UTILIZAREA UNOR DEŞEURI DE TITAN CA SUBSTITUENT AL AGREGATULUI FOLOSIT PENTRU PRODUCEREA MORTARELOR DE CIMENT PORTLAND

USE OF WASTES FROM TITANIUM INDUSTRY AS ALTERNATIVE AGGREGATE FOR PORTLAND CEMENT MORTARS

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This paper presents some physical and mechanical properties of Portland cement mortars prepared with two types of waste as alternative aggregates. These wastes result during the mechanical processing of titanium alloy ingots by shot blasting with steel beads (DS) or by surface abrasion/polishing process with abrasive discs (DSIC).

The total replacement of natural aggregate (sand) with DSIC waste determines an increase of flexural and compressive strengths (with respect to the mortar prepared with sand) most probably due to its high content in Ti (metal and oxide).

The partial replacement of sand or DSIC with DS waste determines a decrease of flexural and compressive strengths both at early ages (3 days) and longer hardening times (28 days).

În lucrare se prezintă o serie de proprietăţi fizice şi mecanice ale unor mortare pe bază de ciment portland în care agregatul (nisip cuarţos) a fost înlocuit cu două tipuri de deşeuri. Aceste deşeuri provin din procesul de prelucrare a lingourilor de aliaje de titan, prin sablare cu alice de oțel (DS) sau prin abraziune/polizare (DSIC).

Înlocuirea totală a nisipului cu deşeul DSIC în mortare, a determinat o creştere a valorilor rezistenţei la încovoiere şi compresiune în comparaţie cu cele înregistrate pentru mortarul preparat cu agregat convenţional (nisip). Acest lucru se poate datora conţinutului mare de titan (metalic sau sub formă de oxid), specific pentru acest tip de deşeu.

Înlocuirea parțială a agregatului natural (nisip cuarţos) sau a celui neconvenţional - deşeu DSIC, cu deşeul DS a determinat o scădere a rezistenţelor la încovoiere şi compresiune ale probelor de mortar, atât la perioade scurte de întărire (3 zile), cât şi la perioade mai îndelungate de timp (28 zile).

Keywords: *Waste, Ti processing, alternative aggregate, Portland cement, mortar.*

1. Introduction

Titanium is one of the most used metals due to its light weight and high resistance to corrosion. The main application domains for this metal are in aerospace industry as well as automotive and ocean engineering [1, 2]. Numerous other applications are connected with medical field i.e. orthopedic titanium rods, pins and plates, surgical instruments, dental implants, and so on. Other applications of Ti metal or alloys include chemical industry, electrical power plants, IT equipments as well as sporting or customer products [2].

Numerous titanium alloys were also developed including vanadium, aluminium, zirconium, molybdenum etc., in order to improve/enhance various properties i.e. strength, ductility, biocompatibility etc.

Metallic titanium is produced in several steps. The raw materials are natural minerals containing TiO_2 (rutile/ilmenite). The first step is the production of titanium sponge by applying the Kroll process, which consists in the chlorination of rutile/ilemnite in order to obtain titanium tetrachloride ($TiCl_4$).This product is reduced by magnesium or sodium at high temperature (800–850°C) and the resulted porous metallic Ti is called titanium sponge.

The next step consists in the processing of Ti sponge in order to obtain alloys, ingots or forged products [1-3].

In order to obtain Ti ingots, the titanium sponge is pressed to obtain electrodes. The electrodes are melted. After the melting, the ingots are mechanically conditioned by plasma welding. The process is followed by a second/third melting and after that the ingot is mechanically finished (cutting, shaping, sanding, shot blasting etc.) [3].

Two types of waste result during the mechanical processing of forged products: DSIC – waste resulted in the surface abrasion/polishing process with abrasive discs; DS- waste resulted in the shot blasting process usually performed with

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steel beads. These wastes are not recyclable in the above mentioned industrial process.

Portland cement and derived composites (mortar, concrete) are frequently used to immobilize various types of waste i.e. contaminated soils, hazardous waste with organic and inorganic contaminants, construction and demolition waste, industrial waste etc. [4-12].

Therefore, the aims of this study were to characterize these two types of waste (DS and DSIC) and to assess the possibility to valorize them in the production of construction materials i.e. Portland cement mortars.

2. Materials and methods

The chemical compositions of DS and DSIC wastes were assessed by inductively coupled plasma optical emission spectrometry (ICP-OES). In order to obtain the solution to be analyzed by ICP-OES, 1 g of waste was treated with a mixture of nitric and hydrochloric acids and then heated on a sand bath. The solution was boiled for 30 minutes, then cooled at room temperature and filtrated. This solution is denominated solution 1. The residue collected on the filter paper was calcined in a platinum crucible. Borax and sodium carbonate were added over the ash and the mixture is melted in an oven at 1200°C for 20 minutes. The melt was cooled and then solubilized with hydrochloric acid. The solution is diluted with bi-distilled water up to 100 ml. The filtrate obtained by successive washings on filtration paper with bi-distilled water was diluted up to 200 ml - this solution was denominated solution 2. Solution 1 was diluted for 10 to 125 times and solution 2 was diluted for 5 up to 50 times. These solutions were analyzed by ICP-OES, with an Optical Emission Spectrometer Agilent 700. This device have a wavelength coverage from 167 to 785 nm and 70 elements can be determinated, with low limits of detection (traces).

The mineralogical composition of the wastes was assessed by X ray diffraction with a Shimadzu XRD 6000 diffractometer. The XRD spectra were obtained using a monochromatic CuKα radiation (λ= 1.5406 Å), range 2θ from 10 to 60 degree.

The microstructure of wastes was assessed with a FEI Inspect F50 High Resolution Scanning Electron Microscopes (SEM) coupled with energy dispersive X ray spectroscopy (EDX). The SEM analyses were performed in fracture of specimens (without metal coating).

DS and DSIC wastes replaced various fractions in the composition of standard aggregate (sand - SR EN 196-1, 2006 [13]) used for Portland cement mortar preparation – see Table 1. The mortar specimens were prepared with a cement to aggregate ratio of 1/3 and water to cement ratio of 0.5.

The mortar specimens were prepared in accordance with the SR EN 196-1 norm; the fresh mortar was cast in rectangular molds (40x40x160mm) and vibrated for 2 minutes. The specimens were cured in the mold (covered with cling film) at room temperature the first 24 hours, then de-molded and immersed in water (20±2 ºC) up to 28 days.

The following characteristics were assessed on mortar specimens cured 3 or 28 days: apparent density, compressive and flexural strengths.

The density of sand, DS and DSIC wastes was assessed with a helium pycnometer-Pycnomatic ATC.

3. Results and discussions

3.1. Characterization of DS and DSIC wastes

The DS and DSIC wastes are granular materials. As it can be seen in Figure 1, DS waste is more homogenous and contains smaller grains opposite to DSIC waste which contains a high amount of coarse grains. This is connected with the mechanical processing in which these two wastes result: DS - results by the shot blasting (with steel beads) of titanium ingots and DSIC results during the surface abrasion/polishing process with abrasive discs of Ti ingots.

The density, assessed with a helium-pycnometer is 6928 kg/m^3 for DS waste and 4217 kg/m^3 for DSIC waste. Both wastes have higher densities as compared with quartz sand i.e. 2070 kg/m^3.

The chemical composition of DS waste (filtrate and melt) assessed by ICP-OES is presented in Table 2. One can notice the high amount of iron (86.56%) – determined by the presence of steel beads remains. The Ti content is 8.23% and is higher in the melt as compared with filtrate solution.

Due to the wide grain size distribution of DSIC waste this material was first separated by sieving in three fractions: DSIC$_f$ – fraction below 400 microns, DSIC$_m$ – fraction with grain size in the range 400 microns and 2 mm and DSIC$_g$-fraction with grains bigger than 2 mm. The amount

Table 1

Composition of aggregates (g) used for Portland cement mortars preparation

Compoziţia agregatelor (g) folosite pentru prepararea mortarelor de ciment Portland

Specimen	Fr<0.15mm (g)			Fr.0.15-0.5mm (g)			Fr. 0.5-1mm (g)			Fr. 1-2mm (g)		
	Sand	DSIC	DS	Sand	DSIC	DS	Sand	DSIC	DS	Sand	DSIC	DS
N	150	-	-	300	-	-	450	-	-	450	-	-
DSIC	-	150	-	-	300	-	-	450	-	-	450	-
N-DS	-	-	150	-	-	300	-	-	450	450	-	-
DSIC-DS	-	-	150	-	-	300	-	450	-	-	450	-

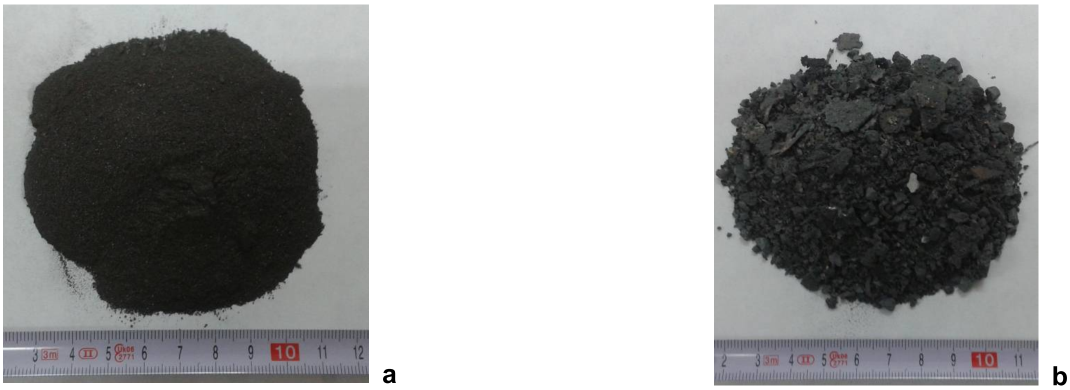


Fig.1 - Visual aspects of wastes: DS (a) and DSIC (b)/ *Aspectul vizual ale celor două deşeuri: DS (a) şi DSIC (b).*

Table 2

Chemical composition of DS waste /*Compoziţia chimică a deşeului DS*

Element (%)	Filtrate	Melt	Total
Al	0.49	0.64	1.13
Cr	0.31	-	0.31
Cu	0.26	-	0.26
Fe	86.26	0.3	86.56
Mn	0.005	-	0.005
Mo	0.005	-	0.005
Ni	0.12	-	0.12
Si	0.24	0.36	0.6
Ti	2.38	5.85	8.23
V	0.1	0.17	0.27
Zn	0.005	-	0.005
C*	0.9		
Total (%)	98.39		

*) C was determined with an automatic gas –analyzer

Table 3

Chemical composition of DSIC waste / *Compoziţia chimică a deşeului DSIC*

Element (%)	$DSIC_f$			$DSIC_m$			$DSIC_g$			DSIC average
	Filtrate	Melt	Total	Filtrate	Melt	Total	Filtrate	Melt	Total	
Al	1.38	6.48	7.86	0.57	15.3	15.87	0.38	11.6	11.98	12.817
Cd	0.005	0	0.005	0.005	0	0.005	0.005	0	0.005	0.005
Cr	0.012	0	0.012	0	0	0	0	0	0	0.003
Fe	2.5	0.14	2.64	1.42	0.39	1.81	0.13	0.8	0.93	1.7799
Mn	0.055	0	0.055	0.032	0	0.032	0.008	0	0.008	0.0313
Ni	0.006	0	0.006	0.005	0	0.005	0.005	0	0.005	0.0053
Pb	0.005	0	0.005	0.005	0	0.005	0.005	0	0.005	0.005
Si	0.18	1.19	1.37	0.085	0.93	1.015	0.039	1.24	1.279	1.175
Ti	17.82	42.12	59.94	29.4	5.6	35	2.22	45.1	47.32	44.561
V	0.94	1.21	2.15	0.33	1.02	1.35	0.22	0.8	1.02	1.4609
Zn	0.012	0.012	0.024	0	0	0	0	0	0	0.006
C	1.6			1.15			0.6			1.114
Total (%)										62.964*

*) The difference up to 100% is due to the oxygen or/and nitrides

of each fraction was: $DSIC_f$ - 25%, $DSIC_m$ - 48%, $DSIC_g$ - 27%. The chemical composition of these three fractions, assessed by ICP-OES is presented in Table 3.

As it can be seen in the Table 3, DSIC waste has a high amount of titanium (44.561%) and this element is distributed in all three grain size fractions. Also the Al content in this waste is important – 12.817%.

The mineralogical composition of DS and DSIC wastes was assessed by XRD – Figures 2 and 3.

As it can be seen in Figure 2, the main phases assessed by XRD in DS waste are iron carbide (Fe_3C) - compound present in steel beads, metallic titanium and titanium oxide – resulted due to the superficial oxidation of Ti ingot.

The main compounds assessed by XRD in DSIC waste (Fig.3) are metallic Ti, titanium oxides (TiO and TiO_2); Al is also present in this waste (see Table 2) as Al_2O_3 and $AlTiO_5$.

The microstructure of DS and DSIC wastes was assessed by scanning electron microscopy (SEM) and the elemental composition of phases was analyzed by EDX (Figs. 4, 5 and 6).

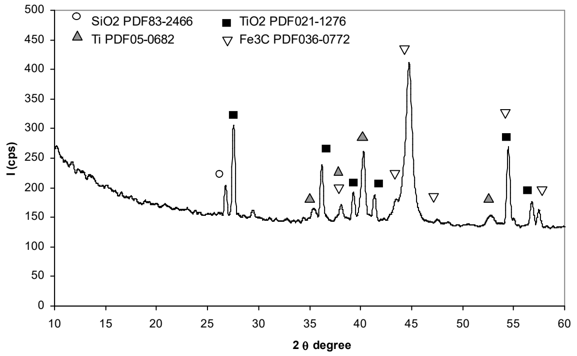


Fig.2 - XRD spectra of DS waste/ *Spectrul de difracţie de raze X al deşeului DS.*

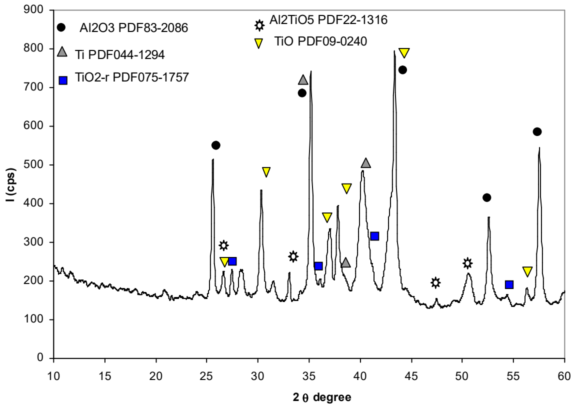
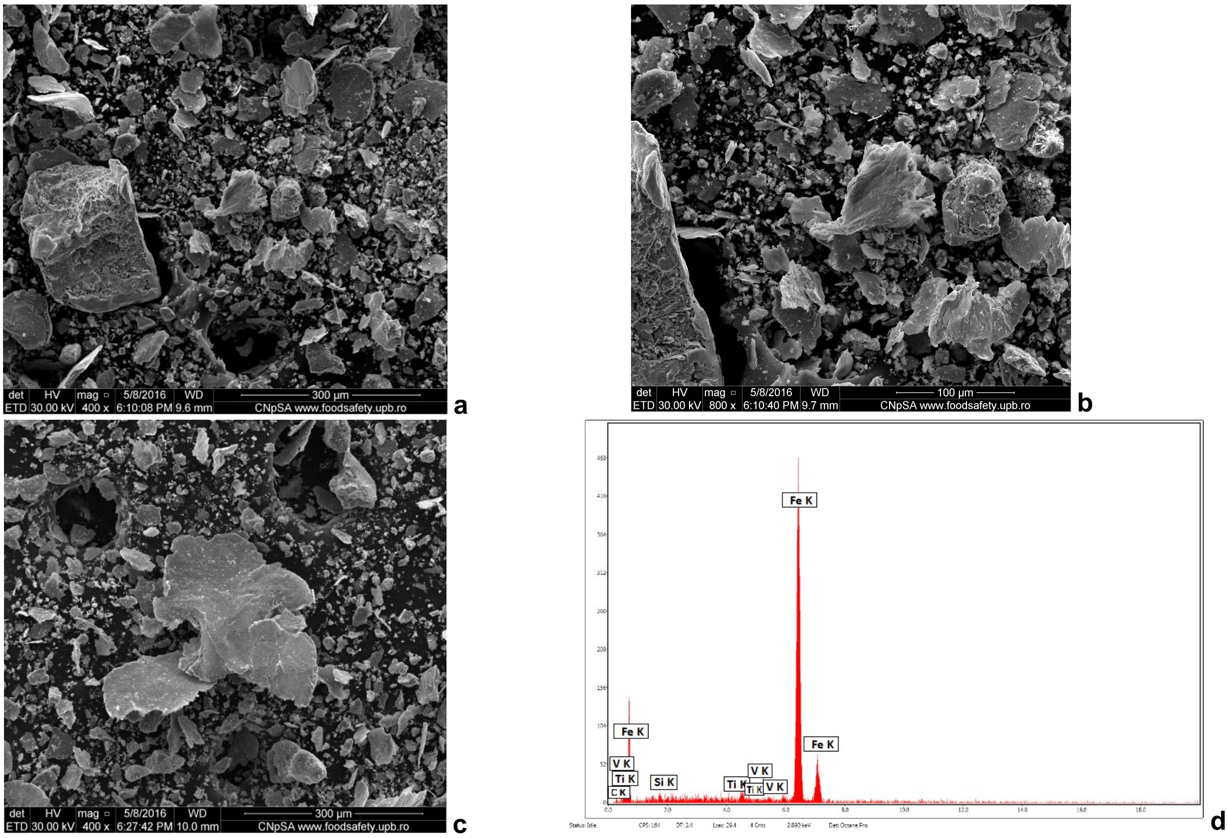


Fig.3 - XRD spectra of DSIC waste/ *Spectrul de difracţie de raze X al deşeului DSIC.*

Fig. 4 continues on next page



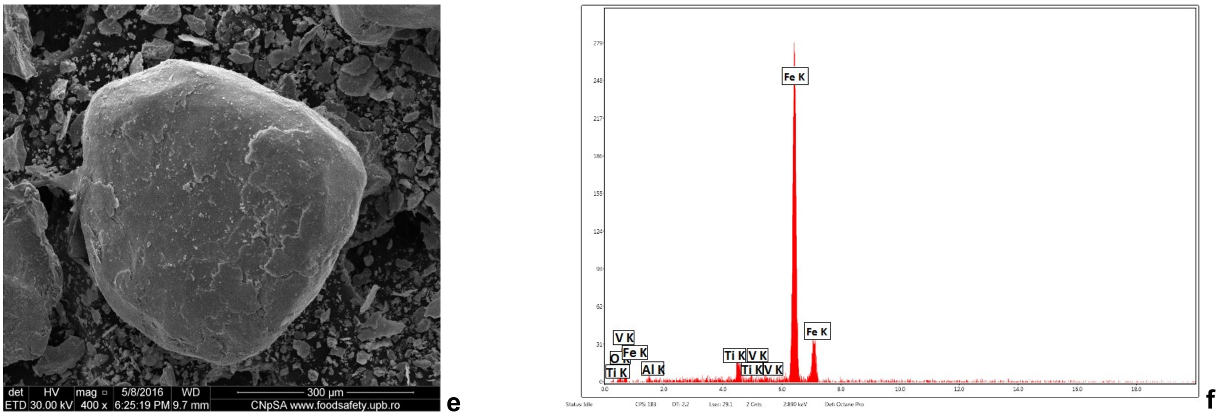


Fig.4 - SEM micrograph (a,b,c,e) and corresponding EDX spectra (d and f) of DS waste/ *Microfotografii SEM (a,b,c,e) și spectrele EDX corespunzătoare (d și f) ale deșeului DS.*

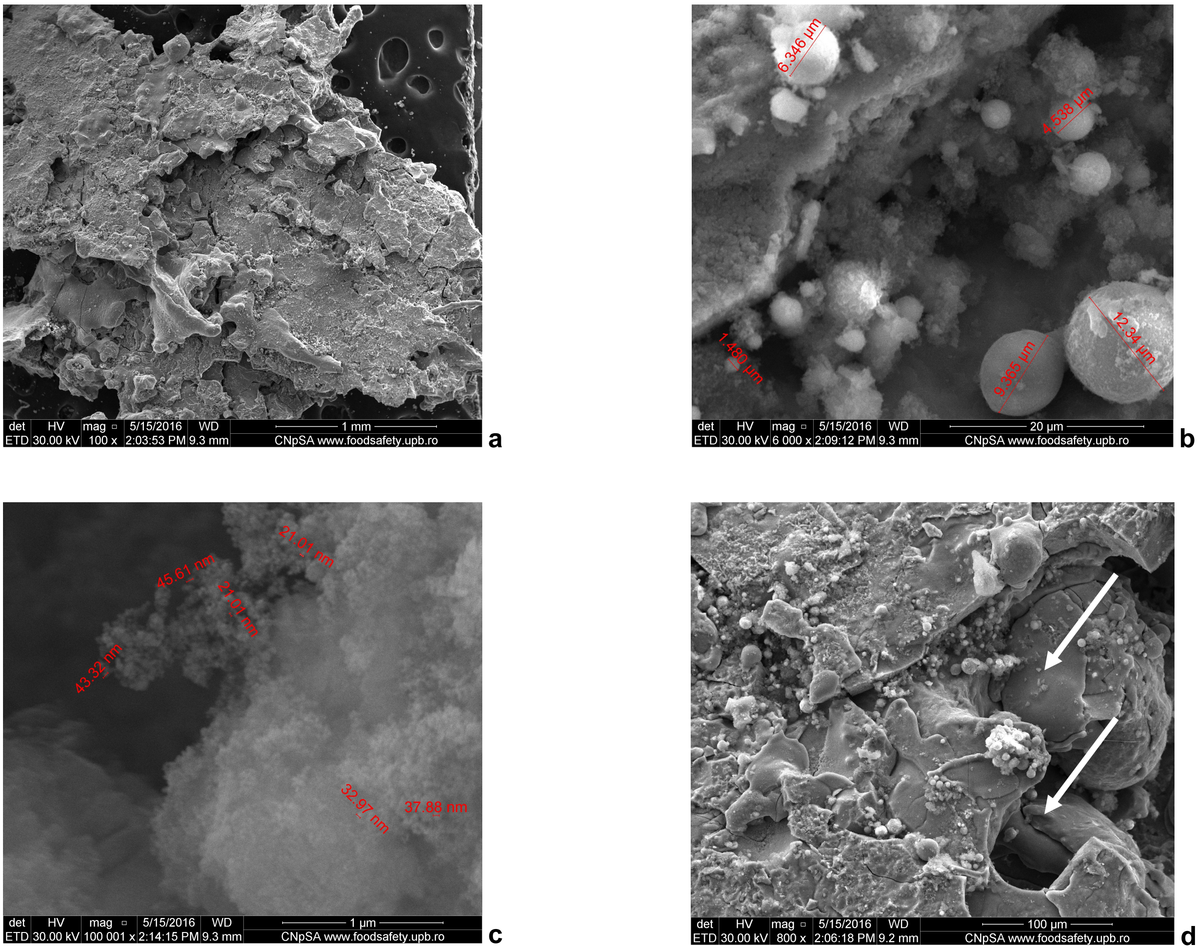


Fig.5 - SEM micrographs of DSIC waste/ *Microfotografii SEM ale deşeului DSIC.*

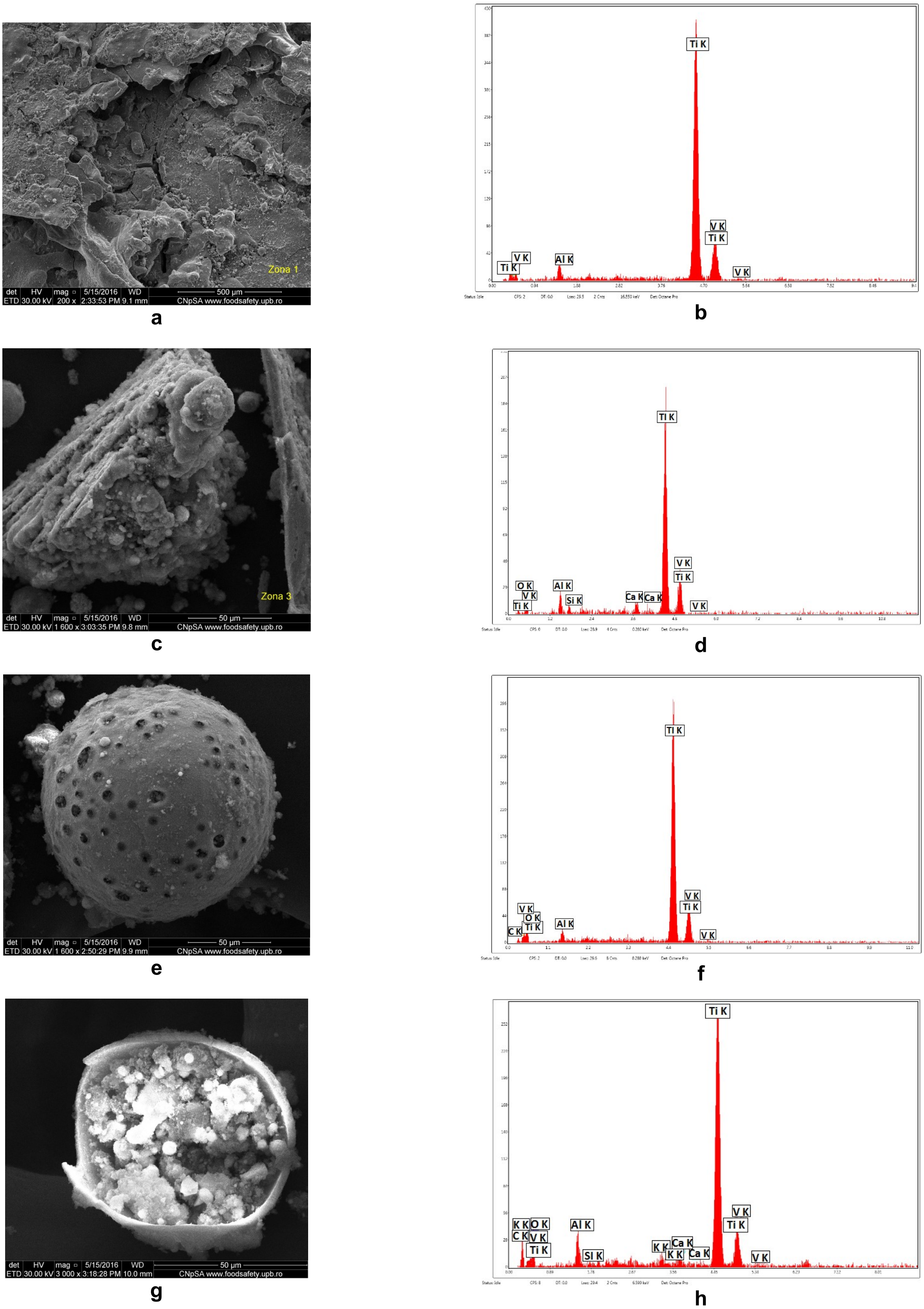
As it can be seen in Figure 4, DS waste consists of grains with various forms (plates, polyhedral and irregular shapes) and sizes (from 5 µm up to 400 µm). The EDX spectra (Figs. d and f) show the presence of iron (in high quantity) along with small quantities of titanium, aluminium and vanadium.

DSIC waste consists mainly in big agglomerations (Fig.5a) of smaller grains (Figs.5b, 5c); one can also assess solidified melt (see arrows in Fig. 5d) that contributes to the aggregate formation.

The main element assessed by EDX analysis in DSIC waste is titanium (Fig. 6). One can also observe hollow of porous microspheres (Figs. 6e and 6g) formed due to the partial melting of titanium alloy during its processing.

3.2. Properties of Portland cement mortars with DS and DSIC as alternative aggregates

The apparent density of mortar specimens prepared with various dosages of sand, DS and DSIC (see Table 1) is presented in Figure 7.



a b c d e f g h

Fig.6. - SEM micrographs (a,c,e,g) and corresponding EDX spectra (b,d,f,g) of DSIC waste/ *Microfotografii SEM (a,c,e,g) şi spectrele EDX corespunzătoare (b,d,f,g) ale deşeului DSIC*

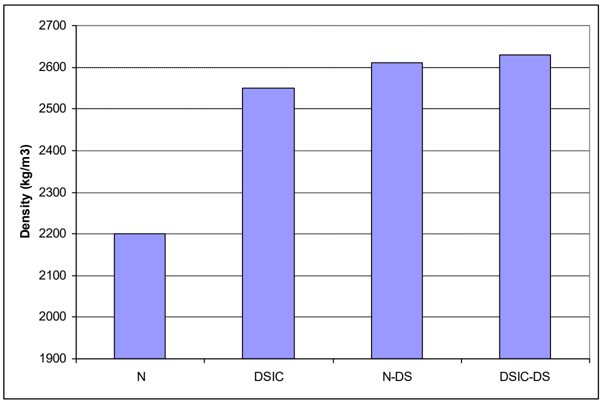


Fig.7 - Apparent density of cement mortar specimens with different types of aggregates/ *Densitatea aparentă a mortarelor de ciment preparate cu diferite tipuri de aggregate.*

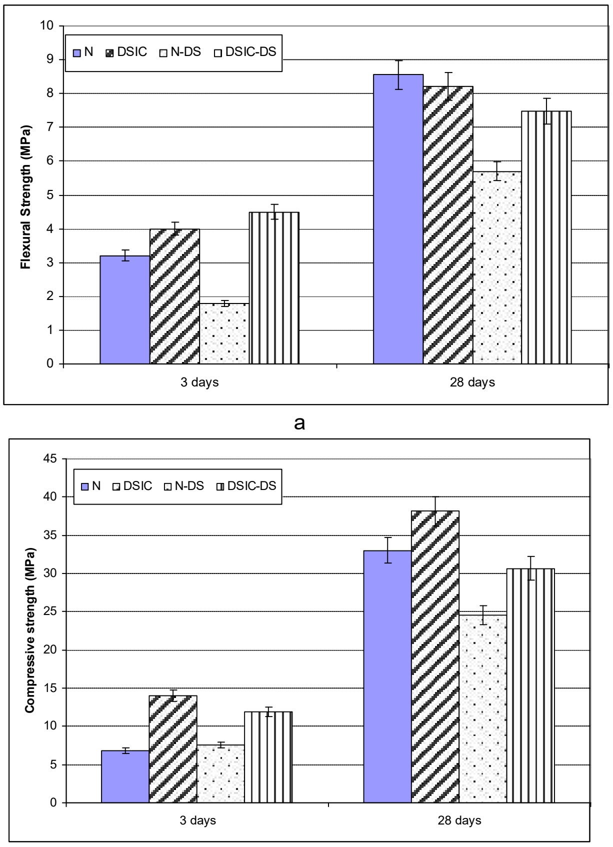
As it can be seen, the mortar specimens in which sand aggregate was replaced totally or partially with various amounts of DS and DSIC waste have higher densities as compared with reference (N). This increase of density values, especially for the mortars with DS waste is in good correlation with the high values assessed for the densities of studied wastes i.e. 6982 kg/m^3 for DS and 4217 kg/m^3 for DSIC.

The values of flexural and compressive strengths assessed on mortar specimens are presented in Figure 8. Both flexural and compressive strengths increase when sand is totally replaced with DSIC waste. That was to be expected, due to the high amount of titanium alloy grains (with high hardness) present in this waste (see § 3.1). The partial replacement of sand (N) and DSIC with DS waste has a negative influence on the mechanical strengths of mortars; N-DS mortars have lower values of flexural and compressive strengths both at early ages (3 days) and longer hardening times (28 days). The negative effect determined by DS waste on the mechanical strengths of mortar specimens is also connected with its grain size and chemical composition i.e. coarse grains with high iron content.

4. Conclusions

The DS and DSIC wastes resulted in titanium alloy mechanical processing (shot blasting or polishing) can be used to substitute the natural aggregate (sand) in the manufacture of Portland cement mortars, as alternative aggregates.

The chemical and mineralogical compositions as well as the grain size distribution of DS and DSIC wastes are influenced by the mechanical process in which are generated. DS, which results by the shot blasting with steel beads, has a high amount of Fe (86.56%) and a smaller Ti content (8.23%). DSIC, which results during the surface abrasion/polishing process with abrasive discs of Ti ingots, has a high Ti (44.56%) and Al (12.81%) content; in this waste Ti is present as metal as well as titanium oxides (in smaller quantities).



a

b

Fig. 8 - Flexural (a) and compressive (b) strengths assessed on mortar specimens with DS and DSIC wastes, hardened for 3 and 28 days/ *Rezistenţa la încovoiere (a) şi la compresiune (b) a mortarelor cu conţinut de deşeuri DS şi DSIC, întărite 3 şi 28 de zile.*

The apparent densities of Portland cement mortars containing DS and DSIC as alternative aggregate are higher as compared with the reference mortar (prepared with sand), due to the higher density of these wastes. The total replacement of sand with DSIC in mortar determines an increase of mechanical strengths both at early ages (3 days) and longer hardening times (28 days). The mortar specimens with DS waste developed lower flexural and compressive strengths as compared with the reference and the mortar with DSIC as alternative aggregate.

Acknowledgements

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ANIVERSARE / ANNIVERSARY

Inginer chimist VIRGINIA MOLDOVEANU

In luna martie doamna inginer Virginia Moldoveanu- **redactor coordonator** la **Revista Română de Materiale**, împlinește o frumoasă vârstă, la a cărei aniversare dorim să-i mulțumim pentru dăruirea cu care ne ajută necondiționat și să îi urăm**: LA MULȚI ANI!**

Așa cum chiar dânsa ne spune: *”Născută în Comuna Boholţ – Făgăraş în anul 1934, a absolvit Liceul „Domniţa Ileana” şi apoi a urmat Facultatea de Chimie Industrială, secţia Anorganică din Institutul Politehnic Bucureşti, unde a avut ca profesori pe magistrul Costin Neniţescu, pe Emilian Bratu,Tudor Ionescu, Eugen Pincovschi şi alţi profesori renumiţi. După absolvirea facultăţii a lucrat ca inginer stagiar la Fabrica de acid sulfuric şi îngrăşăminte fosfatice „Petru Poni” de la Valea Călugărească. Apoi s-a transferat la Editura Didactică şi Pedagogică din Bucureşti, unde timp de 10 ani a fost redactor responsabil la circa 20 de manuale din domeniul industriei chimice. Activitatea consta în primirea manuscrisului şi pregătirea lui pentru tipar şi urmărirea până la apariţia cărţii (lectură informativă, redactare şi discuţie cu autorii, bun de tipar şi bun de difuzat). Pentru exemplificare, câteva titluri: Chimia silicaţilor, autor dr. Aurel Cioară (214 pag), Tehnologia produselor ceramice, autor dr. Dumitru Popescu Haş (368 pag.), Tehnologia ceramicii de construcţii, autor Iulian Givulescu (586 pag.), Tehnologie chimică generală, autori Eugen Pincovschi, Maria Florea, Petru Baltă (238 pag.), Tehnologia materialelor izolatoare, autor Paul Catrinu (144 pag.), Aparate şi instalaţii în industria chimică, (682 pag.), 7 autori (Polihroniade ş.a.) de la IPROCHIM, precum și alte manuale din domeniu: petrochimie, materiale plastice, produse macromoleculare, lacuri şi vopsele, celuloză şi hârtie, acid sulfuric, produse clorosodice, etc., totalizând circa 8000 de pagini.*

A lucrat apoi un an la Laboratorul de lacuri şi vopsele din cadrul unităţii Policolor, după care s-a transferat în ***1971*** *la Centrul de documentare tehnică pentru materiale de construcţii, unde a preluat redactarea Buletinului de informare tehnică şi ulterior* ***a devenit redactor la Revista Materiale de Construcţii.*** *În anul 1973 revista a fost preluată de Institutul de Cercetare și Proiectare Materiale de Construcții-ICPMC în prezent numit PROCEMA. Din 2005 revista este editată de Fundaţia „Şerban Solacolu”.*

A continuat să lucreze la revistă şi după ce în 1994 a ieşit la pensie, până în 2012 când a devenit colaboratoare voluntară, contribuind la apariţia a 183 de numere de reviste. Mentorii săi au fost regretaţii : inginerul Gheorghe Grigorescu, profesorul Ion Teoreanu, cu care a avut colaborări deosebit de fructuoase şi de la care a învăţat foarte mult şi, nu în ultimul rând, de la soţul său chimistul şi cercetătorul pedolog Viorel Blănaru care în mod benevol a scris în revistă despre o serie de monumente (mânăstiri, biserici, palate, castele,cetăţi) şi despre activitatea ştiinţifică a unor personalităţi remarcabile din domeniul respectiv.”

Pentru activitatea îndelungată a doamnei inginer VIRGINIA MOLDOVEANU desfășurată cu pasiune și devotament, încă de la primele numere ale revistei și până în prezent, îi mulțumim și îi dorim putere de muncă și multă sănătate în continuare.

LA MULȚI ANI!

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