

# The use of ion exchange in the recovery of vanadium from the mass of a spent catalyst used in the oxidation of SO<sub>2</sub> to SO<sub>3</sub>

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In the studies on the recovery of vanadium from vanadium catalyst extracts, three types of polymer strongly acidic ion exchangers were used. The ion exchange resins differed in terms of granularity and their ion exchange capacity. As a result, breakthrough curves were made for three main components of the test extract, i.e.: ions of vanadium, iron and potassium. On this basis the optimum conditions for the removal of iron ions from the solution were defined and the technological concept of the process in the semi-technical scale was proposed.

**Keywords:** spent vanadium catalyst, recovery of vanadium, ion exchange, solid waste utilization.

## INTRODUCTION

A contact method using vanadium catalysts is currently the technology most widely used for producing sulfuric acid(VI).

Working in a contact apparatus, the vanadium catalyst gradually loses its catalytic properties and it needs to be replaced. Inactive catalyst's weight is toxic waste for the environment. The content of sulfur oxides adsorbed in the catalyst pores is about 20%<sub>mas</sub><sup>1</sup>. Sulfur oxides react with rainwater and form acidic leachate leaching toxic ingredients of the used catalyst weight. The waste from landfills had high concentrations of vanadium and other heavy metals such as Fe, Pb, Zn, Hg, Cd and As<sup>2</sup>. To date, no effective methods of managing or securing the used catalyst weight have been developed. One way to use this annoying waste is to recover vanadium compounds through leaching with different media such as NaOH, KOH, H<sub>2</sub>SO<sub>4</sub>, CO(NH<sub>2</sub>)<sub>2</sub><sup>1, 3-5</sup>. The solid waste which remains after extraction, after an earlier stabilization and cementation, can be used as building material in road construction or mining<sup>6</sup>. An example of the chemical composition of spent vanadium catalysts is presented in Table 1<sup>1-3</sup>.

The most important research problem is the recovery of the greatest possible amount of vanadium and potassium from solutions after the vanadium catalyst extraction, while ensuring minimal contamination of the product with iron compounds. Iron and vanadium are present in obtained lyes in different ionic forms, which impedes their separation. Methods based on direct selective precipitation of components, depending on the pH of a solution, are characterized by co-precipitation of iron and vanadium compounds<sup>7, 8</sup>.

The aim of this thesis was to determine the applicability of polymeric ion exchangers for the recovery of vanadium and potassium from extracts of a vanadium catalyst.

**Table 1.** The chemical composition of spent vanadium catalysts used for the oxidation of SO<sub>2</sub> to SO<sub>3</sub>

Component	Content [% <sub>mas</sub> .]		
	ref. 3	ref. 4	ref. 5
V <sub>2</sub> O <sub>5</sub>	4.80	4.40	4.68
K <sub>2</sub> O	5.80	7.40	8.70
Fe <sub>2</sub> O <sub>3</sub>	2.10	1.50	2.59
SiO <sub>2</sub>	49.50	38.90	57.31

## MATERIAL AND METHODS

### Material

The equipment used in the studies contained: a spent vanadium catalyst from the landfill of a plant producing sulfuric acid with the contact method, ion exchangers: Amberlite IR – 120 plus (H), Dowex 50W X4 – 100 (H), Dowex 50W X4 (H), hereinafter referred to as J1, J2 and J3 respectively.

### Analytical methods

The concentrations of iron and potassium ions were determined with the FAAS method using Sigma SavantAA GBC spectrometer.

The vanadium ion concentration was determined spectrophotometrically as a complex with hydrogen peroxide. Vanadium ions in concentrated sulfuric acid and 3% aqueous hydrogen peroxide react according to equation 1<sup>9</sup>.



This combination shows the maximum absorption at the wavelength of 450 nm and the molar absorption coefficient is 300 dm<sup>3</sup> · mol<sup>-1</sup> · cm<sup>-1</sup>. The measurements were performed in quartz cuvettes with the optical path length of 10 mm. The determinations were performed using a two-beam spectrophotometer UV – Vis UVD – 3000 LABOMED.

### Research methodology

The material was milled and then divided into appropriate fractions. The fraction of the particle size of 1.5 – 0.75 mm was used in the studies. In the next stage, the catalyst was leached with 5%<sub>mas</sub> H<sub>2</sub>SO<sub>4</sub> in the ratio of solid phase to liquid phase of 1:10 (wt./vol.). The extraction was carried out for 8 hours at a temperature of 293 K, and then the mixture was clarified. The resulting solution was subjected to chemical analysis determining the concentration of vanadium, iron and potassium ions. The composition of lyes: vanadium 2765 ± 23, iron 576 ± 6, potassium 6308 ± 73 mg · dm<sup>-3</sup>.

The column sorption experiments were performed on three ion-exchange resins (Table 2). A constant flow of solution through the ion-exchange column equal 2 ml · min<sup>-1</sup> was used. In order to determine the breakthrough curves for iron, vanadium and potassium ions

**Table 2.** Characteristics of the used ion-exchange beds

Parameter	J1	J2	J3
Particle size [mesh]	16 – 50	50 – 100	100 – 200
Ion exchange capacity [meq · cm <sup>-3</sup> ]	1.82 ± 0.03 (1.8)*	1.17 ± 0.03 (1.1)*	1.11 ± 0.05 (1.1)*
Bed volume [cm <sup>3</sup> ]	32.64 ± 0.08	30.98 ± 0.11	40.5 ± 0.3
Free volume [cm <sup>3</sup> ]	14.7 ± 0.6	13.1 ± 0.7	16.6 ± 1.1
Bed height [cm]	17.08 ± 0.05	15.75 ± 0.06	17.50 ± 0.14

\* value specified by the manufacturer.

effluent collected in known time intervals was analyzed and the concentration of ions was determined. The bed was regenerated by dosing 100 cm<sup>3</sup> of 2M hydrochloric acid solution, the leakage from the column was collected in a volumetric flask with a capacity of 200 or 250 cm<sup>3</sup>, after completing the elution, and subjected to chemical analysis determining the concentration of vanadium, iron and potassium ions.

## RESULTS AND DISCUSSION

Based on the studies conducted, the relationships of vanadium, iron and potassium ion weights were defined with respect to the bed unit volume, retained by ion-exchange resins, and curves for ion exchange, depending on the volume of the solution deposited on the bed

These relationships make it possible to determine: the percentage of exchange for a given metal (A), the breakthrough volume (V<sub>0</sub>) and bed saturation (V<sub>v</sub>), and the practical (Q<sub>A</sub>) and total (Q<sub>v</sub>) ion-exchange capacity, i.e. fundamental parameters describing the characteristics of the test ion-exchange beds. The volumes of V<sub>0</sub> and V<sub>v</sub> were determined graphically from the relations in Figures 1–3, while the other mentioned parameters were calculated according to equations 2–5<sup>10–12</sup>. The determined and calculated parameters are summarized in Table 3.

$$A = \frac{m_{M_0} - m_{M_w}}{m_{M_0}} \cdot 100\% \quad (2)$$

$$Q_v = \frac{(V_0 + 0.5 \cdot \Delta V) \cdot C_0}{V_K} \quad (3)$$

$$\Delta V = V_v - V_0 \quad (4)$$

$$Q_A = \frac{V_0 \cdot C_0}{V_K} \quad (5)$$

where:

m<sub>M<sub>0</sub></sub> – mass of metal deposited to the bed, mg,

m<sub>M<sub>w</sub></sub> – mass of metal in the leakage, mg,

V<sub>v</sub> – bed saturation volume, cm<sup>3</sup>,

V<sub>0</sub> – leakage volume at which the bed breakthrough occurs, cm<sup>3</sup>,

ΔV – leakage volume corresponding to the elution from the work area column, cm<sup>3</sup>,

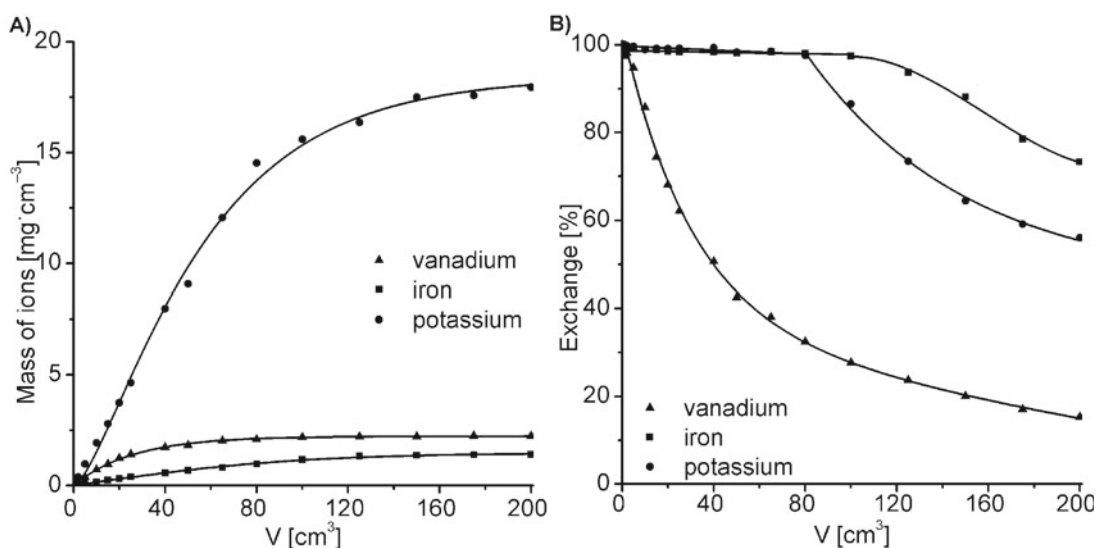
C<sub>0</sub> – initial concentration of metal, mg · cm<sup>-3</sup>,

V<sub>K</sub> – ion exchange bed volume, cm<sup>3</sup>.

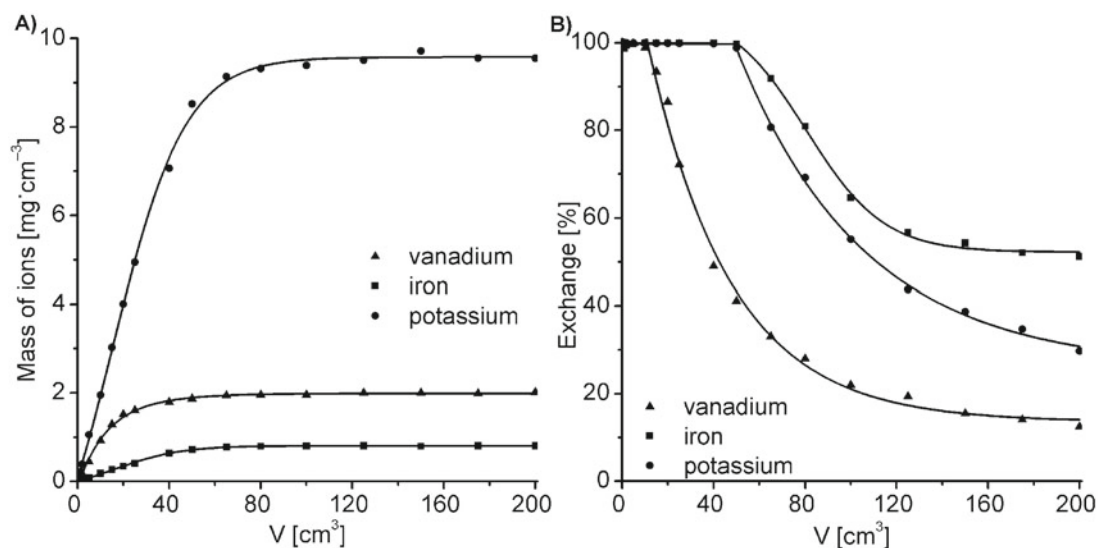
In the applied elution conditions, the affinity of metals for all ion exchange resins used increases in the series (Fe<sup>3+</sup>/Fe<sup>2+</sup>) < K<sup>+</sup> < (VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup>), as illustrated with the relations in Figures 1B, 2B and 3B. It should be noted that with increasing diameter of ion exchange particles, the affinity for vanadium ions decreases while it increases for iron and potassium ions. Almost twice as much potassium ions are exchanged on bed J1 as compared to beds J2 and J3. However, the number of the listed vanadium and iron ions is similar for all ion exchange resins used.

The summary of the practical and total ion exchange capacity for each metal presented in Table 3 shows that these values increase with increasing ion exchange particles. We can also see that the breakthrough volume and bed saturation volume increase with increasing ion exchange particles for ions of iron and potassium. For vanadium ions, however, the breakthrough volume decreases with increasing ion exchange particles, while the bed saturation volume increases.

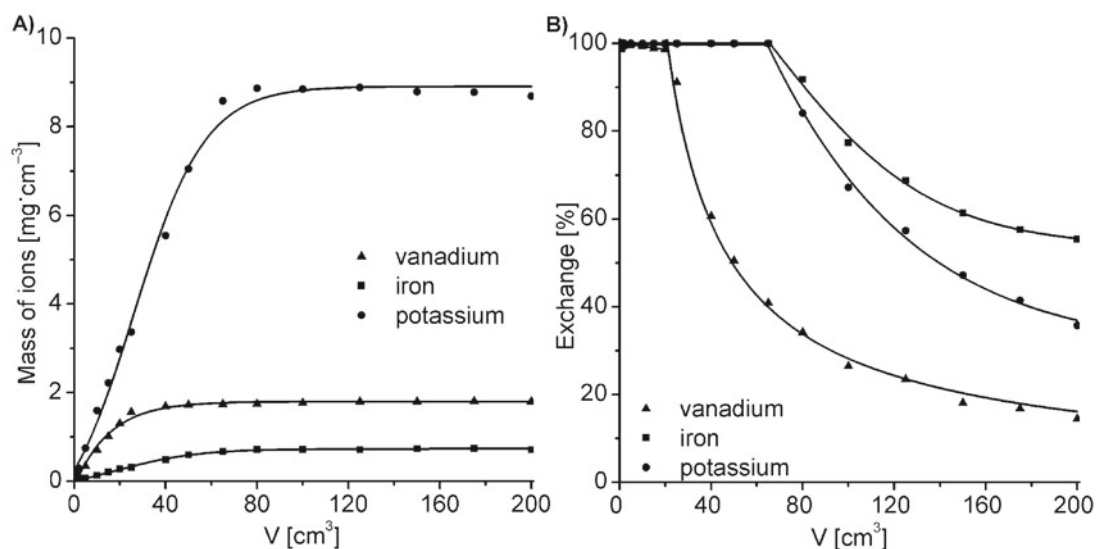
The most important aspect of the studies was to remove the maximum amount of iron ions from the solu-



**Figure 1.** A) The mass of metal exchanged by J1 per 1cm<sup>3</sup> of the bed volume depending on the deposited solution volume. B) The percentage of exchange depending on the solution volume deposited to the ion exchange resin 1



**Figure 2.** A) The mass of metal exchanged by J2 per 1 cm<sup>3</sup> of the bed volume depending on the deposited solution volume. B) The percentage of exchange depending on the solution volume deposited to the ion exchange resin 2



**Figure 3.** A) The mass of metal exchanged by J3 per 1 cm<sup>3</sup> of the bed volume depending on the deposited solution volume. B) The percentage of exchange depending on the solution volume deposited to the ion exchange resin 3

tion with a minimum loss of potassium and vanadium ions. Among the three ion exchange resins used, J1 is characterized by the highest affinity for iron, and at the same time the lowest affinity for vanadium. For the bed breakthrough volume, in relation to iron ions, equal to 90 cm<sup>3</sup>, which is 2.76 of the bed volume, 97.8, 92.1 and 30.1% of iron, potassium, and vanadium ions are respectively removed from the solution. In the case of J2 the bed breakthrough caused by iron ions occurs for a volume of 57.5 cm<sup>3</sup>, which is 1.86 of the bed volume, for this volume it is possible to remove respectively 99.8, 89.8, 37.1% of iron, potassium, and vanadium ions. The third of the used ion exchange resins J3 has the bed breakthrough volume in relation to iron ions of 67 cm<sup>3</sup>, which is 1.65 of the bed volume. For such a volume 100, 99.96 and 39.5% of iron, potassium and vanadium ions are respectively removed from the solution.

Designing a system for recovering vanadium and potassium from vanadium catalyst extracts requires relevant technological assumptions. In order to determine the conduct of the process (i.e. the number and volume of ion exchangers), we should determine the volume of lye production after the vanadium catalyst extraction.

When developing the conditions for vanadium recovery in a semi-technical scale, we can assume that the stream of the extract from the vanadium catalyst will reach 600–1000 dm<sup>3</sup> per day. Using the linear velocity of the eluent flow through the column of 0.63 m · h<sup>-1</sup> and assuming that the working time of the column is 4 hours, we should use two columns with the following internal dimensions: height  $h = 1.16$  m, diameter  $\varphi = 0.5$  m, ion exchange bed volumes  $V = 228.5$  dm<sup>3</sup>. Figure 4 shows a diagram of two columns filled with ion exchange resins, joined in parallel and working alternately.

The spent vanadium catalyst is extracted for 8 hours in an agitator (1), in 5%<sub>mas.</sub> sulfuric acid solution while maintaining the ratio of solid phase to liquid phase 1:10 (wt./vol.). The solution in the next stage is subjected to filtration (3), after separation of solids, and the clear lye is stored in a tank (2). The extract is then dispensed to one ion exchange column (4). After exhausting the practical ion exchange capacity, the column is excluded from work and the extract is sent to the second column on which the exchange takes place. At the same time the ion-exchange resin in the first column is subjected to regeneration. The eluate devoid of iron ions and

**Table 3.** Parameters of the exchange process on beds J1, J2 and J3 for the flow rate of  $1.05 \text{ cm} \cdot \text{min}^{-1}$ 

Parameter	J1	J2	J3
Vanadium			
Bed breakthrough volume [ $\text{cm}^3$ ]	5.0	13.6	22.0
Bed saturation volume [ $\text{cm}^3$ ]	90.0	72.5	45.0
Practical ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	0.42	1.21	1.49
Total ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	4.02	3.84	2.28
Iron			
Bed breakthrough volume [ $\text{cm}^3$ ]	90.0	57.5	67.0
Bed saturation volume [ $\text{cm}^3$ ]	137.5	80.0	75.0
Practical ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	1.59	1.07	0.95
Total ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	2.01	1.28	1.01
Potassium			
Bed breakthrough volume [ $\text{cm}^3$ ]	100	50.0	65.0
Bed saturation volume [ $\text{cm}^3$ ]	225*	100	80.0
Practical ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	19.33	10.18	10.12
Total ion exchange capacity [ $\text{mg} \cdot \text{cm}^{-3}$ ]	31.41	15.27	11.29

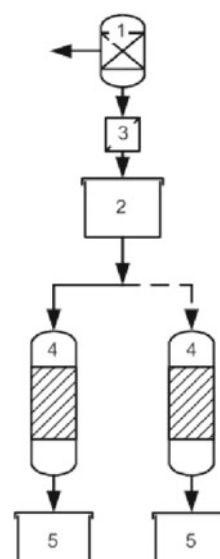
\* extrapolated value.

collected in a tank (5) is further treated chemically to separate vanadium in the form of  $\text{KVO}_3$  or  $\text{V}_2\text{O}_5$ .

Table 4 shows the mass flows of lye components and media used in the process for installation producing 600–1000  $\text{dm}^3$  of the extract per day, where eighty percent utilization of the practical ion exchange capacity of ion exchange resins has been assumed.

The data presented in Table 4 indicate that the highest yield per unit of the apparatus is obtained for bed J1 having the highest ion exchange capacity. However, the lowest level of iron ion removal is obtained for this bed, as compared to the other two ion exchange resins (J2 and J3), where iron ions are removed almost completely.

Due to the composition of the solution obtained after the ion exchange stage, it is most convenient to recover vanadium in the form of  $\text{KVO}_3$  by salting out  $\text{K}_2\text{SO}_4$ . The excess of sulfuric acid used to leach

**Figure 4.** Schematic diagram of iron removal from vanadium catalyst extracts on the ion-exchange bed: 1) agitators, 2) lye tank, 3) filters, 4) ion exchange columns, 5) solution tanks

vanadium catalyst should be neutralized with potassium hydroxide to yield a solution close to saturation in relation to  $\text{K}_2\text{SO}_4$  ( $\sim 0.5 \text{ M}$ ). Under conditions of  $\text{pH} \approx 7$ ,  $\text{KVO}_3$  will crystallize out of solution. Determining the most favourable potassium metavanadate precipitation conditions will require detailed equilibrium studies on the  $\text{KVO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$  system.

The solutions generated during ion exchange resin regeneration and containing significant amounts of hydrochloric acid can be regenerated to recover hydrochloric acid through membrane distillation<sup>13–15</sup>.

## CONCLUSIONS

The studies used three types of ion exchange resins which differed in terms of their particle size and ion-exchange capacity. All test ion exchange beds were

**Table 4.** The mass balance of the process in a one-day cycle without regard to loss between stages

Extraction	Raw materials [kg]		
	Extraction	Extract	Regeneration
Catalyst	100	Fe 0.58	HCl 53.3
$\text{H}_2\text{SO}_4$	51.6	V 2.77	$\text{H}_2\text{O}$ 708.3
$\text{H}_2\text{O}$	980.2	K 6.31	
		$\text{H}_2\text{SO}_4$ 51.6	
		$\text{H}_2\text{O}$ 980.2	
		Ion exchange [kg]	
		Eluate from J2 (capacity of 680 $\text{dm}^3$ )	
Eluate from J1 (capacity of 1000 $\text{dm}^3$ )		Eluate from J3 (capacity of 600 $\text{dm}^3$ )	
Fe	0.012	Fe 0.001	Fe 0
V	1.93	V 1.19	V 1.01
K	0.50	K 0.44	K 0.002
$\text{H}_2\text{SO}_4$	51.6	$\text{H}_2\text{SO}_4$ 35.1	$\text{H}_2\text{SO}_4$ 31.0
$\text{H}_2\text{O}$	980.2	$\text{H}_2\text{O}$ 666.5	$\text{H}_2\text{O}$ 588.2
$\text{H}_2\text{O}$ for rinsing	140	$\text{H}_2\text{O}$ for rinsing 140	$\text{H}_2\text{O}$ for rinsing 140
		Ion-exchange resin regeneration [kg]	
		J2	
		J3	
Fe	0.568	Fe 0.393	Fe 0.348
V	0.84	V 0.69	V 0.65
K	5.81	K 3.85	K 3.78
HCl	53.3	HCl 53.3	HCl 53.3
$\text{H}_2\text{O}$	708.3	$\text{H}_2\text{O}$ 708.3	$\text{H}_2\text{O}$ 708.3
$\text{H}_2\text{O}$ for rinsing	140	$\text{H}_2\text{O}$ for rinsing 140	$\text{H}_2\text{O}$ for rinsing 140



characterized by the greatest affinity for iron ions, and then for ions of potassium and vanadium.

The ion exchange conditions applied allowed to remove from the extraction solution 97.8, 99.8 and 100% of iron ions and 92.1, 89.8 and 99.96% of potassium ions respectively using Amberlite IR – 120 plus (H), Dowex 50W X4 – 100 (H), Dowex 50W X4 (H). There was a simultaneous loss of vanadium ions amounting to 30.1, 37.1 and 39.5% for J1, J2 and J3 respectively.

Taking into account the test results and calculations, the best solution is to use a column filled with Amberlite IR – 120 plus (H). We can get the highest yield per unit of the apparatus and the lowest loss of vanadium for this ion exchange resin. The disadvantage is the incomplete removal of iron ions, yet the reduction in the concentration of that component to the level of  $\sim 12 \text{ mg} \cdot \text{dm}^{-3}$  is satisfactory.

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