

Hydration and hardening processes of Portland cements obtained from clinkers mineralized with fluoride and oxides

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Abstract The hydration and hardening processes of Portland cements prepared from clinkers mineralized with sodium fluoride and/or oxides (SnO_2 or CuO) was studied. Type I cements (CEM I) were prepared by grinding with gypsum (5%) of clinkers obtained by the burning of an industrial raw mix with different mineralizers: sodium fluoride, oxides (CuO and SnO_2) or mixtures of sodium fluoride and oxide ($\text{NaF} + \text{CuO}$ or $\text{NaF} + \text{SnO}_2$). The influence of foreign ions on the clinker morphology was assessed by scanning electronic microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The hydration processes of modified cements were examined by X-ray diffraction analysis (XRD) and thermal analysis techniques (TG and DTA). The main properties of the cements, i.e., flexural and compressive strengths, setting time, and soundness were also determined. A good correlation between the chemically bound water or portlandite content in pastes hydrated 2–28 days and compressive strength developed by mortars was observed. The influence of mineralizers on the kinetic of hydration processes and main properties of cements is different—0.5% NaF and 0.5% SnO_2 and their mixture increase the rate of cement hydration and hardening processes, opposite to 0.5% CuO that reduce the rate.

Keywords Portland cement · Hydration · Mineralizers (NaF, CuO , SnO_2)

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Introduction

The use of different types of alternative fuels, wastes or secondary raw materials in the manufacture of Portland cement represents an attractive approach for energy preservation and reduction of greenhouse gases emissions (especially CO_2). Due to their content in foreign elements alternative materials used as admixtures to the raw mix such as ferrous and non-ferrous slag, foundry sand, fly ashes or as alternative fuels (tiers, oils) can influence the raw mix burning process as well as the reactivity of resulted clinker [1–3]. The elements present in these materials can act as mineralizers, i.e., substances that added in small amounts in raw mix can influence, in a benefic way, the reactions that take place during the burning of cement clinker. The effect of mineralizers can be summarized in changes of chemical, mineralogical, structural, textural, mechanical, and physical properties of the clinker and resulted cement [4]. Available literature on mineralizers presents mainly the influence of individual minor components comprised in one of the following groups: alkalis, transition metals, halogens and p-block elements, and are focused on their effect on the clinker burning process as well as on the assessment of mineralogical composition and texture of modified clinkers [1, 4]. Data on combined effect of different type of compounds or regarding the influence of foreign ions on the cement hydration and hardening processes are less numerous [4–8].

Fluorides are well-known mineralizers and fluxing agents [4, 9, 10] and may enter into the kiln system with raw materials and/or fuels. CuO is a relatively abundant element with rather low potential impact on environment through leaching from concrete [4]. Moreover the copper oxide has a remarkable mineralizing effect on different

Table 1 Sintering temperatures and free lime content in clinkers

Clinker	Mineralizers	Sintering temperature/°C	Free CaO ^a /%
C0	–	1,450	0.87
C1	0.5% NaF	1,400	1.34
C2	0.5% SnO ₂	1,430	0.48
C3	0.5% CuO	1,400	1.86
C4	0.5% NaF + 0.5% SnO ₂	1,380	1.49
C5	0.5% NaF + 0.5% CuO	1,380	1.17

^a Free lime assessment with standard ethylene glycol method SR EN 196-2:2006

Fig. 1 SEM micrographs of reference clinker C0 (without mineralizer): **a** $\times 500$ and **b** $\times 1,500$

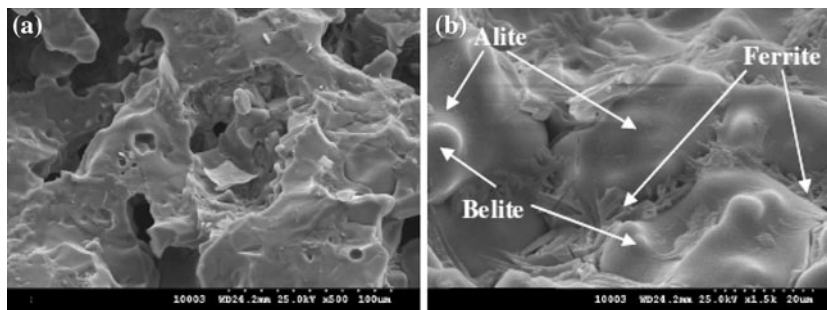


Fig. 2 SEM micrographs ($\times 1,000$) of clinker C1 (with 0.5% NaF)

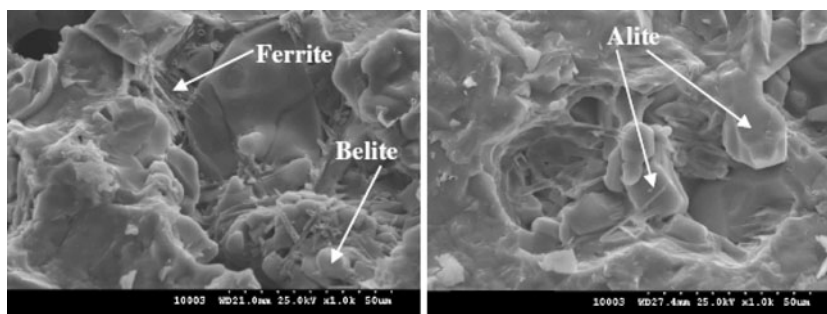
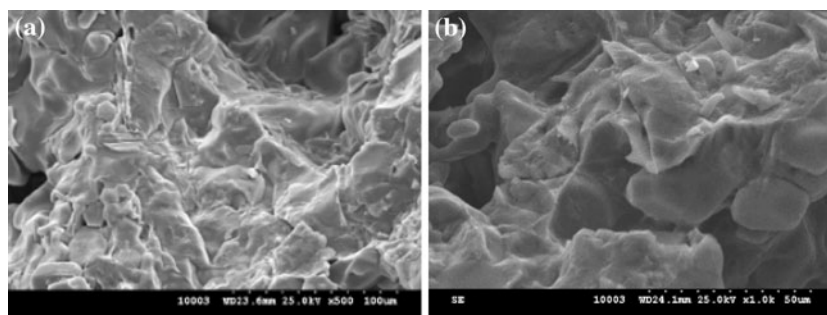


Fig. 3 SEM micrographs of clinker C2 (with 0.5% SnO₂) **a** $\times 500$ and **b** $\times 1,000$



type of clinkers, i.e., with high C₂S or C₃S content [4] or Portland clinkers with 3CaO·3Al₂O₃·CaSO₄ content [5]. Tin (IV) oxide was also reported to be a good mineralizer for Portland cement production [11, 12], but little information is available regarding its influence on the hydration processes of resulted clinker and cement [13]. Due to the simultaneous presence of fluorides and Cu/Sn elements in the raw mix or fuels, the combined effect of these

mineralizers on the cement burning and binding properties can provide useful information for the improvement of environmental issues in cement production.

In previous works [14, 15], the influence of mixtures of fluorides (NaF, KF) and/or copper or tin (IV) oxides on the burnability of the raw mix was studied. Both fluorides and oxides additions decrease the temperature at which starts the dissociation process of calcium carbonate from the raw

Fig. 4 SEM micrographs ($\times 1,000$) of clinker C3 (with 0.5% CuO)

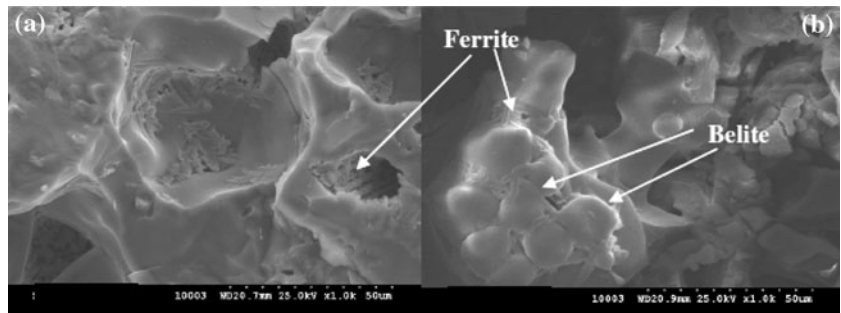


Fig. 5 SEM micrographs of clinker C4 (with 0.5% NaF + 0.5% SnO₂): **a** $\times 500$ and **b** $\times 1,000$

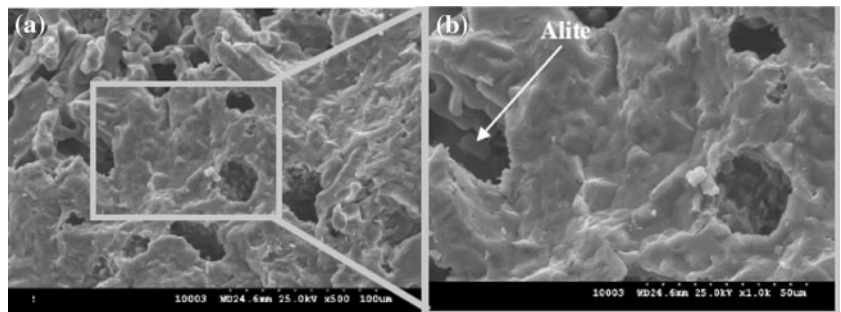


Fig. 6 SEM micrographs of clinker C5 (with 0.5% NaF + 0.5% CuO): **a** $\times 500$ and **b** $\times 1,800$

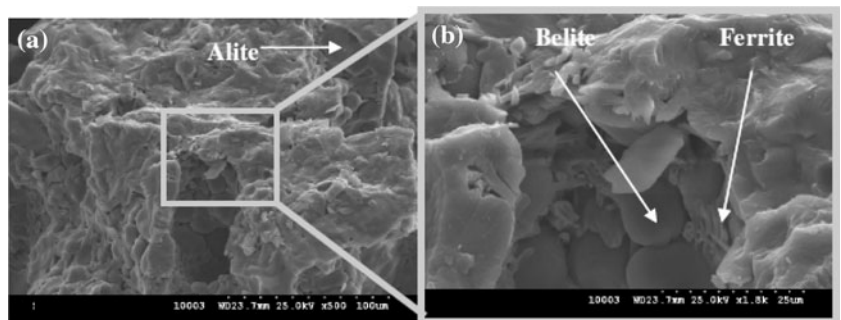


Fig. 7 SEM micrograph of clinker C1 (**a**) and EDX analysis: **b** Si and Ca; **c** Al, Ca and Fe; and **d** Na

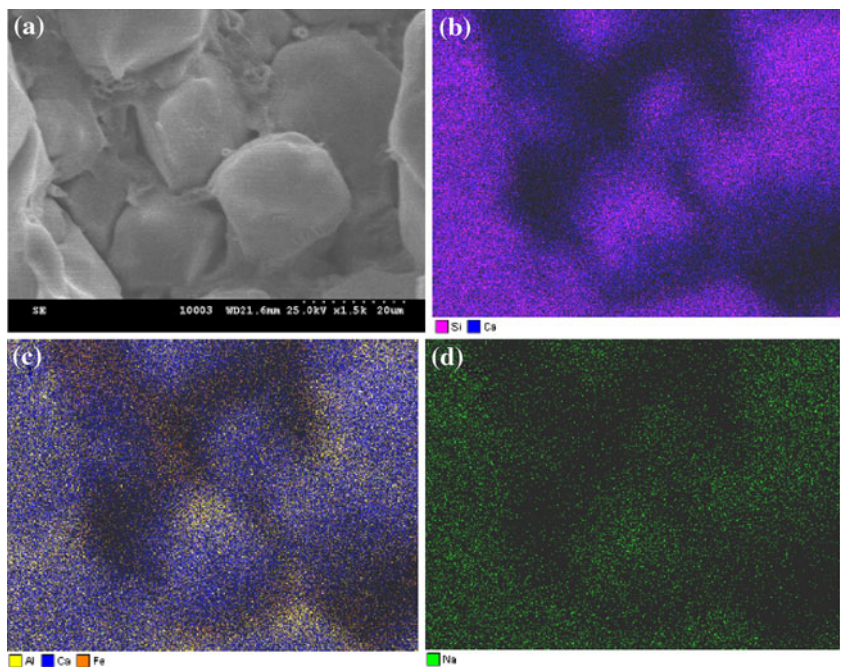


Fig. 8 SEM micrograph of clinker C2 (a) and EDX analysis: b Si and Ca; c Al, Ca and Fe; and d Sn

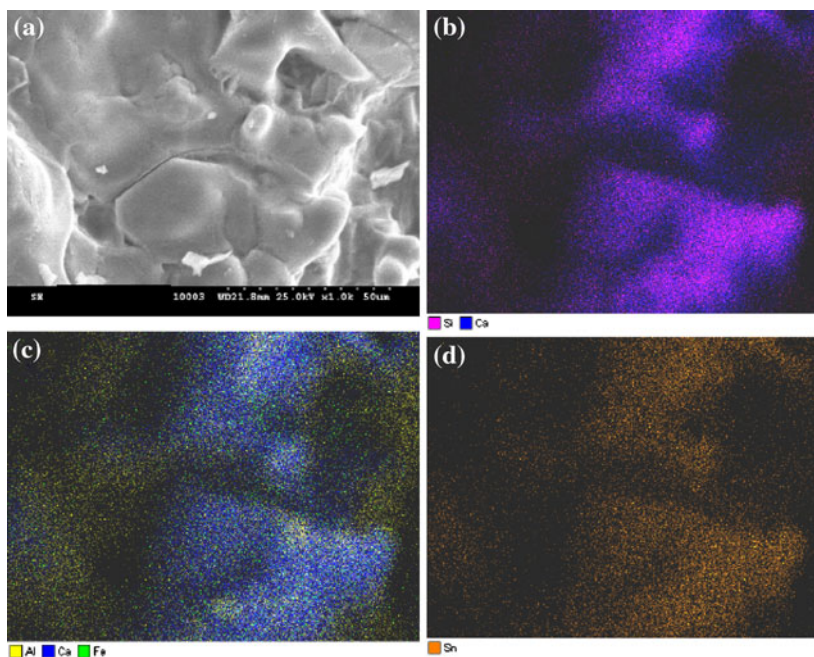


Table 2 Physical and mechanical properties of the studied cements

Cement	Properties:										
	Fineness/ cm ² /g	Water for standard consistency/%	Setting time		Soundness/ mm	Flexural strength/MPa			Compressive strength/MPa		
			Initial/min	Final/h min		2 days	7 days	28 days	2 days	7 days	28 days
C0	3,530	24.4	200	4.00	2.0	3.35	5.93	8.32	15.5	31.7	50.7
C1/C0 + 0.5% NaF	3,520	23.6	190	4.00	0.5	4.5	7.25	8.62	20.8	44.5	56.7
C2/C0 + 0.5% SnO ₂	3,510	24.0	180	4.30	0	4.1	7.4	8.66	20.1	40.4	61.9
C3/C0 + 0.5% CuO	3,530	24.4	225	5.30	0.5	3.42	6.02	8.36	16.6	36.9	54.2
C4/C0 + 0.5% NaF + 0.5% SnO ₂	3,480	24.0	180	3.45	1.5	4.48	7.22	8.10	20.6	42.8	58.3
C5/C0 + 0.5% NaF + 0.5% CuO	3,500	23.4	220	5.00	1.0	3.76	7.49	8.34	16.8	43.8	57.9

mix and increase the alite content in clinker. The combined use of oxides and sodium fluoride has a positive synergic effect on the raw mix burnability [15].

In this article, the influence of mineralizers, i.e., sodium fluoride and/or oxides (SnO₂ or CuO) on the Portland clinker morphology was assessed by scanning electronic microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The hydration and hardening processes of Portland cements (CEM I) prepared from mineralized clinkers were studied by X-ray diffraction (XRD) and thermal analysis (TG and DTA). The main properties of cements, i.e., mechanical strengths, water for standard consistency, setting time, and soundness were also assessed.

Materials and methods

The clinkers were obtained by the burning of an industrial raw meal (with main components limestone, clay, and pyrite ash) with $LSF^1 = 0.96$, alumina ratio² = 1.2, and silica ratio³ = 1.87 [15]. The fineness of the raw mix corresponds to a residue of 2.3% on the 200- μ m mesh sieve and 13.8% on the 90- μ m mesh sieve.

As mineralizers NaF, CuO, and SnO₂—chemical reagent grade, were used.

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 $SR = \% SiO_2 / (\% Al_2O_3 + \% Fe_2O_3)$.

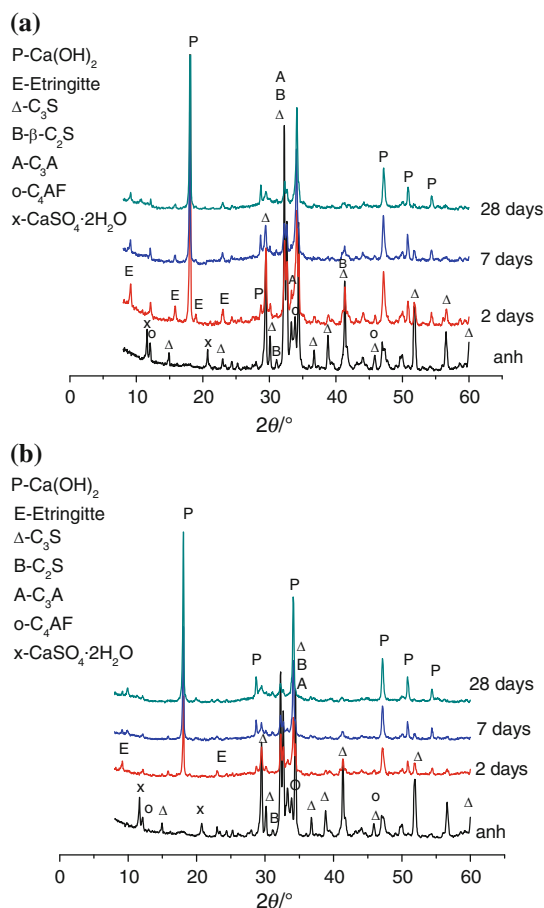


Fig. 9 XRD patterns anhydrous and cement pastes cured for 2, 7, and 28 days: **a** C0 reference Portland cement paste and **b** C1 (with 0.5% NaF)

The raw mixes were pressed to form pellets and thermally treated in an electric furnace at temperatures between 1,380 up to 1,450 °C, for 30 min and cooled rapidly in air. The sintering temperatures (Table 1) were selected based on previous results [14, 15] in order to achieve free lime content below 2%.

SEM analyses were performed on selected clinkers nodules coated with Au using a HITACHI S2600N microscope equipped with EDX with accelerating voltage 25 kV.

The cement pastes were prepared with water to binder ratio of 0.5, sealed in plastic bags and stored for 2, 7, and 28 days. Hydration was stopped by acetone washing and oven-drying at 60 °C for 4 h. The hydrates formed in the cement were assessed by XRD and thermal (DTA and TG) analysis.

The XRD spectra were recorded in the range $2\theta = 5\text{--}60$, with a Shimadzu XRD 6000 diffractometer using monochromatic Cu K_{α} radiation ($\lambda = 1.054 \text{ \AA}$).

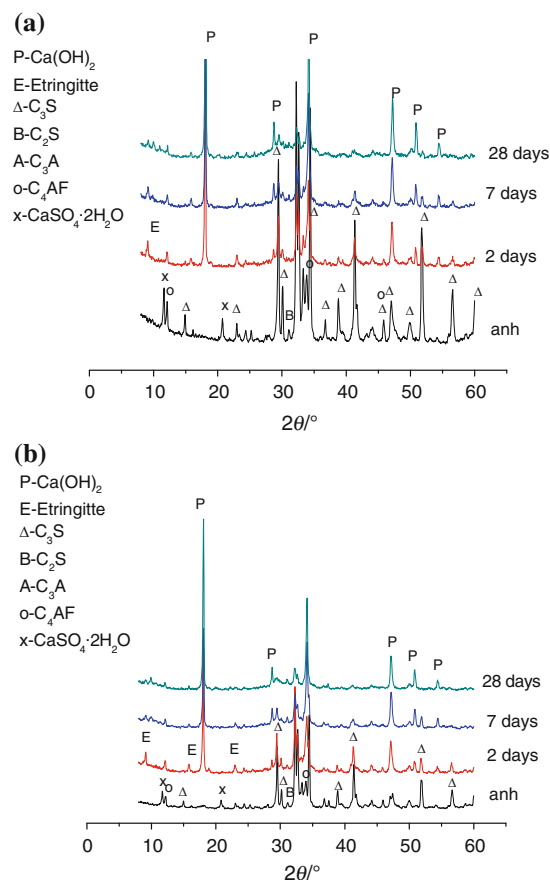


Fig. 10 XRD patterns of anhydrous and cement pastes cured for 2, 7, and 28 days: **a** C2 (with 0.5% SnO_2) and **b** C3 (with 0.5% CuO)

The thermal analysis were performed with a Shimadzu DTA-TG-50H instrument. The thermal analyses were conducted in the following conditions:

- Temperature range: 20–1,000 °C,
- Heating rate: 10 °C/min,
- Furnace atmosphere: air,
- Platinum crucibles (\varnothing 6 mm): uncovered,
- Inert thermal substance: alumina.

The main properties of the cements were assessed using the European and corresponding Romanian standard methods:

- Water for standard consistency, setting time, and soundness—SR EN 196-3;
- Flexural and compressive strength—SR EN 196-1.

Results and discussion

The SEM analyses of clinkers are presented in Figs. 1, 2, 3, 4, and 5. The micrographs are representative for the

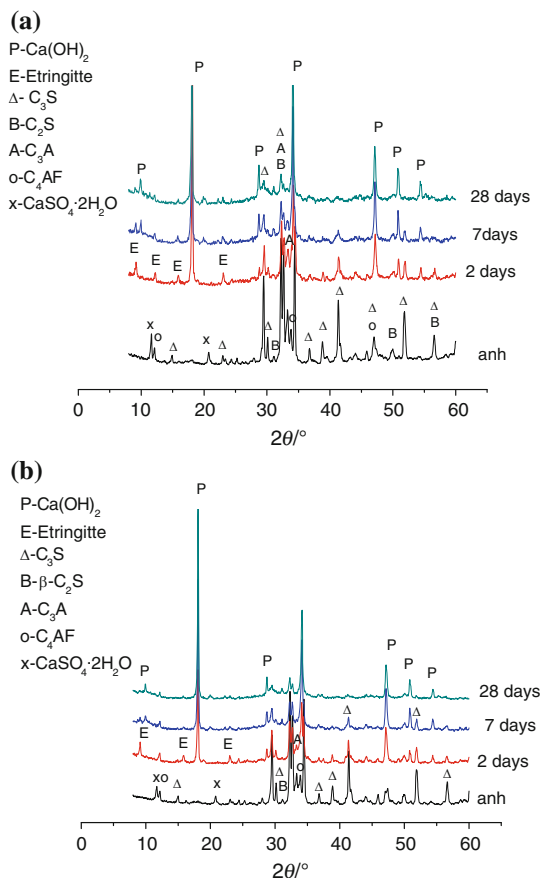


Fig. 11 XRD patterns of anhydrous cements and pastes cured for 2, 7, and 28 days: **a** C4 (with 0.5% NaF + 0.5% SnO₂) and **b** C5 (with 0.5% NaF + 0.5% CuO)

assessment of 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. 1b) large (20–25 μm) prismatic alite crystals along with small (3–6 μm) rounded belite crystals are covered with vitreous phase. Ferrite crystal box works are also present at the border of the big alite grains [15–17].

Figure 2 shows the morphology of the clinker mineralized with 0.5% NaF. This specimen has a slightly different morphology, i.e., bigger alite (20–40 μm) grains along with a higher amount of vitreous phase supports the previous findings regarding the formation of liquid phase at lower temperatures and in higher amount [9–15].

In the specimen containing SnO₂ (Fig. 3) the dimensions of alite crystals increase (over 30 μm) and the vitreous phase, present in high amount, partially covers the alite and belite crystals.

Figure 4 shows the morphology of clinker C3 containing 0.5% CuO. The amount of vitreous phase increases in this specimen as compared with reference (Fig. 4a) and rounded belite grains forms nests (Fig. 4b) [12, 18].

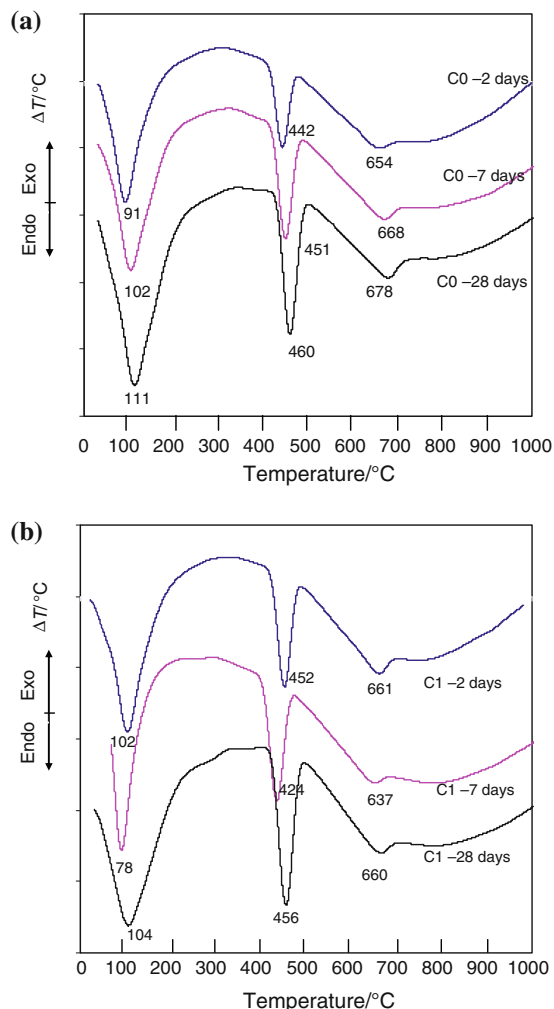


Fig. 12 DTA curves of cement pastes hydrated for 2, 7, and 28 days: **a** C0: reference Portland cement paste and **b** C1 (with 0.5% NaF)

The morphology of the clinker mineralized with NaF and SnO₂ mixture (Fig. 5) suggests the increase of vitreous phase amount as compared with reference, due to the mineralizers' presence.

In the specimen containing NaF and CuO mixture (Fig. 6) clusters of round belite grains are present along with ferrite phase. The amount of vitreous phase is also higher in this specimen as compared with reference clinker and bigger alite crystals (40–50 μm) are also identified.

The SEM examination of the clinkers showed that for those obtained from raw mixes with mineralizers (oxides, fluorides, or mixtures), the size and shape of the silicates and interstitial phases are modified as compared with reference clinker (C0). Also the amount of vitreous phase increase in all mineralized clinkers.

The EDX analysis of clinkers C1 and C2 are presented in Figs. 7 and 8.

As it can be seen from Fig. 7d, Na is present both in interstitial phase and in a bigger amount in calcium

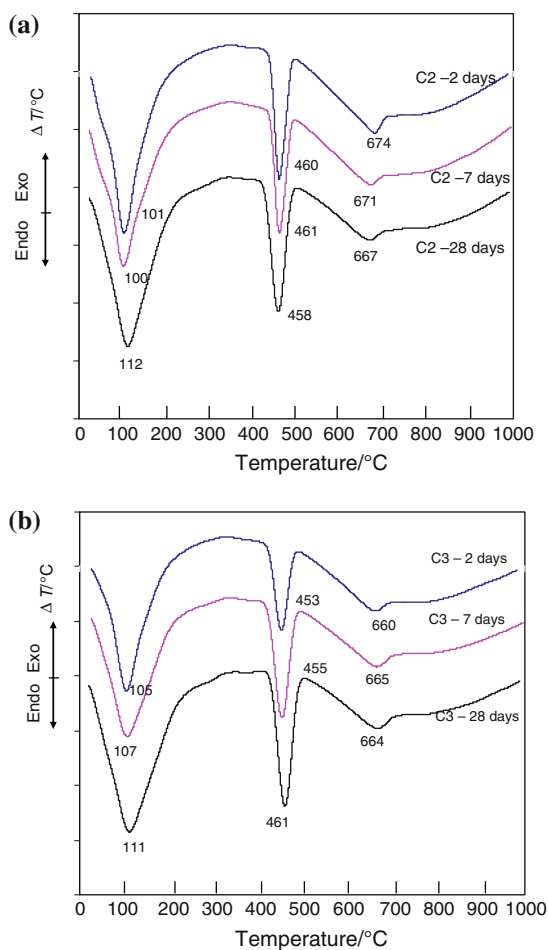


Fig. 13 DTA curves of cement pastes hydrated for 2, 7, and 28 days: **a** C2 (with 0.5% SnO₂) and **b** C3 (with 0.5% CuO)

silicates grains. Sn is assessed mainly in the calcium silicates (Fig. 8a). These data suggests the incorporation of the foreign elements (Na and Sn) in the lattices of silicates minerals and consequently the modification of their reactivity.

The main properties of the CEM I cement prepared with the mineralized clinkers are presented in Table 2.

The values of all assessed properties fulfill the requirements of the European standard EN 197-1:2000.

The use of mineral additions for clinker preparation has no major influence on the value of water for standard consistency (see Table 2). The addition of 0.5% NaF (C1) and 0.5% SnO₂ (C2) slightly decreases the value of initial setting time, as compared with the cement without mineralizer (C0), and increase the values of flexural and compressive strengths especially at early ages (2 and 7 days). If both mineralizers are used for clinker/cement preparation (C4) the sintering temperature can be decrease with 70 °C (see Table 1). The values of mechanical strengths recorded for C4 cement are close to those assessed for C1 and C2 cements as compared with the values recorded for

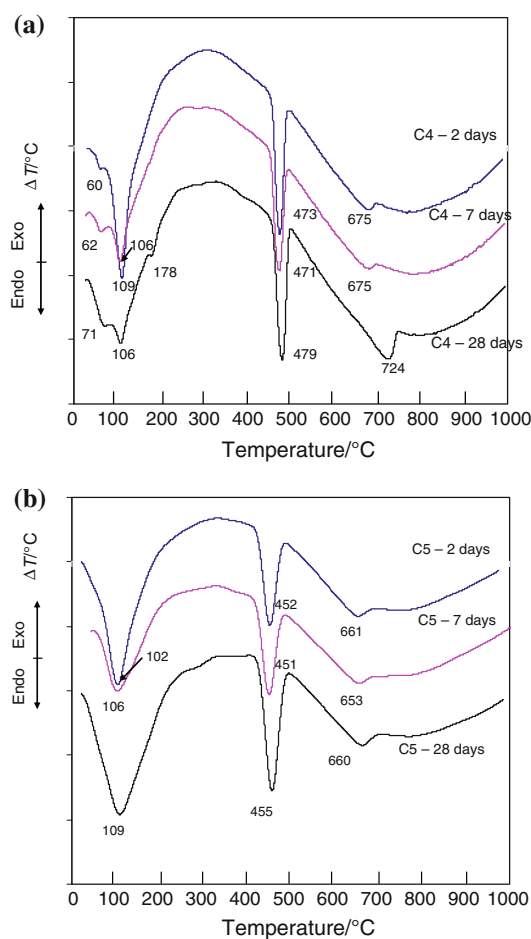


Fig. 14 DTA curves of cement pastes hydrated for 2, 7, and 28 days: **a** C4 (with 0.5% NaF + 0.5% SnO₂) and **b** C5 (with 0.5% NaF + 0.5% CuO)

reference cement (without mineralizer). The increase of the mechanical strengths of the cements mineralized with fluoride or/and SnO₂ can be explained by the incorporation of the foreign elements in the silicates lattice (Figs. 7, 8) and consequently the modification of their reactivity.

The use of 0.5% CuO, as mineralizer, seems to decrease the rate of hydration and hardening processes of resulted cement (C3), i.e., the values of both initial and final setting time are higher as compared with reference cement (C0). Still, both flexural and compressive strengths recorded for all hardening times (2–28 days) are similar or even higher as compared with those recorded for C0.

The combined use of 0.5% NaF and 0.5% CuO as mineralizer for clinker burning seems to reduce the retarding effect determined by the use of CuO alone—the values of initial and final setting time of C5 are smaller as compared with those recorded for C3.

The XRD spectra of anhydrous cement and pastes hydrated 2–28 days are presented in Fig. 9, 10, and 11. XRD patterns of the main mineralogical compounds specific to

Table 3 Weight loss recorded on TG curves for different temperature ranges

Cement	Weight loss /%/ between																	
	20–1,000 °C		20–210 °C		210–400 °C		400–500 °C		500–600 °C		600–1,000 °C							
	2 days	7 days	2 days	7 days	2 days	7 days	2 days	7 days	2 days	7 days	2 days	7 days						
C0	14.86	19.21	22.14	7.11	8.35	9.63	1.94	2.73	3.56	2.55	3.52	4.13	0.57	0.71	0.49	2.69	4.08	4.30
C1/0.5% NaF	16.48	19.77	24.00	7.26	8.50	9.49	2.01	3.24	4.27	3.16	4.12	5.17	0.65	1.00	0.97	3.37	3.27	4.09
C2/0.5% SnO ₂	16.29	19.03	22.82	7.25	8.47	9.65	1.94	2.82	3.93	2.30	4.09	4.72	0.50	0.51	0.82	3.60	3.44	3.69
C3/0.5% CuO	15.29	19.66	23.17	7.25	8.15	9.59	2.24	3.13	4.05	2.79	3.70	4.88	0.41	0.71	0.80	2.60	3.71	3.82
C5/0.5% NaF + 0.5% CuO	14.94	19.30	23.65	7.04	7.40	9.67	2.19	3.39	4.40	2.91	3.98	4.74	0.53	0.88	0.91	2.27	3.64	3.94
C4/0.5% NaF + 0.5% SnO ₂	15.28	20.46	25.70	7.03	8.61	8.75	2.28	3.69	3.98	2.70	3.49	3.59	0.40	0.66	0.78	2.88	4.03	4.97

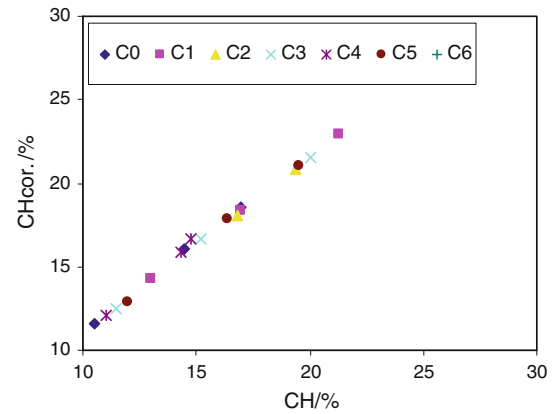


Fig. 15 Corrected portlandite amount—CHcor. (considering the Ca(OH)₂ converted in CaCO₃) versus portlandite amount calculated based on the weight loss on TG curve between 400 and 500 °C

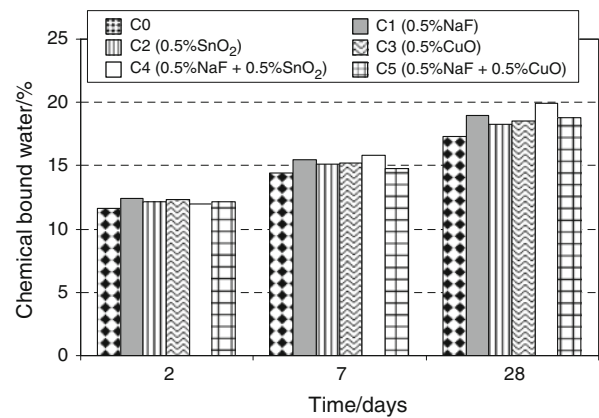


Fig. 16 Chemical bound water in hydrates (weight loss on TG curve between 20 and 500 °C) versus time

Portland cement are present, i.e., alite (3CaO·SiO₂—3.02, 2.77, 2.73, 2.60, and 1.76 Å), belite (β 2CaO·SiO₂—2.79, 2.74, and 2.69 Å), brownmillerite (7.25, 2.77, 2.64, and 1.93 Å), and gypsum (CaSO₄·2H₂O—7.56, 4.27, and 3.05 Å) [16]. The crystalline hydrates assessed by this method on the XRD spectra of hydrated pastes are portlandite (Ca(OH)₂—4.90, 2.63, 1.92, 1.79, and 1.73 Å) and ettringite (3CaO·Al₂O₃·3CaSO₄·31H₂O—9.73, 5.61, and 3.88 Å) [16]. As expected, with the increase of the hydration time, the intensity of XRD patterns specific for anhydrous compounds decreases and the intensity of portlandite and ettringite peaks increases due to the formation of these hydrates in a higher amount and possibly due to the increase of their crystalline degree.

Due to the low amount (0.5%) in which the mineralizers were introduced in the raw mix, on the XRD patterns of the anhydrous cements were not recorded peaks specific for crystalline compounds with Sn or Cu content, reported in other works for clinkers mineralized with 2–2.5% SnO₂ or CuO [5, 11].

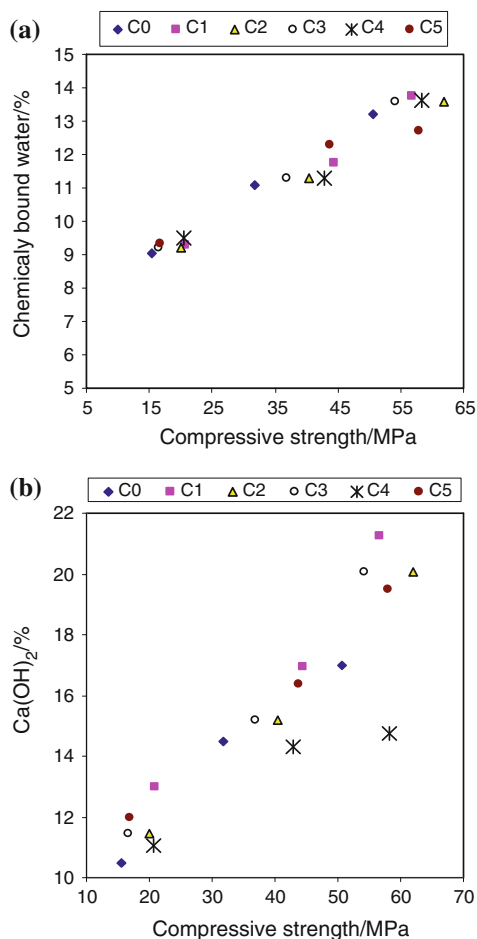


Fig. 17 Chemically bound water (Cbw) **a** Ca(OH)₂ amount in pastes **(b)** versus compressive strength, after 2–28 days of curing

Table 4 R² values for linear regression type between compressive strength (Cs) and chemically bound water in hydrates (Cbw) or formed Ca(OH)₂–CH

Cement	R ² value for linear regression type	
	Cbw ↔ Cs	CH ↔ Cs
C0	1.00	0.97
C1	0.98	0.96
C2	0.95	1.00
C3	0.99	0.99
C4	0.96	0.90
C5	0.95	0.99

Thermal analysis can provide quantitative information regarding both crystalline hydrates (portlandite, AFt, and AFm phases) as well as poorly crystalline hydrates—such as C-S-H, formed in cement pastes after different times of hydration [3, 19–25]. The DTA curves recorded on cement pastes, obtained from clinkers with/without mineralizers, are presented in Fig. 12, 13, and 14.

The endo-effects recorded on DTA curve and the corresponding mass loss determined on TG curves (Table 3) suggests the following processes [3, 19–25]:

- The large endothermic effect from 91 to 111 °C recorded for all cement pastes is assumed to be due to the superposition of more endo-effects. As it can be better noticed for cement 4 (Fig. 14a) this large endo-effect is formed by the superposition of three distinct endothermic effects—the first effect from 60 to 71 °C is most probably due to the loss of humidity, second effect from 106 to 109 °C attributed to loss of water bound in C–S–H phases and the endo-effect from 178 °C can be attributed to water loss from AFt/AFm phases,
- The endo-effect from 424 to 479 °C is assumed to be due to the portlandite dehydration,
- The endo-effect from 660 to 724 °C is generally attributed to the decomposition of CaCO₃ (eventually formed by Ca(OH)₂ carbonation during specimen preparation and curing).

The sensitivity of portlandite to carbonation is well known [19–24]. Some of the researchers convert the weight loss recorded in the range 600–700 °C in equivalent Ca(OH)₂ and then in equivalent H₂O in order to reduce the carbonation influence on the assessment of portlandite amount and chemically bound water in hydrates [3, 11].

In Fig. 15, the portlandite amount corrected by this method (CHcor.) versus the amount of Ca(OH)₂ calculated based on the weight loss recorded between 400 and 500 °C (CH). As it can be seen from Fig. 15, the dependence of the two values is almost linear and if the specimens are prepared, stored, and analyzed in the same conditions the carbonation influence is similar; therefore the comparison of the values of chemically bound water in hydrates or of the portlandite amount formed in hydrated pastes can provide reliable quantitative information regarding the influence of foreign ions on the rate of hydration processes.

TG results presented in Table 3 confirms the positive effect of NaF and SnO₂ additions on the hydration rate of mineralized cements, i.e., the increase of the hydrates amount (assessed by chemically bound water—Cbw (mass loss in the range 20–500 °C) as compared with reference cement (C0)—Fig. 16.

The retarding effect of 0.5% CuO addition (C3) on the setting time is confirmed by the lower values of Cbw in this cement, especially at early ages (2 and 7 days) as compared with the cements based on clinkers mineralized with fluoride and SnO₂ (C1, C2 and C4) and even on non-mineralized cement (C0)—Fig. 16. This inhibition of early hydration processes in the cements with CuO content is most likely due to the formation of amorphous insoluble compounds that cover the cement grains [12].

The chemically bound water in hydrates and/or the amount of formed $\text{Ca}(\text{OH})_2$ can be well correlated with the compressive strength values (Fig. 17). For linear regression the R^2 values are over 0.95 in most of the cases—see Table 4.

Conclusions

The following conclusions can be drawn:

- Sodium fluoride, tin (IV), and copper oxide are good mineralizers for Portland clinker fabrication. Their presence in clinker and in the resulted cements, modify clinker phases morphology and reactivity due to the incorporation of foreign elements, mainly in the lattice of calcium silicates. Consequently, the rate of cement hydration and hardening processes is different for the mineralized specimens as compared with the reference. The use of sodium fluoride and SnO_2 in low amounts (0.5%) increases the rate of early cement hydration and consequently the development of the flexural and compressive strengths; 0.5% CuO has an opposite effect, lowering the rate of hydration and hardening processes at early ages (2 and 7 days).
- The use of mixtures of fluoride and oxides (0.5% NaF + 0.5% CuO or 0.5% NaF + 0.5% SnO_2) seems to have a synergic effect, i.e., increase the rate of hydration and hardening processes, with direct consequence on the main cement properties.
- For all cements prepared with mineralized clinkers, the mechanical strengths values were higher as compared with those obtained for the non-mineralized cement, due to the reduction of sintering temperature with 20–70 °C, as well as the increase of alite reactivity.
- A good linear regression can be established between the chemically bound water values or portlandite amount (assessed by TG) and mechanical strength developed by the cements after 2–28 days of hardening.

References

1. Bhatti JI. Role of minor elements in cements manufacture and use. IL: Portland Cement Association; 1995.
2. Niculae G. Impact of waste co-incineration in the clinker kilns on the emissions and on the clinker and cement. PhD Thesis, University Politehnica from Bucharest; 2009.
3. Perraki M, Perraki T, Kolosov K, Tsivilis S, Kakali G. Secondary raw materials in cement industry. Evaluation of their effect on the sintering and hydration process by thermal analysis. *J Therm Anal Calorim.* 2002;70:143–50.
4. Engelsens CJ. Effect of mineralizers in cement. State of the art. SINTEF report; 2007.
5. Ma S, Shem X, Gong X, Zhong B. Influence of CuO on the formation and coexistence of $3\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$ minerals. *Cem Concr Res.* 2006;36:1784–7.
6. Emanuelson A, Hansen S, Vigghe E. A comparative study of the ordinary and mineralised Portland cement clinker from two different production units. Part. II. Characteristics of the calcium silicates. *Cem Concr Res.* 2003;33:1623–30.
7. Moir GK. Improvements in the early strength properties of Portland cement. *Philos Trans R Soc Lond A.* 1983;310:127–36.
8. Sanjaasuren R, Rymyantsev PF. Synthesis of low temperature Portland cement clinker by using composite mineralizer. In: Justness H, editor. Proceedings of the 10th international congress of the chemistry of cement, Gothenburg; 1997. p. 1i037–46.
9. Teoreanu I, van Huynh T, Stoleriu S. Thermal studies regarding the influence of flour containing mineralisators on calcium carbonate dissociation of Portland clinkers formation. *Rev Roum Chim.* 2003;48:947–53.
10. Kacimi L, Simon-Masseron A, Ghomari A, Derriche Z. Influence of NaF, KF and CaF_2 addition on the clinker burning temperature and its properties. *C R Chim.* 2006;9:154–63.
11. Kolosov GK, Dousis G, Tsivilis S, Kakali G. The effect of SnO_2 on the burnability or raw meal, the structure and the properties of cement clinker. *Zem Kalk Gyps.* 2005;25:81–7.
12. Kolosov KG. Waste ammunition as secondary mineralizing raw material in Portland cement production. *Cem Concr Compos.* 2006;28:133–43.
13. Hill J, Sharp JH. The hydration products of Portland cement in the presence of tin (II) chloride. *Cem Concr Res.* 2003;33:121–4.
14. Paceagiu J, Amzica F, Chendrean T, Paraschiv T. Effect on NaF and SnO_2 on portland cement clinker fabrication. In: D. Acierno, A. D'Amore, L. Grassia, editors. Proceeding of the IV international conference times of polymers (TOP) and composites. Vol 1042. American Institute of Physics; 2008. p. 258–60.
15. Badanoiu A, Paceagiu J, Voicu G. Evaluation of some mineral additions effect on the burnability of raw mix in cement production. *Sci Bull Univ Politeh Buchar B.* 2009;71:23–36.
16. Taylor HFW. Cement chemistry. London: Academic Press; 1990.
17. Campbell DH. Microscopical examination and interpretation of Portland cement and clinker. IL: Portland Cement Association; 1999.
18. Kolosov K, Tsivilis S, Kakali G. SEM examination of clinkers containing foreign elements. *Cem Concr Compos.* 2005;27:163–70.
19. Badanoiu A, Georgescu M, Puri A. The study of DSP binding systems by thermogravimetry and differential thermal analysis. *J Therm Anal.* 2003;74:65–75.
20. Ramachandran VS, Paroli RM, Beaudoin JJ, Delgado AH. Handbook of thermal analysis of construction material. New York: William Andrew Publishing/Noyes; 2002.
21. Stepkowska E, Perez-Rodriguez JL, de Haro MCJ, Sayagues MJ. Study of hydration of two cements of different strength. *J Therm Anal Calorim.* 2002;69:187–204.
22. Mitchell LD, Margeson JC. The effects of solvents on C–S–H as determined by thermal analysis. *J Therm Anal Calorim.* 2006;86:591–4.
23. Stepkowska E, Perez-Rodriguez JL, Sayagues MJ, Martinez Blanes JM. Calcite, vaterite and aragonite forming on cement hydration from liquid and gaseous phase. *J Therm Anal Calorim.* 2003;73:247–69.
24. Goni S, Puertas F, Hernandez MS, Palacios M, Guerrero A, Dolado JS, Zanga B, Baroni F. Quantitative study of hydration of C3S and C2S by thermal analysis. Evolution and composition of C–S–H gels formed. *J Therm Anal Calorim.* doi:10.1007/s10973-010-0816-7.
25. Nochaiya T, Wongkeo W, Pimraska K, Chaipanich A. Microstructural, physical and thermal analysis of Portland cement-fly ash-calcium hydroxide blended pastes. *J Therm Anal Calorim.* 2010;100:101–8.