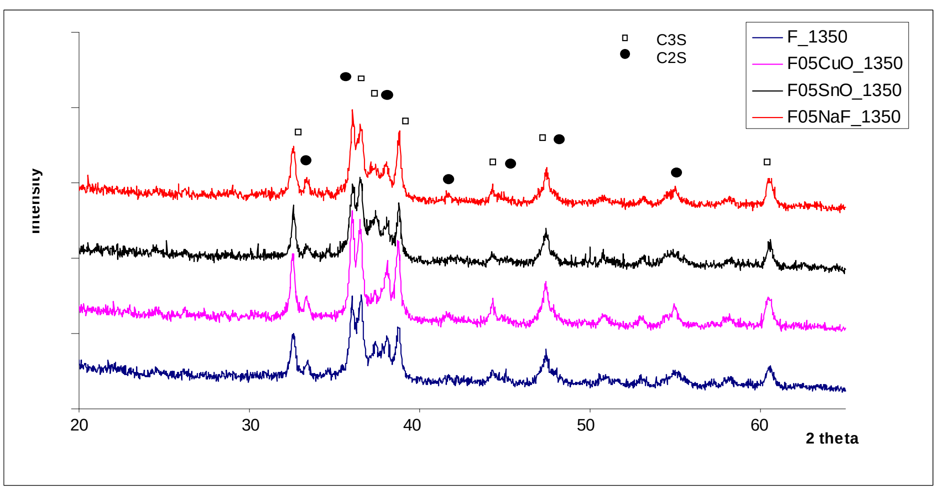


Fig.9. XRD spectra of the clinkers with/without mineralizers burned at 1350°C

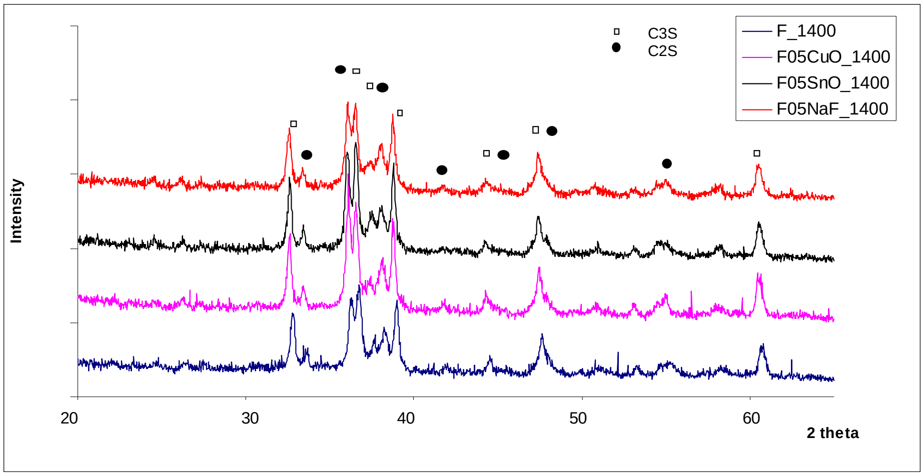


Fig.10. XRD spectra of the clinkers with/without mineralizers burned at 1400°C

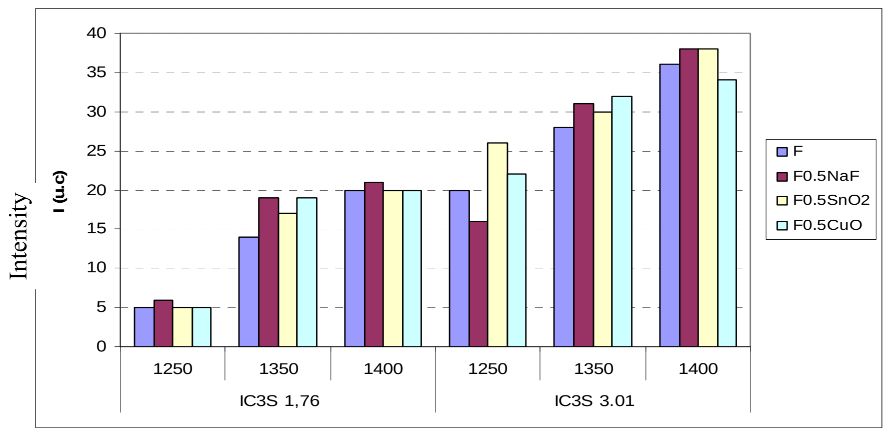


Fig.11. Intensity of XRD peaks specific attributed to C_3S in clinkers with/without mineralizers burned at different temperatures

The SEM analysis of clinkers burned at 1430-1450°C are presented in figures 12-13. The micrographs are representative for assessment of the size and distribution of alite and belite crystals, as well as the amount of vitreous phase formed by rapid clinker cooling.

In the reference specimen (fig.12 a) large (20-25 μm) prismatic alite crystals- A- along with small (3-6 μm) rounded belite-B- crystals are covered with vitreous phase. Ferrite crystal box work – C-are also present at the border of the big alite grains [15].

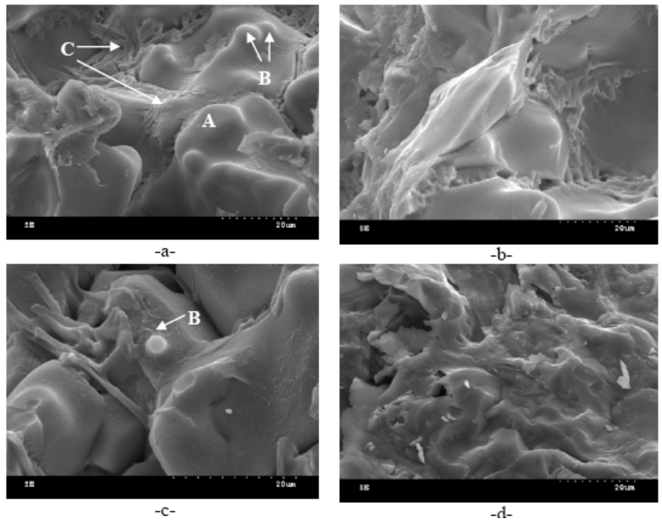


Fig.12. SEM micrographs (x1.5k) of the clinkers: a- reference specimen burned at 1450°C; b-clinker with 0.5%CuO burned at 1450°C; c-clinker with 0.5% SnO_2 burned at 1450°C; d- clinker with 0.5% NaF burned at 1430°C

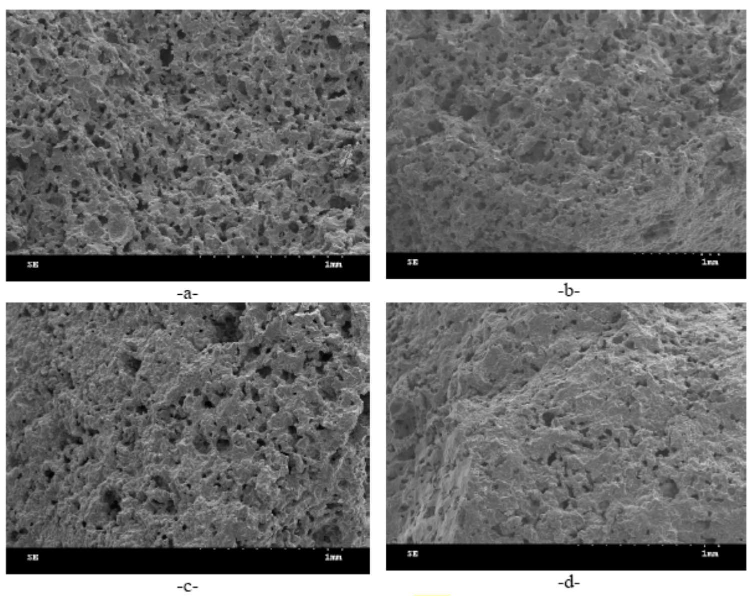


Fig.13. SEM micrographs (x50) of the clinkers: a- reference specimen burned at 1450°C; b-clinker with 0.5%CuO burned at 1450°C; c-clinker with 0.5% SnO_2 burned at 1450°C; d- clinker with 0.5% NaF burned at 1430°C

In the specimens mineralized with CuO (fig.12b) and SnO_2 (fig.12c) the dimensions of alite crystals increases (over 30 μm), while the amount and dimensions of belite nodules decrease. The specimen with NaF content (fig.12d) has a slightly different morphology; the higher amount of vitreous phase present in this specimen supports the previous findings regarding the formation of liquid phase at lower temperatures and in higher amount. The lower porosity of the clinker specimen with NaF content (fig.13d) as compared to reference (fig.13a) and even with the specimen with SnO_2 (fig.13c) confirms this assumption.

6. Conclusions

The following conclusions can be drawn from the present study:

– The additions of oxides (CuO and SnO_2) and fluorides (NaF, KF) decrease the temperature at which starts the dissociation process of the calcium carbonate from the raw mix. The influence of fluorides is more intense as compared to that of oxides. For specimens mineralised with mixtures of oxides and sodium fluoride a positive synergic effect on the raw mix burnability was noticed.

– The presence of mineral additions also favours the binding of free lime; for specimens with SnO_2 the lower values of free lime were obtained for 1% wt. mineralizer and with CuO for 0.3-0.5% wt., respectively. For the specimens mineralised with 0.5-0.8% fluorides it is possible to decrease the clinker burning temperature up to 1400^oC and to obtain a clinker with free lime content under 2%.

– For the raw mixes with mineralizers (oxides, fluorides or mixtures), the C_3S formation is more intense as compared to reference specimen; this can be explained by formation of liquid phase in the mineralized specimens at lower temperatures, phenomenon that promotes the formation of this mineral.

– In specimens mineralized with 0.5%CuO and 0.5%SnO_2 the dimensions of alite crystals increases and the amount and dimensions of belite nodules seems to decrease as compared to reference. There is a higher amount of vitreous phase in a specimen with NaF which determines the lowering of the clinkers porosity, as compared to reference one and even compared to a specimen with SnO_2 content.

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