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DEFLOCCULATION OF CLAY SUSPENSIONS USING SODIUM POLYACRYLATES

P. Jedlicka

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16. Abstract Rheological properties of elutriated kaolin suspensions deflocculated by Na polyacrylate (DAC 3 and DAC 4) were studied and compared to those deflocculated by the conventional Na ₂ CO ₃ water and glass and imported Dispex N40. The deflocculating effect of Na polyacrylate was comparable to that of Dispex N40. The optimum amounts of Na polyacrylate were determined for suspensions based on 5-type kaolin. The Na polyacrylate can be successfully used for decreasing the water content of ceramic slips for casting and spray drying.			
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DEFLOCCULATION OF CLAY SUSPENSIONS USING SODIUM POLYACRYLATES

Eng. Pavel Jedlicka, CSc
Research Institute of Fine Ceramics, Karlovy Vary-Brezova, Czech.

The deflocculation effects of two samples of Na polyacrylates, prepared in the Sokolov Chemical Plants, were compared with those of the imported preparation Dispex N 40. The tests were carried out on elutriated kaolins from several localities in the CSR [Czech Socialist Republic]. The results of measurements indicate that the effects of domestic deflocculation agents are comparable to those of Dispex N 40.

Introduction

Preparation of highly concentrated clay suspensions with rheological properties compatible with a given processing technology is unthinkable without the use of deflocculation agents. The requirements on effectiveness of these agents keep increasing with introduction of more advanced techniques into ceramic operations. Thus, e.g., in processing of ceramic suspensions by spray drying, the concentration of solid phase in suspension distinctly influences the economy of the entire process. The high demands on deflocculation agents apply also to production by casting - particularly in the case of sanitary ceramics where introduction of line production considerably increases demands on the technological properties of casting suspensions. /65*

As a rule, specialized producers worldwide offer an entire assortment of deflocculation agents suitable for certain specific applications - ceramic casting suspensions, spray drying, heat-resistant substances, oxygen ceramics, etc. Among the best known producers is the Zschimmer-Schwarz Company (FRG) which offers a wide assortment of preparations on the basis of huminates, silicates,

* Numbers in the margin indicate pagination in the foreign text.

polyphosphates and synthetic polymers suited for deflocculation of clayey and nonargillaceous materials. Deflocculation agents on the basis of polyacrylates (Dispex N 40 and Dispex A 40) are produced by the Allied-Colloids Company (England), a series of preparations under the trade name Darvan is turned out by the Vanderbilt Company (USA), etc.

On the other hand, the assortment of domestically produced deflocculation agents is relatively limited. In addition to the traditional soda and water glass the market offers one type of huminate (Huminan F) supplied by the J. Fucik Mines in Bilina and several preparations known under the trade name of Kerkotany supplied by the A. Zapotocky Plants in Jaromer. Even though, e.g., Kerkotany are a very effective agent, their application in certain cases is not without problems (sanitary ceramics). Detrimental effects are often constituted by the fact that both the huminates and Kerkotany cause intensive pigmentation of the skin that comes in contact with the agents.

Deflocculation effects are found also in some other industrially produced substances (hexametaphosphate, pyrophosphate, Kortamol NNO, Uniform S, Silifix, Efektan S13, etc.). In view of the fact that these substances are for their major part designed for entirely different applications, their deflocculation effects tend to be considerably unstable.

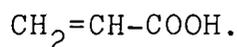
Studies published in literature indicate that very favorable properties are shown by deflocculation agents on the basis of polyacrylates [1-4]. Best known in our country are primarily the preparations of the English company Allied-Colloids, Dispex N 40 and Dispex A 40. In addition to high effectiveness and easy dosing, the most valued attribute of these deflocculation agents is primarily their beneficial effect on the properties of casting slip [2].

The CSSR [Czechoslovak Socialist Republic] producer of the most varied industrially used agents on the basis of polyacrylates are the Chemical Plants in Sokolov. Their production is oriented primarily toward acrylate dispersions for the construction industry, sizing media for the textile industry, polymers used in the leather industry, in production of adhesives, etc. However, none of the routinely produced agents can be used directly for deflocculation of clayey suspensions. Efforts toward expanding the assortment of domestic deflocculation agents and a simultaneous replacement of eventual importation of Dispexes from abroad led to assigning a contract for a technical task the objective of which was to propose a procedure for production of a polymer with properties analogous to those of Dispex N 40. In the course of solving of this task two alternative procedures were worked out for polymerization of acrylic acid in an aqueous and a nonaqueous medium. The resultant product was obtained in both cases by neutralization of the polymerized acid by caustic soda lye. The thus prepared deflocculation agents were designated as DAC 3 and DAC 4. /66

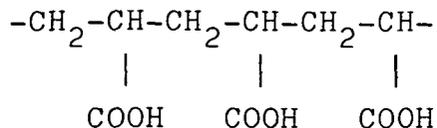
The objective of this study is to provide information regarding the results obtained in verification of the deflocculation efficiency of sodium polyacrylates DAC 3 and DAC 4 with several types of elutriated kaolins from the CSR [Czech Socialist Republic].

Polyacrylates and Their Effects

The initial substance for production of polyacrylates is acrylic acid



Depending on the polymerization conditions, acrylic acid is capable of forming chained models of polyacrylic acid with a varying number of monomer units



The deflocculation agent used in most cases is sodium salt, in some cases also ammonium salt of polyacrylic acid. The deflocculation effects of salts of polyacrylic acid depend to a considerable extent on the length of the polymer chain. An increasing number of monomer units in the polymer entirely changes the nature of their effects on clay dispersions. Polymers with $5 \cdot 10^1$ - $5 \cdot 10^2$ monomer units do produce deflocculation effects, with the number of monomer units on the order of $5 \cdot 10^3$ the polymers act as plasticizing agents and simultaneously improve the mechanical strength of the clay substance after drying. Polymers with more than $5 \cdot 10^5$ monomer units are capable of flocculating clay dispersions [3-4]. Figure 1 shows in the form of a diagram the effects of the chain length of sodium polyacrylate on the progress of the deflocculation dependence of kaolinic clay.

Alston [4] states that the optimum deflocculation effects are achieved with a polymer having 50 monomer units of acrylic acid. An important role is played, according to this author, also by distribution of molecular weights (or chain lengths of individual molecules) in the polymer (Figure 2).

In Figure 2 the polymer A with a narrower distribution of molecular weights will show a higher deflocculation efficiency than polymer B which contains a wide spectrum of molecules of varying length.

The deflocculation effects of polyacrylates are ostensibly connected with their distinctive property of adsorbing themselves on the surface of mineral particles. Joyce and Worrall [5] and other researchers [6] pointed out that it involves a physical

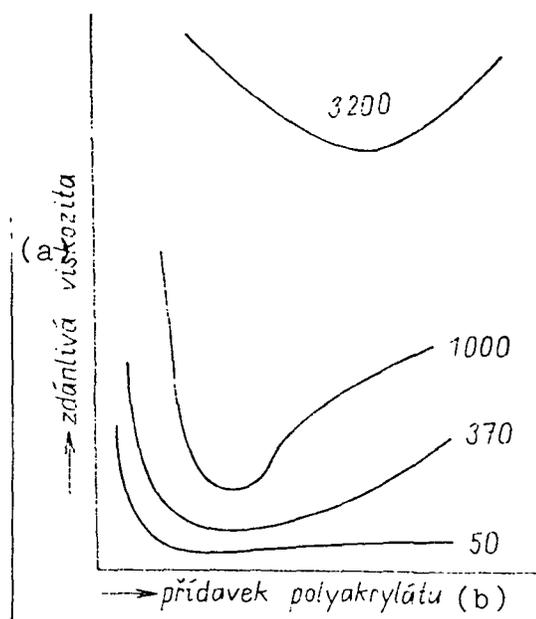


Figure 1. Effects of polyacrylate chain length, expressed by the number of monomer units, on the progress of the deflocculation dependency of a clay suspension (according to [4]).

Key: (a) Apparent viscosity
(b) Polymer addition

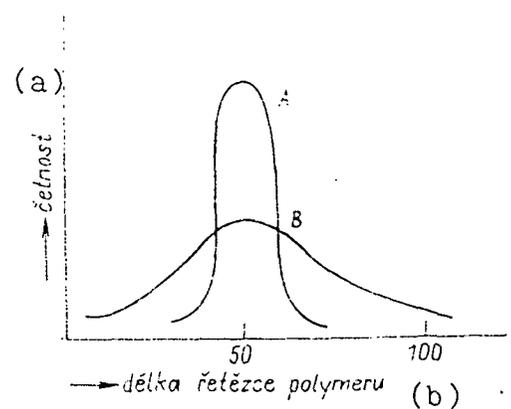


Figure 2. Two varying molecular weight distributions of acrylic acid polymers (according to [4]).

Key: (a) Frequency; (b) Polymer chain length

adsorptions of polymers. Particles covered by adsorbed polyelectrolyte are surrounded by cations and the thus formed electric double layer prevents coagulation as a result of effective repelling forces.

Characteristics of Deflocculation Agents

Verification of the effectiveness of deflocculation agents DAC 3 and DAC 4, produced by the Sokolov Chemical Plants, was carried out through comparison with the foreign preparation Dispex N 40. The tests also included both the conventional deflocculation agents - soda and water glass. Selected characteristic properties of the domestic agents DAC 3 and DAC 4 and those of the foreign preparation Dispex N 40 are shown in Table 1.

Materials and Experimental Method

The effectiveness of the compared deflocculation agents was estimated from the progress of dependency of apparent viscosity of the deflocculated suspension of 5 various samples of elutriated kaolins on water contents in the suspension. Addition

TABLE 1. CHARACTERISTIC PROPERTIES
OF THE TESTED POLYACRYLATES

A	B	C	D	E	F
Označení	Příprava a prostředí	Sůl kyseliny	Molekulová hmotnost	pH	Konz. Na polyakrylátu
Disper N10	G	Na	< 5000	8,5	10 %
DAC 3	H	Na	< 7000	9,2	30 %
DAC 1	H	Na	< 7500	8,6	30 %

Key: A. Designation
 B. Preparation medium
 C. Salt of polyacrylic acid
 D. Molecular weight
 E. pH
 F. Concentration of Na polyacrylate
 G. Nonaqueous
 H. Aqueous

of each deflocculation agent was selected according to the minimum /67 on the dependency curve of apparent viscosity on addition of the given agent (the so-called optimum liquefaction).

The clay materials of which the effectiveness of the compared deflocculation agents was tested are specified in Table 2.

TABLE 2. SELECTED SAMPLES OF ELUTRIATED KAOLINS

Raw Material	Abbrev.	Sampling	Producer
Kaolin Sedlec Ia sample # 1	KS 1	Oct 1981	Kaolin Plants, nat'l. enterpr. Sedlec (KSNP-Sedlec)
Kaolin Sedlec Ia sample # 2	KS 2	Mar 1978	KSNP-Sedlec
Kaolin Kaznejov Sp-ex F	Sp-ex	Feb 1980	West Bohemian Kaolin Plants Horni Briza
Kaolin Chlumcany DS-ex	DS-ex	May 1979	Chlumcany Kaolin Plants Chlumcany
Kaolin Podborany	L/IV	Jun 1981	KSNP-Sedlec

The selected raw materials represent significant kaolin extraction areas in the CSR [Czech Socialist Republic]. In comparison to sample 1, the kaolin Sedlec sample # 2 represents a raw material that is harder to deflocculate by conventional agents. The subsequent tables list some of the properties of selected samples of raw materials. Table 3 lists chemical analyses and Table 5 summarized some of the basic technological properties.

TABLE 3. RESULTS OF CHEMICAL ANALYSIS OF ELUTRIATED KAOLINS

A	Oxidant stability	Zr	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O
KZ 1		13,21	47,61	36,69	0,93	0,21	0,17	0,21	0,96	0,04
KZ 2		13,25	46,72	37,19	0,91	0,23	0,30	0,22	1,17	0,07
Sp-X		12,91	49,69	35,16	0,79	0,81	0,23	0,18	1,15	0,13
Ds-X		12,89	48,11	36,34	0,71	0,65	0,09	0,18	0,87	0,19
LV		12,98	51,91	33,51	0,89	0,32	0,56	0,59	0,93	0,14

Key: A. Designation of raw material

[Commas in tabulated material are equivalent to decimal points]

Measurement of the rheological properties of deflocculated kaolin suspensions was done by means of the rotary cylindrical viscosimeter Rheotest 2 (Medingen Werke - GDR) at a temperature of 24°C. Use was made of the system casing-cylinder designated as S-S₁. For each suspension was determined the dependency of tangential stress on the velocity of shear deformation $\tau = \tau(D)$ in a range of $D = 1.5 \text{ -- } 656 \text{ s}^{-1}$ and the corresponding apparent viscosities were computed according to the relation

$$\eta_2 = \frac{\alpha k}{D}, \text{ where}$$

α = reading from instrument scale,

k = calibration constant of the instrument,

D = velocity of shear deformation.

For additional comparisons of deflocculated substances was selected the apparent viscosity determined at $D = 72.9 \text{ s}^{-1}$.

TABLE 4. SELECTED TECHNOLOGICAL PROPERTIES OF ELUTRIATED KAOLINS

A	Označení sample	T ₀ (sek)	M (Pa)	F (min)	P ₀ (MPa)	P _m (MPa)
KS 1		38,5	18,1	58	2,53	1,26
KS 2		296	35,2	85	3,18	1,39
Spolux		248	2,7	11	0,77	0,47
DeSax		7	6,2	23	2,18	1,15
UV		7	112	92	6,28	2,81

Key: A. Raw material designation; B. (sec)

[Commas in tabulated material are equivalent to decimal points]

- T₀ - Flow-through time for kaolin suspension deflocculated by 0.15% soda at 45% water contents in the suspension. Measured by a standard flow-through viscosimeter immediately after filling.
- M - Extrapolated limit of flow of incompletely deflocculated suspension with 60% of water.
- F - Time needed for filtration of incompletely deflocculated suspension with 60% of water at a pressure of 0.8 MPa and filtering area of 7.7 cm².
- P₀ - Bending strength after drying at 105°C (drawn particles of 10 mm diameter).
- P_m - Bending strength after drying at 105°C and subsequent 24 hour storage in an atmosphere with relative humidity of 52% (the so-called handling strength).

Suspensions were prepared by mixing weighed amounts of the crushed raw material in distilled water into which was added the requisite amount of the deflocculation agent in solution by pipetting. The mentioned additions of deflocculation agents are related to kaolin solids and recomputed to a 100% agent. The suspensions were mixed by a laboratory mixer (about 600 rpm) for 3 hours and then left to rest for 24 hours. Prior to measurement the mixture was agitated for 15 minutes and a sample was taken for determining the precise contents of water in the suspension.

Experimental Results

Determination was made of the amounts of deflocculation agent additions required for attaining a minimum of apparent viscosity

at a constant water content in the suspension. Figure 3 provides an example of plotting the dependence of the apparent viscosity of suspension in kaolin KS-1 on addition of soda and Dispex N 40 with a 45% content of water in the suspension.

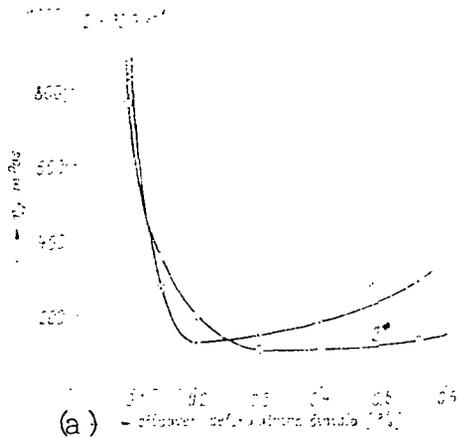


Figure 3 indicates that the minimum of apparent viscosity in the suspension of kaolin KS-1 was achieved by addition of 0.20% of soda and/or 0.30% of Dispex N 40, whereby the apparent viscosity of the suspension was 118 and/or 103 mPas. Additional results are outlined in Table 5.

Figure 3. Dependence of the apparent viscosity of a suspension of kaolin KS-1 on addition of soda (1) and Dispex N 40 (2). Contents of water in the suspension = 45%.

Key: (a) Addition of deflocculant (%)

TABLE 5. OPTIMUM ADDITIONS OF DEFLOCCULATION AGENTS AND THE ATTAINED MINIMUM APPARENT VISCOSITY OF SUSPENSIONS

A Označení suroviny	B Obsah vody %	C Přídavek deflokulačního činidla Zvláštní viskozita suspenze					η _a mPas
		soda %	Dispex %	Dispex DAC 3	Dispex DAC 1		
KS 1	45	0,20 118	0,08 135	0,30 103	0,30 122	0,30 95	
KS 2	45	0,25 607	0,10 270	0,35 111	0,35 140	0,35 156	
Spex	40	0,25 1739	0,06 34	0,15 51	0,20 85	0,20 32	
Dispex	40	0,18 1650	0,08 129	0,15 28	0,10 39	0,10 64	
IV	65	0,15 270	0,15 204	0,20 101	0,15 70	0,15 130	

(see following page for key to Table 5)

Table 5 continued

Key: A. Raw material designation
B. Water contents in %
C. Addition of deflocculent
Apparent viscosity of suspension
D. Water glass

[Commas in tabulated material are equivalent to decimal points]

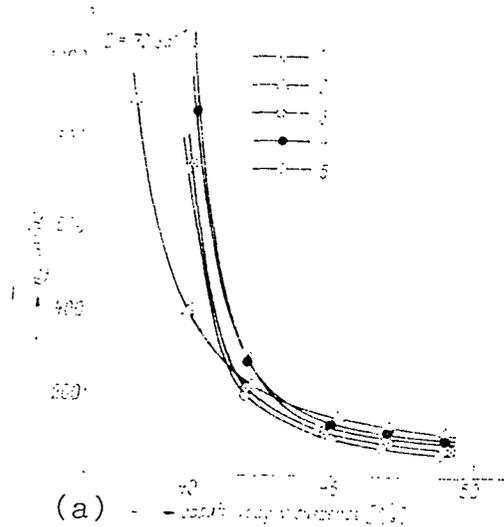


Figure 4. Apparent viscosity of suspension of kaolin KS-1 deflocculated by optimal addition of 5 varying deflocculation agents depending on contents of water in the suspension. 1 - 0.20% Na_2CO_3 , 2 - 0.08% water glass, 3 - 0.3% Dispex N 40, 4 - 0.30% DAC 3, 5 - 0.30% DAC 4.

Key: (a) Contents of water in suspension.

A number of suspensions with varying water contents were prepared from each raw material with optimum addition of the given deflocculation agent on the basis of the results shown in Table 5. Water contents in the given series of suspensions were selected so as to have their apparent viscosities fall into a range of approximately 20-1000 mPas. The measured dependencies of apparent viscosity on water contents in suspension are plotted for all the monitored cases in Figures 4-8.

From the dependencies in Figures 4-8 were read off water contents in suspensions with apparent viscosity of 300 mPas. These data are presented in Table 6.

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TABLE 6. CONTENTS OF WATER IN A SUSPENSION WITH APPARENT VISCOSITY OF 300 mPaS AT OPTIMUM ADDITION OF DEFLOCCULATION AGENT

A označení suroviny	B obsah vody v suspenzi %				
	soda	C sklo	Dispex	DAC 3	DAC 4
KS 1	12,9	40,8	11,3	11,3	11,2
KS 2	11,2	11,9	11,9	11,7	11,2
Spex	19,8	33,7	32,9	33,5	32,7
DAC 3	11,6	33,4	32,8	33,9	33,1
DAC 4	11,9	33,7	32,3	33,7	33,9

Key: A. Raw material designation
 B. Water contents in suspension (%)
 C. Water glass

[Commas in tabulated material are equivalent to decimal points]

Discussion of Results

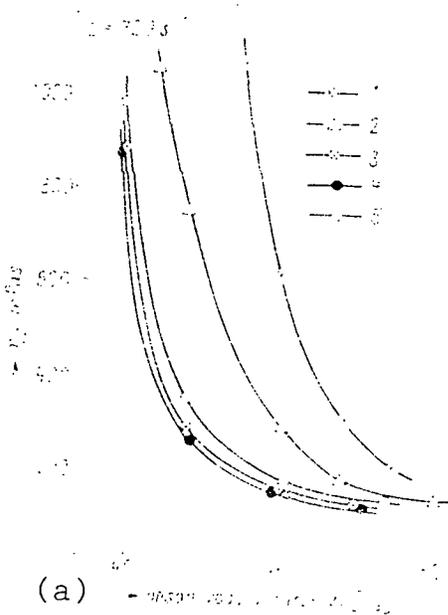


Figure 5. Apparent viscosity of suspension of kaolin KS-2 deflocculated by optimal addition of 5 varying deflocculation agents depending on contents of water in the suspension. 1 - 0.25% Na₂CO₃, 2 - 0.10% water glass, 3 - 0.35% Dispex N 40, 4 - 0.35% DAC 3, 5 - 0.35% DAC 4.

Key: (a) Contents of water in suspension

From the progress of the dependencies plotted in Figures 4-8 and from the data in Table 6 it is obvious that the deflocculation effects of sodium polyacrylates produced by the Sokolov Chemical Plants are entirely comparable to those of the foreign preparation Dispex N 40. The differences found in individual cases fall within the realm of potential dispersion variance of experimental results. From the mentioned dependencies it is also obvious that no significant difference could be found between

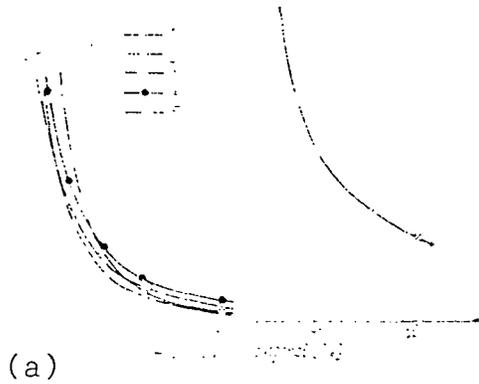


Figure 6. Apparent viscosity of suspension of kaolin Sp-ex deflocculated by optimum addition of 5 varying deflocculation agents depending on contents of water in the suspension. 1 - 0.25% NaCO_3 , 2 - 0.66% water glass, 3 - 0.15% Dispex N 40, 4 - 0.20% DAC 3, 5 - 0.20% DAC 4.

Key: (a) Contents of water in suspension.

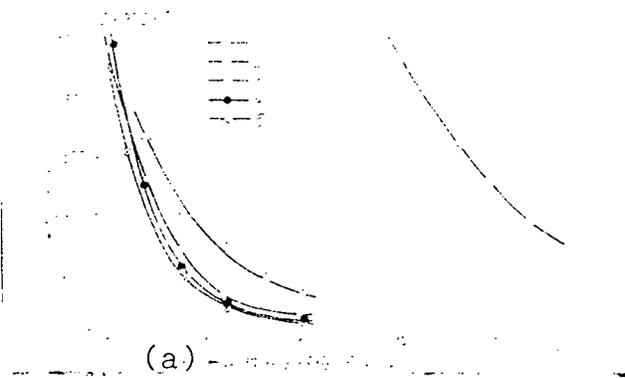


Figure 7. Apparent viscosity of suspension of kaolin Ds-ex deflocculated by optimum addition of 5 varying deflocculation agents depending on contents of water in the suspension. 1 - 0.18% Na_2CO_3 , 2 - 0.08% water glass, 3 - 0.15% Dispex N 40, 4 - 0.10% DAC 3, 5 - 0.10% DAC 4.

Key: (a) Contents of water in suspension

effects of the deflocculation agent prepared by polymerization in a nonaqueous medium (DAC 3) and by polymerization in an aqueous medium (DAC 4). If the next phase of tests - which will be oriented primarily toward verifying the effects on the properties of a casting slip - confirms the present result, selection will be made of a type of polymerization that poses fewer demands from the viewpoint of production. In this case this should involve polymerization in an aqueous medium.

From the measured data it is further possible to derive also some generally valid conclusions regarding deflocculation of kaolin suspensions by sodium polyacrylates. The basic advantage offered by sodium polyacrylates is not constituted by their quantitatively higher effects in comparison to conventional

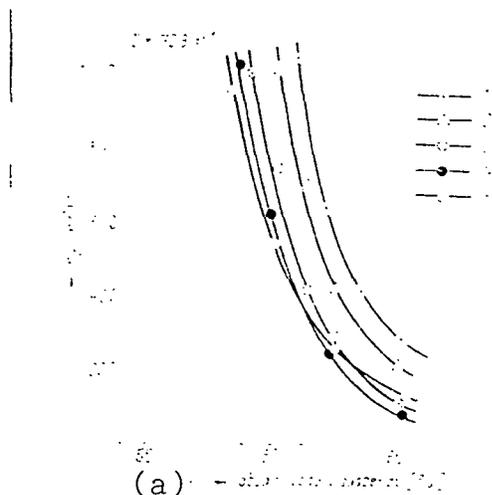


Figure 8. Apparent viscosity of suspension of kaolin I/IV deflocculated by optimum addition of 5 varying deflocculation agents depending on contents of water in the suspension. 1 - 0.15% Na_2CO_3 , 2 - 0.15% water glass, 3 - 0.20% Dispex N 40, 4 - 0.15% DAC 3, 5 - 0.15% DAC 4. Key: (a) Contents of water in suspension

through deflocculation by sodium polyacrylates, while the results obtained with the use of soda and water glass for sample KS-2 are ostensibly poorer.

Very good results with sodium polyacrylates were obtained also in deflocculation of kaolins from the Pilsen region which are difficult to deflocculate by soda. Use of sodium polyacrylates with kaolin Sp-ex/F from Kaznejov yielded results comparable to those obtained with water glass, in the case of kaolin DS-ex from Chlumcany the results obtained with sodium polyacrylates are superior to those obtained with water glass (Figures 6 and 7).

The specified cases of application of sodium polyacrylates point out a wide range of applications for these agents in deflocculation of clay suspensions. Nevertheless, they cannot be

deflocculation agents (soda, water glass), but by their uniformly high effects on a wide scale of raw materials. The dependencies plotted in Figures 4 and 5 can serve as an illustrative example. The plotted curves show progress of the apparent viscosity of suspensions of two different samples of kaolins from Sedlec - sample KS-1 with easy and sample KS-2 with difficult deflocculability by conventional agents. A comparison of the specified dependencies shows that practically identical results were obtained in both cases

expected to be always 100% effective. An example of a less successful application of sodium polyacrylates is deflocculation of kaolin from the Podborany region (Figure 8). Despite the certain amount of improvement achieved in comparison to conventional deflocculation agents, in the case of the suspension of kaolin I/IV it became impossible to adequately suppress the flow limit.

Conclusion

1. Deflocculation agents DAC 3 and DAC 4 prepared by the Sokolov Chemical Plants show effectiveness comparable to that of the foreign preparation Dispex N 40.

2. No significant difference was found between agents prepared by polymerization in aqueous and nonaqueous media.

3. The advantage offered by sodium polyacrylates is their uniformly high effectiveness in deflocculation of various types of kaolins.

4. Kaolins from the Chlumcany, Kaznejov and Sedlec regions showed a high degree of deflocculation efficiency.

5. Kaolin I/IV from Podborany could not be adequately deflocculated by sodium polyacrylates.

Note: Sodium polyacrylates DAC 3 and DAC 4 have not been incorporated into the production program of the Sokolov Chemical Plants at the time of this writing.

REFERENCES

1. Kraho, K., et al., "Contribution to the Forming Behavior of Spray-dried Elastic Fine Ceramic Substances," Silikattechnik 31/3, 81-84 (1980).
2. Alston, E., "Dispersing Agents Suitable for the Deflocculation of Casting Slip," Trans. BCS 74/8, 279-283 (1975).
3. Kunz, W., "Polymer Applications in the Ceramic Industry," Sprechsaal 109/6, 187-189 (1976).
4. Joyce, I.H. and W.E. Worrall, "The Adsorption of Polyanions by Clays and Its Effect on Their Physical Properties," Trans. BCS 89, 211-216 (1970).
5. Bigelow, G. and S.A. Prokopovich, "Sodium Polyacrylate: Deflocculation Mechanism in Clay Slips and Some Properties," J. Austr. Cer. Soc. 13/2, 31-34 (1977).