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Modification of Lime Mortars with Synthesized Aluminosilicates

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Abstract. The increasing attention for restoration of buildings of historical and architectural importance has increased the interest for lime-based binders, which could be applied for manufacturing repair mortars and plasters compatible with historical heritage. Different additives, admixtures or fibers may be incorporated to improve mechanical and thermal features of such materials. In this study synthesized aluminosilicates (SA) were applied as an additive for lime mortar. The technology of synthesis consisted in the deposition of aluminosilicates from a sodium liquid glass by the aluminum sulphate Al2(SO4)3. The goal of this investigation was developing a new method of aluminosilicates synthesis from a sodium liquid glass and using this new material as a component for a lime mortar. Aluminosilicates were precipitated from the solution of aluminum sulphate Al2(SO4)3 and sodium silicate. SA were then used as an additive to calcareous compositions and their influence was tested. Mortars were prepared with commercial air lime and siliceous river sand. Air lime binder was replaced by 5 and 10 wt.% of SA. Calcareous composition specimens were formed at water/lime ratio 1.0. The following analyses were made: grain size distribution of SA, X-ray diffraction analysis (XRD), sorption properties, plastic strength and compressive strength of lime mortars. XRD pattern of the SA shows the presence of thenardite, gibbsite and amorphous phase represented by aggregate of nano-size cristobalite-like crystallites. Application of SA leads to increase of compressive strength after 90 days of hardening by 28% and 53% at SA content 5 and 10% respectively comparing to specimens without this additive. Contents of chemically bound lime in the reference specimens after 28 days of hardening in air-dry conditions was 46.5%, while in specimens modified with SA contained 50.0-55.3% of bound lime depending on filtrate pH. This testifies to high activity of calcareous composition. The new blended lime mortar was developed based on SA. SA in lime composites turned out to be effective as structure-forming additive, both plastic and compressive strength increased after addition of SA.

1. Introduction
The increasing attention for restoration of buildings of historical and architectural importance has increased the interest for lime-based binders. They can be applied for manufacturing repair mortars and plasters compatible with historical heritage. In order to improve mechanical and thermal features of such materials different additives, admixtures or fibers may be incorporated. Lime and/or lime mixed with pozzolanic additives has been widely studied as a potential material for repair of historic buildings [1-6]. The pozzolanic reaction of lime with different additives was studied [7-9]. Lime-based mortars
containing pozzolanic additives of metakaolin, sepiolite and white Portland cement were studied in order to determine their performance as historic masonry conservation mortars [10]. Synthetic fine and coarse zeolite pellets were chosen in the development of air lime–metakaolin mortars for repairing ancient masonry to be used in conservation and restoration of cultural heritage [11]. The performance of air lime mortars modified by the incorporation of large amounts of nanostructured colloidal silica–nanosilica was examined by Duran et al. [12]. In order to enhance physical and mechanical performances of fiber reinforced mortars, the use of zeolitic addition was proposed [13]. Mortars based on air lime binder with additives of palygorskite and metakaolin incorporated as lime binder or sand substitute were studied by Andrejkovičová et al. [14]. It was observed that needle-like palygorskite particles are functional as reinforcing fibers.

The compressive strength development of broad range of hydraulic lime mortars prepared with a range of commercially available aluminosilicate by-products and modern pozzolanic additions (binary and ternary combinations) was investigated [15]. Not only mineral but also organic additives may be applied in lime mortars. Various organic additives were selected on the basis of their properties and historical use [16]: polysaccharides (opuntia used either as a powder or as mucilage), proteins (animal glue and casein) and fatty acids (olive oil). They were all compatible with traditional building materials,

There are reported different methods of synthesis of aluminosilicates. A mesoporous aluminosilicate may be hydrothermally prepared from microcline in an alkaline condition with cetyltrimethylammonium bromide as synthesis directing agent [17]. The electrochemical method to prepare aluminosilicates with high uniformity in terms of surface morphology and the particle size with mullite and quartz as the major phases formed from rice husk silica and aluminum metal was proposed in the study [18]. Aluminum-containing hexagonally ordered mesoporous silica was synthesized using natural clay from low-grade potash ores of a salt lake through liquid-phase transport [19].

Previous investigations proved that thermally and chemically activated diatomite incorporated in lime mortars improved mechanical strength and increased amount of bound lime [20]. In another research aluminosilicates synthesized by adding microfine aluminum powder to sodium silicate at 60°C were used to improve properties of lime finishing compounds [21]. The technology of synthesis applied in this study consisted in a deposition of aluminosilicates from a sodium liquid glass by the aluminum sulphate Al2(SO4)3.

2. Materials and preparation procedures

The first part of the experiment consisted in synthesis of aluminosilicates. Aluminosilicates were precipitated from the solution of aluminum sulfate Al2(SO4)3 and sodium silicate. The sediment was rinsed with water and then dried at 100±2°C. The influence of liquid glass modulus, pH of aluminum sulfate solution and pH of filtrate were examined during development of synthesis technology.

Synthesized aluminosilicates were then used as an additive to calcareous compositions and their influence was tested. Mortars were prepared with powdered commercial air lime with activity 84.5% and siliceous river sand. Air lime binder was replaced by 5 and 10 % wt. of SA. Calcareous composition specimens were formed at water/lime (w/l) ratio equal to 1.0. The samples were cured at air-dry environment: 18±20 °C, relative humidity (RH) 60–70%.

3. Experimental methods

Grain size distribution analysis of aluminosilicates was performed using Laser Particle Size Analyzer - Fritsch Particle Sizer Analysette 22.
XRD examinations were performed in order to determine chemical and phase composition of the newly synthesized product. Evaluation of phase composition was carried on Thermo Scientific ARL™ 9900 X-ray Work Station using CuKα₁,₂ radiation, interval of diffraction angles 2Θ=12-80°, scanning step 0,02°. PDF-2 database of The International Centre For Diffraction Data (ICDD) with the aid of SearchMatch v.2 was used for evaluation of the X-ray diagnosis. Full-profile method of quantitative X-ray analysis with aid of DDM ver. 1.95c software was applied for definite identification of synthesis products. This software applies Rietveld refinement as well as Derivative Difference Minimization (DDM) method. This algorithm is based on minimization of local derivatives on difference curves of experimental and calculated diffraction spectrums.

Structural data for model mineral compositions were sourced from the international Inorganic Crystal Structure Database (ICSD). Concentration of amorphous phase was determined using full-profile X-Ray fluorescence (XRF) with an internal etalon. Anatase (titanium oxide), concentration 30% by weight, was used as the etalon.

Sorption humidification was measured to evaluate sorption properties of the additive in the form of the SA. The specimens in a powder form were first dried at 110±2°C until the steady mass. Then they were placed in desiccators with different relative air humidity (RH) in the range ϕ=18÷97% and the constant temperature t=20±2 °C. Desorption was tested on the humid specimens placed in desiccators with relative air humidity ϕ=10% and the constant temperature t=20±2°C.

Cone penetrator KP-3 was used for plastic strength (or limit shear stress) determination of the modified with aluminosilicates lime compositions. The method consists in immersion of metal cone with the constant mass into the tested material with the specified intervals. The test was performed until the lime composition was set into a lime stone. Plastic strength of lime paste was calculated from the equation:

\[\tau = K_\alpha \frac{F}{h_m^3}\]  

where: \(F\) – the weight of the cone, g; \(h_m\) – the depth of the cone immersion, cm; \(K_\alpha\) - the cone constant.

Compressive strength of lime mortars was tested according to the standard GOST 5802-86 “Construction mortars. Methods of testing”. Cubic specimens 70.7 mm were kept in air-dry conditions at 18÷20 °C and RH=60÷70 %. The number of specimens in each series was not lower than 6. The press used for the test allowed measurement of the force in the range 50÷50,000.

4. Results and discussion

SA is in the form of light gray powder with a bulk density 568.15 kg/m³. According to the grain size distribution analysis, particles 0.010-0.500 µm constitute less than 0.01%, content of grains 100.0-200.0 µm is 0.44%. Less than 5% by mass constitute particles smaller than 3.226 µm and less than 15% - grains lower than 6.985 µm. The detailed grain size distribution is given in table 1. The specific surface area per unit of bulk volume \(S_{SA}=4950.4\) cm²/cm³.

While analyzing synthesis regimes it was determined that when pH of aluminum sulfate solution was 5 there was no precipitation of sediment. Table 2 presents effectiveness of precipitation at different synthesis regimes. The minimum outcome of the synthesized product (33.1%) was obtained at aluminium sulphate solution pH=3 and the maximum outcome equal to 45.9% at pH=1.5. The increase of liquid glass modulus from 2.69 to 2.88 leads to the increase of the outcome from 44.8% to 45.9%. SA have high activity – higher than 350 mg/g. The specific surface area of particles, determined by BET method, is \(S_{sp}=86.5±3.5\) m²/g. Chemical composition of the synthesized product is presented in table 3.
Table 1. Grain size distribution of synthesized aluminosilicates

| Fraction, µm | Contents, % |
|--------------|-------------|
| 0.01-0.5     | 0.01        |
| 0.5-2.0      | 1.81        |
| 2.0-3.0      | 2.55        |
| 3.0-4.0      | 2.8         |
| 4.0-5.0      | 2.73        |
| 5.0-10.0     | 12.61       |
| 10.0-20.0    | 16.61       |
| 20.0-45.0    | 27.2        |
| 45.0-80.0    | 29.14       |
| 80.0-100.0   | 4.09        |
| 100.0-200.0  | 0.44        |

Table 2. Regimes of synthesis and product properties

| pH of aluminum sulfate solution Al₂(SO₄)₃ | Liquid glass modulus | pH of filtrate | Filler activity, mg/g | Outcome of the new product, % |
|-----------------------------------------|----------------------|----------------|----------------------|-----------------------------|
| 5                                       | 2.69                 | -              | >350                 | 41.9                        |
| 3                                       | 2.69                 | 9              | >350                 | 38.9                        |
| 1.5                                     | 2.69                 | 9              | >350                 |                            |
| 5                                       | 2.88                 | -              | >350                 |                            |
| 3                                       | 2.88                 | 9              | >350                 | 34.0                        |
| 1.5                                     | 2.88                 | 9              | >350                 | 42.9                        |
| 5                                       | 2.69                 | -              | >350                 |                            |
| 3                                       | 2.69                 | 5              | >350                 | 40.5                        |
| 1.5                                     | 2.69                 | 5              | >350                 | 44.8                        |
| 5                                       | 2.88                 | -              | >350                 |                            |
| 3                                       | 2.88                 | 5              | >350                 | 33.1                        |
| 1.5                                     | 2.88                 | 5              | >350                 | 45.9                        |

The best synthesis parameters are: aluminium sulphate solution pH=1.5, liquid glass modulus 2.88 and filtrate pH=5.

Table 3. Chemical composition of the synthesized aluminosilicates, % by mass

| SiO₂ | Al₂O₃ | Na₂O | SO₃ | TiO₂ | Fe₂O₃ | MgO | CaO | K₂O | Σ       |
|------|-------|------|-----|------|-------|-----|-----|-----|---------|
| 55.45| 21.24 | 13.91| 8.91| 0.023| 0.038 | 0.11| 0.15| 0.03| 99.861  |

XRD pattern of the SA powder shows the presence of selective diffraction reflections and structural background, so called “diffraction halo”. Crystalline part of the synthesized material is thenardite – rhombic modification of sodium sulphate Na₂SO₄ (PDF 70-1541). Except for it, there is a weak reflection at 2Θ=21.29° which corresponds to gibbsite - one of the forms of aluminium hydroxide Al(OH)₃ (PDF 70-2038). The results of quantitative XRD analysis as a calculation of concentration of crystalline phases is presented in figure 1. Amorphous phase is represented by aggregate of nano-size cristobalite-like crystallites. Contents of the amorphous phase constitutes 77.5% (figure 2).
Figure 1. Calculation of concentration of crystalline phases; the arrow shows reflection of gibbsite.

Figure 2. X-ray diffraction patterns of the synthesized aluminosilicate.

Sorption and desorption isotherms constructed on the basis of the experimental results are given in figure 3. They showed that with the increase of RH regularly increased sorption humidity of the tested material. The process of saturation and drying is described by S-shaped isotherms, which are typical for capillary-porous water-wettable materials. Sorption in RH in the range to 18% obeys the Henry’s law according to the equation:

$$ W = k(\varphi) $$  \hspace{1cm} (2)

It means that sorption moisture is linearly dependant on RH.
When RH is increased to 40%, moisture content in specimens increases according to Freundlich equation. Convex part of isotherm ($\varphi=60\div80\%$) indicates, that only adsorption moisture consisting of one layer of vapour molecules is present in the tested specimens. Increase of RH to 90% leads to formation of the adsorption moisture films consisting of many layers of molecules on the internal surfaces of the material. Sharp increase of sorption moisture starts from RH=80%, which testifies to the process of capillary condensation. Sorption and desorption isotherms converge only at very low and very high RH.

**Figure 3.** Sorption and desorption isotherms of synthesized aluminosilicates: 1-sorption isotherm, 2 – desorption isotherm.

Analysis of the experimental results proved that application of aluminosilicates which were synthesized from aluminium sulphate solution at pH=1.5 leads to increase of compressive strength of samples after 90 days of hardening comparing to samples without this additive by 27.9% and 52.7% at aluminosilicates contents 5% and 10% respectively (figure 4).

**Figure 4.** Compressive strength depending on synthesized aluminosilicates content: 1 – reference sample (without additive); 2 – 5% of aluminosilicates by lime mass; 3 - 10% of aluminosilicates by lime mass.
Contents of chemically bound lime in the reference samples after 28 days of hardening in air-dry conditions was 46.5%. Samples modified with aluminosilicates contained 50.0-55.3% of bound lime depending on filtrate pH (figure 5). This testifies to high activity of calcareous composition.

![Graph showing the increase of chemically bound lime in hardening process.](image)

**Figure 5.** Increase of chemically bound lime in hardening process: 1 – reference samples; 2 – filtrate pH=9; 3 – filtrate pH=5.

While evaluating properties of calcareous compositions with SA in plastic state it was found out that the additive accelerates gain of plastic strength. Fig. 6 presents plastic strength development of lime paste with different additive contents. Incorporation of aluminosilicates additive provokes earlier structure formation of lime paste. Plastic strength after 10 hours from the moment of adding water to the system was equal to 0.0063 MPa when 10% of aluminosilicates by lime mass was added (fig. 6 - line 3); at 5% of additive the strength was equal to 0.0013 MPa (figure 6 - line 2).

![Graph showing the development of plastic strength of lime paste.](image)

**Figure 6.** Development of plastic strength of lime paste: 1 – reference sample; 2 – 5% of aluminosilicates by lime mass; 3 - 10% of aluminosilicates by lime mass.
5. Conclusions
The new blended lime mortar was developed based on synthesized aluminosilicates (SA). The best synthesis parameters are: aluminium sulphate solution pH=1.5, liquid glass modulus 2.88 and filtrate pH=5. Synthesized aluminosilicates in lime composites turned out to be effective as structure-forming additives. The chemical interaction between the additive and lime is revealed based on contents of chemically bound lime. Both plastic and compressive strength increased in samples modified with synthesized aluminosilicates compared with the reference samples.

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