Influence of Lignin-Like Additives on the Solubility of Mechanically Activated Phosphates

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Abstract

The influence of mechanical activation conditions on the solubility of phosphate compounds of phosphorites from the Burenkhan deposit of Mongolia in 2 % solution of citric acid and in water medium was studied. It is established that the efficiency of planetary mill EI-2×150 is considerably higher than that of vibration mill DRM-75T. As the time of activation is increased to 100 min, the assimilable phosphorus content of natural phosphates is heightened. For the vibration mill DRM-75T it is optimal to use as the milling body a steel cylindrical core with a mass of 1000 g. A mechanical activation of phosphorites was carried out with adsorbing additives in the form of lignosulphonates, zeolites and brown coals. The content of assimilable and water-soluble phosphates was determined depending on the composition and nature of additives. As the activation is continued when the amount of assimilable phosphorus is increased, the amount of water-soluble phosphorus is diminished. When lignin-containing additives are used, products with a high degree of phosphorus transition to 2 % solution of citric acid are formed with respect to activated phosphorites under equal treatment conditions. In this way, the possibility of obtaining organophosphorus fertilizers of prolonged action with various assimilability of phosphorus is estimated.

INTRODUCTION

Production of phosphate fertilizers is based on processing of apatite ores and phosphorites. The classical methods of processing of phosphate raw materials are multistage, associated with expenditure of acids for decomposition of the ore and make strict demands of the mineral composition [1].

Among non-traditional ways of processing of natural phosphates, the mechanochemical method is the simplest and ecologically safest one due to the absence of outflows and discharges into the atmosphere [2]. At the same time, there exists a problem of utilization of large-tonnage wastes of the wood working industry containing compounds of lignin which is a promising source of organic nutrient substance [3]. Return of the organic substance lignin to the biological circulation, improvement of the ecological situation, increasing of production of local fertilizers – all this determines the necessity and expediency of processing the lignin into a fertilizer [4].

The use of lignin- and zeolite-containing additives and brown coals is in many respects determined by their adsorption capacity that create conditions for absorption of nutricious substances and their subsequent gradual release. Besides, the enumerated additives can be used both as soil structure formers and as sorbents decreasing the amount of harmful elements in the soil.

The goal of the present work is to study the solubility of phosphate compounds in mechanical activation with adsorbing additives.

EXPERIMENTAL

The objects of study were samples from Mongolian deposits: phosphorites of the Burenkhan deposit with a P_2O_5 content of 36.3 % (No. 1) and 40.8 % (No. 2), zeolites from the Tsagaan Tsabyn deposit, and brown coals from the Ulaan Oboo deposit. The lignosulphonates used in this work containing 2.88 % SO_3 were obtained from wood sawdust whose lignin content was 26–28 %. Mechanical activation was carried out in mills of two types: vibration mill DRM-75T and planetary mill EI-2×150. An 8 g phosphorite weight treatment in the vibration mill was carried out in steel cups with balls of the total mass of 500 g and a cylindrical core of 1000 g for 10, 15, 30, 50, 70, 100 and 120 min. Activation of phosphorite of 3 g in the planetary mill was performed in steel drums with balls with a diameter of 3 mm and the total mass of 200 g for 15 min.

In the initial and in the activated samples, the content of assimilable citric acid-soluble (in a 2 % solution of citric acid) phosphates (CSP) and water-soluble phosphates (WSP) was assayed by differential photometric technique [5]. For estimation of phosphate solubility, according to the method, sample mass of 2 g, and for estimation of the influence of various additive of different nature on the content of soluble phosphate forms taking into account the additive percentage, the weights were heavier than 2 g. X-ray phase analysis was carried out on the device DRON-UM1 with CuK_α irradiation and a Ni filter with a rate of 4 deg/min. Infrared spectra were recorded on devices SPECORD-75 IR using KBr-containing tablets.

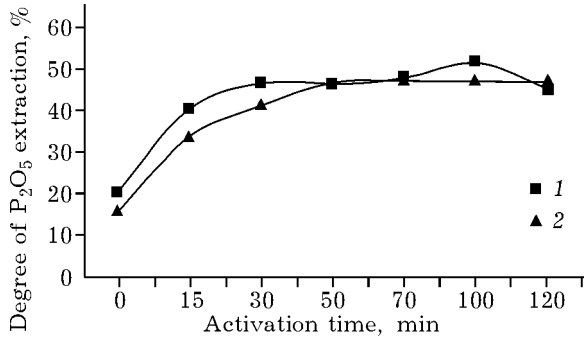

Fig. 1. Influence of the duration of mechanical activation on the extraction of citric acid soluble phosphorus in phosphorites: *1* – specimen No. 1, 36 % P_2O_5; *2* – specimen No. 2, 40.8 % P_2O_5.

RESULTS AND DISCUSSION

Studies of solubility in mechanical activation of phosphorites from the Burenkhan deposit

The task of processing the phosphate raw material consists in transfer of their phosphates to a form assimilable by plants. One of methods of estimating the assimilability of the phosphorus oxide P_2O_5 contained in the fertilizer is the solubility of phosphate compounds in artificial solutions whose acidity is close to that of soil solutions [6].

According to the data of X-ray phase analysis and IR spectroscopy, the initial phosphorites contain quartz, fluorine- and carbon apatites.

We studied the citric acid and water solubility of phosphates with various additives depending on the conditions of mechanical activation, *i. e.* treatment time, type of activators and the mass of the milling bodies.

For the phosphorites of the Burenkhan deposit, the dependence of CSP on the duration

TABLE 1

Phosphate content in phosphorites from the Burenkhan deposit after mechanical activation for 15 min in a planetary EI-2×150 and a vibration DRM-75T mills

Sample number	Total phosphorus (P_2O_5) content, %	Phosphate (P_2O_5) soluble in 2 % citric acid solution, %			
		EI-2×150		DRM-75T	
		absolute	relative	absolute	relative
1	36.3	21.6	59.0	14.63	40.30
2	40.8	23.6	57.8	13.62	33.39

TABLE 2

Influence of lignosulphonates on P_2O_5 extraction into water and in 2 % citric acid solution in phosphorite sample No. 2

Mixture composition, %		Activation time, min	Degree of P_2O_5 extraction, %			
Phosphorite	Lignosulphonate		CSP		WSP	
			absolute	relative	absolute	relative
100	–	0	6.25	15.31	Traces	Traces
		5	7.24	17.76	»	»
		10	8.49	20.83	»	»
		15	10.62	26.03	»	»
		30	11.74	28.79	»	»
		50	14.12	34.62	»	»
		70	14.12	34.62	»	»
		100	14.12	34.62	»	»
88.89	11.11	5	–	–	3.96	12.29
		10	11.41	27.96	2.49	6.14
		15	11.79	28.89	1.53	3.76
		30	13.59	33.30	Traces	Traces
		50	11.50	28.18	»	»
		70	10.93	26.78	»	»
		100	11.29	27.67	»	»
80	20	5	–	–	13.43	32.92
		10	15.95	39.09	10.15	24.87
		15	16.35	40.07	9.47	23.21
		30	14.52	35.58	2.41	5.91
		50	13.10	32.10	Traces	Traces
		70	13.41	32.87	»	»
		100	11.68	28.64	»	»
66.6	33.4	5	15.55	38.11	16.08	39.4
		10	16.68	40.88	19.15	46.93
		15	19.20	47.05	24.75	60.66
		30	18.37	45.02	15.78	38.67
		50	20.80	50.99	12.97	31.8
		70	27.75	68.01	12.39	30.36
		100	28.20	69.10	13.36	32.74
50	50	5	–	–	8.24	20.18
		10	15.92	39.00	10.74	26.32
		15	17.86	43.33	16.62	40.72
		30	24.00	58.82	23.68	58.02
		50	20.96	51.37	28.00	68.62
		70	21.72	53.23	31.2	76.46
		100	22.54	55.24	27.26	66.8

TABLE 3

Influence of zeolites on P_2O_5 extraction into water and in 2 % citric acid solution in phosphorite sample No. 2

Mixture composition, %		Activation time, min	Degree of P_2O_5 extraction, %			
Phosphorite	Zeolite		CSP		WSP	
			absolute	relative	absolute	relative
94.11	5.89	15	7.89	19.34	–	–
		30	7.07	17.34	–	–
		50	9.25	22.67	–	–
		70	10.20	24.99	–	–
		100	11.29	27.67	–	–
88.89	11.11	5	7.72	18.95	–	–
		10	7.44	18.23	–	–
		15	11.25	27.50	–	–
		30	13.12	27.72	–	–
		50	15.18	37.20	–	–
		70	15.88	38.92	–	–
		100	15.32	37.54	–	–
80	20	5	7.65	18.75	–	–
		10	8.90	21.81	–	–
		15	9.83	24.09	–	–
		30	12.18	29.87	–	–
		50	14.52	35.58	–	–
		70	14.68	35.98	–	–
		100	15.00	36.76	–	–
66.6	33.4	5	9.81	24.04	1.30	3.15
		10	9.81	24.04	1.57	3.85
		15	10.35	25.36	0.82	2.01
		30	12.13	29.73	0.49	1.20
		50	14.82	36.32	1.00	2.46
		70	15.88	38.92	0.93	2.26
		100	16.53	40.51	1.12	2.74
50	50	5	11.60	28.43	–	–
		10	10.94	26.81	–	–
		15	11.76	28.82	–	–
		30	12.52	30.68	–	–
		50	14.60	35.78	–	–
		70	16.18	39.65	–	–
		100	18.20	44.60	–	–

Note. Here and in Table 4 the dash means that no measurement has been made.

of mechanical activation in the vibration mill is presented in Fig. 1. One can see that the extraction of assimilable phosphorus is increased as the treatment time is prolonged to 100 min, whereupon a decrease sets on. Depending on the mechanical activation time in the vibration mill, the peaks on diffractograms are widened, their number and intensity being decreased.

At the same time, the efficiency of mechanical activation is considerably influenced by the mass of the milling bodies. Thus, when a cylindrical core with a mass of 1000 g is used, the degree of transition of P_2O_5 to citric acid solution is considerably higher than when the activation is made with steel balls of 500 g (Fig. 2).

TABLE 4

Influence of brown coals on the extraction of P_2O_5 into water and in 2 % citric acid solution in phosphorite sample No. 2

Mixture composition, %		Activation time, min	Degree of P_2O_5 extraction, %			
Phosphorite	Brown coal		CSP		WSP	
			absolute	relative	absolute	relative
90.96	9.04	5	6.45	15.82	–	–
		10	6.61	16.20	–	–
		15	6.60	16.17	–	–
		30	7.78	19.06	–	–
		50	10.28	25.19	–	–
		70	10.96	26.86	–	–
		100	13.34	32.69	–	–
94.11	5.89	5	5.15	12.62	–	–
		10	5.93	14.53	–	–
		15	6.12	15.00	–	–
		30	10.33	25.31	–	–
		50	12.37	30.31	–	–
		70	10.89	26.69	–	–
		100	11.43	28.01	–	–
80	20	5	5.93	14.53	–	–
		10	7.33	17.96	–	–
		15	7.56	18.52	–	–
		30	8.58	21.02	–	–
		50	9.37	22.96	–	–
		70	10.31	25.26	–	–
		100	10.62	26.02	–	–
66.6	33.4	5	6.42	15.73	1.30	3.18
		10	7.48	18.33	3.75	9.19
		15	6.72	16.47	4.12	10.09
		30	8.14	19.95	1.38	3.38
		50	9.61	23.55	1.12	2.74
		70	10.18	24.95	0.93	2.27
		100	10.75	26.34	1.30	3.18
50	50	5	6.40	15.68	–	–
		10	7.42	18.18	–	–
		15	6.66	16.32	–	–
		30	7.94	19.46	–	–
		50	8.56	10.98	–	–
		70	8.56	10.98	–	–
		100	10.76	26.37	–	–

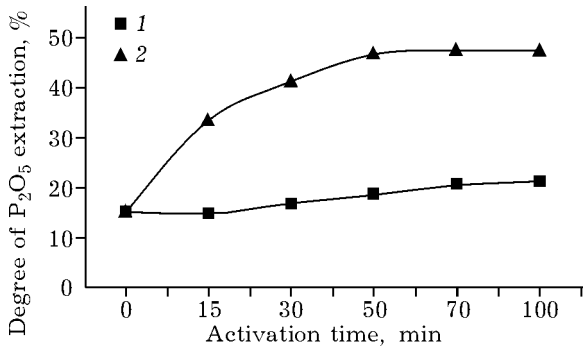

Fig. 2. Influence of the mass of milling bodies on the extraction of assimilable phosphorus in a phosphorite sample No. 2: *1* – 500 g steel balls, *2* – 1000 g cylinder.

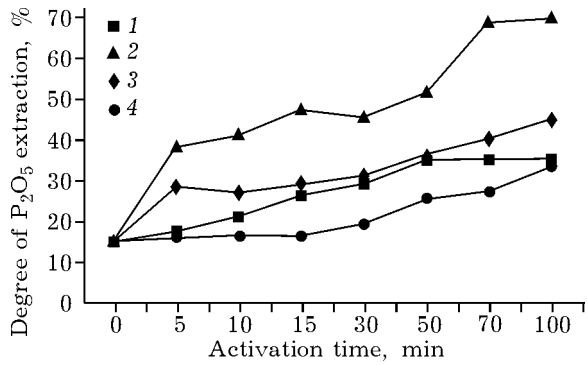

Fig. 3. Influence of additives on the extraction of assimilable phosphorus in mechanical activation: *1* – without any additive, *2* – with lignosulphonate, *3* – with zeolites, *4* – with brown coals.

Comparative data for vibro- and planetary mills tell in favour of the latter, since the solubility achieved after a 15 min activation in the planetary mill exceeds by 1.4–2 times similar data for the vibration mill (Table 1).

Use of adsorbing additives for regulation of solubility of phosphate compounds

For the purpose of estimating the influence of adsorbing additives on the phosphate solubility degree, a combined mechanical activation of phosphorite No. 2 was carried out with additions in the vibration mill using 500 g steel balls and increasing the activation time to 100 min with various ratio of components. From the experimental data it follows that when lignosulphonates are used as additives, activation is accompanied by a negative correlation for the assimilable and water-soluble phosphorus. With different composition of the mixture, an increase of CSP content is accompanied by a decrease of WSP, which, according to our hypothesis, is accounted for by the adsorption properties of lignosulphonates (Table 2). The optimal composition of the phosphorite: lignosulphonate mixture was estimated at 2 : 1. Therein, the degree of extraction of assimilable phosphorus reached 69.10 %, which is by 34.48 % higher tnan that from activated phosphorites under the same activation conditions.

In the process of the experiment it was established that when zeolites and brown coals are used as additives, the solubility of phosphates is lower than when lignosulphonates are used (Tables 3, 4). With respect to efficiency of mechanical activation one can draw up the following increasing series: brown coals, zeolites, lignosulphonates (Fig. 3).

CONCLUSION

From the data obtained it follows that as the duration of treatment of phosphorites of the Burenkhan deposit in the vibration mill increases to 100 min, the content of soluble phosphate forms in them becomes higher.

When lignosulphonates are added in the process of activation in the vibration mill products with a high degree of P_2O_5 transition to citric acid solution are formed. Thus, when the phosphorite : lignosulphonate ratio is 2 : 1, the extraction of assimilable phosphorus increases by 1.5–2 times. By means of varying the composition and the nature of additives in the process of mechanical activation it is established that, judging by thesoluble phosphate content, lignosulphonates display a higher efficiency than zeolites and brown coals.

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