Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 791–796

EFFECTS OF THE TYPE OF CALORIMETER AND THE USE OF PLASTICIZERS AND HYDROPHOBIZERS ON THE MEASURED HYDRATION HEAT DEVELOPMENT OF FGD GYPSUM

V. Tydlitát, P. Tesárek and R. Černý[*]

Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague,
Thákurova 7, 166 29 Prague 6, Czech Republic

Thermal phenomena at the hydration of calcium sulphate hemihydrate ($CaSO_4\cdot 0.5H_2O$) are investigated in the paper. Time development of hydration heat of β-calcium sulphate hemihydrate prepared from flue gas desulphurization (FGD) gypsum is determined using two different types of calorimeter, namely the differential calorimeter DIK 04 and the isothermal heat flow calorimeter KC 01, and the differences in measured data analyzed. Then, the effects of plasticizers and hydrophobizers on the hydration process of analyzed gypsum mixtures are studied.

Keywords: *differential calorimeter, gypsum, hydration heat, isothermal heat flow calorimeter*

Introduction

The hydration process of gypsum when calcium sulphate hemihydrate is converted into dihydrate according to equation

$$CaSO_4\cdot 0.5H_2O+1.5H_2O\rightarrow CaSO_4\cdot 2H_2O+\text{hydration heat} \qquad (1)$$

is known for thousands of years but details of this process were not explained until the past century.

Šatava [1, 2] presented arguments that at the setting process of gypsum suspensions the hydration reaction is realized in such a way that calcium sulphate hemihydrate is dissolved at first in water solution and dihydrate crystallizes from supersaturated solution once nucleation centres are created on defect places of hemihydrate crystal surfaces. Number of the nuclei depends on the water/gypsum ratio, mechanical history of suspensions and temperature.

Hand [3] described the hydration of hemihydrate in similar manner, using the higher solubility of hemihydrate in water (0.65 mass%) compared to dihydrate (0.2%). If hemihydrate is mixed with water and saturated solution is achieved, the solution is oversaturated against dihydrate which is thus separated out the solution. This makes further dissolution of hemihydrate possible, followed by further separation of dihydrate, etc. For the description of hydration kinetics Hand [3] compared three models of crystallization, which were based on analytic functions corresponding to Avrami equation. However, with the experimental data available to him he was not able to decide which of the crystallization models was the most suitable, in an unambiguous way.

Other mechanism of gypsum hydration was proposed by Abriel *et al.* [4] and Bezou *et al.* [5] on the basis of neutron and X-ray powder diffraction studies. They assumed that gypsum suspensions hydrated by a topochemical process where the molecules of water directly entered the crystal lattice of calcium sulphate hemihydrate without previous dissolution.

The first thermodynamic knowledge on the thermal effects at hydration of calcium sulphate hydrates appeared in 1940s. Wirsching [6] presented results of Kelley *et al.* [7] who studied thermodynamic properties of the $CaSO_4$–H_2O system. Eipeltauer [8] in one of the first systematic studies determined integral hydration heats in the $CaSO_4$–H_2O system by solution calorimetry. Bushuev [9, 10] described structural differences between β-calcium sulphate hemihydrate ($CaSO_4\cdot 0.5H_2O$) and α-calcium sulphate hemihydrate ($CaSO_4\cdot 0.67H_2O$) which made possible further insight into the differences in hydration heats of α and β hemihydrates. Freyer and Voigt [11] studied crystallization in the $CaSO_4$–H_2O system. Hydration heats of various compounds in the $CaSO_4$–H_2O system collected from various sources by Wirsching [6] are summarized in Table 1.

Calorimetric measurements are commonly used in gypsum industry for the determination of quality (purity) of gypsum plasters (hemihydrates), which are produced by calcination (dehydration of dihydrate to hemihydrate). Fischer [12], Fietsch and Ramdohr [13]

---

[*] Author for correspondence: cernyr@fsv.cvut.cz

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Hydration heats in the $CaSO_4$–H_2O system [6]

Reaction	Hydration heat of dihydrate at 25°C/J mol^{-1} (J g^{-1})
β $CaSO_4 \cdot 0.5H_2O+1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O$	19300±85 (111.9±0.50)
α $CaSO_4 \cdot 0.5H_2O+1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O$	17200±85 (100.0±0.50)
β $CaSO_4$ III+$2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	30200±85 (175.3±0.50)
α $CaSO_4$ III+$2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	25700±85 (149.6±0.50)
$CaSO_4$ II+$2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	16900±85 (98.0±0.50)

and Gerard [14] referred on the application of results of hydration heat development monitoring in the course of gypsum manufacturing. The hydration heat development data can also be used for controlling the process of calcination (adaptation of maximal temperature, time factor, etc) [6].

As for other applications of thermal analysis and calorimetry in the $CaSO_4$–H_2O system, Folek and Kowol [15] performed calorimetric analysis of various calcium sulphate phases in the course of gypsum hydration. Ambúz *et al.* [16] applied differential calorimeter for monitoring of setting of cement-based silicates containing gypsum. Evju [17] used dynamical corrections during setting of calcium sulphate in a simple isothermal differential calorimeter with a long time constant. The applied calorimeter was a constructional element of the commercially produced calorimeter TAM AIR, [18]. Mtschedlow-Petrossian *et al.* [19] and Oliew and Wieker [20] used accurate isothermal differential calorimeters for monitoring of heat flow. Zdravkov and Pelovski [21] studied the thermal behaviour of gypsum–lime–fayalite composites using DTA/TG and X-ray investigations and identified different hydration products for different ratios of the basic components. Dantas *et al*. [22] used temperature modulated differential scanning calorimetry to identify the different gypsum phases after calcination of $CaSO_4 \cdot 2H_2O$. Rahhal *et al.* [23] performed calorimetric studies of Portland cement with gypsum addition and found that the addition of excess gypsum caused the Portland cement to generate greater heat of hydration per gram.

This paper should contribute to the solution of two basic problems in the measurement of time development of hydration heat of calcium sulphate hemihydrate. The first is how the application of different types of calorimeters can affect the measured results and which of the commonly applied calorimetric techniques is more reliable for monitoring hydration heats in the $CaSO_4$–H_2O system. The second is how the hydration heat development can be influenced by using various admixtures to the gypsum binder.

Experimental

Studied material, its basic classification and modifications

The β-form of calcined flue gas desulphurization (FGD) gypsum produced in the electric power station Počerady, Czech Republic, was used in the experimental studies in the paper. Its purity was higher than 95%.

The basic classification of the studied FGD gypsum was performed according to the Czech standard ČSN 72 2301 [24]. The first criterion of this classification was compressive strength for the time of 2 h after mixing. The lowest compressive strength among three specimens had to correspond to the requirements for the particular classes G-2 to G-25 (the numbers mean compressive strengths in MPa, there are 12 groups altogether). The second criterion was the initial and final setting times using the Vicat device (the classes A to C mean fast, moderate and slow setting). The last criterion was grinding fineness using the 0.2 mm sieve residue where the binder was classified into coarsely, medium and finely milled (classes I to III).

For the first two classification criteria, gypsum mixtures having the so-called ‘normal consistence’ had to be used. The normal consistence was determined using the slump test described in [24]. The standard metal cylinder with the diameter of 50 mm and height of 100 mm was fully filled by water and gypsum mixture. Then the mixture was poured out from the cylinder, the slump measured in two perpendicular directions and the average value calculated. The standard slump corresponding to the normal consistence was 180±5 mm. For the studied gypsum it was achieved for the water/gypsum ratio of 0.627.

The results of the FGD gypsum classification are summarized in Table 2. According to these results the studied FGD gypsum can be classified as G-13 B III.

In the hydration heat development studies in the paper, several modifications of FGD gypsum were investigated. The reference material without any admixtures was denoted as S0. In two of the modifications, which were denoted as S1, S2, the plasticizers PERAMIN SMF 20 and MELAMIN F 4000 were used, respectively. Three other modifications denoted as S3, S4, S5 contained hydrophobizing admixtures, in S3 it was IMESTA IBS 47, in S4 ZONYL 9027 and in S5 ZONYL 301. The exact composition of studied gypsum mixtures is shown in Table 3.

Instruments

Two different types of calorimeters were used in the experimental work in the paper. The first was the commercially produced differential calorimeter DIK 04 [24]. In this type of calorimeter a difference method is used for temperature monitoring of partially insulated hydrating samples. The measurement principle is based on the comparison of the approximately constant temperature of the etalon made of aluminum with the temperature of the hydrating mixture. So, the method is somewhat similar to differential thermal analysis but without external heating. The analyzed system is placed into an upside down positioned Dewar flask. Insertion of the specimen of about 3–5 g in a plastic container into the device including addition of water and mixing takes less than 1 min. However, tempering of both the gypsum specimen and water at least one hour before beginning of the measurement is necessary. An amplifier with A/D converter enables data acquisition using PC. Data can be recorded either in digital or graphic form using software delivered with the calorimeter.

The second device used for the measurements of hydration heat was the isothermal heat flow calorimeter KC 01 which was designed in the Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague. The device is based on the differential measurement of heat flow. Detectors for the heat flow measurement are constructed in the form of copper-constantan thermocouple columns, which are wound up on an insulator plate. The thermocouple joints are placed on the edges of the plate and glued to a copper tube which a cylinder copper reaction vessel with the specimen of about 1–2 g is inserted into. The detectors on the tube where the hydration process takes place are connected differentially with the detectors for determination of heat flow at the reference vessel where no hydration processes occur. The vessels and detectors are arranged in an axial symmetric way. Data collection is performed using the datalogger MS 2 (COMET) with the signal detection range of 0–100 mV and sensitivity of 0.01 mV. The collected data is then transferred from the datalogger to PC and processed. In the measurement of temperature inside the calorimeter the resistance thermometer ALMEMO with the sensitivity of 0.01°C is used.

The calibration of the KC 01 calorimeter was carried out on Joule heat principle, using resistor with the precisely known resistance of 9.99 kΩ placed into the reaction vessel and powered by regulated DC power supply. The voltage was measured by a high-accuracy digital voltmeter. In the range of 0 to 100 mW the applied power [mW] was found to be proportional to output voltage [mV] of the differentially arranged thermocouple columns, with the calibration constant of 14 mW mV^{-1}. In the case of hydration of one gram of calcium sulphate hemihydrate the maximum output voltage of about 10 mV was observed.

The measuring process itself begins with one hour tempering of the gypsum specimen in the reaction vessel of the calorimeter and water outside the calorimeter at the given laboratory temperature. Then, the calorimeter is opened, water quickly added to the gypsum in the reaction vessel, the vessel is sealed and the calorimeter cover closed. This operation takes about 40–60 s. The temperature is registered by the datalogger with the time interval of 15 s.

Table 2 Classification of FGD gypsum using ČSN 72 2301 [24]

	Compressive strength/ MPa	Initial setting time/ min	Final setting time/ min	0.2 mm sieve residue/ %
Measured values	13.3	9	13	1.79
Limiting values	minimum 13.0	earliest time 6	latest time 30	maximum 2
Classification	G-13	B		III

Table 3 Composition of studied gypsum mixtures

Material	Water/gypsum ratio	Type of admixture	Admixture	Concentration
S0	0.627	none	none	none
S1	0.500	plasticizer	PERAMIN SMF 20	0.5 mass%
S2	0.500	plasticizer	MELMENT F4000	0.2 mass%
S3	0.627	hydrophobizer	IMESTA IBS 47	0.5 mass%
S4	0.627	hydrophobizer	ZONYL 9027	5% solution in water
S5	0.627	hydrophobizer	ZONYL 301	5% solution in water

Results and discussion

Comparison of hydration heat development determined using two different types of calorimeters

Figures 1 and 2 show the hydration heat development measured by the calorimeters DIK 04 and KC 01, respectively. Two peaks are noticeable both on the time dependence of temperature difference [K] between the studied sample and the reference sample measured by DIK 04 in Fig. 1 and the time dependence of heat power [mW] determined by KC 01 in Fig. 2. These peaks are quite characteristic for the hydration process of calcined gypsum. According to Fischer [12] the first one, which is developed immediately after addition of water, is due to the wetting heat together with the heat of conversion of β-anhydrite III to β-hemihydrate. The second peak which starts with a short delay after the first peak represents hydration of β-hemihydrate to β-dihydrate.

Table 4 shows a direct comparison of some characteristic features of the hydration heat development curves measured by the calorimeters DIK 04 and KC 01. The differences can be summarized as follows. All the characteristic time points observed on the hydration heat curves were shorter for KC 01 than for DIK 04. The time of the first peak was in the measurements by KC 01 three times shorter, the difference in the times of minimum after the first peak was three minutes, in the times of the second peak achievement twelve minutes. The hydration reaction was in the measurements by KC 01 finished in almost half the time compared to DIK 04. The ratio of magnitudes of the first and second peak was for DIK 04 three times lower than for KC 01.

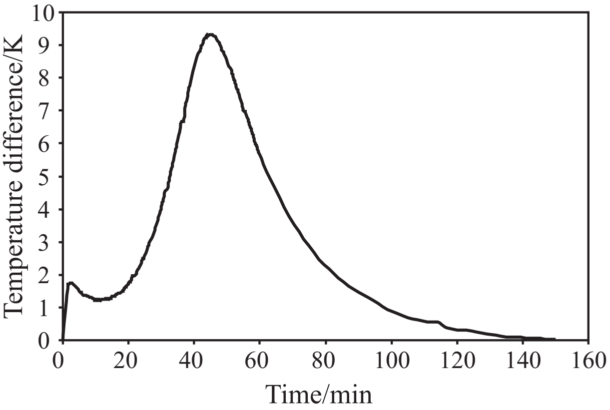

Fig. 1 The hydration heat development of FGD gypsum measured by the differential calorimeter DIK 04

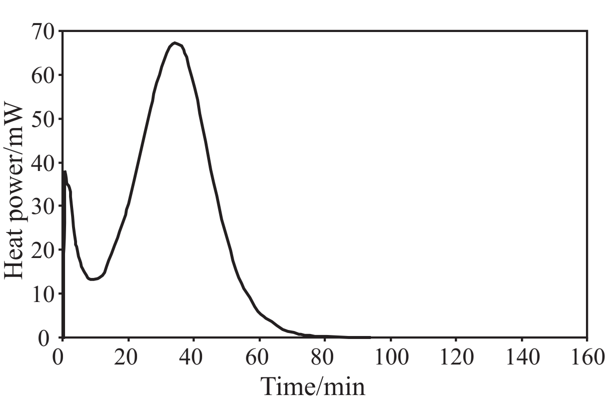

Fig. 2 The hydration heat development of FGD gypsum measured by the isothermal heat flow calorimeter KC 01

Table 4 Comparison of basic parameters of the hydration heat development measured using the calorimeters DIK 04 and KC 01

Parameter	Calorimeter	
	DIK 04	KC 01
The first peak	3 min	1 min
The first minimum	13 min	10 min
The second peak	46 min	34 min
Time of the end of the hydration reaction	150 min	85 min
The ratio of magnitudes of the first and second peak	0.18	0.56

The observed differences in the hydration heat development clearly favour the KC 01 isothermal heat flow calorimeter. Its sensitivity to instantaneous changes in the heat power generation by hydration reactions was remarkably better which was well demonstrated for the first peak, in particular. In addition, KC 01 is able to provide quantitative data in terms of both heat power and total hydration heat directly while DIK 04 would need some additional calibration to convert the temperature difference into the heat power. This calibration, however, could not be done without an exact knowledge of the specific heat capacity and density of the materials in the reaction vessel which may not be an easy task because they are changing during the reaction. Another sound argument for preferring the isothermal heat flow calorimeter KC 01 over the differential calorimeter DIK 04 is that the hydration heat determined by KC 01 is better defined from the physical point of view because the whole reaction process is isothermal (within the limit of approximately 2 K). Measurements by DIK 04 are semi-adiabatic; thus the changes of temperature can be much higher which may affect the reaction process itself in a significant way.

Effect of plasticizers and hydrophobizers on the hydration heat development

The second part of the measurements was done using the isothermal heat flow calorimeter KC 01 only, based

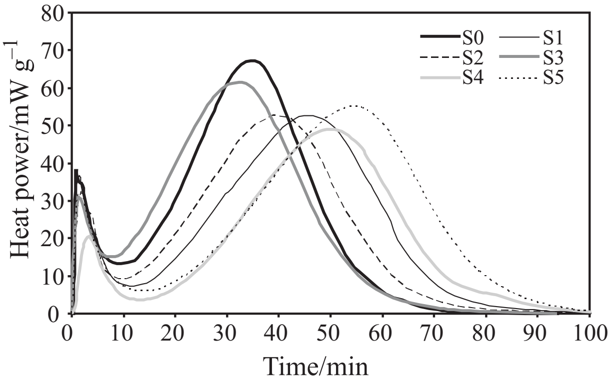

Fig. 3 Comparison of hydration heat development of different FGD gypsum mixtures measured by the isothermal heat flow calorimeter KC 01

on the results of the comparison of both calorimeters in the previous subsection. The comparison of the hydration heat developments of the studied gypsum mixtures containing various admixtures is presented in Fig. 3. Characteristic features of the hydration heat development curves are emphasized in Table 5. The first peak was observed for all gypsum mixtures at approximately 1 min after mixing of gypsum with water, except for S4 where it appeared after 4.5 min. The magnitude of the first peak was highest for the materials S0 and S1, for the most of other materials it was about 20% lower and for S4 even 50% lower. The decrease of power after the first peak began for S0 after 2 min. The minimum was lowest for S4, highest for S3. The magnitude of the second peak was highest for S0 again, for S3 it was about 5% lower, for all other gypsum mixtures approximately 20% lower. The second peak was achieved earliest for S3, 2 min earlier than for the reference material S0. For other studied gypsum mixtures the hydration process was slower than for S0. The maximum delay of the second peak as compared to S0 (21 min) was observed for the material S5. The end of the hydration reaction occurred first for the reference material S0. The latest end of the reaction was observed for the materials S4 and S5, 20 min later than for S0.

The total hydration heats in Table 5 were obtained by integration of the time development curves as average values of 6 measurements. These data are not yet directly comparable with the data measured by other authors. The first reason is that they include two reactions represented by the two basic peaks, namely wetting heat together with the heat of conversion of β-anhydrite III to β-hemihydrate in the case of the first peak and hydration of β-hemihydrate to β-dihydrate for the second one. Therefore, these two reactions were separated analytically in the original total time development curves in a similar way as in [26] and the hydration heats corresponding just to the hydration of β-hemihydrate to β-dihydrate calculated. The results presented in Table 5 do not correspond yet to pure β-hemihydrate because its amount in FGD gypsum is not exactly 100%. Therefore, they were to be recalculated to the real amount of β-hemihydrate which was in the particular studied case determined as 96%. For the reference FGD gypsum (S0) we thus got the hydration heat of β-hemihydrate of $105/0.96=109.4$ J g^{-1}. The comparison with the reference data for β-hemihydrate given by Wirsching [6] in Table 1 shows that the measured value in this paper is lower by 1.5%. This can be considered as a reasonable agreement.

The reduction of water/gypsum ratio from 0.627 to 0.5 (materials S1 and S2) which was achieved using plasticizers was found to have very low effect on the hydration heat of FGD gypsum, the measured difference was lower than 3%. The application of hydrophobization admixtures (materials S3, S4, S5) was for the materials S3 and S5 of very low importance (differences lower than 1%) but for S4 (with ZONYL 9027) the hydration heat was 10% lower than for the reference FGD gypsum. Therefore, the effect of hydrophobizers was not unambiguous which was apparently due to their different composition. IMESTA IBS 47 which was used in S3 is an alloyed hydrophobization powder for gypsum compounds and its application did not exhibit any remarkable effect on basic characteristics of the hydration process.

Table 5 Comparison of basic parameters of the hydration heat development measured using the calorimeter KC 01 for different gypsum mixtures

Parameter/Material	S0	S1	S2	S3	S4	S5
The first peak/min	1.0	1.0	1.5	1.0	4.5	1.0
The first minimum/min	9.5	11.0	11.0	7.5	12.0	14.0
The second peak/min	34.0	44.0	38.0	32.0	49.0	55.0
Time of the end of the hydration reaction/min	80.0	95.0	85.0	85.0	100.0	100.0
The ratio of power values of the first and second peak	0.56	0.65	0.62	0.54	0.41	0.66
Total hydration heat/J g^{-1}	125	121	123	123	112	124
Hydration heat corresponding to the reaction of β-hemihydrate to β-dihydrate (second peak)/J g^{-1}	105	102	104	104	94	105

ZONYL 9027 and ZONYL 301 used in S4 and S5, respectively, are according to the producer fluorochemical solutions that provide a durable, subsurface, transparent, protective barrier against oil and water on porous surfaces. This specification is clearly not sufficient because while the application of ZONYL 9027 led to remarkable differences from the reference material in all characteristic features of the hydration reaction, use of ZONYL 301 resulted only in a prolonged course of the reaction by about 20%. However, a more precise specification of the composition of the hydrophobizers could not be found out due to the lack of necessary information.

Conclusions

Experimental results presented in this paper showed that the accuracy of the measurement of time development of hydration heat of FGD gypsum can be substantially affected by the type of the applied calorimeter. Isothermal heat flow calorimeter was found to be more suitable for practical applications than differential semi-adiabatic calorimeter. Its sensitivity to instantaneous changes in the heat power generation by hydration reactions was much better, the calibration process more straightforward and reliable and the measured hydration heat better defined from the physical point of view because the temperature variations during the measurement were lower.

The effect of plasticizers on the hydration heat of FGD gypsum which came out in the form of decrease of water/gypsum ratio was found to be very low, up to 3%, which does not seem to be very important. The application of hydrophobization admixtures did not lead to unambiguous results. In the particular cases studied in this paper, IMESTA IBS 47 did not exhibit any substantial effect on the hydration heat development of FGD gypsum, ZONYL 301 prolonged the hydration reaction by approximately 20% without any change in total hydration heat, ZONYL 9027 changed all basic characteristic features of the hydration reaction in a significant way, the total hydration heat was about 10% lower as compared with the reference FGD gypsum.

Acknowledgements

This research has been supported by the Ministry of Education, Youth and Sports of Czech Republic, under contract No. MSM: 6840770031.

References

1 V. Šatava, Study of the Setting Process of Gypsum Suspensions (in Czech). Thesis, Institute of Chemical Technology, Prague 1968.
2 V. Šatava, Ceramics-Silikáty, 40 (1996) 72.
3 R. J. Hand, Cem. Concr. Res., 24 (1994) 889.
4 W. Abriel, K. Reisdorf and J. Parnettier, Solid State Chem., 85 (1990) 22.
5 C. Bezou, J. Nonat, A. Mutin, N. Christensen and M. S. Lehmoun, J. Solid State Chem., 117 (1995) 165.
6 F. Wirsching, Calcium Sulfate, Ullmanns Encyclopedia of Industrial Chemistry, Vol. 6. Weinheim: Wiley-VCH Verlag, 1983, pp. 90–94.
7 K. K. Kelley, C. T. Southard and C. T. Anderson, U. S. Bureau of Mines Tech. Paper No. 625 (1941).
8 E. Eipeltauer, Zement-Kalk-Gips, 9 (1956) 501–505.
9 N. N. Bushuev, Dokl. Ak. Nauk, 255 (1980) 1104.
10 N. N. Bushuev, B. M. Maslennikov and V. M. Borisov, Zhurn. Neorg. Chimii, 28 (1983) 2469.
11 C. Freyer and W. Voigt, Monatsh. Chem., 134 (2003) 693.
12 K.W. Fischer, Silikattechnik, 14 (1963) 26.
13 G. Fietsch and H. Ramdohr, Silikattechnik, 42 (1991) 328.
14 H. Gerard, Zement-Kalk-Gips, 44 (1991) 426.
15 S. Folek and K. Kowol, J. Thermal Anal., 9 (1976) 59.
16 V. Ambrúz, J. Havlová and A.Gabrišová, J. Thermal Anal. 33 (1988) 647.
17 C. Evju, J. Therm. Anal. Cal., 71 (2003) 829.
18 TAM AIR User Guide Line, C3 Prozess- und Analysentechnik GmbH, (2005), p. 17.
19 O. P. Mtschedlow-Petrossian, A. Sen and A. Uscherow-Marschak, Silikattechnik, 29 (1969) 229.
20 G. Oliew and W. Wieker, Silikattechnik, 32 (1981) 152.
21 B. Zdravkov and Y. Pelovski, J. Therm. Anal. Cal., 88 (2007) 99.
22 H. F. Dantas, R. A. S. Mendes, R. D. Pinho, L. E. B. Soledade, C. A. Paskocimas, B. B. Lira, M. O. E. Schwartz, A. G. Souza and I. M. G. Santos, J. Therm. Anal. Cal., 87 (2007) 691.
23 V. Rahhal, O. Cabrera, R. Talero and A. Delgado, J. Therm. Anal. Cal., 87 (2007) 331.
24 ČSN 722301 Gypsum Binders – Classification, Common Technical Requirements, Methods of Testing (in Czech). Czech Normalization Institute, Prague 1979.
25 Differential Calorimeter DIK 04, Description and Operating Instructions (in Czech). ELSYST Ltd., Prague 2002, p. 25.
26 M. Hurmanic and H. Roggendorf, Zement-Kalk-Gips, 11 (1990) 550.

Received: September 17, 2007
Accepted: October 30, 2007

DOI: 10.1007/s10973-007-8709-0