INERTIZAREA UNUI DEȘEU INDUSTRIAL BOGAT ÎN CROM ÎN CIMENTURI COMPOZITE PORTLAND INERTIZATION OF AN INDUSTRIAL WASTE RICH IN CHROMIUM IN COMPOSITE PORTLAND CEMENTS

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A common method used for the inertization of industrial waste is solidification / stabilization (S / S); it consists in the mixing of waste with a binder so as the final product meets the standards imposed by environmental agencies. Solidification describes the processes that transform waste into a waterproof solid with strong cohesion, i.e. good physical and mechanical properties. Stabilization is the effect of processes aiming to reduce or even eliminate the mass transfer phenomena of pollutants into water and soil. This paper presents the inertization and immobilization of a chromium-rich waste (from the potassium dichromate industry) in inorganic matrices based on hydraulic binders, namely in special structures called cement C and cement D. It presents also results regarding the influence of waste on hydration-hydrolysis processes and on the main properties of resulted mortars obtained by X-ray diffraction, complex thermal analysis, scanning electron microscopy (SEM and EDX).

O metodă comună utilizată pentru inertizarea deşeurilor industriale este solidificarea/stabilizarea (S / S) se impune amestecarea deșeurilor cu un liant anorganic astfel încât produsul final să respecte standardele impuse de agențiile de mediu. Solidificarea descrie procesele care transformă deșeurile într-un solid rezistent la apă, cu coeziune puternică, adică proprietăți fizice și mecanice bune. Stabilizarea este efectul proceselor care vizează reducerea sau chiar eliminarea fenomenului de transfer de masă al poluanților în apă și sol. Această lucrare prezintă inertizarea și imobilizarea unui deșeu bogat în crom (din industria dicromatului de potasiu) în matrice anorganice bazate pe lianți hidraulici, și anume în structuri speciale numite ciment C și ciment D. De asemenea, sunt prezentate rezultatele privind influența deșeului asupra hidratării hidroliză și asupra proprietăților principale ale mortarelor, rezultate obținute prin difracția razelor X, analiza termică complexă, microscopia electronică de scanare (SEM și EDX).

Keywords: special hydraulic binders, properties, waste, solidification/stabilization processes.

1. Introduction

Global economic and demographic growth, plus the expansion of urbanization and increased purchasing power of consumers are generating increasing amounts of waste. The total amount of waste is 3.4-4 billion tons of municipal and industrial waste generated globally each day and 180 million tons of hazardous waste generated each year [1]. Removing them in a safe and responsible manner is a major global challenge. Often, developing countries do not have the necessary infrastructure, so an increasing amount of their waste reaches landfills or are simply randomly thrown.

A good solution in the management of toxic wastes is to mix them with a binder (organic or inorganic). The hydraulic properties of inorganic binders (such as Portland cement or lime) and their ability to retain harmful elements in their own structure without releasing them in the environment make them eligible candidates for the treatment of toxic wastes. The inertization process of these wastes should be appreciated both in terms of the Various aspects of the use of this technique have been studied over the years, to inert the toxic elements in the composition of certain wastes. Solidification and stabilization of heavy elements in the cementitious matrix were evidenced by the interactions of heavy metals with the binder matrix phases, as well as by checking the efficiency of their inertization through leaching tests [11, 12]. The compositional optimization of binder-waste mixtures has also been studied, taking into account the nature of binder and waste, so that the mechanical and structural properties wouldn't be negatively impacted [13-17].

Among the most harmful elements immobilized by solidification/stabilization in inorganic matrices are Zn, Pb, Cu, Cr Cd and Mn [18-22]. Chromium (III) or chromium (VI) are among the most common forms of toxic metals both in waste and in leaching solutions, due to the relative ease with which they come into complex combina-

ability to immobilize toxic elements and in terms of their influence on the processes that take place in the hydration and hardening processes of corresponding binding systems [2-10].

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tion. Hexavalent chromium is much more toxic than trivalent chromium. Chromium can be immobilized in a Portland cement matrix especially in the ettringite (AFt) structure [22, 23].

In the present paper are presented results regarding the inertization of a chromium-rich waste originating from the potassium dichromate manufacture, in two types of composite Portland cements. The influence of this waste on the cement hydration and hardening processes and the properties or resulted mortars was also assessed.

2. Materials and methods

2.1. Materials

The following materials were as matrices for the solidification/stabilization of a chromium-rich waste resulted in the manufacture of potassium dichromate:

- Cement C - composite Portland cement type II / B-M (S-V) 42.5 N-LH -78%, FA-16%, BPD-6%. This cement has a clinker content of 65-79% and mineral additions between 21-35%; for this type of cement the mineral additions were: slag (S), silicate ash (V), fly ash (FA) and bypass dust (BDP).

- Cement D – composite Portland cement type II / B-M cement (S-V) 42.5 N-LH - 40%, FA-42%, QL-12%; BPD-6%.This cement has similar characteristics with cement C, except for the higher content in fly ash (FA) and the presence of lime (QL).

The oxide and mineralogical compositions of cements C and D are shown in Table 1.

2.2. Methods

For the assessment of chemical and mineralogical composition of chromium waste the following analysis techniques were used:

- X ray fluorescence spectrometry using an Epsilon 5 spectrometer;

- X ray diffraction was carried on a Schimadzu diffractometer XRD 6000-Ni-filtered CuK α (λ =1.5406Å) radiation, scanning speed of 2°/min in 20 range of 5-65°;

- thermal analysis (DTA-TG), using a differential thermal analyzer Shimadzu DTG-TA 51H (30–1000°C temperature range and 10°C/min heating rate).

The chromium waste was dried at 50°C for 48h and then homogenized in a planetary ball mill for 30 minutes, resulting a powder.

The assessment of the morphology of the studied materials was carried out using a Quanta Inspect F scanning electron microscope (1.2 nm resolution) with EDX.

The cement hydration and hardening processes were assessed on pastes with water to binder ratio of 0.5, hardened for 3 up to 90 days. The normal consistency water and setting times of cements were determined according to European and corresponding Romanian standard norm SR EN 196-1:2016 [24].

The density of the cements was measured by Arhimede's method using the helium pycnometer, and their fineness was assessed by to Blaine specific surface area (S_{sp}).

Compressive strength was assessed on mortar specimens prepared with binder : sand = 1:3 and water to binder ratio of 0.5, using as aggregates siliceous sand which met the requirements of both European and corresponding Romanian norms SR EN 196–1, Part 1 [25].The mortar specimens were cast in rectangular molds (15x15x60 mm), vibrated for 2 minutes and cured for 3 up to 90 days in humid air (R.H. 90%). The compressive strength was assessed using a Matest machine and the values represent the

Table 1

The oxide and mineralogical compositions of cements used for waste inertization

· · · · · · · · · · · · · · · · · · ·		3	0		liiizale	e pentru	inertizarea d	eşeulul		
Cement C:	Oxide con	nposition	[%]							
cement type II/B-M (S-V) 42.5 N-LH -78 % , FA-16 %, BPD-	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Mg O	Na ₂ 0	O K ₂ O	SO	3	CI
6%	30.67	10.55	5.54	46.37	2.31	0.6	1.0	2.5	3	0.25
	Mineralog	ical comp	osition [%]							
	C ₃ S/ Alit	C ₂ S/	Tricalcium	aluminate		C ₄ AF/	Gypsum	Calcit	Quart	Lime
		Belit	cC ₃ A/ cubic	oC ₃ A/ orthoedri	с	Celit				
	55.98	8.13	4.55	2.04		7.18	1.47	6.48	6.24	5.25
	N-LH = 78 %; Periclas = 0.36 %; Portlandit = 0.00 %; FA = 16 %; Hemihydrate = 1.49 %; Anhydrate = 0.81%; BPD = 6%									
Cement D:	Oxidie co	mposition	[%]							
cement type II/B-M (S-V) 42.5	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgC)	Na ₂ O	K ₂ O	SO ₃	CI
N-LH – 40 % , FA-42 %, QL- 12%; BPD-6%	18.03	6.74	2.81	62.13	1.31		0.2	0.82	1.45	0.31
12/8, BFD-0/8	Mineralogical composition [%]									
	C ₃ S/ Alit	C ₂ S/		aluminate		C₄AF/	Gypsum	Calcit	Quart	Lime
		Belit	cC ₃ A/ cubic	oC₃A/ orthoedri	c	Celit				
	22.72	4.06	1.62	1.28		2.86	0.82	7.88	3.56	52.67
		,	claz = 0.42 QL = 12 %;	,		= 1.25	%; FA = 42	% Hemil	nydrate =	0.86 %;

average of at least four strength values assessed on specimens cured in similar conditions.

Chromium immobilization in the binding matrices was assessed based on the chromium concentration of the solution (leachate) in which was kept for 24 hours the powder resulted by the grinding of pastes cement hardened for 28 days; the sample preparation was made in accordance with the method presented in SR EN 12457-2 [26]; the chromium concentration in leachate was determined by inductively coupled plasma - optical emission (ICP-OES) technique with a transcribed apparatus Inductively coupled plasma optical emission spectrometer [27].

3. Results and discussions

The chromium waste resulted powder was analyzed by X-ray fluorescence spectroscopy (XRF) - Table 2. One can observe the chromium concentration is 3%, much bigger than concentration of others toxic elements.

The XRD result (Figure 1) shows the main mineralogical components of the waste are calcium carbonate (JCPDS 05-0586), calcium hydroxide(JCPDS 84-1270), calcium chromium oxide hydrate (JCPDS 37-1367) and magnesium hydroxide (JCPDS 44-1482).

The results obtained by XRD are in good correlation with the results provided by complex thermal analysis - Figure 2.

There are present four major endothermic effects with mass loss are highlighted on DTA and TG curves:

i) the endothermic effect from 20°C up to approx. 250°C is attributed to the dehydration of weakly bound hydrates, i.e $CaCrO_4 \cdot 2H_2O$;

ii) the endothermic effect with maximum at approx. 396°C, associated with an weight loss of 8.6 %, is attributed to dehydroxylation of magnesium hydroxide;

iii) the endothermic effect with maximum at approx. at 487°C, associated with weight loss, is attributed to the dehydroxylation of calcium hydroxide (weight loss is 1.4%, corresponding to $5.75 \text{ wt\% Ca} (OH)_2$);

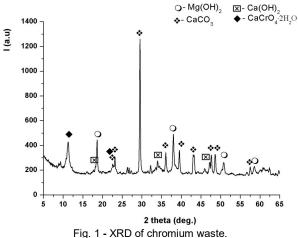
iv) the endothermic effect with maximum at approx. 726°C, also associated with weight loss, is attributed to the decarbonation of magnesium and calcium carbonates.

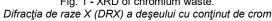
The scanning electron micrographs of chromium waste are presented in Figure 3. The waste consist mainly from particles with different sizes and shapes, which can form agglomerates -Figure 3a. The EDX spectrum (Figure 3b) shows an important content in calcium and magnesium, in

Table 2

Chemical composition, density and specific surface area of chromium waste

		Compoziți	ia chimică, densit	atea și a	nria suprafeţ	ei specifice pentr	u deşeul	cu conţinut	de crom		
Compo- sition	U.M.		Composition	U.M.		Composition	U.M.		Compo- sition	U.M.	
MgO	%	9.567	Ni	ppm	943.767	Cr	%	2.711	v	ppm	415.059
Al ₂ O ₃	%	4.297	Pb	ppm	45.7	As	ppm	11.961	w	ppm	189.884
SiO ₂	%	7.502	Rb	ppm	1.718	Ва	ppm	202.61	Zn	ppm	213.206
Fe ₂ O ₃	%	7.957	Sc	ppm	520.363	Cu	ppm	44.562	Zr	ppm	18.981
SO3	%	1.383	Sr	ppm	92.495	Hg	ppm	0.017	Density	g/cm	2.503
	%			ppm			ppm	573.96	Specific I surface a	rea	
CaO		28.512	Ti		503.142	Mn		7	(S _{sp.} , cm ² /	g)	6548





good correlation with the previously presented results. One can also notice a significant chromium content corresponding to the amount of 2.7%, assessed by chemical methods (Table 1).

The composition of binders obtained by the mixing of the chromium-rich waste and the two studied cements are presented in Table 3; the waste was dosed in order to yield 0.5 and 1% chromium in the mixture (w %).

The density and Blaine specific surface area (S_{sp}) of the cements are presented in Table 4.

The values of water for normal consistency the studied binders are shown in Figure 4a.

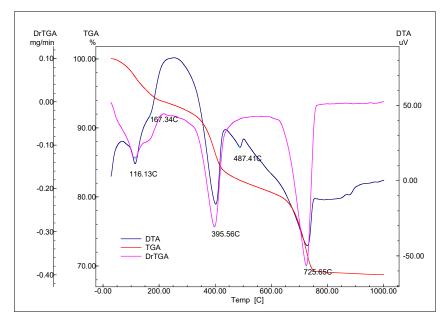


Fig. 2 - Complex thermal analysis for chromium waste / Analiză termică complexă pentru deșeul cu conținut de crom

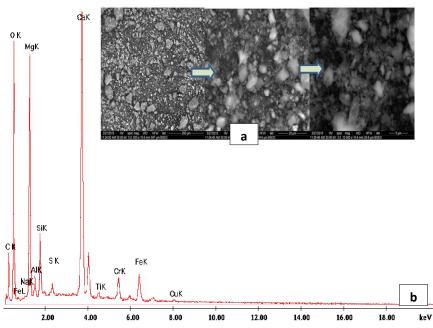


Fig. 3 - Scanning electron microscopy images (a) and EDX spectrum (b) of the chromium waste / Imagini de microscopie electronică de baleiaj (a) și spectrul EDX pentru deșeul cu conținut de crom

Compositions of the bindings studied Compozițiile lianților studiați						
Dindon ormalial	Binder composition (%)					
Binder symbol	C D		Waste			
C0	100	-	-			
C05	81.55	-	18.45			
C1	63.1	-	36.9			
D	-	100	-			
D05	-	81.55	18.45			
D1	-	63.1	36.9			

Table 3

	-

Densitatea și aria suprateței specific pentru lianții						
Binder	Binder composition (%)					
symbol	Density	Ssp.				
	(g/cm³)	(cm²/g)				
C0	2.07	2589				
C05	2.17	2904				
C1	2.25	3057				
D0	2.12	4306				
D05	2.27	4580				
D1	2.34	4790				

Table 4

Density and specific surface area for studied bindings Densitatea și aria suprafeței specific pentru lianții studiați It can be seen that the increase of waste amount in the binder formulations determines the small decrease of the water for standard consistency; this can be due to the dilution of the binders when the waste is added to the cement (see Table 3). It has been observed an important increase of the temperature (over 50°C) during the mixing of D0 cement with water; this exothermic process is mainly due to the presence of lime in the formulation of cement D. This could explain the increase of water normal consistency amount.

The setting time depends significantly on the amount of waste, but also depends on the characteristics of Portland cement - composition, grinding fines, and the amount of water for normal consistency.

The waste presence in binders formulations delays the initial setting times compared to the C0 and D0 references (Figure 4b), but the final setting times varies insignificantly for cement type C and more important for cement type D. These results are in good accordance with literature data [28, 29], which explained the retardation of the cement hydration process due to the formation of heavy metals salts with low solubility and due to the metallic ions adsorption onto the C-S-H gel (hydrogen bonding) which forming an impervious coating on surface of these.

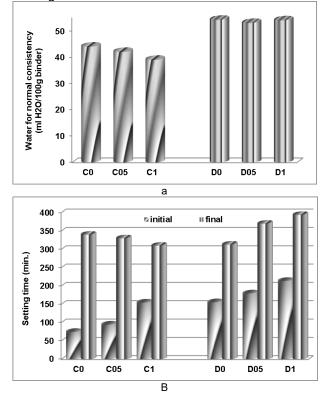


Fig. 4 - The water for normal consistency (a) and setting time (b) determined on studied binders with various chromium content / Apa de consistenţă normală (a) şi timpul de priză (b) determinate pe lianţii studiaţi cu diferite conţinuturi de crom.

The compressive strengths developed by the C and D binders without and with waste are shown in Figure 5.

The mortars based on D-type binders, without and with waste content, do not develop recordable compressive strengths, regardless the curing period; this could be due, most likely, to presence of internal tensions in the hardened structure, generated by the high rate of reaction (in correlation with the high value of hydration heat recorded in these systems).

For the mortars based on C-type binders (without and with waste content) the compressive strength values generally increase in time up to 28 days (Figure 5); after this period, the very small variations of mechanical strengths can be explained by carbonisation process of the sample or by error to measurement. Also, the presence of waste leads to decreasing of compressive strength values and this decrease is more pronounced as the proportion of waste increase. This can be due to the so called "dilution effect" i.e. waste substitutes the cement which is the active component which determines the hardening of the system [28].

The XRD patterns of C and D cement pastes (without and with chromium waste) hydrated for 3, 28, 60, 90 days are shown in Figures 6 and 7.

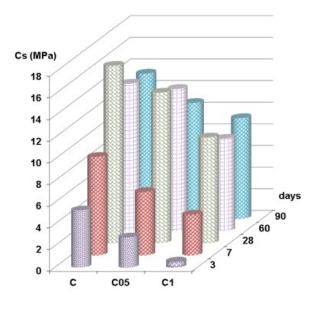


Fig. 5 - Compressive strength of C-type binder without and with waste content / *Rezistența la compresiune pentru liantul de tip C fără și cu conținut de deșeu.*

From the data presented in Figs. 6 and 7, one can observe the increase of calcium hydroxide XRD peaks in time, a clear indication of cement hydration process;

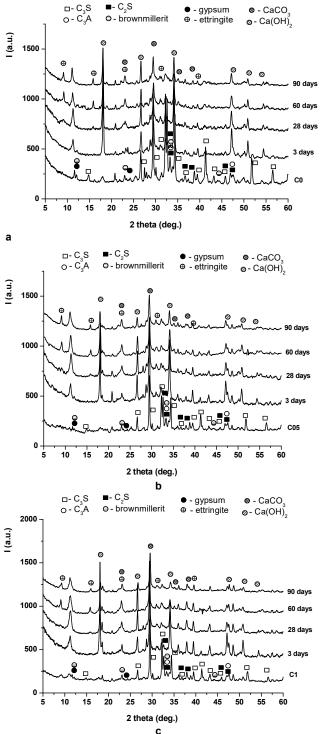


Fig. 6 - XRD patterns of C binders, without and with waste content, anhydrous and hydrated for 3, 28, 60, 90 days: a-C0, b-C05, c-C1 / Imaginile DRX pentru lianții de tip C, fără şi cu conținut de deşeu, anhidrii şi hidrataţi 3, 28, 60, 90 zile: a-C0, b-C05, c-C1.

The presence of chromium waste in binder formulations inhibits the cement hydration process and consequently inhibits the formation of hydrates including calcium hydroxide. The "dilution effect" can be another explanation for the lower intensities of XRD peaks specific for $Ca(OH)_2$ in the systems

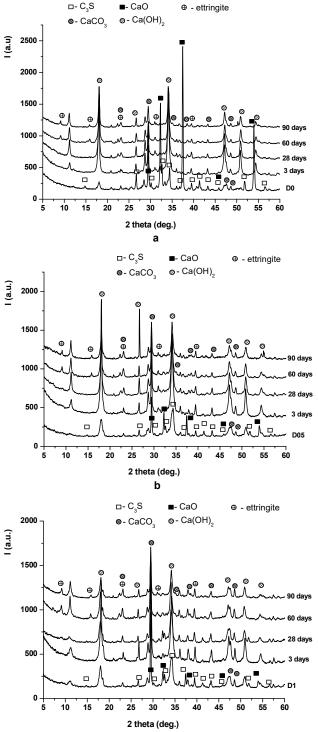


Fig. 7 - XRD patterns of D binders, without and with waste content, anhydrous and hydrated for 3, 28, 60, 90 days: a-D0, b-D05, c-D1 / Imaginile DRX pentru lianţii de tip D, fără şi cu conţinut de deşeu, anhidrii şi hidrataţi 3, 28, 60, 90 zile: a-D0, b-D05, c-D1.

С

with waste content.

Ettringite (AFt) is another crystalline hydrate formed during Portland cement hydration; it's specific peaks can be assessed on the XRD patterns of cement pastes, after 28 days of hydration.

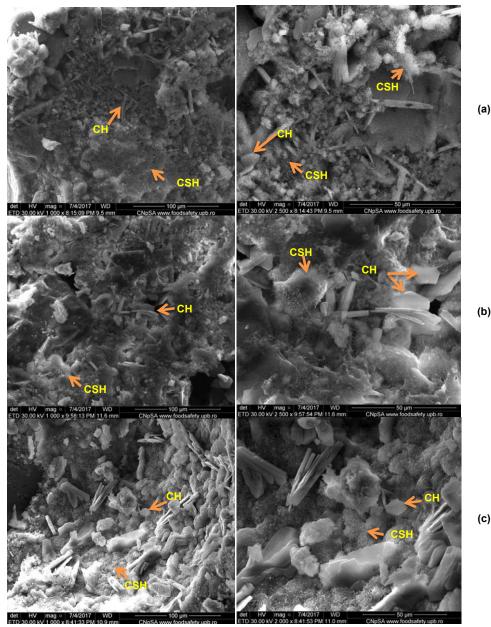


Fig. 8 - Scanning electron microscopy images for mortars based on C cement without and with chromium waste content: a) 0% Cr, b) 0.5% Cr and c) 1% Cr, hydrated 28 days / Imagini de microscopie electronică de baleiaj pentru mortare pe bază de ciment de tip C fără şi cu conținut de deşeu cu crom, întărite 28 zile: a) 0% Cr, b) 0,5% Cr and c) 1% Cr.

The intensity of XRD peaks specific for AFt is discontinuous in time, as a result of its partial transformation into the monosulfated compound (AFm) [30]. AFm is detected on XRD patterns by low intensity peaks, which makes difficult its clear detection; on the XRD patterns of C0 paste hardened for 90 days (fig. 6a) can be noticed the disappearance XRD peaks specific for ettringite (AFt) but the XRD specific lines for AFm cannot be assessed. Considering literature information [31], a low crystallinity degree of AFm can be assumed, as a result of its incorporation or interlaying into poorly crystalline calcium silicates hydrates. Also, in cement paste with chromium waste content, the formation of ettringite (AFt) seems to be favored i.e. the intensities of its XRD peaks being more

intense than in the waste free cement paste. The same variation / influence is noticed when fly ash is present in the binder formulation (see C versus D).

The SEM images of mortars (without and with chromium waste content) hardened at 28 days are presented in Figures 8 and 9.

For all types of studied mortars, the hydrated phases evolve in time. Thus, the calcium silicates hydrates (CSH with specific morphology foils or thin needles) evolve to well-formed phases; one can also notice the presence of hexagonal crystals specific for calcium hydroxide (CH) [32].

The immobilization capacity of chromium by the C and D cements was assessed by a static test (SR EN 12457-2). The chromium

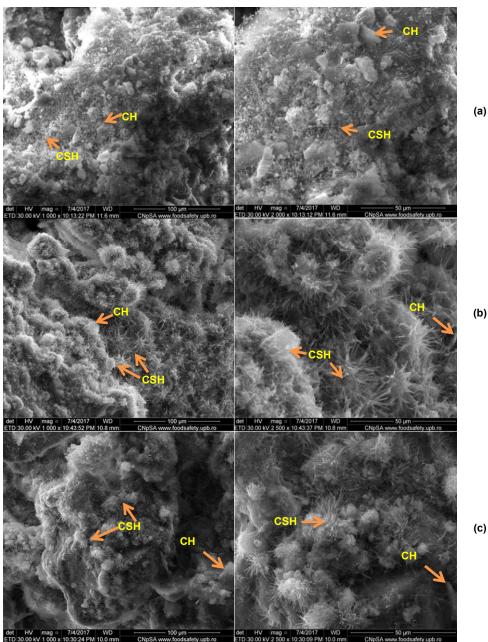


Fig. 9 - Scanning electron microscopy images for mortars based on cement D, without and with waste content: a) 0% Cr, b) 0.5% Cr and c) 1% Cr, hydrated 28 days / Imagini de microscopie electronică de baleiaj pentru mortare pe bază de ciment de tip D fără şi cu conținut de deşeu cu crom, întărite 28 zile: a) 0% Cr, b) 0,5% Cr and c) 1% Cr.

concentration in leachate resulted is presented in Table 7.

According to European and national regulation [26, 27] the maximum values for Cr content in leachate is 70 mg / Kg. The data presented in Table 7 highlight for C and D binding systems, with waste content corresponding to 0.5% chromium, values for chromium in the leachate just below the limit value i.e. 70 mg / Kg; the increase of waste dosage (corresponding to 1% chromium content), increases very much the chromium concentration in leachate, suggesting a poor immobilization of chromium in this type of materials.

Chromium concentration in the leachate Concentratia cromului în levigat

	alai ili ieviga
Sample	[Cr]
	ppm
Distilled water	0.0013
C0	0.52
C05	69.33
C1	205.67
D0	0.14
D05	69.97
D1	193.10

Table 7

4. Conclusions

The following conclusions can be drawn:

- The solidification/stabilization of the waste resulted in potassium dichromate manufacture can be achieved with two types of Portland cements (with various admixtures i.e. slag, fly ash, lime and bypass dust), but only for small dosages (0.5% chromium).

The presence of waste in binder formulation based on these two types of Portland cements modifies the kinetic of hydration and hardening process and the morphology of formed hydrates; this has direct consequences of the i.e. water specific properties for standard consistency, setting time and compressive strengths.

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