

VALORIFICAREA CENUȘII REZULTATE LA ARDEREA REZIDUURILOR PETROLIERE CU CONȚINUT DE HIDROCARBURI LA OBTINEREA LIANȚILOR ANORGANICI CU CONȚINUT DE SULFAT DE CALCIU VALORIZATION OF ASH RESULTED FROM THE COMBUSTION OF HYDROCARBON-CONTAINING RESIDUES FROM PETROLEUM INDUSTRY IN THE MANUFACTURE OF INORGANIC BINDERS WITH CALCIUM SULFATE CONTENT

CRISTINA DIMA (VĂDUVA), ALINA BĂDĂNOIU *, ȘTEFANIA STOLERIU, DIANA LUCA

University Politehnica of Bucharest, Str. G. Polizu nr. 1-7, cod 011061, Bucharest, Romania

The study presents one possible way for the valorization of an ash resulted from the combustion of hydrocarbon-containing residues from petroleum industry (waste A). The substitution of gypsum binder with 5 wt.%, 20 wt.% and 30 wt.% waste A, results in the modification of compressive strength values; the increase of ash A amount (from 5 wt.% to 30 wt.%) determines the increase of setting time, therefore the composition with 30 wt.% ash A, has a setting time similar with the one specified in gypsum binder standard. The activation of ash A with sulfate salts shortens the setting time and increases the compressive strengths (with reference to plain ash A paste).

Studiul prezintă o posibilitate de valorificare a cenușii rezultate prin arderea unor reziduuri cu conținut de hidrocarburi din industria petrolieră (deșeurile A). Înlocuirea ipsosului cu 5%, 20% și 30% (procente gravimetrice) de deșeu A, are ca rezultat modificarea rezistenței la compresiune; creșterea proporției de cenușă A (de la 5% la 30%) determină o întârziere a prizei astfel încât la un dozaj de 30% cenușă, timpul de priză este similar cu cel impus de normative pentru lianții de ipsos. Activarea cenușii A cu adaosuri de săruri (sulfați) scurtează timpul de priză și mărește rezistența la compresiune a pastelor liante.

Keywords: valorization, waste ash, gypsum, accelerator additions

1. Introduction

Exploitation of natural resources, energy consumption and wastes resulted from technological processes are the main cause of environmental damage. In this context, the protection of natural environment is a fundamental requirement of the continuity of economic and social life.

The elaboration of a broad and circular economy policy led to the implementation of legislative and institutional policies, for the valorization of different types of wastes such as: furnace slag, fly ash and glass wastes.

For example, in the European Union it is available the European standard EN 450-1 Fly ash for concrete. Part 1: Definition, specifications and conformity criteria [1]; this norm specifies the conditions for physical and chemical properties as well as the quality control process for fly ash used as Type II addition in concrete production.

The above mentioned European standard does not apply to ashes resulted from the burning

of household wastes or from petroleum industry.

Due to the different composition (less silica and high carbon content) the heavy oil ash resulted from the combustion of heavy oil from petroleum industry for power generation has a limited utilization [2-4].

This study aims to find a possible way to valorize a different type of ash resulted from the combustion of high sulfur content petroleum residues in the presence of lime. The main component of this ash is anhydrite – CaSO_4 . Therefore, in this study the ash was mixed with gypsum plaster or activated with sulfate salts.

It is well known that during the thermal treatment of gypsum (the raw material used for the manufacture of gypsum binder), several phases can be obtained in correlation with the thermal treatment temperature [5]. At temperatures around 107°C the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is transformed in calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$); further increase of the temperature (over 170 - 207°C) determines the formation of anhydrite (CaSO_4). The reactivity of anhydrite vs. water is

* Autor corespondent/Corresponding author,
E-mail: alina.badanoiu@upb.ro

Table 1

Chemical composition of ash A (wt.%) / *Compoziția chimică a cenușii A (% grav.)*

L.O.I	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O
2.90	5.97	2.16	0.65	48.66	0.52	38.78	0.19	0.16

Table 2

Compositions of studied binders / *Compoziția lianților studiați*

Code	Gypsum plaster [wt.%]	Ash A [wt.%]	Fe ₂ SO ₄ [wt.%]	K ₂ SO ₄ [wt.%]
I	100	0	0	0
5A	95	5	0	0
20A	80	20	0	0
30A	70	30	0	0
100A	0	100	0	0
100A+FeSO ₄	0	100	3*	0
100A+K ₂ SO ₄	0	100	0	1*

*Salts were added in addition to the ash A dosage

correlated with the temperature of thermal treatment i.e. the anhydrite obtained at high temperatures (over 1200°C) called anhydrite I has a very low reactivity as compared with the anhydrite III which is obtained at lower temperatures (around 350°C) [5].

The setting and hardening of gypsum binder (with/without additions) is due to the hydration of its main component i.e. calcium sulfate hemihydrate (CaSO₄·0.5H₂O) with the formation of gypsum (CaSO₄·2H₂O).

According to Lewry and Williamson [6, 7], the reaction with water of CaSO₄·0.5H₂O occurs in three different stages: i) dissolution of CaSO₄·0.5H₂O to form a supersaturated solution of CaSO₄·2H₂O; ii) nucleation and growth of CaSO₄·2H₂O crystals (needles) and their interlocking; iii) depletion of CaSO₄·0.5H₂O.

Anhydrite (CaSO₄) can also react with water to form gypsum, but the reaction rate is smaller as compared with calcium sulfate hemihydrate and depends also on the temperature at which anhydrite is obtained [5]. In order to activate the anhydrite hydration several additions can be used including sulfate salts [8].

2. Materials and methods

The following materials were used:

- gypsum binder (I) for building purposes, in conformity with EN 13279-1 [9], i.e. content of calcium sulfate over 50%, initial setting time 15-20 minutes and a fineness corresponding to 99% passing through 315 microns sieve.

- ash (waste A) obtained from the combustion of hydrocarbon-containing residues from petroleum industry in the presence of limestone (for in-furnace desulfurization).

The oxide composition of ash A is presented in Table 1.

The compositions of the studied binders are presented in Table 2.

In order to prepare the pastes, the binders were homogenized in dry state and subsequently

mixed with water. The water to solid ratio for all compositions was 0.5.

The mineralogical composition of ash A was assessed by X-ray diffractions (XRD). The XRD patterns were obtained using a monochromatic CuKα radiation (λ = 1.5406Å), range 2θ from 10° to 60°.

The compounds resulted in hydration processes were assessed by XRD and SEM analyses, performed on pastes with the composition presented in table 2, cured in air for 3 and 7 days.

SEM analyses were performed on paste specimens (fracture surfaces) coated with Ag, using a HITACHI S2600N microscope.

Apparent (geometrical) density was assessed on paste specimens (20x20x20 mm) after 7 days of hardening in air (at 23 ± 2°C and 50 ± 5% R.H).

Setting time and compressive strength were determined on paste specimens, in conformity with the methods presented in European Standard EN 13279-2 for gypsum binders and gypsum plasters [10].

3. Results and discussion

Figure 1 presents the XRD patterns of ash obtained from the combustion of hydrocarbon-containing residues from petroleum industry.

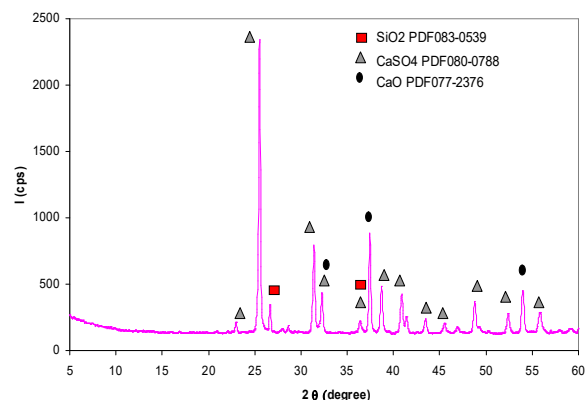


Fig.1 – X-ray diffraction pattern of ash A / Difractograma cenușii A.

The main *mineralogical compounds* identified by this method are anhydrite (CaSO₄), calcium oxide (CaO) and quartz (SiO₂).

The *setting times* of the studied binders are presented in Table 3.

The substitution of gypsum plaster with 5 wt.% and 20 wt.% ash A, determines an important shortening of both initial and final setting times as compared with gypsum plaster (I). This acceleration is most probably due to the presence of calcium oxide in the composition of ash A, which can participate to the hydration processes therefore determining the rapid setting and hardening of the system.

Table 3

Setting time / *Timpul de priză*

Composition	Setting time (h-min)	
	initial	final
I	0-13	0-20
5A	0-4	0-6
20A	0-7	0-10
30 A	0-14	0-20
100A	8-45	12-15
100A+FeSO ₄	2-35	5-28
100A+K ₂ SO ₄	3-32	5-58

It is interesting to note that the increase of ash A dosage from 5 wt.% to 20 wt.% exerts a retardation of setting i.e. the values of setting times of 20A composition are almost double as compared with 5A composition but remains much smaller as compared with gypsum binder (I). This apparent mismatch is due, in our opinion, to the complex composition of ash A resulted in the combustion of hydrocarbon-containing residues from petroleum industry i.e. this material contains also traces of organic substances – see Figure 2. These organic substances can form films at the surface of anhydrous calcium hemihydrate and calcium oxide grains therefore hindering their hydration process.

The increase of ash A dosage increases not only the content of CaO but also the content of organic substances.

The increase of ash A dosage up to 30% delays the setting times up to values similar to plain gypsum plaster (see A30 vs. I – Table 3).

The setting of ash A paste (100A) is much longer as compared with the systems based on gypsum binder (Table 3); this is explained by the lower reactivity vs. water of the anhydrite formed at high temperatures during the combustion of hydrocarbon-containing residues. Moreover, the presence of organic substances, as previously presented, contributes to the retardation of setting and hardening process in this system.

In order to accelerate the setting and hardening of ash (100A) two additives were used

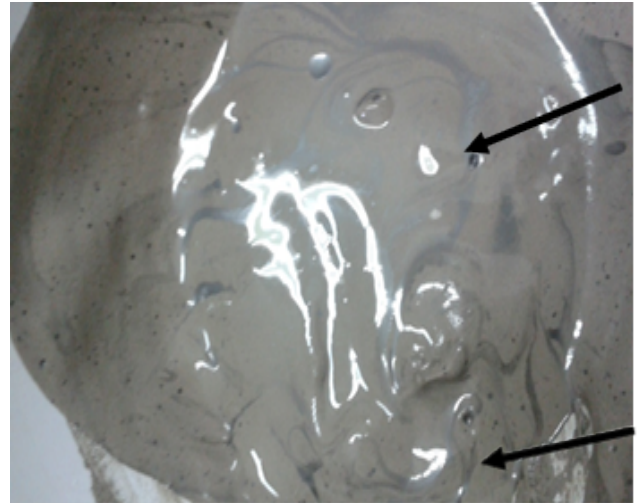
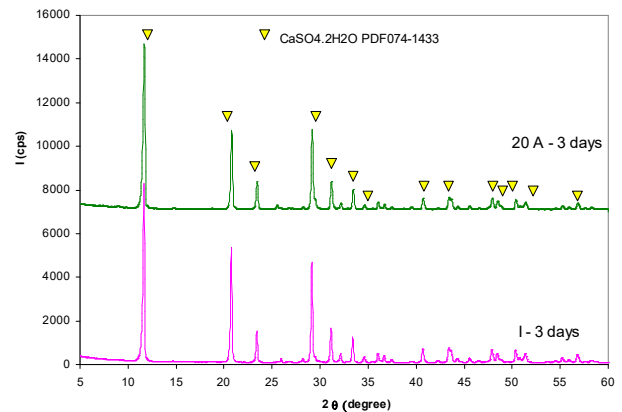
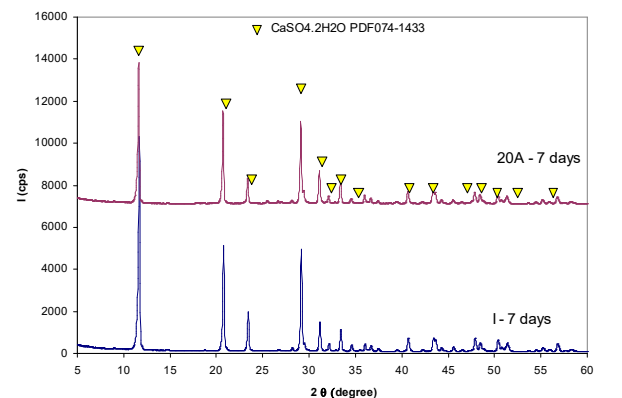


Fig.2 - Visual aspect of 100A paste immediately after mixing of ash A with water/ *Aspectul probei 100A imediat după amestecarea cenușii A cu apa.*

i.e. K₂SO₄ (100A+K₂SO₄) and FeSO₄ (100A+FeSO₄); the setting of these mixtures proceeds faster compared to the setting of ash A (100A). The setting time values are closer to those specific for portland cement, but much longer compared with gypsum binder (I).



a



b

Fig.3 - XRD patterns of binders I and A20 after: a) 3 days of hydration; b) 7 days of hydration/ *Difractogramele pastelor liante I și 20 A după: a) 3 zile de hidratare; b) 7 zile de hidratare.*

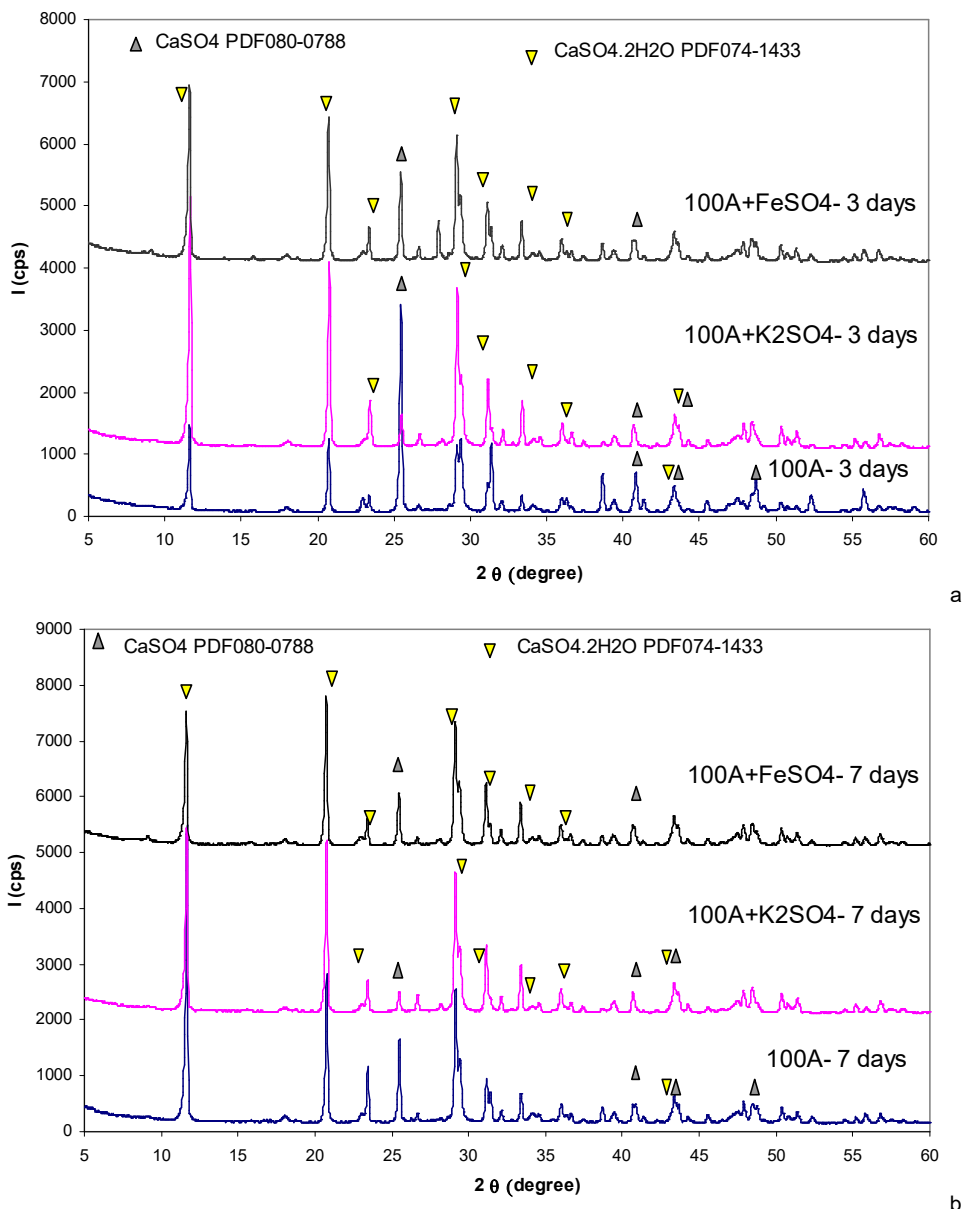


Fig.4 - XRD patterns of pastes based on ash A with/without activator additions after different periods of hydration: a) 3 days; b) 7 days / *Difractogramele pastelor pe bază de cenușă A cu/fără adaos de activator după diferite perioade de hidratare a) 3 zile; b) 7 zile.*

The use of 3 wt.% FeSO_4 addition seems to have a higher impact on the acceleration of setting as compared with 1 wt.% K_2SO_4 and confirms the results obtained by other authors [8].

The XRD patterns of I and 20A pastes, hydrated 3 and 7 days (Fig. 3) shows the presence of gypsum as main crystalline phase; this compound results by the hydration of calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) from gypsum binder as well as of anhydrite from ash A (for 20A).

Due to the presence of anhydrite (in high amount) and calcium oxide (in lower amount) in ash A, this material has cementations properties i.e. hardens, but with a much lower rate as compared with gypsum binder. The crystalline phases assessed on the XRD patterns of 100A

paste, after 3 and 7 days of hydration (Fig. 4), are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4). The presence of anhydrite on XRD patterns, even after 7 days of hardening, confirms its low hydration rate; therefore, two additions were used to increase the hydration rate i.e. K_2SO_4 and FeSO_4 .

The influence of these two accelerator additions is more intense for shorter hardening times (3 days - Fig.4a), the intensity of gypsum peaks being higher in 100A+ K_2SO_4 and 100A+ FeSO_4 as compared with plain ash A (100A).

The apparent density assessed on the binder pastes after 7 days of hardening at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ R.H is shown in Table 4.

The substitution of gypsum with ash A or

the use of accelerator admixture in combination with ash A, do not cause a significant change in the apparent density of these pastes.

Table 4
Apparent density of studied mixtures after 7 days of hardening/
Densitatea aparentă a amestecurilor studiate după 7 zile de întărire

Composition	Apparent density (g/cm ³)
I	1.47
5A	1.40
20A	1.43
30 A	1.46
100A	1.36
100A+FeSO ₄	1.48
100A+K ₂ SO ₄	1.52

In Table 5 are presented the compressive strength values determined on pastes based on gypsum binder with/or ash A, after different curing times. It can be seen that the substitution of gypsum binder with 5 wt.% and 20 wt.% ash A, results in an increase of the compressive strength values for short (2 hours, 1 day) and longer (7 days) curing periods.

The further increase of ash A dosage up to 30 wt.% determines a reduction of compressive strength values for all hardening times; nevertheless, these values are comparable with those assessed for gypsum binder (I).

This decrease could be due to a "dilution effect" determined by the replacement in a high amount of the active binder i.e. gypsum binder.

The ash paste (100A), develops very low compressive strengths and only after longer hardening times (3 and 7 days); the use of setting accelerator salts determines an increase of compressive strengths (as compared with 100A) at longer curing times (3 and 7 days). The presence of ferrous or potassium sulfates in binding systems results in a faster kinetics of the stiffening (setting) (Table 4).

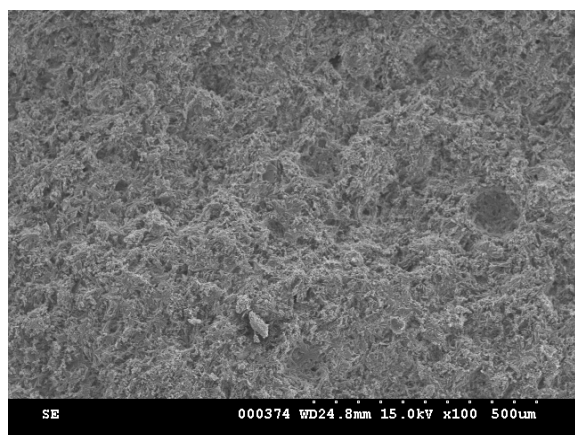
Table 5
Compressive strength of pastes after different periods of hardening/
Rezistența la compresiune a pastelor după diferite perioade de întărire

Composition	Compressive strength (N/mm ²)			
	2 hours	1 day	3 days	7 days
I	2.95	3.76	8.08	8.33
5A	5.53	5.65	7.25	11.5
20A	7.1	7.12	8.01	9.5
30A	2.75	4.4	7.5	8
100A	0	0	1.25	2.65
100A+FeSO ₄	0	2	6.98	7.82
100A+K ₂ SO ₄	0	nd	2.93	6.32

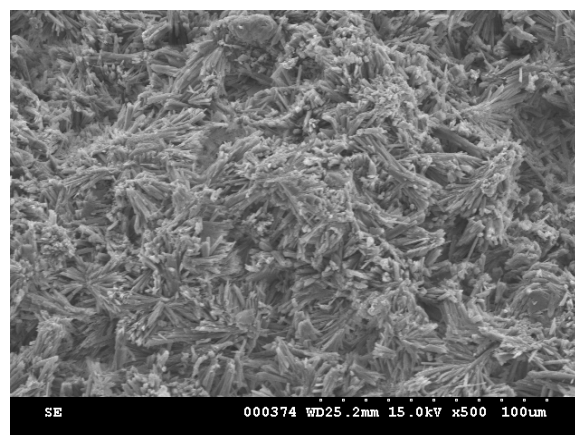
nd- not determined/ *nedeterminat*

The scanning electron micrograph (SEM) images of selected pastes hardened for 7 days are shown in the Figures 5 -8.

In the gypsum paste (I) - Fig. 5, one can notice the presence of needle like crystals, specific for calcium sulfate dihydrate (gypsum) formed by the hydration of calcium sulfate hemihydrate. The higher interlocking degree of these crystals is essential for the development of a good mechanical strength.



a



b

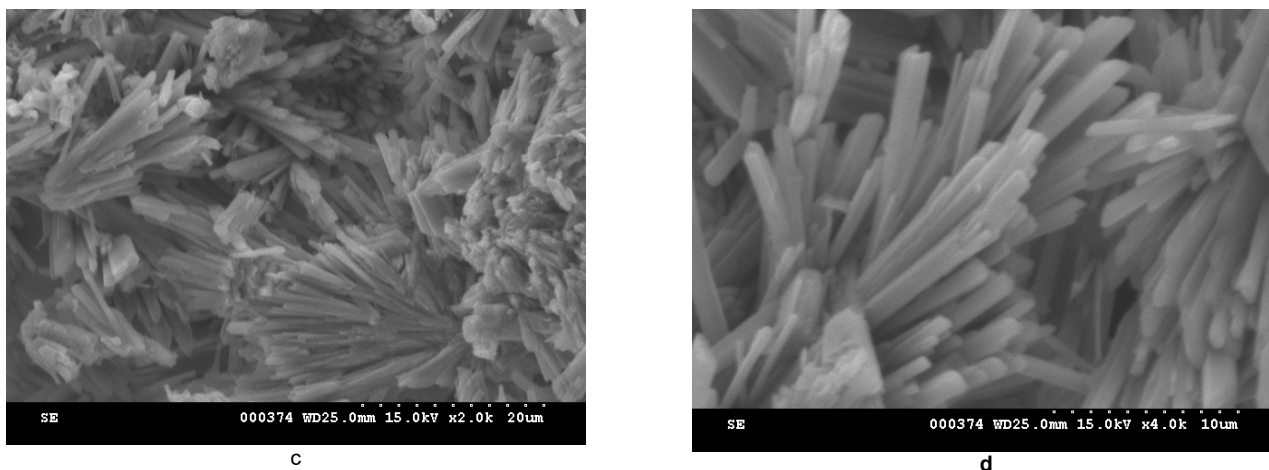


Fig.5. – SEM images of gypsum binder (I) hardened for 7 days/ *Imaginile SEM ale ipsosului (I) întărit 7 zile.*

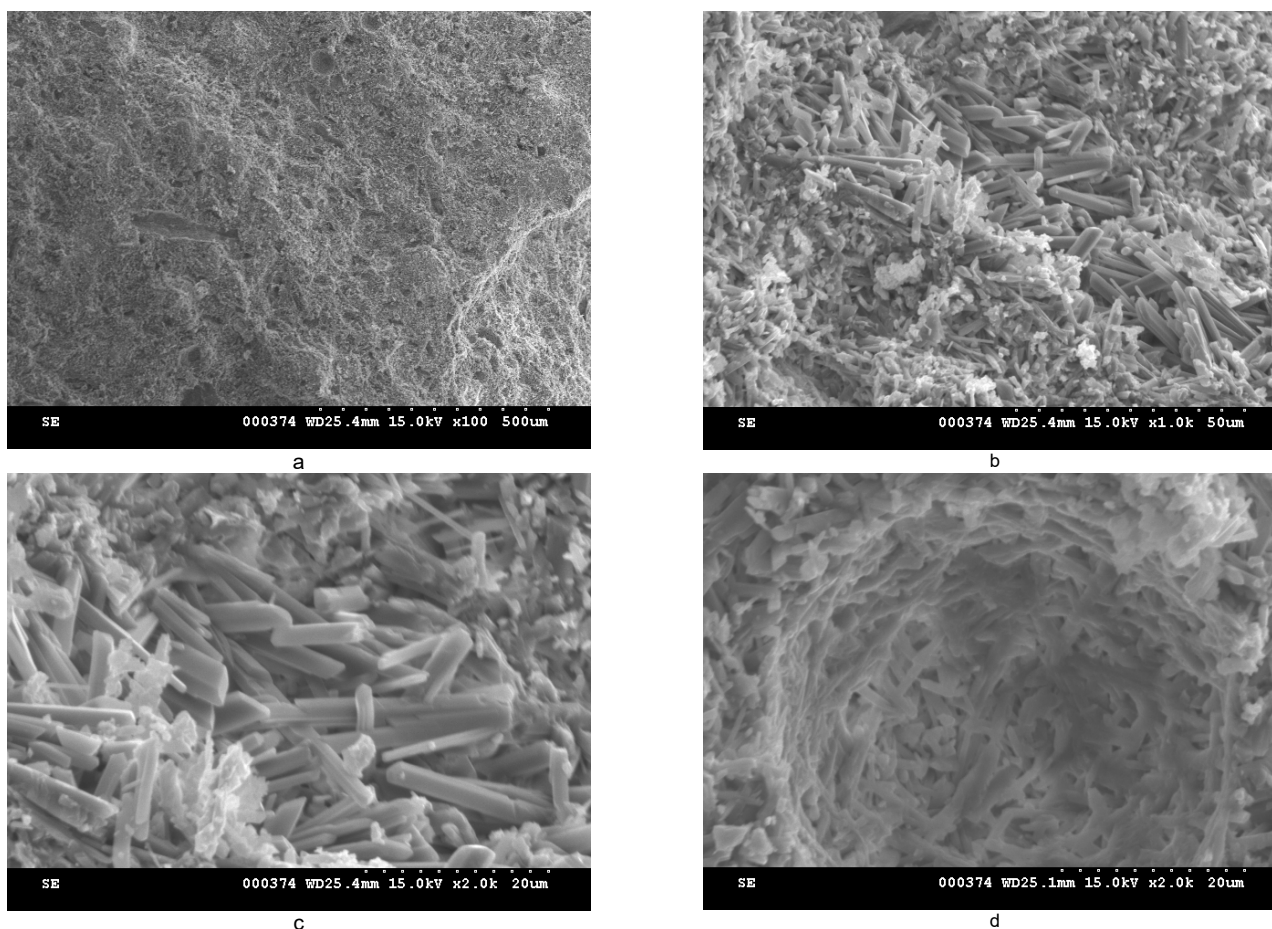


Fig.6 – SEM images of 20A hardened for 7 days/ *Imaginile SEM ale probei 20A după 7 zile de întărire.*

In the SEM images of the 20A paste, one can notice the presence of bundles of needle like gypsum crystals along with another less crystalline phases (see Fig. 6b); the interlocking of gypsum needle like crystals is high (see fig. 6d) therefore the mechanical strengths of this specimen are good (see also Table 5).

For the paste based of ash A (100A) one can assess a microstructure consisting of agglomerates grains (Fig.7); between these phases one can also assess needle-shaped crystals specific for gypsum

(see the arrow in Fig. 7c) or hexagonal plates – specific for portlandite (the arrow in Fig. 7d). The amount and interlocking degree of gypsum crystals is low which explain the small values of compressive strengths assessed for 100A paste.

In the case of ash A paste with ferrous sulfate addition (Fig. 8), the amount of needle like crystals is much higher and is due to the formation of a larger amount of gypsum by the anhydrite hydration, favored by the presence of $FeSO_4$ [8].

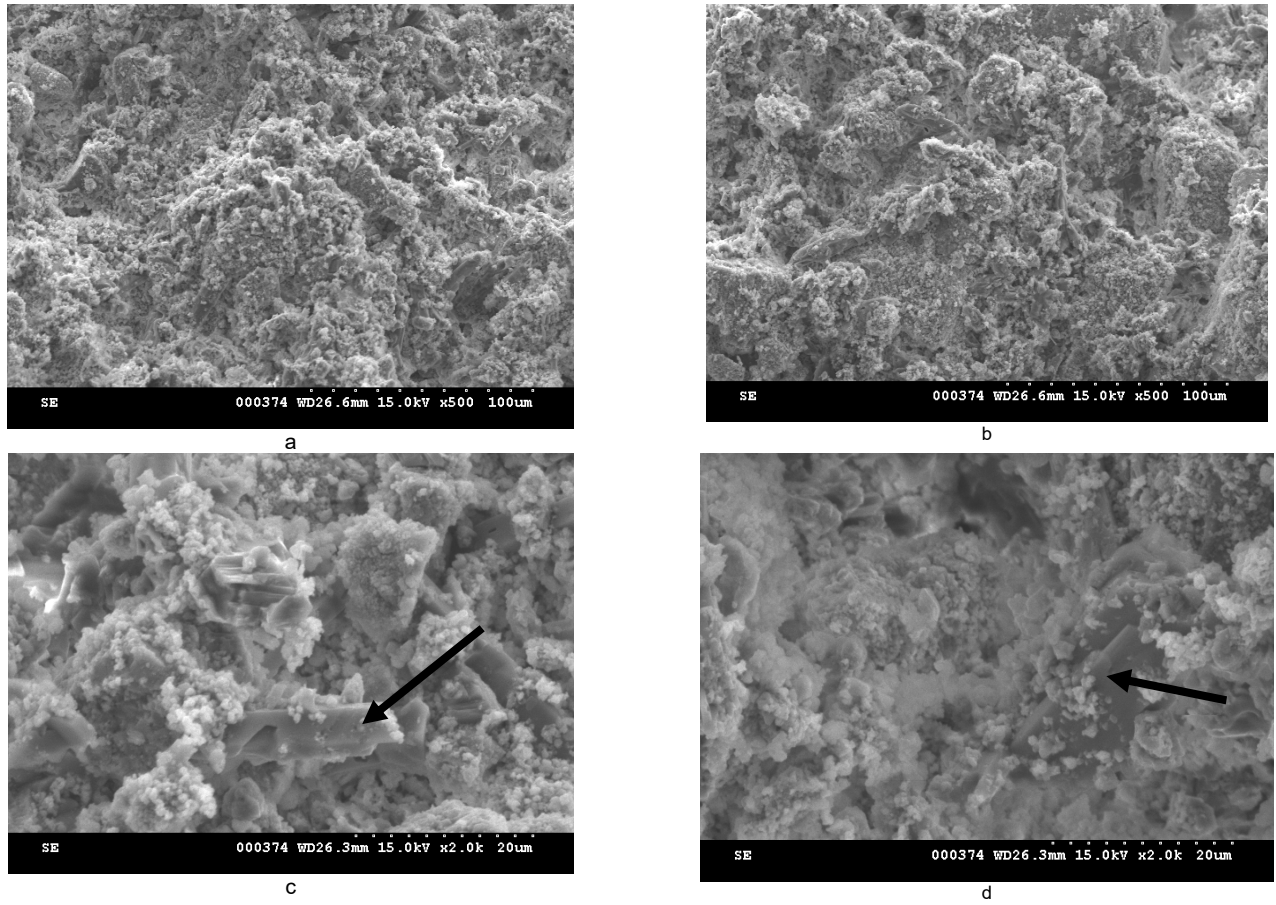


Fig.7 – SEM images of 100A hardened for 7 days / Imaginile SEM ale probei 100A după 7 zile de întărire.

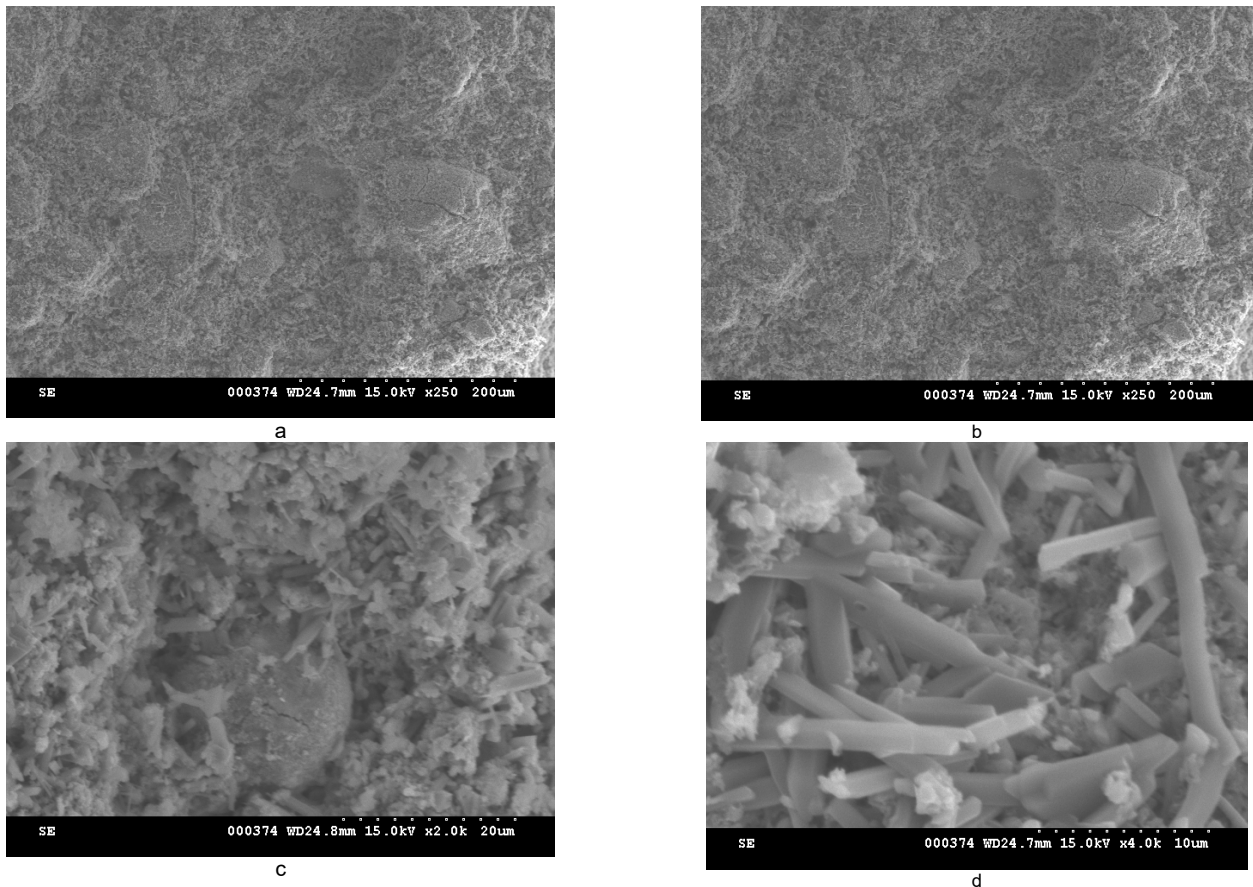


Fig.8 - SEM images of sample 100A+FeSO₄, hardened for 7 days/ Imaginile SEM ale probei 100A+FeSO₄ după 7 zile de întărire.

4. Conclusions

Based on this study the following conclusions can be drawn:

- The substitution of gypsum with 5 wt.% and 20 wt.% ash A results in an increase of the compressive strength values for both short (2 hours) and longer (7 days) curing periods; further increase of ash A dosage (30 wt.%) decreases the compressive strength values (as compared with 5A and 20A) but the values are comparable with those developed by the gypsum binder.

- The setting times of pastes with 5 wt.% and 20 wt.% ash A are much shorter as compared with the value imposed by the norm specific for gypsum binder (i.e. 20 minutes) therefore these compositions cannot be used in practice; the substitution of gypsum binder with 30 wt.% ash A further delays the setting time and the values are comparable with those specific for gypsum binder. The composition 30A fulfil the requirements of specific norms for gypsum binders and plasters.

- The rates of setting and hardening processes of ash A paste are very small, due to its specific composition i.e. anhydrite, low amount of CaO and organic substances.

- The use of accelerator additions (sulfate salts) in combination with ash A, shortens the setting time and increases the compressive strengths of paste; the setting times for 100A+K₂SO₄ and 100A+FeSO₄ pastes are closer to the values specific for portland cement i.e. initial setting time of 2-3 hours and final setting time – 5-6 hours.

- The values of compressive strength, after 7 days of hardening, of pastes based on ash A with sulfate additions increase with more that 130% (with reference to ash A paste) and are comparable with those specific for gypsum binder (I).

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