Leaching of vanadium(V) from the mixture after potassium metavanadate synthesis based on KCl and spent vanadium catalyst

Urszula Kiełkowska[*], **Katarzyna Białowicz, Sebastian Drużyński**

Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarin Street, 87-100 Toruń, Poland
[*]*Corresponding authors: e-mail: ulak@chem.umk.pl*

The results of the leaching of vanadium(V) from the mixture after potassium metavanadate synthesis from KCl and spent vanadium catalyst in the presence of steam were presented. Spent vanadium catalyst was obtained from the waste storage of a chemical plant producing sulfuric acid(VI) by the contact method. The reaction mixture was leached using different solutions: 1 M Na_2CO_3, 20% $CO(NH_2)_2$, 15% NaOH, 15% KOH, 2 M H_2SO_4. The effect of time and temperature was studied. The results showed that for reaction mixture leached for 4 h at 303 K in the presence of 15% sodium hydroxide solution at a liquid:solid ratio of 10:1, the extent of leaching of vanadium(V) was 95.43%.

Keywords: KVO_3 synthesis, spent vanadium catalyst, leaching, recovery, iron, vanadium(V).

INTRODUCTION

A vanadium catalyst used in the oxidation of SO_2 to SO_3 gradually loses its catalytic activity, inter alia, due to impurities introduced together with gases containing SO_2. This is an irreversible process, and thus the catalyst must be partly or wholly replaced from time to time. Vanadium catalyst operating time is dependent on technological process parameters, as well as its mechanical strength. The yearly amount of waste catalyst is limited by the size of H_2SO_4 production and its stability which is estimated at 10 years. Vanadium catalysts that have been subjected to mainly thermal and chemical deactivation are withdrawn from the production cycle and stored near plants at waste heaps or in concrete silos[1, 2]. A spent vanadium catalyst contains a range of pollutant, it is a heterogeneous material. Vanadium catalysts derived from sulfur installations, in contrast to catalysts derived from metallurgical installations, have no micropollutants such as copper, mercury, cadmium and lead[3].

Deactivated vanadium catalyst handling is an important research problem. The complex structure and texture make it difficult for utilization. The development of optimal methods for spent catalyst utilization is important not only for environmental, but also economic reasons. Vanadium(V) oxide contained in the catalyst is a valuable resource. The estimated average annual increase in waste vanadium catalyst in Poland is 78.8 tons/year. This hazardous post-production waste contains about 5% of vanadium calculated as V_2O_5, precipitated on diatomaceous earth. This enables recovery of 3.9 tons of V_2O_5 /year in the whole country[2, 3].

This paper is a continuation of research on the utilization of spent vanadium catalyst from H_2SO_4 using the contact method[4–14]. This is of vital importance for the natural environment protection. Research on the use of spent vanadium catalyst is carried out in two directions:
1. extraction of spent vanadium catalyst components[4–9],
2. its use for the synthesis of KVO_3 or $NaVO_3$[10].

One of the possible utilization methods is the reaction of vanadium(V) oxide from waste catalyst with potassium chloride in the presence of steam in accordance with the reaction equation[10, 14]:

$$2KCl + V_2O_5 + H_2O_{(p)} \rightarrow 2KVO_3 + 2HCl\uparrow \qquad (1)$$
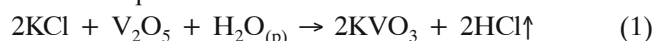
The paper presents a study on optimal conditions for the extraction of vanadium(V) from the mixture after KVO_3 synthesis – reaction (1).

EXPERIMENTAL

Materials

The spent vanadium catalyst was obtained from the waste storage of a chemical plant producing sulfuric acid by the contact method. $CO(NH_2)_2 \geq 98\%$ (PPH Standard, Poland), H_2SO_4 95%, NaOH 98,8%, KOH 85%, Na_2CO_3 of 99.8% all by POCh Gliwice S.A., Poland were used for all experiments. Before the research the catalyst was divided into appropriate granulometric fractions with the FRITSH (Germany) set of sieving.

The research was conducted in two steps:
1. The KVO_3 synthesis from KCl and spent vanadium catalyst in the presence of steam.
2. Leaching of KVO_3 from the post-reaction mixture.

The synthesis of KVO_3 based on KCl and spent vanadium catalyst in the presence of steam was carried out under constant conditions[10, 14]: reaction temperature 873 K, grain diameter of catalyst f = 0.355–0.250 mm, time of processing 3 hours. The synthesis was performed with the use of 20% excess of KCl in the reaction mixture, relative to mass of spent vanadium catalyst. The steam flow through the reactor of 0.883 g · min^{-1} was constant during the experiments. The analysis of the composition of spent vanadium catalyst used in the study was performed on a PANalytical BV XRF spectrometer MiniPAL4[15]. For the synthesis reaction used a single about 10 g of the catalyst. Before studies, the sulfur oxides from spent vanadium catalyst was removed. The catalyst was calcined at the temperature of 1073 K for 21 hours. The schematic diagram of the reactor, in which the synthesis of KVO_3 was performed, was published in a previous paper[14].

The yield of KVO_3 synthesis was determined based on the number of gaseous products extracted during the process, which were absorbed in scrubbers filled with approximately 5 M aqueous NaOH solution[14]. The chloride ions concentration (after the neutralization) was determined argentometrically by means of the potentiometric titration method (716 DMS Titrino titrator,

Switzerland), with a combined silver electrode[16]. Each analysis was performed in triplicate, the relative error did not exceeded 1%.

The qualitative analysis of the post-reaction mixture was carried out by XRD, using the X-ray powder diffractometer Philips X'Pert PRO.

The effect of various leaching solutions and time on the efficiency of vanadium(V) recovery from the mixture after KVO_3 synthesis was studied. The study was conducted at the temperatures of 293 and 303 K, at a constant ratio of solid to liquid phases 1:10. The effect of 15% NaOH, 15% KOH, 20% $CO(NH_2)_2$, 2 M H_2SO_4, 1 M Na_2CO_3 on the degree of vanadium(V) recovery was examined. The concentrations of extraction solutions were chosen based on previous studies on the recovery of spent vanadium catalyst components[4–9, 17].

Samples of the post-reaction mixture (10±0.0002 g) were put into the Erlenmeyer flasks with the magnetic stirrer. Then accurately 100 cm^3 of a particular leaching solution was added. Next, the samples were placed in a thermostated bath and stirred magnetically. The temperature was kept constant with the BIOBLOCK-SCIENTIFIC thermorelay. The extraction was carried out at variable time t = 1–4 hours. After the required time the solution was separated by vacuum filtration. The clear solution was transferred into the flask, diluted with the distilled water and analyzed to determine the concentration of vanadium and iron compounds. The concentration of vanadium(V) and iron(III) in the solutions was determined using the atomic absorption spectroscopy method[18–20]. Analyses were performed using the AAS Avanta Sigma GBC.

RESULTS AND DISCUSSION

A synthesis of potassium metavanadate(V) with KCl was performed, using a spent vanadium catalyst as a source of vanadium(V) oxide in the presence of steam. The yield of KVO_3 synthesis was calculated based on the reaction (1) assuming for the calculations that the spent vanadium catalyst contains 5.15% V_2O_5. The average degree of conversion from V_2O_5 to KVO_3 was 98%. Roentgenographic analyses of post-reaction mixtures clearly confirmed the presence of KVO_3.

Chemical analyses of the test solutions and the results obtained showed the possibility of recovering vanadium(V) compounds from the mixture after the synthesis of potassium metavanadate(V) by extraction using various leaching solutions. In addition, the concentration

of iron(III) ions was determined in the post-extraction solutions. The effect of time (1–4 h) and temperature (293 K and 303 K) on the efficiency of the leaching of vanadium and iron compounds from the spent catalyst was investigated.

Table 1 summarizes the results of vanadium(V) extraction from the mixture obtained after synthesis of potassium metavanadate(V). Based on these results, the effect of the leaching solution and the extraction time on the degree of vanadium(V) recovery from the post-synthesis mixture at temperatures of 293 K and 303 K was defined. The obtained experimental data show that the efficiency of vanadium(V) extraction increases with increasing contact time of the solid and liquid phases. The highest effect of the extraction time was observed when vanadium(V) was leached in 1 M Na_2CO_3 and 15% KOH. Rising temperatures and longer leaching time has a positive effect on the extraction efficiency. Extraction in 15% NaOH for 4 hours at 303 K gave the highest degree of vanadium(V) recovery from the mixture after synthesis of potassium metavanadate(V) using a spent vanadium catalyst.

When analyzing the data presented in the Table 1 in order to determine the effect of the leaching agent on the efficiency of vanadium(V) extraction at other fixed parameters (temperature and extraction time), it can be seen that the type of extraction agent is significant. The best leaching agent for vanadium(V) at the two temperatures is 15% NaOH, while the lowest results were obtained for 20% $CO(NH_2)_2$.

The contact time of the solid and liquid phases has no significant effect on the recovery of iron(III) ions (Fig. 1). Most iron(III) ions go into solution when 20% $CO(NH_2)_2$ is the leaching agent. The poor leaching of iron compounds may be due to the different forms of iron present in the catalyst. The iron oxide decreases in time due to the formation of $Fe_2(SO_4)_3$, this in turn reacts with the active phase to form such as $K_3V_{1-x}Fe_x(SO_4)_3$. These compounds are very stable and inactive at low temperatures. Their activity increases with the increasing molar fraction of iron.[2] Therefore isolation of these compounds from the catalyst mass requires more aggressive leaching conditions.

CONCLUSIONS

Based on the chemical analyses of the test solutions and the compiled results, the possibility of recovering vanadium(V) from the mixture after synthesis of potas-

Table 1. The results of vanadium(V) recovery from the mixture after synthesis of potassium metavanadate by extraction using different leaching solutions

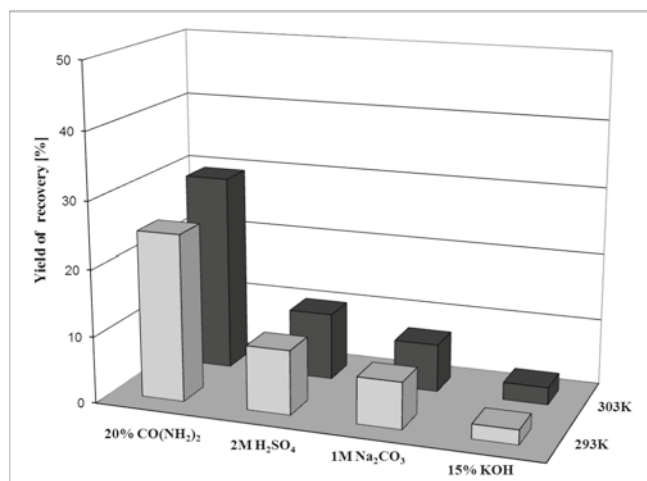| Time of leaching [h]	Yield of vanadium(V) recovery [%]				
	T = 293 K				
	15% NaOH	15% KOH	20% $CO(NH_2)_2$	2 M H_2SO_4	1 M Na_2CO_3
1	92.22	88.54	84.36	90.11	88.32
2	92.51	88.72	84.62	90.33	88.51
3	92.93	89.00	84.94	90.68	88.89
4	93.12	89.28	85.27	90.95	89.17
	T = 303 K				
	15% NaOH	15% KOH	20% $CO(NH_2)_2$	2 M H_2SO_4	1 M Na_2CO_3
1	94.30	89.68	84.75	91.30	89.47
2	94.81	89.97	84.98	91.57	89.85
3	95.22	90.20	85.46	91.79	90.03
4	95.43	90.45	85.87	92.15	90.32

Figure 1. Dissolution of the iron(III) in different leaching solutions (time = 4h; S:L=1:10 (g:cm^3))

sium metavanadate by extraction using various leaching solutions was presented. The extraction was carried out at temperatures of 293 K and 303 K.

It was found that:

1. The longer the contact time of the solid and liquid phases, the higher the efficiency of the extraction process.

2. The highest efficiency of vanadium(V) recovery from the mixture after synthesis of potassium metavanadate(V) using a spent vanadium catalyst (95.43%) was obtained at the following extraction parameters: 15% NaOH, t = 4 h, T = 303 K, 1:10 (g:cm^3) L:S ratio.

Using urea solution as a leaching reagent, it was possible to obtain an iron extraction yield of 29% under optimal leaching conditions of 1:10 (g:cm^3) L:S ratio, 303 K leaching temperature, 20% $CO(NH_2)_2$ and 4 hours reaction time.

ACKNOWLEDGMENTS

LITERATURE CITED

1. Grzesiak, P. (2002). Sulfuric acid - Methods and technologies of sulfuric acid production. Poznań, Poland, IOŚ.

2. Grzesiak, P. & Grobela, M. (2002). Sulfuric acid – Effect of iron on some properties of the vanadium catalyst used for the oxidation of SO_2. Poznań, Poland, IOŚ.

3. Trypuć, M., Grzesiak, P., Mazurek, K. & Grobela, M. (2007). Complex development of hazardous waste vanadium catalyst used for the oxidation of SO_2, Volume 1 – Characteristics of processes and catalysts for the production of sulfuric acid. Toruń – Poznań, Poland, IOŚ.

4. Mazurek, K. (2012). Studies on the optimum conditions for leaching the spent vanadium catalyst from metallurgical plants with sodium hydroxide solutions. Przem. Chem. 91(2), 234–238.

5. Mazurek, K., Białowicz, K. & Trypuć, M. (2010). Extraction of vanadium compounds from the used vanadium catalyst with the potassium hydroxide solution. *Pol. J. Chem. Techn.* 12(1), 23–28. DOI: 10.2478/v10026-010-0005-2.

6. Mazurek, K. & Trypuć, M. (2009). Recovery of the components of the spent vanadium catalyst with sulfuric(VI) acid solutions. *Przem. Chem.* 88(11), 1248–1251.

7. Mazurek, K. (2013). Recovery of vanadium, potassium and iron from a spent vanadium catalyst by oxalic acid solution leaching, precipitation and ion exchange processes. Hydrometallurgy 134–135, 26–31. DOI: 10.1016/j.hydromet.2013.01.011.

8. Mazurek, K., Białowicz, K. & Trypuć, M. (2010). Recovery of vanadium, potassium and iron from a spent catalyst using urea solution. Hydrometallurgy 103(1–4), 19–24. DOI: 10.1016/j.hydromet.2010.02.008.

9. Mazurek, K. (2012). Extraction of vanadium and potassium compounds from the spent vanadium catalyst from the metallurgical plant. *Pol. J. Chem. Techn.* 14(2), 49–53. DOI: 10.2478/v10026-012-0070-9.

10. Kiełkowska, U. (2009). Spent vanadium catalyst using to synthesis of potassium metavanadate in the presence of steam. *Przem. Chem*. 88/1, 70–72.

11. Trypuć, M., Białowicz, K. & Mazurek, K. (2001). Investigations on the Synthesis of $NaVO_3$ and Cl_2 from NaCl and V_2O_5 in the Presence of Oxygen. *Ind. Eng. Chem. Res*. 40(3), 731–735. DOI: 10.1021/ie000687w.

12. Trypuć, M., Torski, Z. & Białowicz, K. (2001). Investigations on the influence of silicon dioxide introduced as a neutral carrier on V_2O_5 conversion into KVO_3. *Pol. J. Chem. Tech.* 3(1), 28–32.

13. Trypuć, M., Białowicz, K. & Mazurek, K. (2004) Investigations on the synthesis of KVO_3 and Cl_2 from KCl and V_2O_5 in presence of oxygen. *Chem. Eng. Science* 59(6), 1241–1246. DOI: 10.1016/j.ces.2003.12.017.

14. Trypuć, M., Torski, Z. & Kiełkowska U. (2001) Experimental determination of the optimum conditions of KVO_3 synthesis based on KCl and V_2O_5 in the presence of steam. *Ind. Eng. Chem. Res*. 40(4), 1022–1025. DOI: 10.1021/ie000588i.

15. Brouwer, P. (2006) Theory of XRF. Almelo, Netherlands: PANalytical B.V.

16. Hermanowicz, W. (1999). Physico-chemical investigation of water and wastes. Warsaw, Poland, Arkady.

17. Kiełkowska, U., Białowicz, K., Trypuć, M., Mazurek, K. & Grzesiak, P. (2008) Extraction of vanadium compounds from spent vanadium catalyst using NaOH solution. Sulfuric Acid – New Opportunities, 311–317. Poznań, Poland: IOŚ. ISBN 978–89867–30–8.

18. Sánchez-Viñas, M., Bagur, G.M., Gázquez, D., Camino, M. & Romero, R. (1999). Determination of tin, vanadium, iron, and molybdenum in various matrices by atomic absorption spectrometry using a simultaneous liquid-liquid extraction procedure. *J. Anal. Toxicol.* 23(2), 108–112. DOI:10.1093/jat/23.2.108.

19. Fernandes, K.G., Nogueira, A.R.A., Gomes Neto, J.A. & Nóbrega, J.A. (2007). Determination of vanadium in human hair slurries by electrothermal atomic absorption spectrometry. Talanta 71(3), 1118–1123. DOI: 10.1016/j.talanta.2006.06.008.

20. Skoog, D.A., Holler, J.F. &, Nieman T.A. (1998) Principles of instrumental analysis (5th Ed.) Philadelphia, USA, Saunders.