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ГИДРОФТОРИДНАЯ ПЕРЕРАБОТКА ОТХОДОВ МОКРОЙ МАГНИТНОЙ СЕПАРАЦИИ ТИТАНОМАГНЕТИТОВ С ПОЛУЧЕНИЕМ АМОРФНОГО ДИОКСИДА КРЕМНИЯ

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Разработано вскрытие кремнийсодержащего техногенного сырья водным раствором гидрофторида аммония (NH_4HF_2) с последующим получением аморфного кремнезема. В работе использованы хвосты мокрой магнитной сепарации (хвосты, tailings) – отходы обогащения железных титаномагнетитовых руд, которые в огромных количествах образуются и складируются в шламохранилищах обогатительных фабрик. Основными породообразующими минералами хвостов мокрой магнитной сепарации (ХММС) являются упорные силикаты – пироксен, амфибол, плагиоклаз и оливин с общим содержанием около 50% SiO_2. Было установлено, что фторирование кремнийсодержащих минералов начинается при механическом диспергировании реакционной смеси в сухом виде при комнатной температуре. Термодинамические расчеты подтверждают активное взаимодействие компонентов в составе минеральных комплексов уже при 25 °C, при этом часть процессов являются экзотермическими с запасом энтропии. Увеличение температуры до 90 °C и продолжительности выщелачивания до 5 ч повышает извлечение кремния в виде растворимого фторосиликата аммония. В нерастворимом остатке содержатся нерастворимые фториды кальция и магния и малорастворимые в условиях выщелачивания фторометаллаты аммония, а также часть непрореагировавшей породы. В наиболее эффективных условиях обескремнивания (20% раствор NH_4HF_2, соотношение Ж:Т=4:1, 2 ч) остаточное содержание кремния снижается до 1–2% SiO_2. Синтез высокодисперсного аморфного кремнезема (SiO_2) проводили гидролитическим осаждением при снижении величины pH осветленного раствора фторосиликата аммония путем введения аммиака. Показано, что постепенное введение водного раствора аммиака (5 мл/ч) в разбавленный кремнефторидный раствор с концентрацией менее 5 г/л Si при постоянном перемешивании приводит к формированию сферических наночастиц кремнезема. Степень извлечения кремния из хвостов в процессе гидрофторировании 20% раствором NH_4HF_2 при 90 °C в течение 2 ч составила 98%, а содержание примесей в аморфном кремнеземе не превысило 1–2%. Отделение тонкодисперсной взвеси нерастворимых фторидов, а также примесей гидроксидов, образующихся при ступенчатом гидролизе кремнефторидного раствора до величины pH не более 5, являются необходимыми условиями для получения чистого кремнезема SiO_2. Конечный продукт, близкий по свойствам к «белой саже», характеризуется преимущественным размером частиц в интервале 2-20 нм, высокой площадью поверхности 230-360 м^2/г и низкой пикнометрической плотностью 1,62 г/см^3.

Ключевые слова: хвосты мокрой магнитной сепарации, кремнийсодержащие техногенные отходы, фторирование, гидрофторид аммония, аморфный кремнезем, гексафторосиликат аммония

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HYDROFLUORIDE PROCESSING OF TAILINGS FROM WET MAGNETIC SEPARATION OF TITANOMAGNETITE TO OBTAIN AMORPHOUS SILICON DIOXIDE

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A method for the opening of silicon-containing technogenic feedstock using an aqueous solution of ammonium bifluoride (NH_4HF_2) with subsequent production of amorphous silica has been developed. In this work we examined wet magnetic separation tailings (WMST) – iron titanium-magnetite ore enrichment rejects that are formed in huge quantities and stored in sludge depositories at concentrating plants. The main rock-forming minerals of WMST are resistant silicates – pyroxene, amphibole, plagioclase and olivine with the total SiO_2 content of about 50%. It was established that fluorination of silicon-containing minerals begins during mechanical dispersion of a dry reaction mixture at room temperature. The thermodynamic calculations confirm active interaction of components in the composition of mineral complexes already at 25 °C, some of the processes being exothermic with entropy reserve. When the temperature increases to 90 °C and the duration of leaching to 5 h, the extraction of silicon in the form of soluble ammonium fluorosilicate grows. Insoluble calcium and magnesium fluorides and sparingly soluble under leaching conditions ammonium fluorometallates, as well as a part of unreacted rock are formed in the insoluble residue. Under the most effective desilication conditions (20% NH_4HF_2 solution, L:S=4:1, 2 h), the residual content of SiO_2 decreases to 1–2%. The synthesis of finely dispersed amorphous silica (SiO_2) was performed by hydrolytic deposition when the value of pH of clarified ammonium fluorosilicate solution was reduced by adding ammonia. It was shown that gradual introduction of hydrous ammonia (5 ml/h) into diluted fluorosilicate solution with a concentration of less than 5 g/l Si while constant stirring leads to the formation of spherical silica nanoparticles. The degree of silica extraction from tailings in the process of hydrofluorination of 20% NH_4HF_2 solution at 90 °C for 2 h was 98%, and the content of impurities in amorphous silica did not exceed 1–2%. Separation of finely dispersed suspension of insoluble fluorides and hydroxide impurities formed during stepwise hydrolysis of fluorosilicate solution to pH value less than 5 is a necessary condition for producing pure silica SiO_2. The final product, similar to "white soot" in properties, is characterized by predominant particle size in the interval of 2-20 nm, a large surface area 230-360 m^2/g and a low pycnometric density 1.62 g/cm^3.

Key words: tailing, fluorination, silica-based raw materials, ammonium bifluoride, ammonium hexafluorosilicate, amorphous silica

INTRODUCTION

Silicates and finely dispersed silica belong to the group of top requested materials of modern science and engineering. The base of inert high-specific-surface-area thermally stable catalyst carriers, sensors and components of magnetic devices, nontoxic sorbents and absorbers [1] is finely dispersed amorphous silica – "white soot". Colored and transparent ceramics, glass, inorganic and organic polymers, as well as chemical sensors and composite materials consume cheap silica of different quality. The fields of silica application are largely determined by the degree of its purity, which depends on the composition of initial feedstock and method of production [2]. Expensive pyrogenic silica is vastly superior in properties to precipitated silica produced by sulfuric acid hydrolysis from solutions of alkaline metal silicates, for which the initial raw material is silica sand. In order to obtain various morphological forms of silica nanoparticles, sol-gel methods have been developed recently, which employ organic silicon-containing compounds, in particular, tetraethyl orthosilicate (TEOS) [3]. One of the most important problems of larger-scale production of “white soot” remains the production of precipitated silicon dioxide by a cheap method, which would have the characteristics close to those of pyrogen product.

Technogenic waste is an economically accessible feedstock increasingly attracting the attention in terms of ecology. Silicon oxide is the main component of enrichment rejects, metallurgy slags, fly ash, rice hull etc. [4-7]. Involvement of waste in processing implies both their direct use as additions without destruction of mineral matrix, for example, in construction materials, as geopolymer binders [8] and opening with separation of components and isolation of desired product by various methods. Silicon-selective are ammonium fluoride and bifluoride, whose action leads to the production of soluble ammonium fluorosilicate (the values of solubility in water are 217.8 g/l at 26.7 °C and 369.3 g/l at 68.3 °C) [9]. High-temperature treatment of silicon-containing feedstock by ammonium bifluoride results in selective separation of silicon by sublimation of the same complex $(NH_4)_2SiF_6$ at a temperature of 350 °C, which is used in analytical chemistry of silicon [10]. The technology for bifluoride opening of high-silicon quartzites by sintering was proposed for the precipitation of “white soot” from a pure solution obtained by absorption of sublimate. High-energy processes of sintering leading to the formation of a gaseous product can be completely replaced by hydrometallurgical processes, which are less energy intense and more environmentally friendly.

In the case of industrial waste, concerned in this paper, these fine materials are composed mostly of silica, together with iron, magnesium, calcium oxides, alumina, and other minor minerals. At present, silicon-containing waste such as wet magnetic separation tailings of titanium magnetite ore beneficiation at the Kachkanar ore mining and processing enterprise EVRAZ with silicon content up to 50% are directed to mud storage area. They occupy huge areas and are located in close proximity to settlements. More than 1500 mln tons of WMST have been accumulated in dumps during field development and processing of titanium-iron-vanadium ores and about 50 mln more tons are received annually. Thus, the disposal of tailings is becoming a necessity also because the quantity of accumulated components often exceeds the content of these components in the raw ores. Therefore, it is important to develop mechanisms and to find solutions to reduce the costs for waste storage. WMST are a rebellious hard-to-open feedstock that has not been processed to date because of the lack of an effective technology. Only some exploratory studies are known that are directed to extract scandium and other REE [11]. However, their realization is considerably restricted because it is necessary to break down and open the minerals of the feedstock and transfer simultaneously a considerable amount of components to a sulfuric acid solution. Close attention is paid to the fluorination process, which helps to reduce the environmental impact, saving space required for the disposal of waste, and provides low processing temperatures, and at the same time to the creation of materials with well-developed surface morphology and a broad spectrum of applications.

Thus, the aim of our endeavor is to study the interaction of tailings with NH_4HF_2 and develop a fluoride method for obtaining valuable products such as ammonium hexafluorosilicate and nano silica. In this work we considered fluorination of polycomponent technogenic materials by hydrochemical synthesis.

MATERIALS AND METHODS

Wet magnetic separation tailings of titanium magnetite (tailings) were received from the Kachkanar ore mining and processing enterprise located in the Ural region (EVRAZ KGOK, Russia). Before controlling the chemical composition, tailings were further dried at 125 °C for 24 h (initial moisture content was about 10-20 wt.%) and comminuted. High-purity ammonium bifluoride (NH_4HF_2) with ammonia (20% NH_4OH) were chosen as starting reagents. The grinding of the initial large source into powder was carried out using a planetary mill (MLW 4600 KM1) with an agate mortar and a ball, since hard refractory materials will not fully open.

Hydrochemical fluorination of wet magnetic separation tailings was conducted using 1-20% NH_4HF_2 solution with the liquid: solid ratio L:S = = 100:1 in fluoroplastic vessels at 80-90 °C for 30 min to 5 h. Then the obtained mixture was carefully filtered to separate the Si-containing solution from the slurry. The decomposition of $(NH_4)_2SiF_6$ solution by hydrolysis was carried out by dripping ammonia water while stirring to precipitate silica. The pH of the solution was monitored and the precipitation stopped when pH reached 8-9. Silica (SiO_2) was separated from the ammonium fluorine solution by centrifugation. When the precipitate was silicon dioxide, distilled water was used for the washing stage. The SiO_2 gel was fully dried at 100 °C until a stable weight of the final product.

The leaching degree of silica was calculated according to Eq. (1).

$$\omega = 100\% \times (C_2 \times m_2)/(C_1 \times m_1), \tag{1}$$

where C_1 and C_2 are the content of silicon in per unit or wt.% in initial tailings and residue with their masses m_1 and m_2 (g), respectively.

The mineralogical composition of raw materials and final products was characterized using X-ray powder diffraction (XRD) analysis. The XRD patterns were collected on a Shimadzu XRD-7000 automatic diffractometer (Cu$K\alpha_1$ radiation) in the 2θ angle range of 10-70° with a step of 0.03° and 5 s acquisition time. The PDF2 database (ICDD, USA, Release 2016) was applied for phase analysis. Elemental analysis of multicomponent solutions and solids was carried out with the use of an Elan 9000 inductively coupled plasma–atomic emission spectrometer (ICP-AES, Perkin Elmer). The calibration solutions and all samples were prepared by dilution with 2 wt% HNO_3. The morphology of the solids was examined using a scanning electron microscope (SEM, JEOL-JSM LA 6390 and MIRA 3 TESCAN) under the accelerating voltage of 5–20 kV. Energy dispersive X-ray (EDX) analysis was performed by using a JEOL JED-2300 detector coupled to the microscope. The pH values were measured with an ionometer ANION 4154 (Infrapak-Analit, Russia) coupled with a glass pH-electrode.

A Gemini VII 2390t analyzer (Micrometrics, USA) was used to determine the specific surface area (Brunauer-Emmett-Taylor method, BET) and the pore size (Barrett-Joyner-Halenda method, BJH) of powdered materials. Prior to gas adsorption measurement, the specimens were degassed at 100 °C under vacuum for 2 h. The dispersed parameters (particle size and particle size distribution functions) of amorphous silica were received using a particle size analyzer HORIBA LB-550. Infrared (IR) spectra were recorded on an FTIR spectrometer (Spectrum One, Perkin Elmer, England) using a diffuse reflectance attachment (DRA) over 400-4000 cm^{-1}.

RESULTS AND DSCUSSION

Tailings from the Kachkanar ore mining and processing enterprise located in the Ural region (Russia) were used as a source of silicon for the production of silica according to the diagram presented in Fig. 1. According to the chemical composition provided in the form of oxides in Table 1, silicon dioxide is the main component of the employed tailings. As can be seen from the XRD pattern (Fig. 2), the tailings consist of several crystalline phases: 74.4% pyroxene ($CaMgSi_2O_6$), 14.2% amphibole ($Ca_2(Al,Fe,Mg,Ti)_5Si_8O_{22}(OH)_2$), 8.0% plagioclase ($NaAlSi_3O_8 – CaAl_2Si_2O_8$), 1.5% titanomagnetite (Fe_2TiO_4), 1.3% olivin ($Fe_2Mg_8O_{20}Si_5$), 0.6% ilmenite ($FeO{\cdot}TiO_2$). The tailings have a characteristic grey color of particles of irregular shape not less than 10 μm in size, 80% of which have a diameter within the range of –1.6–0.074 mm with an average size of –0.5–0.2 mm. The particle size after grinding was achieved 0.25 μm.

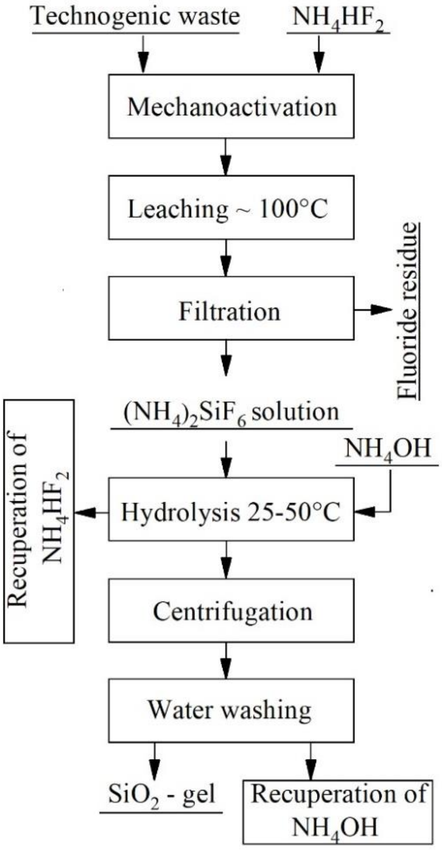

Fig. 1. Proposed flowsheet of silica leaching from tailings
Рис. 1. Предлагаемая технологическая схема выщелачивания кремнезема из хвостов

The separation of tailing components during hydrochemical interaction with ammonium bifluoride in solution is based on the formation of fluorine-containing compounds having various physicochemical properties. The thermodynamic simulation showed that fluorination reactions of silicon-containing oxide phases and most of minerals begin at temperatures below 200 °C and are accompanied by heat release [12-14].

Table 1

Composition of employed samples, wt.%

***Таблица 1.* Состав используемых образцов, мас.%**

SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	TiO_2	∑REE
47.9	20.2	13.7	7.6	6.5	3.3	0.7	0.044

The interaction of NH_4HF_2 with the basic mineral pyroxene $CaMgSi_2O_6$ to form poorly soluble and highly soluble simple and complex fluorides is possible under standard conditions according to eq. 2, $\Delta G^\circ_{298} = -850.3$ kJ/mol:

$$CaMgSi_2O_6 + 8NH_4HF_2 = CaF_2 + MgF_2 + \\ + 2(NH_4)_2SiF_6 + 6H_2O\uparrow + 4NH_3\uparrow \quad (2)$$

Readily soluble ammonium hexafluorosilicate $(NH_4)_2SiF_6$ is a product of decomposition of ammonium heptafluorosilicate $(NH_4)_3SiF_7$, which is formed in the first place during hydrofluorination of silicate-containing compounds, by analogy with individual SiO_2 [7]:

$$SiO_2 + 7NH_4HF_2 = \\ = 2(NH_4)_3SiF_7 + 4H_2O\uparrow + NH_3\uparrow, \quad (3)$$

$$(NH_4)_3SiF_7 \rightarrow (NH_4)_2SiF_6 + HF\uparrow + NH_3\uparrow \quad (4)$$

Solid-phase sintering of ilmenites, scheelite, wolframite, non-bauxite ores (kaolins, high-alumina shales, anorthosites, alkaline aluminosilicates etc.) with NH_4HF_2 or NH_4F revealed that the fluorating agent is in molten state [12-16]. We also found that mixing and grinding at room temperature lead to intensive wetting of the reaction mixture due to the formation of ammonia and water. Upon addition of water to reach the ratio L:S = 100:1, at the reagent concentration from 1 to 20% NH_4HF_2, the pulp was kept at a temperature of 90 °C for 30 min to 5 h. Then the fluorosilicate solution was separated from insoluble residue. As can be seen from the XRD pattern (Fig. 2), the leaching residue during leaching with 20% NH_4HF_2 solution for 2 h consists mainly of complex fluorides of different composition. The fluoride compounds in the residue are present simultaneously with a part of unreacted diopside, therefore the composition of the leaching residue in Table 2 is given in the elemental form. The degree of silicon extraction from tailings to solution is as high as 98% and the residual silicon content is about 1-2%.

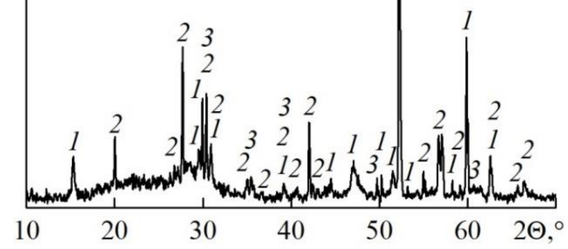

Fig. 2. XRD of leaching residue, identified minerals: 1 – (Na, K)$MgAlF_6$, 2 – $Ca(Mg,Fe,Al)(Si,Al)_2O_6$, 3 – $CaMg_2Al_2F_{12}$
Рис. 2. РФА остатка выщелачивания, идентифицированные минералы: 1 – (Na, K)$MgAlF_6$, 2 – $Ca(Mg,Fe,Al)(Si,Al)_2O_6$, 3 – $CaMg_2Al_2F_{12}$

Since finely-dispersed sols are formed in solutions during fluorination, insoluble magnesium and calcium fluorides may pass through filtering materials and be found in the silicon-fluoride solution separated from the residue. The fluorination products – complex fluorides $(NH_4)_3FeF_6$, $(NH_4)_3AlF_6$ and $(NH_4)_2TiF_6$ – are characterized by different values of solubility in water [16], but in ammonium bifluoride solution they may often go into it. Since impurity components will be also subjected to hydrolysis during neutralization of the solution, it is necessary to preliminarily remove them before precipitation of silica according to eq. 5:

$$(NH_4)_2SiF_6 + 4NH_3 + (n+2)\ H_2O = \\ = SiO_2 \cdot nH_2O\downarrow + 6NH_4F \quad (5)$$

Table 2

Composition of leaching residue with 20% NH_4HF_2 at 90 °C for 2 h, wt.%

Таблица 2. **Состав остатка выщелачивания 20% NH_4HF_2 при 90 °C в течение 2 ч, мас.%**

Ca	Mg	Al	Fe	Si	Na	Ti	Zr	Sc
17.2	10.65	6.7	4.4	1.6	0.75	0.35	0.07	0.01

Besides the precipitation of silica by eq. (5), ammonia is necessary for the neutralization of fluorohydric acid formed according to eq. (4) with regeneration of NH_4F and NH_4HF_2 reagents. To avoid the removal of light volatile substances of the solution, the temperature during precipitation did not exceed 50 °C. However, temperature reduction below 40 °C and rapid addition of ammonia lead to increased coagulation and agglomeration of silica gel particles. As a result, the quality of the product is degraded, which is confirmed by enhanced particle size and decreased specific surface area.

The studies performed revealed that the composition of the decomposition products depends on the initial concentration of silicon-fluoride solution and the pH value during neutralization. At the stage of tailing leaching, solutions containing more than 11 g/l Si were obtained, which corresponds to a rather high content of the complex compound $(NH_4)_2SiF_6$ – above 125 g/l. Therefore, already a small increase in pH to 1-2 induces the crystallization of $(NH_4)_2SiF_6$ due to decreased solubility. Silica gel is formed from a diluted solution with a concentration of less than 5 g/l Si (55 g/l $(NH_4)_2SiF_6$) at pH of about 7-8, its amount increases with further growth of pH to 8-9. In the region of medium concentrations from 5 to 11 g/l Si in the solution, the product consists of a mixture of silica SiO_2 and ammonium fluorosilicate $(NH_4)_2SiF_6$ in different ratios, which are formed due to simultaneous running of the processes of hydrolysis by eq. (5) with neutralization of solution and crystallization with decrease of solubility.

Thus, in order to produce pure SiO_2, the concentration of silicon in the initial solution should not exceed ~5 g/l Si. Hydrolytic precipitation should be carried out after preliminary removal of metal impurities at pH not more than 5-6. The optimal conditions for almost complete silica precipitation with the formation of well-filterable precipitate include slow addition of ammonia (5 ml/h) to pH 8-9, temperature 40-50 °C and agitation for minimum 2 h. The average content of impurities that are entrapped from initial feedstock during leaching and are co-precipitated with silica did not exceed 2 wt.%, as shown in Table 3 for two different samples dried at 25 °C and 200 °C.

Table 3

Concentration of trace elements in SiO_2 samples, wt.%

***Таблица 3.* Концентрация микроэлементов в образцах SiO_2, мас.%**

No.	T, °C	Al	Ca	Ti	Mg	Fe	Zr
1	25	0.1	0.1	0.5	0.08	1.0	0.007
2	200	1.08	0.5	0.1	0.08	0.07	0.007

Since silica SiO_2 is X-ray amorphous, the IR spectra were studied using the products from Table 3 as an example. The spectra of both SiO_2 samples have a typical set of vibrational bands of Si–O–Si bonds in the tetrahedral structure of SiO_4–matrix: a complex intense band ν_{as} at 1000-1200 cm^{-1}, a medium-intensity band ν_s at 800 cm^{-1} and an intense band δ at 460 cm^{-1} [17]. The medium-intensity band at 950 cm^{-1} on curve *2* (shoulder of curve *1*) is responsible for the Si–OH bond that is duplicated by the stretching vibrations of single silanol groups Si–(OH) at 3750 cm^{-1}. The absence of Si–O–Si vibrations in the region of 800-600 cm^{-1} and the regular shape of ν_s (800 cm^{-1}) indicate that the structure of condensed orthosilicates, for example $[Si_2O_7]^{2-}$ groups, is absent. It is also known that the replacement of silicon atoms by other metals (Fe, Ca, Al and Mg) during silica gel precipitation may result in spectrum complication by splitting of SiO_4 tetrahedron vibrations and in shifting of the main bands into the low-wave region [18]. Thus, it is safe to say that the product obtained under the selected precipitation conditions is silica SiO_2 in segregated form.

The broad band in the absorption region 3500-3000 cm^{-1} and a small band at 1630 cm^{-1} correspond to vibrations of H−O−H of sorbed and structural water. As a result of thermal treatment, the intensities of these bands decrease (curve *2*), and modes of symmetric and asymmetrical stretching vibrations of N–H bonds in the region of 2860-3210 cm^{-1} and modes of deformation vibrations $\delta_s(NH_4)$ of tetrahedral cation NH_4^+ at 1430 cm^{-1}, which are present on curve 1, disappear. The presence of ammonium ions in the product characterizes the ammonia method for silica production and a high sorption capacity of silica gel during precipitation in solution. No vibrational modes of bonds of other impurity compounds (Me–O, Me–F, Si–F) were found in the spectra.

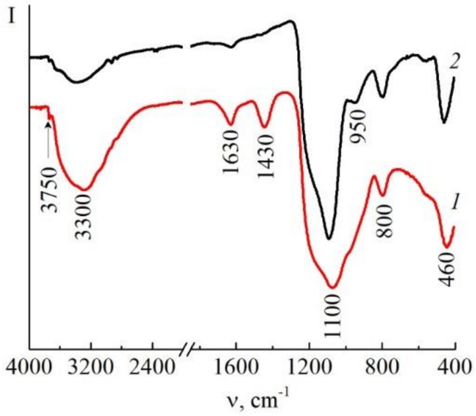

Fig. 3. IR spectra of SiO_2 from technogenic waste, treatment temperature: *1* – 25 °C, *2* – 200 °C

Рис. 3. ИК спектры SiO_2, полученного из техногенных отходов, температура термообработки: *1* – 25 °C, *2* – 200 °C

For practical application of silica SiO_2, of importance are the surface characteristic and particle morphology established by the BET and electron microscopy methods. According to Fig. 4a, the N_2 adsorption/desorption curve shows a steep hysteresis loop, indicating a week connection between N_2 and SiO_2. The sharp rise at a relative pressure (p/p_0) of ~0.9 points to the existence of mesopores with a rather narrow pore size distribution. This is because the slit-like mesoporosity was built within SiO_2 particles by Van der Waals' force. The sorption isotherms according to IUPAC classification [19] correspond to type IV isotherms having a capillary condensation hysteresis loop for mesoporous substances with constantly changing pore groups. As shown in Fig. 4b, in terms of the Barrett-Joyner-Halenda theory, both SiO_2 samples have a pore size distribution in the range of 2-120 nm and most of them are in the range of 2-20 nm. The BET surface area (S_{BET}) of SiO_2 is 230 m^2/g and 360 m^2/g, suggesting that the thermal modification can result in a significant decrease in the surface area of silica. The pore volume of SiO_2 samples was, respectively, 0.28 cm^3/g and 0.18 cm^3/g. Thus, the thermal treatment to 200 °C, leading to a certain decrease in the surface area S_{BET}, had scarcely any effect on the pore type, quantity and size.

Fig. 4c,d display SEM images of the as-synthesized SiO_2 nanoparticles (in different magnifications) obtained by hydrolysis and calcination at 200 °C demonstrating globular nanoparticles with the average diameter between 10-20 nm and agglomerated particles up to 1 μm in size. The value of pycnometric density of sample *2* (upon thermal treatment) was ρ ≈ 1.62 g/cm^3, which is smaller than the corresponding density defined in GOST standard for “white soot” SiO_2, equal to 1.9-2.2 g/cm^3 [20]. Proceeding from the spherical form of nanoparticles and the values of surface area S_{BET}, the average diameter (D) of SiO_2 particles was calculated by the formula (6):

$$D = {}^{6}\!/_{S_{BET}} \cdot \rho \qquad (6)$$

The values of *D* were 15 nm and 10 nm for the smallest and the largest S_{BET} values, respectively, which confirmed the BET results.

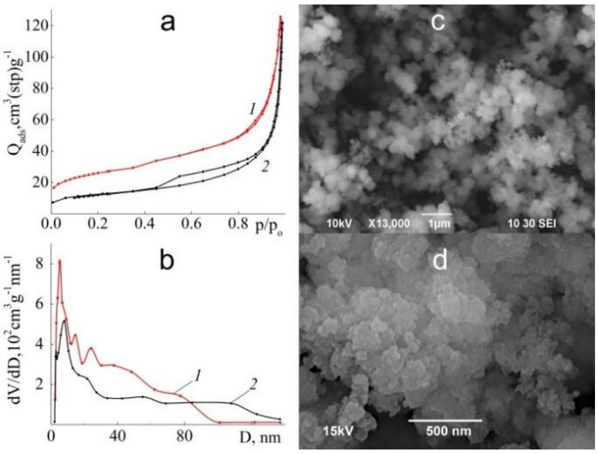

Fig. 4. Nitrogen adsorption curves (a), pore distribution curves (b) for SiO_2 samples: *1* – 25 °C, *2* – 200 °C; and typical SEM images (c, d)
Рис. 4. Кривые адсорбции азота (a) и распределения пор (b) для образцов SiO_2: *1* – 25 °C, *2* – 200 °C. (c, d) - СЭМ вид образцов

CONCLUSION

The data obtained showed that tailings are a rebellious hard-to-open for hydrochemical fluorination silicon-containing feedstock. To achieve the 98% degree of silicon extraction, the initial material was grinded to about 0.25 μm and used a 20% solution of ammonium bifluoride. It was shown that before precipitation of silica, it is necessary to remove the impurities of Ca, Fe, Ti and Al compounds passing into the leaching solution through the filtering material in the form of finely-dispersed suspension. The precipitation of silica is most optimal from diluted solutions by neutralization with ammonia to pH not less than 8 to increase the yield. If the concentration of silicon in solutions is greater than 5 g/l Si, in acidic or neutral medium ammonium fluorosilicate crystallizes. The composition and morphological properties of the obtained silica allow us to assign this product to “white soot” produced in industry.

Thus, a rather effective method has been proposed for the extraction of SiO_2 from ore-processing plant tailings, which have no sensible application at present and are stored in sludge depositories in huge quantities. From the obtained research results it can be concluded that technogenic waste such as wet magnetic separation tailings offers a feasible alternative to silica source.

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CONFLICT OF INTERESTS

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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