Rheological Properties of Building Gypsum Fresh Pastes

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Abstract

The study presents results of laboratory tests of rheological properties of fresh pastes made of building gypsum at a wide range of water-gypsum ratios W/G = 0.4–1.5. The tests were carried out in a rotary-type viscosimeter RHEOTEST-2. The rheograms characterize dynamic changes in shearing stress τ of the gypsum pastes in the course of setting. By the addition of setting retarders rheostable gypsum pastes were obtained for the period of the experiments, which enabled the taking of rheograms of the shearing stress τ , described by analytical functions based on Bingham's and Herschel-Bulkley's plastic bodies. There were determined relations between the yield stress τ_0 as well as plastic viscosity η_{pl} and the W/G ratios. The results have considerable heuristic and practical values for rheology of fresh gypsum pastes.

Key words: gypsum, gypsum plaster, rheology, plastic viscosity, yield stress

Notation

<i>k</i> , <i>n</i>	-	coefficients of the equation (14), describing the Herschel-Bulkley's model,
L	_	length of the internal measuring cylinder [m],
М	_	torque in the rotational viscosimeter [Nm],
Q	_	heat generated during reaction [J],
R_1	-	radius of the internal cylinder in the rotational viscosimeter [m],
R_2	-	radius of the external cylinder in the rotational viscosimeter [m],
t	_	time elapsed from the moment of preparation of the gypsum paste [s, min],
α, k_f	_	rheogram transformation coefficients, see Fig. 5,
β	_	angle of slope of the pseudo-rheograms $\tau_{R1} = f(\dot{\gamma}_p)$,
γ̈́	-	true deformation rate $[s^{-1}]$,

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γ_p	-	apparent deformation rate $[s^{-1}]$,
η	_	absolute viscosity [Pa·s],
η_{pl}	_	plastic viscosity [Pa·s],
τ	_	shearing stress [Pa],
$ au_{R1}$	-	shearing stress on the surface of the internal cylinder of the rotational viscosimeter [Pa],
$ au_0$	_	yield stress [Pa],
$ au_{1L}$	_	shearing stress, see Fig. 5, an auxiliary value used for transformation of rheograms, [Pa],
$\omega = W/G$	_	water-gypsum ratio,
Ω	_	angular velocity $[s^{-1}]$.

1. Introduction

Building gypsum is commonly used for finishing of buildings (plasters, white coats, stuccowork) and for production of prefabricated units like gypsum plaster board GK, PRO MONTA plate elements for partition walls, hollow masonry units for building of walls in dwelling houses (Meuś and Rzepecki 1963, Klin 1998, Mikoś 2004). In such applications the gypsum binders are used as pure gypsum pastes or as multicomponent mixes, consistency of which is adopted for the particular application, and may be plastic, semi-liquid or even liquid. Rheological properties of gypsum mixes decide as to the effectiveness of application and quality of products.

Building gypsum is the gypsum binder in the form of β -CaSO₄·0.5H₂O, obtained by partial dehydratation of natural or synthetic gypsum dihydrate CaSO₄·2H₂O, due to calcination in rotary kilns or calciners in low-moisture atmosphere (Kurdowski 2003). The indispensable operation is comminution of the calcined material in ball mills, recently substituted by roll mills (Zisselmar 1985).

Mixing with water gives the gypsum paste characterized by relatively fast hydration process, which leads again to the dihydrate, according to the following chemical reaction:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O + Q.$$
(1)

Setting of gypsum is an exothermic process (Magnan et al. 1976), characterized by considerable kinetics (Uszerow-Marszak 1979, Karamazsin, Comel and Murat 1983, Ostrowski and Czamarska 1991). Heat generated by the reaction progressively accelerates the setting rate. Setting time of gypsum is short and may amount from a few to approximately 30 minutes, in functional dependence upon the W/Gratio (Klin 2005). In industrial applications, setting time of gypsum is prolonged by addition of setting retardants (Ostrowski 1983, Moissey 1985). Different hydration rate of particular grain sizes of gypsum results in steady setting, according to relation (1) until the total setting of the whole paste. Consistence of the gypsum paste and its rheological properties (η_{pl} , τ_0) are time dependent variables. However, by application of effective setting retardants, such as, for example, sodium thiosulfate, added in amounts beginning from 0.04%, one can obtain pastes almost rheostable for a somewhat longer time. It enables finishing indispensable operations in the process of shaping of gypsum products in construction sites, or determination of initial rheological characteristics of gypsum pastes in laboratories. In the study, rheological properties of gypsum pastes are described basing on mathematical descriptions of models elaborated by: Wilkinson (1963), Parzonka (1968), Kembłowski and Kaczmarczyk (1975), Czaban (1987), Kempiński (2001).

2. Examination of Rheological Properties of Fresh Gypsum Pastes Described in Scientific Literature

As compared with well investigated problems of rheological properties of cement mortars, including analysis of issues of mechanics of shearing (Szwabowski 1999, Chandler and Macphee 2003), influence of plasticizers on the rheological properties of cement slurries (Kucharska 2000, Chandra and Björnström 2002, Grzeszczyk and Sudoł 2003), interactions between cement and plasticizers (Hanekara and Yamada 1998), elucidation of the influence of plasticizers on consistency of cement slurries by means of spin resonance and X-ray technique (Roncero et al. 2002), influence of plasticizers on stability and mechanical properties of cured concrete (Marin et al. 2001, Czarnecki and Łukowski 2003) – problems of rheology of fresh gypsum pastes are much less known.

Lehman, Mathiak and Kurpiers (1970) examined the suitability of various laboratory methods for examination of fresh gypsum pastes and mortars to determine their workability. They compared results obtained by means of the modified Vicat apparatus, with a cylindrical tip according to ASTM C 26-54 standard to results obtained with a conical consistencemeter of Kuntze, according to ASTM C 472-64. In both the methods, the measure of consistence is depth of penetration of cylindrical or conical tips in the fresh gypsum mortars.

Lehman, Mathiak and Kurpiers (1970) designed a rotary plastometer, for comparison of stress of rotation of a cylinder with perpendicular pins, immersed in fresh gypsum pastes and in gypsum plaster mixes. The plastometer gave reliable results, useful in practical applications, but not determined by any physical parameters, like η_{pl} and τ_0 , which might be used for elucidation of the shearing mechanics.

Examination of rheology of fresh gypsum pastes, carried out with rotational rheometers, proved that from the moment of preparation of a paste begins a fast increase of shearing stress $\tau = f(t)$ being a function of time t (Colussi et al. 1982)

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and there is a close relation between specific surface of the material and shearing stress of fresh gypsum pastes (Skvara and Vancurova 1973). Moreover, there are elaborated comparative curves for the relation $\eta_{pl} = f(\dot{\gamma})$, determined for pastes made of natural gypsum and for two various synthetic gypsum grades (Hurbanic et al. 1994); but for the same W/G ratio according to DIN 1168, that is for one consistence level, only.

Peng et al. (2005), which determined effect of plasticizing agents, like sulfonated β -naphthalenes (BNS) and polycarboxylates (PC), on reduction of water demand and on effectiveness of plasticizing, proved that the preparations may be added in amounts of 2% of the total weight of the binding material, maximum. The effect of plastification of gypsum pastes may be observed for approximately 4 minutes, only. Then, it suddenly disappears.

For anhydrite binders, which have much slower curing rates, Sebök and Vondruška (2000) determined interactions between soluble anhydrite CaSO₄ II and plasticizing agents like melamine-formaldehyde polycondensates (MSFC), with some K_2SO_4 added as a curing accelerator. Continuing the studies, they determined effects of plasticizing agent of the MSFC type on some properties of anhydrite mortars, like consistency and compression strength on setting (Sebök et al. 2001). The study provides original technological directions enabling optimization of plasticizing effects of the MSFC type agents in anhydrite mortars.

To recapitulate results of the hitherto made studies on rheological properties of gypsum, it should be concluded that rheology of fresh gypsum pastes, made of building gypsum of the β -CaSO₄·0,5H₂O grade, and particularly the shearing processes, are much less elucidated as compared with these for cement mortars.

3. Objective and Methods of Rheometric Measurements

Rheological properties of fresh gypsum pastes were examined with the rotary-type rheometer RHEOTEST-2 (Fig. 1), which consisted of two coaxial cylinders with radii R_1 and R_2 (Fig. 5) and the motor, which provided the torque and rotated the internal cylinder at the rotational speed of Ω . The tests were carried out with cylinders in the S3 system, with the following parameters: $R_1 = 32$ mm, $R_2 = 40$ mm, $\alpha = R_2^2/R_1^2 = 1.56$, volume of the sheared mixture V = 50 ml.

Both the examination methods and interpretation of results are described by Parzonka (1977).

The examinations were aimed at elucidation of phenomena of shearing of fresh gypsum pastes, made of building gypsum and at determination of functional relations describing:

- characteristics of changes of shearing stresses τ versus deformation rate $\dot{\gamma}$ for pastes with various consistencies, that is with various W/G ratios, in the form of the relation $\tau = f(\dot{\gamma}, \omega = \text{const.})$,



Fig. 1. The test stand for measurement of rheological properties of fresh gypsum pastes – RHEOTEST-2

- characteristics of changes of plastic viscosity η_{pl} and of yield stress value τ_0 for gypsum pastes within practically full range of the W/G ratios: from W/G = 0.4 (thick plastic) to W/G = 2.0 (castable).

Moreover, an important goal was analysis of rheological models of fresh gypsum pastes, for various consistence levels. The tests were carried out with building gypsum β -CaSO₄·0.5H₂O, calcined in coal fired rotary kilns, produced from natural raw materials, the mineral composition of which is specified in Table 1.

Standard spreading of the gypsum samples at a diameter of $D_r = 18$ cm, measured with Southard's table (according to PN-86/B-04360) was measured for W/G = 0.72.

For wide range comparative studies on various methods used for examination of consistency of fresh gypsum pastes were performed, including effective original methods, see the separate study (Klin 2005). The examinations of rheological properties of fresh gypsum pastes, carried out by means of rotary-type rheometers, are the II stage of the work.

No.	Component	Percentage [%]
1	2	3
1.	$CaSO_4 \cdot 0.5H_2O$	82.43
2.	Anhydrite III	0.00^{*}
3.	Stabilized anhydrite II	1.78
4.	Anhydrite II	0.26
5.	$CaSO_4 \cdot 2H_2O$	4.26
6.	Inactive material	10.74
7.	Moisture	0.53
	Total	100

Table 1. Mineral composition of the building gypsum examined

*Anhydrite III was completely stabilized as CaSO₄·0.5H₂O phase.

4. Changes in Rheological Properties of Natural Gypsum Pastes

Fig. 2 presents the $\tau_{R1} = f(t)$ diagrams of fresh gypsum pastes without any setting retardants prepared at W/G = 0.5-1.5. Very rapid increase of shearing stress



Fig. 2. Diagrams of $\tau_{R1} = f(t)$ for building gypsum pastes at W/G = 0.5–1.5. Results of measurements carried out with rotational rheometer RHEOTEST-2

 $\tau_{R1} = f(t)$ may be noticed. The shearing stress values τ were measured after the time $t_0 = 1.5$ min. It was the time required for preparation of the paste and the rheometer for tests.

Process of setting of freshly prepared gypsum paste begins just in the moment of mixing of water and gypsum. In pastes with high contents of the binder, at W/G = 0.5-0.7, the process is realized very rapidly. The lower is concentration of binder in the paste, the slower proceeds setting. The pastes prepared at W/G= 0.8-0.9 set slower; and the castable pastes with W/G = 1.0-1.5 set the slowest.

In pastes of W/G = 1.5, that is having consistency of castable and low-viscosity liquids, sedimentation of coarser grains of the binder occurs, resulting in some resistance increase, due to friction forces, followed by considerable change of structure of the paste, accompanied by a sudden drop of its shearing stress.

Fig. 3 shows increasing shearing stress τ_{R1} in the three-parameter space, $\tau_{R1} = f(\omega, t, \dot{\gamma}_p = \text{const})$. It may be noticed that both increase of the binder in the paste, represented by W/G ratio, and time t elapsed from the moment of preparation of the paste, result in continuous increase of the shearing stress τ_{R1} .



Fig. 3. Increasing shearing stress τ_{R1} of gypsum pastes shown in the three-parameter space $\tau_{R1} = f(\omega, t, \dot{\gamma}_p = \text{const} = 16.2 \text{ s}^{-1})$

5. Rheological Properties of Rheostable Gypsum Pastes Modified with Setting Retardants

From theoretical and practical points of view, results of examination of rheological properties of fresh gypsum pastes modified with setting retardants, which make them relatively rheostable, seem to be interesting. For the tests the commonly used retardant, sodium citrate, was applied. At concentrations of 0.04–0.1% of gypsum weight, the retardant gave pastes characterized by the function $\tau = f(\dot{\gamma})$ practically constant within 10 minutes, that is for the time required for full accomplishment of one test series. Rheostability of the test samples of the pastes was every time controlled by initial repeatability testing of the diminishing and increasing of pseudo-curves of flow $\tau = f(\dot{\gamma}_p)$, in a cycle with a time bias for accomplishment of particular measuring loops.

Fig. 4 shows the pseudo-curves of flow $\tau_{R1} = f(\dot{\gamma}_p)$ for rheostable gypsum pastes at various $\omega = W/G$ ratios. They characterize the relation between shearing stress τ_{R1} and apparent deformation rate $\dot{\gamma}_p$, for various W/G ratios, pointing out that for description of the flow mechanics different models of viscous-plastic bodies are needed, as described in Section 7.



Fig. 4. Pseudo-curves of flow $\tau_{R1} = f(\dot{\gamma}_p)$ for rheostable building gypsum pastes

6. Approximation of Pseudo-Curves of Flow

In the rotating viscosimeter, full shearing of visco-plastic paste occurs when the shearing stress τ_{R2} in outermost bands at a distance of R_2 from the rotation axis are larger from the yield stress τ_0 (Fig. 5), according to the relation of:

$$\tau_{R2} = \frac{M}{2\pi L R_2^2} > \tau_0.$$
 (2)



Fig. 5. Pattern of velocity ΩR and shearing stress values τ in the Couette-Searle type viscosimeter for the Bingham's body (Parzonka 1977)

Full shearing always occurs in Newtonian liquids, for which the relation $\tau = f(\dot{\gamma})$ is a linear function:

$$\tau = \eta \dot{\gamma}. \tag{3}$$

Within the range of small deformation rates $\dot{\gamma}_p$ partial shearing may occur, as shown in Fig. 5. It occurs in the case of:

$$\tau_{R1} = \frac{M}{2\pi L R_1^2} > \tau_0 > \tau_{R2} = \frac{M}{2\pi L R_2^2}.$$
(4)

Basing on results of measurements of torque M for various rotational velocities Ω pseudo-rheograms $\tau = f(\dot{\gamma}_p)$ may be obtained, where $\dot{\gamma}_p$ – is apparent deformation rate described by Parzonka (1977) as:

$$\dot{\gamma}_p = \frac{2\Omega}{1 - \frac{R_1^2}{R_2^2}} = \frac{2\Omega}{1 - \frac{1}{\alpha}}.$$
(5)

Apparent deformation rate $\dot{\gamma}_p$ equals actual deformation rate $\dot{\gamma}$ for Newtonian bodies only, that is when the following relations occur:

$$\dot{\gamma} = \dot{\gamma}_p$$
 and $\tau_{R1} = f(\dot{\gamma}_p)$ equals $\tau = f(\dot{\gamma})$. (6)

As non-Newtonian bodies are characterized by the following relations:

$$\dot{\gamma} \neq \dot{\gamma}_p$$
 and $\tau_{R1} = f(\dot{\gamma}_p)$ is not equal to $\tau = f(\dot{\gamma})$, (7)

therefore for such bodies apparent deformation rate $\dot{\gamma}_p$ differs from the true deformation rate and the shearing stress $\tau_{R1} = f(\dot{\gamma}_p)$ differs from the true shearing stress $\tau = f(\dot{\gamma})$.



Fig. 6. Approximation of pseudo-curves of rheograms $\tau_{R1} = f(\dot{\gamma})$ with the Bingham model (Parzonka 1977)

Fig. 6 shows the partial flow zone. In case of partial shearing, the shearing stress $\tau_{R1} = f(\dot{\gamma}_p)$ is greater than shearing stress $\tau = f(\dot{\gamma})$ from the true flow curve. To obtain values of true flow curve and the true shearing stress $\tau = f(\dot{\gamma})$ – for the full-shearing state within the whole range of deformation rates – one should compare the pseudo-curve (measured) and the true curve. The pseudo-curves of flow, which for shearing stress equal:

$$\tau_{R1} > \tau_{1L} = \tau_0 \alpha \tag{8}$$

are rectilinear, that is when the derivative $d\tau_{R1}/d\dot{\gamma}_p = \text{const}$, may be equalized with the Bingham model of viscous-plastic body, described by the following function:

$$\begin{aligned} \tau &= \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad \text{for} \quad \tau \ge \tau_0 \\ \dot{\gamma} &= 0 \qquad \text{for} \quad \tau < \tau_0. \end{aligned}$$
 (9)

Fig. 6 shows an example of graphical equalization of pseudo-curve of flow with the Bingham model, taken from the work of Parzonka (1977). Both the curves, that is the curvilinear pseudo-curve and rectilinear true one cross the axis at the same point of τ_0 . Considering the lesser accuracy of results of measurements used

for determination of the curvilinear pseudo-curve in the partial shearing zone, as the most reliable was assumed the rectilinear section of the pseudo-curve, which in extension crosses the τ axis at:

$$\tau_0' = \frac{\tau_0}{k_f}.\tag{10}$$

The required yield stress τ_0 is derived from the following relation:

$$\tau_0 = \tau'_0 \cdot k_f,\tag{11}$$

where: the curve equalization parameters, k_f and α , theoretically depend exclusively on geometrical dimensions of the cylinders and amount to:

$$\alpha = \frac{R_2^2}{R_1^2},$$
 (12)

$$k_f = \frac{1 - \frac{1}{\alpha}}{\ln \alpha}.$$
(13)

For the RHEOTEST-2, used for the measurements, the coefficients α and k_f are equal to $\alpha = 1.56$ and $k_f = 0.81$.

7. Discussion of Results

7.1. Rheological Models Dependent upon the W/G Ratio of the Gypsum Paste

Considering rheological properties of the gypsum pastes examined, they may be classified into two groups, namely:

- I Group, including pastes of $W/G \ge 0.7$ (1.5; 1.0; 0.8; 0.7), for which the pseudo-curves of flow $\tau_{R1} = f(\dot{\gamma}_p)$, shown in Fig. 4, may be described with Bingham's model (Eq. 9);
- II Group, including the pastes of W/G < 0.7 (that is W/G = 0.6; 0.5; 0.45 and 0.4). For these pastes, characterized with high concentration of the binder, the pseudo-curves of flow are evidently curvilinear for the whole range of deformation rates used $\dot{\gamma}_p = 0 145.8 \text{ s}^{-1}$. For description of the pseudo-curves of flow of such pastes the generalized three-parameter rheological models are required, for example the Herschel-Bulkley's model (applied by Eckstädt 1984, Czaban 1987, Kempiński 2000), described by the following equations:

$$\begin{aligned} \tau &= \tau_0 + k \cdot \dot{\gamma}^n \quad \text{for} \quad \tau \ge \tau_0, \\ \dot{\gamma} &= 0 \qquad \text{for} \quad \tau < \tau_0, \end{aligned} \tag{14}$$

where: τ_0 , k, n – parameters of the model.

7.2. Functional Description of Rheological Properties of Liquid Gypsum Pastes at $W/G \ge 0.7$

The parameters τ_0 and η_{pl} for gypsum pastes of $W/G \ge 0.7$, specified in Table 1, were determined with the graphical method of Parzonka (Fig. 6), by approximation of pseudo-curves of flow with Bingham's model.

No.	W/G ratios	Rheological characteristic τ'_0 [Pa]	Yield stress values calculated from the condition (11) τ_0 [Pa]	Plastic viscosity η_{pl} [Pa·s]
1	2	3	4	5
1.	1.5	0.87	0.70	0.0272
2.	1.0	1.68	1.35	0.0299
3.	0.8	5.68	4.57	0.0522
4.	0.7	10.27	8.28	0.0794

Table 2. Parameters of rheological properties of Bingham's model τ'_0 , η_{pl} and τ_0 for freshly prepared building gypsum pastes (I Group, $W/G \ge 0.7$, Fig. 7)



Fig. 7. Approximation of pseudo-curves of flow of gypsum pastes at $W/G \ge 0.7$ with the Bingham model

As expected, coefficients of plastic viscosity for gypsum pastes of the I Group reduce their values at increasing $\omega = W/G$ ratios. It was found that the relation may be described with exponential function (Fig. 8) of the following type:

$$\eta_{pl} = 0.026 + 11.1e^{-7.623\omega} \tag{15}$$

at considerable correlation $R^2 = 0.997$.



Fig. 8. Approximation of the functional relation between plastic viscosity η_{pl} and the W/G ratio

As expected, the rheological characteristics τ'_0 (Fig. 6), as well as the flow threshold values τ_0 according to (Eq. 11), increase as increases concentration of gypsum in the pastes.

The phenomena of yield stress appearance are observed even for the castable pastes at W/G = 1.5. Reliability of the data obtained in such a way may be confirmed by the fact, that yield stress τ_0 was observed in case of bottom deposits from the Odra river, sampled from the vicinity of the stage of fall Brzeg Dolny. The bottoms being products of erosion of clay soil, include dust fractions. The yield stress τ_0 was noticed at a concentration of solids in water of $C_v \ge 5\%$ (Głowski et al. 1995).

Approximation of the relation $\tau_0 = f(\omega)$ proved (Fig. 9), that the empirical formulas describe the exponential function with considerable correlation degrees, as follows:

$$\tau_0 = 0.5743 + 1011e^{-6.959\omega}; \quad R^2 = 0.998. \tag{16}$$

After inserting of the empirical relations (15) and (16) to equation (9), one can obtain the relation (17), which describes true rheological flow curves for liquid gypsum pastes at $W/G \ge 0.7$:

$$\tau = 0.5743 + 1011e^{-6.959\omega} + \left(0.026 + 11.1e^{-7.623\omega}\right)\dot{\gamma}.$$
 (17)

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Fig. 9. Approximation of the function of the yield stress values versus W/G ratios, $\tau_0 = f(\omega)$



Fig. 10. Approximation of the pseudo-curves of flow for gypsum pastes prepared at W/G < 0.7 (Hershel-Bulkley's model)

7.3. Description of Rheological Properties of Gypsum Pastes at W/G < 0.7

The description refers to pastes with consistency of semi-liquid (W/G = 0.6), plastic (W/G = 0.5), and thick plastic (W/G = 0.45-0.4).

Pseudo-rheograms of flow for pastes from the II Group (Fig. 4) at W/G < 0.7 require approximation with three-parameter rheological models, like the Herschel-Bulkley's model described by:



$$\tau = \tau_0 + \tau_1 = \tau_0 + k_1 \cdot \dot{\gamma}_p^{n_1}.$$
 (18)

Fig. 11. Diagrams of changes of plastic viscosity $\eta_{pl} = \frac{d\tau}{d\dot{\gamma}_p}$ for pastes at W/G < 0.7

Fig. 10 presents measuring points of the pseudo-rheograms $\tau_{R1} = f(\dot{\gamma}_p)$ for pastes prepared at W/G = 0.4; 0.45; 0.5 and 0.6, and descriptions of pseudo-curves of flow approximated with functions of the Herschel-Bulkley's model.

Derivative of the function (18), described with the relation

$$\dot{\tau}_{R1} = \frac{d\tau_{R1}}{d\dot{\gamma}_p} = k_1 \cdot n_1 \cdot \dot{\gamma}_p^{n_1 - 1}$$
(19)

illustrates variability of the slope of the tangent to the given point of the pseudo-curve of flow. The $\dot{\tau}_{R1}$ may be interpreted as plastic viscosity η_{pl} in this point of the pseudo-curve of flow $\tau_{R1} = f(\dot{\gamma}_p)$.

The variability of $d\tau_{R1}/d\dot{\gamma}_p$ is particularly high at small deformation rates $\dot{\gamma}_p = 0-27 \text{ s}^{-1}$.

The data presented in Fig. 11 evidence also considerable effect of the W/G ratios: the thicker pastes, at lower W/G, the higher are values of the shearing

stress τ_{R1} (Fig. 10) and of the $d\tau_{R1}/d\dot{\gamma}_p$ derivative. At deformation rates exceeding 27 s⁻¹ variability of the derivative $\dot{\tau}_{R1}$ considerably stabilizes, giving moderate linear growths. Analysis of derivatives of pseudo-rheograms of flow, like in Fig. 11, may be useful just for qualification and selection of a suitable rheological model: from the two-parametric Bingham's model for $d\tau_{R1}/d\dot{\gamma}_p = \text{const.}$, to other multi-parametric models, like for example the Herschel-Bulkley one.

8. Conclusions

The study provides results of examination of rheological properties of fresh gypsum mortars, obtained by means of rotary-type rheometers for practically full range of consistencies, that is from thick-plastic (W/G = 0.4) to castable (W/G = 1.5), including analysis of rheological models of plastic flow of pastes, diversified depending on concentration of the binder in the paste, as represented by the W/G ratio.

It was found that gypsum pastes having consistencies of from liquid to castable (W/G = 0.7 to 1.5, respectively) behave as the visco-plastic Bingham's bodies, and the pseudo-curves of flow $\tau_{R1} = f(\dot{\gamma}_p)$ of the pastes for this W/G range may be described with two-parameter relation as in the Bingham model (Eq. 9). Basing on results of own work on this group of pastes, the empirical formula describing relations between change of plastic viscosity η_{pl} and the water-to-gypsum ratio $\omega = W/G$ (Eq. 15), and other empirical formula (16), which evidences changes of the yield stress values $\tau_0 = f(\omega)$ in relation to the W/G ratio of the examined building gypsum pastes were derived.

Moreover, it was found that for the second group of the pastes, more concentrated and characterized by $\omega = W/G < 0.7$, pseudo-curves of flow are evidently curvilinear, the plastic viscosity coefficient $\eta_{pl} \neq \text{const.}$ and the rheograms $\tau = f(\dot{\gamma})$ should be described by the three-parametric model proposed by Herschel-Bulkley's (Eq. 14). Due to considerable complexity of statistical calculations, it was qualified for discussion in a separate paper.

Both the empirical results and analytic relations may be directly used for designing of gypsum paste transport systems based on pumping methods.

Results of examination of the pastes from group I, characterized with $\omega = W/G \ge 0.7$ may be utilized in production of gypsum prefabricated units and the gypsum plaster boards, because as liquid pastes with $\omega = 0.7 - 0.8$ are used. The results of rheological examinations of pastes characterized by $\omega > 0.8$, may be used for designing of castable paste systems used for production of light aerated gypsum elements.

Results of examination of the fresh gypsum pastes belonging to the second group, with $\omega < 0.7$, may be used for various industrial applications, from production of flexible gypsum plasters, generally applied with plaster units, to production of vibro-pressed elements at $\omega \le 0.4$.

References

- Chandler H. W., Macphee D. E. (2003), A model of the flow of cement pastes, *Cement and Concrete Research*, 33, 265–270.
- Chandra S., Björnström J. (2002), Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars. Part I, *Cement and Concrete Research*, 32, 1605–1611, Part II, 32, 1613–1619.
- Colussi I., Lapasin R., Papo A. (1982), Shear-dependent behavior of gypsum plasters, *Ind Eng. Chem. Process Des.*, 21.
- Czaban S. (1987), Determination of Parameters of Hydraulic Transport in Pipelines for Rheostable Diphase Mixtures (in Polish), Prace Naukowe Akademii Rolniczej we Wrocławiu, No. 60.
- Czarnecki L., Łukowski P. (2003), Effect of admixtures and polymer additives on durability of concrete (in Polish), *Cement Wapno Beton*, 6, 300–310.
- Eckstädt H. (1984), Druckrohrströmung von Rinder-Schweinegülle. Ein Beitrag zur Mechanik von Mehrphasensystemen, Dissertation, Universität Rostock.
- Głowski R., Kempiński J., Parzonka W. (1995), Silting-up of the Odra river above the Brzeg Dolny barrage (in Polish), Zeszyty Naukowe Akademii Rolniczej we Wrocławiu, nr 270, Konf. X, t. 2, 43–53.
- Grzeszczyk S., Sudoł M. (2003), Effect of structure of acrylic super-plasticizers on rheological properties of cement pastes (in Polish), *Cement Wapno Beton*, 3, 156–160.

Gypsum Binders and Gypsum Plasters – Part 2: Test Methods (2004), EN-13279-2:2004.

- Hanekara S., Yamada K. (1999), Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology, *Cement and Concrete Research*, 29, 1159–1165.
- Hurbanic M., Böse H., Reatker F. (1994), Comparative investigations into the sedimentation and rheology of non-formulated multiphase gipsum plaster made natural and FGD gypsum, *Zement Kalk Gips*, 9, 242–248.
- Karamazsin A., Comel C., Murat M. (1983), Etude des systèmes Ca-SO₄-H₂O par calorimétrie isotherme, *Cements Bétons Plâtres Chaux*, 740, 47–50.
- Kembłowski Z., Kaczmarczyk A. (1975), Mathematical models of rheology of some viscous/plastic fluids (in Polish), *Inżynieria chemiczna*, 5, 283-285.
- Kempiński J. (2001), Flow characteristics of homogenous mixture in laminar flow zone, Archives of Hydro-Engineering and Environmental Mechanics, Vol. 48, 4, 57–86.
- Klin S. (1998), Gypsum in the building industry in Poland (in Polish), *Materiały Budowlane* 10, 42–47.
- Klin S. (2005), Analysis of the variation of strength and deformability of gypsum in various states of stress and humidity (in Polish), Zeszyty Naukowe Akademii Rolniczej we Wrocławiu, nr 510, rozprawy CCXXVIII.
- Kucharska L. (2000), Conventional and modern additives used for reduction of water in cement pastes (in Polish), *Cement Wapno Beton*, 2, 46–61.
- Kuczyński W. (1976), Watertightness of Concrete Tanks in Theory and Praxis (in Polish), Prace Naukowe Instytutu Inżynierii Lądowej Politechniki Wrocławskiej, 19, 4.
- Kurdowski W. (2003), *Chemistry of Building Materials* (in Polish), Uczelniane Wydawnictwo Naukowo-Dydaktyczne, Akademia Górniczo-Hutnicza Kraków.
- Lehman H., Mathiak H., Kurpiers P. (1970), Über die Messung der Verarbeitbarkeit von Gipsmörteln, *Tonindustrie Zeitung*, 1, 94–96.
- Magnan R., Cottin B., Gardet J. (1976), Mechanism of hydration of β gypsum semi-hydrate (in Polish), *Cement Wapno Gips*, 3, 61–64.

- Marin V., Tenoudji F., Feylessoufi A., Richard P. (2001), Superplasticizer effects on setting and structuration mechanisms of ultrahigh-performance concrete, *Cement and Concrete Research*, 31, 63–71.
- Meuś W., Rzepecki R. (1963), Elements and Structures Made of Gypsum and Gypso/Concrete Materials (in Polish), Arkady, Warszawa.
- Mikoś J. (2004), *Building of Gypsum. Informator* (in Polish), Wydawnictwo Instytutu Ekonomiki Przemysłu Chemicznego a/Gliwice, Konsultant AG Sp. z o.o., Gliwice.
- Moissey J. M. (1985), Modificateurs de prise de plâtres, Cements Bétons Plâtres Chaux, 5, 765-766.
- Nowak J. (2002), History and the future of gypsum plasters from "Dolina Nidy" (in Polish), Cement Wapno Beton, 5, 189–194.
- Ostrowski C. (1983), Retardants for gypsum semihydrate (in Polish), *Biuletyn Informacji Budownictwa*, 7–8, 24–25.
- Ostrowski C., Czamarska D. (1991), Studies on kinetics of heat generation in processes of hydration of gypsum semi-hydrate and clinker-based materials comprising gypsum semi-hydrate and gypsum dihydrate (in Polish), *Cement Wapno Gips*, 8, 212–224.
- Parzonka W. (1968), Characteristic of laminar flow of the non-Newtonian fluids with the three-parameter rheological model (in Polish), *Rozprawy Inżynierskie*, 3, 16, 281–298.
- Parzonka W. (1977), The Scientific Basis for Hydraulic Transport of Two-Phase Mixtures (in Polish), Skrypty Akademii Rolniczej we Wrocławiu, nr 139.
- Peng J., Qu J., Zhang J., Chen M., Wan T. (2004), Adsorption characteristics of water-reducing agents on gypsum surface and its effect on the rheology of gypsum plaster, *Cement and Concrete Research*, 35, 527–531.
- PN-86/B-04360. Gypsum Binders. Test Methods. Testing of Physical Properties (in Polish).
- Prince W., Edwards-Lajnef M., Aitcin P. C. (2002), Interaction between ettringite and a polynaphtalene sulfonate superplasticizer in a cementitious paste, *Cement and Concrete Research*, 32, 79–85.
- Roncero J., Valls S., Gettu R. (2002), Study of the influence of superplasticizers on the hydration of cement paste using nuclear magnetic resonance and X-ray diffraction techniques, *Cement and Concrete Research*, 32, 103–108.
- Sebök T., Vondruška M. (2000), Interaction of anhydrite and melamine-formaldehyde polycondensates in aqueous suspensions, *Cement and Concrete Research*, 30, 993–1003.
- Sebök T., Vondruška M., Kulisek K. (2001), Influence of MSFC-type dispersant composition on the performance of soluble anhydrite binders, *Cement and Concrete Research*, 31, 1593–1599.
- Singh M., Garg M. (1997), Retarding action of various chemicals on setting and hardening characteristics of gypsum plaster at different pH, Cement and Concrete Research, 27, 947–950.
- Skvara F, Vancurova M. (1973), The effect of particle size distribution on apparent viscosity of a dispersion system, *Silikaty*, 17, 1, 9-20.
- Szwabowski J. (1999), *Rheology of Mixtures Containing Cement Binders* (in Polish), Wydawnictwo Politechniki Śląskiej, Gliwice.
- Uszerow-Marszak A. W., Urzenko A. M., Lassis A. J., Morkynene W. A (1979), Kinetics of heat generation at hydration of gypsum semi-hydrate (in Russian), *Stroitielnyje Materialy*, 10, 27–29.
- Wilkinson W. L. (1963), Non-Newtonian Fluids, Pergamon Press Limited, England.
- Ziesselmar R. (1985), Zur Pressaglomeration von Rauchgasgips mit Waltzenpressen, Zement Kalk Gips, 5, 243–246.