COALESCENCE OF PHOSPHORUS-CONTAINING SLUDGE: HYDRO-MECHANICAL METHOD OF UTILIZATION

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Abstract

The following article is a continuation of research that examines the problem of utilization of phosphorus-containing sludge that is produced in the phosphorus industry. Using models for coagulation and coalescence of the sludge, both within its hydraulic mix and following sedimentation in a ribbon mixer apparatus, very important parameters were identified. Those parameters are: the "energetic barrier" of the coalescence, power that is spent on mixing dispersed particles of sludge in conditions of complete coalescence, duration of coalescence, duration of sedimentation of particles of various aggregates and volume of liquid phosphorus that is secreted out of the sludge. Within the coalescence process we identified the prevailing impact of upper particles energy and mixing energy. Using a concrete example, we determined that during mixing and sedimentation, both the production of concentration and the average volume of the produced aggregates of particles is constant.

Keywords: Phosphorus-containing sludge, utilization, coalescence, modeling, technological parameters

1. INTRODUCTION

The only practical way for industrial scale production of elementary yellow phosphorus is its reproduction from natural phosphates in ore-thermal electric furnaces with different capacities, using carbon in the presence of silica [1]. As a result of the electro-thermal process, furnace gas is formed. This gas contains up to 20 % phosphorus in mass and 5 - 7 % in volume. It contains vapors of phosphorus, organic materials, bounds of flour, silicon, carbon and other gas bounds, as well as dust with different degrees of dispersion. The furnace gas passes through electro filters and enters into a condensation system, where it is secreted as liquid phosphorus. The liquid phosphorus is condensed together with the dust and gas bounds, producing raw phosphorus and phosphorus-containing sludge. The mechanism of creation, classification, composition, main characteristics and ways of utilization of the phosphorus-containing sludge are explored and described in the research [2]. **Fig. 1** shows a scheme of phosphorus stabilization by molecules of surfactants and water, mineral and carbon particles. Phosphorus-containing sludge is a poly-dispersed system with normal distribution of phosphorus particles in the volume. The degree of dispersion of the particles determines the sludge types: "clay" - d_p = (1 - 9)·10^{-5} m, "sand" - d_p = (2 - 16)·10^{-5} m, "grain" - d_p = (1 - 8)·10^{-4} m, "plasticine" - d_p = (1.6)·10^{-3} m. "Rich" phosphorus-containing sludge (60 - 80 % P_4), which is first involved in the recycling, is an emulsion of phosphorus in water with stabilizers such as organic materials and thinly dispersed dust at phase interfaces. Less stable are the "grain" sludge types; these are easily stratified after previous intensive mixing within apparatuses with a blender. After analyzing the different ways of recycling and utilization of sludge, the hydro-mechanical method of dividing sludge was accented. This method is based on using ribbon mixers and multidirectional screws, which were industrially tested in the phosphorus industry in Kazakhstan.

Research objectives:

- Examination of coagulation, coalescence and sedimentation of phosphorus-containing sludge within a hydro-mechanical method of utilization.
- Definition of the most important technological parameters of the process as energetic barrier of the coalescence ΔE; power that is spent on mixing dispersed particles of sludge in conditions of complete

coalescence N_*; duration of coalescence t_{cl}; duration of sedimentation of aggregates of particles t_s and volume of liquid phosphorus V_{ph} that is secreted from the sludge.
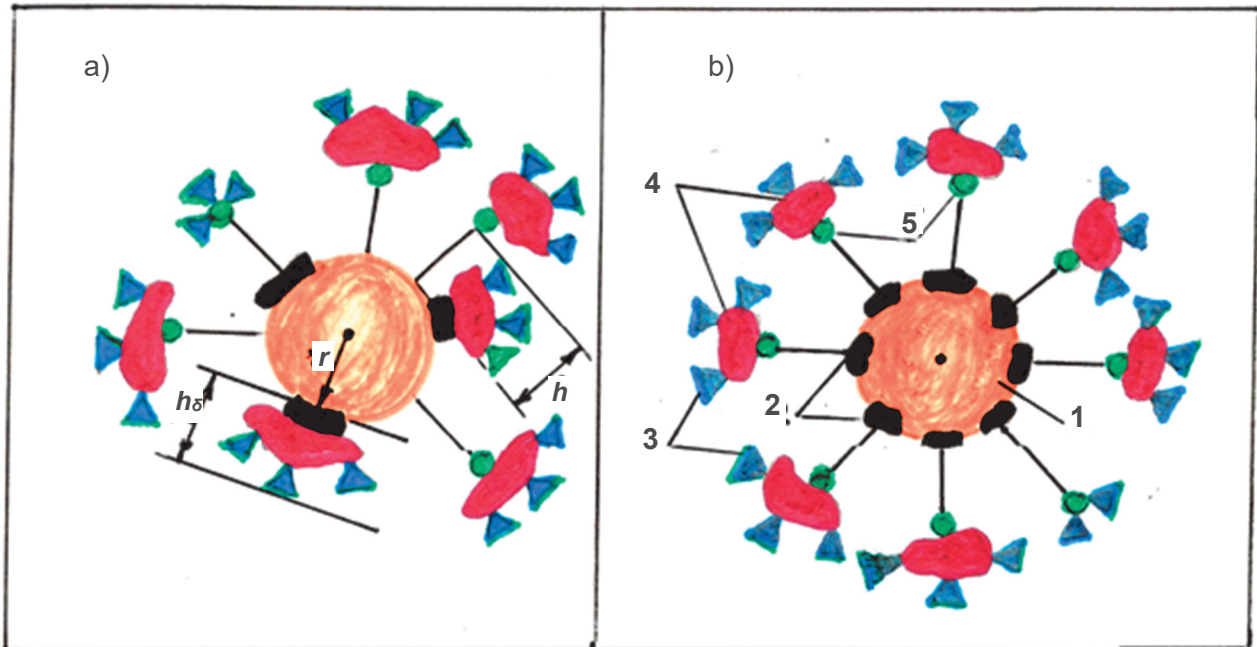

Fig. 1 Schemes of stabilization of phosphorus drops. 1 - drop of phosphorus; 2 - hydrophobic particles; 3 - water molecules; 4 - hydrophilic mineral particles; 5 - surfactant molecules
r - radius of single "clean" particle of phosphorus; h - distance between surface of "clean" particle of phosphorus and surfactant molecules (if they exist ; h_δ - thickness of the structure-mechanical barrier.

2. COAGULATION AND COALESCENCE OF PHOSPHORUS-CONTAINING SLUDGE DURING HYDRO-MECHANICAL AGITATION AND SEDIMENTATION

2.1 Coagulation of phosphorus-containing sludge

In order to achieve the previously mentioned objectives, an equation of ceaseless coagulation was examined and resolved and is presented in [3]. Concentration $n(t)$ and average volume $V_*(t)$ of produced aggregates of particles at time t are defined in the formulas (1):

$$n(t) = n_0 \left[1 - \left(\frac{K_{cg}\,t}{1 + K_{cg}\,t} \right) \right] \exp \left\{ \frac{2}{\sigma} \left(\frac{K_{cg}\,t}{1 + K_{cg}\,t} \right) \left[a + \frac{\sigma\,K_{cg}\,t}{1 + K_{cg}\,t} \right] \right\},$$

$$V_*(t) = V_0 \left(\frac{\beta_D + K_{cg}\,t}{\beta_D} \right) = \frac{V_0\,n_0}{n(t)} \tag{1}$$

where t - current time (s); $K_{cg} = 4\,\pi\,D_*\,R_*\,n_0 = \beta_D\,K^*_{cg} = \beta_D\,4\,\pi\,D_*\,R_*\,n_0$ - constant of coagulation (s^{-1}) ; D_* - coefficient of diffusion (dispersion) of particles (m^2/s), defined using diffusive and deterministic-stochastic models of mass transfer, examined in [2, 4]; β_D - proportionality factor for the constant K^*_{cg} in which Brownian diffusion coefficient is replaced by the factor D_*; R_* - radius of "sphere of influence" of single particles (m); $n_0 = n_{t=0}$ - initial concentration of particles (m^{-3}); α, σ - the Gauss parameters of sludge particles distribution in the volume (m^3) $\cdot$ V_0, V_{max} - the minimum (average) and maximum volume of single particles, respectively (m^3), defined by equations (2):

$$V_0 = \frac{1}{2}\left[\sigma \exp^{-\frac{1}{2}\left(\frac{a}{\sigma}\right)^2} + a\sqrt{\pi/2} \right], \quad V_{max} = \left(\sigma/2 + V_0\right) \tag{2}$$

The process of production new volumes of aggregates of particles $V_*(t)$ with a concentration of $n(t)$ during mixing sludge is also correct within sludge sedimentation. At this point the coagulation constant K_{cg} is respectively replaced by $K_{cgS} = 4\pi D_{*S} R_{*S} n(t_h)$, where $n(t_h)$ (m^{-3}) - concentration of produced aggregates of particles at the moment of dispersion homogenization t_h. The meanings of parameters D_{*S}, t_h for different volumes of apparatuses with ribbon mixers are shown in [2, 4].

Counting that the micelles of phosphorus-containing sludge are particles of phosphorus, that are protected by the structure-mechanical barrier, which prevents their coalescence(**Fig. 1**),the radiuses of the "spheres of influence" of single particles R_* and their aggregates R_{*S}, which are part of coagulation constants K_{cg}, K_{cgS} will be shown as (3):

$$R_* = \xi_*\left(r + h_\delta + h\, e^{\frac{\Delta E}{kT}} \right), \quad R_{*S} = \xi_{*S}\left(r_S + h_\delta + h_S\, e^{\frac{\Delta E_S}{kT}} \right), \tag{3}$$

where h_δ - is the thickness of the structure-mechanical barrier; r, r_s - are the radiuses of single "clean" particles of phosphorus and theirs aggregates; h, h_s - are the distances between surfaces of "clean" particles in the aggregates and between the aggregates themselves, as defined by the theory of distribution of" direct neighbor" [3]: $h = 0.55396\sqrt[3]{V_0}$, $h_S = 0.55396\sqrt[3]{V_*(t_h)}$; ξ_*, ξ_{*S} - is the number of paired interactions of particles within aggregates and of the aggregates themselves, as received from the condition of dense packing of particles (or aggregates of particles), that are located on "orbits" around the examined particles or their aggregates: $\xi_* = \pi (2 + h/r)$, : $\xi_{*S} = \pi (2 + h_S/r_S)$; kT is thermal energy (N m), in which k - the Boltzmann constant, T - temperature (K). Values ΔE, ΔE_S, that are included in the formula (3), are energetic barriers of coalescence within mixing and sedimentation of sludge, respectively. These can be best presented by the Gibbs thermodynamic potential [2]. In simpler cases (for example, where there is a constant temperature, or an absence of chemical reactions, or both) individual terms ΔE, ΔE_S are defined by experiments, or by known semi-empirical dependencies. In particular, the energetic barrier of coalescence ΔE is presented as an algebraic sum:

$\Delta E = E_e + E_a + E_g - E_v - E_d$, where E_e - energy of electrostatic repulsion between double electric layers with an identical charge; E_a - energy of adhesion of phosphorus and aqua to the surface of sludge mineral particles; E_g - surface Gibbs's energy, that count changes of the surface tension on the interfacial surface area; E_v - attraction energy (van der Waals energy attraction); E_d - dissipative energy of mixing that is applied to the volume V_0 - of the coalescing particles. During the mixing process the relationship $\Delta E\, /\, kT$ is affected a considerable degree by the surface energy of the structure-mechanic barrier of phosphorus particles ($E_a + E_g$) and dissipative energy E_d, which depends on the power of mixing. As follows from [3], a significant excess of the energetic barrier ΔE on kT almost terminates the process of coagulation.

2.2 Coalescence and sedimentation of phosphorus-containing sludge. Energy of agitation

Our objective is to define conditions in which single particles with average volume V_0 with a radius of the "sphere of influence" R_* will, when collected in aggregates with volumes $V_*(t)$, merge together, thereby creating a single drop. Following [5], a condition to this is "loss of emulsion layer", meaning destruction of the structure-mechanical barrier on surfaces of "clean" phosphorus particles with a radius r (**Fig. 1**).

The condition to coalescence of particles, when collected in aggregates, and aggregates of particles is implementation of the energy balance: $\Delta E = \Delta E_S = 0$, when ($h_\delta = 0$), meaning implementation of equality:

$E_d = E_e + E_a + E_g - E_v$. Hence, coalescence of sludge within the mixing process can be managed by variation of mechanic energy or power N_*, supplied to the volume of the particles. The objective of defining the power N, that is spent on the mixing of "clean" (without particles) liquids, is resolved in [6] by examining the dynamic interaction of ribbon screws mixer with viscous liquids, using the building vortex hydrodynamic model. Power N_*, which is spent on mixing in conditions of complete coalescence of initially discreet particles in the volume of apparatus V_a, the duration of coalescence of sludge particles, located in aggregates t_{cl}, and the duration of sedimentation aggregates t_S are shown in the following formulas (4) and (5):

$$N_* = \frac{E_d \, \rho_{av} \, V_a}{\rho_l \, V_0 \, t_{cl}} = N + N_{in}, \tag{4}$$

in which the summand N_{in} takes into account the power from inside forces of interaction between particles of phosphorus-containing sludge and constitutes approximately 8 % of N_*. ρ_l, ρ_{av} - is respectively the density of the environment around sludge particles and its average density.

$$t_S = \frac{1}{K_{cgS}} \left[\frac{\beta_D^2 \, n_0}{(\beta_D + K_{cg} \, t_h) \, n(t_S)} - \beta_D \right], \quad t_{cl} = a_* \left(t_h + t_{cg} \right) = a_* \left(t_h + \frac{\beta_D}{4 \, \pi \, D_* \, n_0 \, \xi_* (r + h)} \right), \tag{5}$$

t_{cg} - the duration of coagulation within which, in accordance with [5], the concentration sum of the particles decreases to $n_0/2$; t_h - is the time homogenizing dispersions, defined in [2, 4]; $\alpha_* = 0.166$ is the coefficient of proportionality that matches the occasion when dispersed particles of phosphorus are completely covered by adsorption particles that are present in sludge [2]; $n(t_S) = 1$ m^{-3} - the concentration of initially discreet particles that are merged in one large volume (drop) for case $\Delta E_S = 0$.

3. EXPERIMENTAL STUDY OF COAGULATION, COALESCENCE AND SEDIMENTATION OF PHOSPHORUS - CONTAINING SLUDGE. CALCULATION OF PROCESS PARAMETERS

Experimental research into coagulation processes and coalescence of phosphorus-containing sludge within hydro-mechanical mixing and sedimentation were conducted directly in laboratories and workshops in plants of the southern Kazakhstan phosphorus industry. Initial physical parameters are taken from [2]. Examples of calculation technological parameters during mixing and sedimentation of the "sand" type sludge in laboratory apparatus with a ribbon mixer are given in **Table 1** below.

Table 1 Example of calculation of process parameters with stirring and sedimentation of phosphorus-containing " sand "type sludge in the device with opposite helical screws

Original data:
$d_{p \, max} = 2 \, r = 1.6 \cdot 10^{-4}$ m; $a = 0.68 \cdot 10^{-12}$ m^3; $\sigma = 0.77 \cdot 10^{-12}$ m^3; $V_0 = 0.69 \cdot 10^{-12}$ m^3; $V_{max} = 1.07 \cdot 10^{-12}$ m^3;
$n_0 = 4.663 \cdot 10^{11}$ m^{-3}; $h = 4.895 \cdot 10^{-5}$ m; $h_\delta = 12 \cdot 10^{-10}$ m; $\xi_* = \xi_{*S} = 9.09$; $\rho_{av} = 1300$ kg/m^3;
$\rho_l = 1000$ kg/m^3; $T = 353$ K; $k = 1.38 \cdot 10^{-23}$ N m/K; $D_* = 2.3 \cdot 10^{-3}$ m^2/s; $D_{*S} = 2.6 \cdot 10^{-3}$ m^2/s;
$\beta_D = 100$; $\alpha = 0.166$; $V_a = 0.036$ m^3; $V_w = 0.2 \, V_a$; $\omega = 4 \, \pi$ (rad/s); $N_{* \, exp} = 40$ w; $t_h = 55$ s.
Calculated data:
$E_e = 0$; $(E_a + E_g) = 6498 \cdot 10^{-12}$ N m; $E_v = 17 \cdot 10^{-20}$ N m; $(7) \to t_{cg} = 6.3 \cdot 10^{-6}$ s ≈ 0; $t_{cl} = 9.13$ s;
$(5) \to E_d = 6.46 \cdot 10^{-9}$ N m; $\Delta E = - 3.68 \cdot 10^{-11}$ N m < 0; $(3) \to \exp(\Delta E / k \, T) = \exp(-0.75 \cdot 10^{10}) \to 0$;
$R_* = 7.3 \cdot 10^{-4}$ m; $(1) \to K_{cg} = 9.8 \cdot 10^{-6}$ s^{-1}; $n(t_h) = 764764$ m^{-3}; $V_*(t_h) = 3.72 \cdot 10^{-6}$ m^3; $V_{ad} = 4.5 \cdot 10^{-5}$ m^3.
Law of conservation of mass: $V_*(t_h) \, n(t_h) = 0.278 \approx V_0 \, n_0 = 0.322$; $\Delta_V \, n = 14$ %.
Technological parameters for coalescence conditions (symbol ') during agitation and sedimentation.
Agitation:
$(4) \to \Delta E' = \Delta E'_S = 0 \to \Delta E'_d = E_a + E_g - E_v = 6498 \cdot 10^{-12}$ N m; $R' = 1.17 \cdot 10^{-3}$ m; $K'_{cg} = 1.58 \cdot 10^7$ s^{-1};
$(7) \to t'_{cl} = 9.13$ s; $(5) \to N'_* = (E'_d \, \rho_{av} \, V_a)/(\rho_L \, V_0 \, t'_{cl}) = 40.227$ w $\to N'_* = N_{*exp}$; $\Delta N_* = 0.5$ %.
Sedimentation:
$r'_S = d'_S / 2 = 0.5 \sqrt[3]{(6 \, V_* \, t_h)/\pi} = 9.612 \cdot 10^{-3}$ m; $h_S = 8.583 \cdot 10^{-3}$ m; $(3) \to R'_S = 0.165$ m; $K_{cgS} = 4040$ s^{-1}.

Time of sedimentation: $(7) \to t_S = 2141$ s $= 35.7$ min.
Liquid volume of phosphorus after sedimentation: $V_{ph} = V_a - V_w - V_{ad} = 0.0287$ m$^3 \approx 0.8 \, V_a$.

The obtained value for time of sedimentation t_S matches condition $n(t_S) = 1$ m^{-3} of merging all phosphorus into one large drop in the volume of the apparatus, which is equal 1 m^3. In reality the volume of secreted phosphorus $V_*(t_S)$ cannot exceed the difference between the volume of apparatus V_a and the volume of water V_w and impurities V_{ad} that are present in sludge: $V_{ad} \approx 4 \pi n_0 (r + 0.5 h_\delta)^2 h_\delta + V_{mpw}$, in which V_{mpw} - the volume of free mineral particles in dispersion medium - water. Parameters V_a, V_w, V_{ad} and limitation of mixing duration $t = t_h$ are set by the regulation process.

CONCLUSIONS

The results of this research phase show that coagulation and coalescence models of "rich" (60 - 80 % P_4) phosphorus-containing sludge with hydro-mechanical mixing and following sedimentation can be used as an application to resolve the problem of additional secretion of yellow phosphorus from phosphorus-containing sludge. The main results of mathematic and physical models discussed above are:

- The results showed compliance with the law of conservation of mass, that means that production $n(t)$ $V_*(t)$ of concentration and average volume of aggregates of particles is constant within mixing and sedimentation of phosphorus-containing sludge.

- There is a concretized conception of the coalescence energetic barrier for the particles of phosphorus-containing sludge. The results showed the prevailing impact of the surface energy of particles ($E_a + E_g$) and the energy of mixing E_d in the process of coalescence.

- For conditions of compete coalescence of initially discreet particles within the time of mixing and sedimentation ($\Delta E = \Delta E_S = 0$) we obtained analytical formulas for time t_{cl} and power N_* of coalescence and functional dependence which allows us to define the time of aggregates sedimentation t_S and the volume of secreted phosphorus from sludge V_{ph}.

- The above obtained formulas became a basis for explore mechanisms of coagulation and coalescence of phosphorus-containing sludge in order to utilize it. These can be also applied for practical calculations of mixing processes of different types of dispersions, such as suspensions and emulsions in different dynamic conditions of their interaction.

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