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VANADIUM RECOVERY FROM SPENT CATALYST: FROM LAB TO INDUSTRY

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Abstract: The recovery of secondary raw materials from hazardous waste is currently an important focus of research worldwide. One example of interesting waste is spent catalysts used in the production of sulfuric acid using the contact process. These residues contain between 3–9% vanadium pentoxide and must be stored indefinitely as there is no processing strategy in the country concerned, Cuba. The aim of the research is to carry out studies on the treatment of catalytic waste aimed at recovering vanadium, an element that is considered strategic. A first paper explains the research path to develop the technical process as a laboratory solution. This second paper spans from the production process in the laboratory to the necessary industrial realization, including logistics. The paper proposes a hydrometallurgical processing strategy for catalytic residues. This is followed by an evaluation of the aspects required for processing the residues on a pilot plant scale based on logistical criteria. Overall, the developed process represents a viable alternative for the treatment of spent vanadium–containing catalysts, enabling the recovery of a metal in a critical state and contributing to the protection of the environment.
Keywords: vanadium, spent catalysts, recovered product, processing strategy, scaling

1. INTRODUCTION

In Cuba, the protection and conservation of the environment is a policy of the country, for which reason strategies have been drawn up to control and adequately treat the industrial waste generated. The Ministry of Science, Technology and Environment (CITMA) of Cuba is responsible for proposing environmental policy and directing its execution [1].

A few years ago, Cuba established the National Confinatorium of Hazardous Wastes to control and confine hazardous wastes generated in the country. The first wastes analyzed for confinement at this center were residues containing vanadium, such as spent catalysts from sulfuric acid manufacturing.

Vanadium catalysts are utilized in the contact process for sulfuric acid production because they facilitate the conversion 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 permanently the costs and the amount of residual stored [2].

According to a report from 2018, more than 900 tons of catalytic waste are stored in Cuba.

They come from the production of sulfuric acid in Plant A in Pinar del Río, in the westernmost part, and from Plant B in Holguín, in the eastern region of Cuba [3].

On the other hand, investments were made in plants B and C in Matanzas to further increase the production of sulfuric acid. This will lead to an increase in the amount of catalytic waste produced, in addition to the waste already stored in the country. To date, there is no defined processing strategy.

In the case of Plant C in Matanzas, also located in the west of the country, the catalyst residues generated are mixed with cement for paving surfaces as an additive [3], which avoids the environmental problems caused by the catalysts, but eliminates the possibility of recovering the vanadium they contain.

The spent catalysts from the manufacture of sulfuric acid contain more than 3% V_2O_5, resulting in an important source of vanadium (≥ 1.68% V), a strategic metal of which there are no reported deposits in Cuba. There are few deposits in the world with high concentrations of this element, which is obtained industrially from different ores and industrial residues [4].

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 [5, 6].

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.

The importance of the research topic results summarized from 3 main aspects:

- Waste: Existing and increasing waste from production that contains vanadium and requires permanent, expensive storage.

- Demand: Vanadium is a strategic material, there is the need to provide vanadium for various industrial applications.
- There are global only few own deposits of Vanadium & high prizes: Largely depleted and expensive extraction of the raw material worldwide, as well as no own deposits in Cuba.

Therefore, as a result of experiments carried out in the laboratory, a technology for processing spent catalysts to recover the vanadium contained in them is obtained, which is thought according to economic technical criteria and Cuban conditions, which was presented in a first paper. From the results obtained, it is then necessary to move on to the next stage of the research, which is the scaling up of the procedure. Therefore, the objective of this work is to analyze the possibility of transferring the methodology developed in the laboratory to a pilot plant scale, based on general logistic criteria.

2. MATERIALS AND METHODS

Basic considerations

To achieve the research objectives, it is essential to utilize equipment that can be feasibly assembled in Cuba, primarily using reagents of national origin. Consequently, the results of the process hinge on establishing key operational parameters such as temperature, concentration, and others that directly influence output variables like yield and vanadium concentration.

The proposed treatment for spent catalysts contributes significantly to environmental preservation by enabling the processing of catalytic residues considered pollutants. Moreover, it offers the opportunity to extract vanadium from these catalysts.

Table 1 summarizes the analysis carried out to develop the research and the work methods applied during its development [7].

Table 1. Design of the research

Problem	Chance
Hazardous waste containing vanadium	Vanadium source
High cost to deposit	Waste treatment methodology
Research questions	**Research methods**
Are there regulations in Cuba for treatment of spent catalytic?	Expert consultation
What methods can be used for treatment of spent catalysts with vanadium?	Literature review Laboratory experiments
What are the applications of the products obtained?	Consultation with experts Literature review
Is it possible to scale up the selected procedure?	Expert analysis
What aspects must be considered to move to a larger scale of the process?	Expert analysis Literature review

Methods of catalytic waste treatment

In the case of spent catalysts from sulfuric acid manufacturing, which utilize vanadium pentoxide as an active component, their final disposal as solid waste typically involves two primary methods: recovery of vanadium or landfill disposal [3]. The metal can be recovered as a vanadium salt or as ferrovanadium. It has been determined that the vanadium pentoxide content in the waste must be higher than 3% to proceed with recovery, establishing the following parameters for the catalytic waste [4]:

- 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: 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 [4].

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, specifically carbothermic and aluminothermic processes. Carbothermic methods are generally not economically viable unless large quantities of spent catalysts are processed and vanadium metal prices are high [8]. This method is characterized by high energy consumption, making it impractical for application in Cuba. On the other hand, aluminothermic processing results in relatively low vanadium content in the alloy [9].

Another traditionally employed method is hydrometallurgical processing, which involves using liquid solutions to extract and recover metals from ores and residues, with leaching playing a fundamental role [10]. In these cases, leaching can be acidic or basic. For the specific case of Cuba, leaching with sulfuric acid is preferred because it is produced domestically in the same plants where the waste is generated, facilitating a stable supply of raw materials for processing.

Therefore, through proper chemical processing of spent catalysts from sulfuric acid manufacturing, it is possible to recover the vanadium they contain without generating new polluting residues. To develop this strategy effectively, it is essential to consider technical and economic factors that enable the recovery of vanadium.

Raw material and reagents

The spent catalyst sample selected for the study was obtained from Plant A in the province of Pinar del Río, which has been inactive for more than two decades. These catalysts are currently stored at the plant site. Chemical characterization was conducted by the Center for Environmental Studies of Cienfuegos using X–ray fluorescence [11], and the results are presented in Table 2.

Table 2. 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

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

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.

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.

On the other hand, the determination of vanadium in the recovered product was carried out by atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

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 [6].

Spent catalysts from sulfuric acid manufacture consist of an inert support with a highly porous surface, typically natural or synthetic cristobalites. The pores contain a mixture of vanadium pentoxide as the active component, along with alkali metal sulfate promoters, usually potassium sulfate or cesium sulfate. Additionally, they may contain small concentrations of other elements, depending on the catalyst manufacturer and the characteristics of the sulfuric acid production process [12].

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 sulfur, requiring a temperature higher than 450 °C, thereby increasing the production costs [13].

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Considering 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, 14].

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 processes aimed at obtaining a product of higher purity. Several authors have conducted studies involving solvent extraction, selective precipitation, oxidation, among others [5]. These operations necessitate additional steps and equipment in the overall scheme, resulting in a significant increase in the process costs.

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

The final product obtained is reduced to obtain metallic vanadium or ferrovanadium, depending largely on the final application of the product. Sometimes this product is refined to improve its purity, especially if the intention is to market it directly, but this operation is also unnecessary given the intended use of the alloy.

The reduction of the metal oxides obtained in the recovered product must be carried out by aluminothermic reduction, a process capable of sustaining itself from the heat generated by the redox reactions. Therefore, it does not require additional energy supply, only the energy needed to initiate the process.

Proposed processing scheme

Based on the conducted on this subject and the procedures developed [11, 15, 16], Figure 1 illustrates the proposed diagram. In the diagram it can be observed the entry of the raw material into the system, in this case the spent catalyst. In addition, it adds to the system the materials necessary to carry out the processing. Also, it can be observed that as output products of the process, were obtained a recovered product containing vanadium and two new residuals.

Then, are developed a sequence of steps in the process, represented by the diagram of flow located in the interior of the image. The flow chart inside the image shows the different stages the process goes through and the products that are generated in each of them.

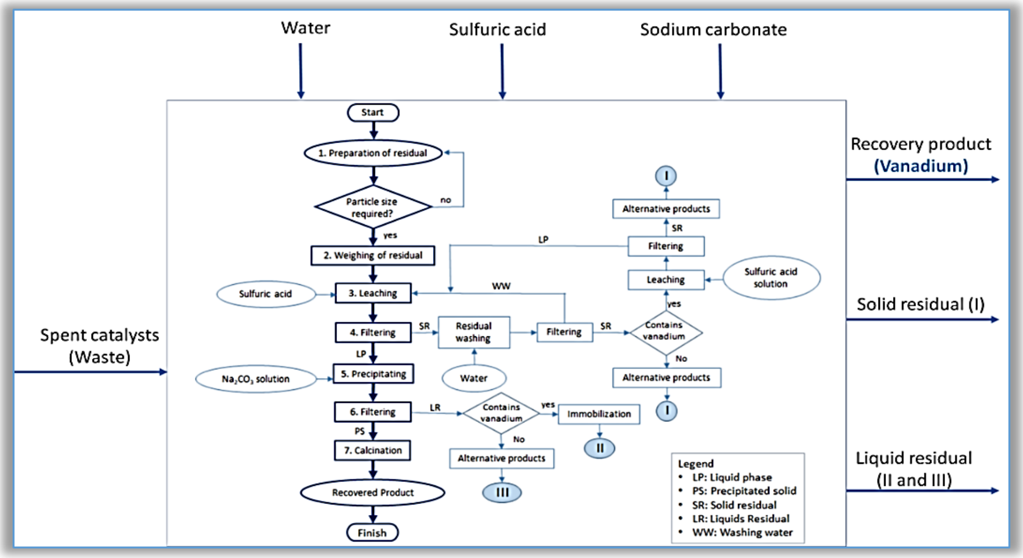

Figure 1. Schematic diagram of catalytic residue processing

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 2 shows a figure with the different forms in which the V_2O_5 catalyst can be presented [4].

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.

Figure 2. Shapes of the vanadium pentoxide catalyst. a) Pellets, b) Rings, c) Stars [8]

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 [17].

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 [18, 19, 20]. A particle size of less than 0.25 mm was selected, which agrees with several researchers [19, 21]. It is important to maintain control of the working particle size to ensure vanadium recovery values at similar levels.

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 considered [17].

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 [13, 20, 22], also using organic acids such as citric acid, oxalic acid [18]. As for basic lixiviants, sodium and potassium hydroxide, sodium carbonate and ammonia solutions have been studied [5, 19, 23].

Alkaline leaching is selective for vanadium over iron, but dissolves some silica and is more expensive in terms of reagents [5]. On the other hand, good results have been obtained using sulfuric acid [13, 22], 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, considering the vanadium content in the catalytic residual. These results are shown in Table 3.

Table 3. Leaching stage results

V (mg/L)	Leaching yield (%)
3611.7	93.9

Vanadium solutions in acidic media are found in VO_2^+ form as $(VO_2)_2SO_4$ and in VO^{2+} form as $VOSO_4$. Also, in the presence of sulfate ions, VO_2^+ cations form compounds such as $VO_2SO_4^-$. Thus, 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 [24].

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 [13, 20, 22].

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 [6].

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 [6].

On the other hand, Na^+ ions can combine with vanadium during precipitation to form sodium polyvanadate, which crystallizes later. 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 [13, 22], the latter being used to achieve and maintain the ideal pH during precipitation [25].

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. As a result of this stage, the product shown in Figure 3 was obtained.

This product contains the recovered vanadium, so it was analyzed by atomic absorption spectroscopy, obtaining a V_2O_5 content of 37.8 %, which indicates that the recovery was favorable.

Figure 3. Recovered product

Waste generated from processing

After the sulfuric acid leaching stage, a solid residue formed mainly by silica is generated [11], 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.

Solid residual (Product I, in Figure 1): The vanadium–free solid residue is an output product. 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 [23].

Therefore, if the solid residue does not contain vanadium, it can be considered not to be a contaminant.

Liquid residual (II and III, in Figure 1): 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 1), 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 1), 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.

Vanadium for the manufacture of electrodes in Cuba. Uses, background & perspectives

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 the installed capacity, mainly due to the lack of raw materials. On the other hand, electrodes for hardfacing are not produced in Cuba, so it is necessary to import them. 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 [26].

In 1986 a pilot plant was set up for the manufacture of electrodes for manual welding of 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, which made it possible to replace nickel and nickel iron–based electrodes in many applications [27], and the vanadium used for its manufacture 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.

However, not much research has been carried out in Cuba to obtain vanadium alloys. Table 4 summarizes the studies carried out in this field. The alloy developed by Morales Rodríguez [28] was the first vanadium alloy obtained in Cuba.

Table 4. Vanadium alloys developed in Cuba and their applications

Autor	Morales Rodríguez [28]	Perdomo González [9, 29]
Alloy	Cr–V alloy	Vanadium alloys
Method	Carbothermal processing in an electric arc furnace	Aluminothermic processing
Raw materials	Cuban chromites and spent catalysts from the manufacture of sulfuric acid	Catalytic residues from the manufacture of sulfuric acid from the B and A plants
Alloy applications	Manufacture of electrodes for manual electric arc welding, obtaining welding deposits with 17% Cr and 1.89% V [30]	Manufacture of coated tubular electrodes, where they were combined with other ferroalloys [31, 32, 33]

In the case of the research carried out by Perdomo González [9, 29], the maximum vanadium content obtained in the alloy is limited by the characteristics of the residue and the method of obtaining it. However, the evaluation of the alloys obtained by Perdomo González in the manufacture of electrodes has resulted in improvements in the properties of the strands obtained, especially those related to wear resistance.

All the previously mentioned validates the importance of obtaining vanadium concentrates from the chemical processing of spent catalysts, feasible to process by aluminothermic, 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 pieces 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.

Logistic analysis for the processing of vanadium catalytic residues at pilot plant level

According to a 2018 report, Plant B generates about 21 tons of catalytic waste per year and plant C generates about 7 tons every year. Therefore, it can be estimated that around 28 tons of waste would be generated per year, in addition to the more than 900 tons of waste that were accounted for in the report [3]. So, and according to the consultation with several experts, the proposed processing can be scaled up to pilot plant level. Considering the amount of waste that is generated annually, and the amount that is already stored, the reactor could be designed to process about 200 kg of waste per working day [34].

Thus, it should be analysed which site would be appropriate for the installation of a possible plant. Criteria should be considered to allow the operation of such a plant in the future [35].

Selection of the possible processing site

For the location of a possible 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 4 shows a map of Cuba with the location of the sulfuric acid plants that exist in the country and the proposed location of the waste processing plant (PP). Figure 4 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.

Figure 4. Location of the sulfuric acid plants and the proposed residuals processing plant

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.

The province of Cienfuegos is characterized by its industrial development, with several industries of national scope, so it has access by rail, road and sea. In addition, near the bay of Cienfuegos is the National Hazardous Waste Confinatorium, the institution in charge of controlling hazardous waste in the country, making this city a strategic site or place to locate the pilot plant.

Mind map of the research

To scale up the proposed process it is important to consider several technical, economic and environmental criteria. Figure 5 shows the mind map from which it was made an analysis of the proposal. Table 5 shows a group of questions necessary to address the analysis of the proposal [35].

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The map shown (Figure 5) is designed with the objective of achieving the scale–up of the vanadium production process using as raw material the spent catalysts from the sulphuric acid manufacturing (input product). To achieve this objective, it is proposed a methodology for the processing of the catalysts, which was developed in the laboratory, as described above, obtaining satisfactory results.

As a result of the methodology studied, it is obtained as output products: the recovered product containing vanadium, the solid residual (I) and the liquid residual (II and III). Therefore, following is an assessment of the aspects to be considered in order to scale up the developed procedure.

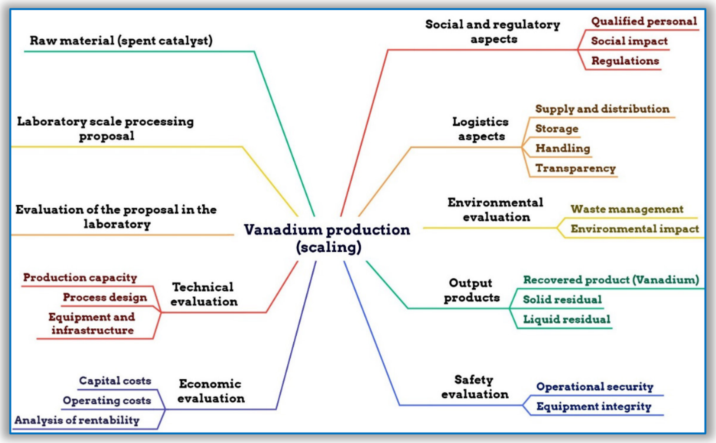

Figure 5. Mind map of scaled production

Table 5. Questions for carrying out the scaling analysis

Questions	Data
What are the characteristics of the raw material?	Industrial residual – Mixture of powders and pellets – 4–9 % V_2O_5 – Contaminant
What are the stages of the procedure to be escalated?	Crushing and screening – Leaching – Precipitation – Filtration – Filtration – Calcination – Handling of raw materials, intermediate and final products
What results have been obtained from its application at laboratory scale?	Intermediate product: liquid phase (94 % vanadium extraction) – Product recovered with 38% V_2O_5 – Solid residue (>90 % silica) – Liquid residue (sodium sulfate solution)
What technical aspects must be known to scale up the procedure?	Proposal: production capacity 200 kg/day of catalyst – Plant dimensions – Scaling criteria – Available space – Possible failures – Materials selection
What economic aspects should be considered?	Cost of infrastructure – Equipment – Total expenses – Model cost – Selling price
What technological and environmental safety measures must be followed?	Hazardousness of reagents – Chemical plant safety protocols – Risk prevention plan
What logistical aspects should be considered?	Material flow; Transportation; Storage; Material handling; Planning; Process control; Flow of empty
What social impact would the plant have?	Study of the area of interest – Improvement of local living conditions

Technical evaluation

The first point to be evaluated is the technical analysis of the process, which is based on the production capacity of the plant, being necessary to guarantee the processing of 100% of the waste generated, with a constant and efficient supply of the required raw materials.

Provided that the flow of spent catalyst is constant, this plant can be set up on a pilot plant scale, capable of processing 200 kg/day of residual, as mentioned above. The processing of 200 kg of catalyst per day would allow the processing of about 48 tons of catalyst in the year, obtaining about 6.5 tons of recovered product. In the case of Cuba, the recovered product will be used to obtain vanadium alloys (FeV), which will be marketed for the manufacture of welding consumables, mainly for the recovery of parts exposed to wear, for example, in the sugar industry. Cuba currently has facilities capable of producing the alloy and welding consumables.

Another aspect within the technical evaluation is the design of the process, which includes the criteria to be taken into consideration for its scaling up, without compromising efficiency, and the optimization of operating parameters, especially in the leaching and precipitation stages. All this contributes to the quality of the product obtained, which must be assured during production.

To develop the scaling of equipment it is necessary to consider similarity principles, among these by geometric similarity. In this case, both leaching and precipitation are carried out in a reactor that is a stirred tank, and the basic design parameters are: geometry, construction material, design and location of baffles and design of the agitator, taking as scale factor 50 [36]. In the case of leaching, it requires temperature control. In addition, the design of the plant must consider the space requirements of the plant, since it is necessary to have an area for information and administrative procedures, an area for physical examination, space for standard equipment and the area for storage of raw materials and intermediate and final products. In addition, it is important to ensure the stable and efficient operation of the plant by considering the factors that can cause system failures. Among these factors 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.

As for the precipitation stage, as mentioned above, among the fundamental factors are pH control and agitation. The selection of equipment and infrastructure is a fundamental aspect that allows the correct operation of the process [37, 38]. The equipment must be adequately designed and dimensioned to guarantee production at the expected levels, and it is necessary to make an adequate selection of material resources, including storage systems, pumping systems, mill and sifter, reactors, filtration systems and muffles for calcination. In addition, it must consider the corrosive characteristics of the substances to be handled, so that they are resistant to them.

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 [39, 40], 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 100ºC. 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 60ºC.

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.

In the case of precipitation stage, this 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.

Economic evaluation

Another criterion that must be evaluated is the economic analysis of the process, which requires an analysis of capital costs, operating costs and profitability. First, there is an initial investment to be made for the installation of the facility, acquisition of the equipment and start–up of the technology. Then, there is a cost associated with raw materials and reagents, required labour, and energy and maintenance costs of the facility, among others.

As for the acquisition costs of raw materials, since it is a residual, the cost of the spent catalyst would be basically that related to its transportation. The cost of the sulphuric acid, a reagent used in the leaching stage, is about 200 – 250 USD/ton and that of the sodium carbonate, used in the precipitation stage, is 180 USD/ton [41]. These prices correspond to the international market. In addition, a profitability analysis must be performed, considering criteria such as return on investment, which allows determining the economic viability of the project, and the selling price. The selling price of the recovered product (vanadium) involves an analysis of the production cost of the product, as well as the possible additional income from the sale of the by–products obtained (solid and liquid residues). In this case, the price of one kilogram of vanadium pentoxide in the international market is ~20 USD.

Safety evaluation

Regarding the safety of the process, it must be taken measures for the development of the operations, considering that hazardous substances will be handled, for example, pollutants such as vanadium or corrosive substances such as sulphuric acid [42, 43]. There must be strict control during the transfer and storage of concentrated sulphuric acid [42], capable of causing serious accidents to plant operators. Therefore, it should be implemented safety protocols appropriate to the characteristics of the process and it should be ensured that all personnel are trained and use appropriate personal protective equipment within the facility. The installation must have showers installed and easily accessible in case of contact with any reagent and adequate materials in case of fire or spill in the installation [42, 43].

During all stages of plant operation, the safety and work protection rules established for chemical plants must be followed [43]. On the other hand, it must be scheduled preventive maintenance of the facility and ensure the use of corrosion resistant materials in equipment and containers, so that the integrity and efficiency of the equipment is not compromised.

Environmental evaluation

Another important aspect to consider is the environmental assessment, especially given the characteristics of the raw material being processed. In this regard, solid and liquid waste generated during the process must be properly managed, as well as the water resulting from product washing and facility cleaning operations, which must be adequately treated before discharge. For the products leaving the process, classified as new waste, the possibility of reusing them in other industrial applications must be evaluated. The water generated from the solid waste washing operations, as mentioned above, can be reused in the preparation of the leaching solution.

Control over solid and liquid residues must be maintained, especially in relation to the vanadium content, to prevent the release 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. The catalytic residue must also be stored in safe conditions.

In the case of spent catalysts, the main environmental risk is due to their V_2O_5 content, as this dissolves in water forming toxic mixtures. Additionally, the presence of sulfate, free sulfite, and water in spent catalysts can lead to an acidic leachate (pH around 1 – 2) [24].

In general, vanadium compounds are classified as acute toxicity health hazards, being harmful if ingested or inhaled. The toxicity of vanadium compounds increases with increasing oxidation state, with V^{5+} being the most toxic, which has been reported to cause respiratory organ damage, changes in heart rate, biochemical alterations in blood and changes in albumin and cholesterol concentration [44].

Regarding the environmental aspect, it is necessary to evaluate the impact that the installation of a facility of this type would have on the ecosystem, identifying possible impacts and seeking ways to mitigate them, so that the process complies with the environmental regulations established both locally and internationally.

Logistics

Logistics in this case is essential to ensure that all processes are carried out efficiently, safely and cost–effectively, from the sourcing of incoming products into the system to the delivery of outgoing products. Logistics encompasses several key areas: transportation, warehousing and distribution, each with its own considerations and strategies [35]. Important here is the adequate and reliable supply of the required raw material and reagents, in addition to other material inputs that may be needed, and the distribution of the products obtained, primarily the recovered vanadium–containing product. For all this to be possible, it is necessary to have adequate means of transportation between the different units, either by rail, sea or road access. In addition, routes must be planned to minimize the risk of accidents and avoid densely populated or environmentally sensitive areas, and factors such as road conditions, weather and traffic must be considered.

On the other hand, storage facilities must be secured, where different areas must be provided for the storage of incoming materials, intermediate products and the final products of the plant. Also, a storage area for packaging material must be provided [45]. In this regard, appropriate and resistant containers should be used for the storage of spent catalysts and chemical reagents. These must protect against corrosion and prevent any leakage or contamination.

The design of storage facilities must be analysed and prepared to handle the necessary volumes, thus avoiding interruptions in production due to lack of raw materials [46]. Considering the toxicity of vanadium compounds, mentioned in the previous section, various safety precautions must be observed when storing and transporting vanadium–containing products, corresponding to Storage Class (TRGS 510): 6.1B: Non–flammable, acutely toxic category 1 and 2 / very toxic hazardous substances, according to the German Hazardous Substances Regulation. For storage it is important to ensure that the containers containing the spent catalyst or the product recovered from the process are tightly closed and made of suitable material, stored in a cool place and that the storage area is properly labelled and

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marked. Access to these areas should be restricted to qualified personnel. Transportation should be by authorized vehicles, packed in secure containers and properly labelled with appropriate hazard labels and markings. Emergency plans and equipment should be in place to respond to possible accidents involving these products. On the other hand, it is important to ensure good ventilation in the workplace [47, 48].

In addition to these measures, specific national and international regulations and guidelines for handling hazardous substances should always be observed to ensure the safety of people and the environment.

Social and regulatory aspects

Finally, it is important to analyse the social impact that the installation of a facility would have by creating jobs and training personnel, and the relationships that this would bring with the surrounding communities by establishing open communication with their inhabitants and addressing their concerns. In terms of regulatory compliance, it must obtain all necessary permits and licenses for large–scale operation and comply with all occupational health and safety regulations.

In Cuba, the Ministry of Science, Technology and Environment (CITMA) is responsible for proposing environmental policy and directing its implementation through a set of decrees and laws approved by the Council of State. Examples of this are the DECRETO–LEY No. 309 "On Chemical Safety" and the Cuban standards NC: 229:2014 on occupational safety and health and NC 1039: 2014 on personal protective equipment [49–51].

4. CONCLUSIONS

- The chemical processing proposed for the spent catalysts from plant A allows obtaining a vanadium concentrate of ~38% V_2O_5, which can be used in the development of welding electrode prototypes.
- 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 processing technology for the recovery of vanadium from spent catalysts is feasible to scale up to the pilot plant level taking logistics criteria into consideration. Qualified tasks must be developed for this purpose
- The proposed technology constitutes a contribution to the environment and the economy, complying with the principles of the circular economy.

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