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Products of Apatite-Nepheline Ore Processing in the Synthesis of Low-Modulus Zeolites

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ABSTRACT

The article presented the results of studies on the production of low-modulus zeolites from two types of technogenic resources containing a sufficient amount of silicon in their composition. The raw materials were nepheline concentrate and silica gel, which are products of the processing of apatite-nepheline ore. Directly before the synthesis of low-modulus zeolites, the morphology, chemical composition, and particle size of the starting materials were analyzed. The optimal parameters for sample preparation and purification of the raw materials used were also selected. The influence of the ratio of components in the reaction mixture on the type of synthesized zeolite and its characteristics were studied. The properties of synthesized zeolites from the proposed type of raw material were compared with the properties of zeolites synthesized today using the popular technology from kaolin clay, which is currently offered as an inexpensive natural raw material.

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1. INTRODUCTION

The development of mineral resources and fuel and energy complexes is associated with the creation of new technical solutions and technologies to produce knowledge-intensive commercial products guided by the principles of energy efficiency and sustainable development (Litvinenko *et al.*, 2022; Litvinenko *et al.*, 2020).

Currently, mining enterprises are actively extracting widely used apatite-nepheline ores. Apatite concentrate obtained from this ore is in demand on the world market, as it is a high-quality raw material for the production of phosphate fertilizers, and the products of its processing are a promising resource of valuable components (Ponomareva *et al.*, 2021). The composition of apatite-nepheline ore includes nepheline (up to 60 wt. %) (Slipenchuk *et al.*, 2019; Nevskaya *et al.*, 2019; Elbendary *et al.*, 2020), from which nepheline concentrate can be obtained, suitable as a raw material for the production of metallurgical alumina (aluminum hydroxide; Al_2O_3). However, only a small part of the nepheline concentrate is used for the production of alumina, the rest is practically not used in the production (Sizyakov & Brichkin, 2018; Elbendary *et al.*, 2019; Ponomarenko *et al.*, 2021). To date, about 1 billion tons of nepheline-containing waste have accumulated in the dumps of enrichment plants, and annually they are replenished in the amount of 15-20 million tons (Siziakova *et al.*, 2019; Chukaeva & Matveeva, 2018; Sizyakov *et al.*, 2020).

On the other hand, nepheline-containing raw materials are a valuable source of alumina (Al_2O_3) and silica (SiO_2). It may be promising to use nepheline not only in the production of metallurgical alumina but also in the synthesis of low-modulus zeolites, as well as active boehmite aluminum hydroxide (Golubev & Litvinova, 2021). At the same time, obtaining zeolites from pre-crushed nepheline is carried out mainly by fusing the silicon- and aluminum-containing components with alkali (Gembitskaya & Gvozdetskaya, 2021). The general scheme for obtaining potential products from nepheline raw materials is shown in **Figure 1**.

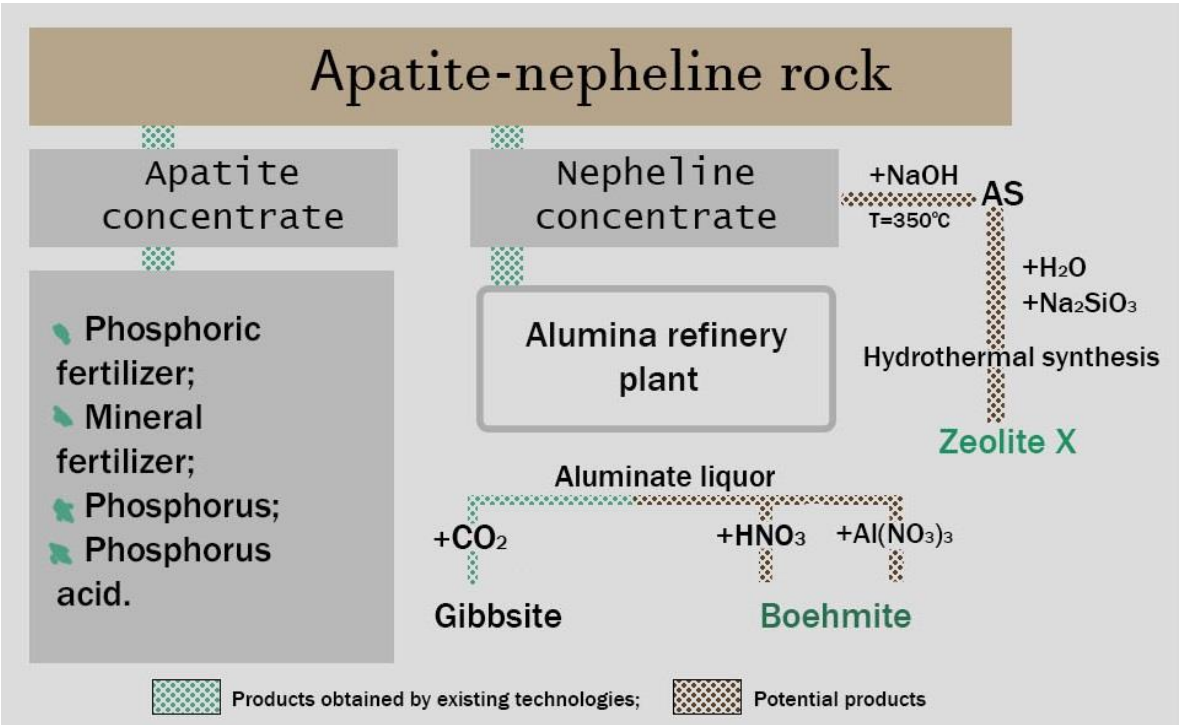

Figure 1. General scheme for obtaining potential products from nepheline raw materials.

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Secondary products of apatite concentrate processing are sent to the production of aluminum fluoride, where silica gel is formed. It is another by-product, which, like nepheline, is sent to dumps. And if nepheline is a source of both aluminum and silicon, silica gel is a valuable raw material with a high content of valuable amorphous silicon dioxide. Usually, the content of finely dispersed silicon dioxide in silica gel is more than 60 wt. % (Vaičiukynienė *et al*., 2021; Girskas *et al*., 2016). Most of the existing scientific developments related to silica gel are directed at the preparation of liquid glass (Sviridov *et al*., 2013; Evgenii Andreevich *et al*., 2019). The quality of the resulting liquid glass from silica gel is not inferior to the quality of liquid glass obtained by traditional technology. However, from this point of view, it is more promising not to stop at obtaining only a sodium silicate solution, but also to study the possibility of obtaining more popular and expensive products, namely, low-modulus zeolites.

Zeolites are microporous materials that are currently used in various industries as adsorbents, ion exchangers, and catalysts (Tran *et al*., 2018; Konoplin & Kondrasheva, 2021; Cherermisina *et al*., 2019; Ren *et al*., 2020; Verrecchia *et al*., 2020). The traditional method for obtaining zeolites is hydrothermal synthesis, in which chemically pure reagents are used as raw materials. Reaction mixtures for synthesis usually consist of sodium silicates, sodium aluminate, aluminum salts, or colloidal silicon dioxide in strongly alkaline solutions. On the other hand, the synthesis of zeolites from inexpensive raw materials is also widely considered to reduce the cost of production (Ruiz *et al*., 1997; Chen *et al*., 2022; de Aquino *et al*., 2020; Gualtieri, 2001; Pacewska *et al*., 2007). Among non-traditional sources of raw materials, the use of kaolin clay is the most studied (Wang *et al*., 2020; Foroughi *et al*., 2021; Alaba *et al*., 2017; Wang *et al*., 2013), which, in turn, is a promising source of valuable components (ElDeeb *et al*., 2021). Zeolites of types A, X, and Y are of the greatest interest. Synthetic zeolites of types X and Y are analogs of natural faujasite, which can be determined by the ratio of SiO_2:Al_2O_3 in the range from 2 to 3 for zeolite X and more than 3 for zeolite Y (Wang *et al*., 2021; Zhang *et al*., 2013).

Zeolites have a high capacity for ion exchange since their structure is a three-dimensional framework consisting of AlO_4^{-5} and SiO_4^{-4} tetrahedral units linked by oxygen atoms (Sekhon *et al*., 2004). The substitution of Si^{4+} for Al^{3+} leads to the appearance of a negative charge in the framework of zeolites, which is compensated by cations of alkali and alkaline earth metals in the cavities (on the surface) of zeolites (Koohsaryan *et al*., 2020). Due to the exchange of these cations, zeolites are widely used as ion exchangers. The most pronounced ion exchange ability is shown by type A zeolite, which is used as an additive to detergents to reduce water hardness due to its ability to remove Ca^{2+} and Mg^{2+} ions (Ayele *et al*., 2016; Nasief *et al*., 2021; Xue *et al*., 2014). Despite its high Ca^{2+} removal efficiency, type A zeolite exhibits low Mg^{2+} removal capacity, especially at ambient temperature (Smith & Fritz, 1998; Ghadamnan *et al*., 2019). In the case of type X zeolite, the removal of Mg^{2+} ions are more efficient. Therefore, the possibility of using zeolite X together with zeolite A as additives to detergents is being considered.

In this regard, this work was devoted to studying the possibility of synthesizing low-modulus zeolites of types A and X using apatite-nepheline ore processing products as raw materials. Since in modern literature kaolin clay is proposed as the most famous natural inexpensive raw material in the synthesis of zeolites, we also investigated the possibility of obtaining zeolites from this type of raw material. The results of morphological studies of zeolites obtained from kaolin clay were compared with the results of zeolites obtained from nepheline and silica gel.

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2. METHODS

2.1. Materials

As objects of study, various factory samples of nepheline concentrate and kaolin clay were used, which were selected from Russian enterprises. The hydrated silica gel used for the second series of experiments was taken from an aluminum fluoride production facility and contained up to 50% wt. of moisture. The names of enterprises are classified information; however, the quality of the secondary product is the same for the production of this sector. The composition of the original dried silica gel was as follows: 65,3 % wt. SiO_2, 26,9 % wt. F, 7,8 % wt. Al_2O_3. Sulfuric acid solutions with a concentration of 0.5 % wt. were used to purify industrial silica gel. To prepare a solution of liquid glass, a solution of sodium hydroxide with a concentration of 7-8 % wt. was used. The sodium hydroxide pellets used were analytically pure.

The aluminate solution used for the synthesis of zeolites from silica gel was prepared by dissolving commercial gibbsite in a sodium hydroxide solution at 80°C and had the following characteristics: 277 g/L Al_2O_3, 308 g/L Na_2O и $\rho = 1,58$ g/cm^3. The initial aluminum hydroxide powder for the preparation of the aluminate solution was analytically pure.

2.2. Characterization

The morphology of the precipitates obtained was analyzed using a TESCAN scanning electron microscope (Vega 3sem). The image of the electron microscope sample was obtained from secondary electrons (SE) in resolution scan mode, HV - 10 kV.

The surface area of the samples was determined by the BET method based on low-temperature adsorption of liquid nitrogen on a NOVA3200 instrument. The analysis of the used raw materials and the obtained substances was carried out using an X-ray powder diffraction apparatus "Shimadzu" XRD-7000 with CuKα radiation. Correspondence of the structure of the obtained zeolite samples to the structures of types A and X was determined by X-ray diffraction. X-ray exposure was maintained at long accumulation times (2 s) and a scanning step of 0.02°. The description was carried out using the JCPDS and ICSD databases. To refine the lattice parameters and determine the quantitative content of phases in the samples, we used the method of full-profile X-ray diffraction analysis of polycrystals (the Rietveld method).

2.3. Synthesis of Zeolite

2.3.1. Synthesis of zeolite from nepheline concentrate and kaolin clay

In the work, we used the original factory nepheline concentrate with a particle size of no more than 250 μm, ground in a ball mill. Three series of samples were obtained.

Sample set A. For this experiment, a sample of nepheline concentrate weighing about 50 g, mixed with caustic soda in a given ratio was used. The mixture was kept in a muffle furnace at a temperature of 350°C, then placed in an autoclave, where the prepared sodium silicate solution and distilled water were also added. At the end of the synthesis, the precipitate was filtered off from the solution and washed with hot distilled water with a pH of 7–8. The precipitate was dried for 2 hours at 120°C, then calcined for 4 hours at 650°C. The calculation of the necessary components was carried out based on the molar ratio of the components in the reaction mixture: SiO_2/Al_2O_3 from 3,8 to 6,2; Na_2O/SiO_2 from 1,2 to 2,6; H_2O/Na_2O from 20 to 70. The synthesis temperature varied from 75 to 105 °C, the synthesis time was from 12 to 24 hours.

Sample set B. In this experiment, a sample of nepheline concentrate of about 50 g without heat treatment was used. It was placed in an autoclave, where the prepared sodium silicate solution and distilled water were also added. The calculation of the necessary components was carried out based on the molar ratio of the components in the

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reaction mixture: SiO_2/Al_2O_3 = 4,8; Na_2O/SiO_2 = 1,2; H_2O/Na_2O = 40. The synthesis temperature was 95°C, and the synthesis time was 24 hours.

Sample set C. A sample of kaolin weighing about 50 g was amorphized by calcination at 650°C in the presence of sodium hydroxide. The heat treatment temperature was determined from DTA data at the transition point of kaolin to metakaolin. The calculation of the necessary components was carried out based on the molar ratio of the components in the reaction mixture: SiO_2/Al_2O_3 = 2,8; H_2O/Na_2O = 50. The temperature of hydrothermal synthesis was within 90 °C, synthesis time was 2 hours with and without stirring.

2.3.2. Synthesis of zeolites from silica gel

Waste silica gel was used to prepare a sodium silicate solution. Zeolite synthesis was carried out according to the order shown in **Figure 2**. Before using, the silica gel was purified by treatment with a low-concentration sulfuric acid solution. To obtain a liquid glass solution, a sample of purified silica gel with a SiO_2 content of at least 99.8 wt. % was dissolved in a sodium hydroxide solution with a concentration of 7.5 wt. % at a process temperature of 95–100 °C and a stirring speed of 400 rpm. At the end of the process, the resulting solution was filtered from the undissolved part of the silica gel. Further, the obtained liquid glass was analyzed and sent to derive D-series zeolites samples.

Samples set D. Synthesis of zeolites was carried out following traditional hydrothermal technology. A solution of sodium aluminate was poured into the silicate solution at a temperature of 50°C and a stirring speed of 750 rpm until a thick aluminosilicate gel was formed. The resulting solution was placed in an autoclave and kept for 1 hour at a synthesis temperature of 95°C. Upon completion of the synthesis, the precipitate was filtered off from the solution and washed with hot distilled water until pH 7–8. The precipitate was dried for 3 hours at a temperature of 120 °C. The calculation of the required amount of components was carried out based on the molar ratio of the components in the reaction mixture: SiO_2/Al_2O_3 from 2,0 to 2,2; Na_2O/SiO_2 from 1,1 to 2,0; H_2O/SiO_2 from 30 to 100.

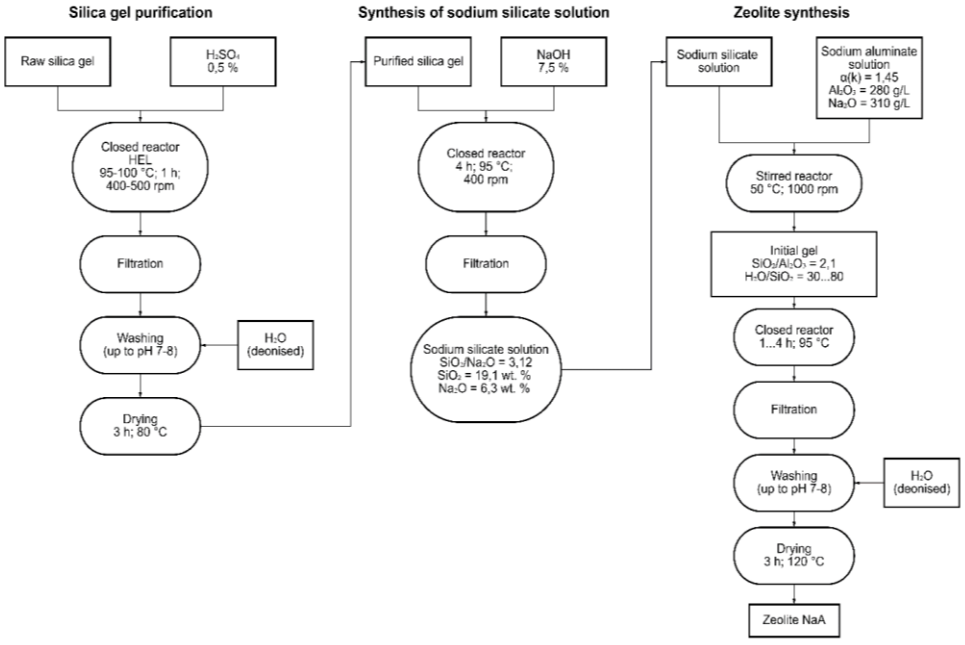

Figure 2. Scheme for obtaining zeolite from silica gel.

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3. RESULTS AND DISCUSSION

3.1. Synthesis of Type X Zeolite

3.1.1 Activation of initial raw material synthesis with NaOH

Table 1 presents the X-ray fluorescence analysis of raw materials, which are the main source of aluminum and silicon in the hydrothermal synthesis of zeolites.

Table 1 shows that the main components of the nepheline concentrate are SiO_2 and Al_2O_3, which make up about 69.2 wt. %. The total amount of all alkaline impurities in the raw material (Na_2O, K_2O, CaO, and Rb_2O) is approximately 24.98 wt. %. There are no differences in the chemical composition between the separately isolated fractions of nepheline concentrate. The main contaminant of the nepheline concentrate is Fe_2O_3 in an amount of about 4.02 wt. %. However, the Fe_2O_3 content can be significantly reduced by magnetic separation and acid treatment of the nepheline concentrate with 1-2 M HCl, H_2SO_4, or HNO_3 (Garcia *et al.*, 2016). In this case, acid treatment with mineral acids will also have a positive effect on the amorphization of the nepheline concentrate before thermal treatment with alkali, as described in (Drag *et al.*, 1985). In Zhu *et al.* (2011) and Burriesci *et al.* (1984), raw materials with an iron content of up to 3.5 wt. % was used, and therefore, in this work, the initial nepheline concentrate was not subjected to additional purification to extract iron impurities.

The only operation for preparing the raw nepheline concentrate before synthesis was its grinding in a ball mill. Grinding of nepheline concentrate was carried out to increase the area of its contact with NaOH. The particle size of the raw nepheline concentrate did not exceed 250 µm. The largest percentage of particles, which is about 40 vol. %, was in the range from 98 to 150 µm. After grinding, the percentage of particles of this size decreased to 20%, and the percentage of particles ranging in size from 20 to 80 µm increased.

The X-ray diffraction pattern of the crude nepheline concentrate powder shown in **Figures 3a** and **3b** shows that the crude nepheline concentrate mainly consists of the nepheline phase. After activation of the nepheline concentrate with NaOH in atmospheric air at 350°C for 2 h, the main sharp peaks of nepheline disappear on the X-ray pattern, which indicates the formation of a more reactive amorphous aluminosilicate (AS).

Morphological studies confirm the data of X-ray diffraction analysis. **Figure 4a** shows pure nepheline crystals that break down when activated with alkali, as shown in **Figures 4b** and **4c**.

Table 1. The chemical composition of the initial aluminosilicate raw materials used in the synthesis.

Parameter / Clay sample	Mass fraction of the component, %							SiO_2/Al_2O_3
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	$K_2O + Na_2O$	CaO	
Nepheline concentrate	45.21	25.21	0.46	3.02	0.32	23.89	1.09	3.05
Kaolin clay 1D	56.88	34.29	5.29	1.56	0.68	-	-	2.81

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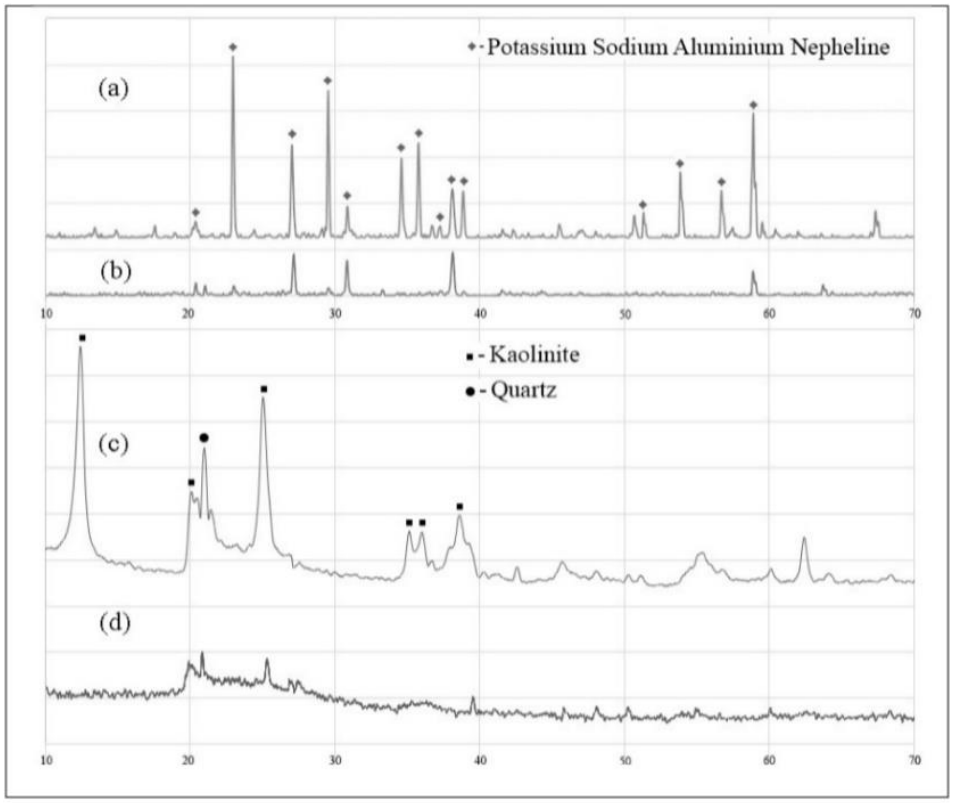

Figure 3. XRD: (a) - original nepheline concentrate without activation; (b) - nepheline concentrate after thermal activation in the presence of sodium hydroxide; (c) - kaolin clay prior to activation in the presence of sodium hydroxide, (d) – kaolin clay after thermal activation in the presence of alkali.

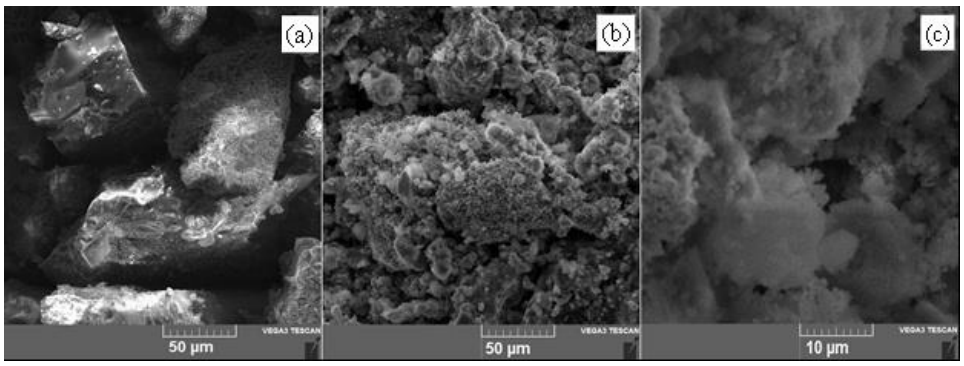

Figure 4. Electron microscope images (a) - raw nepheline concentrate; (b) and (c) - nepheline concentrate after activation in the presence of sodium hydroxide.

3.1.2. Hydrothermal reaction to form zeolite

The radiographs of the resulting precipitates were compared with the radiographs of commercial zeolite, as shown in **Figure 5**. The phase composition of the precipitates obtained in samples of series A after hydrothermal synthesis showed that aluminosilicate (AS) was zeolite X, which was confirmed by the presence of characteristic peaks in the X-ray diffraction patterns in the angles 2θ = 11.72, 15.48, 18.48, 20.12, 23.38, 26.72, 30.36, 31.04, 32.08, 33.66, 37.44, 40.94. In addition, zeolite type A was present in some samples of series A, which was confirmed by the presence of peaks in the angles 2θ = 13.90, 16.06, 21.68, 24.18, 27.16, 29.62, 34.34 on the X-ray patterns.

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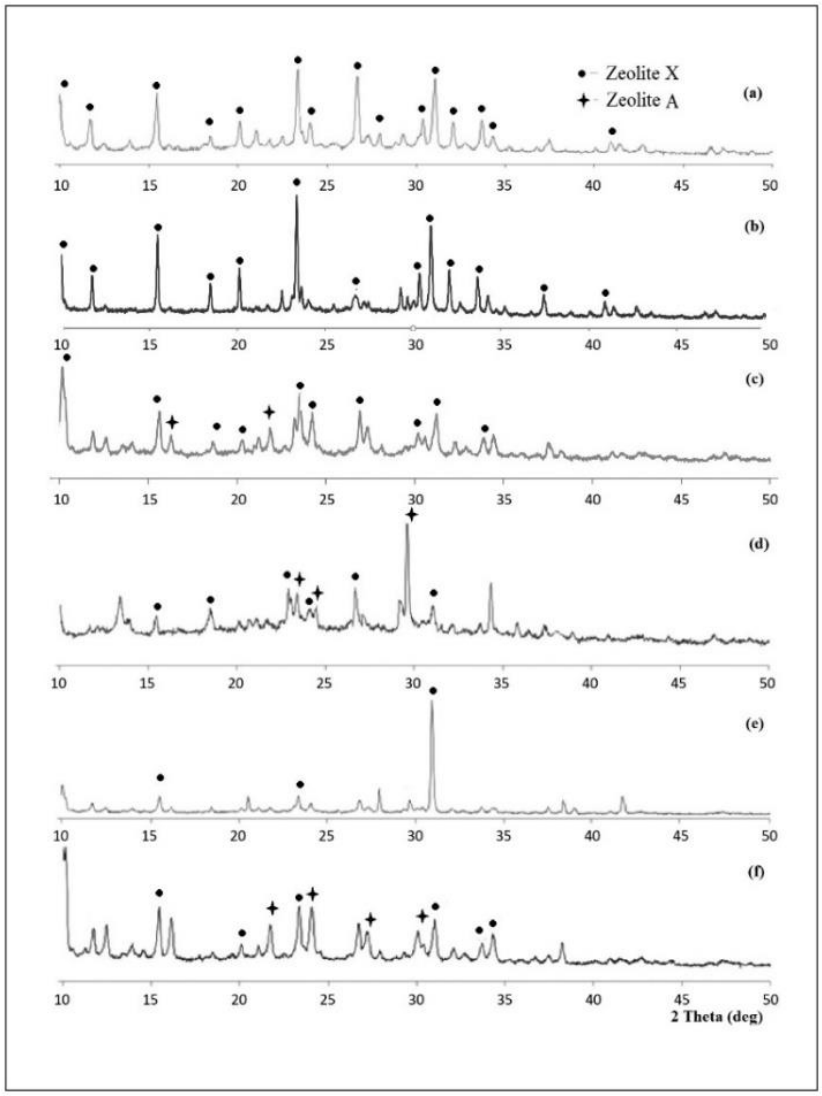

Figure 5. XRD (a) - commercial zeolite X; zeolite obtained from nepheline concentrate at a synthesis time of 24 hours and a temperature of 95°C: (b) - SiO_2/Al_2O_3 = 4,8; Na_2O/SiO_2 = 2,0; H_2O/Na_2O = 40; (c) - SiO_2/Al_2O_3 = 3,8, Na_2O/SiO_2 = 1,2, H_2O/Na_2O =70; (d) - SiO_2/Al_2O_3 = 4,3; Na_2O/SiO_2 = 1,4; H_2O/Na_2O = 50; (e) - SiO_2/Al_2O_3 = 4,6; Na_2O/SiO_2 = 1,2; H_2O/Na_2O = 60; (f) - SiO_2/Al_2O_3 = 4,6; Na_2O/SiO_2 = 1,2; H_2O/Na_2O = 70

With a synthesis time of 24 hours and a temperature of 75°C, the samples of series A were a mixture of zeolites A and X. An increase in the synthesis temperature to 95 °C led to the complete crystallization of zeolite X. A further increase in temperature to 105°C led to the appearance of zeolite A in the precipitate. At a SiO_2/Al_2O_3 ratio of 4.3, the crystallization product is predominantly zeolite A. An increase in the H_2O/Na_2O ratio in the reaction mixture to 60 and a decrease to 30 led to a deterioration in the crystallization of zeolites and a low degree of crystallinity.

The X-ray powder diffraction of the zeolites obtained from the obtained kaolin was also carried out, as shown in **Figure 6**. The obtained zeolites were type A zeolites. The morphology of samples obtained using kaolin clay, nepheline concentrate, and bauxite is shown in **Figure 7**.

According to the research results, it was found that the time of the hydrothermal reaction significantly affects the crystallinity of the synthesized powders of zeolite X. With a synthesis time of 12 hours and a temperature of 95 °C, zeolite crystals have already formed.

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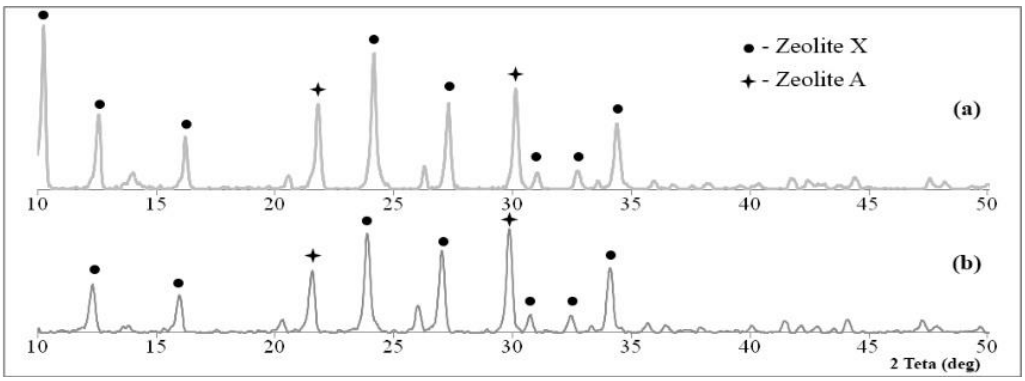

Figure 6. XRD of zeolites derived from kaolin clay.

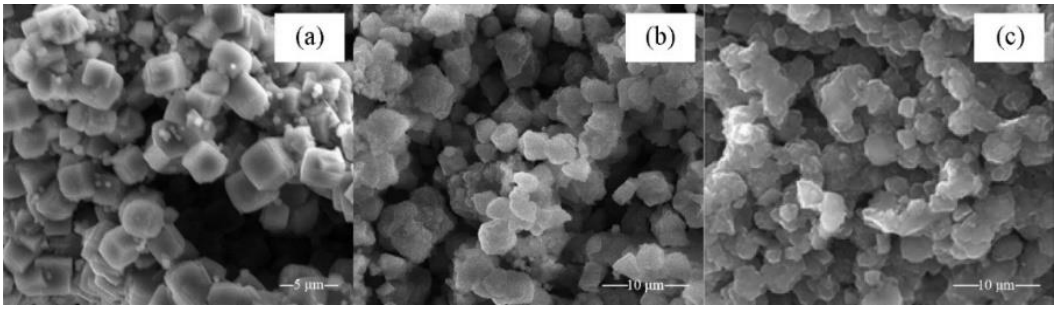

Figure 7. SEM samples: (a) – zeolite obtained after hydrothermal synthesis of activated kaolin clay: synthesis time 3 hours, synthesis temperature 95 °C; (b) – zeolite obtained on the basis of crushed nepheline concentrate: synthesis time 24 hours, synthesis temperature 95 °C; (c) zeolite derived from bauxite (Belviso, 2013).

However, these particles were not fully formed octahedral crystals. A similar morphology was observed in zeolites synthesized from nepheline concentrate and zeolites obtained from bauxite Belviso *et al.* (2013) at a synthesis time of 24 hours and a temperature of 95 °C (**Figure 7**). But, despite the presence of a higher modulus type X zeolite, samples of zeolite A obtained from kaolin clay had a more regular crystal shape and better crystallinity. A study of series B samples showed that the use of nepheline concentrates without thermal activation did not ultimately lead to the formation of any zeolite. Series B samples were large aluminosilicate globules (up to 100 µm). According to the given data, it becomes obvious that the stage of activation of the nepheline concentrate at a high temperature (more than 350 °C) and in the presence of alkali is necessary to obtain type X zeolite.

The BET for specific surface area of the obtained zeolite samples ranged from 156 to 282 m^2/g, while the value of the specific surface area of commercial zeolite was 420 m^2/g. Thus, the production of zeolite from a nepheline concentrate can be considered from the point of view of the cheapness and redundancy of the feedstock, but in this case, it is necessary to take into account the quality of the resulting product. Also, a positive result of this work can be considered the possibility of recycling part of the waste from the processing plant to obtain additional marketable products.

3.2. Synthesis of Zeolite from Silica Gel

3.2.1. Purification of silica gel

The original silica gel contained about 55 wt. % moisture, which was reduced to 3 % by weight using an air-drying process. **Table 2** presents the results of X-ray fluorescence analysis (XRF) of dehydrated silica gel, which is further the main source of SiO2 in the hydrothermal synthesis of zeolites.

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Table 2. Chemical composition of dehydrated silica gel.

Parameter / Name	Mass fraction of the component, %		
	SiO_2	Al_2O_3	F
Dehydrated silica gel	65.32	26.91	7.77

The **Table 2** shows that silicon dioxide is the main component of silica gel; fluorine and aluminum impurities account for more than 30 wt %. These impurities can be removed by acidic or alkaline treatment of the feedstock since impurities of fluorine and aluminum compounds have a negative effect on the subsequent production of a liquid glass solution (Mamchenkov *et al.*, 2015). In this case, acid treatment will have a positive effect on the amorphization of silica gel before its dissolution in sodium hydroxide solution. Purification of industrial silica gel in this case was carried out by interaction with a solution of sulfuric acid with a concentration of 0.5 wt. % at a process temperature of 95–100 °C and a stirring speed of 450 rpm. In the course of purification, aluminum compounds present in the crude silica gel passed into solution in the form of $Al_2(SO_4)_3$, and fluorine compounds were removed in the form of HF and SiF_4 gases due to the decomposition of the resulting H_2SiF_6. After the purification operation, the resulting mixture was filtered, and the solid residue was washed with distilled water until pH 7-8. The content of silicon dioxide in the purified silica gel was determined by XRD and was more than 99.8 wt. %. Further, after preparing a solution of liquid glass according to the method described above, experiments were carried out on the synthesis of zeolite.

3.2.2. Hydrothermal reaction to form zeolite

The results of the X-ray phase analysis of the obtained samples of series D are shown in **Figure 8**. The crystalline phase of the powders was identified as a monophase of a zeolite of structural type A, which was confirmed by the presence of characteristic peaks in the X-ray diffraction patterns at the angles 2θ = 10.19, 12.49, 16.14, 20.46, 21.72, 24.04, 26.17, 27.2, 30.01, 30.9, 32.62, 34.26 и 44.26. Despite the fact that the crystalline part was a zeolite monophase, an amorphous phase was present in the samples, and the zeolite crystals themselves had different sizes. This was assessed using scanning electron microscopy. The results of the study of samples of series D are presented in **Figures 9** and **10**. Thus, at a temperature of 95 °C, a synthesis time of 1 hour, and an H_2O/SiO_2 ratio of about 100, the presence of characteristic zeolite crystals was already observed, but amorphous aluminosilicate predominated. With a decrease in this H_2O/SiO_2 parameter to the region of 80, clear octahedral zeolite crystals already predominated. The crystals have a regular shape with rounded edges, characteristic of a zeolite of structural type A.

The granulometric composition of zeolite samples, shown in **Figure 11**, showed that the main fraction of zeolite crystals has sizes from 2 to 10 μm. At the same time, it is observed that a decrease in the H_2O/SiO_2 ratio leads to the formation of crystals with a smaller average particle size. Since low-modulus zeolites are mainly used as an additive to detergents, they are subject to requirements for a minimum degree of crystallinity, crystal shape and average particle diameter. A high degree of crystallinity indicates the purity of the resulting product (Ayele *et al.*, 2016). Cubic zeolite A crystals with sharp edges cause damage to textile fibers and the formation of scale on materials and machine parts, while crystals with flatter edges, on the contrary, prevent this (García *et al.*, 2015). The requirements for the average particle size for the use of zeolites as a modifier is from 1 to 10 μm, since crystals smaller than 1 micron can linger in the fibers of the fabric and damage them, and more than 10 μm can

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cause deposits on fabrics and machine parts (Fruijtier-Pölloth, 2009).

Based on the results of the work, it can be concluded that the use of liquid glass based on silica gel for the synthesis of zeolites of the NaA structural type is a promising direction of research due to the high content of silicon in the waste silica gel. The use of silica gel for the production of commercial liquid glass and zeolites will reduce the accumulated reserves and send it to recycling.

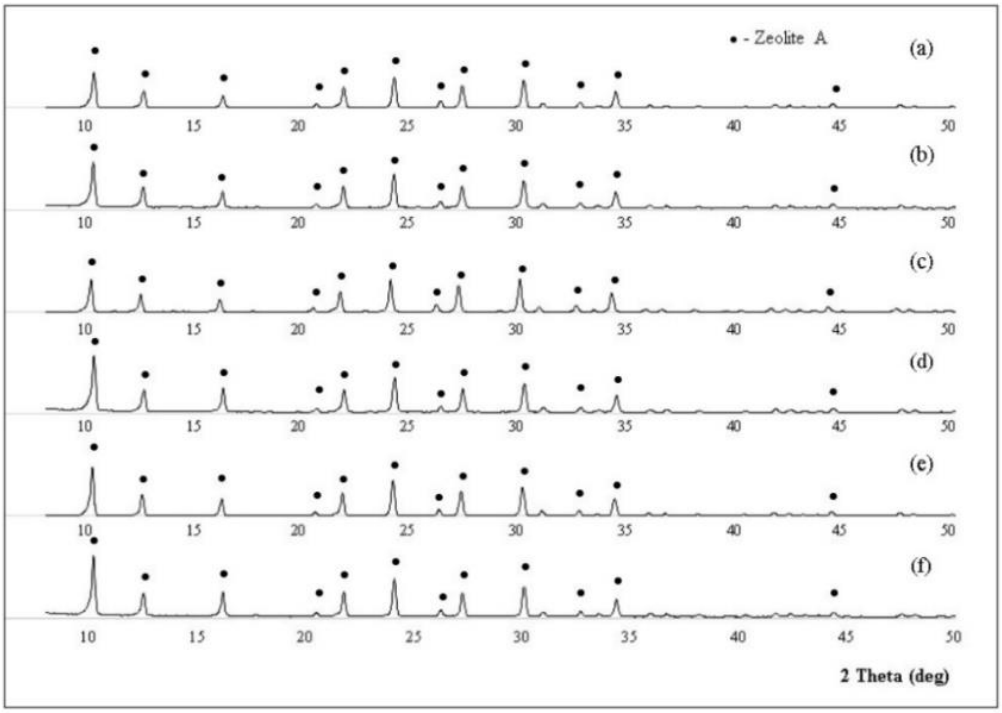

Figure 8. XRD of samples set D: (a) – commercial zeolite A; zeolite obtained by the proposed method with the use of silica gel (synthesis time - 1 hour, synthesis temperature - 95°C): (b) - SiO_2/Al_2O_3 = 2,13; Na_2O/SiO_2 = 1,89; H_2O/SiO_2 = 80; (c) - SiO_2/Al_2O_3 = 2,06; Na_2O/SiO_2 = 1,92; H_2O/SiO_2 = 70; (d) - SiO_2/Al_2O_3 = 2,03; Na_2O/SiO_2 = 1,93; H_2O/SiO_2 = 60; (e) - SiO_2/Al_2O_3 = 2,19; Na_2O/SiO_2 = 1,87; H_2O/SiO_2 = 50; (f) - SiO_2/Al_2O_3 = 2,12; Na_2O/SiO_2 = 1,12; H_2O/SiO_2 = 40; (g) - SiO_2/Al_2O_3 = 2,07; Na_2O/SiO_2 = 1,14; H_2O/SiO_2 = 30.

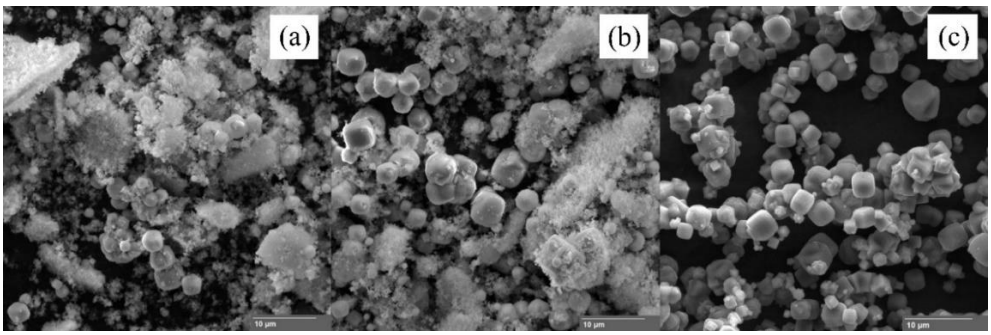

Figure 9. SEM of samples set D: (a) – SiO_2/Al_2O_3 = 2,24; Na_2O/SiO_2 = 4,15; H_2O/SiO_2 = 100; (b) – SiO_2/Al_2O_3 = 2,09; Na_2O/SiO_2 = 3,98; H_2O/SiO_2 = 90; (c) – SiO_2/Al_2O_3 = 2,13; Na_2O/SiO_2 = 4,03; H_2O/SiO_2 = 80.

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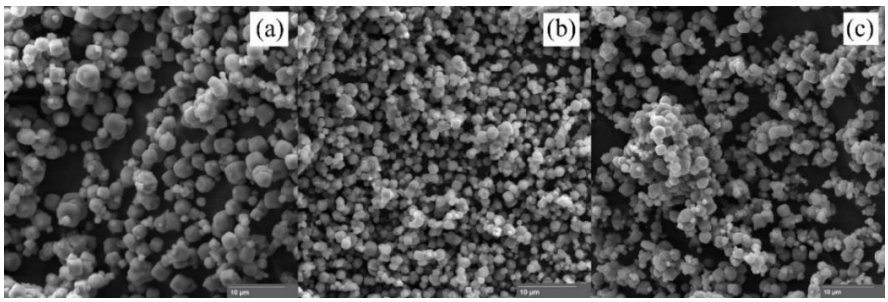

Figure 10. SEM of samples set D: (a) – SiO_2/Al_2O_3 = 2,06; Na_2O/SiO_2 = 3,95; H_2O/SiO_2 = 70; (b) – SiO_2/Al_2O_3 = 2,19; Na_2O/SiO_2 = 4,09; H_2O/SiO_2 = 50; (c) – SiO_2/Al_2O_3 = 2,07; Na_2O/SiO_2 = 2,36; H_2O/SiO_2 = 30.

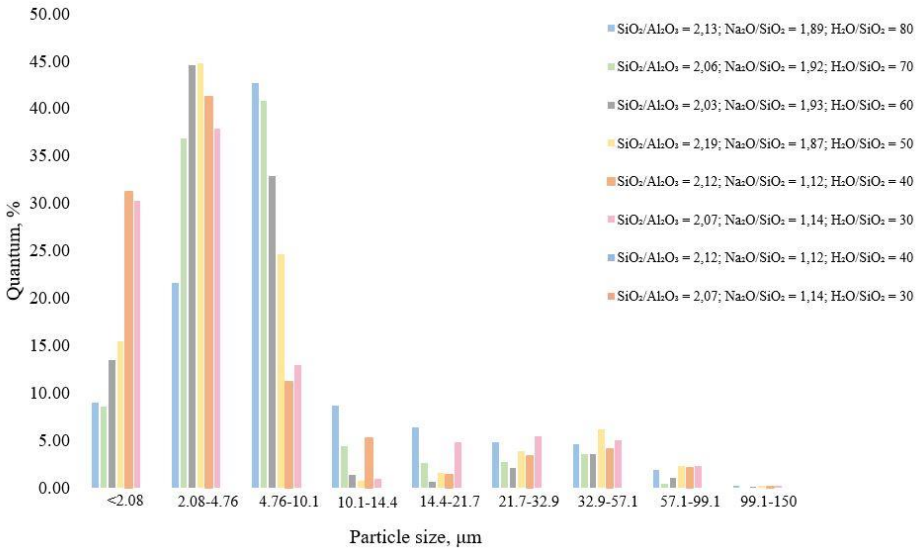

Figure 11. Granulometric composition of samples of zeolite series D.

4. CONCLUSION

The results of this work indicate that the nepheline concentrate obtained from the processing of apatite-nepheline waste can be used as a raw material for obtaining a valuable zeolite product. After activation in the presence of alkali and treatment at a temperature of 350 ^oC, the nepheline concentrate easily turns into type X zeolite, while the untreated nepheline concentrate does not react. The ratio of components in the reaction mixture affected only the purity of the products obtained, where zeolite A acted as a by-product.

The resulting products in the presence of all impurities can be used as feedstock in the formation of granules of zeolite-containing sorbents. Also, a by-product of production - silica gel - can be used to produce commercial liquid glass with a silicon module from 2.8 to 3.2. The subsequent use of the liquid glass solution based on silica gel in the synthesis of low-modulus zeolites makes it possible to obtain a monophase zeolite of the NaA structural type at a ratio SiO_2/Al_2O_3 = 2,0…2,25, Na_2O/SiO_2 = 1,1…2,0 and H_2O/SiO_2 = 30…80. The resulting zeolites are characterized by a high degree of crystallinity and a regular octahedral crystal shape, which subsequently makes it possible to use the resulting product as an additive to detergents.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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