The properties of composite materials of ternary mixtures based on gypsum

D Dobias¹, M Vokac¹ and P Pokorný¹

¹ Klokner Institute, Czech Technical University in Prague, Solinova 7, Prague 6, Czech Republic

E-mail: daniel.dobias@cvut.cz

Abstract. In this paper, properties of composite materials containing ternary binders are determined. Except gypsum, ternary binders containing also pozzolans and alkaline component, which serve as an activator of pozzolanic reaction. The main aim of this research was to investigate changes in physical and chemical properties and pore structural characteristics due to additions of ternary binders. Experimental results showed that changes in the properties of the composite depend not only on the amount of the addition, but also on the kind of pozzolan.

1. Introduction

Gypsum application in building structures has its difficulties. One of them is partial solubility of solid gypsum in the water when about 256 mg of gypsum would dissolve in 100 grams of water. It means that during a long-term contact of gypsum or gypsum-based material (gypsum boards, gypsum blocks, gypsum plasters) with humidity, the solid gypsum binder is gradually dissolving. Quantity of such dissolved material depends on quantity of the water in contact with the material. Dissolution is more intense if the water is repeatedly replaced as the solution is not saturated. Gypsum solubility in the water can be reduced by presence of calcic or sulphate ions, on the contrary, solubility of plaster increases in solutions containing acids or other ions. Solubility can cause loss of cohesion during the time.

Another disadvantage of application of chemically clean gypsum (i.t. without admixtures and additives), is the fact that gypsum is changing substantially its mechanical properties due to change of humidity and temperature. Increased humidity of gypsum by 12% reduces its strength by about 50% and therefore application of gypsum is not recommended in the environment with air humidity higher than 60%.

The last important factor limiting applicability of gypsum at increased humidity is its corrosive effect on metals. This occurs, when the calcium sulphate solution reaches pH 5 and less (under RH more than 60%). This humidity is causing corrosion of metal which is in contact with gypsum thus creating rusty spots on the gypsum surface [1].

Gypsum properties can be improved by application of pozzolanic admixtures. Many authors are describing increased humidity resistance in these materials. In order to act actively, pozzolans require presence of calcium hydrate (Ca(OH)₂) or portland cement as their addition is increasing pH of the mixture allowing the so called pozzolanic reaction. In mixtures without alkaline additives, pozzolans would act only as an inert aggregate. Materials based on gypsum binder with admixture of pozzolan and activator (calcium hydrate, portland cement) are marked as ternary binders. Ternary binders preserve from major part their gypsum properties but have bulk density and heat-carrying capacity.
Ternary binders on calcined gypsum basis are more promising. Addition of a second binder such as portland cement or lime can lead to activation of applied pozzolan [2, 3], thus to an effective use of all three components. Application of gypsum and lime together in a binder appears as particularly suitable because properties of both of them are complementary. While the lime shrinks during setting, the gypsum slightly expands [4], the setting of lime is slow, the gypsum sets quickly, and the workability of gypsum-lime blends is better. Application of pozzolan in such kind of binder is thus a logical solution.

In the ternary calcined gypsum-lime-pozzolan blends, which were studied to date, fly ash was the most frequently used. Singh and Garg [5] investigated a blended binder consisting of 40% calcined phosphogypsum, 40% fly ash and 20% hydrated lime and observed an increase in compressive strength up to 90 days. Shen et al. [6] analysed several ternary mixes and achieved best results for the binder composed of 8-12% lime, 18-23% phosphogypsum and 65-74% fly ash. Kumar [7] in similar experiments reported the highest compressive strength for the blend with 40% fly ash, 30% gypsum and 30% lime.

Article is dealing with observation of the impact of application of pozzolanic admixtures (silica fume, slag, brick powder) in the gypsum based binder on mechanical and physical properties of composite materials.

2. Materials and experimental details

As pozzolanic admixtures were used materials formed as secondary products of industrial production, specifically silica fume (marked T-M), slag (T-S) and brick powder (T-B). Lime hydrate (calcium hydrate) was selected to act as activator of pozzolanic reaction. For comparison also reference admixture was prepared without any pozzolan (marked T-0).

Pozzolan component was proposed in such a way so the rate of material quantity of calcium in lime hydrate and of silicon in amorphous SiO\textsubscript{2} contained in the pozzolan is equal to 1.5. This value was proposed based on previous experiments [8]. In case this rate value is lower, the calcium hydrate would be quickly exploited and no products of pozzolan hydration would form in the mixture. On the other hand, if the rate value is higher, some mixtures might not fulfil the condition of proportional representation of plaster.

Composition of individual mixtures is described in table 1. Water coefficient was calculated per binding compound of mixtures (i.e. overall quantity of gypsum, lime and pozzolanic admixture) and was modified according to required process ability. Upon determination of water coefficient it was decided, based on previous experiments [8], that the value of dispersion of all mortar mixtures would be between 180 – 190 mm, so all wet mixtures can be easily processed and too quick hardening of material is avoided. In order to determine behaviour of mixtures, dispersion tests were performed according to ČSN EN 13454 [9].

Tests prisms were produced from individual mixtures with dimension 160x40x40 mm. Once the solid the samples were demoulded they were set for 24 hours in laboratory conditions (temperature 20°C and relative humidity 50% ± 15%). Then they were set in the water until the time of tests.

| Sample marking | Pozzolan type | Pozzolan [% wt] | Lime [% wt] | Gypsum [% wt] | Water-binder ratio | Spill [mm] |
|---------------|---------------|----------------|-------------|---------------|-------------------|-----------|
| T-M           | silica fume   | 8.5            | 15.0        | 76.5          | 0.70              | 189       |
| T-0           | 0             | 15.0           | 85.0        |               | 0.77              | 180       |
| T-S           | slag          | 15.0           | 15.0        | 70.0          | 0.72              | 190       |
| T-B           | brick powder  | 30.0           | 15.0        | 55.0          | 0.68              | 187       |
3. Measuring method

3.1. Determination of bulk density, absorption capacity and open porosity

For determination of bulk density, absorption capacity and porosity were used the method of hydrostatic weighing. Tests were performed on samples treated in the water for 28 days. Test specimens were dried prior testing to a stable weight - \( m_d \). Samples were set in desiccator and with use of vacuum pump the vacuum was reached. Test specimens remained in this environment for 2 hours. Then such a quantity of isopropanole was added to wet the bottom part of samples. From this moment such quantity of isopropanole was added during 30 minutes until samples were fully immersed. Isopropanole was added until the moment when the level at least 20 ± 5 mm above the upper level of test bodies was reached. When no air bubbles were visible on the surface of samples, the vacuum pump was switched off. Test specimens were removed from vacuum vessel, slightly dried and weighed - \( m_f \). Samples were subsequently hydrostatically weighed under the level of isopropanole - \( m_{sF1} \) in order to determine bulk density. Absorption capacity and open porosity were determined from obtained values.

For calculation were used following formulas:

\[
\rho = \frac{m_d \cdot \rho_{F1}}{(m_s - m_{sF1})} \quad [\text{kg/m}^3] \tag{1}
\]

\[
V_p = \frac{(\rho \cdot m_{F1}) \cdot 100}{(\rho_{F1} \cdot m_d)} \quad [%] \tag{2}
\]

\[
N = \frac{(m_s - m_d) \cdot 100}{m_d} \quad [%] \tag{3}
\]

where \( \rho \) is bulk density of test specimen, \( \rho_{F1} = 998 \text{ kg/m}^3 \) is specific weight of test liquid, \( m_{F1} \) is weight of the liquid absorbing the tested specimen, \( m_{sF1} \) is weight of saturated test specimen in the liquid, \( m_d \) is weight of dried test specimen, \( m_s \) is weight of test specimen soaked with the liquid, \( V_p \) is open porosity and \( N \) is absorption capacity.

3.2. Mechanical tests

Also some mechanical properties were tested in the samples of mortars containing ternary binders, as fracture energy, which is the basic parameter for non-linear modelling of quasi-brittle materials and bending strength evaluated from this test. Tests were performed on samples treated in the water for 28 days. Fracture energy was tested on testing specimens 40 x 40 x 160 mm in three-point bending test. The span was 120 mm. Notch about 10 mm deep defining the crack area was prepared in the middle of the span. During the actual test the specimen is loaded by displacement. Acting force and sample deflection are measured. These values are transferred to the load displacement diagram, see figure 1. The fracture energy related to unit of fracture area is calculated by integration of L-D diagram and the following formula based on recommendation of FMC1 [10] was used:

\[
G_t = A_{iip}(W_0 + mg\delta_0), \tag{4}
\]

where \( G_t \) is fracture energy, \( A_{iip} \) size of the failure area, \( W_0 \) value of integral under load displacement diagram, \( m \) weight of testing specimens between supports, \( g = 9.81 \text{ m/s}^2 \) is acceleration of gravity and \( \delta_0 \) deformation at failure. We can also calculate from this test the tensile strength in bending \( f_{db} \), resp. its estimate, as normal tension in the section is affected by the notch.

3.3. Thermal analysis of ternary mortars

In order to determine composition of solid binders the samples of individual mixtures were tested by thermal analyses. Thermal analysis is the method during which some physical properties of tested matter are monitored in relation to time or temperature.

Simultaneous thermal analysis consisting of differential scanning calorimetry (DSC) and thermogravimetry (TG) was used to find and quantify hydration products of all studied samples. This method analyzes heat effects associated with phase transitions or chemical reactions as a function of temperature in a chosen atmosphere (inert or reactive).
The experiments were done in the temperature range from 25 to 1000 °C in a nitrogen atmosphere with a flow rate of 40 mL min\(^{-1}\). The heating rate was 20 °C min\(^{-1}\). Samples were tested in the age of 120 days.

4. Results and discussion

4.1. Bulk density, absorption capacity and open porosity

Results shown in the table 2 prove that differences in tested materials are very small but certain changes of behavior can be detected in material with pozzolanic admixtures. All mixtures with pozzolanic admixtures proved higher bulk density, lower absorption capacity and open porosity than the mixture without pozzolan (T-0). It is evident from the results that pozzolanic admixtures, mainly hydrated microsilica and slag created together expected CSH phase and secondary ettringit, which are products filling pores in the material. Porosity in the mixture T-B with brick dust was almost the same as in the reference mixture T-0.

| Sample marking | Bulk density ρ [kg/m\(^3\)] | Porosity V\(_p\) [%] | Absorption capacity N [% wt] |
|----------------|------------------------------|---------------------|-----------------------------|
| T-M            | 1058.59                      | 41.44               | 39.5                        |
| T-0            | 1030.54                      | 42.91               | 41.6                        |
| T-S            | 1077.87                      | 41.64               | 38.6                        |
| T-B            | 1068.73                      | 42.83               | 40.0                        |

4.2. Mechanical properties

Resulting values of fracture energy and tensile strength in bending are shown in table 3. Three testing specimens were tested for each mixture, figure 1 is showing curves of one representative sample of the given mixture and table 3 is showing average values.

![Figure 1](image-url)
Table 3. Values of fracture energy $G_f$ and tensile strength in bending $f_{mb}$ (average from 3 samples).

| Sample | 1 T-M | 2 T-S | 3 T-B | 4 T-0 |
|--------|-------|-------|-------|-------|
| $G_f$ [N/m] | 7.50  | 7.26  | 7.28  | 7.08  |
| $f_{mb}$ [MPa] | 1.25  | 1.05  | 0.90  | 0.84  |

Diagram on figure 1 and table 3 contain individual mixtures arranged according to bending strengths and fracture energies. There is of course strong dependence between these values. A lowest value of tested mechanical quantities has the mixture without pozzolanic admixtures. Parameters were improved in all cases with added pozzolanic admixtures, namely the strongest in microsilica (improvement of bending strength in average by 49 %), further in slag (25 %) and ground brick fragment (7 %). Increasing of fracture energy is not so significant, e.g., in case of microsilica only by 6 %.

4.3. Thermal analysis

Results of thermal analysis are shown in diagrams (figure 2-5) and in the table 4.

![Figure 2. DTG curves of samples of ternary binders.](image)

Table 4. Mass defects and calculated quantity of individual phases in samples of binders.

| Sample | Mass defects [%] | Content [%] | CaSO$_4$·2H$_2$O | CaCO$_3$ | Ca(OH)$_2$
|--------|------------------|-------------|------------------|---------|--------|
|        | 30-120°C | 120-200°C | 400-500°C | 650-800°C |        |        |        |
| T-0    | 0.79 | 14.72 | 0.33 | 5.97 | 70.3 | 13.6 | 1.4 |
| T-M    | 1.14 | 13.44 | 0.00 | 4.50 | 64.2 | 10.2 | 0.0 |
| T-C    | 5.68 | 8.90  | 0.10 | 4.14 | 42.5 | 9.4  | 0.4 |
| T-S    | 3.98 | 12.39 | 1.48 | 1.76 | 59.2 | 4.0  | 6.1 |
Figure 3. DSC curves of samples of ternary binders.

From thermogravimetry curves of individual binder samples are well visible 4 changes of mass defect. Under the temperature 30-120 °C residual humidity is releasing and CSH phase is disintegrated. Under the temperature 120-200°C gypsum rock is dehydrating into hemihydrate and anhydrite. It is evident that size of the peak depends on quantity of gypsum component in the mixture. Under the temperature 400-500°C portlandite disintegrates into calcium oxide and water and under the temperature 650-800°C the CaCO₃ disintegrates into calcium oxide and carbon dioxide. Behavior of curves of thermal analysis in all materials with pozzolanic admixture shows very similar trend. Based on the quantity of portlandite in samples of binders it is best comparison of reactivity of individual pozzolans. It is evident that slag reaction is slowest compared to silica fume, where the portlandite is already exhausted by pozzolanic reaction.

5. Conclusions
Obtained results shown, that application of pozzolanic admixture in the gypsum-based binder is significantly improving material properties of test specimens of binders. It is evident from results that application of pozzolan caused in the samples products pozzolanic reaction, which has positive impact on water transport properties. Ternary binders with pozzolan have higher bulk density and on the contrary lower absorption capacity and open porosity than mortars without pozzolan. Also values of tested mechanical quantities were higher in all binders with pozzolan. Best results were obtained in samples with admixture of microsilica when all monitored parameters got improved. This improvement was most probably reached due to highest pozzolanic reactivity of microsilica as proved results of the thermal analysis.

More extensive tests will be performed based on these first results which proved positive impact of pozzolan in ternary binders which might lead to wider application of gypsum-based material in building structures.

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