

Processing strategy for catalytic residues containing vanadium

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Abstract

Vanadium is a strategic element which is on the list of raw materials in a critical state, mainly due to the depletion of the mineral deposits that contain it, so it is important to recover it from industrial wastes that contain it. Among these wastes are the spent catalysts from the manufacture of sulfuric acid, which contain between 4-9 % of V_2O_5 , and are therefore classified as contaminants. The objective of the work is to develop a strategy for processing catalytic residues from sulfuric acid manufacture, to recover the vanadium contained in them, without generating new pollutant residues. The work proposes a hydrometallurgical processing strategy for the waste from the Patricio Lumumba Plant, which consists of leaching with sulfuric acid and subsequent precipitation with sodium carbonate. The result is a recovered product with ~38 % V_2O_5 . On the other hand, the process generates a solid residue, consisting of 98 % silica, and a liquid residue consisting mainly of sodium sulfate and water. The proposed process allows the recovery of vanadium in the form of concentrate and the generation of two new residues, without vanadium, which can be used in other applications. The developed process constitutes a viable alternative for the processing of spent catalysts from the manufacture of sulfuric acid, which allows the recovery of a metal considered strategic and contributes to the protection of the environment.

1. Introduction

Vanadium is a metal of strategic and industrial importance due to its applications in many technological fields, which is on the list of raw materials classified as critical. This, together with the low vanadium grade in ore concentrates and the depletion of ore concentrate deposits in the world, makes it necessary to make full use of secondary resources containing vanadium, including spent catalysts [1], [2].

The spent catalysts from the manufacture of sulfuric acid contain more than 3% V_2O_5 , resulting in an important source of vanadium ($\geq 1.68\%$ V), a strategic metal of which there are no reported deposits in Cuba. There are few deposits with high concentrations of this element, which is obtained industrially from different ores and industrial residues [3].

Spent catalysts are among the preferred secondary raw materials for vanadium extraction, as they contain 4 to 9 wt% V_2O_5 along with other valuable components, in the form of oxides or sulfates, and have an average lifetime of 2 to 5 years (up to 10 years) [4], [5].

Vanadium catalysts are used in the sulfuric acid production process by the contact method, since they contribute to the transformation of SO_2 into SO_3 . With the pass of time the catalyst is spent "poisoning" and must go out of service, being considered hazardous waste, so it is obligatory for the companies to store it indefinitely, increasing the costs and the amount of residual stored [6].

According to a 2018 report, Cuba stores more than 900 tons of catalytic waste from the production of

sulfuric acid from plant A in Pinar del Río, located in the westernmost part of the country, and plant B in Holguín, in the eastern region of Cuba [7]. On the other hand, investments have been made in plants B and C in Matanzas to increase the production of sulfuric acid, which leads to an increase in the amount of catalytic waste generated, in addition to those already existing in the country, for which there is no defined processing strategy. Plant B generates about 21 tons of catalytic waste per year and plant C generates about 14 tons every two years. In the case of Plant C in Matanzas, also located in the western region, the catalytic residues generated are used as an additive mixed with cement for paving surfaces [7], which avoids the environmental problems generated by the catalysts, but misses the possibility of recovering the vanadium contained in them. In Cuba there is currently no defined processing strategy for catalytic wastes, and they are stored indefinitely in the National Confinement of Hazardous Wastes, in the province of Cienfuegos, an institution created to confine hazardous wastes in the country, which is located in the central and southern region of the country. The confinement of waste solves the environmental problem in the short term, but since the space available is limited, it is not a viable option on a permanent basis. These aspects validate the need to find alternatives for processing spent catalysts in order to avoid their confinement and environmental contamination, and also to recover the vanadium. Therefore, the objective of this research is to evaluate at laboratory scale a procedure for the treatment of spent catalysts from sulfuric acid manufacturing to recover vanadium. In order to realize the objective, it is necessary to use equipment that is feasible to assemble in Cuba, using mainly reagents of national origin. Therefore, the results of the process can be achieved from the establishment of the main operation parameters, such as temperature, concentration, among others, which influence the output variables of the process, such as yield, vanadium concentration, etc. Then, the research is important because the treatment proposed for the spent catalysts contributes to the preservation of the environment, since it would allow processing the catalytic residues considered pollutants. In addition, it offers the possibility of extracting the vanadium contained in the catalysts, a strategic metal of which there are no deposits in Cuba, and whose import cost is high, due to the price of the metal and the difficulties Cuba has to import products in the international market.

2. Methods or experimental part

2.1. Methods of catalytic waste treatment

In the case of spent catalysts from the manufacture of sulfuric acid, which use vanadium pentoxide as an active component, it is generally established that their final disposal as solid waste can be carried out in two fundamental ways: processing to recover the vanadium or disposal in landfills [3]. The metal can be recovered as a vanadium salt or as ferrovandium, for which it has been established that the vanadium pentoxide content in the waste must be higher than 3%, establishing the following as the required parameters of the catalytic waste [3]:

- V_2O_5 : min. 3% weight
- K_2O : max. 10% weight
- P: max. 0.5% weight
- Sn, Pb, As, Sb, Bi, Cu, Zn, Cd, Hg: max. 0.1% weight

Landfill disposal can be carried out in two ways: by fixation or direct landfill. In the case of fixation, the residue is fixed in an inert matrix, usually concrete or glass, prior to controlled deposit in an authorized landfill, a process designed to avoid leaching of metals. For direct landfill, the catalyst is deposited directly into a suitable licensed landfill, and it is common practice to mix it with lime to neutralize the acidity of the residue [3].

From the options available for the final disposal of catalytic residues, several studies have focused on the extraction of vanadium, due to its high cost and industrial importance.

Among the methods used for the recovery of vanadium from spent catalysts are pyrometallurgical methods, using for this purpose: carbothermia and aluminothermia. In the case of carbothermia, it is not a generally economical route unless a large amount of spent catalyst is processed and the prices of vanadium metal are high [8], a method characterized by its high energy consumption, which is why it would not be feasible to apply in Cuba. As for aluminothermic processing, the vanadium content in the alloy would be relatively low [9]. Another traditionally used method is hydrometallurgical, in which liquid solutions are used for the extraction and recovery of metals from ores and residues, in which leaching plays a fundamental role [10]. In these cases, leaching can be acidic or basic, selecting for the particular case of Cuba leaching with sulfuric acid because it is produced in the country in the same plants where the waste is generated, which facilitates the supply of raw materials for processing.

Therefore, if an adequate chemical processing of the spent catalysts from the manufacture of sulfuric acid is carried out, it is possible to recover the vanadium present in them, without the

generation of new polluting residues. In order to develop this strategy, it is necessary to take into account technical and economic factors that allow the recovery of vanadium.

2.2. Selection of the catalytic residual and processing site

For the development of the research, catalysts from Plant A, which has not worked for more than two decades, were selected. These catalysts are still stored in the plant installations.

On the other hand, for the location of the catalytic waste processing plant, the province of Cienfuegos was considered to be the most appropriate place, due to its location in the central region of the country and the Bay of Cienfuegos to the south of the province, which would facilitate the logistics of control and collection of catalytic waste from the sulfuric acid plants located at the ends of the country.

Figure 1 shows a map of Cuba with the location of the sulfuric acid plants mentioned and the proposed location of the waste processing plant.



Figure 1: Location of the sulfuric acid plants and the proposed residuals processing plant

Figure 1 shows the location of Plant A at the westernmost tip of Cuba, about 455 km from the province of Cienfuegos, via the East-West Highway and the National Highway. On the other hand, the distance from Plant B to Cienfuegos would be about 709 km and from Plant C about 172 km, both along the Central Highway of Cuba. Another aspect that influences the location of the processing plant is its proximity to the sulfuric acid factory located at Plant C (172 km), a reagent necessary to develop the leaching stage of chemical processing.

2.3. Raw material and reagents

The spent catalyst sample selected for the study came from Plant A, in the province of Pinar del Río. The chemical characterization was carried out by the Center for Environmental Studies of Cienfuegos by means of X-ray fluorescence [11] and the results are shown in Table 1.

The spent catalyst sample was crushed in a disk mill to a particle diameter < 0.25 mm [11]. The following reagents were used to process the catalytic residue:

- technical grade sulfuric acid for leaching.
- sodium carbonate solution to neutralize the excess acid and as a precipitating agent.

Table 1: Elemental chemical composition of the spent catalysts from the Sulfometal Plant

Content (%-wt)		Content (mg/kg)	
Si	30,03	P	809,20
S	7,17	Mn	323,37
Fe	6,35	Ni	269,13
V	1,92	Zn	183,25
Na	1,09	Cr	181,40
Mg	0,78	Cu	139,73
Ca	0,62	As	64,57
Pb	0,16	Sr	62,09
Total	48,12	Total	2032,74

2.4. Processing of spent catalyst

The first stage of the working procedure consisted of mixing the spent catalyst sample with a dilute sulfuric acid solution (leaching agent), in order to separate the soluble (leachable) elements from the rest of the compounds that make up the residual, which remain as insoluble residues [11].

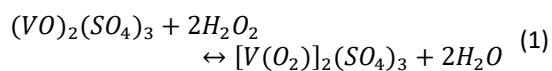
When the leaching stage is finished, the mixture is filtered under vacuum and the liquid phase is separated from the solid residue. The solid residue is washed with water to remove any remaining solution and then dried at 120 °C.

The second processing stage consists of adding a sodium carbonate solution to the liquid phase obtained, until a pH value of pH=7 is reached, then

the precipitated product is filtered and separated by filtration, generating a liquid residual. The precipitated product is calcined at 450 °C for two hours.

2.5. Product characterization

The determination of the vanadium content in the liquid phase coming from the leaching and in the liquid residual remaining after the precipitation stage was carried out by means of visible ultraviolet spectroscopy, applying a technique available at the Spectroscopy Laboratory of the Agricultural Research Center, belonging to the Faculty of Agricultural Sciences, at the "Marta Abreu" Central University of Las Villas. The technique consists of the formation of a complex between hydrogen peroxide and vanadium. Vanadium ions in sulfuric acid and hydrogen peroxide react according to equation 1 to form a reddish brown color, where the color intensity depends on the concentration of vanadium [12]. Measurement of solution absorbance at a wavelength of 455 nm can be used for quantitative analysis of vanadium.



The phasic characterization of the recovered product and the solid residual generated was carried out by X-Ray Diffraction (XRD). The diffractograms were processed using the software X Pert High Score Plus (2011) and Profex version 5.1.1. The databases used for the identification of the phases present were the Crystallographic Open Database 2014 and the ICSD Database FIZ Karlsruhe 2008-2.

3. Results and Discussion

3.1. General methods for obtaining vanadium from residuals by leaching

Vanadium processing depends largely on the nature of the raw material, but all processes have common features, which include the stages of physical beneficiation, roasting, leaching, solution purification and precipitation [13].

In the case of spent catalysts, the surface may be poisoned with organic compounds, unburned substances, carbon residues, sulfur, which often requires preliminary calcination. These catalysts are used in processes such as hydrosulfurization (HDS), fluidized catalytic cracking (FCC), hydrotreating (HDT) and sulfuric acid production, so their chemical composition is very varied [14]. Therefore, the roasting stage is performed with the aim of removing substances from the catalyst, such as water, light hydrocarbons, and carbon and sulfur by oxidation [15].

In the case of spent catalysts from sulfuric acid manufacture, they consist of an inert support with a highly porous surface, typically natural or synthetic cristobalites, with pores containing a mixture of vanadium pentoxide as the active component, together with alkali metal sulfate promoters, usually potassium sulfate or cesium sulfate. In addition, they may contain small concentrations of other elements, which is a function of the catalyst manufacturer and the characteristics of the sulfuric acid production process [16].

Therefore, the catalytic residues from the manufacture of sulfuric acid do not contain the same pollutants as the rest. In these, the main pollutant is sulfur.

In the case of the catalyst studied, the roasting stage was not included. Table 3.1 shows the chemical composition of the catalyst, where it is possible to observe the presence of sulfur as the main contaminant, and to a lesser extent other elements such as phosphorus, arsenic, strontium and lead. These elements should be found as $Ca_3(PO_4)_2$, As_2S_5 , SrO , PbO and sulfur in its elemental form [11].

Therefore, the roasting stage would only eliminate the sulfur, for which a temperature higher than 450 °C would be necessary, making the production process more expensive [17].

Taking into account the possible reactions that must occur during leaching between the components of the catalyst and the sulfuric acid [11], sulfur and As_2S_5 are not dissolved, so they will remain as insoluble residues, forming part of the residue generated. $CaSO_4$, $PbSO_4$ and $SrSO_4$ should form precipitates, which would become part of the insoluble solid residue [11], [18].

Therefore, these elements that are found contaminating the catalytic residue should not interfere with the quality of the main product of the process, i.e., the vanadium concentrate.

On the other hand, the precipitation stage is accompanied by separation and purification, with the aim of obtaining a product of higher purity. In this sense, several authors have carried out studies with solvent extractions, selective precipitation, oxidation, among others [4], operations that require adding certain steps and equipment to the general scheme, which implies a considerable increase in the cost of the process.

The vanadium concentrate to be obtained will be used in the production of welding consumables. Therefore, none of the operations mentioned previously is essential, since the other elements that precipitate with the vanadium (iron, magnesium, chromium fundamentally) would not affect the development of the electrode, since they commonly form part of its composition.

The final product obtained is reduced to obtain metallic vanadium or ferrovandium, which depends largely on the final application of the product. Sometimes this product is refined to improve its purity, especially if the purpose is to market it directly, an operation that is also not required in view of the intended use of the alloy. The reduction of the metal oxides obtained in the recovered product must be carried out by means of aluminothermia, a process that is capable of developing in a self-sustained manner from the heat generated by the redox reactions, so it does

not require additional energy supply, only that necessary to start the process.

3.2. Proposed processing scheme

Based on the studies carried out on this subject and the procedure developed [11], [19], the diagram shown in Figure 2 is proposed. The diagram shows the different stages through which the process passes and the products generated in each one of them.

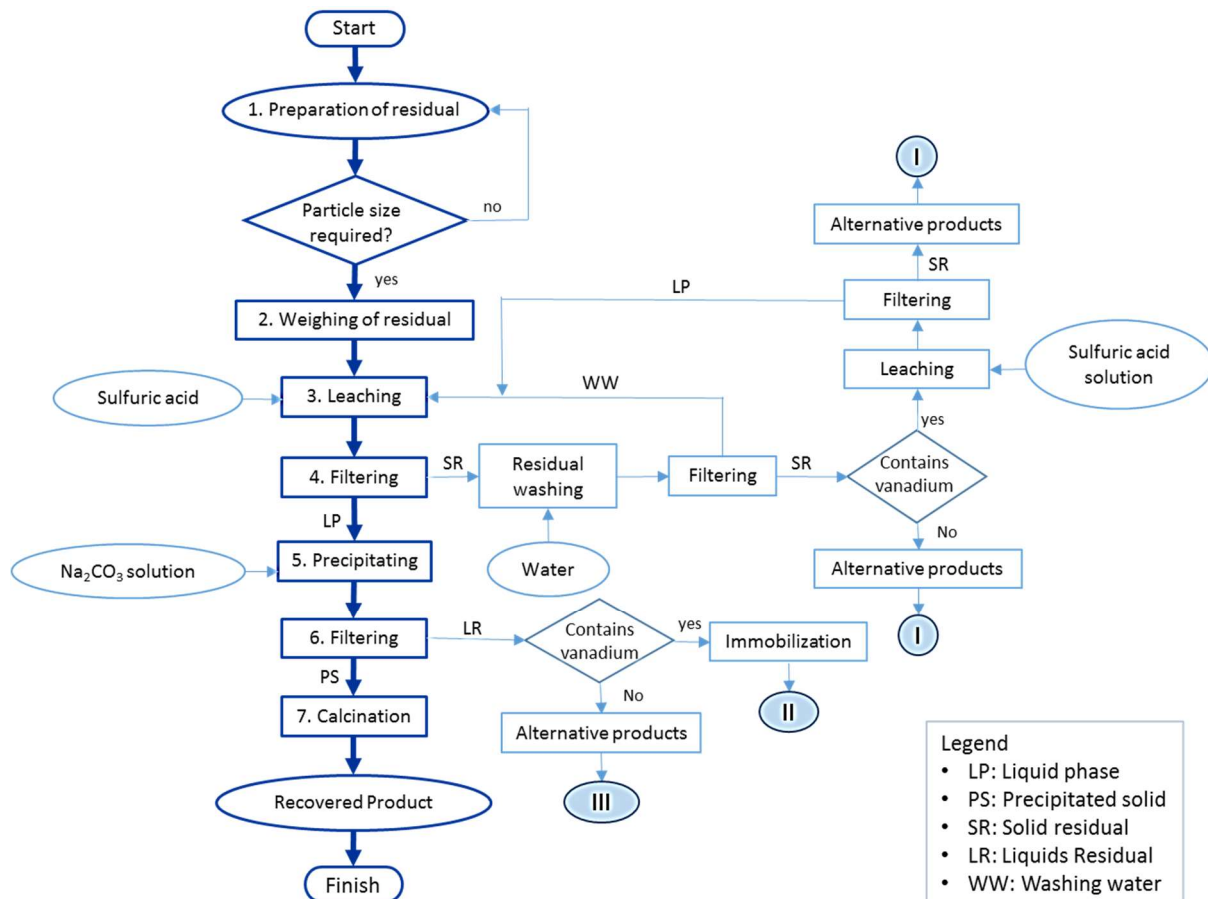


Figure 2: Schematic diagram of catalytic residue processing

3.2.1. Catalyst preparation

The first step in the processing of the catalyst is the preparation of the raw material: crushing and screening, since the catalysts are commercialized in different forms such as pellets, rings or stars. Figure 3 shows a figure with the different forms in which the V_2O_5 catalyst can be presented [3].



Figure 3: Shapes of the vanadium pentoxide catalyst. a) Pellets, b) Rings, c) Stars [8]

Generally, these catalysts have ceramic separators whose function is to avoid caking of the catalyst pellets, and thus guarantee the SO_2 flow through the adsorption towers. These parts must be removed prior to catalyst milling. Particle size is one of the factors involved in the efficiency of the extraction process, since the smaller the particle size, the greater the interfacial area between the solid and the liquid and therefore the greater the transfer and the shorter the distance that the solute must diffuse within the solid. However, the production of very fine material that can occupy the interstices of the larger particles and impede the flow of the solvent must be avoided [20].

Several authors have carried out studies varying the particle size, selecting values in the range of 0.1 to 4 mm depending on the operating conditions [21], [22], [23].

A particle size of less than 0.25 mm was selected, which is in agreement with several researchers [22, 24]. It is important to maintain control of the working particle size to ensure vanadium recovery values at similar levels.

3.2.2. Acid leaching

Leaching is performed in a reactor and a set of factors such as solvent, solid-liquid ratio, leaching time, agitation, temperature, etc. must be taken into account [20].

The leaching agent can vary, and the use of various reagents is found in the literature. Among the acid leaching agents, the most studied are nitric, sulfuric and hydrochloric acids, using in some cases mixtures of them in different proportions [17], [23], [25], [26], also using organic acids such as citric acid, oxalic acid [21]. As for basic lixiviants, sodium and potassium hydroxide, sodium carbonate and ammonia solutions have been studied [4], [22], [27].

Alkaline leaching is selective for vanadium over iron, but dissolves some silica and is more expensive in terms of reagents [4].

On the other hand, good results have been obtained using sulfuric acid [17], [25], which is a reagent produced in Cuba, currently in two plants: Plant C in Matanzas and Plant B in Holguín.

As a result of the leaching stage, a greenish colored liquid phase was obtained, from which the vanadium content was determined by UV-visible spectroscopy and from this value the leaching yield was determined, taking into account the vanadium content in the catalytic residual. These results are shown in Table 2.

Vanadium solutions in acidic media are found in VO_2^+ form as $(VO_2)_2SO_4$ and in VO^{2+} form as $VOSO_4$. Furthermore, in the presence of sulfate ions, VO_2^+ cations form compounds such as $VO_2SO_4^-$.

Therefore, three ionic species of vanadium can be found in solution, which have characteristic colors: VO_2^+ , with a pale yellow coloration, VO^{2+} , with a blue coloration, and $VO_2SO_4^-$, with a yellow coloration. The combination of these ions in solution produces a greenish coloration [5].

Table 2: Leaching stage results

V (mg/L)	Leaching yield (%)
3611,7	93,9

Table 2 shows that as a result of the leaching stage, approximately 94 % of the vanadium present in the catalyst could be extracted to the liquid phase.

These values are in similar ranges to those reported in the literature [17], [23], [25].

3.2.3. Precipitation

Once the liquid phase is obtained after leaching, precipitation takes place, with the objective of converting the metallic sulfates present in the liquid phase into solids (precipitate).

This is the final processing operation in which pH control and the addition of the precipitation agent are key or fundamental parameters [13].

Different compounds (salts or hydroxides) have been studied for precipitation, the most widely used being ammonium compounds, which lead to a high purity of the product, but produce large quantities of waste water and gases containing ammonia, constituting a threat to the environment [2], [13], [28].

On the other hand, Na^+ ions can combine with vanadium during precipitation to form sodium polyvanadate, which crystallizes later [2]. Several authors have evaluated the use of sodium compounds, such as sodium hydroxide and sodium carbonate of concentration 1 mol/L or 2 mol/L [17], [25], the latter being used to achieve and maintain the ideal pH during precipitation [29]. Therefore, based on these criteria, sodium carbonate was selected as the precipitating agent for precipitation.

Once the precipitation was completed, the mixture was filtered and the precipitated product was calcined at 450 °C for two hours.

As a result of this stage, the product shown in Figure 4 was obtained, which was analyzed by XRD, obtaining the diffractogram shown in Figure 5.



Figure 4: Recovered product

From the diffractogram obtained, the presence of several phases can be observed, among them ternardite (Na_2SO_4), which is produced as a consequence of precipitation with a sodium salt. In addition, it is observed that vanadium is present in the phases of molecular formula: $Fe_4Mn_3V_6O_{24}$, $KNaV_2O_6$, V_2O_5 , V_3O_8 , $Ca_3MnNaV_5O_{17}$ predominating the latter, which represents 12.6 % of the recovered product. On the other hand, the determination of the vanadium content in the recovered product gave a value of 37.8 % of V_2O_5 , which indicates that the recovery was favorable.

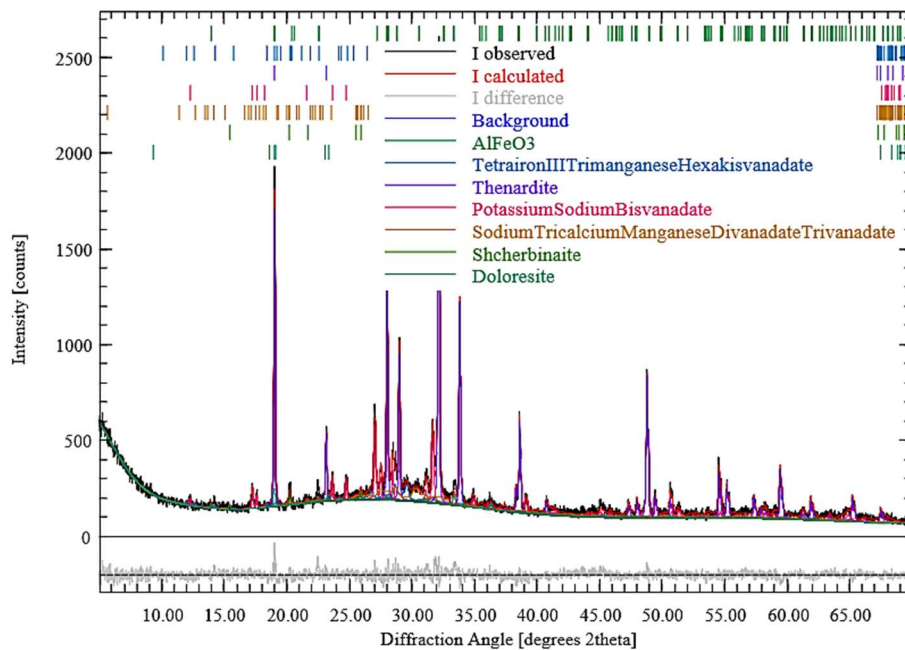


Figure 5: X-ray diffractogram of recovered product

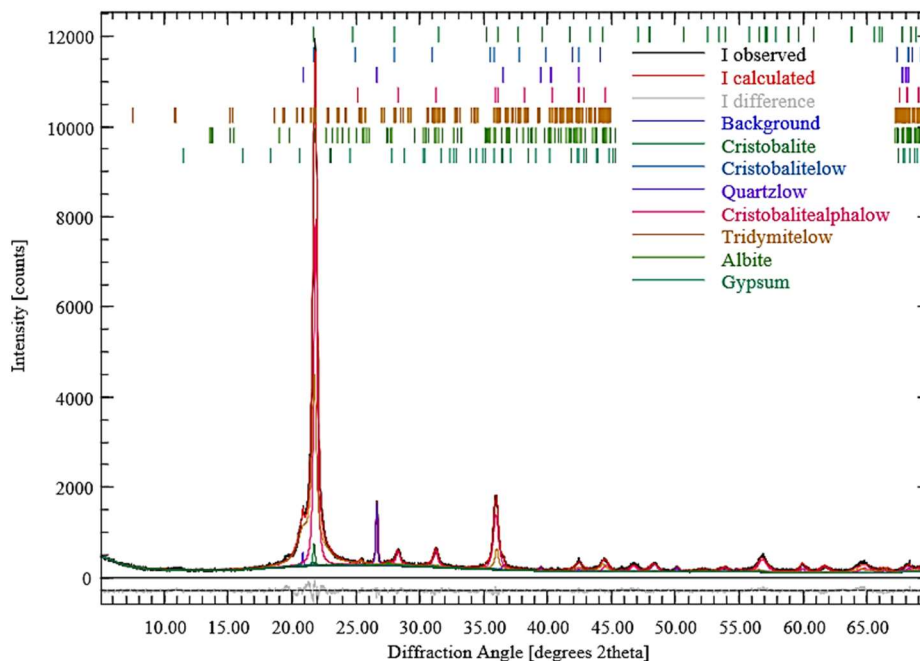


Figure 6: X-ray diffractogram of solid residual

3.2.4. Waste generated from processing

After the sulfuric acid leaching stage, a solid residue formed mainly by silica is generated, which must be washed, since it is contaminated with vanadium from the liquid phase. The wash water resulting from this stage must be recirculated to the leaching reactor in order to take advantage of the metallic elements that were removed from the residual during washing. Finally, the residue is dried at 120 °C.

In the case of the catalytic residual sample analyzed, the solid residual obtained after leaching was analyzed by XRD, obtaining the diffractogram shown in Figure 6, from which the preliminary

semi-quantitative analysis was carried out, obtaining the data shown in Table 3, where it can be seen that the residual is composed of 98 % silica.

Table 3: Preliminary semi-quantitative analysis of solid residual (%-wt)

Phase	H ₂ O	Na ₂ O	Al ₂ O ₃	SiO ₂	SO ₃	CaO
%-wt	0,28	0,14	0,24	98,31	0,62	0,44

The vanadium-free solid residue is an output product (product I in Figure 2). In this case, since it consists mainly of silica, its use in other

applications can be valued, for example, in construction materials as industrial aggregate or filler material [27].

It is important to highlight in this case the absence of peaks corresponding to vanadium compounds, evidencing the non-presence of the element in the residual, indicating that the extraction during leaching was efficient. Therefore, it is affirmed that the residue generated from the chemical processing of the spent catalysts does not constitute a pollutant for the environment.

On the other hand, during the precipitation stage, a liquid residue is also generated as a result of the reactions between the excess sulfuric acid and the metal sulfates with the sodium carbonate. In this case, the residual consists mainly of sodium sulfate and water.

In the precipitation stage, pH control plays a fundamental role in order to avoid redissolution of the vanadium into the liquid phase.

If the liquid waste contains vanadium (product II in Figure 2), it must be immobilized, which can be achieved by incorporating it into construction materials. If it is free of contaminating metals (e.g. vanadium), alternative uses can be evaluated (product III in Figure 2), especially to take advantage of the sodium sulfate content present in the waste.

The qualitative determination of vanadium in the liquid waste with hydrogen peroxide showed that the waste does not contain vanadium.

3.3. Basic process considerations

From the study developed at laboratory level, it is important to point out some aspects that should be taken into consideration for a possible scaling up of the evaluated procedure, which would allow to achieve the highest efficiency in the processing of catalytic wastes, and therefore the highest vanadium recovery. It is therefore important to control each stage of the process.

Among the main factors that can cause failures in the system are those associated with the leaching stage, since the maximum extraction of vanadium and the avoidance of generating a new contaminated waste depends on it. In this case, there may be aspects related to the operation of the leaching reactor, such as the temperature of the system due to problems in the heating system or in its control system. Another problem may be related to the agitation of the mixture, which is necessary to favor the transfer of matter between the phases.

Fundamental aspects to guarantee the stable operation of the plant are those related to the plant's equipment in each of its operations. In the leaching stage, an acid pulp is processed, which is filtered under pressure. Therefore, the equipment

required for the development of these operations must be resistant to sulfuric acid solutions.

According to Perry and Peters [30], [31], alloys of aluminum-bronze, copper, cast iron with 14 % silicon and lead are resistant to sulfuric acid solutions with concentrations < 50 % and at temperatures of 20, 60 and 100 °C. In addition, some polymeric materials such as polytetrafluoroethylene (Teflon), polychlorotrifluoroethylene (PCTFE or kel-F), polyvinylidene fluoride (PVDF), among others, can be used. In the case of polyvinyl chloride (PVC), it is limited to working temperatures of up to 60°C. Therefore, it is necessary to give special attention to the selection of the pumping system and the filter. In addition, it is advisable to install a second pump to increase the reliability of these operations.

As for the precipitation stage, as mentioned above, among the fundamental factors are pH control and agitation. In this case, the precipitation stage begins in an acid medium, where the pH of the medium gradually increases to a neutral value, therefore, the reactor must be made of a material resistant to sulfuric acid solutions, but the pumping equipment and the filtration of the pulp (precipitate) can be carried out with conventional pumps and filters.

In this second stage it is also advisable to duplicate the pump to guarantee stability in the process.

On the other hand, it is advisable to maintain control over the solid and liquid residual, especially in relation to the vanadium content, which avoids the exit of a contaminating product from the process. The storage and handling of raw materials, intermediate and final products must be taken into consideration to avoid possible spills or contamination of these products.

In the case of raw materials, there must be strict control during the transfer and storage of concentrated sulfuric acid, since it is a highly corrosive reagent [32], capable of causing serious accidents to plant operators.

The catalytic residue must also be stored in safe conditions.

During all stages of plant operation, the safety and work protection rules established for chemical plants must be followed [33].

With respect to the proposal for a pilot plant to scale up the procedure evaluated at the laboratory level, it should be taken into account that the quantities of catalytic waste generated in Cuba are relatively low; therefore, the pilot plant should be capable of processing other industrial waste containing vanadium, such as the ashes from oil combustion.

3.4. Importance of vanadium in the development of electrodes for the recovery of parts in Cuba

In Cuba there are two plants for the manufacture of coated electrodes, with an installed capacity of five thousand tons per year, whose production does not correspond to this capacity, mainly due to the lack of raw materials; neither does it satisfy the demand, in variety or quantity, for the electrodes required by the country's economy. In addition, the electrodes for hardfacing are not produced in Cuba, so it is necessary to import them. The demand for electrodes for the recovery of parts and, specifically, for manual electric arc welding hardfacing is not satisfied due to financing limitations. These electrodes are priced much higher than conventional welding electrodes (E6013 and E7018). For example, the UTP 620 electrode, widely used in the sugar industry for hardfacing a wide variety of parts, is 10 times more expensive than conventional electrodes [34]. In Cuba, at the José A. Echevarría Polytechnic Institute in 1986, a pilot plant was set up to manufacture electrodes for manual welding hardfacing, mainly for the sugar industry, with a production capacity of 200 tons per year. Among the electrodes produced in Cuba at that time was the Vanadin 25 electrode, an electrode with a basic coating for welding and cold filling of lamellar and spheroidal gray cast iron. This electrode made it possible to replace in many applications the nickel and nickel iron base electrodes [35], the vanadium used for the manufacture of the Vanadin 25 electrode was imported. Retaking the manufacture of these electrodes by using the capacities installed in the factories and using part of the raw materials of national origin for the coating contributes to reduce imports and costs.

Morales Rodríguez [36], obtained by means of carbothermal processing in an electric arc furnace, a Cr-V alloy, which was evaluated in the manufacture of electrodes for manual electric arc welding, obtaining welding deposits with 17% Cr and 1.89% V, feasible to use in the recovery of parts working in abrasive wear conditions [34], resulting in this being the first alloy with vanadium obtained in Cuba, using Cuban chromites and catalytic residues from the manufacture of sulfuric acid.

Subsequently, Perdomo González obtained vanadium alloys from the aluminothermic processing of catalytic residues from the manufacture of sulfuric acid from the B and A plants, where the maximum vanadium content obtained in the alloy is limited by the characteristics of the residue and the method of obtaining it [37], [9]. These alloys have been evaluated by Rodríguez Pérez [38], [39], [40] in the manufacture of coated tubular electrodes for the

recovery of parts, where they were combined with other ferroalloys.

For example, the effect of V and Si, incorporated from the Fe-V-Si alloy obtained, on the microstructure of the deposits obtained with high Mn content (Hadfield) was evaluated. As a result of the work, the properties of the obtained strands were improved, especially those related to wear resistance [37]. Coated tubular electrodes were also developed, using FeCrMn alloys, evaluating the influence of the addition of the Fe-V-Si alloy on the abrasive wear of the deposits obtained by welding, achieving a significant improvement in the properties of these deposits [38].

On the other hand, FeSiV alloys were used in different proportions of the alloy load in coated tubular electrodes, which allowed studying their influence on the microstructure of hypoeutectic white cast iron, being able to determine their behavior for their use in the surface coating of parts subjected to low or moderate abrasive wear [39].

All the previously mentioned validates the importance of obtaining vanadium concentrates from the chemical processing of spent catalysts, feasible to process by aluminothermia, which will allow obtaining vanadium alloys suitable for their use in the manufacture of welding consumables. Using these alloys, it will be possible to obtain different variants of hardfacing electrodes, which will allow covering a greater number of applications in the recovery of parts in Cuba. These special electrodes developed with these alloys constitute a contribution to the development of welding consumables, allowing the country to be independent from the international market, thus constituting an economic contribution and contributing to the preservation of the environment.

4. Conclusion

- The chemical processing proposed for the spent catalysts from the A plant allows obtaining a vanadium concentrate of ~38 % V_2O_5 .
- From the chemical processing of the spent catalysts, two new residues are generated, one solid and one liquid, which do not contain vanadium, being possible their reuse in other industrial applications.
- The control of the process parameters and the selection of the appropriate equipment is important to achieve efficiency and stability during processing.
- The proposed methodology constitutes a contribution to the environment and the economy, complying with the principles of the circular economy.

- The obtaining of a concentrate with 38% of V2O5, will allow its use in the development and evaluation of welding electrode prototypes.

5. References

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