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HYDROMETALLURGICAL TESTS FOR VANADIUM EXTRACTION FROM BLACK LIMESTONES FROM PUYANGO SECTOR, LOJA PROVINCE, ECUADOR

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INTRODUCTION

The following study is directed to the vanadium hydrometallurgy, a trace element distributed throughout the earth's crust with great commercial and economic importance, used in the steel industry forming alloys with titanium (for aerospace applications) and iron in order to improve its mechanical properties such as hardness, resistance to fatigue and stress [1], in addition to its use as a catalyst in the form of vanadium pentaoxide, in the manufacture of sulfuric acid, replacing platinum and in the production of batteries (for example in Li3V2(PO4)3 in batteries for electric cars) [2].

In the Puyango sector, Ecuador, geochemical anomalies of vanadium and uranium have been detected in samples of black bituminous limestones, with about 1.6% of V2O5. However, when starting from samples of a material different from that used in other countries, it is necessary to carry out a more specific study of the characterization (physical, chemical and mineralogical) of the samples, allowing to determine, analyze and obtain the necessary information of the composition of them, in addition to identifying the mineral phases to which vanadium is associated to carry out the hydrometallurgical tests using the acids necessary for the extraction thereof.

METHODS AND RESULTS

Preparation of the sample

The sample was set to a series of processes of particle size reduction, starting with a primary fragmentation of the material into more manageable pieces and subsequent drying. Then a crushing was performed in a jaw crusher, until the material has a grain size of 2 mm. After this a homogenization was performed to obtain a representative sample, the technique of quartering (with device and manual) was used, from which 100 g of sample was taken and weighed to be pulverized in a disc mill, under operating conditions of three minutes and 700 rpm. The powdered has a D80 of mesh 200 (0.075 mm), granulometry used in the process.

Determination of head grade of V2O5.

A preliminary chemical analysis of the different samples collected in the sector was carried out to determine the percentage of V2O5 present in them, using portable X Ray Fluorescence (pXRF). From this sample, the highest percentage obtained was 1.6% of V2O5, which was used for subsequent processes.

Mineralogical characterization.

The mineralogical analysis was carried out through X Ray Diffraction (XRD) where the sample presented the following mineralogical composition: calcite (79%), quartz (15%), uranospatite (3%), apatite (1%), sherwoodite (1%), and minor amounts (<1%) of illite, biotite, kaolinite, rossite and ronneburgite.

Occurrence state of vanadium.

Operating conditions were set such as the leaching time comprised in three hours, the solid/liquid ratio of 1:10, granulometry of 0.075 mm, conditions taken from other hydrometallurgical tests of vanadium [3,4,5]. For the agitation speed, 300 revolutions per minute were set, since in previous tests it was verified that at the speed of 200 rpm there was no longer any dependence between the agitation speed and the percentage of leaching [6].

Leaching with distilled water.

10 g of powdered sample were weighed in a beaker (in triplicate). To these samples were added 100 ml of distilled water and they were brought to constant agitation for a period of three hours at an agitation speed of 300 rpm, in this way all the material has contact with the water and the leaching is carried out [3].

For this procedure, the operating variables were the leaching temperatures of 35, 48 and 61 °C, which were fixed experimentally. After the leaching time the mixtures were allowed to settle for 10 minutes, the liquid was taken to centrifugation to completely separate it from the solid, a process that was carried out at 7830 rpm for a lapse of 15 minutes. The remaining solid was dried in an oven at 105 °C for 12 hours, this tail was finally analyzed by pXRF.

To calculate the percentage of leaching, the percentage of V₂O₅ present in the head grade of the sample minus the percentage of V₂O₅ in the solid (leaching tail) result was taken as percentage, being the initial concentration of V₂O₅ 100% vanadium present. In the sample used, a 6.25% leaching of V₂O₅ with distilled water was registered, a value that denoted the presence of vanadium (V) slightly absorbed in the surface of organic matter and detrital minerals. [3].

Leaching with hydrochloric acid (HCl).

For this process, 5 g of pulverized sample were weighed in four beakers and the initial operating conditions were kept fixed, in addition to the leaching temperature, which was maintained at 25 °C to evaluate the action of the acid alone. on the sample, without the intervention of the temperature [3].

The operation variable was the concentration of hydrochloric acid. To each glass was added 50 ml of HCl of different concentration: 15%; 21%; 27% and 32%. These concentrations were established establishing a range of four percentages comprised within the highest concentration available in the laboratory, which was 32%.

Once the time of three hours of leaching had passed, the mixture was allowed to settle, the liquid part was brought to centrifugation and the remaining solid was dried on a heating plate at a temperature of 150 °C. For the reading of the resulting solid the pXRF equipment was used, by subtraction with respect to the initial concentration of V₂O₅ the percentage of leaching with HCl was obtained. To this result the percentage of V₂O₅ leached with distilled water was subtracted to obtain the percentage of vanadium (V) strongly absorbed in the surface of the organic matter and the detrital minerals that was of 43.11% of the sample used for the process [3].

Leaching with sulfuric acid (H₂SO₄).

Finally, leaching was carried out with different concentrations of sulfuric acid, which was used due to the universal use for the leaching of vanadium in other projects consulted, in addition to the low percentage of aluminosilicates, which is why HF was not used [6].

As in the previous leaching, factors such as agitation speed, leaching time, solid / liquid ratio and temperature of 25 °C were kept constant. Four beakers of precipitation were prepared, where 5 g of pulverized sample was weighed in each one and 50 ml of sulfuric acid were added at different concentrations: 7%; 15%; 25% and 35%. As with HCl, it was decided to set these concentrations based on the highest available concentration of sulfuric acid. Leaching was carried out with higher concentrations of sulfuric acid (50% and 75%) but no better results were recorded than those previously obtained at lower concentrations.

After three hours of leaching, the samples were allowed to settle and then the solid phase was separated from the liquid phase. The liquid was taken to centrifuge, where speed and time parameters of 7830 rpm and 15 minutes were set, respectively. The resulting solid was dried on a heating plate at 150 °C, and analyzed by pXRF.

The percentage of V₂O₅ leached with sulfuric acid was calculated with respect to the concentration of V₂O₅ present in the head grade, which in turn was subtracted the sum of the percentage of vanadium leached with distilled water plus the leaching with HCl to thus calculate the percentage shared between vanadium in state (V), which is strongly absorbed in the surface, and vanadium (IV) that is strongly linked to organic matter [3], which was 33.13%.

When adding the three percentages of leaching (H₂O + HCl + H₂SO₄) it is assumed to obtain the percentage of total vanadium leaching in state (IV) and (V), which when subtracted from 100% of the head law, results in a 17.5% of vanadium existing in state (III), the same that is unable to be leached with the use of acids [4].

Hydrometallurgical tests of vanadium.

Variables such as the choice of leaching acid, the optimum concentration of this medium, the ideal temperature at which to carry out the process and whether the oxidation of the sample is significant before and after being attacked by the selected medium were involved in this trial.

Choice and determination of the concentration of the leaching medium.

As a result of the vanadium speciation, the leaching percentage information was used with each of the media, and leaching was carried out with nitric acid at different concentrations, where there was no satisfactory leaching, leaving the highest percentage of vanadium in the solid (tailings), so it was determined as the best

means of leaching, the sulfuric acid at the concentration of 15%, denoting the percentage of leaching yield of 82.5%.

Variation of temperature.

The operating conditions verified in the previous tests were fixed, the sulfuric acid was selected as a leaching agent at a concentration of 15%. The variable of this test was the temperature, which was established at 25 °C, 37 °C, 50 °C and 75 °C, temperatures set experimentally, since above this range (as used in other methodologies [1,6,7]) there was no adequate separation between the solid residue and the leachate, due to the high viscosity of the mixture.

Like the previous experimental processes, the mixture was left to settle for a lapse of 10 minutes and for its subsequent centrifugation at 7830 rpm for 15 minutes, after this time the solid was separated from the leachate. The solid was dried on the heating plate at 150 °C and analyzed by pXRF, which showed inferior results to those obtained at 25 °C.

Oxidation of vanadium (III)

The solid residue, product of the leaching at 25 °C with 15% H₂SO₄, was used as starting material for the oxidation process.

It started with the division into three equal parts of the solid waste and according to its weighing, the volume of the hydrogen peroxide solutions of 10 volumes (3% concentration) was added, in concentrations of 10, 20 and 30 g / L [7, 8] to maintain the solid / liquid ratio of 1:10. The agitation time and speed of 3 hours and 300 rpm, respectively and 25 °C of temperature, were maintained.

Once oxidized the material was left to rest for 10 minutes and the liquid was centrifuged at 7830 rpm and 15 minutes, then the solid was allowed to dry at room temperature (inclemency), spread on a glass watch. With the help of a spatula the solid was removed and measured with the use of pXRF, the result was maintained, so there was no loss of vanadium in this process.

Second leaching.

Each solid residue resulting from the oxidation was weighed and according to this the volume of the acid was added, to maintain the solid / liquid ratio of 1:10, in addition to the other operating conditions. The medium used for the second leaching was sulfuric acid at a concentration of 15%. Optimal conditions according to previous tests.

Once the leaching time was over, which was three hours, the solid was allowed to settle and again centrifuged at the same conditions and the solid was dried on a heating plate at 150 °C, the same as measured by pXRF and finally it was determined that the concentration of hydrogen peroxide required to achieve the highest oxidation of the vanadium in state (III) was 20 g / L. Subsequently, the percentage of the total vanadium yield of the leaching process that was 96.95% was calculated.

DISCUSSION AND CONCLUSIONS

In the case of the selected bituminous black limestone sample, vanadium is found mostly in state (V) approximately 43.12%, occurring in minerals such as sherwoodite and, to a lesser extent, in minerals such as ronneburgite and rossite, notwithstanding a percentage notable (33.13%) is found as vanadium (IV), which is strongly bound to organic matter and 17.5% vanadium (III) which can be found in the illite, replacing Al.

Due to its leaching action, sulfuric acid was taken into account as a means for leaching, giving approximate percentages of 82.5% in the first process. When carrying out the oxidation of vanadium (III) to vanadium (IV) or (V), it could be leached, increasing the yield of the process to 96.95%, which is why the oxidation process, with H₂O₂ as an oxidizing agent, must be taken into account to obtain an efficient process.

Conclusions

The best leaching agent was H₂SO₄ at a concentration of 15%, using operating conditions such as temperature of 25 °C, solid / liquid ratio 1:10, time and rate of leaching agitation of 3 hours and 300 rpm, respectively.

Vanadium (III) can not be leached by acids (with the exception of HF), like the other states (IV and V), reason why oxidation is an indispensable process for the increase of the total yield, where the best concentration experienced it was 20 g / L of H₂O₂ (10 volumes), this procedure being very useful, since there is no greater economic demand due to the low prices of hydrogen peroxide.

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Country or International Organization

Ecuador

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