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MODELE EXPERIMENTALE DE MATERIALE COMPOZITE, CU CAPACITATE POTENŢIALĂ DE ÎNCAPSULARE A DEŞEURILOR CU NIVEL SCĂZUT DE RADIOACTIVITATE
EXPERIMENTAL MODELS OF GROUT TYPE COMPOSITE MATERIALS, WITH POTENTIAL CAPACITY OF LOW LEVEL RADIOACTIVITY WASTES ENCAPSULATION

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The main objective of this work is to identify, based on experimental physical characteristics investigation, the grout types with potential capacity of residual radionuclides stabilization into storage container of low level radioactivity waste (LLW).

The grouts matrix based on Portland cement or special cement with lead slag addition and various fillers (limestone, L or pulverized fly ash, PFA) were carried out with river fine sand or lead slag recycled fine sand. The Portland cement /PFA or L ratios have had values of 30/70; 50/50 and 70/30, and cement/sand ratio was of 1/1.

There were tested on the physical characteristics – fluidity which assesses the filling ability of the LLW storage container, the density which reflects radionuclide shielding capacity, the shrinkage correlated with the microcracking potential and mechanical strengths evolution required of the long time secure LLW management.

Obiectivul principal al acestei lucrări este de a identifica, pe baza datelor experimentale de investigare a caracteristicilor fizice, tipurile de grout cu capacitate potenţială de stabilizare a radionuclizilor reziduali în containerul de stocare a deşeurilor solide cu nivel redus de radioactivitate (LLW).

Grouturile cu matrice de ciment Portland sau ciment special cu adaos de zgură plumbică, şi diferite filere (calcar, cenuşă zburătoare) s-au realizat cu nisip natural sau cu nisip reciclat (de zgură plumbică). Raportul ciment Portland /cenuşă sau filer de calcar a fost de 30/70; 50/50 şi 70/30, iar raportul ciment/nisip a fost de 1/1. Au fost testate caracteristicile fizice - fluiditatea care evaluează capacitatea de umplere a containerului cu deşeuri solide LLW, densitatea ca măsură a capacităţii de ecranare la radionuclizi, contracţia corelată cu potenţialul de fisurare şi evoluţia rezistenţelor mecanice, cerută pentru gestionarea în siguranţă, pe termen lung, a LLW. Modificările microstructurale şi elementale ale matricei pe bază de ciment cu zgură plumbică au fost investigate prin analiza SEM-EDAX.

Keywords: *grout, special cement, lead slag, pulverised fly ash, encapsulation, low level radioactivity waste*

1. Introduction

The developing of technological and functional performance of advanced composites for encapsulation / immobilization of radioactive waste with cumulated ability of ionizing radiation absorption/shielding is derived from necessity to protect health and the environment in the context of increasing impact nuclear technology in various applications and volume of radioactive waste.

The stabilization-solidification of radioactive waste process principle consists of encapsulate of solid waste, solidify liquid waste (included tritiated water), stabilise contaminated soils, stabilize tank-heel residues after tanks are emptied, and as low permeability barriers [1] Processing and immobilization of radioactive waste includes the operations that change physico-chemical characteristics such as pretreatment, treatment and conditioning. The conditioning may or may not include immobilization. Immobilisation reduces the potential for migration or dispersion of radionuclides. As according to IAEA [1] immobilization is defined as conversion of waste into a waste form by solidification, embedding or encapsulation.

The radioactive wastes are stabilized by converting the radionuclides to a less mobile form as a result of various physico - chemical process as adsorption and chemical reactions, but the waste solidifying improves their mechanical performances. There are required for facilitate of handling, transportation storage and safety disposal of radioactive waste [1 - 3].

The grouts research materials proposed for research are advanced composite materials of functional type because they can provide special functions in the application. In this category are the selfcompacting grouts with LLW encapsulating/ immobilizing capacity.

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The main objective in managing and disposing of radioactive (or other) waste is to protect people and the environment. In July 2011 the European Union adopted a directive for the disposal of used nuclear fuel and radioactive wastes which requires member countries to develop national waste management plans for European Commission review by 2015 [4].

Ionizing radiations include alfa rays, beta rays, protons, neutrons, gamma rays and X rays which cause ionisation when passing through the matter, and is specifically divide into direct ionizing radiation and indirect ionizing radiation. In particular, gamma rays, X-rays or neutrons directly act on atoms or molecules, thus changing the main structure of DNA or proteins. When this type of radiation acts on the generative cell of a living organism, a probability for inducing mutation to thus bring about malformation and malfunction may be increased. The radioactive wastes require a appropriate system for radionuclides immobilizing by solidification/stabilisation into impermeable grout matrix and concrete barrier towards radionuclides diffusion. Also, the the area to which radiation is applied essentially requires a radiation shielding system able to shield gamma rays, X-rays or neutrons harmful for human body and environment [5]. Low level wastes (LLW) contain radioactive materials where activity does not exceed 4 GBq/te of alpha or 12 GBq/te of beta/gamma [6, 7]. Intermediate level wastes (ILW) where radioactivity levels exceed those for LLW, but where heating is not an issue for storage or disposal facilities. The encapsulating/immobilizing into impermeable grouts is a appropriated method recommended and used in LLW and ILW radioactive waste disposal [8 - 10]. The method effective is due to compositional and functional modeling ability to achieve the set performance level. The grout main component is the cement and the high density, inert and pozzolanic or cementitious powder.

The grouts matrices are used as carriers for the radiation shielding composite materials and offer desired engineering and thermal attributes for various radiation management applications [8-11]. Properties of the cement and additives of grouts determine the long term durability of the protective material, the key property of these encapsulation systems. Many research projects are aimed for improving the durability of cement based composites as radioactive waste encapsulation or shielding systems by appropriate modification [11-16].

An upgraded solution for the existing technology of LLW encapsulation is proposed with a new advanced composite materials compatibles ensuring long term radionuclide confination. The main self-compacting grouts (SCG) technical characteristics are high fluidity and segregation stability, capacity to fill the narrowest spaces between comminuted LLW, and very low gas and liquid permeability of hardened state. The functional characteristics are described by the matrix compatibility with the LLW, due to solidification/stabilization (immobilization) capacity, of radionuclide from LLW solid and liquid with long life time.

In this context the paper presents the grout compositional factors influence on the structure and on the physical characteristics, appropriated to radioactive solid wastes encapsulation such as ensure the stability of the solidified wastes into container. The studied main characteristics which determine radionuclide diffusion transfer are:

- Fluidity, filling ability, stability of segregation and bleeding.
- Density.
- Dimensional stability on long term.
- Mechanical strengths evolution.

The obtaining and testing model of grout for LLW encapsulation, developed in this work, is schematic showed in Figure 1.

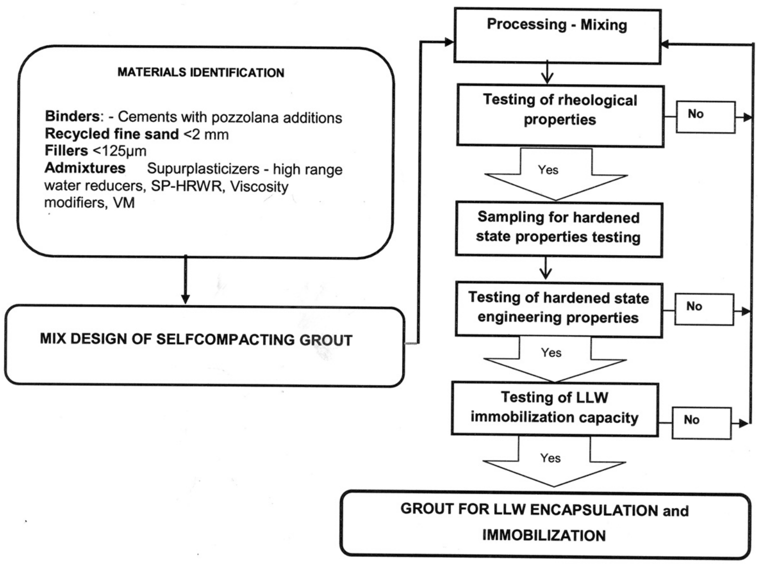


Fig 1 - Model of obtaining and testing of grout for LLW encapsulation/ *Model experimental de obținere şi testare a grouturilor pentru încapsularea deşeurilor cu radioactivitate scăzută*

Table 1

The characteristics of blended cements with lead slag content
Caracteristicile cimenturilor cu adaos de zgură plumbică

Characteristics/*Caracteristica*		ZPb1-2	ZPb1-3
Density/*Densitate*, g/cm^3		3.30	3.35
Blaine specific surface area/*Suprafaţa specifică Blaine*, cm^2/g		4100	4090
/Water for standard consistency/*Apă de consistenţă standard*, %		24.0	24.9
Setting time/*Timp de priză*	Initial/*Inceput*	>8 h	
	Final/*Sfârşit*	< 24 h	
Stability/*Stabilitate*, mm		0.5	4.0
Cement type/*Clasa de rezistenţă*		42.5N	32.5R

Table 2

The chemical composition (average values) of pulverised fly ash /*Compoziţia chimică (valori medii) a cenuşii zburătoare*

Content/*Conţinut*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	PC	S Sulfides/ *Sulfuri*
Pulverised fly ash	52.0	24.7	7.9	8.6	2.3	0.9	0.7	1.4	1.8	0.13
SR EN 450	> 70%			> 5	< 4	< 3	< 1	< 2.4	< 3	-

2. Experimentals

2.1 Materials

The matrix of grouts contains two types of cements: CEM II/A-V 42.5N (provided by Lafarge Romania) and specially blended cements with slag lead addition of 20% (ZPb1-2) and 30% (ZPb1-3), obtained by CEPROCIM. The physical characteristics of cements with lead slag addition are presented in Table 1.

The grouts contain two types of mineral powders: pulverized fly ash (PFA) and limestone filler (L) which partially substitute the cement. The oxidic composition of PFA is given in Table 2.

Limestone filler used in grouts have the following characteristics: % CaO-53.5%, residue on 0.125 mm sieve- 9.8%, density-2700kg/m^3.

The used superplastifiants admixtures (SP) were based on the modified carboxilated polyethers provided by Chryso and noted as SP1, SP2.

Lead primary slags (ZPb) were supplied by former ROMPLUMB S.A. dump. The ZPb was the secondary product of lead obtaining process. There are few areas of primary lead slag recovery as addition into cementitious grout and concrete. There are not identified in our country work of primary lead slag valorization in grouts and concretes, but exist attempts referring to inorganic polymers [17].

The ZPb used in this research were characterized by various content of lead and copper. The ZPb contains 6.6% PbO and 4.6% CuO. The lead primary slag was used as addition in cement and also as substitute of the fine sand in grout mix. The main mineralogical components of lead slags, determined by X-ray diffraction, were marganosite ($Ca_2PbSi_3O_9$), gehlenite ($Ca_2Al[AlSiO_7]$) and quartz (SiO_2). The ZPb was grinded and used as substitute of fine river sand. The characteristics were: density-3850 kg/m^3, bulk density- 1880 kg/m^3 and water absorption-0.4%.

2.2 *Grout mixes*

Blended cement based on the partial replacement of Portland cement by secondary materials is currently used for encapsulation of radioactive waste. Up to 75% PFA is employed in encapsulation grouts, which is much higher values than those used in the construction industry. These percentages are selected to help reduce the heat released during cement hydration and avoid thermal cracking [18, 19].

This principle has been applied to the design of grout mixes based on secondary resources as partial substitutes of Portland cement or of river sand. The design of grout mixes was based on the modelling principle refering to rheological characteristics and compactity required by effective LLW encapsulation. The self compacting grouts are characterised by filling ability of the smalest gapes into containers with stored solid LLW. In this context, were carried out various grout mixes refering to type of components and their weight ratios.

2.2.1. The grout mixes with limestone filler and pulverised fly ash

The grout mixes are showed in the Tables 3-5.

The grout mixes contain cement type CEM II/A-V 42.5N and limestone filler or PFA as partial cement substitutes. The Portland cement /PFA or L ratios have values of 30/70; 50/50 and 70/30. The grout mixes are showed in Table 3.

2.2.2. The grout mixes with lead slag

The grout mixes contain primary lead slag both as blended cement addition and substitute of fine river sand. The lead slag led to the grout density required for a better shielding capacity at ionizing radiation. According with the obtained research results referring to L and PFA mixes were carried out two groups of lead slag grout mixes with powder/ZPb sand ratio of 30/70 and, respectively, of 50/50.

The first group of grout mixes with cement/filler ratio of 70/30, powder/ ZPb sand ratio of 30/70, water/powder ratio of 0.5 and SP1 of 1.6% is presented in Table 4.

Table 3

The grout mixes with limestone filer (L) and pulverised fly ash (PFA) as partial cement substitute
Compoziția grouturilor cu filer de calcar şi cenuşă zburătoare ca substituenți ai cimentului

	Code	CEM II/A-V 42.5N, %	L,%	PFA,%	Water/Cement ratio/ *Raport A/C*	Water/Power weight ratio/ Raport *Apa/Pulberi*	SP1
1	P3V7	30		70	1.67	0.5	1.6
2	P5V5	50		50	1	0.5	1.6
3	PV2	70		30	0.7	0,5	1.6
4	P3C7	30	70		1.67	0.5	1.6
5	P5C5	50	50		1	0.5	1.6
6	PC2	70	30		0.7	0.5	1.6

Table 4

The grout mixes with lead slag as recycled fine sand/ *Compoziția grouturilor cu nisip reciclat de zgură plumbică*

	Code	CEM II/A-V 42.5N, %	L, %	PFA, %	ZPb	
					0-1mm, %	1-2mm, %
1	Reference/*GR referința*	100			10	90
2	GC	70	30		10	90
3	GV	70	0	30	10	90

Table 5

The grout mixes with lead slag as addition to blended cement and lead slag as recycled fine sand
Compoziția grouturilor cu ciment cu adaos de zgură plumbică şi nisip reciclat de zgură plumbică

Code	Powders/*Pulberi*					Sand/*Nisip*				W/C/ *A/C*
	Cement/ *Ciment*			L, %	PFA, %	ZPb		River sand/*Nisip de râu*		
	CEM II/A-V 42.5N, %	ZPb1-2, %	ZPb1-3, %			0/1 mm, %	1/2 mm, %	0/1 mm, %	1/2 mm, %	
GR1	100	-	-	-	-	90	10	-	-	0.5
GC1	70	-	-	30	-	90	10		-	0.71
GV1	70	-	-	-	30	90	10		-	0.71
GRN	100	-	-	-	-	45	-	45	10	0.5
GZ2	-	100	-	-	-	-	-	90	10	0.5
GZ3	-		100	-	-	-	-	90	10	0.5

The second group of grout is characterized by the cement/filler ratio of 70/30, powder/ ZPb sand ratio of 50/50, water/powder ratio of 0.5 and SP1 of 1.6% is presented in Table 5.

2.3 Methods

2.3.1. The cement-superplastifiant compatibility

The cement-superplastifiant compatibility (C-SP) consist of assessment of correlations between paste viscosity decreasing and type and content of SP admixture. The viscosity is influenced by the C3A and alkaline sulfate content in cement and specific surface. The SP is compatible with cement whether leads to fluidity increasing simultaneous with water/cement ratio decreasing. Also, cement-SP compatibility is emphasized by keeping constant paste initial consistency for a long time period. The cement–superplasticizer compatibility can be investigated by measuring realized flow time of grout as according with several researches [20-22]. The cement paste fluidity usually is represented by a curve indicating the flow time C–SP system according to superplasticizer dosage at various times. Saturation superplasticizer dosage corresponding to a break in the curve when superplasticizer is added over the saturation point; it does not improve any more the fluidity of C–SP but only increases the risk of sedimentation and delays the cement setting time.

The C-SP compatibility was carried out as following:

- Establishment of the minim standard consistency water at various SP amounts of the ZPb cement type.
- Measuring of the flow time of the paste by con Marsh method.

Grout mixes as fresh and hardened state were monitored for: fluidity, segregation resistance and bleeding, setting time, dimensional stability and cracking and compressive strength. The grout compressive strength acceptance criterion for secure LLW encapsulation is minim 10 MPa at 28 days. The bending strength testing is need as information about cracking potential. The dimensional stability and the mechanical strengths were tested on 4x4x16 cm samples. All values presented in the paper are the average value of three determinations.

The microstructure of the some hardened grouts was described by SEM method.

3. Results

3.1 The cement-SP compatibility

The results of lead slag cement-SP compatibility are graphically showed in Figure 2. The minimum water amount for standard consistency into range of 17...18% were obtained at the 1.7…1.8% SP content.

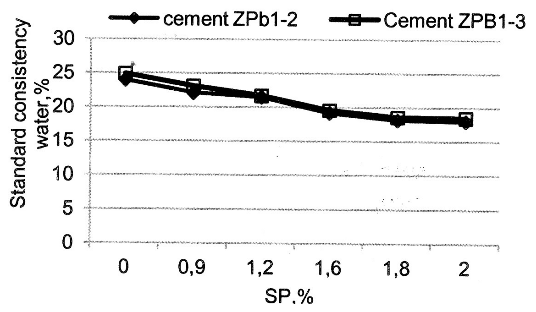


Fig. 2 - The compatibility of the blended cements with lead slag with HRWR superplasticizer/*Compatibilitatea cimenturilor cu adaos de zgură de plumb cu aditivul superplastifiant puternic reducător de apă.*

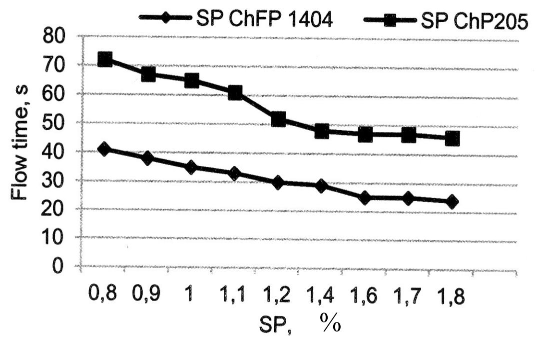


Fig 3 - The variation of flow time versus superplasticizer, tested at water/cement ratio of 0.5/ *Variația fluidității, ca timp de curgere, în funcție de aditivul superplastifiant, la raport A/C=0.5*

The cement type CEM II/A-V 42.5N is characterised by flow time values according to experimental data graphically showed in the Figure 3.

The C-SP compatibility was investigated for two SP types of admixtures appart to carboxilated polyethers class. It is found the minimum flow time values are different depending on SP type at the same saturation concentration of 1.6...1.8% range values. Thus, the SP1 is more efficient than SP2., because the flow time was of 25 s and, respectively, 48 s at the same saturation concentration of the 1.6% .

3.2 The characteristics of the fresh grouts

The compositional influences factors were verified by testing of engineering self compacting grouts. These characteristics are controlled by the mix parameters such as powder types and cement/addition ratios, water/cement (powder) ratio, cement/sand ratio and SP admixture. The characteristics of different mix design grouts are briefly presented in Table 6.

The fluidity of grouts measured as flow time through Marsh funnel (aperture diameter of 10 mm) varied with grout mix design namely type of cement, filler (limestone or pulverized fly ash) and sand (river sand or recycled lead slag).

The PFA influences the fluidity in the compositional context meaning the powder type. Thus, the PFA increase the flow time (viscosity) in cement-PFA system in comparison with cement-limestone filler system. The increasing of filler content modified grout viscosity. Increasing the content of PFA from 30% to 50% and, respectively, 70% in cement-PFA system leads to significant increasing of grout flow time from 70 to 500 seconds, although the water/cement ratio was from 0.7 to 1.67. The grout P5V5 is distinguished by higher resistance of segregation and bleeding than the others. The high content PFA grouts maintain initially consistency a longer time than those with lower content of PFA.

Different behavior was observed at cement-limestone filler couple; increased of limestone content insignificantly decreased the flow time (from 18 to 8 seconds) at the same values of W/C ratio with cement-PFA couple.

The obtained results showed that the fluidity of the grout decreases with the introduction of the fillers, this reduction is proportional to their replacement level and type, according to data obtained by other authors [20- 22].

The experimental grout fluidity values as flow times were significantly influenced by the content and fineness of lead slag. The recycled lead slag as fine sand in grout mix leads to increasing of the fluidity. Thus, the increasing of lead slag fine sand from 50 to 70 % resulted in constantly decreasing of flow time. The obtained values were influenced by the other factors namely filler type (limestone or PFA) and water/cement ratio. The results are showed in Table 7.

The data referring to grout mixes of powder/ZPb recycled sand ratio of 30/70 lead to the following:

- The cement-limestone couple had the fluidity very good (flow time of 8 seconds) appropriated to encapsulate by confining of the solid LLW.

Table 6

The characteristics of the fresh grouts with limestone filler and fly ash
Caracteristicile grouturilor cu filer de calcar şi cenuşă zburatoare, în stare proaspătă

	Code	Cement/PFA ratio Cement/L ratio *Raport ciment/cenuşă* *Ciment/filer calcar*	Flow time/*Timp de curgere*, s	Unit weight/*Masa volumică*, kg/m^3
1	P3V7	30/70	500	1309
2	P5V5	50/50	100	1601
3	PV2	70/30	70	1730
4	P3C7	30/70	8	1718
5	P5C5	50/50	8	1700
6	PC2	70/30	18	1865

Table 7

The characteristics of the fresh grouts with lead slag content
Caracteristicile în stare proaspătă ale grouturilor cu zgură plumbică

Description /*Descriere*	Flow time/*Timp de curgere*, s	Unit weight/*Masa volumică*, kg/m^3
Powders/lead slag weight ratio = 30:70 / *Raport pulberi/zgură plumbică = 30:70*		
GR	36	2576
GC	43	2584
GV	No flow / *Nu curge*	2380
Powders/lead slag weight ratio = 50:50 / *Raport pulberi/zgură plumbică = 50:50*		
GR1	124	2447
GC1	86	2441
GV1	61	2093
GRN	26	2159
Grouts with lead slag addition blended cement; cement/sand ratio = 50:50 *Grouturi pe bază de ciment cu zgură plumbică; raport ciment/nisip = 50:50*		
GZ2	43	2229
GZ3	45	2275

- The recycled sand of lead slag has an unfavorable influence on the segregation resistance of the grout mix.
- The great difference between density of cement-filler (limestone, pulverized fly ash) and lead slag is an obvious cause of fresh grout segregation.
- The lead slag has contributed to relevant grout density increase, from 2380 to 2576 kg/m^3, as a beneficial factor for radionuclide diffusion barrier function.

The data referring to grout mixes of powder/ZPb recycled sand ratio of 50/50 lead to the following:

- The decreasing of powder/ZPb result in increase of flow time (viscosity).
- The PFA has had a beneficial role on the fresh grout mobility at cement/PFA ratio of 70/30 and the same water/powder ratio, and SP type and content.
- The partial substitution of the ZPb slag recycled sand with river sand of the same particle size lead to diminishing of the segregation and to decreasing of the flow time from 61 to 26 seconds.

3.3 The characteristics of the hardened grouts

The apparent density reflects the grout mix components. The apparent density values of grouts with PFA were into range from 1200 to 1420 kg/m^3, while those with limestone filler have a density from 1500 to 1600 kg/m^3. The density values of grouts with lead slag recycled as fine sand were of 2200…2412 kg/m^{3}closer to the heavy concrete. Considering that these grouts with recycled lead slag as fine sand correspond in terms of segregation stability, they constitute an appropriate compositional model, with notable potential for encapsulation / immobilize both physically by high impermeability and chemically by Pb content.

The compresssive strength and bending strengths were tested. The obtained results are graphically showed in Figures 4-6.

The mechanical strength decreased significantly with increasing water / powder regardless of the type of powder.

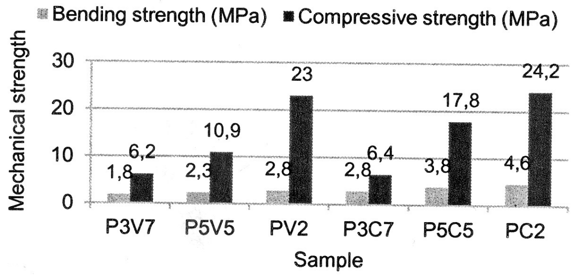


Fig. 4 - The influence of filler (PFA or limestone) on the 28-days- mechanical strengths/*Influența filerului (calcar sau cenuşă zburătoare) asupra rezistențelor mecanice la 28 zile.*

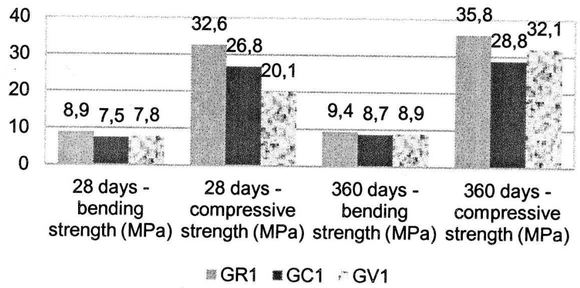


Fig. 5 - The mechanical strengths evolution of the grouts with the cement/filler ratio of 70/30, powder/ lead slag recycled sand ratio of 50/50, and water/powder ratio of 0.5/ *Evoluția rezistențelor mecanice ale grouturilor cu raport ciment/filer=70/30, raport pulberi/nisip reciclat de zgură plumbică = 50/50 şi raport apă/ciment = 0,5*

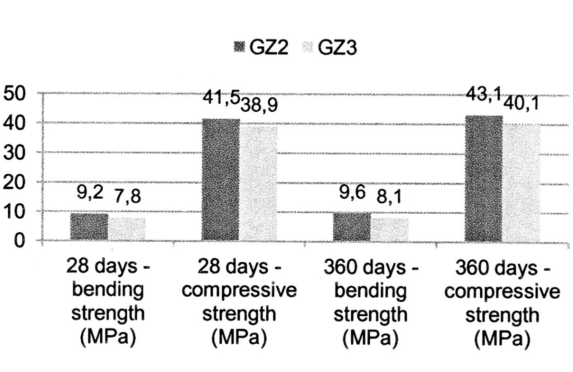


Fig. 6 - The mechanical strengths evolution of the grouts based on cement with lead slag addition/*Evoluția rezistențelor mecanice ale grouturilor cu ciment cu adaos de zgură de plumb.*

The data of figure 4 show that increasing the amount of filler (PFA or L) has led to a considerable decrease of the mechanical strengths. The grouts with PFA addition show lower values of mechanical strength than those with limestone filler for the same water/cement ratio. This phenomenon can be attributed to the greater shrinkage of grouts with PFA, according to experimental obtained data.

Figure 5 shows the influence of filler on the compressive and bending strengths of the grouts at different ages.

The lead slag recycled as fine sand had an positive influence on the mechanical strength at powder/ ZPb recycled sand ratio of 50/50. This report can be considered an optimal value as a result of LLW encapsulation grout compositional modeling, to achieve target performances related to segregation stability, flowability and mechanical strength.

The greatest compressive and flexural strength of 32.6 respectively of 8.9 MPa had a GR1 grouts with powder/ ZPb recycled sand ratio of 50/50. The cementitious grout with PFA showed compressive strengths values above 10MPa compressive strength, the minimum level required for LLW waste encapsulation.

Figure 6 shows the mechanical strengths time evolution for the grouts based on cement with 20% and 30% ZPb slag addition.

The mechanical strength of grout based on cement with lead slag addition had a positive evolution up to 360 days. Increasing the amount of slag from 20 to 30% has led to a decrease in the mechanical strengths.

3.4 The shrinkage

The shrinkage of grouts varied depending on the filler type, at the same cement/filer ratio of 70/30, the same W/C ratio, but with different SP admixtures. Some obtained results are presented graphically in Figure 7. The shrinkage increased continuously over time, up to 1 mm/m for PFA based grout ash and up to 0.72 mm/m for limestone filler based grouts.

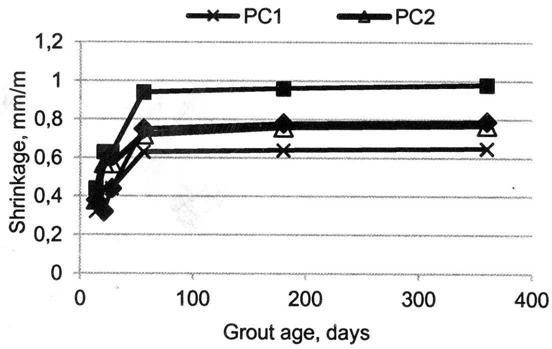


Fig. 7 - The grouts shirinkage evolution depending on the filer type and SP admixture/*Evoluția în timp a contracției, în funcție de tipul de filer şi aditiv superplastifiant.*

It is found that SP admixture influences shrinkage evolution as a consequence of the viscosity modifier role. So, the SP1 admixture had a smaller contribution to increase fluidity, but favored segregation resistance and bleeding diminishing with beneficial role on the shrinkage and cracking potential decrease.

3.5. Microstructure

The Figures 8 and 9 represent SEM images of GZ2 and GZ3 grout samples.

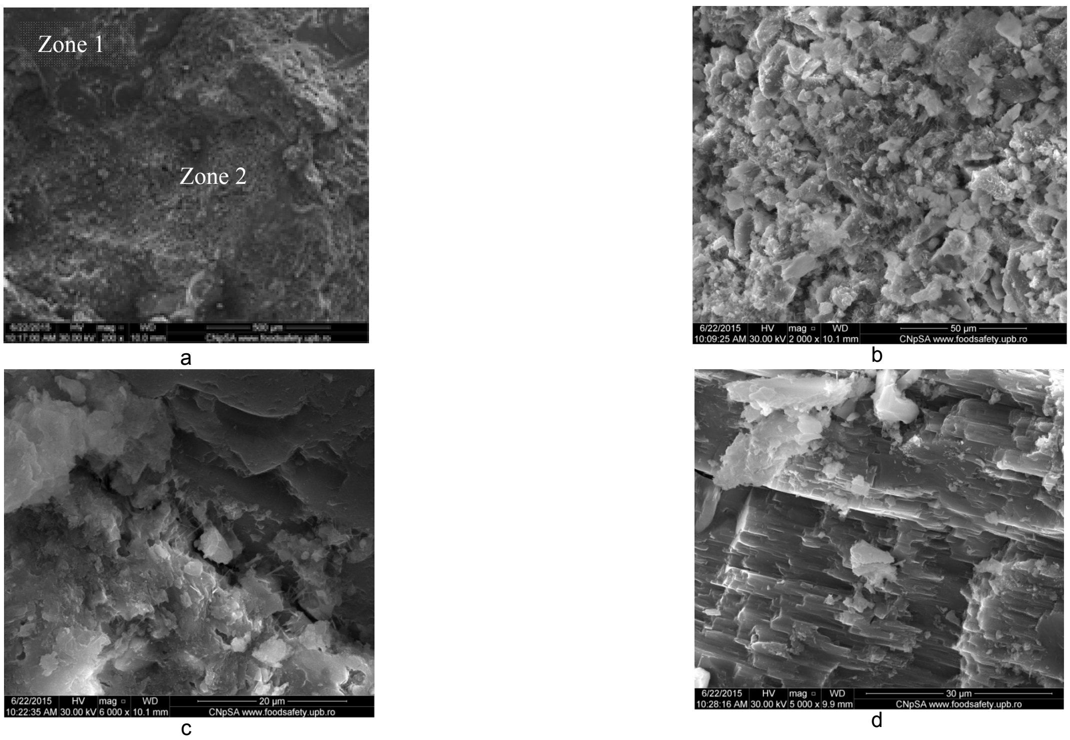


Fig. 8 - SEM images of GZ2 sample/*Imagini electronomicroscopice ale probei GZ2.*

SEM images of GZ2 grout show two types of crystals:

- Original crystalline phases from primary lead slag used as addition to cement (fig. 8d);
- New phases formed by hydrolyse of clinker.

The zone 1 represent siliceous aggregate (river sand) while zone 2 shows the cement matrix. The main hydrates present in the cement matrix are small crystallized calcium silicate hydrates (CSH) and needle like crystallized ettringite (Fig. 8c). The zone 3 contains feldspars, according to elemental analysis, which are components of lead slag.

The SEM images of GZ3 grout (Fig. 9), show a weaker microcrystalline aspect of cement matrix in comparison with sample GZ2 that contains a lower content of lead slag (as addition to cement)-Fig. 9a, d. This difference could be a consequence of a lower rate of hydration. The zone 1 shows unreacted lead slag from cement matrix. The matrix maintains its morphology of lead slag components. On the surface of lead slag seems to grow some ettringite crystals. The silicate hydrates are also present.

4. Conclusions

The paper presents experimental data referring to cementitious grouts with waste materials as substitutesof of both the Portland cement and fine river sand [8,9, 13, 15]. The grout solid components were powders - Portland cement or cement with lead slag addition, pulverized fly ash, limestone filler, river sand and recycled fine sand of lead slag. The modeling of compositional factors was focused on achieving of functional performance of grouts, required by LLW encapsulation proces.

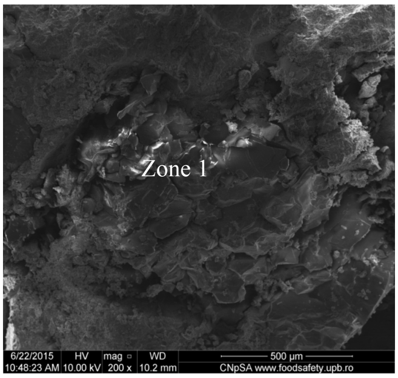
The compositional factors considered were the water / cement (or powder) ratios from 0.5 to 1.83; cement / filler ratios of (70/30; 50/50 30/70); powders / slag lead ratio (30/70 and 50/50) and two superplasticizers types.

The increasing of filler content modified grout viscosity. The PFA increase the flow time (viscosity) in cement-PFA system in comparison with cement-limestone filler system Increasing the content of PFA from 30% to 50% and, respectively, 70% in cement-PFA system leads to significant increasing of grout flow time. The obtained results showed that the fluidity of the grout decreases with the introduction of the fillers proportionally to their replacement level and type, according to data obtained by other authors [21- 22].

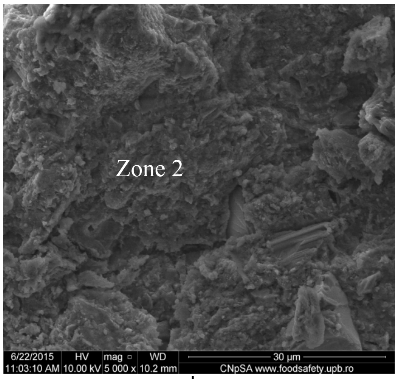
The lead slag has contributed to relevant grout density increase, from 2380 to 2576 $kg/m^{3,}$ as a beneficial factor for radionuclide diffusion barrier function.

The partial substitution of the ZPb slag recycled sand with river sand of the same particle size lead to diminishing of the segregation and to decreasing of the flow time from 61 to 26 seconds.

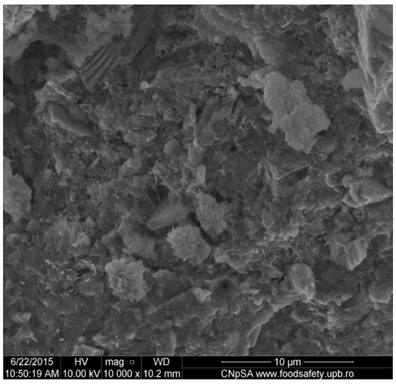
The greatest compressive and flexural strength of 32.6 respectively of 8.9 MPa have had the grouts with powder/ ZPb recycled sand ratio of 50/50.



a



b



c

Fig. 9 - SEM images of GZ3 sample/ *Imagini electronomicroscopice ale probei GZ3.*

The SEM images of grout with blended cement with lead slag show various types of crystals as following: initial crystalline phases of lead slag, as addition to cement; new phases formed by hydrolyses of clinker. The grout with 30% ZPb addition in cement showed a weaker microcrystalline structure than the grout with 20% ZPb addition in cement.

The grout mixes GC1, GV1, GZ2 SI GZ3 may be used in LLW encapsulation process according to obtained experimental data referring to flow time, shrinkage and mechanical strengths. Also, the content of the recycled materials (PFA, lead slag) was taken into account. These grout mixes are going to test on the encapsulation ability by specifically leaching test of the interested radionuclide at IFIN-HH.

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REFERENCES

1. International Atomic Energy Agency, Radioactive Waste Management Glossary, Vienna, 2003 Edition
2. M.I. Ojovan and W.E. Lee, Introduction to Nuclear Waste Immobilisation, 2nd edition, Imprint Elsevier, 2014
3. R. Rakhimov, N. R. Rakhimova and M. I. Ojovan, Cementitious Materials for Nuclear Waste Immobilisation, Editor John Wiley & Sons, 2014
4. http://www.world-nuclear.org/info - Radioactive-Waste-Management April 2012. Department of Energy and Climate Change (DECC) and the Nuclear Decommissioning Authority (NDA), Radioactive Wastes in the UK: A Summary of the 2010 Inventory
5. J. Kim, Y. Uhm, B. Lee, J. Jung, C. Kyu Ree, M. Lee and S. Lee, Radiaton shielding members including nanoparticles as a radiation shielding material and method for preparing the same. U S Patent, no 8 318 045. B2, 2012, Nov**. 27**.
6. F. Berkhout, Radioactive Waste: Politics and Technology. The Natural Environment: Problems and management, Edited by Routledge, 2003.
7. C. Bayliss and K. Langley, Nuclear Decommissioning, Waste Management, and Environmental Site Remediation, Edited by Butterworth-Heinemann, 2003.
8. http://www.rsc.org/ N. Milestone, Immobilisation Science Laboratory Department of Engineering Materials University of Sheffield, Nuclear Waste Immobilisation – Cementation
9. A. Sugaya, K. Tanaka and S. Akutsu, Cement Based Encapsulation Experiments for Low-Radioactive Liquid Waste at Tokai Reprocessing Plant, Waste Management Conference, February 27-March 3, 2011, Phoenix.
10. K. Akkurt, C. Günoglu, C. Basisgit and A. Akka, Cement Paste as a Radiation Shielding Material Acta Physica Polonica, 2013, **2**(123), 341.
11. I. Teoreanu, N. Deneanu and M. Dulamă, Matrix materials for the conditioning organic radioactive wastes, Romanian Journal of Materials 2010, **40**(2), 112.
12. E.H. Ahrens, M. Onofrei and M.B. Pinawa, Ultrafine cement grout for sealing underground nuclear waste repositories, Processing of Conference: 2. North American rock mechanics symposium: tools and techniques in rock mechanics, 19-21 Jun 1996, Montreal.
13. A. Lowinska-Kluge and P. Piszora, Effect of Gamma Irradiation on Cement Composites Observed with XRD and SEM Methods in the Range of Radiation Dose, Acta Physica Polonica, 2010, **2(**114), 399.
14. Y. Lv and Y. Gao, Protective concrete for weakening the intensity of proton radiation. US Patent No 7819970 B2, oct. 26, 2010.
15. S. Dasharatham, Composite materials and techniques for neutron and gamma radiation shielding, US7250119 B2, Jul. 31, 2007.
16. S. Finsterle, M. Conrad, M. Kennedy, T. Kneafsey, K. Pruess, R. Salve, G. Su, and Q. Zhou, Mobility of Tritium in Engineered and Earth Materials at the NuMI Facility, Fermilab, Progress Report, Lawrence Berkeley National Laboratory , March 2007.
17. S. Onisei, Y. Pontikes, T. Van Gerven, G.N. Angelopoulos, T. Velea, V. Predica and P. Moldovan, Synthesis of inorganic polymers using fly ash and primary lead slag, Journal of Hazardous Materials, 2012, **205–206**, 101.
18. P. H. R. Borges, J. O. Costa, N. B. Milestone, C.J. Lyndsdale and R. E. Streatfield, Carbonation of CH and C-S-H in composite cement pastes containing high amounts of BFS. Cement and Concrete Research, 2010, **40**, 284.
19. J. Sun, Carbonation Kinetics of Cementitious Materials Used in the Geological Disposal of Radioactive Waste, Thesis submitted for the degree of Doctor of Philosophy of the University of London Department of Chemical Engineering University, 2010.
20. L. Ferrari, P. Boustingorry, A. Pineaud and L. Bonafous, From cement grout to concrete scale: a study of superplasticizer-design-controlled thixotropy to match SCC Application requirements 7th RILEM International Conference on Self-Compacting Concrete and 1st RILEM International Conference on Rheology and Processing of Construction Materials, Paris, 2013, 285. http://www.researchgate.net/publication/
21. P. C. Aitcin, C. Jolicoeur and J.G. MacGregor, Superplasticizers – how do they work and why they occasionally don't, Concrete International, 1994, **16**(5), 45.
22. A. Hallal, E. H. Kadri, K. Ezziane, A. Kadri and H. Khelafi, Combined effect of mineral admixtures with superplasticizers on the fluidity of the blended cement paste, Construction and Building Materials 2010, **24** (8), 1418.

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