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RECOVERY OF VANADIUM PENTOXIDE FROM SPENT CATALYST USED IN THE MANUFACTURE OF SULPHURIC ACID

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Abstract

Vanadium has many industrial uses and its contribution to environmental contamination is increasing all the time. Recovery of vanadium pentoxide from spent sulphuric acid catalysts was performed using a three-step process involving acid leaching, oxidation and precipitation. Several different acids were used in the leaching process. Finally, sulphuric acid was used in various concentrations, solid to liquid ratios, stirring times and temperatures.

A high solid/liquid ratio in the leaching stage was used to obtain high concentration of vanadium pentoxide and low acid consumption that allowed direct precipitation without the use of extraction by rather expensive organic solvents. Sodium carbonate solution of one mole/liter concentration was used in the precipitation stage. An industrial application including material balance and operating conditions with an overall vanadium pentoxide recovery efficiency of (70%) was proposed.

Keywords: catalyst, leaching, precipitation, vanadium

1. Introduction

Vanadium has many and continuously increasing industrial uses. Today over 85% of the world production of vanadium is consumed in carbon and stainless steel-production, as an alloying agent to produce ferro-vanadium. Vanadium is employed for the manufacture of a variety of vanadium compounds, many of which in turn are employed to prepare catalysts such as hydrocarbon oxidation catalysts and catalysts for the manufacture of sulphuric acid [1]. LOZANO and JUAN [2] stated that vanadium could be recovered from sulfate solutions derived from the leaching of spent catalysts by means of solvent extraction with primary aliphatic amine. OTTERNUM and STRANDEL [3] described a process for the recovery of vanadium from sulfate leaching solution using organic phase containing di(2-ethylhexyl) phosphoric acid combined with tributyl phosphate. HO et al. [4] compared the di(2-ethylhexyl) phosphoric acid and amine extractants and investigated the relative extracting performance of quaternary amine in the case of a range of vanadium (V) anionic species between pH 6 and 13. Alkaline leaching is more selective for iron but dissolves some silica and is more costly in terms of reagent [5]. IKEYAMA [6] describes a process in which vanadium and molybdenum were recovered as sodium vanadate $[(NH_4)_3VO_4]$ and H_2MoO_4, with yields of 96% and 92%, respectively.

The purpose of the present work is to study the possibilities for the recovery of vanadium pentoxide by dissolving the spent catalyst with suitable acid media and oxidize the vanadium to higher oxidation state, then precipitate it directly by converting the vanadium into simple vanadate compounds which is insoluble in the pH adjusted solution without the use of relatively expensive organic extraction solvents.

2. Experimental

2.1. Materials

Spent catalyst mass used in the manufacture of sulphuric acid was supplied by the General Fertilizer Company GFC Homs/Syria containing 5.5% V_2O_5 and 11.84% moisture. Samples were ground to fine particles to improve leaching efficiencies and they were dried. All acids, sodium carbonate and hydrogen peroxide employed were analytical grade Merck products.

2.2. Apparatus and Procedures

All leaching tests were carried out in a beacher with a magnetic stirrer placed in a thermostat to control the temperature. The mixtures were filtered under a vacuum unit. Acidity degree was adjusted using a pH-meter.

The total amount of vanadium as V(V) was determined. Vanadium was oxidized with potassium permanganate and the excess of permanganate was reduced with sodium nitrite. Urea was added to decompose the excess of nitrite, and the vanadium was titrated with standard ferrous ammonium sulfate using sodium diphenylaminesulphonate as an indicator [7, 8]. This method is used as the high precision assay of vanadium, a relative standard deviation of 1% was achieved.(*Fig. 1*)

3. Results and Discussion

3.1. Selection of a Suitable Leaching Acid

Leaching was carried out by the following acids: sulphuric acid 50% v/v, nitric acid 65% wt., a mixture of sulphuric acid 50% v/v and nitric acid 65% wt. 2:1 and a mixture of sulphuric acid 50% v/v, nitric acid 65% wt., hydrofluoric acid 40% wt. and perchloric acid 70% wt. 57:28:6:9 under the same experimental conditions ($T = 60$ °C, solid/liquid $= 1/10$ g/ml, mixing time $= 30$ min) . The results are plotted in *Fig. 2*. The efficiency was nearly the same except for nitric acid where it

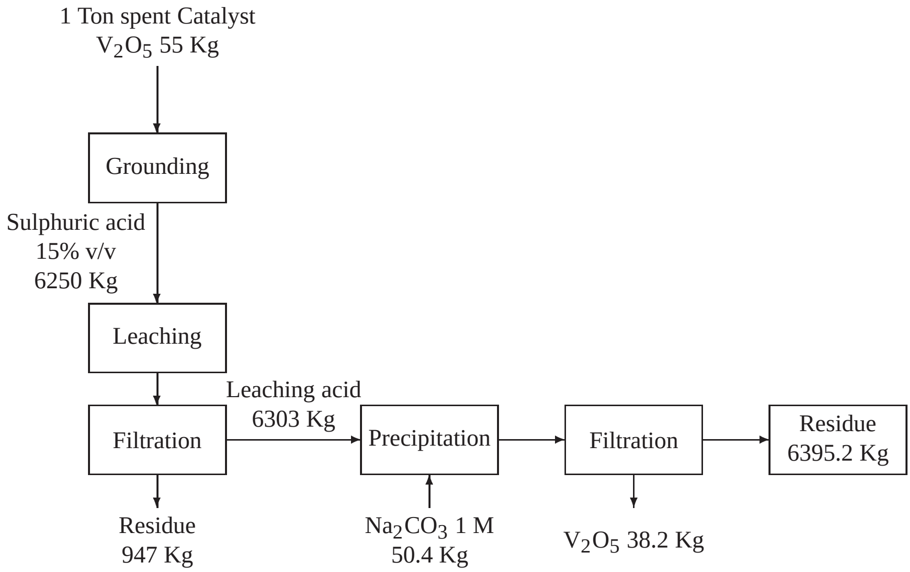

Fig. 1. Proposed flowsheet with material balance

was lower. Consequently sulphuric acid was used to perform the following leaching experiments.

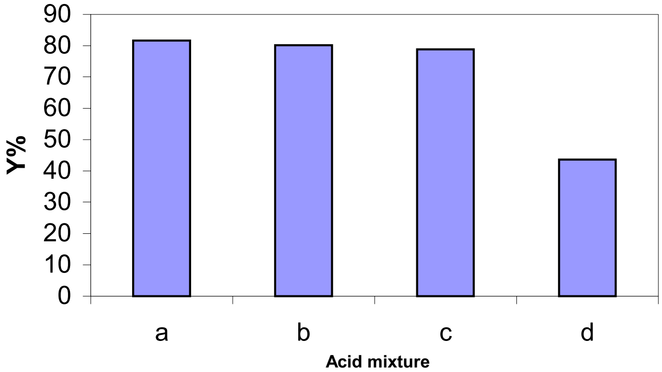

Fig. 2. The effect of acid mixtures on leaching efficiency ($T = 60$ °C, leaching time $= 30$ min, S/L $= 1/10$ g/ml)

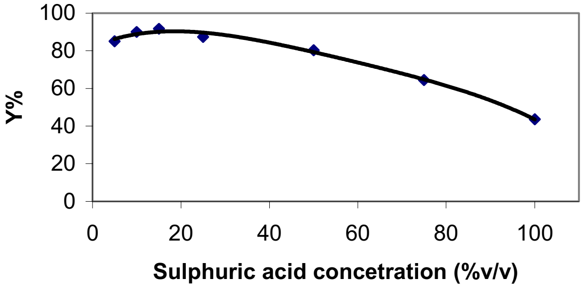

Fig. 3. The effect of sulphuric acid concentration on leaching efficiency ($T = 60$ °C, leaching time = 30 min, S/L = $1/10$ g/ml)

3.2. *Effect of Sulphuric Acid Concentration*

The effect of sulphuric acid concentration was studied by varying the concentration of the acid from 5% v/v to 100% v/v while keeping other conditions constant ($T = 60$ °C, solid/liquid = $1/10$ g/ml, mixing time = 30 min). The results are presented in *Fig.* 3. The results show, that above the acid concentration of 15% v/v the efficiency decreases significantly so sulphuric acid of 15% v/v was selected for further experiments.

3.3. *Effect of Time of Mixing*

The leaching was carried out by varying the time of mixing from 10 min to 4 hours while keeping other conditions constant ($T = 100$ °C, solid/liquid = $1/10$ g/ml, sulphuric acid 15% v/v). The results are presented in *Fig.*4 in the form of efficiency versus time of mixing. The efficiency was constant after 30 min so it is enough to fix the mixing time at one hour for other experiments.

3.4. *The Effect of Temperature*

The effect of temperature was investigated by varying the temperature from 60°C to 100 °C with other conditions constant (mixing time = 60 min, solid/liquid = $1/10$ g/ml, sulphuric acid 15% v/v). The results are plotted in *Fig.*5. It is clear that the efficiency increases negligibly after 80 °C so the temperature was fixed at 100 °C for other experiments.

3.5. The Effect of Solid/Liquid Ratio on the Efficiency

Different solid/liquid (S/L) ratios were studied using sulphuric acid 15% v/v and a mixing time of one hour at 100 °C. The results are presented in *Table 1*. The three phase ratios S/L = 1/15, 1/10, 1/5 g/ml give the highest efficiency but S/L = 1/5 g/ml was found to be the best as a result of the trade-off between the vanadium recovery (96.8%) and the concentration of V_2O_5% in the sulphuric acid solution (0.71%).

Table 1. The effect of S/L ratio on leaching efficiency and the concentration of V_2O_5% in the sulphuric acid solution

S/L ratio [g/ml]	Efficiency [%]	V_2O_5 [%] in the sulphuric acid solution
1/15	96.3	0.25
1/10	95.9	0.35
1/5	96.6	0.71
1/3	91.6	1.12
1/2	90	1.65

3.6. Vanadium Oxidative Precipitation

One liter of leaching solution (0.71%V_2O_5) was prepared by adopting the previous typical conditions (mixing time = 60 min, solid/liquid = 1/5 g/ml, sulphuric acid 15% v/v). Oxidative precipitation of vanadate was performed. At first, H_2O_2 (concentration: 30%) was added to the leaching solution to oxidize vanadium to vanadium pentoxide. When the entire vanadium component in the leaching solution was supposed to be in the pentavalent state, then pH was adjusted to be between 6 and 7 using sodium carbonate solution of one mole/liter concentration to allow precipitation of vanadium as insoluble simple vanadate. The efficiency of precipitation process of 73% was achieved.

In agreement with VITOLO et al. [9] and SCHEMEL et al. [10] precipitation at a pH higher than 7 had to be avoided to prevent the precipitation of nickel and other metals. In addition, iron precipitation occurs at the same $pH = 6 - 7$, but the oxidation stage reduces it considerably.

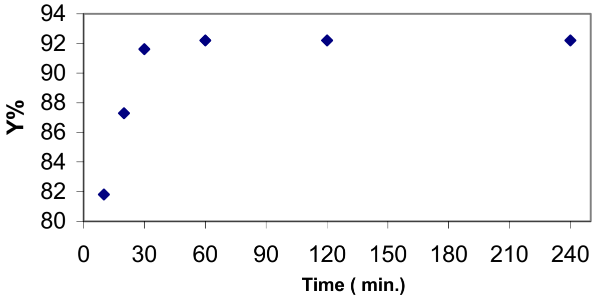

Fig. 4. The effect of mixing time on leaching efficiency ($T = 60$ °C, concentration of sulphuric acid 15% v/v, S/L = $1/10$ g/ml)

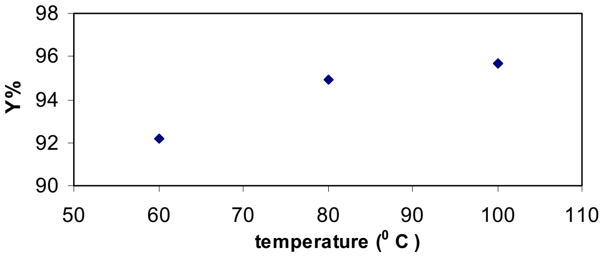

Fig. 5. The effect of temperature on leaching efficiency (mixing time = 60 min, concentration of sulphuric acid 15% v/v, S/L = $1/10$ g/ml)

4. Conclusions

Sulphuric acid was found to be the best leaching solution. The efficiency of recovery decreases by increasing the concentration of the acid. Leaching efficiency of 96.6% was achieved and the concentration of vanadium in the spent catalyst was tested to be 0.187%. It is not toxic and by adding it to the second leaching stage it is possible to reduce the concentration of vanadium in the waste. The efficiency of the precipitation process was 73% and the concentration of vanadium in the filtrate was 0.19%, it is not toxic either. Vanadium pentoxide can be recovered from the initial spent catalytic mass with an overall efficiency of 70% using a three-step process which consisted of acid leaching, oxidation and precipitation. The proposed flowsheet can be economically favorable, as well as it avoids environmental contamination with untreated spent catalyst waste.

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