

Leaching of vanadium from sulphuric acid manufacture spent catalysts^(*)

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Abstract Recovery of vanadium contained in spent catalysts from the manufacture of sulphuric acid has been studied in this work, resulting in an industrial multistage process for the treatment of them avoiding direct deposition or dumping. Characterization of supplied spent catalysts samples, confirmed vanadium levels showed in the literature. The study of variables influencing leaching process: type of leaching agent, leaching agent concentration, S/L ratio, stirring speed and temperature, allows to fix the most advantageous conditions using industrial application criterion and verifying that the process is diffusion controlled. The work is completed by developing an industrial leaching cycle simulation with the aim of reproducing real performance of spent catalyst, proposing operating conditions, and verifying the non-toxic character of the final residue obtained.

Keywords Spent catalysts. Vanadium pentoxide. Leaching. Sulphuric acid manufacture.

Lixiviación de vanadio de catalizadores agotados procedentes de la fabricación del ácido sulfúrico

Resumen En el presente trabajo se ha estudiado la recuperación del vanadio contenido en los catalizadores agotados procedentes de la fabricación del ácido sulfúrico, planteando un proceso industrial multietapa para el tratamiento de estos residuos, evitando su deposición o vertido directos. La caracterización de las muestras de catalizadores agotados disponibles confirmó los valores encontrados en la bibliografía. Se estudiaron las variables que influyen en el proceso de lixiviación (tipo de agente de lixiviación y concentración del mismo, relación S/L, velocidad de agitación y temperatura) definiendo las condiciones más adecuadas desde el punto de vista industrial y verificando que el proceso está controlado por mecanismos difusionales. El trabajo se completa con la simulación de un ciclo industrial de lavado del catalizador y la verificación de la nula toxicidad de los lixiviados obtenidos por degradación del residuo final.

Palabras clave Catalizadores agotados. Pentóxido de vanadio. Lixiviación. Fabricación de ácido sulfúrico.

1. INTRODUCTION

The increase of environmental concerns and legislation over the disposal of hazardous residues is forcing to companies and countries to process their own waste products and residues. Options available depends on local conditions, markets and existing technology. Spent catalysts containing Mo, Cr, and V are processed at specified centralised facilities due to their value and scarcity of primary processing plants. Vanadium has many industrial uses and its contribution with environmental contamination is growing every day.

In the last 10 years research about the vanadium effects on living beings, has been increasing substantially, due to its presence in the environment from different sources. Interest for vanadium and their compounds is due to its toxic effects and uses in some biomedical areas: such antineoplastic, cholesterol and glucose level blood, diuretic, oxygen haemoglobin affinity^[1 y 2]. Vanadium toxic effects are so due to the fact of its property of inhibiting many enzymatic systems. Vanadate and vanadyl ions make chemical complexes exhibiting the property of inhibiting or increasing the activity of the enzymes participating

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in the DNA and RNA synthesis. They also induce mutagenic and genotoxic effects^[3].

Today, over 85 % of world production of vanadium are consumed in carbon and stainless steel making as also as an alloying agent to produce ferro-vanadium. Other industrial applications can be found in ceramic and chemical industries. Vanadium batteries are being developed in Australia and Japan utilizing vanadium pentoxide electrolyte as the core material for use in electrical load leveling in power-generating units. Smaller, rechargeable vanadium pentoxide lithium batteries are already in production. 1997 worldwide demand for vanadium pentoxide was estimated in february 1998 to be 160 million pounds up from 100 million pounds in 1994. Nearly 30 % of demand worldwide for vanadium pentoxide came from the USA, most of which was imported. Demand from traditional uses is expected to grow at about 5 % annually over the next 10 years. China Russia, South Africa and the USA produce vanadium pentoxide from vanadium bearing magnetite ores, concentrates and slags while Japan and USA produce vanadium pentoxide from petroleum residues, ash and spent catalysts^[4].

There is a wide variety of approaches for treating alumina based spent catalysts, which are usually contaminated with 10-20 % oil residues^[5]. Commercial operations focus on vanadium and molybdenum recovery by roasting at high temperatures and leaching remaining metal oxides to dissolve vanadium and recover it from leach solutions using solvent extraction techniques^[6 y 7], alkaline pressure leaching and later precipitation as its hydroxide^[8 y 9] or salt roasting and leaching, recovering vanadium by precipitation of ammonium metavanadate^[10-12].

Spent catalysts from the manufacture of sulphuric acid are used in the process of catalytic oxidation of sulphur dioxide to sulphur trioxide and consists of a relatively pure mixture of V(IV) and V(V) salts, probably $\text{VO}(\text{SO}_4)$ and $(\text{VO}_2)_2\text{SO}_4$, as well as V_2O_5 dispersed in a melted mixture of alkaline pirosulphates (mainly sodium and potassium) over a silica substrate. Vanadium content is around 4-5 % w/w. Alkaline leaching is selective for vanadium over iron but dissolves some silica and is more costly with reagents. Sulphuric acid leaching does not dissolve silica, and can be modified to produce a leach solution containing either V(IV) or V(V) for further processing.

Dilute sulphuric acid has been used at 60-90 °C, alone own^[13], and in the presence of hydrazine^[14],

oxalic acid^[15], or sulphur dioxide^[16] as reducing agents for V(V). This prevents the precipitation of vanadic acid and maximises the extraction of vanadium, but the leach solution must be re-oxidised before V_2O_5 can be precipitated. More concentrated sulphuric acid leaching or roasting the catalyst in its own acid at 200 °C and water leaching, is equally effective and results in an acidic V(IV)/V(V) leach liquor for oxidation and neutralisation. The main problem is that $\text{Fe}(\text{OH})_3$ co-precipitates with vanadic acid around pH 1.5-2.5 and contaminates the final product.

However, solvent extraction of vanadium offers the greatest selectivity and highest purity V_2O_5 product. There is no reference of existing plants for recovery of vanadium from these silica based spent catalysts. The actual treatment of this toxic and hazardous residue consists of spent catalyst vitrification and later controlled dumping in dedicated areas. The purpose of the present work is to study optimum leaching conditions for this kind of industrial waste using several reagents and establish mechanism controlling the process.

Recovery of vanadium from leach process solutions was attempted following two ways: precipitation as V_2O_3 either directly or after reduction with Na_2SO_3 , or solvent extraction. Direct precipitation (pH>10) with KOH yields low recovery of vanadium and high contents of this metal in residual solution while a previous reduction gets a gelatinous solid with 50 % of V_2O_3 and residual humidity up to 85 %. That means a serious inconvenient in order to handle this product and recover potassium sulphate.

Organic solvent extraction of vanadium with primary amines and mixtures with phosphine oxides dissolved in kerosene allows a 99 % recovery of this metal, which is finally obtained as ammonium metavanadate. Results of organic solvent extraction of vanadium in this media will be discussed in a next paper.

2. EXPERIMENTAL

Spent catalyst mass used in manufacture of sulphuric acid were supplied by *Española del Zinc S.A.* and *AEMEDSA* in Cartagena, Spain. The samples were ground to a particle size K_{80} between 2 and 4 mm, since lower grain sizes did not improve leaching efficiencies in preliminary tests. Chemical analysis of samples supplied are shown in table I. V, Fe, Co, Ni, Al, Ca and Mg contents were determined by atomic absorption spectroscopy, Na

Table I. Elemental composition of spent catalyst samples

Tabla I. Composición elemental de las muestras de catalizadores agotados

Element	Sample A	Sample B
	(% w/w, dry basis)	
V	4.04	4.38
S	6.37	12.50
Na	0.26	0.93
K	6.86	6.03
Fe	0.70	0.96
Co	<0.01	<0.01
Ni	0.02	<0.01
Al	0.58	0.58
Ca	0.42	0.31
Mg	0.06	<0.01
Insoluble	48.18	48.20

and K were analyzed by flame spectroscopy and sulphur were gravimetrically determined as barium sulphate. Mixtures of both samples (1/1) were used for all experiments, except for industrial leaching cycle tests.

All leaching tests were conducted in an 1 L glass vessel submerged in a thermostatic bath at atmospheric pressure. The vessel had four necks: one for the stirrer, one for the thermometer, one for the inlet of the sample and the last served the purpose of withdrawal of samples at regular intervals of time. Volume correction after sample collection were not carried out since volume of samples withdrawn (slurry) were negligible and perfectly homogenized inside the reactor. Temperature range investigated was from room values to 65 °C. Minimum agitation speeds were fixed to ensure total suspension of solids in the fluid. All chemicals employed were AR grade.

3. RESULTS AND DISCUSSION

3.1. Leaching with sulphuric acid

The influence of temperature, agitation speed and sulphuric acid concentration in leaching solutions were investigated. Figure 1 shows leaching kinetics of all tests performed. It can be seen that 95 % of total vanadium recovered in each test is solubilized in the first five minutes of experiment.

The data given in figure 1 were analysed with the aid of established shrinking core model^[17]. The respective diffusion through insoluble product layer plots using Crank model, shows a linear

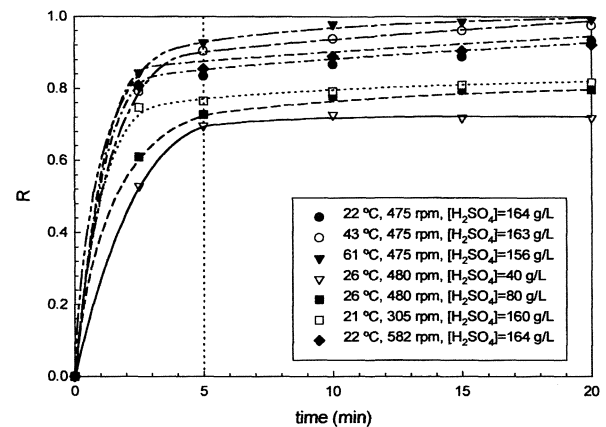


Figure 1. Leaching kinetics of spent catalysts using sulphuric acid solutions.

Figura 1. Cinética de lixiviación de catalizadores agotados empleando disoluciones de ácido sulfúrico.

relationship between the terms $1 - \frac{2}{3}R - (1-R)^{2/3}$ and reaction time when $t < 10$ min.

$$1 - \frac{2}{3}R - (1-R)^{2/3} = k \cdot t$$

where R is the fraction of vanadium leached and k is the apparent rate constant according to:

$$k = \frac{2bMDC}{pr^2}$$

where k =stoichiometric coefficient (dimensionless). M =molecular weight. D =diffusion coefficient of vanadium in porous medium (m^2/min), C =Concentration of leaching agent (mol/m^3), σ =density of residue (kg/m^3) and r =radius of unreacted particle (m).

Values of regression coefficients are showed in table II.

An arrhenius plot was constructed using apparent rate constants calculated in order to evaluate activation energies and verify that the process is diffusion controlled (Fig. 2).

The slope of the line obtained gives an activation energy of 18.4 $kJ mol^{-1}$ with a correlation coefficient >0.9999 . This low value of activation energy confirms that the process is mainly diffusion controlled.

The effect of stirring and sulphuric acid concentration on vanadium leaching is summarized in fig 3. The results show that the rate of vanadium dissolution increases as those two parameters increases, finding linear relationships

Table II. Regression coefficients for diffusion through insoluble product layer models

Tabla II. Coeficientes de regresión para los modelos de difusión a través de superficie de producto insoluble

Conditions			
T (°C)	Agitation speed (rpm)	Sulphuric acid concentration (g/L)	r
22	475	164	0.9992
43	475	163	0.9230
61	475	156	0.9128
26	480	40	0.9566
26	480	80	0.9111
21	305	160	0.9926
22	582	164	0.9901
Average			0.9550

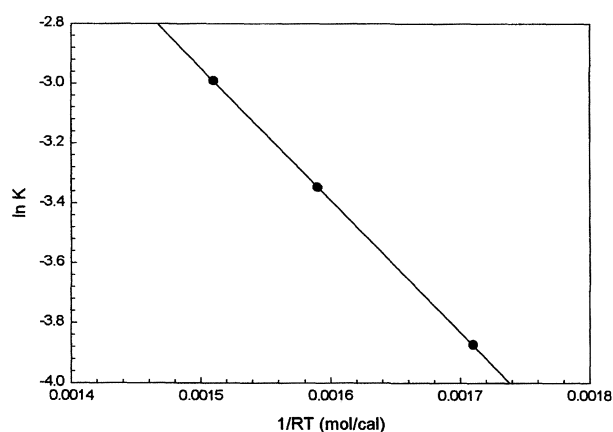


Figure 2. Arrhenius plot of the \ln of apparent rate constant, k , against $1/RT$ (T = bulk solution temperature) in acid media.

Figura 2. Gráfica de Arrhenius del \ln de la constante de velocidad aparente, k , frente a $1/RT$ (T = Temperatura de la disolución) en medio ácido.

between them and apparent kinetic constants with regression coefficients > 0.9990

Finally a relationship between final vanadium leaching yield and initial sulphuric acid concentration (g/L) in leach solutions was found:

$$\%R = 61.15 + 0.23 \cdot [H_2SO_4] \quad r = 0.9999$$

That means that using 160 g/L sulphuric acid solutions at room temperature, up to 98 % of vanadium can be recovered. It was found no relationship between final acidities of solutions and vanadium recovery yields.

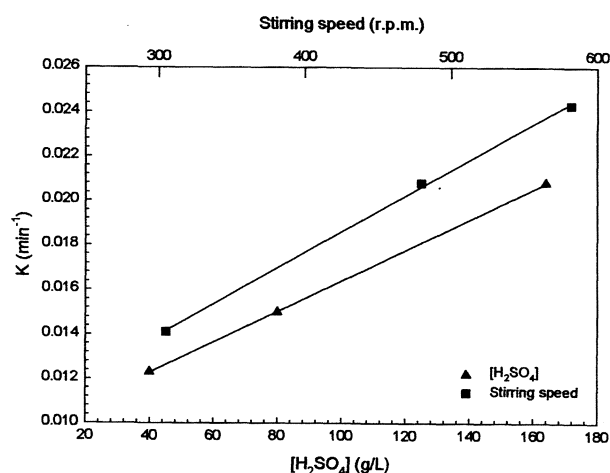


Figure 3. Effect of stirring speed and sulphuric acid concentration on vanadium dissolution rate.

Figura 3. Efecto de la velocidad de agitación y la concentración de ácido sulfúrico en la velocidad de disolución del vanadio.

3.2. Leaching with alkaline reagents

Alkaline leaching of spent catalysts were carried out following the same methodology that used for sulphuric acid tests. Figure 4 shows leaching kinetics of all tests performed in alkaline media (NaOH and KOH). It can be seen that total vanadium recovery is reached but it is necessary longer times than in acidic media in similar conditions.

The data given in figure 4 were fitted to a shrinking core model with diffusion controlled mechanism. The activation energies obtained for

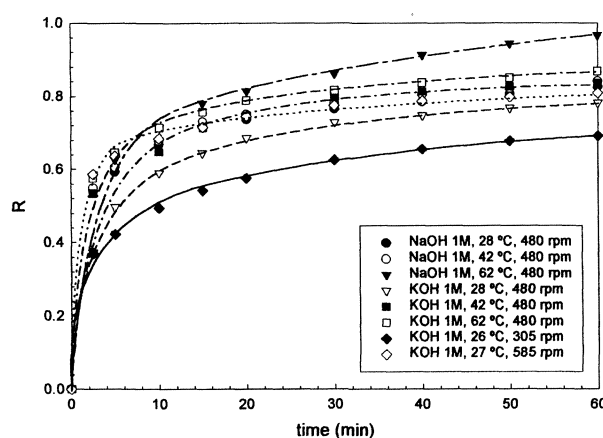


Figure 4. Leaching kinetics of spent catalysts using alkaline solutions.

Figura 4. Cinética de lixiviación de catalizadores agotados empleando agentes alcalinos.

both KOH and NaOH can be obtained using Arrhenius plots showed in figure 5, and confirms that the hypothesis of a diffusion controlled process is correct (2.98 kJ mol⁻¹ for NaOH and 12.1 kJ mol⁻¹ for KOH)

The effect of stirring was investigated using KOH solutions as leaching agents. Since diffusion controlled mechanism is proposed, an increase in agitation speed would have result in faster kinetics. This conclusion is confirmed and can be seen in figure 6.

3.3. Simulation of an industrial leaching cycle

Allowing for results obtained in previous experiments, an industrial leaching cycle to simulate real conditions was developed. Theoretically, in order to obtain a final residue with less than 0.03 % (w/w) of vanadium using a leach solution 20 g/L H₂SO₄, and a S/L ratio 1/2.5, it is necessary a three stage countercurrent process. The scheme for this conditions is showed in figure 7 and summarized results are given in table III.

Toxicity of final residue was determined using EP tests. Leach obtained from this test were analyzed using the Mutatox Test^[18], which uses a special dark strain (M169) of luminescent bacteria to detect the presence of genotoxic agents. EC50 values for 5 min were 231 % and 264.7 % in 15 min. That values ensures the absence of genotoxic chemicals in effluent streams from biological degradation of final residues obtained.

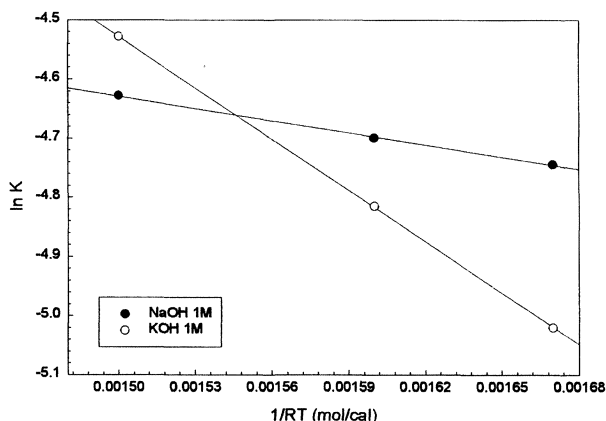


Figure 5. Arrhenius plots of the ln of apparent rate constant, k, against 1/RT (T = bulk solution temperature) in alkaline media.

Figura 5. Gráfica de Arrhenius del ln de la constante de velocidad aparente, k, frente a 1/RT (T = Temperatura de la disolución) en medio alcalino.

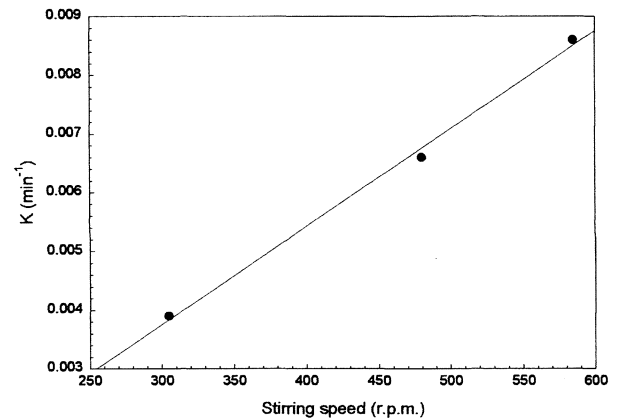


Figure 6. Effect of stirring speed on vanadium dissolution rate in alkaline media.

Figura 6. Efecto de la velocidad de agitación en la velocidad de disolución del vanadio en medio alcalino.

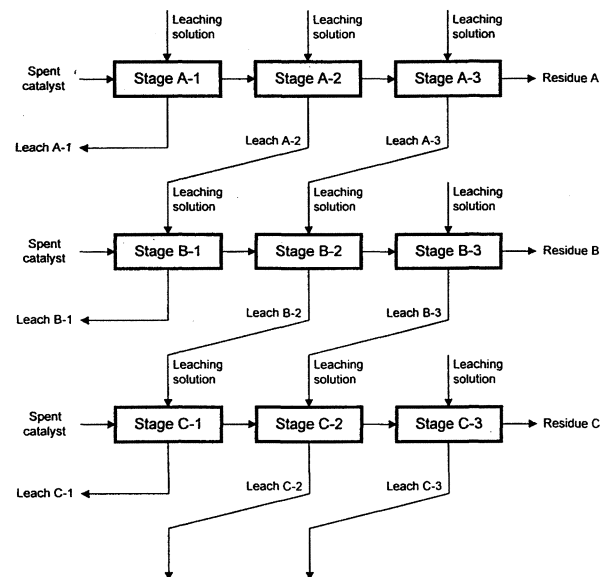


Figure 7. Industrial leaching cycle.

Figura 7. Ciclo industrial de lixiviación.

4. CONCLUSIONS

Vanadium spent catalysts from the manufacture of sulphuric acid are a hazardous and toxic waste. Best results were obtained using sulphuric acid solutions. The values obtained of activation energies (18.44 kJ mol⁻¹) inform that leaching of these residues with sulphuric acid is a very fast diffusion controlled process in the conditions tested (R>95 % when t<10 min). A relationship between final vanadium leaching yield and initial sulphuric acid concentration (g/L) in leach solutions confirms that using 160 g/L sulphuric

Table III. Final results for industrial leaching process simulation tests using spent catalyst type B

Tabla III. Resultados finales para los ensayos de simulación del proceso industrial de lixiviación con catalizador agotado tipo B

Leaching solution	S/L Ratio (g/mL)	Catalyst mass (g)	Residue mass (g)	% V residue (% w/w)	Leach volume (mL)	[V] solution (g/L)	Recovery yield (%)
H ₂ SO ₄ (20 g/L)	1 / 2.5	1000	690.0	0.34	1645	22.11	94.51
H ₂ SO ₄ (20 g/L)	1 / 5	1000	715.0	2.32	3940	6.22	61.24
K ₂ SO ₄ (50 g/L)	1 / 2.5	1000	755.0	2.30	1580	14.9	59.43
H ₂ SO ₄ (20 g/L) + K ₂ SO ₄ (50 g/L)	1 / 5	1000	685.0	0.10	4020	9.95	98.39
H ₂ O	1 / 2.5	500	382.9	2.81	740	13.38	49.72
H ₂ O	1 / 5	1000	665.0	2.38	3950	9.94	54.34
H ₂ O	1 / 12.5	250	153.2	2.17	2690	2.68	68.93

acid solutions at room temperature, up to 98% of vanadium can be recovered and the use of water as leaching agent can achieve a recovery of 60% vanadium. An industrial leaching process in three countercurrent stages gets a final residue with less than 0.1% of vanadium and a total recovery of this metal >95 %.

The use of alkalyne reagents (NaOH, KOH) results in slower kinetics and a diffusion controlled process is also verified.

Direct precipitation of vanadium as trioxide is not a commercial possibility, and a solvent extraction process for vanadium is recommended for the recovery of this metal.

5. ACKNOWLEDGEMENTS

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