

PHOSPHORUS REMOVAL FROM SOLUTIONS BY CARBONACEOUS WASTES

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Abstract. The suitability of fine carbonaceous wastes, decomposed by heating at 700–900°C, for the removal of phosphates from solutions was established. The phosphate binding ability of the wastes depended directly on the content of free calcium and magnesium oxides, which, in its turn, depended on the composition of the wastes and the conditions of their heating. To completely remove phosphate from waste water containing less than 300 mg $\text{PO}_4 \cdot \text{l}^{-1}$, it was necessary to add 1 kg of the sorbent made from limestone heated at 900°C to 1 m³ of waste water. Insoluble amorphous and finely crystallized Ca and Mg phosphates with a high specific surface area were formed.

Key words: limestone, dolomite, sorption, waste water, binding ability.

INTRODUCTION

The phosphorus contained in waste waters discharged into water bodies is not yet sufficiently removed. Mechanical-biological treatment removes only 20–30% of the phosphorus. The amount of phosphorus discharged annually into the Baltic Sea is evaluated at about 1400 tonnes, mainly in the form of orthophosphate ion. In 1996 at least 90% of phosphorus had to be removed from waste water. This means that the concentration of phosphorus in the water could not exceed 1.5 mg·l⁻¹ (4.5 mg $\text{PO}_4 \cdot \text{l}^{-1}$) [1]. This can be achieved by additional chemical treatment, either by precipitation of phosphates with lime or some other reagent or by its fixation on the surface of solid sorbents [2–4].

In order to decrease the cost of phosphorus removal from waste water, the possibilities of using industrial wastes – fine fractions formed in crushing carbonaceous rock – were investigated in the present study. The results obtained were compared with those achieved by using oil shale ash.

EXPERIMENTAL

The chemical composition of the rock samples used and of the products of their heating are presented in Table 1. The sample of dolomite represents the waste of crushing Adavere dolomite rock, the sample of limestone – the same from Maardu limestone. Adavere rock waste contains 46.1% CaCO_3 and 43.3% MgCO_3 , Maardu rock waste – 71.4% CaCO_3 and 8.8% MgCO_3 . The rock samples were heated in a muffle furnace at different temperatures (in the interval from 600 to 900°C) for two hours. The thermograms of the samples detected by an MOM derivatograph in an air stream are presented in Fig. 1. The lower than expected content of free oxides (CaO , MgO) in the heated samples can be explained by their partial reaction with the accompanying rock minerals (silicates etc.) during heating. The sample of oil shale ash is typical Baltic Power Plant cyclone ash.

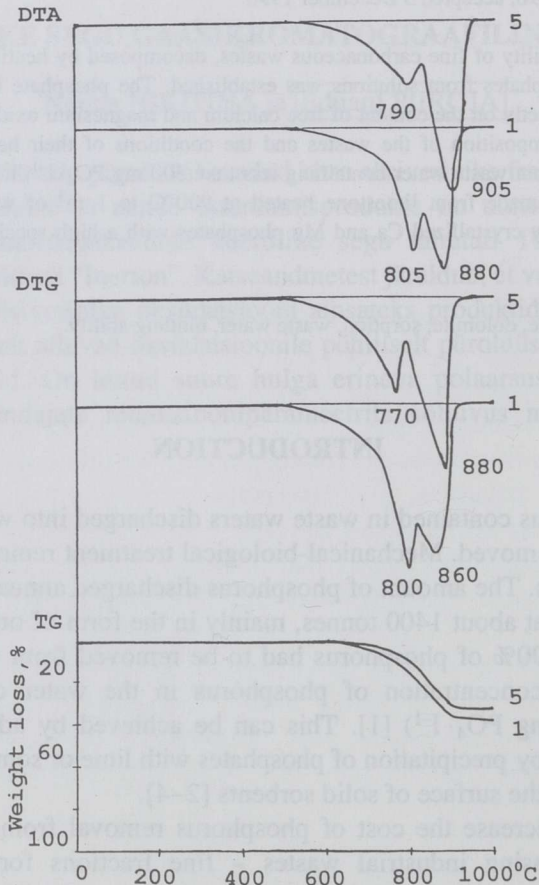


Fig. 1. Thermograms of dolomite (1) and limestone (5), rate $10^\circ/\text{min}$.

Table 1

Composition of the sorbents

Sample*	Sorbent	Content, Wt %					Specific surface area, m ² /g	(CaO+MgO) _{free} moles/100 g
		CaO	CaO _{free}	MgO	MgO _{free}	insoluble residue		
1	Adavere dolomite	25.80	0	20.76	0	14.30	2.1	0
2	Dolomite heated at 600°C	27.04	0.13	21.76	2.80	15.00	2.6	0.071
3	Dolomite heated at 700°C	27.80	0.13	21.80	5.90	15.30	3.9	0.148
4	Dolomite heated at 900°C	43.00	27.05	34.60	6.20	23.83	5.0	0.636
5	Maardu limestone	40.00	0	4.22	0	13.60	5.0	0
6	Limestone heated at 700°C	42.10	0.70	4.44	0.85	14.32	3.0	0.0335
7	Limestone heated at 900°C	61.50	41.30	6.50	0.17	20.92	3.2	0.741
8	Oil shale ash	49.10	18.70	5.10	n.d.	24.50	1.5	0.333

* The particle size of samples 1-7 was 0.5-2 mm; n.d., not determined.

Both batch and continuous column experiments were carried out. The main objective of the batch experiments was to compare the phosphorus binding ability and the kinetics of different sorbents to find out the best ones. For this purpose the phosphate binding ability ($\text{mg PO}_4 \cdot \text{g}^{-1} \text{ sorb.}$) and rate ($\text{mg PO}_4 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) were calculated. The aim of the column experiments was to investigate the influence of the flow rate of the solution on the phosphate binding kinetics, to establish the breakthrough time of the phosphate, the saturation time of the sorbent, and the binding capacity of the sorbent.

In the batch experiments a fixed amount of the sorbent (1 or 5 g) was added to one litre of the solution. The mixture was stirred in an Erlenmeyer flask with a magnetic stirring bar at room temperature. Pure KH_2PO_4 was used for preparing the phosphate solution [2]. The phosphate content in the solution varied in an interval of 25–1030 $\text{mg PO}_4 \cdot \text{l}^{-1}$. The lowest value was selected as a rather common one in waste water, the highest – for a more rapid saturation of the sorbent and, thus, for the determination of its binding capacity. During stirring, the samples of the mixture were taken out and after filtration the pH and the content of phosphate were determined.

The column experiments were carried out by pumping the initial solution ($25 \text{ mg PO}_4 \cdot \text{l}^{-1}$) through a glass column (diameter 34 mm) with 100 g sorbent (height of the sorbent layer 100 mm), varying the flow rate of the solution (0.6, 1.2, $2.4 \text{ l} \cdot \text{h}^{-1}$). Sample 3 (Table 1) with 0.5–2 mm particle size was used. During the experiments the pH and the phosphate content in the outflowing solution were fixed.

For the determination of the composition of the phases and the identification of the compounds formed at sorption, methods of chemical analyses, infrared spectroscopy (Specord 75IR), and X-ray diffraction techniques (Dron 3M) were used. Phosphate was analysed by the colorimetric method with the formation of phosphorus–molybdenum yellow complex, calcium by the volumetric method using KMnO_4 solution, and magnesium by atomic absorption spectrometry (AAS-1). The content of free CaO in the heated samples was determined by the ethylene glycol method [5], the content of free MgO by the method presented in [6]. The specific surface area of the samples was determined by the BET method (sorptionmeter EMS-53).

RESULTS AND DISCUSSION

The experiments with initial dolomite and limestone showed that they bind almost no phosphate. The phosphate binding agents of heated carbonate rocks are first of all free oxides (CaO, MgO) formed by heating. Depending on the origin of the rock and the heating conditions, the formation of free oxides starts at 500–600°C, first as a result of dolomite decomposition. When heating is continued

at higher temperatures, two opposite processes take place: decomposition of carbonates, which brings about an increase in the content of free oxides, and the reaction of free oxides with silicates and other components of the rock, which decreases the content of free oxides and increases the insoluble residue content (Table 1). In our experiments the content of free oxides reached its maximum at 900°C (which is the temperature that guarantees the maximum content of free CaO in carbonaceous rocks), amounting to 33.2 and 41.5% by mass (or 0.636 and 0.741 moles per 100 g) for the heated dolomite and limestone, respectively. For oil shale ash these indicators are lower (18.7% and 0.333 moles).

Besides the free oxides content, the amount of phosphate bound by a sorbent depends also on the mass ratio of the sorbent to the solution, the initial content of phosphate, the pH of the solution, and the time of interaction (Table 2).

In the batch experiments phosphate was bound with the sorbent in a maximum amount when the samples were heated at 900°C and solutions with a higher phosphate content were used (experiments 5 and 11) and when the sorbents were totally saturated by phosphate or the same samples, but solutions with lower phosphate content were used and phosphate was completely removed from the solution (experiments 4 and 10). In these experiments 300–600 mg PO₄ was bound per 1 g sorbent.

The binding ability of the samples heated at lower temperatures was much lower, first of all due to the smaller content of free oxides. If we express the phosphate binding in moles PO₄ per moles of free oxides, i.e. by the ratio $S = \text{moles PO}_4 : \text{moles (CaO + MgO)}_{\text{free}}$, omitting experiment 2 where a big excess of sorbent was used, this ratio varies within the limits 0.25–1.1. Such a wide interval shows that the binding capacity of the sorbent was not always fully used (at lower values of the ratio S) and phosphates with different PO₄:(CaO + MgO) ratio were precipitated as a result of the reactions. At pH values higher than 9–10 mainly (Ca, Mg)₁₀(PO₄)₆(OH)₂ (with the ratio PO₄:(CaO + MgO) = 0.6) and (Ca, Mg)₃(PO₄)₂ (0.67), and at pH values lower than 9–10 (Ca, Mg)HPO₄ (1.0) should be formed. The results of the experiments carried out under comparable conditions indicate that when samples with a higher MgO content (in comparison with CaO content) are used the degree and rate of phosphate removal from solutions are lower. This phenomenon can be explained by a lower solubility of Mg(OH)₂ and a higher solubility of magnesium phosphates compared to the respective compounds of calcium.

The sorbents react with phosphates relatively rapidly, mainly during the first 5–15 minutes, depending on the origin of the sorbent and the ratio of the sorbent to solution (Fig. 2). For complete phosphate removal in case the phosphate content in the solution is lower than 300 mg · l⁻¹, it is enough to take 1 g of heated at 900°C limestone per 1 litre of the solution and to have them interact for 5 min.

Oil shale ash is somewhat inferior to heated limestone in the ability and rate of phosphate removal; nevertheless, it can be used successfully for the same purpose.

Table 2

Phosphorus removal parameters of different sorbents in batch experiments

No. of exp.	Sorbent	Temperature, °C	Sorbent-solution ratio, g·l ⁻¹	Concentration of solution, mg PO ₄ ³⁻ l ⁻¹		Time, min	pH	Binding ability, mg PO ₄ ³⁻ g ⁻¹	Binding rate, mg PO ₄ ³⁻ ·min ⁻¹ , 0-5 min	Molar ratio PO ₄ ³⁻ /(CaO+MgO) _{free}
				initial	final					
1	Dolomite	600	5	300	185	240	8.5	23	0.52	0.338
2	Dolomite	700	5	25	2.7	60	9.4	4.4	0.14	0.0316
3	Dolomite	700	5	300	127.5	180	10.0	34.6	2	0.245
4	Dolomite	900	1	300	0	60	9.8	300	59	0.503
5	Dolomite	900	1	1032	474	300	11.2	558	66	0.937
6	Limestone	700	1	25	6.5	50	8.5	20.0	0.66	0.579
7	Limestone	700	1	50	23	15	8.2	27.0	4	0.847
8	Limestone	700	1	100	65	30	7.6	35.0	4	1.090
9	Limestone	700	5	300	123	120	9.0	35.6	3	1.113
10	Limestone	900	1	300	0	5	11.3	300	60	0.427
11	Limestone	900	1	1032	430	120	9.8	600	96	0.856
12	Oil shale ash	-	1	260	30	15	11.0	230	36	0.726

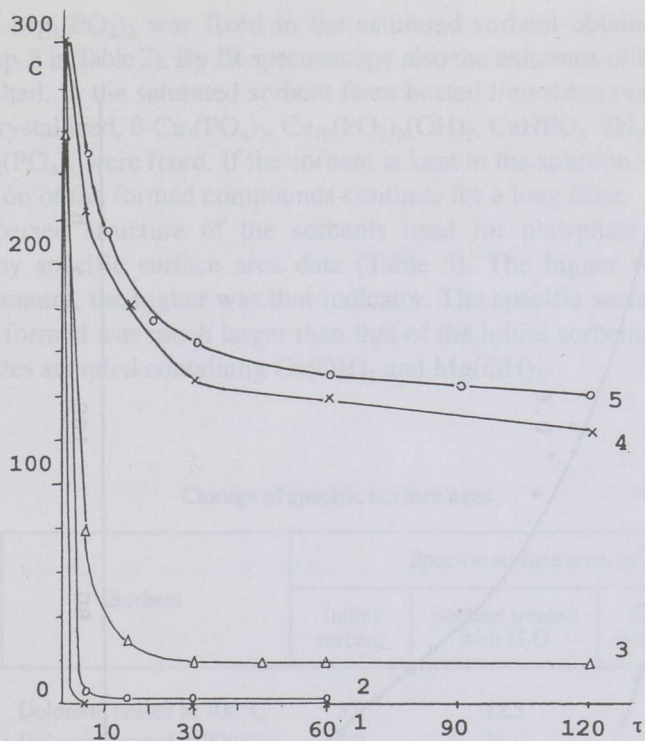


Fig. 2. Dependence of phosphate ion concentration (c , $\text{mg PO}_4 \cdot \text{g}^{-1}$) in the solution on contact time (τ , min) for different sorbents in batch experiments: 1, limestone 900°C ; 2, dolomite 900°C ; 3, oil shale ash, solid-liquid ratio $1 \text{ g} \cdot \text{l}^{-1}$; 4, limestone 700°C ; 5, dolomite 700°C , solid-liquid ratio $5 \text{ g} \cdot \text{l}^{-1}$.

The column experiments with dolomite heated at 700°C showed that at the beginning of the experiment the phosphate content in the outlet is equal to zero (Fig. 3). After the phosphate breakthrough at moment τ_1 , the phosphate content begins to increase and its initial value is achieved by the moment τ_2 . The time of sorbent saturation, τ_2 , is inversely proportional to the solution flow rate: 75–80 h by flow rate $1.2 \text{ l} \cdot \text{h}^{-1}$ and 35–40 h by $2.4 \text{ l} \cdot \text{h}^{-1}$. The amount of bound phosphate at the moment τ_2 does not depend on the solution flow rate and is the same in all three experiments – $24 \text{ mg PO}_4 \cdot \text{g}^{-1}$. It is lower than the value fixed in analogous batch experiments ($35 \text{ mg PO}_4 \cdot \text{g}^{-1}$). The reason might be a lower contact area between the phases as well as the leaching of part of the active magnesium and calcium compounds from the sorbent. If the purpose is to achieve final phosphate content on a level $4.5 \text{ mg PO}_4 \cdot \text{l}^{-1}$ and to carry out the purification process with a high intensity, the actual amount of phosphate bound by the sorbent is about $7\text{--}8 \text{ mg PO}_4 \cdot \text{g}^{-1}$.

The phosphates precipitated are mainly amorphous, especially when a magnesium-rich sorbent is used. Therefore, in X-ray diffraction analysis only the

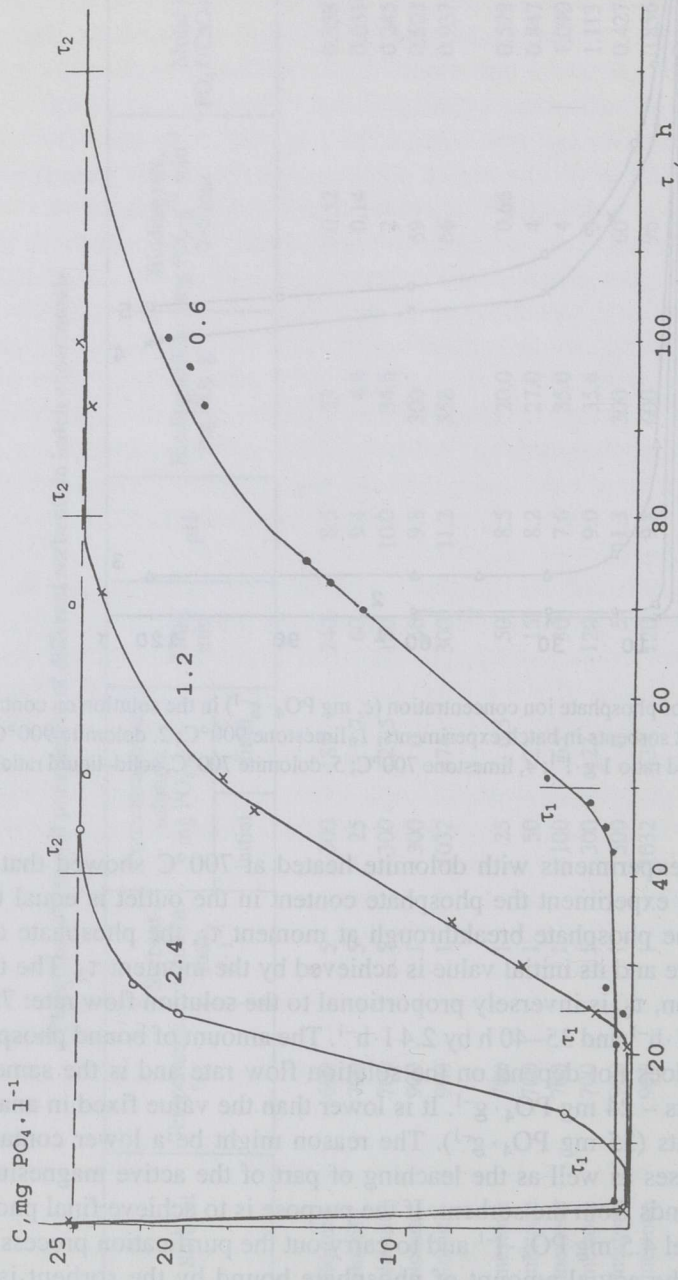


Fig. 3. Comparison of PO₄ breakthrough curves at different flow rates (l·h⁻¹) in continuous column experiments, sample No. 3 in Table 1. c, phosphate ion concentration; τ, contact time; τ₁, phosphate breakthrough moment; τ₂, sorbent saturation time.

presence of $Mg_3(PO_4)_2$ was fixed in the saturated sorbent obtained by heating dolomite (exp. 5 in Table 2). By IR spectroscopy also the existence of $MgHPO_4 \cdot 3H_2O$ was established. In the saturated sorbent from heated limestone (exp. 11), which was better crystallized, $\beta-Ca_3(PO_4)_2$, $Ca_{10}(PO_4)_6(OH)_2$, $CaHPO_4 \cdot 2H_2O$, $Mg_3(PO_4)_2$, and $Ca_4Mg_5(PO_4)_6$ were fixed. If the sorbent is kept in the solution, crystallization and nucleation of the formed compounds continue for a long time.

The dispersed structure of the sorbents used for phosphate removal was confirmed by specific surface area data (Table 3). The bigger was the bound phosphate content, the higher was that indicator. The specific surface area of the compounds formed was much larger than that of the initial sorbents and also that of the hydrates sampled containing $Ca(OH)_2$ and $Mg(OH)_2$.

Table 3

Change of specific surface area

No. of experiment in Table 2	Sorbent	Specific surface area, $m^2 \cdot g^{-1}$		
		Initial sorbent	Sorbent treated with H_2O	Sorbent treated with PO_4 solution
3	Dolomite heated at 700°C	3.9	12.5	16.1
4	Dolomite heated at 900°C	5.0	33.6	52.4
9	Limestone heated at 700°C	3.0	7.0	14.5
10	Limestone heated at 900°C	3.2	21.7	100.0

The PO_4 content in saturated sorbents from dolomite and limestone was 38.4 and 40.7%, respectively, from which 93–98% is soluble in 2% citric acid solution. Consequently, the discarded sorbent can be used as phosphorus fertilizer.

CONCLUSIONS

1. The fine fractions formed as a waste by crushing limestone and dolomite that are heated for decarbonization can be successfully used for the removal of phosphate from waste water. The phosphorus binding ability of the sorbents depends on the composition of the initial material and the temperature of heating, most directly on the content of free calcium and magnesium oxides formed at heating. Samples of limestone waste heated at 900°C have the highest binding ability.

2. The amount of the sorbent required for phosphate removal depends on the initial and the permissible final content of phosphate in waste water. For complete removal of phosphate from waste water containing less than $300 \text{ mg } PO_4 \cdot l^{-1}$, it is

necessary to add to 1 m³ of water 1 kg of the sorbent prepared from limestone by heating it at 900°C. Phosphate fixation takes place mainly during the first 5–15 minutes.

3. By phosphate binding amorphous or finely crystallized calcium and magnesium phosphates are formed. As a result of phosphate precipitation the specific surface area of the sorbent increases up to ten times, amounting to 100 m²·g⁻¹. The discarded sorbent can be used as a phosphorous fertilizer.

4. The phosphate binding ability of oil shale ash is lower in comparison with the thermal treatment products of limestone due to its smaller content of free calcium oxide, nevertheless it can be successfully used for phosphate removal from waste water.

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FOSFAATIDE EEMALDAMINE LAHUSTEST KARBONAATSETE JÄÄTMETE ABIL

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On kindlaks tehtud karbonaatsete kivimite (dolomiit, lubjakivi) töötlemisel tekkivate ja 700–900°C juures kuumutatud heitmete sobivus fosfaatide eemaldamiseks lahustest. Nende fosfaadisidumisvõime sõltub otseselt vabade kaltsium- ja magneesiumoksiidide sisaldusest, viimane omakorda on seotud heitmete koostise ja nende kuumutamistingimustega. Protsessi tulemusel tekivad lahustamatud amorfsed ja peenkrustallilised suure eripinnaga Ca–Mg-fosfaadid.