Ternary gypsum-based materials: Composition, properties and utilization

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Abstract. In spite of the fact that gypsum is one of the most environmentally friendly binders, utilization of gypsum products is relatively narrow. The main problem of gypsum materials is their low resistance to the wet environment and radical decrease of mechanical properties with increasing moisture. The solution of the problem could be in use of composed gypsum-based binders, usually ternary, comprising gypsum, pozzolan and alkali activator of pozzolan reaction. These materials have a better moisture resistance and often also better mechanical properties. Paper provides literature survey of the possible compositions, properties and ways of utilization of the composed gypsum-based binders with latent hydraulic and pozzolan materials together with some results of present research performed by authors.

1. Introduction
Gypsum is one of the most environmentally friendly binders, because the energy consumption at its production is substantially lower compared to the cement or lime and it can be also produced from the numerous waste products. It is also nearly indefinitely recyclable. To the other advantages of gypsum belong its excellent fire behaviour, good workability, good acoustic properties and aesthetics. Unfortunately the utilization of the gypsum as a building material is restricted to the use in dry environment only, because gypsum loses its mechanical properties significantly when wet. There were several attempts to improve the water resistance of gypsum products, either by the modification of the gypsum material or by the impregnation of the surface.

Gypsum could be modified e.g. by clay minerals [1], by acrylic latex [2] or by composed waterproofing additives. Jianquan Li et al. prepared the water-proofing additive by emulsifying polyvinyl alcohol and stearic acid together, and mixing it with alunite, carboxylic acid sodium and aluminum sulfate [3]. The surface impregnation of the gypsum is also possible, but the durability of such a treatment is shorter-lived in comparison with the modification of the gypsum material. Colak found, that the impregnation of the gypsum surface by the epoxy resin could improve the water-resistance of gypsum significantly, but only for relatively short period [2].

Best results in the attempts to obtain water resistant gypsum-based materials were achieved by use of the composed binders with latent hydraulic and pozzolan materials. Because pozzolan reaction needs the alkali environment and because gypsum is neutral or slightly acid, these binders have to contain also some alkaline component (usually hydrated lime or cement). Such materials are called ternary, because three main components create the binder. The possible compositions of these materials, their properties and ways of their utilization are described.
2. Gypsum-based systems with the latent hydraulic or pozzolan materials

The difference between the latent hydraulic and pozzolan materials lays in the principles of their hydration reaction and their composition. While latent hydraulic materials are able to set and harden in the water after reaction with some activator, pozzolans need also the presence of the calcium hydroxide for reaction. Pozzolan materials usually do not contain the calcium oxide (or contain it only in small amount), while in the latent hydraulic materials contain the calcium oxide in higher amount [4].

Both types of materials need for the hydration alkaline environment, which is a reason, why they cannot be usually used in the gypsum directly, because pH of gypsum lies between 5 - 7. Therefore an alkaline environment have to be established in the gypsum mixture to start pozzolan reaction. The addition of calcium hydroxide (most often in the form of hydrated lime or as a product of cement hydration) seems to be most obvious choice, especially for the pozzolans. The calcium sulphate (either in the form of gypsum or anhydrite) is used very often in the latent hydraulic materials as an activator (although other activators could be used too), therefore their combination in the gypsum-based binders is logical. Sometimes even an additional source of calcium hydroxide is not necessary, if the mixture of gypsum and latent hydraulic material is alkaline sufficiently.

2.1. Hydration of the gypsum-based systems with the latent hydraulic and pozzolan materials

While the setting of gypsum could be described by the simple chemical reaction (1), the hydration of gypsum-based systems with latent hydraulic and pozzolan components is very complex, because very complicated CaO–SiO₂–Al₂O₃–CaSO₄–H₂O systems are created.

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\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O} + 1,5 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\] (1)

The main products, occurring from the hydration reactions are hydrated silicates (C-S-H), hydrated aluminates (C-A-H), ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) and gypsum (CaSO₄·2H₂O) [5]. The presence of ettringite was found in the system by several authors [6, 7, 8]. Some hydration products were found also by authors in the binder composed from commercial calcined gypsum, hydrated lime and granulated blast furnace slag (Fig. 1).

\[\text{ettringite} \quad \text{gypsum} \quad \text{amorphous phase (C-S-H)}\]

**Figure 1.** SEM image of composed binder from gypsum, hydrated lime and granulated blast furnace slag.

The existence of ettringite was proved also by the differential scanning calorimetry (DSC) thermal analysis of the composition of calcined gypsum - hydrated lime - blast furnace slag at the age 7 days. At temperature about 120 °C can be seen peak, which could be accredited to the decomposition of ettringite.
2.2. Volume stability of the gypsum-based systems with the latent hydraulic and pozzolan materials

Sometimes there are concerns about the volume changes related to the delayed ettringite formation and about subsequent loss of the mechanical properties. Most of the authors do not confirm that, mostly the constant increase of the strength is described even after longer periods (90-360 days) [9, 10]. We found that the presence of ettringite does not causes any decrease of strength after 90 days in the ternary materials, composed from gypsum, hydrated lime and silica fume or granulated blast furnace slag [11]. However, there were reported problems with volume changes in some gypsum-based binders. Bizzozerro et al. [12] found, that systems of calcium aluminate cement and calcium sulfoaluminate cement, both with added gypsum, show unstable expansion due to ettringite formation when gypsum is added above a given threshold. Also Ioannou et al. [13] report the volume expansion in the binary binder, formed by calcium sulfoaluminate cement and calcium sulphate (both dihydrate and anhydrite), when the amount of calcium sulphate is higher than 50 %.

In the materials without the cement the volume expansion was observed less frequently. It seems that in these materials the formation of ettringite takes place mostly in the porous systems because gypsum contains bigger pores than cement. Pure gypsum has unimodal porous system with the pore diameters between 0.1-1 μm, while the pores in cement materials are usually smaller (under 0.1 μm).

The volume expansion was observed also by Hung and Lin [14] in the material, composed from phosphogypsum, steel slag, ground granulated slag and limestone. In this case the unsoundness was attributed to the steel slag over dosage. Değirmenci [15] described the occurrence of cracks and loss of strength in the material, made from 50 % of raw phosphogypsum, 40% of fly ash and 10 % of hydrated lime, when stored in water. When calcined phosphogypsum was used instead of raw phosphogypsum, than any significant volume change was not observed.

In our present, yet unpublished research we found that some clay minerals, contained in pozzolan additions could cause volume changes and cracking of the material. The phenomenon was observed in the ternary materials made from calcined gypsum, hydrated lime and either metakaolin or ground ceramic brick. In the material with the metakaolin (Fig. 3) the volume instability could be attributed to the residual kaolinite and in the material with the ground ceramic brick the illite was found by the XRD analysis and it is also visible on the SEM of the material (Fig. 4).
2.3. Properties of the gypsum–based systems with the latent hydraulic and pozzolan materials

Pozzolan materials are used in cement-based materials as a partial cement replacement mainly from ecological and economic reasons. Therefore, the evaluation of these materials is based mostly on the verification, that latent hydraulic or pozzolan addition does not cause significant decrease of the properties (mainly mechanical).

Use of pozzolan materials in the gypsum-based materials follows different objective – mainly to improve their behaviour in the wet environment. Another problem of gypsum is sometimes low strength, which could be improved by the pozzolan and latent hydraulic materials also [16].

Several authors observed the improved resistance to the wet environment. Fraire-Luna et al. [6] compared the materials, prepared from gypsum (or anhydrite), ground granulated blast-furnace slag and metakaolin with pure gypsum or anhydrite. While the pure anhydrite lost more than 50% of one-day strength after 360 days in water, the strength of ternary composition achieved more than 400% of one-day strength. Camarini and DeMilito [17] measured the strength of the panels exposed to the external conditions for three years. The panels, made only from gypsum lost more than 2/3 of its original strength. Strength of the panels, prepared from 75% of hemihydrate and 25% of ground granulated blast-furnace slag stayed the same. We tested the strength of ternary material, composed from calcined gypsum, hydrated lime and metakaolin, stored in the water. While the compressive strength of material without metakaolin (from commercial gypsum and hydrated lime only) decreased, the strength of material with metakaolin increased by 11% after 180 days in water (Fig. 5).

Colak tested the frost resistance of gypsum-based materials [18]. He found that the strength of pure gypsum decreased by 90% after 5 freeze-thaw cycles already, while binder composed from 41% of gypsum, 41% of cement, 18% of pozzolan and 1% of superplasticizer had 78% of original strength after 30 freeze-thaw cycles. The frost resistance was improved significantly.

The strength development of different gypsum-based materials is in table 1.

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**Figure 3.** Cracks in composed binder from gypsum, lime and metakaolin.

**Figure 4.** SEM image of composed binder from gypsum, lime and ground ceramic brick.
Figure 5. Compressive strength of binders, composed from calcined gypsum, hydrated lime and with/without metakaolin.

Table 1. Strength development of some gypsum-based binders in the wet environment.

| Source   | Binder composition* [%] | Compressive strength [ MPa ] | Age [days] |
|----------|-------------------------|------------------------------|------------|
|          |                         | 1   | 3   | 7   | 28  | 90  | 120 | 180 | 360 | 1080 |
| [6]      | 100 HH b                | 3.1 | 3.1 | 2.7 | 2.7 | 2.4 | 1.2 | 1.2 | 1.7 |
| [6]      | 100 AH                  | 4.1 | 5.0 | 5.7 | 4.6 | 3.9 | 4.3 | 4.3 | 4.8 |
| [6]      | 75 AH, 25 GGBS          | 2.6 | 2.5 | 4.4 | 9.4 | 9.2 | 10.6| 13.8|     |
| [6]      | 75 AH, 15 GGBS, 10 MK   | 3.4 | 5.3 | 6.0 | 8.6 | 13.7| 14.7|     |     |
| [9]      | 80 HH, 10 GGBS, 5 PC, 5 LH | 4   | 7   | 10  | 15  |     |     |     |     |
| [10]     | 70 AH, 10 AF, 20 PC     | 8.4 | 13.0| 15.0| 16.0| 18  | 31  |     |     |
| [13]     | 65 DH, 35 CSAC          | 6.8 | 8.1 | 9.4 | 16.3| 10.2|     |     |     |
| [13]     | 50 AH, 50 CSAC          | 11.9| 21.9| 25.8| 43.3| 47.1|     |     |     |
| [14]     | 45 AH, 40 GGBS, 10 MV, 5 SS | 1.3 | 3.5 | 8.1 |     |     |     |     |     |
| [17]     | 75 HH, 25 GGBS          | 5   |     |     |     | 5.2 | 5.3 |     |     |
| [18]     | 41 HH, 41 PC, 18 NP     | 8   | 10  | 18  |     |     |     |     |     |
| [19]     | 70 AH, 24 GGBS          | 13  | 21  | 23  | 22  |     |     |     |     |
| [19]     | 50 AH, 50 GGBS          | 19  | 25  | 29  | 33  |     |     |     |     |
| [20]     | 75 AH, 10 GGBS, 15 PC   | 15  | 23  | 23  | 29  | 30  |     |     |     |
| [21]     | 40 HH, 40 AF, 20 LH     | 1.8 | 2.0 | 2.0 | 3.0 | 8.5 |     |     |     |
| [21]     | 40 HH, 40 AF, 10 LH, 10 PC | 2.0 | 2.5 | 4.5 | 8.8 | 12.1|     |     |     |
| [22]     | 50 AH, 34 AF, 16 PC     | 11  | 20  | 26  | 28  |     |     |     |     |
| [23]     | 40 HH, 40 AF, 20 LH     | 1.8 | 2.0 | 2.0 | 3.0 | 8.5 |     |     |     |
| [24]     | 30 HH, 40 P, 30 LH      | 5.6 | 5.9 | 6.8 | 7.2 |     |     |     |     |
| c        | 71 HH, 10 LH, 11 MK     | 28.9| 28.3| 29.8| 33.8|     |     |     |     |

* Main components only, additions up to 5 % are not mentioned
b Abbreviations: GGBS - ground granulated blast-furnace slag
HH - CaSO₄·0,5 H₂O AF - fly ash
AH - CaSO₄ LH - lime hydrate
MK - metakaolin NP - natural pozzolan
GL - ground limestone

c Authors unpublished work
3. Conclusions
By the utilization of composed gypsum-based materials with latent hydraulic and pozzolan materials can be solved main problem of gypsum binders, which are low water resistance and the loss of strength in the wet environment. These materials do not lose the mechanical properties in the wet environment; on the contrary their strength usually increases. For pozzolan components ternary binders seems to be the best solution, while for latent hydraulic components sometimes binary binders are sufficient. The mechanical properties and frost resistance could be improved by the latent hydraulic or pozzolan additions also. In some composition the volume instability, caused by ettringite formation was reported, but in smaller extent than in cement-based binders and it can be avoided by the right design of material. The presence of some clay minerals could cause the volume changes also.

Composed gypsum-based materials can be used for production of water-resistant gypsum boards, self-levelling floors, bearing blocks for outer walls, fire-proofing constructions and similar products.

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4. References
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