

EXTRACCION DE VANADIO A PARTIR DE MINERALES DE BAJA LEY.

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Se estudia la extracción de vanadio a partir de menas portadoras de vanadinita que contienen 0.108% de V_2O_5 .

Los ensayos preliminares permitieron determinar que el ácido sulfurico es el mejor agente lixiviante, evaluándose el efecto de la temperatura, granulometría, etc.

Se realizaron dos ensayos de extracción en corrientes cruzadas. La modelación matemática de los resultados experimentales obtenidos determinó, para el primer ensayo, el límite de máxima concentración de vanadio que puede lograrse en la solución lixiviante y para el segundo ensayo, el mínimo contenido remanente de vanadio en el residuo sólido.

Para la recuperación del vanadio en forma económica, por precipitación, será necesario aumentar la concentración de vanadio en la solución ya sea por preconcentración del mineral o por adsorción del vanadio en superficies activas o por extracción con solvente. La lixiviación sobre un preconcentrado de mayor ley -para las mismas condiciones experimentales- muestran un aumento en el límite porcentual de extracción, manteniéndose la misma concentración de vanadio en el residuo final.

POSSIBILITIES OF VANADIUM EXTRACTION IN LEACHING OF LOW GRADE VANADIUM ORES

Vanadium extraction from 0.108% of V_2O_5 vanadinite low grade ores has been studied. Preliminary tests have been performed in order to evaluate the effect of the experimental variables: leaching agent, temperature, particle size etc.. The maximum vanadium concentration in the leaching liquor and the minimum vanadium remaining in the residue, for a crosscurrent multistage extraction system were obtained by mathematical modelation of the experimental data. The mathematical modelation of the experimental data, for a multistage crosscurrent extraction system gave the minimum amount of vanadium in the leaching residue and the maximum vanadium concentration in the leaching liquor. For the economical recovery of vanadium from the leach liquor by precipitation of the red cake, the preconcentration of the ore before leaching or the increase of the vanadium concentration by selective adsorption on active surfaces or solvent extraction have been proposed. Complementary leaching tests have shown an increase in the vanadium recovery when preconcentrated ore was leached.

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INTRODUCTION

Vanadium is one of the widely distributed element throughout the earth crust, in more than 50 minerals.

Few of its minerals are of commercial significance and few deposits with more than 1-2% of vanadium are known.

Largest deposits of vanadium minerals occur in Peru like patronite, a vanadium sulphide.

The vanadium reserves are in deposits in which the vanadium could be obtained as by-product of the extraction of other minerals from titaniferous magnetites, in USSR, China, South Africa, Finland and Australia; phosphatic shales and phosphate rocks in USA (Utah and Wyoming); uranium-bearing minerals in USA (Colorado, Utah, Arizona); copper, lead and zinc vanadates in Namibia, Zambia, Mexico and Argentina, and certain petroleum crude oils and tars, especially from South America.

In Argentina, vanadium minerals are vanadates originated in the action of vanadium waters on lead, zinc and uranium oxidized compounds. The exploitation of the vanadium deposits began in 1929. From then on, the production was discontinued during different periods and for different deposits. No recovery of vanadium from the processing of uranium minerals are registered.

Very little can be gained from the literature about the extractive metallurgy of vanadium from vanadinite or descloizite.

Acid leaching of ores and concentrates is far the commonest method of hydrometallurgical attack. Alkaline leaching using alkali metal hydroxides and carbonates is potentially applicable to those metals which form anionic complexes.

The aim of this work is to develop the process for the vanadium extraction from low grade vanadinite ores. In that way, preliminary tests have been performed to evaluate the effect of the experimental variables: leaching agent, temperature, particle size and solid:liquid ratio. A multistage crosscurrent extraction system was simulated in the laboratory, and the experimental data was mathematically modeled.

THEORETICAL BACKGROUND

The mineralogy of vanadium is exceedingly complex because of its sensitivity to oxidation potential, its strong amphoteric behaviour in its higher valence states, and its tendency to form complex polyions of high molecular weight in its higher valence state (1).

The equilibrium diagram of Fig 1, represents the stability of various vanadium compounds in presence of water in terms of oxidation potential (E_h) vs pH and is drawn on the basis of the thermodynamic data for anhydrous oxides (1).

Shaded areas are fields of stability of solids in which the solubility of vanadium is less than approximately 0.01mole/l

Unshaded areas are fields in which predominant dissolved vanadium species exceeds 0.01 mole/l.

Boundaries between dissolved species are drawn where they are in equal molar concentration. This boundary lines may shift slightly with changes in the ionic strength or in the ionic concentration.

Actually, the solid oxides are precipitated from aqueous solutions in hydrated forms which have different free energy contents.

According to the estimated free energies of hydration of the oxides, the equilibrium diagram has been redrawn in Fig 2.

Vanadium (V) forms pervanadyl cation VH_2^{+} only at low pH: the isoelectric point is between pH 1 and 2, the solubility falls to a minimum, as is evidenced by the stability field of hydrated V_2O_5 . Above this pH, vanadium can be polymerized reversibly to different polyvanadates anions, changing the pH conditions. In general, they change colour from deeply coloured -highly polymerized- at low pH to colourless -less condensed- ions at high pH values.

Different complex anions that can be present in a solution in terms of a total vanadium concentration and the hydrogen concentration are presented in Fig 3 (2).

In particular, Fig 4 shows the influence of pH on the solubility of V_2O_5 at 25°C. The boundaries of V_2O_5 with ionic species as drawn use the equilibrium formulas based on

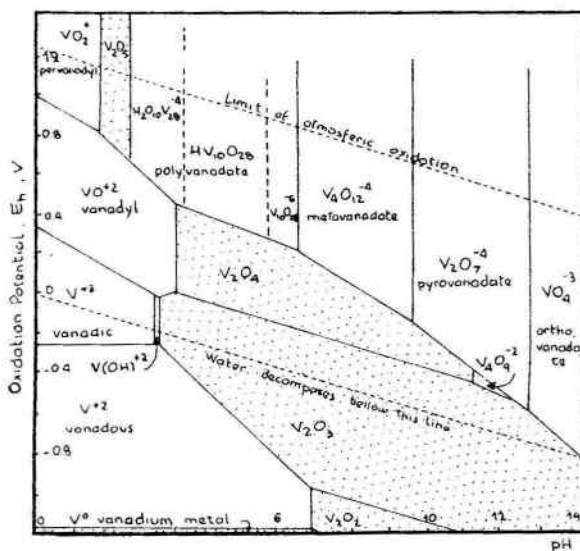


Fig 1: Stability ranges of various solids and solution phases

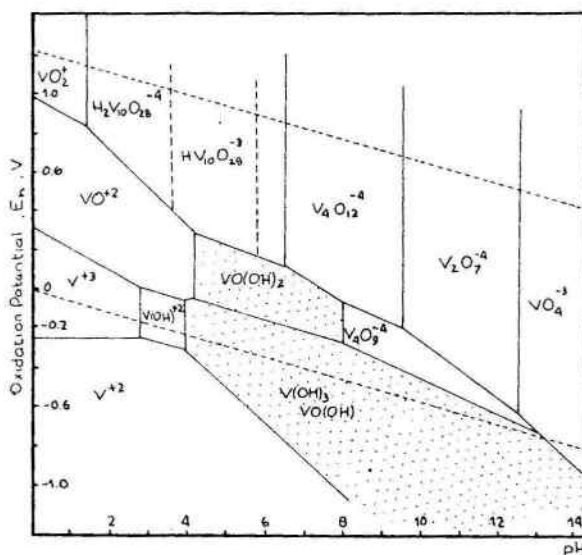


Fig 2: Domains of relative predominance of various dissolved forms of vanadium

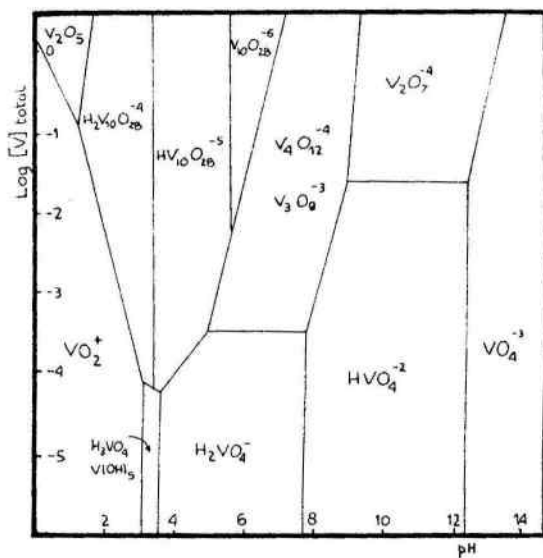


Fig 3: Domain for different vanadium species vs. pH

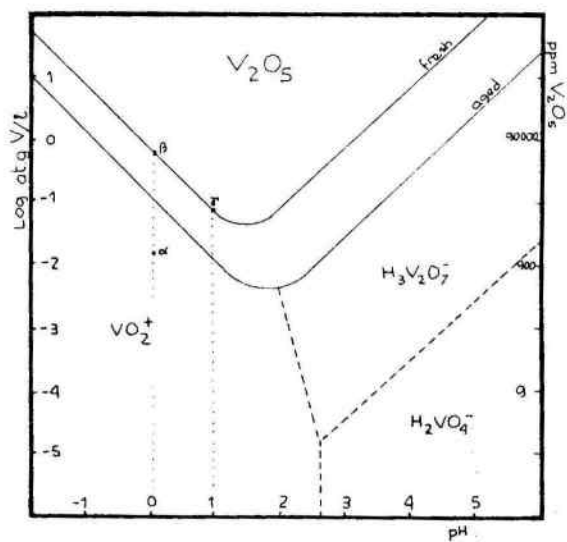


Fig 4: Influence of pH on the solubility of V_2O_5

thermodynamic data for the "aged" material and the "freshly precipitated oxide.

Aged material is more stable than newly precipitated. The standard free energy of formation is -344000 kcal/mole against -342000 kcal/mole for the fresh material.

Rapid neutralization of an acid solution of VO_2^+ permits passage from this ion to the orange polyvanadates without precipitation of the hydrated or fresh pentoxide, whereas the same titration, if done slowly, results in formation of the yellow-brown oxide.

The increase of stability with time may be correlated with a decrease in hydration as well as with a change in crystalline state.

EXPERIMENTAL

The low grade vanadium ore, was mined from the San Fermín Mine, in the mining district El Guárico, located in the NW of Cordoba province.

The mineralogical analysis has shown the presence of quartz, feldspar and biotite like the major constituents. Disemitted pyrochlore has also been detected.

The vanadium specie is vanadinite which seems to be included in apatite grains and is associated with cerussite and quartz. Magnetite, hematite and pyrochlore have also been detected. The sample assayed 0.11% V_2O_5 .

The size distribution of the ground ore was:

US sieve	+20	20-30	30-60	60-100	-100
w %	10.9	23.8	36.0	14.6	20.7

All the reagents used, were of analytical grade. Distilled water have been used.

The leaching tests were performed in 600 ml glass reactor equipped with a stainless steel stirrer, vertically mounted, running at 800 rpm.

165 to 175 g. of ground mineral and 250 ml of leaching agent were used in all the tests. After the completion of a particular experimental run, the suspension was filtered and

the cake was washed with fresh solvent for additional vanadium recovery.

Different preliminary tests have been performed in order to evaluate the effect of some experimental variables.

Sulfuric acid 4.3, 8.5 and 16% w/v; sodium carbonate 15% w/v, sodium bicarbonate 10% w/v, have been tested like leaching agents.

Temperatures of 19°C and 59°C and leaching periods of 1.5, 3 and 6 hours have been used in different tests.

Test n°10 was performed changing the solid:liquid ratio.

Test n°11 was performed in order to evaluate the effect of size particle upon the leaching time and the vanadium recovery. Ground mineral 100% under 100 mesh and the experimental conditions of test n°7 were used.

Leaching kinetic was followed by taking liquor samples at prefixed time intervals of 15 minutes.

The experimental conditions used in different tests are resumed in Table I.

Table I: Experimental conditions for preliminary tests.

TEST	LEACHING AGENT	CONCENTRATION % w/v	SOLID:LIQUID RATIO	TIME (hrs)	TEMP (°C)
1	Na_2CO_3	15	0.7:1	6	19
2	Na_2CO_3	15	0.7:1	6	59
3	NaHCO_3	10	0.7:1	6	19
4	H_2SO_4	8.5	0.7:1	3	19
5	H_2SO_4	8.5	0.7:1	3	59
6	H_2SO_4	8.5	0.7:1	3	19
7	H_2SO_4	8.5	0.7:1	1.5	19
8	H_2SO_4	16	0.7:1	3	19
9	H_2SO_4	4.3	0.7:1	1.5	19
10	H_2SO_4	8.5	1.8:1	1.5	19
11	H_2SO_4	8.5	0.7:1	1.5	19

Besides one stage extraction tests, a multistage cross-current extraction system tests were performed.

In test A, the leach liquor is successively contacted with fresh solid in batch stages, in the conditions detailed in Table II.

Table II: experimental conditions for test A

STAGE n	SAMPLE WEIGHT	LEACHING SOLUTION	SOLID:LIQUID RATIO	TIME (min)
1	165.4	H ₂ SO ₄ 8.5% w/v	1.7:1	100
2	164.9	liquor stage 1	1.7:1	100
3	163.3	liquor stage 2	1.7:1	100
4	175.9	liquor stage 3	1.7:1	60
5	175.5	liquor stage 4	1.7:1	60
6	175.3	liquor stage 5	1.7:1	60

Single stages were done at 13°C. After each extraction, the suspension was filtered and the filtering cake was washed with fresh solvent.

The final leaching liquors and the washing solutions were assayed for vanadium.

The leaching kinetic was followed by vanadium assay of liquor samples took at prefixed time intervals for the three initial stages.

For the three initial stages, the concentration vs. time data were mathematically modelled using the expression for a first order system:

$$C = C_{\infty} (1 - \exp(-t/T)) \quad (1)$$

The following kinetic parameters could be obtained for the three initial stages:

C_{∞} : final equilibrium vanadium concentration.

T : time required for obtaining the 63% of the final equilibrium concentration, in minutes.

The ultimate vanadium concentration in the leaching liquor, after infinite leaching contact stages with fresh solids, could be obtained with the C_{∞} values.

In test B, a multistage crosscurrent extraction system wherein the raffinate is successively contacted with fresh solvent in batch stages, was experimented with the original mineral sample.

Additional test C, was done with a tabling preconcentrated

ore, with a size distribution 100% under 100 mesh, and 0.173% of V_2O_5 assayed.

Tests B and C were conducted using the experimental conditions resumed in Table III.

Table III: experimental conditions for test B and C

STAGE n ^o	SAMPLE LEACHED	LEACHING AGENT	SOL:LIQ RATIO	TIME (min)	
				test B	test C
1	195.4g	H ₂ SO ₄ 8.5% p/v	0.7:1	105	40
2	raff.stage 1	H ₂ SO ₄ 8.5% p/v	0.7:1	60	40
3	raff.stage 2	H ₂ SO ₄ 8.5% p/v	0.7:1	60	40
4	raff.stage 3	H ₂ SO ₄ 8.5% p/v	0.7:1	60	40

All the single stages were done at 16°C. After each single extraction stage, the suspension was washed with fresh solvent.

All leaching samples and washing liquids were analysed for vanadium.

The maximum vanadium extraction after an infinite batch extraction stages were mathematically obtained by modelation of the mg of V_2O_5 extracted vs. stage data, using the following mathematical expression:

$$G = G_0 \left(1 - \frac{1}{2^{N+1}} \right) \quad (1)$$

where:

G: mg extracted under N extraction stages

G₀: mg extracted under infinite extraction stages

N*: number of the stage when 50% of the ultimate recovery was reached.

RESULTS

Table IV resumes the percentage of V_2O_5 extraction obtained in the preliminary tests.

Table IV: % of V_2O_5 extracted in preliminary tests

TEST N ^o	% extracted	TEST N ^o	% extracted	TEST N ^o	% extracted
1	1.2	2	2.7	3	1.6
4	37.8	5	46.7	6	37.5
7	38.7	8	38.4	9	31.0
10	36.7	11	39.6		

The obtained results have shown that extraction of vanadium is possible using sulfuric acid.

Extraction is increased with the increase of the vanadium concentration from 4.3 to 8.5% w/v with no additional extraction when 16% w/v sulfuric was used.

Practically, no extraction is possible by use of sodium carbonate or sodium bicarbonate.

It was seen that an increase in the vanadium extracted takes place when temperature reaches 60°C .

No difference in the extraction is detected by changing the solid:liquid ratio.

Similar vanadium extraction values are obtained with leaching times longer than 1.5 hours.

For test 11, no additional vanadium extraction is obtained by reducing the particle size and the maximum extraction is reached after 15 minutes.

For the multistage crosscurrent extraction system tests, the maximum vanadium concentration in solution and the minimum vanadium concentration in the raffinate are calculated.

The results obtained for the kinetic parameters (test A) are resumed in Table V.

Table V: kinetic parameters obtained in test A

STAGE N°	1	2	3	4	5	6
C_x (ppm V_2O_5)	235	432	580	745	877	998
T (minutes)	11.8	18.0	34.0			

The maximum vanadium concentration in the leaching solution under infinite contact stages with fresh solids would be 1849ppm of V_2O_5 . The 63% of this maximum concentration would be reached in 7.72 ideal stages.

The results for the experiences performed for determining the minimum vanadium concentration in the raffinate are resumed in Table VI. According to eq.[2], the maximum vanadium extracted under infinite extraction stages with fresh solvent would be for test B, 50.5% of the total inicial vanadium (170 mg. V_2O_5), and for test C, 61.9% of the total inicial vanadium (294 mg. V_2O_5).

The 50% of the maximum extraction would be reached, for test B in the stage 0.35, and for test C in the stage 0.16.

Table VI: % of V_2O_5 extraction in tests B and C

STAGE N°	TEST B			TEST C		
	mgV_2O_5 extracted	% (tag)	Accumul. %extrac.	mgV_2O_5 extracted	% (tag)	Accumul. %extrac.
1	35.6	49.6	32.5	157.4	157.7	53.6
2	7.3	72.8	42.6	2.5	167.3	54.8
3	4.4	77.0	45.2	5.1	172.4	58.6
4	4.5	81.5	47.9	4.7	177.1	60.1

DISCUSSION AND CONCLUSIONS

The mathematical modelling of the results obtained in test A, has shown that a magnificable increase in vanadium concentration is not allowable by increasing the extraction leaching stages on the low grade vanadinite ore from San Fermín mine. The maximum vanadium concentration obtainable in leaching liquors, is by 1849 ppm of V_2O_5 (like VO_2^+ ion) and the resulting solution pH was 0-0.2 (see point x in Fig.4).

At the vanadium concentration of this point, vanadium pentoxide would be obtained by increasing the pH by neutralization or by increasing the vanadium concentration.
INCREASING THE SOLUTION PH:

The recovery of V_2O_5 by rapid neutralisation would not be probable, unless very controlled conditions are used.

Nevertheless, pervanadyl cation has its isoelectric point between pH 1 and 2. Then, maximum vanadium adsorption on activated charcoal or solvent extraction by neutralizing the solution to pH 1.5-2.0 can be proposed like an alternative for processing low grades ores by other economical techniques i.e heap leaching.

INCREASING THE VANADIUM CONCENTRATION:

At pH 0, of fresh vanadium pentoxide is precipitated from the solution at about 76200 ppm of V_2O_5 (see point B in Fig.4).

At pH 1, fresh vanadium pentoxide is precipitated from the solution at about 7699 ppm of V_2O_5 (see point y in Fig.4).

Comparing the results for vanadium extraction in test C and A, greater vanadium concentration in solution was obtained using a pre-concentrated ore.

It could be concluded that the use of high vanadium grades ores or concentrates is the alternative for the V_2O_5 recovery by precipitation from leach liquors in which the free acid content has been controlled in order to avoid undesirable reactions or excessive neutralizing agent consumption.

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