INFLUENCE OF ZINC SALTS ON THE PORTLAND CEMENT PROPERTIES WITH OR WITHOUT SLAG ADDITION

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Cimentul portland unitar, precum şi lianţii silicatici micşti derivaţi din acesta, pot constitui matrici eficiente pentru imobilizarea unor substanţe nocive, cu conţinut de metale grele.

Evaluarea eficienţei procedeului de inertizare a deşeurilor/substanţelor cu conţinut de metale grele în matrici liante trebuie apreciată atât sub aspectul capacităţii de solidificare / stabilizare a compuşilor cu conţinut de metale grele în materialele liante în care sunt înglobate, cât şi sub aspectul influenţei pe care o exercită asupra proprietăţilor sistemului întărit. În funcţie de acestea, prin solidificarea/stabilizarea deşeurilor nocive în matrici liante se poate asigura depozitarea lor controlată sau, eventual, betoanele care le înglobează, se pot folosi pentru infrastructuri rutiere.

În această lucrare se prezintă date privind influenţa zincului, adăugat sub formă de săruri, asupra proprietăţilor unor sisteme liante pe bază de ciment portland şi ciment portland cu 30% zgură de furnal granulată.

Unitary Portland cement, as well as mixed silicates binders derived from it, can constitute effective matrices for the immobilization of some hazardous substances containing heavy metals.

The efficiency evaluation of the inertization procedure of noxious wastes/substances with heavy metals content in binding matrices should be considered according to the capacity of solidification/stabilization of heavy metal into the binders in which there are embedded, and also to the influences exerted toward the hardened system. Based on that, the controlled disposal of hazardous wastes might be assured through their solidification/stabilization into binding matrices, or eventually, the concretes which contain them could be used for roads infrastructure.

This paper presents data regarding the influence of zinc, added as salts, onto the properties of some binding systems based on Portland cement and Portland cement with 30% granulated blast furnace slag.

Keywords: portland cement, blast furnace slag, heavy metal, setting time, compressive strength.

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1. Introduction

The air and soil pollution through hazardous substances migration is the fundamental restrictive criterion for the handling of industrial wastes by disposal or recycling. This kind of threats determined the researches oriented toward the stabilization of hazardous substances in mixture with materials which are able to provide a stable matrix.

The binding matrices based on Portland cement (unitary or mixed) are considered nowadays an efficient and cheap inertization way by the solidification/stabilization of some hazardous substances with heavy metals content [1 – 7]. The immobilization process presumes a complex mechanism based on physical and chemical phenomena [2, 3, 8-10].

The hazardous substances could modify the properties of the mortars and concrete when they are added. The stabilizing capacity of the wastes is influenced by the properties of the material containing the stabilized waste: water permeability, soluble substances content and mechanical strengths

Substances with zinc content can be well stabilized into the cement stone, including by the formation of some hard soluble hydrates like $CaZn_2(OH)_6.2H_2O$ [1, 10-13]. The binders with slag content show even a better immobilization capacity of Zn [11, 14-16].

The efficiency evaluation for the inertization procedure of noxious substances in binding matrices should be mainly considered with regard to the capacity to fix and to retain such materials, and also concerning the changes produced by their embedment toward the properties of the concretes containing these binding matrices. Based on that, the controlled disposal of hazardous wastes might be assured by their solidification/stabilization into binding matrices, or eventually, the concretes which contain them could be used for roads infrastructure.

2. Experimental

During the researches the following binder types have been considered: ordinary Portland cement type CEM I – 52.5R and cement with 30% added blast furnace slag content (derivate from CEM I- 52.5R);

The compositional characteristics of the materials used are presented in the Table 1.

Table 1

Compositional characteristics of the cementitous materials

Binder materials	Specific surface area [cm^2/g]	Oxide composition [%]					
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
CEM I – 52.5R	3391	18.89	5.48	4.39	62.62	1.50	0.8
Slag	3870	32.57	16.82	1.48	40.19	4.74	-

Zinc salts considered in researches were: zinc chloride ($ZnCl_2$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and zinc sulphate ($ZnSO_4 \cdot 7H_2O$), added in ratios of 0.01%, 0.02% and 0.03% (molar zinc) reported to cement [14, 15].

The binding mixtures with zinc sulphate (CS), nitrate (CN) or chloride (CCl) which were investigated are shown in the Table 2.

Table 2

Binding investigated compositions

Symbol of binder*)	Portland cement [%]	Furnace slag [%]	$ZnSO_4 \cdot 7H_2O$ [%]	$Zn(NO_3)_2 \cdot 6H_2O$ [%]	$ZnCl_2$ [%]
C0	100.0	-	-	-	-
CS1	97.12	-	2.88	-	-
CS2	94.24	-	5.75	-	-
CS3	91.37	-	8.63	-	-
CN1	97.03	-	-	2.97	-
CN2	94.06	-	-	5.94	-
CN3	91.09	-	-	8.91	-
CCl1	98.64	-	-	-	1.36
CCl2	97.27	-	-	-	2.73
CCl3	95.91	-	-	-	4.09
CZ0	70.0	30.0	-	-	-
CZS1	67.99	29.13	2.88	-	-
CZS2	65.97	28.27	5.75	-	-
CZS3	63.96	27.41	8.63	-	-
CZN1	67.92	29.11	-	2.97	-
CZN2	65.84	28.22	-	5.94	-
CZN3	63.76	27.33	-	8.91	-
CZCl1	69.05	29.59	-	-	1.36
CZCl2	68.09	29.18	-	-	2.70
CZCl3	67.14	28.77	-	-	4.09

*) S = $ZnSO_4 \cdot 7H_2O$; N= $Zn(NO_3)_2 \cdot 6H_2O$; Cl = $ZnCl_2$; 1. 2. 3 = addition of 0.01%M; 0.02%M; 0.03%M Zn^{2+}. added as salts

The main investigated properties were:

- setting time – measured on normal consistency paste;

- compressive strengths – measured on microsamples with size dimensions of 15 x 15 x 60 mm, made of plastic mortar with binder/sand ratio of 1/3 and water/binder ratio of 1/2; the samples were kept for hardening one day in moulds, isolated from atmosphere, and then in a humidity saturated atmosphere, up to the testing terms (2 – 270 days).

3. Results and Discussion

Setting time

The setting time has been measured on normal consistence pastes. The quantity of water for the normal consistence binder pastes is presented in Table 3.

Table 3

Normal consistency water of the binder pastes – without/with addition of zinc salts*

Symbol of binder	H_2O_{nc} (ml/100g)	Symbol of binder	H_2O_{nc} (ml/100g)
C0	30.3	CZ0	26.4
CS1	30.4	CZS1	30.8
CS3	31.8	CZS3	32.2
CN1	28.2	CZN1	25.1
CN2	27.2	CZN2	24.71
CN3	25.6	CZN3	24.58
CCl1	33.4	CZCl1	32.4
CCl2	37.8	CZCl2	34.8
CCl3	39.6	CZCl3	35

*) S – sulphate; N – nitrate; Cl – chloride

The presence of zinc salts influences, in different ways the value of the water for normal consistency pastes, depending on their chemical nature: $ZnSO_4$ and $ZnCl_2$ determine increases of the water values for normal consistency pastes, while $Zn(NO_3)_2$ determines for the two types of binders some diminution of the water for water for normal consistency pastes.

Setting time determined on the normal consistency pastes, prepared with the two types of binders, is shown in the Figs. 1 and 2.

The additions of $ZnSO_4$ and $ZnCl_2$ (Fig. 1 a, b and Fig. 2 a, b) shorten significantly the setting time, the influence being more evident for a higher salt content. These results allow to consider that at low proportions (0.01 – 0.03%M) these salts exert a favorable influence on the initial hydration of the binders with formation of gel silicate hydrates, specific compounds for the cement setting period. Shortening the setting time is more important for Portland cement.

The addition of $Zn(NO_3)_2$ influences differently the setting time (Fig. 1 c and Fig. 2 c), meaning:

- in lower amounts (0.01 and 0.02%M) it produces the setting time delay, both for Portland cement and for slag Portland cement;
- in higher amounts (0.03%M) the delaying effect is much diminished for the slag Portland cement and it is even opposite for Portland cement.

The presented data reveal that the nature of anion contained in the salt influences in high degree the initial hardening period (setting).

The setting time diminution by $ZnSO_4$ could be explained by its possible participation in the formation of some additions hydrates as AFt or AFm, according to the reactions 1 and 2:

$$ZnSO_4 + Ca(OH)_2 + H_2O \rightarrow Zn(OH)_2 + CaSO_4 \cdot 2H_2O \quad (1)$$

$$CaSO_4 \cdot 2H_2O + C_3A(C_4AF) + H_2O \rightarrow AFt / AFm \quad (2)$$

During the hydration of the cements with aditions, of $ZnCl_2$, it is possible to occur the formation of one complex hydrate of type $C_3A(Ca.\ Zn)Cl_2 \cdot 10H_2O$.

Compressive strengths

The compressive strengths for periods of 2 days - 270 days are shown in Figs. 3 and 4.

From graphical representations it is ascertained that the compressive strengths increase in the time for the period of 2 days – 270 days for all considered binder systems (witness and/or zinc salt addition).

The presence of zinc salts (sulphate. nitrate and chloride) in amounts of 0.01 – 0.03% M. produces some diminishing of compressive strengths compared to witness samples C0 and CZ0. The mechanical strengths developed during the first 7 days of hardening, excepting Portland cement with low salt amount (CS1. CN1. CCl1) are significantly affected by these salts.

The compressive strengths decrease for the two binders with Zn salts additions is associated with their delaying effect on the hydration of Portland cement.

The diminution of compressive strengths for the binders with zinc salts additions is more evident as the amount of the salt is higher.

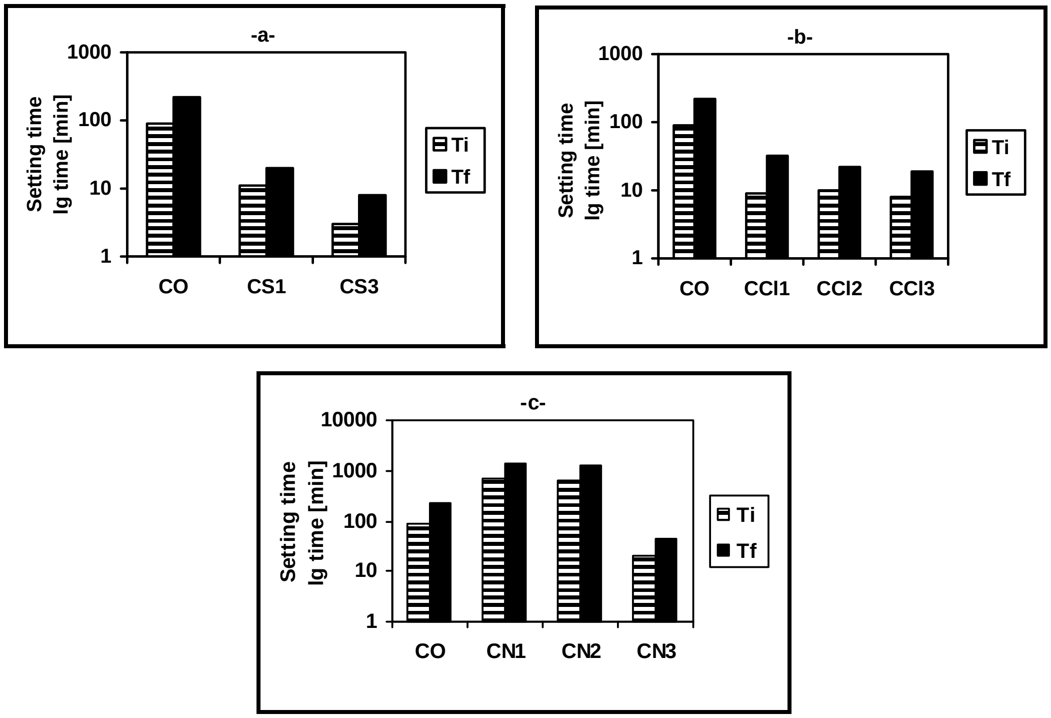
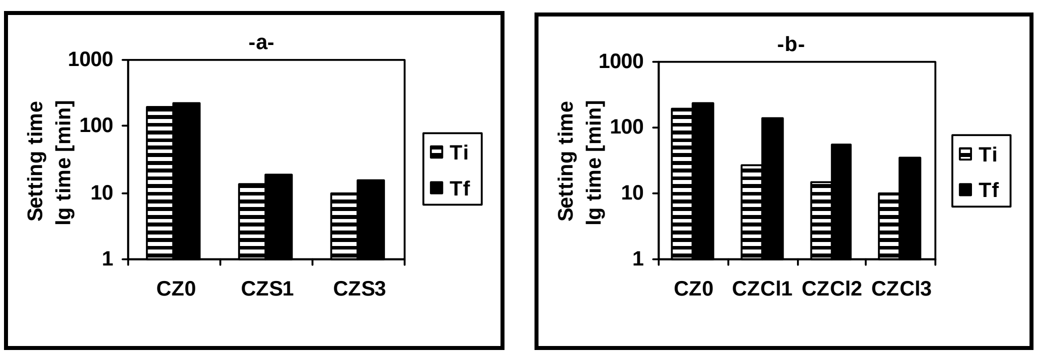


Fig. 1 Setting time for Portland cement pastes – without/with zinc salts addition: (a) - sulphate; (b) - chloride; (c) – nitrate



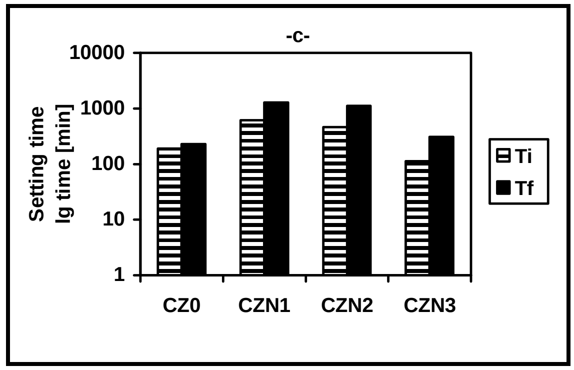


Fig. 2 Setting time of slag based cement pastes – without/with zinc salts addition: (a) - sulphate; (b) - chloride; (c) - nitrate

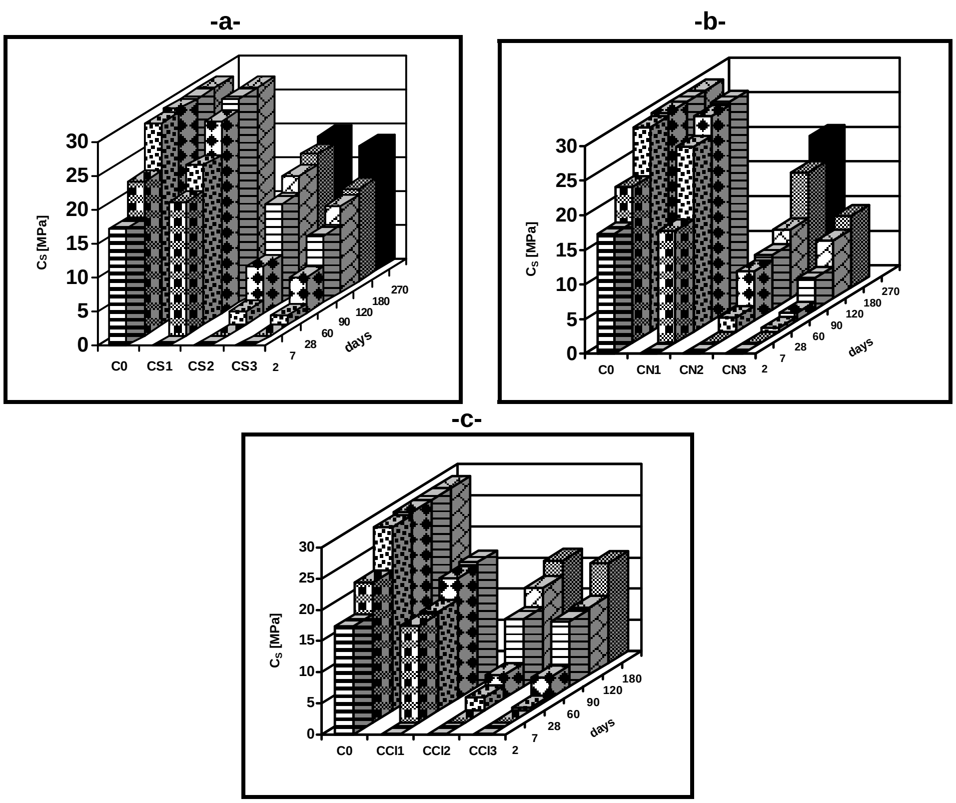


Fig. 3 Compressive strengths of Portland cement – without/with zinc salts addition: (a) - sulphate; (b) - chloride; (c) – nitrate

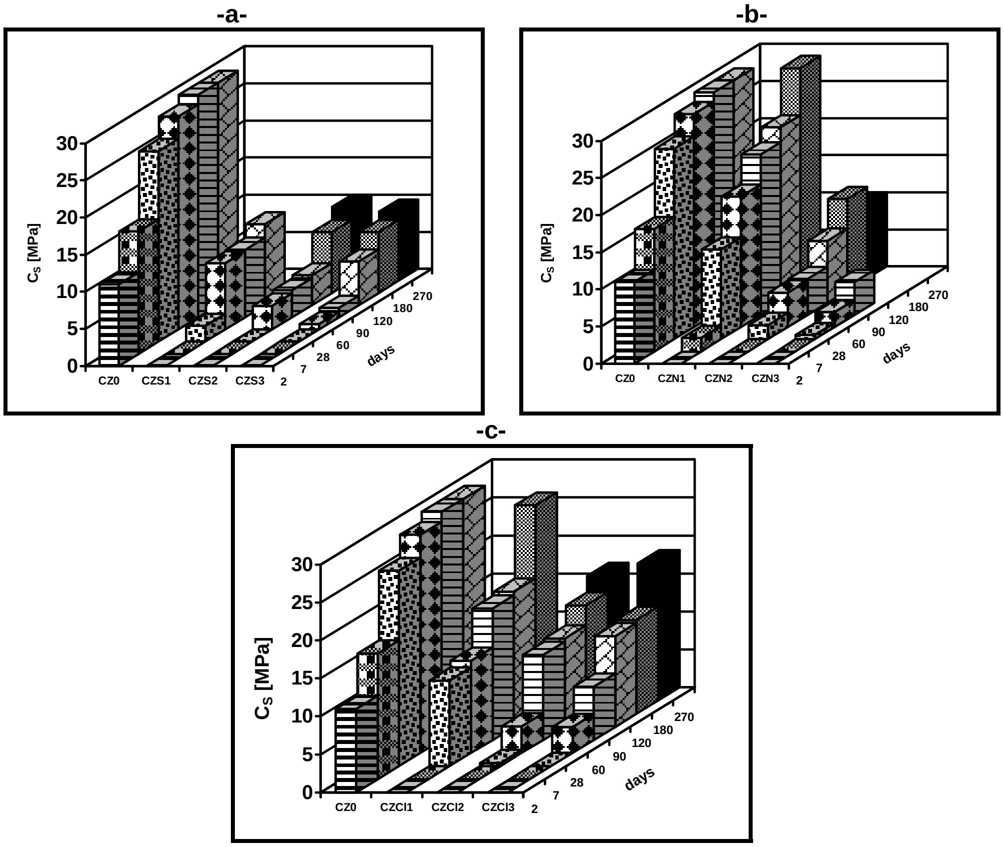


Fig. 4 Compressive strengths of slag based cement – without/with zinc salts addition: (a) - sulphate; (b) - chloride; (c) - nitrate

4. Conclusions

The zinc salts additions influence differently the initial hardening period of the investigated cements, in function of the nature of the anion they contained. The additions of $ZnSO_4$ and $ZnCl_2$ shorten significantly the setting time, the influence being more evident for higher salt addition. The addition of $Zn(NO_3)_2$ influenced differently the setting time; for lower amounts (0.01 and 0.02%M) it produces a delay of the setting time, but at higher amounts (0.03%M) the delaying effect is more diminished for the slag cement and it is even opposite for Portland cement.

The presence of zinc salts (sulphate. nitrate and chloride) in amount of 0.01 – 0.03%M Zn produces a significant diminution of the compressive strengths developed during the hardening of the binders as Portland cement and Portland cement with 30% slag, especially at short hardening periods of time. The diminution of compressive strengths for the binders with zinc salts content is higher as the amount of the salt is higher.

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