Comparison of structure and properties of gypsum mortars with different types of aggregates

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Abstract. Gypsum is one of the most environmentally friendly building materials and therefore its importance increases nowadays. Since the gypsum is mostly used in the form of the paste, the influence of aggregates on properties of gypsum mortars is not investigated very often. The article deals with the structure and properties of gypsum mortars with two different aggregates (silica sand and basalt). It was found, that even if the chemical composition and shape of particles of both aggregates differs significantly, the structure and properties of gypsum mortars with both types of aggregates are similar and the properties of the gypsum composite depends more on the aggregate granulometry and the quality of its surface. The aggregate with rougher surface of particles has more distinct interfacial transition zone, higher porosity and higher compressive strength.

1. Introduction

Even if gypsum is one of the oldest building binders, the knowledge of its structure, properties and behavior is very often based only on the historical experience or on the knowledge obtained from the study of other binders. While in the cement- and lime-based materials the presence of aggregates is inevitable, because they provide better dimensional stability at setting [1], gypsum does not shrink during setting; to the contrary it expands slightly [2]. Therefore the aggregates in gypsum are used less frequently and mostly from economic reasons. They could also improve the behavior of gypsum-based materials in fire [3, 4]. Even if the gypsum is considered as an excellent fire resistant material, gypsum paste shrinks considerably at high temperatures and the presence of aggregates can improve the volume stability of gypsum based material significantly [4].

It is known that the size, shape and texture of the aggregate particles influence the properties of the cement-based material. The properties of the aggregates affect the workability of the fresh mixture, the mechanical properties and the durability of the hardened cement mortars or concretes [1]. It was verified that the properties of aggregates influence the gypsum-based materials in similar way as cement-based materials [5].

Nevertheless the influence of normal types of aggregates on the gypsum materials is not studied very often. Mostly the lightweight aggregates are tested [6, 7, 8, 9]. Also large scale of waste products was used in gypsum-based materials, e.g. recycled expanded polystyrene [10], waste PUR [11] or ground rubber [12, 13].

Gypsum mortars with two different types of aggregates (silica sand and basalt) were studied. The mortar with silica sand was used as a reference material and basalt was chosen in order to improve the fire behavior of gypsum mortar. Basic physical and structural properties of both mortars were tested and compared in the paper.
2. Materials and methods

The commercial gypsum plaster (calcium sulfate hemihydrate, \( \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} \)) was used as a binder. Plaster was type A2, according ČSN EN 13 279-1:2009 [14] and it was calcined from flue gas desulfurization product (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)) by producer Saint-Gobain Construction Products CZ, branch RIGIPS, Czech Republic.

Silica sand, which complies with CEN, ČSN EN 196-1 [15] and crushed basalt (producer KÁMEN Zbraslav, ltd.) were used as a fine aggregates. Set retarder Retardan-200 P (producer SIKA, Germany) was used in all mortars.

The chemical composition of raw materials, obtained by XRF analysis and their mineral composition, obtained by XRD analysis are given in the table 1 and 2. The granulometry of the aggregates can be seen in figure 1 and their bulk density and specific gravity is given in table 3. The bulk density and specific gravity of basalt are slightly higher than values of silica sand, but the difference was not significant. The granulometries of both aggregates obtained by the sieve analysis were similar, silica sand was slightly rougher. Nevertheless there was significant difference in the size and amount of smallest particles, obtained by laser analysis. Crushed basalt contained considerably larger amount of dust particles smaller than 20 \( \mu \text{m} \) (figure 2).

| Oxide  | Na\(_2\text{O}\) | MgO | Al\(_2\text{O}_3\) | Si\(_2\text{O}_2\) | SO\(_3\) | K\(_2\text{O}\) | CaO | TiO\(_2\) | Fe\(_2\text{O}_3\) |
|--------|----------------|-----|----------------|----------------|--------|--------|------|--------|----------|
| Gypsum | -              | -   | 0.4            | 0.6            | 53.9   | -      | 44.5 | -      | -        |
| Standard sand | -        | -   | 1.1            | 97.7           | -      | -      | 0.2  | -      | 0.4      |
| Basalt  | 3.3            | 7.3  | 17.2           | 42.2           | -      | 1.2    | 12.7 | 3.2    | 11.6     |

Table 1. Chemical composition of raw materials.

| Mineral          | Gypsum [wt. %] | Silica sand [wt. %] | Basalt [wt. %] |
|------------------|----------------|---------------------|----------------|
| Bassanite        | CaSO\(_4\) \cdot 1/2\text{H}_2\text{O} | 89                | -              |
| Anhydrite        | CaSO\(_4\)    | 6                   | -              |
| Calcite          | CaCO\(_3\)    | 4                   | -              |
| Muscovite        | K\(\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2\) | 1                | -              |
| Quartz           | SiO\(_2\)     | -                   | 100            |
| Diopside         | CaMgSi\(_2\)\(_6\) | -               | -              |
| Nepheline        | (Na,K)\text{AlSiO}_4 | -               | -              |
| Plagioclase      | Na\text{AlSi}_3\text{O}_8 - Ca\text{Al}_2\text{Si}_2\text{O}_6 | -               | -              |
| Anorthite        | Ca\text{Al}_2\text{Si}_2\text{O}_8 | -               | -              |
| Analcim          | Na\text{AlSi}_3\text{O}_6 \cdot \text{H}_2\text{O} | -               | -              |
| Forsterite       | Mg\(_2\)\text{Si}_4 | -               | -              |
| Aegirine         | NaFe\(_{3+}\)\text{[Si}_2\text{O}_6\] | -               | -              |
| Tobermorite      | Ca\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O} | -               | -              |
| Biotite          | K(Mg,Fe\(_{3+}\)\text{(AlSi}_3\text{O}_{10})(\text{F,OH})_2 | -               | -              |
| Magnetite        | Fe\(_{2+}\)Fe\(_{3+}\)\text{O}_4 | -               | -              |

Table 2. Mineral composition of raw materials.
Table 3. Bulk density and specific gravity of aggregates.

|                | Silica sand | Basalt |
|----------------|-------------|--------|
| Bulk density   | [kg m⁻³]    | 2575   | 2631   |
| Spec. gravity  | [kg m⁻³]    | 2831   | 3015   |

**Figure 1.** Granulometry of used aggregates.

**Figure 2.** Results of laser particle size analysis.

### 2.1. Composition and preparation of mortars

The composition of the mortars was designed for the same volume of gypsum and aggregate in both mortars in order to compare the structural changes in the gypsum matrix. Composition of mortar with silica sand (GS) was designed according ČSN EN 196-1 [15]. The mass ratio between the gypsum powder and sand was 1 : 3. Amounts of 450 g of gypsum and 1350 g of sand were used for one batch of mortar. The mass of basalt aggregate in mortar GB was calculated from its density $\rho_B$ and the volume of silica sand $V_S$ in mortar GS. By that way both mortars contained the same volume of aggregate.
The amount of water was determined for a flow tests diameter value of 165±5 mm. Amount of water in GB mortar was higher because basalt contained higher amount of very fine particles and therefore more water was needed to achieve same workability. The amount of retarding agent was 0.02% from dry gypsum weight in both mortars. Composition of tested materials is given in table 4.

| Material | Aggregate | Gypsum [g/batch] | Aggregate [g/batch] | Retardant [ml/batch] | Water [ml/batch] |
|----------|-----------|------------------|---------------------|---------------------|-----------------|
| GS       | silica sand | 450              | 1350.0              | 0.09                | 270             |
| GB       | basalt    | 450              | 1379.4              | 0.09                | 330             |

The materials were prepared according to ČSN EN 13454-2 [16]. Dry gypsum powder was mixed with the retarding agent and dry mixture was poured into the required amount of water in the mixing bowl and the bowl was put into the automatic mixer. Total time of mixing was 4 minutes. Mixing consisted from 30 s at low speed (140 rpm), 30 s of adding aggregates at low speed, 30 s mixing at high speed (285 rpm), pause 90 s during which the mixture was manually wiped from the bowl wall and finally mixing for 60 s at high speed. Then the mortar was poured into a mold and was firstly manually and then mechanically compacted. Three prismatic samples (40 × 40 × 160 mm) were prepared from each mortar. The hardened samples were put out of the molds after 60–90 min and stored at 20 ± 5°C and relative humidity of 50 ± 5% for 28 days.

2.2. Methods

The particle size distribution of used aggregates was determined according to ČSN EN 933-2 [17]. Standard sieves with apertures of 0.063 mm, 0.09 mm, 0.125 mm, 0.25 mm, 0.5 mm, 1.0 mm, 2.0 mm and 4.0 mm were used.

The bulk density of aggregates was determined by the immersion of aggregate in the volumetric cylinder and counted from dry mass of aggregate and the increase of water level in volumetric cylinder. This method is not standardized.

The bulk density of mortars was calculated from the mass and dimensions as a ratio of mass and volume. The dimensions of samples were measured by the digital calliper and their mass was determined by weighing. Volume of samples was calculated from dimensions.

The specific gravity of aggregates and tested mortars was determined by the helium pycnometry using Pycnomatic ATC (Thermo Fisher Scientific). This method uses a gas displacement technique and it is not standardized.

The microstructural morphology of the gypsum mortars and aggregate grains was studied by scanning electron microscopy (SEM) using a Phenom XL electron microscope. The samples were dried and they were not coated or polished.

The grain and fracture surface roughness was determined by the 3D Roughness Reconstruction software, based on “shape from shading” technology from SEM images, obtained by the device Phenom XL. Roughness was determined as the three-dimensional arithmetical mean roughness value SRa [µm], which is an analogy to the arithmetical mean deviation of the profile Ra (two dimensional roughness) according to ISO 468 [18].

The porosity of mortars p [%] was calculated from the bulk density ρs and the specific mass ρ according equation 1.

\[ p = (1 - \frac{\rho_s}{\rho}) \times 100 \]  

Mercury intrusion porosimetry (MIP) was used for describing of pore system of studied composites. The measuring apparatus was composed of devices Pascal 140 and Pascal 440. The software evaluated the cumulative curve of pores and the distribution curve of pores.
The **flexural and compressive strength** were determined according ČSN EN 13454-2 [16] on standard test samples. The experiment was performed as a common three-point bending test. The measurements were carried out 28 days after mixing. The compressive strength was measured on the halves of the specimens left over from the bending test.

The **modulus of elasticity** was measured according ČSN EN 12504-4 [19] by the Pundit Lab Ultrasonic device (Proceq) using the ultrasonic method. The modulus of elasticity was calculated from bulk density $\rho_v$ and pulse velocity $v$ according equation 2.

$$E = \rho_v \times v^2$$ (2)

3. Results and discussion

Basic properties of both mortars GS and GB are given in table 5 together with values of surface roughness of both aggregates and the fracture surface roughness of mortars. The values of all properties are discussed in the following chapters.

**Table 5.** Properties of tested mortars.

|                     | GS   | GB 
|---------------------|------|------
| Specific gravity    | 2754 | 2938 |
| Bulk density        | 1916 | 1903 |
| Total porosity      | 30.4 | 35.2 |
| Compressive strength| 12.7 | 13.8 |
| Flexural strength   | 5.9  | 5.0  |
| Modulus of elasticity| 3434 | 2936 |
| Grain surface roughness| 591  | 633  |
| Fracture surface roughness| 0.30 | 0.37 |
| Thermal conductivity| 1.8  | 0.7  |

3.1. XRD analysis of mortars

XRD analysis showed that used aggregates did not react with the gypsum matrix. The mineral composition of both mortars contained the same minerals, which were found in the raw materials, only bassanite (calcium sulphated hemihydrate) in calcined gypsum powder was hydrated to the gypsum (calcium sulphate dihydrate). It is evident that both aggregates were chemically inert in gypsum environment. The mineral composition of both mortars is given in table 6.

**Table 6.** Mineral composition of mortars.

| Mineral            | GS [wt.%] | GB [wt.%] |
|--------------------|-----------|-----------|
| Gypsum             | CaSO$_4$·2H$_2$O | 38        | 46        |
| Bassanite          | CaSO$_4$·1/2H$_2$O | 1         | 2         |
| Anhydrite          | CaSO$_4$   | -         | 0         |
| Muscovite          | KAl$_2$(AlSi$_3$O$_{10}$)(OH)$_2$ | - | 5 |
| Quartz             | SiO$_2$   | 61        | -         |
| Diopside           | CaMgSi$_2$O$_6$ | -         | 22        |
| Nepheline          | (Na,K)AlSiO$_4$ | - | 4         |
| Plagioclase        | NaAlSi$_3$O$_8$–CaAl$_2$Si$_2$O$_8$ | - | 4         |
| Anorthite          | CaAl$_2$Si$_2$O$_8$ | - | 2         |
| Mineral   | Formula                                      | Image   | Value |
|-----------|----------------------------------------------|---------|-------|
| Analcim   | NaAlSi$_2$O$_6$·H$_2$O                      | a)      | 2     |
| Forsterite| Mg$_2$SiO$_4$                               |         | 3     |
| Aegirine  | NaFe$_{3+}$[Si$_2$O$_6$]                    |         | 2     |
| Tobermorite| Ca$_5$Si$_6$O$_{16}$(OH)$_2$·4H$_2$O          |         | 0     |
| Biotite   | K(Mg,Fe)$_3$(AlSi$_3$O$_{10}$)(F,OH)$_2$     |         | 2     |
| Magnetite | Fe$_{2+}$Fe$_{3+}$O$_4$                      |         | 2     |

3.2. SEM observations and surface roughness evaluation

The shape and quality of the surface of the aggregate grains were studied by the SEM. From each aggregate several grains were chosen and the surface roughness SRa was determined 10 times for each aggregate at 20 μm wavelength and the mean value was calculated. SEM images of typical grain surface and height map generated by 3D Roughness Reconstruction software can be seen in figure 3.

Both aggregates were crushed, therefore their surface was not smooth, nevertheless the basalt surface was rougher and there can be seen (figure 4), that the ITZ between gypsum paste and aggregates was more pronounced in the GB mortar. The size and shape of gypsum crystals in the vicinity of aggregate particles were similar in both mortars.

![SEM images of typical grain surface and height map](image-url)
Figure 3. SEM image at 1000× magnification (a) and height map (b) of typical grains.

Figure 4. SEM image of mortars at 1000× (a) and 3000× (b) magnification.
3.3. **Porosity and pore size distribution of mortars**

The total porosity of mortar with silica sand GS was 30.4%, porosity of mortar with basalt GB was 35.2%. Even if the specific gravity of mortar with basalt aggregate (GB) was higher than specific gravity of mortar with silica sand (GS), its bulk density was lower, because it contained more water.

The increase of porosity of GB mortar was therefore caused mainly by the higher amount of water and partly by larger ITZ in this mortar (as can be seen in SEM images). The size of more porous ITZ increases with the roughness of the aggregate particles [5].

The pore size distribution curves are given in figure 5. The distribution curves of both mortars are similar. They have nearly unimodal pore size distribution with highest amount of pores between 1–10 μm, which is typical for gypsum pastes [20]. The higher amount of pores larger than 10 μm in mortar GB was caused by the higher amount of water. Mortar GB contained also more very small pores (< 0.01 μm), which correspond with the fact that smaller pores appears in the gypsum mortars with rougher surface of particles [5].

![Cumulative pore volume vs. Pore size graph](image)

**Figure 5.** Pore size distribution curve of mortars.

3.4. **Mechanical and thermal properties of mortars**

The compressive strength of mortar GS was 12.8 MPa and mortar GB had the compressive strength 13.2 MPa. The higher compressive strength of mortar GB with basalt was caused by the higher surface roughness of basalt particles compared to the silica sand. This corresponds with the conclusions in the [5] and also with the behaviour of cement based materials [1]. The higher porosity of the mortar GB had no impact on the compressive strength, because the effect of surface roughness prevailed. The flexural strength was more influenced by the porosity and therefore the flexural strength of GB mortar was about 15% lower than flexural strength of mortar GS.

The modulus of elasticity decreased with increasing porosity (from 3434 MPa for GS to 2936 for GB), which is common for porous materials [21, 22].

The thermal conductivity of mortar with basalt GB decreased significantly (at about 50%), compared to the thermal conductivity of mortar with silica sand GS, which conforms to the higher porosity of the mortar GB.
4. Conclusions
Mortars with two different types of nonporous aggregates were studied. The mortar with silica sand was used as a reference material. Basalt was used in order to improve the fire behaviour of gypsum mortar. The comparison of mortars with both types of the aggregates was performed at normal temperature before subjecting them to the elevated temperatures.

It was found, that both aggregates did not chemically react with the gypsum matrix at normal temperature and the differences in the structure and properties of both mortars were caused by the aggregate particle size distribution and the quality of particles surface.

We found that:

- the shape and size of crystals of gypsum matrix were similar in both mortars
- the ITZ in the mortar with basalt was more pronounced, which was caused by the higher roughness of basalt surface
- the pore size distributions of mortars was unimodal with most of the pores having diameter 0.1–1 \( \mu \)m
- higher porosity of mortar with basalt aggregate was caused by higher amount of mixing water, caused by higher amount of very fine particles in basalt aggregate
- the thermal conductivity of mortar with basalt aggregate was lower at about 50%

The research will continue by the testing of both materials at the elevated temperatures (up to 1000°C). The behaviour of mortar with silica sand will be compared with the behaviour of the mortar with basalt aggregate and also with the behaviour of gypsum paste. Silica sand is generally considered as less suitable for use at high temperatures, because of its volume instability \([23]\) and therefore its substitution by other material could be beneficial for utilization of gypsum based materials as a fire protecting materials.

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