

ELECTROPLASMA ENRICHMENT OF NATURAL DIATOMITE

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Preliminary Note – Prethodno priopćenje

Method of electrohydraulic enrichment of natural diatomite from the Kazakhstan deposit as a multipurpose nano-material has been developed. Electrohydraulic method is based on separation of diatomite from the clay component under the influence of plasma energy arising in a short electric discharge. Complex study of enriched diatomite by spectral, X-ray diffraction (XRD), silicate (chemical) and thermal analysis methods was carried out. Independent methods of analysis applied show almost identical results for the degree of diatomite enrichment with silicon oxides (SiO_2), being in the range of 78 - 80 %.

Keywords: diatomite, electrohydraulic method, silicon oxide, enrichment, methods of analysis

INTRODUCTION

In modern conditions new effective enriching methods are promising for obtaining diatomite with the given functional properties, allowing to expand the fields of its application: construction (heat insulating, sound- and waterproofing materials, paints and glass); agriculture (mineral fertilizers that increase crop yields and ensure crop safety); animal husbandry (livestock feed); chemical and oil industries (filters and adsorbents); medicine [1-3].

The basic composition of diatomite consists of three oxide components SiO_2 , Al_2O_3 , and Fe_2O_3 .

Diatomite has a porous structure and contains up to 70 - 80 % cavities [4-6] as an analogue of activated carbon.

Methods of purification and enrichment of diatomite with the use of proven technologies are still insufficient for obtaining diatomite based nanomaterials with unique properties. In this regard, enrichment of diatomite by electrohydraulic method with use of plasma energy is proposed.

RESEARCH METHODOLOGY

Enrichment of diatomite raw materials was carried out by electrohydraulic method, the essence of which is to separate the clay component using plasma energy arising from a short electric discharge. Electrohydraulic shaking of diatomite and clay mixture leads to their separation. Since the densities of diatomite and clay are within $380 - 1\,000\text{ kg/m}^3$ clay $1\,400-1\,700\text{ kg/m}^3$ correspondingly, the clay, as a heavier material will settle in the bottom layer, and diatomite will concentrate on the top.

Electrohydraulic method is based on the Utkin effect [7]. A similar technology is used, in particular, for colloidal enrichment of ores and separation of gold from clay [8]. Depending on physical and chemical properties of materials, the operation mode of electrohydraulic device is adjusted for brittle, hard and plastic substances [8,9]. We have developed the operating mode of electrohydraulic device for natural diatomite separation [7-9].

RESULTS RESEARCH

The technology of diatomite enrichment based on the electrohydraulic method consists in the separation of diatomite into two components containing pure diatomite and clay. Due to the fact that the clay (with density of $1\,400-1\,700\text{ kg/m}^3$) is heavier than diatomite (with density in the range of $380 - 1\,000\text{ kg/m}^3$), the clay will settle in the bottom layer of the water suspension, and diatomite will float to the surface of the mixture, as it is shown in Figure 1.

Comparative analyses of natural diatomite and diatomite enriched by electrohydraulic methods by spectral, X-ray diffraction methods, silicate (chemical) and thermal analyses were carried out.

Spectral analysis was performed on a Vista MRX Simultaneous ICP-OES Series\$ atomic emission spectrometer.



Figure 1 Slurry after electrohydraulic impact:
1- water layer, 2- diatomite, 3- clay

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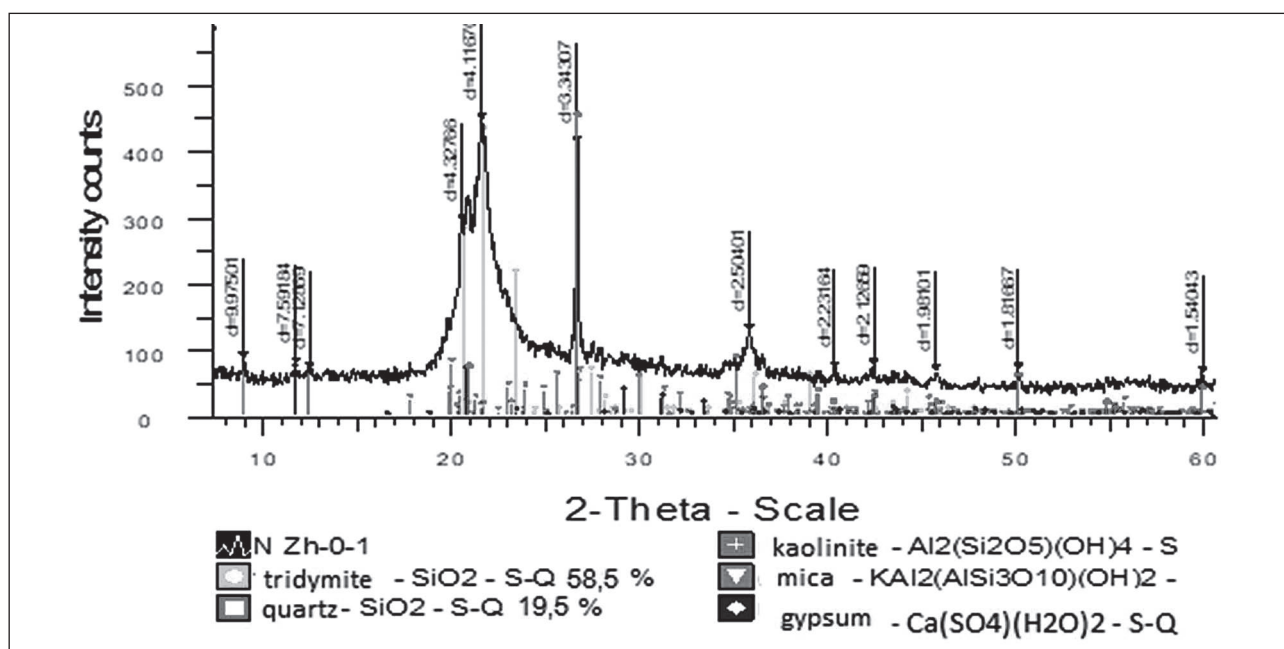


Figure 2 Diffractogram of enriched diatomite

The method of spectral analysis based on plasma determination of oxides in diatomite consists in decomposition of the analyzed material, its dissolving, introduction of the obtained solution in the form of aerosol in inductively coupled plasma and measuring the spectral line intensity of determined elements on the atomic emission spectrometer.

The matrix effect has the greatest and least controllable effect on the result of analysis. To account for unstable analysis conditions, an internal standard is used that is added to each sample before it is introduced into the plasma, as well as highly diluted solutions. The reference element is lithium, which has a spectral line at 670,783 nm (Table 1). Using spectrophotometric analyses of various samples, their concentrations for natural and enriched by electrohydraulic method diatomite were determined using the characteristic spectral lines of the oxides listed in Table 1.

Results of spectral analysis show (Table 1) that after diatomite enrichment by electrohydraulic method [17-

18] content of SiO₂ in it has markedly increased (up to 79,95 %), and concentrations of Al₂O₃ and Fe₂O₃ decreased to 13,49 % and 2,9 % respectively. Nevertheless, Al₂O₃ and Fe₂O₃ concentrations remain quite noticeable; apparently, additional measures are required to adjust the operating modes of electrohydraulic device depending on physical and chemical properties of diatomite.

X-ray diffraction analysis tuned to the characteristic emission of the copper line - ($Cu_{K\alpha}$) was carried out on an automated diffractometer DRON-3. The operating mode of the X-ray unit during the diffractogram registration corresponded to 35 kV voltage and the current of 20 mA. The scale was designed for 2000 pulses. The goniometric registration parameters were θ -2 θ by detecting 2 deg/min. X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the equal weight method. Quantitative ratios of crystalline phases were determined.

A diffractogram of enriched diatomite is shown in Figure 2.

Table 1 Results of spectral analysis of enriched and natural diatomite, and sludge component

Component	Actual measured content / %					
	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
	1	2	3	4	5	6
Emission wavelength / nm	308,215	238,204	318,127	285,213	588,995	766,491
Enriched diatomite / %	13,49	3,65	0,21	1,48	0,37	1,43
Natural diatomite / %	14,36	3,1	0,74	2,48	3,3	1,45
Sludge component / %	16,63	3,17	7,38	1,37	0,26	1,32

Component	Actual measured content / %				
	SiO ₂	P ₂ O ₅	SO ₃	MnO	TiO ₂
	7	8	9	10	11
Emission wavelength / nm	251,611	213,618	181,972	257,610	334,941
Enriched diatomite / %	79,95	0,071	0,18	0,018	0,38
Natural diatomite / %	64,13	0,094	1,26	0,018	0,68
Sludge component / %	59,41	0,153	9,87	0,013	0,43

Table 2 Results of semi-quantitative X-ray phase analysis of crystalline phases of sludge component, natural and enriched diatomite

Mineral	Formula	Natural diatomite / %	Sludge component / %	Enriched diatomite / %
Tridymite	SiO ₂	-	-	58,5
Quartz	SiO ₂	22,9	7,8	19,5
Kaolinite	Al ₂ (Si ₂ O ₅)(OH) ₄	40,2	51,3	14,3
Mica	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	9,8	6,7	4,6
Halite	NaCl	4,4	3,0	-
Gypsum	Ca(SO ₄ (H ₂ O) ₂)	-	-	3,1
Smectite	(Na, Ca) 0,3(Al,Mg)2Si ₂ O ₁₀ (OH) ₂ nH ₂ O	22,7	-	-
CCM	K-Na-Al-Si-O-(OH)	-	31,2	-
TOTAL		100 %	100 %	100 %

Table 3 Results of silicate (chemical) analysis

Samples	Element content / wt. %											
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Moisture	Residue	Σ	d
Natural diatomite	53,9	7,29	4,22	4,93	4,63	2,54	0,94	2,53	7,0	11,47	99,45	2,57
Enriched diatomite	81,8	4,55	2,5	2,42	2,73	0,44	0,62	1,61	2,2	0,77	99,64	2,40

Table 4 Results of thermal analysis of the sludge component, natural and enriched diatomite

Mineral	Formula	Natural diatomite / %	Sludge component / %	Enriched diatomite / %
Tridymite	SiO ₂	-	-	60
Quartz	SiO ₂	25	20	20
Kaolinite	Al ₂ (Si ₂ O ₅)(OH) ₄	18,4	22,4	5,3
Hydromica	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	13,5	11,3	11,3
Gypsum	Ca(SO ₄ (H ₂ O) ₂)	-	-	3,4
Smectite	(Na, Ca) 0,3(Al,Mg)2Si ₂ O ₁₀ (OH) ₂ nH ₂ O	23,1	21,2	-
Thermally inert minerals (Halite, Mica, Albite, etc.)	K-Na-Al-Si-O-(OH)	20	25	-
TOTAL		100 %	100 %	100 %

The main trend for oxides concentration in diatomite as a function of electrohydraulic action can be seen from Table 2. Concentration of SiO₂ reaches 78 % in the enriched diatomite. At the same time concentration of kaolinite is almost 3 times less compared with the natural diatomite, where the content of kaolinite is 40,2 %. The concentration of mica decreases by a factor of 2.

Thus, based on the experimental data obtained from X-ray phase analysis, the effectiveness of electrohydraulic method of diatomite enrichment can be seen.

Silicate (chemical) analysis of natural and enriched diatomite samples was carried out by fusion method. Diatomite sample fusion was carried out in a muffle furnace at a temperature of 1000° C. Results of silicate (chemical) analysis of natural and enriched diatomite samples are shown in Table 3.

The Table 3 shows that in the enriched diatomite content of SiO₂ is 81,8 %. At the same time, concentration of Al₂O₃ is decreased to 4,55 % and that of Fe₂O₃ is reduced to 2,5 %. In contrast to the spectral analysis (Table 1), which shows complete purification of enriched diatomite from CaO (7,38 % →0,21 %) and SO₃ (9,87 % →0,18 %), the chemical analysis (Table 3) gives an insignificant difference in favor of diatomite purification.

Similar absorption bands were predicted in [10] according to the refractive index calculation, where the refractive coefficients were attributed to the modification of

amorphous silicon. A promising area of research is the development of technology for the synthesis of strategic material - amorphous silicon from the enriched diatomite.

Thermal analysis of natural and enriched diatomite samples was carried out by recording the changes in thermochemical and physical parameters of substance at heating.

The results of thermal analysis of samples are presented in Table 4 for three fractions: natural, slimy and enriched [11,12].

Enriched diatomite is represented predominantly (~ 80 %) by the silica minerals tridymite and quartz, as indicated in Table 4. Quartz was determined by the endothermic peak at 500 °C, which is associated with its polymorphic transition from α to β-modification. At pointed temperature region, this thermal effect is overlapped by endothermic effect caused by kaolinite dehydroxylation.

Tridymite detected in the sample also leaves a very weak appearance on the curve due to its transition (at 870 °C) into α-quartz. After subtracting the detected thermally active components from the sample composition, the share of silicon dioxides is about 80 % of the sample mass. Of these, in a qualitative comparison of the peak intensities of the putative minerals, quartz should be assigned < 20 % and tridymite <60% of the mass of studied system. The total composition of the enriched sample of diatomite is /in %: tridymite - 60; quartz - 20; kaolinite - 5,3; hydromica - 11,3 and gypsum - 3,4.

CONCLUSIONS

The electrohydraulic method was used for the first time for the enrichment of natural diatomite. The results of spectral, X-ray diffraction, silicate (chemical) and thermal analyses show that the concentration of SiO_2 diatomite enriched by electrohydraulic method significantly increased to 78 - 81,8 %, while concentrations of Al_2O_3 and Fe_2O_3 decreased to 3 %.

It should also be stated that the content of kaolinite in all presented samples identified by thermal analysis as result of dehydration of diatomite structure is slightly lower (5,3 %, Table 4) than that detected by X-ray diffraction analysis (14,3 %, Table 2). Apparently, this effect is due to the lack of hydroxyls in the silica-oxygen framework of the indicated system, as well as caused by the presence of defects in the crystal structure of this clay mineral.

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Note: The responsible for England language is Nurgul Zhanturina, Aktobe, Kazakhstan