

Recovery of Vanadium from Acid and Basic Leach Solutions of Spent Vanadium Pentoxide Catalysts

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Abstract: The vanadium pentoxide catalysts are used in the sulfuric acid manufacture, but as an inherent consequence of the process, they are deactivated or poisoned, because of that they need to be renewed. In Ecuador, the increase of environmental pollution concerns and the legislation related with the final dispose of hazardous residues is forcing to companies to process their waste products and residues. For the present investigation, catalysts samples were characterized using AAS (atomic absorption spectroscopy), XRD (X-ray diffraction), surface area (BET) and SEM-EDS (scanning electron microscopy). Results show presence of 6-5% w/w of vanadium pentoxide (V_2O_5), 10-11% w/w of potassium oxide (K_2O) and 55-60% w/w of silicon oxide (SiO_2). The material presents a pore size of 3 nm and a specific surface area of 200 m^2/s . The spent catalyst was firstly pulverized in a powder mill until 200 μm was attempted, then a calcination at 450 °C was made. Different leaching agents were used: nitric, sulfuric, hydrochloric acid and sodium hydroxide with variation of percentage of solids, particle size, leaching agent concentration and leaching time. Sodium carbonate was added to the solution to obtain a precipitate. A final calcination step was made at 450 °C to obtain vanadium pentoxide. The best results were obtained by using sulfuric acid at 75 g/L, 20 w/w percentage solids, environmental temperature, agitation speed was maintained 750 rpm and 30 minutes leaching, the recovering vanadium rate was 94.41%. In the precipitation stage 92.2% of sodium meta vanadate, for that a pH 7 was required. Finally, precipitation was calcinated getting vanadium pentoxide at 97% purity and it costs is \$104.5 per 500 grams.

Key words: Vanadium, deactivated, poisoned, catalyst, spectroscopy, diffraction, leaching, calcinations.

1. Introduction

The vanadium pentoxide catalysts are used in the sulfuric acid manufacture, but as an inherent consequence of the process they are deactivated or poisoned, reason why they need to be renewed. The vanadium content is around 4-5% w/w, this element has many industrial uses and it is categorized as dangerous and toxic for environment [1, 5].

In Ecuador, the increase of environmental pollution concerns and the legislation related with the final dispose of hazardous residues is forcing the companies to process their waste products and residues [3, 4].

Industries supplied vanadium pentoxide catalyst used in its manufacture of acid sulphuric acid for the production of detergents, oil refining, treatment of steel,

soap, fertilizers and others. In the last year the industries have in stock metric tons of catalytic residues and they are forced to seek environmental managers to process them, otherwise they have to pay high fines. The actual treatment of toxic and hazardous residues consists of spent catalysts vitrification and later controlled dumping in specific areas [1, 5, 6].

The purpose of the present work is to study the possibilities for treat the catalyst residues and to study optimum vanadium pentoxide recovery from spent vanadium pentoxide catalyst. The recovery consists in leaching, following of precipitate by converting the vanadium into vanadate and finally calcination a high temperature of the obtained vanadium pentoxide [2].

Today, over 85% of the world production of vanadium is consumed in carbon and stainless steel making alloying agents to produce ferro vanadium, in ceramic and chemical industries. Demand from uses in

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expected to grow at about 5% annually. China, South Africa and the USA produce vanadium pentoxide from vanadium bearing magnetite ores, concentrates and slags while Japan produce vanadium pentoxide from petroleum residues, ash, and spent catalysts. Actually, vanadium pentoxide at > 97% purity costs \$104.5 per 500 grams [5, 6].

2. Experiment

2.1 Chemical Characterization

Catalysts samples were characterized using atomic absorption spectrophotometry in a Perkin AA300. The mineralogical composition was determined by X-ray diffraction Bruker D8 Advance. The surface area and Porosity was determined by BET. SEM images of samples were obtained by using equipment Vega-Tescan.

2.2 Leaching Process

2.2.1 Pretreatment of the Catalyst

Spent catalysts samples were firstly pulverized in a powder mill for 15 minutes in order to obtain different particle micro sizes. Later, the samples were calcined at 450 °C in a furnace for 3 hours to remove coal and sulfur waste in the form of gas, as CO_x and SO₂. After calcination, the samples were cooled at environmental temperature.

2.2.2 Leaching Process

Different leaching agents were used: nitric, sulfuric, hydrochloric acid and sodium hydroxide to extract vanadium from samples. Different factors were studied in the leaching process were pretreatment of samples, variation of percentage of solids, particle size, leaching agent concentration and leaching time. After that, the solution was filtered obtaining clarified solution and solid residue silicon oxide.

All the leaches were realized at environmental

temperature with a constant mixing velocity of 750 rpm. Vanadium percent recovery is determined by dividing the mass of leached solution with the initial mass of the sample.

2.3 Vanadium Precipitation

Solution sodium carbonate 2 M was added to the leaching solution to obtain a precipitate of sodium meta vanadate (NaVO₃). Later, the precipitate was calcined at 450°C to obtain vanadium pentoxide (V₂O₅).

3. Results and Discussion

3.1 Chemical Characterization

Two samples of vanadium pentoxide catalyst were characterized, one called activate state and spend state. Vanadium pentoxide catalysts present the following vanadium composition observed in Table 1.

In Table 1 the vanadium content of each sample is shown. Vanadium is around 5.2 percentage inside activated catalysts, but in consequence of the catalytic process, they are deactivated or poisoned and the vanadium percentage reduce around 4 percentage for the spend catalyst. The temperature, time reaction and the raw material proprieties in the process are the main factors that cause the reduction of vanadium content.

Vanadium pentoxide catalysts present the following mineralogical composition observed in Table 2.

In Table 2 the active catalyst and the spend catalyst composition is shown. The amount of pentoxide vanadium, potassium oxide and silicon oxide is fewer than the amount of these three components on the active catalyst, this happens because of the catalyst uses. The ferric oxide appears on the spend catalyst, because the iron is part of the alloy that conforms the reactor material where the process takes place.

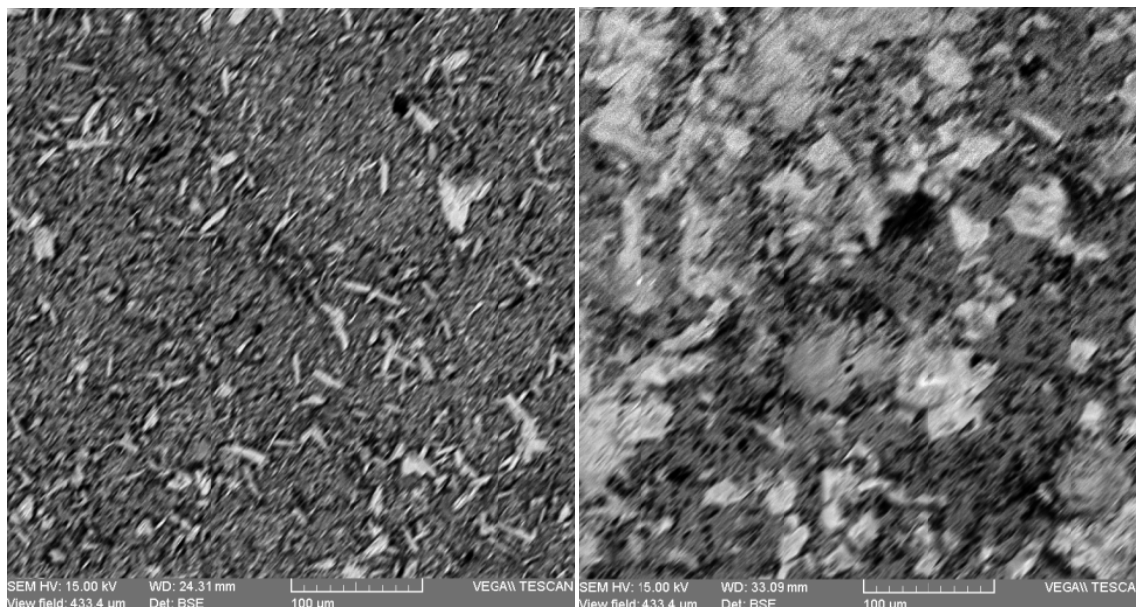
A comparison of the two types of catalyst is shown by the SEM images obtained in figure 1 a) section of

Table 1 Vanadium composition of vanadium pentoxide catalysts.

Sample	State	Vanadium content (%)
Vanadium pentoxide catalysts	Activate	5.2
Vanadium pentoxide catalysts	Spend	4

Table 2 Mineralogical composition of vanadium pentoxide catalysts.

Compound	Formula	% (Active catalysts)	% (Spent catalysts)
Vanadium pentoxide	V_2O_5	8	6
Potassium oxide	K_2O	16	15
Silicon oxide	SiO_2	76	74
Ferric oxide	Fe_2O_3	-	< 2

**Fig. 1 a) section of activated vanadium pentoxide catalysts (increased = 500x) and b) section of spent vanadium pentoxide catalysts (increased = 500x).**

activated vanadium pentoxide catalysts (increased = 500x) and b) section of spent vanadium pentoxide catalysts (increased = 500x).

As observed Fig. 1a) section of activated vanadium pentoxide catalysts the porous surface is uniform, cleaned, and without waste while the b) section of spent vanadium pentoxide catalysts presents a porous surface covered by a residual layer and incrustations because sulfur, organic and inorganic residues du the process. Finally, the catalyst presents a pore size of 3 nm and a specific surface area of 200 m²/s.

3.2 Leaching Process

3.2.1 Pretreatment Influence

Pretreatment of the catalyst was studied in the leaching process and the Table 3 shows the results. Leaching conditions were as leaching agent sulfuric acid (98%) with concentration of 50 g/L, 10 w/w solids

percentage, environmental temperature, agitation speed was maintained 750 rpm and 4 hours time leaching.

The results show the influence of the pretreatment, the increasing recovery of vanadium by using a calcination pretreatment for 3 hours at different fractions evaluated.

3.2.2 Leaching Agents Influence

Leaching agents and pretreatment influence were studied in the vanadium recovery and the Table 4 shows the results. Various leaching agents: sulfuric acid (98%), hydrochloric acid (36%) nitric acid (60%) and sodium hydroxide (99%) in 50 g/L concentration were used in the process. Leaching conditions were 10 w/w solids percentage, environmental temperature, agitation speed was maintained 750 rpm and 4 hours time of leaching.

Table 4 shows that the recuperation percentage

Table 3 Vanadium recovery from spent vanadium pentoxide catalysts at different particle size and pretreatment influence.

Mesh size	Pretreatment	Recovery
#150-#200		77.75%
#150-#200	Calcination	96.20%
#200-#235		75.67%
#200-#235	Calcination	95.11%
#325-#400		76.72%
#325-#400	Calcination	97.14%

Table 4 Vanadium recovery from spent vanadium pentoxide catalysts using different agents leaching.

Leaching agent	Pretreatment	Recovery
Sulfuric acid (98%)		75.67%
Sulfuric acid (98%)	Calcination	96.20%
Hydrochloric acid (36%)		78.94%
Hydrochloric acid (36%)	Calcination	87.67%
Nitric acid (60%)		74.95%
Nitric acid (60%)	Calcination	78.37%
Sodium hydroxide (99%)		55.61%
Sodium hydroxide (99%)	Calcination	71.88%

Table 5 Vanadium recovery from spent vanadium pentoxide catalysts at different percentage of solids.

Percent solids	Concentration Vanadium (g/L)	Recovery
10 w/w	3.61	96.20%
15 w/w	6.30	86.72%
20 w/w	8.70	82.88%
25 w/w	10.71	75.18%
30 w/w	10.93	72.36%

Table 6 Vanadium recovery from spent vanadium pentoxide catalysts at different percentage of solids and leaching agent concentration.

Concentration	Recovery		
	(10 w/w)	(20 w/w)	(25 w/w)
Sulfuric acid (98%)-50 g/L	96.20%	82.88%	75.18%
Sulfuric acid (98%)-75 g/L	97.41%	94.41%	88.77%
Sulfuric acid (98%)-100 g/L	97.34%	96.14%	91.42%

depends on the leaching agent and the pretreatment that was used. Sulfuric Acid (98%) was the best leaching agent in the vanadium recovery if a calcination pre treatment is done, giving 96.2% of recovery.

3.2.3 Percentage of Solids Influence

Percentage of solids were evaluated in the vanadium recovery using as agent leaching sulphuric acid (98%) in 50 g/L concentration, calcined sample, environmental temperature, agitation speed was maintained 750 rpm and 4 hours time of leaching. Table 5 shows the results.

Vanadium concentration increase as the percentage solids increase too, but the vanadium recovery decreased, that is why its important in order to obtain a higher concentration and a higher recovery by using the least amount of leaching agent.

3.2.4 Leaching Agent Concentration Influence

The leaching agent concentration was determined at different percentage solids using as the leaching agent sulfuric acid, calcined sample, environmental temperature, agitation speed was maintained 750 rpm and 4 hours time of leaching. The Table 6 shows the results of vanadium leaching at 10 w/w, 20 w/w and 25

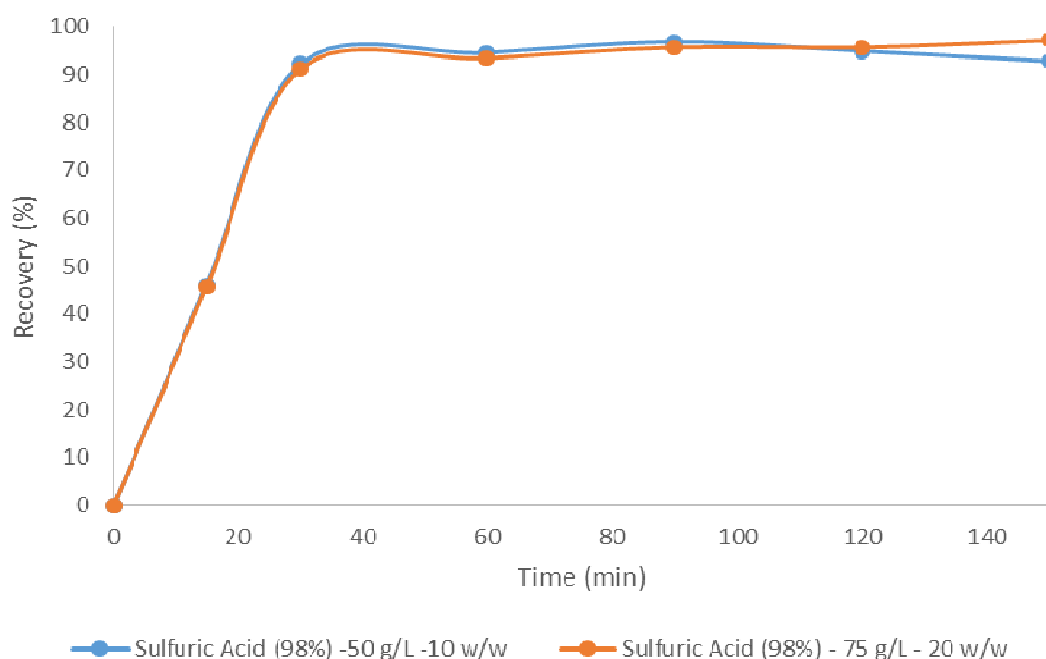


Fig. 2 Vanadium recovery (%) during the time reaction (min).

Table 7 Vanadium precipitation at different pH.

Parameters	pH = 3	pH = 7	pH = 12
Volume sodium carbonate (mL)	12	36	64
Vanadium recovery (%)	16.69	92.2	44.15

w/w solids percentage each one with sulfuric acid at 50 g/L, 75 g/L and 100 g/L.

Vanadium recovery increased as leaching agent concentration increased too, during all the process. Leaching at 10 w/w was similar, recovering around 97%, leaching at 20 w/w the recovery increased from 82.88% to 96.14% and leaching at 25 w/w the recovery increased 75.18% to 91.42%.

3.2.5 Leaching Time Influence-Kinetic of the Reaction

Kinetic of the reaction was studied at the best two better conditions of vanadium recovery, leaching with sulfuric acid at 50/L, 10 w/w solids percentage and the other leaching was realized with sulfuric acid at 75 g/L and 20 w/w solids percentage. Results are presented in Fig. 2.

Vanadium recovery increased in the first thirty minutes, after that the recovery remained constant, for this reason thirty minutes was the optimum leaching

time, during this time the recovery was high and the energy consumption by agitation was minimal. The best results were obtained by using sulfuric acid at 75 g/L, 20 w/w solids percentage and 30 minutes of leaching. The recovering vanadium rate was 94.41%.

3.3 Vanadium Precipitation

3.3.1 Effect of pH in Vanadium Precipitation

Solution sodium carbonate 2 M was added to the leaching solution to obtain a precipitate of sodium meta vanadate; the pH was changed in the process and it influence on the amount of sodium meta vanadate precipitation as Table 7 shows. The pH was controlled by adding different volume of solution sodium carbonate, three pH values are studied = 3, 7, 12.

The pH 7 was the optimal condition in the vanadium precipitation, because the ion meta vanadate was formed at this value. Later, the precipitate was calcined at 450 °C to obtain vanadium pentoxide.

4. Conclusions

Vanadium recovery was increased when the catalyst is pretreated by calcining at 450 °C for 4 hours to remove coal and sulfur waste in the form of gas, as CO₂ and SO.

The best results in vanadium leaching were obtained by using the following conditions: leaching agent sulfuric acid at 75 g/L, 20 w/w percentage solids, environmental temperature, agitation speed was maintained 750 rpm and 30 minutes leaching. The Recovering vanadium rate was 94.41%.

Finally, in the precipitation stage 92.2% of sodium meta vanadate, for that a pH 7 was required.

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