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ON THE POSSIBILITY OF PHOSPHATES REMOVAL FROM WASTE WATERS AND OBTAINING OF MIXED FERTILIZERS WITH NATURAL ZEOLITES

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ABSTRACT

The possibility of utilization of phosphates' saturated zeolites as raw materials for the obtaining of mixed phosphorous fertilizers has been substantiated. Taking into consideration that the regeneration of the sorbing agent is economically baseless, the proposed alternative solution presents an interest.

It has been demonstrated that the adsorbed in the structure of the zeolite phosphate ions are in the form of P_2O_5, able to be assimilated. The cation less and modified forms of the different clinoptilolites' samples preserve their structure and adsorption capacity. The quantities of the total P_2O_5 and of the citrate's soluble P_2O_5 in the calcium and potassium modified forms are more important that in the natural zeolites. In spite of the lower content of able to be assimilated phosphorous in the potassium form in comparison with the calcium modified, the first one is recommended as a raw material for obtaining mixed phosphorous fertilizers, due to the introduction in the ground of the essential for the plants potassium.

INTRODUCTION

The widespread natural zeolites, including in our country, find a polyvalent application in several areas of the industry and the agriculture. Today predominates their use as catalysts or catalysts' matrix in petrochemical industry and oil refining processing, as adsorbing agents in order to solve ecological problems, as nutritional additives to insure useful and essential microelements for the breeding and the plant-growing.

Their unique adsorption's and molecularly sieve's properties initiated the studies on the natural clinoptilolites, beginning from the 60th years of the XX century, in order to remove phosphate ions from waste and washing waters from phosphates' productions. The economically baseless regeneration of phosphates' saturated adsorbing agents represents a prerequisite for the search of an alternative solution for their posterior utilization. It is known that the mechanic mixture of clinoptilolite and super phosphate (Lian, et al., 1978) ensures the more complete phosphorous assimilation by the plants and the possibility of supplementary ground's enrichment with useful microelements, as well as the amelioration of its structure.

For this purpose, the synthesis of phosphorous containing zeolites has been tested, by substitution of Al from the network with phosphorous, applying a controlled copolymerization and coprecipitation in homogeneous phase. However, the characteristics of the obtained products are their reduced thermic stability and adsorption capacity, that sometimes reach 50 % of that of the non-containing phosphorous zeolites (Flanigen, et al., 1971).

That why the investigations on the phosphates' removal by adsorption with natural zeolites and the use of the enriched sorbing agents as a raw material for the obtaining of mixed mineral fertilizers represent an interest.

Currently phosphates' removal is carried out by neutralization with lime or by intermediary flocculation with polyelectrolytes (0,20 - 0,25 mg/cm^3) with pH $\approx$ 11. The degree of extraction reaches 90 %.

RESULTS AND DISCUSSIONS

In order to study the sorption's mechanism of the phosphate ions on clinoptilolote, comparative researches on the sorption capacity of samples coming from some bulgarian deposits and one from Georgia, whose chemical composition is presented in table 1, have been accomplished.

Table 1. Chemical composition of the tested clinoptilolites' samples

№	Sample	Chemical composition, %							Silicate module SiO_2/Al_2O_3	Mineral content in the sample, %
		SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3		
1	BG-green	66.60	11.32	1.58	3.37	2.16	0.23	0.88	9.98	90
2	BG-pink	68.90	11.63	1.93	3.76	1.85	0.37	0.88	10.05	90
3	BG-white	66.40	12.30	1.87	3.50	2.00	0.52	2.21	9.16	70
4	Georgia-Dzegvi	68.04	14.41	2.08	1.80	6.87	2.20	3.93	8.30	65

Admixtures of β-quartz, β-tridymite, orthoclase, albite, anorthite, biotite, chrysotile (in the green clinoptilolite BG-green) have been established.

The preliminary researches concern studies on the influence of particle dimensions on the adsorption capacity of the samples. The experiments have been carried out using three samples of each type with particles' dimensions in the interval respectively 0.2 – 0.5 mm, 0.8 – 1.0 mm, 1.2 – 1.5 mm. The effect of the granulation composition of the clinoptilolite on the adsorption is presented in fig. 1. The obtained results allow to admit that the following tests have to continue by using samples with particles' dimensions 0.2 – 0.5 mm.

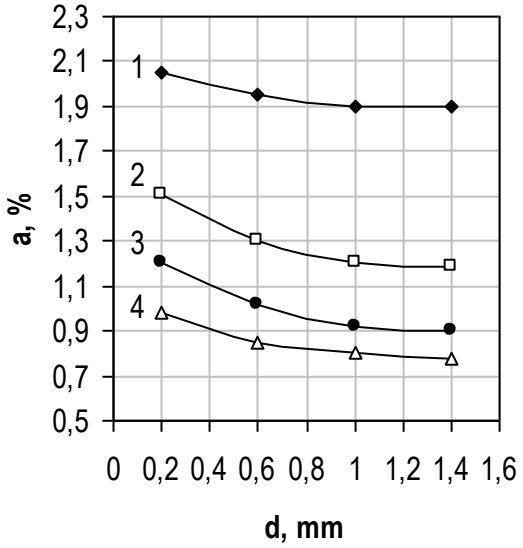

Figure 1. Influence of the clinoptilolite particles'dimensions on the sorption capacity, %:
1) BG-green; 2) BG-pink; 3) BG-white; 4) Dzegvi.

In fig. 2 are presented the adsorption isotherms obtained at ambient temperature and with particles' dimensions of clinoptilolite 0.2 – 0.5 mm. A direct relationship between the adsorption capacity and the stability towards acids has been observed, as well as of the purity of the mineral. The important quantity of limestone in the zeolite from Dsegvi - Georgia explains its higher capacity against P_2O_5, that will be mentioned again below.

It is known that an important characteristic of the phosphorous fertilizers represents the quantity of the able to be assimilated P_2O_5, i.e. phosphorous soluble in water and in citrates.

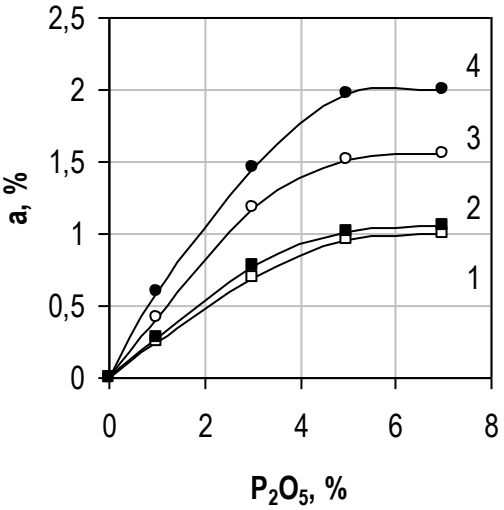

Figure 2. Adsorption isotherms of P_2O_5 at 20°C on clinoptilolite with particles'dimensions 0.2 – 0.5 mm:
1) BG-green; 2) BG-pink; 3) BG-white; 4) Dzegvi.

It is interesting to test under what form is the adsorbed phosphate. For this purpose an experiment has been accomplished, during which samples of clinoptilolite with similar particles' dimensions have been saturated with an aqueous solution of P_2O_5 with a concentration of 3%. Then the samples have been treated respectively with Petermann reagent (ammoniac solution of ammonium citrate), with distilled water and with HCl 20 %. The quantities of the different forms of phosphates in the filtrate have been established, as shown in table 2.

Table 2. Solubility of the adsorbed by the clinoptilolite phosphorous

№	Clinoptilolite	SiO_2/Al_2O_3	Water soluble		Citrate soluble		Acid soluble		Total P_2O_5, %
			%	% total	%	% total	%	% total	
1	BG-green	9.98	2.09	91	0.07	3.00	0.14	6.00	2.30
2	BG-pink	10.05	2.46	88	0.10	5.50	0.24	8.50	2.80
3	BG-white	9.16	9.55	77	0.37	3.00	2.48	20.00	12,40
4	Dsegvi	8.32	9.76	63	0.78	5.00	4.65	30.00	15.19

The obtained results allow concluding the following:

1. As much the silicate module is great, i.e. as much the quantity of aluminum in the structure is small, as much the adsorption capacity of the clinoptilolite expressed via P_2O_5 is low and as much is the relative content of its soluble in water form.

2. The soluble in citrates phosphorous that, as it is known, is a phosphate of alkaline earth elements and especially of the calcium is the best to the plants form of P_2O_5, able to be assimilated. Its constant quantity in all samples with the exception of that from Dsegvi, in which it is approximately 1.5 times greater represents again a proof for the higher quantity of limestone in this sample, who's chemical and Rö-structural analysis confirm that the $CaCO_3$ content reaches 40 %.

3. In order to increase the sorption activity of the clinoptilolite's natural tuff, expressed via P_2O_5 and taking into consideration data in table 2, experiments using aluminum less and modified

samples have been carried out. For this purpose, the zeolite BG-green has been treated with HCl 4 mol/L at 25°C by applying a standard methodology [3] and a cation exchange has been accomplished, transforming it in a hydrogenated form. The partial Al substitution in this case increases the silicate module and leads to a supplementary widening of the structural pores. This insures a higher adsorption capacity. Parts of the obtained dehydrogenated form are transformed in calcium and potassium forms by treatment with $CaCl_2$ 1 mol/L and with KCl 1 mol/L respectively. This kind of modification is chosen in order to increase the quantity of the citrates' soluble phosphorous and to ameliorate the nutritional properties of the mixed fertilizer by the addition of a third important for the plants element, the potassium. Aside this, it is known, that when in the structure of the zeolite are introduced cations with greater dimensions than those in the natural zeolites, its thermic stability and elements' arrangement in its structure are ameliorated. Thermodynamic and Rö-structural studies show that the skeleton is conserved, while the results of the chemical analysis are given in table 3.

Table 3. Chemical composition of the modified clinoptilolites' samples

№	Sample	Components, %							SiO_2/Al_2O_3	Degree of aluminum exchange, %
		SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3		
1	BG-green	66.60	11.32	1.58	3.37	2.16	0.23	0.88	9.98	-
2	H-BG-gree	70.30	9.14	0.46	2.86	0.56	0.19	0.55	1.,08	19.25
3	Ca-BG-gree	71.01	9.20	0.65	2.98	4.20	0.18	0.68	13.11	18.72
4	K-BG-gree	70.85	9.08	0.55	5.25	1.16	0.20	0.86	13.26	19.78

The obtained modified and cations less forms have been saturated with P_2O_5 in static conditions and at ambient temperature. Each of the samples, in quantity of 1.0 g, has been treated during 1.5 – 2 hours with H_3PO_4, containing 4 % of P_2O_5. It has been established after analysis, that the calcium form contains 4.76 % of total P_2O_5 and 0.15 % of citrate soluble P_2O_5, while in the potassium form these values are 4.07 % of total P_2O_5 and 0.13 % of citrate soluble P_2O_5, what is approximately 50 % more than of P_2O_5 forms in the natural clinoptilolite.

In spite of the lower adsorption capacity of the potassium form, it is recommended as a raw material for obtaining mineral mixed fertilizers, because of the introduction of the third essential for the plants' grow element, the potassium.

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