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J. ZYCH[*]

MONITORING THE THIXOTROPIC EFFECT IN WATER-CLAY SLURRY SYSTEMS USED AS A BINDER FOR MOULDING SANDS

MONITOROWANIE ZJAWISKA TIKSOTROPII W PASTACH UKŁADÓW WODNO-GLINOWYCH STANOWIĄCYCH LEPISZCZE (SPOIWO) MAS FORMIERSKICH

The work presents results of studies concerning the reological stability of water-clay pastes. The dynamic viscosity of bentonite pastes was assesed by an ultrasonic method. The studies were focused on kinetics changes at so called restoring period. Changes occuring in that period are the result of thixotropy phenomenon, which is common in dispersed system. It is shown that the degree of the viscosity change is distinctive enough to play an important role in the green moulding sand technology (it amounts to over 240 kPa·s with paste concentration of 75%). The studies were original both in a methodology and obtained results. The dynamic viscosity of bentonite pastes was assessed in the function of their concentration ($\eta = f(\%$ of clay$)$). The empirical relationship between bentonite paste stretching durability and dynamic viscosity was assessed ($R_m = f(\eta)$). The unmonotonous nature of the dependence of dynamic viscosity on temperature was found ($\eta = f(T)$). The viscosity of concentrated water-clay systems reaches it's minimum in the temperature of about 30°C. The research of dynamic viscosity was conducted using an ultrasound method devised by the author.

Keywords: ultrasonic, thixotropy, viscosity, reology,moulding sand

Przedstawiono wyniki badań stabilności reologicznej stężonych roztworów wodno-glinowych. Lepkość dynamiczną past bentonitowych wyznaczano metodą ultradźwiękową. Badania dotyczyły wyznaczania kinetyki zmian lepkości w tzw. okresie odstawania, czyli po zakończeniu ścinania. Zmiany w tym okresie są skutkiem zjawiska tiksotropii, które jest typowe dla roztworów dyspersyjnych. Wykazano, że skala zmian lepkości jest na tyle duża (wynosi ponad 240 kPa·s przy stężeniu pasty 75%), iż może mieć istotne znaczenie w całym procesie technologicznym przygotowania i wykorzystania wilgotnych mas formierskich. Wyznaczono lepkość dynamiczną past bentonitowych w funkcji ich stężenia ($\eta = f(\%$ gliny$)$). Wyznaczono empiryczny związek pomiędzy wytrzymałością na rozciąganie i lepkością dynamiczną pasty ($R_m = f(\eta)$). Stwierdzono niemonotoniczny charakter zależności lepkości dynamicznej od temperatury ($\eta = f(T)$). Lepkość stężonych układów wodno-glinowych osiąga minimum w temperaturze około 30°C. Badania lepkości dynamicznej past wykonano metodą ultradźwiękową opracowaną przez autora.

1. Introduction

In terms of rheology, green moulding sands with binders produced by processing of argillaceous materials are considered to be visco-elastic bodies. The viscosity is conferred by the binder, the elasticity – by the sand. In argillaceous materials, in a water-clay system, the effect of thixotropy takes place [1]. The systems, in which the effect of thixotropy occurs (suspensions and slurries), are rheologically unstable. Their apparent viscosity depends not only on the shear rate but also on the shear "history".

Moreover, the structure of thixotropic systems is spontaneously recovering as soon as the process of shearing (mixing, stirring) ends, which results in increase of viscosity, and in the case of slurries also in decrease of elasticity. Moreover, in slurries included into the thixotropic systems, the mechanical properties (R_m, R_t) are observed to increase upon completing of the stirring process.

The effect of thixotropy in water-based systems of clay binders used by foundry industry is practically unknown. Changes in technological and mechanical properties of green moulding sands observed after their preparation are usually ascribed to variations in humidity, or to the, so called, bentonite swelling behaviour. The behaviour of synthetic sands in technological process could be better understood, if in the analysis, the rheological instability of binder resulting from the thixotropy of water-clay systems was taken into consideration.

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[*] DEPARTMENT OF TECHNOLOGY OF CASTING MOULDS, FACULTY OF FOUNDRY ENGINEERING, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KRAKOW, POLAND

The article presents the results of the author's genuine work on the development of a new method to investigate the rheological properties of concentrated thixotropic systems, called slurries. The new method of investigations is based on the technique of ultrasounds. The water-clay ratio in the examined bentonite slurries corresponds to that which occurs in true green moulding sands. Applying the new method, the rheological stability of green moulding sands was evaluated, determining also the effect of slurry concentration on its strength. The effect of temperature on the dynamic (absolute) viscosity of bentonite slurries was examined as well.

2. The effect of thixotropy

The term "thixotropy" denotes every process in which - due to destruction of the internal structure of the system – the isothermal decrease of internal friction of the liquid (slurry) occurs with the lapse of shear time, followed by a sufficiently slow (measurable in time) return to the original consistency while at rest [2]. Thixotropy is understood as an ability of some dispersion systems of spreading under the effect of sufficiently strong mechanical forces (stirring, shaking) and resetting when these forces cease to act. Thixotropy is the feature typical of some coagulation structures which can be destroyed many times but each time recover completely and return to their original properties [1, 2]. The mechanical properties of thixotropic structures are characterised by the three main parameters

- η_o – the highest effective viscosity of virgin structure,
- $\eta_{\min}$ – the lowest effective viscosity of the ultimately destroyed structure,
- P_o – the boundary deformation stress.

The relationship between the effective viscosity η of a thixotropic system and the applied deformation stress P can be described by equation (1):

$$\eta = \eta_{\min} + (\eta_o - \eta_{\min}) \cdot \frac{P/P_o}{\sinh(P/P_o)} \tag{1}$$

With low values of P, which do not impair the structure or induce only an insignificant degree of flow, the system structure has the properties of a solid body, which means that, under given conditions, the rate of its recovery exceeds the rate of destruction. When $P \gg P_o$ the system is destroyed totally and forms the structure of a very low viscosity $\eta_{\min}$. The stress P_o expresses the stability of undestroyed structure.

The oscillating of a thixotropic system between the two extreme conditions corresponding to minimum and maximum viscosity is related with a kinetics of this system, which depends on many different factors. Figure 1 shows a model of changes in the viscosity of thixotropic systems during shearing (stirring) and resetting while "at rest". To get transformed from a stable condition (η_o) to the condition in which the apparent viscosity is the lowest ($\eta_{\min}$), the system needs certain amount of work to be performed, indispensable during the repeated shearing at a stress value higher than the flow limit of the system. The value of the minimum viscosity ($\eta_{\min}$), which the system can reach, depends on the shear rate; when the shear rate increases, the viscosity is decreasing.

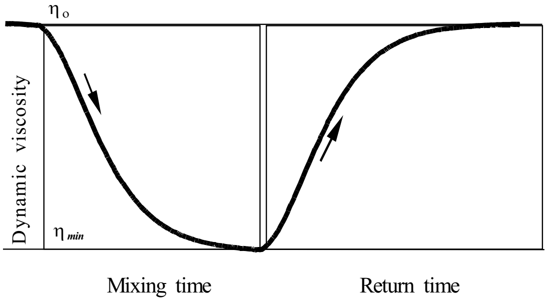

Fig. 1. Viscosity change in a thixotropic system during shearing and return to the equilibrium state (model of the process)

3. Studies of the thixotropic effect in water-clay slurries

3.1. Ultrasonic wave propagation in viscous media

It has been proposed to use ultrasonic technique in investigations of the viscosity of bentonite slurries and rheological stability of green moulding sands. The wave propagation rate in loose media (viscous and visco-elastic bodies) changes with the changing viscosity of the medium (or of one of its components). For longitudinal waves propagating in a viscous medium only in direction of the axis x, a general equation of rheology can be written in the form [3]:

$$\rho_o \frac{\partial^2 \xi}{\partial t^2} = \frac{1}{\beta_{ad}} \frac{\partial^2 \xi}{\partial x^2} + \eta \frac{\partial^3 \xi}{\partial x^2 \partial t} \tag{2}$$

where: β_{ad} – coefficient of adiabatic compressibility, η – absolute viscosity, ξ – particle displacement from the state of equilibrium.

After introducing the complex coefficient of elasticity $\left(K^* = \frac{1}{\beta_{ab}} + i \cdot \omega \cdot \eta\right)$, the equation gives a solution which enables the wave velocity to be determined [3].

$$c_L = \left(\sqrt{\frac{K}{\rho_o}}\right) \cdot \sqrt{\frac{2 \cdot (1 + \omega^2 \cdot r^2) \cdot (\sqrt{1 + \omega^2 \cdot r^2} - 1)}{\omega^2 \cdot r^2}} \tag{3}$$

where: $r = \frac{\eta}{K} = \frac{\eta}{\frac{1}{\beta_{ab}}} = \eta \cdot \beta_{ab}$, i – imaginary unit of complex number, K – complex coefficient of elasticity, ω – wave frequency.

Bentonite slurries of concentration corresponding to the concentration which occurs in moulding sands are characterised by high viscosity. With very high level of viscosity ($\omega \cdot r \gg 1$), equation (3) is reduced to a much simpler form of equation (4) [3]:

$$c_L = \sqrt{\frac{2 \cdot \omega \cdot \eta}{\rho_o}} \tag{4}$$

3.2. Research methods

In moulding sands, the clay binder present in a water-clay system has the form of a slurry. The concentration of this slurry depends on water content in the sand mixture (usually it is from 3.0 to 6.0%) and on the content of bentonite (6.0–10.0%) Under such assumptions, the concentration of bentonite in moulding slurries is comprised in a range from ~55 to 75%. The viscosity of the slurry with concentration >50% is so high that its measurement with traditional rotational or capillary rheometers is practically impossible [1–2, 4–6]. Therefore, for the measurements of viscosity an ultrasonic technique has been proposed. The parameter measured is the velocity of longitudinal wave (c_L). The dynamic viscosity of the slurries can be determined from relationship (5), basing on the results of the wave velocity measurement (c_L) generated at a frequency w, and on the measurement of the density of the slurry itself (ρ_o).

$$\eta = \frac{\rho_o \cdot c_L^2}{2 \cdot \omega} \tag{5}$$

In monitoring the kinetics of the thixotropic effect in slurries, it is necessary to take measurements in an "on line" mode at selected time intervals. In ultrasonic examinations, the wave velocity is determined at short time intervals. The measurements start immediately after preparation of the slurry or after the successive operation of its stirring (shearing). The ultrasonic measuring head cooperating with computer enables continuous recording of changes in wave velocity in the examined medium within any arbitrarily selected time interval. The research concept and the method were described in studies of the thixotropic effect in bentonite slurries [7, 8]. The studies referred to the period when in the examined slurry the process of restructuring takes place after the previously experienced effect of shearing ("destruction"). The return of the structure to the state of equilibrium, accompanied by continuous increasing of absolute viscosity is a spontaneous process. To monitor this process, the applied method of taking measurements should be such as not to cause "destruction" of the recovering structure. The applied ultrasonic technique with energy at a level generated by the transmitting head of the tester seems to be free from any effects that might cause any traceable changes in the recovering structure. The lack of such effects can be proved by a comparison made between the kinetics of changes in wave velocity recorded during continuous monitoring (the slurry is subjected to the wave effect emitted every 1 second) with the kinetics obtained at single ultrasonic impulses emitted, e.g., every 10 minutes. The measurements taken in this way have not revealed any difference in the kinetics of the examined slurries restructuring. The wave energy transmitted by the ultrasonic measuring head is not high enough to induce the traceable disturbances in the process of restructuring caused by the thixotropic effect. This mainly refers to the strong water-clay slurries with bentonite concentration above 30%, which are the subject of the described investigations.

3.3. The results of investigations

The kinetics of changes in wave velocity during storage of bentonite slurries after their previous shearing was examined. The process of shearing (stirring) of the slurries was carried out each time for a period long enough to make the wave velocity stabilised at a lower level of values. In this way it was attempted to obtain the state in which the slurry had the lowest viscosity (the structure "totally destroyed"). The samples of the slurry prepared in this way were placed in a probe (Fig. 2), and next in a chamber of the ultrasonic testing instrument; the temperature in the chamber was stabilised.

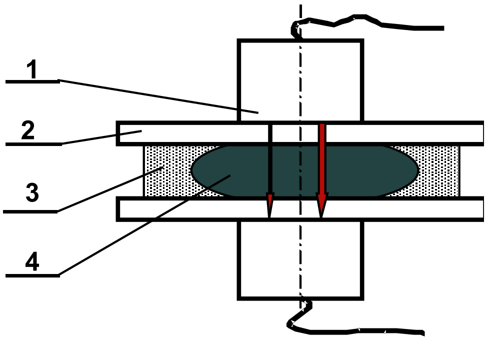

Fig. 2. Measuring system for ultrasonic testing of the thixotropic behaviour of water – clay slurries: 1 – ultrasonic heads, 2 – ceramic plates, 3 – sample sealing system, 4 – sample of slurry

The changes of wave velocity in the slurries at a concentration of 33–75% are plotted in Figure 3. Basing on the measured wave velocity values and using relationship (5), changes in absolute viscosity of the slurries during storage were determined.

During storage, the viscosity of the slurries increases; the intensity of these changes is shown in Figure 4. The stronger is the slurry, the greater are the increments in its absolute viscosity. The time and rate of shearing (stirring) have an important effect on the value of the viscosity measured immediately after stirring. Therefore, the increments in viscosity during storage do not depend only on the concentration and type of the slurry, but also on the "degree" of its structure destruction through shearing. If the increments in dynamic viscosity of the examined slurry are examined after the lapse of 4h (Fig. 4), then – for example – at a concentration of 33%, the increment $d\eta \cong 40$ kPa·s, while at a concentration of 75%, $d\eta \cong 240$ kPa·s, and so it is nearly 6 times higher.

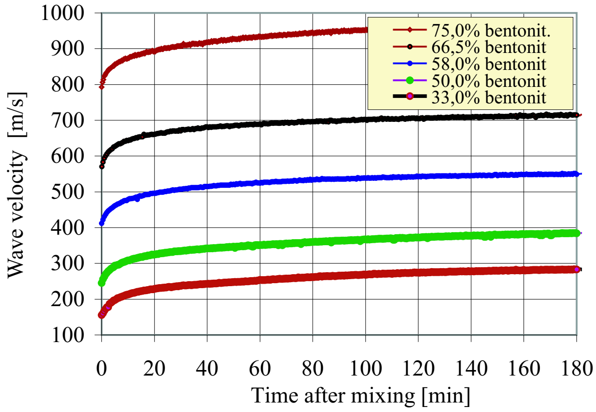

Fig. 3. Course of changes of wave velocity in samples of bentonite slurry during resetting (after shearing). $T = 20°\mathrm{C}$; Specjal bentonite

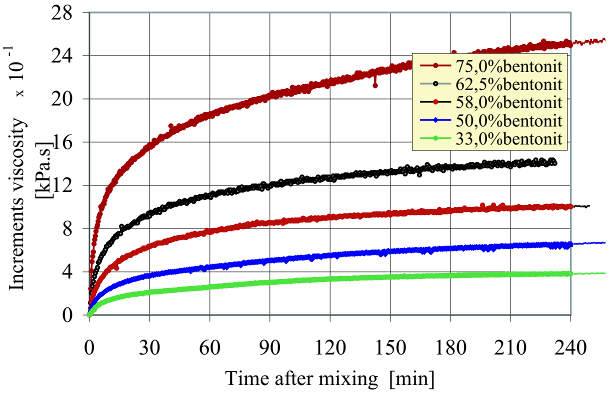

Fig. 4. Increments of absolute viscosity in bentonite slurries of 33–75% concentration during resetting: Specjal bentonite (75% montmorillonite), $T = 20°\mathrm{C}$

With increasing concentration of the slurry, its density is also increasing as well as the wave velocity. According to relationship (5.1), its dynamic viscosity is increasing, too. Because of the thixotropic properties of slurries, the effect of their concentration on the viscosity can be determined only during some selected periods of time after stirring, e.g. directly after stirring (when $\eta_x \cong \eta_{\min}$), or after having achieved the state close to equilibrium (when $\eta_x \cong \eta_{\max}$). Figure 5 shows a relationship determined for Specjal bentonite after about 3h of storage, when changes in viscosity are already proceeding much more slowly. The mere shape of the curve suggests that between the absolute viscosity of the slurry determined by the newly developed ultrasonic method and its strength properties a well correlated relationship should occur.

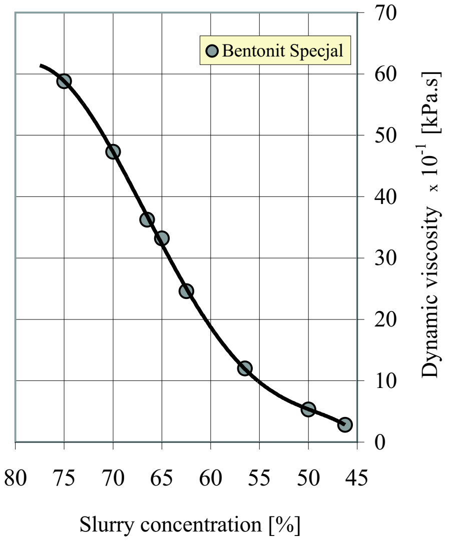

Fig. 5. Effect of slurry concentration on dynamic viscosity determined after 3 hours of resetting: Specjal B bentonite, $T = 20°\mathrm{C}$

The conclusion results from a similarity that is noted to exist between the curve describing the effect of slurry concentration on the absolute viscosity and the curve describing the effect of moisture content in bentonite-bonded sand on the sand strength. The results of the investigations which aimed at a verification of this thesis are shown in Figure 6. The tensile strength R_m was determined by means of a split probe described in [9]. With increase of the slurry concentration, its tensile strength R_m increases immediately after stirring and after 24h which elapse since the moment when the stirring operation has been completed. Moreover, with increased shear rate, the value of minimum viscosity of the destroyed bentonite structure ($\eta_{\min}$) is decreasing. This phenomenon is typical of the thixotropic systems. In moulding sands it has a very measurable technological impact, viz. the sands subjected to quick shearing in modern turbine mixers are characterised by definitely much better utilisation properties if compared with the sands processed in conventional paddle mixers or edge runner mixers.

The increase in absolute viscosity of bentonite slurries observed after shearing is very adequately described by logarithmic equations. Similar equations describe changes in the mechanical parameters of the slurries

(Fig. 7). The similarity of changes in the dynamic viscosity determined by ultrasonic method and in the strength of the slurries is the next proof that by measuring the viscosity of the slurry at a given time instant it is possible to determine also its strength. It should be stressed that the ultrasonic testing is of a non-destructive character. Changes in the viscosity and strength of the slurries included in thixotropic systems can be monitored *on line* at any arbitrarily selected time instant.

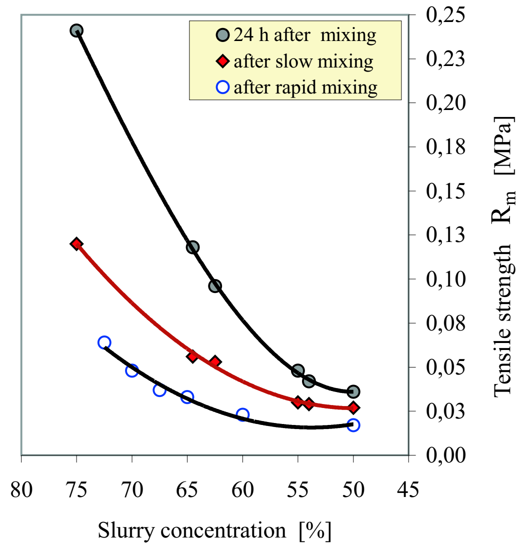

Fig. 6. Effect of slurry concentration on the tensile strength (R_m) determined directly after stirring and in 24h after the sample has been prepared: Specjal bentonite, T = 20°C

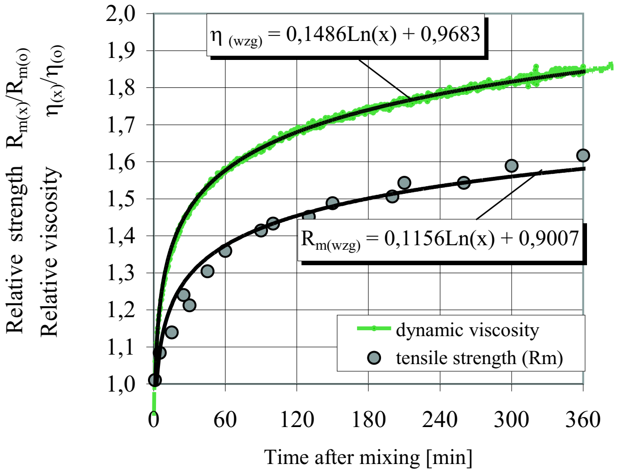

Fig. 7. Course of changes in dynamic viscosity and tensile strength (R_m) of the bentonite slurry during resetting. Slurry of 55% concentration, Specjal bentonite, T = 20°C

The temperature of bentonite slurry determines its dynamic viscosity. Usually, the increase of temperature is accompanied by decreased viscosity of fluids, solutions and slurries. Applying the developed method of ultrasonic testing, the effect of temperature on the absolute viscosity of strong bentonite slurries was examined. The prepared bentonite slurry was moulded in a probe shown in Figure 2 and was cooled for 24h to a temperature close to 0°C. The probe was next placed in the chamber of an ultrasonic testing apparatus, where the temperature of 50°C was maintained. Parallel with heating of the slurry, its temperature and ultrasonic wave velocity were measured. This enabled monitoring the changes in the viscosity of the slurry in function of temperature (Fig. 8). Preheating of the slurry to a temperature of about 30°C makes its absolute viscosity decrease, while further increasing of temperature results in a considerable increase of viscosity. Non-monotonic run of the viscosity-temperature relationship ($\eta_{\max} = f(T)$) is not typical of fluids, solutions and/or slurries. In other studies [10] it has been proved that similar effect is exerted by temperature on the strength of green moulding sands, using bentonite (bentonite slurry) as a binder. The determination of temperature at which the slurries included in water-clay systems achieve their minimum viscosity is also very important in the technology of green sand moulding. In a like manner, owing to the common occurrence in nature of these systems (water and clay), the fact that the minimum viscosity is available at a temperature of about 30°C may be of some significance for many other sectors of industry and economy.

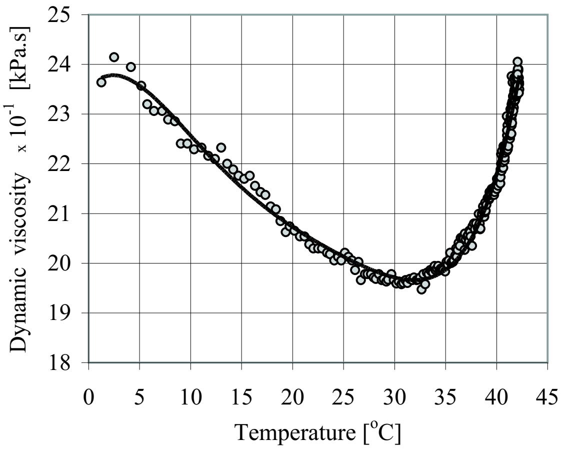

Fig. 8. Effect of temperature on dynamic viscosity of bentonite slurry

4. Summary

The phenomenon of thixotropy observed in colloidal systems, water-clay systems included, may be of some significance for numerous technological processes. This significance is the greater, the greater are the changes in the rheological parameters of the system (its viscosisty and plasticity), and the higher is the kinetics of changes of these properties. The studies conducted so far enable drawing some detailed conclusions. The most important are the following ones:

- the effect of thixotropy taking place in slurries can be monitored by ultrasonic technique, basing on the results of measurements of the longitudinal wave velocity,
- using the results of the ultrasonic measurements makes possible the determination of dynamic (absolute) viscosity of slurries, including slurries prepared from the montmorillonite clay,
- the range of viscosity changes depends on the slurry concentration, the higher is this concentration, the greater are the changes of viscosity (and of the strength),
- the rate at which the recovery of the thixotropic structure occurs after the shearing process (stirring, mixing) depends on the type of slurry, its concentration and temperature,
- slurries from the water – clay systems reach their minimum dynamic viscosity at a temperature of about 30°C.

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