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A NEW WAY FOR V_2O_5 /Fe_2O_3 SEPARATION AND RECOVERY FROM SPENT CATALYSTS

BY

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Abstract. The paper presents data on the study of V_2O_5 and Fe_2O_3 spent catalysts used in the sulphuric acid obtaining process. During oxidation of SO_2 to SO_3 the spent catalysts undergoes a series of physical and chemical transformations, the most important is the reduction of V^{5+} and Fe^{3+} ions in contact with sulphur dioxide. Thus, V^{5+} is reduced to V^{4+} and V^{3+} resulting VO_2, $VOSO_4$ and $V_2(SO_4)_3$ and Fe^{3+} ions are reduced and passing at $FeSO_4$. Resulting sulphates are soluble in water and can be separated by filtering support (mass of) insoluble. Vanadium oxides VO_2 and V_2O_3 or V_2O_5 surface retain some quantities of SO_2 and SO_3. Due to these processes, novel compounds are resulting that can hydrolyse in contact with water, and creating acidic solutions - corrosive agents which are environmental pollutants. Also, the separating process of vanadium (V^{4+} and V^{3+}) from spent catalysts as V_2O_5 and Fe^{3+} and Fe^{2+} in the form of Fe_2O_3 is presented. The resulting V_2O_5 and Fe_2O_3 oxides are insoluble and can be separated from initial solutions and reused.

Key words: spent catalysts, divanadium pentoxide, sodium hypochlorite, sodium acid phosphate, ion exchange, precipitation, separation, neutralization.

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1. Introduction

In sulphuric acid industry, one of the main stages of the technological process is the catalytic oxidation of sulphur dioxide to sulphur trioxide: $SO_2 \rightarrow SO_3$. Currently, all facilities from SO_2 to SO_3 oxidation used a catalyst based on divanadium pentoxide, V_2O_5, 6-11%. In practice, the catalysts used in the oxidation of SO_2 to SO_3 are the type V_2O_5-K_2O (Na_2O) - SiO_2. In addition to these components, active catalyst also contains ferric oxide, Fe_2O_3, whose rate ranging between 2.5-3%. During the catalytic process divanadium pentoxide is reduced by SO_2 oxides at V(IV) and V(III) and VO_2, V_2O_3, which reacts with SO_3 to form $VOSO_4$ and $V_2(SO_4)_3$ as well as other compounds of vanadil vanadat respectively $Na_2V_2O_4 \cdot 5V_2O_5$ or $Na_2V_2O_4 \cdot 4V_2O_5$, etc.. Meanwhile, ferric oxide Fe_2O_3 is reduced to Fe (II) or FeO. Iron oxide reacts also with sulfur trioxide to form $Fe_2(SO_4)_3$ and $FeSO_4$, soluble in water (Balasanian & Leonte, 1984; Clark, 1968).

During to the chemical reaction, V_2O_5 percentage decreases, while the Fe_2O_3 percentage increases, the catalyst changes its structure and composition, and is inactivated. The study based on V_2O_5/Fe_2O_3 used catalysts follow the separation of soluble compounds contained in the spent catalyst, which in contact with water pass into solution and can be separated. Resulting solutions have a low pH and is corrosive, toxic and polluting to the environment. Strong acid character of the solutions is because resulted sulphates (contact stove) or $FeSO_4$, $Fe_2(SO_4)_3$, $V_2(SO_4)_3$, $VOSO_4$, that are soluble in water, hydrolysed and form sulphuric acid, a strong acid.

Sulphurous gases SO_2 and SO_3 react with water to form the corresponding acids H_2SO_3 and H_2SO_4. V_2O_5 is slightly soluble in water; however small amount of it reacts with water to form HVO_3 - metavanadic acid. According to above processes, the resulting solution has a strong acidic pH, about 1.5 to 2.5 (Balasanian & Leonte, 1984; Calistru & Leonte, 1972; Dumitriu & Hulea, 1997; Foca *et al.*, 2010).

At this pH values, Fe^{2+}, Fe^{3+}, V^{3+} and VO^{2+} ions exist freely in solution, are stable and can be dosed and separated individually. The resulting solutions after vanadium and iron ions separation are neutral, presenting pH around 6.5 - 7.

Most important problem that arises in the study of catalysts used based on V_2O_5 is the oxidation of ions Fe^{2+}, V^{3+} and V^{4+} (VO^{2+}) in oxidation state maximum Fe^{3+} or V^{5+}, and separation of these cations, which is quite difficult.

2. Experimental

The study presented in this paper has considered active catalyst, but in particular, the spent catalyst. Table 1 shows the composition of the active and spent catalyst, the percentage of V_2O_5 and Fe_2O_3 determined by physicochemical methods, namely alkaline oxidizing melting and spectrophotometric method used to determine the concentration of Fe^{3+} or V^{5+} ions in solution (Bîlbă & Tofan, 2004; Vicol & Berdan, 1986).

Table 1

V_2O_5 and Fe_2O_3 Content of the Active and Spent Catalyst

Number of determinations	active catalyst		spent catalyst	
	% V_2O_5	% Fe_2O_3	% V_2O_5	% Fe_2O_3
1	5.75	1.25	3.42	2.65
2	5.80	1.30	3.25	2.75
3	6.15	1.80	3.2	2.50
4	6.00	1.75	3.55	2.80
5	6.12	1.45	3.35	2.49

From Table 1 it is found that due to chemical reactions, the catalyst composition it is changed leading to disable it. Vanadium V(V) from V_2O_3 and Fe (III) from Fe_2O_3 pass into soluble compounds such as $FeSO_4$, $Fe_2(SO_4)_3$, $V_2(SO_4)_3$, $VOSO_4$, soluble in water, which can be separated by filtration of the insoluble catalyst (SiO_2, V_2O_5 and Fe_2O_3 catalyst mass remaining). By physico-chemical methods Fe(III) and V(V) are separate and can be precipitated as insoluble compounds. Spent catalyst is finely milled powder shows a yellow-green, partially soluble in cold water, forming a green solution because soluble components such as $FeSO_4$, $Fe_2(SO_4)_3$, $VOSO_4$ but especially complex ion $[V(H_2O)_6]^{3+}$ (Krishan *et al.* 1996, Schriver *et al.* 1998, Spacu *et al.* 1998, Roşca *et al*, 1991).

The spent catalysts thermal behaviour. Vanadium oxides V_2O_5, VO_2 and V_2O_3 are able to retain on their surface important quantities of SO_2 and SO_3 forming additive compounds such as $V_2O_5{\cdot}SO_2$, $V_2O_5{\cdot}SO_3$, $VO_2{\cdot}SO_2$, $VO_2{\cdot}SO_3$, $V_2O_3{\cdot}SO_2$, $V_2O_3{\cdot}SO_3$, this sulphur oxides are bound to vanadium oxides by physicochemical relatively strong bonds, which gives them a high thermal stability (Cretescu *et al.*, 2006; Doniga, 2000).

We followed the variation in weight of catalyst used exactly weighed samples (50 g) at several temperatures, namely 125°C, 250°C, 500°C, 700°C and 850°C in an oven with forced bars. After annealing for 5 h, the samples were weighed again and have found the following:

− When the sample is heated at lower temperatures, 125-150°C, the weight remains constant;

− If the sample is heated to 500°C, weight loss is about 5%;

− At temperatures between 575°C and 625°C, weight loss is about 16%;

− If the samples are burnt at 700 C, the weight loss is about 25%, a number of sulphates as $FeSO_4$, $Fe_2(SO_4)_3$, $V_2(SO_4)_3$, $VOSO_4$ are decomposed, releasing SO_2 and SO_3, which influences the experimental data. If the spent catalyst is subjected to calcination at 850°C, it is found that the samples have the same weight because although some compounds decompose leaving catalyst simultaneously occurring reactions such as oxidation of V(III) and V(IV) to V(V), the reaction of SO_3 and K_2O support or reactions between oxides of Fe(II) and Fe(III) with SO_3.

The spent catalyst behaviour in aqueous solution. Dissolution stages to follow the transition in soluble components were followed under the next aspects:

− The behaviour in aqueous solution of the spent catalyst is determined by the soluble components that go into solution in contact with distilled water;

− The optimum contact time: spent catalyst - distilled water for complete solubilisation

− The time evolution of pH in the system: spent catalyst - distilled water;

− The kinetic reaction of sulphur trioxide retained on the catalyst with distilled water;

The concentration of Fe^{3+} and V^{5+} ions was determined on solutions resulting from spent catalyst in contact with distilled water by spectrophotometric method (Scheme 1). To study the behaviour of the spent catalyst in aqueous solution were weighed exact amount of catalyst (50 g) were brought in over the 2L bottles and 1L distilled water was added to obtain the ratio 20 parts water - 1 part spent catalyst, components for total solubilisation followed SO_2, SO_3, $FeSO_4$, $Fe_2(SO_4)_3$, $V_2(SO_4)_3$, $VOSO_4$, K_2SO_4. Samples were left in contact with distilled water for 6, 8, 12, 24 and 48 h, and then separating the insoluble was filtered. After filtration, the insoluble mass was dried in an oven at 150°C and then reweighed. In all cases, weight loss of the sample was approximately 3.5%. The resulting solution was determined after filtration pH (2 - 2.5). Nature of the acid solutions is due to chemical reactions between compounds contained in the spent catalyst and distilled water, respectively:

The chemical reactions that occur in the studied system are presented in eqs. (1) - (7).

$$\mathrm{SO_2 + H_2O \leftrightarrow H_2SO_3} \tag{1}$$

$$\mathrm{SO_3 + H_2O \leftrightarrow H_2SO_4} \tag{2}$$

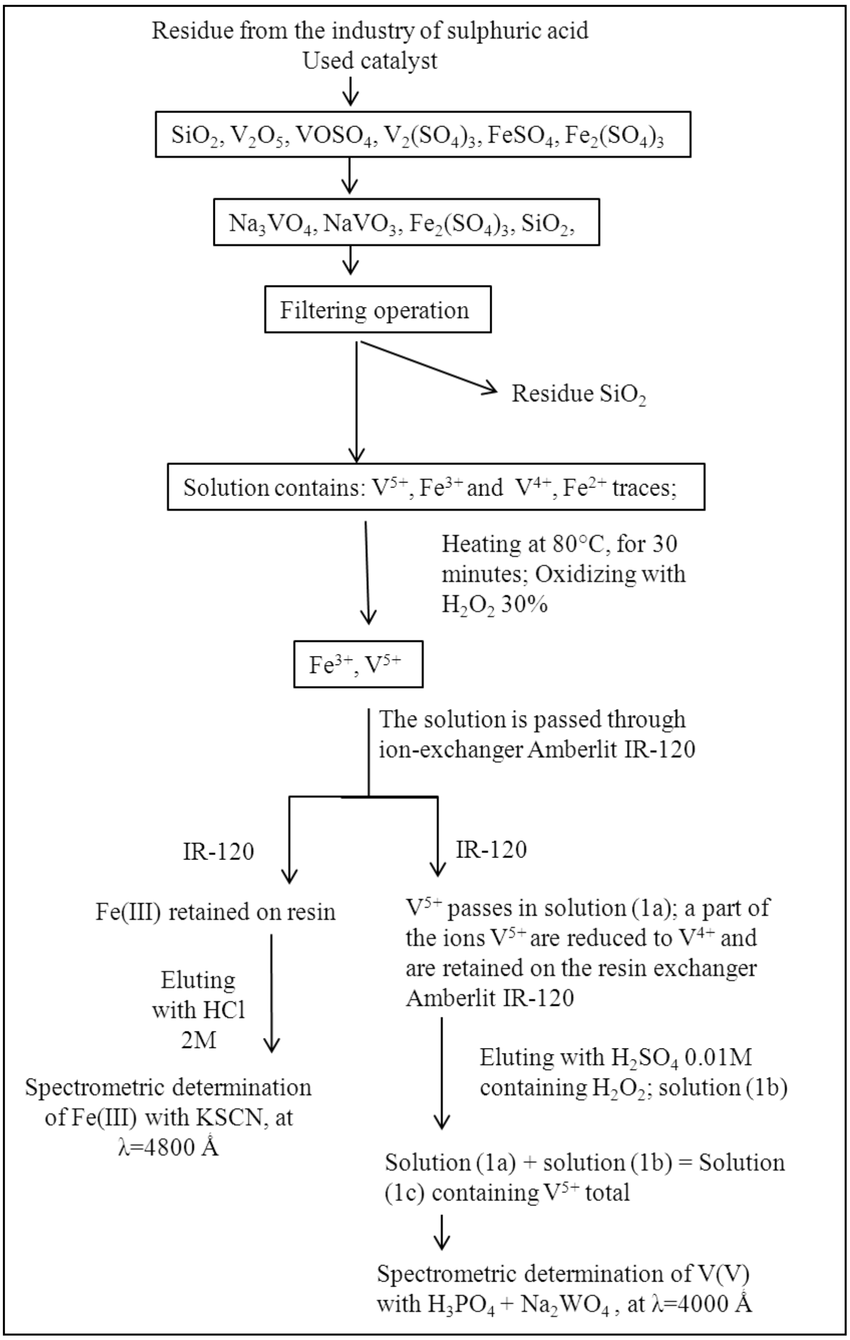
$$\mathrm{FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2 + H_2SO_4} \tag{3}$$

$$\mathrm{Fe_2(SO_4)_3 + 6H_2O \leftrightarrow 2Fe(OH)_3 + 3H_2SO_4} \tag{4}$$

$$\mathrm{VOSO_4 + 2H_2O \leftrightarrow VO(OH)_2 + H_2SO_4} \tag{5}$$

$$\mathrm{V_2(SO_4)_3 + 6H_2O \leftrightarrow 2V(OH)_3 + 3H_2SO_4} \tag{6}$$

$$\mathrm{V_2O_5 + H_2O \leftrightarrow 2HVO_3} \tag{7}$$



Scheme 1 − The behaviour of used catalysts based on V_2O_5 in aqueous solution, separation and determination of V^{5+}/Fe^{3+} ions (Sutiman *et al.*, 2012).

The pH values were determinate in solutions from spent and raw catalyst and have been subjected to heat treatment at different temperatures. 5 g of spent catalyst from each sample was weighed and was placed in contact with 100 mL of distilled water. The pH values of the resulting solution were performed after 24 h and the experimental data are shown in Table 2:

Table 2

PH Values of the Spent Catalyst- Distilled Water, Contact Time 24 h

Sample no.	$m_{\text{spent catalyst}}$ [g]	Vol H_2O, [mL]	Sample characteristics	Contact time, [h]	Determined [pH]
1	5	100	homogeneous	24	2.47
2	5	100	uniform sieving	24	2.30
3	5	100	Dry at 125C	24	2.33
4	5	100	Dry at 250C	24	2.50
5	5	100	Burnt at 600C	24	2.99
6	100	200	homogeneous	24	2.11

The pH values were determined on several systems spent catalyst - distilled water, watching its variation over time. Determinations were performed in static but also in dynamic conditions (stirring) using an analyser CONSORT 831C type multi parameter coupled with a computer.

In Figs. 1 and 2 are given the pH variation in time for spent catalyst samples (raw or heated).

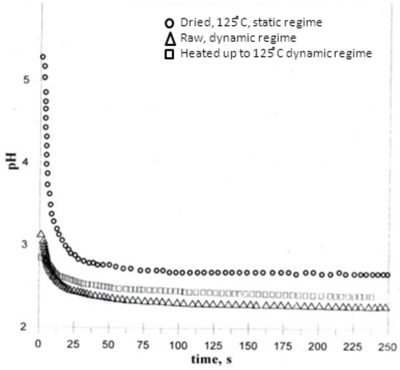


Fig. 1 − The pH variation in time for spent catalyst samples (raw or heated), static regime.

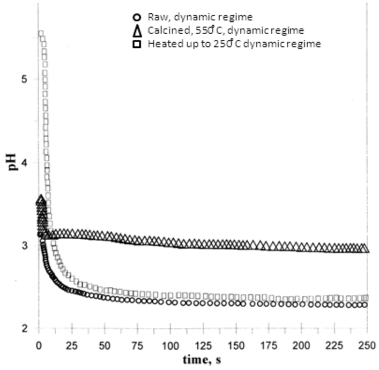


Fig. 2 − The pH variation in time for spent catalyst samples (raw or heated), dynamic regime.

By doing Similarly, the electrical conductivity was determined during the time the $mScm^{-1}$ variation, the evidence of raw or heat-treated catalyst (Dăneț, 1996). The results of experimental determinations are shown in Figs. 3 and 4.

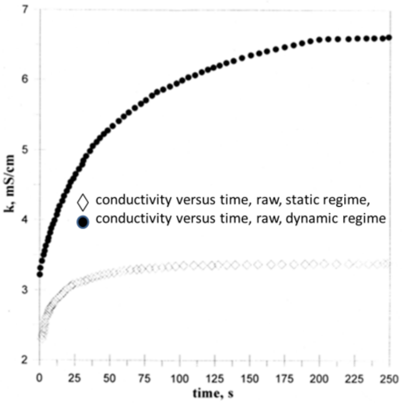


Fig. 3 − The electrical conductivity variation for raw spent catalyst.

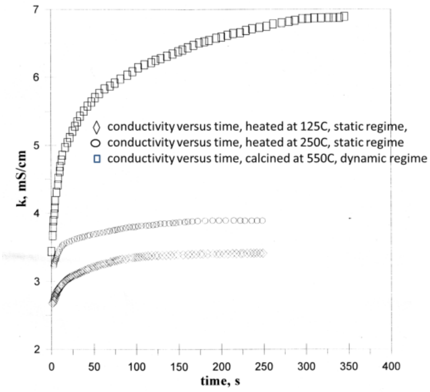


Fig. 4 − The electrical conductivity variation for heated spent catalyst.

Analysing the variation of pH and electrical conductivity for several systems spent catalyst - distilled water is observed that:

− Speed of dissolution of soluble components in the system both in static and dynamic system is maximum when used catalysts in distilled water;

− Increasing the pH and conductivity as Figs. 1-4 is highest in the first few minutes of exposure to the spent catalyst with distilled water;

− Diluents speed soluble catalyst component decreases over time and after about 30 min remains constant, the curves describing the variation of pH and conductivity while flattening;

− Most of the soluble components of the catalyst used in solution pass in the first 30 min of contact;

− The study pH and conductivity variation in time for spent catalyst - distilled water system can appreciate optimum contact time for the system to obtain a complete dissolution of all components soluble;

− Basically, it is considered that the optimum contact between the catalyst used - water for complete dissolution of soluble components is 4-6 h.

Fe^{3+}/V^{5+} *ions separation.* The Fe^{3+}/V^{5+} ions separation involves two steps:

− Oxidation solution (filtrate) obtained from spent catalyst contact with distilled water,

− Separation of ions Fe^{3+} /V^{5+} ions by chemical or ion exchange.

The spent catalyst after contact with distilled water for 6-8 h, separated by vacuum filtration of the insoluble green solution, SiO_2, Fe_2O_3 and V_2O_5 unreacted part.

The resulting solution contains cations V^{3+}, VO^{2+}, V^{5+}, Fe^{2+} and Fe^{3+}, which to be separated, must be brought high oxidation state (Fe^{3+} or V^{5+}), which is made with various oxidizing agents. For this purpose can be used oxidants such as $KMnO_4$, $K_2Cr_2O_7$, H_2O_2, HNO_3, etc. In this case the oxidation was performed with sodium hypochlorite, the reaction can be carried out cold or hot and takes place at high speed. Oxidation reaction is performed under niche, adding small amounts of sodium hypochlorite so that the resulting solution is yellow to clear, pH approximately equal to 4. The solution thus obtained is heated until the chlorine smell disappeared, then proceed to separate the V^{5+} ions Fe^{3+}.

a) *Precipitation of* $Fe^{3\ +}$ *ions with chemical reagents*. For separating ions oxidized Fe^{3+} in solution, it is treated with a mixture of Na_2HPO_4 + CH_3COONa (1:1) when Fe^{3+} ions precipitate as ferric orthophosphate form, according to the reaction:

$$\begin{aligned} \mathrm{Na_2HPO_4 + 2CH_3COONa + Fe_2(SO_4)_3} \\ \mathrm{= 2FePO_4\ + 3Na_2SO_4 + 2CH_3COOH} \end{aligned} \tag{8}$$

Ferric orthophosphate is a sparingly soluble precipitate and separate from the solution by vacuum filtration. The resulting solution after filtration contains only ions V(V) and is used further precipitation of compounds V(V): V_2O_5 or NH_4VO_3.

To precipitate V_2O_5 final solution (filtrate) is treated with NaClO (pH = 10) when rainfall $V_2O_5{\cdot}nH_2O$, insoluble in water, which is separated by filtration and then ash at 600°C, when their reaction is:

$$\mathrm{V_2O_5 \cdot n\,H_2O \rightarrow V_2O_5 + n\,H_2O} \tag{9}$$

In the second version, the solution containing ions V(V) is treated with a solution of ammonia (NH_4OH, approximately 25%) when V^{5+} ions precipitate metavanadat form of ammonium NH_4VO_3 that calcined lead to pure V_2O_5.

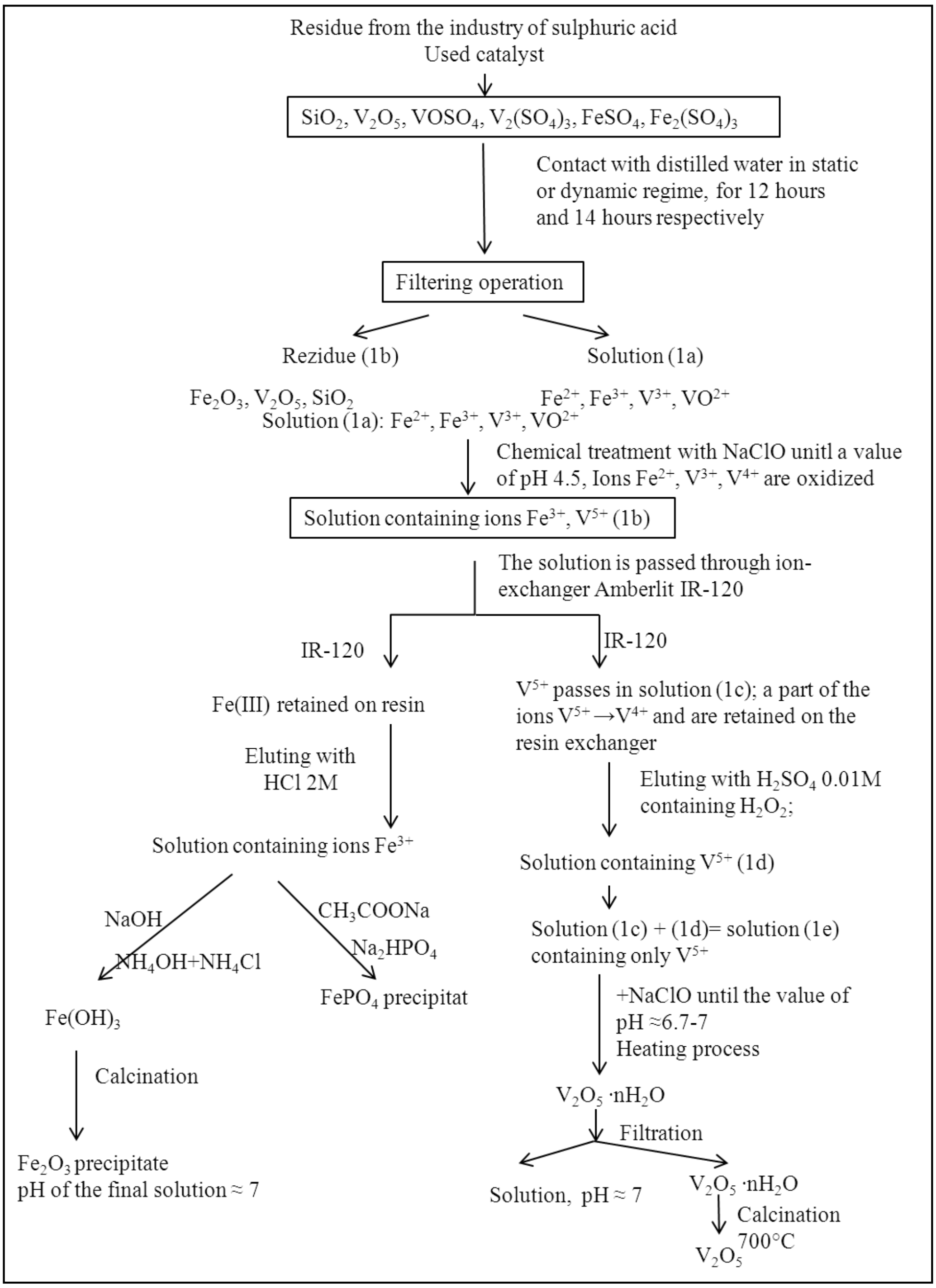
$$\mathrm{2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O} \tag{10}$$

b) *ion exchange method.* For separating Fe^{3+} by V^{5+} ions in solution resulting from oxidation were used two types of ion exchange resins: Amberlite IR120 and Purolite C-150, cationic form H^+, which at lowered pH can retaining only Fe^{3+}ions. V^{5+} ions pass into the solution to collect effluent in a glass bowl (Ionescu, 1964; Luca *et al.*, 1983; Macoveanu *et al.*, 2002).

Fe^{3+} ions retained on the ion exchange resin Amberlite IR120 are passed into solution by treating it with a solution of 10% H_2SO_4 and collected separately.

From this two solutions, we can separate NH_4VO_3 and $Fe(OH)_3$ by treating solutions containing Fe^{3+} ions with a solution of 25% NH_4OH. The precipitates obtained are calcinated to obtain V_2O_5 and Fe_2O_3 respectively. Final results were neutral solutions.

The separation of Fe^{3+} to V^{5+}, Fe_2O_3 and V_2O_5 form of the catalyst used is shown in Scheme 2.



Scheme 2 − The V^{5+}/Fe^{3+} ions from spent catalyst separation.

4. Conclusions

In the process of obtaining an industrial sulphuric acid, oxidation of SO_2 to SO_3 is achieved using catalysts such as V_2O_5 + Fe_2O_3 + K_2O supported on SiO_2. Due to the reducing of SO_2, oxides of composition V_2O_5 and Fe_2O_3 catalyst that undergoes a series of redox transformations and the compounds formed are unfriendly to the environment. This method allows efficiently the separation and determination of useful components from spent catalysts. It also makes possible their recovery and reintroduction as raw materials in new processes. During separation stages are followed some aspects regarding pollution reducing, in order to diminish the amount of wastewater discharged in the environment.

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METODĂ DE SEPARARE ŞI RECUPERARE A V_2O_5/Fe_2O_3 DIN CATALIZATORI UZAŢI

(Rezumat)

Lucrarea se axează pe studiul catalizatorilor uzaţi pe bază de V_2O_5, Fe_2O_3 şi K_2O rezultaţi din procesul de oxidare a gazelor sulfuroase din procesul de obţinere a acidului sulfuric la nivel industrial. În timpul oxidării SO_2 la SO_3 catalizatorii uzaţi suferă o serie de transformări fizice şi chimice, cea mai importantă este reducerea ionilor V^{5+} şi Fe^{3+}. Astfel, V^{5+} se reduce la V^{4+} şi V^{3+} rezultaţi ca VO_2, $VOSO_4$ şi $V_2(SO_4)_3$ şi ionii Fe^{3+} sunt reduşi la Fe^{2+} sub formă de $FeSO_4$. Sulfaţii rezultaţi sunt solubili în apă şi pot fi separaţi prin filtrare de suportul (masa) insolubilă. Oxizii de vanadiu VO_2, V_2O_3 sau V_2O_5 pot reţine cantităţi importante de SO_2 şi SO_3 pe suprafaţa lor iar la contactul cu apa, produşii de hidroliză formaţi sunt toxici şi corozivi. Această lucrare îşi propune să prezinte procesul de separare a ionilor de vanadiu (V^{4+} şi V^{3+}) şi de fier (Fe^{3+}) din catalizatori uzaţi pe bază de V_2O_5 şi Fe_2O_3.