

INFLUENȚA ADAOSULUI DE CENUȘĂ DE PLOP ȘI CENUȘĂ DE SĂLCIE ASUPRA PROPRIETĂȚILOR MORTARULUI DE TENCUIALĂ

INFLUENCE OF POPLAR ASH AND WILLOW ASH ADMIXTURE ON PLASTERING MORTAR PROPERTIES

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The purpose of the present paper is to investigate the influence of ash coming from the complete burning of poplar wood and willow wood, respectively. For this purpose, plaster mortar with ash with 2 and 5% admixtures to a commercial reference mortar was prepared. The major elements in the investigated wood ash are calcium, magnesium, potassium and carbon. Sulfur, phosphorus and manganese are present at around 1%. Silicon, sodium, iron, aluminum, copper, zinc, and boron are present in relatively smaller amounts. Strong peaks corresponding to $\text{Ca}(\text{CO}_3)_2$ were identified in both ash. The willow ash contains relatively higher amounts of potassium compared to poplar ash and show strong peaks corresponding to $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Willow ash being richer in sulphur and potassium has $\text{K}_2\text{Ca}(\text{SO}_4)$. Similarly, poplar, being richer in sodium, displays very weak peaks corresponding probably to $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$ compound. The addition of ash, regardless of its nature (poplar or willow) or its amount did not contribute to the increase of the resistance of the commercial reference mortar after 3 days, 7 days or 28 days of hardening. Their role was mainly of filler together with pre-existing silica aggregates from the commercial mortar. Finally, the compressive strengths determined experimentally after 28 days of hardening place these mortars with ash admixtures below the values accepted by the starting reference mortar class. However, the use of poplar or willow ash generated after calcinations at 650°C as admixtures for binder materials in mortar seems to be effective for their recycling in plastering mortars.

Scopul prezentei lucrări este de a investiga influența cenușii provenind din arderea completă a lemnului de plop și respectiv a lemnului de salcie. În acest scop, s-au preparat mortare de tencuială cu adaos de cenușă în pondere de 2 și 5% raportat la masa unui mortar de referință comercial. Elementele majore din cenușa lemnoasă investigată sunt calciul, magneziul, potasiul și carbonul. Sulfur, fosforul și manganul sunt prezente în pondere de aproximativ 1%. Siliciul, sodiul, fierul, alumiul, cuprul, zincul și borul sunt prezente în cantități relativ mai mici. În ambele cenuși, au fost evidențiate interferențe puternice de difracție cu raze X corespunzătoare $\text{Ca}(\text{CO}_3)_2$. Cenușa de salcie conține cantități relativ mai mari de potasiu în comparație cu cenușa de plop și prezintă interferențe puternice corespunzător $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Cenușa de salcie fiind mai bogată în sulf și potasiu are în compoziția mineralogică $\text{K}_2\text{Ca}(\text{SO}_4)$. În mod similar, plopul, fiind bogat în sodiu, prezintă interferențe foarte slabe, care corespund probabil compusului $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$. Adăugarea de cenușă, indiferent de natura sa (plop sau salcie) sau de cantitatea sa nu a contribuit semnificativ la creșterea rezistenței la compresiune a mortarului de referință comercial după 3 zile, 7 zile sau 28 de zile de întărire. Rolul lor a fost în principal de umplură împreună cu agregatele de silice preexistente din mortarul comercial. În cele din urmă, rezistențele la compresiune determinate experimental după 28 de zile de întărire plasează aceste mortare cu adaosuri de cenușă sub valorile acceptate de clasa mortarului de referință. Cu toate acestea, utilizarea acestor cenuși de plop sau de salcie generată după calcinarea lemnului la 650°C ca adaosuri pentru materialele liante din mortare pare să fie eficientă pentru reciclarea lor la tencuieli.

Keywords: Ash, Willow, Poplar, Wood, Mortar, Waste Recycling

1. Introduction

In the current climate change scenario, woody energy crops appear as a very attractive way to produce lignocelluloses biomass which can be locally used in power plants and/or combined heat and power (HP) systems, thus also promoting the economic and social development of the regions involved [1]. The forestry species with the highest interest in Europe are poplar (*Populus* spp.) [2], willow (*Salix* spp.) [3], eucalyptus (*Eucalyptus* spp.) [4] and to a lesser extension, black locust (*Robinia pseudoacacia*) [5]. All of them are a fast-growing tree plantation and therefore, a

promising source of biofuel with a large potential to feed the demand of raw materials from the energy sector and other conventional industrial purposes [6]. Moreover, the *Salicaceae* family provides a valuable source of woody fuel in areas with high water availability such as those located in Northern Europe [7 -10]. Wood ashes are a source of macronutrients for plants. Their contents can be presented in the following series of decreasing values: $\text{Ca} > \text{C} > \text{K} > \text{Mg} > \text{P} > \text{S} > \text{N}$. Out of 1 t of wood ash, approx. 160 kg C, 6 kg N, 20 kg P, 98 kg K, 302 kg Ca, 39 kg Mg and 18 kg S can be introduced into the soil. The content of heavy metals in the analyzed ashes was acceptable

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according to the standards for their content in waste materials intended for liming soils. Generally, ashes contain significant amounts of basic oxides and can be used as amendment for the acidic soils [11-13]. Given the high contents of potassium, phosphorus and micronutrients, ash can also be used as a potassium-phosphorus fertilizer [14-16] or for composting sewage sludge in combination with ash for soil reclamation [12]. Starting from a promising perspective of various industrial ash valorization in the field of building materials manufacturing in conjunction with the growing concern with respect to topics related to the environment [17-24], the aim of this study was to determine the usefulness of ashes obtained following the combustion of poplar and willow wood in construction materials sector as addition to mortars. The mortars used in construction works are well homogenized mixtures of binder, water and sand (sometimes other additions), which are applied in thin layers on some substrate, which they adhere to and which they work with in operation. The hardening of the mortars leads to the obtaining of an artificial stone, with a sandstone appearance. *Ordinary mortars* are used for the binding in a monolith of natural or artificial masonry stones (masonry mortars), or for the protection, finishing and maintenance of the built surfaces (plaster and special mortars).

Masonry mortar is used in the execution of masonry; they have a variable composition depending on the nature of the masonry (load bearing, unsuitable), the nature of the stone (compact, porous), the environment in which the masonry will be found (dry, wet).

Plaster mortar, which is applied to the built surfaces, in order to protect against the weather, thermal, sound or fireproof insulation finishing.

Special mortars, which can be decorative, corrosion resistant, waterproofing, thermal insulation, refractory, for the combination of precast concrete elements.

The components of mortars have a different role and influence by their nature, quality and quantity the properties of mortars, thus determining their field of use. The binder, by binding the sand granules, gives the mortar mechanical strength, and by its nature and proportion in the mortar largely determines the workability of the fresh mortar and the hardening speed. Sand is the predominant quantitative component in the composition of mortars, having a great influence on their structure and general properties (both fresh and hardened). In the case of cement mortars, the sand contributes to reducing the shrinkage of the cement stone. The sand must meet the standard quality conditions (content of impurities, granularity, maximum grain size and shape) and the requirements imposed by the field of use and the

type of mortar. Water ensures both hydration of the binder and the workability of the fresh mortar. The water used in the preparation of mortars must comply with the quality conditions established by the standard ISO 456:2000. Additives are organic or inorganic substances, which can be used in some cases, in small quantities, to improve properties of fresh or hardened mortars. The influence of poplar ash and willow ash admixture on plaster mortar mechanical and microstructure properties was investigated.

2. Experimental

The *chemical composition* of the mortar was determined by X-ray Fluorescence (XRF) with Panalytical AXIOS X-ray fluorescence spectrometer operating at 60 KV and current of up to 160 mA with dual multi-channel analyzer (DMCA) and by using the software Super Q, analytical programs (IQ +, WROXI).

Elemental and chemical compositions of the wood ash were obtained using Inductively Coupled Plasma Emission Spectroscopy (ICPES) and X-Ray Diffraction (XRD). Samples for ICPES were prepared by first drying the ash in an oven and then dissolving approximately 100 mg of the dried ash in 4 ml of reagent grade, concentrated hydrochloric acid. The mixture was left standing for a couple of hours for complete dissolution. This solution was later diluted to approximately 100 g using distilled, deionized water so that the concentration of various elements was within the linear range of detection for the Spectrometer. The solution was analyzed for concentrations of Si, Fe, Mn, P, B, Al, Na, K, Ca, Mg, S; Zn. Samples for XRD were first finely ground and then mounted on a glass slide using an adhesive layer to hold the ash on to the glass surface. The powder was ground fine to ensure random orientation of the crystals so that there are sufficient amount of crystals to generate detectable signals at all angles and that the background noise is kept to a minimum.

Mineralogical phase analyses were performed by X-ray diffraction method with parallel beam - scanning axis $2\theta / \theta$, on bulk samples. A Shimadzu XRD 6000 diffractometer with the radiation generator tube power of 1200 W, with Cu-K α characteristic radiation ($\lambda = 1,541874 \text{ \AA}$) was employed. Scanning range (2θ) of goniometry was located between 10° and 70° , with $5^\circ/\text{minute}$ angular speed and 0.02° step.

The morphology and microcomposition of mortars and ash admixtures were analyzed by Scanning Electron Microscope- Quanta Inspect F coupled with Energy-Dispersive X-ray Spectroscopy EDXS on gold sputtered surface.

General physical characterization of cumulative average samples was focused to

Table 1

The chemical composition of the reference mortar (ME) determined by XRF spectroscopy/
Compoziția chimică a mortarului de referință (ME) determinată prin spectroscopie XRF

L.O.I	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₃ O ₄	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	V ₂ O ₅	SrO	BaO
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
22.60	68.26	0.28	6.47	1.47	0.05	0.42	19.33	2.13	1.08	0.09	0.38	0.01	0.01	0.02

L.O.I. Loss of ignition determined at 1200°C/ Pierdere la calcinare determinată la 1200°C

Table 2

The elemental composition of poplar ash& willow ash (w% of ash)
Compoziția elementară a cenușii de plop și a cenușii de salcie (în% din cenușă)

Content	Si	Ca	Al	Fe	Mg	Zn	Na	K	P	S	B	Cu	Mn
	%	%	%	%	%	%	%	%	%	%	%	%	%
Poplar ash	0.13	26.08	0.33	0.36	8.98	0.03	2.42	7.87	0.96	1.01	0.05	0.02	0.43
Willow ash	0.11	22.09	0.13	0.24	3.57	0.32	0.07	11.47	1.16	0.81	0.06	0.04	0.15



Fig. 1 - The appearance of poplar ash (a) and of the willow ash (b)
Aspectul cenușii de plop (a) și a cenușii de salcie (b).

establish the limits of variation for the basic parameters, as: moisture content (according to SR ISO 331:1994, Total moisture content), bulk density (STAS 5630-73, Determination of bulk density).

The mechanical compressive strengths were determined on cubic test bodies, with dimensions of 30x30x30 mm kept under standard conditions in air until the test age and considered as average of six individual attempts. For the determination of mechanical resistance by static compressive strength of standard mortar samples (without ash addition), respectively of mortar samples with willow and poplar ashes additions, a WPM --Werkstoffprüfsysteme Leipzig test machine (Germany) was used. During our study we followed the evolution of the compressive strength at short hardening intervals (3 days, 7 days) and at 28 days, considered the standard duration for the mortar class.

The influence of the additions of poplar ash (CP) and willow ash (CS) on the compressive strengths of a reference M20 mortar type according to GP SR EN 998-1: 2011 (coded ME) was investigated. The chemical oxide equivalent composition of the reference mortar (ME) determined by XRF analysis is shown in Table 1.

Technical characteristics of the M20 reference mortar (ME) are: setting time: 3 hours; reaction to fire class A1; maximum granulation: 1.4 mm, compressive strength: > 3.5 N / mm²,

adhesion :> 0.2 N / mm², water vapor diffusion coefficient: 5-20 mm²/s, thermal conductivity (λ10, dry): 0.54 W / m.K, Cr⁶⁺ content: <2 ppm.

2.1 Admixtures of wood ash

2.2.1. Elemental composition of poplar ash and willow ash was determined by ICPES spectroscopy is shown in Table 2. The particle size distribution for poplar ash is as follows: d₁₀ at 3.17 μm, d₅₀ at 23.85 μm, and d₉₀ at 40.33 μm. Willow ash had the particle size distribution detail as follows: d₁₀ at 2.47 μm, d₅₀ at 46.02 μm, and d₉₀ at 99.53 μm.

The major elements in the wood ash are calcium, magnesium and potassium. Sulfur, phosphorus and manganese are present at around 1%. Silicon, sodium, iron, aluminum, copper, zinc, and boron are present in relatively smaller amounts. The aspect of the poplar ash and willow ash used in our experimental works is shown in Fig.1 (a, b).

2.2.2. Structural and morphological analyzes of wood ash

X-ray diffraction analyzes were performed in order to see the possible phase differences that could occur due to the addition of ash in some mortar binder materials. The ash used as additives were of two types, namely from the complete burning of poplar wood waste, respectively willow.

Typical XRD patterns at temperatures of 650 °C are shown in Fig.2. Strong peaks corresponding to $\text{Ca}(\text{CO}_3)_2$ were identified in both ashes. The willow ash contains relatively higher amounts of potassium compared to poplar ash and show strong peaks corresponding to $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Willow ash being richer in sulphur and potassium has $\text{K}_2\text{Ca}(\text{SO}_4)$. Similarly, poplar, being richer in sodium, displays very weak peaks corresponding probably to $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$ compound. It appears that when the ash is left standing in air, calcium oxide reacts with atmospheric water vapor to form calcium hydroxide; however calcium hydroxide is unstable at temperatures over 600°C.

2.2.3 SEM and X-ray energy dispersion spectroscopy (EDAX) analysis

In order to be able to understand the curing behavior of the mortars as well as the evolution of the mechanical resistances at different curing periods, the morphological identification of the phases was performed. Because the important aspect was related to the final behavior of the reinforced material, these analyzes were performed exclusively on the 28-day hardened samples, whose mechanical resistance to compression also gives the product brand. The comparative analysis is in this case more useful as it was worked with a standardized, commercial mortar. Fig.3 shows the SEM image

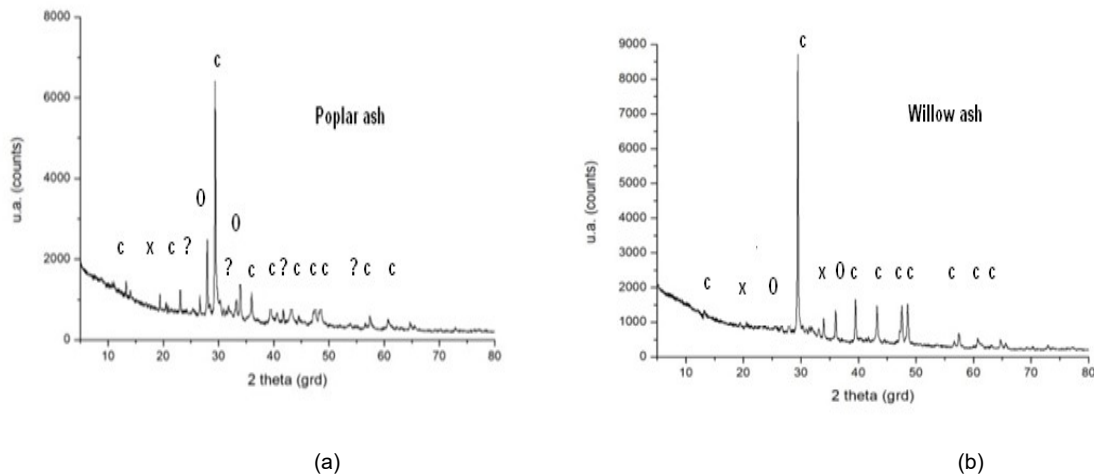


Fig.2 - X- ray diffraction pattern for poplar ash (a) and willow ash (b) respectively / Diffractograma cu raze X pentru cenușa de plop (a), respectiv pentru cenușa de salcie (b).
Legend: c- CaCO_3 , 0 – $\text{K}_2\text{Ca}(\text{CO}_3)_2$, x- $\text{K}_2\text{Ca}(\text{SO}_4)$, ?- $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$

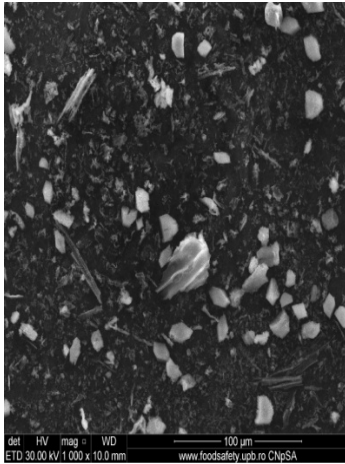


Fig.3 - SEM image of poplar ash / Imaginea SEM a cenușii de plop.

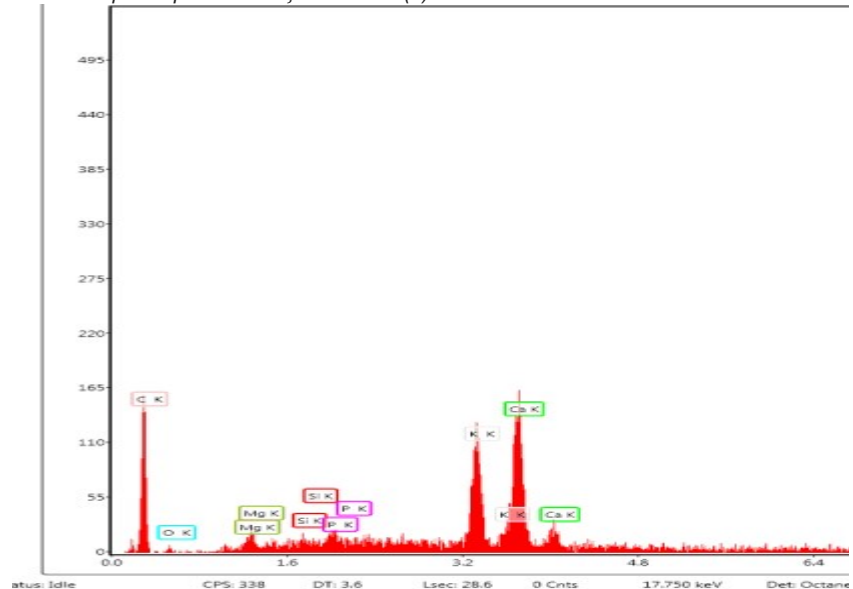


Fig.4 - EDAX spectrum of poplar ash / Spectrul EDAX pentru cenușa de plop.

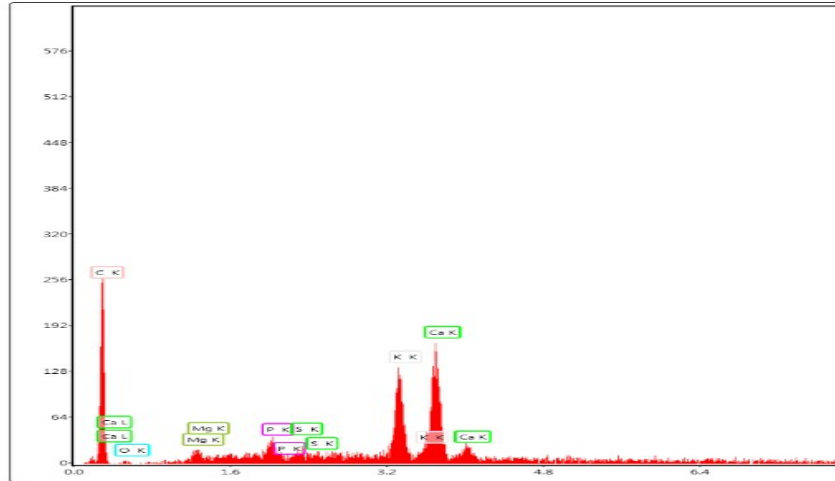


Fig.5. - SEM image of willow ash
Imaginea SEM a cenușii de salcie.

Fig.6 - EDAX spectrum of willow ash / Spectrul EDAX pentru cenușa de plop.

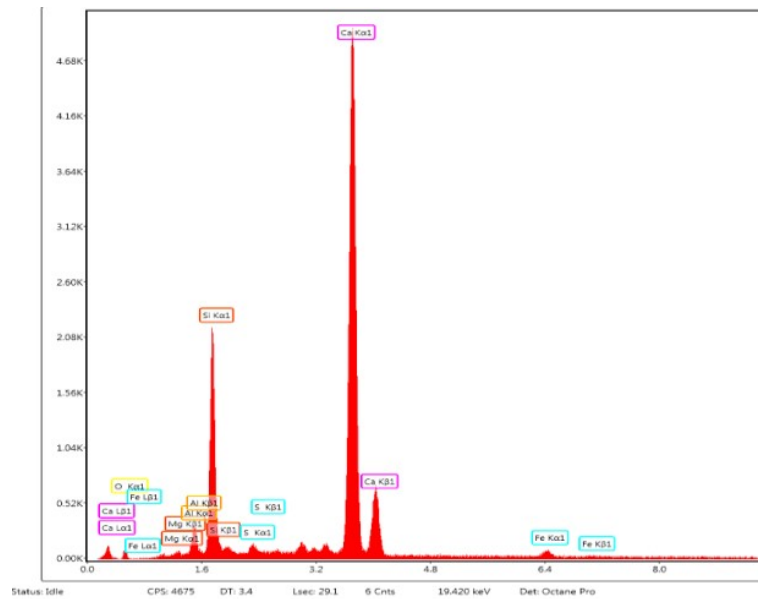
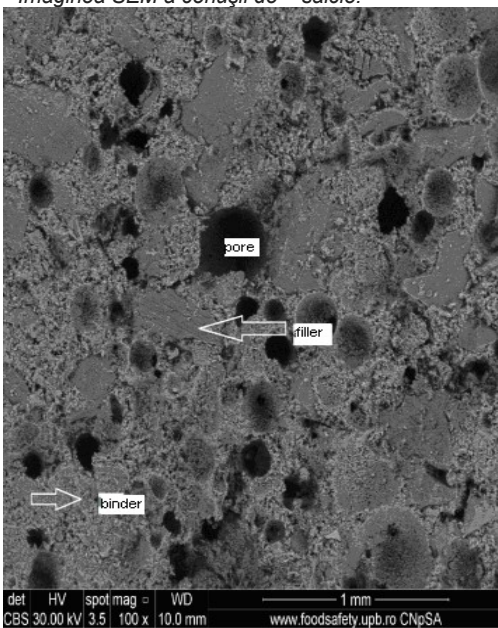


Fig.7 - SEM image on fracture surface of reference mortar ME
Imaginea SEM pe suprafața de rupere a mortarului de referință ME.

Fig.8 - EDAX spectrum on fracture surface of reference mortar ME / Imaginea SEM pe suprafața de rupere a mortarului de referință ME.

of poplar ash, obtained after combustion in a rotary oven at 650°C. We can observe the various phases existing in the analyzed ash where unburned carbon fibers are next to crystalline phases which have been identified by X-ray analysis and presented above. Elemental analysis (see Fig.4) highlighted the presence of carbon together with several elements such as Ca, Si, K, Mg, P and O, constituents of inorganic salts or complex oxides determined by X-ray diffraction. - have been integrated in the mineralogical products formed at the mortar hardening, except for carbon fibers and residue. The willow ash, as mentioned above, is practically no different from the poplar ash phase. Fig.5 shows the SEM image of willow ash resulting from burning at 650°C. There are

several very visible differences in relation to poplar ash, especially since the burning of the wood material occurred at a lower temperature. Thus, as in the case of poplar ash, the crystalline phases due to salts formed or already existing in the willow can be clearly distinguished prior to the combustion process and which are like those of poplar ash, as demonstrated by X-ray diffraction analysis.

The carbon phases are distinguished with great clarity, in the almost natural form and where the gaps left by the nutrient transport vessels within the plant can be highlighted. These fragments are quite large, in the order of tens of microns, but they are extremely fragile and therefore their size is expected to decrease with the mixing process after integration into the mortar.

Their existence also justifies the need to use a higher amount of mixing water to obtain a normal consistency of the mortar at the start, some of the water being physically absorbed in the capillaries of carbon fibers and which prevents its participation in hydration-hydrolysis reactions typical of cement mortar. Elemental analysis of EDAX performed on willow ash reveals the same elements, in principle as in the case of poplar ash. The EDAX spectrum of the elemental analysis for willow ash is shown in Fig. 6. The only notable difference in this case is the presence of sulfur and the lack of silica, but these probably depend on the structural nature of the wood origin. One can remark that oxygen and carbon are also present, but were not determined by ICPEs.

2.2.4. Reference mortar (no ash content)

Fig.7 shows the SEM image of the reference mortar hardened 28 days and has undergone compression until breaking. In the fractured section can be seen how the aggregate (usually sand and carbon particles) of various shapes and sizes are distributed almost evenly in the binder matrix (cement paste). Also, typical of mortars, there is also certain porosity, where the average pore size varies approximately in the range of 18-120 microns. This porosity is necessary if we think that the applications of mortars are usually made on surfaces that require adhesion and the capillary forces are pronounced strongly at the pore level of the hardened material. The particle distribution mode of the aggregate in the binder mass is clearly observed from the EDAX spectrum performed on the standard sample (see Fig.8) but especially from the mapping made on the breaking surface of the same standard sample.

Fig.9 shows a detail of an area of the SEM image shown in Fig.7. One can be seen the aggregate granules, mainly sand containing silicon dioxide but also minor phases with iron content (impurities existing in natural aggregates).

2.2.5. Preparation of experimental mortars

In order to study the influence of ashes admixtures on mortar hardening properties used, four types of compositions were used in addition to the standard (ash-free mortar-ME), namely with 2%, 5% poplar ash (coded MCP2 and MCP5), respectively with willow ash (coded MCS2 and MCS5). These compositions were all derived from the standard composition of the M20 mortar (commercially available). The dosage of the mortars prepared with ash admixtures in which, each amount is expressed gravimetrically is shown in Table 3. The amount of water needed to prepare mortars, as this depends largely on the nature and fineness of the sand, as well as on the absorption capacity of the substrate and must be the one required to ensure the consistency imposed by the application conditions.

The casting masses were made by gravimetric dosing of the solid components and by volumetric dosing of the water, followed by manual homogenization for 10 minutes in batches of 500 grams of mortar of the reference M20 plaster mortar to which the water respectively the ash additions was added according to dosage recipes (see Table 2). The homogenized mortar batches of 500 g were poured into metal mould with 10 nests of cubes of 30x30x30 mm was obtained. The molded samples were compacted on the vibrating

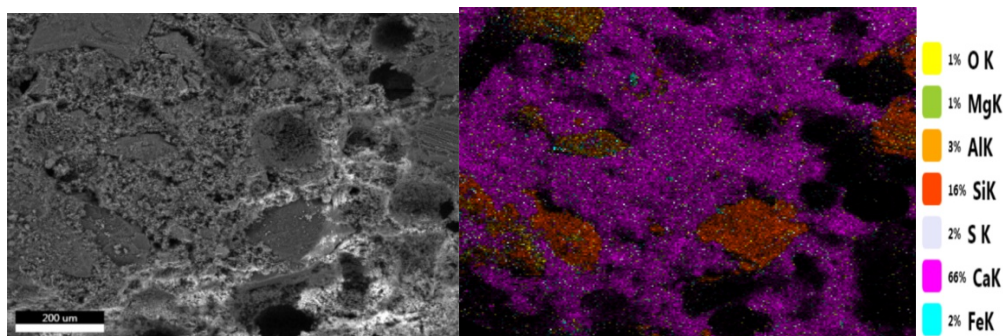


Fig.9- Mapping of elemental distribution on hardened reference mortar surface/*Distribuția elementelor pe suprafața mortarului de referință*

Table 3

Component dosage of the experimental mortars with ash additions
Dozarea componentelor mortarelor experimentale cu adaosuri de cenușă

Nr. crt.	Water (g/500 g solid batch)	Reference mortar ME %	Poplar ash admixture (% over 100% solid ME)	Willow ash admixture (% over 100% solid ME)
ME	100	100	0	0
MCP2	110	100	2	0
MCS2	110	100	0	2
MCP5	130	100	5	0
MCS5	130	100	0	5

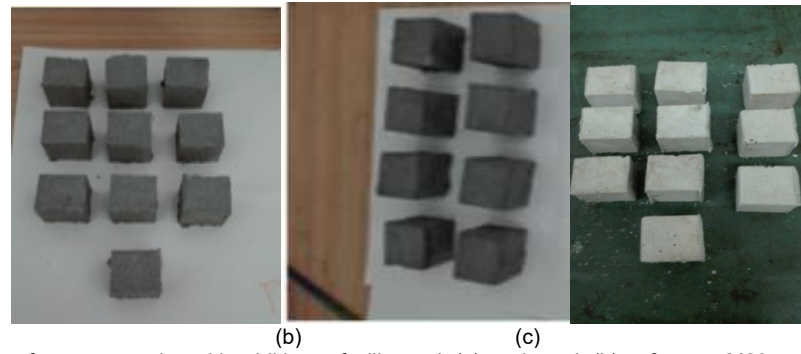


Fig. 10 - Appearance of mortar samples with additions of willow ash (a) poplar ash (b), reference M20 mortar (c)
 Apariția probelor de mortar cu adăugare de cenușă de salcie (a) cenușă de plop (b), mortar de referință (c)

table in three sequences of 45 seconds each until a smooth surface on the surface of the mortar as seen in Fig. 10.

3. Results and discussion

The main properties of hardened mortars are the mechanical resistance, drying shrinkage, freeze-thaw resistance and adhesion to the support.

3.1. Compressive strength

The mechanical resistance to compression and bending depends on several factors, such as: nature of components, dosage, conservation conditions, etc.

In our work we have investigated the mechanical, microstructure and morphological evolution of mortars with willow ash poplar ash additions respectively after 3 days, 7 days and 28 days of hardening. The evolution of the compressive strength after 3 days of hardening of the experimental samples made with poplar ash (MCP2, MCP5), respectively with willow ash (MCS2, MCS5), comparatively to the reference plaster mortar (ME) is presented in Fig.11.

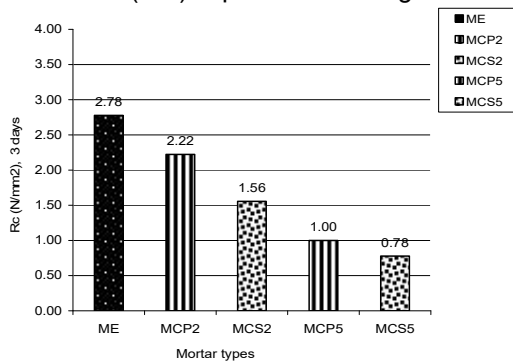


Fig.11 - Evolution of the compressive strength of the experimental samples made with poplar ash (MCP2, MCP5), respectively with willow ash (MCS2, MCS5), compared to the reference plaster mortar (ME) after 3 days of hardening / Evoluția rezistenței la compresiune a probelor experimentale realizate cu cenușă de plop (MCP2, MCP5), respectiv cu cenușă de salcie (MCS2, MCS5), comparativ cu mortarul de referință (ME) după 3 zile de întărire.

The experimental data show that after 3 days of hardening, the ash content in mortars cause a decrease of the mechanical strengths regardless of their type and dosage. However, a more pronounced effect in this regard is recorded for the willow ash. As the amount of ash in the mortar composition increases, a more pronounced decrease in mechanical strength is observed (for example, in the case of MCP5 mass it drops by ~ 2.8 times, and in the case of MCS5 mass it decreases by ~ 3.6 times).

The evolution of the compressive strength after 7 days of hardening of the experimental samples made with poplar ash (MCP2, MCP5); respectively with willow ash comparatively to the standard plaster (ME) mortar is given in Fig.12.

The experimental data show that after 7 days of hardening, the mortars with the increase of ash content also determine a decrease of the mechanical strengths regardless of their type and concentration. However, a more pronounced effect in this regard has the poplar ash. As the weight of the ash in the mortar composition increases, a more pronounced decrease in mechanical strength is observed (for example, in the case of MCP5

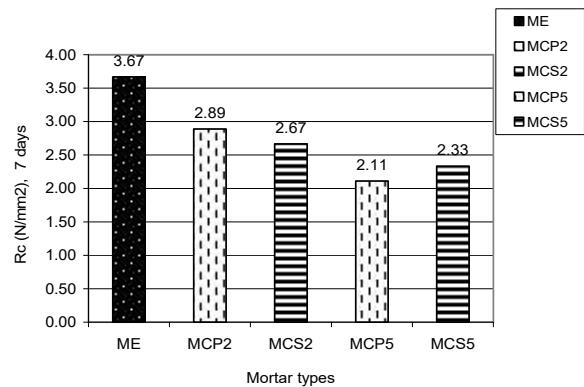


Fig.12 - Evolution of the compressive strength of the experimental samples made with poplar ash (MCP2, MCP5), respectively with willow ash (MCS2, MCS5), compared to the reference plaster mortar (ME) after 7 days of hardening / Evoluția rezistenței la compresiune a probelor experimentale realizate cu cenușă de plop (MCP2, MCP5), respectiv cu cenușă de salcie (MCS2, MCS5), comparativ cu mortarul de referință (ME) după 7 zile de întărire.

mass it drops by ~ 1.7 times, and in the case of MCS5 mass it decreases by ~ 1.6 times).

After 28 days of hardening of the experimental samples made with poplar ash (MCP2, MCP5), respectively with willow ash (MCS2, MCS5) comparatively with the standard plaster (ME) mortar, the evolution of the compressive strength is represented in Fig. 13.

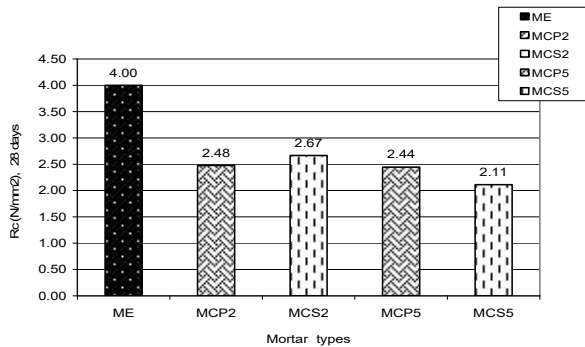


Fig.13 - Evolution of the compressive strength after 28 days of hardening of the experimental samples made with poplar ash (MCP2, MCP5), respectively with willow ash (MCS2, MCS5), 2% and 5% by weight dry component) compared to the reference plaster (ME) mortar / *Evoluția rezistenței la compresiune a probelor experimentale realizate cu cenușă de plop (MCP2, MCP5), respectiv cu cenușă de salcie (MCS2, MCS5), comparativ cu mortarul de referință (ME) după 28 zile de întărire.*

The experimental data show that after 28 days of hardening, the ash content mortars also cause a decrease of the mechanical strengths regardless of their type and concentration. However, a more pronounced effect in this regard is the poplar ash. As the weight of the ash in the mortar composition increases, a more pronounced decrease in mechanical strength is observed (for example, in the case of MCP5 mass it drops by ~ 1.6 times, and in the case of MCS5 mass it decreases by ~ 1.9 times).

The appearance on XRD spectrum at small angles of poplar ash and willow ash indicates the possible presence of a non-crystalline, glassy phase, which most likely integrated the rest of the detected microelements. The identified phases are not hydraulically active, and therefore do not contribute to the formation of hardening structure through hydration - hydrolysis reactions together with the mineral components in the cement.

It should be noted that the possible carbon residues in ash are not detectable by X-ray diffraction but are highlighted by scanning electron microscopy (SEM) analysis and further by X-ray energy spectroscopy (EDAX). These residues do not interact with the oxide phases or with hydration-hydrolysis products having the simple filler role. Their presence may affect the mechanical characteristics of hardened mortars. Their role was only filler (aggregate) along with pre-existing aggregates in the reference mortar. The lack of interactions at the interface with the binder (cement in this case) a kind of delaminating that not only does not contribute to the development of resistance structures but can provided stress concentration points that subsequently affect the mechanical strengths. Probably for this reason, the mechanical strengths determined experimentally after 28 days of hardening place these mortars with ash additions below the values accepted by the mortar class. The aspect of the breaking surface is almost similar to the standard mortar, in the sense that the binder phases can be distinguished, as regards the aggregate, it has a similar appearance to that of the standard but in addition small integrated carbon residues (grey colour) can be observed in the formed cement stone. As with poplar ash additives, willow ash additives have a similar quasi-morphological structure. Thus, in the EDAX mapping images shown in Fig. 14 and Fig.15 for

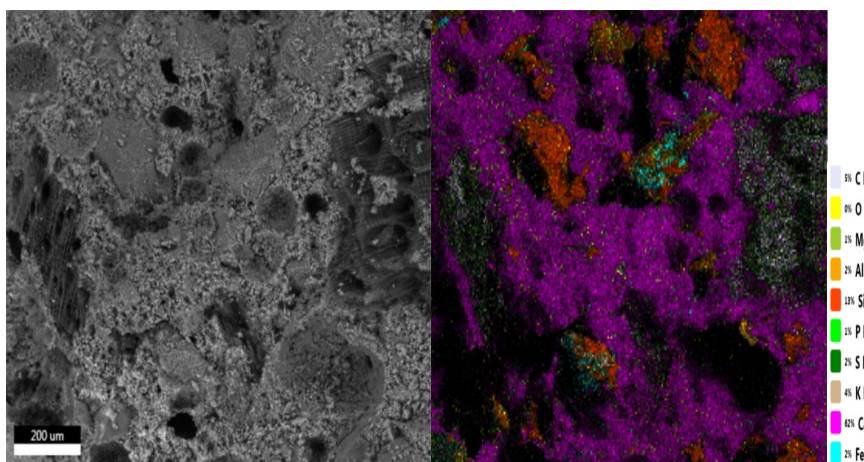


Fig.14 - SEM image and EDAX mapping on MCS2 mortar (with 2% willow ash) fractured after 28 days of hardening / *Imagine SEM și distribuția elementorevidențiate prin tehnicaEDAX pe mortarul MCS2 (cu 2% cenușă de salcie) după 28 de zile de întărire.*

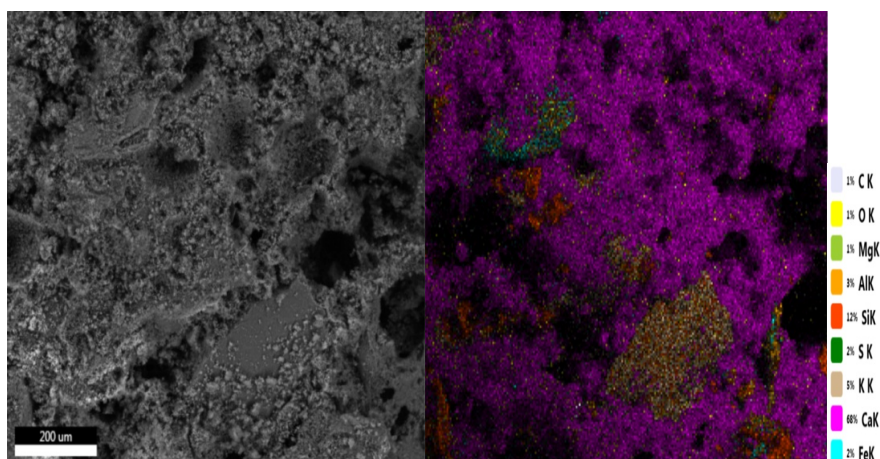


Fig.15 - SEM image of the MCS5 mortar with 2% poplar ash fractured after 28 days of hardening/ Imagine SEM și distribuția elementelor prin EDAX pe mortarul MCS2 (cu 2% cenușă de plop) după 28 de zile de întărire

the mortars with 2% ash, where the same types of aggregates distributed evenly in the binder matrix can be observed. The aspect in this case is the fact that the carbonic remains in the mortar appear clearly, being obviously individualized in the cement stone. It can also be observed that the structure of the carbon residues retains the capillary structure of the initially woody tissue, probably due to the lower calcinations temperature from which the ash resulted.

4. Conclusion

The ash used as additives were of two types, namely from the complete burning of poplar wood waste, respectively willow. The major elements in these woods ash are calcium, magnesium, potassium and carbon. Sulfur, phosphorus and manganese are present at around 1%. Silicon, sodium, iron, aluminum, copper, zinc, and boron are present in relatively smaller amounts. The major elements in the investigated wood ash are calcium, magnesium, potassium and carbon. Sulfur, phosphorus and manganese are present at around 1%. Silicon, sodium, iron, aluminum, copper, zinc, and boron are present in relatively smaller amounts. Strong peaks corresponding to $\text{Ca}(\text{CO}_3)_2$ were identified in both ash. The willow ash contains relatively higher amounts of potassium compared to poplar ash and show strong peaks corresponding to $\text{K}_2\text{Ca}(\text{CO}_3)_2$. Willow ash being richer in sulphur and potassium has $\text{K}_2\text{Ca}(\text{SO}_4)$. Similarly, poplar, being richer in sodium, displays very weak peaks corresponding probably to $\text{Na}_2\text{Ca}(\text{SiO}_2)_3$ compound. The appearance on XRD spectrum at small angles of poplar ash and willow ash indicates, the possible presence of a non-crystalline, glassy phase, which most likely integrated with the rest of the detected microelements was detected. The identified phases are not hydraulically active, and therefore do not contribute to the formation of hardening structure through hydration - hydrolysis reactions together with the mineral components from the cement.

It should be noted that the carbon residues in ash are not detectable by X-ray diffraction but are highlighted by scanning electron microscopy (SEM) analysis and further by X-ray energy spectroscopy (EDAX). These residues do not interact with the oxide phases or with hydration-hydrolysis products having the simple filler role. Their presence may affect the mechanical characteristics of hardened mortars.

The addition of ash, regardless of its nature (poplar or willow) or its amount did not contribute to the increase of the resistance of the commercial reference mortar after 3 days, 7 days or 28 days of hardening. Their role was mainly of filler together with pre-existing silica aggregates from the commercial mortar. Finally, the compressive strengths determined experimentally after 28 days of hardening place these mortars with ash admixtures below the values accepted by the starting reference mortar class. However, the use of poplar or willow ash generated after calcinations at 650°C as admixtures for binder materials in mortar seems to be effective for their recycling in plastering mortars.

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ANIVERSĂRI



20 septembrie (1459) – Ziua orașului București

La această dată se împlinesc 560 de ani de la prima atestare documentară a existenței Orașului București, într-un hrisov emis de cancelaria voievodului Vlad Țepeș. În ordine cronologică, orașul București a devenit treptat, în secolele următoare, cea de a patra capitală a Țării Românești a Munteniei (dupa Câmpulung, Curtea de Argeș și Târgoviște) și prima capitală a României Mari după Războiul de Întregire Națională din 1916 – 1918.