Effect of water-binder ratio on properties of phosphogypsum binder

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Abstract. Technological, physical and mechanical properties of mineral binders are often defined by the amount of water add to the binder known as W/B ratio. The role of water is contributed to the workability of fresh paste, hydration processes, porosity, mechanical performance and durability of the material. Present research summarizes the relationship between gypsum based binder W/B ratio in mixture composition to properties of hardened gypsum binder, giving a marginal borders of properties affected by W/B. The W/B ratios evaluated were from 0.3 to 1.15. Dihydrate phosphogypsum (PG), which is a waste of phosphorus fertilizer industry and commercial gypsum binder were used as a raw material for production of gypsum samples and results compared to commercial gypsum binder. At the beginning PG was dried at 60°C and afterwards homogenized by milling it in ball mill or by collision milling in disintegrator. Samples were made with plasticizers, mineral additives and foam forming additive. In this work 26 dense and 9 porous mixture compositions was summarized, from which 18 compositions were made from commercial binder for comparison. A series of performance properties of the binders were investigated, such as density, porosity and 14d compression strength regarding to W/B ratio used to prepare the samples. The chemical and mineralogical composition of PG used was determined by XRF and XRD. The results indicate that plasticizers in PG based gypsum binder could reduce W/B ratio from 1.15 down to 0.4. The PG binder bulk density for samples without pore forming admixture was in range from 726 – 1600 kg/m³, total porosity 35 – 71 vol.% and compressive strength from 1.4 to 28.7 MPa at the age of 14 d. Ultra porous gypsum material was obtained with the pore forming agent, which allowed to obtain gypsum based material with bulk density from 213 – 726 kg/m³, total porosity from 67.9 – 90.6 % and compressive strength from 0.2 – 0.8 MPa. Results show that the material density and strength decreases while porosity tends to increases with the increase of W/B ratio. These tendencies are true both for dense and porous specimens. It was concluded, that lowest W/B of dense PG specimens was 0.43, otherwise the workability of a binder decreased dramatically and decrease of compressive strength was observed. With the same W/B ratio the technological properties of PG binder may be affected by gypsum treatment parameters and selected mixture composition, allowing to improve the properties of gypsum binder obtained from same raw material.

1. Introduction

Nowadays gypsum is a common building material with wide range of application, i.e. it is used in production of gypsum binders for direct use on site or to produce gypsum plasters (including plasters for special purposes) or manufactured elements (blocks, tiles, plasterboards). Historically, gypsum is used also as paints created from lime-gypsum suspension [1]. Besides of natural gypsum a synthetic
gypsum is available which in most cases is described as a by-product from industrial production and it has a potential of replacement of natural gypsum. Flue gas desulfurization-FGD gypsum and phosphogypsum (PG) is the most common forms of synthetic gypsum [2], [3]. PG is a primary by-product from phosphoric acid production and in most cases it is accumulated in open stack-piles occupying large areas near plants and bringing environmental problems (figure 1) [3], [4].

Figure 1. Dihydrate phosphogypsum stacks in Kedainiai, Lithuania (author picture)

PG could be contaminated with technological impurities which reduce the potential disposal of the PG in production of building materials [5], [6]. There are several ways to remove or neutralize the impurities, i.e. washing with water [7], neutralizing with alkaline additives [8], adding adsorbents [6]. Some of them are combined with the milling process of PG as during milling process, PG crystals are destroyed and unfavorable P₂O₅ released and modified while the compressive strength increases as specific surface area increases [9]. P₂O₅ is a powerful desiccant and dehydrating agent therefor it may attract water that could increase the moisture content in gypsum material lowering its properties [5]. The water-gypsum (W/B) ratio has an influence on the basic physical characteristics of hardened gypsum, such as its volume density, total open porosity and other related characteristics like its moisture, mechanical, thermal and sound insulation properties. The strength values of hardened gypsum significantly depend on the water-gypsum ratio as well. The theoretical W/B ratio necessary for the hydration of calcium sulphate hemihydrate into calcium sulphate dihydrate is 0.187 while the additional water, in a so-called over-stoichiometric quantity, is necessary for the processing of the hardening gypsum paste [10].

There are researches where PG is evaluated as potential binder with W/B ratio from 0.54 to 0.70 giving a compressive strength from 5 to 19 MPa after 7d hardening [11]. In other researches W/B ratio is defined in the interval of 0.6 to 0.8. [10]. The highest W/B ratios researched was from 0.9-1.3 which resulted with density from 880-1080 kg/m³ of the obtained binder with compressive strength from 4.2-16 MPa [12].

Effective way to improve workability and reduce W/B is to use superplasticizers (SP). Superplasticizers are used from 0.2–1% from the weight of gypsum and the most common plasticizers used are naphthalene, melamine and polycarboxylate, citric acid which may act both as gypsum setting time retarders or accelerators [13]–[15]. To use SP efficiently, often an increase of pH of binder is needed. To increase alkaline media of fresh binder thus involves electrostatic effect of SP the amount of lime which is necessary to add is about 2 to 2.5% by gypsum mass [16].

This research summarizes the experimental results of PG based binder regarding to W/B ratio in mixture composition to properties of hardened gypsum specimens, giving a marginal borders of properties affected by W/B and is compared with commercial gypsum material.
2. Materials and methods

Phosphogypsum dihydrate (PG) from AB Lifosa (Lithuania) and commercial construction gypsum (Knauf Baugips - BG) were used for investigation. The chemical compositions of the gypsum were determined using a Thermo Scientific ARL PERFORM'X Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF) with a Rh-target x-ray tube and the UniQuant program. Prior to the measurements, samples were dried at 60°C and heated at 950 °C; a fused bead was then prepared with lithium tetraborate 50%/lithium metaborate 50%, with a 1:10 mixture of the PG and flux heated at 1085 °C. The chemical composition of PG is given in Table 1. BG is commercial gypsum used in this research, PG_raw is secondary raw material obtained from production plant and PG is binder obtained from PG at 180°C for 4h.

| Component | BG     | PG raw | PG     |
|-----------|--------|--------|--------|
| LOI 950°C | 22.43  | 19.24  | 6.89   |
| Na₂O      | 0.31   | 0.48   | 0.47   |
| MgO       | 3.92   | 0.21   | 0.16   |
| Al₂O₃     | 1.68   | 0.71   | 0.96   |
| SiO₂      | 3.73   | 1.07   | 0.94   |
| P₂O₅      | 0.00   | 0.57   | 0.66   |
| SO₃       | 30.90  | 37.38  | 43.21  |
| CaO       | 35.64  | 37.16  | 43.25  |
| TiO₂      | 0.05   | 0.11   | 0.08   |
| Fe₂O₃     | 0.46   | 0.22   | 0.21   |
| As₂O₃     | 0.07   | 0.09   | 0.13   |
| SrO       | 0.23   | 2.25   | 2.52   |
| CeO₂      | 0.01   | 0.24   | 0.24   |
| TOTAL     | 99.42  | 99.74  | 99.73  |

The particle size distribution of gypsum binders is given in Figure 2. 100% of particles are below 0.3 mm which is in accordance with standard LVS EN 13279-1:2008. PG has finer nature comparing to BG. The characteristic value of d₁₀ was 0.05 mm, d₅₀ – 0.075 mm, d₉₀ – 0.12 mm for PG and 0.08, 0.13 and 0.22 mm for BG respectively. The high fineness of gypsum could lead to increased W/B ratio and reduced setting time similar as for Portland cement reported previously [17].

![Figure 2. Particle size distribution of commercial gypsum (BG) and phosphogypsum after collision milling in disintegrator and heating at 180°C (PG).](image-url)
The mineralogical composition of PG transformation through dehydration and hydration processes is given in Figure 3. The main mineral in dihydrate PG was synthetic calcium sulfate hydrate (\(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\), ref. 33-0311). The dehydration at 180°C for 4h results in weight loss of 18 wt% of chemically bonded water and new phase – calcium sulfate hemi-hydrate (\(2\text{CaSO}_4 \cdot \text{H}_2\text{O}\), ref. 02-0667) was detected. For hardened samples prepared from PG treated at 180°C main mineral indicated was calcium sulfate hydrate (ref 72-0568) indicating reverse hydration reaction to dehydration.

**Figure 3.** Mineralogical composition of phosphogypsum and commercial gypsum. DH – calcium sulfate hydrate (33-0311), PH - calcium sulfate hydrate (02-0667)

Results and discussion

The effect of W/B ratio on density of gypsum samples is given in figure 4. The results can be divided in three groups: density range for commercial gypsum (i), PG binder (ii) and porous gypsum based samples. It can be clearly seen that material based on PG has increased demand to W/B ratio so that material could be prepared and casted which is associated with increased fineness of PG and constituents which may attract extra water. However, there is a range of density, where PG properties could be compared with commercial gypsum. The W/B ratio from 0.43-0.60 could be used for both binders and the density of the material could be in range from 1100-1400 kg/m³. It must be noted, that such a low W/B ratio of PG binder could be achieved only with the use of superplasticizers. For commercial binder the W/B ratio could go as low as 0.30 where maximum density from 1500-1600 kg/m³ could be reached. The porous gypsum remains low W/B ratio (from 0.22-0.78) which is associated with the prepared foam volume and the binder distribution in the foams which act as surfactants. The density of porous gypsum obtained with foaming agents could be as low as 200 kg/m³ while the upper limit is slightly below the margin of density for PG binder with high W/B ratio (1.00-1.15) and could reach up to 750 kg/m³.

**Figure 4.** The relationship between water-binder ratio and density of gypsum based material.
The total porosity is strongly related to the W/B ratio as extra free-water, which is necessary to ensure workability of the prepared binder evaporates from the structure, creating air voids as open pores, which reduce the density and strength of the gypsum binder, similar as for Portland-cement based materials [18]. The total porosity obtained for commercial gypsum binder was around 38–40 vol.% with the W/B ratio from 0.3 while the same total porosity for PG binder could be reached with W/B ratio of 0.43 (figure 5). The total porosity for porous PG samples could reach up to 90 % giving a promising result to obtain ultra-lightweight gypsum material.

Figure 5. The relationship between water-binder ratio and total porosity of gypsum based material.

The W/B ratio has strong impact on compressive strength of gypsum material (Figure 6). The strength with high W/B ratio could be from 1-5 MPa while the decrease of W/B ratio gradually increase the strength up to 29 MPa. Comparing the compressive strength properties of PG and commercial binder it could be seen that there is a range where the W/B and compressive strength relationship is overlapping giving a promising potential for PG as substitution of natural gypsum. The possibility to reduce W/B ratio of commercial gypsum increased material strength up to 24 MPa, while the fine nature of PG gives higher compressive strength results even at higher W/B ratio. It must be also noted that even with similar W/B ratio the wide range of compressive strength results might be obtained indicating the importance of preparation of gypsum binder and selection of its mixture composition.

The porous gypsum materials have lower compressive strength comparing to its dense counterparts. The dependence of W/B ratio on porous material compressive strength has minor effect as the increase of W/B from 0.2 to 0.8 did not change compressive strength of porous material (0.1-0.8MPa).

Figure 6. The relationship between water-binder ratio and compressive strength of gypsum based material.
Good correlation between compressive strength and density of gypsum material was obtained (Figure 7). Also there is some deviation of the results which might be affected by the treatment conditions of PG and the physicochemical properties of PG after its production, the overall tendency is clear. Again, the overlapping region between PG and commercial gypsum can be observed. With gypsum based binder the density in range from 200-1600 kg/m$^3$ could be covered and compressive strength from 0.1-29 MPa obtained.

Figure 7. The relationship between density and compressive strength of gypsum based material.

The results obtained in this research were compared with other literature studies addressing the study of natural or synthetic gypsum regarding to its properties depending from W/B ratio and results are show in Table 2. The performance of the PG gypsum in this research complies with data reported in literature (see table 2). However, the scattering of results is possible as different gypsum treatment conditions and mixture compositions could be prepared.

| Gypsum type | W/B ratio | Bulk density, kg/m$^3$ | Total porosity, vol.% | Compressive strength, MPa | Ref |
|-------------|-----------|------------------------|-----------------------|---------------------------|-----|
| Gypsum plaster | 1.3 | 880 | n/d | 4.0 | [12] |
| | 0.9 | 1080 | n/d | 14.5 | |
| Phosphogypsum 1 | 1.15 | 800 | 64.5 | 4.0 | This work |
| natural gypsum and gypsum from a chemistry industry, ratio 1:1 | 0.71 | 1130 | 46* | 9.4 | [10] |
| Commercial gypsum 1 | 0.6 | 1135 | 55.5 | 11.5 | This work |
| Phosphogypsum | 0.6 | 1200 | 52* | 12 | |
| Commercial hemi-hydrate gypsum | 0.45 | 1400-1920 | n/d | 5-15 | [19] |
| Phosphogypsum 2 | 0.43 | 1400 | 46 | 26 | This work |
| Commercial gypsum 2 | 0.3 | 1580 | 38.0 | 23.0 | This work |
| Foamed β-gypsum | 0.70 | 658 | n/d | 0.41 | [20] |
| Foam gypsum 1 | 0.77 | 213 | 91 | 0.1 | This work |
| Foam gypsum 2 | 0.27 | 430 | 81 | 0.19 | This work |

*calculated from bulk density and density of matrix

Table 2. Properties of waste gypsum and natural gypsum reported in literature.

3. Conclusions

Results indicate that commercial gypsum based binder could be effectively altered with waste-stream gypsum based binder – phosphogypsum. The phosphogypsum has finer nature comparing to natural gypsum binder and also harmful constituents might be present which brings negative effect on demand of water. The increase of water necessary to prepare fresh gypsum paste reduce the strength of the binder as the total porosity increased. The other effect of water increase in paste gives reduction of material
density. The water demand of phosphogypsum binder could be reduced by the use of superplasticizers reducing the W/B ratio to 0.43 and strength increase to 29 MPa. By the use of foaming agent, the density of gypsum material decreased from 700 to 200 kg/m³ with a reasonable compressive strength (0.1-0.8 MPa). The scattering of results is possible with similar W/B ratios which is associated with the different gypsum treatment conditions and selection of mixture composition showing the importance of selection proper materials and approaches for production of gypsum based materials.

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