

## PROPERTIES OF BLENDED CEMENTS WITH HAZARDOUS WASTE CONTENT

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An efficient method for the safe disposal of heavy metals pollutants (industrial wastes) is their stabilization/solidification (s/s) in organic or inorganic matrices. The s/s of heavy metals in cementitious matrices based on portland cement should be assessed not only from the point of view of its efficiency, but also from the point of view of their influence on the binder's hydration and hardening processes.

This study was carried out on blended cements with limestone filler, fly ash and volcanic tuff additions in order to estimate the opportunity of using these blended binders as matrices for the stabilization/solidification of industrial hazardous wastes with high chromium content and to identify possible uses for the resulted materials.

The paper presents data regarding the influence of the hazardous waste content on the main properties of blended cement matrices *i.e.* workability, setting time and mechanical strength. The degree of immobilization of the heavy metals brought by the industrial waste in the studied matrices, assessed by a static monolithic leaching test, was very high.

### INTRODUCTION

The waste streams management is an important environmental issue.<sup>1-4</sup> In 2002, the amount of industrial wastes in Romania (including those resulted in the mining and energy production industries) was of 372.4 millions tones; from the total waste amount 31% was re-used and 69% was eliminated (by burning and as landfill).<sup>2</sup> According to the statistics, in 2002, in Romania were recorded 680 industrial waste deposits with an estimated surface of 6400 ha from which, 147 deposits contained hazardous wastes generated especially in the mining activities and metal production.<sup>2</sup>

Stabilization/solidification (s/s) is considered to be an effective technology for the commercial treatment of a number of waste streams including inorganic waste and contaminated soil.<sup>3</sup> Inorganic and organic binders are used in this technique as a matrix for the immobilization of the contaminated material to enable its disposal.<sup>4</sup> The solidification process of powder or liquid wastes renders it into a form that is easily stored and transported, and further inhibits the environment pollution.

The implementation in Romania of the EU legislation regarding the environmental protection

and specifically of the Landfill Directive (Council Directive 1999/31/EC) is very likely to stimulate the recovery of wastes (instead of disposal) due to the increase of the landfill costs (pre-treatment of the waste is required before landfill).

A number of projects have been carried out in order to identify the possible uses for the stabilized wastes, particularly in association with construction.<sup>3,4</sup>

Therefore, the study of the influence of hazardous wastes on the main properties of different types of inorganic binders is justified.

The main objective of this paper is to assess the influence of the hazardous wastes with heavy metals content on the main properties of the binding matrices with limestone filler, fly ash and volcanic tuff.

### EXPERIMENTAL

#### Materials

Type I portland cement, limestone filler, fly ash and volcanic tuff, were used for the preparation of binary and ternary blended cements. The oxide composition and the materials specific surface area are presented in table 1. The composition of the blended cements is presented in table 2.

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Based on the binders presented in table 1, specimens with 0.5%, 1% and 2% Cr content were prepared. The Cr and other heavy metals were brought in the binding

systems by a hazardous industrial waste admixture. The the heavy metals content of the industrial waste (R) is presented in table 3.

Table 1

Chemical characteristics and specific surface area of the cement and admixtures

Composition (%)	Portland cement (C)	Limestone filler (L)	Fly ash (F)	Volcanic tuff (T)
SiO <sub>2</sub>	18.24	n.d.	53.53	55.47
Al <sub>2</sub> O <sub>3</sub>	5.50	n.d.	26.44	10.97
Fe <sub>2</sub> O <sub>3</sub>	3.87	n.d.	9.33	2.55
CaO	63.65	48.96	4.00	9.83
MgO	1.09	3.34	1.94	1.18
K <sub>2</sub> O	0.85	n.d.	2.23	1.62
Na <sub>2</sub> O	0.30	n.d.	0.77	1.55
P.C.	3.18	n.d.	0.80	15.14
Specific surface area (cm <sup>2</sup> /g)	2956	5193	3040	5562

n.d. – not determined

Table 2

The composition of blended and composite cements

Binder	Portland cement (%)	Limestone filler(%)	Fly ash (%)	Volcanic tuff (%)
C	100	-	-	-
CL	80	20	-	-
CF	80	-	20	-
CLF	80	10	10	-
CT	80	-	-	20
CLT	80	10	-	10

Table 3

Heavy metals content in the industrial waste R

Heavy metals content (%)					
Cd	Cr	Cu	Ni	Pb	Zn
0.5005	13.5145	1.8560	0.1324	0.2646	6.5535

The main elements in the waste R (assessed by EDX analysis) are the heavy metals (Cr, Zn, Pb, Cu and Cd) and P, Al, Si, Ca and Fe – figure 1.

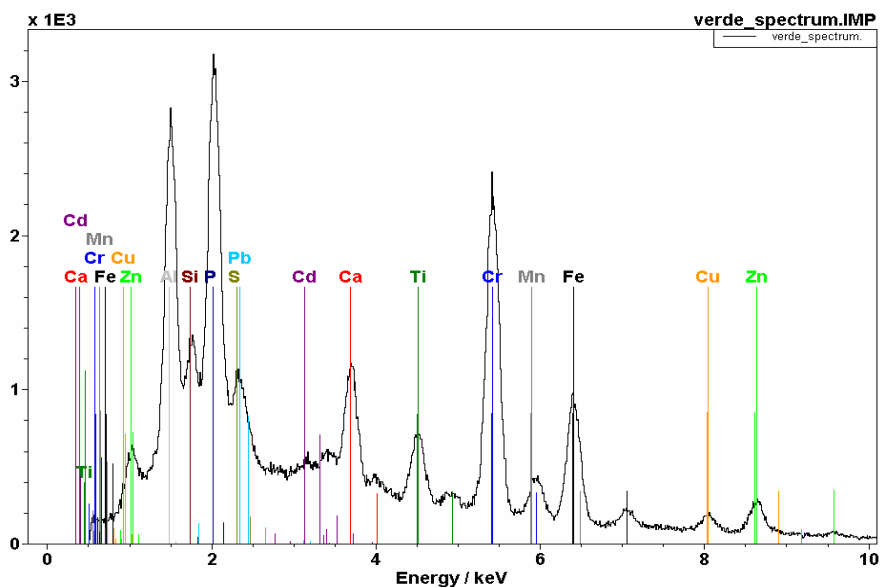


Fig. 1 – EDX analysis of waste R.

The reactivity of the pozzolanas was assessed by a conductometric method – evolution vs. time of the electrical conductivity of a lime supersaturated solution in which 1 g of pozzolana was added. The data presented in figure 2 suggest a higher reactivity for the natural pozzolana (volcanic tuff - T) as compared with the fly ash (F).

The lower reactivity of the fly ash, compared with the volcanic tuff, can be explained by its higher content of well-crystallized  $\alpha$ -quartz<sup>5</sup> and by its smaller specific surface area (see table 1).

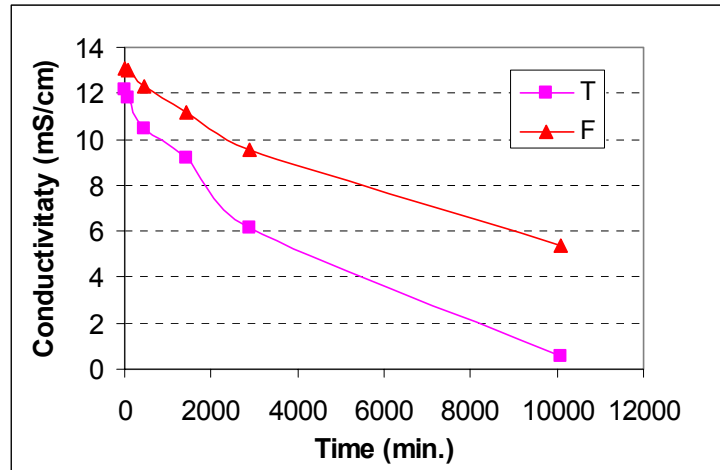


Fig. 2 – Electrical conductivity vs. time of the lime saturated solution containing 1 g of fly ash (F) and volcanic tuff (T).

#### Testing procedures

The binding matrices capacity to achieve the stabilization/solidification of the heavy metals was assessed by the atomic absorption analysis of the leaching solutions; these solutions resulted by the immersion of hardened mortar samples (monoliths) with 2% chromium content (brought by the waste R) in distilled water (water/solid = 5) for different periods of time - 28 and 60 days.

The viscosity of the cement pastes with water to binder ratio of 0.65, with/without waste R content was determined with a RHEOTEST -2 viscosimeter.

The water content for the standard paste and the setting time were assessed using the EN 196-3:1994 method.<sup>6</sup>

The compressive strength was assessed on mortar specimens (15x15x60mm) with binder/sand = 1/3 and water/binder=0.5, hardened for 2 up to 60 days in moist room (95% R.H.).

## RESULTS AND DISCUSSION

The heavy metals content in the samples and the concentrations in the leaching solutions are presented in table 4.

Table 4

Heavy metals content in mortar samples and leaching solutions

Sample	Time [days]	Concentration [mg/L]					
		Ni	Zn	Cd	Cu	Cr	Pb
<i>Potential content</i> *)		<b>21.558</b>	<b>1066.8</b>	<b>68.75</b>	<b>302.08</b>	<b>2200</b>	<b>43.08</b>
C2	28	0.0003	u.d.l	0.0018	0.1162	0.0479	u.d.l
	60	0.0123	0.0005	u.d.l	0.2738	0.0429	u.d.l
CL2	28	0.0050	u.d.l	0.0029	u.d.l	0.0354	u.d.l
	60	0.0069	0.0118	u.d.l	0.2331	0.044	u.d.l
CF2	28	0.0089	u.d.l	0.0018	0.2161	0.0289	u.d.l
	60	n.d	0.0205	n.d	0.3374	n.d	u.d.l
CLF2	28	0.0185	u.d.l	0.0011	0.0289	0.0217	u.d.l
	60	n.d	u.d.l	n.d	n.d	n.d	u.d.l
CT2	28	0.0148	u.d.l	0.0026	0.1394	0.0355	0.0027
	60	n.d	0.0019	u.d.l	0.3608	0.0587	u.d.l
CLT2	28	u.d.l	u.d.l	0.0025	0.0065	0.0081	u.d.l
	60	0.0272	0.0048	u.d.l	0.2048	0.0584	u.d.l

n.d. – not determined; u.d.l. – under detection limit ( $< 10^{-4}$ )

\*) calculated based on the waste content in mortar specimens and heavy metal content in waste.

The data presented in table 4 suggests a very good stabilization/solidification (s/s) of the heavy metals from the waste R in the studied cementitious matrices. The increase of the contact time between the monolith sample and solution causes, as expected, the increase of the heavy metal concentration in the leaching solution; still, the heavy metals concentration values are under the regulatory requirements.<sup>7,8</sup>

Alba *et al.*<sup>9</sup> reported also a good immobilisation of metals such Zn, Cd and Pb found in industrial residues in blended binders containing slag and

pulverised fly ash (PFA). According to Poon *et al.*<sup>10,11</sup> and Jones *et al.*<sup>12</sup> the Cr, Zn and Cd presence in the cement based mixtures promotes the ettringite formation; this hydrate exhibits extensive ionic substitution potential, therefore it provides an effective chemical immobilisation of this type of contaminants.<sup>4</sup> Cr, Zn, Cd, Pb and Ni can be also immobilised by sorption or substitution in the C-S-H structure.<sup>13</sup>

The viscosity of the studied cement pastes with/without hazardous waste (with to 2% Cr content) is presented in figure 3.

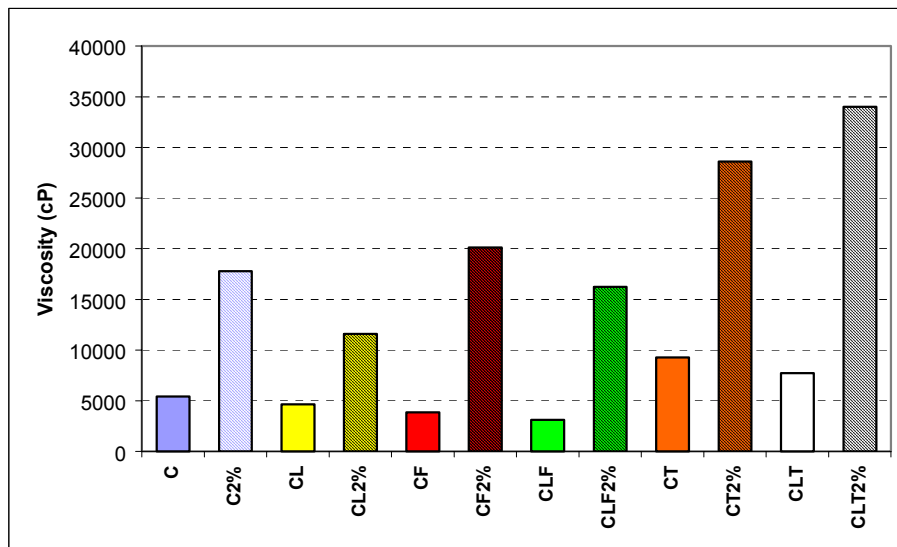


Figure 3 – The viscosity of pastes (water/binder=0.65): C – Portland cement; C2% - Portland cement cu 2% Cr (waste R); CL – Portland cement +20% limestone filler; CL2% - CL with 2% Cr (waste R); CF – Portland cement +20% fly ash; CF2%- CF cu 2% Cr (waste R); CLF – Portland cement +10% limestone filler +10% fly ash; CLF2% - CLF cu 2% Cr (waste R); CT – Portland cement +20% volcanic tuff; CT2% - CT cu 2% Cr (waste R); CLT – Portland cement +10% limestone filler +10% volcanic tuff; CLT2% - CLF cu 2% Cr (waste R).

The addition of 20% limestone filler causes, as expected, a certain decrease of the cement pastes viscosity *i.e.* improvement of the workability. This behaviour is due to the improvement of the grain size distribution curve (in the fine range) of the cement that causes the so-called “particle packing effect”.<sup>14,15</sup>

The addition of 20% fly ash also decreases the viscosity of the pastes. This reduction of the viscosity is explained by Malhorta and Mehta<sup>15</sup> by the “particle packing effect” and by the spherical shape and smooth surface of the particles, which helps to reduce the interparticle friction, thus facilitating their mobility. The mixture of the fly ash and limestone filler decreases furthermore the viscosity of the cement paste (see CLF and CF), most probably due to the increase of “particle packing effect”.

The addition of 20% volcanic tuff has an opposite influence *i.e.* increases with almost 50% the cement paste viscosity, mainly due to its higher specific surface area. For the composite cements with limestone filler and volcanic tuff (CLT), the positive effect induced by the limestone filler causes the decrease of the pastes viscosity.

The addition of the waste R causes, for all the studied binders, an important increase of the pastes viscosity.

The assessment of water content of the standard consistency pastes (figures 4 - 6) provides supplementary information on the fresh pastes workability. The increase of the waste dosage (corresponding to the chromium concentration of 0.5% and 1%, respectively) causes the reduction of the pastes workability (*i.e.* increase of the water demand).

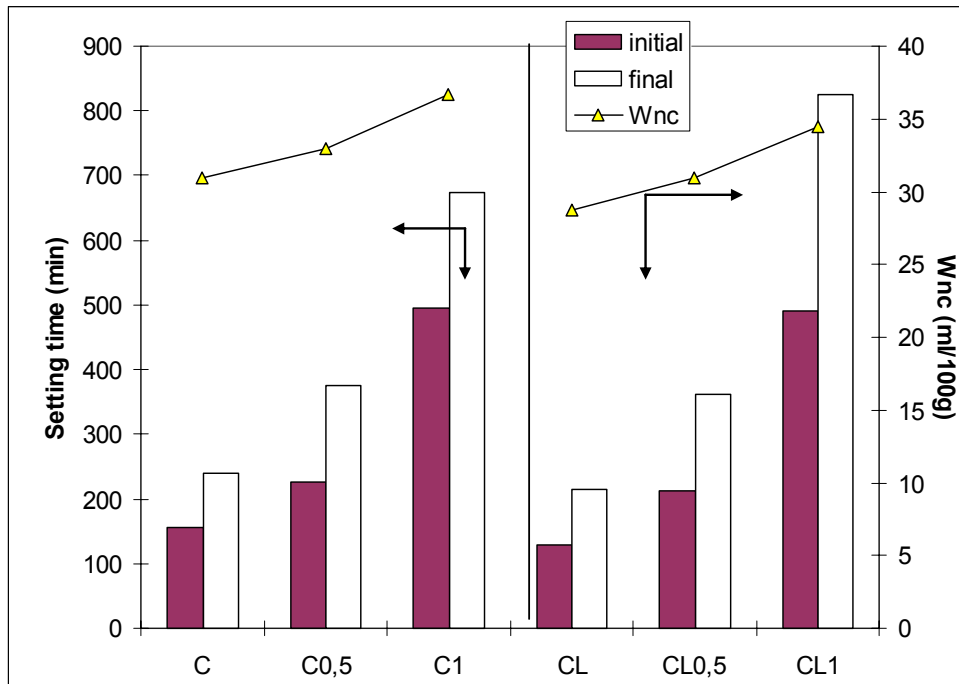


Fig. 4 – Water content of the standard consistency pastes and setting time for: C – Portland cement; C0.5 - Portland cement with 0.5% Cr (waste R); C1- Portland cement with 1% Cr (waste R); CL – Portland cement+20% limestone filler; CL0.5 - CL with 0.5% Cr (waste R); C1 - CL with 1% Cr (waste R).

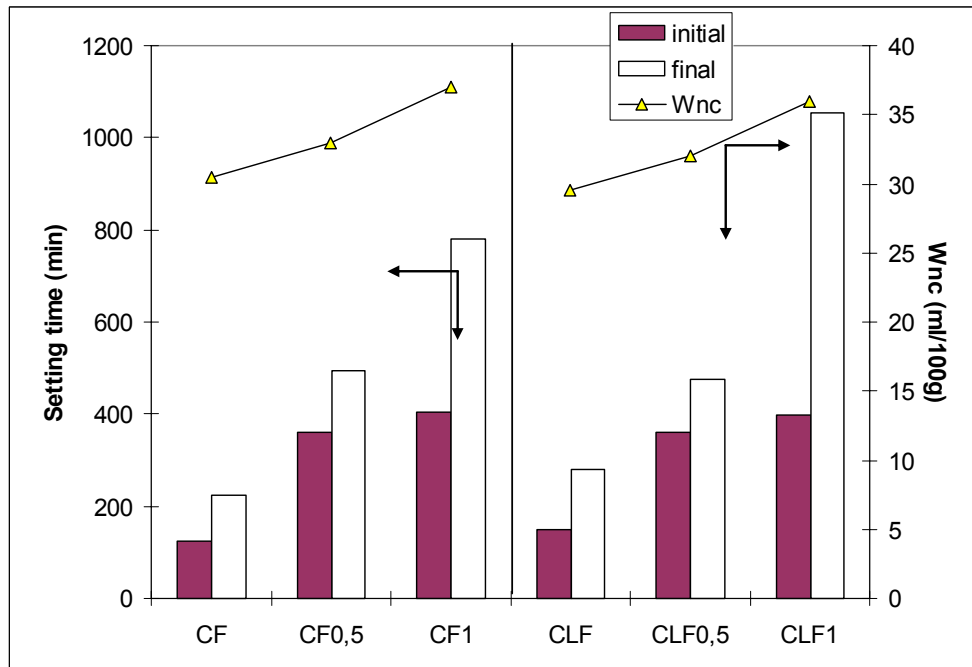


Fig. 5 – Water content of the standard consistency pastes and setting time for: CF – Portland cement+20% fly ash; CF0.5 - CF with 0.5% Cr (waste R); CF1 - CF with 1% Cr (waste R); CLF – Portland cement+10% limestone filler+10% fly ash; CLF0.5 - CLF with 0.5% Cr (waste R); CLF1 - CLF with 1% Cr (waste R).

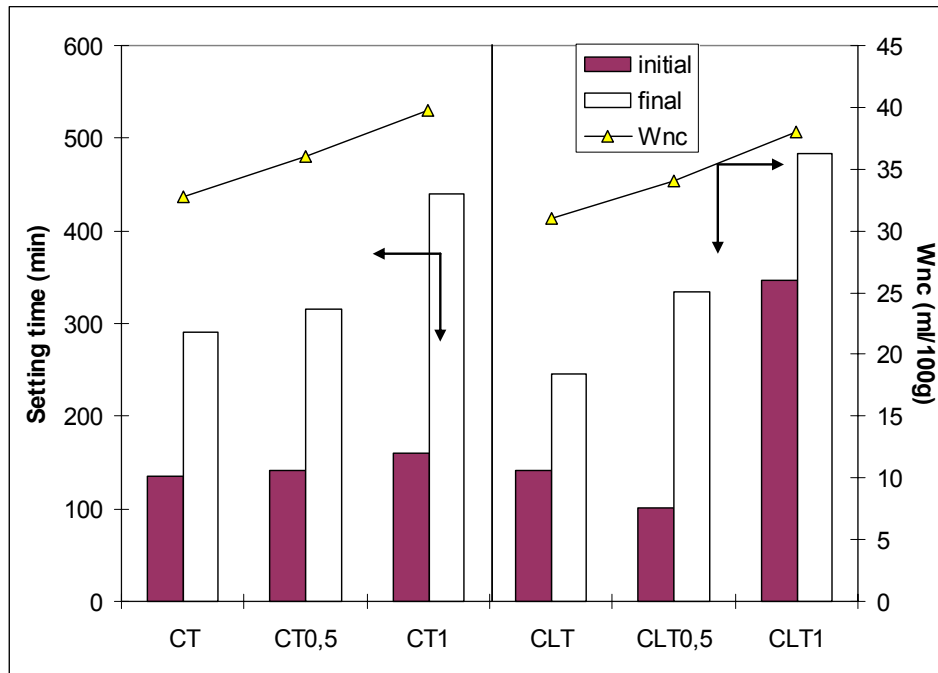


Figure 6 – Water content of the standard consistency pastes and setting time for: CT – Portland cement+20% volcanic tuff; CT0.5 - CT with 0.5% Cr (waste R); CT1 - CT with 1% Cr (waste R); CLT – Portland cement+10% limestone filler+10% volcanic tuff; CLT0.5 - CLT with 0.5% Cr (waste R); CLT1 - CLT with 1% Cr (waste R).

The presence of waste in the cement pastes exerts an important delaying effect upon the setting. The initial and final setting times increase with the increase of the waste amount. Similar data were reported in previous papers<sup>16,17</sup> for inorganic matrices based on portland–limestone filler-slag cements and alkali activated slag; this delay could be the consequence of the formation of heavy metals salts with low solubility which hinders the cement hydration processes. According to Bone *et al.*<sup>4</sup> the retardation of the cement hydration process could be also due to the metallic ions adsorption onto the C-S-H gel (hydrogen bonding) to form an impervious coating that stifles future hydration. This mechanism may explain the important setting delay noticed in the systems with limestone filler (which promotes the C-S-H formation at early ages) and a high waste content (corresponding to 1% Cr).

The increase of the waste content also causes an important setting delay of the blended cement with fly ash. Still, it has to be noted that, the cements with volcanic tuff (with/without limestone filler) have the smallest values for the initial and final setting time, even for higher waste content (1%). Such behaviour is in good correlation with the higher reactivity of the volcanic tuff as compared with the fly ash.

The compressive strengths of the studied cements with/without hazardous waste content are presented in the figures 7-9.

The presence of the hazardous waste in these cements determines a reduction of the compressive strength values, for all the studied cements. For the samples based on portland cement (figure 7a) the increase of the waste content hinders the mechanical strength development, especially at early ages – the sample with 2% Cr (C2) had no compressive strengths until 28 days of hardening. This behavior may be correlated with the increase of the water content of the standard consistency pastes when the waste content increases, as well as with the important setting delay.

For the blended cements with limestone filler the negative effect induced by the hazardous waste is of a smaller importance – the specimen CL2 has compressive strengths at early ages (7 days) in contradiction to C2 specimen (no strengths after 2 and 7 days and very small values after 28 days). The limestone filler presence in the binding system induces two effects: “particle packing effect” and intensification of the portland cement hydration process.<sup>14,16</sup> Therefore, the negative (delaying) effect determined by the waste on the portland cement hydration and hardening processes is partially compensated by the positive (accelerating) effect determined by the limestone and by its physical effect.

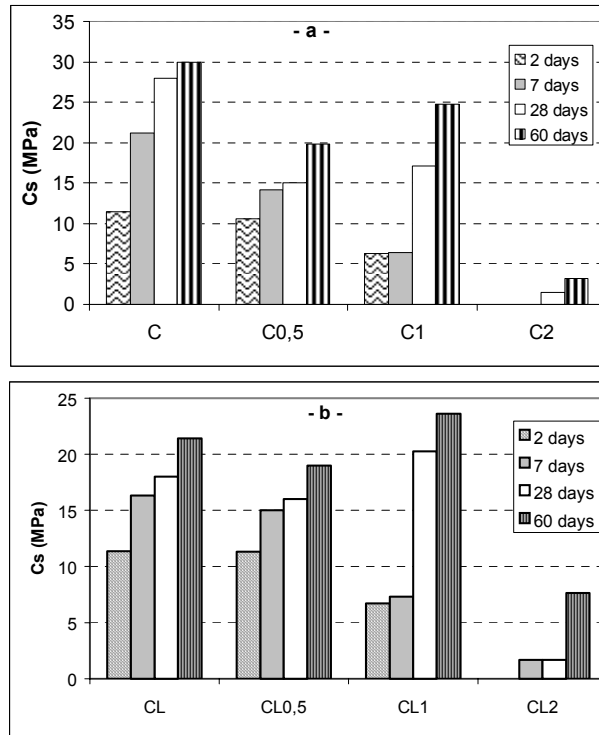


Fig. 7 – Compressive strength (Cs) vs. time for mortar samples with 0.5%, 1% and 2% Cr – brought by the hazardous waste: a) Portland cement; b) Portland cement +20% limestone filler.

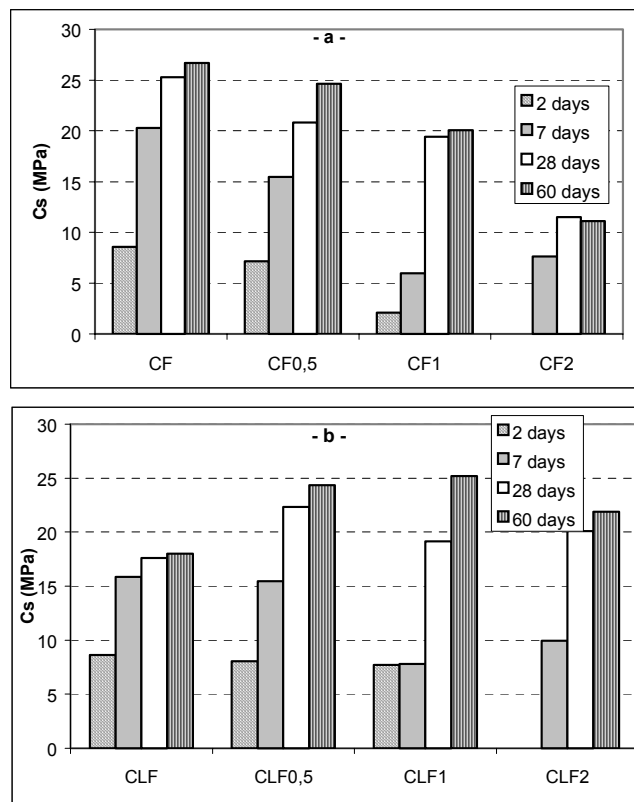


Fig. 8 – Compressive strength (Cs) vs. time for mortar samples with 0.5%, 1% and 2% Cr – brought by the hazardous waste: a) Portland cement+20% fly ash; b) Portland cement +10% limestone filler+10%fly ash.

The influence of the hazardous waste on the strength development in blended cement with fly ash content, presented in figure 8, is less important

compared with the systems based on portland cement, especially for longer ages.

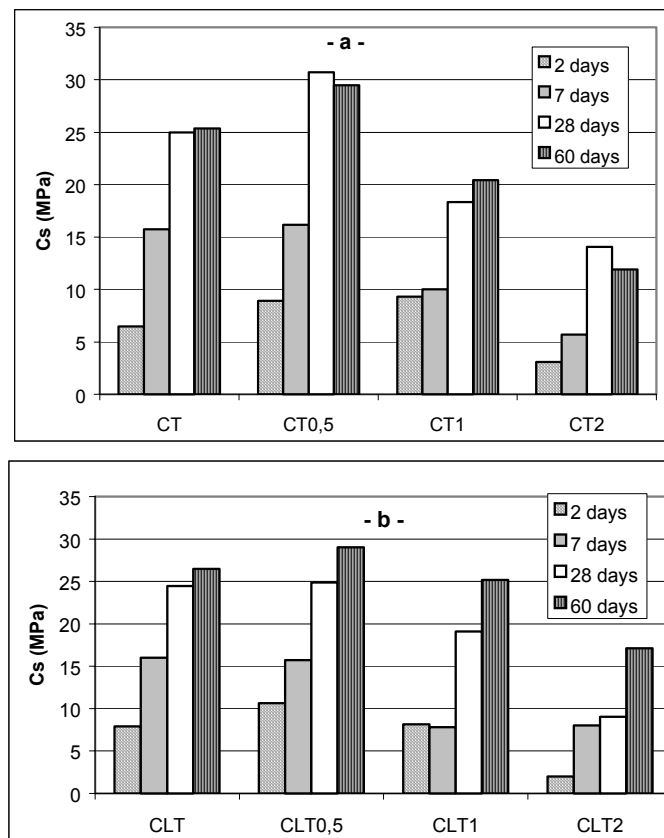


Fig. 9 – Compressive strength (Cs) vs. time for mortar samples with 0.5%, 1% and 2% Cr – brought by the hazardous waste: a) Portland cement+20% volcanic tuff; b) Portland cement +10% limestone filler+10% volcanic tuff.

The presence of the hazardous waste in the blended cements with volcanic tuff determines a decrease of the compressive strengths but this influence is smaller compared with the portland cement system. This behaviour may be the consequence of the intensification, at early ages, of the portland cement hydration process in the presence of the volcanic tuff, as well as the development of a higher amount of hydrates at later ages.<sup>18</sup>

In the portland composite cements, CLF and CLT, the synergic effect of the limestone filler and pozzolana additions has a positive influence on the mechanical strength development (see figures 8b and 9b), and a reduction of the negative influence of the hazardous waste.

## CONCLUSIONS

Hazardous wastes with heavy metals content can be solidified/stabilized in blended cements

with limestone filler and pozzolanas (volcanic tuff or fly ash).

The workability of blended cements with pozzolana or/and limestone filler is influenced by the amount and nature of each addition; the portland cement substitution, with limestone filler and fly ash decreases the pastes viscosity and water demand. The presence of the waste with heavy metals content in these binding systems, increases the water content for the standard consistency pastes *i.e.* reduces the workability of fresh pastes and mortars.

The mechanical strengths developed by the blended cements are in good correlation with the single or synergic influence of the admixtures and with the workability of the fresh mortars.

The mechanical strengths of the blended cements with hazardous waste decrease with the increase of the hazardous waste content, especially at early ages, in correlation with the increase of the setting time.



The negative influence determined by the hazardous waste on the mechanical strengths of the blended and composite portland cements is smaller if compared with the portland cement system. This could be the consequence of the “particle packing effect” and of the intensification of the cement hydration processes in the presence of pozzolana.

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