PROSPECTS FOR THE USE OF GYPSUM WASTE FOR THE PRODUCTION OF BUILDING GREEN CERAMICS

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Abstract

The study considers the prospects of using large-scale wastes of gypsum molds from the ceramic industry and phosphogypsum to produce blocks/bricks for the construction industry. The technology was based on the principle of obtaining gypsum concrete. To initiate the binding properties of gypsum wastes, they were subjected to low-temperature treatment in the range of 200-300 °C. Additionally, phosphogypsum was subjected to neutralization without subsequent washing from newly formed compounds. Compressive strength tests of samples showed that for mixtures of Portland cement-gypsum molds $F_{comp.}$ varies from 170 to 90 kg/cm^2 at a cement content of 90-10 wt%. For mixtures of Portland cement-phosphogypsum $F_{comp.}$ varies from 150 to 100 kg/cm^2 at a content of 90-60 wt% cement. For comparison, similar mixtures of Portland cement and commercial semi-aqueous gypsum were prepared.

Keywords: Portland cement, waste gypsum molds, phosphogypsum, glass fibers, concrete, green ceramics

1.   Introduction

Gypsum in the form of $CaSO_4 \cdot 0.5H_2O$ and $CaSO_4$ is widely used both in construction [1-4] and in the production of fine ceramics (porcelain, semi-porcelain, faience, etc.) [5], when slip is poured into gypsum molds. As a result, the production and use of gypsum products is accompanied by the accumulation of large volumes of waste. As a rule, gypsum wastes are represented by $CaSO_4 \cdot 2H_2O$. One of the most important properties of such gypsum wastes is the relative ease of obtaining new (secondary) binders from them, namely, $CaSO_4 \cdot 0.5H_2O$ [4, 6, 7]. It is known that primary dihydrate calcium sulfate ($CaSO_4 \cdot 2H_2O$) when heated in the temperature range of 140–170 °C turns into hemihydrate calcium sulfate ($CaSO_4 \cdot 0.5H_2O$). However, for waste from spent gypsum molds, as established in [4], the transition temperature ($CaSO_4 \cdot 2H_2O$) → ($CaSO_4 \cdot 0.5H_2O$) can reach 300 °C due to the accumulation of electrolyte solutions introduced into the clay to liquefy it by the gypsum matrix. This feature of gypsum waste should be taken into account for the complete conversion of $CaSO_4 \cdot 2H_2O$ into $CaSO_4 \cdot 0.5H_2O$.

Phosphogypsum is a by-product of the production of phosphorus-containing mineral fertilizers and phosphoric acid [8]. These large-tonnage wastes are removed from the territories of enterprises to sludge storages, which turn out to be environmental pollutants. Phosphogypsum contains from 80 to 98% gypsum and can be classified as a gypsum raw material, so the most promising areas for the utilization of phosphogypsum is its use in the production of gypsum binders. However, the presence in their composition of acidic fluorine- and phosphorus-containing impurities, which pass into the gaseous phase during heat treatment, significantly complicates the direct use of phosphogypsum as a high-temperature or low-temperature binder. To overcome the negative impact of steam and gas emissions on the environment in the technological process of obtaining "pure gypsum", as a rule, procedures are used to neutralize and wash off waste phosphogypsum [9, 10]. This leads to significant capital and energy costs and hinders the large-scale processing of this type of waste.

Phosphogypsum can be used in the cement industry to produce Portland cement, as well as a mineralizer during firing and an additive in clinker grinding [11]. Phosphogypsum can be used as an additive and filler in mixed binders without the use of heat treatment to obtain phospho concrete [12, 13].

The aim of the work was to study the properties of unfired building blocks/bricks obtained both on the basis of Portland cement and waste gypsum molds, and Portland cement and phosphogypsum subjected to the neutralization of aggressive acid-base properties, but without washing off the newly formed compounds.

2. Preparation of specimens

In this work, we investigated the properties of samples obtained from three types of mixtures: a. portland cement-commercial gypsum ($CaSO_4 \cdot 0.5H_2O$); b. portland cement - $CaSO_4 \cdot 0.5H_2O$), obtained during the processing of gypsum mold waste; c. Portland cement - ($CaSO_4 \cdot 0.5H_2O$), obtained by processing phosphogypsum.

To obtain semi-aqueous gypsum from spent gypsum molds (option b), the latter were crushed and then subjected to heat treatment at 300 ºC to convert ($CaSO_4 \cdot 2H_2O$) to ($CaSO_4 \cdot 0.5H_2O$) [4]. To obtain semi-aqueous gypsum from phosphogypsum (option c), these wastes were also ground, then neutralized with $CaO/Ca(OH_2)$ to obtain Ph = 6 - 7. This powder was subjected to heat treatment at 200°C for 2 h to transfer ($CaSO_4 \cdot 2H_2O$) in ($CaSO_4 \cdot 0.5H_2O$).

Water was added to homogenized powder mixtures of Portland cement-$CaSO_4 \cdot 0.5H_2O$ to obtain molding pastes. As the content of hemihydrate gypsum increased, the water content was increased from 35 ml to 50 ml per 100 g of the mixture (or water/solid changed from 0.35 to 0.5). The 10 g of glass fiber 2 cm long and 0.1 mm thick were introduced into the molding pastes. The resulting pasty mixtures were poured into molds 2x2x2 cm in size. After hardening, the samples were removed from the molds. The properties of the samples were studied after exposure to air for 72 h.

The obtained specimens were investigated by the X-ray diffraction (XRD) method in Cu Kα radiation (Siemens D-500 diffractometer). Electron microscopy study and electron-probe microanalysis were performed with the use of installations SU1510 HITACHI, and Oxford X-Act. The mechanical properties of the ceramics were by standard investigation techniques [14]. The hydrogen index (pH) was determined with the use HANNA instrument HI2550 pH/ORP&EC/TDS. The water absorption was determined by the formula: W, % = $[(P_1 – P_0)/ P_0] \cdot 100$, where P_0 is the initial weight of a specimen and P_1 is the weight of the specimen after water absorption. To determine the leaching of the samples, the destroyed samples were boiled in distilled water for 2 h.

3. Results and discussion

3.1.X-ray data

It has been found that in all mixtures, as the cement content in the mixture increases, the intensity of the two-water gypsum ($CaSO_4 \cdot 2H_2O$) peaks decreases and the intensity of the $Ca_2SiO_3(OH)_2$ or C-S-H peaks increases (see **Fig. 1**). Along with these main phases, there are a number of other hydro silicates of various compositions, the content of which is much lower. The phase composition of samples obtained from mixtures a-c containing gypsum components of various origins is almost identical. The differences are only in the intensity of the peaks, that is, in the content of these phases (see **Fig. 2**).

3.2 SEM/EDS data

Fig. 3 shows that samples with different content components are a set of agglomerates of different sizes. As the gypsum content increases, a looser structure is formed. Such a transformation of morphology should lead to a decrease in the strength of the samples and an increase in water absorption.

Fig. 4 a shows the glass fibers present in the samples, and **Fig. 4 b** shows the change in the content of the main elements of the elements: Ca, S, and Al. The decrease in the aluminum content is consistent with the decrease in the content of Portland cement in the samples. Since Ca and S are present in both components of mixtures, the change in their content reflects only the total value of these elements

3.3. Water absorption of specimens and corrosion stability

In **Fig. 5** it can be seen that with a high content of Portland cement in the initial mixtures (90-50 wt.%), water absorption (W) is largely determined by the cement component of the compositions. However, as the content of Portland cement in

mixtures decreases (40-10 wt.%), the amount of water absorption increases significantly. This is due to the fact that the gypsum component of the mixtures is less stable in the aquatic environment. This is most clearly manifested during prolonged boiling of the samples (see **Fig. 6**), which can be considered as a test for the corrosion resistance of the samples.

Some differences in the W value of samples obtained from different mixtures (see Fig. 5a-c) depend on the properties of the gypsum component used, and ultimately on the temperature of the conversion of $CaSO_4 \cdot 2H_2O$ to $CaSO_4 \cdot 0.5H2O$ [4]. It can be assumed that with the complete transformation of waste gypsum dihydrate into hemihydrate gypsum, the water absorption will decrease.

Since the absorption properties of ceramics/products depend on the system of open pores in the material under study, it can be concluded that in the area of concrete formation (90-50 wt.% Portland cement) the corrosion resistance of the material is significantly higher than in the area of gypsum material formation (40-10 wt .% Portland cement).

The durability and strength of concrete and brick materials depend on the development of physicochemical and chemical corrosion processes [14]. These types of corrosion are largely dependent on the composition of the mineral components that form the solid/product.

Corrosion resistance testing of samples of Portland cement-gypsum hemihydrate under extreme conditions (boiling water) revealed leaching of both the cement and gypsum components (see **Table 1**). This is evidenced by the invariance of the pH of the aqueous solution during the processing of various compositions of Portland cement-gypsum components. According to [15], corrosion occurs due to the release of $Ca(OH)_2$. It is the leaching process that causes an increase in the porosity of the material. However, a significant increase in water absorption and porosity when processing samples with a high content of the gypsum component indicates active leaching of the gypsum component as well (see **Figs. 5, 6**). As a result of the leaching of the main components of the mixtures (Portland cement and gypsum), there is an apparent increase in the content of glass fibers in the samples (see **Fig. 6**). It can be concluded that the effect of the destruction of the macrostructure of the composite material depends on the ratio of the components.

3.4. Strength properties of specimens

Compressive strength tests of samples showed (**Fig. 7**) that as the content of the gypsum component in the initial mixtures $F_{comp.}$ decreases. Samples obtained using virgin (commercial) $(CaSO_4) \cdot 0.5H_2O$ have the best characteristics (**Fig. 7 a**). Depending on the content of semi-aqueous gypsum, it is possible to obtain concretes that can be used for laying foundations with a low load ($F_{comp.} \sim$ 100-120 kg/cm²), for concreting load-bearing structures of low-rise buildings ($F_{comp.} \sim$ 130-160 kg/cm²), for the installation of monolithic foundations and ceilings, buildings of normal height, concreting of retaining walls ($F_{comp.} \sim$ 190-300 kg/cm²). Samples containing $\sim$10 wt.% $(CaSO_4) \cdot 0.5H_2O$ have the best strength properties. From such mixtures it is possible to obtain concrete intended for devices of critical structures ($F_{comp.} \sim$ 330 kg/cm²). At the same time, mixtures with a Portland cement content of 10-50 wt.% are suitable for the manufacture of brick products for various purposes.

When using waste from gypsum molds and phosphogypsum, the compressive strength of the samples is significantly lower than in the previous case (see **Fig. 7 b, c**). If from mixtures (90-10) wt.% Portland cement - (10-90) wt.% waste gypsum molds, you can get samples with a strength that satisfies wall brick products for various purposes, then from mixtures (90-10) wt.% Portland cement - (10-90) wt.% phosphogypsum To obtain wall bricks, mixtures containing only (10-40) wt.% phosphogypsum should be used.

4. Conclusions

The basis for obtaining unfired/green ceramics is the principle of preparing composite mixtures from Portland cement and large-tonnage wastes of gypsum molds of ceramic production and phosphogypsum. The conducted studies have shown that:

• when using these types of waste, it is necessary to carry out their low-temperature treatment in the range of 200-300 ºC to transform $(CaSO_4 \bullet 2H_2O) \rightarrow (CaSO_4 \bullet 0.5H_2O)$ and the neutralization of the acidic properties of phosphogypsum by the introduction of $CaO/Ca(OH)_2$ aqueous solution up to pH = 6- 7 without subsequent washing from newly formed soluble and insoluble compounds;

• By changing the content of secondary $CaSO_4 \cdot 0.5H_2O$ in Portland cement, it is possible to obtain building blocks-bricks of various strengths. For Portland cement-gypsum mold waste composites, the content of the gypsum component can be changed from 10 to 90%. For composites Portland cement-phosphogypsum waste the content of the gypsum component can be changed from 10 to 40%;

• to increase the compressive strength of unfired ceramics in a mixture of Portland cement-gypsum waste, fibrous material of various types, such as glass fibers, should be introduced;

The developed non-firing technology is not only energy-saving and water-saving, simple in technological design but also ensures environmental sustainability, preventing soil and water pollution.

Figure captions

Fig. 1. X-ray patterns of specimens obtained from different mixtures of $(CaSO_4) \cdot 0.5H_2O$-Portland cement. (a) mixtures from industrial materials. For (b, c) the $(CaSO_4) \cdot 0.5H_2O$ obtained from the treatment of wastes.

Fig. 2. Change of peaks intensity of $(CaSO_4) \cdot 2H_2O$ and $Ca_2SiO_3(OH)_2$ (b) depending on the content of portland cement and $(CaSO_4) \cdot 0.5H_2O$ in mixtures.

Fig. 3. SEM image of fracture surfaces of samples with different content of cement and gypsum components. a) Portland cement- commercial gypsum; b) Portland cement- molds gypsum; c) Portland cement- phosphogypsum.

Fig. 4. SEM image of the fracture surface of the specimen with 50 wt.% Portland cement - 50 wt.% phosphogypsum (a), and (b-d) changes in elements content on the fracture surface of specimens.

Fig. 5. Changes in the water absorption of samples depending on the composition of the initial mixtures. For specimens Portland cement- commercial gypsum mixtures (a); for specimens Portland cement- molds gypsum mixtures (b); for specimens Portland cement- phosphogypsum mixtures (c).

Fig. 6. SEM images of specimens after boiling in water for 2 h.

Fig. 7. Change in the compression (a–c) strength of specimens depending on the initial composition of mixtures. (a) for initial mixtures of Portland cement-commercial gypsum; (b) for initial mixtures of Portland cement-waste plaster molds; (c) for initial mixtures of Portland cement-waste phosphogypsum.
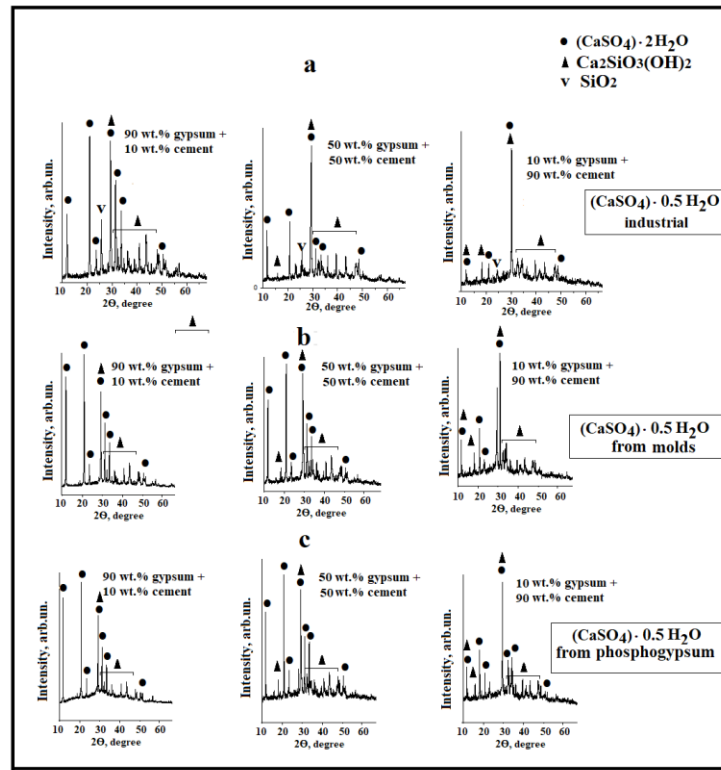
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Table 1. pH values of water after boiling destroyed samples for 2 h.

Composition x wt.% cement- y wt% gypsum	Cement - gypsum comercial	Cement- gypsum moldes	Cement – phospho- gypsum
90 : 10	12	12	12
80 : 20	12	12	12
70 : 30	12	12	12
60 : 40	11	12	12
50 : 50	11	12	12
40 : 60	11	12	12
30 : 70	11	11	11
20 : 80	11	11	11
10 : 90	7.7	7.5	11

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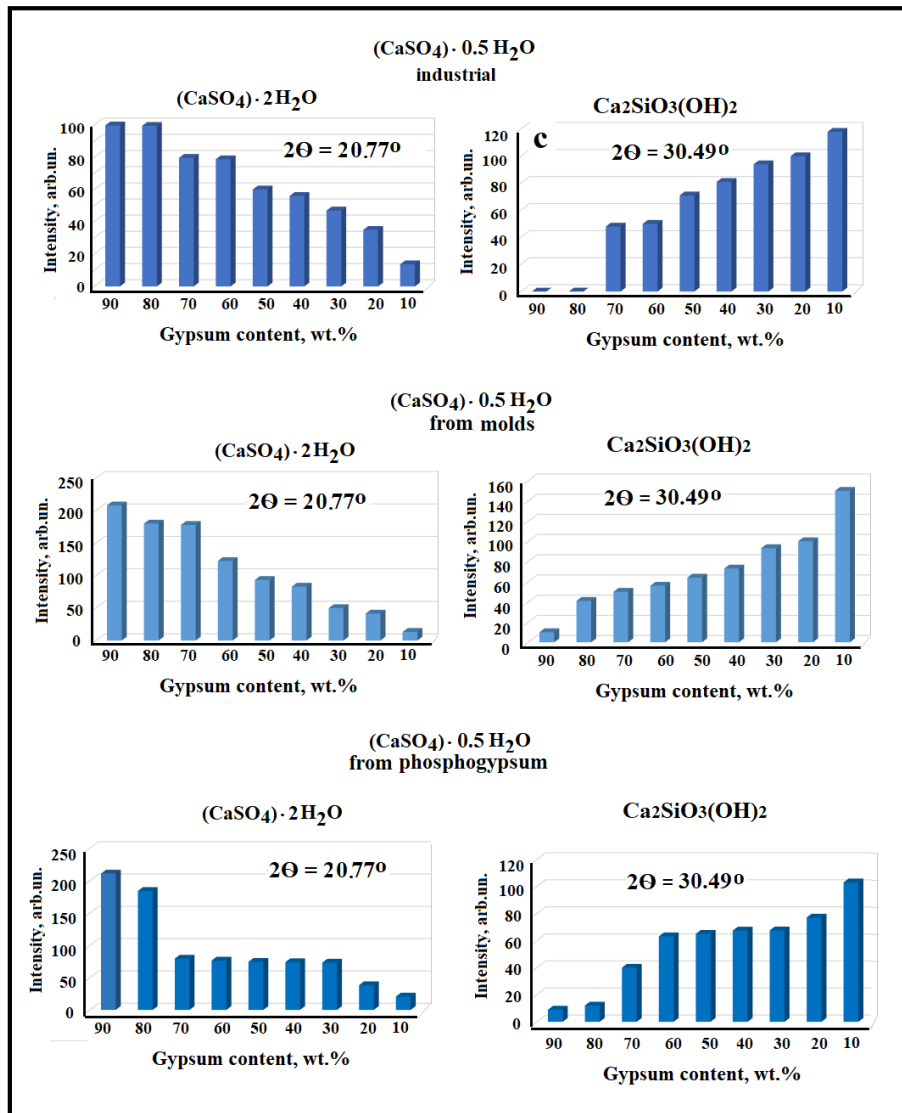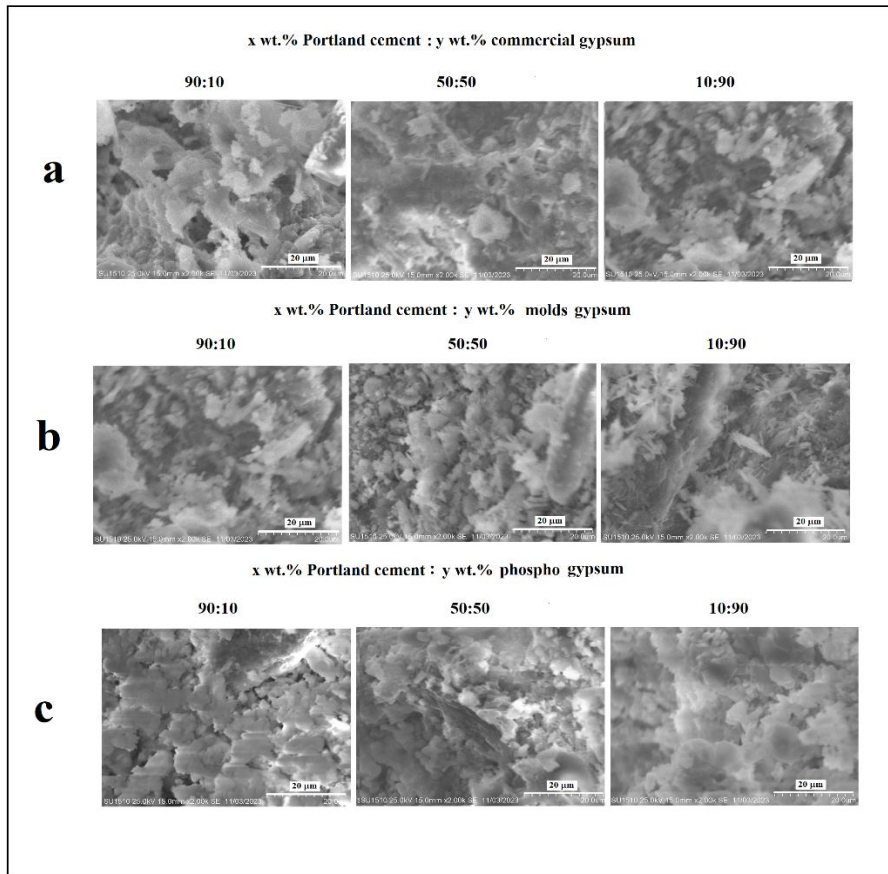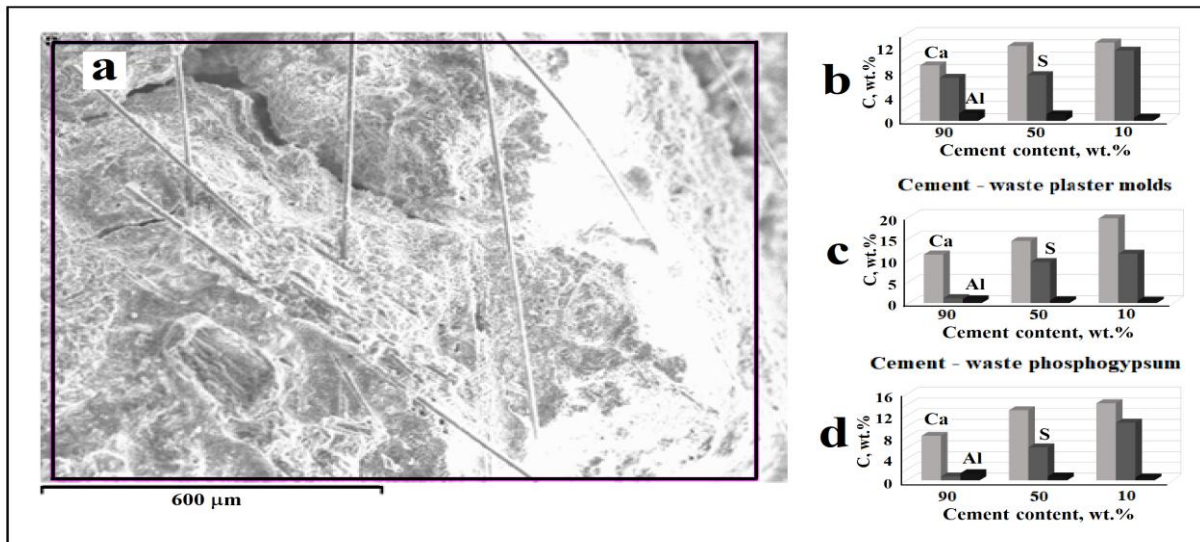
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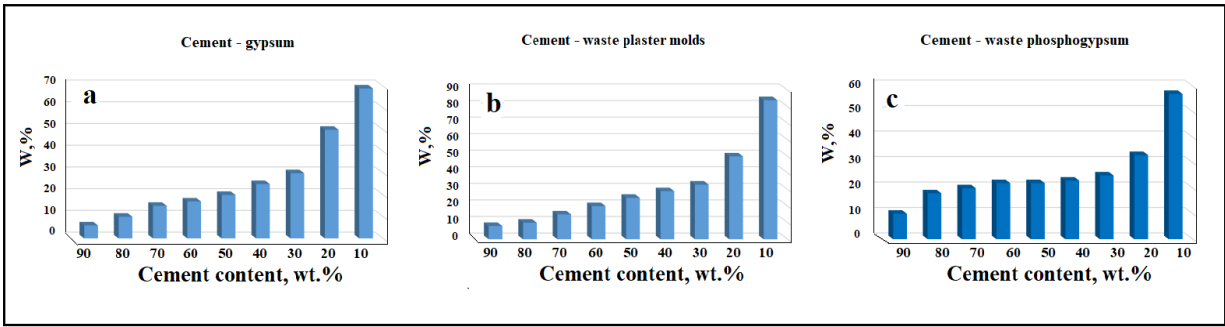
Fig. 5. Changes in the water absorption of samples depending on the composition of the initial mixtures. For specimens Portland cement- commercial gypsum mixtures (a); for specimens Portland cement- molds gypsum mixtures (b); for specimens   Portland cement- phosphogypsum mixtures (c).
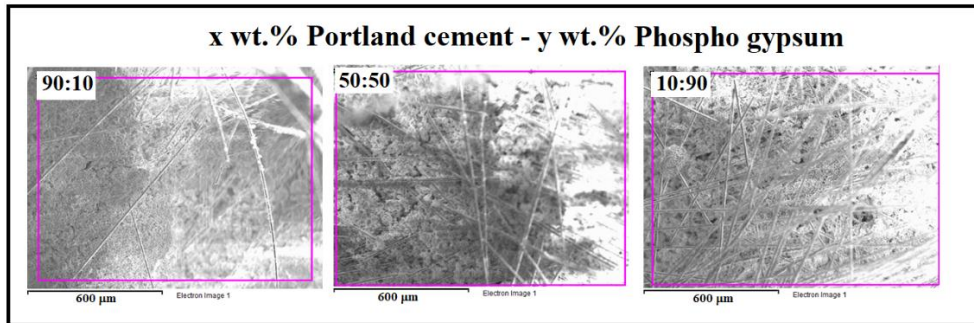

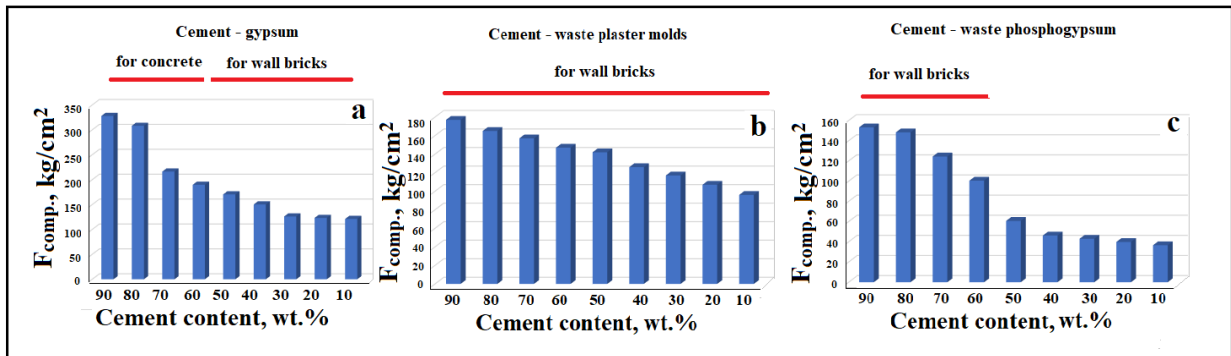**Fig. 6**. SEM images of specimens after boiling in water for 2 h.

Fig. 7. Change in the compression (a–c) strength of specimens depending on the initial composition of mixtures. (a) for initial mixtures of Portland cement-commercial gypsum; (b) for initial mixtures of Portland cement-waste plaster molds; (c) for initial mixtures of Portland cement-waste phosphogypsum.