Egyptian Journal of Chemistry

Recovery of Aluminum and Vanadium Compounds from Karatau Phosphorites for Application in the Synthesis of Aluminum-Vanadium Containing Carbon Nanoparticles

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Abstract

The chemical composition of Karatau phosphorite raw materials and of solid waste phosphogypsum was determined, and the percentage of aluminum and vanadium elements quantified by chemical and physicochemical methods. Aluminum and vanadium compounds were extracted from the phosphorite ores and from the phosphogypsum for the preparation of aluminum-vanadium nanosorbents. Carbon nanotubes were then grown by chemical vapour deposition over previously adsorbed carbon nanotubes on the aluminum-vanadium nanosorbents (CN-CVD-100 method). Characterization results confirm the successful preparation of nanocatalysts and nanosorbents composed of ready-made aluminum and vanadium carbon nanotubes.

Keywords: Karatau phosphates; phosphogypsum; nanoparticles; nanosorbents; carbon nanotubes

1. Introduction

Phosphate raw materials are one of the main sources of phosphorus to produce phosphorus fertilizers, phosphoric acid salts, detergents and other valuable products and tools used in agricultural machinery. Phosphorus ores are divided into three types, namely apatites, phosphorites and complex apatite component ores. Phosphorite fertilizers are produced from phosphorites containing the element phosphorus. Depending on the amount of phosphorus, phosphorus ores can be classified as very high (35% P_2O_5), high (28-35% P_2O_5), medium (18-28% P_2O_5), poor (10-18% P_2O_5), very poor (5-10% P_2O_5) and phosphoric rocks (0.5-5% P_2O_5). The phosphate content of these ores is 39% of the value of phosphorite, which is higher than that of apatites. Apart from phosphorus, phosphorites typically also contain aluminum and vanadium in their composition. Accordingly, the purpose of this work is to develop a technology for the extraction of aluminum and vanadium compounds from phosphorite raw materials and from the solid waste phosphogypsum formed as a by-product of the production of fertilizers from phosphorites. Aluminum and vanadium compounds are not mined. For example, they are in the form of an impurity in the chemical composition of phosphorites at the Karatau deposit, Zhambyl region, Republic of Kazakhstan. Previous studies show that during the purification of phosphorites of the Karatau deposit, transitional and rare earth elements were separated as compounds, and sorbents and catalysts can be prepared from these valuable compounds. Further, nanosorbents and nanocatalysts can be grown from the obtained sorbents and catalysts using the CN-CVD-100 method in a carbon nanotube device of the Japanese company ULVAC JAPAN, Ltd. Nanosorbents and nanocatalysts in chemical and petrochemical production work very effectively in the purification of gas and liquid phases. To date, carbon nanotubes are mostly produced by arc discharge, ablation and chemical vapor deposition (CVD), but by far CVD is the most simple and economical processes for growth of carbon nanotubes. These materials play an important role in innovative technologies, including

the production of adsorbents and catalysts. Many experts predict the growth of this industry in the coming years.

According to previous results of analysis, three groups of element-impurities were identified in Karatau phosphorites: (i) rare earth elements (REE) and yttrium, which differ in large amounts in the phosphorites of potassium phosphorus and chalcophilic basins; (ii) arsenic, cadmium, copper, lead, rubidium, gallium, thorium and uranium, the average content of which differs two to three times; (iii) other elements showing low concentrations. Regarding group (i), the average value of rare earth elements for Karatau phosphorites is 700-800 g/t. Karatau phosphorites are found to be low in heavy rare earth elements. Efforts for sustainable development of REEs resources have been paid on the following aspects: (1) recycle REEs from manufacturing rare earth scrap/residues [1], (2) reclaim REEs from End-of-Life products [2–4], (3) extract REEs from landfill mining of industrial wastes or residues [5]. Several studies have recently been carried out to investigate the feasibility of extracting REEs through recycling of low value waste streams such as bauxite residue, mine tailings, PG, slag and waste waters [6–8].

Regarding group (ii), two chalcophilic elements, lead and copper, are found as 40 g/t Pb and 7 g/t Cu in the Karatau basin. The content of strontium in the basin phosphorites is 5-8 g/t, the content of aluminum is 50-90 g/t. The content of gallium is also small, 0.7 g/t, and the content of vanadium is 0.14 g/t. In the third group of compound elements are included elements for which significant and systematic differences are not detected in the samples of the two basins being compared. They are close in content of zinc, nickel, chromium, molybdenum, tin, niobium and other metals. There are not many differences in the amount of beryllium, silver, tungsten and tin. In previous works zinc, selenium and lead compounds were isolated from Karatau phosphorites and a zinc-containing sorbent and a selenium-lead catalyst were prepared. The zinc sorbent and the selenium-lead catalyst were prepared in the form of tablets and placed on a metal tray (ULVAC JAPAN, Ltd.). The device of the Japanese company was made of carbon nanotubes and zinc-containing nanosorbent [9] or nanocatalysts containing selenium-lead [10].

In the present work, aluminum is found to range between 3,57 and 6,93% in the chemical composition of phosphorites, which compares with the previously formed zinc element (2,5-4,8%), and with the lead element content (0,4-0,6%). The high percentage of aluminum in phosphorites affects the higher weight loss of the formed sorbents. Further, when making aluminum-vanadium nanotubes in carbon nanotubes, the content of aluminum oxide is adequate. Aluminum-vanadium catalysts are used in the production of sulfuric acids, for the purification of sulfurous and hydrogen sulfide gases. Therefore, recommendations for the approximation of processing to the place of use of aluminum-vanadium nanocatalysts can dramatically reduce the cost of raw materials, process heat and water supply.

2. Experimental

2.1. Materials and Preparation Procedures

Phosphate raw materials were collected in the Karatau basin of Kazakhstan, country that has the largest reserves of phosphorites in the world. The synthesis of phosphorite waste and phosphogypsum is highly dependent on the nature of both raw materials and precipitating agents. First, a mixture of concentrated nitric (100 mL of HNO_3 (65-68% by mass)) and hydrochloric (300 mL of HCl (32-35% by mass)) acids (royal vodka), taken in a ratio of 1:3 by volume (mass ratio, in terms of pure substances, about 1:2) was prepared. Then, 50 g of phosphorus and 50 g of phosphogypsum were placed in 2 different volumetric flasks, to which were added 100 mL of distilled water and 200 mL of royal vodka. All the precipitate remains insoluble and the filtrate was filtered with a filter paper in order to recover the insoluble precipitate [11]. The precipitate was rinsed on the filter paper several times with hot water and distilled water was added to the mark of the volumetric flask. Following the separation of the precipitate, the subsequent analytical results were used to recover the aluminum and vanadium sorbents from the resulting liquid solution.

2.2. Recovery of the vanadium sorbent from the phosphorite raw material residues and from phosphogypsum

To recover the vanadium-containing sorbent from the liquid solution of the phosphorite raw material decomposed in royal vodka, 3-4 g of $CH_3COONa.3H_2O$ were added to 10 mL of a 2 N acidic solution. CH_3COOH was added and heated until $V(OH)_2$ precipitate is completely formed. The hot solution was filtered and the precipitate was washed

with a 0.1 N CH_3COOH solution. Then placed in a beaker, mixed with H_2SO_4 and dry $H_2C_2O_2.2H_2O$ added and evaporated until total evaporation. After cooling, the mixture was diluted with 200 mL of water and the infusion repeated. The following steps were performed to meet the required settling conditions again. A few drops of methyl red were added to 200 mL of a solution containing 5 g of ammonium chloride or an equivalent amount of free hydrochloric acid and no oxidizing agents (e.g. nitric acid) that can destroy the indicator, and heat the solution to the boiling point. Dilute (1:1) ammonia solution was carefully added until the solution turns light yellow and boiled for 1-2 minutes. If the solution changes color to orange or red, ammonia was added and filtered immediately. The precipitate was thoroughly washed with a 2% solution of ammonium chloride and recovered by filtration.

The precipitate was further dissolved with hot diluted hydrochloric acid, the filter washed with hot water and stored. Then vanadium was added and so a precipitate was again formed. The precipitate was filtered and washed as before. The final settling should be done with filter paper and the solution should drain well from the precipitate. After filtration, VO_2 was dried. The conversion factor for vanadium was 0.5995 [10,11]. Ammonia filters and effluents were combined for treatment and the precipitate was dried as described above and further analyzed.

The precipitate measured from ammonia was melted with pyrsulfate and dissolved in dilute (1:20) sulfuric acid. The resulting solution was divided into approximately equal parts, one part treated with a few drops of hydrogen peroxide (30%) and the color of the two parts was compared. This test detects the presence of visible particles of titanium or vanadium. The appearance of pure yellow-orange color of the solution indicates the presence of vanadium, the reddish-brown color indicating the presence of vanadium, and the absence of color change indicating the absence of both elements [10-12].
The above method was used to decompose phosphogypsum in royal vodka and to recover the vanadium-containing sorbent from the resulting liquid solution, but no precipitate was formed.

2.3. Recovery of the aluminum sorbent from the phosphorite raw material residues and from phosphogypsum

In a typical procedure, aluminum is precipitated from ammonia along with many other elements such as iron, titanium, zirconium, vanadium, phosphorus, and silicas of aluminum are observed when the hydroxide or oxide is treated with hydrochloric acid, dried and carefully fired after evaporation.

2.4. Growing of carbon nanotubes over the aluminum and vanadium sorbents

A pressstep was prepared as a 1 cm^2 tablet of dry powder containing aluminum and vanadium, which was recovered from the raw phosphorite and solid residual phosphogypsum in royal vodka. Then, a carbon nanotube reactor was used to grow carbon nanotubes by chemical vapour deposition (CN-CVD-100 method). The synthesis was conducted in the following sequence [10,12]: 1) process gas (methane, hydrogen) enters the reactor chamber; 2) the plasma is ignited through a quartz window by injecting microwave radiation into the reactor chamber; 3) the growth of carbon nanotubes occurs by placing the pressed tablet in a metal tray (ULVAC JAPAN, Ltd.). The sample accommodates a metal substrate with a diameter of 1 inch (25 mm). The device of the Japanese company is embedded in a carbon nanotube and sending it to the microwave. Each tablet was processed feeding methane gas for 10-15 minutes at a temperature of 600ºC and pressure of 260-280 kPa. In this process, methane gas burns and hydrogen gas decomposes, and the free carbon atoms gradually settle on the surface of the tablet and are adsorbed and grown as carbon nanotubes. The device was remotely controlled with a touch screen using the "CN-CVD-100" method.

2.5. Characterization of materials and analytical methods

The functional composition and symmetry of the synthesized sorbents were confirmed by infrared spectroscopy. The method of oscillating IR spectroscopy consists on the passage of light through a substance, which absorbs certain frequencies that correspond to the natural oscillation frequency of atoms (ions). The method of IR spectroscopy is sensitive in some cases, but X-ray allows determining the mixed phases, unlike the method of phase analysis. IR absorption spectra were prepared on the KBr substrate in the form of thin tablets by Infraspek, Model FSM 1201 (Russia, St. Petersburg) in the wavelength range of 1400-400 cm^{-1}.
Scanning electron microscopy (SEM) was performed to provide information about the surface of the samples in high (up to 0.4 nanometers) space, as

well as the composition, structure and other properties of the surface layers. It is based on the principle of interaction in the electronic bundle of the sample.

The growth of carbon nanotubes was carried out on the carbon nanotubes of the company "CN-CVD-100". This device is based on the cultivation of carbon nanotubes by placing the test compounds or substances in the form of tablets in a press and placed on a metal bed (metal substrate) with a volume of 1 cm^3. The device consists of 3 systems; 1) Cultivation system, 2) Vacuum system, 3) Electrical system. The inner diameter of the cultivation chamber is 55 mm and the length is 240 mm. Inside the chamber there is a metal screen equipped with a cooling air blower. The test objects are placed on a metal tray (ULVAC JAPAN, Ltd.) with a diameter of 1 inch (25 mm). The vacuum system is equipped with a pre-vacuum pump with a capacity of 100 L/min. The measuring device is equipped with a diaphragm vacuum gauge. The gas supply system has 2 gas meters. Gas meters ensure the release of hydrogen and methane gases. The vacuum injection in the control system is manually controlled by a touch screen. 1) In the gas delivery system, the gas delivery speed is controlled, hydrogen and methane gases being released at 100 cm^3/second. Gaseous nitrogen is used to dilute process gas, the gas flow rate should be 20 L/min. 2) After loosening the lower bolt, a half-flange is installed and the cooling fan is switched on. 3) After installing the test substance in the device and activating the carbon nanotube, the readiness of the CN-CVD-100 to be tested on the touch screen is indicated by a signal. 4) After placing the test substance on the metal tray, attaching it to the device and directing the plasma-supplied quartz glass tube to the carbon nanotube, methane gas is supplied from the gas supply system at a pressure of 260-280 kPa. The free carbon gradually settles on the surface of the test substance. As a result of the study, the color of the tablet changes to black. The tablet was removed from the device, cooled and its microstructure was studied.

Results and discussion

2.6. Elemental composition of the phosphorous raw material
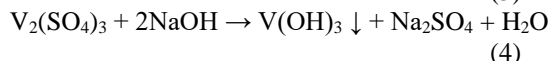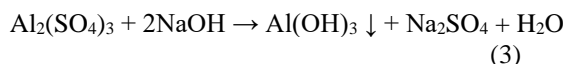
The composition of the ore from which aluminum and vanadium compounds were extracted from phosphorite multicomponent concentrate, by leaching with sulfuric acid solutions, is given in Table 1.

As can be seen from Table 1, the maximum contents of aluminum (Al) and vanadium (V) in the studied phosphorite is 6.93 and 0.14%, respectively. As vanadium is an active catalyst, it is important in the chemical industry. Vanadium catalyst (V_2O_5) is used in the production of sulfuric acid and also as catalyst in various organic chemical reactions. The reactions described in equations (1) and (2) occur when the ore reacts with sulfuric acid [13,14]:

$$Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2 \uparrow \quad (1)$$

$$V + 6H_2SO_4 \rightarrow V_2(SO_4)_3 + H^+ \uparrow \quad (2)$$
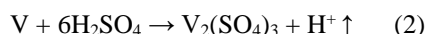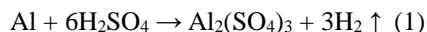
Based on the composition of the ores and on the properties of aluminum and vanadium, it can be assumed that all these elements are successfully transferred to the product solution during leaching with sulfuric acid solutions. When the raw phosphorite is decomposed in sulfuric acid, filtered and then poured into a liquid phase 10-15% NaOH solution, aluminum and vanadium compounds precipitate according to equations (3) and (4) [15,16].

$$Al_2(SO_4)_3 + 2NaOH \rightarrow Al(OH)_3 \downarrow + Na_2SO_4 + H_2O \quad (3)$$

$$V_2(SO_4)_3 + 2NaOH \rightarrow V(OH)_3 \downarrow + Na_2SO_4 + H_2O \quad (4)$$

The precipitates were further filtered and physicochemical studies were carried out on the elements aluminum and vanadium in the solid waste.

2.7. IR spectroscopy of the recovered aluminum and vanadium compounds

The study of the IR spectrum of compounds allows to obtain important information about the structure, composition and interaction of the structural components (fragments) that make up the substance, both in solid state (crystalline or amorphous) and in solution. IR spectra also provide information about the state of molecules absorbed or located on the surface of a substance, depending on the presence of channels, holes, layers and spaces between the grain space.

Table 1 Elemental composition of the phosphorous raw material

Sample point	O, %	Na, %	Mg, %	Al, %	Si, %	P,%	S,%	Cl,%	Ca,%	Ti, %	V, %	Mn, %	Fe, %	total, %
1	20,80	19,16	5,77	5,27	0,29	0,24	0,09	27,87	7,71	0,12	0,012	0,34	12,31	100
2	15,88	24,79	4,14	3,57	0,23	0,28	0,82	36,36	5,30	0,00	0,04	0,36	8,23	100
3	27,86	11,56	7,10	6,93	0,48	0,21	0,41	18,60	11,27	0,00	0,14	0,29	15,16	100
average	21,51	18,51	5,67	5,25	0,34	0,24	0,44	27,61	8,09	0,04	0,05	0,33	11,92	100

IR spectra of absorption bands characteristic of crystallized aluminum in the structure of the phosphorous raw material of the synthesized compound are shown in Figures 1 and 2. Table 2 shows the IR spectrum of absorption bands of aluminum obtained from phosphogypsum (solid residue after decomposition of phosphorites), and Table 3 shows the IR spectrum of absorption bands of aluminum obtained from phosphorous raw materials of the Karatau deposit.

Analytical lines of the aluminum element are located mainly in the visible and ultraviolet regions of the spectrum. It should be noted that the study of the protective layer by IR spectroscopy in the region of 4000-400 cm^{-1} shows that the structure of the aluminum oxide-hydroxide layer is heterogeneous. In addition to the absorption bands characteristic of aluminum oxides, oscillations of the Al-OH bond associated with aluminum hydroxide are observed. The IR spectrum of the initial mixture contains absorption bands characteristic of tetrahedral coordinated aluminum containing γ-Al_2O_3 (753.2 and 777.3 cm^{-1}).

According to literature [17-18], the range of intensive absorption of 935.5 cm^{-1} corresponds to the deformation oscillations of Al-OH. Slight absorption bands appear at 577.5, 554.3 and 869.1 cm^{-1}, attributed to the structure of θ-Al_2O_3. It also contains gibbsite $Al(OH)_3$,121.9.9; 1100,1; There may also be a set of strips 493.1 and 419.3 cm^{-1} [12-14]. A band at 1030.0 cm^{-1} indicates the presence of $Al(OH)_3$ bayerite. Aluminum is a white polycrystalline powder obtained from the synthesized phosphorous raw material, and the aluminum sample made of phosphogypsum is a light-yellow crystalline powder. The spectra of all bands were predicted based on the group theory of absorption. According to the data shown in Table 2, the absorption band at ~3400 cm^{-1} belongs to the surface OH-groups. There are also structural hydroxo-groups, whose chronic oscillations are visible at the level of 3036.5 and 3290.1 cm^{-1}. The range at 1630 cm^{-1} corresponds to the deformation oscillations of water, and the ranges at 1022, 970, 800 and 740 cm^{-1} are caused by the deformation oscillations of the OH-hydroxide groups. The Al-O bond provides absorption bands in the region of 500-422 cm^{-1}.

Phosphorus tetrahedrons O-P-O are associated to the elongated asymmetric oscillations of the band appearing at 1039-1080 cm^{-1} in this region of the IR spectrum, and the single-band ν(P-O) = 509-592 cm^{-1} is assigned to valence symmetrical P-O oscillations. The lowest frequency of the spectral maximum in the valence band belongs to the oscillations of P-O bonds in $(PO_4)^{3-}$ phosphate anions and in $(P_2O_7)^{4-}$.

Table 2 IR spectrum of absorption bands of aluminum obtained from phosphogypsum and grown on carbon nanotubes

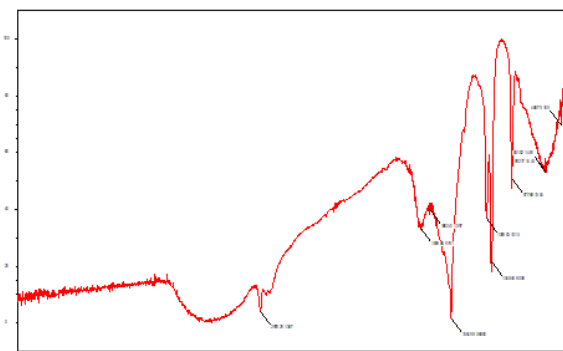| Functional groups	Al sorbent recovered from phosphogypsum	Al nanosorbent in the grown carbon nanotubes
H_2O (νOH)	3400	3412
C	-	2179-2056
Al-NO_3	1639	1618
Al-P_2O_7	1384	1442
O–P–O	1089	1080
ν(P–O)	592	509-592
Al-O	466	420

Fig. 1. IR spectrum of aluminum recovered from phosphogypsum
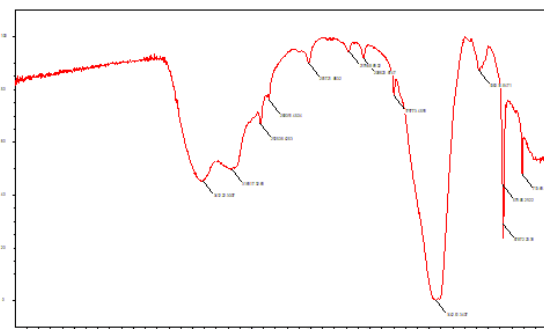

Fig. 2. IR spectrum of aluminum recovered from phosphogypsum in the grown carbon nanotubes

In the IR spectrum of aluminum compounds derived from phosphogypsum it also observed activity in the region of 1628 cm^{-1} and in the range 580–820 cm^{-1}, due to chronic oscillations of the v(Al-O) bond [17-19]. In addition, Al-NO$_3$ bonds are visible in the range 1618-1699 cm^{-1} and are defined by intensive absorption bands, due to their symmetry. The IR spectra of nanotubes grown on powdered samples at a temperature of 600°C in carbon nanotubes grown on aluminum nanosorbent corresponded to the symmetrical and asymmetrical oscillations of carbon bonds in the range of 2133-2235 cm^{-1}, in contrast to the previous powder. According to the data given in Table 3, the absorption band at ~3400-3300 cm^{-1} belongs to the surface OH-groups. The range 1626 cm^{-1} corresponds to the deformation oscillations of water. Phosphorous tetrahedrons belong to the O-P-O oscillations with respect to the elongated asymmetric oscillations of the band appearing at 1087 cm^{-1} in this region of the IR spectrum. The lowest frequency of the spectral maximum in the valence band belongs to the oscillations of P-O bonds in $(PO_4)^{3-}$ phosphate anions and $(P_2O_7)^{4-}$. The two bands δ (ClO_3) = 711-713 cm^{-1} correspond to the predicted bands of oscillations of asymmetric deformation [20,21].

The bands of anhydrous aluminum dihydrogen phosphate correspond to the deformation oscillations of the bonds at 1136-1398 cm^{-1}. However, some complex aluminum cations and NO$_3^-$ anions are visible around 1626 cm^{-1} and are characterized by intense absorption bands due to their symmetry. Table 4 shows IR spectra of aluminum nanosorbent present in the grown carbon nanotubes at a temperature of 600°C were found in powder samples, which, in contrast to unburned powder, correspond to symmetrical and asymmetrical oscillations of carbon bonds in the range of 2850-2924 cm^{-1}.

The IR spectrum of vanadium obtained from raw phosphorite and grown in carbon nanotubes are given in Figures 3 and 4, respectively. According to these Figures, the weak bands at a frequency of 2363-2365 cm^{-1} are characteristic of phosphoric acid, and the intense bands at a frequency of 1618 and 1402 cm^{-1} are characteristic of vanadium sulfate or nitrate ions. The frequencies in the region 1384-1402 cm^{-1} correspond to the deformation oscillations of Ti-O and V-O bonds, the band at 1107-1047 cm^{-1} to the deformation frequencies of Ti-OH and V-OH bonds, and that at 871 cm^{-1} to the valence oscillations of TiO compounds. According to the results of the obtained IR spectrum, vanadium can be in the form of compounds of sulfate and phosphate ions. IR spectra of vanadium-containing nanosorbent grown on powder nanotubes at a temperature of 600°C were determined, which differs from the original powder in that it corresponds to symmetrical and asymmetrical oscillations of carbon bonds in the range of 2850-2924 cm^{-1}.

Table 3 IR spectrum of absorption bands of aluminum obtained from phosphogypsum and grown on carbon nanotubes

Functional groups	Al sorbent from phosphogypsum	Al nanosorbent grown on carbon nanotubes
H$_2$O (vOH)	3400-3300	3400-3300
C	-	2920
Al -NO$_3$	1793	1799
Al-P$_2$O$_7$	1384	1404
O – P – O	1087	-
δ (ClO$_3$)	711	713
v(P–O)	599	509

Table 4 : IR spectrum of vanadium absorption bands obtained from phosphorous raw materials

Functional groups	V sorbent from phosphogypsum	V nanosorbent grown on carbon nanotubes
H$_2$O (vOH)	3138-3414	3138-3414
C	-	2850-2924
H$_3$PO$_4$	2363	2365
V-NO$_3$	1618	1616
V-O	1384-1402	1402
V-OH	1107-1047	1112
VO	871	711-871

Fig. 3. IR spectrum of vanadium recovered from raw phosphorite
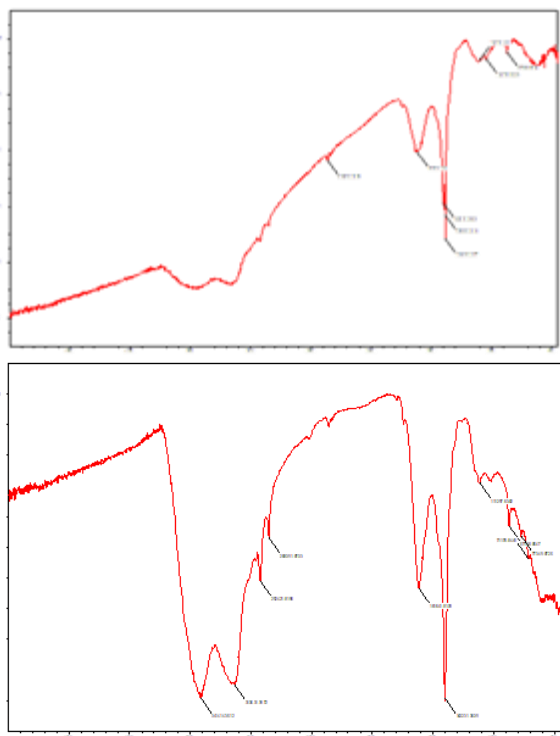
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Fig. 4. *IR spectrum of vanadium-containing compounds derived from phosphorite raw materials in the grown carbon nanotubes*

Fig. 5. *SEM microphotography of aluminum compounds recovered from phosphorite raw materials*

2.8. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD)

According to the data obtained, it was proved that the formation of phosphate compounds containing magnesium, strontium and vanadium was observed in the IR spectrum [21,22]. The study of the morphology of aluminum and vanadium compounds revealed that the elements obtained from aluminum and vanadium contain other elements (Table 5). This table shows that the amount of aluminum obtained from the raw material of phosphorite is 2.96 - 3.03. In addition, it contains elements of oxygen, sodium, calcium, iron, including large amounts of oxygen.

Figure 5 shows the results of scanning electron microscopy of the aluminum compounds recovered from phosphorite raw materials. The details of these specimens show that they present form of leaves. Aluminum ions in the micrographs of the studied samples are observed in the form of particle sizes with hexagonal structure. This inhibits the growth of crystals of aluminum phosphates [21,22].
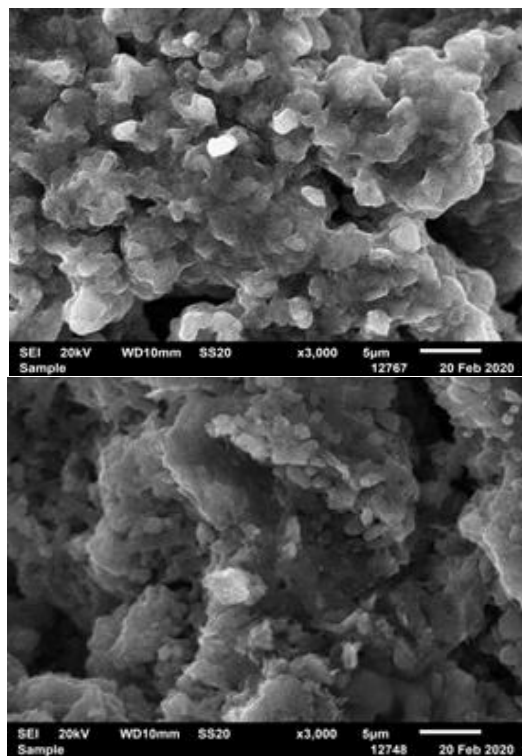
Figure 6 shows the results of scanning electron microscopy of aluminum nanoparticles recovered from raw phosphorite in grown carbon nanotubes. The composition of aluminum elements on this grown carbon nanotubes was studied and it was found to contain other elements. It is shown that the content of aluminum from phosphorite raw materials is 2.3-2.59. In addition, it contains elements of oxygen, sodium, calcium, iron, including a large amount of oxygen [23-25].

As shown in Figure 6, the morphology of the samples reveals that the surface structure of the nanoparticles is in the form of leaves. According to the results of the study, the effectiveness of small differences in the amount of nanostructured aluminum is observed. A new compound was formed by determining the composition of the aluminum element derived from phosphorite raw materials in the grown carbon nanotubes.

The examination of the obtained vanadium precipitate with the help of scanning electron microscopy showed that the particle size is lower than 5-10 nm in porous agglomerates. Aggregates have different sizes depending on the conditions of synthesis. The resulting vanadium precipitate formed an amorphous structural product in the form of

colloidal, hydrated particles of variable composition VO, which is structured as follows due to the interaction of OH groups [26]. The results of the V compound obtained from the phosphorite feedstock determined by SEM method are shown in Figure 7 and Table 5, detailing the elements that are formed in this compound.

It was found that these compounds contain oxygen, sodium, magnesium, aluminum, silicon, phosphorus, chlorine, calcium, titanium, vanadium, manganese and iron. Among these elements, the precipitate contained 0.14 % of vanadium compounds.

As can be seen from the microphotography in Figure 7, the metal particles are expressed in the form of grains, meaning that the addition of ammonium hydroxide causes the deposition of large grain precipitates. The processing performed in royal vodka allows to obtain micro-smooth surfaces with crystalline layers of precipitated V oxide.

The composition of vanadium elements derived from phosphorite raw materials in carbon grown nanotubes was studied and it was found that they contain many elements and that the amount of the element V obtained from phosphorite raw materials is around 0.14%. In addition, it contains elements of oxygen, sodium, magnesium, aluminum, silicon, phosphorus, chlorine, calcium, titanium, vanadium, manganese, iron, including large amounts of chlorine [27]. After growing this sample on a carbon nanotube, Al and V compounds can be seen that it contains 12.7 carbon atoms. In contrast to the previous model of V nanosorbents obtained from phosphorite raw materials, it was found that they contain a C atom. The content of these elements is given in Table 6.

By determining the composition of the V-containing nanosorbent compounds derived from phosphorite raw materials and in grown carbon nanotubes, it was proved that a new compound

$C_4O_5Na_3MgAlSiPCl_3SaTiVMnFe$ was formed. In most cases, the content of vanadium in the raw material of phosphorite does not exceed 1%, but sometimes it can be as high as 5%. The presence of vanadium is more frequent and requires quantitative analysis of many other substances, such as ores, refractory materials and metallurgical products. In this regard, methods of separation and determination of vanadium are very important.
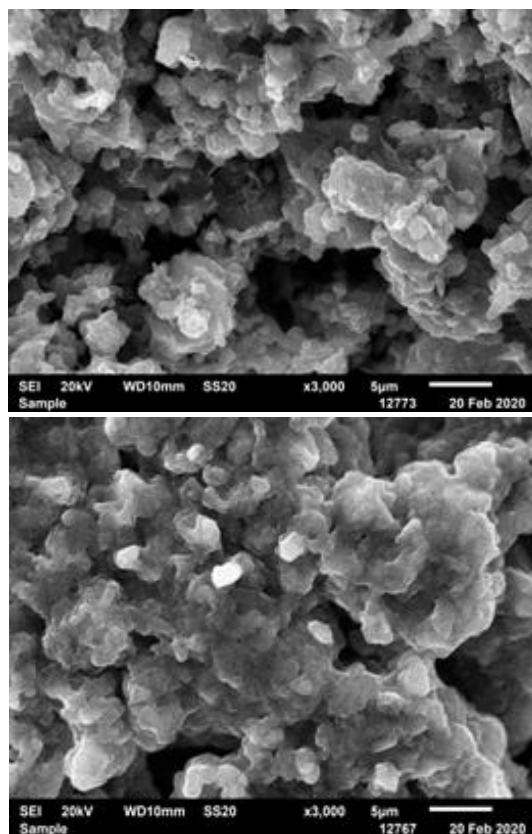

Fig. 6. *SEM microphotography of aluminum nanotubes recovered from phosphorite raw materials in grown carbon nanotubes*

Table 5 : Composition of the vanadium compounds derived from phosphorite raw materials

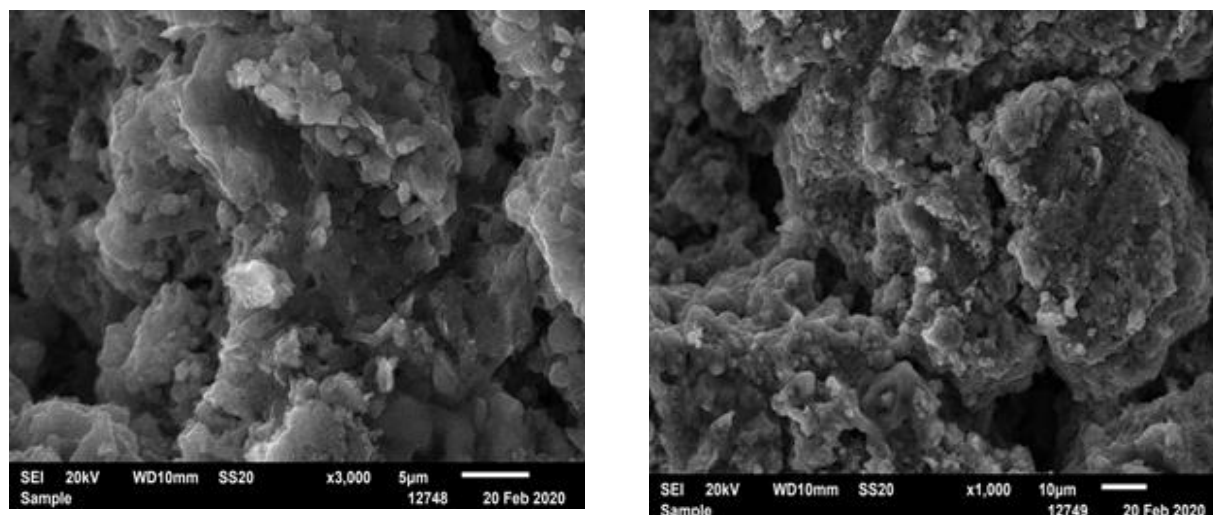| X-ray phase sample	O, %	Na,%	Mg, %	Al,%	Si, %	P,%	Cl,%	Ca,%	Ti, %	V, %	Mn, %	Fe, %	total, %
1	40,35	16,87	4,30	3,55	0,14	0,22	13,63	11,85	0,00	0,04	0,24	8,63	100
2	36,60	18,92	4,16	3,59	0,11	0,22	16,36	11,11	0,00	0,06	0,33	8,36	100
3	37,01	19,96	4,31	2,84	0,22	0,12	16,09	11,35	0,11	0,14	0,00	7,98	100
Average	37,99	18,58	4,26	3,33	0,16	0,19	15,36	11,44	0,11	0,14	0,19	8,36	100

Fig. 7. *Images of vanadium obtained from phosphorite raw materials by scanning electron microscopy*

Table 6 Composition of vanadium elements derived from raw phosphorite and in grown carbon nanotubes

X-ray phase sample	C, %	O, %	Na, %	Mg, %	Al, %	Si,%	P,%	Cl,%	Ca,%	Ti,%	V, %	Mn, %	Fe, %	total, %
1	12,9	20,8	19,1	5,77	5,27	0,29	0,24	27,8	7,71	0,12	0,04	0,34	12,3	100
2	12,5	15,8	24,7	4,14	3,57	0,23	0,28	36,3	5,30	0,01	0,06	0,36	8,3	100
3	12,8	27,8	11,5	7,10	6,93	0,48	0,21	18,6	11,2	0,02	0,14	0,29	15,2	100
average	12,7	21,5	18,5	5,67	5,25	0,34	0,24	27,6	8,09	0,12	0,14	0,33	11,9	100

Table 7: Composition and mass fraction of vanadium-containing nanosorbents in grown carbon nanotubes obtained from phosphorous raw materials of the Karatau deposit

Sample	Elements	Mr, g	W, %	W/Mr, %	Arithmetic calculation Result
1	C	12	12,7	1,06	4,24
2	O	16	21,5	1,34	5,36
3	Na	23	18,5	0,8	3,2
4	Mg	24	5,67	0,24	0,96
5	Al	27	5,25	0,19	0,76
6	Si	28	0,34	0,012	0,048
7	P	31	0,24	0,008	0,032
8	Cl	35,5	27,6	0,77	3,08
9	Ca	40	8,09	0,2	0,08
10	Ti	48	0,12	0,0025	1
11	V	51	0,14	0,0027	1,08
12	Mn	55	0,33	0,006	0,024
13	Fe	56	11,9	0,21	0,84
Formula	$C_4O_5Na_3MgAlSiPCl_3CaTiVMnFe$ C-O-Na-Mg-Al-Si-P-Cl-Ca-Ti-V-Mn-Fe-..........				

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Conclusions

The chemical composition of the phosphorous raw materials of the Karatau deposit and the phosphogypsum solid residue were studied, the percentage of aluminum and vanadium elements was determined, and a method for extracting aluminum and vanadium compounds from phosphorous raw materials and phosphogypsum solid residue was developed. According to the developed method, aluminum and vanadium compounds were isolated, sorbents were obtained, and carbon nanotubes were grown on the obtained catalysts in the device of the company from Japan "ULVAC JAPAN, Ltd.". Thus, the results of the study showed that the extraction of valuable aluminum and vanadium compounds from the phosphorous raw materials of the Karatau deposit can be used to obtain sorbents and catalysts containing aluminum and vanadium, as well as carbon aluminum-vanadium-containing nanocatalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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