The Deflocculation of Kaolin Suspensions – the Effect of Various Electrolytes

Pěnkavová, Věra
2013

Dostupný z `http://www.nusl.cz/ntk/nusl-161341`

The deflocculation of kaolin suspensions – the effect of various electrolytes

V. Pěnkavová[1], M. Guerreiro[2], J.Tihon[1], J.A.C.Teixeira[2]
[1] Institute of Chemical Process Fundamentals AS CR, v.v.i., Rozvojová 135, 165 02 Prague, Czech Republic, E-mail: penkavova@icpf.cas.cz, tihon@icpf.cas.cz;
[2] University of Minho, 4710-057 Braga, Portugal, E-mail: a66188@alunos.uminho.pt, jateixeira@deb.uminho.pt

Keywords: *kaolin suspensions, deflocculants, viscosity measurements, stability of suspensions.*

Abstract:
The deflocculation effect of conventional additives to kaolin suspensions is evaluated from the results standard rheological measurements. Several widely used electrolytes (NaOH, Na_2CO_3, Na_2SiO_3, SHMP = sodium hexametaphosphate, and CMC = sodium salts of carboxymethyl-cellulose) have been tested. The optimal concentrations of these deffloculants, in respect to reaching the maximum reduction of initial suspension viscosity, are found. The stability of deflocculated kaolin suspensions against sedimentation is evaluated and different aspects of the observed flow enhancement discussed. Inorganic electrolytes are found to be more effective in viscosity reduction, but on the other hand, low-molecular organic CMC additives produce more stable final suspensions.

1. Introduction

Deflocculation of kaolin suspensions is a technological process widely used in ceramic, paper and dye industry. To decrease viscosity and thus to facilitate transport, aqueous kaolin suspensions are mixed with various electrolytes. Mineral kaolinite is a dominant compound of kaolin clays. Kaolinite particles with their two-face layer structure (the octahedral alumina layer covered by hydroxyl groups and the tetrahedral silica layer with excreted oxygen [1, 2]) are susceptible to create hydrogen bonds and thus exhibit strong electrochemical interactions in aqueous media. This is the reason why a small addition of electrolyte influences the finally achieved flowability and stability of aqueous kaolin suspensions. Adsorption of chemical agents onto different parts of kaolin structure (faces or edges) is strongly affected by pH value of the prepared suspension.

The intensity of electrochemical interactions can be demonstrated via zeta-potential. Its value gives us information on the difference of potentials between slipping layers covering particles and surrounded medium. If zeta-potential is high, repulsion forces between particles are strong, interacting particles do not aggregate, and the prepared suspension is stable and having low viscosity. A lot of works deal with the measurement of zeta-potential of mineral suspensions in dependence on the content of additives and the actual value of pH [3-9]. But due to the complex structural character of kaolinite (silica and alumina faces have different surface potentials [10]), the information obtained from zeta-potential measurement of kaolin suspensions is not easy to interpret. Six kinds of inter-particle interactions can occur in kaolin suspensions: alumina face - silica face, alumina face - alumina face, silica face - silica face, edge - alumina face, edge - silica face and edge-edge. Energy of these interactions has been studied and from the results different internal particle structures have been deduced [3, 11]. The dominant inter-particle interactions influence the internal structure and consequently also the rheological behavior of kaolin suspensions. Thus the rheology measurements can provide fundamental information on the quality of suspensions.

Changes in flow behavior of mineral suspensions caused by additives are usually described in the form of the dependence of yield stress on the content of additives and the actual value of pH [3, 4, 8, 9]. The normalized value of yield stress has been found to be inversely proportional to square of zeta-potential and directly proportional to a power of the volume fraction of solid particles in suspension [3].

Only few works deal with detailed rheological measurements of kaolin suspensions (see [12] for primary and [13-19] for deflocculated suspensions). Unfortunately, these works are focusing on a limited number of additives and their concentrations. The observed viscosity curves exhibit mostly shear thinning character, but in some cases shear thickening [13, 18] or even anti-thixotropy [19] has been observed. Practically all used additives (both organic and inorganic) decrease viscosity of original aqueous kaolin suspensions. Only additives with the presence of Ca^{2+} ions play an opposite role, working as flocculants and increasing suspension viscosity [18].

The objective of this work is to study systematically the effect of additives on rheological behavior of kaolin suspensions. The results of viscosity measurements carried out for inorganic (five different electrolytes) and organic (one polyelectrolyte at three molecular weights) additives, all widely used as deflocculants, are presented. The stability of resulted deflocculated suspensions against sedimentation is also classified and discussed.

2. Experimental

2.1. Materials

Kaolin "Zettlitz Ia", produced by Sedlecký Kaolin, a.s., has been used to prepare kaolin suspensions. This kaolin contains more than 90% of mineral kaolinite ($Al_2O_3.2SiO_2.2H_2O$) with wide particle size distribution (typically 60% of particles are smaller than 2μm, just negligible amount of particles is larger than 60μm). The BET surface area is 18.57 m^2/g. The list of electrolytes used as deflocculation additives is presented in Table 1.

Table 1: List of the additives used as deflocculants

Electrolyte	Molecular weight [g/mol]	Producer
SHMP*	611.77	Penta
NaOH	40.00	Penta
Na_2SiO_3	122.06	Kittfort
Na_2CO_3	105.99	Penta
SHMP/Na_2CO_3 (1:1)		Penta
CMC**	90000	Aldrich
CMC	250000	Aldrich
CMC	700000	Aldrich

* Sodium hexametaphosphate

** Sodium carboxymethylcellulose

Primary kaolin suspensions (with 30, 35 and 40% wt. concentrations) have been prepared by pouring kaolin with distilled water. Resulted suspensions have been let at rest for 3 days and then mixed until reaching homogeneous state. Deflocculated kaolin suspensions have been prepared by a similar way, i.e. addition of electrolyte solutions into kaolin powder. Suspensions have been again keeping at rest for few days, just shaking from time to time. After becoming homogeneous, they were used for rheological measurements.

2.2. Methods

Brookfield viscometers (LVDV-II+Pro Extra and HBDV-III Ultra) have been used to carry out rheological testing of prepared aqueous kaolin suspensions. The configuration of coaxial cylinders equipped with a small sample adapter has been applied instead of traditional Brookfield spindles. It assures a very good temperature control of a small amount of tested samples. The spindle SC4-18 and SC4-31 have been used for high (up to 330 s^{-1}) and low (up to 68 s^{-1}) shear rates, respectively.

The working ranges and measuring accuracies of used viscometer configurations are given in Table 2. The optimal viscometer configuration for each suspension has been chosen according the consistency of a tested sample, which was ranging over several orders of magnitude from 11000 mPa.s (primary kaolin suspensions at low shear rates, non-Newtonian shear thinning behavior) and 5 mPa.s (deflocculated kaolin suspensions over the whole range of shear rates, Newtonian behavior).

Table 2: Limits and accuracy of viscosity measurement

Viscometer	Spindle	Spring Torque	Shear Rate Range		Viscosity Range		Torque Accuracy
			min* RPM	max* RPM	min RPM	max RPM	
		mN.m	s^{-1}	s^{-1}	mPa.s	mPa.s	% full range
LVDV-II+Pro Extra	SC4-18	0.0673	6.6	264	600	15	1
LVDV-II+Pro Extra	SC4-31	0.0673	1.7	68	6000	150	1
HBDV-III Ultra	SC4-18	5.7496	6.6	330	51200	1024	1

* Minimum and maximum angular velocity is 5 RPM (min) and 200 RPM or 250 RPM (max, for LVDV or HBDV), respectively.

An example of flow curves measured for primary and deflocculated kaolin suspensions is shown in Figure 1a. Rheological data are presented for three kaolin suspensions (primary, addition of 0.25% and 0.5% wt. SHMP) and for two independent samples of each suspension (labeled in the legend as “a” and “b”). The concentration of an additive is expressed in weight percentage relatively to the mass of kaolin powder. The results suggest a very good reproducibility of measurements. The flow curves are fitted by a simple power law rheological model:

$$\tau = K \dot{\gamma}^{n}, \tag{1}$$

where the coefficient of consistency K and the flow index n are the parameters relating to the shear stress τ and shear rate $\dot{\gamma}$. The change from the non-Newtonian rheological behavior of primary kaolin suspensions (shear thinning with $n \cong 0.15$) to the Newtonian behavior of deflocculated kaolin suspensions (here $n \cong 1$ for 0.5% SHMP) is apparent. As seen in Figure 1b the viscosity of kaolin suspensions is shear rate dependent. Therefore to facilitate the comparison of consistency of deflocculated kaolin suspensions, the viscosity values at a reference shear rate of $100s^{-1}$ (marked in the figure by a dash line) are stated hereinafter.

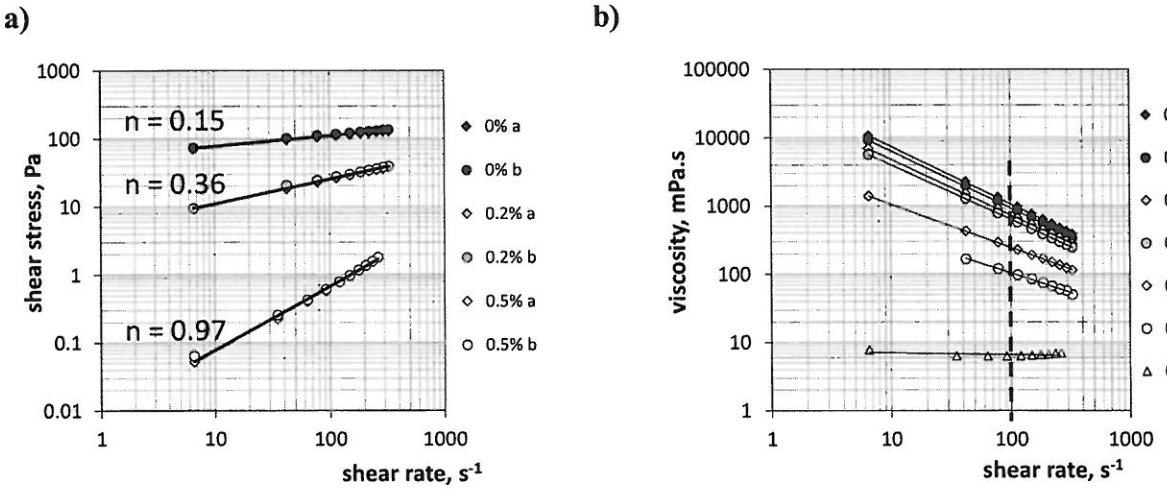


Figure 1: Rheological data measured for 40% kaolin suspensions with addition of SHMP: a) flow curves, b) shear rate dependent viscosity.

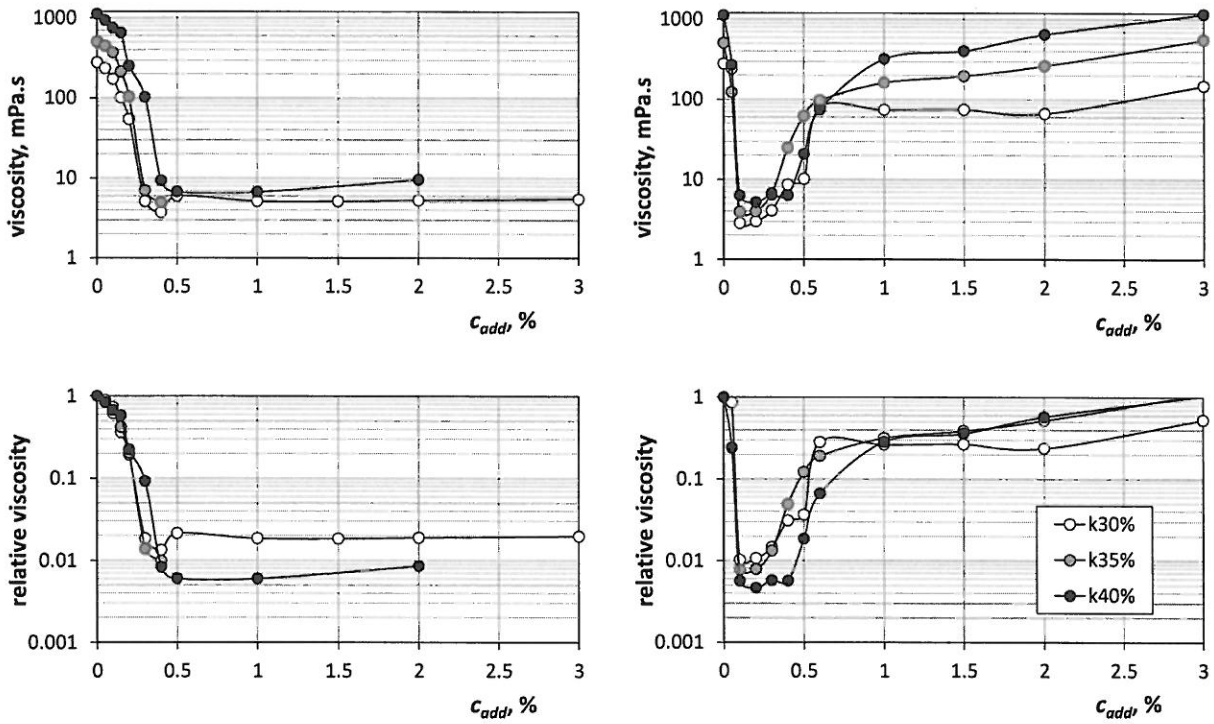
3. Results and discussion

The efficiency of various electrolytes as deflocculation agents of aqueous kaolin suspensions can be evaluated from the results of rheological measurements. However, not only low viscosity but also good homogeneity and stability are needed to classify the final suspension as well deflocculated. In this section, first the suspension viscosity and stability results are separately discussed, and then final evaluation of all used deflocculants is given.

3.1. Viscosity of suspensions

Inorganic additives

The rheological measurements with three different primary concentrations of primary aqueous kaolin suspensions (30, 35 and 40% wt.) have been done first with the objective to find the best viscosity versus concentration scaling. As seen in Figure 2, where viscosity data obtained for suspensions with SHMP and NaOH additives are presented, the relative concentration based on the ratio between the mass of additive and kaolin give satisfactory results (i.e. the relative viscosity curves match and the optimal concentrations corresponding to the maximum viscosity reduction are practically the same). Strong viscosity effect of additives is apparent especially at small concentrations, where a rapid decrease of viscosity is observed before reaching the minimum value of viscosity. After that subsequent addition of the electrolyte either does not change (for SHMP, see Figure 2a) or increase again (for NaOH, see Figure 2b) the viscosity of final suspensions. As this viscosity trend is qualitatively the same for all studied kaolin concentrations, all other experiments have been performed only with 40% kaolin suspensions.


a) SHMP

b) NaOH

Figure 2: Variation of viscosity and relative viscosity (related to the viscosity of primary kaolin suspension) with the concentration of additives: a) SHMP, b) NaOH.

(Viscosity is calculated from the shear stress at the reference shear rate100 s^{-1})

The efficiency of all used inorganic electrolytes for deflocculation of 40% aqueous kaolin suspension is compared in Figure 3. All these additives are able to reduce the viscosity to the level less than 1% of the initial value of primary suspension. This is usually achieved for optimal concentrations several tenths of percent (for 0.3% Na_2CO_3, 0.3% SHMP/Na_2CO_3, 0.4% SHMP), but also just for 0.1% NaOH and 1% Na_2SiO_3. After reaching the minimal value the viscosity remains practically the same, just increases slightly with the content of additives. However, anomalous viscosity behavior is observed during addition of NaOH, when a subsequent addition of electrolyte results in a significant increase of viscosity. The resulting viscosity of kaolin suspension with addition of 3% NaOH is even higher than the initial one.

As seen in Figure 3c, the flow index *n* follows viscosity changes caused by additives and its value is ranging between 0.1 (shear thinning suspensions with high viscosity) and 1 (Newtonian suspensions with low and shear rate independent viscosity). Complex rheological behavior is observed for the kaolin suspensions with addition of NaOH, for which strong shear thinning behavior with the flow index $n \approx 0.2$ is detected over two distinct ranges of small and high concentrations of NaOH.

Additional information on measured pH values of suspensions is given in Figure 3d. This parameter vary from neutral ($pH \approx 7$ for SHMP suspensions) to strongly alkalic ($pH \approx 13$ for NaOH suspensions) values. With respect to the isoelectric point of kaolin suspensions located at $pH \approx 3$ [5, 6, 8], all tested suspensions should exhibit high negative zeta-potential values.

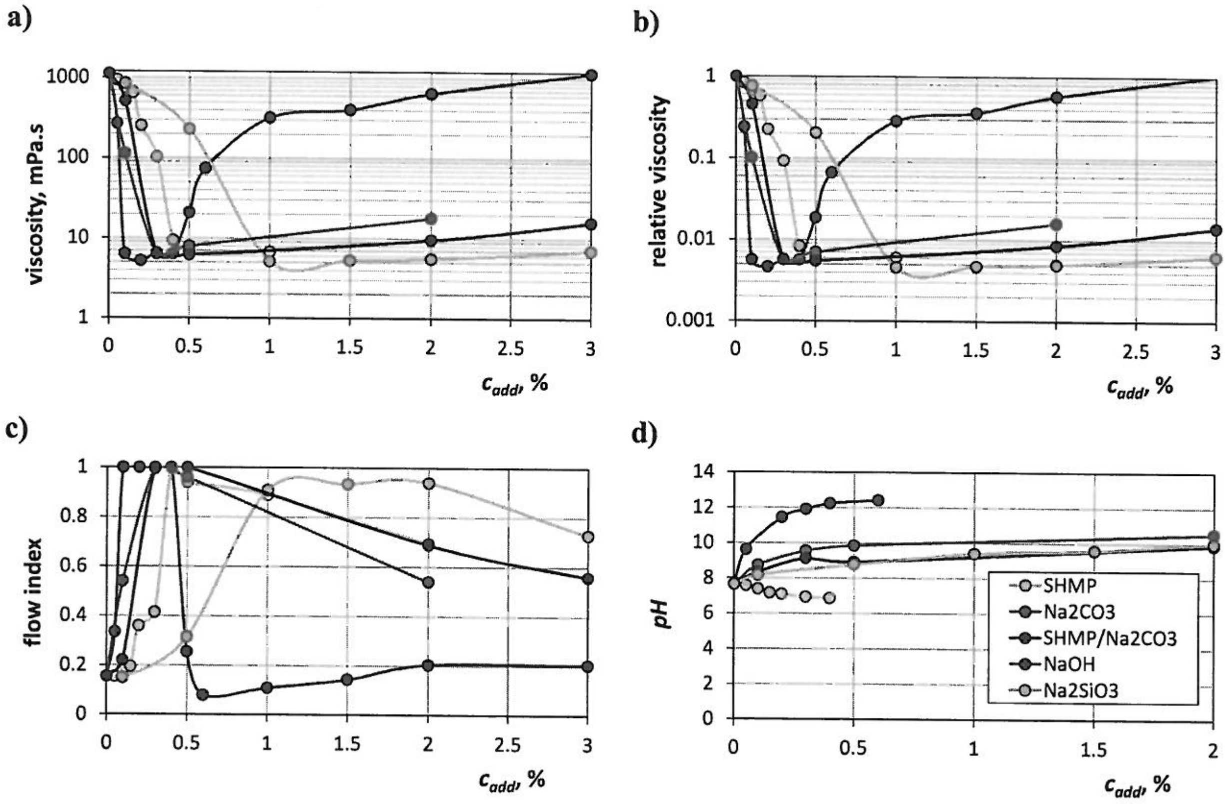


Figure 3: Variation of viscosity (a), relative viscosity (b), flow index (c), and pH (d) of 40% kaolin suspensions in dependence on the concentration of inorganic electrolytes.

(Viscosity is calculated from the shear stress at the reference shear rate100 s^{-1})

Organic polyelectrolyte additives

The results of similar measurements carried out with an organic additive (the sodium salt of carboxymethylcelulose, CMC) having three different molecular weights (M = 90000, 250000 and 700000 g/mol) are shown in Figure 4. The effect of polyelectrolyte molecular weights is obvious. The high-molecular CMC cannot be used as a deflocculant agent. A small decrease of viscosity is observed only for small concentrations of this additive, but already at CMC concentration about 0.3% wt. the viscosity of suspension starts to increase again due to the effect of an added polymer. Both medium and low molecular CMC decrease the viscosity of kaolin suspensions, but low molecular CMC is more effective (80% against 95% viscosity reduction reached at the optimal additive concentrations 0.5% and 0.8%, respectively). The viscosity of suspensions deflocculated with low molecular CMC is also less sensitive to an excessive addition of polymer. The value of flow index increases gradually with a decrease of suspension viscosity (from 0.2 to 0.8), but no one from prepared suspensions behaves as the Newtonian liquid. Values of pH are close to 8, thus not differing from pH of the primary 40% kaolin suspension.

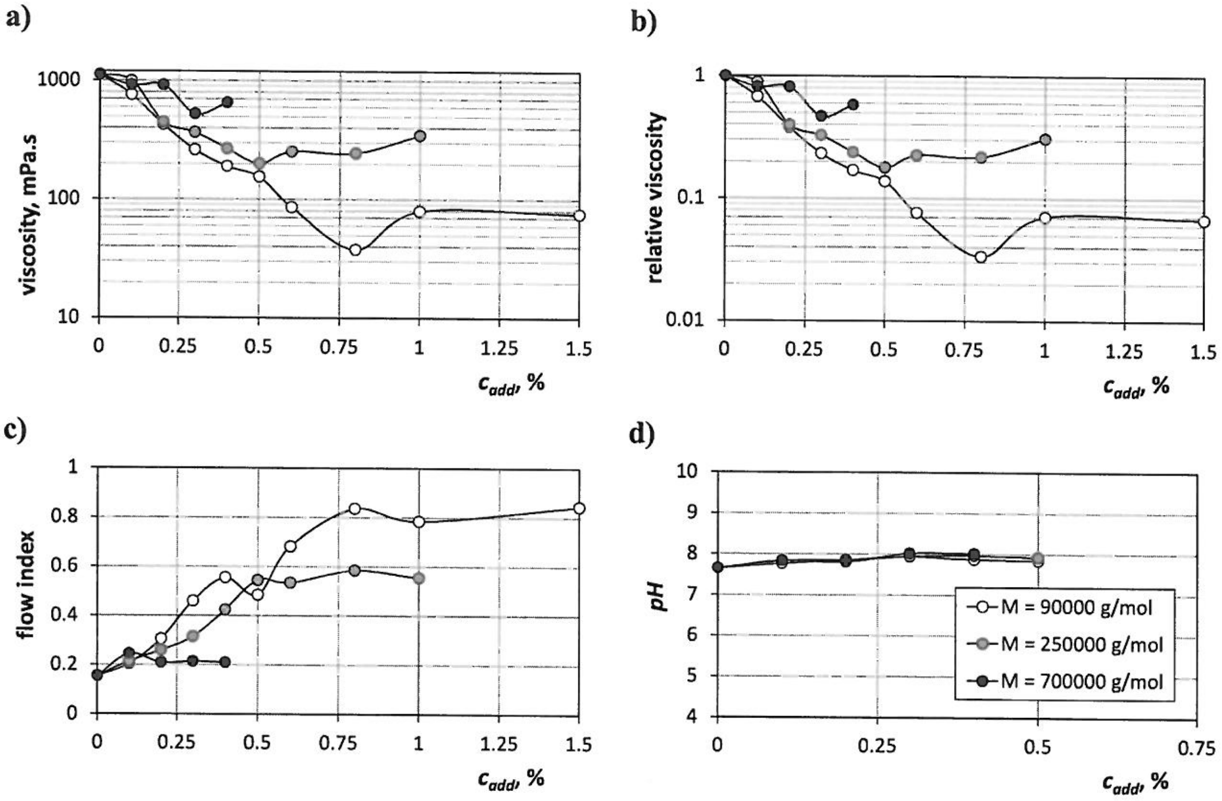


Figure 4: Variation of viscosity (a), relative viscosity (b), flow index (c), and *pH* (d) of 40% kaolin suspensions in dependence on the concentration of CMC polyelectrolytes.

(Viscosity is calculated from the shear stress at the reference shear rate100 s^{-1})

3.2. Stability of suspensions

The stability against sedimentation is a really important parameter of colloidal suspensions. Therefore the sedimentation stability has been also observed and its subjective classification is given in Table 3. The observed stability of suspensions exhibits large differences in dependence on both, the used additive and its concentration, e.g. see a poor stability of Na_2SiO_3 suspensions and, on the contrary, a good stability of NaOH suspensions. Concerning inorganic additives, with an exception of NaOH, they produce not very stable deflocculated kaolin suspensions with a certain tendency to sedimentation. On the other side, the sedimentation stability of suspensions deflocculated by CMC polyelectrolytes is very good, even for suspensions having low viscosities.

3.3. Evaluation of deflocculants

Concerning used inorganic electrolytes, Na_2SiO_3 can be evaluated as the worst deffloculation agent. In comparison with other electrolytes, the highest additive concentration (1%) is needed to reduce the suspension viscosity to its minimum value. Also its stability against sedimentation is the worst (see Table 3). On the other hand, NaOH exhibits the lowest optimal concentration (0.1%) and the most stable suspensions. But in this case some care should be taken, because an excessive addition of the electrolyte results in a re-increase of suspension viscosity at higher concentrations. Thus to avoid this undesirable effect, another two electrolytes (SHMP, Na_2CO_3, or their mixture) can be considered. For these electrolytes the optimal concentration of additives is practically the same (about 0.3%), just the suspensions containing SHMP are little more stable. However, from an ecological point of view, the application of Na_2CO_3 deflocculants can be recommended as more environment-friendly. All prepared suspensions containing inorganic electrolytes are found to be less stable against sedimentation then primary kaolin suspensions.

Table 3: Classification of the sedimentation stability of kaolin suspensions based on a subjective evaluation: a) inorganic additives, b) organic additives

(The highest score 5 corresponds to stable suspensions and the lowest score 1 to unstable, quickly settling suspensions. The gray fields mark the stability score obtained for the optimal additive concentrations).

a)

concentration % / additive	0	0.05	0.1	0.15	0.2	0.3	0.4	0.5	0.6	1	1.5	2	3
SHMP	5	4	3	3	3	3	3	3		2	2	2	2
NaOH	5	5	3		3	3	4	5	5	5	5	5	5
Na_2SiO_3	5		3					3		1	1	1	1
Na_2CO_3	5		3			2		2				2	
SHMP:Na_2CO_3	5		3			2		2				2	

b)

concentration % / additive	0	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1	1.5
CMC M = 90000 g/mol	5	4	3	3	3	3	5	5	5	5
CMC M = 250000 g/mol	5	4	4	5	5	5	5	5	3	
CMC M = 700000 g/mol	5	5	4	4	5	5				

If we compare our results with that obtained by Rossington et al. [14] in their experimental study using similar electrolytes, surprisingly large discrepancies in the additive evaluation are observed. Contrary to our findings, Na_2SiO_3 is classified as a very good deflocculant, whereas Na_2CO_3 (although recommended by kaolin producers) as an additive just with a mediocre ability to reduce viscosity of kaolin suspensions. A probable explanation for such different results can consist in different compositions and qualities of used kaolin minerals (e.g. the specific surface area 26.9 and 18.6 m^2/g is stated for Florida (USA) and Sedlec (Czech Republic) deposits, respectively).

From the organic polyelectrolytes, low molecular CMC (M = 90000 g/mol) is found to be a good deffloculant. It is able to reduce significantly the viscosity of kaolin suspensions (up to the level of 10% of the initial value) and create very stable suspensions. The optimal concentration needed to reach the minimum viscosity is little bit higher than for inorganic electrolytes (about 0.8%). Medium molecular (M = 250000 g/mol) is found to be a less effective deffloculant. The application of high molecular CMC (M = 700000 g/mol) bring about the rise of viscosity already at relatively small CMC concentrations. From the viscosity results obtained for three different CMC polyelectrolytes can be deduced the existence of a molecular weight which will be optimal for using this substance as a deffloculant agent. All the suspensions prepared by using CMC polyelectrolytes are very stable.

4. Conclusions

The deflocculation of aqueous kaolin suspension by using various inorganic and organic electrolytes is evaluated from the results of viscosity measurements and suspension stability observations. The relative mass content of additives in respect to kaolin is first confirmed to be the most suitable choice of concentration scaling. The optimal additive concentration expressed in this way is thus independent of the content of kaolin in a primary suspension. All tested electrolytes with an exception of high-molecular CMC are then found to reduce significantly the viscosity of primary kaolin suspensions. Inorganic electrolytes are found to be more effective in such a viscosity reduction, but on the other hand low-molecular organic CMC additives produce more stable resulting suspensions.

Acknowledgement

The support by Czech Science Foundation GACR through the contract P101/12/0585 is gratefully acknowledged.

5. References

[1] Brindley G.W., Robinson K.: The structure of kaolinite, 1946, Mineral. Mag. 27, 242-253

[2] Gupta V., Hampton M.A., Nguyen A.V., Miller J.D.: Crystal lattice imaging of the silica and alumina faces of kaolinite using atomic force microscopy, 2010, Journal of Colloid and Interface Science 352, 75-80

[3] Johnson S.B., Franks G.V., Scales P.J., Boger D.V., Healy T.W.: Surface chemistry - rheology relationship in concentrated mineral suspensions, 2000, Int. J. Miner. Process. 58, 267-304

[4] Zhou Z., Scales P.J., Boger D.V.: Chemical and physical control of the rheology of concentrated metal oxide suspensions, 2001, Chemical Engineering Science 56, 2901-2920

[5] Hu Y., Liu X.: Chemical composition and surface property of kaolins, 2003, Minerals Engineering 16, 1279-1284

[6] Alkan M., Demirbas O., Dogan M.: Electrokinetic properties of kaolinite in mono- and multivalent electrolyte solutions, 2005, Microporous and Mesoporous Materials 83, 51-59

[7] Cunha F.O., Torem M.L., D'Abreu J.C. : On the fundamentals of kaolin rheology applied to the paper industry, 2006, Minerals Engineering 19, 1462-1464

[8] Teh E.J., Leong Y.K., Liu Y., Fourie A.B., Fahey M.: Differences in the rheology and surface chemistry of kaolin clay slurries: The source of the variations, 2009, Chemical Engineering Science 64, 3817-3825

[9] Addai-Mensah J., Ralston J.: Investigation of the role of interfacial chemistry on particle interactions, sedimentation and electroosmotic dewatering of model kaolinite dispersions, 2005, Powder Technology 160, 35-39

[10] Gupta V., Miller J.D.: Surface force measurements at the basal planes of ordered kaolinite particles, 2010, Journal of Colloid and Interface Science 344, 362-371

[11] Gupta V., Hampton M.A., Stokes J.R., Nguyen A.V., Miller J.D.: Particle interactions in kaolinite suspensions and corresponding aggregate structures, 2011, Journal of Colloid and

Interface Science 359, 95-103

[12] Nuntiya A., Prasanphan S.: The rheological behavior of kaolin suspensions, 2006, Chiang Mai J. Sci. 33, 271-281

[13] Garrido L.B., Volzone C., Torres Sanchez R.M.: OH-Al polymers and HMP adsorption on kaolinite: experimental conditions and viscosity of deflocculated suspensions, 1997, Colloids and Surfaces A: Physicochem. Eng. Aspects 121, 163-171

[14] Rossington K.R., Senapati U., Carty W.M.: A Critical Evaluation of Dispersants for Clay-Based Systems, 1998, Ceram. Eng. Sci. Proc. 19, 77-86

[15] Sjoberg M., Bergstrom L., Larsson A., Sjostrom E.: The effect of polymer and surfactant adsorption on the colloidal stability and rheology of kaolin dispersions, 1999, Colloids and Surfaces A: Physicochemical and Engineering Aspects 159, 197-208

[16] Penner D., Lagaly G.: Influence of anions on the rheological properties of clay mineral dispersions, 2001, Applied Clay Science 19, 131-142

[17] Marco P., Labanda J., Llorens J.: The effects of some polyelectrolyte chemical compositions on the rheological behaviour of kaolin suspensions, 2004, Powder Technology 148, 43-47

[18] Andreola F., Castellini E., Ferreira J.M.F., Olhero S., Romagnoli M.: Effect of sodium hexametaphosphate and ageing on the rheological bahaviour of kaolin dispersions, 2006, Applied Clay Science 31, 56-64

[19] Tombasz E., Szekeres M.: Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite, 2006, Applied Clay Science 34, 105-124