Vanadium Recovery from Bayer Process Liquor Residue

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The objective of this work is to develop a vanadium recovery process from a liquor residue of Bayer process. Vanadium finds application in strategic industrial sectors such as steel production and energy storage. The recognized importance of vanadium has pushed academic and industrial research towards the development of technologies for its recovery from different types of secondary sources. The developed process refers to a sodium fluorovanadate sludge from a spent Bayer liquor. The resulting filter cake was characterized to determine its composition and a vanadium recovery process was studied and optimized. This starts with a solubilization of the filter cake by water, followed by a precipitation step of aluminum through pH adjustment with sulfuric acid till 9.2. Vanadium is then recovered as ammonium metavanadate by precipitation with ammonium sulfate using a ratio $(NH_4)_2SO_4$/salt cake = 2.25 w/w; the precipitate was calcined at $T = 500°C$ to obtain vanadium as V_2O_5. The results showed an overall vanadium recovery of about 95%, with a purity > 99.6%. The innovative contribution here addressed is represented by the feasibility of producing high-purity V_2O_5 from the Bayer liquor through a relatively simple precipitation route.

INTRODUCTION

Currently, vanadium (V) is a material of strategic importance from the industrial production point of view. Vanadium finds application in strategic industrial sectors such as steel production and energy storage.[1] Most of the V extracted is concentrated in the Earth's crust,[2] while its presence in sea water is negligible, and then the extraction is economically unsustainable because of its dilution. The main deposits consist of vanadiferous titanomagnetite, igneous rocks that can be found worldwide.[3] V can be found in fossil fuels[4] but also mined as a secondary product from production processes such as iron and steel, uranium, alumina, phosphorus, lead and zinc.[5] Since 2017, the strategic importance of V has been reflected in its presence in the list of critical raw materials published by the European Commission.[6,7] The list represents a selection of metals which present a high supply risk and, at the same time, are of great importance for the EU economy. Europe is dependent on non-EU countries for V supply.[8] The main EU supplier in the period 2010–2014 was Russia with a share of 71%, but China is currently the main supplier (∼60%). V demand has increased by about 45% since 2011, reaching 102.1 kilotons in 2019.[9] Forecasts show that consumption will grow up to 130.1 kilotons by the end of 2024 with an annual growth rate of 5%. The price of vanadium iron (used as an indicator) in the period 1980–2020 has varied significantly with continuous fluctuations until reaching a peak in 2018 (113 US $ kg^{-1}) before decreasing again in 2019 to 40 US $ kg^{-1}.[10] Considering its strategic importance in many industrial sectors and its high supply risk, it is fundamental to assess the current state of the art of V extraction from both primary and secondary sources, focusing on the processes of extraction and recovery from multiple matrices[11–14] and on the effects of V on the environment and human health.[15,16] Several techniques have been studied for the recovery of V from primary and

secondary sources. The very first techniques found in the available literature were based on aluminothermic and silicothermic reduction processes with low recovery efficiency.[17,18] Marafi et al.[19] and Ray et al.[20] applied pyrometallurgical and hydrometallurgical methods with low efficiency; meanwhile, Chen et al., Gomes et al. and Liu et al.[21–23] achieved 90% leaching efficiency through selective electro-oxidation. To reduce costs and harmful effects on the environment, calcification-roasting was studied, obtaining however impure vanadium products.[13,24,25] To reduce the leaching times and improve efficiency, microwave heating[26–28] and ultrasound-assisted techniques[29] have been tested. Another recent technique is the assisted leaching of microorganisms (bioleaching), which has the advantages of low production costs and negligible environmental impact;[30] however, V leaching efficiency is low (about 75%). Precipitation with NaOH, H_2 and NH_4Cl resulted in high V recoveries of 99%.[31–33] However, these results are associated with difficult multi-steps, very high temperatures and the formation of secondary products potentially harmful to the environment.

V recycling rates are currently still low and, as seen before, the main criticalities in the development of recycling methods are the selective separation from other metals, the recovery efficiencies as well as technical obstacles (e.g., the high temperatures employed, use of multi-step processes, formation of secondary products that can corrode the equipment and be harmful to the environment), which make their scale-up to the industrial level difficult. In terms of environmental assessment, factors such as pollution, safety, heat release, toxicity, residues, etc., have to be considered.[1]

The present paper focuses on the recovery of V from a residue of the Bayer liquor process, which is the NaOH-based hydrometallurgical extraction and refinement process of alumina from bauxite.[34] In the Bayer process, V is dissolved during the leaching step and then removed from loaded leachate as vanadium cake in the evaporation unit.[35] A method of recovering V from the Bayer process products was already studied in 1990.[36] Over time, the recovery processes have been optimized from both a technical point of view—evaluating for example the temperature parameters and the most suitable reagents with their concentration—and from the perspective of the economic and industrial applicability, while attention given to environmental aspects has been steadily growing. Table I reports the recovery studies carried out on Bayer slags highlighting their criticalities. Several authors proposed green alternatives based on the replacement of traditional leaching agents with urea, chelating agents, supercritical fluids and surfactants.[37–42] These methods resulted however in relatively low recovery yields (60–70%). Numerous studies have been carried out and others are in progress that show innovative approaches for the exploitation of different waste.

However, most of the methods developed require too specific reaction conditions to industrialize the process in a simple and automatic way. The main challenge remains the possibility to selectively recover V, which implies the use of pre-treatment step specific for the type of waste.

In the present study, a process was developed for recovering V from a filter cake derived from the Bayer liquor process. Proposed method is based on a relatively simple precipitation-filtration route which exploits the different solubility of compounds contained in samples.

MATERIALS AND METHODS

A vanadium filter cake sample (about 800 g) was provided by RUSAL. The sample was produced by batch precipitation of sodium fluorovanadate sludge from a volume of evaporated spent Bayer liquor resulting from alumina alkaline extraction process.

All solutions were prepared with analytical grade reagents and using distilled water. All reagents were purchased from Sigma Aldrich and used as received without further treatments. Vanadium filter cake samples were homogenized using a PM100CM (Retsch) planetary ball mill. Leaching and precipitation batch tests were performed in glass reactors with the capacities of 0.5–1 L at 25°C and under stirring at a controlled rate. The concentrations of metal ions in solution were measured by Microwave Plasma-Atomic Emission Spectrometer (4100 MP-AES, Agilent Technologies) and Atomic Absorption Spectrophotometer (AA-6300 Shimadzu). All experiments were performed in quadruplicate as a check on the experimental technique and precision; the total error associated with the experimental measurements was estimated to be within ± 5% (given by the sum of the systematic and random errors).

Characterization of the Filter Cake Sample

To determine the granulometry of the starting material, a weighted portion of the salt cake was passed through a set of four standard sieves with mesh size ranging from 850 μm to 38 μm. pH measurements were performed by titration using an acid/base instrument (888 Titrando, Metrohm).

The elemental composition was determined by dissolving the filter cake in distilled water at 25°C and by measuring the obtained solution with spectrophotometric techniques.

Thermal analysis was performed in alumina crucibles (75 μL volume) using about 10 mg sample with a thermogravimetric analyzer (Mettler Toledo TGA DSC1, STAR EVALUATION software) between 25°C and 1000°C, with a heating rate of 10.0°C min^{-1} under a 80 mL min^{-1} air flow rate. Preliminary "blank experiments" were carried out before each run. The instrument was calibrated by melting standard metals (In at 157°C and Ag at 962°C) at heating rates between 2 and 15°C min^{-1}.

Table I. Vanadium recovery from Bayer process residues

Treated material	Leaching agent	Adsorption/ desorption step	Precipitation step	Remarks	Criticalities	Refs.
Bayer sludge	Hot H_2O	Activated carbon/ NH_3 solution (10%)	H_2SO_4 or HCl + calcination	Constant T (85°C)	Difficult to apply in the industrial field	36
Bayer liquor	–	–	CaO	1 h precipitation T > 150°C	Low recovery percentages Multistep precipitation	43
Vanadium cake	H_2SO_4 + Na_2SO_3	–	NaOH	1 h leaching T = 70°C 96% $Fe_3(VO_4)_2$ laboratory recovery 95% $Fe_3(VO_4)_2$ semi-pilot recovery	Leaching performances depend on salt concentration	35
Vanadium sludge	Air + CO_2 + aluminate solution	–	$(NH_4)_2SO_4$	The produced metavanadate was converted into polyvanadate with H_2SO_4 and subsequently into V_2O_5 T = 560°C	Difficult process High temperature	44
Bayer liquor	–	Amidoxime resin (LSC 700)	–	Rapid, efficient and homogeneous resin adsorption capacity	Desorption method under development	45

Table II. Characterization of the filter cake before and after thermal treatment (1000°C)

Element	% (w/w) as received	% (w/w) after thermal treatment
Na	30.9	39.2
V	7.6	9.4
Al	4.6	5.8
As	0.4	0.2
Ca	0.4	0.4
*Others	< 0.04	< 0.04

*Others include: Cu, Ni, Ba, Fe, Ti,, Mg, Sr, Mn, Pb, Cr, Cd, Co, Sn, Zn and Ga.

The uncertainty for temperature was determined to be 0.5°C.

Vanadium Recovery

The first step of the proposed recovery process comprises the selective removal of Al by precipitation. After dissolving the sample in distilled water, Al insoluble compound formation was studied as a function of pH. The pH has been adjusted using H_2SO_4, HNO_3 and HCl. Al concentration was measured in the pH range 1.8–10.7. After Al precipitation, the obtained solid and liquid phases were separated by a vacuum filtration system (0.45 μm).

The leachate obtained after Al removal was treated adding solid $(NH_4)_2SO_4$; the reaction between the $Na_2V_2O_7$ and $(NH_4)_2SO_4$ led to the formation of ammonium metavanadate (NH_4VO_3). After V precipitation, the solid and the liquid phases were separated by a vacuum filtration system (0.45 μm).

RESULTS AND DISCUSSION

Characterization of the Filter Cake Sample

The particle size of the treated sample was in different granulometry (80% between 38 and 425 μm, 16% < 38 μm without exceeding 850 μm), where each collected fraction was indicated as a percentage of the total weight (wt.%).

Regarding sample solubility, it was observed that the salt cake powder was completely soluble in distilled water at room temperature up to a concentration of 66 g L^{-1}. This vanadium salt cake solution ([V] = 5.1 g L^{-1}) titration was performed using HCl 0.5 N. The sample was very alkaline and needed 0.0085 eq.(HCl) g^{-1}(salt cake) to be neutralized.

The elemental composition of the filter cake—obtained after sample dissolution in distilled water and metal analysis—is reported in Table II.
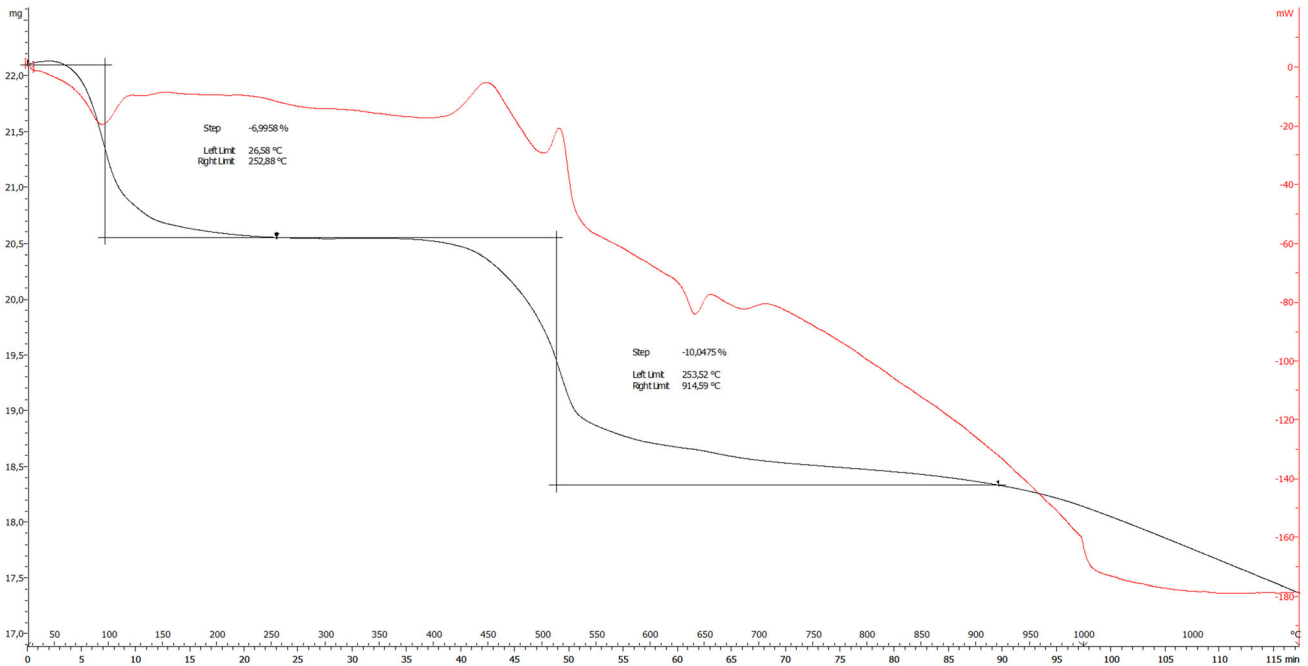
Fig. 1. Vanadium sample cake TGA thermogram. Details of the instrument used are in 2.1 paragraph.
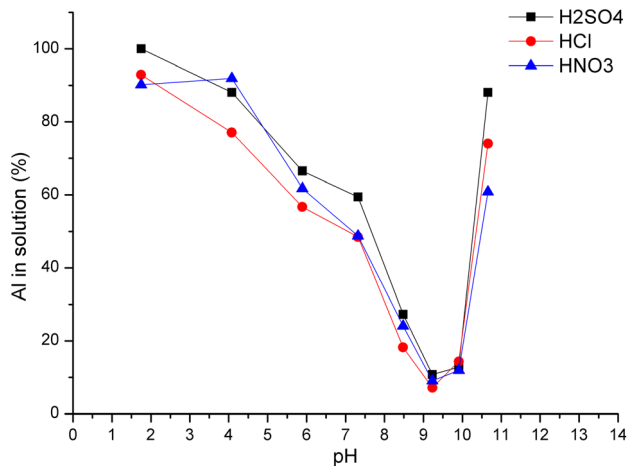

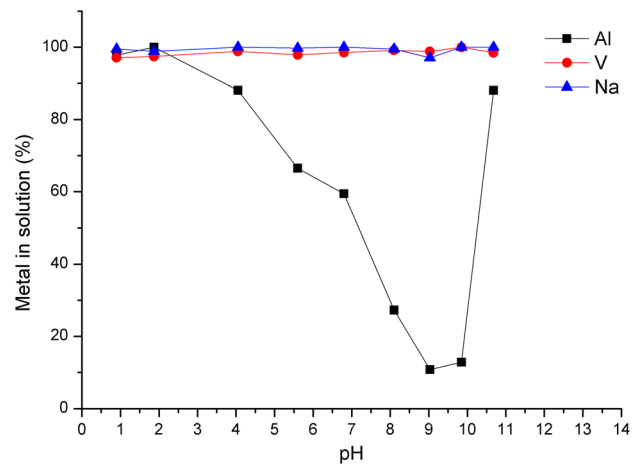Fig. 2. Aluminum precipitation as function of pH.

Fig. 3. Metal precipitation as function of pH.

Vanadium concentration in the salt cake is 7.6% w/w, while Na and Al content is 30.9 % and 4.6%, respectively.

Regarding thermal analysis, by examining the TG curve (Fig. 1), a 7% mass decrease was observed between room temperature and 250°C corresponding to the loss of interstitial water. The step occurring at higher temperature shows a weight loss of about 10%, corresponding to thermal degradation (250–600°C) and As loss (600–950°C), the latter confirmed by As weight concentration values before and after TGA. After reaching $T = 1000$°C, sample weight remains constant. Notably, there are

two exothermic transitions in the range 400–550°C (circled in Fig. 1), which suggests a thermal reaction. Another sample portion was heated at 1000°C for 3 h: this treatment produces a color change in white, and the final weight confirms the loss of 17% already measured by TGA. To check the chemical composition, the sample, after thermal treatment, was solubilized in distilled water, and the obtained leachate was analyzed by spectrophotometric techniques. The increased content of some elements, in particular Na, V and Al, could be due to the loss of water caused by heat treatment, while the decrease in As content can be explained with the formation of volatile compounds.
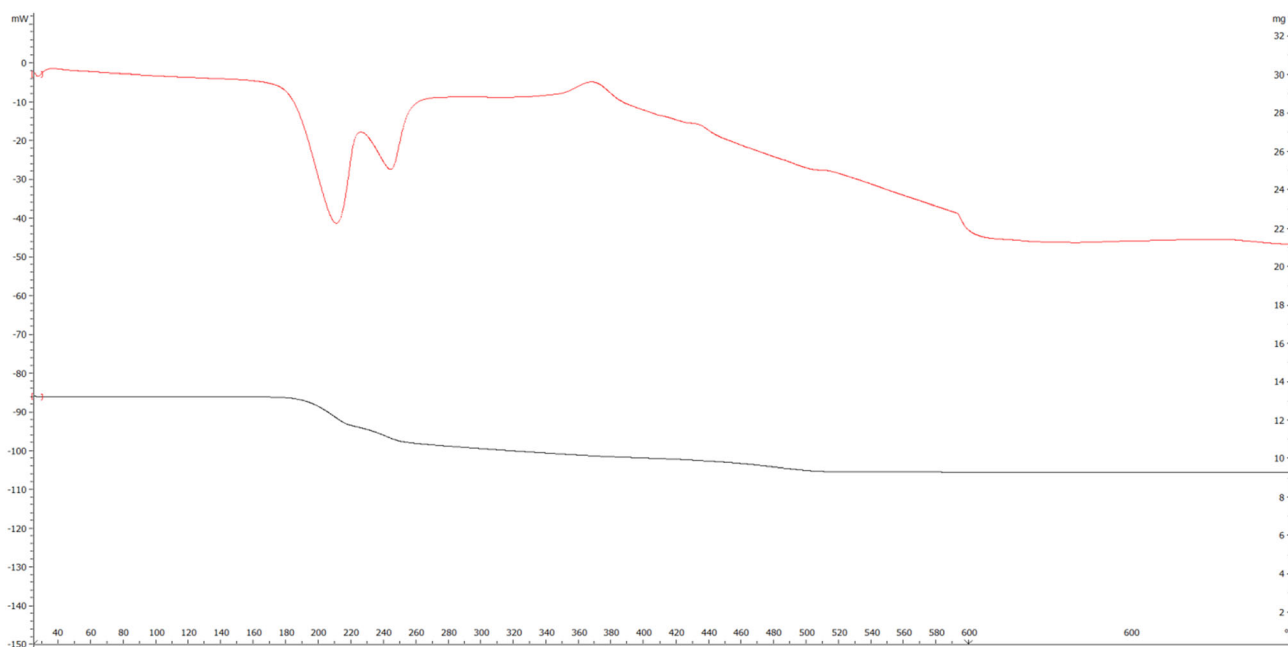
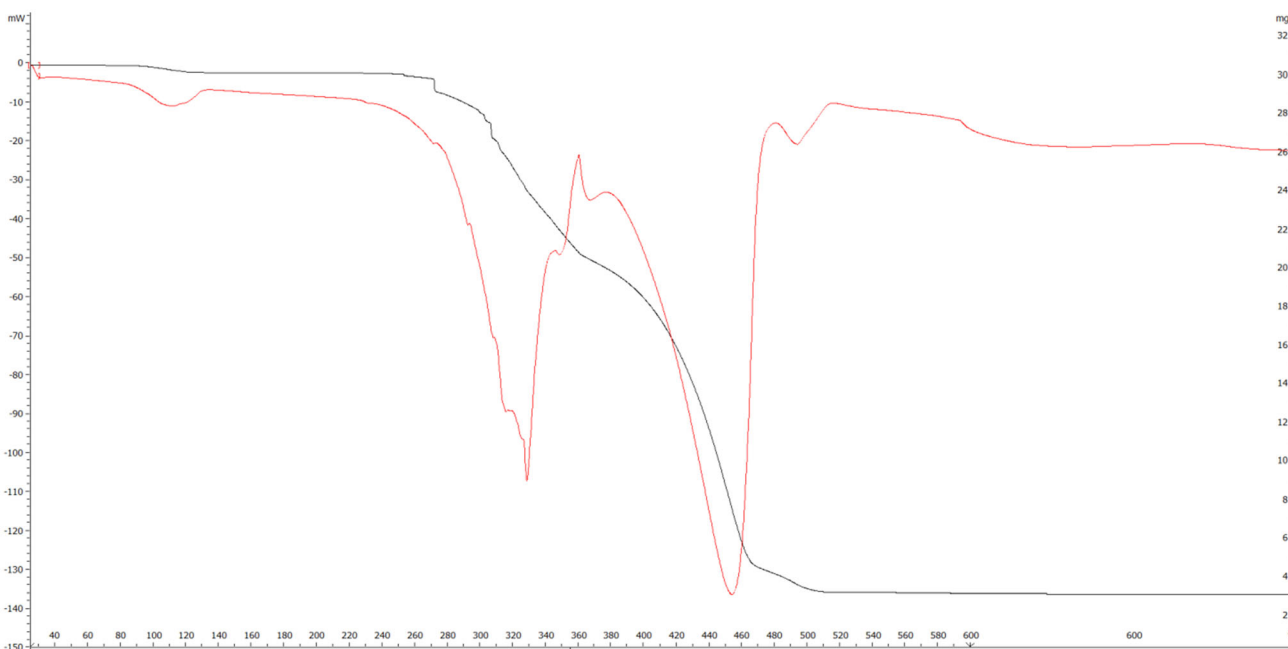Fig. 4. Thermal analysis (TGA-DSC) of ammonium-vanadate precipitate.

Fig. 5. Thermal analysis (TGA-DSC) of ammonium sulfate. Details of the instrument used are in 2.1 paragraph.

Vanadium Recovery

The first step of the proposed V recovery process consists of a prior Al precipitation. Since the salt cake is completely soluble in water, Na and Al cannot be removed by applying a washing step. Al removal was thus performed by precipitation. By gradually adjusting the pH conditions, it was observed that at pH 9.2 Al reaches the lowest concentration (about 10%) regardless of the acid used. Sulfuric, nitric and hydrochloric acids have been tested for pH variation; however, to avoid the introduction of other anions during V purification step (usually made by ammonium and sulfate anion), it is preferable to decrease the pH using H_2SO_4. In this condition, Na and V ions do not precipitate (Figs. 2 and 3).

The solid phase contains 90% and 75% of the initial Al and As content, respectively, and the
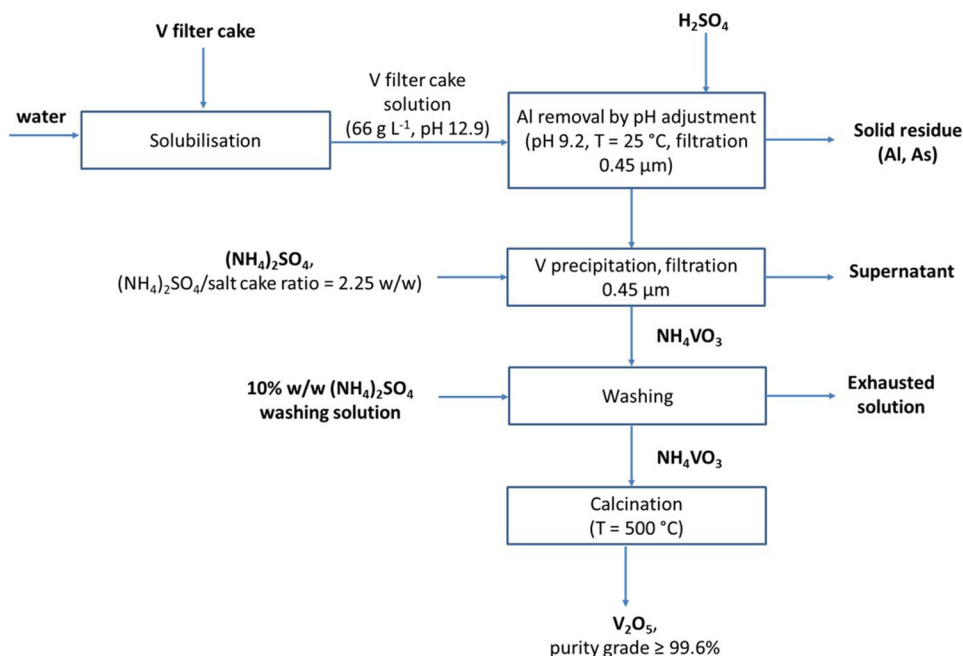
Fig. 6. Vanadium recovery process flow sheet.

remaining solution still contains the initial amount of Na and V.

The second step involves V precipitation from the liquid phase; therefore, the pH 9.2 solution has been treated adding solid ammonium sulfate. Reaction between the sodium vanadate and ammonium sulfate probably led to the formation of ammonium metavanadate according to the reaction in Eq. 1.[46]

$$Na_2V_2O_7 + 4NH_4^+ = 2NH_4VO_3 + 2NH_3 + 2Na^+ + H_2O$$

(1)
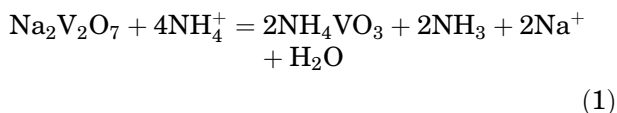
$(NH_4)_2SO_4$ allowed quantitative precipitation of V, while Na and Al remain in solution. Using a $(NH_4)_2SO_4$/salt cake ratio of 2.25 (w/w), V precipitation was > 94%, which can be considered a good compromise between process efficiency and reagents consumption. V precipitation through $(NH_4)_2SO_4$ was also studied at other pH values (2.5, 4.1 and 7.1); however, in these cases the precipitation was not quantitative.

The precipitate was treated by a 10% w/w $(NH_4)_2SO_4$ solution to wash off the soaked Na and Al.

Finally, a third process step is considered necessary to remove ammonium and sulfate ions from solid phase formed during vanadium precipitation. To check the suitable conditions to remove ammonium and sulfate ions through thermal treatments, TGA and DSC have been performed on the dried washed precipitate and on an ammonium sulfate sample (Figs. 4 and 5). These tests show that under oxidizing conditions, the decomposition of ammonia takes place at 170°C up to 280°C, but the thermal

degradation of $(NH_4)_2SO_4$ is complete at 500°C. In conclusion, therefore, achieving a final temperature of 500°C is necessary for the complete removal of ammonium and sulfate ions from this precipitate.

To determine the composition and purity of the final product, an aliquot was solubilized in aqua regia and then analyzed. The resulting chemical speciation is V_2O_5 with a purity grade > 99.6%.

The proposed recovery process flow sheet is shown in Fig. 6. After Al removal by adjusting the pH of the solution to 9.2 with H_2SO_4, precipitation of ammonium metavanadate was obtained by adding solid $(NH_4)_2SO_4$; the subsequent 500°C thermal treatment on the precipitate allowed obtaining V as V_2O_5 with a recovery rate of about 95% and purity grade > 99.6%.

CONCLUSION

The aim of the present work was to recover vanadium—a critical element for the European economy—from a filter cake derived from a waste liquor originating from Bayer process performed to refine bauxite. This study demonstrated the feasibility of producing high-purity V_2O_5 through a relatively simple precipitation-filtration route, allowing the simultaneous removal of aluminum. A precipitation-based approach was performed as it is more economical compared to other recovery methods such as solvent extraction and electrowinning. The proposed process can be considered an efficient method in accordance with circular economy principles. It leads to better recovery rate, product purity and environmental safety. Furthermore, vanadium recovery can be considered a smart

strategy to face the long-term challenge of ensuring a sustainable supply of raw materials, essential for main European industries' sustenance.

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