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Recovery by solvent extraction of vanadium from spent catalysts leaching solutions using Primene 81R(•)

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Abstract Recovery of vanadium contained in solutions coming from spent catalysts leaching process by means of solvent extraction techniques using primary amine Primene 81R, has been studied in this work, resulting in an industrial multistage process for the treatment of these effluents. Results obtained allows to propose an extraction mechanism for vanadium(V) with this amine in acidic media, verifying the great influence of pH on the process and fix adequate ranges for variables: O/A ratio, organic phase composition, pH, stirring speed and phase separation speed. These values were simulated in industrial conditions. Vanadium is finally recovered by means of precipitation as ammonium metavanadate and later calcination to obtain vanadium pentoxide of commercial grade.

Keywords Spent catalysts. Solvent extraction. Vanadium. Primene 81R.

Recuperación mediante extracción con disolventes de vanadio de soluciones procedentes de la lixiviación de catalizadores agotados empleando Primene 81R

Resumen En el presente trabajo se ha estudiado la recuperación del vanadio contenido en soluciones procedentes del proceso de lixiviación de catalizadores agotados, por medio de la técnica de extracción con disolventes, empleando la amina primaria PRIMENE 81R, planteando un proceso industrial multietapa para el tratamiento de estos efluentes. Los resultados obtenidos permiten proponer un mecanismo de extracción para el vanadio(V), con esta amina en medio ácido, verificando la gran influencia del pH en el proceso y fijando los rangos adecuados para las siguientes variables: relación O/A, composición de la fase orgánica, pH, velocidad de agitación y velocidad de separación de fases. Esos valores se simularon en condiciones industriales. El vanadio se recupera finalmente precipitándolo como metavanadato amónico y posterior calcinación para obtener pentóxido de vanadio de calidad comercial.

Palabras clave Catalizadores agotados. Extracción con disolventes. Vanadio. Primene 81R.

1. INTRODUCTION

In 1998, vanadium production was limited to material recovered from various industrial waste streams. In U.S., fewer than 10 firms processed such materials, as vanadium-bearing ferrophosphorus slag, iron slag, fly ash, petroleum residues, and spent catalysts to produce vanadium pentoxide, ferrovanadium, and vanadium metal. Recycling of vanadium is negligible; only small quantities of vanadium-based catalysts and vanadium-aluminum alloy are recycled[1].

Leaching of spent catalysts with sulphuric acid followed by solvent extraction (L-SX) is one of the alternatives for the recovery of this metal and offers the greatest selectivity and highest purity V_2O_5 product[2].

Solutions coming from leaching process of spent catalysts used in the manufacture of sulphuric acid contains up to 4 g/L vanadium in sulphate media, and pH values ranging between 2 and 4.5, to avoid precipitation as brown vanadic acid ($V_2O_5 \cdot n\ H_2O$). In these liquors vanadium (IV) and vanadium (V) predominate. Vanadium (V) is a strong oxidant in

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dilute acid when it is present as $[VO_2]^+$. This cation hydrolyzes easier, forming oxianions (1) which polymerize, releasing protons to make up a series of partially protonated polymerised polyanions of general formula $[H_yV_{2x}O_{5x+2}]^{y-4}$, even though the predominant polymeric specie for some authors takes the form $[H_yV_{2x}O_{5x+3}]^{y-6}$ (2), were x usually takes the values 1.2 or 5 [3 and 4].

$$2\,[VO_2]^+ + 3H_2O \Leftrightarrow [H_3V_2O_7]^- + 3H^+ \qquad (1)$$

$$5[H_3V_2O_7]^- \Leftrightarrow [H_5V_{10}O_{28}]^- + 4OH^- + 3H_2O \qquad (2)$$

The solvent extraction of vanadium has been developed to treat neutral, acidic and basic solutions containing either vanadium (IV) or vanadium (V) species. Commercial plants have focussed on either the extraction of vanadium(IV) as $[VO]^{2+}$ from acid solutions using D2EHPA, or the extraction of vanadium(V) as one of its many anionic species using tertiary or quaternary amines[2]. Tertiary amines extract vanadium more effectively at pH 1.5-4 [5 and 6], but quaternary amines function over a wide pH range of 1.5-12, reaching optimum values in the range 6-9 [7-9].

The U.S. Bureau of Mines developed a process for extraction of vanadium resulting from sulphuric acid leaching of dolomitic shale[5]. Best results were obtained according to the next order for extraction reagents:

Adogen 363 > Amberlite LA-2 > TIOA > Primene JMT,

thus primary amines show the worst extraction yields under these conditions.

Schroetterova[10 and 11] has studied the extraction of U(VI), Mo(VI), V(V), Ce(IV), Zr(IV), Fe(III) and Al(III) with Primene JMT in sulphate media. Results obtained shows that predominant species for vanadium in this media are several decavanadates. Non ideal behaviour of this extraction system are due to hydration phenomena of present vanadium species.

Commercial tertiary amines reported from some authors for the extraction of vanadium are Alamine 336 [9, 12 and 13] and Adogen 364 [2], while quaternary ammonium salts reported are Aliquat 336 [14 and 15], tri-octyl-methyl-ammonium chloride[16 and 17] and Adogen 464 [2].

The purpose of the present work is to study the possibilities for the recovery of vanadium from sulphate solutions coming from leaching of spent catalysts used in the manufacture of sulphuric acid, by means of solvent extraction with the primary amine Primene 81R.

2. EXPERIMENTAL

Synthetic liquors were made up by dissolving solid V_2O_5 (analytical reagent quality) in 2M sulphuric acid solutions until saturation and later filtration. Vanadium was analyzed by atomic absorption spectrometry (AAS). Primene 81R was obtained from Rohm & Haas and was used as received. This amine has a composition of >99 % primary aliphatic amine, with the general estructure $R_1R_2R_3$-C-NH_2, where the total carbon number is 12-14, has an experimental molecular weight of 200 and a density of 812 kg/m^3. As diluent of the organic phase several aliphatic and aromatic hydrocarbons were tested, while several alcohols were used as modifiers. All chemicals were AR grade.

Vanadium extractions were carried out by shaking volumes of the organic and aqueous phases in separatory funnels at room temperature and for the time necessary to achieve equilibrium. Equilibrium pH were adjusted by addition of measured quantities of solutions 1M H_2SO_4. Coalescence tests were carried out in 500 mL graduated tubes by mixing volumes of loaded organic phase (Primene 81R + isodecanol + kerosene) with aqueous raffinate, measuring the height of the sharply defined interfase at various running times.

Vanadium stripping from the loaded organic phase was carried out with aqueous solutions of NH_3 in a similar manner that described for extraction tests, although pH adjustment was not neccessary. Simulation of industrial multistage solvent extraction cycle were carried out following the scheme showed in figure 1.

3. RESULTS AND DISCUSSION

3.1. Diluents and modifiers influence

Distribution ratios (D) for the extraction of vanadium from leach liquors containing 1.9 g/l of this metal with organic phases made up of mixtures of Primene 81R (2 % v/v), isodecanol (5 % v/v) as modifier and several diluents are shown in table I. The agitation time used in these experiments were three periods of 3 minutes, adjusting the pH value prior to each period as indicated in previous section. O/A ratio were 1/1 in all cases.

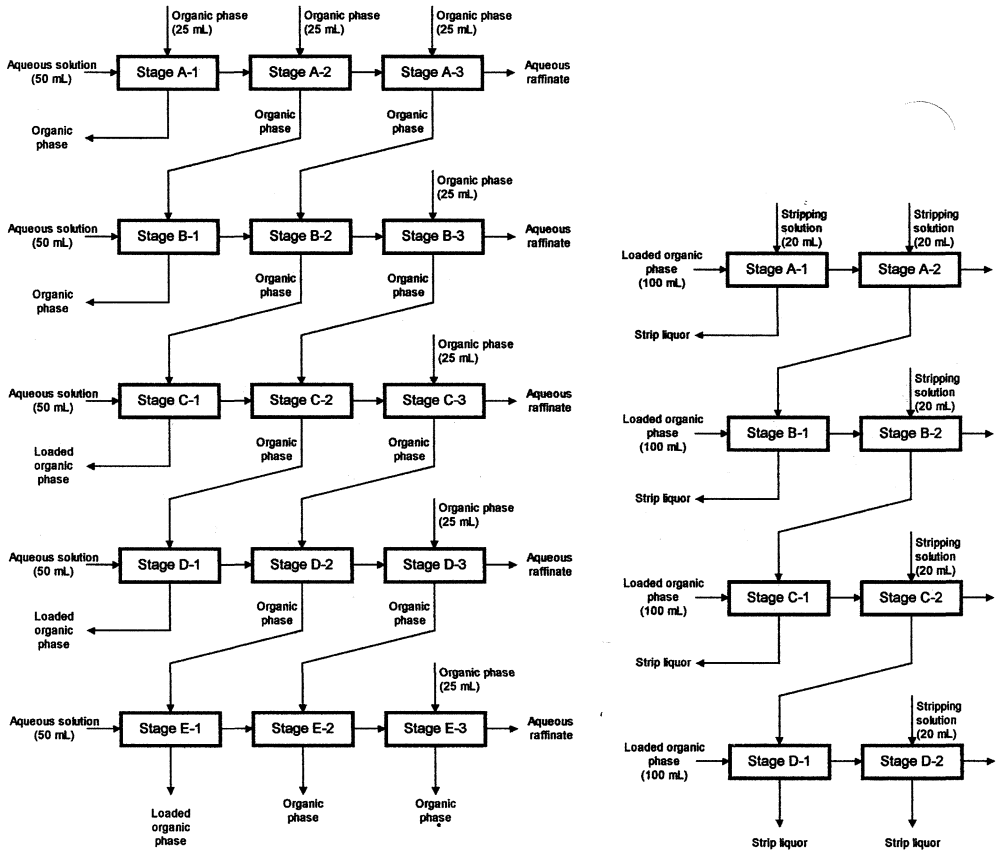

Figure 1. Scheme of the pattern for the simulation of industrial solvent extraction cycle.

Figura 1. Diagramas de flujo para la simulación de los ciclos industriales de extracción con disolventes.

Table I. Influence of the diluents on vanadium solvent extraction of by Primene 81R in acid media

Tabla I. Influencia de los diluyentes en la extracción con disolventes del vanadio con Primene 81R en medio ácido

Diluents	$[V]_{aq}$ (g/L)	$[V]_{org}$ (g/L)	pH	D	R (%)
Toluene	0.110	1.823	2.33	16.57	93.82
Benzene	0.133	1.799	2.35	13.53	92.60
Ciclohexane	0.102	1.851	2.29	18.15	94.32
Kerosene	0.102	1.833	2.34	17.97	94.32
n-hexane	0.130	1.840	2.31	14.15	92.76
n-heptane	0.108	1.845	2.35	17.08	93.99
n-octane	0.110	1.860	2.32	16.92	93.82

These extraction systems were also studied without modifier, but after equilibration time the presence of a third phase in all cases was observed, which is a serious drawback for industrial purposes. Small differences were observed among these diluents, so kerosene was used due to its low cost and easinest availability.

Several alcohols were tested as possible modifiers in similar conditions that indicated above (methanol, ethanol, 2-propanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol and isodecanol). The best results were obtained with the higher molecular weight alcohol, although differences observed were negligible. Taking into account this fact, isodecanol was chosen as modifier.

3.2. Agitation time influence

The necessary agitation time to reach the equilibrium was studied by means of extractions carried out at room temperature with organic phases of Primene 81R 10 % v/v and isodecanol 10 % v/v in kerosene and aqueous phases containing 2.3 g/L V(V) (O/A ratio = 1/1). Agitation times from 15 sec. to 5 min. were tested. Results show that vanadium extraction is decreased from 93 to 85 %. This result is assumed due to the increase of equilibrium pH reached (>7), since this parameter has not been adjusted in these tests.

3.3. Effect of extraction reagent concentration

The optimum concentration of Primene 81R in the mixture was first studied to obtain higher metal extractions. The extraction experiments were carried out by using aqueous phases of V(V) 2.7 g/l and organic phases with different contents of Primene 81R expressed as a percentage and isodecanol as modifier.

As expected, the graph of log D versus log [RH2] (Fig. 2) shows a linear relationship and gives a slope of 0.53, indicating that the ratio of extractant to metal is 0.5 when pH = 2.5. Similar results were obtained when different initial metal concentrations were used.

Taking into account that vanadium(V) exists in the form of protonated polyanions (decavanadates) at pH 2.5 - 6 ($HSO_4^- << SO_4^=$) the next equilibria are possible:

$$2[RNH_2]_{org} + H_2SO_4 \Leftrightarrow [2(RNH_3)^+(SO_4)^{2-}]_{org} \quad (3)$$

$$2[(V_{10}O_{28})^{6-}]_{aq} + 6[2(RNH_3)^+(SO_4)^{2-}]_{org} \Leftrightarrow$$
$$\Leftrightarrow 2[(RNH_3)^+_6.(V_{10}O_{28})^{6-}]_{org} + 12\ SO_4^{2-} \quad (4)$$

$$2[(HV_{10}O_{28})^{5-}]_{aq} + 5[2(RNH_3)^+(SO_4)^{2-}]_{org} \Leftrightarrow$$
$$\Leftrightarrow 2[(RNH_3)^+_5.(HV_{10}O_{28})^{5-}]_{org} + 10\,SO_4^{2-} \quad (5)$$

$$2[(H_2V_{10}O_{28})^{4-}]_{aq} + 4[2(RNH_3)^+(SO_4)^{2-}]_{org} \Leftrightarrow$$
$$\Leftrightarrow 2[(RNH_3)^+_4.(HV_{10}O_{28})^{4-}]_{org} + 8\,SO_4^{2-} \quad (6)$$

Direct extraction by the amine is not probably since neutral vanadium species are not predominant at this pH. Assuming the next overall extraction reactions for this system:

$$6[RNH_2]_{org} + 6H^+_{aq} + [(V_{10}O_{28})^{6-}]_{aq} \Leftrightarrow$$
$$\Leftrightarrow [(RNH_3)^+_6.(V_{10}O_{28})^{6-}]_{org} \quad (7)$$

$$5[RNH_2]_{org} + 5H^+_{aq} + [(V_{10}O_{28})^{5-}]_{aq} \Leftrightarrow [$$
$$\Leftrightarrow [(RNH_3)^+_5.(VH_{10}O_{28})^{5-}]_{org} \quad (8)$$

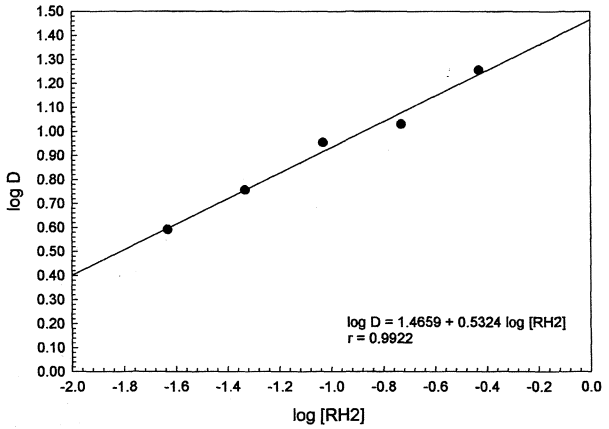

Figure 2. Vanadium distribution coefficient versus Primene 81R concentration at pH = 2.5.

Figura 2. Coeficiente de distribución vs. concentración de Primene 81 R a pH = 2,5.

$$4[RNH_2]_{org} + 4H^+_{aq} + [(H_2V_{10}O_{28})^{4-}]_{aq} \Leftrightarrow$$
$$\Leftrightarrow [(RNH_3)^+_4.(H_2V_{10}O_{28})^{4-}]_{org} \quad (9)$$

in which RNH_2 represents the amine Primene 81R and aq and org the aqueous and organic phases, respectively. Considering that $[(HV_{10}O_{28})^{5-}]_{aq}$ is the predominant polymeric specie, it can be deduced:

$$K_{ext} = \frac{[(RNH_3)_5^+ \cdot (HV_{10}O_{28})^{5-}]_{org}}{[RNH_2]^5_{org}[H^+]^5_{aq}[(HV_{10}O_{28})^{5-}]_{aq}} \quad (10)$$

and from this:

$$\log D_v = \log K_{ext} - 5pH + 5\log[RNH_2] \quad (11)$$

3.4. Initial metal concentration influence

Figure 3 shows the distribution coefficient for vanadium versus initial vanadium concentration in aqueous phase at pH=2. The organic phases used had the composition: Primene 81R 5% v/v, isodecanol 5 % v/v in kerosene. In this figure it can be seen that, under the present experimental conditions, the optimum vanadium concentration for the aqueous solutions is around 2 g/l.

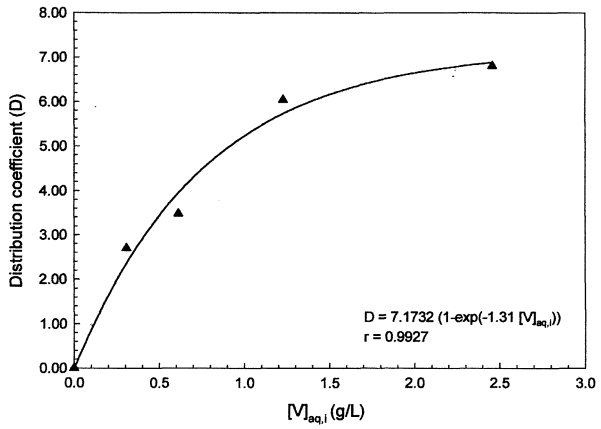

Figure 3. Relationship between vanadium distribution coefficient and initial concentration of this metal in aqueous solution in acid media.

Figura 3. Relación entre el coeficiente de distribución del vanadio y la concentración inicial de este metal en la solución acuosa en medio ácido.

3.5. Extraction isotherms

Graphical presentation of the variation of metal concentration in the organic phase with metal concentration in the aqueous phase are showed in figure 4 for several concentrations of Primene 81R in the organic phase. The graph on the left shows the total curve obtained, while the figure on the right side is an extended view of the initial shape of this isotherm. Data were obtained by shaking volumes of organic and aqueous phases at O/A ratios ranging from 10/1 to 1/10 and maintaining pH values around 2-2.5.

Shaped curves obtained confirms data reported on vanadium extraction by amines[18]. The shape is due to the presence of non-extractable metal complexes, or polymerisation in the organic phase at low metal concentrations in the aqueous phase.

3.6. Phase disengagement

The rate at which the dispersed phases disengage are of prime importance in the operation of a solvent extraction system, since this governs the size of the settling area and throughput of a plant. Figure 5 plots the height of the interfase vs. time when disengagement of loaded organic phases (Primene 81R 2 % v/v, iso-decanol 5 % v/v dissolved in kerosene) from aqueous raffinate using the same agitation speed that for previous extraction tests. The continuous phase was determined by the initial position of the stirrer.

Parameters obtained for each test are summarized in table III Specific area (cm.s) is determined by numerical integration of the curve obtained by plotting the height of the sharply defined interfase vs. time:

$$A_{org} = \int_0^t h(t)_{org} dt \qquad A_{aq} = \int_0^t h(t)_{aq} dt \tag{12}$$

Equivalent time is defined as:

$$t_{org} = \frac{2A_{org}}{h_{org}} \qquad t_{aq} = \frac{2A_{aq}}{h_{aq}} \tag{13}$$

Thus, coalescence velocity (m/s) is defined as follows:

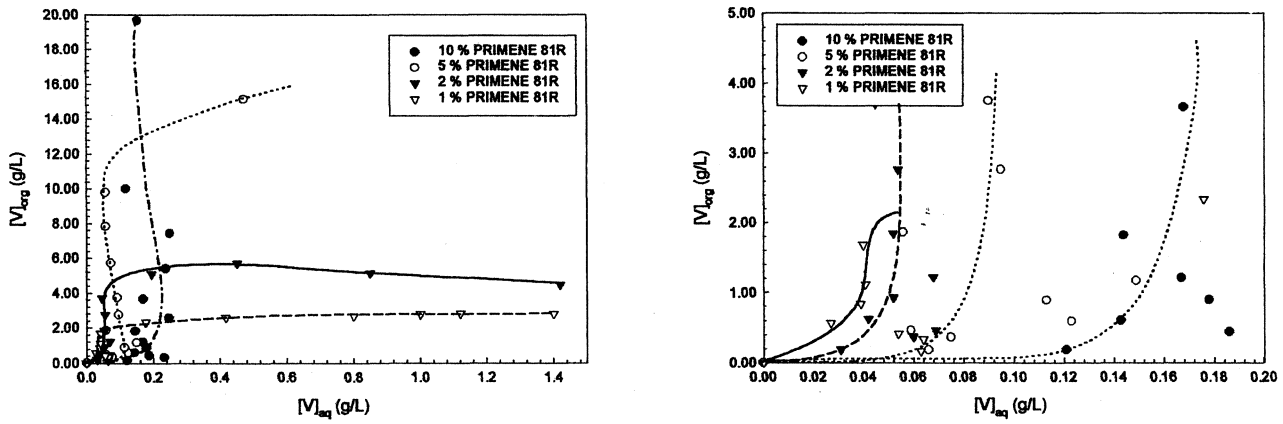

Figure 4. Vanadium extraction isotherms at pH around 2 - 2.5.

Figura 4. Isotermas de extracción del vanadio a pH 2 - 2,5.

Table II. Equilibrium data for the extraction system Primene 81R- vanadium (V) using kerosene as diluent and isodecanol as modifier

Tabla II. Datos de equilibrio para el sistema de extracción Primene 81R - Vanadio (V) empleando queroseno como diluyente e isodecanol como modificador

10 % PRIMENE 81R			5 % PRIMENE 81R			2 % PRIMENE 81R			1 % PRIMENE 81R		
D	$[V]_{aq}$ (g/L)	$[V]_{org}$ (g/L)	D	$[V]_{aq}$ (g/L)	$[V]_{org}$ (g/L)	D	$[V]_{aq}$ (g/L)	$[V]_{org}$ (g/L)	D	$[V]_{aq}$ (g/L)	$[V]_{org}$ (g/L)
1.62	0.121	0.177	3.82	0.066	0.178	8.12	0.031	0.185	3.38	0.063	0.162
1.52	0.233	0.334	5.76	0.075	0.357	7.34	0.060	0.365	6.04	0.064	0.327
2.41	0.186	0.436	9.10	0.059	0.454	7.78	0.069	0.454	8.58	0.054	0.410
4.34	0.143	0.598	5.51	0.123	0.583	16.68	0.042	0.616	22.51	0.027	0.560
5.34	0.178	0.889	8.89	0.113	0.886	19.85	0.052	0.925	23.20	0.039	0.840
7.74	0.167	1.210	8.82	0.149	1.170	19.27	0.068	1.215	28.92	0.041	1.114
13.18	0.144	1.819	35.97	0.056	1.861	37.59	0.052	1.841	44.04	0.040	1.676
10.92	0.246	2.588	31.14	0.095	2.764	53.30	0.054	2.760	13.78	0.176	2.337
22.36	0.168	3.656	44.08	0.09	3.746	85.35	0.045	3.699	6.55	0.417	2.602
23.76	0.237	5.425	83.24	0.072	5.728	26.90	0.194	5.093	3.55	0.800	2.667
31.12	0.249	7.430	145.48	0.056	7.844	13.10	0.452	5.731	2.95	1.000	2.773
87.88	0.117	10.016	180.54	0.056	9.807	6.28	0.85	5.145	2.74	1.120	2.807
131.22	0.153	19.652	32.96	0.472	15.153	3.42	1.42	4.476	2.32	1.400	2.800

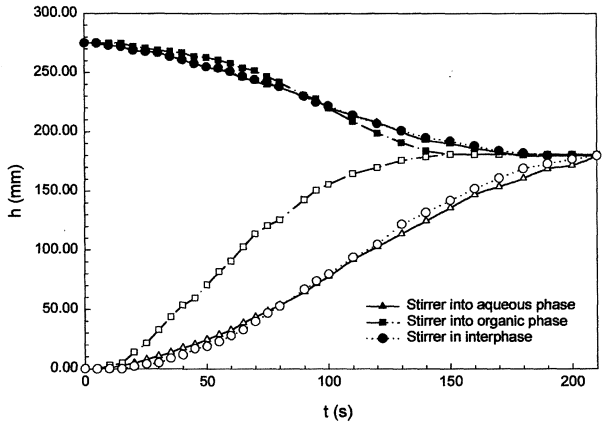

Figure 5. Plot of height of interphase vs. time in coalescence tests for vanadium extraction with Primene 81R.

Figura 5. Representación de la altura de la interfase frente al tiempo en los ensayos de separación de fases para la extracción de vanadio con Primene 81R.

$$\upsilon_{org} = \frac{h_{org}}{t_{org}} \qquad \upsilon_{aq} = \frac{h_{aq}}{t_{aq}} \qquad (14)$$

Finally, specific settling capacity (C_e) is defined as the minimum of both coalescence velocities ($m^3/s \cdot m^2$)

Table III. Results obtained in coalescence tests for vanadium extraction with Primene 81R

Tabla III. Resultados obtenidos en los ensayos de separabilidad de fases para la extracción de vanadio con Primene 81R

	Stirrer placed into aqueous phase	Stirrer placed into organic phase	Stirrer placed in interphase
A_{org} (cm/s)	870	846.5	886.25
A_{aq} (cm/s)	1983.25	1131.75	1956.5
t_{org} (s)	183.16	180.11	186.58
t_{aq} (s)	220.36	125.06	217.39
υ_{org} (m/min)	0.0311	0.0313	0.0306
υ_{aq} (m/min)	0.0490	0.0868	0.0497
C_e ($l/min \cdot m^2$)	31.1	31.3	30.6

$$C_e = Min\{\upsilon_{org}, \upsilon_{aq}\} \qquad (15)$$

Differences observed when placing stirrer in each phase are negligible because in all cases studied, coalescence of organic phase is the rate determining stage.

3.7. Vanadium stripping

The concentration of the stripping solutions and agitation time necessary were carried out with organic phases (Primene 81R 2 % v/v and isodecanol 5 % v/v dissolved in kerosene) loaded with 2.5 g/L V and solutions of NH_3 ranging from 0 to 5 N, using A/O ratios = 1/1. The results are showed in table IV and indicate an asympthotic tendency for vanadium recovery. That means that the maximum vanadium recovery in one single stage is around 70 %. Solvent losses were not observed in the tests performed.

Stripping kinetics are showed in figure 6. The test were carried out with the same loaded organic phase that reported previously using several NH_3 solutions and A/O ratio 1/1. The plot indicates slower reaction kinetics than for extraction tests in all cases, and minimum contact times of 5 min to achieve equilibrium.

Figure 7 shows the vanadium stripping isotherms obtained with organic phases of Primene 81R 2 % v/v and isodecanol 5 % v/v dissolved in kerosene loaded with 2.449 and 3.089 g/L V(V) respectively, and stripping solution of NH_3 2 N, using various A/O relationships.

Table IV. Results of stripping tests for vanadium using NH_3 aqueous solutions at A/O ratio 1/1

Tabla IV. Resultados de los ensayos de reextracción para el vanadio empleando soluciones acuosas de NH_3 y una relación A/O = 1/1

$[NH_3]$ (M)	Vanadium stripped (%)
0	3.87
0.4874	61.06
0.9045	63.04
1.4020	65.33
1.8391	65.91
2.8190	66.36
3.6481	66.52
4.6431	66.94
5.3969	67.13

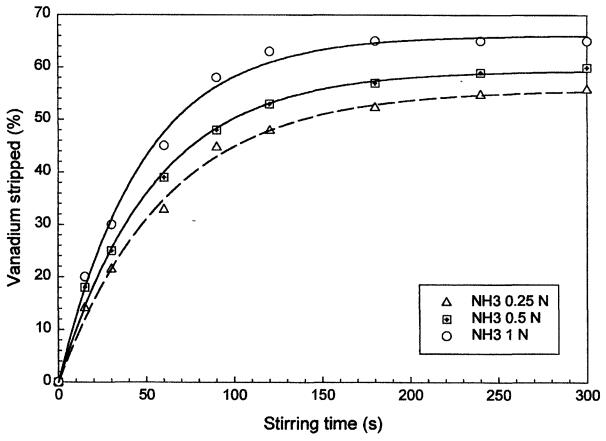

Figure 6. Stripping kinetics of vanadium using NH_3 aqueous solutions at A/O ratio 1/1.

Figura 6. Cinética de reextracción del vanadio empleando soluciones acuosas de NH_3 y una relación A/O = 1/1.

3.8. Simulation of industrial SX cycle

According to results obtained in previous tests, the industrial conditions showed in table 5 were fixed in order to check the validity of the method proposed for the recovery of vanadium from leach liquors coming from treatment of spent catalysts used in the manufacture of sulphuric acid.

Results of industrial SX cycle simulated are summarized in table 6. From the results obtained it can be assumed the validity of the method proposed. Vanadium is finally recovered from the strip liquor by evaporation as ammonium metavanadate and later calcination to obtain V_2O_5 of commercial grade (>99 %).

4. CONCLUSIONS

The results obtained with the primary amine Primene 81R dissolved in kerosene indicate that this reagent can be used to extract vanadium (V) from sulphate media at acid pH values. The presence of a modifier is neccesary in order to avoid cruds or third phase formation and pH must be

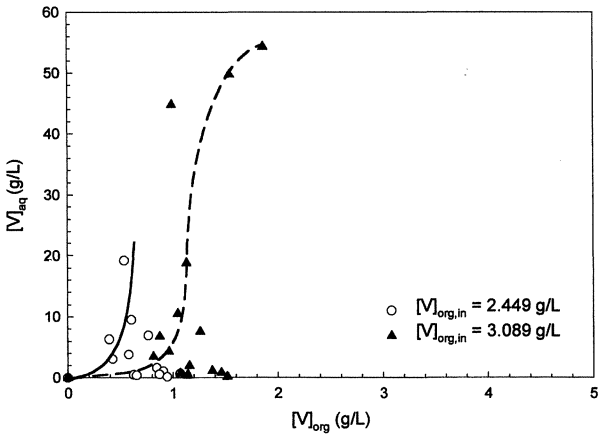

Figure 7. Vanadium stripping isotherms.

Figura 7. Isotermas de reextracción del vanadio.

Table V. Experimental conditions for simulation tests of industrial solvent extraction cycle for recovery of vanadium

Tabla V. Condiciones experimentales para los ensayos de simulación industrial de un ciclo de extracción con disolventes para la recuperación del vanadio

Leach liquor	Solvent extraction	Stripping
[V] < 2.5 g/L	Reagent: Primene 81R (2 % v/v)	Reagent: NH3 aqueous solutions (2 N)
pH < 4.5	Modifier: Isodecanol (5 % v/v)	
$[SO_4^{=}]$ > 1.5 M	Diluent: kerosene	
	O/A ratio: 1/2	A/O ratio: 1/5
	pH adjustment: 2-2.5	pH adjustment: Not necessary
	Number of stages: 3	Number of stages: 2
	Contact time: 3 intervals of 3 minutes each	Contact time: 5 min
	Flow pattern: countercurrent	Flow pattern: countercurrent
	Scrubbing stage: Not necessary	Scrubbing stage: Not necessary
	[V] in loaded solvent < 3.5 g/L	[V] in strip liquor < 20 g/L

Table VI. Global results for the simulation of industrial solvent extraction cycle for the recovery of vanadium

Tabla VI. Resultados globales para la simulación de un ciclo industrial de extracción con disolventes para la recuperación del vanadio

Line	Extraction yields (%)	Stripping yields (%)
A	94.78	69.12
B	90.68	71.58
C	90.82	70.78
D	90.74	71.88
E	92.88	

kept in the range 2-2.5. Experimental data obtained confirms that predominant polymeric specie for vanadium at those pH is $(HV_{10}O_{28})^{5-}$ and the overall extraction mechanism proposed is:

$$5[RNH_2]_{org} + 5H^+_{aq} + [(HV_{10}O_{28})^{5-}]_{aq} \Leftrightarrow$$

$$\Leftrightarrow [(RNH_3)^+_{5}.(HV_{10}O_{28})^{5-}]_{org}$$

Extraction isotherms confirms S-shaped curves cited in previous references. Vanadium stripping can be achieved with aqueous NH_3 solutions. Simulation of a industrial solvent extraction cycle (three countercurrent stages for solvent extraction and two countercuerrent stages for stripping), allows to propose a method for the recovery of this metal from leaching liquors coming from the treatment of spent catalyusts used in the manufacture of sulphuric acid. Vanadium is finally recovered as V_2O_5 of commercial grade.

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