EFFECT OF DRYING TEMPERATURE ON PROPERTIES OF HARDENED GYPSUM

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Abstract:
Experimental research dealing with the effect of drying temperature on the properties of hardened flue gas desulphurization (FGD) gypsum is presented in the paper. The measurements of basic thermal and hygric parameters of FGD gypsum modified by the addition of hydrophobization substances and plasticizers are carried out, using the specimens subjected to two different thermal drying regimes, with the maximum temperatures of 40 °C and 80 °C, before the measurements. Bulk density, open porosity, thermal conductivity, volumetric heat capacity, water absorption coefficient and apparent moisture diffusivity are determined and compared to the properties of hardened gypsum without any admixtures.

Keywords:
hardened gypsum, thermal stability

INTRODUCTION

Thermal stability of hardened gypsum belongs to the tasks which are not yet resolved with clear outputs. This is one of the reasons why gypsum is not used in exterior applications. The problem of water removal from gypsum is relatively complex mainly because samples of hardened gypsum contain both physically and chemically bound water.

Calcined gypsum – hemihydrate $CaSO_4 \cdot ½\ H_2O$ – can be produced by various technologies. Nowadays, still relatively new but already very promising seems to be its production using the dehydration of waste flue gas desulfurization (FGD) gypsum – dihydrate $CaSO_4 \cdot 2H_2O$ – at the temperatures of 110 to 150 °C. Then, β-form of hemihydrate (calcined gypsum) is formed according to the equation, which describes the process of calcination:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot ½\ H_2O + 1\ ½\ H_2O. \quad (1)$$

The solid structure of calcined gypsum is created by reverse hydration from hemihydrate to dihydrate according to equation

$$CaSO_4 \cdot ½\ H_2O + 1\ ½\ H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (2)$$

Factors which affect the removal of chemically and physically bound water are temperature, relative humidity and pressure (air pressure or vacuum). If the critical temperature when starts the

dehydration of calcium sulfate dihydrate to hemihydrate is exceeded gypsum is somewhere between the two stages: dihydrate and hemihydrate.

The opinions of various researchers on the critical temperature are very different. Schulze et al. [1] and Řičánek [2] state that this temperature is 40 °C or 42 °C, respectively. Šatava [3] dried gypsum samples at the temperature of 40 °C. These values of critical temperature are similar to the drying temperature of gypsum samples recommended by the Czech standards [4] and [5]. However, in another studies Kupilík [6] and Wirsching [7] determined the critical temperature to be higher than 70 °C. Turk and Bounini [8] compared world standards for gypsum and gypsum plasters. They found that the recommended drying temperatures for gypsum were between 35 °C and 50 °C. The same authors, however, presented their own DTA results which showed that gypsum samples after drying over 80 °C always exhibited two peaks but separation of these peaks was complicated.

In this paper, the effect of two thermal drying regimes of hardened FGD gypsum specimens, with the maximum temperatures of 40 °C and 80 °C and at atmospheric pressure, on the measured hygric and thermal properties is investigated.

EXPERIMENTAL METHODS

Basic physical properties, namely bulk density, matrix density and open porosity, were measured by water vacuum saturation method [9]. Each sample was dried in a drier to remove majority of the physically bound water. After that the samples were placed into desiccator with distilled water. During three hours air was evacuated with vacuum pump from the desiccator. The specimen was then kept under water not less than 24 hours.

The water absorption coefficient and apparent moisture diffusivity representing the moisture transport parameters were determined from a one dimensional water sorption experiment [10]. The specimen was water and vapor-proof insulated on four lateral sides and the face side was immersed 2 mm in the water. A constant water level in the tank was achieved using a bottle placed upside down. The known water flux into the specimen during the suction process was then employed to the determination of the water absorption coefficient. The apparent moisture diffusivity was calculated using the water absorption coefficient and saturated water content [10].

Thermal conductivity and volumetric heat capacity were determined using the commercial device ISOMET 2104 (Applied Precision, Ltd.). ISOMET 2104 is a multifunctional instrument equipped with various types of optional probes. Needle probes are for porous, fibrous or soft materials, surface probes are suitable for hard materials. The measurement is based on the analysis of the temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor heater having a direct thermal contact with the surface of the sample.

MATERIALS AND SAMPLES

β-form of calcined gypsum with purity higher than 98 % of flue gas desulfurization (FGD) gypsum was used in the investigations. It was produced in the electric power station Počerady, CZ. The reference material without any admixtures was denoted as S0.

Two plasticizers and three hydrophobization admixtures were used for modifications of the basic calcined gypsum. For the first modification (denoted as S1) we used the plasticizer PERAMIN SMF 20 with a concentration of 0.5% of the mass of the solid phase. The second modification S2 was done using the plasticizer MELMENT F 4000 with a concentration of 0.2% of mass of the solid phase. The amount of plasticizers was chosen in such a way that the consistence of the gypsum paste was approximately the same as that of the reference material. The third modification contained the hydrophobization admixture IMESTA IBS 47, an alloy

hydrophobization powder for gypsum compounds produced by Imesta Inc., Dubá u České Lípy, CZ. Concentration of this admixture for material which was demoted as S3 was 0.5% by mass. The modified gypsum material denoted as S4 contained the admixture ZONYL 9027 (a fluorochemical solution that provides a durable, subsurface, transparent, protective barrier against oil and water on porous surfaces) produced by Du Pont, USA. This admixture was used as 5% water solution. The last modification denoted as S5 contained 5% water solution of the hydrophobization admixture ZONYL 301 produced by Du Pont again.

Two different temperatures were used for drying of gypsum samples, namely 40 and 80 °C. Therefore, the particular samples are denoted as either 40 or 80 to distinguish between the chosen drying regimes. Table 1 shows the detailed composition of gypsum mixtures including the water/gypsum ratio.

Table 1 Composition of measured materials

Material	Type of the admixture	Name of the admixture	Concentration	Water/gypsum ratio
S0	-	-	-	0.627
S1	plasticizer	Peramin SMF 20	0.5 % by mass	0.500
S2	plasticizer	Melment F 4000	0.2 % by mass	0.500
S3	hydrofobization admixture	Imesta IBS 47	0.5 % by mass	0.627
S4	hydrofobization admixture	Zonyl 9027	5% solution	0.627
S5	hydrofobization admixture	Zonyl 301	5% solution	0.627

The samples were mixed according to the Czech standard ČSN 72 2301 [11]. For the measurements of particular physical, thermal and hygric parameters, we used the following specimens: basic properties and apparent moisture diffusivity – 6 specimens 50 x 50 x 23-25 mm, thermal conductivity and volumetric heat capacity – 6 specimens 70 x 70 x 70 mm.

EXPERIMENTAL RESULTS AND DISCUSSION

The basic properties of both reference and modified gypsum for the drying temperatures of 40 and 80 °C are shown in Table 2. The values of bulk density and porosity were similar for the materials S0, S3, S4 and S5, the differences being up to 10% no matter the drying temperature. This can be explained by the same water/gypsum ratio used in the preparation of reference and hydrophobized materials. The application of plasticizers (S1 and S2) led to decrease in porosity by about 10% and increase in bulk density up to 10% compared to the reference specimens. This is an expected consequence of the application of plasticizers and the decrease of the water/gypsum ratio. The comparison of results achieved for samples dried at the temperatures of 80 °C and 40 °C shows that higher bulk density and lower porosity had the materials which were dried at 40 °C. This means that some originally chemically bound water was removed after drying to 80 °C.

Table 2 Basic physical properties of measured materials

Material	Bulk density [kgm^{-3}]	Matrix density [kgm^{-3}]	Open porosity [% by volume]
S0-80	1019	2530	60
S1-80	1124	2495	55
S2-80	1089	2577	58
S3-80	998	2530	61
S4-80	962	2530	62
S5-80	930	2530	63
S0-40	1170	1900	38
S1-40	1270	1950	35
S2-40	1250	1935	35
S3-40	1100	1900	42
S4-40	1060	1900	44
S5-40	1120	1900	41

Table 3 shows thermal and hygric properties of studied materials. The samples used for measurements were dried at first and then stored at laboratory conditions: relative humidity 50% and temperature about 20 °C. The materials dried at 80 °C had all almost the same values of thermal conductivity and volumetric heat capacity. For the drying temperature of 40 °C the differences were higher. The lowest thermal conductivity exhibited the material S4, the highest had the materials S1 and S2 produced using plasticizers. This corresponds with the open porosity measurements in Table 2. The values of thermal conductivity of samples dried at 80 °C were about two times lower then for materials dried at 40 °C. This is also in good agreement with the measured basic properties (see Table 2). The volumetric heat capacity was not affected by the drying temperature in a significant way. The differences were only up to 5%.

From the point of view of water transport properties the application of hydrophobization admixtures was successful for S4 (ZONYL 9027) and S5 (ZONYL 301). The water absorption coefficient decreased about 5 times and apparent moisture diffusivity more by one order of magnitude compared to the reference specimens. In the material S3 (IMESTA IBS 47) the hydrophobization had a lower effect which was quite comparable with the use of plasticizers (S1 and S2). The drying temperature affected only water transport properties of the materials S1, S2 and S3 in a significant way. Water absorption coefficient of the specimens dried at 40 °C was about two times lower than for those dried at 80 °C. This is in basic accordance with the open porosity data in Table 2. The hydrophobization used for the materials S4 and S5 was the same successful for both drying temperatures. On one hand, this confirms the proper function of both hydrophobization admixtures, no matter the drying temperature. On the other, this effect may also be partially due to the secondary hydration after the specimens dried at 80 °C came in contact with water because the

water absorption coefficient of the reference material was found to be basically unaffected by drying temperature as well.

Table 3 Thermal and hygric properties of measured materials

Material	Thermal conductivity [$Wm^{-1}K^{-1}$]	Volumetric heat capacity [$Jm^{-3}K^{-1}$]	Water absorption coefficient [$kgm^{-2}s^{-1/2}$]	Apparent moisture diffusivity [m^2s^{-1}]
S0-80	0.22	1.49 E+6	0.31	2.6 E-7
S1-80	0.22	1.50 E+6	0.25	2.1 E-7
S2-80	0.23	1.50 E+6	0.31	2.5 E-7
S3-80	0.22	1.48 E+6	0.25	1.5 E-7
S4-80	0.21	1.46 E+6	0.06	7.3 E-9
S5-80	0.21	1.46 E+6	0.11	2.6 E-8
S0-40	0.43	1.58 E+6	0.30	6.1 E-7
S1-40	0.53	1.63 E+6	0.14	1.6 E-7
S2-40	0.54	1.64 E+6	0.13	1.4 E-7
S3-40	0.40	1.56 E+6	0.14	1.2 E-7
S4-40	0.36	1.55 E+6	0.06	1.9 E-8
S5-40	0.43	1.53 E+6	0.06	2.0 E-8

CONCLUSIONS

The measurements of basic physical, hygric and thermal properties in this paper have shown that the drying temperature was an important factor affecting the properties of gypsum in a significant way. Drying at 80 °C was apparently not a suitable treatment because already the basic properties of both reference and modified gypsum materials were changed very remarkably in a comparison to drying at 40 °C. Apparently, some originally chemically bound water was removed after heating to 80 °C which meant that the material was not thermally stable at this temperature any longer. Therefore, it can be concluded that the critical temperature for the dehydration of calcium sulfate dihydrate to hemihydrate lies somewhere between 40 and 80 °C. The relatively close results obtained for water transport properties of specimens dried at 40 and 80 °C for some studied materials which was in a clear contradiction to the measured data of bulk density and open porosity were probably achieved due to the secondary hydration taking place after the contact of the specimens with water.

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