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RESISTANCE MANAGEMENT AND STRUCTURAL-RHEOLOGICAL PROPERTIES OF THE SUSPENDED LIQUID COMPLEX FERTILIZERS BASED ON ACTIVATED GROUND PHOSPHATE ROCK

At flotation Belarusian phosphate, along with high-quality flotation concentrate, the high-stable suspension with good structural and rheological properties formed in dewatering process of the fine fractions. The results of obtaining of different brands suspended liquid complex fertilizes with a broad content of useful substances on the basis of phosphate slurry and monoammonium phosphate, potash and nitrogen fertilizers are presented. The ways of regulating the physicochemical and structural and rheological properties of their suspensions are investigated.

Introduction. With the creation and development of the agro-industrial complex the problem of a rational cost-saving production and use of fertilizers is becoming increasingly sharp, as fertilizer industry refers to large-tonnage and capital-intensive industries. In this connection extremely important is to address the matter efficient use of fertilizers. The main source of the solid mineral fertilizer losses, except mechanical losses during transport and land application, is extremely low and inefficient use of nutrients introduced by plants [1].

Existing assortment of solid fertilizers allows us to solve the problem of supplying plants with nutrients, but not fully satisfies the growing needs of agriculture. Moreover, the solid fertilizer application does not allow achieving mixture homogeneity and its uniform application to the soil, which in turn, leads to a substantial overexpenditure of fertilizer, reduction of productivity and environmental pollution.

According to leading foreign and domestic experts, the basic requirements for fertilizers, especially when foliar application, can only be met by using the liquid forms of fertilizers. Agricultural science and practice of the last three decades of the previous century show clearly that the place of traditional solid fertilizers is increasingly taken by liquid ones, in other words, the future belongs to the liquid complex highly concentrated mineral fertilizers. Their rapid spread is considered as a "revolution" of liquid fertilizers. Among them suspended liquid complex fertilizers (SLCF) are quite promising [2, 3].

Suspensions of liquid complex fertilizers are brines in which fine crystals (particles) of insoluble salts, stabilizing agents and other substances are dispersed. Suspensions combine the advantages of both traditional complex two-, three-component solid fertilizers, namely high ≈40% concentration of nutrients and liquid complex fertilizers (LCF). The main advantages of SLCF over solid fertilizers are full mechanization and reduction of losses on the preparation, transportation, storage and application; more qualitative (uniform) distribution at the surface broadcast application, the ability to combine the application with other agricultural practices of tillage, planting, watering, and bringing in growth stimulants, pesticides, trace elements.

Since the component solubility in the suspensions does not play such an important role, as in the LCF solutions, the SLCF advantage is also the possibility of using cheaper poorly soluble materials, in our case, ground phosphate rock, as one of cheaper and additional nutrient sources, in particular P_2O_5. Thereby SLCF obtaining can extend the fertilizer blending resource base.

The suspended liquid fertilizers have high viscosity, which varies during storage, i.e. thixotropy phenomenon is observed. Therefore, they should be mixed assisted by powerful pumps, pipelines. The presence of solid particles in the mixtures increases the abrasive properties of the suspensions as compared to solutions, which leads to deterioration of the pumps and other equipment during production and introduction. Despite the difficulties, it does not prevent the suspensions to be the most promising type of fertilizer. It is the high concentration of nutrients suspended in fertilizers that compensate all these shortcomings, and these fertilizers are becoming more common in foreign practice.

The largest suspension manufacturer in foreign countries is currently the United States. SLCF in significant volumes is used in Western European countries such as England, France, Denmark, Italy, Belgium, the Czech Republic and Hungary.

As noted previously [4, 5], at the development of technology of Belarusian rock phosphate flotation, along with high flotation concentrate, in the dewatering process of fine-dispersed fractions, highly stable suspension is formed. Drying of this suspension even in the most efficient spray dryers is associated with high energy expenditure. In consideration of their high stability and good structural-rheological and technological properties, it was proposed to use them as suspended liquid compound fertilizers, in giving them the required amount of potassium chloride and nitrogen fertilizers.

On the basis of ground phosphate rock, ammonium phosphate, urea, potassium chloride, ammonium sulfate, produced by the chemical industry of the Republic of Belarus, we have developed compositions SLCF NPK-fertilizers of various brands with a broad content of useful substances. To achieve high suspension quality and high concentration of nitrogen and P_2O_5 we used ammophos as a base solution instead of currently applicated for these purposes costly and energy-intensive ammoniated polyphosphoric acids. The technological properties of the suspended compositions are studied.

Since suspensions contain, except dissolved salts, part of the salts in the form of particulate matter (nitrogen and potassium salts, phosphate powder), then the question arises of keeping the particles in suspension, preventing their precipitation and crystal growth from supersaturated solutions during suspension storage. In other words, it's about getting dispersion system which is stable enough. It is shown that the initial suspensions based on ground phosphate rock, nitrogen salts and fine-grained potassium chloride are semistructured systems with high water yield values and the proportion of the clarified layer, with low values of thixotropy and stability.

Experiment results to determine the stability of the phosphorite-salt dispersion of ground phosphate rock, urea, potassium chloride composition 12.4–6.3–0 и 10.6–5.2–11.5 ($N : P_2O_5 : K_2O$), a liquid phase of which are concentrated salt solutions shown in Fig. 1.

These data indicate that the suspension on the basis of ground phosphate rock are unstable systems with a high proportion of clarified layer in a short time. Thus, the clarified layer proportion of the indicated compositions within an hour is 38 and 30 wt. % respectively (curves 1, 2). Introduction of the stabilizer – bentonitic clay in an amount of 2.3 wt. % reduces the delamination degree sharply, the clarified layer is about 12%, at a flow rate of greater than (4 wt. %) – only 2% at the same time of the suspension sedimentation (curves 3 and 4).

The mineral fertilizer suspensions are inherently coarse systems, so to make them homogeneous throughout the volume and resistant to delamination, the stabilizers, increasing the system viscosity to the required level and slowing the clarification rate must be given to their composition.

Clays used as stabilizers must have certain properties, the chief of which is their ability to swell. bentonitic clays were used for studies. For these clays is specific not only capillary suction, but also inside crystallization of water causing high swelling degree. When observed in the electronic microscope the fine particles of montmorillonite give characteristic lamellar, foliaceous crystals. The smallest thickness of the montmorillonite particles, like of a lot of clays, is 0.001 mm, the specific weight 2.5–2.6 g/sm^3. Bentonitic clays have a high ability to cation exchange. Exchange capacity essentially determines the physical and chemical properties of clays. Clays containing alkali metals, mainly sodium, swell more than clays whose composition includes calcium.

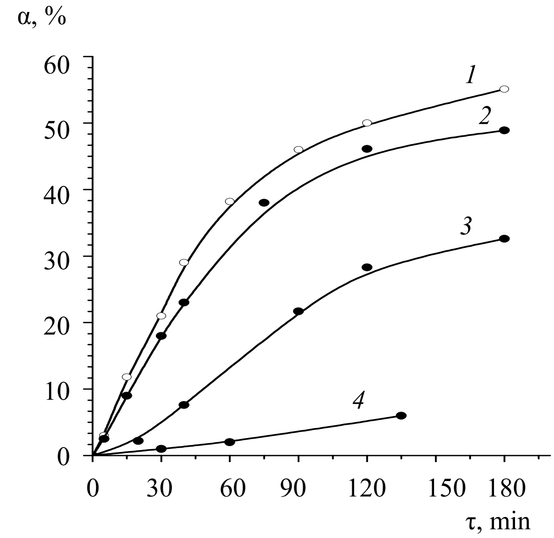

Fig. 1. Dependence of the clarifying degree (α) of phosphorite-salt dispersions on the duration:
1 – suspension of 12.4 : 6.3 : 0; *2* – 10.6 : 5.2 : 11.5;
3, *4* – bentonitic clay 2 and 4 wt. % respectively

For the preparation of the starting clay suspension the clay was preliminarily pulverized to a particle size of 0.071 mm, was mixed with hot water at vigorous stirring, a weight ratio of 1 : 6; 1 : 10; 1 : 15 and a temperature of 70°C. Sodium and calcium bentonitic clay forms were used for studies. It was found that bentonitic clay, consisting of Na-montmorillonite, swells very rapidly, and even at normal temperature is converted into a gel, which is a very viscous structured system stable for several months. For improving the Ca-form swelling and obtaining sufficiently viscous and gelatinous clay the alkaline component (soda) was added thereto in an amount up to 5 wt. % from the clay weight, which facilitated the transition to Na-form, simultaneously fine-dispersed calcium carbonate was formed, which is an additional suspending agent.

SLCF NPK-fertilizer compositions of different brands were obtained on the basis of ammophos, phosphate rock, phosphate urea, potassium chloride.

Tab. 1 shows the characteristics of the major brands of triple fertilizers prepared by mixing the base solution of ammophos, bentonitic clay, phosphate rock, dry urea and potassium chloride. The amount of nutrients depending on the brand ranges from 23.0 to 29.9 wt. %. The share of P_2O_5 from phosphate fertilizer in suspension ranges from 1.78–2.38 wt. %, from ammophos – 12.69–14.31 wt. %. The density of the solution is in the range 1.267–1.430 g/cm^3, the ratio of T : L from 0.86 to 1.16, the dynamic minimum viscosity is 80–1200 mPa·s.

Tab. 1 shows the ternary SLCF characteristics obtained using a concentrated solution containing 40 wt. % of urea, in which ammonium phosphate was dissolved by heating to 70°C and at vigorous stirring, the gelatinous bentonitic clay, phosphate rock and ammonium sulfate powder were introduced here. The resulting suspensions have the same characteristics as in the first case, the density at 20°C 1.35–1.43 g/cm^3, the viscosity is somewhat higher 180–370 mPa·s, the ratio of solid to liquid is within 1.0–2.2 .The kinetic stability of the obtained composite structures has been established. The results are shown in Fig. 2.

The obtained data show that the use of ammophos as basic solutions due to the fluorophosphate sludge contained in them contributes to the stabilization of suspended fertilizers even in the absence of bentonitic clay. The proportion of clarified suspension layer, for example of 7.5–9.3–6.9, for 24 hours is 2.5% and for four days only 6.5% (curve 2, Fig. 2).

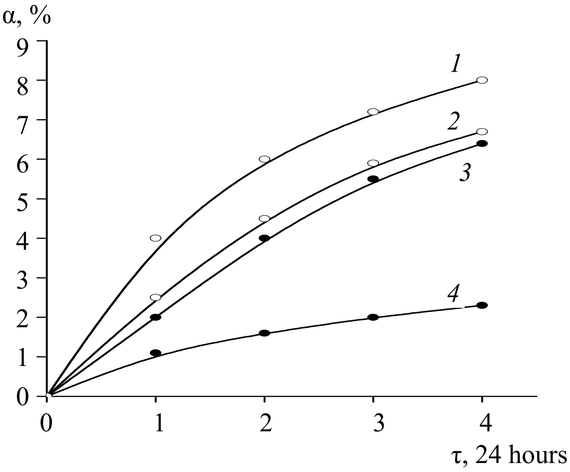

Fig. 2. Dependence of the clarified layer fraction (α) on the duration of suspension maturation: *1* – No. 4 (Table 1); *2* – No. 9 (Table 1); *3* – No. 6 (Table 1); *4* – No. 5 (Table 1)

P_2O_5 content in a fertilizer due to ammophos is 7.52 wt. %. Suspensions containing large quantities of ammophos (25–31 wt. %) in the presence of phosphate rock represent stable high strength structured systems with high thixotropy gelled at lower temperatures to a pasty state, necessitating their periodic mixing.

Table 1

Characteristics and technological properties of ternary (SLCF NPK) compositions on solution basis: ammophos (1–9), urea (10–12) and solid fertilizers (phosphate rock, urea, potassium chloride) (No. 8–9 – introduced Na-CMC)

No. sp.	$N : P_2O_5 : K_2O$, wt. %	Salt composition, wt. %						η_{min}, mPa·s	ρ, g/cm^3	p_{k2}, Pa	T : Zh	pH value
		ammophos	urea	phosphate rock	KCl	bentonitic clay	H_2O					
1	5.4 : 15.5 : 4	27.75	4.54	12.61	6.3	2.10	46.67	100	1.354	166	1.16	7.1
2	6.2 : 19.1 : 4.6	31.8	5.19	14.43	7.4	–	41.38	–	–	–	1.43	7.3
3	4.8 : 14.8 : 3.5	24.64	4.03	11.2	5.6	1.12	53.39	80	1.340	30	0.86	7.2
4	5.4 : 16.7 : 4	27.75	4.54	12.61	6.3	–	48.78	200	1.408	50	1.04	7.1
5	5.2 : 16.0 : 3.8	26.63	4.35	12.10	6.1	1.21	49.63	170	1.267	180	1.00	7.4
6	5.4 : 16.7 : 4.0	27.87	4.56	12.66	6.3	0.92	47.63	–	–	–	1.10	7.3
7	8.7 : 13.8 : 7.6	26.12	11.9	–	11.9	2.37	47.66	500	1.430	105	1.10	7.1
8	8.1 : 10.1 : 7.4	16.82	9.25* 7.56	10.93	12.6	–	42.05	–	–	–	1.60	7.2
9	7.5 : 9.3 : 6.9	14.49	7.97* 6.52	9.42	10.9	–	50.72	1200	1.350	280	1.00	7.2
10	5.8 : 10.6 : 7.4	13.3	10.66	26.6	13.3	3.0	39.3	–	–	–	2.0	7.3
11	6.7 : 10.0 : 7.0	12.5	6.25* 9.4	25.0	12.5	2.8	31.2	–	–	–	2.2	7.1
12	9.1 : 11.8 : 9.6	15.2	16.2	20.3	15.2	1.4	39.6	–	–	–	2.2	7.2
13	7.0 : 9.5 : 6.6	11.8	14.1	23.5	11.8	2.6	36.3	500	1.430	265	1.8	7.4
14	7.8 : 9.0 : 6.3	11.1	5.5* 13.2	22.2	11.1	2.5	34.1	180	1.420	190	2.0	7.1

* (1–9) – NH_4NO_3 ; (10–15) – $(NH_4)_2SO_4$.

We have defined structurally rheological properties of developed by us suspended fertilizers with various compositions using bentonitic clay as stabilizer. Structurally rheological properties were studied on a rotary viscometer "Reotest 2". The resulting flow curves are shown in Fig. 3, 4. They indicate that the suspensions are structured liquid-like systems related to non-Newtonian fluids. It had been found that with increasing of solid content in the suspensions the strength of their structure significantly increases, as evidenced by an increase in the rheological properties of $p_{к2}$ and η.

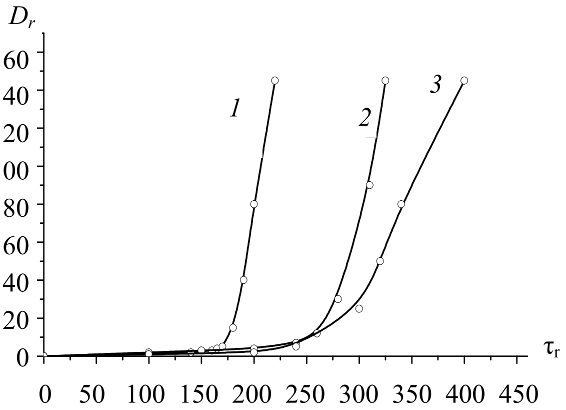

Fig. 3. The rheological flow curves of suspended fertilizers with various compositions: D_r – the velocity gradient, C^{-1}; τ_r – shear stress in Pa (similar to Fig. 4): *1* – No. 5 (Table 1); *2* – No. 6 (Table 1); *3* – No. 9 (Table 2)

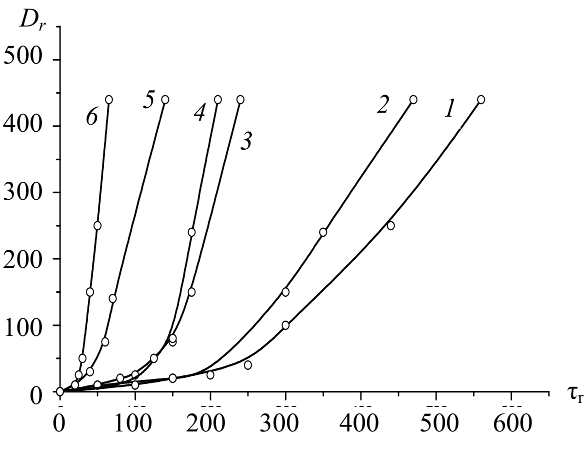

Fig. 4. The rheological flow curves of suspended fertilizers: *1*, *3–6* – No. 1 (Table 1); *2* – No. 4 (Table 2)

For example, at a ratio of S : L = 1–1.5 and S : L = = 2 the limit stress in the first case is 50–100 Па, a η_{min} = 0,1–3,0 Pa · s, and in the second it increases to 200–300 Pa and the viscosity – to 1 Pa · s or more.

Comparing the rheological data for the suspension stability it was found that systems with high solids are stable for several days. Suspensions with low solids stratified within three days by 26–30%. Analyzing the data, we can see that by changing of the original component content, the suspension structure can be changed. Thus, the introduction of a solution containing 40 wt. % of urea the SLCF stability is considerably higher than when using urea as a solid.

To stabilize the phosphorus-salt suspensions instead of expensive and scarce bentonitic clays, we proposed to use clay-carbonate slurries and available for agriculture calcium compounds. It was shown that the suspensions obtained both on base solution 10–34–0 and assisted by phosphate rock, ammophos, soluble nitrogen-containing salts of potassium chloride in the presence of CaO, $CaCO_3$, $CaSO_4 \cdot 2H_2O$ have good physical-chemical properties. The quality of obtained suspended fertilizers is not inferior to those using bentonitic clay (Table 2).

Stable, for a long time (a week or more) non-stratifying binary and ternary compositions SLCF were obtained with the amount of nutrients 26–30 wt. % in binary and 23–35 wt. % in ternary NPK-fertilizers. The density of fertilizers depending on their composition ranges from 1.31–1.61 g/cm^3, viscosity – 0.97–4.40 Pa · s. The P_2O_5 content in suspensions due to phosphate ground rock is 3.4–5.7 wt. %, the amount of suspending agent (GSSH) – 0.7–4.0 wt. %.

Using clay slurry with chalk or lime helps to increase the stability of the obtained suspensions while maintaining sufficiently high flow ability. To determine the flow ability the methodology was used which is based on the ability of the suspension to flow under its own weight. It was determined by the spreading of the suspension flowing from a standard cone.

To increase the fluidity of various kinds of suspended systems in practice, both inorganic and organic compounds are used as reagents-diluents. Inorganic diluents most widely used in the industry are salts of weak and medium acids, giving a strongly pronounced alkaline reaction (Na_2CO_3, $NaHCO_3$, Na_2SiO_3, $Na_2P_3O_{10}$). The soda ash was used as inorganic diluent of suspended fertilizers. Application of soda together with suspending stabilizers (chalk, lime, clay slimes) provides stable and mobile suspensions, moreover, contributes to the pH value, which plays an important role in their usage. For example, the use of chalk (1 wt. %) in combination with sodium (1 wt. %) increases the fluidity of the suspension from 91 to 95 mm, the pH value from 4.2 to 5.0, and also the stability of the suspension compared with the case when only chalk is used. A similar pattern is observed when using clay slurry together with soda.

Table 2

The influence of various reagents-stabilizers on physicochemical properties SLCF on the basis of phosphate rock from Polpinski deposit, ammophos and soluble fertilizers (1–3 mark 1: 1.1: 1; 4–10 – mark 1: 0.6: 0.9)

N	Salt composition, wt. %					Stabilizing agent, wt. %		Viscosity Pa · s		Density g/cm^3	Value pH	Stability	
	Urea	Ammo-mo-phos	Phosphate rock	KCl	K_2SO_4	$CaCO_3$	Clay sludge	max	min			24 hours	Percentage of clarifi-cation
1	20.0	17.4	21.8	17.5	–	1.7	–	86.02	0.23	1.51	4.5	1	0
2	18.6	16.2	20.2	16.2	–	0.8	–	22.7	0.4	1.48	4.2	1	2
3	17.4	15.1	18.9	15.1	–	0.75	–	14.0	0.25	1.45	4.2	1	4
4	29.3	11.7	17.4	21.3	–	0.5	1.0	26.7	0.64	1.49	4.3	2	0
5	27.3	8.3	23.1	19.8	–	–	1.8	17.1	0.31	1.47	4.7	1	0
6	26.2	8.0	22.1	19.0	–	1.8	–	22.6	0.1	1.48	5.3	–	–
7	27.2	8.3	23.0	–	23.0	1.8	–	99.6	1.7	1.50	4.7	2	0
8	24.7	7.5	20.9	–	20.9	1.6	–	23.9	0.2	1.51	4.5	2	2
9	25.8	7.8	21.8	–	21.8	–	–	21.4	0.27	1.46	5.2	1	0
10	26.2	8.0	22.1	–	22.1	1.8	–	80.0	0.67	1.49	4.6	2	0

It is shown that the use of Na-CMC additives as a suspending agent of clay-salt slurry has an additional stabilizing effect on SLCF. Within 7 days and even more the suspensions are practically not stratified, the proportion of the clarified layer is almost zero. Good results have been achieved when using small additions of Na-CMC (0.1–0.5 wt. %) in combination with soda. In this case, the fluidity of the slurry is increased to 95 mm at a lower viscosity and maintaining the same stability.

From a large number of raw sludge diluents or clay mud viscosity reducers for dilution high-strength structures it was proposed to use lignosulfonates (LS) and alkaline waste of caprolactam production (AWCP), as well as other by-products of the industrial enterprises of the Republic of Belarus LS introduction in 2–5 wt. % on solid contributes to SLCF dilution, lowers the viscosity to 1.25–2.50 Pa · s, increases the fluidity up to 98 × 98 mm, while maintaining good stability.

With further increase in the LS concentration the fluidity decreases and the viscosity increases, which is consistent with the data of the LS effect on the rheological properties of clay-salt dispersions and is associated with increased structure formation in the system.

It is shown that in the case of AWCP application in small concentrations it has a stabilizing effect on the system, thereby increasing the stability of the suspension (1.2–1.4% clarification instead of 25% without it), decreasing the fluidity, raising the viscosity and then with increasing concentration the gradual viscosity reduction of the suspension and as a result the fluidity increase are observed. When using binary compositions of proposed SLCF diluents based on AWCP and LS with concentration increasing the slurry fluidity increases and their viscosity decreases at some loss of stability.

Conclusion. It has been established that the proposed suspended fertilizers containing 30.3 wt. % useful components have a strong structure that growths with the stabilizer increase in it – bentonitic clay in one form or another. With increasing of the aqueous phase concentration in the suspensions their stability and strength of the overall structure decrease.

It is proposed to use the mixture of LS and AWCP for structure dilution (viscosity reduction). The introduction of the reactants, the viscosity reducers in an amount of 2–5 wt. % contributes to SLCF dilution, to fluidity increase up to 98 × 98 mm (MChTI), to the viscosity reduction to 1.25–2.50 Pa · s, while maintaining stability. The differences in the diluent action on SLCF in the presence of urea and ammonium sulfate has been established.

To stabilize the phosphorus-salt suspensions instead of expensive and scarce natural clays, it is proposed to use along with clay-carbonate slurry calcium compounds available for agriculture. It was shown that the obtained suspensions both as on base solution 10–34–0 and assisted by phosphate rock, ammophos, soluble nitrogen-containing salts of potassium chloride in the presence of CaO, $CaCO_3$, $CaSO_4 \cdot 2H_2O$ have good physicochemical properties. The quality of the obtained suspended fertilizers is not inferior to those using bentonitic clay.

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