



Studies of Acid Activation and Thermodynamic Characteristics of Aluminosilicates in Sorption Process of Phosphorus Release from Sludges

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ABSTRACT

One of the actual problems of the phosphoric industry is complex usage of all got raw materials and processing of technogenic waste with receiving products. One of the main waste of phosphoric production are the phosphorus-containing sludges which are formed on stages of condensation of vaporous phosphorus. Despite numerous researches on suppression and processing of phosphoric sludges, today the universal way of their processing meeting the requirements of phosphorus production isn't found yet. In this regard, we offer a sorption method of phosphorus release from phosphorus-containing sludges. Various aluminosilicate minerals, including bentonites, vermiculites, refractory clays, etc. can act as sorbents. The specified minerals possess high sorption ability with an advanced surface. Results of thermodynamic researches of heterogeneous system phosphorus - water - solid mineral impurity are given. The thermodynamic probability of the main of reaction and systems characteristic for sorption process of phosphorus release from sludges is shown. For modifying the surface of minerals of the montmorillonite group entering into bentonites and vermiculites acid activation is used. For increase in hydrophilic surface of minerals are considered exchange cations of Al^{+3} , H^+ , Na^+ . It is shown that hydrophilic materials can be received at normal saturation by exchange cations. At its supersaturate hydrophilily can reach initial (before processing) values.

Keywords: Sorbents, Vermiculite, Bentonite, Montmorillonite, Thermodynamics, Acid activation, Hydrophilily.

INTRODUCTION

In the course of phosphorus production is formed a quantity phosphorus-containing sludges which depend on many factors-qualities and

preparation mode of raw materials, technological mode of carrying out process, etc. The problem of utilization of sludges, despite significant progress in this question, at the existing enterprises still remains actual problem¹⁻³.

Therefore, the researches directed to search for new ways of refining the phosphorus-containing sludges with usage sorbents on the basis of the bentonites possessing the developed mesoporosity are of a great interest.

Such sorbents containing up to 70% pores in the conditions of dynamic process are capable to absorb effectively organic and mineral impurity stabilizing a phosphorus emulsion in water. Adhesion of droplets of phosphorus a sorbent is followed by spreading on the surface of the solid body, with subsequent agglomeration under the influence of superficial energy. The formed large drops easily separate from sorbent by gravity⁴.

Bentonite clays represent available sorbents for various substances such as ions of heavy metals, organic compounds, etc. Sorption happens due to existence in composition of clays of layered silicates (smectit) such as montmorillonite, illit^{5,6}.

The main rock-forming mineral of aluminosilicates is montmorillonite which structure includes layers of silicate-oxygenous tetrahedrons between which are concluded aluminum oxide octahedrons. Feature of montmorillonite structure is extending crystal lattice due to which mineral can be modified by large organic molecules therefore the area of practical applications of vermiculites and bentonites sharply extends.

Acid activation of clays is a widespread method of receipt of porous sorbents for organic and inorganic substances. Activation shall be cost-efficient. When carrying out handling of initial substances acid it is necessary to aim to use whenever possible more diluted acid, and also to low temperatures and time of activation^{7,8}.

Washing of clay from excess of acid is quite labor-intensive process therefore in most cases it is necessary to calculate previously optimum concentration of acid, considering features of a chemical composition of natural clay, and also availability of impurity in them. It is known that at the initial stage of acid activation exchange cations are replaced on hydrogen ions, so-called N-bentonite turns out. Further depending on concentration of

acid, there is a washing away of structural cations in following order: $Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+}$.

The crystal lattice of all smectit consists of several layers. 3 layers enter into elementary cell which form: extreme top and lower layers of a package consist of tetrahedrons of Al, SiO_4 and are called tetrahedral. Between tetrahedral layers is located layer consisting of octahedrons of Al and Fe, called octahedral. The three-layer package has the negative charge caused by replacement of trivalent elements (Al, Fe) in an octahedral layer on bivalent elements (Mg, Fe) or tetravalent Si on trivalent Al in a tetrahedral layer. The option is possible when the negative charge of a package is caused by replacement reactions, as in octahedral, and tetrahedral layers.

Due to a negative charge, on the surface of a package settle down positive one - two - and trivalent cations. It is, mainly, Na, K, Ca, Mg and Fe. As a result of interaction with water around these cations hydrate covers can be formed and the aggregate packages at the same time bulks up. It is characteristic that the volume of a hydrate cover for different cations is various. Ions of alkaline metals and first of all sodium possess the greatest hydrating ability. Significantly the smaller hydrating ability ions of alkali earth metals possess: calcium and magnesium.

The specified feature of smectit to bulk up, increasing in volume at 2-20 times extremely important property for their industrial usage. Among smectit montmorillonite in which the main exchange cation Na possesses the highest bulking-up ability. These bentonites have received the name of alkaline bentonites. Bentonites in which among exchange cations Ca prevails have received the name of calcic. Except Ca at montmorillonite in a significant amount there can be Mg. In some bentonites magnesium holds the prevailing position in relation to calcium. Most often are met calcium-magnesian (alkali-earth). Calcic and calcium-magnesian bentonites can be transferred to the category sodium by their processing by solutions of sodium salts. Such sodium bentonites are called activated, and process of ion-exchange replacement with activation.

It should be noted that the choice of acid depends on the chemical composition of initial clay. Nitric and sulfuric acids easily oxidize organic components which are present at samples of clays. Hydrochloric acid promotes transfer of smectit to the N-form without collateral processes of oxidation. Therefore most often hydrochloric acid is applied to acid activation of clays.

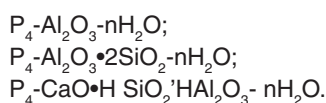
The choice of acid type and definition of optimum conditions of acid activation of clays with preservation of structure of clay minerals is the major task. The research on the influence of impact of the diluted solutions of phosphoric acid on the chemical composition and structure of vermiculites and bentonites of the South Kazakhstan minefields is conducted in the given work. The choice of phosphoric acid for activation is caused by the fact that the fulfilled sorbents on the basis the aluminosilicate of minerals, can be used for receiving the phosphor fertilizers where phosphorus with alkaline metals is the main component for fertilizers.

MATERIALS AND METHODS

The method of intensive hashing for receiving homogeneous mass of the studied clays, a centrifugation method was used for fraction separation in the given work. Chemical and mineralogical structures of tests were analyzed by means of the chemical analysis and on the scanning electronic microscope "JEOL JSM 700 F"⁹.

The thermodynamic analysis is carried out by means of the program HSC-5.1 complex of the Outokumpu companies founded on the fundamental principle of a minimum of energy of Gibbs.

Considering conditions of formation of phosphoric sludges and chemical composition, and also adsorption with use of bentonites thermodynamic modeling of the working systems characteristic of the adsorptive process of release of phosphorus of phosphoric slime is carried out to areas 283-343 K with various pressure of the following systems^{10,11}.



The full thermodynamic analysis of systems was carried out with usage of the program HSC-5.1 complex Finnish metallurgical the Outokumpu companies, the minimum of energy of Gibbs based on the fundamental principle taking into account that

$$G(x) = \sum_{a=1}^f \cdot \sum_{j=1}^{i_a} X_j \left(C_j + \ln \left(\frac{X_j}{X_a} \right) + \ln y_j \right) \rightarrow G(x)_{min} \quad \dots(1)$$

at restrictions in a look:

$$\begin{cases} \sum_{j=1}^m a_i X_j = b_i \\ \sum_{j=1}^{L_a} X_j = X_a \end{cases} \quad \dots(2)$$

where f – a total number of phases of system; b_i – a total number of moles of an independent component i in the system; C_j – empirical thermodynamic function; X_a – total number of moles of a phase and in system; X_j/X_a – a molar share of dependent j -of a component in the phase a .

Distribution of elements and structure of a gas phase of systems were considered in temperature area (T) 283-343K.

Graphic dependence of change of elements distribution and connections of working stoichiometric structure (in kg) from temperature of process of phosphorus release from aluminosilicate calcium mixes has been defined.

Acid activation of bentonites clay was carried out on the known techniques⁶.

RESULTS AND DISCUSSIONS

System $P_4-Al_2O_3-nH_2O$

The system in the studied area of temperatures 283-343K is characterized by participation in interaction of 17 connections: $PH_3(g)$, $H_2(g)$, SiO_2 , H_3PO_4 , $P_4O_{10}(g)$, $P_2O_3(g)$. The main connections by a quantitative index are P, Al_2O_3 , $AlPO_4$, $H_2(g)$.

Quantitative data on the interaction of substances in the final interval of temperatures $T=343\text{K}$ at change of number of water moths with 0,5 to 2,0 are provided in table 1.

The analysis of quantitative indexes of the main participants of system on change of number of water moths confirms proportional dependence of change of phosphorus mass and formation of phosphate of aluminum and phosphine (table 1).

Extent of phosphorus transition to the AlPO_4 connections and $\text{PH}_3(\text{g})$ were counted at $T=343\text{K}$ and value of moths number H_2O from 0,5 to 2,0. at $n=1$

$$\alpha_{\text{P}(\text{AlPO}_4)_2} = 0,223 \cdot 48,781 = 10,88\% \text{ at } n=0,5$$

$$\alpha_{\text{P}(\text{AlPO}_4)} = 0,223 \cdot 24,57 = 5,48\%$$

$$\alpha_{\text{P}(\text{PH}_3)} = 0,7352 \cdot 0,088 = 0,065\% \text{ at } n=1,5$$

$$\alpha_{\text{P}(\text{AlPO}_4)} = 0,223 \cdot 73,164 = 16,32\%$$

$$\alpha_{\text{P}(\text{PH}_3)} = 0,7352 \cdot 0,28 = 0,21\% \text{ at } n=2,0$$

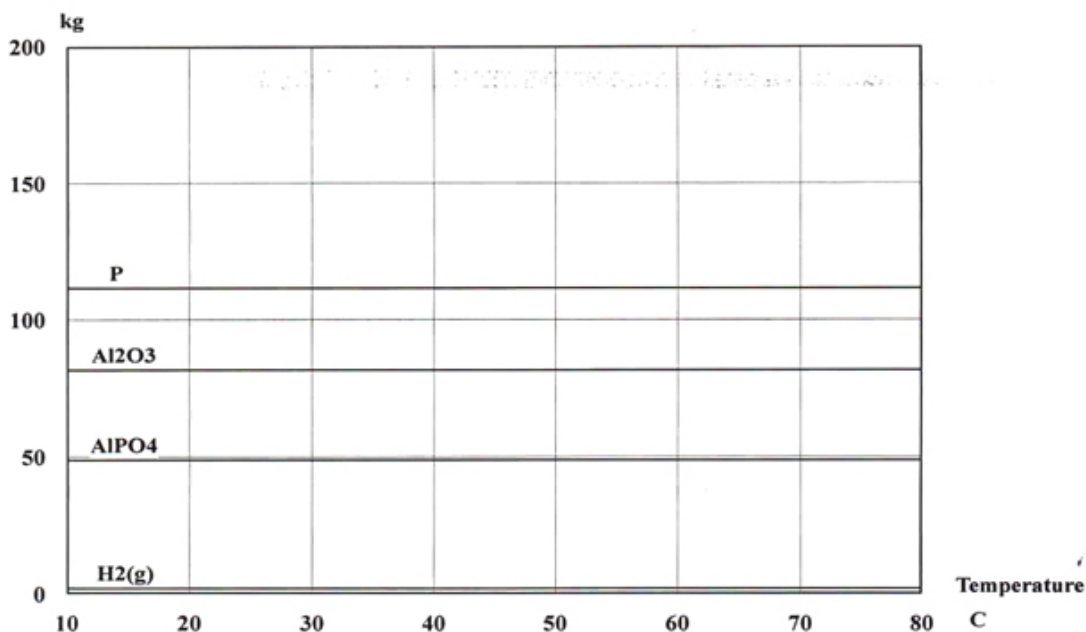
$$\alpha_{\text{P}(\text{AlPO}_4)} = 0,223 \cdot 97,561 = 21,76\%$$

$$\alpha_{\text{P}(\text{PH}_3)} = 0,7352 \cdot 0,371 = 0,28\%$$

It should be noted that at increase in number of water moths with 1,5 to 2,0 substantial increase of phosphorus transition to AlPO_4 from 16,32 to 21,76% is observed. Transition of phosphorus to phosphine is increased to 0,28% at $n=2,0$.

System $\text{P}_4\text{-Al}_2\text{O}_3 \cdot 2\text{SiO}_2\text{-nH}_2\text{O}$

24 connections participate in the studied area of temperatures 283-343K in interaction. The main characteristic connections are P, SiO_2 , Al_2O_3 , AlPO_4 , $\text{N}_2(\text{g})$. Nature of dependence of change



Temperature:	283.150 K
Pressure:	1.000 bar
Raw Materials:	kmol
$\text{N}_2(\text{g})$	1.0000E-01
Al_2O_3	1.0000E+00
H_2O	9.9999E-01
P	4.0034E+00

Fig. 1: Influence of temperature on equilibrium distribution of the $\text{P}_4\text{-Al}_2\text{O}_3\text{-nH}_2\text{O}$ system at $n=1$

of quantitative indexes of formation of these connections on temperature, demonstrates minor changes in process of temperature increase with 283 to 343K.

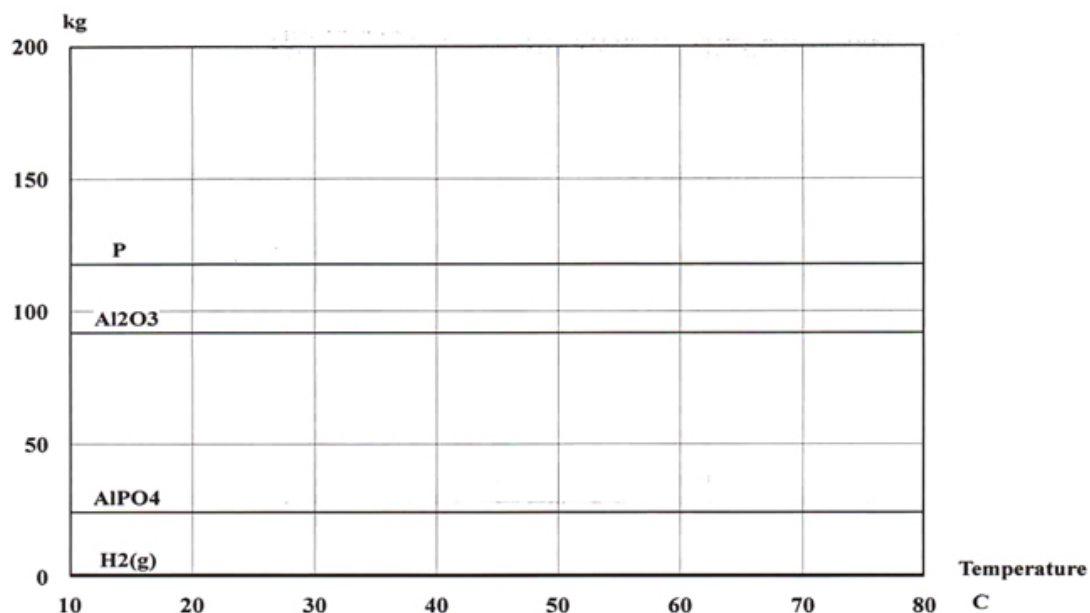
Quantitative tabular data of the formed connections from keeping in system of number of water moths from 0,5 to 2,0 are provided in table 21. The general regularity of settlement indicators is that in process of reduction of amount of phosphorus in the system sharp increase in formation of phosphate of ammonium is observed, at increase in system of number of water moths from 0,5 to 2,0.

Thermodynamic modeling of the systems characteristic of phosphorus release from phosphoric slime with using silicate, alum silicate connections corresponding to betonies clays has shown the general regularities of formation of H_3PO_4 and PH_3 (g) in the studied systems. And, formation of H_3PO_4

in process of increase in number of moths of H_2O on 0,5 to 2,0 increases to 29,7%. The $P_4-Al_2O_3-nH_2O$ and $P_4-Al_2O_3 \cdot 2SiO_2-nH_2O$ systems have the general nature of formation of $AlPO_4$. The maximum extent of transition of phosphorus to $AlPO_4$ is observed in the $P_4-Al_2O_3-nH_2O$ system at number of water moths $n=0,5$ reaches the maximum value of 29,8%.

For using betonies as sorbents they were subjected to heat treatment at temperatures of 500-900°C within 1-4 hours. Bentonite clays were crushed, mixed with water, granulated in spherical shape with a diameter of 8-12 mm, further dried in air within a day. Granules were exposed to heat treatment in the muffle furnace and mechanical durability which results are shown in table 2 is determined.

The results of heat treatment has shown at a temperature of 300°C that with increase in duration



Temperature:	283.150 K
Pressure:	1.000 bar
Raw Materials:	kmol
N2(g)	1.0000E-01
Al2O3	1.0000E+00
H2O	4.9958E-01
P	4.0034E+00

Fig. 2: Influence of Temperature on Equilibrium Distribution of the $P_4-Al_2O_3-nH_2O$ System at $n=1,5$

of roasting diameter of granules of bentonite clays of minefields Syrdarya and Darbaza are increased to 8-10%. Heat treatment of samples of 500°C clays of Darbaza minefield leads to destruction of granules structure. It can be explained, insignificant inclusions of ferrous connections as a part of clays which at thermal influence are characterized by transition of Fe (II) → Fe (III) providing high extent of gas generation in a consequence bringing to destruction of granules.

Bentonite clays are characterized by existence of the main mineral of montmorillonite which structure includes layers of silicate oxygenous and aluminium oxygenous connections. The main characteristic of montmorillonite is the extending crystal lattice due to which bentonite clay is capable

to distend actively therefore the area of practical applications of bentonite clays extends. In this regard for increase in durability and porosity of granules of bentonite clay activation methods by hydrochloric acid, and also with an additive are carried out to composition of clay of waste high aluminate and silicate waste of coal mining. For carrying out researches of activation of bentonite clay were used fractions of clays of Syrdarya and Darbaza minefields and waste of coal mining of the Lenger minefield in the ratio 70:30,80:20. Results of the received researches on chemical activation of bentonite clay with use of additives of waste of coal mining are given in tables 3 and 4. The analysis of the received results demonstrates and the fact that at increase in concentration of HCl contents alkaline and alkali earth decreases by 50% of-90%. At the

Table 1: Equilibrium quantitative distribution of the main connections in system $P_4-Al_2O_3-nH_2O$

n	Input	kg	%	Output	kg	%	
1	1,0	P ₄	124	50,86	P ₄	111,496	45,70
		Al ₂ O ₃	101,961	41,79	AlPO ₄	48,781	20,0
		H ₂ O	18,015	7,38	H ₂ (r)	2,005	0,82
					Al ₂ O ₃	81,569	33,43
					Other compounds	0,125	0,05
	Total	243,976	100		243,976	100	
0,5	0,5	P ₄	124	52,77	P ₄	117,756	50,11
		Al ₂ O ₃	101,961	43,39	Al ₂ O ₃	91,752	39,05
		H ₂ O	9,007	3,84	AlPO ₄	24,37	10,37
					H ₂ (r)	1,002	0,43
					PH ₃ (r)	0,088	0,04
	Total	234,968	100		234,968	100	
1,5	1,5	P ₄	124	49,02	P ₄	105,243	41,60
		Al ₂ O ₃	101,961	40,30	AlPO ₄	73,164	28,92
		H ₂ O	27,022	10,68	Al ₂ O ₃	71,376	28,21
					H ₂ (r)	2,006	0,79
					PH ₃ (r)	0,28	0,11
	Total	252,983	100	Other compounds	0,914	0,37	
					252,983	100	
2,0	2,0	P ₄	124	47,33	P ₄	98,986	37,76
		Al ₂ O ₃	101,961	38,92	AlPO ₄	97,561	37,22
		H ₂ O	36,03	13,75	Al ₂ O ₃	61,177	23,34
					H ₂ (r)	4,009	1,53
					PH ₃ (r)	0,377	0,14
	Total	261,991	100		261,991	100	

Table 2: Results of heat treatment of bentonite clays of two minifields

Number of sample	Temp., °C	Diameter of granules before burning, mm	Diameter of granules after burning, mm			
			1 hour	2 hour	3 hour	4 hour
1 Syrdarya	300	8-11	9-11	9-12	11-12	12-13
	500	8-11	10-11	11-12	11-12	12-13
	700	8-11	10-12	12-13	11-12	12-14
2 Darbaza	300	8-10	8-12	12-13	11-13	9-12
	500	Destruction	-	-	-	-
	700	Destruction	-	-	-	-

Table 3: A chemical composition of samples of bentonite clay with an additive of waste of coal mining at a ratio 80:20

Sample	Initial test of clay	Activated 0,1 M HCl clay	Activated 1,5 M HCl clay
Substance composition		Composition, %	
SiO ₂	51,2	52,4	53,2
Al ₂ O ₃	12,2	14,01	13,94
Fe ₂ O ₃	7,81	8,05	6,42
CaO	0,86	0,29	0,09
MgO	1,47	0,89	0,73
K ₂ O	0,92	0,91	0,88
Na ₂ O	0,54	0,19	0,04
SO ₂	0,013	0,012	0,05
TiO ₂	1,09	1,12	0,91

Table 4: A chemical composition of samples of bentonite clay with an additive at coal mining waste at a ratio 100:30

Sample	Initial test of clay	Activated 0,1 M HCl clay	Activated 1,5 M HCl clay
Substance composition		Composition, %	
SiO ₂	58,1	58,4	59,3
Al ₂ O ₃	13,4	14,7	14,56
Fe ₂ O ₃	8,15	8,07	7,15
CaO	0,95	0,45	0,10
MgO	1,25	1,17	1,23
K ₂ O	0,95	0,98	0,96
Na ₂ O	0,65	0,35	0,26
SO ₂	0,028	0,025	0,10
TiO ₂	1,23	1,27	0,98

same time, the content of silicon increases by 2%, aluminum of 13%. Results of the analysis of chemical activation with an additive of waste of coal mining are characterized by minor improvements of indicators what without additive.

On result of chemical activation of bentonite clays hydrochloric acid concentration of 0,1 M observes decrease in maintenance of cations such as, by Ca^{2+} , Mg^{2+} and Na^+ . It should be noted that concentration of ions decreases by 53,7%, 0,7% and 46% respectively. Concentration of ions of aluminum and silicon when processing by hydrochloric acid concentration of 0,1 M and 1,5 M slightly increases that demonstrates preservation of structure of clay minerals.

CONCLUSIONS

Thus, by means of a program complex the full thermodynamic analysis of system phosphorus - mineral impurity – water is carried out. Equilibrium distribution of elements and connections in the considered systems is defined. Characteristic dependences of change of quantitative indices on formation of these connections are studied.

Acid activation of samples of bentonite clays with an additive of carboniferous materials and without them is carried out. It is shown that the additive of coal mining waste promotes some increase the quality indicators of the process.

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