Review of modern scientific developments in the field of extraction of vanadium oxide from petrochemical catalysts

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A review of the scientific and technical literature on hydrometallurgical methods for extracting high-purity vanadium oxide from spent catalysts in the petrochemical industry has been carried out. Currently, high-purity vanadium oxide ($V_2O_5 \geq 99.5\%$) is not produced in Russia. The main consumer of high-purity vanadium oxide is the rapidly developing production of vanadium-containing master alloys for the manufacture of titanium alloys. In the chemical industry, high-purity vanadium oxide is used to produce catalysts for the synthesis of phthalic and maleic anhydrides.
One of the promising sources of vanadium is spent (deactivated) vanadium catalysts (SVC), in which the content of the valuable component in terms of pentoxide (V_2O_5) can reach 4–8%. It is much higher than in most processed ore raw materials. Spent catalysts are a secondary raw material, since during operation there is a loss of catalytic properties (activity, conversion, selectivity). After several cycles of regeneration, such a product is a subject of recycling to obtain valuable components.
It should also be noted that there is an increase in demand for hydrotreating catalysts, which may cause an excess of spent catalysts in the future. In this regard, there is an urgent need to develop a highly efficient technology for processing catalysts in order to extract valuable components.
The review of the scientific and technical literature shows that there are many methods for processing spent catalysts. The article describes the methods of acid, alkali, soda leaching, as well as the performance indicators of these processes. But the existing scientific developments in this area need further development in order to improve the efficiency of the vanadium oxide leaching process.

Key words: vanadium oxide, alkaline leaching, acid leaching, soda leaching, hydrometallurgy, spent petrochemical catalysts.

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Introduction

Vanadium is a trace rare element and is at number 23 in the D.I. Mendeleev periodic table of chemical elements. According to [1], the mass content of metal in the earth's crust is $1.6\times10^{-2}\%$, in the world ocean — $3\times10^{-7}\%$, however, vanadium is not found in free form. Vanadium compounds are widely used in the petrochemical industry in the production of catalysts , steel, and are also known as "vitamins of modern industry" [2].

The main sources of vanadium are vanadium titanomagnetite, coal, slag and others. Particular attention is paid to the extraction of vanadium from spent (deactivated) catalysts (SVC). Typically, the content of the valuable component in such a multi-component raw material is about 4-8%, which is higher than in most processed ore raw materials.

Currently, there is an increase in the demand for catalysts in the oil refining and petrochemical industries **(Fig. 1)**. Thus, in 2020, the volume of catalysts consumption in Russia amounted to more than 17.5 thousand tons. According to the forecast, by 2030 this figure will reach 26 thousand tons [3].

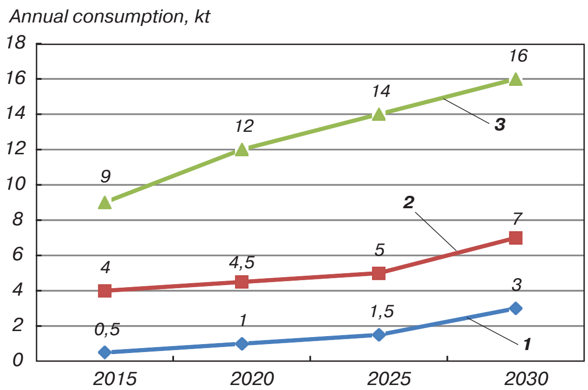

Fig. 1. Demand for catalysts by types, thousand tons per year [3]:
1 — hydrocracking; *2* — hydrotreating; *3* — catalytic cracking

Research methods and results

Due to the increase in demand for petrochemical products, a problem arises in the recycling of catalysts used in the technological cycle of hydrocarbon processing. In this regard, there is also a need to develop an integrated technology for processing catalysts. Thus, in the study [4], a complex technology for processing **(Fig. 2)** a spent vanadium catalyst for the synthesis of sulfuric acid was developed. The original catalyst contained in the mass. %: V_2O_5 – 4.7; SiO_2 – 57.3; K_2O – 8.7; Fe_2O_3 – 2.6; the rest is others. To extract vanadium from the catalyst, leaching with a 2% oxalic acid solution was used at a temperature of 50 °C for 4 h at a solid to liquid ratio ($S : L$) = 1 : 25. During the study, it was found that vanadium, potassium and iron ions pass into the solution, which makes it difficult to further separate the elements.

To separate vanadium, ionic resins Amberlite IR-120 plus (H), Dowex 50 W X4-100 (H) and Dowex 50 W X4 (H) were used, which have the lowest affinity for vanadium compared to potassium and iron. After sorption, the eluate, purified from impurities, was subjected to chemical precipitation to obtain crystalline vanadium oxide, or used to regenerate the vanadium catalyst by the wet method. Recovery of V, K and Fe were 91%, 92% and 63%, respectively.

The work [5] describes pyro- and hydrometallurgical methods of processing SVC in order to extract vanadium and associated valuable elements. The pyrometallurgical method for extracting vanadium from spent catalysts consists in two-stage roasting of SVC, the first of which is carried out in air and is aimed at cleaning the catalyst from carbon, and the second is oxidative, carried out with the addition of NaCl. As a result of the pyrometallurgical processing of the SVC, the extraction of vanadium did not exceed 77%. The work also notes high energy costs and low environmental friendliness of pyrometallurgical methods for processing of SVC. As an alternative to pyrometallurgical technologies, hydrometallurgical schemes for the processing of vanadium are proposed, consisting of the treatment of SVC with aqueous solutions, the leaching of a valuable component and its further isolation from the solution. Extraction of vanadium from SVC is 85%.

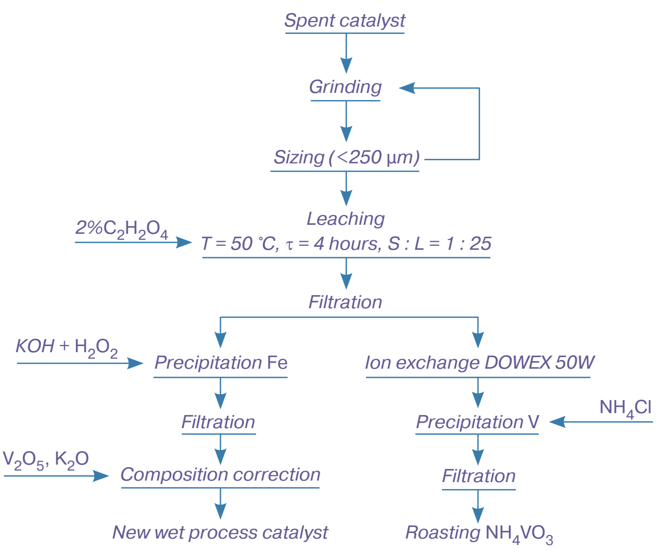

Fig. 2. The proposed technological scheme for the integrated processing of spent catalysts [4]

In [6], the influence of water leaching modes on the degree of vanadium extraction from slags of titanium-magnesium ores obtained by soda technology was studied **(Fig. 3)**. It is noted that the degree of extraction of vanadium for the JSC EVRAZ NTMK slag increased by 50% (from 43 to 65%) with an increase in temperature from 50 to 80 °C. For the slag after the ITmk3 process, a similar dependence was established, however, the highest degree of extraction was 37%.

The method of processing SVC in the production of sulfuric acid is described in [7]. The spent catalyst is subjected to a two-stage leaching **(Fig. 4)**. The extraction of vanadium into the solution was 92.5%. Next, tetravalent vanadium is oxidized to pentavalent one using a three-chamber electrolyzer. The solution is poured into the anode space. After that, V_2O_5 precipitates to 85%, and the solid residue contains up to 90% vanadium.

A known method of processing SVC of sulfuric acid production [8], which includes preliminary grinding of the catalyst and leaching with sulfuric acid. This method makes it possible to obtain up to 98% of vanadium compounds with a yield of up to 87% in the finished product.

A method has been developed [9] for processing vanadium-containing raw materials. The technology includes a two-stage heap leaching, vanadium sorption, as well as additional strengthening of sorption circulating mother liquors with sulfuric acid. This development shows the degree of vanadium extraction into solution of about 75.7%.

Known is the development of a method for obtaining vanadium from spent catalysts for the production of sulfuric acid, in which vanadium is obtained by two-stage leaching (acidic and reductive) [10]. According to the proposed technological scheme, it is possible to completely process all by-products and obtain V_2O_5 with a purity of 85–87%. According to the technology, solid

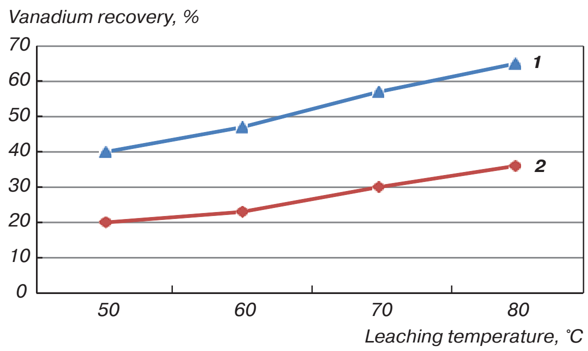

Fig. 3. The proposed technological scheme for the complex processing of spent catalysts [6]:
1 – JSC EVRAZ NTMK slag; *2* — ITmk3 process slag

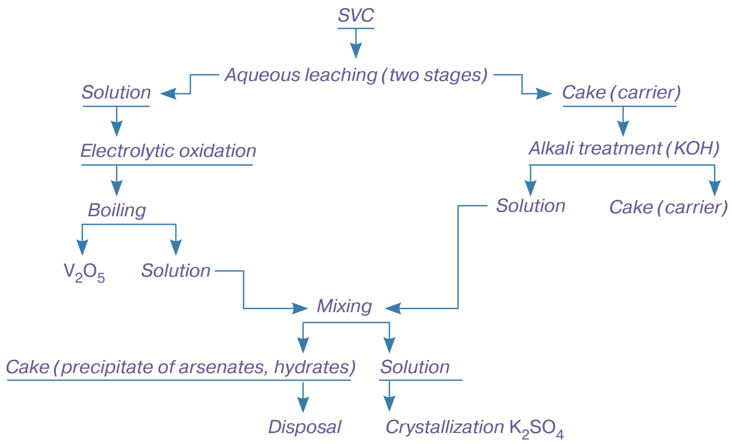

Fig. 4. Technological scheme for processing spent vanadium catalysts [7]

residues can be used for the production of building materials, coagulants, and also as fertilizers in agriculture. The spent vanadium catalysts can also be used for the production of fritted colored glazes [11].

The authors of the article [12] study the process of leaching a spent vanadium catalyst with a KOH solution **(Fig. 5)**. The maximum degree of extraction of vanadium oxide into the solution was 87%. The authors evaluated the use of hydroxide to extract vanadium from spent vanadium catalyst. The obtained yields of vanadium compounds are satisfactory from a technological point of view. Vanadium can be isolated, purified and recovered from the solution by ion exchange. The solution after leaching can be used to produce fresh catalyst.

According to the method [13], the initial catalyst preliminarily crushed in a vibratory mill and separated into fractions through sieves was leached with 5% sulfuric acid at $S : L = 1 : 20$, process temperature 50 °C. The maximum degree of leaching reached the level of 91%.

In [14], the influence of the concentration of reagents, temperature, and leaching time on the degree of extraction of vanadium and tungsten from selective catalytic reduction catalysts was studied. For leaching, the catalyst was ground and sieved. A solution containing H_2O_2 and $(NH_4)_2CO_3$ was chosen as the leaching agent. The degree of extraction into solution for W was 99%, and for V, 98%.

Sulfuric acid production generates a large volume of spent catalyst containing vanadium. Thus, in [15], the efficiency of vanadium oxide leaching was studied. The original catalyst, in addition to a valuable component, contained mainly iron oxide, sulfur, potassium and silicon oxides. Hydrogen peroxide was used to oxidize sulfur to form sulfuric acid, which leached out the vanadium. The efficiency of the process is directly proportional to the concentration of hydrogen peroxide, and inversely proportional to the duration of leaching **(Figs. 6, 7)** and stirring rate **(Fig. 8)**. The maximum extraction of vanadium into the solution was 92.2%.

Currently, a leaching using pressure is quite common. Extraction of vanadium and tungsten from spent catalysts autoclave leaching with caustic soda is used [16]. Nana et al. used spent catalysts from thermal power plants, an XRF 1800 spectrometer was used to determine the chemical composition of the catalysts. A YZPR-100 reactor was used for the leaching process.

The results showed that alkaline pressure leaching allows the extraction of high purity vanadium and tungsten, 96% and 98%, respectively. This method takes less time. Also, this method reduces the concentration of the leaching agent, thereby reducing resource consumption.

The authors of the article [17] carried out the leaching of vanadium and tungsten from spent catalysts of the $V_2O_5 - WO_3/TiO_2$ system for the selective catalytic reduction. The raw materials were leached to transfer valuable components from the solid phase to the liquid one using a sealed autoclave reactor with a capacity of 1 l. Sodium hydroxide (Junsei Chemicals, 97%, Japan) was

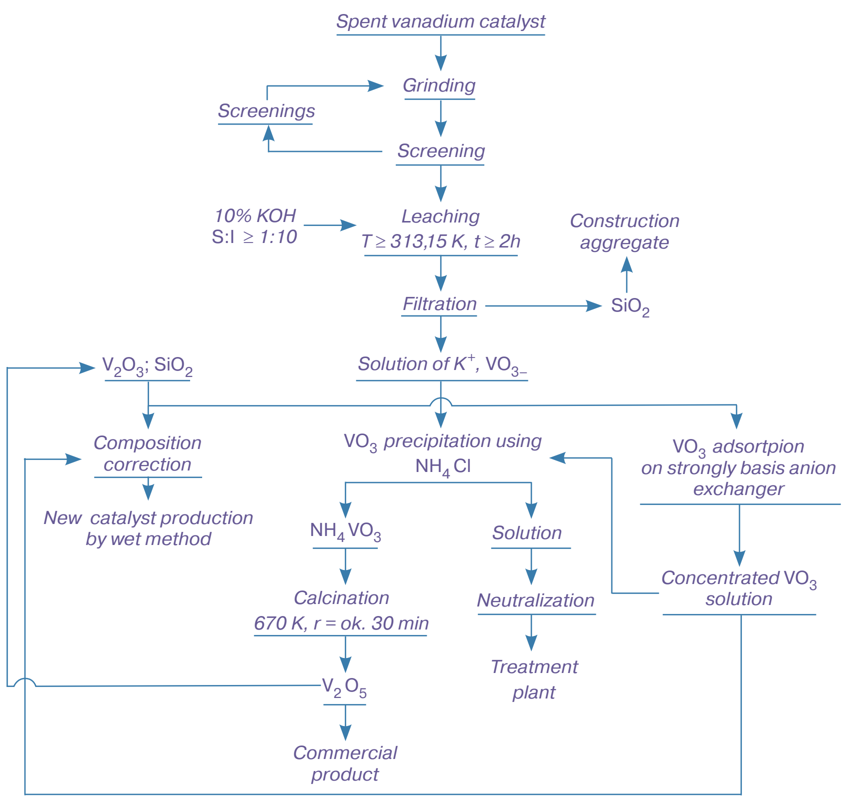

Fig. 5. Technological scheme for the extraction of vanadium from the spent catalyst by leaching with a potassium hydroxide solution [12]

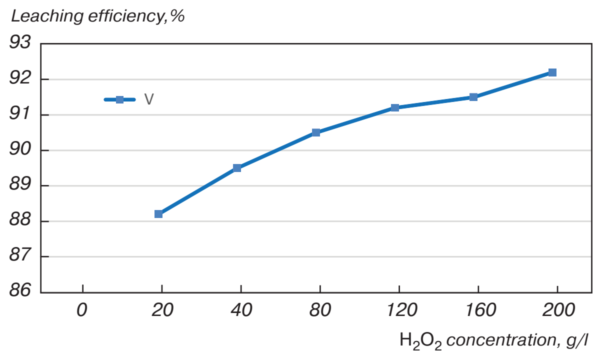

Fig. 6. Effect of H_2O_2 concentration on leaching efficiency V [15]

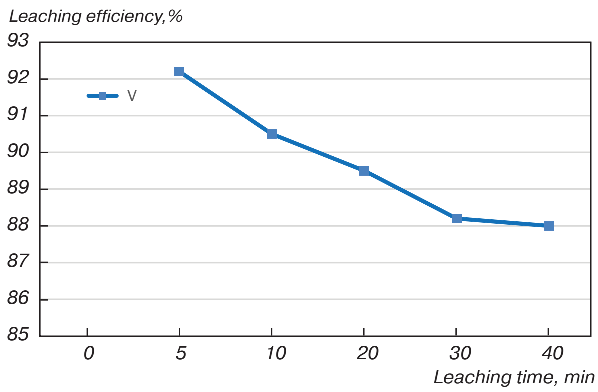

Fig. 7. Influence of duration on V leaching efficiency [15]

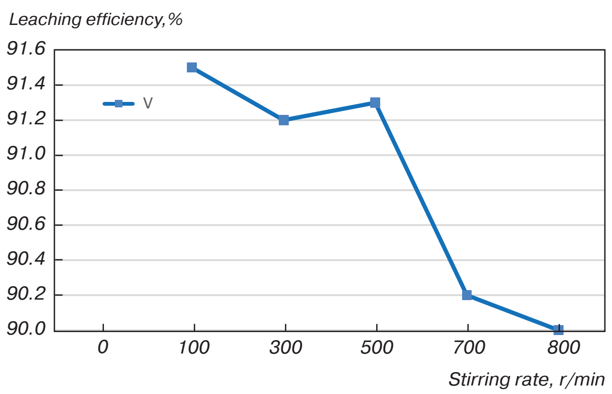

Fig. 8. Influence of stirring rate on V leaching efficiency [15]

used as an alkaline agent. The recovery of vanadium and tungsten into the solution was 98 and 91.5%, respectively.

In [18], the possibility of direct leaching of vanadium from a spent oil hydrotreatment catalyst using a sulfuric acid solution as a leaching agent was considered. As a result of a series of experiments, it was determined that the maximum extraction of vanadium into the solution is 88% with the following process parameters: the ratio $S : L = 1 : 10$, the concentration of sulfuric acid is 0.45 M at a leaching temperature of 80 °C for 2 hours.

Thus, methods for extracting vanadium from catalysts have been developed. All of them mainly include grinding of the feedstock, vanadium leaching, conversion into various compounds (precipitation, extraction, ion exchange), but the efficiency of the technology and the quality of the resulting product will depend on the indicators of the leaching process.

Conclusions

A review of the scientific and technical literature shows that most researchers choose the hydrometallurgical scheme for processing vanadium-containing spent catalysts. The use of pyrometallurgical schemes is associated with large losses of valuable components due to the volatility of their vapors at high temperatures.

In general, the method of leaching vanadium from such a multicomponent raw material has not yet been fully studied; in accordance with this, further modernization of the process is required, associated with the correct selection of optimal modes, the study of the influence of various factors on process indicators, as well as the search for instrumentation.

The results of R&D were achieved during the implementation of the project using measures of state support for the development of cooperation between Russian educational institutions of higher education, state scientific institutions and organizations of the real sector of the economy implementing complex projects to create high-tech production, provided for by Decree of the Government of the Russian Federation dated April 9, 2010 No. 218. An agreement on the provision of subsidies from the federal budget for the development of cooperation between a Russian educational organization of higher education and an organization in the real sector of the economy in order to implement a comprehensive project to create a high-tech production "Creation of an import-substituting production of high purity vanadium oxide for deep processing of hydrocarbon raw materials" was concluded between the Ministry of Science and Higher Education of the Russian Federation and JSC " Company Wolfram " dated June 25, 2021 no. 075-11-2021-053.

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