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INFLUENCE OF CATHODE RAY TUBES (CRT) GLASS WASTE ON HYDRATION PROCESSES IN PORTLAND CEMENT - WATER AND SLAG CEMENT - WATER SYSTEMS

Ana - Maria PANAIT[1], Maria GEORGESCU[2]

Environmental protection involves the continuous need to find ways for recovery of wastes with heavy metals content. The binders based on Portland clinker represent a solution for immobilization of these wastes.

The present paper brings information regarding to the influence of lead, from glass (CRT) waste, immobilized in cement matrices, on hydration processes of Portland cement – water and slag cement – water systems. For this purpose, binder pastes with water/binder ratio of 0.4 and CRT glass waste dosed in amounts corresponding up to 10% Pb^{2+} were prepared. Samples were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: Portland cement, slag cement, cathode ray tubes waste, lead immobilization, hydration processes, X-ray diffraction, scanning electron microscopy

1. Introduction

Due to the rapid development of technology which determined, in a relative short time, the replacement of electronic equipment type of TV sets and computer monitors, with LCD or LED technology, annually a large quantity of CRT glass is collected [1]. The main problem related to the management and storage of these wastes is high content of lead in their composition (>15%). The lead, once arrived in ecosystem, can cause serious environmental problems. Therefore, the interest in ways of recycling and reuse of waste, which does not lead to the release of Pb into the environment, is important.

There are some literature data [2-6] concerning the effect of Pb^{2+} addition (as waste or soluble salts) on hydration - hydrolysis processes of hydraulic binders and some of them [5,6] are about of the re-use of CRT glass waste in Portland cement concretes as fine aggregate replacement. As aggregate replacement, the authors mentioned the washing of the CRT glass (before adding in concrete

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[1] PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania, e-mail: anamaria.moncea@gmail.com

[2] Prof., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

composition) with an acid solution in order to remove the PbO existing on glass surface.

The Portland cement – with/without admixtures, was used since 1950, as matrix for nuclear waste immobilization [7]. Currently, among the many research concerning the stabilization/solidification of waste with heavy metals content in aluminosilicates matrices type of alkali activated slag and geopolymers, the cement matrix still remains an adequate solution to immobilize of these wastes [8-15].

The immobilization possibility of many type of waste in Portland cement is due to the adsorption of noxious compounds on the surface of hydrates formed in cement stone (calcium aluminate silicate hydrates and aluminate sulphate phases – AFt and AFm). The cement capacity to encapsulate pollutants in the hardening structure and the high pH (<12) of intergranular solution that favor the precipitation of stable heavy metals compounds (hydroxides) are key factors for toxic elements immobilization [12-15].

The present paper brings information regarding the influence of Pb, from CRT glass waste, on hydration processes and hydrates formed in Portland cement – water and slag cement – water systems. Binding pastes, in which the active component (cement) was replaced by CRT glass waste up to 40.8%, were prepared and kept for hardening up to 28 days. Subsequently, the hardened pastes stones were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

The materials used to prepare the binding systems were ordinary Portland cement (OPC) type CEM I 42,5 R, slag cement (SC) – CEM III A, containing 36% slag and CRT glass waste with high lead content (>15%.). The same materials were used for investigations regarding the lead immobilization too, in different binding systems, including OPC and SC and reported in the paper [16]. The materials composition and fineness are shown in Table 1

Pastes with water to binder ratio of 0.4 were prepared. The CRT waste, obtained by fine grinding of neck, funnel and panel glass from TV sets and discarded monitors, has a Blaine specific surface area of 3010 cm^2/g. The compositions of studied binders are shown in Table 2.

The XRD analyses were performed on hardened binder pastes in order to obtain information regarding the hydration processes and hydrates formed after 2, 7 and 28 days of hardening. The hydration of binder was stopped by acetone washing and oven-drying at 60ºC for 3 hours. Information regarding the micro-structural characteristics of binding pastes with 10% Pb content, hardened 28 days, were obtained by SEM analyses.

3. Results and discussions

The XRD analysis performed on the OPC pastes – without/with Pb content, hardened up to 28 days are shown in Fig. 1.

After the first two days of hydration, on XRD pattern are identified, as main hydrates $Ca(OH)_2$ (at 2θ values of 18.1°, 28.7°, 47.1°) and ettringite (at 2θ value of 9.2°, 15.9°). The amount of calcium hydroxide increases during time due the calcium silicates hydration:

$$C_3S\ (C_2S) + H_2O = C_nSH_y + mCH \qquad (1)$$

After two days of hydration for composition OPC 2, and after 28 days for OPC, the ettringite is partial transformed in monosulphate aluminate hydrate. The $CaCO_3$ peaks are present on XRD patterns, as secondary compound, even since two days of hydration; this compound is most probably resulted by carbonation of $Ca(OH)_2$ formed in the specimens during their processing and curing.

Table 1

Composition and fineness of materials

Ordinary Portland cement		**Cement slag**	**CRT Glass waste**	
Oxides	**Composition (%)**	**Composition (%)**	**Elements**	**Composition (%)**
SiO_2	18.96	24.92	Si	33.99
Al_2O_3	4.98	7.32	Pb	15.45
Fe_2O_3	3.20	2.68	Na	10.97
CaO	64.02	53.87	Ba	8.84
MgO	1.00	3.19	K	8.24
SO_3	3.31	3.46	Al	2.58
Na_2O	0.23	0.46	Ca	2.22
K_2O	0.65	0.72	Sr	1.71
Cl^-	0.007	0.007	Mg	0.94
LOI	3.44	3.37	Sb	0.40
HCl ins. Rez.	0.47	-	Fe	0.16
			minor elements	0.37
Specific surface area (cm^2/g)	**2595**	**3143**	**Specific surface area (cm^2/g)**	**3010**

Waste additions corresponding to 2 – 10% Pb (with reference to cement content), exert a delaying effect on cement hydration processes. The intensities of calcium silicates peaks at 2θ=32° - 34°, are lower after two days of hydration as compared to those assessed on XRD spectra of OPC specimen (see Figs. 1*b*, 1*c* and 1*d*).

Table 2

Binding compositions

Binder indicative	Solid components (%)			water/ binder ratio	CRT waste (g)
	OPC	Slag	Pb		
OPC	100	-	-	0.4	-
OPC 0.18	99.82	-	0.18	0.4	1.2
OPC 0.37	99.63	-	0.37	0.4	2.4
OPC 0.74	99.26	-	0.74	0.4	4.8
OPC 2	98	-	2	0.4	13.1
OPC 4	96	-	4	0.4	26.2
OPC 10*	90	-	10	0.4	65.53
SC	64	36	-	0.4	-
SC 0.18	63.9	35.9	0.18	0.4	1.2
SC 0.37	63.8	35.87	0.37	0.4	2.4
SC 0.74	63.5	35.7	0.74	0.4	4.8
SC 2	62.4	35.3	2	0.4	13.1
SC 4	61.4	34.6	4	0.4	26.2
SC 10*	57.6	32.4	10	0.4	65.53

* 0.5% polycarboxilate superplasticizer type CHRYSO®Fluid Premia 180 was added

The lower intensities of XRD peaks of crystalline hydrates, $Ca(OH)_2$ in particular, for all periods of hardening, sustain this idea.

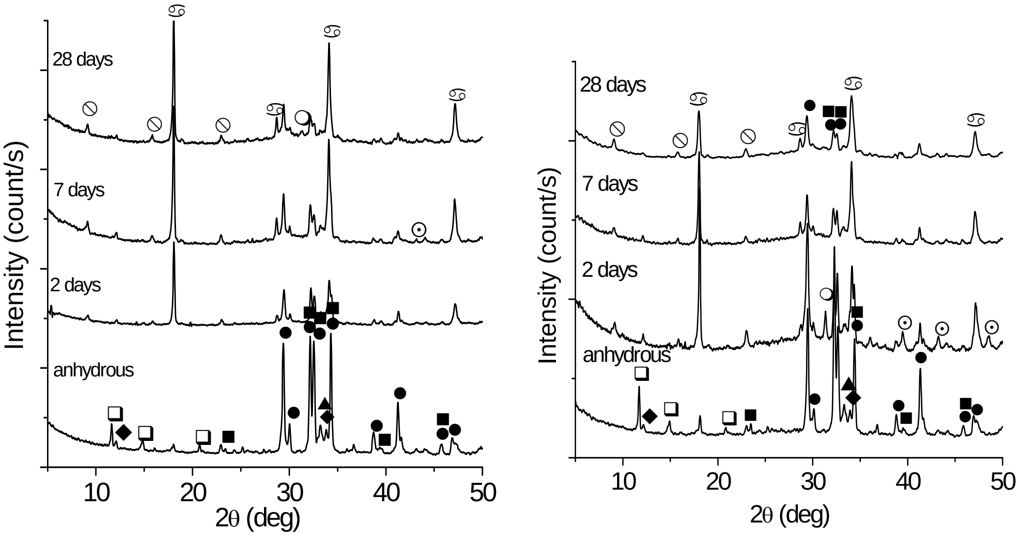


Fig 1 - a *b*

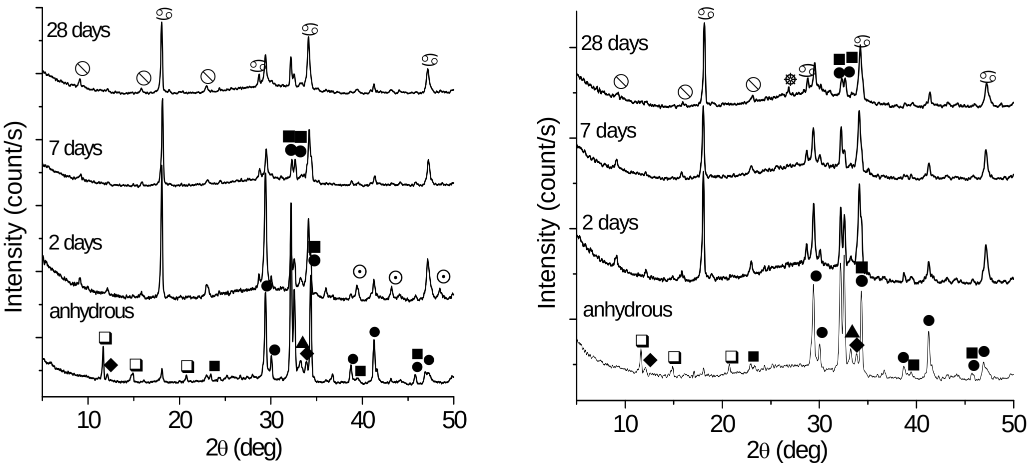


Fig. 1 - c *d*

Fig. 1. XRD patterns of OPC binders – without CRT waste (a) and with CRT waste, corresponding to 2% Pb (b), 4% Pb (c) and 10% Pb (d). The notations corresponds to: ● C_3S; ■ C_2S; ◆ C_4AF; ▲ C_3A; ❑ Gypsum; ♋ CH; ⦸ Ettringite; ❍ Monosulphate aluminate hydrate (Hydrocalumite); ⊙ $CaCO_3$; ❆ $PbCO_3$.

The formation of Pb compounds i.e. carbonates with low crystallinity degree (2θ=26.8°) is also possible - see XRD pattern of OPC 10 (Fig. 1*d*).

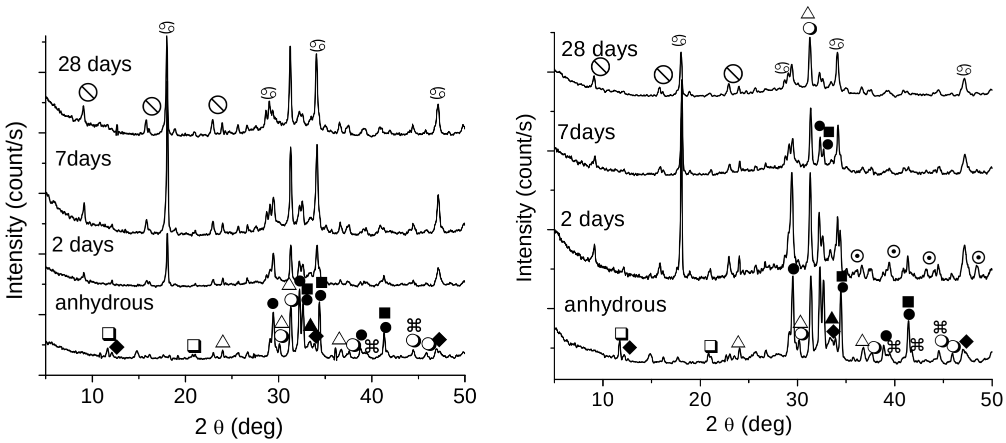


Fig. 2.- a *b*

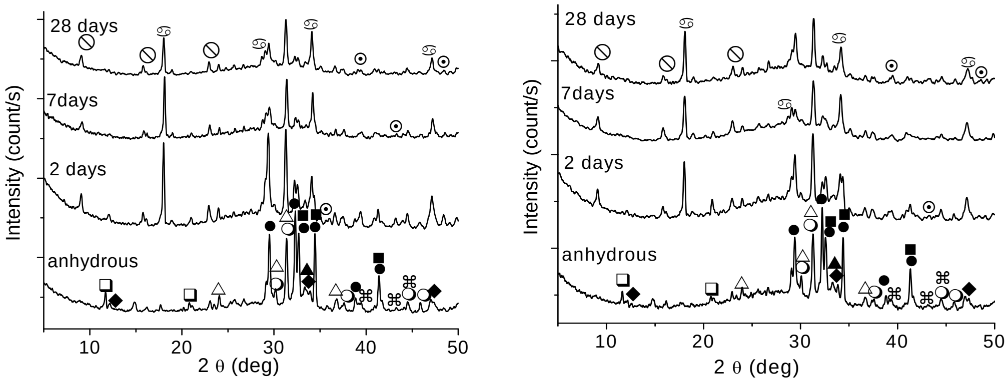


Fig. 2. - c *d*

Fig. 2. XRD patterns of SC binders – without CRT waste (a) and with CRT waste, corresponding to 2% Pb (b), 4% Pb (c) and 10% Pb (d). The notations corresponds to: ● C_3S, ■ C_2S, ◆ C_4AF, ▲ C_3A, ○ C_2MS_2, △ C_2AS, ⌘ C_3MS_2, ❑ Gypsum, ♋ CH, ⊘ Ettringite, ⊙ $CaCO_3$.

The XRD patterns of SC binders – without/with Pb are presented in Fig. 2. After two days of hardening, $Ca(OH)_2$ and ettringite, as crystalline hydrates are present on the spectra. The $Ca(OH)_2$ amount formed by calcium silicates hydration, is lower as compared with OPC binder, due to lower content of Portland clinker (in SC) and also due to its partial consumption by slag hydration. Crystalline compounds with Pb were not assessed by this method. Some chemical interaction between Pb and hydrates formed in cement paste could be supposed due to the shifting of ettringite characteristic peak to higher values of 2θ angles (Fig. 3).

The XRD patterns of SC binding pastes – without/with Pb content, hardened for 28 days, show the presence of ettringite (peaks for $2\theta=8$ -10°), see Fig. 3. As it can be seen, the decrease of 9.8 Å peak intensity (at 2θ value of 9°), and the splitting and shifting at higher values of 2θ occurs in series: SC → SC 2 → SC 4 → SC 10. This can be explained by the interactions between Pb and hydrates of Portland cement, mentioned in some literature data [14, 17, 18]:

- the substitution of Ca^{2+} with Pb^{2+} ions in ettingite structure can reduce its crystallinity and can even form solid solutions;
- the precipitation of some compounds with low solubility formed by interactions between Pb^{2+} and both SO_4^{2-} (available for ettringite formation) and CO_3^{2-} ions, with possible compositions of $Pb_4SO_4(CO_3)_2(OH)_2$ and $3PbCO_3{\cdot}2Pb(OH)_2{\cdot}H_2O$ [17, 18].

Considering the characteristic peaks of calcium silicates at d=2.77 Å and d=2.18 Å (2θ=30-34), the hydration degree of OPC and SC binders was calculated (formula 2). The obtined data are shown in Fig. 4.

$$G_h = \frac{I_0 - I_t}{I_0} \times 100 \qquad [\%] \qquad (2)$$

Io is the intensity of the peak on XRD pattern of anhydrous binder; It – the intensity of the peak on XRD pattern of paste hydrated *t* days.

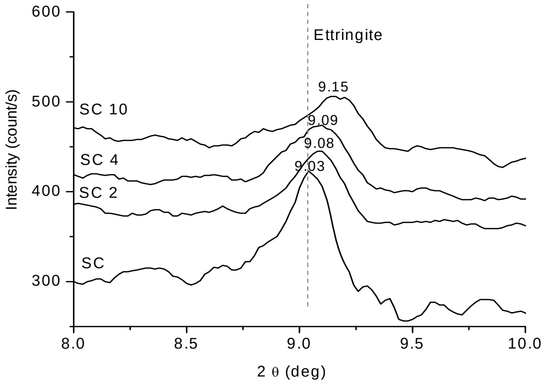
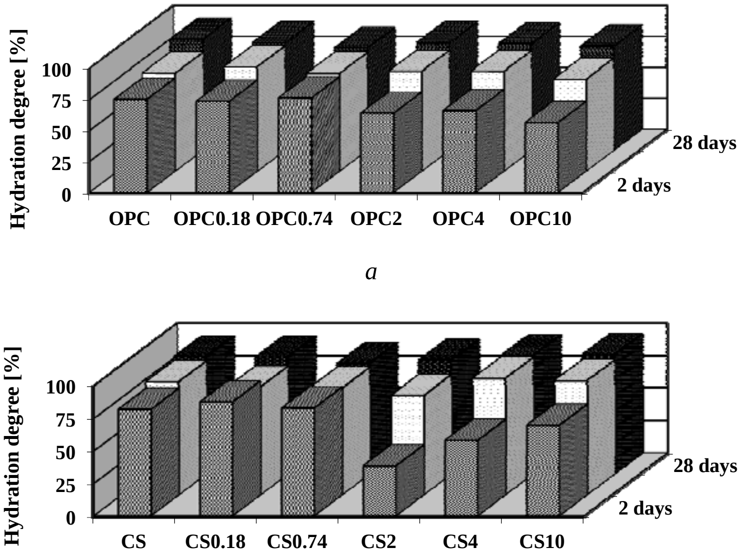


Fig. 3. XRD patterns of SC pastes without and with 2 – 10% Pb, after 28 days of hydration

As it is shown in Fig. 4, the hydration degree of OPC and SC binders is not affected by the small amounts of Pb additions (0.18 - 0.74%); higher Pb additions (2 - 10%), lead to the decreases of hydration degree, especially at early ages (2 days). After 28 days of hydration, the negative influence of Pb on the hydration degree of binders is reduced or even eliminated. This can be explained by the hydration mechanism suggested by Gineys et all. [8] and Lee et all. [17, 18] consisting in precipitation of low solubility lead salts as a low permeable membrane, around the cement grains, hindering the hydration processes in the early stages. Due to low permeability of this membrane, there is still a slow hydration of cement grains, and consequently a release of Ca^{2+} in the space between cement grain and membrane which cause the increase of osmotic pressure until its destruction; in these conditions, the hydration of cement grain will continue until a new membrane of Pb compounds will form, thus generating a new cycle.

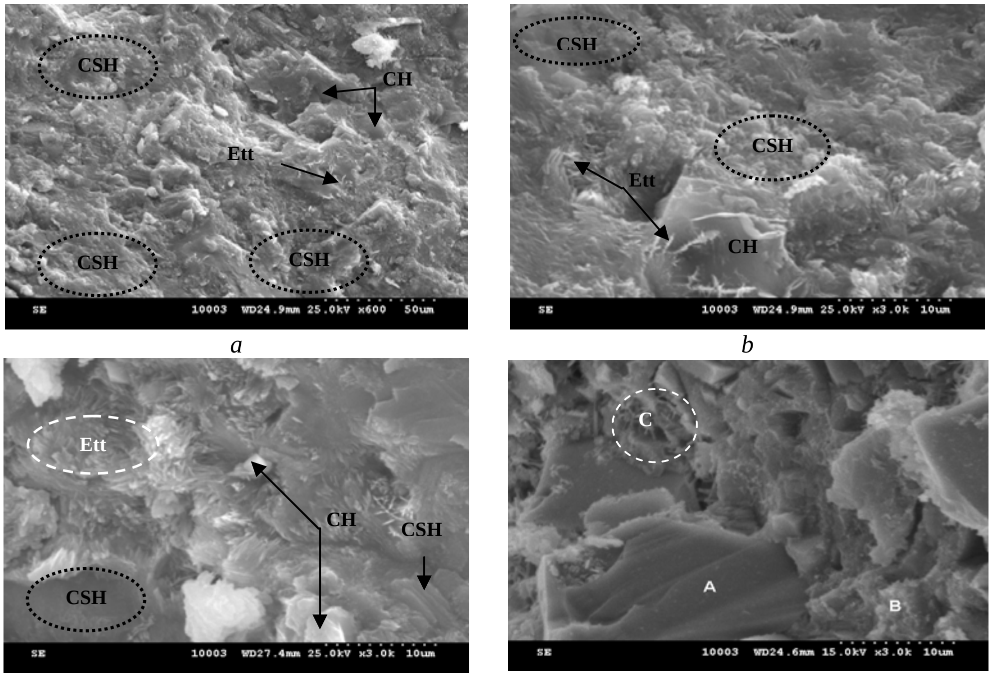
The SEM analysis performed on OPC, OPC 0.74 and OPC 10 type of binders, are shown in Fig. 5. The SEM images of OPC binder show the presence, as preponderant hydrate phases, of calcium silicate hydrates with an irregular aspect (Figs. 5*a* and 5*b*); the acicular crystals can be assigned to the ettringite and the $Ca(OH)_2$ is present as plaques.



a

b

Fig. 4. Hydration degrees according to XRD data for OPC (a) and SC (b) type of binders, hardened up to 28 days



a *b*

c *d*

Fig. 5. SEM images of OPC (a, b), OPC 0.74 (c), OPC 10 (d), hardened 28 days

The addition of 0.74% Pb as CRT glass waste, does not cause structural and morphological changes compared with binder without Pb content (Fig. 5*c* compared with Fig. 5*b*)

The SEM image of OPC 10 (fig. 5*d*), shows a porous microstructure in which glass grains (A) may be easily distinguished. In the pores of the cementitious matrix (B), the ettringite (C) can be observed as needle-liked crystals.

The SEM images of SC, SC 0.74 and SC 10 are shown in Fig. 6. Beside the calcium silicates hydrates, present as low crystalline formations (Fig. 6*a*) it can be seen, on SC microstructure, the abundant presence of ettringite, suggested by the agglomerated needle-liked crystals (Figs. 6*a* and 6*b*). The abundance of ettringite can be explained by lower proportion of calcium aluminates hydrates (due to clinker substitution with slag) which could react with ettringite leading to hydrocalumite formation.

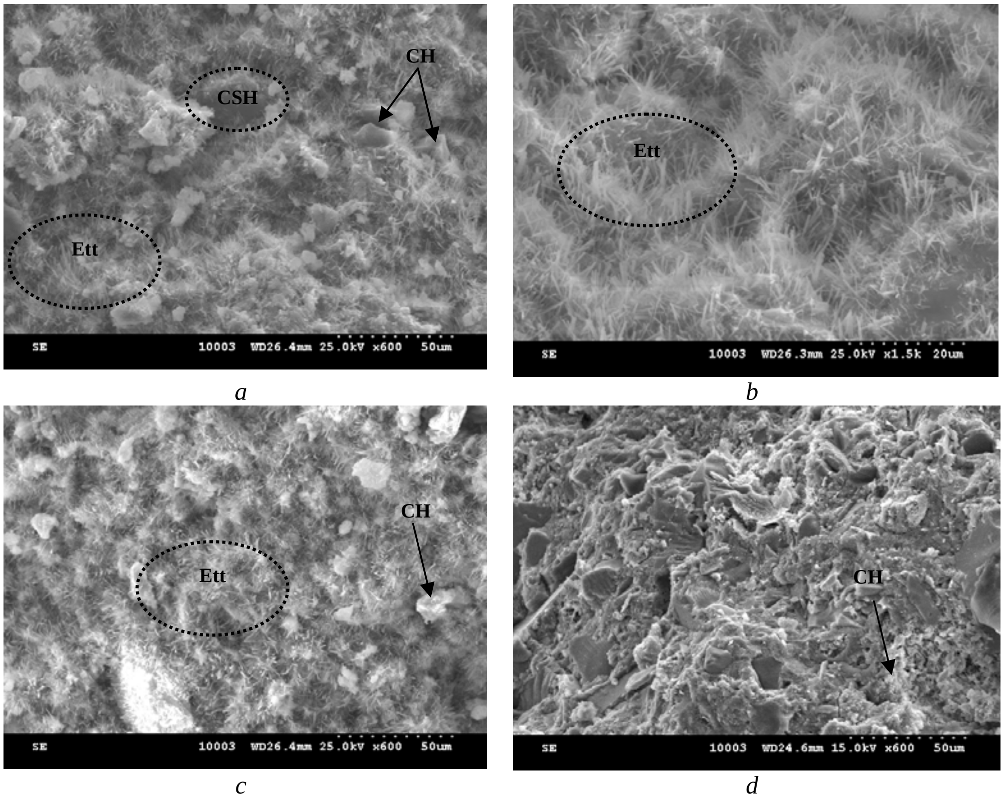


Fig. 6. SEM images of SC (a, b), SC 0.74 (c), SC 10 (d), hardened 28 days

The addition of 0.74% Pb, do not causes major changes in morphology of hydrates formed in slag cement stone. Beside the less crystalline CSH phases, it can be assessed the presence of ettringite and of some hexagonal crystals assigned to $Ca(OH)_2$; this compound is present in smaller quantities in this binder compared with OPC.

On the SEM image of SC 10 binder can be seen some differences as compared to SEM images of CS and SC 0.74. In case of SC 10, the needle-liked crystals assigned to ettringite does not seem to be in the same amount and/or crystallinity as in SC and SC 0.74 binders (Fig. 6*d* compared to 6*a* and 6*c*); the glass grains embedded in cementitious matrix can be seen too.

4. Conclusions

The XRD analyses performed on OPC and SC type of binders with different Pb addition, hardened up to 28 days, have shown the evolution of hydration-hydrolysis processes and the formation as crystalline hydrates of CH, ettringite and calcium carbonates. In OPC 10 binder lead carbonates was identified too. The $Ca(OH)_2$ content in SC binders is lower than in OPC binders due both to lower clinker content and its partial consumption by slag hydration.

The hydration-hydrolysis processes of OPC and SC type of binders are favored by small amounts of Pb (0.18 - 0.74) and are delayed by higher amounts of Pb (2 – 10%); the hydration degree of binders with 0.18 – 0.74% Pb, generally higher, compared with those of binder with 2 – 10% Pb, sustain this idea.

SEM analysis suggests a microstructure with low crystallinity degree of OPC 10 and SC 10 pastes as compared with those of binder without Pb or with 0.74% Pb content. The lower frequency of ettringite crystals in SC 10 binder could be explained by formation of Pb insoluble precipitates with SO_4^{2-} and CO_3^{2-} ions against ettringite formation. Beside the less crystalline CSH hydrates, the SEM images showed the presence of some needle-liked crystals designed to ettringite and some hexagonal crystals assigned to $Ca(OH)_2$.

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