EXTRACTION OF VANADIUM FROM PET-COKE GASIFICATION CINDER PART 1: LEACHING KINETIC STUDIES IN SULPHURIC ACID MEDIUM

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Abstract

Petcoke cinder is a solid by-product generated during the gasification of petcoke, accounting for three to five percent of the petroleum coke mass. It commonly contains valuable metals such as V, Ni, Al, and Fe, highlighting its potential as a resource for vanadium extraction. Therefore, it may be considered an emerging secondary source of vanadium and other critical metals. The conventional pyro-cum-hydrometallurgical process for vanadium recovery relies on alkali roasting, which is not only energy-intensive but also contributes to greenhouse gas emissions. Given environmental concerns and high energy consumption, this study presents a state-of-the-art, economically feasible, and energy-efficient process for extracting V from petcoke cinders. This paper discusses the acid-leaching method for vanadium extraction from petcoke cinders and examines various parameters, including acid concentration, temperature, process duration, percentage of H_2O_2, amount of sodium dodecyl sulfate (SDS), and solid-liquid phase ratios. The optimal recovery rate of V, 95.62%, was achieved under the following conditions: 4 M sulfuric acid at 90 °C for three hours, with a solid-liquid ratio of 15%, H_2O_2 at 20%, and SDS at 6%. Leaching kinetics were investigated using a shrinking surface-controlled model, revealing a reaction order of 1.29 with respect to sulfuric acid concentration. According to the Arrhenius equation, the apparent activation energy of leaching was approximately 27.67 kJ/mol, and the empirical equation representing the acid leaching kinetics of vanadium was established as $1-(1-\alpha)^{1/3}=kt=(9.261\times10^3)[H_2SO_4]^{1.2916}exp[-27674/RT]T$.

Keywords: Petcoke cinders; Acid leaching; SDS; Leaching kinetics; Apparent activation energy

1. Introduction

Petcoke gasification cinder, often known as petroleum coke cinder, is a by-product of gasification plants. The refining and upgrading of crude oil produce heavy residues. In the coking process, the long-chain hydrocarbons in these heavy residues break down into condensed, carbon-rich solid products called petcoke. This petcoke is used as a raw material in gasification plants. During gasification, petcoke is converted into lighter products, mainly syngas, while the heavier molecules remain behind. The solid residue left over from this process is called petcoke gasification cinder, which contains significant amounts of metals such as vanadium (V), nickel (Ni), aluminum (Al), and iron (Fe) [1]. In recent decades, petcoke gasification plants have dramatically increased and generated an unavoidably large quantity of leftover cinder. Consequently, the disposal of petcoke cinder in landfills has sparked growing concerns. Therefore, recovering V and other critical metals from the cinders is not only beneficial for humans, the environment, and the economy, but also reduces the burden of waste management and exploitation of the primary resources [2, 3].

Vanadium is the most strategic and valuable transition metal and plays a crucial role in both ferrous and nonferrous industries. Its unique properties have gained worldwide attention, including high thermal strength, excellent conductivity, strong creep resistance, and low neutron scattering [4, 5]. As a result, vanadium and its alloys have several essential applications in the iron and steel industries (~85%), un-substitutable in the near future, such as Contact's process catalyst for producing sulfuric acid and, more importantly, in the manufacturing of high storage capacity secondary batteries (vanadium redox flow batteries (VRFBs)), which are becoming increasingly popular. VRFBs are becoming increasingly popular for their high-safety features, large-scale environmental friendliness, and medium- to long-term energy storage capability. Their effectiveness and sustainability make them indispensable to our energy future [6, 7].

In today's technology-driven world, it is also essential for manufacturing advanced aerospace,

automobiles, defense, and spacecraft materials, and making electronic devices like cell circuits [8-10]. Since 2011, worldwide vanadium consumption has risen by approximately 45%, with 102.1 kilotons consumed in 2019 and 125.13 kilotons in 2021. It is also expected to increase further, reaching 130.1 kilotons by the end of 2025, with a CAGR of 8.5% due to its growing importance in various industry applications [11].

The scarcity of primary resources and the increasing demand for vanadium production have heightened future supply security concerns [12, 13]. To fulfill this demand and ensure the safe disposal of hazardous materials, many countries around the world are paying attention to the comprehensive utilization of secondary and lean-grade sources for the recovery of vanadium, such as fly ash of heavy fuel power plants, petcoke [1, 14], spent catalysts [8], Bayer alumina sludge, vanadium-containing wastewaters [7], vanadium slags [2, 15] and cinders from petcoke gasification plants, etc. [1, 16]. Among the secondary sources, petcoke gasification cinders are considered a new and emerging source of vanadium (2.5-4%) as they contain an extractable amount of vanadium like other secondary sources such as spent catalysts (0.3-15%) [17], fly ash (1.5-3%) [18], alumina sludge (10-20%) [19], and vanadium slag (6-24%) [20].

In the last few years, the pyro-cum-hydrometallurgy process used to extract vanadium from its corresponding resources included alkali roasting methods such as NaCl, Na_2SO_4, NaOH, Na_2CO_3, $NaHCO_3$, and calcium salt roasting with or without additives, followed by water, alkali, or acid leaching which led to the emission of serious toxic gases like CO_2, CO, Cl_2, SO_2, HCl etc. In addition, many new innovative techniques are employed to leach vanadium, including microwave leaching, electro-oxidation, acid leaching, manganese salt roasting-acid leaching, liquid oxidation, etc. Due to cost constraints, only a few of these approaches are utilized in industrial production. Compared to high-temperature roasting and newly developed processes, direct acid leaching is a cost-effective approach for recovering vanadium from secondary sources because of its high efficiency and applicability [21-26]. Numerous studies have established that petcoke, known for its high energy value, is employed in a range of industrial processes, including fuel production, aluminum and iron manufacturing, and the creation of various products such as steel, glass, paint, and fertilizer. Furthermore, petcoke contains a lower concentration of vanadium compared to gasification cinders, rendering it economically unviable for vanadium extraction [1, 14, 27].

Although vanadium recovery from secondary sources has been widely investigated, little literature is available concerning the processing of petcoke gasification cinders for valuables' extraction. In view of the foregoing, we developed an effective method for the extraction of vanadium and other metals through direct acid leaching without roasting, followed by solvent extraction and precipitation of vanadium from the petcoke gasification cinders. However, this paper focuses on the acid leaching and leaching kinetic mechanism. The main objectives of this paper (part-1) are to investigate (i) the recovery of vanadium from petcoke gasification cinders using sulfuric acid and (ii) the effects of various process parameters, including the concentration of sulfuric acid, hydrogen peroxide, SDS, dissolution temperature, time, and solid-liquid (S/L) ratio on vanadium leaching efficiency. Furthermore, the leaching kinetics, apparent activation energy, and reaction order are established to reveal the mechanism responsible for the vanadium recovery process and improve the scalability of the experiments.

2. Materials and methods
2.1. Materials and reagents

The spent vanadium-bearing petcoke gasification cinder was obtained from a gasification plant and comprised primarily fine powders and medium-sized particles, with sizes ranging from less than 2 cm. Before introducing the vanadium extraction process, the samples were dried at 150 °C for 2 hours and sieved to a particle size of less than 105 μm to concentrate the metal fraction from the petcoke cinder by eliminating the carbon-rich fraction. The metal-rich fraction (above 105 μm) materials were crushed and ground into a powder with a particle size of less than 75 μm. All chemicals, including acid, SDS, and hydrogen peroxide, used during the experiment were of analytical grade.

2.2. Characterization

The spent petcoke cinder, leach residue, and value-added products were characterized using different techniques, such as ICP-OES, ultimate and proximate analysis, scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS), and X-ray powder diffraction (XRD). The chemical compositions of the leach liquor and digested solid samples were determined by ICP-OES (5100 Agilent Technologies, India). The mineralogical phases present in the samples and leach residues were analyzed using XRD (Bruker D8-discover). The XRD peaks were obtained with Cu Kα (k = 1.54178 A^0) (ranging from 2θ = 20° to 80° at a scanning rate of 2°/min). Morphological interpretation of the samples was performed through SEM-EDS (SEM-EDS AZtech). In proximate analysis, moisture, ash content, volatile matter, and

fixed carbon were measured using a 701 Thermo Gravimetric Analyser (LECO). In the ultimate analysis, carbon, nitrogen, and hydrogen contents were measured using C, H, and N Analysers, elemental (SV Instrument), while sulfur was assessed using the Total Sulfur Determinator (LECO).

2.3. Leaching methodology

The beneficiated metal-rich fraction, with a particle size of less than 75 μm, was blended homogeneously and employed for leaching experiments. These experiments were carried out in a 500 ml beaker on a ceramic magnetic hot plate with a stirrer, allowing for continuous agitation. The sample was added continuously once the desired temperature was achieved.

The leaching experiments were carried out under different molar concentrations of acid, from 1 M to 5 M, with S/L ratios ranging from 5% to 25%, over a leaching duration of 0.5 to 4 hours, with various H_2O_2 percentages from 0% to 20%, under different SDS percentages of 0% to 6%, and at temperatures from 60 °C to 90 °C to investigate the effects of these parameters on vanadium leaching efficiency. The

the volume of the filtrate (*L*), *M* refers to the mass of the sample taken for the experiment (*g*), and *α* is the percentage of a specific metal in the sample (*wt%*).

3. Results and discussion
3.1. Test and characterization

Prior to initiating the vanadium extraction process, a thorough characterization analysis is conducted to identify the various mineral phases and their relationships within the samples. The petcoke gasification cinder was generally composed of powders and medium-sized particles that contained a significant amount of ash. The gasification cinder was

Table 1. *Chemical analysis of the various sieve fractions of petcoke gasification cinder*

Size (μm)	Fraction (wt%)	Chemical analysis (wt%)			
		V	Al	Fe	Ni
Mixed particle (< 75)	4.95	0.31	1.26	0.81	0.09
150 - 75	5.76	1.69	4.19	2.69	0.57
250 - 150	4.67	2.88	7.98	2.48	0.66
500- 250	11.82	1.79	4.79	2.09	0.6
> 500	72.76	3.57	10.12	5.46	1.42

Table 2. *Proximate and ultimate analysis of petcoke cinder (wt%)*

Sample	Ash (%)	Moisture (%)	VM (%)	Fixed C (%)	C (%)	H (%)	N (%)	S (%)
Raw	79.2	0.22	1.93	18.65	21.8	0.52	0.23	1.72
+150 μm	84.10	0.15	1.39	14.36	16.99	0.3	0.13	1.42
-150 μm	57.20	0.68	4.12	38	46.74	0.86	0.48	2.95

solid-liquid ratio refers to the volume of water (ml) compared to the sample weight (g). After the completion of leaching, vacuum filtration was used to separate the leachate and the residue, and then the residue was in situ washed once using distilled water. The obtained leach liquor was analyzed to determine the concentrations of V, Ni, Fe, Al, and other impurities. The leach residues were dried in an oven at 110 °C for 24 hours and then weighed. The content of vanadium and other metals in the sample, leach liquor, and the dried residues was determined by chemical analysis to calculate the metal leaching efficiency.

The extraction efficiency (E) of metals from the petcoke gasification cinder was calculated according to the following Equation (1):

$$\%E = \frac{CV}{M\alpha} \times 100\% \qquad (1)$$

Where *E* represents the leaching efficiency of a certain element (*wt%*), *C* indicates the concentration of the element in the aqueous phase (*g/L*), *V* denotes

sieved into fractions of different sizes to concentrate the metal fraction, and the complete analysis of the sieve fractions is shown in Table 1. The entire proximate and ultimate analysis of the raw petcoke cinder, +150 and -150 μm of cinder, is given in Table 2. It was observed that -150 μm petcoke cinder has a high fixed carbon content of 38% and 2.95% sulfur. In contrast, +150 μm petcoke cinder contains only 14.36% fixed carbon, 1.39% volatile matter, and 1.42% sulfur.

The spent petcoke cinders often contain high amounts of common metals, such as calcium, aluminium, and magnesium. Additionally, they include several catalytically active metals, like iron, vanadium, and nickel, indicating that the cinders possess excellent catalytic activity.

The major chemical compositions of the petcoke gasification cinders were determined using ICP-OES, as shown in Table 3.

It was found that the primary compounds in waste petcoke cinder are Fe_2O_3, Al_2O_3, CaO, NiO, and V_2O_3, with percentages of 4.4%, 13.48%, 19.13%, 1.2%, and 4.29%, respectively.
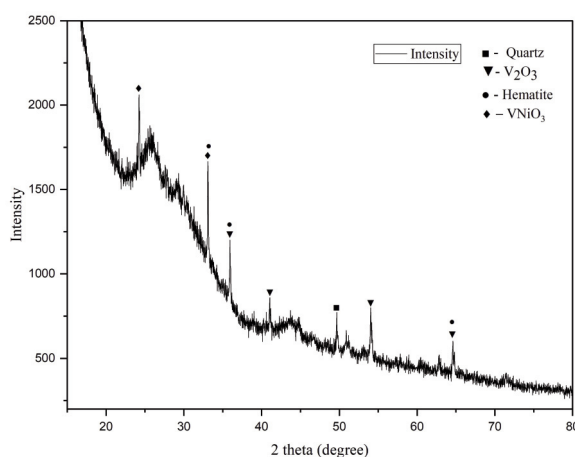
Table 3. Chemical composition of the petcoke cinder (mass fraction%)

Compound	V_2O_3	Al_2O_3	Fe_2O_3	NiO	CaO	SiO_2	SO_3	MgO	Na_2O
Content (%)	4.29	13.48	4.4	1.2	19.13	23.82	13.58	1.03	0.4

3.2. Characterization studies

The mineralogical phase composition of the petcoke cinder was analyzed using XRD, and the result is displayed in Fig. 1. This result confirms that the spent petcoke cinder contains both amorphous and crystalline structures. It can be seen that the prominent characteristic peaks of the sample are amorphous in nature, indicating the presence of unburned carbon, SiO_2, and Al_2O_3. Broader peaks in the range of (2θ) 24°- 27°, along with wide peaks between 41°- 44°, indicate the amorphous nature of unburnt carbon. At the same time, the minor crystalline mineral phases identified in the samples include quartz, hematite, and vanadium (III) oxide. The nickel phase was found in trace amounts, overlapping the vanadium and iron phases. The

Figure 1. XRD pattern of spent petcoke cinder

elemental distribution of the petcoke cinder was analyzed by SEM-EDS, and the results are shown in Fig. 2. The SEM images of the gasification cinder have numerous irregular spherical shapes, as presented in Fig. 2(a, b). The bulk EDS spectra analysis (Fig. 2(c)) illustrates that the elements V, Al, Ni, and Fe are present in significant quantities. The EDS elemental mapping indicates that all the elements are distributed within the exact crystal grain. However, V is comparatively more concentrated at the center of the grain, as shown in Fig. 2(e). The elemental percentages obtained from the EDS analysis closely align with the ICP-OES results and show a relatively higher percentage of V than the primary ores. Therefore, this spent petcoke gasification cinder could be considered a valuable treasure for V and other critical metals.

3.3. Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the leaching efficiency of vanadium was investigated over a wide range, from 1M to 5M. Meanwhile, the values for H_2O_2, SDS, reaction temperature, S/L ratio, and time were kept constant at 15%, 6%, 90 °C, 20%, and 3 hours, respectively. The results are shown in Fig. 3. The H^+ ion concentration increases with the increase in sulfuric acid concentration, which could intensify the dissolution of the target metal. Initially, the leaching efficiency was about 50.12% with 1M acid; in comparison, a leaching efficiency of approximately 67.74% was achieved at 2M acid concentration, which improved significantly to about 95.62% at 4M.

Concurrently, at 4M acid concentrations, the leaching efficiencies of Fe, Ni, and Al increased to 94.56%, 96.4%, and 96.45%, respectively. However, the leaching ratio only marginally improved when the acid concentration increased from 4M to 5M. The dissolution of metals at extremely low acid concentrations is inadequate, so a minimum concentration of 4M acid is necessary to enhance leaching effectiveness. Conversely, high concentrations of acid may reduce the solubility of oxygen, which decreases the oxidation of vanadium and, as a result, decreases vanadium dissolution. Therefore, considering the cost reductions and high leaching efficiency, a sulfuric acid concentration of 4M was utilized in the subsequent experiment.

3.4. Effect of pulp density

The solid-to-liquid ratio is an important parameter that affects the volume of filtrate and the concentration of the intended product in the leaching process. Multiple experiments were undertaken to determine an optimal S/L ratio for achieving high leaching efficiency of vanadium. The effect of the S/L ratio on metal dissolution from petcoke cinder was studied at ratios ranging from 5% to 25%, using 4M sulfuric acid, a temperature of 90 °C, a reaction time of 3 hours, 15% H_2O_2, and 6% SDS. Figure 4 shows that the dissolution efficiency of all metals significantly decreases as the S/L ratio increases from 5% to 25%. While vanadium extraction efficiency drops slightly from 99.1% to 95.62% when the S/L ratio increases from 5% to 20%, it falls sharply to 74.8% at the S/L ratio of 25%. Likewise, the leaching efficiencies for Fe, Al, and Ni declined from 94.56%, 96.45%, and 96.4% to 68.8%, 82.93%, and 79%, respectively, as the S/L increased from 20% to 25%.
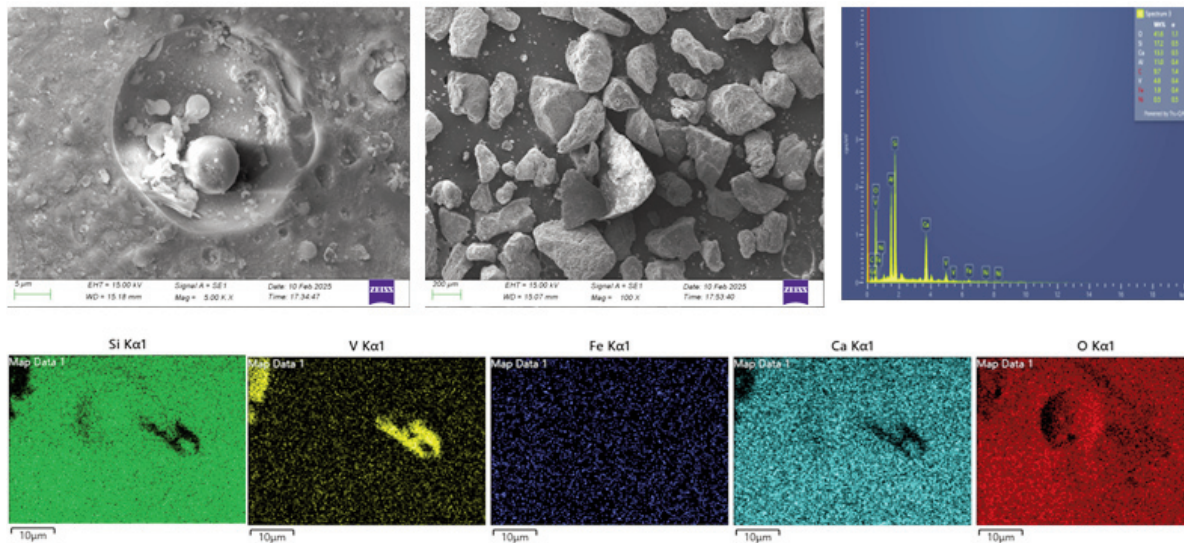
Figure 2. *(a, b) SEM of petcoke cinder; (c) EDS spectra marked; EDS elemental distribution: (d) Si, (e) V, (f) Fe, (g) Ca, and (h) O*
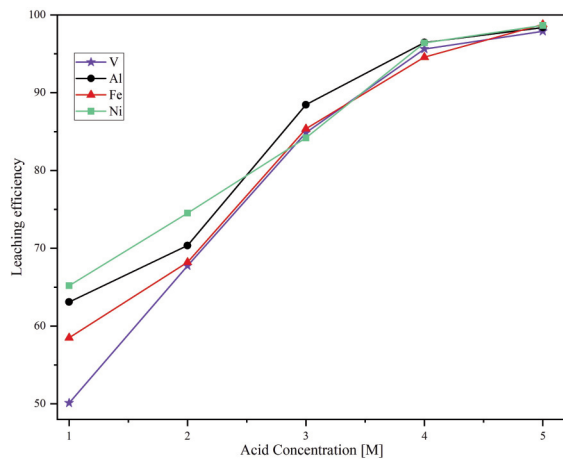

Figure 3. *Effect of sulfuric acid concentration on the metals leaching efficiency at time-3h, H_2O_2-15%, SDS-6 %, S/L ratio-20 %, and Temperature-90 °C*
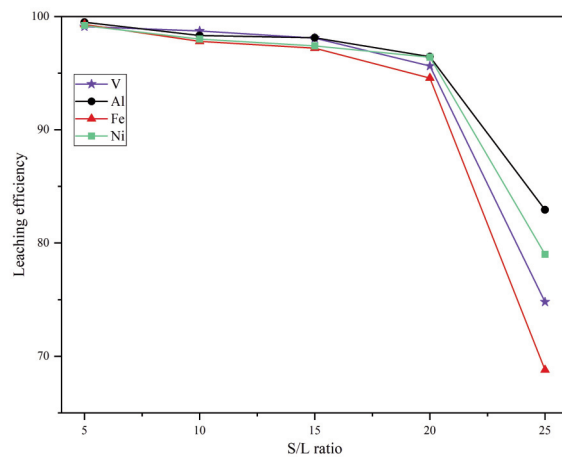

Figure 4. *Effect of solid-liquid ratio on the metals leaching efficiency at $[H_2SO_4]$-4M, Time-3h, H_2O_2-15%, SDS-6%, and Temperature-90 °C*

These results suggest that a maximum S/L ratio of 20% is optimal for metal recovery.

3.5. Effect of oxidant on leaching

The leaching efficiency of different metals from the petcoke cinder sample was investigated by varying the H_2O_2 concentration from 0% to 20% (v/w). At the same time, other conditions remained constant, such as the sulfuric acid concentration of 4M, temperature of 90 °C, reaction time of 3h, S/L ratio of 20%, and surfactant concentration of 6% SDS. H_2O_2 is a common oxidizing agent, which was found to significantly enhance the leaching rate of vanadium, as shown in Figure 5. The vanadium extraction yield increased from 65.98% to 95.62%

after 3 h, while the H_2O_2 concentration rose from 0% to 15%. This demonstrates that the increase in peroxide concentration positively affects the leaching of the gasification cinder. Similarly, the dissolution rates of other metals, such as Fe, Al, and Ni, in this sulfuric acid leaching process are directly proportional to the concentration of H_2O_2. The solubility of vanadium rises with the oxidation of V; thus, as H_2O_2 increases, vanadium is more easily oxidized and leached into the solution. This was also confirmed in our leaching tests, as shown in Fig. 5. No substantial increase in leaching efficiency was observed with excessive amounts of H_2O_2. Considering the costs associated with the leaching process, a concentration of 15% H_2O_2 appears to be the optimum level.
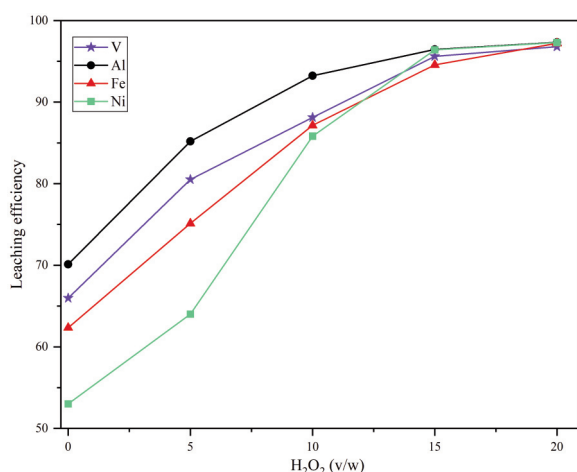
Figure 5. *Effect of H_2O_2 on the metals leaching efficiency at [H_2SO_4]- 4M, Time-3h, SDS-6%, S/L ratio-20%, and Temperature-90 °C*

Figure 6. *Effect of SDS on the metals leaching efficiency at [H_2SO_4]–4 M, Time-3h, H_2O_2-15%, S/L ratio-20%, and Temperature-90 °C*

3.6. Effect of additives

The sodium dodecyl sulfate (SDS) is a sodium salt of a long-chain sulfonated organic compound having the general formula $CH_3(CH_2)_{11}$-O-S(=O)$_2$-O$^-$ Na$^+$. It is utilized in the leaching process because it enhances the leaching in several ways, including reducing surface tension and improving wettability by contact between the material and the leaching reagents.

The effect of SDS on the leaching efficiency of petcoke cinder is shown in Fig. 6. When coal cinders are leached with SDS concentrations ranging from 0% to 6% at 90 °C for 3 hours, leaching efficiency increases as the SDS concentration rises. Without SDS, only 71.58% of vanadium was leached. Moreover, when the SDS concentration increased from 0% to 6%, the leaching efficiency of vanadium increased significantly to 95.62%.

Similarly, the leaching efficiencies for Fe, Al, and Ni improved from 74.85%, 70.12%, and 69.2% to 94.56%, 96.45%, and 96.4%, respectively, while SDS wt% increased from 0% to 6%.

The petcoke cinder contains unburnt carbon and sulfur particles, which exhibit hydrophobic properties and prevent contact between the reagent and materials. But, in the presence of SDS, it adsorbs on the surfaces and micro-porous cracks of metal particles, creating an absorbing coating that reduces the surface tension of the leaching solution and the contact angles, consequently promoting the wetting, penetration, and dispersion activities.

It also improves the processes of molecular and convective diffusion; thus, more acid penetrates the interior of the petcoke cinder particles, leading to a higher dissolution fraction of vanadium and other metals, which shortens the leaching time.
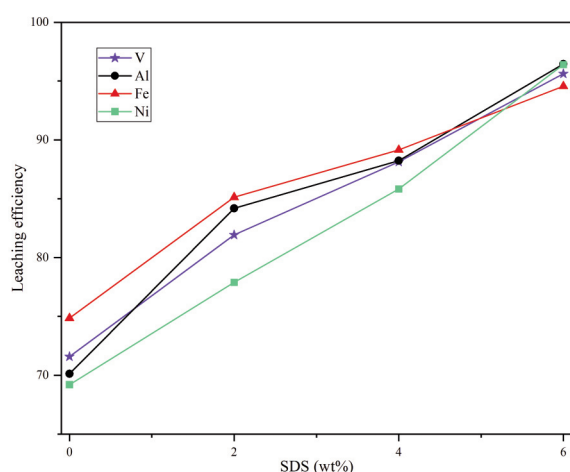
3.7. Effect of leaching duration

The leaching experiments were investigated under different leaching durations, ranging from 30 to 240 minutes, with a sulfuric acid concentration of 4 M, SDS at 6%, H_2O_2 at 15%, S/L ratio of 20%, and a temperature of 90 °C. Figure 7 clearly illustrates that the leaching efficiencies for vanadium, iron, aluminium, and nickel increase rapidly with the increase in leaching duration. The leaching efficiency of V increases from 41.68% to 95.62% as the duration extends from 30 to 180 minutes, indicating that vanadium can be continuously leached from the gasification cinder. While the maximum reaction takes 180 minutes, further increases in time lead to only marginal improvements in efficiency. Therefore, a leaching duration of 180 minutes is considered optimal, particularly when factoring in the cost of electric energy.
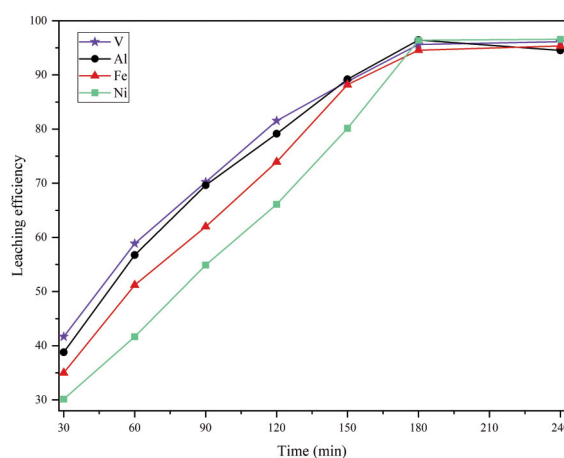

Figure 7. *Effect of leaching duration on the metals leaching efficiency at [H_2SO_4] - 4M, H_2O_2-15%, SDS-6%, S/L ratio-20%, and Temperature-90 °C*

3.8. Effect of temperature

The reaction temperature was another important parameter that significantly influenced the leaching process of vanadium from both thermodynamic and kinetic perspectives. Figure 8 summarizes the effect of reaction temperature on the leaching efficiency of vanadium and other metals under standard conditions: a sulfuric acid concentration of 4 M, H_2O_2 of 15%, a reaction time of 3h, S/L ratio of 20%, and surfactant SDS of 6%. Higher temperatures reduce viscosity and enhance H^+ diffusion, leading to better accessibility and reactivity with metals and improving vanadium leaching efficiency. When the reaction temperature was increased from 60 °C to 90 °C, the leaching efficiency of vanadium significantly increased from 63.37% to 95.62 %. This indicates that a higher temperature can facilitate the reaction rate. This is largely attributed to the higher solubility of vanadium at higher temperatures, which benefits the leaching reaction and enhances the extraction efficiency of vanadium and other metals. Therefore, 90 °C was chosen for further experiments on other variables.
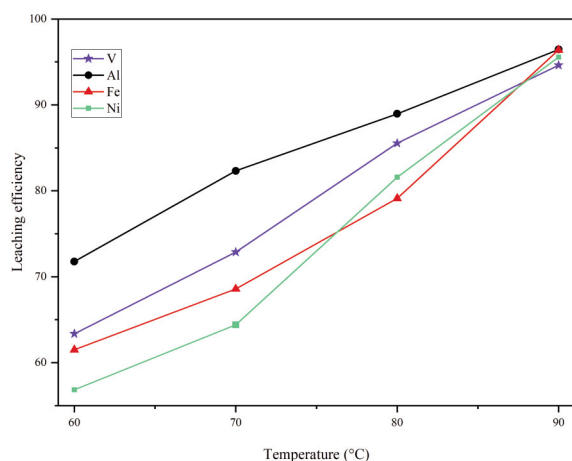

Figure 8. Effect of temperature on the metals leaching efficiency at [H_2SO_4] - 4M, Time-3h, H_2O_2-15%, SDS-6%, and S/L ratio-20%

4. Kinetics analysis
4.1. Kinetic analysis of vanadium leaching

The sulfuric acid leaching of petcoke cinder is a solid-liquid reaction whereby the thickness of the dissolved product of the outer surface progressively decreases. At the same time, the inner core of the reacted particle increases. Under optimal leaching conditions, kinetic modelling is investigated to obtain comprehensive information about leaching parameters, scale-up experiments, and the dissolution mechanism of vanadium from the petcoke gasification cinder. To establish a solid-liquid heterogeneous

reaction kinetics model, some assumptions are taken into consideration: (i) the particles are spherical, (ii) the process is irreversible, and (iii) a solid residual layer forms; it frequently employs the shrinking core model (SCM). SCM primarily focuses on two non-catalytic heterogeneous reaction kinetics models: the rate of chemical reaction at the surface layer of the sample and the rate of diffusion of metal through the product layer in the leaching process. It illustrates that the process is primarily controlled by two mechanisms:

Chemically controlled reaction:

$$1-(1-\alpha)^{1/3} = k_1 t \qquad (2)$$

Solid product diffusion-controlled reaction:

$$1-3(1-\alpha)^{2/3}+2(1-\alpha) = k_2 t \qquad (3)$$

Where α is the vanadium leaching efficiency (*wt.%*), 't' is reaction time (*min*), and k_1 and k_2 are the apparent reaction rate constants.

To explain the rate-controlling mechanism during the acid leaching of vanadium, the experimental results were substituted in Eqs. 2 and 3 to calculate k_1 and k_2, respectively. The calculated apparent rate constants (k_1 & k_2) and regression coefficients (R^2) at different temperatures are shown in Table 4, and the fitting curves of R^2 were used to evaluate the controlling factors of the rate of reaction during the leaching.

A fitting of the kinetic equation plot of $1-(1-\alpha)^{1/3}$ against time is illustrated in Fig. 9. The linear correlation coefficient is perfectly fitted, indicating that the vanadium dissolution reaction is chemically regulated and produces a product following the chemically controlled reaction (Eq. (2)), with correlation values of $R^2 = 0.9891$. Analogously, a fitting of the kinetic equation plot of $1-3(1-\alpha)^{2/3} + 2(1-$
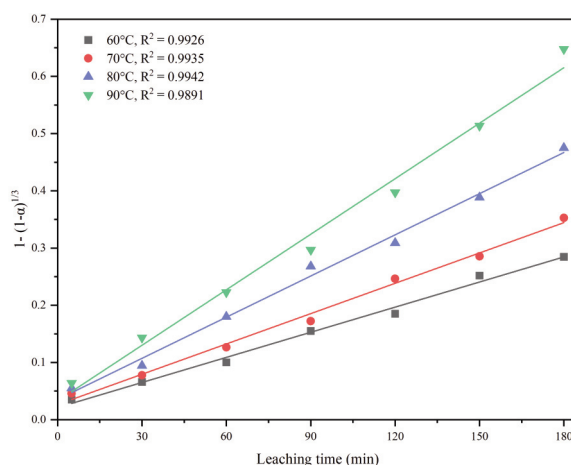

Figure 9. A Fitting plot of $1-(1-\alpha)^{1/3}$ vs time (t) at different temperatures for V recovery

Table 4. Analysis of the leaching kinetics model under the variation of temperature

Metal	Temperature (°C)	Chemically controlled reaction		Solid product diffusion	
		K_1 (min^{-1})	R^2	K_2 (min^{-1})	R^2
V	60	7.8×10^{-4}	0.9926	5.91×10^{-4}	0.9634
	70	9.1×10^{-4}	0.9935	8.32×10^{-4}	0.9671
	80	1.3×10^{-3}	0.9942	1.33×10^{-3}	0.9897
	90	1.77×10^{-3}	0.9891	1.96×10^{-3}	0.9645

α) against time is illustrated in Fig. 10. This linear relationship indicates that the leaching reaction mechanism is influenced by the diffusion of reactants and products according to the solid product diffusion-controlled reaction (Eq. (3)) with a correlation coefficient value of $R^2 = 0.9645$.

The R^2 values of the chemically controlled model were all greater than 0.989 and properly satisfied the condition. As a result, these values suggested that the vanadium leached from the petcoke cinder through the chemically controlled reaction instead of a solid product diffusion-controlled reaction.

4.2. Estimation of apparent activation energy

According to the Arrhenius Equation, the apparent activation energy (E_a) of a reaction can be calculated as follows:

$$K = Ae^{-Ea/RT} \tag{4}$$

This is an exponential equation that can be simplified by applying the logarithm to both sides, and the modified equation is as follows:

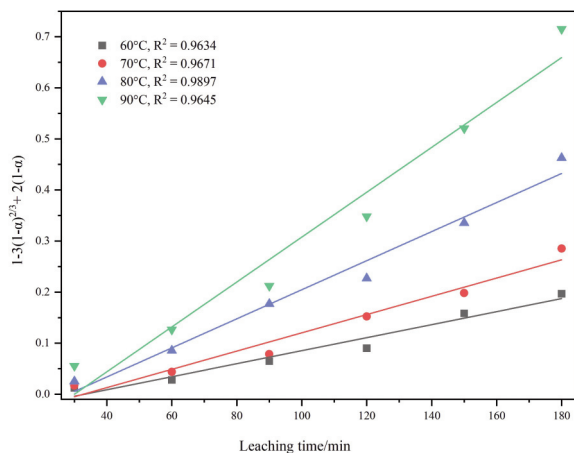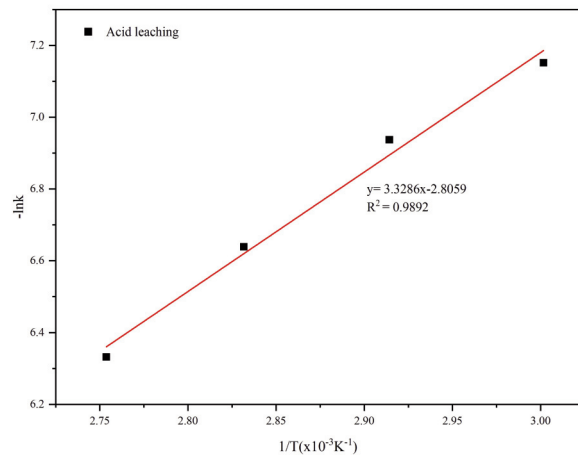$$lnk = (-E/R).1/T + lnA \tag{5}$$

where k = apparent reaction rate constant, E= activation energy (*kJ/mol*), R= universal gas constant (*8.314J/(mol K)*), T= absolute thermodynamic

temperature (*K*), A= frequency factor (min^{-1}).

The rate constant for vanadium dissolution was evaluated from the slopes of the plot line in Fig. 9. By calculating Equation 5, a linear relationship can be drawn between the lnk vs 1/T, and the slope of the line is -E/R. The apparent activation energy of the chemical reaction is obtained by calculating the slope (-E/R) of the line. The relation between the logarithm of the apparent reaction rate constant (k) of gasification cinder in sulfuric acid leaching and the reciprocal of absolute temperature T (1/T) is demonstrated and depicted in Figure 11. Linear fitting of the correlation coefficient (R^2) was above 0.989, indicating a flawless match. The intercept and slope of the Arrhenius fitting plot are used to compute pre-factor A (lnA) and the activation energy for the leaching process of vanadium, respectively. The activation energies calculated from the Arrhenius equation plot were 27.66 kJ/mol for vanadium and provided additional evidence to support that the acid leaching process was governed by a chemically controlled mechanism.

4.3. Estimation of reaction order

The overall reaction order of the leaching process is determined by the chemical reactions of the reactants and the principle of mass transfer. By substituting the experimental results in Equation 2, a linear fitting plot is drawn between $1-(1-\alpha)^{1/3}$ and

Figure 10. A fitting plot of $1-3(1-\alpha)^{2/3} + 2(1-\alpha)$ vs time (t) at different temperatures for V recovery

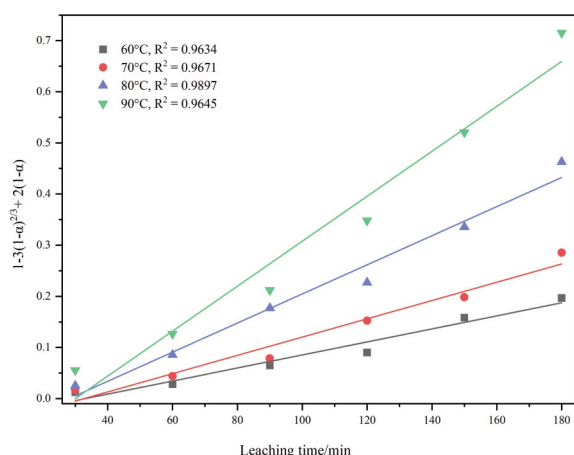

Figure 11. Arrhenius fitting plot of -lnK versus 1/1000T

Figure 12. *A fitting plot of 1-(1-α)^{1/3} vs time (t) at different temperatures for V recovery*

Figure 13. *A fitting plot of lnK versus ln [H₂SO₄]*

leaching time (t), and the result is illustrated in Figure 12. The apparent rate constant (k) was determined by calculating the slope of the fitted line in Fig. 12.

The reaction order depends directly on the leaching rate formula, which can be calculated using the following equation.

$$-lnk = lnk_0 - E / RT + nlnC \qquad (6)$$

where k = apparent reaction rate constant, E= activation energy (*kJ/mol*), R= universal gas constant (*8.314J/(mol K)*), T = absolute thermodynamic temperature (*K*), and n = order of reaction, and C = concentration of sulfuric acid (*[M]*).

To evaluate the reaction order, a graph was plotted against the logarithm of the rate constant 'k' and the logarithm of acid concentration; the result is illustrated in Fig. 13. The resultant slope of the linear fit for lnK vs. ln[H₂SO₄] is 1.29, indicating that the empirical order of the reaction is determined concerning sulfuric acid concentration.

Meanwhile, the frequency constant (A) could be calculated approximately 9.261×10^3 by using the intercept of the linear fitting plot. As a result, the leaching kinetics model of vanadium is controlled by the diffusion through a product layer, which could be the empirical order of reaction stated as follows:

$$1-(1-\alpha)^{1/3} = k_1 t = \\ (9.261 \cdot 10^3)[H_2SO_4]^{1.2916} exp[-27674 / RT]T \qquad (7)$$

In this study, the activation energy was calculated to be 27.67 kJ/mol, and the apparent order of the reaction was 1.29. This indicates that the presence of sulfur and silicon in the petcoke cinder inhibited the chemical diffusion within the surface layer; as a result, the leaching efficiency of vanadium was impeded. Silicon in petcoke cinder reacts with sulfuric acid to form an insoluble H₄SiO₄ compound,
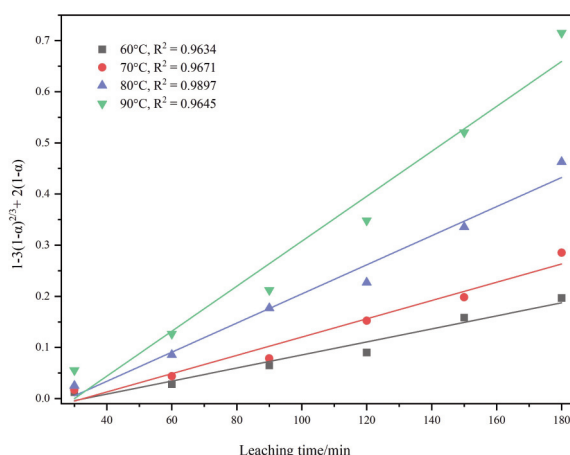
which is highly compact. Along with H₄SiO₄, sulfur and unburned carbon cover the surface of the reaction particle, providing resistance to diffusion. Therefore, the activation energy of the reaction was relatively high, and the leaching process was regulated by the chemically controlled product layers. The reaction mechanism of leaching kinetics corresponds to Cai et al.'s (2016) "Shrinking Core-Shrinking Particle Model".

5. Characterization of leach residue

The leach residue generated after 4M sulfuric acid leaching at 90 °C from the petcoke cinder was characterized by chemical analysis, SEM, and XRD. After leaching, the residues are thoroughly washed and dried at 110 °C for 24 hours. Under the optimized conditions, the amount of leached residue produced was approximately 20% more than that of the original petcoke cinder input sample. This increase is due to the formation of higher molecular weight compounds, including gypsum, silicic acid (H₄SiO₄), and its various polymerized or hydrated forms, such as colloidal silica or silica gel. The overall chemical composition of the leach residue is shown in Table 5. The results of the XRD pattern of leach residue are shown in Fig. 14. The prominent peak in the residue indicates the presence of crystalline SiO₂, gypsum, and anhydrite. Impurities like alunogen are found in very low quantities.

The SEM-EDS image of the residue indicates that the surface of the particles was significantly changed by the reagent during leaching, the results are shown in Fig. 15. The EDS mapping study highlighted the notable relevance of Si, Ca, and O. Additionally, the

Table 5. *Chemical multiple elemental analysis of leach residue*

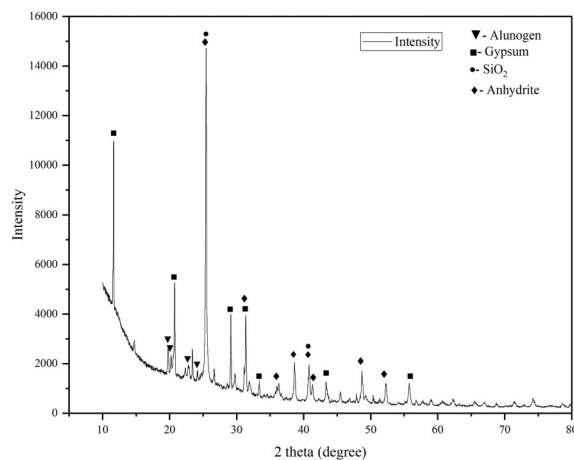| Compound	V_2O_5	Al_2O_3	Fe_2O_3	NiO	CaO	SiO_2	SO_3
Content (%)	0.19	0.3	0.38	0.06	13.58	19.26	25.25

Figure 14. XRD pattern of leach residue

EDS spectra analysis revealed that the Ca concentration was 8.5%, which closely matched the chemical analysis result of 9.8%. Moreover, the presence of silicate and calcium in the leached residue indicated that it could be a valuable commodity for future applications.

characterization techniques were employed to conduct a comprehensive investigation of the material. The results indicated that a notable percentage of critical metals, 4.4% Fe_2O_3, 13.48% Al_2O_3, 1.2% NiO, and 4.29% V_2O_3 are present in this material. A novel energy-efficient sulfuric acid leaching method in the presence of SDS and H_2O_2 was developed to extract vanadium from the petcoke cinder. Under optimal conditions such as a sulfuric acid concentration of 4M, H_2O_2 at 15%, a reaction time of 3 hours, a S/L ratio of 20%, a SDS surfactant of 6%, and a temperature of 90 °C, the maximum leaching efficiencies of 95.62%, 96.45%, 94.56%, and 96.46% for V, Al, Fe, and Ni, respectively were achieved. According to the kinetics of leaching, the process mechanism was controlled by a shrinking core diffusion model. The system's apparent activation energy was 27.67 kJ/mol. Simultaneously, the reaction order of the sulfuric acid concentration was calculated to be 1.29. To better understand the reaction model, an exponential mathematical formula $\{1-(1-\alpha)^{1/3} = k_1t = (9.261 \times 10^3) [H_2SO_4]^{1.2916} \exp[-27674/RT] \, T\}$ was derived by calculating both the apparent activation energy and the order of the reaction.
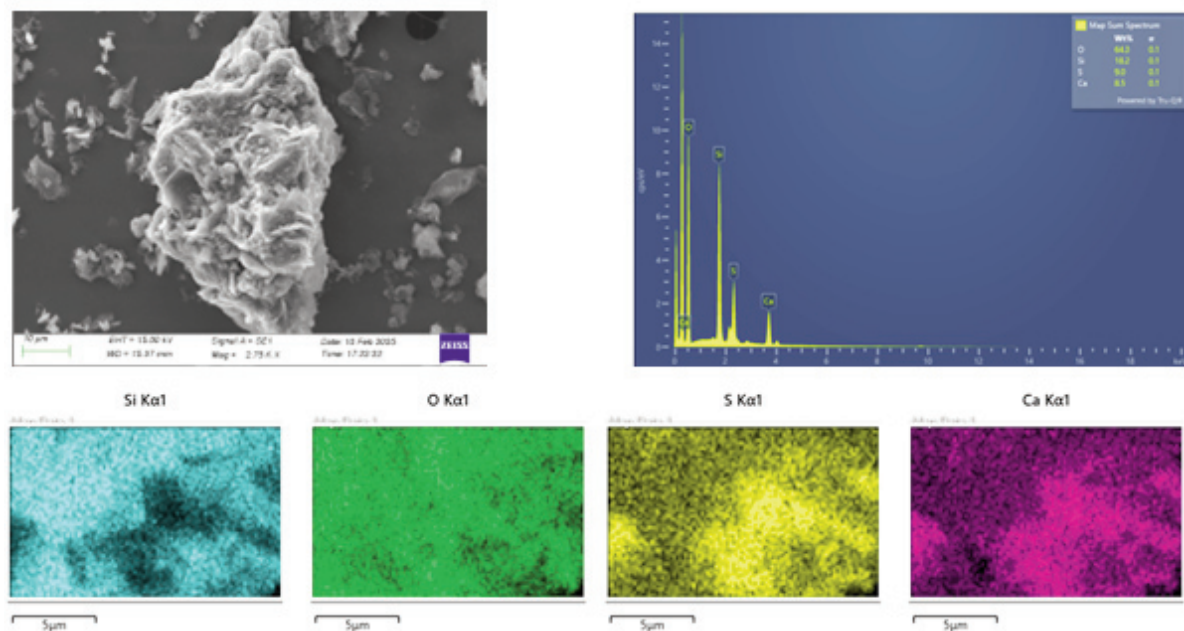

Figure 15. (a) SEM image of leach residue, (b) EDS spectra of leach residue, EDS elemental mapping distribution (c) O, (d) Ca, (e) Si, and (f) S

6. Conclusions

The petcoke cinder, a by-product of petcoke gasification plants, is a highly underutilized and emerging potential source of vanadium, capable of significantly fulfilling the global vanadium demand for years to come. Various physicochemical

Author Contributions

Shibsundar Das designed and performed the experiments, wrote the original draft; Susmita Mohanta and Akshay Kumar analyzed the data and edited; Devabrata Mishra designed, planned, wrote and reviewed; K. K. Sahu provided visualization and supervised the paper.

Data availability

The data for this article can be acquired by emailing the corresponding author.

Conflict of interest

The authors declare no conflict of interest.

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EKSTRAKCIJA VANADIJUMA IZ PEPELA NASTALOG GASIFIKACIJOM PET-KOKSA DEO 1: ISPITIVANJE KINETIKE LUŽENJA U SREDINI SUMPORNE KISELINE

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Apstrakt

Pepeo pet-koksa predstavlja čvrsti nusproizvod koji nastaje tokom procesa gasifikacije pet-koksa i čini oko tri do pet procenata mase petrol-koksa. Ovaj materijal obično sadrži vredne metale kao što su V, Ni, Al i Fe, što ukazuje na njegov potencijal kao sirovine za ekstrakciju vanadijuma i zbog toga se može smatrati novim sekundarnim izvorom vanadijuma i drugih kritičnih metala. Konvencionalni pirometalurško-hidrometalurški postupak za dobijanje vanadijuma zasniva se na alkalnom prženju, koje je energetski intenzivno i doprinosi emisiji gasova sa efektom staklene bašte. Uzimajući u obzir ekološke izazove i veliku potrošnju energije, ova studija predstavlja savremen, ekonomski isplativ i energetski efikasan proces za ekstrakciju V iz pepela pet-koksa. U radu se razmatra proces kiselinskog luženja za izdvajanje vanadijuma iz pepela pet-koksa i analiziraju se različiti parametri, uključujući koncentraciju kiseline, temperaturu, trajanje procesa, udeo H_2O_2, količinu natrijum-dodecil-sulfata (SDS) i odnos čvrste i tečne faze. Optimalni stepen izdvajanja vanadijuma, 95,62%, postignut je pod sledećim uslovima: 4 M rastvor sumporne kiseline na 90 °C tokom tri sata, uz odnos čvrsto-tečno od 15%, uz dodatak 20% H_2O_2 i 6% SDS. Kinetika luženja ispitivana je primenom modela kontraktujuće površine, koji je pokazao da je red reakcije u odnosu na koncentraciju sumporne kiseline 1,29. Na osnovu Arhenijusove jednačine, prividna aktivaciona energija procesa luženja iznosi približno 27,67 kJ/mol, a empirijska jednačina koja opisuje kinetiku kiselinskog luženja vanadijuma utvrđena je kao: $1-(1-\alpha)^{1/3}=kt=(9.261 \times 10^3) [H_2SO_4]^{1.2916} exp[-27674/RT]T$.

Ključne reči: *Pepeo pet-koksa; Kiselinsko luženje; SDS; Kinetika luženja; Prividna aktivaciona energija*