

Removal of vanadium, potassium and iron from spent vanadium catalyst by leaching with citric acid at atmospheric pressure

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The effect of time, temperature, the catalyst particle size and the ratio of the catalyst weight to the leaching solution volume (S:L) on the treatment of spent vanadium catalyst components was determined using citric acid solutions at atmospheric pressure. The optimal parameters of catalyst leaching in 10% acid solutions at atmospheric pressure are: $T = 323\text{ K}$, $t = 4\text{ h}$, the particle size of less than 0.160 mm , the S:L ratio below 0.1. Under these conditions it was possible to dissolve about 90% of vanadium and potassium compounds and more than 60% of iron compounds contained in the catalyst. These results fall within the scope of research on a comprehensive method for recovering spent vanadium catalyst components.

Keywords: citric acid, sulphur oxide, spent vanadium catalysts, leaching, recovery.

INTRODUCTION

In view of the on-going depletion of natural resources and increasing environmental pollution, industrial waste has become a valuable source of raw material acquisition¹⁻⁷. The re-use of waste reduces the exploitation of natural resources and the amount of accumulated waste. The main challenge of the current generation is a sustainable development aimed at reducing the negative impact on the natural environment while maximizing process efficiencies. This also involves the concept of recycling, i.e. the use of resources that were previously considered as waste and that can become a valuable source of raw materials and energy. In 1990, 155 million tons of municipal wastes were landfilled on the area of the current 27 member states of the European Union, and only 28 million tons were recycled or composted. In 2008, the landfill was reduced to 103 million tons, while the amount of recycled waste was increased to 104 million tons. The European Environment Agency estimates that in 2020 this proportion will reach 78 to 136 million tons, respectively⁸.

The same applies to industrial waste. In Poland, over 110 million tons of industrial wastes were “produced” in 2008⁹. This waste comes mainly from mining – black coal, brown coal and non-ferrous metals, as well as the processing of these minerals. 75% of the waste is subjected to land use and the remainder is preserved and stored in a variety of ways.

Spent vanadium catalysts are among the industrial wastes that can be used in the recycling process. It is estimated that the accumulated amount of this waste in Poland is about 3000 tons¹⁰. The problem of deactivated and decommissioned industrial catalysts has not yet been solved in a comprehensive manner and constitutes a serious problem for plants producing sulphuric(VI) acid. The amount of accumulated waste, the structure complexity and toxicity of some components fully justify the research on a method for recovering spent vanadium catalyst components¹⁰⁻¹⁷.

Lee et al.¹⁸ and Zeng & Cheng¹⁹ indicated the possibility of using organic acids (oxalic acid and citric acid) for a selective leaching of vanadium compounds from a spent catalyst used in hydrodesulfurization processes (HDS). According to these reports, the use of both leach-

ing agents makes it possible to leach vanadium. Oxalic acid has been found to be more selective with respect to vanadium compounds. Citric acid in this study also allowed for the leaching of other metals contained in the catalyst (mainly iron, nickel and molybdenum)^{18, 19}. On this basis it was decided to check the possibility of using citric acid as the leaching agent to separate the major components of the spent vanadium catalyst used for the oxidation of SO_2 and determine the optimum parameters of leaching process.

EXPERIMENTAL SECTION

Reagents

The vanadium spent catalyst used in the study came from a landfill of a plant producing sulphuric(VI) acid with the contact method. The catalyst consisted of: 5.44% V_2O_5 , 8.57% K_2O , 0.91% Fe_2O_3 . The catalyst was ground and divided into appropriate granulometric fractions. The citric acid used was of analytical grade – POCh Gliwice, $\geq 99\%$.

Experimental part

Weighed samples of the catalyst (5.000 g) were placed in conical flasks with a capacity of 100 cm^3 , and an appropriate amount of the leaching agent was added using a disposable pipette. The samples were vigorously stirred for a certain time and at a constant temperature. After a suitable time, the samples were filtered with suction and the clear solution was sampled for quantitative analysis.

Analytical methods

The concentration of all ions in solutions was determined using the EDXRF method, using a PANalytical's MiniPal4 compact energy dispersive X-ray spectrometer²⁰.

RESULTS AND DISCUSSION

The effect of time on the degree of dissolution of the test compounds

Figure 1 shows the relationship between the degree of dissolution of the tested compounds and the leaching process time. The curves show clearly that time plays an

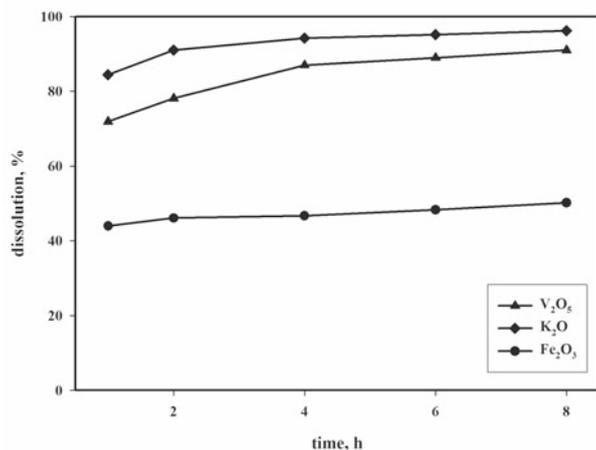


Figure 1. Dissolution of vanadium, potassium and iron compounds as a function of time ($\phi = 0.750\text{--}0.160$ mm; $c_{\text{C}_6\text{H}_8\text{O}_7} = 10\%$; $T = 293$ K; $S:L = 0.1$ (g:cm³); $p = 0.1$ MPa)

important role in the leaching of vanadium, potassium and iron compounds. The highest increase in the degree of vanadium leaching was observed between 1 and 4 hours.

Previous studies on leaching vanadium compounds from the spent vanadium catalyst in acidic environment conducted by other authors also showed that the greatest increase in the degree of the element leaching occurs in the first hours of leaching^{15, 17, 21, 22}. Further extension of time results in much smaller increments of the process efficiency obtained.

Qualitative results on spent vanadium catalysts have showed the presence of vanadium at different oxidation states (+5, +4) and in the form of simple and complex non-stoichiometric compounds (V_nO_{2n-1} , $K_3V_{1-n}Fe_n(SO_4)_3$ and $KV_{1-n}Fe_n(SO_4)_2$). Some of these may be more or less soluble, depending on their composition. A similar behaviour was observed in the case of potassium compounds, and the leaching percentage was higher than vanadium compounds. The leaching of iron was lower and not changes in the leaching were observed in time.

Comparing the experimental data with the results published in the literature, it should be noted that in the case of vanadium compounds, the results obtained after the first hour of leaching at 293 K are similar to the results obtained for a 10% solution of sulphuric(VI) acid (67%)¹⁵, but considerably lower than in the case of application of 15% NaOH as the leaching agent (78%)²³.

The effect of temperature on the degree of dissolution of the test compounds

Figure 2 shows the effect of temperature on the leaching of vanadium, potassium and iron compounds from the spent catalyst with a citric acid solution. It is clear that the higher temperature, the degree of leaching of all elements increases. In the case of vanadium and potassium compounds, the highest increase is observed when the temperature rises from 293 to 303 K, and it is 7 and 9% respectively. The degree of dissolution of vanadium and potassium compounds at a temperature of 333 K is increased by 18 and 15%, respectively, of that observed at 293 K. The degree of leaching of iron compounds grows linearly with increasing temperature.

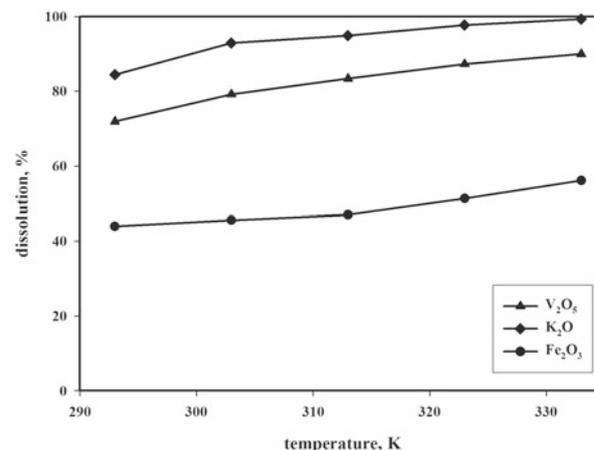


Figure 2. Effect of temperature on the dissolution of vanadium, potassium and iron compounds ($\phi = 0.750\text{--}0.160$ mm; $c_{\text{C}_6\text{H}_8\text{O}_7} = 10\%$; $t = 1$ h; $S:L = 0.1$ (g:cm³); $p = 0.1$ MPa)

The highest value was obtained at 333 K, and it was 56%, and the lowest 44% – at 293 K.

The presented data show that the efficiency of leaching of spent vanadium catalyst components with a citric acid solution is dependent on temperature to a much greater extent than in the case of sulphuric(VI) acid where the effect of temperature is much less significant. Khorfan et al.²² found that with increasing temperature from 333 to 383 K, the yield of leaching vanadium compounds from the catalyst with 15% H₂SO₄ grows up by only 2%.

It should be noted at that the catalyst used in the tests contained relatively small amounts of iron (below 1%). Research conducted by Grzesiak and Grobela^{11, 24–27} on the effect of iron compounds on the properties of vanadium catalysts have shown that iron builds up in the structure of a catalyst to form compounds with vanadium $K_3V_{1-x}Fe_x(SO_4)_3$ and $KV_{1-x}Fe_x(SO_4)_2$ and without it $KFe(SO_4)_2$. All of these compounds are very stable chemically and completely inactive at low temperatures. In addition, the degree of their chemical inactivity increases significantly with increasing mole fraction of iron. Low iron content in the test catalyst may cause that vanadium, and potassium are more readily leached out from the spent catalyst than from a catalyst containing a much larger amount of iron in its composition.

The effect of the particle size on the degree of dissolution of the test compounds

Figure 3 shows the effect of the spent catalyst size on the degree of leaching of vanadium, potassium and iron compounds from the spent vanadium catalyst. The curves clearly show that the greatest impact of the spent catalyst size on the leaching occurs in the case of iron compounds. The increase is almost linear and with a catalyst particle size of 0.088 mm allows the leaching of iron compounds with a yield of about 20% higher than that achieved for the catalyst with the largest particle diameter tested. In the case of vanadium and potassium compounds, it can be clearly seen that the maximum increase in the degree of leaching is achieved when the catalyst is ground to a particle diameter of less than 0.160 mm. Further fragmentation does not significantly affect the degree of leaching of the test compounds.

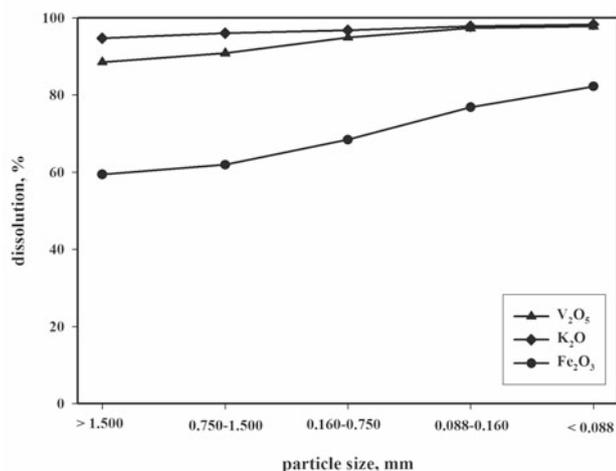


Figure 3. Particle size effect on the degree of dissolution of vanadium, potassium and iron compounds ($c_{C_6H_8O_7} = 10\%$; $T = 323\text{ K}$; $t = 4\text{ h}$; $S:L = 0.1$ ($\text{g}:\text{cm}^3$); $p = 0.1\text{ MPa}$)

X-ray spectrometry (EDS) of the crushed catalyst conducted by Grzesiak and Grobela^{11, 21-24} revealed the presence of typical spheroids resembling dendritic structures formed by the previously mentioned K-V-F-S compounds. The catalyst with particle size below 0.160 mm probably reduces the leaching agent access restrictions resulting from the existence of these structures.

The effect of the S:L ratio on the degree of dissolution of the test compounds

For the ratio $S:L = 0.2$, Figure 4, the degree of leaching of vanadium, potassium and iron compounds were to 88, 91 and 58%, respectively. The higher degree of leaching is achieved at the $S:L$ ratio of 0.025 with recoveries of – 98, 99 and 78%, respectively. Literature data indicate that the optimal concentration of vanadium ions in the solution to enable easy their precipitation should be in the range from 3 to 5 $\text{g}\cdot\text{dm}^{-3}$. Therefore, to maintain the appropriate concentration of vanadium compounds in the solution after leaching, the solid to liquid phase ratio should not be less than 0.03.

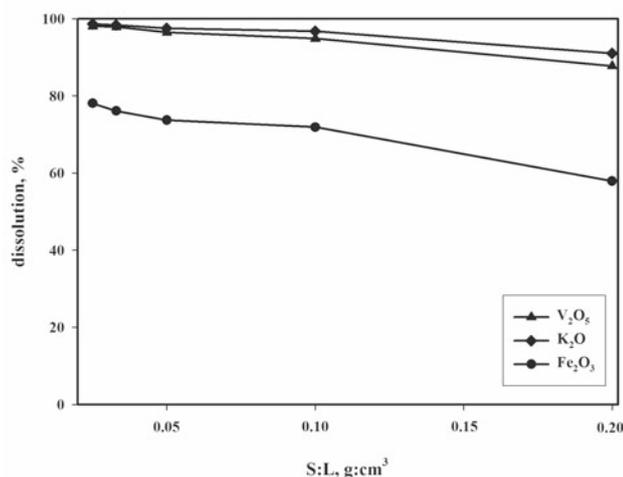


Figure 4. Effect of the $S:L$ ratio on the dissolution of vanadium, potassium and iron compounds ($\phi = 0.750\text{--}0.160\text{ mm}$; $c_{C_6H_8O_7} = 10\%$; $T = 323\text{ K}$; $t = 4\text{ h}$; $p = 0.1\text{ MPa}$)

CONCLUSION

Citric acid solutions can be successfully used for leaching active phase components (vanadium and potassium compounds) from a vanadium catalyst. When the spent catalyst was treated with a 10% citric acid solution at 323 K, $t = 4\text{ h}$, the particle size less than 0.160 mm, and the $S:L$ ratio below 0.1 over 90% of vanadium and potassium compounds can be leached. At the same time in addition to those elements, depending on the leaching parameters used (time, temperature, particle size, $S:L$), from 40 to 80% of iron compounds contained in the catalyst are leached.

The solution after leaching may be used for the production of the fresh catalyst weight. For this purpose, it is necessary to separate iron compounds from the solution (by changing the pH to the alkaline using KOH), evaporate some water and adjust the composition of the solution by the addition of appropriate amounts of vanadium and potassium compounds. The content of citrates in the solution is very advantageous from the viewpoint of the production of new catalyst. Released in the processes of catalyst calcination and chemical formation, free carbon(IV) oxide would positively affect the structure and porosity of the catalyst.

ACKNOWLEDGEMENT

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