Národní konference s mezinárodní úcastí

INŽENÝRSKÁ MECHANIKA 2002

13. – 16. 5. 2002, Svratka, Ceská republika

THINNING OF KAOLIN SLURRY

Vlasák Pavel, Chára Zdeněk, Konfršt Jiří

Abstract

After mixing kaolin with water attractive and repulsive forces between kaolin particles initiate process of coagulation and peptisation, respectively. The coagulation process in the kaolin slurry gives rise to voluminous aggregates of kaolin particles, where a great deal of water is fixed. A modification of the physico-chemical environment of the slurry by addition of a peptising agent produces repulsive forces between particles. It results in destruction of the aggregates and water originally fixed in aggregates is liberated, the viscous friction can play a larger role in the slurry, which is liquefied. To prove this process kaolin slurry with and without the peptising agent was measured on experimental pipeline loop. It was demonstrated that even very low concentration of peptising agent results in a significant reduction of the apparent viscosity and of the yield stress.

Key words: rheology of suspension, drag reduction, kaolin slurry, coagulation, peptisation, experimental investigation

1. Introduction

The flow behaviour of concentrated slurries is strongly affected by physically-chemical forces acting in the slurry and by the mutual particle-particle and particle-liquid interaction. The presence of the fine solid particles in a Newtonian liquid evokes complex rheological behaviour of the slurry due to many physical and chemical factors acting in the both, liquid and solid components. During the slurry flow shear-induced translation and rotational motions of the particles. It resultsd in particle collisions and formation of temporary multiples of particles caused by hydrodynamic interactions. Such interactions lead to an increase of the bulk viscosity of the slurry. Non-hydrodynamic inter-particle interactions evoke non-Newtonian behaviour of the slurry. They originate from random Brownian motion of particles and colloidal forces due to the van der Waals attractive forces and the electrostatic repulsive forces.

In highly concentrated fine-grained suspensions both types of interactions exist and their relative influence on the rheology is a function of the physical and electrochemical characteristics of the particles, the nature of the carrier liquid and on the type and intensity of the flow, Nguyen and Boger [2].

Ing. Pavel Vlasák, DrSc., Ing. Zdeněk Chára, CSc., Ing. Jiří Konfršt, Institute of Hydrodynamics, ASCR, Pod Patankou 5, 166 12, Praha 6, Czech Republic, E-mail : vlasak@ih.cas.cz, chara@ih.cas.cz

If the attractive forces acting in the slurry prevail, process of coagulation and sedimentation is initiated. However, a simultaneous existence of the repulsive forces enables to stabilise the slurry and keeps individual particles separated. The effect of the electro-static repulsive forces on the stabilisation process could quite well explain a mechanism of clay slurries liquefying, Satava [3].

2. Physical-chemical behaviour of kaolin slurry

Let us see in more details the kaolin particle behaviour in water environment. Kaolin particle is actually a table shaped crystal of kaolinite. The kaolinite crystal can be imagined as a packet of „cards“, where each card consists of two units - the first layer is built from tetrahedrons of silicon dioxide SiO_4, the second layer from hexahedrons of aluminium hydroxide $Al(OH)_6$, mutually connected by covalent bonds.

A sketch of this aggregate - the double-layer constituent - is given in Fig. 1. The double-layers are situated one by one in parallel position with higher or lower regularity according to the quality of the kaolinite crystal. Except some irregularity we can find also some imperfection due to the isomorphic substitution of quartz by aluminium or by iron in a crystal grid of kaolinite. Due to the substitution the kaolin surface becomes not electrically-neutral and at the locus of substitution an unsaturated negative charge exists, which play an important role in the slurry behaviour. Further on the kaolinite crystals could be imperfect also from the macroscopic point of view, they could be broken or their edge could be knocked off. Consequently the bonds between atoms of quartz or aluminium and oxid in the crystal grid are also broken and the impaired surface of the kaolinite adsorbs anionts OH^- from dissociated carrier liquid, e.g. from water.

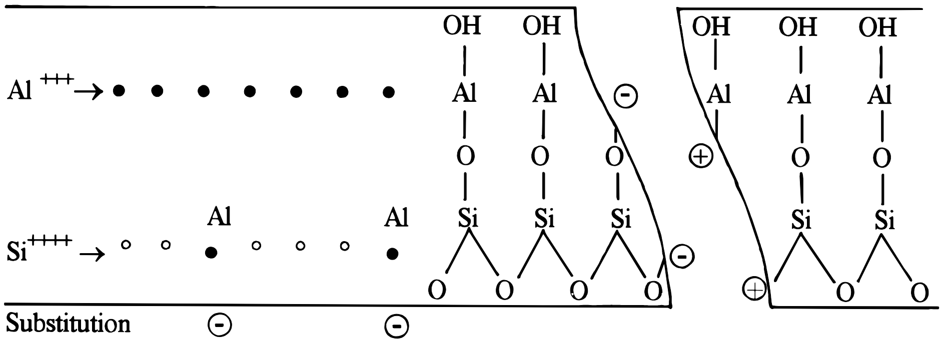

Fig. 1 Sketch of quartz substitution and break of kaolinite crystal

A number of negative charges on surface of the kaolin particle is originated due to the substitution in the crystal grid and electrolytic dissociation of Si - OH or Al - OH groups. Around the charged particle a layer consisting of cations dissociated in the carrier liquid is formed, which together with charged surface create an electrical double-layer.

The thickness of the double-layer depends on the value of surface charge and a kind and concentration of dissociated cations, which have to balance the charge of surface. The greater is charge and concentration of the cations and smaller is their size, the thinner surrounding layer could serve to compensate the charge of particle surface. Hence, the large hydrated monovalent cations as e.g. Na^+, Ka^+, Li^+, NH_4^+ with small specific iont charge produce a thick iont “atmosphere” around the particle. The medium thickness of the double-layer is evoked by bivalent ionts of calcium C^{++} or of magnesium Mg^{++} and the thinnest double-layer arises if the surface charge is compensated by trivalent aluminium ionts Al^{+++}.

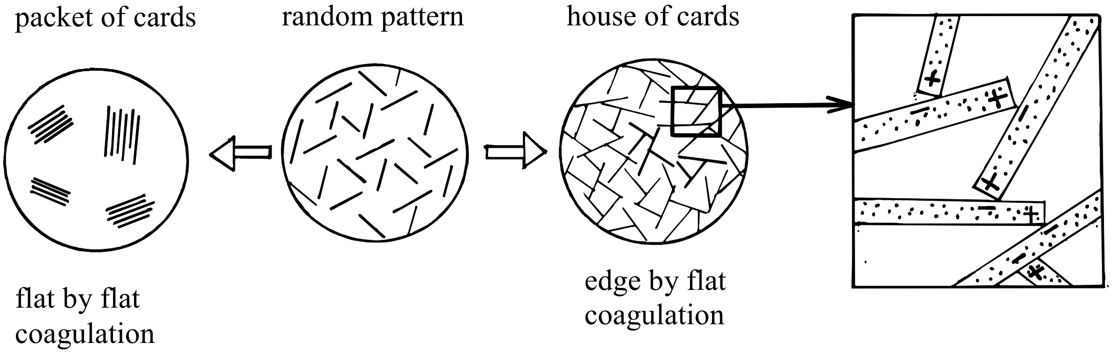

Fig. 2 Mechanism of coagulation of kaolin slurry

In the suspension the particles tend to bunch into bigger aggregates since it decreases the total energy of the system. Electrical double-layers are created around particles, their thickness depends on valence of dissociated cations. The thinner is electrical double-layer, the closer individual particles can come near each other and process of coagulation in the slurry gives rise to voluminous aggregates with a loose structure where a large deal of water is fixed. If the repulsive forces due to the change of ion content prevail, the aggregates are destroyed on individual particles and/or small clusters of particles.

We can distinguish two patterns of coagulation depending on acidity of the slurry. On the flat surface of the kaolinite crystal only negative charges can exist due to the quartz substitution, but on the edges and fractures the charge depends on pH of the slurry and is given by the process of dissociation.

For pH > 7 the Si-OH and Al-OH groups liberate hydrogen cation H$^+$ and on the edges of kaolinite crystal the negative charges remain. Thus only the negative charges exist on the surface of solid particles and the table shaped crystals of kaolinite attach together flat by flat and create so called ”packet of cards” (see Fig. 2) during the process of coagulation. On the contrary, for pH < 7 the anionts OH$^-$ are dissociated from the Si-OH and Al-OH groups on he edges of crystals, so that negative charges are on the plains of crystals while on edges positive charges exist. Due to Brownian motion the solid particles turn up so that negative and positive charges mutually compensate and resulting inner structure of the slurry can be described as irregular “honey combed” or as a “house of cards” pattern.

For higher concentration of solids, this structure could fill up the whole volume of the slurry. It means that for the low pH slurry a viscous friction in the kaolin-water mixture can act only in a small-scale, more energy is consumed on the aggregate deformation. If due to the change of the slurry environment (change of pH and/or content of dissociated cations) the voluminous aggregates are destroyed on individual particles or smaller packets of particles, water originally fixed in aggregates is liberated, the slurry becomes peptised. Energy is no more consumed on the aggregate deformation, the viscous friction can exert in much more scale and values of an apparent viscosity as well as a yield stress decreases and slurry is liquefying, Vlasak et al [6].

3. Experimental equipment and procedure

To prove the possibility of liquefying of the kaolin slurries three kinds of the kaolin were tested. The individual kind of kaolin differs by the particle size distribution (see Table 1) and also by a chemical composition (see Table 2). All the investigated kinds of kaolin have the similar content of the basic components (quartz, aluminium and iron oxides mass content is about 85 %) but the difference in the calcium and magnesium oxide is rather significant. Horsley and Snow [1] have shown that for determination of the yield stress and the apparent viscosity of a slurry a chemical composition is equally important as the solid concentration and particle size distribution. It was found that high content of magnesium and calcium compounds in the slurry obstructs modification of the slurry behaviour.

Rotational and capillary rheometers and also experimental pipeline loop were used to determine the flow behaviour of kaolin slurry without and with peptising agent. The flow behaviour of the kaolin slurry was measured by the capillary viscometer and by the rotational viscometer Haake Rotavisco RV 20 for three mass concentrations c_m = 0.39, 0.50 and 0.55. With the capillary viscometer velocity gradient up to 10^4 s^{-1} was reached. The rotational viscometer was used for velocity gradient range from 0 to 200 s^{-1}. Measurements provided on the both types of viscometer are in a good agreement.

The sodium carbonate and soda water-glass were used as a peptising agent in the mass concentration varying from c_a = 0.05 to 1 %. The both additives can supply the slurry by Na^+ cations for the compensation of the surface charge. The calcium ionts in the slurry are precipitated in the form of insoluble calcium carbonate or low-soluble calcium silicate, respectively.

Tab. 1 Particle size distribution

Kaolin	d_{50} μm	ρ kgm^{-3}	d μm	< 1	1-2	2-4	4-6	6-10	10-20	20-30	d_{max} μm
Sedlec-S1a	1.5	2507	mass	41	18	19	10	9	3	-	15
Sedlec-MK	6.0	2505	content	21	7	9	9	17	32	5	30
H.Bříza-HB	2.8	2549	[%]	28	12	22	21	11	6	-	20

Tab. 2 Chemical composition of the kaolin

Kaolin	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Σ CaO +MgO	residue
Sedlec - S1a	47.84	35.83	0.92	0.50	0.37	1.11	0.06	0.24	0.87	13.13
Sedlec-MK	50.56	34.56	1.08	0.21	0.29	1.61	0.07	0.39	0.50	11.23
H. Bříza-HB	50.33	35.06	0.67	0.07	0.20	1.38	0.09	0.93	0.27	11.27

An experimental re-circulation pipeline loop with test section from hydraulically smooth stainless steel pipe of inner diameter D = 17.5 mm was used to prove the flow behaviour and the process of peptisation during flow of kaolin-water slurry in pipe, Vlasak et al [8]. Kaolin slurry was forced by a screw pump with phase advancer from agitated storage tank. The installation makes possible to operate in laminar and in turbulent regime up to average slurry velocity $V_{av} \approx 8$ m/s. Pressure losses were measured by differential pressure transducers Hottinger-Baldvin PD-1 monitored by computer. At the pipe outlet a box divider was mounted which allowed mass flow rate and volume concentration measurement, Vlasak & Chara [7].The temperature of the slurry was kept in range $t \approx 18$ °C by help of heat exchanger situated at the beginning of transport pipe.

The kaolin from the workstation Horni Briza and sodium carbonate as a peptising agent were used. Two types of slurries, i.e. kaolin-water slurry and kaolin-water-sodium carbonate slurry of different volumetric concentrations, varying from $\boldsymbol{c_v}$ = 3 to35 %, were tested for laminar, laminar/turbulent transition and turbulent regimes. Based on experience, Vlasak et al [5,6], from measurement realised on rotational and capillary viscometers, the kaolin Horni Briza was used due to its average sensibility to the peptisation process. Rheometr Haake RheoStress 300 was used to determine the flow behaviour of kaolin slurry without and with peptising agent after measurement in pipe loop. The peptising agent/kaolin mass ratio was varied from c_a = 0.05 to 0.30 %, which corresponds with optimum efficiency, Vlasak et al [6]. Due to the peptising agent we could study kaolin slurry up to volumetric slurry concentration $\boldsymbol{c_v}$ = 36 %.

4. Results and Discussion

The effect of the both additives, the sodium carbonate and soda water-glass, and their concentration for different slurry concentration and kind of kaolin was investigated.

The behaviour of the system is determined by a mutual effect of the attractive and the repulsive forces between the solid particles. A magnitude of the forces is determined by physical and chemical properties of the both phases. By addition of the appropriate cations into the slurry the repulsive forces between particles prevail and the viscosity and the yield stress decrease. The effect depends on the peptising agent concentration (see Fig. 3). With increasing concentration of the agent, the apparent viscosity and the yield stress at first quickly decrease, after exceeding the optimal value of the agent concentration, the both rheological quantities again increase and the re-coagulation process resumes, Vlasák et al [4].

A similar effect of agent concentration was observed for the different slurry concentration (see Fig. 3), the tendency of re-coagulation seems to be nearly independent on concentration of solids, but it was observed to be higher for the lower velocity gradient value.

The effect of the kind of peptising agent is illustrated in Fig. 4. For higher agent concentration the efficiency of water-glass is higher that of sodium carbonate, for the low agent concentration the opposite is valid. From the point of view of the sort of kaolin, the best results were gained for kaolin Sedlec MK. The peptisation effect for the other two sorts is similar, but considerably lower (see Fig. 4). Very low concentration of peptising agent results in rather remarkable decrease of both yield stress and apparent viscosity. If the agent concentration increases, its efficiency decreases and the process of slurry re-coagulation can be observed, as well as the increase of pH from the original value about pH = 6 up to pH ~ 10.5 for c_a = 1.0%.

The present investigation confirms that the addition of peptising agent can serve to reduce the yield stress and viscosity of kaolin slurries by orders of magnitude and can help to reach much higher solids concentration together with the lower energy consumption for pipeline transport of kaolin slurries. A similar principle, e.g. the change of chemical environment of the transported slurry, can be used also for another fine-grained dense hydromixture, as was described for instance by Horsley and Snow [1] for different mine tailings or by Nguyen and Boger [2] for bauxite residue.

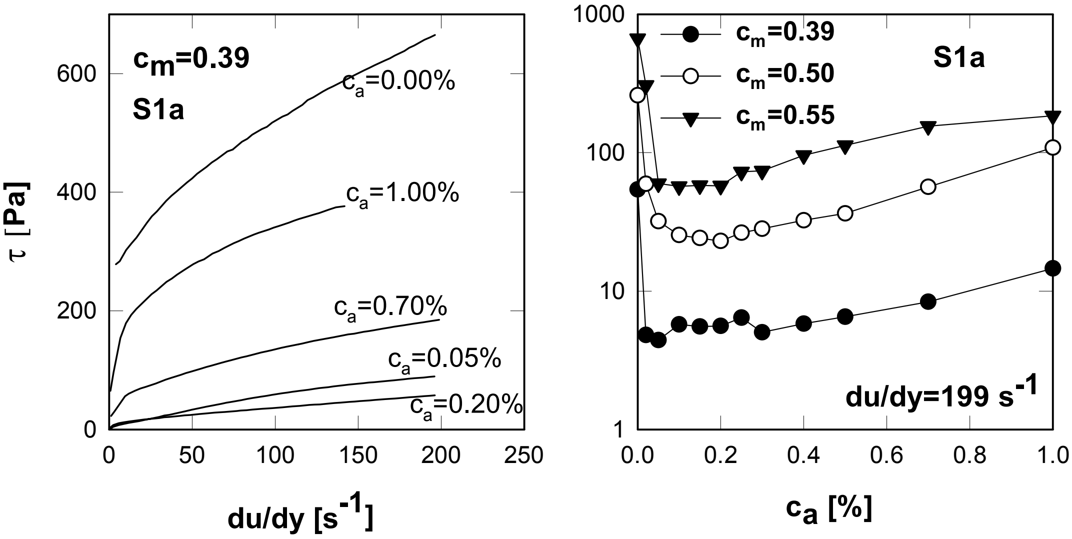

Fig. 3 Effect of sodium carbonate and of kaolin concentration on shear stress

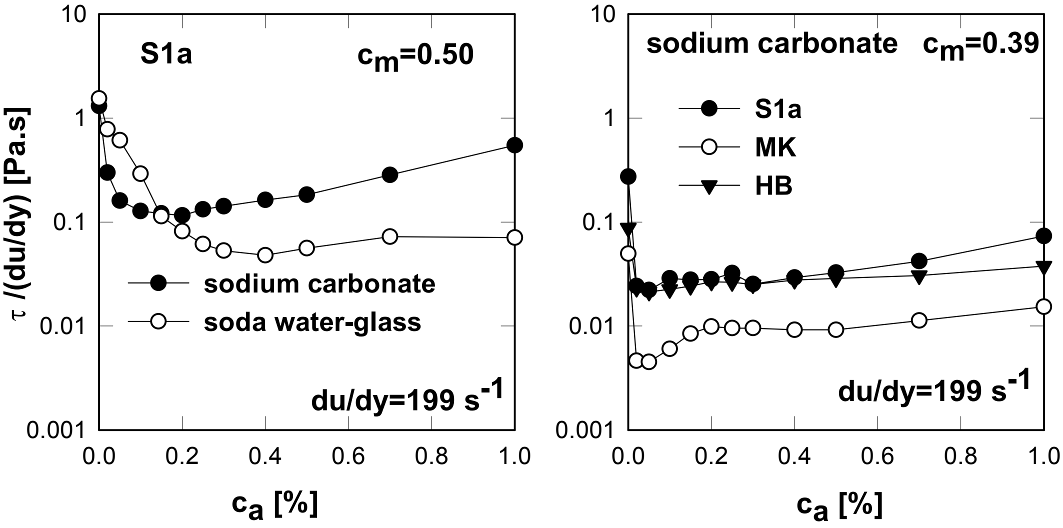

Fig. 4 Effect of kind of peptising agent and of kaolin on shear stress/shear rate ratio

Similar results were obtained for kaolin slurry measured after processing of the slurry in pipeline loop. Difference of slurry flow behaviour of kaolin slurry without peptising agent and with peptising agent was characterised by shear stress over shear rate relationship, see Fig. 5. The untreated kaolin slurry was measured on rheometr

Haake RheoStress 300 for volumetric concentration varied from c_v = 3 % up to 23 %. and kaolin slurry with sodium carbonate was measured for volumetric concentration c_v = 10, 23, 27 and 36 % and sodium carbonate/kaolin mass ratio c_a = 0.05 ÷ 0.30 %.

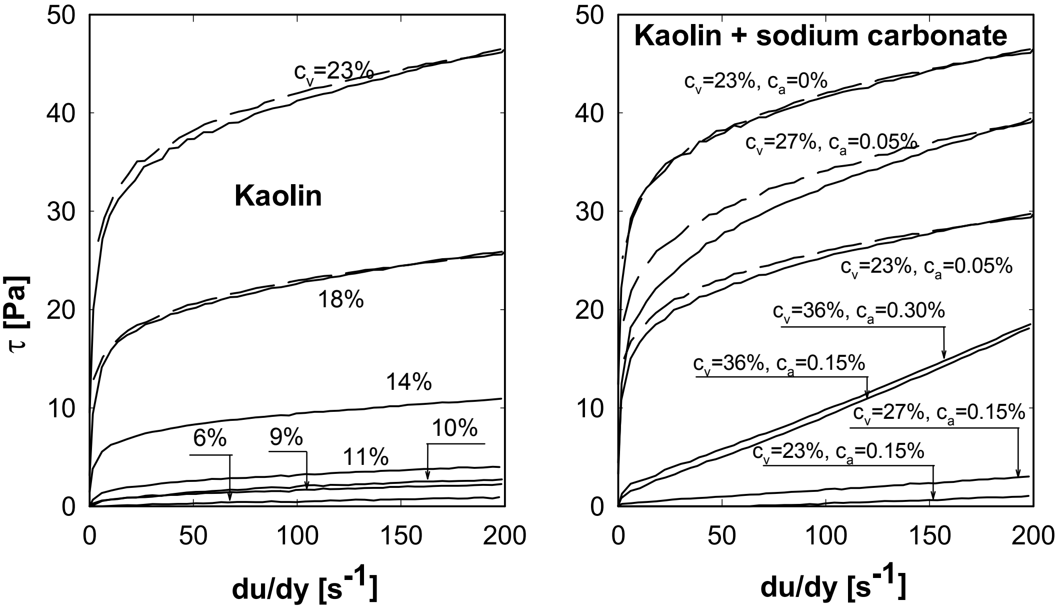

Fig. 5 Shear stress τ over shear rate *du/dy* relationship for kaolin slurry and for peptised kaolin slurry measured on rotational rheometer Hake RheoStress 300

The results are very similar to the results obtained former for kaolin slurry, Vlasak & Chara [7,9] or peptised kaolin slurry, Vlasak et al [4,5,6]. However, because concentration of the slurry measured in the pipe loop was lower than that of slurry used formaly for rheometrical measurement only (c_v = 39, 50 and 55 %), there are some differences, but more or less only of quantitative character. We can see also hysteresis of shear stress/shear rate relationship, which is more marked for peptised slurry (solid line indicates the ascending branch and dash line the descending one).

The untreated and peptised slurries of c_v = 10, 23, 27 and 36 % were measured also on experimental pipeline loop to prove the effect of peptisation on kaolin slurry during pipe flow under laminar and turbulent condition. The flow behaviour of peptised and untreated kaolin slurry is considerable different, see Fig. 6 and 7. Efficiency of peptising agent depends on slurry and peptising agent concentration and on flow regime. The agent efficiency increases with its concentration and it is higher for lower flow velocities.

For low slurry concentration the peptising agent acted in laminar region only. The yield stress practically vanishes and the hydraulic gradient/velocity relationship is very close to water alone values. Practically no difference between peptised and untreated slurry in transient and turbulent regime can be found for higher velocity region. The effect of peptisation becomes essential for higher values of slurry concentration ($c_v \approx 25$ %). In laminar regime it is strongly positive and substantial decrease of hydraulic gradient about 30 % was watched. At turbulent region the positive effect depends on slurry flow velocity V_{av} and on peptising agent/kaolin mass ratio c_a. We can see only slight decrease of the velocity value corresponding to the transient point, from about V_{tr} ~ 7.8 m/s to V_{tr} ~ 6.3 m/s for slurry concentration c_v = 23 % and peptising agent/kaolin mass ratio c_a = 0.05 %. Behind the transient point the hydraulic gradient i_m of peptised slurry quickly increases and at V_{av} ~ 6.7 m/s exceeds the value of untreated slurry.

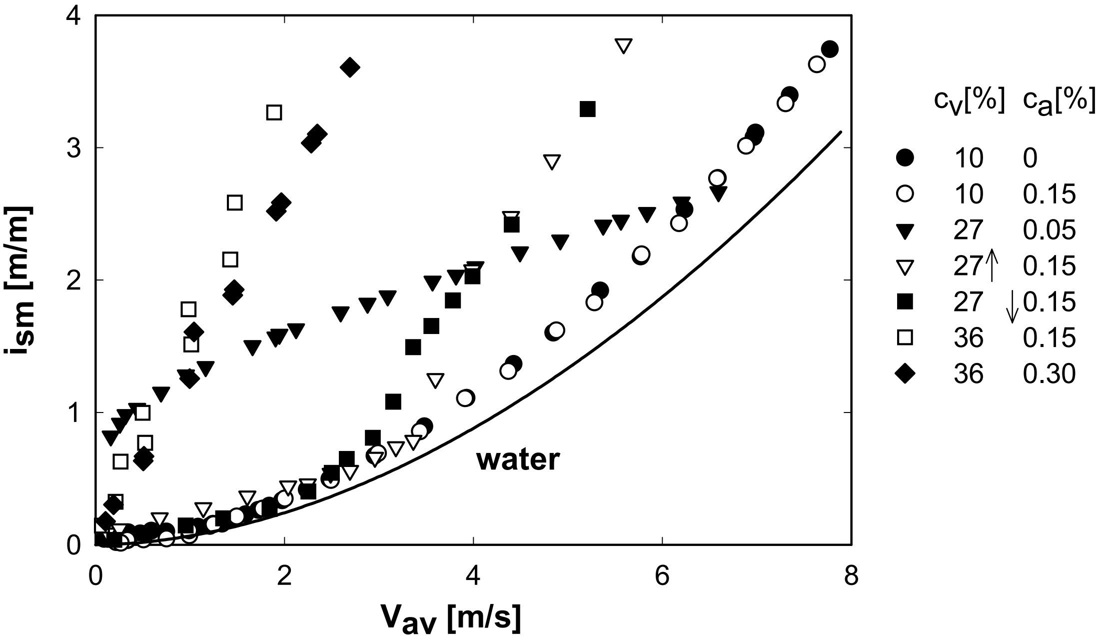

Fig. 6 Effect of peptising agent/kaolin mass ratio c_a on hydraulic gradient i_m (kaolin slurry of c_v = 10, 27 and 36 %)

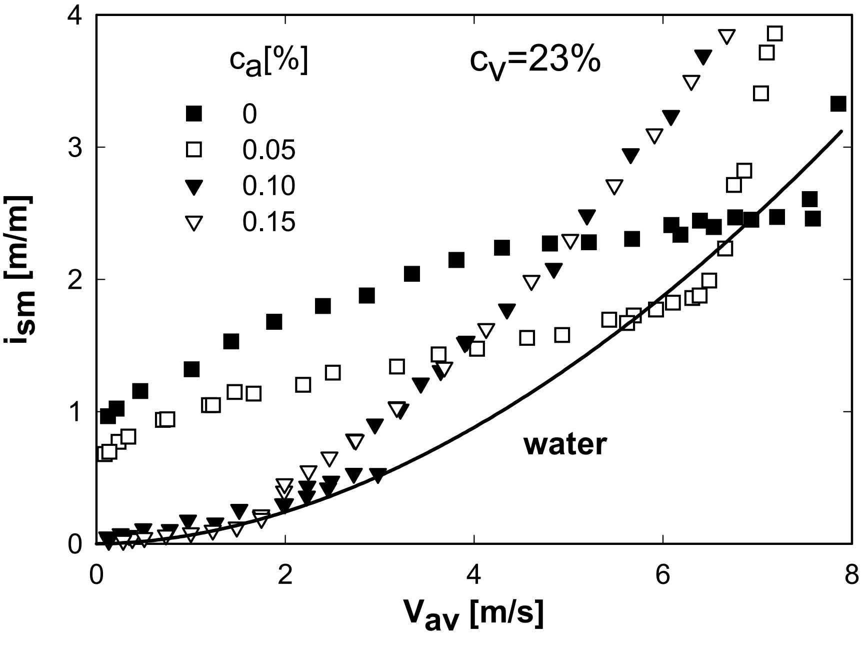

Fig. 7 Effect of peptising agent/kaolin mass ratio c_a on hydraulic gradient i_m (kaolin slurry of c_v = 23 %)

For peptising agent/kaolin mass ratio c_a = 0.10 % the peptised slurry shows only slightly non-Newtonian behaviour. The laminar/turbulent transient point is about slurry velocity V_{tr} ~ 3.0 m/s. At transient region hydraulic gradient steeply increases and in turbulent region the peptised slurry behaves practically as Newtonian liquid with viscosity and density higher than those of water. For c_a = 0.15 % the peptised slurry seems to be Newtonian liquid even in the laminar regime. The transient region is reached at slurry velocity V_{tr} ~ 2.0 m/s and behind it the slurry hydraulic gradient/velocity relationship continues similarly as for the slurry of c_a = 0.10%. However, at slurry velocity about V_{av} ~ 5.0 m/s hydraulic gradient of peptised slurry exceeds values valid for untreated slurry and a profit from peptisation vanishes.

For very high slurry concentration (about $\boldsymbol{c_v}$ = 36 %) peptisation suppresses yield stress and the hydraulic gradient/velocity relationship can be approximated by very steep linear dependence. Unfortunately, it is impossible to compare flow behaviour of peptised and untreated slurry since without addition of the peptising agent the slurry of so high concentration is no more flowing in pipe.

It was demonstrated, see Fig. 8, peptisation results in significant decrease of the yield stress. Effect of the peptising agent is higher for higher kaolin concentration and peptising agent/kaolin mass ratio. The pipe loop investigation confirmed the results obtained by rheometrical measurement of very super-concentrated kaolin slurry, Vlasak et al [5,6].

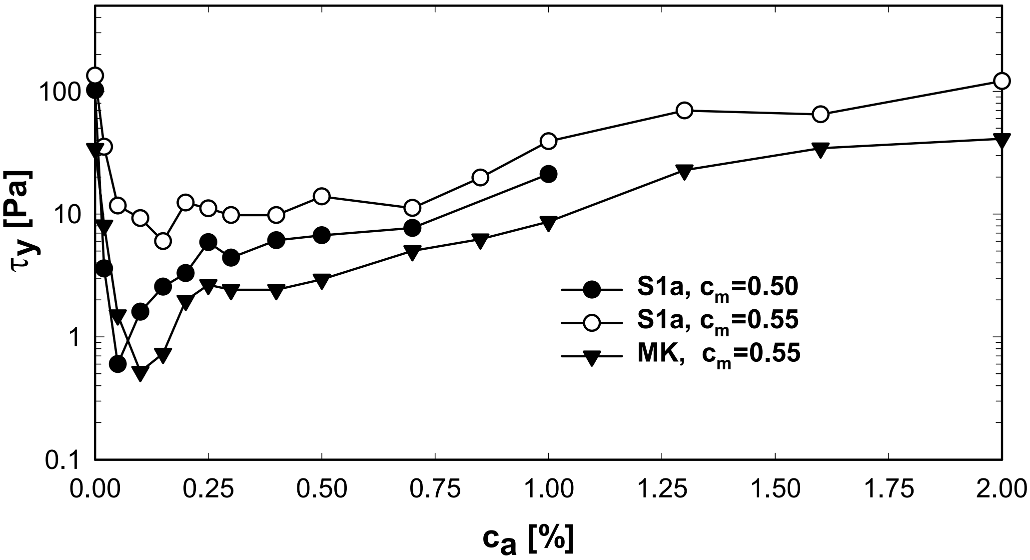

Fig. 8 Effect of kind of kaolin and peptising agent concentration on yield stress

4 Conclusions

The effect of the peptising agent and its concentration for different kaolin slurry concentrations was investigated. The behaviour of the kaolin slurry is controlled by a mutual effect of the attractive and the repulsive forces between the solid particles given by physical and chemical properties of the both phases.

The peptising agent (sodium carbonate) supplies the slurry by Na^+ cations for the compensation of the surface charge of particles, affects significantly flow behaviour of kaolin slurries and helps to reach much higher concentrations of solids and/or lower energy consumption during slurry flow in pipe. With increasing concentration of the peptising agent the apparent viscosity and the yield stress gradually decrease, the later one even vanishes. For high peptising agent content transition from non-Newtonian to Newtonian behaviour was observed. Efficiency of the slurry liquefying process depends on the peptising agent and the solids concentrations and flow velocity of the slurry. Effect of the peptising agent increases with kaolin concentration and it is higher for laminar regime. The laminar/turbulent transition point is reached for peptised slurries at significantly lower flow velocity compared to the untreated slurry. For laminar/turbulent transition and especially for turbulent regimes the positive energy consumption effect has to be evaluated for each event.

The control of physical-chemical behaviour and of an inner structure of a slurry makes possible to optimise both the energy and water consumption, to improve quality and economy of the transport, handling and processing of the slurry.

References

[1] R.R. Horsley and R.J. Snow - The rheology of some Australian mine tailings. Progress and Trends in Rheology II, Prague (Czechoslovakia), 17-20 June, 1986, Ed. H. Giesekus, M. F. Hibberd, Steinkopff, Darmstadt, 1988, 34

[2] Q.D. Nguyen and D.V. Boger - Exploiting the rheology of highly concentrated suspensions. In: Proc. of IX. Int. Congress on Rheology, Acapulco, Mexico, 8-13 October, 1984, Ed. B.Mena, 153.

[3] V. Satava - Teorie ztekucovani keramickych litych brecek a optimalizace procesu liti. *Sklar a keramik*, **XXIII**, 1973, 195 (in Czech)

[4] P. Vlasak, Z. Chara, P. Stern: The effect of additives on flow behaviour of kaolin-water mixtures. Progress and Trends in Rheology V, Portoroz (Slovenia), 6-11 September 1998, Ed. I.Emri, Steinkopff, Darmstadt, 1998, 605

[5] P. Vlasak, Z. Chara, P. Stern: Liquefying of dense clay-water mixtures, Problems in Fluid Mechanics and Hydrology, IH ASCR, Prague (Czech Rep.), 23-26 June 1999, 190

[6] P. Vlasak, Z. Chara, P. Stern: Effect of peptisation on flow behaviour of clay suspension, Hydrotransport 14, BHR Group Conf. Series No. 36, Maastricht (The Netherlands), 8-10 September 1999, 347

[7] P. Vlasak, Z. Chara: Laminar and turbulent flow experiments with yield-power law slurries. *Powder Technology*, **104**, 1999, 200

[8] P. Vlasak et al: Flow behaviour and drag reduction of kaolin suspensions, Hydrotransport 15, BHR Group Conf. Series, 3.-5. June 2002 (in press)

[9] P. Vlasak, Z. Chara: Laminar and turbulent flow of dense Kaolin and ash hydromixtures, *Handbook of Conveying and Handling of Particulate Solids,* (Ed.: A.Levy, H. Kalman), Elsevier Sciences, 2001, 473

Acknowledgement

The support under project No. S 2060007 of ASCR R&D Program and under Grant No. A 2060701 of Grant Agency of ASCR is gratefully acknowledged.