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Experiments on bleaching of kaolin from the Khodjakulskoye deposit

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Abstract. This paper presents the results of experiments on the bleaching of kaolin from the Khodjakul deposit. Various methods for removing coloring impurities were investigated, including acid leaching, treatment with chemical reducers, and physico-chemical methods. The effectiveness of using various reagents, such as oxalic, sulfuric, and hydrochloric acids, as well as nitric acids, was evaluated. The optimal processing conditions for achieving the maximum degree of whitening were determined. The whiteness index was established. The whiteness of the samples was analyzed using the SBDY-1P whiteness meter. The obtained results allow the conclusion that certain methods hold promise for improving the quality of kaolin from this deposit and its further industrial use. Comparative studies were conducted on the original, enriched, and acid-treated kaolins. To improve whiteness, methods regulated by GOST 21286-82 "Enriched kaolin for ceramic products. Technical requirements" were applied. The whiteness level was determined according to standard methods specified in GOST 16680-79 "Enriched kaolin. Methodology for measuring whiteness".

1 Introduction

In the Aral Sea region, there is a large reserve of natural minerals widely used in various sectors of the national economy [1, 2]. Among them, kaolin is a natural mineral applied in industries such as ceramics, paper production, cosmetics, and pharmaceuticals. Bleaching of kaolin is an important technological process that enhances its quality and broadens its areas of application. The development of new processing methods, especially environmentally friendly ones, plays a key role in improving the characteristics of kaolin and reducing its environmental impact. However, natural kaolin often contains impurities that decrease its whiteness and degrade the quality of the final product.

To increase the efficiency of using domestic kaolin mineral resources, methods of its enrichment have been studied [3, 4]. This will, in the future, improve the quality of finished products and establish the production of scarce grades of kaolin based on local raw materials, which are currently predominantly imported from neighboring countries. The reserves of natural kaolin with reduced levels of coloring oxides (Fe_2O_3 and TiO_2) are limited. The geographic distribution of kaolin raw materials in the CIS countries is shown in Figure 1.

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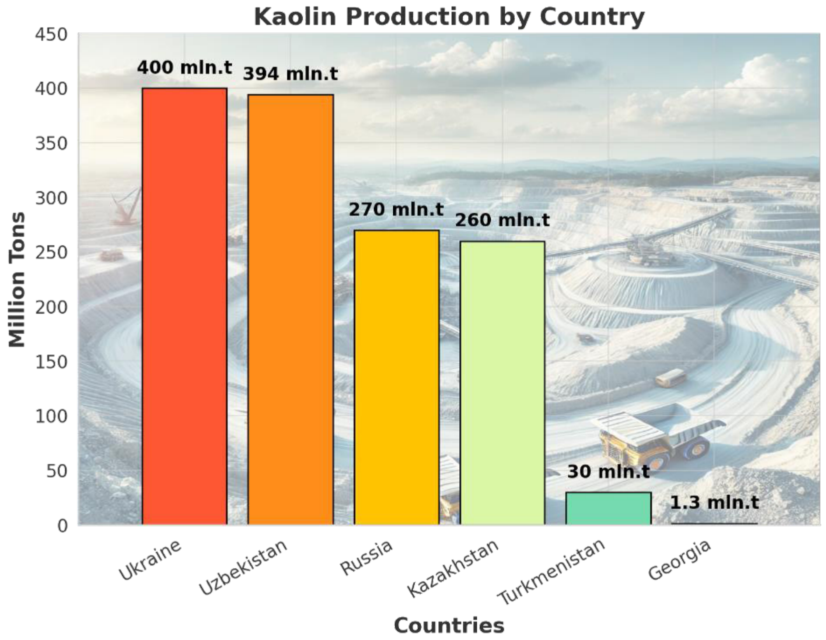


Fig. 1. Distribution of kaolin raw materials across the CIS countries.

Given the scarcity of natural kaolins with lower content of coloring oxides in the territory of the Republic of Uzbekistan, our goal is to improve the quality of kaolin from the Khodjakul deposit. To enhance the quality of kaolin, various bleaching methods are applied, including:

Chemical bleaching – this method is based on the use of reagents that oxidize or reduce the color-forming impurities, such as iron and organic substances. In oxidative bleaching, substances like hydrogen peroxide (H_2O_2), ozone (O_3), and sodium hypochlorite (NaClO) are used. They effectively break down colored organic impurities and oxidize iron-containing compounds. In reductive bleaching, chemical compounds such as sulfur dioxide (SO_2) or sodium hydrosulfite ($Na_2S_2O_4$) are applied, which reduce iron from the colored trivalent form (Fe^{3+}) to the colorless divalent form (Fe^{2+}). The presence of iron and titanium compounds in kaolins and other components of ceramic mixtures contributes to a decrease in whiteness and the emergence of undesirable hues. In kaolin and clays, iron is found in the form of free minerals (goethite, hematite, etc.), as oxide films covering the surface of silicate particles, or integrated into the crystalline structure of silicates [5].

Froth flotation enrichment allows the removal of organic impurities and iron-containing minerals by using special reagents (collectors) that selectively bind with the contaminating particles, enabling their removal in the form of foam.

In the biological method, an alternative approach is the use of microorganisms capable of synthesizing organic acids that break down the color-forming impurities in kaolin. Screening of such microorganisms and their application for kaolin treatment has shown promising results in improving its quality. The authors of the work [6] proposed a kaolin bleaching method that involves the bioreduction of Fe(III) to Fe(II) using activated microflora, followed by magnetic separation and treatment with ammonium oxalate solution. This method allows for a significant reduction in the content of color-forming impurities and an increase in the whiteness of kaolin.

Magnetic separation – this method is used to remove ferromagnetic and paramagnetic impurities. During the treatment process, kaolin passes through a magnetic field, in which iron and other metal impurities are held. This method is particularly effective when there is a high concentration of iron compounds.

One of the methods of whitening is heat treatment. Calcination in the range of 600–900°C promotes the decomposition of organic compounds and reduces the concentration of colored impurities. However, this method can lead to transformations in the mineral's crystal structure, which is not always acceptable. In industry, various technologies are used to remove coloring impurities from kaolins, including mechanical, chemical, biotechnological methods, as well as their combinations [7, 8]. Proper selection of the cleaning method ensures maximum effectiveness in removing these inclusions.

The choice of method depends on the composition of impurities, the intended purpose of the final product, and economic feasibility. In industry, a combination of several methods is often used to achieve the best effect.

Among the physico-chemical methods, kaolin enrichment in a fluidized bed stands out. Studies show that drying and selective grinding of kaolin in a fluidized bed with a heat carrier allow for effective removal of impurities and improvement of the final product quality [9].

In kaolin, the concentration of strongly magnetic or non-associated iron-containing compounds with clay minerals is usually minimal compared to the presence of iron in the form of weakly magnetic, low-crystalline, or amorphous phases. These inclusions can be located inside the aggregates of clay particles or form surface coatings, making their removal difficult using physical and chemical processing methods. For this reason, many researchers have analyzed methods of acid leaching carried out in solutions of both organic and inorganic acids. This process can be carried out either without the use of reducers or with their addition to improve the removal of contaminating components. Organic and inorganic reagents are used as chemical reducing agents for removing iron-containing impurities. During the reaction, reducers interact with (hydro)oxides of iron, converting them from an insoluble state to soluble Fe(II) compounds, which are then removed by filtering the clay minerals. The main mechanism ensuring the rapid dissolution of (hydro)oxide particles is their reduction. However, in a neutral environment, this process occurs extremely slowly, requiring the creation of optimal conditions for the effective removal of impurities. In practice, kaolin is also used as an adsorbent for bleaching vegetable oils.

2 Research methods

For the tests, a technological sample of the initial kaolin from the Khodjakul deposit was selected. The bleaching operation was carried out using methods regulated by GOST 21286-82 “Enriched kaolin for ceramic products. Technical conditions”. The whiteness degree was determined according to the standard methods of GOST 16680-79 “Enriched kaolin. Method for determining whiteness.” This method is based on measuring the reflectance coefficient of the surface of the analyzed sample.

For conducting scientific experiments, the selection of kaolin samples was carried out according to established standards regulating the requirements for kaolin. The average portion of kaolin was reduced to a mass of (50±5) g. All drying stages at a temperature of (105±5) °C were conducted in specialized drying equipment. After undergoing the wet enrichment stage, the material was initially air-dried, then the fragments were ground in a porcelain mortar and sieved through sieve No. I until fully passed, evenly distributed in a thin layer, and dried until a stable weight was achieved.

The whiteness of kaolin was determined using the SBDY-1P whiteness meter, which operates on the basis of the photoelectric effect and is equipped with a D65 light source (R457), intended for the analysis of the whiteness of powdered materials. For measurements, the required amount of kaolin was poured onto a sheet of paper, then lightly tamped by folding the paper in half and gently pressing it with the palm of the hand. Afterward, the sample was thoroughly mixed with a spoon, poured into a cuvette included in the leukometer set, and lightly tapped at the base to remove any voids, forming a cone-shaped pile of the material with a height of 4–6 mm. The surface of the layer was leveled with a clean glass plate without any defects, removing excess kaolin from the edges of the cuvette. Then, by pressing again, the surface was brought to the level of the cuvette edges without shifting the glass to avoid the appearance of gloss, which could distort the measurement results. The microstructure of kaolin was analyzed using the SALD-7500nano electron microscope, equipped with a semiconductor UV laser with a wavelength of 405 nm and a power of 40 W, as well as the Tescan Vega 3 Sbh scanning electron microscope, equipped with an Azteclive Lite Xplore 30 energy-dispersive microanalysis system with a tungsten cathode for thermionic emission. For sample preparation for the electron microscope examination, a one-step platinum-carbon replication method was used.

3 Results of experimental studies

The analysis of the chemical and mineral composition of the initial kaolin sample from the Khodjakul deposit showed that all the tested samples contain the same minerals, although their proportions vary, with kaolinite and quartz being the predominant minerals. The elemental composition of this kaolin sample is presented in Figure 2.

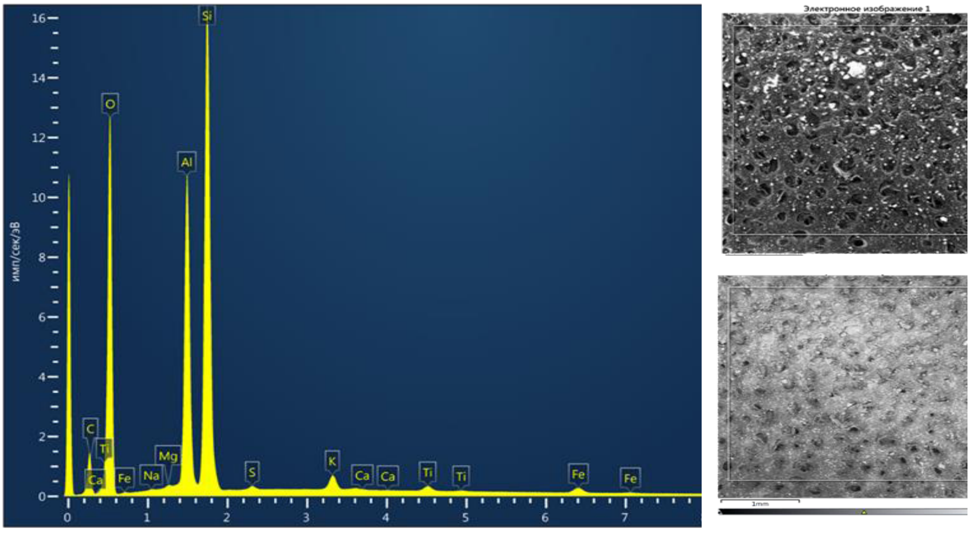


Fig. 2. Elemental composition of the original kaolin from the Khodjakul deposit.

The quality of kaolins is impaired by limiting impurities such as iron and titanium compounds. In this kaolin sample, the average content of Fe_2O_3 and TiO_2 is 1.21% and 0.71%, respectively. It should be noted that part of the iron and titanium is isomorphically incorporated into the kaolinite structure. To identify the presence of iron-containing impurities, a microstructural characterization of the initial kaolin was conducted. Figure 3 shows electron microscope images of the original and enriched kaolin from this deposit.

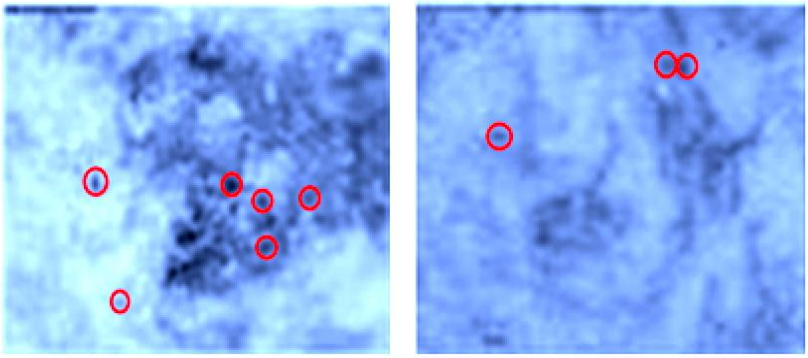


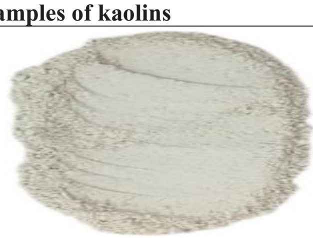
Fig. 3. Electron microscope image of the original and enriched kaolin.

The analysis of the obtained data shows that this kaolin sample belongs to the category of polymineral raw materials, and the iron-containing particles present in it have high dispersity and are represented by the mineral hematite. The enrichment of kaolin is presented in our previous works.

For this kaolin sample, the method of acid treatment was selected. In laboratory tests dedicated to the whitening of kaolin using acid treatment, H_2SO_4, HCl, HNO_3, and $C_2H_2O_4$ were used. Both the initial and the kaolin enriched by the wet method were subjected to whitening. The experiments were conducted using solutions of the specified acids with concentrations ranging from 5 to 20% at a temperature of 100°C for 2 hours, with a solid-to-liquid ratio (S:L) of 5:1, followed by multiple washings and filtration. To evaluate the whiteness level of kaolin, a blue light filter with a working wavelength of 457 nm was used. The instrument setup and measurement procedure were carried out according to the operating manual, and the obtained data were rounded to 0.1%. After completing each measurement cycle, which included 16-20 measurements, the leukometer was calibrated using a calibration plate, the whiteness of which closely matched the whiteness value of the sample under investigation.

When using H_2SO_4, HCl, and HNO_3 at the specified concentrations, the whiteness of the kaolin did not meet the requirements of GOST 16680-79 “Enriched Kaolin. Method for Determining Whiteness.” The best whitening result was achieved with a 20% oxalic acid ($C_2H_2O_4$) solution. The obtained results with different acids are presented in Table 1.

Table 1. Comparative results of kaolin after acid treatment.

Samples of kaolins		Original sample (comparison)
Enriched kaolin		
Enriched kaolin with H_2SO_4		

Continuation of Table 1.

Enriched kaolin with HCl		
Enriched kaolin with HNO_3		
Enriched kaolin with $C_2H_2O_4$ (Oxalic acid)		

The analysis of the obtained experimental data allows us to conclude that the reduction of unwanted impurities, including iron oxide (Fe_2O_3) and titanium oxide (TiO_2), which directly affect the whiteness of kaolin, was successfully achieved through chemical whitening. As a result of the conducted laboratory studies, it was found that the application of a 20% oxalic acid solution achieved an impurity removal efficiency of 13.20%. This conclusion is fully supported by the obtained numerical values of the whiteness index for the kaolin samples, which were determined using the high-precision whiteness meter model SBDY-1P (Table 2).

Table 2. Results of chemical whitening.

№	**Raw material**	**Leaching conditions concentration, %**		**Content, %**				**Whiteness index, R (457)**
				Fe_2O_3	**TiO_2**	**Al_2O_3**	**SiO_2**	
1	Non-enriched kaolin	-		1,21	0,71	31,14	64,90	68,80
2	Enriched kaolin	-		0,99	0,55	32,81	61,10	75,30
3	Enriched kaolin with $C_2H_2O_4$	$C_2H_2O_4$	5	0,97	0,50	32,93	60,99	76,66
			10	0,95	0,47	33,80	60,66	78,43
			15	0,93	0,44	35,92	60,21	80,15
			20	0,92	0,42	37,61	59,10	82,40

To clearly demonstrate the dynamics of kaolin whiteness changes at different stages of processing, specific experimental indicators should be considered. In its initial, unprocessed form, the whiteness index of kaolin was 68.80%, due to the presence of impurities that reduce its optical properties. After the wet enrichment stage, the whiteness level increased to 75.30%, indicating partial removal of contaminating compounds. The highest whiteness index was recorded after chemical treatment of kaolin: as a result of exposure to active reagents, particularly oxalic acid, a whiteness index of 82.40% was achieved, confirming the effectiveness of this purification method. Figure 4 shows a diagram of the chemical bleaching results.

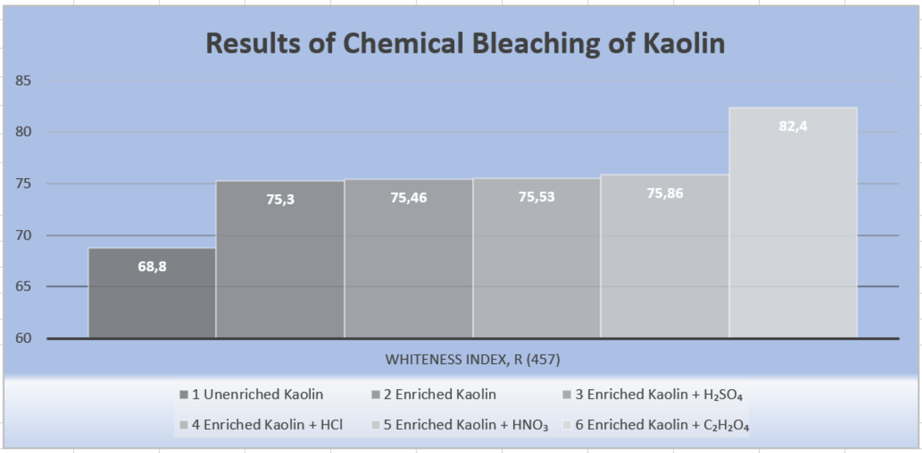


Fig. 4. Results of chemical bleaching.

Figure 5 shows the results of the elemental composition analysis of the enriched kaolin sample from the Khodjakul deposit after acid treatment, obtained using a scanning electron microscope.

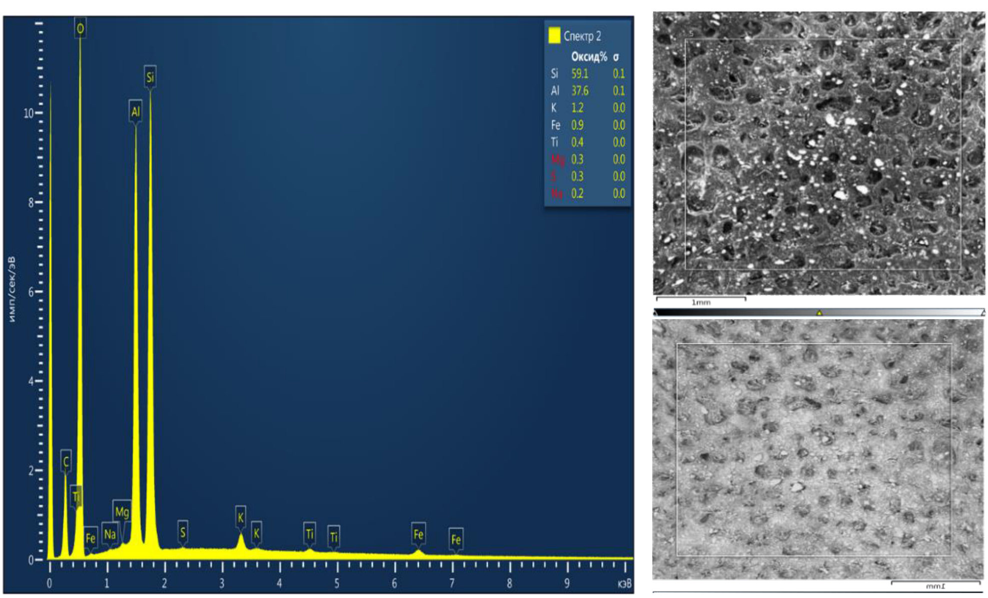


Fig. 5. SEM image of the enriched kaolin from the Khodjakul deposit after acid treatment with 20% C2H2O4.

The analysis results show that the content of Al increased from 31.14 to 37.60 compared to the non-enriched kaolin; the amount of Si decreased from 64.90 to 59.10; the amount of Fe decreased from 1.21 to 0.92; and Ti decreased from 0.71 to 0.42.

4 Conclusion

The conducted experiments on kaolin bleaching from the Khodjakul deposit involved the study of various methods for removing coloring impurities, such as iron and titanium oxides. The research showed that the most effective method was acid leaching using oxalic acid, particularly at a 20% concentration, which resulted in a significant increase in kaolin whiteness. Physicochemical methods, including magnetic separation and treatment with chemical reducers, also demonstrated certain effectiveness, but their application requires optimization of the processing conditions. The whiteness analysis of the treated samples, performed using the SBDY-1P whiteness meter, confirmed that the selected technologies could significantly improve kaolin quality and expand its potential applications. The results suggest that the developed methods can be used for industrial processing of kaolin from the Khodjakul deposit, which will increase its competitiveness and reduce dependence on imported analogs. Further research could focus on improving the technological parameters of bleaching processes and studying the environmental aspects of chemical reagent application.

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