

INERTIZAREA DEȘEURILOR LICHIDE ÎN LIANȚI MAGNEZIANO-FOSFATICI LIQUID WASTE INERTIZATION IN CHEMICALLY BONDED PHOSPHATE CERAMIC (CBPC)

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This paper presents experimental results for liquid waste inertization in chemically bonded phosphate ceramic (CBPC). This process turns waste hazardous in non-hazardous waste.

It was studied the inertization of liquid wastes containing heavy metals (Ba, Cd, Cu, Ni, Pb) with concentrations between 3000 mg/l and 30000 mg/l in CBPC versus inertization in portland cement paste. As the CBPC is a fast setting system, it was also used boric acid as retarder in concentration of 3% (based on the amount of magnesium oxide and potassium dihydrogen phosphate). To increase the efficiency of cadmium inertization, phosphoric acid was added. Also it was studied the influence of sodium dimetilditiocarbamate. It was determined the maximum temperature of the obtained systems, the setting time and compression strength. To determine the effectiveness of waste inertization it was performed leaching tests in water and in acid solution, and the obtained values were compared with regulated limits.

Lucrarea prezintă rezultatele experimentale pentru inertizarea deșeurilor lichide în lianți magneziano-fosfatici (CBPC). Prin acest proces deșeurile periculoase se transformă în deșeuri nepericuloase.

S-a studiat inertizarea deșeurilor lichide cu conținut de metale grele (Ba, Cd, Cu, Ni, Pb) cuprins între 3000 mg/l și 30000 mg/l, în CBPC comparativ cu inertizarea în pastă de ciment portland. Deoarece sistemul CBPC este unul cu întărire rapidă, s-a utilizat ca întârziator de priză acidul boric în concentrație de 3% (raportat la cantitatea de oxid de magneziu și fosfat diacid de potasiu). Pentru a mări eficiența inertizării cadmiului s-a adăugat acid fosforic. De asemenea, s-a studiat influența adăugării dimetilditiocarbamatului de sodiu. S-a determinat temperatura maximă a sistemelor obținute, timpul de început de priză și rezistența la compresiune. Pentru determinarea eficienței procesului de inertizare a deșeurilor s-au realizat teste de levigare în apă și în soluție acidă, valorile obținute comparându-se cu cele reglementate.

Keywords: waste inertization, heavy metals, chemically bonded phosphate ceramic, CBPC, portland cement, leachate, TCLP

1. Introduction

According to the legislation, the liquid wastes are not accepted for storage in the waste deposits. They must be previously treated, stabilized, solidified. The non-hazardous waste landfill permit the storage of stable, non-reactive hazardous waste, such as those solidified vitrified, having a proper leaching behavior [1].

Stabilization processes change the dangerousness of the waste components and therefore transform hazardous waste into a non-hazardous one.

Solidification processes only change the physical state of the waste (for example, from liquid to solid) by using additives without changing the chemical properties of the waste.

A waste is considered as partly stabilized if after the stabilization process dangerous constituents which have not been completely changed to harmless can be released in the environment in the short, medium and long term [2].

Immobilisation is not able to reduce the content of any contaminant in the waste, only change the chemical composition by chemical reactions. These techniques are most likely to be effective in the treatment of inorganic wastes. With this technique, a large range of wastes can be treated (liquids, solids, many chemical pollutants, ashes, etc.). [3]

For stabilization/solidification of wastes can be used Portland cement or CBPC.

CBPC is prepared by an acid-basic reaction between a metallic oxide (MgO) and an acid phosphate (KH₂PO₄), in presence of water, resulting hydro-phosphates that crystallize further into a monolithic ceramic, according to the following reaction [4]:



The formation of this ceramic is a three step process [5]:

- the oxide is dissolved in a solution of the acid phosphate and metal ions are released into solution;

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- aquasols formed from the phosphate anions react with cations to form a gel of metal hydrophosphate;
- the gel crystallized and grows in a monolithic ceramic.

Because the reaction is too fast, for obtaining a proper CBPC, MgO should be calcined at temperatures above 1000°C [8] and must be used retarders such as boric acid (H₃BO₃) [4].

CBPC presents some advantages over inertization in Portland cement: allows higher waste and salts loadings compared with Portland cement [6, 7].

The scope of this work is to evaluate the effectiveness of heavy metals (Ba, Cd, Cu, Ni, Pb) inertization from hazardous liquid waste using Portland cement and CBPC.

2. Experimental

Six solutions containing heavy metals (Ba, Cd, Cu, Ni, Pb) were prepared:

- Solution I: 3000 mg metals/l (500 mg Ba/l, 1000 mg Cd/l, 500 mg Cu/l, 500 mg Ni/l, 500 mg Pb/l); density 1.0040 g/cm³
- Solution II: 6000 mg metals/l (1000 mg Ba/l, 2000 mg Cd/l, 1000 mg Cu/l, 1000 mg Ni/l, 1000 mg Pb/l); density 1.0088 g/cm³
- Solution III: 9000 mg metals/l (1500 mg Ba/l, 3000 mg Cd/l, 1500 mg Cu/l, 1500 mg Ni/l, 1500 mg Pb/l); density 1.0136 g/cm³
- Solution IV: 10000 mg Ba/l; density 1.0099 g/cm³
- Solution V: 20000 mg Ba/l; density 1.0205 g/cm³
- Solution VI: 30000 mg Ba/l; density 1.0311 g/cm³

The solutions were prepared using the following salts:

- BaCl₂·2H₂O
- Cd(CH₃COO)₂·2H₂O
- CuCl₂·2H₂O

- Ni(NO₃)₂·6H₂O
- Pb(NO₃)₂

The compositions of each solution, expressed in % gravimetric, are presented in Table 1. For the preparation of these solutions, salts were dissolved one by one. In the table are specified also the properties which render the waste hazardous, according to Commission Regulation (EU) No 1357/2014 [9].

2.1. Waste samples stabilized with cement

The waste samples stabilized with cement were prepared as follows:

- 45 ml of waste metal solution was added to 100 g of cement (compositions expressed in % gravimetric are presented in Table 2), it was stirred with a glass rod until a paste was obtained, it was poured into molds and left them 21 days to harden.

Then they were removed from molds and it was determined the compressive strength.

It was used a press HECKERT FP 100/1 and were measured two samples for each composition. From these compositions were obtained 6 samples, presented in Table 2. It was used cylindrical forms with height equal with diameter (4 cm).

2.2. Waste samples stabilized with CBPC

To obtain CBPC it was used MgO calcined at 1100°C for 3 hours and KH₂PO₄. As a retarder was used boric acid. It was used equimolar quantities of KH₂PO₄ and MgO.

In some compositions it was added phosphoric acid (about 5% (volume %) reported to the liquid waste quantity) or sodium dimethyl-dithiocarbamate (about 5 times the amount of metal from the waste) to study the effect of above mentioned solution on waste inertization efficiency.

The phosphoric acid precipitates heavy

Table 1

Salts amounts used for solutions preparation, expressed in % gravimetric; Properties of waste which render it hazardous
Cantitățile de săruri utilizate pentru prepararea soluțiilor, exprimate în mg/l; Proprietățile care fac deșeurul periculos

Salt Sare	Solution I Soluția I, % gr	Solution II Soluția II, % gr	Solution III Soluția III, % gr	Solution IV Soluția IV, % gr	Solution V Soluția V, % gr	Solution VI Soluția VI, % gr	Properties of waste which render it hazardous* <i>Proprietăți care determină caracterul periculos al deșeurului</i>
BaCl ₂	0.08	0.15	0.23	1.55	3.13	4.75	HP6 "Acute toxicity", if concentration > 0.1% HP6 "Toxicitate acută", dacă concentrația > 0,1%
Cd(CH ₃ COO) ₂	0.21	0.42	0.63	-	-	-	HP7 "Carcinogenic", if concentration > 0.1% HP7 "Cancerigen", dacă concentrația > 0,1%
CuCl ₂	0.11	0.21	0.32	-	-	-	-
Ni(NO ₃) ₂	0.16	0.31	0.47	-	-	-	HP7 "Carcinogenic", if concentration > 0.1% HP7 "Cancerigen", dacă concentrația > 0,1%
Pb(NO ₃) ₂	0.08	0.16	0.24	-	-	-	-
Total salts <i>Total săruri</i>	0.63	1.26	1.89	1.55	3.13	4.75	-

* According to Commission Regulation (EU) No 1357/2014

Table 2Samples compositions for waste stabilized with Portland cement / *Compoziția probelor de deșeu stabilizat cu ciment*

Sample code <i>Codul probei</i>	Sample composition <i>Compoziția probei</i>	Percentage composition, % gravimetric <i>Compoziția procentuală, % gravimetrice</i>	
		Cement <i>Ciment</i>	Liquid waste solution <i>Deșeu lichid</i>
A	cement + solution I / <i>ciment + solutie I</i>	68.88	31.12
B	cement + solution II / <i>ciment + solutie II</i>	68.78	31.22
C	cement + solution III / <i>ciment + solutie III</i>	68.68	31.32
D	cement + solution IV / <i>ciment + solutie IV</i>	68.75	31.25
E	cement + solution V / <i>ciment + solutie V</i>	68.53	31.47
F	cement + solution VI / <i>ciment + solutie VI</i>	68.31	31.69

Table 3Sample composition of waste stabilized with CBPC/ *Compoziția probelor de deșeu stabilizat cu CBPC*

Sample code <i>Codul probei</i>	Sample composition <i>Compoziția probei</i>	MgO % gr	KH ₂ PO ₄ % gr	H ₃ BO ₃ % gr	Heavy metals solution <i>Soluții metale grele</i> % gr	H ₃ PO ₄ % gr	Na dimethildithiocarbamate <i>Dimetilditio-carbamat de sodiu</i> % gr
1	Blank I: MgO + KH ₂ PO ₄ + H ₃ BO ₃ +water	11.72	39.85	1.55	46.88 (water)	0.00	0.00
2	Blank II: KH ₂ PO ₄ + H ₃ BO ₃ +water + MgO	11.72	39.85	1.55	46.88 (water)	0.00	0.00
3	MgO+KH ₂ PO ₄ +H ₃ BO ₃ + solution I	11.70	39.78	1.54	46.98 (solution I)	0.00	0.00
4	KH ₂ PO ₄ +H ₃ BO ₃ +solution I + MgO	11.70	39.78	1.54	46.98 (solution I)	0.00	0.00
5	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution I + H ₃ PO ₄	11.25	38.25	1.48	45.17 (solution I)	3.85	0.00
6	KH ₂ PO ₄ + H ₃ BO ₃ + solution I + H ₃ PO ₄ + MgO	11.25	38.25	1.48	45.17 (solution I)	3.85	0.00
7	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + Na dimethildithiocarbamate + solution I	11.63	39.54	1.54	46.71 (solution I)	0.00	0.58
8	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution II	11.67	39.69	1.54	47.10 (solution II)	0.00	0.00
9	KH ₂ PO ₄ + H ₃ BO ₃ + solution II + MgO	11.67	39.69	1.54	47.10 (solution II)	0.00	0.00
10	MgO + KH ₂ PO ₄ + H ₃ BO ₃ solution II +H ₃ PO ₄	11.22	38.16	1.48	45.29 (solution II)	3.84	0.00
11	KH ₂ PO ₄ + H ₃ BO ₃ + solution II + H ₃ PO ₄ + MgO	11.22	38.16	1.48	45.29 (solution II)	3.84	0.00
12	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + sodium dimethildithiocarbamate + solution II	11.54	39.23	1.52	46.56 (solution II)	0.00	1.15
13	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution III	11.65	39.60	1.54	47.22 (solution III)	0.00	0.00
14	KH ₂ PO ₄ + H ₃ BO ₃ + solution III + MgO	11.65	39.60	1.54	47.22 (solution III)	0.00	0.00
15	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution III + H ₃ PO ₄	11.20	38.08	1.48	45.41 (solution III)	3.83	0.00
16	KH ₂ PO ₄ + H ₃ BO ₃ + solution III + H ₃ PO ₄ + MgO	11.20	38.08	1.48	45.41 (solution III)	3.83	0.00
17	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + sodium dimethildithiocarbamate + solution III	11.45	38.92	1.51	46.41 (solution III)	0.00	1.72
18	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution IV	11.67	39.67	1.54	47.13 (solution IV)	0.00	0.00
19	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution V	11.61	39.47	1.53	47.39 (solution V)	0.00	0.00
20	MgO + KH ₂ PO ₄ + H ₃ BO ₃ + solution VI	11.55	39.28	1.52	47.65 (solution VI)	0.00	0.00

metals as insoluble phosphates. Sodium dimethyl-dithiocarbamate was used to improve the precipitation of metals from liquid waste.

The samples stabilized with CBPC were prepared using the material quantities presented in Table 3 (in the order specified in Table).

Samples were well mixed with a glass rod and it was recorded the maximum temperature reached by systems and the setting time. At the beginning, the material was very fluid and after a period of mixing, formed a thick but pourable paste, which was transferred into cylindrical moulds, with diameter equal to the height (4 cm). The paste was immediately hardened. After 2 days the samples were removed from the moulds.

2.3. Unconfined compressive strength

Unconfined compressive strength was determined after 21 days of hardening on samples with surface of 12.56 cm². It was used a press HECKERT FP 100/1 and were measured two samples for each composition.

Unconfined compressive strength was measured to establish the cohesiveness of the materials. It also represents the effectiveness of the solidification and stabilization of the binder with the waste.

According to the United States Environmental Protection Agency (USEPA) regulations, solidified and stabilized waste products must have a minimum unconfined compressive strength of 0.35 MPa after 28 days [10].

2.4. Leachate Test Results (ratio solid: water = 1:10)

After 21 days from sample preparation it was performed the leaching test for a report between stabilized solid waste: water report = 1:10. The resulting suspension was stirred for 24 hours with an orbital shaker at a speed of 10 rotations per minute, according to STAS SR EN 12457-4:2003 [11], then it was filtered and preserved with HNO₃ to pH <2 for the metals analyses.

Analyses for the determination of metals in leachate were performed by inductively coupled plasma spectrometry with optic emission (ICP-OES) according to SR EN ISO 11885/2009 [12].

2.5. Leaching Procedure TCLP - EPA Method 1311 [13]

In order to carry out this procedure can be used one from the following extraction fluids:

- Fluid 1: add 5.7 ml glacial acetic acid to 500 ml distilled water, add 64.3 ml of 1N NaOH and dilute to a volume of 1 liter with distilled water. pH of this solution is 4.93±0.05

- Fluid 2: dilute 5.7 ml glacial acetic acid with distilled water to a volume of 1 liter. pH of this solution is 2.88±0.05

To determine which of the two extraction fluids should be used proceed as follows:

- weigh out 5 g solid waste with particle size of approximate 1 mm in a 500 ml Erlenmeyer flask and then add 96.5 ml distilled water;
- cover with a watch glass and stir vigorously for 5 minutes using a magnetic stirrer;
- measure and record pH (value pH I);
- if the pH is lower than 5, it is used extraction fluid 1;
- if the pH is greater than 5, add 3.5 ml of 1N HCl, mix, cover with a watch glass, heat to 50°C and maintained at this temperature for 10 minutes. Cool at room temperature and measure the pH.(value pH II);
- if the pH is less than 5, it is used extraction fluid 1;
- if the pH is greater than 5 is used extraction fluid 2.

For TCLP extraction the wastes stabilized both with CBPC and with cement were grounded to a particle size below 9.5 mm, then were placed in contact with the extracting fluid in ratio solid: liquid=1:20, were stirred for 18 hours at 30 rotations per minute, filtered, acidified with HNO₃ to pH <2 and analyzed for metal content.

2.6. X-ray diffraction

X-ray diffraction analyzes were carried out using an X-ray diffractometer Empyrean produced by PANalytical the Netherlands), using an X-ray beam characteristic with K α 1 ($\lambda = 1.540598$) equipped with PSD and PIXcel3D detector. Analyses were performed using the Bragg-Brentano geometry ("Theta-2Theta") for angles 2 θ in range 10 to 80.

2.7. Scanning electron microscopy (SEM)

Investigation of samples was performed using scanning electron microscope F QUANTA INSPECT equipped with electron gun with field emission - FEG (field emission gun) with a resolution of 1.2 nm and energy dispersive X-ray spectrometer (EDS) with resolution of 133 eV at MnK α .

3. Results and discussions

The values for maximum temperature, setting time and compressive strength obtained on these compositions, after 21 days of hardening, are presented in Table 4.

All wastes stabilized with cement or CBPC meet the USEPA specification regarding the minimum unconfined compressive strength of 0.35 MPa.

From the waste samples stabilized with CBPC, the highest compressive strength and the highest value for setting time were recorded for those with phosphoric acid addition.

The analyses results for determinations of Cu and Pb in water leachate (solid:liquid ratio = 1:10) are presented in Table 5 and for Ba, Cd, Ni in Figures 1-3.

The maximum regulated values for leachate 1:10 (solid: liquid) in distilled water – expressed in mg/kg of solid waste - according to Order 95/2005 [14], are presented in Table 6.

Table 4

Temperature values, setting time and compressive strength for the obtained systems
 Valorile temperaturii, timpului de început de priză și rezistenței la compresiune pentru sistemele obținute

Sample code Codul probei	Temperature °C Temperatura °C	Setting time, minutes Timp de priză, minute	Compressive strength Rezistența la compresiune MPa
1	57	19	4.07
2	55	29	4.32
3	55.8	25	4.11
4	52.8	25	3.31
5	62.2	52	9.36
6	62	62	5.56
7	56.3	18	3.37
8	54.7	20	4.99
9	56.2	23	5.14
10	63.1	43	6.45
11	60	53	7.67
12	55.8	19	3.57
13	53.8	26	3.92
14	57.6	29	5.09
15	61.5	72	9.78
16	55.6	66	9.45
17	54.9	19	2.84
18	57.9	18	3.78
19	54.4	24	6.05
20	50.1	29	5.16
A	-	-	16.9
B	-	-	16.4
C	-	-	13.2
D	-	-	11.6
E	-	-	12.2
F	-	-	17.2

Table 5

Metals (Cu, Pb) concentrations in water leachate for stabilized samples with CBPC and Portland cement
 Concentrația de metale (Cu, Pb) în levigatul în apă pentru probele stabilizate cu CBPC și ciment Portland

Sample code Codul probei	Cu, mg/kg	Pb, mg/kg
1	<0.2	<0.2
2	<0.2	<0.2
3	<0.2	<0.2
4	<0.5	<0.5
5	<0.5	<0.5
6	<0.5	<0.5
7	<0.2	<0.2
8	<0.2	<0.2
9	<0.2	<0.2
10	<0.5	<0.5
11	<0.4	<0.4
12	<0.2	<0.2
13	0.2	<0.2
14	<0.2	<0.2
15	<0.5	<0.5
16	<0.5	<0.5
17	<0.2	<0.2
A	<0.5	<0.5
B	<0.5	<0.5
C	<0.5	<0.5

Table 6

The maximum regulated concentrations of metals in water leachate, for solid: liquid ratio = 1:10
 Concentrația maximă reglementată a metalelor în levigatul în apă, pentru raportul solid:lichid = 1:10

Waste classification Clasificare deșeu	Metals, mg/kg / Metale, mg/kg				
	Ba	Cd	Cu	Ni	Pb
Inert waste Deșeu inert	20	0.04	2	0.4	0.5
Non-hazardous waste Deșeu nepericulos	100	1	50	10	10
Hazardous waste that may be classified as non-hazardous Deșeu periculos care poate fi clasificat ca nepericulos	100	1	50	10	10
Hazardous waste Deșeu periculos	300	5	100	40	50

In Figures 1 - 3 are presented the metals concentrations in leachate (values are expressed

in mg/kg) versus the maximum regulated concentrations of Ba, Cd, Ni in leachate.

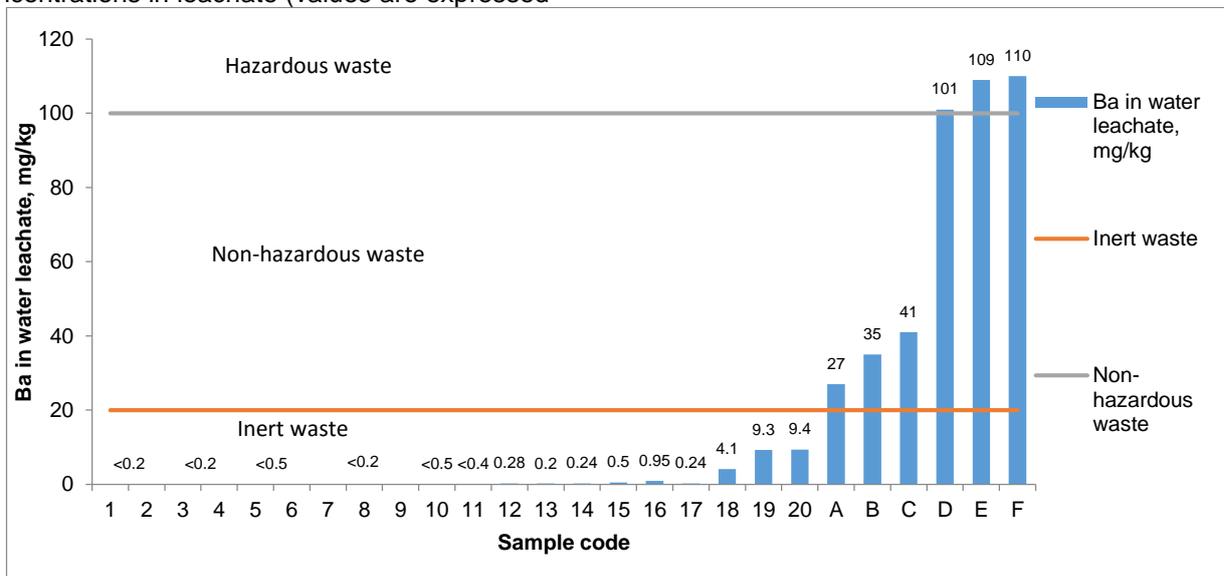


Fig. 1 - Ba concentration in water leachate (solid:water ratio=1:10), versus the maximum regulated concentrations of Ba in leachate [14].
 Concentrația de Ba în levigatul în apă (raport solid:apă=1:10) comparativ cu concentrația maximă admisă a Ba în levigat [14].

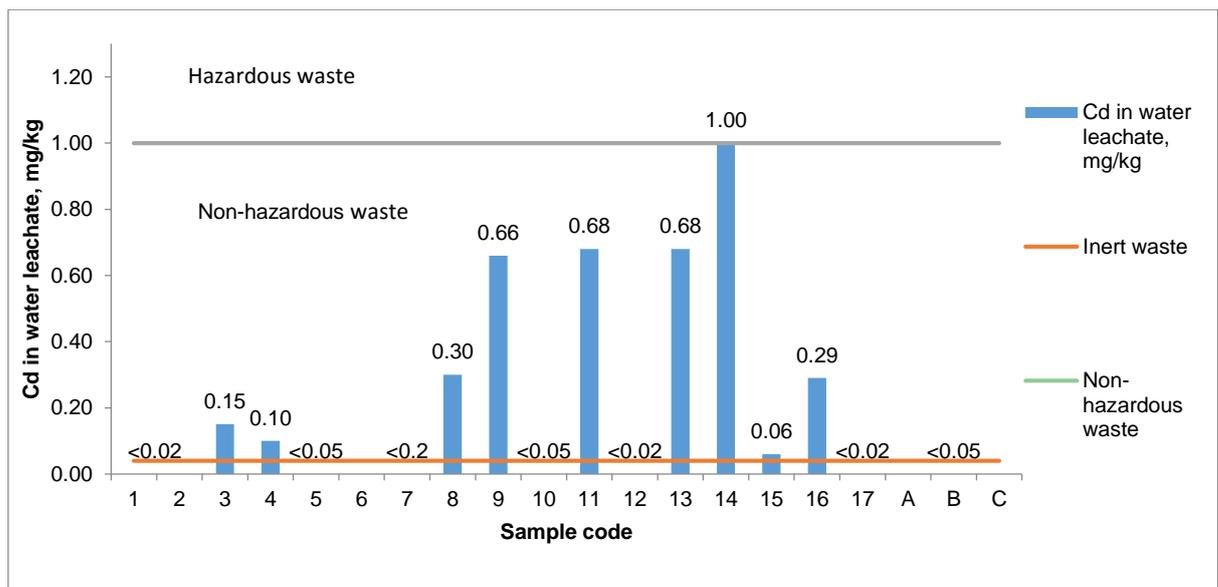


Fig. 2 - Cd concentration in water leachate (solid:water ratio=1:10), versus the maximum regulated concentrations of Cd in leachate [14].
 Concentrația de Cd în levigatul în apă (raport solid:apă=1:10) comparativ cu concentrația maximă admisă a Cd în levigat [14].

For Ba, all stabilized wastes in CBPC are classified as inert and those stabilized in cement are non-hazardous (samples A, B, C) or hazardous (samples D, E, F).

For Cd, all waste stabilized with CBPC are classified as non-hazardous and those stabilized with cement are inert.

As can be seen from Figure 2, for samples 3, 4, 8, 9 and 13, 14 prepared from MgO, KH₂PO₄, water and liquid waste containing increasingly cadmium concentrations (samples 3 and 4 contain liquid waste with 1000 mg/l Cd, samples 8 and 9 contain 2000 mg/l Cd and samples 13 and 14 contain 3000 mg/l Cd) the amount of cadmium in leachate increases proportionally with the initial amount of Cd in liquid waste, so that for sample 14 reaches the maximum admissible value for non-hazardous waste - 1 mg/kg.

Also, the order of addition of raw materials MgO and KH₂PO₄ is important, so for samples 8 and 9 that have the same composition, differing only components mixing order is found a higher value for cadmium concentration in leachate for sample 9 where MgO was added at the end, compared to sample 8 where MgO was mixed dried with KH₂PO₄, then it was added boric acid, and finally cadmium solution. The situation is similar for samples 13 and 14, leading to the conclusion that for a more effective stabilization of cadmium is needed dry mixing of MgO and KH₂PO₄ at the beginning, then addition of the retarder and the liquid waste should be added at the end.

This could be explained by the fact that magnesium oxide must be present in solution from the beginning to release ions in solution that would combine with phosphate ions by acid-basic reactions, resulting phosphate hydrates that crystallize further into a monolithic ceramic.

The most effective stabilization for the liquid waste with cadmium it was obtained for the version with initial solid mixture between MgO and KH₂PO₄ and addition of phosphoric acid in the liquid waste (samples 5, 10 and 15). Cd reacts with H₃PO₄ to form the respective phosphate or phosphate hydrate that is chemically insoluble. It is further encapsulated physically in the dense CBPC matrix [4, 15, 16]. This compound wasn't identified on the XRD spectra being below detection limit of the method (Figure 5).

It is found that the samples with addition of phosphoric acid present the highest values for compressive strength (about two times higher than those without phosphoric acid). These samples show the highest setting time, which has allowed the phosphate gel resulted to crystallize slowly in a network well-ordered, without interruptions, resulting in a solid monolithic with a high compressive strength as will be further presented (SEM analysis).

For Ni, all wastes stabilized with CBPC and cement are classified as inert or non-hazardous.

For Cu and Pb concentrations in leachate are very small and have not been plotted, all compositions are classified as inert.

For samples (7, 12 and 17) in which sodium dimethyldithiocarbamate was added, metals in leachate concentrations are extremely low, all are classified as inert, but they have the lowest values for compressive strength. An explanation could be that the samples stabilized with sodium dimethyldithiocarbamate present the shortest setting time, which is insufficient for a proper crystallization.

For TCLP procedure, in order to establish the extraction fluid used, it was measured the pH of the obtained systems after adding distilled water and HCl 1N. Values are presented in Table 7.

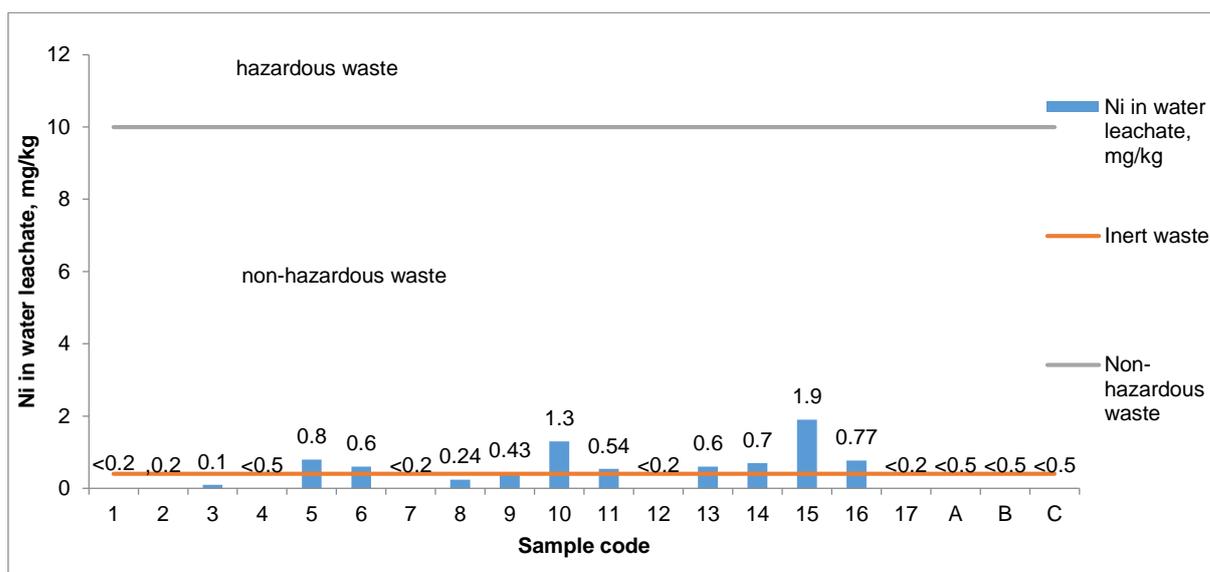


Fig. 3 - Ni concentration in water leachate (solid:water ratio=1:10), versus the maximum regulated concentrations of Ni in leachate [14] *Concentrația de Ni în levigatul în apă (raport solid:apă=1:10) comparativ cu concentrația maximă admisă a Ni în levigat [14].*

Table 7

pH values for establishing of extraction fluid / Valorile pH-ului pentru stabilirea fluidului de extracție

Sample code / Codul probei	Value pH I / Valoare pH I	Value pH II / Valoare pH II
1	8.22	7.69
2	8.52	7.42
3	8.83	7.27
4	9.34	7.16
5	7.88	7.3
6	7.97	7
7	9.58	7.35
8	9.12	7.46
9	9.01	7.16
10	8.14	6.79
11	8.04	7.01
12	9.02	7.24
13	8.84	7.66
14	8.70	7.11
15	7.95	7.04
16	7.82	6.4
17	9.27	7.51
18	8.93	7.27
19	9.01	7.43
20	8.98	7.39
A	12.01	11.32
B	11.95	11.46
C	11.96	11.47
D	11.95	11.45
E	11.88	11.37
F	11.93	11.48

Table 8

Metal concentrations values in TCLP extract for samples stabilized CBPC and cement
Valorile concentrațiilor metalelor în extractul TCLP pentru probele stabilizate cu CBPC și ciment

Sample code Codul probei	Ba TCLP, mg/l	Cd TCLP, mg/l	Cu TCLP, mg/l	Ni TCLP, mg/l	Pb TCLP, mg/l
1	<0,05	<0,005	<0,05	<0,05	<0,05
2	<0,05	<0,005	<0,05	<0,05	<0,05
3	0,14	0,025	<0,05	0,05	<0,05
4	0,05	0,100	0,075	0,08	<0,05
5	0,095	<0,005	<0,05	0,48	<0,05
6	0,095	<0,005	<0,05	0,5	<0,05
7	0,195	<0,005	<0,05	<0,05	<0,05
8	0,365	0,075	<0,05	0,045	<0,05
9	0,145	0,075	<0,05	0,165	<0,05
10	0,1	0,008	<0,05	0,7	<0,05
11	0,35	0,060	<0,05	2,25	<0,05
12	0,4	<0,005	<0,05	<0,05	<0,05
13	0,15	0,100	<0,05	0,21	<0,05
14	0,1	0,150	<0,05	0,9	<0,05
15	0,1	0,010	<0,05	1	<0,05
16	0,17	0,045	<0,05	0,1	<0,05
17	0,3	<0,005	<0,05	<0,05	<0,05
18	0,95	-	-	-	-
19	1,9	-	-	-	-
20	1,7	-	-	-	-
A	2,4	<0,005	<0,05	<0,05	<0,05
B	3,1	<0,005	<0,05	<0,05	<0,05
C	3,7	<0,005	<0,05	<0,05	<0,05
D	15	-	-	-	-
E	20	-	-	-	-
F	20	-	-	-	-

Table 9

Regulated limits for TCLP procedure, values are expressed in mg/l
Valori maxime admise pentru procedura TCLP, valori exprimate în mg/l

Metal	Maximum allowable concentrations TCLP extract, according EPA and Onyx Waste Acceptance Landfilling Protocol, mg/l <i>Concentrația maximă admisă pentru extractul TCLP, conform EPA și protocolului Onyx de acceptare la depozitare, mg/l</i>
Ba	100
Cd	1
Cu	200
Ni	35
Pb	5

So, for all the samples the pH values are less than 5 by addition of 1N HCl and it was used the extraction fluid 2.

The analysis results for TCLP extract using fluid 2, performed by ICP-OES, are shown in table 8 (values are expressed in mg/l), and in Table 9 are presented the regulated limits for TCLP procedure.

In terms of the leachability according to TCLP procedure for Ba, Cu, Ni, Pb and Zn all waste stabilized both with CBPC and cement are below the maximum allowed limit for this procedure.

From X-ray diffraction pattern was identified as a single crystalline phase $KMg(PO_4) \cdot 6H_2O$ [ICDD 04-009-4123] with orthorhombic structure. In the Figures 4, 5 are presented X-ray diffraction spectra for samples 3 and 5 after 21 days from preparation.

Microstructural appearance of the sample 3 (without H_3PO_4) and sample 5 (with addition of H_3PO_4) after 21 days from preparation, is shown by scanning electron microscopy images (backscatter electron images BSED) in figure 6 a, b, c and d and in Figure 7 a, b, c, d, e and f.

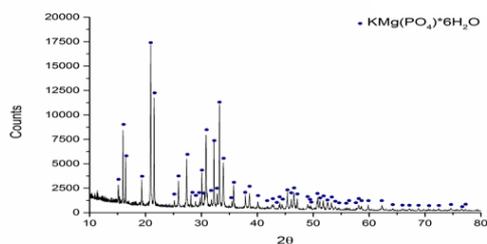


Fig. 4 - X-ray diffraction spectra for sample 3 /Spectrul de difracție de raze X pentru proba 3.

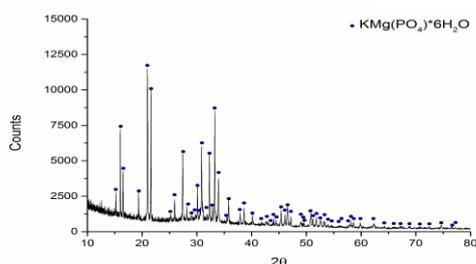


Fig. 5 - X-ray diffraction spectra for sample 5 /Spectrul de difracție de raze X pentru proba 5.

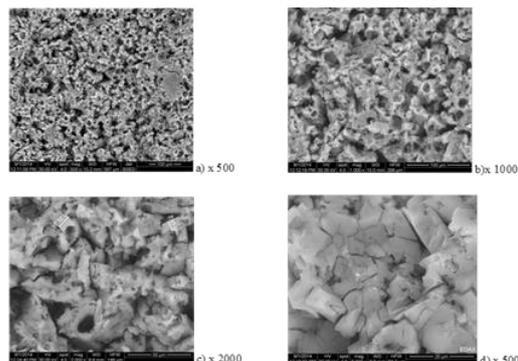


Fig. 6 a, b, c and d - SEM images for sample 3 /Imagini SEM pentru proba 3.

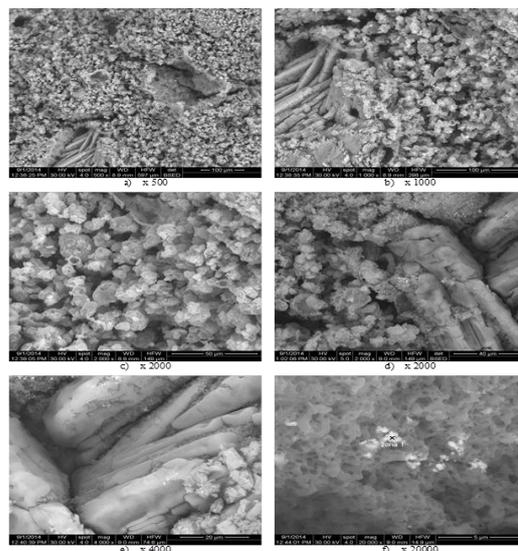


Fig. 7 a, b, c, d, e and f - SEM images for sample 5 /Imagini SEM pentru proba 5.

For the sample 3, can be observed pores and polyhedral particles with maximum size between 5-12 μm . For the sample 5, one can notice the presence of agglomerates of polyhedral particles having maximum size of 10 micrometres (width) and some fine particles round up to 2 μm . Sample 5 (with H_3PO_4) is more compact, less porous, which is reflected in the mechanical properties - samples with phosphoric acid added shows the highest compressive strength among all samples of waste immobilized in CBPC.

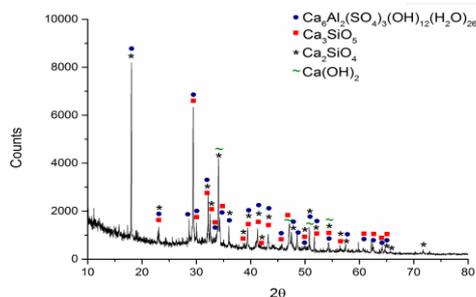


Fig. 8 - X-ray diffraction spectra for sample A /Spectrul de difracție de raze X pentru proba A

In the Figure 8 is presented the XRD spectra for sample A (cement + solution I (3000 mg/l metals)). From XRD spectra there were identified the following crystalline phases: $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ (ettringite) [ICDD 04-011-5267] with hexagonal structure, Ca_3SiO_5 (alite) [ICDD 00-055-0740] with monoclinic structure, Ca_2SiO_4 (belite) [ICDD 01-083-0461] with monoclinic structure and $\text{Ca}(\text{OH})_2$ (portlandite) [01-076-0571] with hexagonal structure.

4. Conclusions

- For the inertization of Ba (Ba concentration in liquid waste is up to 30000 mg/l) all samples stabilized in CBPC are classified as inert; samples stabilized in cement are non-hazardous (for concentrations of barium in solution until to 10000 mg/L – 1%) or hazardous (for concentration of barium in solution over 10000 mg/l – 1%).

- For the inertization of Cd (Cd concentration in liquid waste is up to 3000 mg/l) is necessary an initial mixing between MgO and KH_2PO_4 in solid state, adding boric acid as a retarder and the final addition of liquid waste with phosphoric acid in concentration of 5% (volume %) relative to the amount of liquid waste. Adding of H_3PO_4 in liquid waste increase the compressive strength and decrease the porosity of final product. The samples with phosphoric acid present the longest setting time, which permit an appropriate crystallization, conducting to the highest compressive strength of the system.

- For the inertization of Cu and Pb (Cu and Pb concentrations in liquid waste is up to 1500 mg/l of each metal) all waste stabilized with both CBPC and cement are classified as inert.

- For the inertization of Ni (Ni concentration in liquid waste is up to 1500 mg/l) all waste stabilized with both CBPC and cement are classified as inert or non-hazardous.

- Inertization of Ni and Pb is effective both in CBPC and in cement.

- Addition of sodium dimethyl-dithiocarbamate is very efficient from the leaching point of view: the compressive strength is lower than other samples, but meets the USEPA criterion. The samples stabilized with CBPC and sodium dimethyldithiocarbamate shows the shortest setting time, which is insufficient for a proper crystallization. From this cause these samples present the lowest compressive strength.

REFERENCES

1. Government of Romania decision HG 349/21.04.2005 concerning waste storage
2. Government of Romania decision HG 856/16.08.2002 concerning the waste management records and approving the list of wastes, including hazardous wastes
3. European Commission - Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Waste Treatments Industries, August 2006
4. Arun S. Wagh - Chemically Bonded Phosphate Ceramics, Twenty-first century materials with divers applications, Aragonne National Laboratory, Elsevier, 2004
5. Arun S. Wagh, Seung Z. Jeong - Chemically Bonded Phosphate Ceramics: I, A Dissolution Model of Formation, J. Am. Ceram. Soc., 2003, **86** (11)..
6. Sandip Chattopadhyay - Evaluation of Chemically Bonded Phosphate ceramics for Mercury Stabilization of a Mixed Syntetic waste, National Risk management research Laboratory, USEPA, 2003
7. Dileep Singh, Kartikey Patel - Modified Phosphate Ceramics for Stabilization and Solidification of Salt Mixed Wastes, Energy Technology Division, Aragonne National Laboratory, 1999
8. Arun S. Wagh, Dileep Singh - Chemically Bonded Phosphate Ceramics for Stabilization and Solidification of Mixed Waste, Energy Technology Division, Aragonne National Laboratory
9. COMMISSION REGULATION (EU) No 1357/2014 of 18 December 2014 replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives
10. USEPA OSWER Directive 9437.00-2A, USEPA 1989
11. STAS SR EN 12457-4:2003 Part 4: Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)
12. SR EN ISO 11885/2009 Water quality. Determination of selected elements by optical emission spectroscopy inductively coupled plasma (ICP-OES)
13. Environmental Protection Agency, EPA, Method 1311 – Toxicity Characteristic Leaching Procedure
14. Order 95/2005 – Government of Romania – Ministry of Environment and Water Management – Order for establishing the acceptance criteria and preliminary waste acceptance procedures at storage and the national list of waste accepted in each class of waste deposit
15. Arun S. Wagh, Dileep Singh, Seung Young Jeong – Mercury Stabilization in Chemically Condensed Phosphate Ceramics, Energy Technology Division, Aragonne National Laboratory, 2000
16. Arun S. Wagh - Recent Progress in Chemically Bonded Phosphate Ceramics, ISRN Ceramics, 2013
