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Flocculation abilities of industrial cationic starches

RAPID COMMUNICATION

Summary — Flocculation abilities of five industrial cationic starches were investigated. The research was performed on suspensions of kaolin, bentonite and natural clay. Time dependence of turbidity was determined using the nephelometric method. It was found that modified cationic starches are quite good flocculants for aluminosilicate suspensions, especially for natural clay. The highest flocculation efficiency showed the potato starch BORCET SZ 2000 characterized with the highest substitution degree.
Keywords: cationic starch, suspension turbidity, kaolin, bentonite, natural clay.

ZDOLNOŚCI FLOKULACYJNE PRZEMYSŁOWYCH SKROBI KATIONOWYCH
Streszczenie — Określono właściwości flokulacyjne skrobi kationowych różniących się pochodzeniem oraz stopniem podstawienia (tabela 1). Badania przeprowadzono w zawiesinach glinokrzemianów: kaolinu, bentonitu oraz naturalnej gliny. Zmiany zmętnienia w czasie oznaczano metodą nefelometryczną. Stwierdzono, że zmodyfikowane skrobie kationowe mogą pełnić rolę flokulantów przyspieszających sedymentację glinokrzemianów, a w szczególności naturalnej gliny. Klarowanie zawiesiny zachodzi tym efektywniej im większy jest stopień podstawienia skrobi (rys. 1). Najlepszą efektywność zaobserwowano stosując BORCET SZ 2000. W porównaniu z flokulantami syntetycznymi, skrobie kationowe zapewniają nieco mniejszą wydajność procesu (tabela 2), jednak posiadają wiele zalet, takich jak: nietoksyczność, zdolność do biodegradacji oraz niska cena.
Słowa kluczowe: skrobia kationowa, zmętnienie zawiesiny, kaolin, bentonit, glina naturalna.

Water-soluble polymers are known as effective aids for flocculation of colloidal particles and are applied for water clarification, sludge dewatering, pulp sedimentation *etc*. The most widely used flocculant is polyacrylamide [1] due to its good water solubility, high molecular weight and possibility to create both anionic and cationic forms [2, 3]. Unfortunately, polyacrylamides are not biodegradable. That is why searching for natural-based flocculants appears to be a very important task. Among alternative flocculants one can find polysaccharides grafted by polyacrylamide [4, 5] as well as those substituted with various functional groups [6, 7]. Starch derivatives proved to be effective flocculants in suspensions of both low [7] and high [6] concentrations. In concentrated kaolin suspension the flocculation ability of cationic starch has been found to be dependent on solubility and substitution degree of the starch used [6]. Flocculation abilities of cationic starches in that system have been found to be worse than that of cationic polyacrylamide because of low molecular mass of the polysaccharide polymers. Investigations carried out on modified starches towards low-concentrated suspensions of silica [7] and kaolin [4] have shown that flocculation performance of modified polysaccharide depends on length of grafted chains as well. In this case [7] cationized starch appeared to be more effective flocculant than starch grafted with polyacrylamide and a variety of commercial flocculants.

In this work five commercially available cationized starches of various origin and substitution degree have been examined. The examined starches are destined for paper production and wastewater treatment but there is no detailed information concerning their dosage for flocculation of aluminosilicate minerals. For that reason quantitative studies of flocculation abilities of modified starches have been performed on suspensions of clay minerals of various kinds.

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EXPERIMENTAL

Materials

Cationic starches of BORCET series used for experiments have been produced by the Bochem chemical company (Pionki, Poland). Cationization of the starches has been performed by the producer with 2,3-epoxypropyltrimethylammonium chloride according to the standard method described in European patent [8]. The modified starches have been signed according to their origin (potato — SZ, wheat — SP) and substitution degree values (*SD*), as it has been shown in Table 1.

T a b l e 1. Characteristics of cationic starches of BORCET series used as flocculants (according to the producer)

Type of starch	*SD*	Solubility, %
BORCET SZ 2000	0.180—0.200	20
BORCET SZ 1500	0.135—0.150	24
BORCET SP 1500	0.135—0.150	84
BORCET SP 400R	0.035—0.040	32
BORCET SP 150R	0.0135—0.015	23

The commercially available nonionic polyacrylamide Rokrysol WF1 (Rokita, Poland) and cationic polyacrylamide Optifloc C496 (Kemipol, Poland) have been used as reference flocculants. Model suspensions of aluminosilicates were prepared using commercial kaolin KOM (SURMIN-KAOLIN, Poland), reagent grade bentonite (Aldrich) and natural clay from Kujawy (North-West Poland). The natural clay corresponds to the Poznań loam type and contains very small quantities of organic matter as well as non-clay minerals [9].

Suspension preparation and testing

Suspensions of clays of 4 g/dm^3 concentration have been prepared at room temperature, just before the test. Each time 1 g of dried aluminosilicate has been stirred with 200 cm^3 of distilled water for 10 min; then suspensions were poured into test cylinders, added with a dose of fresh-prepared flocculant solution of 50 or 100 mg/dm^3, completed with distilled water up to the volume of 250 cm^3 and mixed by turning the cylinders for 5 times by 180°. Test samples were periodically collected from the top layer of the sedimentation cylinders. Turbidity of the samples was determined with the nephelometric method using spectrofotometer type Spekol 11 with wave length λ = 555 nm. The results have been presented as a nephelometer signal expressed in mV, which increases proportionally to the increase of suspension turbidity.

RESULTS AND DISCUSSION

Kinetic curves of sedimentation of the aluminosilicate suspensions have been presented in Figure 1, as dependence of nephelometric signals (proportional to turbidity of samples) in time.

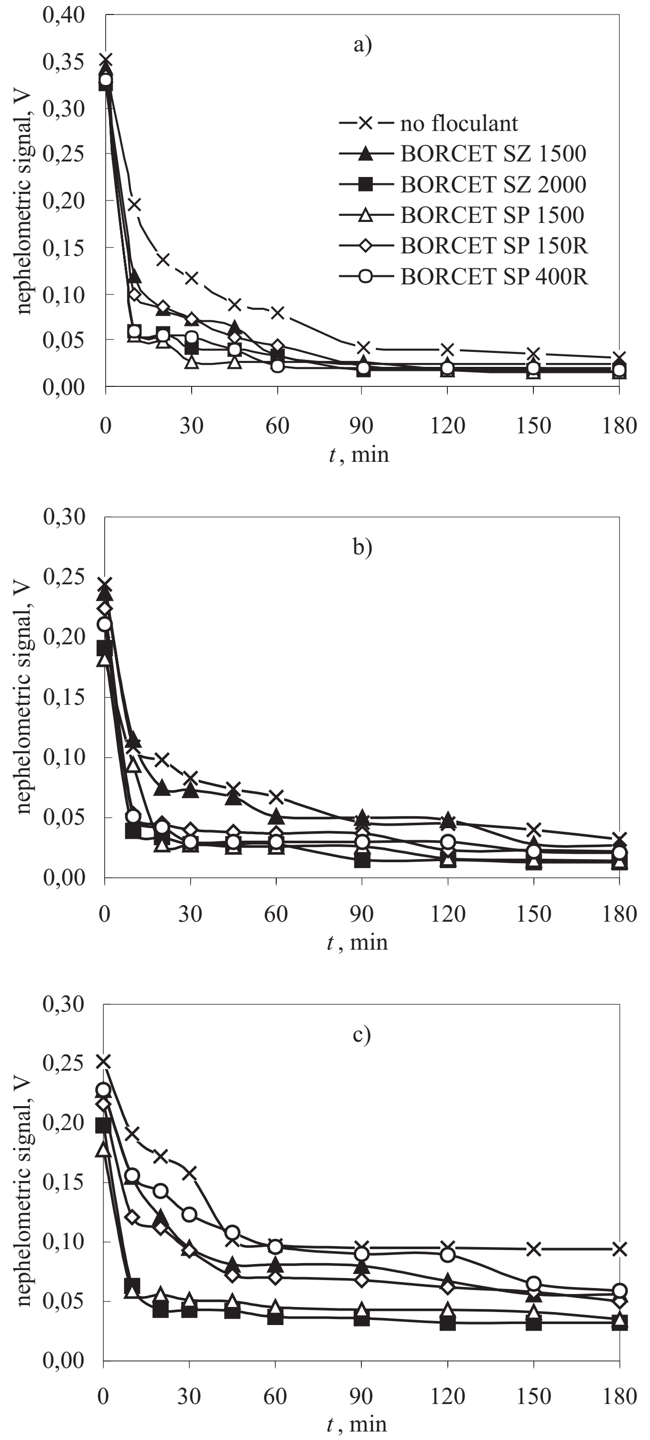

Fig. 1. Changes of nephelometric signal in time for suspensions of 4 g/dm³ concentration of kaolin (a), bentonite (b) and natural clay (c) without flocculant and in the presence of various flocculants with dose of 10 mg/dm³

Suspensions of kaolin, bentonite and natural clay have various stability (compare Figs. 1a—1c). The considerable turbidity of the natural clay suspension registered after a long period of sedimentation (Fig. 1c) indicates a high concentration of colloidal particles. Addition of cationic starches considerably accelerates this suspension sedimentation (Fig. 1c). For all the examined systems the flocculation effect of cationic starches was the most visible in the first 60 min of measurements (Figs. 1a—1c). Reduction in the turbidity after 180 min of measurements was 22—48 % for kaolin, 15—59 % for bentonite and 37—66 % for natural clay suspensions. The highest flocculation efficiency showed potato starch BORCET SZ 2000 and wheat starch BORCET SP 1500 which are characterized with the highest values of *SD*. It is obvious that relatively high positive charge on a macromolecule, corresponding to high value of *SD*, is needed to neutralize negative charge of clay particles facilitating their agglomeration into larger aggregates. One more important feature of cationic starches is their solubility. BORCET SP 1500 starch has better solubility and better flocculation efficiency in comparison with BORCET SZ 1500 characterized by the same *SD* value (Fig. 1, Table 1). Detailed description of flocculation ability of the most effective cationic starch BORCET SZ 2000 has been given in Table 2.

T a b l e 2. Nephelometric signal for kaolin suspension with initial concentration of 4 g/dm^3 in the presence of natural and synthetic flocculants

Type of flocculant	Flocculant concentration mg/dm^3	Nephelometer signal, mV	
		after 20 min	after 90 min
none	—	183	78
BORCET SZ 2000	1	99	42
BORCET SZ 2000	2	86	51
BORCET SZ 2000	4	40	36
BORCET SZ 2000	6	38	27
BORCET SZ 2000	8	24	33
BORCET SZ 2000	10	20	30
Optifloc C496	1	70	55
Rokrysol WFl	1	51	43

As one can see, in the first stage of the flocculation process (*i.e.* up to 20 min) cationic starch is less effective than the reference polyacrylamide flocculants Rokrysol WF1 and Optifloc C496. Flocculation efficiency of cationic starch can be improved by increase of its quality. It has been noted that cationic starch (BORCET SZ 2000) applied in amount higher then 2 mg/dm^3 both after 20 min and after 90 min gives similar results as polyacrylamide flocculants used in doses of 1 mg/dm^3 (Table 2). Extension of flocculation time levels the flocculants efficiencies. Above observations are important from the economical point of view. The studied starch polymers are over a half cheaper than the synthetic ones and have environmental advantages such as non-toxicity and biodegradability. One can conclude that cationic starches of BORCET series are promising flocculants for water clarification.

CONCLUSIONS

The studied cationic starches effectively accelerate sedimentation of aluminosilicate suspensions. Flocculation ability of both potato and wheat starches increases with their substitution degree. Applying cationic starches requires doses 2 to 4 times higher as compared to polyacrylamide flocculants to reach comparable sedimentation ability.

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