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The influence of leaching solution pH and addition of peroxide hydrogen on the recovery of some components from the used vanadium catalyst with urea solutions

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The research was conducted to determine the influence of the pH of the leaching solutions and hydrogen peroxide addition on the efficiency of the recovery of vanadium, potassium and iron compounds from the used vanadium catalyst from the node of oxidation of sulfur dioxide to sulfur trioxide.

Keywords: sulfuric acid, sulfur oxide, urea solutions, used vanadium catalysts, leaching process.

INTRODUCTION

Industrial vanadium catalyst is a complicated phase system, in which the active phase consists of vanadium compounds (5 to 9% V_2O_5) and potassium compounds (8 to 12% K_2O), frequently modified with the cesium or sodium compounds[1]. The active phase is spread on the carrier surface – the natural silica.

In the industrial processes, the vanadium catalysts are deactivated by the changes occurring in their structure and texture[2]. The coefficient of relative deactivation, which is a measure of decrease of the catalyst activity, is a function of time and the conditions of the catalyst use. Higher values of the coefficient of relative deactivation are found for the catalysts used in the metallurgy type installations or in the wet catalysis, due to the metallic impurities such as: Fe, Pb, Zn, Hg, Cd and As[3].

The used catalysts constitute the chemically and granulometrically heterogeneous material. The composition of these catalysts strongly depends on the conditions of their usage, source of sulfur dioxide, as well as the conditions of their storage after withdrawal from the process. Table 1 presents an example of the composition of the used vanadium catalysts[1].

Table 1. Chemical composition of the spent vanadium catalyst

Component	Content [%]
V_2O_5	6.18
SiO_2	48.40
K_2O	10.03
Fe_2O_3	1.43
Na_2O	2.32
Al_2O_3	2.18
SO_3	22.32

The amount of that waste, which could be estimated as close to 3000 – 4000 Mg in Poland[2], and their composition indicate the necessity of the research on developing the method of their complex utilization.

So far there has been no such method enabling the complex utilization of that waste[4]. Therefore, the authors decided to develop a method that would be safe for the environment and economically justified.

The research on the use of urea solutions with such a method was initiated based on the numerous papers reporting that urea significantly affects the solubility of inorganic compounds in water[5–7]. In most cases it reveals the salt in effect. Urea forms the double salts with many compounds, which reveal significantly larger solubility in water, than pure salts.

EXPERIMENTAL PART

Reagents

The used vanadium catalyst was sampled from the waste deposit of POLCHEM, Toruń, Poland, the factory producing the sulfuric acid in the contact process; $CO(NH_2)_2$ (purity of 98%) – PPH „Standard", Poland; H_2O_2 (purity of 98%) – POCh Gliwice, Poland; NaOH (purity of 98%) – POCh Gliwice, Poland; H_2SO_4 95% (purity of 98%) – POCh Gliwice, Poland).

Before the research, the catalyst was milled in the vibrational mill, and divided into the appropriate granulometric fractions with the FRITSH set of sieves. Also the contents of the water and sulfur oxides were determined[8].

Experimental methods

The effect of the pH of the leaching solution and hydrogen peroxide addition on the ratio of the recovery of vanadium, potassium and iron compounds from the used vanadium catalyst was investigated with the use of catalyst grains of 0.250 – 0.180 mm diameter at 293 K.

Samples of the used vanadium catalyst (5.000 g) were put into the Erlenmeyer flasks with the magnetic stirrer. Then, 50 cm^3 of the urea solution of 20% mass concentration and addition of appropriate reagent (H_2O_2, H_2SO_4 or NaOH) were pipetted into the flask, the flask was closed. Next, the samples were transferred to a thermostated bath and stirred magnetically for 120 minutes.

The temperature was kept constant with the BIOBLOCK-SCIENTIFIC thermorelay.

After the desired time interval, stirring was discontinued. The solution was separated from the insoluble remainder of the catalyst with a sintered glass crucible by a vacuum filtration.

The clear solution was transferred into the flask, diluted with the distilled water and analyzed to determine the concentration of vanadium, potassium and iron compounds.

Analytical methods

The concentration of vanadium(V) in solutions was determined spectrophotometrically by the peroxide method[9]. This method might be applied for the vanadium concentration range between $8 \cdot 10^{-3}$ – 2.16 $mol \cdot dm^{-3}$. The concentration of vanadium, corresponding to the measured absorbance, was calculated from the calibration curve. Each analysis was performed for three samples, and the error of the vanadium determination had not exceeded 2%.

The total concentration of iron in the solutions was determined spectrophotometrically with the use of sulfosalicylic acid[10]. The analysis is performed at λ = 430 nm. The determination was performed for three samples, with the error had not exceeding 2%.

The analyses were performed with the double-beam Hitachi U-2000 UV/Vis spectrophotometer, which allows the analyses at the wavelength range 190 – 1100 nm and -1 to 3 ABS. The 10 mm quartz absorption cells were used.

The concentration of potassium ions in the solutions was determined by flame photometry[11]. Flame photometry relies upon the fact that the compounds of the alkali and alkaline earth metals can be thermally dissociated in a flame and that some of the atoms produced will be further excited to a higher energy level. When these atoms return to the ground state they emit radiation, which lies mainly in the visible region of the spectrum. The analyses were performed with the PFP7 Jenway, a low temperature single channel emission, flame photometer, designed for the routine determination of sodium and potassium. Each analysis was performed for three samples, and the error of the potassium determination had not exceeded 2.5%.

Additionally, a qualitative analysis of the selected solutions was performed using EDXRF method[12]. In this method the sample is irradiated with X-rays emitted by an X-ray tube and the resulting characteristic X-rays, generated in the sample (fluorescent X-rays) are detected. By measuring the energies of the radiation emitted by the sample it is possible to determine which element are present – qualitative analysis. By measuring the intensities of the emitted energies it is possible to determine how much of each element is present in the sample – quantitative analysis. The analyses were performed with the MiniPal4 PANalytical compact energy dispersive X-ray spectrometer.

Results and discussion

The results of the analyses of the solutions, revealing the effect of pH of the leaching solution on the recovery ratio of vanadium, potassium and iron compounds are presented in Table 2. The reported data include the addition of reagents, the pH, the solution density (g·cm^{-3}), the vanadium, potassium and iron ions concentration in g·dm^{-3} and the colour of clear solutions.

The data listed in Table 2 indicates that with increasing the pH of the solutions, the Fe^{3+} concentration in the solutions is systematically decreased. The highest concentration of iron ions was observed for the solutions with the addition of 10 cm^3 H_2SO_4 (1:3) – pH = 2.1. In this solutions concentration of $Fe_3{}^+$ of 0.424 g·dm^{-3} was reported. For the leaching solution with 8 cm^3 4M NaOH addition (pH = 13.9) the iron ions concentration amount only 0.016 g·dm^{-3}. Then the Fe^{3+} concentration is decreased by 96%.

The results of the research imply clearly that with increasing the concentration of OH^-, the K^+ concentration is systematically increased. The potassium ions concentration reaches the highest value of the pH of the leaching solution – 13.9. The difference between the K^+ concentration in the solution at pH = 2.1 and at pH 13.9 is 32%.

The experimental data presented in Table 2 indicate that the vanadium ions concentration in the solutions results from three effects. The concentration of V^{5+} increases with the sulphuric acid addition to 2.149 g·dm^{-3}. With the NaOH addition the vanadium ions concentration initially decreases to pH = 6. At this point the vanadium concentration is 0.371 g·dm^{-3}. Numerous reports in the scientific literature concluded that between pH 5 and 7 precipitation of vanadium oxides from the solution occurs.

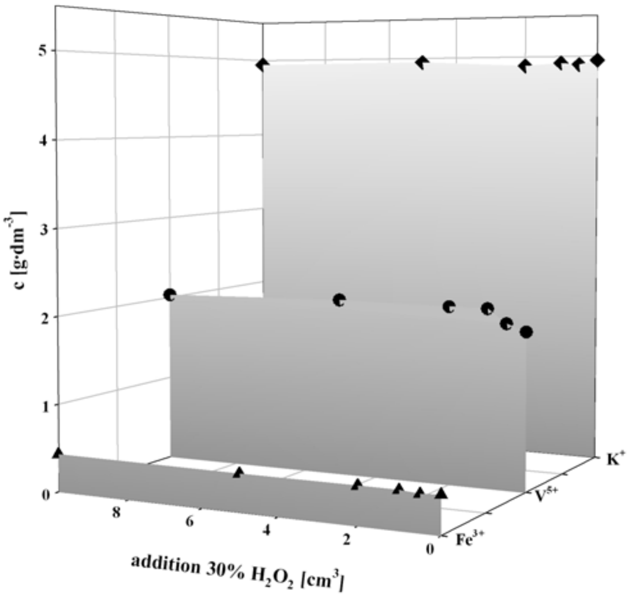

Figure 1. The influence of the hydrogen peroxide addition on the recovery ratio of vanadium, potassium and iron compounds

Table 2. The influence of the pH of the leaching solutions on the efficiency of the recovery of vanadium, potassium and iron compounds

Sample	Addition	pH	ρ [g·cm^{-3}]	c [g·dm^{-3}]			Colour of clear solution
				V^{5+}	K^+	Fe^{3+}	
1	10 cm^3 H_2SO_4 (1:3)	2.1	1.101	2.149	4.507	0.424	green
2	5 cm^3 H_2SO_4 (1:3)	2.4	1.082	1.997	4.937	0.431	green
3	-	3.0	1.062	1.910	5.124	0.429	light green
4	1 cm^3 NaOH (2M)	4.1	1.068	1.573	5.307	0.132	yellow
5	2 cm^3 NaOH (2M)	4.9	1.064	1.121	5.022	0.089	yellow - green
6	3 cm^3 NaOH (2M)	5.5	1.061	0.759	5.066	0.076	dark green
7	4 cm^3 NaOH (2M)	5.9	1.057	0.271	5.254	0.075	dark green
8	6 cm^3 NaOH (2M)	8.6	1.076	0.426	6.037	0.016	colourless
9	4 cm^3 NaOH (4M)	9.8	1.066	0.498	6.440	0.015	colourless
10	6 cm^3 NaOH (4M)	13.0	1.076	1.723	6.768	0.015	colourless
11	8 cm^3 NaOH (4M)	13.9	1.078	1.764	6.728	0.016	colourless

Above this pH the V^{5+} concentration is systematically increased toward the point of pH 13.9. In this solution vanadium ions concentration is 1.764 $g \cdot dm^{-3}$.

The reported data indicate, that it is possible to recover the chosen components of the used catalysts steering the pH of the leaching solution. For example, an addition of the 4M NaOH solution in proportion 1:0.16 (cm^3:cm^3) leads to the recovery of only the active-phase compounds – vanadium and potassium compounds.

The results of the qualitative analysis of the hydrogen peroxide addition influence of recovery ratio of vanadium, potassium and iron compounds are presented on Figure 1.

The course of the curves plotted on Figure 1 indicates that there is no effect of H_2O_2 presence on the iron ions solubility. The Fe^{3+} concentration is practically constant with the increasing H_2O_2 concentration.

The vanadium ions concentration initially increased with increasing the addition of hydrogen peroxide and reaches the maximum at the ratio (mass vanadium catalyst to H_2O_2 addition) S/L = 1:0.2. Above this ratio the V^{5+} concentration is practically constant with the increasing hydrogen peroxide addition.

Figure 1 implies clearly that there is no effect of hydrogen peroxide presence on the potassium ions solubility.

Remarks

The presented research indicated that the pH of the leaching solution significantly affects the efficiency of the recovery of vanadium, potassium and iron compounds from the used vanadium catalyst.

The collected results indicated a small effect of hydrogen peroxide addition on the efficiency of the recovery of vanadium compounds.

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