

Extraction of vanadium compounds from the used vanadium catalyst with the potassium hydroxide solution

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The paper presents the results of the research on the degree of the recovery of vanadium(V) from the used vanadium catalyst with the use of KOH solution. The extraction was performed at 293 – 323 K, for 0.5 to 4 h and the catalysts of the variable grain diameter. The concentration of the extracting solution was varied in the range 5 – 20%. The optimal ratio of solid to liquid phase S/L was determined. Additionally the degree of the recovery of total iron ions was presented.

Keywords: vanadium catalyst, leaching, recovery, vanadium, iron, sulfuric acid, potassium hydroxide

INTRODUCTION

For the contemporary industry, utilization of the vanadium catalyst deactivated during the industrial process, is one of the fundamental problems requiring the complex solution. The vanadium catalyst used in the technological process of SO₂ oxidation to SO₃ loses its activity. The waste generated in that process includes the oversize from every step of the catalyst sieving, a catalyst withdrawn from the process due to the loss of its activity, as well as the deposit of the catalyst from the industrial installations stopped due to the decreasing economical activity¹⁻³.

The vanadium catalyst withdrawn from the process of H₂SO₄ production is usually stored on the factory dump, therefore being a troublesome waste because of the large amount of toxic substances (eg. V₂O₅, H₂SO₄, alkalies), which are eluted with the precipitation into the soil. The necessity of the environment protection and high price for V₂O₅ make the utilization of the vanadium catalyst a very significant problem.

Every year 100 – 140 tons of catalyst are required to fill the medium size installation of a production capacity about 300 000 MH. That gives the estimate for the catalyst usage and also justifies the necessity for the research on the utilization of such large amount of vanadium waste.

There are numerous literature reports on the methods of the utilization of the used vanadium catalyst or methods for the recovery of vanadium(V) oxide⁴⁻¹⁰. Among the most frequently used are:

- addition of a certain amount of the used catalyst to the new catalytic mass
- production of ferrovandium
- recovery of vanadium compounds from the solution by chemical methods

Chemical methods of extraction of vanadium from the used vanadium catalyst could be divided into two groups; those requiring the thermal pre-processing or not.

The former include sintering of the raw material containing vanadium with fluxing agents such as NaCl, Na₂CO₃, Na₂SO₄, and subsequent elution of the sinter with different solutions (acids, bases or solutions containing vanadium(II)).

Among the chemical methods of vanadium extraction from the used vanadium catalyst mass with no prior thermal processing, the frequently reported is the extraction

with NaOH solutions. Based on the results of the previous research^{4,7} the general conditions of extraction of the used catalyst with NaOH were determined:

- before the extraction, the catalyst should be granulated and should be granulometrically homogeneous (the grain size should not exceed 0.2 mm)
- the concentration of the NaOH solution used in the extraction should be 5%
- the ratio of the solid to liquid phase should be 1 : 10
- the ratio of the solid phase to the volume of H₂O₂ used should be 1 : 0.175
- the time of extraction with the constant steering – 1 h

The extracts obtained under these conditions contain circa 4.5 g V₂O₅/dm³ but also some impurities introduced together with vanadium compounds.

The method described above was an inspiration for the research on the determination of optimal conditions for vanadium(V) extraction from the used vanadium catalyst with the use of KOH solutions.

This paper presents the results of a fragment of the research^{1,2,11-14} conducted at the Department of Chemical Technology UMK on the determination of the conditions for the extraction of the components of the used vanadium catalyst. The paper presents the results of the research on the degree of the recovery of vanadium(V) with the use of KOH solutions of different concentration. The influence of temperature, time of extraction, KOH concentration and the ratio of solid to liquid phase (S/L) on the concentration of vanadium(V) in the raffinate were also determined.

Additionally, authors have determined the concentration of iron compounds in the analyzed solutions, since these compounds are the main contaminant in the catalyst mass recovered from the sulfur-type installations. Iron causes a significant deterioration of the catalytic and physical properties of the catalyst despite its amount and form in which it was introduced. Therefore the authors decided to control the amount of the recovered iron to determine the possibility of the use the post-extraction lye to obtain new catalyst mass.

Recovery of V₂O₅ from the used vanadium catalyst with the use of chemical methods seems to be the most rational way of the utilization of that waste. Therefore most of the research on the utilization of the vanadium catalyst focus on these methods.

EXPERIMENTAL SECTION

Reagents used

The used vanadium catalyst was obtained from the dump of the plant POLCHEM, Toruń, producing the sulfuric acid with the contact method. The used vanadium catalysts are chemically and granulometrically heterogeneous materials. Their composition strongly depends on the conditions of their use, source of sulfur dioxide, as well as on the way of their storage. The catalyst samples were analyzed to determine the chemical composition with the use of the EDXRF method. The results of the analyses are presented on Table 1 and Figure 1.

Table 1. Chemical composition of the used vanadium catalysts

Compound	Content [%]
V ₂ O ₅	4.68
SiO ₂	57.31
K ₂ O	8.70
Fe ₂ O ₃	2.59

Before the research, the catalyst was granulated and divided into the required granulometric fractions with the use of the FRITSH sieve set.

KOH (analytical grade) POCh Gliwice.

Methods

Research on the determination of conditions of vanadium(V) and iron extraction from the used catalyst with KOH solution was divided into four steps:

The first step focused on the effect of the time and the concentration of the leaching solution on the rate of the process of vanadium(V) and iron recovery. The experiments were conducted at 303 K for the catalyst grains of 0.16 – 0.075 mm diameter. The ratio of the solid to

liquid phase S/L was kept constant at 1/10 [g/cm³]. The concentration of KOH solutions was 5%, 10%, 15% and 20%. The extraction time was 0.5, 1, 2, 3 and 4 h, respectively. The starting parameters were selected based on the results obtained for the use of NaOH solutions^{4,7}.

The 5g samples of the used vanadium catalyst with the grain diameter of 0.16 – 0.075 mm were put into the 100 ml Erlenmeyer flasks with a magnetic stirrer. Next, 50 cm³ of KOH solution of a required concentration was added. The flasks were thermostated and intensely stirred for 0.5 – 4 h. Then the solution was filtered with the sintered glass crucible. The obtained filtrate was diluted as required and subjected to the chemical analysis.

In the second step, the ratio of solid to liquid phase (S/L) [g/cm³] was optimized and the effect of the grain diameter on the ratio of vanadium(V) and iron recovery was determined. The extraction was performed at 303 K for 1 h, using 15% KOH solution. The S/L ratio varied from 1/2 to 1/10 and four catalyst fractions differing by the grain diameter were investigated. The method of the experiments was the same as described for the first step.

In the third step, the effect of temperature on the ratio of vanadium(V) and iron recovery was determined for the constant concentration of the extracting solution (15% KOH). The temperature ranged from 293 to 323 K, the reaction time was 1 and 4 h.

In the last step the extraction from the used catalyst was conducted under optimal conditions determined in the previous steps.

The yield of recovery was calculated as:

$$Y_{\%} = \frac{[m_{M_xO_y}]}{[Z \cdot m_{catalyst}]} \cdot 100\% \quad (1)$$

where:

M = V or Fe,

m = mass [g]

Z = contents of the investigated oxides in the catalyst (V₂O₅ – 5% and Fe₂O₃ – 1.65%).

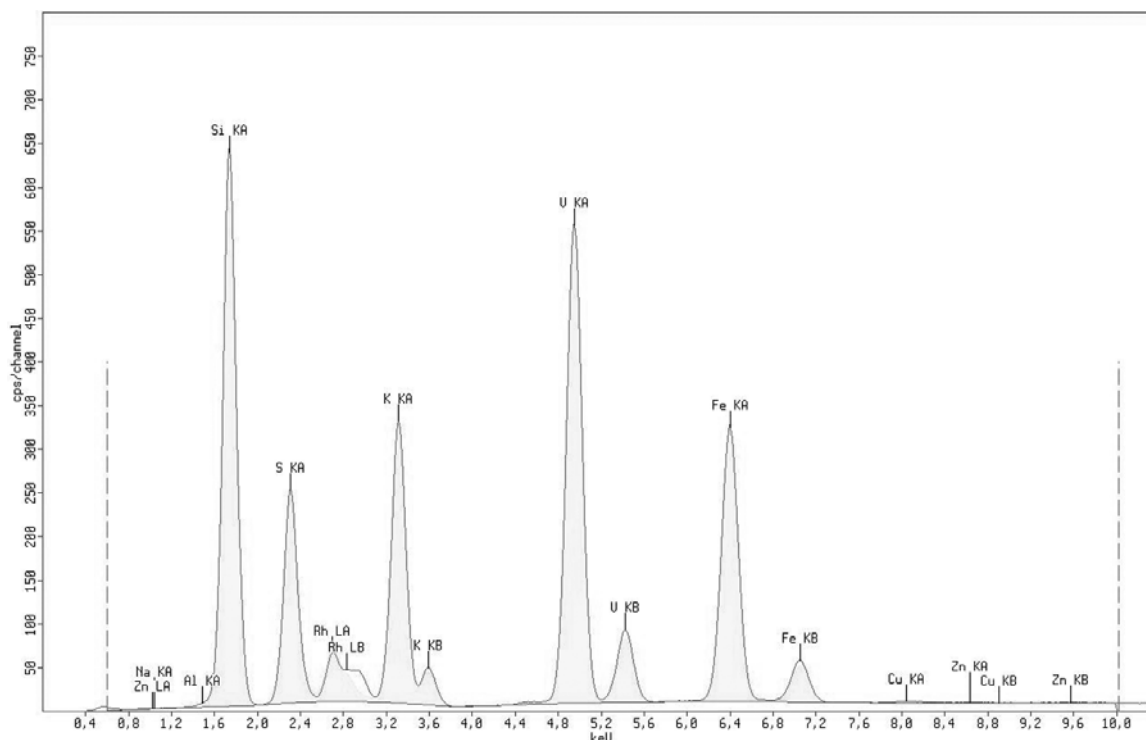
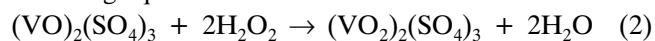


Figure 1. Quantitative composition of the spent vanadium catalyst

Analytical methods

The concentration of vanadium(V) ions in the solutions was determined spectrophotometrically, using the peroxide method¹⁵. This method is based on the ability of vanadium(V) to form in the presence of sulfuric acid and hydrogen peroxide, the compounds VO_2X or VO_2X_5^- where X is a monoanion. Vanadium(V) and hydrogen peroxide react in the equimolar amounts according to the following equation:



forming the stable red-brown complex. That compound, revealing a maximum absorbance at wavelength 450 nm and the molar absorption coefficient is $300 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, is suitable for the spectrophotometric determination of the vanadium amounts.

The analyses were performed with the double-beam U-2000 UV/Vis spectrophotometer (HITACHI).

The total concentration of iron in solutions was determined using the EDXRF method¹⁶. The analyses were performed with the MiniPal4 PANalytical compact energy dispersive X-ray spectrometer.

RESULTS AND DISCUSSION

Table 2, figures 2 and 3 presents the results of chemical analyses obtained in the first step and used to determine the effect of the concentration of KOH solutions and the time of contact between the solid and liquid phases on the degree of vanadium(V) and iron recovery. The concentration of vanadium(V) in the raffinate increases with the increasing time of extraction for the constant KOH concentration. However, that increase is not larger than 4%. The degree of vanadium(V) recovery increases with the increasing concentration of the extracting solution. The smallest increase of vanadium(V) concentration in the raffinate was found with the KOH concentration change

Table 2. The effect of KOH concentration and the extraction time on the degree of vanadium(V) recovery from the used vanadium catalyst ($T = 303\text{K}$, $S/L = 1/10$; $\phi: 0.16 - 0.075 \text{ mm}$)

KOH concentration [%]	Time [h]	Degree of vanadium(V) recovery [%]
5	0.5	68.08
	1	68.92
	2	69.75
	3	70.60
	4	71.44
10	0.5	71.43
	1	72.25
	2	73.11
	3	73.96
	4	74.79
15	0.5	73.97
	1	74.80
	2	75.63
	3	76.45
	4	77.32
20	0.5	74.25
	1	75.43
	2	76.47
	3	77.12
	4	78.16

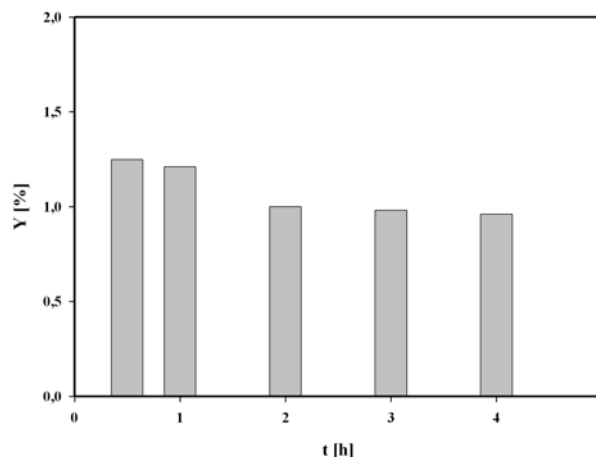


Figure 2. Dependency on the efficiencies of the iron compounds leaching process on the time of the catalyst leaching ($c_{\text{KOH}} = 15\%$; $T = 303 \text{ K}$; $S/L = 1/10$; $\phi: 0.16 - 0.075 \text{ mm}$)

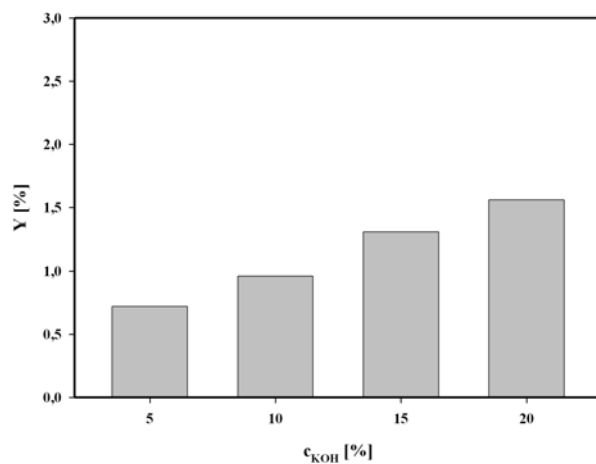


Figure 3. Dependency of the yield of iron compounds recovery on the potassium hydroxide concentrations in the leaching solution ($T = 303 \text{ K}$; $S/L = 1/10$; $\phi: 0.16 - 0.075 \text{ mm}$)

from 15% to 20%. Therefore, the subsequent investigations were performed with the use of 15% KOH solution.

Data presented in Figure 2 indicate that the yield of the recovery of iron compounds decreases in time at the temperature 303 K and reaches the minimum past 4 hour leaching process.

The reported data in Figure 3 indicates that the potassium hydroxide concentration has the smallest effect on the yield of the recovery of iron compounds. In that case the increase of the KOH concentration from 5 to 20% by mass results in the yield increase by approximately 0.8%.

The raffinate density varies from 1.063 to 1.173 g/cm^3 .

Table 3 presents the results of the second step focusing on the effect of catalyst granulation and changes of the ratio of solid to liquid phase (S/L) on the amount of eluted vanadium(V).

The data analysis reveals that the degree of vanadium(V) recovery increases with the increasing granulation for the constant S/L ratio. Also for every catalyst fraction, the vanadium(V) concentration in the raffinate increases with the S/L changing from 1/2 to 1/10. The best results in this step were obtained for the catalyst fraction with the small-

Table 3. The effect of the S/L ratio and the catalyst grain diameter on the degree of vanadium(V) recovery ($T = 303\text{K}$, $c_{\text{KOH}} = 15\%$, $t = 1\text{h}$)

Catalyst grain diameter [mm]	S/L [g/cm ³]	Degree of vanadium(V) recovery [%]
0.75 – 0.385	1/2	67.76
	1/4	68.54
	1/6	69.29
	1/8	71.03
	1/10	71.77
0.385 – 0.16	1/2	69.15
	1/4	70.26
	1/6	71.57
	1/8	72.40
	1/10	73.68
0.16 – 0.075	1/2	70.05
	1/4	72.24
	1/6	73.04
	1/8	73.43
	1/10	74.80
< 0.075	1/2	72.10
	1/4	74.05
	1/6	75.11
	1/8	76.00
	1/10	77.88

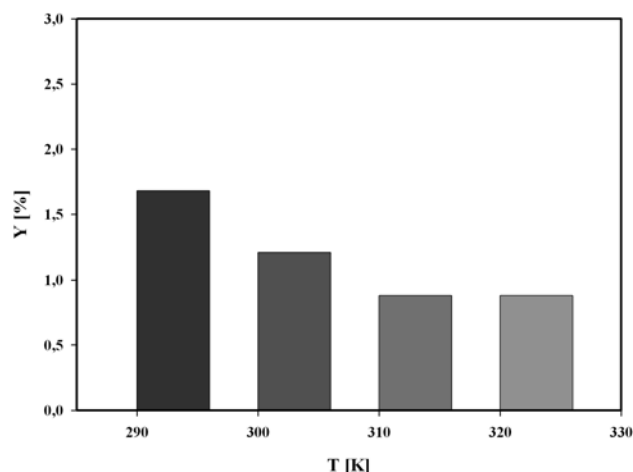
est grain diameter (ϕ below 0.075mm) and the solid to liquid phase ratio $S/L = 1/10$. The yield obtained for these conditions was 77.88% of vanadium(V) contents in the catalyst.

In the next step the effect of temperature was determined. The extraction was performed with 15% solution of KOH for 1 and 4 h and ratio $S/L = 1/10$, for the catalyst fraction of ϕ below 0.075mm. The results are presented in Table 4 and in Figure 4. The data reveal the increase of the degree of vanadium(V) recovery with the increasing temperature for the selected time of extraction. For both the 1 h and 4 h period of extraction that increase was 7% with the temperature changed from 293 to 323 K. Also, the longer time of extraction results in the increase of the vanadium(V) concentration in raffinate. The highest concentration was obtained at 323 K for 4 h extraction time. The range of raffinate density was 1.126 – 1.141 g/cm³, and the density increased with the increasing temperature and the time of elution.

Data presented in Figure 4 indicate that the yield of recovery of iron compounds decreases systematically with the increasing temperature from 293 to 313 K. Further

Table 4. The effect of temperature on the degree of vanadium(V) recovery from the used vanadium catalyst ($c_{\text{KOH}} = 15\%$, $S/L = 1/10$; ϕ : below 0.075mm)

Temperature [K]	Time [h]	Degree of vanadium(V) recovery [%]
293	1	75.92
	4	78.15
303	1	77.88
	4	80.37
313	1	81.70
	4	85.42
323	1	83.12
	4	86.29

**Figure 4.** Dependency on the efficiencies of the iron compounds leaching process on the temperature of the catalyst leaching ($c_{\text{KOH}} = 15\%$; $S/L = 1/10$; ϕ : below 0.075 mm)

raising of the temperature does not lead to a significant decrease of that concentration.

The research was concluded with the extraction of vanadium(V) from the used catalyst under the following conditions: 15% KOH, $T = 323\text{K}$, $t = 4\text{h}$, $S/L = 1/10$, the catalyst grains ϕ : below 0.075mm. The achieved degree of the recovery of vanadium(V) from the catalyst was 86%. Apart from vanadium and potassium compounds a small amount of iron compounds, whose concentration is 10 – 20 ppm, goes to the solution

The selected catalyst samples after the extraction with the use of KOH solutions were analyzed to determine the chemical composition with the use of the EDXRF method. The results of the analyses are presented in Table 5 and Figure 5. The large increase in the content of potassium compounds in the catalyst sample after the extraction compared to the catalyst before the extraction is related to the K_2SO_4 precipitation. The qualitative composition of the solution sample after the extraction is presented in Figure 6.

Figure 7 presents the comparison of the results of the temperature influence of the leaching process on vanadium compounds recovery using potassium hydroxide and sodium hydroxide solutions for the optimal conditions ($t = 4\text{h}$, $c = 15\%$, $S/L = 1/10$, ϕ : below 0.075). The degree of vanadium(V) recovery is similar for both leaching solutions¹⁷. However, the method of the spent vanadium catalyst utilization with NaOH requires an additional step – separation of vanadium compounds from the solution⁴⁻⁷. The direct precipitation yielded low recovery of vanadium and the high contents of this metal in the residual solution. It is necessary to apply the organic solvent extraction. But it greatly increases the costs of the process. The use of KOH solution doesn't require separation of

Table 5. Chemical composition of the used vanadium catalyst sample after the extraction

Compound	Content [%]
V_2O_5	0.72
SiO_2	57.5
K_2O	21.7
Fe_2O_3	3.50

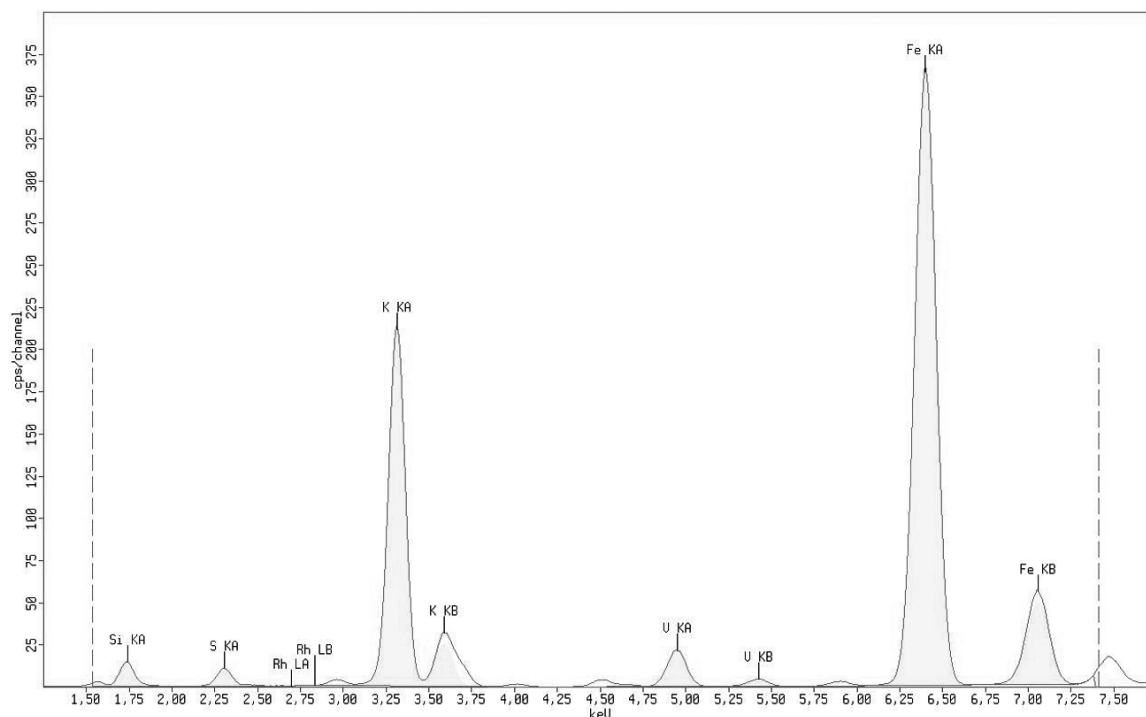


Figure 5. Quantitative composition of the spent vanadium catalyst after the extraction

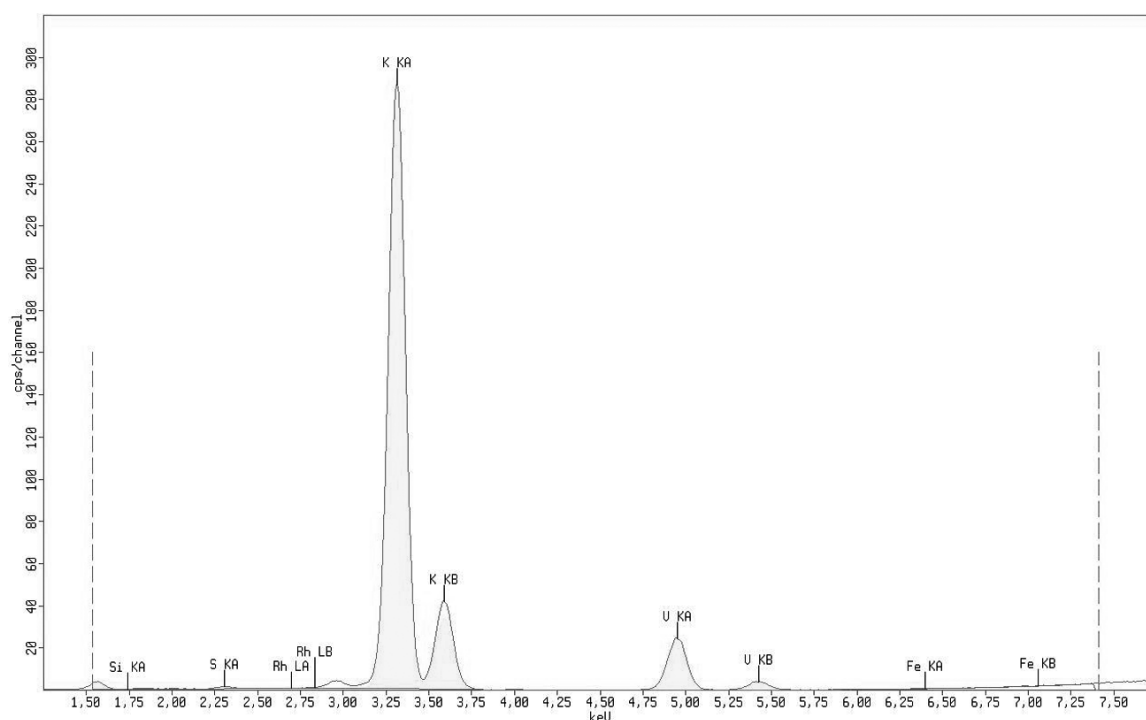


Figure 6. Quantitative composition of the solution after the extraction

vanadium from the solution. The solution, after the correction of its composition, can be directly used for the production of the new mass of vanadium catalyst.

Figure 8 presents the conceptual process flow sheet for the recovery of vanadium from the spent catalyst with potassium hydroxide solutions and the production of the new catalyst.

The new catalyst will be produced using the wet technique based on the recovered compounds:

- natural or recovered SiO_2 (min. 85% SiO_2 ; max 0.5% Fe_2O_3), roasted ($T = 673 \text{ K}$),
- technical V_2O_5 (grain size: below 0.075 mm) and KOH, for the correction of the solution composition,

- K_2CO_3 ,
- ground sulfur,
- sulfuric(VI) acid,
- texture modifier.

A possible production process will proceed according to the flow sheet presented in the manuscript¹⁸.

Summary

1. The degree of vanadium(V) recovery from the used vanadium catalyst increases with the increasing concentration of the extracting solution. The optimal concentration of KOH solution is 15%, and higher concentrations cause only an insignificant increase of the degree of recovery.

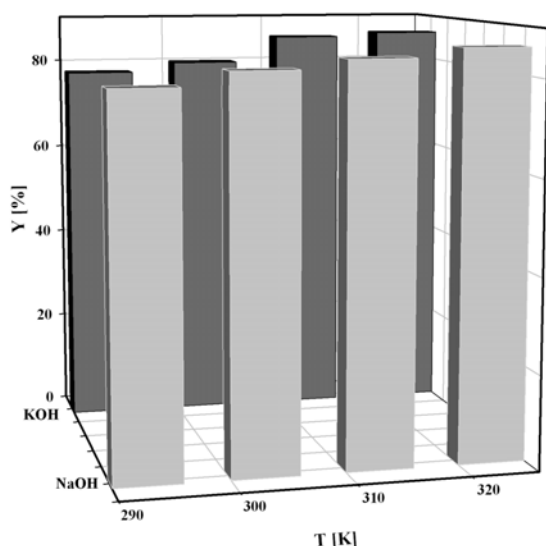


Figure 7. The comparison of the results of vanadium compounds recovery using potassium hydroxide and sodium hydroxide solutions

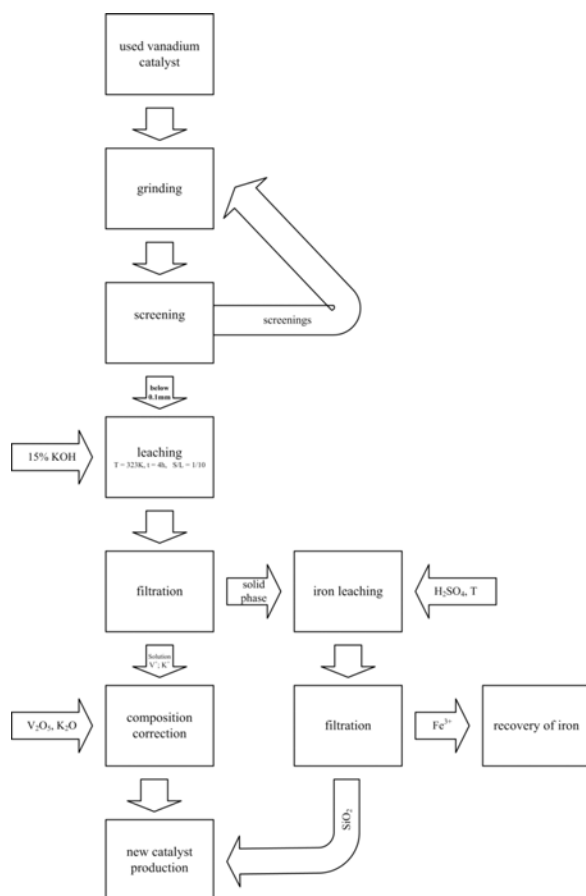


Figure 8. A conceptual process flow sheet for the recovery of vanadium from a spent catalyst with potassium hydroxide solutions and the new catalyst production

2. Extension of the time of the contact between the solid and liquid phases results in the increase of the extraction yield.

3. The degree of vanadium(V) recovery increases with the increasing temperature.

4. Concentration of vanadium(V) in raffinate increases with the decreasing size of the catalyst grains.

5. Maximum degree of vanadium(V) recovery from the used vanadium catalyst (86%) was achieved for the extraction conditions: 15% KOH, $T = 323\text{K}$, $t = 4\text{h}$, $S/L = 1/10$, ϕ : below 0.075mm .

6. Low leakage of iron compounds from the catalyst into the solution was observed.

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