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ECOLOGICAL MINERAL MATRIX FOR CONSTRUCTION

BY

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Abstract. The addition of calcium sulphate (CS) as replacement of cement in the traditional mixture develops a so-called *ecological mineral matrix* with favourable influence on the setting time of the material, speeding up the hardening, improved workability, compactness, homogeneity of material with convenient mechanical properties. In this paper the authors analyse the properties of this binder obtained by partial replacement the Portland cement in the production of concrete with a product obtained from recycled wastes. The analysis of the micro structure and the evaluation of most important technological and mechanical properties confirm the suitability of the obtained matrix for applications in construction.

Key words: green cement; mineral matrix; recycling; microstructure; blended cement; SEM analysis; tensile and compressive strength.

1. Introduction

Sustainable development is often associated to the notions "green economy", „clean technology" and „final waste" that results in minimizing the

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existent industrial wastes (Van den Heede & De Belie, 2012). Large quantities of waste issue from refineries, chemical and metallurgical industries (Tayibi *et al*., 2009; Kuryatnyk *et al*., 2008; Guo & Shi, 2008) as well as gas emissions and solid waste are mainly resulting, among others phosphogypsum, gypsum, flue gas desulphurization (FGD), lactogypsum, citrogypsum, etc.

The mineral matrices provide an efficient way of utilizing the materials properties leading to important raw material saving, one of the main objectives of sustainable development (Mobasher, 2012). These materials increase the new structures performances and can be utilized for composites in the rehabilitation of the structures that exceeded their service life. It is anticipated that the cement and concrete industry needs to become soon a „green industry" more ecologically friendly (Aitcin, 2000; Damtoft *et al*., 2008). From an environmental perspective, it is obvious that a high content of cementitious by-products in blended cements is desirable (Van den Heede & De Belie, 2012).

A novel binder has been obtained from an irretrievable industrial waste that does not involve carbon emissions and sustain the possibility to re-recycle the material, recalcinating its wastes and to obtain a fresh product (WO 2010/003827 A1). Over a billion tons of wastes could be reused (Tayibi *et al*., 2009; Kuryatnyk *et al*., 2008; Guo & Shi, 2008) avoiding the big energy and natural resources usage as in the case of clinker production for construction industry. A research team from the Technical University of Iaşi has developed a research program dedicated to attracting the wastes/subproducts in the construction process (Toma *et al*., 2011; Hohan *et al*., 2011) and in the efficient association of some individual materials within multifunctional composite products.

In this paper the authors analyse the properties of a new binder obtained by partial replacement of the Portland cement in the fabrication of concrete with a product obtained from recycled wastes. The analysis of the micro structure, chemical composition, and the evaluation of most important technological and mechanical properties confirm the suitability of the obtained matrix for applications in construction.

2. Ecological Mineral Matrix for Construction Composite Elements

A mineral matrix can be utilized to obtain simple reinforced composites, by adding aggregates as reinforcing particles (Fig. 1), or double reinforced composites by adding aggregates and fibrous reinforcing materials (Fig. 2). The ideal structure of a composite material with simply reinforced mineral matrix is represented by a network formed from the aggregates encased in a thin layer of paste or binder and the water strictly needed for hydration, as presented in Fig. 1. The adherence is obtained through mechanical anchorage of

the matrix in the asperities of the grains and through the chemo-absorption of the hydrated binder on the granules.

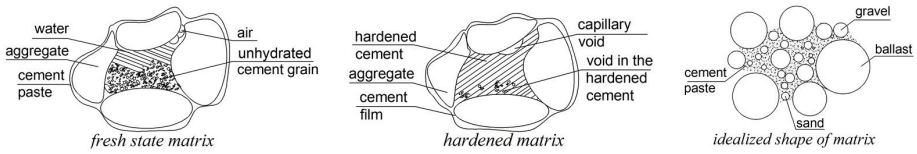


Fig. 1 – Simple reinforced composite with mineral matrix.

The double reinforced mineral matrix composites are obtained through the embedment of fibres or textile reinforcement in the previous mixture (Fig. 2).

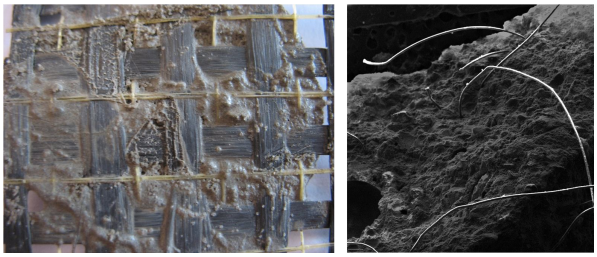
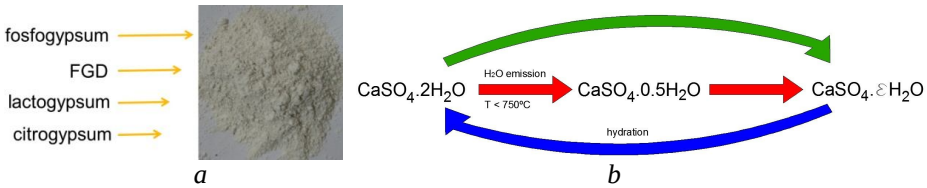


Fig. 2 – Optical and scaning electrons microscope images of double reinforced mineral matrix composites.

2.1. The Components of the Proposed Blended Cement

A partial replacement of the Portland cement in the production of concrete or mortars with a product obtained exclusively from recycled wastes has been operated and the properties of the new product have been analysed. This possible admixture is obtained from irretrievable industrial wastes like phosphogypsum, flue gas desulfurization (FGD), lactogypsum and citrogypsum (Fig. 3 *a*).



a *b*

Fig. 3 – Composition of calcium sulphate (CS).

The admixture is based on an anhydrous calcium sulphate β type, a mixture between a hemihydrate ($CaSO_4.0.5H_2O$) and an anhydrite III ($CaSO_4$).

The final product is named as *calcium sulphate* (CS) *based binder*. Heating gypsum ($CaSO_4.2H_2O$) at relatively low temperatures, compared to those used to produce clinker, results in eliminating only water from its microstructure (Fig. 3 *b*). Thus, obtaining CS will not involve carbon emissions and even more there is the possibility to re-recycle the material, re-calcinating the product after its expiry date. To obtain anhydrite III, the typical dehydrate will be heated resulting in calcium sulphate with low percentages of water in its composition, $CaSO_4.\varepsilon H_2O$ with $0.06 < \varepsilon < 0.11$. When rehydrated the chemical reaction enables the return to the initial dehydrate form (WO 2010/003827 A1).

2.2. Mixtures of the Proposed Mineral Matrix for Microstructural Analysis

Through microtechnology the mixtures can be drafted so that the final material has the intended properties. Applying at the micro level an adequate chemical design strength increase and cracking restraint can be obtained. The standard mixture is cement, aggregate and water mix while the newly proposed mixtures involve the addition of CS, a powdery material. The addition of CS as replacement of cement in the traditional mixture (Fig. 4 *a*) develops the so-called *ecological mineral matrix* (Fig. 4 *b*).

a *b*

Fig. 4 – Aspect and composition of the mineral matrix:
a – traditional mixture; *b* – modified mixture.

The cement used was CEM I 42.5R, a type I pure Portland cement. The sand had a grain size between 0.1 and 1.0 mm. A 0.4 water/binder ratio has been constantly selected for all mixtures. The constituents of the mixtures are presented in Table 1.

Table 1
Mixture Constituents (in percentages)

Sample	Water/binder ratio	CS	Cement	Sand
1	40	100	–	–
2	40	30	70	–
3	40	15	35	50

The traditional cement and sand blended with water is the well known micro concrete. The composition has a grey colour; it is very viscous and hard to pour in the moulds requiring compaction (Fig. 4 *a*). The mixture with a 15% CS in the composition is more fluid and has a lighter colour; the material was much easier poured in the moulds (Fig. 4 *b*). A 6...7 times faster hardening of the samples containing CS has been noticed. For the SEM analyses, three samples have been prepared (Figs. 5 *a*, 5 *b*, 5 *c*).

a) *Sample 1*

The first mixture is a calcium sulphate binder, obtained mixing CS and water. The obtained composition was very fluid with a whitish aspect. The anhydrite reacted slowly with water. During the hydration of the sample no bulking of the material was noticed, but the material experienced small shrinkage during drying.

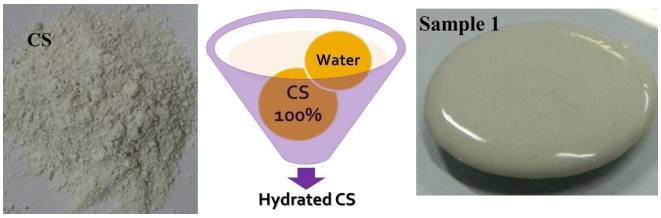


Fig. 5 *a* – Calcium sulphate binder.

b) *Sample 2*

The second composition is a mixture of CS and cement. It resulted in a grey fluid mixture and the chemical reaction of the constituents discharged heat. The setting and hardening of the material occurred very quickly. No bulking or shrinkage was observed during hydration and drying.

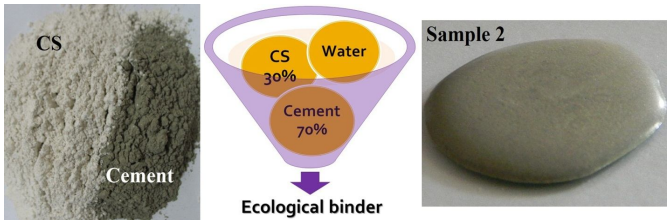


Fig. 5 *b* – Calcium sulphate and cement binder.

c) *Sample 3*

The third mixture was created by adding sand to the previous mix. The composition had the same grey colour but was a little more slurry. It was noted

that the sand addition slowed down the setting time and the hardening of the sample when compared to the CS and cement binder. The chemical reactions discharged heat. The material had no volume change during hydration and drying of the sample.

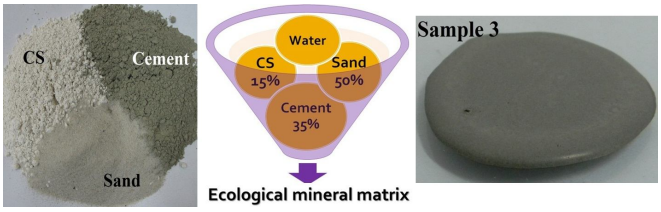
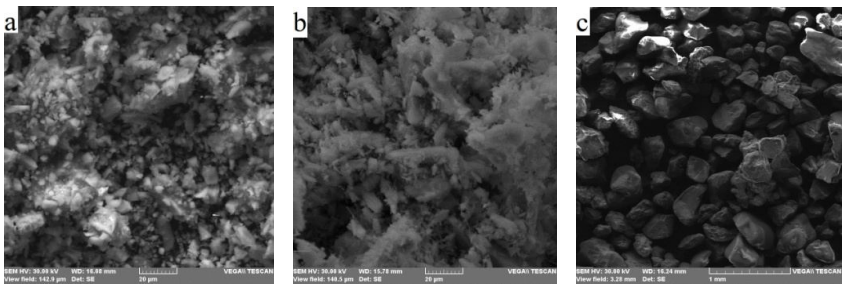


Fig. 5 *c* – Proposed mineral matrix.

3. Microstructural Analysis of the Proposed Mineral Matrix

Scanning electrons microscope (SEM) results were obtained using secondary electrons (SE) detector of Vega Tescan LMH II equipment. The images of the investigated microstructures were taken at a working distance of approximately 16 mm with same amplification scale. A first series of analyses was performed on the individual constituents cement, CS and sand respectively. Their microstructural aspect is shown in Fig. 6.



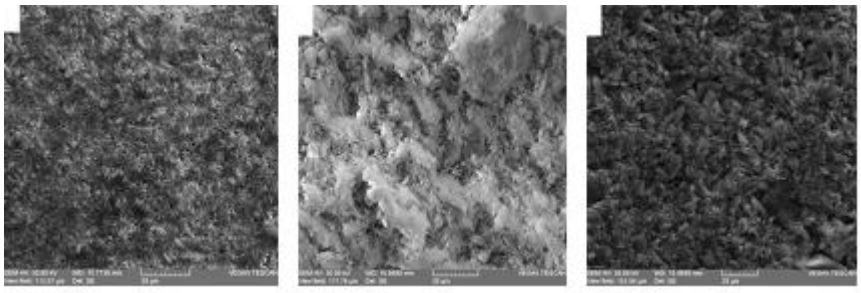
a *b* *c*

Fig. 6 – Microstructure of unhydrated elements: *a* – cement; *b* – CS; *c* – sand.

The second series of SEM analyses has been performed on the three mixtures. Materials were analysed as small parts (25 g weight) and no mechanical operations were applied so the initial state of the mixtures has been preserved. The images shown in Figs. 7,…,9 characterize the microstructure of the studied material at a 2.5 kx aggrandizement for time intervals of 24 h, 7 days and 28 days, respectively, from the material casting.

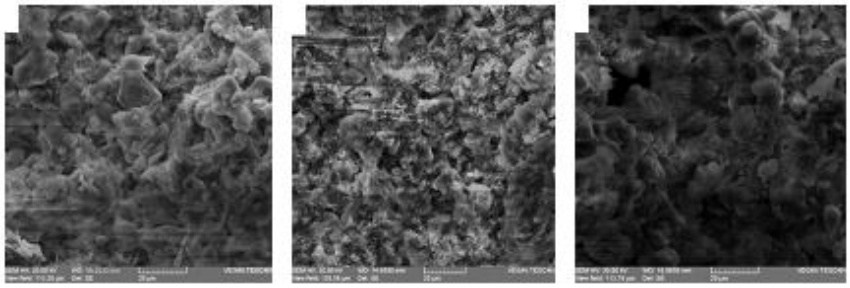
The first sample has a rapid increase of the needle-shape crystals that start felting, thus the forming of the paste reduces and results in a brittle and rigid mass. The microstructure with finished setting time is composed of an

acicular shape crystals network. After the water evaporation from the saturated structure the microstructure is transformed into an intergrown crystal mass. The parallelepipedic formations of micrometer dimensions, between 2…7 μm, and sub micrometer ones, between 0.2…0.8 μm, creating the mass connection between the larger elements, can be observed in Fig. 7 *a*. In this mix, small black spots or holes of approximately 0.5 μm can be visualized, at 24 h (Fig. 7 *a*), defects that after 7 days (Fig. 7 *b*), disappear or are very small leading to the idea that the material is better configured, denser and thus leading to better strengths. The sample keeps the crystal structure, mostly with rhombic and hexagonal forms, typical for phosphogypsum morphology (Tayibi *et al.*, 2009).



a *b* *c*

Fig. 7 – Microstructure of sample 1 at: *a* – 24 hours; *b* – 7 days; *c* – 28 days.

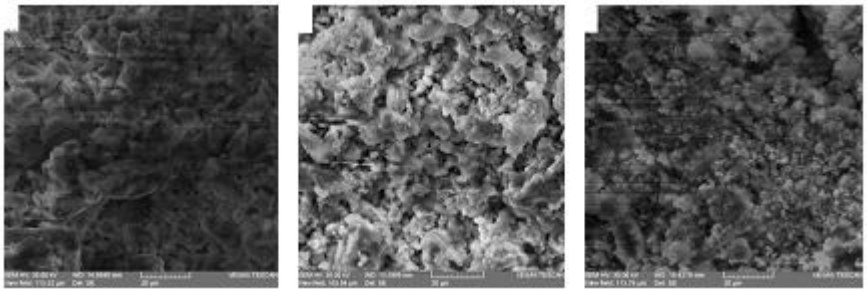


a *b* *c*

Fig. 8 – Microstructure of sample 2 at: *a* – 24 hours; *b* – 7 days; *c* – 28 days.

The other two mixtures, sample 2 (Fig. 8), and sample 3 (Fig. 9), have a spongious aspect but compact composition regardless the curing age. The microstructure of the second sample presents a good chemical reaction, between cement and CS, creating a homogeneous material. The sharp parallelepipedic configuration of the simple CS binder (Fig. 7) disappears, obtaining for the second type binder a structure with a pulpy aspect. No special influence of the CS percentage can be observed on the third sample.

Looking at the binder microstructure, at 28 days (Fig. 8 *c*), some holes are noticeable, corresponding probably to capillary voids that lead to material microstructural defects. In sample 3 (Fig. 9 *c*), that has an addition of sand, the fine grains are being perfectly bonded with the CS and cement binder, and thus, a more idealized shape for a mineral matrix is obtained.



a *b* *c*

Fig. 9 – Microstructure of sample 3 at: *a* – 24 hours; *b* – 7 days; *c* – 28 days.

4. Chemical Analyses of the Proposed Mineral Matrix

For chemical analysis the EDX (Energy-dispersive X-ray spectroscopy) analyses has been utilized. The equipment used is a Bruker brand (Quantax X-flash 5030 technology for environmental and cold field emission field SEM). The chemical composition obtained on the three mixtures is given in Table 2. The results have been expressed on a 9 mm^2 sample surface in a 3 min time analysis and automatic work type. The samples for chemical investigations were used as-cast with no interfering elements on the material surface. The output of an EDX analysis is an EDX spectrum, an analytical technique that enables the chemical characterization of a sample. The energy *vs*. intensity spectrums for each sample are presented in Table 3, and show that the expected main elements of the individual constituents exist in the mixtures.

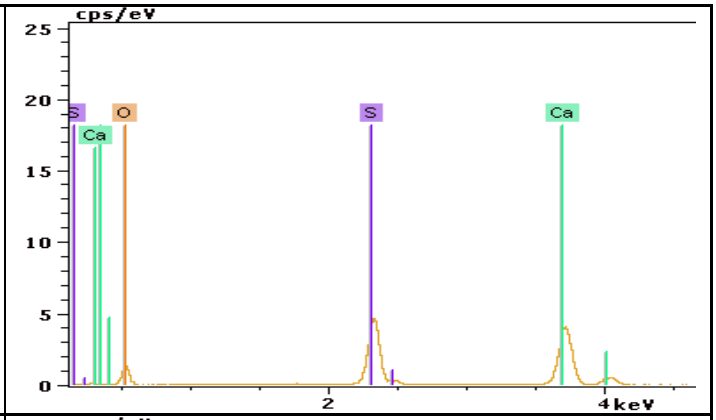
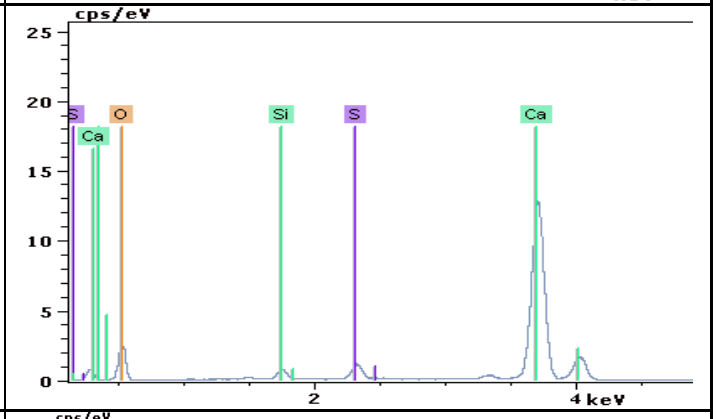
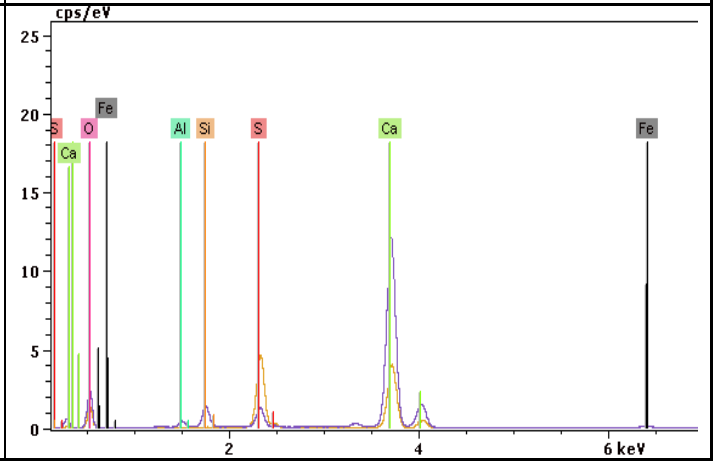
Table 2

Chemical Composition of the Mixtures

Sample 1			Sample 2			Sample 3		
Element	Norm. wt.%	Norm. at%	Element	Norm. wt.%	Norm. at%	Element	Norm. wt.%	Norm. at%
Oxygen	47.031	66.821	Oxygen	51.467	72.155	Calcium	45.345	26.803
Calcium	30.845	17.495	Calcium	44.500	24.956	Oxygen	43.865	64.950
Sulphur	22.123	15.683	Sulphur	2.626	1.837	Silicon	4.475	3.775
			Silicon	1.316	1.051	Sulphur	3.488	2.577
						Aluminium	1.533	1.346
						Iron	1.292	0.548

Table 3

Energy vs. Intensity Spectrums for each Mixture

Sample 1	
Sample 2	
Sample 3	

5. Mechanical Properties

Several experiments have been carried out at the Technical University of Iaşi to determine the tensile and compressive strengths of the proposed mineral matrices. The samples were made with traditional binders, sample *T*, and ecological binders, sample *E*. The mixtures percentages are presented in Table 4.

Table 4

Mixture Constituents (in percentages)

	Cement	CS	Sand	W/B*
Sample *T*	50	–	50	40
Sample *E*	35	15	50	40

*W – water; B – binder.

To obtain the tensile and compressive strengths of each mixture a total number of 24 prismatic samples with dimensions 16 × 16 × 40 mm were casted (Figs. 10 *a*, *b*).

a *b* *c* *d*

Fig. 10 – Preparation and testing of samples: *a* – samples casting; *b* – prismatic samples; *c* – bending test; *d* – compression test.

a *b*

Fig. 11 – Experimental results of mechanical testing of traditional and ecological mineral matrix, [MPa]: tensile strength; *b* – compressive strength.

The casting and testing were performed according to the EU based standards. The tensile strength was obtained from three point loading test (Fig. 10 *c*), while the compressive strength was determined through the

compressive testing of the half prisms resulted from bending failure (Fig. 10 *d*). The samples were tested at four time intervals: 24 h, 72 h, 7 days and 28 days. The mean values obtained on the samples are presented in Fig. 11.

Analysing the results it can be concluded that in the first 24 h both types of matrices are in the same range. The next two time intervals record a strength decrease for the ecological samples. In the last time interval, of 28 days, an increase of 25% of the tensile strength for the ecological mineral matrix with respect to the traditional one it is noticed. On the other hand, at 28 days, the compressive strength of ecological matrices is almost half when compared to the results obtained on the traditional matrices.

6. Conclusions

1. The mineral matrix obtained by replacing the classical Portland cement with other environmental safe admixtures brings not only ecological solutions in the construction industry but also improves the overall properties of the material.

2. The addition of calcium sulphate (CS) influences the setting time of the material, speeding up the hardening and removal of moulds.

3. The mineral matrices with CS based binder have an improved workability, facilitating the pouring in complex shapes.

4. In addition, a reduced water/binder ratio improves the microstructure, limiting the capillary voids and the result is a compact, homogeneous material with good mechanical performances.

5. The mechanical tests of mineral matrices with partial replacement of cement by CS have lead good results of strength properties characteristic convenient to civil engineering applications.

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MATRICE MINERALĂ ECOLOGICĂ PENTRU CONSTRUCŢII

(Rezumat)

Adaosul de sulfat de calciu (CS) ca înlocuitor al cimentului în amestecul tradiţional dezvoltă o aşa-numită matrice minerală ecologică cu influenţă favorabilă asupra prizei materialului, reducerea timpului de întărire, îmbunătăţirea lucrabilităţii, compactităţii şi a omogenităţii materialului cu proprietăţi mecanice convenabile. Se analizează proprietăţile liantului obţinut prin înlocuirea parţială a cimentului Portland la producerea betonului cu un produs obţinut din deşeuri reciclate. Analiza microstructurală şi evaluarea proprietăţilor mecanice şi tehnologice confirmă adoptarea matricei obţinute pentru aplicaţii în construcţii.