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Original Research

Characterization of Opoka as a Basis for its Use in Wastewater Treatment

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Abstract

Opoka, as a silica-calcite sedimentary rock, occurs in south-eastern Europe and Russia. Stratigraphical studies down to 8 m depth were performed in Bełżec, Poland, where samples were taken for further analyses. Vertical layers represented a heavy-weight opoka consisting of relatively more $CaCO_3$ than the horizontal layers of lightweight opoka dominated by SiO_2. Opoka had a mean bulk density of 1.34 g/cm^3, a porosity of 44.5 % and a specific surface area of 64 m^2/g. Opoka, especially after heated to over 900^oC can be used as reactive filter media for phosphorus removal. Maximum sorption capacity was 119.6 g PO_4-P/kg. Element analysis of the rock did not reveal any anomaly from that expected, and it was concluded that its element content does not devaluate opoka as a sorbent used in ecological wastewater treatment .

Keywords: calcination, fertilizer, gaize, opoka, phosphorus sorption, Polonite®, reactive media

Introduction

Opoka belongs to the group of silica-calcite sedimentary rock, a marine deposit composed of the remains of minute marine organisms from the late Cretaceous period called Mastrych. This formation is mainly found in deep strata covering an area from the North Sea, Poland, Lithuania and Ukraine. Deposits are found in Russia as well [6,15]. In the southeastern parts of its distribution area in Poland, outcrops of opoka have been found [19] where it easily can be quarried. Turnał-Morawska [20] suggested the term opoka as it was used by Russian scientists. Kuźnicki et al. [12] and Buraczyński [3] distinguish opoka and "geza" among silica-carbonate rock. In Polish literature this type of rock can be classified either as geza (synonymous with gaize) when the silica content is high or as opoka when calcite dominate. Its high porosity and other properties made it excellent for insulation and for moisture protection.

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According to Russian literature, opoka has properties that qualify it for use in water purification [17]. The authors of this article have since 1995 put research efforts in the development of opoka as an industrial product for wastewater treatment. Due to its high $CaCO_3$ and SiO_2 content we first suggested a high sorption capacity of PO_3-P, but we also considered its metal removal properties. Water colored by dyes or humus can be cleaned efficiently by powdered opoka as found in a dye adsorption methylen-blue test [5]. Today, opoka is considered a promising sorbent in municipal wastewater treatment, as a result of research we headed [2, 4, 5, 8, 10, 11, 13, 14, 16]. Natural materials are more environmentally friendly and more effective for releasing P to plants in agricultural production after use in the treatment process, compared to the artificial precipitation chemicals [7, 11]. Other possibilities instead of using natural materials such as opoka to remove phosphate ions from aqueous solutions are to apply cementitious by-products like fly ash and blast furnace slags [1,8].

Fig.1. Soil profile down to 1.5 m showing superficial, horizontal layers of opoka.

A Swedish company is excavating and manufacturing opoka. From the raw material, a wastewater treatment product Polonite® is developed by a procedure of thermal treatment where the material is becoming more reactive for P sorption. There are many other possible uses of opoka. These include, for instance, its use as an addition for the production of Portland cement and for ceramic tile production.

The objectives of this study are to describe the chemical composition and some physical properties of the bedrock opoka and to evaluate its usefulness in wastewater treatment.

Materials and Methods

The samples of opoka were taken in Bełżec in south-eastern Poland. The altitude above sea level is 306 m. The samples were taken from depths of 1 to 8 meters in order to cover variation in the material (Figs. 1, 2). The material was dried in the air and then in an oven at 105°C. Then material was ground and sieved with a screen of mesh diameter 0.25 mm. For element analyses, samples of natural opoka (OPN-1, OPN-2) and samples of opoka calcinated at 900°C (OPC-1, OpC-2, OpC-3) were placed in a teflon vessel and soaked in 7 M nitrite acid in a microwave oven. Some oxides were determined after melting the samples with lithiummetaborate, followed by dissolution in diluted nitrite acid. A combination of ICP-AES and ICP-SFMS were used for analyses of the elements in solution. This was performed by SGAB Analytica, Luleå, Sweden. The pH of the opoka was determined in solutions with H_2O and in 1 M KCl at a proportion of 1:1.

The mineral composition of sample OPN-1 was investigated by means of X-ray diffractometer, a Philips PW 1729 with Cu Kα radiation (XRD). The description of the rock was made on the same sample by using a Leitz Ortholux polarisation microscope with transmitted and reflected light. One polished thin section was prepared. Transmission Electron Microscope (TEM) was used to study mineral crystals and Scanning Electron Microscope (SEM) to study remains of organisms forming the biogenic silica of the bedrock. Samples were prepared in vaccum, sprayed by silver and gold silt.

Density of the solid phase was determined by pycnometric method. Bulk density was determined by strew method using 100 cm^3 volume cylinder.

Total porosity (%) was calculated from the equation:

$$P = (\delta - \delta_b) / \delta \times 100$$

Where:
P = total porosity
δ = solid phase density
δ_b = bulk density

Specific surface area was determined according to the BET method (using a Micromeritics Flow Sorb II 2300 apparatus. Loss of ignition (LOI) was determined on 5 g samples of opoka in a muffle furnace at the following temperatures; 250, 500, 750, and 1000°C. After 2.5 hours heating and additional time of cooling in exsiccator, the weight of opoka was measured. The phosphate sorption capacity of natural opoka and opoka heated to the above-mentioned temperatures was performed by batch experiments. Artificial phosphorus solutions were prepared by dissolving K_2HPO_4 in distilled water. The amount of phosphate sorbed was calculated from the difference in

Fig.2. The bedrock opoka at approximately 5 m depth, appearing at this place in vertical layers.

Table 1. Chemical composition of natural (OPN) and calcinated (OPC) opoka.

Compound (% dry weight)	Natural opoka		Opoka heated at 1000 °C		
	OPN-1	OPN-2	OPC-1	OPC-2	OPC-3
SiO_2	52.10	37.20	52.50	40.20	25.40
CaO	19.30	28.20	32.30	42.60	51.30
MgO	0.69	0.58	0.78	0.71	0.70
Al_2O_3	5.75	3.82	5.67	4.25	3.08
Fe_2O_3	1.80	1.79	2.34	1.88	1.80
K_2O	1.05	0.71	1.14	0.70	0.35
Na_2O	0.13	0.12	0.19	0.09	0.05
TiO_2	0.37	0.24	0.35	0.27	0.18
P_2O_5	0.03	0.04	0.05	0.06	0.05
MnO_2	0.01	0.02	0.03	0.02	0.03
Summa	81.23	72.72	95.35	90.78	82.94
LOI	17.40	24.70	2.90	7.70	13.50
Total	98.63	97.42	98.25	98.48	96.44

concentration between the initial and final solution, i.e. when the concentration of the solute was in equilibrium with the sorbent. The phosphate concentration was analyzed colorimetrically by means of Flow Injection Analyzer (autoanalyzer Aquatech-Tecator).

Results and Discussion

In the area investigated, opoka is deposited as regular beds and formed in horizon layers. However, in the same stratigraphy are also found some vertical layers indicating tectonic processes, which took place during the Tertiary period (Figs. 1, 2). Opoka found in these layers is very hard, compact and enriched with calcium carbonate. Opoka consists mainly of SiO_2 and $CaCO_3$ (Table 1). The microscope investigation showed that opoka is rich in silica of organic origin. Remains of *Radiolaria*, diatomes and sponges are frequent (Fig. 3). Other main components are calcite, quartz, clay minerals and amorphous SiO_2. The calcite is mostly very fine grained but some crystals have also been observed (Figs. 4, 5). Crystalline goethite and hemathite were also observed on amorphous silica in opoka. In high magnification, using SEM, the occurrence of biofossils are visible (Fig. 6).

The chemical composition of opoka in its natural and calcinated forms is shown in Table 1. During thermal treatment, bounded water is evaporated at 100°C and crystal water at approximately 750°C, which causes

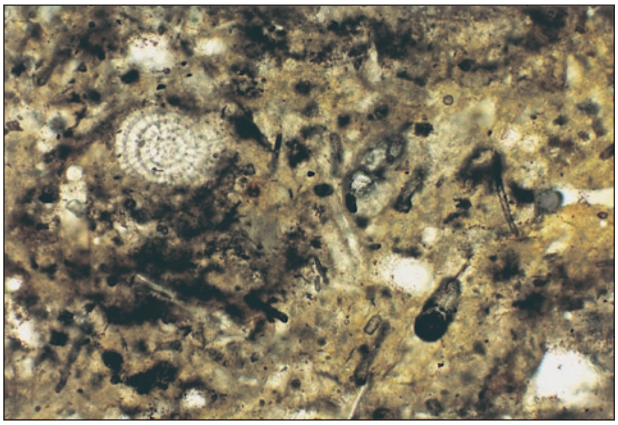

Fig.3. Photo showing different remains of fossil organisms, quartz and feldspar (white). Magnification 160x.

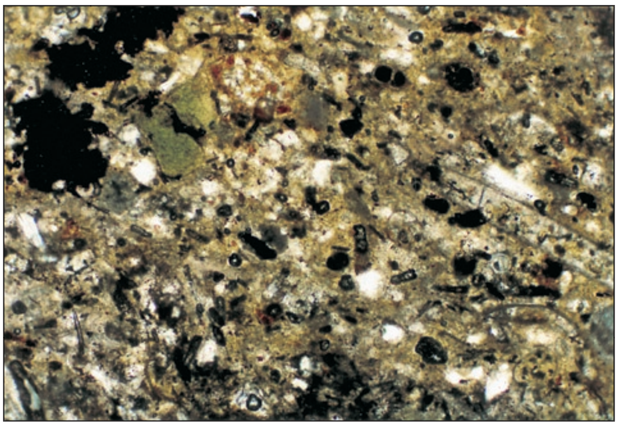

Fig.4. Photo showing different mineral particles; quartz (white), opak (black), clorite (green) and muskovite (white, left side). The material between consists of finegrained calcite, silica and clay mineral. Magnification 160x.

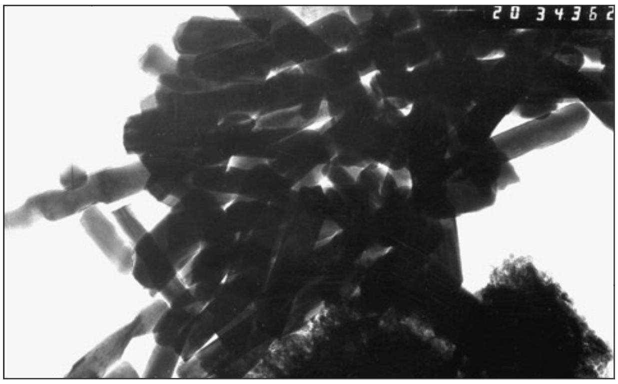

Fig.5. Visible needles in natural opoka (TEM, magnification 660x) interpreted as crystals of calcite.

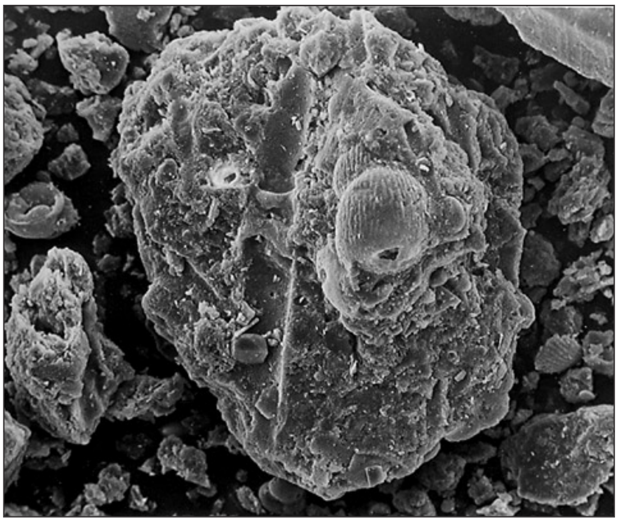

Fig.6. Remains of minute marine organisms in opoka (SEM, magnification 300x).

weight losses. Dissociation of calcium carbonate takes place and terminates in temperatures over 900^{o}C. However, calcinated opoka do not react with water as calcinated limestone do. It is suggested that the high content of silica is the reason for that behavior. However, the low water reactivity of calcinated opoka increases its usefulness in wastewater treatment.

In natural opoka the silica content range from 37.5 to 52.1%, while the calcium carbonate content range from 34.5 to 50.4%. Silica in the form of opal - $SiO_2 \cdot nH_2O$ (quartz occurring only in trace amounts), which is of biogenic origin (Figure 3), increases the total porosity of opoka (Table 3) and makes this bedrock soft and enhances its water holding capacity. Natural opoka has additional amounts of CaO (2.54%) not bounded as $CaCO_3$. It is suggested that this surplus of calcium comes from other minerals such as feldspars and others, which occur in trace amount in this material. Opoka with high content of SiO_2 and high porosity is called ”light opoka”. Also occurring is ”heavy opoka” in vertical layers as mentioned above, which has a more compact structure due to its higher content of $CaCO_3$.

Calcination of both kinds of opoka starts at an approximate temperature of 750^{o}C and terminates at 900^{o}C for light opoka, but over 1000^{o}C for heavy opoka. Heating of the latter one at 1000^{o}C up to 3 h does not even dissociate completely $CaCO_3$ to CaO and CO_2. However, some small amounts of dolomite (Ca, Mg)CO_3 was recognized, which can be a reason for the incomplete dissociation.

Aluminium as Al_2O_3 is a third component of opoka. This compound does not show great variation both in samples of natural and heated opoka (Table 1). Iron as Fe_2O_3 also occurs in opoka. This element has properties comparable with aluminium. Heating of opoka can slightly increase its content by oxidation of two valent Fe to three valent.

K, Mg, Mn, Na, Ti, and P are found in opoka, however occurring in trace amounts (Table 1).

The content of heavy metals and some other elements are shown in Table 2. The main trace element in opoka is strontium. According to Smulikowski [18], this element occurs in substantial amounts in all marine deposits, especially in calcareous rock. Strontium carbonate is accumulated by marine organisms and occurs in limestone and opoka, but not in the radioactive form. Thus, it is not dangerous for the environment. There are some contents of barium (Ba), wolfram (W), vanadium (V), chromium (Cr), zink (Zn), and zirconium (Zr). All these elements are accompanying deposits of marine origin and are at concentrations considered as general background in most soils. Zirconium silicate Zr(SiO_4) (also called zirconium) is a hard mineral and difficult for weathering but occurs in appreciable amounts in marine deposits.

Contents of trace elements in natural opoka in decreasing succession are as follows:

$$Sr > Zr > Ba > W > V > Cr > Zn > Sn > Ni > Y > La > Nb > Cu > Co > Sc > Be$$

There were only slight changes in the amount of trace elements in opoka after heating, except for strontium, which showed an increase of about 35 to 40% (Table 2). It has been emphasized that such contents of trace elements in opoka mentioned above do not devalue this bedrock material as a sorbent used in ecological wastewater treatment. We argue that opoka can be applied in cultivation as a silica-calcium-phosphorus fertilizer. Opoka, appropriate technologically prepared, is able to bound from 12 to 15% of dissolved phosphorus in comparison to dry weight material.

Heating of opoka gradually activates its sorption capacity because the physico-chemical properties are changed (Table 3). Natural opoka has a high pH (7.5-7.8), but remarkable increase in pH starts when opoka is heated over 750^{o}C, reaching pH values close to 13. This bedrock increases slightly its solid phase density from 2.52 g/cm^3 (OPN) to 2.94 g/cm^3(OPC) on average during heating

Table 2. Content of some trace elements in natural (OPN) and calcinated (OPC) opoka. The amount of several elements are under the detection limit of the instrument used (shown with <).

Element (mg/kg dry weight)	Natural		Heated at 1000°C		
	OPN-1	OPN-2	OPC-1	OPC-2	OPC-3
Sr	682.0	638.0	852.0	931.0	972.0
Zr	119.0	91.4	147.0	93.7	70.6
Ba	124.0	83.6	135.0	89.0	59.9
W	<52.9	<51.5	<54.4	<54.3	<55.8
V	52.1	35.0	49.0	42.3	30.7
Cr	46.8	31.4	50.0	41.5	39.5
Zn	31.2	31.6	54.0	49.1	28.1
Sn	<21.1	<20.6	<21.8	<21.7	<22.3
Ni	14.2	15.1	21.5	17.8	11.1
Y	12.2	13.4	13.8	11.0	7.5
La	15.0	7.3	14.4	11.2	<5.6
Nb	8.8	97.9	8.5	8.8	<5.6
Cu	<5.3	<5.2	<5.4	<5.4	<5.5
Co	<5.3	<5.2	<5.4	<5.4	<5.6
Sc	5.3	2.8	5.1	4.4	2.3
Be	<0.5	<0.5	<0.5	<0.5	<0.6

Table 3. Mean values of some physical properties of natural opoka and as heated at different temperatures. Measured P-sorption capacities are also given.

Properties	Natural Opoka	Heating temperature (°C)				Sum of LOI (%)
		250	500	750	1000	
Loss of ignition (LOI) (%)	-	2.40	3.40	4.40	20.00	30.20
Density (g/cm^3)	2.52	2.58	2.64	2.72	2.94	-
Bulk density (g/cm^3)	1.34	1.30	1.26	1.20	0.86	-
Porosity (%)	44.5	49.6	52.4	55.9	70.7	-
Specific surface area (m^2/g)	64	n.d.	n.d.	n.d.	0.7	-
pH (H_2O)	7.20	7.20	7.40	7.60	12.6	-
pH (KCl)	6.80	7.00	7.20	7.30	12.1	-
Sorption capacity PO_4-P (g/kg)	19.6	60.5	72.0	86.8	119.6	-

from room temperature to 1000°C. The high temperature treatment changes the colour of opoka, and it is possible that new minerals are created. The bulk density decreases when opoka is thermally treated at 1000°C 0.86 g/cm^3 on average (range 0.70-0.98). Total porosity of opoka increases parallel to the heating treatment. The transformation of $CaCO_3$ to CaO should leave some empty spaces after the release of CO_2; however, contradictory evidence shows that the specific surface decreased remarkably after heating (Table 3). Thermal treatment should be applied if better sorption and/or immobilization properties of opoka will be achieved for the removal of, for instance, phosphates, ammonium, other biogen elements and heavy metals. Due to the extraordinary properties of opoka, it should be considered as an industrial mineral and as a promising wastewater treatment material and sorbent, especially for phosphorus. When saturated with phosphorus after use in wastewater treatment, the material should be recycled in agriculture as a fertilizer and soil improver, especially for acid soils. Sorbed phosphorus can also be extracted easily from the opoka matrix by using chemical methods.

Conclusions

Opoka consists mainly of SiO_2 and $CaCO_3$. Depending on the ratio between those compounds opoka can be classified as light-weight (more SiO_2) or heavy-weight (more $CaCO_3$). Opoka has a potential to be developed as a product for wastewater treatment. Its unique natural properties can be exploited for the removal of phosphorus. The sorption capacity is very high, up to 119 g P/ kg material. The chemical composition of this silica-calcium rock is not dangerous for the soil environment. The heavy metal content equals that normally found in most agricultural soils. Hence, opoka can be used as a phosphorus sorbent in wastewater treatment and in agriculture as a multi-component fertilizer. However, in that situation its ability to trap heavy metals also has to be considered.

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