Influence of leaching parameters on the vanadium extraction from petroleum coke

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Abstract: More than 60 trace elements, including rare metals, can be found in heavy oils. The most valuable component of oils and petroleum products is vanadium. It is used as an alloying agent to create extra strong steel, as a cathode for lithium-ion batteries, and also as a catalyst in the chemical industry. Nowadays studies of various methods for extracting vanadium from heavy oils and petroleum products are actively carried out. This work presents the method of alkaline and acid leaching of vanadium from petroleum coke and also results of the examination of influence of factors such as the duration of the process (0.5, 1.5 and 2.5 h) and the ratio of solid and liquid phases (1:2, 1:3 and 1:4). The highest yield of vanadium 80% is observed using sulfuric acid with the process duration is 1.5 hours and the ratio S/L = 1:4

1 Introduction

In connection with the depletion of light oil reserves, the question of processing of heavy metal oils arose [1]. However, the metals contained in oils adversely affect the quality of the obtained products, deactivate catalysts for oil refining processes, and cause corrosion of the equipment[2-4]. At the same time, trace elements are contained in oils are valuable incidental components, of which vanadium is an important strategic metal, due to it use as an alloying additive to high-strength steel, a cathode for lithium-ion batteries, catalysts, etc.[5].

Vanadium is the single element that is currently extracted from heavy oils, but only abroad. This is due to the fact that the content of vanadium in heavy oils is comparable or higher than its content in the ores from which it is extracted. Therefore, the process of extracting vanadium from oil can become more cost effective, and it can also provide products for metallurgical production because its demand for vanadium is constantly growing[4]. In addition, extraction of vanadium in the form of porphyrin complexes by extractive methods is also important for the petrochemical industry [6-8].

About 95% of all vanadium amount gets concentrated in petroleum coke during the coking process [9,10], so it a promising raw material for the recovery of vanadium. Spent catalysts and ash from boilers of thermoelectric power plants using fuel oil and petroleum coke can also serve as raw materials for vanadium recovery. A large number of studies have been carried outon the extraction of vanadium using ash from thermal power plants as a raw material [11-16] and few research is devoted the study of coke as a raw material for the recovery of vanadium [17,18].

V.A. Rudko [17] studied the influence of the ratio of the solid (coke) to the liquid (acid) phase, as well as the time of the process on the yield of vanadium in the process of acid leaching. To carry out the process, petroleum coke was ground to a particle size of 100 μm. Concentrated and diluted sulfuric acid and a mixture of concentrated nitric and sulfuric acids in a 1:1 mass ratio were used as leaching agents. It was shown that with a decrease in the ratio of the solid and liquid phases from 1:3 to 3:1, the degree of extraction of vanadium also decreases.

M.R. Tavakoli [18] studied the leaching process using vanadium pent oxide as the raw material. Sulfuric acid and sodium hydroxide were used as leaching agents. It was shown that a decrease in the pH and temperature of the process for acid leaching leads to an increase in the solubility of vanadium. The opposite data was obtained for alkaline leaching. Moreover, the solubility of vanadium in sulfuric acid solution was found to be higher than in solutions of nitric and hydrochloric acids. This is due to the formation of a complex of the vanadylion with sulfate.

Y.L. Zhang [19] studied the effect of sodium sulfate on the leaching process. Prior to the experiment, the coke was ground and sieved to the particle size range of 74 μm. It was shown that a small amount of sodium sulfate (about 0.7 g) increases the leaching rate.

Thermodynamic calculations show that it is most advantageous to carry out the leaching process with a dilute sodium hydroxide solution as a reagent in order to extract vanadium. However, according to experimental data, the highest yield of vanadium is obtained when using concentrated sulfuric acid. This discrepancy between calculations and experimental data can be explained by the influence of factors that thermodynamics does not take into account, for example, the difference in the passage of the reagent into the pores of the coke.

Thereby, in this work, we compared the effect of acid and alkali agents on the extraction of vanadium from petroleum coke by the leaching method. We used different parameters of the process, such as the ratio of liquid and solid phases and the duration of the process, to the compare the vanadium recovery from petroleum coke.

2 Experimental

2.1 Materials

An industrially obtained sample of petroleum coke from a mixture of West Siberian oils was taken from a delayed coking unit.

The main technological parameters of the delayed coking process were:
• Coking temperature at the reactor's inlet: 505 °C
• Coking pressure in the reactor: 0.35 MPa (excessive)
• The load factor for raw materials: 1.2.
The materials balance of the delayed coking process is presented in Table 1:

Table 1. The materials balance of the delayed coking process.

Input		Output	
Atmospheric residue	85.0	Gas	5.4
HGOCC *	15.0	Petrol	9.8
		Lightgasoil	28.5
		Heavy gasoil	29.9
		Coke	27.3
Total:	**100.0**	**Total:**	**100.0**

*HGOCC – stands for heavy gasoil catalytic cracking
Quality indicators of petroleum coke are indicated below.
• The yield of volatile substances: 7.8%

• Ash content: 0.11%
• Content, %, of other components: S - 1.6911, V - 0.0198, Si - 0.0010, Fe - 0.0009.

2.2 Leaching of vanadium from petroleum coke

Experiments on the leaching of vanadium from petroleum coke were carried out in stainless steel reactors 60 mm high and of 40×30 mm in diameter. Each reactor was charged with 1 g of petroleum coke (particle size of about 0.1 mm) and the necessary amount of leaching agent (acids or alkali) were placed in each reactor. Then the reactors were placed in a drying oven and kept at the temperature of 100 °C from 0.5 to 2.5 hours.

NaOH 10% and H_2SO_4 12% were used as leaching agents. Acid or alkali was added to the coke so that the ratio of solid and liquid (S/L) phases was 1:2, 1:3 and 1:4.

After the leaching process petroleum coke was filtered using a "white tape" filter paper and washed with 30-40 ml of water. Then it was dried in a drying oven at the temperature of 110 °C to constant weight.

2.3 Photometric analysis of the solutions after leaching

Analysis of the solutions after leaching was carried out using a PE-5400 UV spectrophotometer (LLC "ECROSCHIM"). The degree of vanadium extraction from petroleum coke was determined according to GOST 10364 "Oil and petroleum products. Vanadium determination method."

40 ml of the solution after leaching, 2 ml of diluted sulfuric acid 1:1, 5 ml of diluted phosphoric acid, and 2.5 ml of sodium tungstate solution were placed in a 100 ml beaker. After adding each reagent, the contents of the beaker were mixed by shaking. The resulting solution was heated to 40–70 °C and then cooled down to room temperature. Then the solution was quantitatively transferred into a 50 ml volumetric flask and adjusted to the mark with distilled water. The solution was left for 60 minutes.

A control solution was prepared for photometric analysis. 2 ml of sulfuric acid 1:1, 5 ml of diluted phosphoric acid, and 2.5 ml of sodium tungstate solution were placed in a 50 ml flask. The resulting solution was adjusted to the mark with distilled water. The optical density of the solution after leaching was determined relative to the control solution. The mass of vanadium in mg contained in 50 ml of the solution was determined according to the calibration plot (Figure 1).
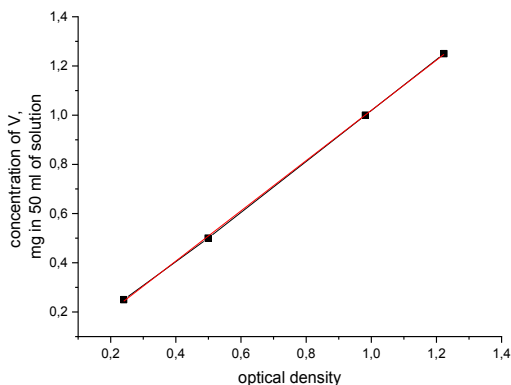
Fig. 1. Calibration plot for determining the content of vanadium in the solution.

The concentration of vanadium in mg per kg of raw material is calculated by Equation (1):

$$C = \frac{m_1 \cdot 1000 \cdot 50}{m \cdot V},\tag{1}$$

where m_1 – is the mass of vanadium in the solution, determined according to the calibration plot, mg; m – is the sample weight, g; 50 – is the volume of solution made for photometric analysis, ml; V – is the aliquot of the solution taken for photometry analysis, ml.

The degree of extraction of vanadium from petroleum coke in the leaching process is determined by Equation (2):

$$E = \frac{C}{C_{coke}} \cdot 100\%,\tag{2}$$

where C –is the concentration of vanadium in solution, mg/kg; C_{coke}–is the concentration of vanadium in petroleum coke, mg/kg.

2.4 X-ray fluorescence analysis

The content of sulfur and trace elements in the obtained samples of petroleum coke was determined using X-ray fluorescence spectrometry without preliminary ashing of the samples using the addition method on a sequential wave dispersive X-ray fluorescence spectrometer XRF-1800 Shimadzu[20,21]. The device is equipped with an x-ray tube with an anode of Rh with a power of 2.7 kW. A detailed method for the determination of sulfur and trace elements is described in [22].

2.5 Derivatographic analysis

Thermogravimetric analysis and differential scanning calorimetry were performed on a SDT Q600 thermal analyzer. This device allows to conduct these analyzes simultaneously, which significantly reduces the time spent on examining samples. The sample weight for analysis was taken with an accuracy of 10^{-3} mg. The mass of carbon material was taken in the range from 15.494 mg to 5.406 mg. Heating was carried out from 50 to 1000 °C at a rate of 20 °C/min. The oxidizing environment was the air.

2.6 X-ray diffraction analysis

X-ray diffraction analysis of samples of carbon materials was carried out using aXRD-7000 Shimadzu X-ray diffractometer(CuKα radiation, 2.7 kW) at room temperature using the polycrystal method. Radiographs were taken at large accumulation times (2 s) and a scanning step of 0.02°.

The asymmetric reflections of petroleum cokes were decomposed into peaks. Their profile is described by a Gaussian with a maximum at angles of 2θ characterizing certain structural components of the samples.

In this work, we used the inter-planar distance of the (002) and (110) diffraction maxima, as well as the sizes of the coherent scattering region in the directions of the axes "c" (average crystallite height L_c) and "a" (average diameter of hexagonal layers L_a) for a detailed assessment of the fine structure of carbon materials by the X-ray diffraction method. The inter-planar distance (d_{002} and d_{110}) in Å of the obtained samples of petroleum coke was calculated according to the Wulf-Bragg equation [23,24]:

$$d = \frac{\lambda}{2 \cdot sin\theta}, \tag{3}$$

where $\lambda = 1.5406$ – is the X-ray wavelength for CuKα, Å; θ – is the Bragg diffraction angle, rad.

The average linear size of crystallites L_c and L_a was determined in Å according to the Scherrer Equation [25]:

$$L_c = \frac{0.89 \cdot \lambda}{\beta_{002} \cdot cos\theta_{002}} \text{ and } \quad L_a = \frac{0.89 \cdot \lambda}{\beta_{110} \cdot cos\theta_{110}}, \tag{4}$$

where 0.89 – is the Scherer constant, which for cokes was conditionally set the same for the uniformity in the published results [26]; β – is the width of the diffraction line at half the maximum height (in rad) minus the hardware peak width $b = 0.2°$.

3 Results and discussion

3.1 Leaching and analysis of product solutions

The degree of vanadium extraction was determined according to paragraph 2.3. The optical density of the solution was recalculated to the degree of extraction using Equations 1 and 2. The received data are presented in Table 2.

Table 2. The degree of vanadium extraction.

Time, h	Leaching agent	S/L	Optical density	Mass of coke, g	Concentration of V, mg in 50 ml of solution	Concentration of V, mg/kg	Degree of extraction, %
0.5	H_2SO_4	1:2	0.091	1.0035	0.092	115	55
		1:3	0.107	1.0082	0.108	134	64
		1:4	0.101	1.0089	0.102	127	60
	NaOH	1:2	0.068	1.0018	0.068	85	40
		1:3	0.074	1.0066	0.075	93	44
		1:4	0.096	1.0007	0.097	121	58
1.5	H_2SO_4	1:2	0.065	1.0013	0.065	81	39
		1:3	0.082	1.0060	0.083	103	49
		1:4	0.134	1.0016	0.135	169	80
	NaOH	1:2	0.090	1.0078	0.091	113	54
		1:3	0.088	1.0094	0.089	110	52
		1:4	0.119	1.0018	0.121	151	72
2.5	H_2SO_4	1:2	0.079	1.0033	0.079	99	47
		1:3	0.087	1.0043	0.088	110	52
		1:4	0.092	1.0064	0.093	116	55
	NaOH	1:2	0.065	1.0040	0.065	81	39
		1:3	0.112	1.0027	0.113	141	67
		1:4	0.063	1.0016	0.063	79	38

Earlier in our laboratory it was shown that from the point of view of thermodynamics, sodium hydroxide is the best leaching agent. However, as can be seen from Table 1, the recovery of vanadium is higher when sulfuric acid is used. This is due to the fact that, in addition to thermodynamic factors, other parameters influence the leaching process, such as pore size, reagent diffusion, etc.

The recovery of vanadium increases with an increase in the S/L ratio and the duration of the process, if sodium hydroxide or dilute sulfuric acid are used as a leaching agent. However, if the process is carried out for 2.5 hours, the degree of extraction decreases; that is also described in the works [11,14]. This may be due to the predominance of adverse and substitution reactions, whereby solubility of vanadium decreases.

The highest recovery of vanadium (80%) is observed in the leaching process in the presence of sulfuric acid for 1.5 hours with a phase ratio of 1:4. The maximum of vanadium recovery for sodium hydroxide (72%) is observed under the same conditions. Thus, the maximum of vanadium recovery can be obtained by carrying out the process for 1.5 hours at a phase ratio of 1:4.

The spent solution after the alkylation of isobutene with olefins can be used like sulfuric acid as leaching agent in production [27].

3.2 Analysis of the composition and structure of the carbon residue after leaching

3.2.1 X-ray fluorescence analysis

The composition of the solid residue after leaching was studied by X-ray fluorescence analysis. The obtained data are presented in Table 3.

Table 3. The composition of the solid residue after leaching.

Time,h	Leaching agent	S/L	Content of element, %					
			V	Ni	S	Fe	Al	Ca
0.5	H_2SO_4	1:2	0.0095	0.0100	1.9119	0.0259	0.0046	0.0041
		1:3	0.0076	0.0171	1.3976	0.0189	0.0049	0.0033
		1:4	0.0083	0.0114	1.8702	0.0360	0.0056	0.0260
	NaOH	1:2	0.0125	0.0155	1.8826	0.0484	0.0131	0.0096
		1:3	0.0117	0.0130	1.8980	0.0286	0.0180	0.0107
		1:4	0.0089	0.0094	1.6805	0.0270	0.0857	0.0246
1.5	H_2SO_4	1:2	0.0129	0.0144	2.8792	0.0408	0.0074	0.0183
		1:3	0.0107	0.0126	1.9173	0.0198	0.0061	0.0040
		1:4	0.0041	0.0150	0.9374	0.0366	0.0028	0.0046
	NaOH	1:2	0.0097	0.0113	1.8730	0.0222	0.0041	0.0139
		1:3	0.0100	0.0134	1.8198	0.0167	0.0043	0.0122
		1:4	0.0059	0.0185	1.1460	0.0269	0.0026	0.0083
2.5	H_2SO_4	1:2	0.0111	0.0118	1.9178	0.0174	0.0051	0.0048
		1:3	0.0100	0.0117	1.8670	0.0404	0.0059	0.0129
		1:4	0.0094	0.0097	1.8843	0.0308	0.0044	0.0068
	NaOH	1:2	0.0129	0.0138	1.8251	0.0220	0.0051	0.0084
		1:3	0.0069	0.0090	1.3881	0.0530	0.0050	0.0141
		1:4	0.0131	0.0145	1.8110	0.0190	0.0046	0.0079

As can be seen from the table, the sulfur content is higher in the samples obtained by leaching in the presence of sulfuric acid. Sulfur is a more harmful impurity than vanadium, therefore the sodium hydroxide is better to use for improving the quality of coke obtained after leaching.

The content of aluminum and calcium is higher in the samples obtained using sodium hydroxide, so alkali has a higher selectivity for the extraction of vanadium compared to acid.

3.2.2 Derivatographic analysis

The chemical reactions taking place in the solid residue after the leaching process with increasing temperature were studied by the method of thermogravimetry (Figure 2). Two processes are noticeable on the obtained curves: decomposition of the carbon part (600 °C) and oxidation (400°C).

The mass of the samples for the study was not constant, therefore, to compare the oxidation state, the increase in the mass of the sample in percent was calculated using Equation 5:

$$M = \frac{m_{ox}}{m_{sam}} \cdot 100\% , \qquad (5)$$

where M – is the sample weight increase, %; m_{ox} – is the maximum mass of the sample after oxidation, mg; m_{sam} – is the sample weight taken for research, mg.

Table 4 presents the data calculated according to Equation 5.
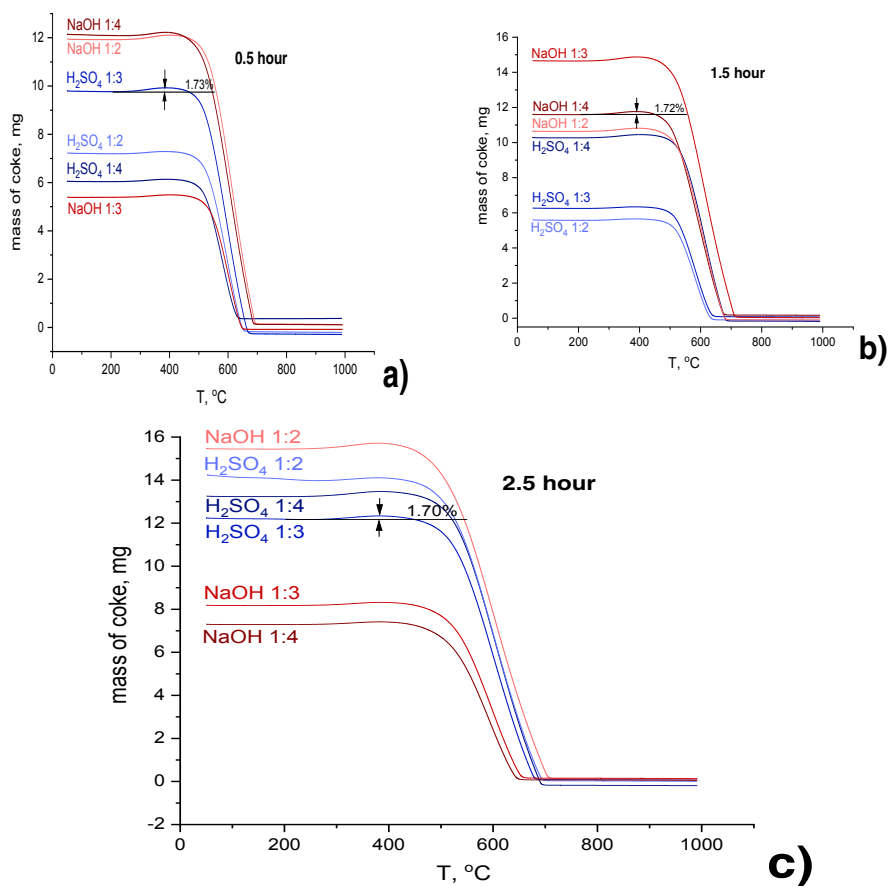
Fig. 2. Thermo gravimetric analysis: the duration of the process is a) 0.5 hours, b) 1.5 hours, c) 2.5 hours.

Table 4. The results of thermogravimetric analysis.

Time, h	Leaching agent	S/L	Mass of samples, mg	Maximum mass after oxidation, mg	Increase massof samples, %
0.5	H_2SO_4	1:2	7.252	0.10	1.38
		1:3	9.833	0.17	1.73
		1:4	6.074	0.10	1.65
	NaOH	1:2	11.960	0.17	1.42
		1:3	5.406	0.10	1.85
		1:4	12.165	0.14	1.15
1.5	H_2SO_4	1:2	5.615	0.07	1.25
		1:3	6.293	0.07	1.11
		1:4	10.316	0.22	2.13
	NaOH	1:2	10.683	0.18	1.68
		1:3	14.698	0.22	1.50
		1:4	11.639	0.20	1.72
2.5	H_2SO_4	1:2	14.343	0.14	0.98
		1:3	12.329	0.21	1.70
		1:4	13.281	0.24	1.81
	NaOH	1:2	15.494	0.27	1.74
		1:3	8.199	0.14	1.71
		1:4	7.326	0.14	1.91

The mass of the samples obtained using sodium hydroxide increases more than for the samples obtained using sulfuric acid. This fact confirms the previous conclusion about the higher selectivity of sodium hydroxide for the vanadium extraction as compared to sulfuric acid. This is due to the fact that sulfur and metals, remaining in the samples after leaching, are subjected to oxidation[28,29]. The more metals and sulfur are left in the sample, the more its mass will increase during the oxidation process.

More oxidation is observed in the samples in the presence of sulfuric acid, when the ratio of solid and liquid phases is 1:4. This may be due to an increase of the sulfur content in these samples. The fact that the sulfur content in these samples is higher than in the samples obtained using alkali was shown in section 3.2.1.

The curves that were obtained by the method of differential scanning calorimetry (DSC) show one peak corresponding to the decomposition of the sample. There are no peaks corresponding to oxidation, because the oxidation process only affects 2% of the total mass and has little effect on the overall heat balance of the system (Figure 3).
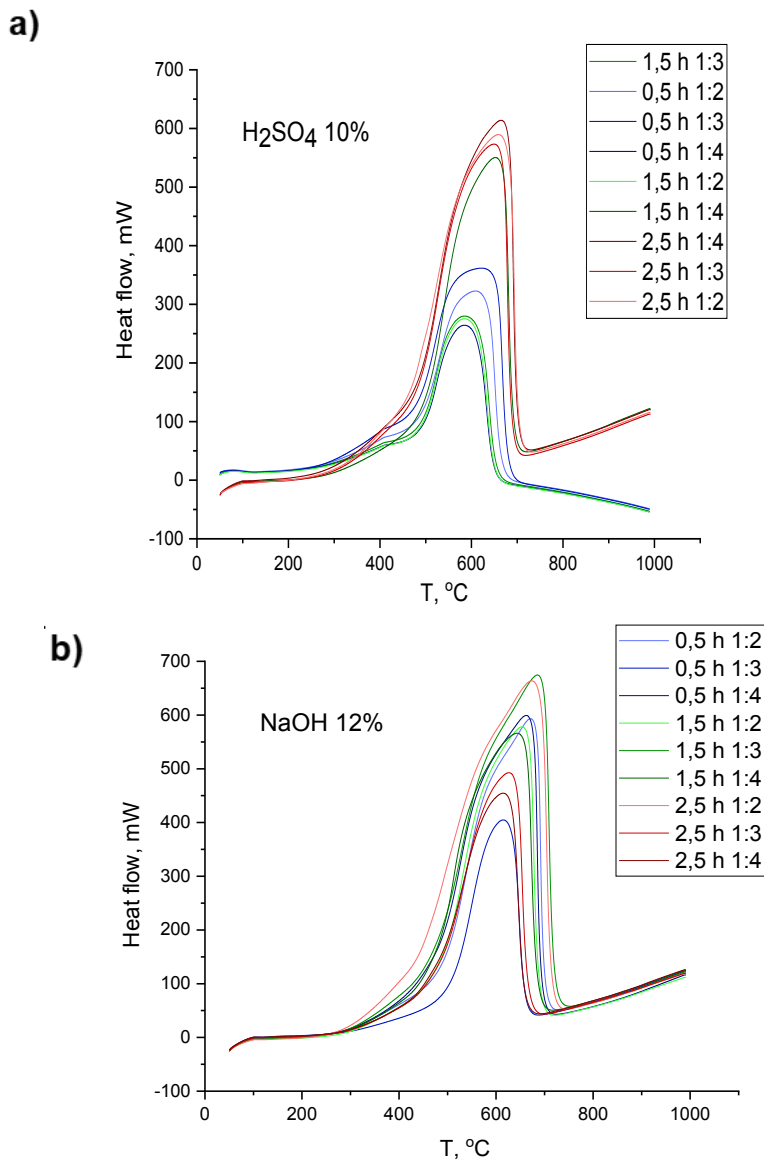
Fig. 3. DSC curves for samples were obtained using NaOH (a) and H_2SO_4 (b).

The average decomposition temperature of the sample was calculated according to the DSC curves. Table 5 presents the obtained data.

The decomposition temperature of the sample is 640 ℃.

Table 5. Decomposition temperatures of samples.

Time, h	Leaching agent	S/L	Decomposition temperature, ℃
		1:2	609
0.5	H_2SO_4	1:3	622
		1:4	584
	NaOH	1:2	671

| | | 1:3 | 615 |
		1:4	662
1.5	H_2SO_4	1:2	585
		1:3	585
		1:4	652
	NaOH	1:2	653
		1:3	685
		1:4	643
2.5	H_2SO_4	1:2	659
		1:3	649
		1:4	665
	NaOH	1:2	673
		1:3	626
		1:4	615
The average			636

3.2.3 X-ray diffraction analysis

Petroleum coke is amorphous carbon with a low degree of crystallinity. Amorphous carbon transforms into graphite during high-temperature processing. Crystallites formed in the amorphous matrix of petroleum coke during the thermolysis have a turbostract structure that differs from the graphite one [30]. The main structural parameters of such crystals are the inter-planar distances d_{002}, d_{110} and the sizes of the coherent scattering regions in the direction of the crystallographic axes "c" and "a", L_c and L_a, respectively. For graphite, d_{002} and d_{110} are 3.354 and 1.232 Å, respectively, and for a turbostratic structure, d_{002} varies from 3.37 to 3.60 Å, and d_{110} from 1.215 to 1.230 Å [31].
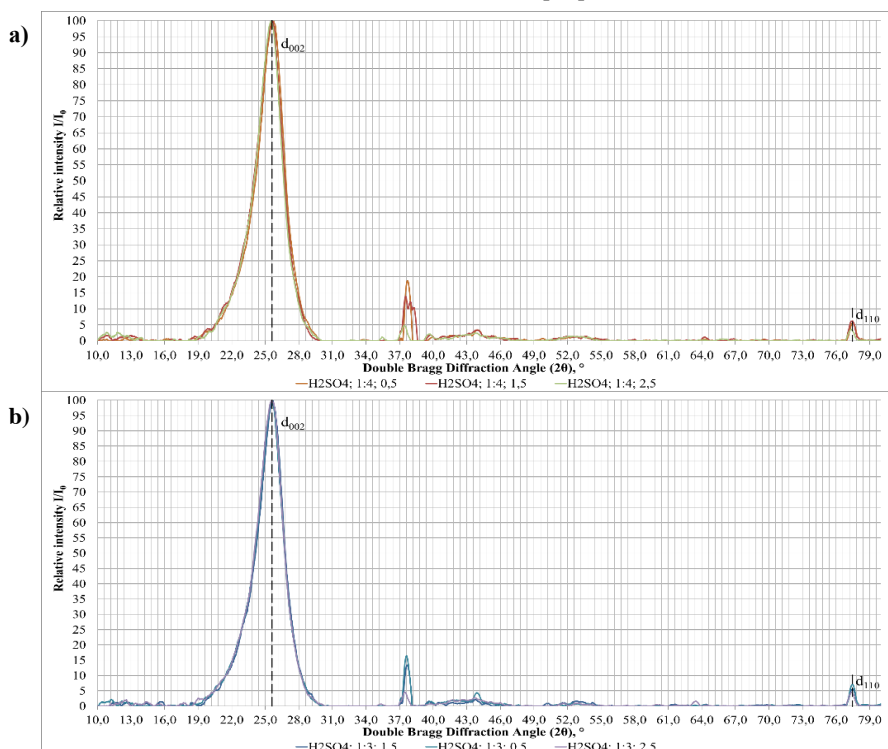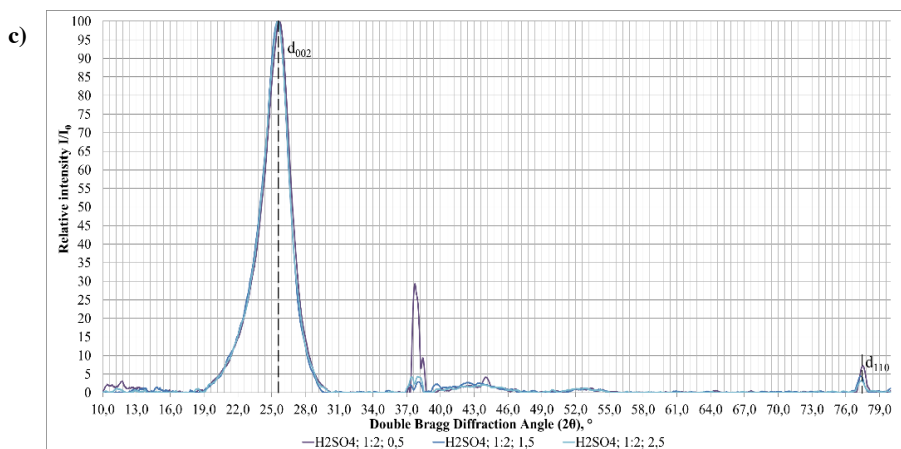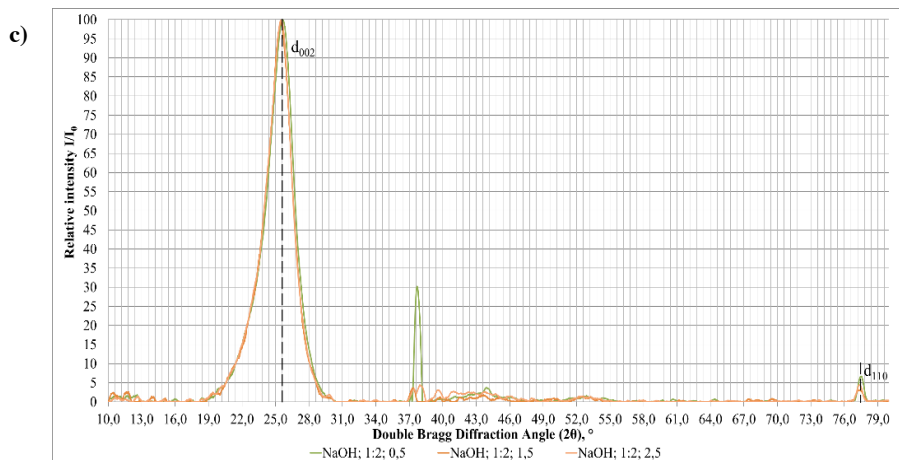
Fig. 4. Comparison of the diffraction patterns of the carbon material after vanadium recovery in presence of H_2SO_4 at 0.5, 1.5 and 2.5 h: a) S:L = 1:4; b) S:L = 1:3; c) S:L = 1:2.

Figures 4 and 5 show a comparison of the diffractograms of the carbon material after the leaching process in the presence of H_2SO_4 and NaOH, respectively.

c)
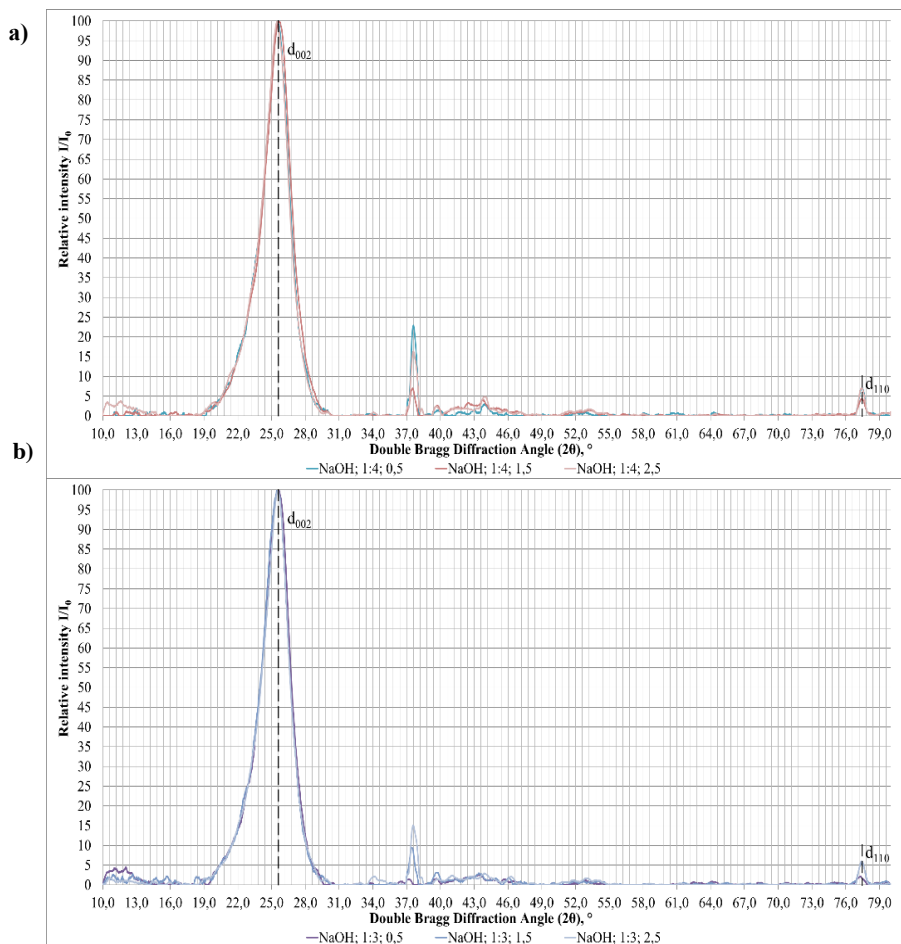
Fig. 5. Comparison of the diffraction patterns of the carbon material after vanadium recovery in presence of NaOH at 0.5, 1.5 and 2.5 h: a) S:L = 1:4; b) S:L = 1:3; c) S:L = 1:2.

Peaks with a maximum of 2θ angles in X-ray diffractograms are about 25° and 77°, respectively responsible for reflections $2\theta_{002}$ and $2\theta_{110}$, are clearly expressed characteristic of petroleum coke. The angular position of the reflexes ($2\theta_{002}$ and $2\theta_{110}$) in the X-ray diffraction pattern is determined by the corresponding inter-planar distance (d_{002} and d_{110}) [32,33]. The diffractometric analysis results and values calculated from (002) and (110) reflections for the carbon material after vanadium recovery are shown in Table 6.

Table 6. Results of diffractometric analysis of carbon material.

Characteristics	Reflex (002)				Reflex (110)			
	2θ, °	Halfwidth, °	d_{002}, Å	L_c, Å	2θ, °	Halfwidth, °	d_{110}, Å	L_a, Å
H_2SO_4; 1:3; 1.5	25.6000	2.6800	3.4769	29.4672	77.4400	0.6000	1.2315	173.9979
H_2SO_4; 1:2; 0.5	25.6600	2.7600	3.4689	28.6119	77.5000	0.6200	1.2307	167.7915
H_2SO_4; 1:3; 0.5	25.6200	2.7000	3.4742	29.2489	77.4600	0.5800	1.2312	180.8176
H_2SO_4; 1:4; 0.5	25.7200	2.7400	3.4609	28.8253	77.4800	0.6000	1.2309	174.0467
H_2SO_4; 1:2; 1.5	25.6000	2.7600	3.4769	28.6085	77.3000	0.6600	1.2333	156.3386
H_2SO_4; 1:4; 1.5	25.6000	2.8000	3.4769	28.1977	77.4400	0.6400	1.2315	161.9023
NaOH; 1:2; 0.5	25.6600	2.7000	3.4689	29.2512	77.5200	0.6200	1.2304	167.8150
NaOH; 1:3; 0.5	25.5200	2.7600	3.4876	28.6040	77.3000	0.7000	1.2333	146.5845
NaOH; 1:4; 0.5	25.5600	2.7000	3.4822	29.2454	77.4600	0.6000	1.2312	174.0223
NaOH; 1:2; 1.5	25.4800	2.6600	3.4930	29.6829	77.3200	0.7600	1.2331	134.1298
NaOH; 1:3; 1.5	25.4800	2.7200	3.4930	29.0246	77.4400	0.6800	1.2315	151.4458
NaOH; 1:4;	25.70	2.8000	3.463	28.203	77.46	0.6600	1.231	156.513

Characteristics	Reflex (002)				Reflex (110)			
	$2\theta, °$	Halfwidth, °	d_{002}, Å	L_c, Å	$2\theta, °$	Halfwidth, °	d_{110}, Å	L_a, Å
1.5	0		6	3	0		2	5
H_2SO_4; 1:4; 2.5	25.540	2.6400	3.4849	29.9127	77.360	0.6200	1.2325	167.6272
H_2SO_4; 1:3; 2.5	25.580	2.7400	3.4796	28.8173	77.380	0.6000	1.2323	173.9250
H_2SO_4; 1:2; 2.5	25.540	2.7200	3.4849	29.0280	77.420	0.7000	1.2317	146.7074
NaOH; 1:2; 2.5	25.580	2.6800	3.4796	29.4660	77.400	0.6000	1.2320	173.9493
NaOH; 1:3; 2.5	25.600	2.6400	3.4769	29.9162	77.440	0.6000	1.2315	173.9979
NaOH; 1:4; 2.5	25.500	2.6400	3.4903	29.9103	77.460	0.6000	1.2312	174.0223

The inter-planar distance d_{002} for samples of the carbon material after vanadium recovery varies from 3.4636 to 3.4930 Å, and d_{110} from 1.2304 to 1.2333 Å. The character of the microstructure of petroleum coke can be judged according to the results of X-ray phase analysis by the ratio of the average height L_c and the average diameter L_a of crystallites [34,35]. In this case, the ratio of L_c/L_a varies from 0.16 to 0.22, so petroleum coke has a flattened structure of crystallites because of thermo baric conditions during the formation of petroleum coke.

In the X-ray diffraction patterns of most samples of carbon materials, in addition to the peaks (002) and (110), there is also a peak with the maximum value of the doubled Bragg diffraction angle 2θ of about 37°, which is not typical for of the crystal lattice of petroleum coke and reflects the content of impurities.

The results of the analysis show that the relative intensity of this peak, which characterizes the content impurities, has a general tendency to decrease with an increase of the duration of the leaching process from 0.5 to 2.5 hours, but with a minimum at 1.5 hours at a ratio of S:L = 1:4 and using sulfuric acid or sodium hydroxide as a leaching reagent. The trend to decrease remains at L:S = 1:3 and others parameters equal, however withno minimum at 1.5 hours. The relative intensity of the peak at S:L = 1:2 passes through a maximum at 1.5 hours and returns to the original range of values.

The relative intensity of the peak of 37° at a leaching time of 0.5 h and a decrease in the content of the leaching reagent H_2SO_4 or NaOH (the S:L ratio varies from 1:4 to 1:3 and 1:2) increases. However, the relative intensity of this peak decreases at 1.5 and 2.5 hours and others parameters the same.

4 Conclusion

It was shown that the extraction of vanadium after the leaching process increases with an increase in the ratio of the S/L phases and the duration of the process. It was also shown that sulfuric acid is the best leaching agent, although it increases the sulfur content in coke. Alkali is a more selective solvent compared with sulfuric acid.

The highest recovery of vanadium (80%) was observed when the process was carried out in the presence of sulfuric acid for 1.5 hours with a phase ratio of 1:4. The maximum of vanadium recovery using sodium hydroxide was observed under the same conditions and amounted to 72%.

The obtained crystals of petroleum coke have a turbostract flattened crystal structure, because of the thermobaric conditions for the formation of petroleum coke.

This work has also shown that petroleum coke is a promising raw material for the production of vanadium at an industrial scale.

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