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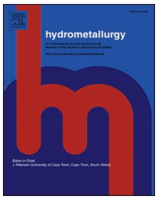

Selective recovery of vanadium pentoxide from spent catalysts of sulfuric acid production: Sustainable approach

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ABSTRACT

Spent vanadium catalysts of sulfuric acid production (main elemental composition in wt%: 7.5 V, 9.1 K, 10.2 S, 23.2 Si and 1.4 Fe) can be used as a secondary source of vanadium. Extraction of vanadium was studied using two-step leaching (acidic and reductive) of spent vanadium catalysts with further oxidizing of leaching solutions. The factors leaching and hydrolysis temperature, concentration of leaching (H_2SO_4, Na_2SO_3) and oxidizing ($(NH_4)_2S_2O_8$) reagents, solid/liquid ratio, mixing parameters, and time of leaching and thermohydrolysis were systematically investigated. The solubility of V_2O_5 was investigated as a function of temperature, pH of sulfuric acid solutions, and concentration of Na_2SO_3. The kinetics of V_2O_5 solubility and reduction were also studied. The vanadium leaching yield after a two-step recovery was 98 wt% after acidic (H_2SO_4, pH 1.2–1.3) leaching with ultrasonic treatment for 5 min at ambient temperature, followed by reductive leaching in 0.01 Mol/L Na_2SO_3 solution for 15 min at ambient temperature. The highest vanadium extraction yield from leaching solutions was 98 wt% obtained through oxidizing of leaching solutions by 30 wt%. $(NH_4)_2S_2O_8$ with a molar ratio $n(V_2O_5)/n((NH_4)_2S_2O_8)$ of 5/1 for a reaction time of 5 min at 80–90 °C. the extracted vanadium product was V_2O_5 with a purity of 85–87 wt%. The technological scheme has been developed to recycle all obtained products and sub-products

1. Introduction

Vanadium is a valuable metal widely dispersed in the Earth's crust (the 22nd most abundant element). It is found in over 50 different minerals (Habashi 1998; Habashi 2002; Moskalyk and Alfantazi 2003), however, it is never found in its pure state (Perron 2001). Nowadays, vanadium is recovered as a by-product or a co-product from mineral resources where its content ranges from 0.01–0.2 wt% to 2 wt% (Gupta and Krishnamurthy 1992; Nikiforova et al. 2017). The current primary resources are not sufficient to satisfy the vanadium demand (Liu and Yu, 2003) because of the increasing industrial interest in vanadium applications.

The steel industry is the largest consumer of vanadium. Today, its consumption in metallurgy is up to 85% of total vanadium consumption; vanadium is used as an alloying component introduced into steel as ferro-vanadium (Erust et al. 2016; Nikiforova et al. 2016). Furthermore, vanadium is widely used for the producing of vanadium redox flow batteries (VRBs) (Wang et al. 2011; Skyllas-Kazacos et al. 2011; Cheng et al. 2011). VRBs have unique advantages for large-scale application and a long cycle life in comparison with other energy storage technologies (Zhang et al. 2013; Aaron et al. 2013). Vanadium is also widely used within the chemical and petrochemical industry, where it is employed for the production of a variety of vanadium compounds, used for instance to prepare catalysts (Khorfan et al. 2001). Vanadates are also widely used as a less hazardous substitute of chromium compounds in the production of yellow-colored pigments (Zharskiy et al. 2015) and as a corrosion inhibitor for aluminum alloys (Kharitonov et al. 2017, 2018, 2019).

Growing industrial interest to vanadium requires to other ecological and economic sources to produce vanadium and its compounds. One

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source is vanadium-containing waste: spent vanadium catalyst (SVC), fly ash, converter and smelter slag (Orehova et al. 2012; Zharski et al. 2012). SVC is one of the most preferable secondary raw materials for vanadium extraction, as it contains 5–10 wt% of vanadium along with other valuable components, such as Cu, Ni, Mo, and Co, in the form of oxides or sulfates (Akcil et al. 2015; Erust et al. 2016). The average service life of this catalyst is about 2–5 years (up to 10 years) (Ullmann 's 1994). During production of sulfuric acid, about forty thousand tons of SVC are produced annually worldwide (Mauskar, 2007), which would cause several pollution problems if wasted. There are several advantages with the recycling of vanadium-containing waste. Costs of vanadium extraction from these raw materials are lower compared with natural deposits. Also, ecological arguments become increasingly important (Tadao et al. 2001; Rajendran et al. 2016; Liu et al. 2019). The United States Environmental Protection Agency classifies spent catalysts as hazardous wastes (USEPA, 2003). Vanadium is considered the major source of contamination (WHO, 2011; Navarro et al. 2007; Montiel-Davalos et al., 2012).

A number of hydro- and pyro-metallurgical processes have been proposed for metal recovery from secondary raw materials. The metals are recovered as mixed solutions and then separated through conventional separation techniques (solvent extraction, selective precipitation and ion-exchange) (Ognyanova et al. 2009).

Hydrometallurgical processes are preferred for SVC treatment. It involves leaching with alkaline (sodium hydroxide, sodium carbonate, ammonia) or acidic solutions (sulfuric, nitric, hydrochloric, oxalic acids) (Peng 2019).

Alkaline leaching is selective for vanadium (solubility of vanadium in alkaline media is more than 10 times higher than in acidic media) over iron but dissolves some silica and is more expensive in terms of reagents (Ho et al. 1994).

Khorfan et al. (2001) described a three-step process of SVC utilization involving acidic leaching, oxidation and precipitation to recover vanadium pentoxide but the efficiency of this method was rather low – 70 wt%.

It is obvious that the method of SVC utilization must be highly efficient from technological, economic, and ecological points of view. Because of that, our approach was to develop a hydrometallurgical method of SVC utilization using reagents with a composition close to the composition of SVC to prevent contamination. Moreover, reagents were used that are the main product of plants producing SVC, such as sulfuric acid, sulfites and persulfates. This study aimed to generate a technological scheme that could be used directly on plant. This work focused on selective metal extraction, and aimed to understand different extraction/utilization parameters of leaching and oxidation to recover vanadium in an efficient way and with high purity of obtained V_2O_5.

2. Experimental

2.1. Materials and sample preparation

Spent vanadium catalyst sulfovanadate on silica gel type, used in this study, was provided by JSC Grodno Azot, Belarus. The catalyst samples (cylindrical, with an average diameter of 6 mm and 20 mm in length) were ground in the planetary ball mill PULVERISETTE 6 (FRITSCH, Germany) with a crushing time of 30 s to improve leaching efficiencies. Then, they were dried at 100 °C for 1 h.

Sulfuric acid was used as a leaching agent and it was prepared by diluting concentrated acid (Sigma-Aldrich, 98%) with distilled water to the desired concentration or pH. All acids, sodium sulfite, ammonium persulfate, and vanadium pentoxide were of analytical grade (Merck).

2.2. Analysis of materials

Morphology and elemental composition of the sample surface were investigated by Scanning Electron Microscopic (SEM) analysis using a Scanning Electron Microscope JSM 5610 LV equipped with the Energy-dispersive X-ray spectroscopy system EDX JED 2201 JEOL (Japan). At least three samples were investigated for each condition. The surface analyses were conducted with magnifications up to 5000× for a minimum of 10 different locations.

The phase compositions of the initial SVC samples and the synthesized V_2O_5 and solid leaching residues were determined by means of X-ray diffraction analysis with a Panalytical X'PERT PRO diffractometer (Netherlands) [wavelength Cu Kα (1.5405 A) and software Philips X'PERT suite]. The PDF2 database was used as the reference data. The software HighScore Plus was used for Rietveld refinements. The peak profile was refined by pseudo-Voigt function.

A Confotec MR350 instrument was used for confocal Raman spectroscopy measurements, using a 532 nm laser (no filter). The sample was inspected before and after analysis to ensure no laser-induced oxidation.

Thermogravimetric analysis (TGA) of SVC and obtained V_2O_5 was done with a TA Q500 instrument. 40 mg of the sample was placed into an alumina pan without a lid and heated from ambient temperature to 1000 °C (SVC) and to 600 °C (V_2O_5) at 5 °C/min under a nitrogen purge flow of 100 mL/min.

Particle size distribution was determined by Fritsch Particle Sizer Analysette 22 (Germany) in distilled water suspension.

2.3. Solubility and kinetics

The solubility testing of V_2O_5 and SVC was performed in a glass flask with a magnetic stirrer and heater (Velp, Arec). The solubility and kinetics of SVC were also studied in an ultrasonic (US) installation with piezoelectric emitter IL 100–6/1 (Inlab, Russia), an installation power of 630 W, an operating frequency of 22 ± 10% kHz, a vibration amplitude of at least 40 μm, and a 50 mL volume of the processed suspension. The concentration of the aqueous suspension of SVC during processing in the ultrasonic installation was up to 20 wt%. The pH was continuously monitored by a controller connected to a computer. The final solution was filtered using an ashless syringe filter paper and analyzed for weight loss using a mass balance by weighing the remaining solid after each test and calculating the extent of leaching based on the initial weight. The composition and quantity of extracted vanadium compounds and solid residues after the leaching were determined by SEM and XRD methods. The triplicate experiments for every point have been done.

The effect of pH, temperature, sodium sulfite and ammonia persulfate (peroxydisulfate) concentration on kinetics was studied. Gravimetric studies, Atomic Absorption Spectroscopy (AAS), Electronic Paramagnetic Resonance (EPR), and UV–Visible Spectroscopy (UV–Vis) were applied to analyze vanadium (IV/V) concentration in solution (Kanamori et al. 1999; Yang and Gould 2003). For the study of reduction kinetics, sulfuric acid solution of V_2O_5 with adding of 0.01 mol/L Na_2SO_3 was used. The pH of the reduction solution was changing with time (0–1500 s) from 1.30 to 1.13.

The content of vanadium (V) after reduction by Na_2SO_3 was determined by AAS analysis using a spectrometer Avanta GBC Scientific Equipment (Australia).

EPR spectra were recorded at 1000 G and 298 K in X-band range (operating frequency 9.3 GHz) in a magnetic field up to 7 T, with a power of 5 mW, by means of a Varian E112 spectrometer. The RF Modulation Amplitude (100 kHz) was 1.0 G. Intense signals were attenuated 8–256 times. EPR was used to determine the vanadium oxidation state in the reduction solutions of V_2O_5 and SVC, because it is known that the vanadyl ion VO^{2+} shows an EPR spectrum – an octet with a constant on vanadium of the order of 10.8 mT (Hanson and Berliner 2009; Krzystek et al. 2015).

UV–Vis absorption spectra of V_2O_5 in reduction solutions were recorded at $\lambda = 277.6$ nm (maximum light absorption by sulfuric acid solution of V_2O_5) (Santini et al., 1952; Samchuk and Pilipenko, 1987) and 298 K by means of a SPECORD 200 PLUS (Analytik Jena AG, Gemany). The initial concentration of V_2O_5 in sulfuric acid solutions was

$6.3 \cdot 10^{-5}$ mol/L, the pH was 1.5, the measuring range was 190–1100 nm, the wavelength step was 0.1 nm, the speed was 5 nm/s, the integration time was 0.02 s, and the points of data fixation was 0.2 s. The molar coefficient of light absorption ε (L / (mol · cm)) was calculated as:

$$\varepsilon = A/(C \cdot l) \tag{1}$$

where A – absorption or optical density; C – concentration of V_2O_5 in solution; l – solution layer thickness.

The substance conversion rate was determined as:

$$v = \Delta C/t \tag{2}$$

where ΔC – concentration difference of V_2O_5 in solution before and after reaction; t – reaction time.

2.4. Synthesis

It was hypothesized that iron could be present in SVC not only as a part of its phase composition but also as solid iron particles from contact absorber shelves. To remove solid iron particles, SVC samples were handled with magnet before leaching and SVCm was obtained.

2.4.1. Leaching tests

The acidic and reductive leaching tests were performed in glass shake flasks (100 mL) with a magnetic stirrer at ambient temperature. The acidic leaching tests were also performed in the ultrasonic installation. The S/L ratio and the concentration of sulfuric acid and sodium sulfite were selected according to optimal experimental conditions. The S/L ratio was 10 ± 0.0005 g of SVCm in 50 mL of H_2SO_4 (S/L = 1/5) and the pH of the solution was 1.2–1.3. The contact time was 5 min, after which the samples were filtered. Magnani et al. (2000) used sodium thiosulfate to reduce vanadium (V) to vanadium (IV) and reported that it could be dissolved in the form of oxy-sulfate ($VOSO_4$) by means of sulfuric acid leaching of spent sulfuric acid catalyst. In the present work, the solid residue from acidic leaching was used with the addition of the reducing agent sodium sulfite (Na_2SO_3) at 0.01 mol/L to reduce vanadium (V) to vanadium (IV), the S/L ratio was 1/5, the solution pH was 2.6–2.8, and the reaction time was 15 min. The solid phase was filtered and dried. Filtrates from acidic and reductive leaching were combined and were used for extraction of vanadium.

2.4.2. Extraction tests

It is known that vanadium in acidic leach liquor can be presented in the form of VO_2^+ as $(VO_2)_2SO_4$ and in the form of VO^{2+} as $VOSO_4$ (Eatough et al. 1984). To extract vanadium from leaching solutions in form of V_2O_5, filtrates were oxidized with 1.0 mL of ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) at 30 wt% in solution. Oxidized solutions were processed by thermohydrolysis: they were heated to the boiling point, the time of boiling was 5 min, and the precipitated V_2O_5 was filtered and dried. The filtrate after the vanadium extraction was recycled and included in the acidic leaching step. The filtrate was neutralized periodically with ammonia solution (25 wt%) to obtain $Al(OH)_3$. $NH_3 \cdot H_2O$ was added in an optimal amount to increase the pH from approximately 3 (pH of leaching solution after vanadium extraction) to 5–6 (pH of $Al(OH)_3$ precipitation). The precipitated $Al(OH)_3$ was separated by filtration and was dried. The filtrate after $Al(OH)_3$ separation was vaporized to reach concentration of 20 g/L K^+.

3. Results and discussion

3.1. Compositional analysis

XRD patterns and SEM images of SVC are presented in Supplementary Information (SI, Figs. S.1*a-b*). The main phases of SVC were cristobalite and quartz. Apart from the support phase, crystalline phases of potassium sulfates, disulfates, pyro-sulfato-vanadates, and pyrosulfates were identified, according to (Nikiforova et al. 2016). The elemental composition of the initial SVC sample is listed in SI, Table S.1. Vanadium was present in SVC in the following compounds: 41.6 wt% – anorthic crystal system $V_{10}O_{18}$; 34.1 wt% – monoclinic crystal system V_4O_{10}; 14.7 wt% – anorthic crystal system $V_{20}O_{36}$; 8.6 wt% – other phases. DTA and TG analysis of SVC showed the number of SVC decomposition stages with total mass loss 21.1 wt% and endothermic thermal effects corresponded to the removal of physically bound water (Figueiredo et al. 1999) and sulfate decomposition (SI, Fig. S.2).

The amount of iron in the SVCm as compared to the SVC sample (SI, Fig. S.1*c*) after magnetic separation decreased from 1.41 to 0.85 wt% (SI, Table S.1). XRD patterns (SI, Fig. S.1*a*) show the same phase composition for the SVCm sample as in the initial SVC sample but with a small left shift of peaks because of the smaller amount of magnetic phases (less than 5%). The median particle size of the SVCm sample after magnetic separation decreased by 2.3 times in comparison with the initial SVC sample from 17.867 μm (SI, Fig. S.3) to 7.764 μm (SI, Fig. S.4). This supports our hypothesis on the presence of iron both in the phase composition of the catalyst and as solid iron particles from contact absorber shelves in the SVC. Such solid iron particles can be easily recycled after magnetic separation from SVC.

3.2. Solubility and kinetics analysis

The solubility and kinetics study were done to obtain optimal extraction/utilization parameters of SVC leaching. The V_2O_5 solubility in water was studied as a function of temperature. As Fig. 1*a* shows, the content of V_2O_5 in the saturated solution (pH = 2.8) is 0.2 g/L at a temperature of 20°C. With an increase in temperature from 20 to 90°C, the solubility of V_2O_5 in solution was 4-fold higher and reached 0.81 g/L. A further increase in temperature led to boiling of solution with an increase in hydrolysis processes and a decrease in the V_2O_5 content in solution. Obtained data corresponded to (Woolery 1997; O'Neil, 2001) showing an increase in V_2O_5 solubility from 0.30–0.35 g/L at 25°C to 0.7 g/L at 100°C (pH = 2.8). Upon dissolution in water, V_2O_5 forms crystalline hydrates with three, two or one molecule of water, which correspond to the forms of ortho-, pyro- and methavanadic acid (Jahr et al. 1963). The process of electrolytic dissociation of methavanadic acid is equal for both directions (Jahr et al. 1963):

$$VO_3{}^- + H^+ \rightleftarrows VO_2OH \rightleftarrows VO_2{}^+ + OH^- \quad K = 3.0\ 10^{-5} \tag{3}$$

It was reported (Ivakin 1966) that in acidic solutions (pH < 1.5) methavanadic acid could be mostly present in the form of VO_2^+ or in the form of $[H_nV_{10}O_{28}]^{(6-n)-}$. The ion VO_2^+ is characterized by its high oxidation properties. The content of $[H_nV_{10}O_{28}]^{(6-n)-}$ is increasing with increasing pH.

The solubility of V_2O_5 in sulfuric acid solutions is presented in Fig. 1*b*. The experimental data shows a significant increase for V_2O_5 solubility in sulfuric acid solutions. The most probable forms of vanadium (V) in such solutions are (Pletnev et al. 1986):

$$10VO_2{}^+ + 8H_2O = [H_2V_{10}O_{28}]^{4-} + 14\ H^+, K = 10^{-6.75} \tag{4}$$

$$[H_2V_{10}O_{28}]^{4-} = [HV_{10}O_{28}]^{5-} + H^+, K = 10^{-3.6} \tag{5}$$

$$[HV_{10}O_{28}]^{5-} = [V_{10}O_{28}]^{6-} + H^+.K = 10^{-6.8} \tag{6}$$

In a non-complexing aqueous acidic solution, the pentavanadyl ion (VO_2^+) is the only dominant cation in the solution. It was found that the solubility of V_2O_5 reaches its maximum point (5.8 g/L) at pH < 1 (Fig. 1*b*). This fact could be explained by the formation of a monosulfate complex (VO_2HSO_4) according to the following reactions (Ivakin 1966; Rakid and Durand, 1996; Puigdomenech 2004):

$$VO_2{}^+ + SO_4{}^{2-} = VO_2SO_4{}^- \tag{7}$$

$$VO_2{}^+ + HSO_4{}^- = VO_2HSO_4 \tag{8}$$

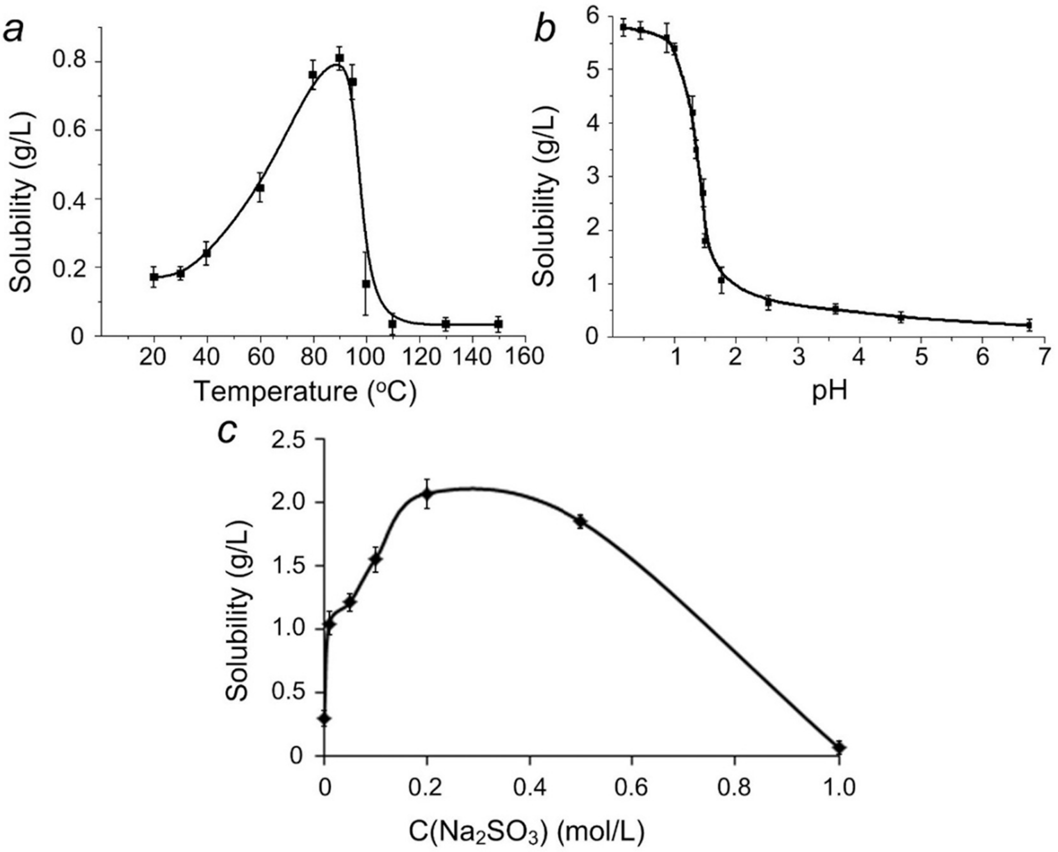

Fig. 1. Solubility of V_2O_5 versus temperature (a), pH of sulfuric acid solutions (b), and concentration of Na_2SO_3 in solution (c).

An increase of pH in sulfuric acid media led to a significant decreasing of V_2O_5 solubility to less than 0.3 g/L at pH 5.5–7.0. In this solution, the most probable form of vanadium (V) is $[H_nV_{10}O_{28}]^{(6-n)-}$ (Ivakin 1966). Hence, our study suggests that the most optimal pH of sulfuric acid solution for the acidic leaching of vanadium (V) from SVC is pH 1.2–1.3 in terms of the ratio of V_2O_5 solubility and quantity of sulfuric acid.

Since vanadium (IV) has a higher solubility than vanadium (V) in acidic media (Pourbaix 1974; Puigdomenech, 2004; Ivankovic et al. 2006), the solubility of V_2O_5 in reducing sodium sulfite solutions was studied (Fig. 1c). The addition of sodium sulfite in aqueous solutions of V_2O_5 at a quantity of 0.01–1.0 mol/L led to a change of the solution color from yellow to dark green, which can be explained by the formation of blue vanadium (IV) compounds or green vanadium (III) compounds according to:

$$V_2O_5 + 6H^+ + 2e^- \rightarrow 2VO^{2+} + 3\ H_2O \tag{9}$$

$$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O \tag{10}$$

As shown in Fig. 1c, the solubility of V_2O_5 in acidic solutions with Na_2SO_3 contents ranging from 0.01 to 0.20 mol/L (constant pH = 2.8) increased from 1.05 to 2.07 g/L. The solubility of V_2O_5 in sodium sulfite solutions is hence higher than in water and in sulfuric acid solutions because of the formation of vanadium (IV) and vanadium (III) compounds or mixed polyanions $[V_3^{+5}V_7^{+4}O_{24}H]^{4-}$ and $[V_7^{+5}V_3^{+4}O_{26}H]^{4-}$ (Pletnev et al. 1986). However, the increase of the Na_2SO_3 concentration to more than 0.2 mol/L led to a decrease of the solubility, Fig. 1c. This might be explained by the formation of sparingly soluble sulfates and sulfites of vanadium. In order to prevent reagents overconsumption and based on obtained data (Fig. 1c), it was suggested to use 0.01 mol/L solution of sodium sulfite for the reductive leaching of vanadium (V) from SVC.

The kinetics of V_2O_5 reduction in sodium sulfite solutions are shown in Fig. 2a. The highest degree of V_2O_5 reduction (92 wt%) was reached after the first 5 min of reaction time. During the next 40 min, the content of reduced V_2O_5 in the solution was reduced to 61 wt%. After 90 min of the reduction process, the quantity of reduced V_2O_5 reached 78 wt% and did not change further.

As the obtained data showed, there was a reversible reaction for the reduction of V_2O_5 by sodium sulfite in sulfuric acid solutions. During the first 5 min, the maximum of the reduction of V_2O_5 was detected and the color of the solution was changed from yellow (vanadium (V) compounds) to blue (vanadium (IV) compounds). Then, formed vanadium (IV) compounds were oxidized to vanadium (V) compounds and the solution color changed to light green (a mixture of vanadium (IV/V) compounds). Such fact when reduction is caused by an oxidizing agent and, conversely, oxidation is caused by a reducing agent is mentioned by Remy (1973).

The EPR analysis of reductive solutions showed the spectrum of VO^{2+} in sulfuric acid, proving the existance of vanadium (IV) in solution in the form of vanadyl sulfate $VOSO_4$. Fig. 2b shows the intensity of the 4th peak of the spectrum EPR (I_4) of VO^{2+} in acidic sodium sulfite solutions as a function of reaction time. In agreement with the AAS and gravimetric results, a maximum of reduction occurred after 5 min of the process, a minimum of reduction after 45 min, and a plateau was reached after 90 min.

The rate of V_2O_5 reduction by sodium sulfite was calculated for the first 5 min of reaction time from Fig. 2c (detailed calculation is presented in SI). An average molar absorption coefficient was calculated by (1) $\varepsilon = 2535$ L/(mol·cm). An average conversion rate of the was calculated by (2) $v = 1.97 \cdot 10^{-7}$ mol/(L·min).

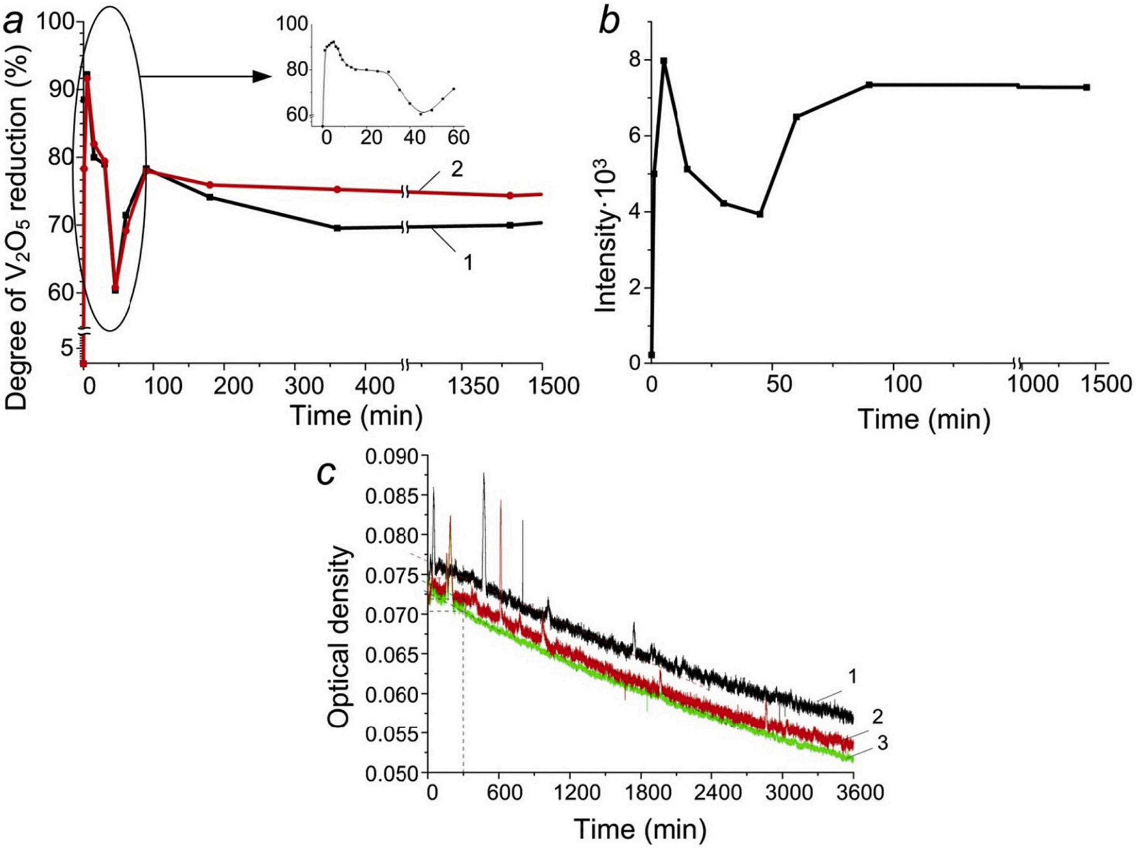

Fig. 2. Kinetics studies of V_2O_5 reduction in acidic Na_2SO_3 solutions.
V_2O_5 reduction versus time of contact with Na_2SO_3 (a): 1 – gravimetric analysis; 2 – AAS.
VO^{2+} EPR spectra intensity versus reaction time with Na_2SO_3 (b).
UV–Vis absorption spectra optical density of V_2O_5 versus reaction time Na_2SO_3 (c): 1, 2, 3 – parallel experiments.

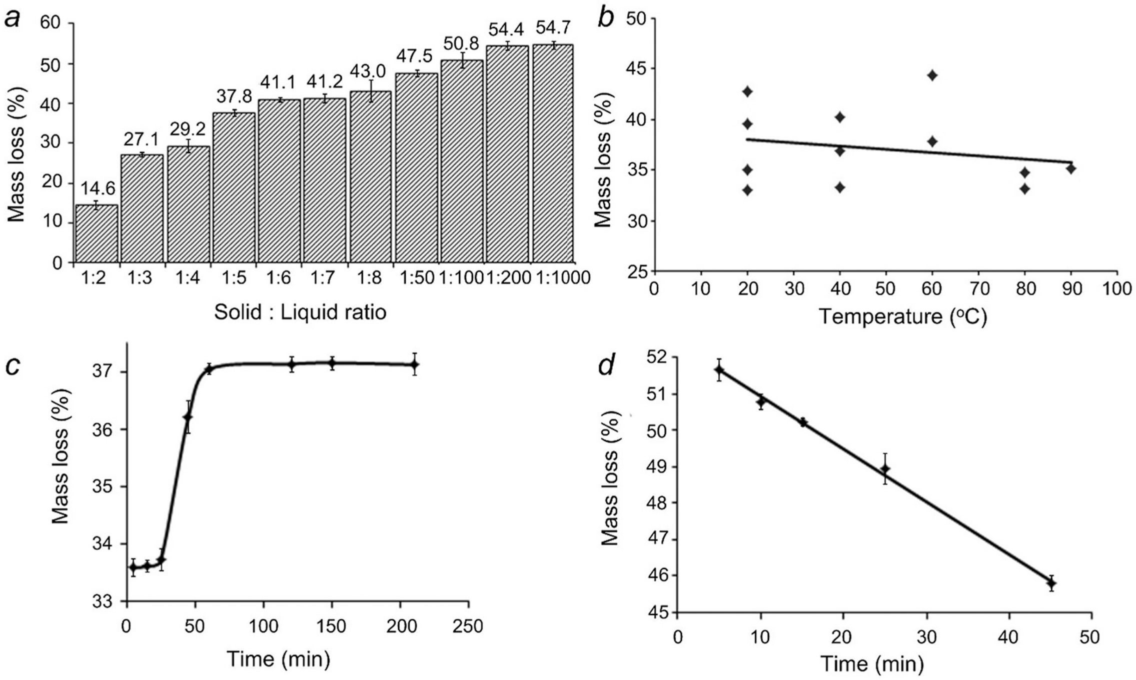

Fig. 3. SVCm mass loss versus the solid/liquid ratio (a), the temperature of process at S/L = 1/5 (b), time of mixing with magnetic stirrer at S/L = 1/5 (c), the time of ultrasonic (US) treatment at S/L = 1/5 (d).

3.3. Leaching of vanadium

As Fig. 3a shows, the S/L ratio had a significant effect of SVCm mass loss in the interval from 1/2 to 1/5. A further increase of water volume increases the SVCm mass loss slightly: in the interval of S/L ratio from 1/5 to 1/50 it increases by 10% and from 1/200 to 1/1000 it remains almost constant – 54.5 ± 0.2%. Obtained results of the dependence of SVCm mass loss on the S/L ratio assisted in choosing the minimum solvent volume, at which the most rational ratio “water consumption – vanadium extraction” was achieved.

The increase of temperature did not influence the SVCm mass lost and its value varied from 32 wt% to 45 wt% at any temperature of the interval from 20 to 90 °C (Fig. 3b).

The results of the kinetics studies of SVCm mass loss as a function of different types of mixing are presented in Fig. 3c,d. The data showed that the first 5 min of mixing of the SVCm water solution with a magnetic stirrer led to 32 wt% of SVCm mass loss and after 60 min the maximum of SVCm mass loss (37 wt%) was reached (Fig. 3c), after which the leaching was constant. US treatment increased the mass loss of SVCm significantly as compared to the magnetic stirrer and it reached the maximum value after the first 5 min of US mixing – 51–52 wt% (Fig. 3d). Such SVCm mass loss is comparable with a S/L ratio of 1/100–1/1000 (Fig. 3a). Moreover, it led to the increase of vanadium leaching from SVCm to 60%. This effect is explained by the formation of particles with smaller sizes (9.466 μm, SI, Fig. S.5) in comparison with the size of particles formed in the solutions with magnetic stirrer mixing (12.455 μm, SI, Fig. S.6). The further decrease of SVCm solubility under US treatment can be explained by the formation of particle agglomerates with larger sizes, which correlates to our previous experimental data (Zharskiy et al. 2015) and literature data (Khan et al. 2013).

Obtained results showed that the S/L ratio 1/5 and 5 min of US treatment at ambient temperature led to salvation of all soluble SVCm components. The high solubility of SVCm in water (in comparison with V_2O_5) is explained by the presence of highly soluble compounds such as potassium and sodium sulfates and polysulfates in the SVCm composition (SI, Fig. S.1). Furthermore, the presence of disulfates in the SVCm leads to sulfuric acid formation in the water solution of SVCm. The solution pH becomes 1.5–1.6, which facilitates the solvation of both vanadyl sulfate $VOSO_4$ and V_2O_5 in the solution. The main component of the SVCm solid residue after leaching was insoluble SiO_2 in sulfuric acid solution.

As was shown before, the presence of a reducing agent in water solutions led to the formation of vanadium compounds in low oxidation states that are significantly more soluble than V_2O_5 (Figs. 1c and 2). Fig. 4 shows that the mass loss of SVCm and the degree of its vanadium leaching depends on the presence of sodium sulfite in water. The concentration of Na_2SO_3 did not significantly influence the SVCm mass loss (44–46 wt%) and the vanadium leaching degree (33–35 wt%). However, an increase of Na_2SO_3 in the solution led to their slight decrease due to an induced pH increase. This study proved that using 0.01 mol/L Na_2SO_3 for the technological process of reductive leaching of vanadium (V) from SVC is possible and advantageous.

Fig. 4b shows the same trend of the vanadium reduction degree as shown for V_2O_5 reduction (Fig. 2). The maximum of vanadium (V) reduction was after 5–15 min of the process, the minimum of vanadium (V) reduction was after 45–90 min of the process, and a plateau was reached after 180 min.

The influence of pH on the SVCm mass loss and degree of vanadium leaching was investigated in highly acidic solutions with pH values lower than 1.56 (pH of SVCm water solution). Fig. 5 shows the results for different steps of the leaching with developed optimal conditions as a function of the pH of the sulfuric acid leaching solutions. Represented data prove the increase of the SVCm mass loss in strong acidic solutions. It reaches maximum values at a pH lower than 1.3 for all samples. At the first step of SVCm leaching in sulfuric acid solutions, mixing with a magnetic stirrer, the mass loss increased to 47–48 wt% (SVCm-1 L-MX). The use of US treatment for mixing the sulfuric acid leaching solutions of SVCm raised the mass loss to 54–56 wt% (SVCm-1 L-US). The second step of SVCm leaching, reductive leaching in 0.01 mol/L solutions of sodium sulfite, led to the increase of SVCm mass loss for solutions with both types of mixing: to 50–51 wt% for SVCm-2 L-MX and to 58–60 wt% for SVCm-2 L-US. The increase of mass loss led to the increase of vanadium leaching from SVCm, however, at a pH lower than 0.7, it was impossible to extract V_2O_5 from the leaching solutions. The composition of solid residues at every step of leaching is presented in Fig. 6 and Table S.2 (SI). The difference in particle sizes was found only for the first step of leaching with different types of mixing (SI, Fig. S.5 and Fig. S.6) and, after the reductive leaching, the particle sizes were comparable for both samples: 8.484 μm for SVCm-2 L-MX (SI, Fig. S.7) and 8.108 μm for SVCm-2 L-US (SI, Fig. S.8).

Thus, this study showed that the optimal condition for vanadium recovery from SVCm was a two-step leaching process. The first step was leaching in sulfuric acid solutions with a constant pH interval from 1.2 to 1.3 and 5 min of ultrasonic treatment (22 ± 10% kHz). It led to the leaching of more than 90 wt% of vanadium of its initial content in SVCm (Fig. 6b, SVCm-1 L-US). The second step was reductive leaching in 0.01 mol/L sodium sulfite with a reaction time of 15 min, leading to the leaching of more than 98% of vanadium of its initial content in SVCm (Fig. 5b, SVCm-2 L-US). The residual amount of vanadium in solid residues after the two-step leaching did not exceed 0.16 wt% of its initial content in SVCm. As the solid residues were mainly SiO_2 with small impurities of sulfur, potassium and iron (Fig. 6*a*, SI, Table S.2), it could be used in different industrial processes. Our study highlights the possibility to use obtained solid residues in the production of building

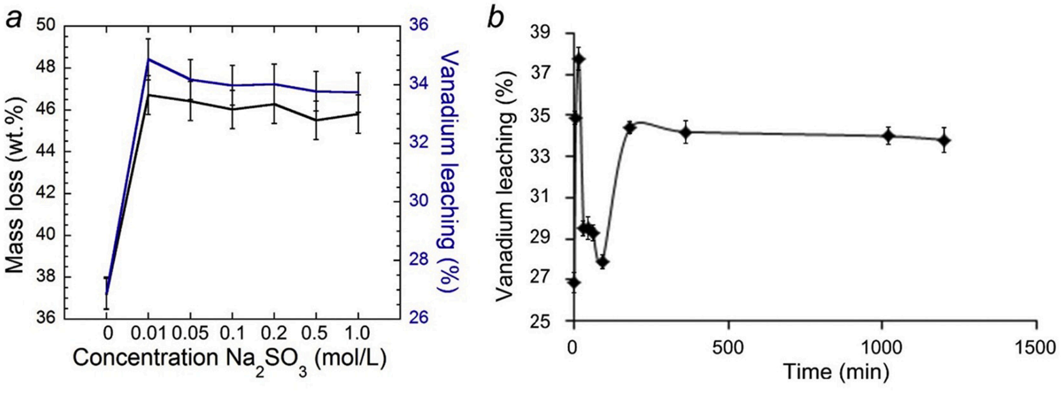

Fig. 4. Effect of reductive leaching of SVC in sodium sulfite solution.
SVCm mass loss and vanadium leaching (%) from SVC versus concentration of reducing agent Na_2SO_3 (a). Effect of leaching time in 0.01 mol/L Na_2SO_3 solution on vanadium leaching (%) from SVC (b).

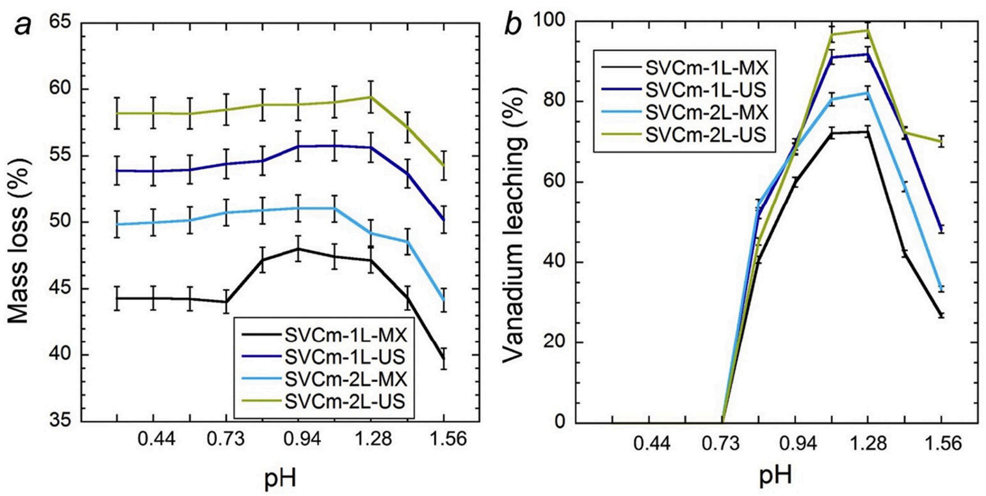

Fig. 5. Effect of leaching solution pH on SVCm mass loss (a) and quantity of leaching from SVCm vanadium (b). SVCm-1 L-MX – the first step of leaching in H_2SO_4 solutions, mixing with magnetic stirrer, time of leaching 5 min. SVCm-1 L-US – the first step leaching in H_2SO_4 solutions, mixing with US treatment, time of leaching 5 min. SVCm-2 L-MX – the second step of leaching in 0.01 mol/L Na_2SO_3 solution, time of leaching 15 min. SVCm-2 L-US – the second step of leaching in 0.01 mol/L Na_2SO_3 solution, time of leaching 15 min.

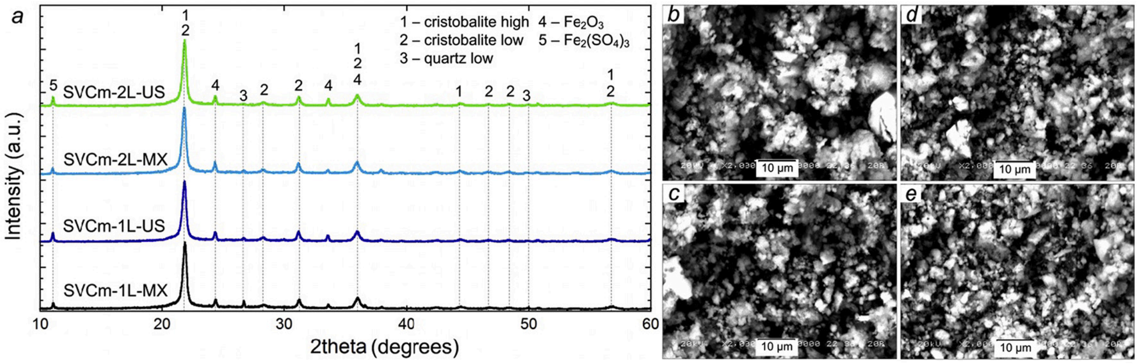

Fig. 6. XRD patterns (a) and SEM-EDX of the SVCm solid residues after leaching: SVCm-1 L-MX (b); SVCm-1 L-US (c); SVCm-2 l-MX (d); SVCm-2 L-US (e).

materials, such as ceramic bricks (Kryshilovich et al. 2017).

3.4. *Extraction of V_2O_5*

It is well known that vanadium can be extracted from solution by hydrolysis as V_2O_5 (Muzgin and Khamzina, 1981). Some authors (Vegliò et al. 2006; Ognyanova et al. 2009; Erust et al. 2016) reported about using hydrogen peroxide (H_2O_2) as an oxidizing agent for vanadium leaching, leading to an intensification of the V_2O_5 hydrolytic extraction. Our previous studies showed the possibility to use H_2O_2 for oxidation of SVC leaching solutions and further extraction of V_2O_5 from solutions by thermohydrolysis with boiling time 5 min (Orehova et al. 2013). The vanadium extraction degree was about 92 wt% and the molar ratio of extracted V_2O_5 to used H_2O_2 was 1 to 2 (Orehova et al. 2013). To increase the amount of extracted V_2O_5 and to decrease the oxidizing agent consumption, ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) was used for SVC leaching solutions oxidation. Ammonium peroxydisulfate has the same O—O bond as H_2O_2, why it was decided to use $(NH_4)_2S_2O_8$ as an oxidizing agent. Furthermore, ammonium peroxydisulfate is used in water and wastewater treatment, as it has high oxidizing properties, is nontoxic, and a cheap reagent (Wacławek et al. 2017). Fig. 7 shows that using $(NH_4)_2S_2O_8$ helped to extract 98 wt% of vanadium from the

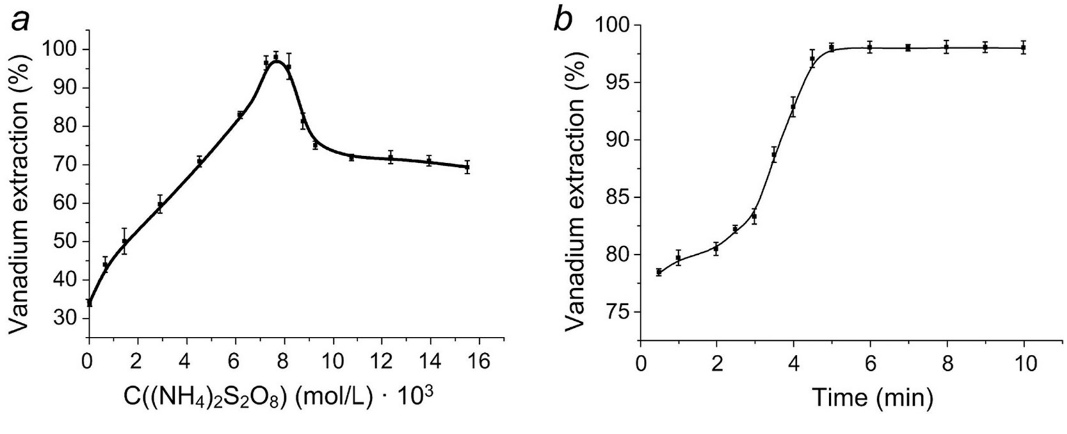

Fig. 7. Vanadium extraction versus concentration of oxidizing agent $(NH_4)_2S_2O_8$ (a) and time of reaction (molar ratio $n(V_2O_5)/n((NH_4)_2S_2O_8) = 5/1$) (b).

leaching solutions. The optimal molar ratio of extracted V_2O_5 to used $(NH_4)_2S_2O_8$ was 5 to 1 and the maximum of vanadium extraction was reached after 5 min of thermohydrolysis at 80–90°C. The residual concentration of vanadium in terms of V_2O_5 was not less than 0.0033 mol/L and did not depend on the initial vanadium concentration or quantity of the oxidizing agent.

The elemental composition and morphology of extracted vanadium compounds is presented in Fig. 8 and Table S.2 (SI). As shown, for both methods of leaching, the obtained product was V_2O_5 with some impurities of potassium, silica, iron and sulfur. XRD patterns and SEM images of the obtained product show that after the thermohydrolysis the amorphous hydrated $V_2O_5 \cdot nH_2O$ formed with a small contamination of VO_2. The average size of the particles of V_2O_5 extracted from SVCm leaching solutions prepared with magnetic stirrer mixing was 84.323 μm (SI, Fig. S.9). The average size of particles for V_2O_5 extracted from SVCm leaching solutions prepared with ultrasonic treatment was almost in 7 times lower – 12.157 μm (SI, Fig. S.10).

DTA/TG analysis of extracted V_2O_5 shows two decomposition stages with total mass loss 11 wt% and thermal effects corresponded to the removal of physically and crystalline bound water (SI, Fig. S.11).

$V_2O_5 \cdot nH_2O$ was heated to 500°C for 1 h. After the heating, V_2O_5 with a purity of 85–87 wt% was obtained that is higher in comparison with other known technologies (Khorfan et al. 2001; Peng 2019). XRD analysis (Fig. 8d) showed the presence of V_2O_5 phase with a small impurity of nonstoichiometric vanadate $K_{0.23}V_2O_5$ in both samples.

The crystalline quality of obtained V_2O_5 was also evaluated using Raman spectroscopy. Fig. S.12 (SI) shows the Raman bands corresponding to the characteristic phase of V_2O_5 samples (Shvets et al. 2019; Sundeep et al. 2019; Wachs 2013) (see the full peak explanation in SI).

Fig. 9 shows the developed optimal technological scheme of V_2O_5 recovery from spent vanadium catalyst of sulfuric acid production. The mass balance of V_2O_5 recovery from SVC of sulfuric acid production is presented in SI, Fig. S.13.

With time, K^+, Na^+ and Al^{3+} ions accumulate in the leaching solutions. These ions are the raw material for the production of fertilizers and $Al(OH)_3$ for coagulant production. In order to obtain these products, the stage of periodical neutralization of leaching solutions by $NH_3 \cdot H_2O$ was included in the technological scheme.

4. Conclusion

As a result, a new resource and energy-saving, low-cost and environmentally friendly method of vanadium recovery from SVC of sulfuric acid production has been developed. The method includes grinding; magnetic separation of iron; two-step leaching of vanadium at S/L ratio 1/5: the first step – vanadium leaching in sulfuric acid solutions with pH = 1.2–1.3, ultrasonic treatment for 5 min; the second step – vanadium reductive leaching in 0.01 mol/L Na_2SO_3 solutions at ambient temperature for 15 min; oxidation of leaching solution by 30 wt% solution of $(NH_4)_2S_2O_8$; thermohydrolytic extraction of V_2O_5 for 5 min at temperature 80–90°C; periodic neutralization of leaching solutions by $NH_3 \cdot H_2O$ solution; drying; recycling of leaching solutions. The degree of vanadium recovery from SVC was 98 wt%. The purity of obtained V_2O_5 was 85–87 wt%. Using of $(NH_4)_2S_2O_8$ as an oxidizer helped to obtain less corrosive solutions compares with using of H_2O_2. All sub-products can be used in other industrial processes: solid residues (SiO_2) for building materials production, $Al(OH)_3$ for coagulant production, and concentrates of Na^+ and K^+ as fertilizers in agriculture. The technology was developed in a way to prevent any secondary waste. All spent solutions are recycled back to the process. The evaluated capital cost of the technology is about 120–125 k$ (depends on using equipment), payback period is not more than 1 year.

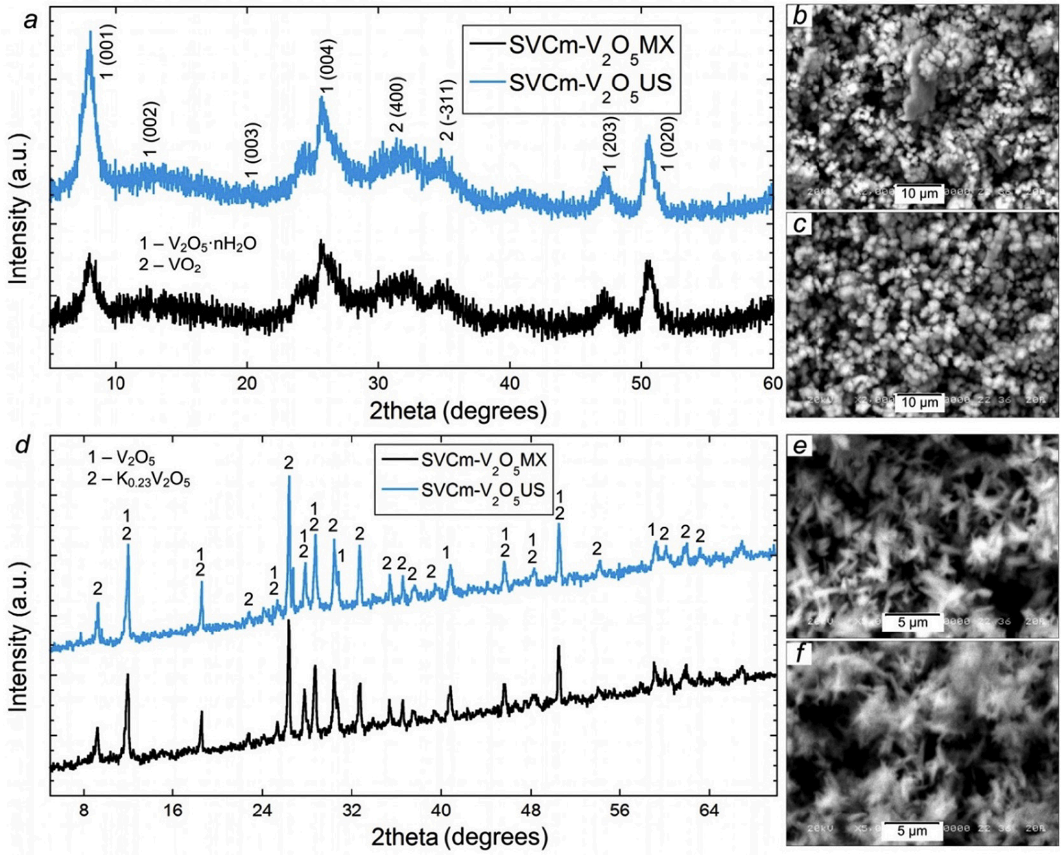

Fig. 8. XRD patterns of extracted V_2O_5 (a) and V_2O_5 after heating at 500°C (d) and SEM-EDX of the extracted vanadium product from SVCm leaching solutions: SVCm-V_2O_5MX (b, e); SVCm-V_2O_5US (c, f).

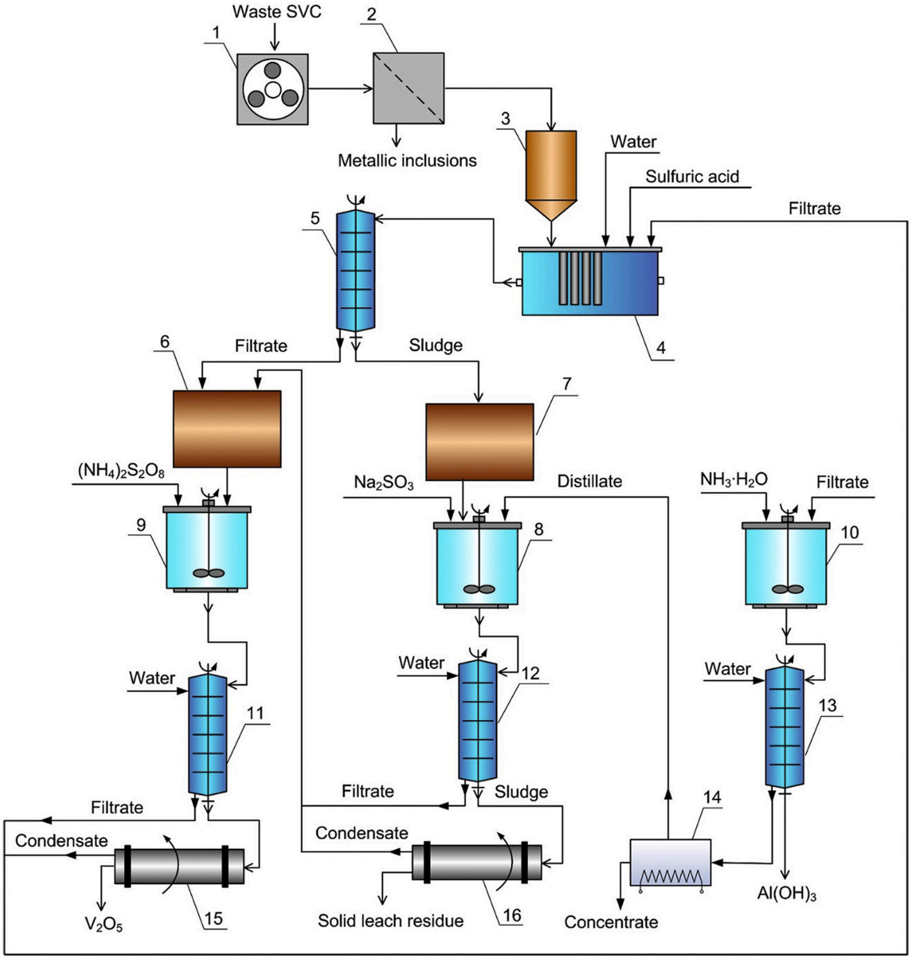

Fig. 9. Technological scheme of vanadium recovery from spent vanadium catalyst of sulfuric acid production: 1 – mill; 2 – magnetic separator; 3 – hopper; 4 – ultrasonic installation with a piezoceramic emitter; 5, 11–13 – filter; 6, 7 – storage tank; 8 – reactor for leaching; 9 – reactor for thermohydrolysis; 10 – reactor for filtrate neutralization; 14 – evaporator; 15, 16 – drum dryer.

Such a sustainable approach could be adapted for the recovery of vanadium from other wastes, such as SVCs of different types, ash residues of fuel oil, petroleum coke.

CRediT authorship contribution statement.

Elena Romanovskaia: Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Visualization, Validation, Funding acquisition, Writing – Original Draft.

Valentin Romanovski: Investigation, Visualization, Funding acquisition, Writing – Review & Editing.

Witold Kwapinski: Formal analysis, Funding acquisition.

Irina Kurilo: Conceptualization, Project administration, Supervision, Funding acquisition, Writing – Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2021.105568.

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