Analysis of Hydrometallurgical Methods for Obtaining Vanadium Concentrates from the Waste by Chemical Production of Vanadium Pentoxide

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Abstract: The paper describes hydrometallurgical methods to recycle wastes of vanadium pentoxide chemical fabrication. Sludges containing a significant amount of V₂O₅ can be considered as an additional source of raw materials for vanadium production. We studied the one-stage leaching method using various iron-based reductants for converting V⁵⁺ to V⁴⁺ in a solution allowing to precipitate V when its concentration in the solution is low. As a result of the reduction leaching with further precipitation, we obtained concentrates with V₂O₅ content of 22–26% and a high amount of harmful impurities. Multistage counterflow leaching can be used to fabricate solutions with vanadium pentoxide concentration suitable for vanadium precipitation by hydrolysis and adding ammonium salts. The solutions with V₂O₅ content of ≈15 g/L can be obtained from the initial sludge by three-stage counterflow vanadium leaching. A concentrate with a content of 78 wt% V₂O₅ can be precipitated from these solutions at pH = 2.4 by adding ammonium chloride. Additionally, concentrate with V₂O₅ content of ≈94 wt% was precipitated from the solution with a concentration of >20 g/L V₂O₅ obtained from the roasted sludge. The concentrates were purified for increasing the vanadium content to 5–7%. The consumption and technological parameters of the considered processes are presented in the paper.

Keywords: vanadium; vanadium pentoxide; concentrate; waste; sludge; leaching; reduction; vanadium alloys; precipitation; hydrolysis

1. Introduction

Vanadium is an important strategic metal widely used in various fields of industry. In ferrous metallurgy, V in the form of ferrovanadium is used for steel alloying [1–3] and in non-ferrous metallurgy in aluminum-vanadium alloys for alloying titanium-based structural materials used in aerospace engineering (engines, fuselages of high-speed aircraft) [4–7]. In the chemical industry, vanadium compounds are used as catalysts [8]. Additionally, materials based on vanadium oxides (V₂O₅, VO₂ and V₂O₃) are used in memristors (resistors with memory), bolometers (thermal infrared detectors), biosensors [9,10]. The application of vanadium in medicine for the manufacture of dental implants is described in [11].

Currently, the main sources for vanadium production are titanomagnetite ores [12–15]. Additionally, vanadium is extracted from coal [16–18], fly ash [19,20], spent catalysts [21,22], and other sources [23]. Titanomagnetite ores are processed to produce vanadium converter slag, from which vanadium pentoxide is obtained by chemical means [7,12,24–28]. Vanadium in converter slags is presented mainly in spinel (FeO-V₂O₃) practically insoluble in acid solutions. Therefore, in order to convert vanadium into soluble forms, preliminary slag oxidation roasting is carried out [7,12,24–33].
During the alkaline roasting, the formation of toxic salts of hexavalent chromium \( \text{CrO}_4^{2-} \) [7,12,32] is possible. With this technology due to the complexity of disposal, exhausted sodium-containing solutions are thrown into the water basin polluting the environment. Roasting of slag with calcium-containing additives (lime, limestone) is considered more environmentally friendly when vanadium in the spinel is forming acid-soluble phases \( \text{Ca}_x\text{V}_y\text{O}_z \), \( \text{Ca}_2\text{V}_2\text{O}_7 \) and \( \text{Ca}_3\text{V}_2\text{O}_8 \) [7,12,33].

Vanadium is precipitated from leaching solutions by hydrolysis, as a result, technical vanadium pentoxide with impurities Mn, Si, Fe, etc., is acquired. To obtain a cleaner vanadium pentoxide, precipitation is carried out with the addition of ammonium salts (for example, \( \text{NH}_4\text{SO}_4 \), \( \text{NH}_4\text{Cl} \)) [7,12,30]. Thus, the concentration of solutions before precipitation is usually higher than 15 g/L \( \text{V}_2\text{O}_5 \).

A significant amount of vanadium remains after leaching (<4.5 wt% \( \text{V}_2\text{O}_5 \)) [33–36] in sludges (wastes of hydrometallurgical production of vanadium pentoxide), therefore, it can be considered as a technogenic source of raw materials for vanadium production. Vanadium in sludges similarly to initial vanadium slags exists in the form of spinel (\( \text{V}^{3+} \)), also part of vanadium is in acid-soluble forms \( \text{V}^{4+} \) and \( \text{V}^{5+} \) [36]. Consequently, hydrometallurgical methods that are used in the production and research practice of vanadium slags processing should also be effective for this type of vanadium-containing raw materials.

The research was aimed at studies of hydrometallurgical methods of vanadium-containing sludge processing to produce vanadium concentrates.

Previously [34,35] it was shown that multi-stage counterflow leaching is necessary to obtain vanadium concentrates from sludges suitable for further smelting of vanadium alloys. In three stages of leaching, solutions with \( \text{V}_2\text{O}_5 \) content of \( \approx 10 \) g/L can be obtained from the initial sludges and more than 20 g/L \( \text{V}_2\text{O}_5 \) from the roasted sludges in two stages.

It is known that vanadium can exist in aqueous solutions in the form of compounds with oxidation degrees from +2 to +5 [37,38]. All known methods of vanadium precipitation are based on the vanadium extraction into a concentrate in the form \( \text{V}^{5+} \). In this work, new methods for vanadium precipitation in the form of \( \text{V}^{4+} \) using reagents that are not used in production practice are studied. Additionally, the production of vanadium concentrates by ammonium methods was studied.

2. Materials and Methods
2.1. Materials

The original vanadium-containing sludges were obtained from the EVRAZ Vanadii Tula plant (Tula, Russia). The samples were obtained at various periods and the content of \( \text{V}_2\text{O}_5 \) somewhat differs.

The chemical analysis was performed with the X-ray fluorescence spectrometer AX-IOSmax Advanced (PANalytical, Almelo, The Netherlands) using the method described in [36,39]. Table 1 shows the chemical composition of sludges.

2.2. Methods
2.2.1. Leaching

The important parameters of the leaching process are the following: concentration of the sulfuric acid solution, leaching temperature and duration, and solid to liquid ratio S/L. To select optimal process parameters the samples were leached by \( \text{H}_2\text{SO}_4 \) solution with a concentration of 1–20% at 20–80 °C during 5–60 min and S/L = 1/1–1/10 (g/mL).

The leaching process was performed in the 10-L stainless steel reactor with an upper agitator. After the end of leaching, the pulp was filtered under vacuum and washed with water at a ratio of S/L = 1/0.5 (g/mL). The filtrate and washing water were not mixed.

Chemical analysis of leaching solutions before and after vanadium deposition was carried out using an atomic emission spectrometer with inductively coupled plasma Agilent 725 Radial (Agilent Technologies, Santa Clara, CA, USA). Standard solutions from High-Purity Standards were used for calibration.
Table 1. Chemical composition of vanadium-containing sludge samples, wt%.

| Component   | Sludge No. | #1  | #2  | #3  |
|-------------|------------|-----|-----|-----|
| V₂O₅        |            | 2.25| 2.78| 3.59|
| V₂O₅a.s     |            | 0.94| 1.61| 1.4 |
| MgO         |            | 1.36| 1.53| 1.04|
| Al₂O₃       |            | 2.28| 2.2  | 1.56|
| SiO₂        |            | 11.69| 11.2 | 11.8|
| P₂O₅        |            | 0.03| 0.03 | 0.03|
| K₂O         |            | 0.10| 0.11 | 0.11|
| CaO         |            | 12.2| 11.4 | 12.1|
| TiO₂        |            | 7.14| 7.69 | 7.3 |
| Cr₂O₃       |            | 3.13| 3.14 | 3.34|
| MnO         |            | 6.50| 6.67 | 6.52|
| Fe₂O₃       |            | 40.9| 39   | 36.8|
| SO₃         |            | 14.5| 14.25| 15.81|

V₂O₅a.s.—acid-soluble form of V₂O₅. Method of determination is described in [33].

Leaching rate was calculated as:

\[ \eta(V₂O₅)_{sol} = \frac{m(V₂O₅_{sol})}{m(V₂O₅_{total})} \times 100, \% \]  

where \( V₂O₅_{sol} \)—the mass of \( V₂O₅ \) in solutions after leaching, g; \( V₂O₅_{total} \)—the total mass of \( V₂O₅ \) in the sample of sludge, g.

2.2.2. Reducing Leaching

Reducing leaching was carried out by two methods using iron sulfate and metallic iron powder as reducing agents.

In the first method, FeSO₄·7H₂O (99 wt% FeSO₄·7H₂O) was added to the solution after sulfuric acid leaching of the sludge under optimal conditions and pulp filtration. The filtrate was heated to 80 °C using a heating plate with constant stirring, then brucite Mg(OH)₂ was added to increase pH = 2–3 and FeSO₄·7H₂O was added at the rate of 1 g per 1 g of \( V₂O₅ \) in solution. After that, the pH of the solution was adjusted to ≈ 5.5 by adding brucite and the solution was kept under constant heating and stirring for 1 h.

In the second method, metallic iron powder (99.7 wt% Fe) was added during the process of vanadium leaching from sludge. Water and concentrated H₂SO₄ dropwise to pH ≈ 1.6 were added to the sample of sludge (at optimal S/L), the pulp was heated to 80 °C. Metallic iron powder was added at the rate of 2 g per 1 g of \( V₂O₅ \). Stirring and heating were carried out for 1 h. The resulting solution after filtration was heated to 80 °C once more, Mg(OH)₂ was added to pH ≈ 5.5 and exposed 1 h.

After filtration and washing the sediment was roasted in a muffle furnace at 550 °C for 2 h, then the content of the main components in the vanadium-containing concentrate was measured.

The chemical composition of brucite, wt% was the following: moisture 0.20; calcination loss 32.0; MgO 64.5; Al₂O₃ 0.06; SiO₂ 1.00; CaO 2.15; Fe₂O₃ 0.15.

Recovery rate of vanadium into the concentrate from the sludge was calculated as:

\[ \eta(V₂O₅)_{conc} = \frac{m(V₂O₅_{conc})}{m(V₂O₅_{total})} \times 100, \% \]  

where \( V₂O₅_{conc} \)—the mass of \( V₂O₅ \) in the concentrate, g; \( V₂O₅_{total} \)—the total mass of \( V₂O₅ \) in the sample of sludge, g.

2.2.3. Multistage Counterflow Leaching

To obtain a strong \( V₂O₅ \) solution from the original and roasted sludge (>10 g/L \( V₂O₅ \)), multi-stage counterflow leaching was carried out. This method includes the following:
the filtrate after leaching with H$_2$SO$_4$ solution in the first stage is used for leaching a new portion of the charge in the second stage; filtrate after the second stage is used similarly for the third stage, and so on until the final solution reaches a concentration V$_2$O$_5$ $\approx$ 10 g/L.

2.2.4. V$_2$O$_5$ Sedimentation by Ammonium Salt

V$_2$O$_5$ was sedimented from solutions with a content of V$_2$O$_5$ > 10 g/L by adding solid ammonium chloride NH$_4$Cl (99.5 wt% NH$_4$Cl) at a flow rate of 30–45 g/L and pH = 1–8. For this, the solution was preliminarily neutralized by adding NaOH (99 wt% NaOH) in the form of granules permanently monitoring the pH values using a pH-meter.

The recovery rate of V$_2$O$_5$ into the concentrate from the solution was calculated as Equation (2), substituting the value of V$_2$O$_5$ content in the solution into the denominator.

3. Results and Discussion

3.1. Selection of Leaching Conditions

Investigations aimed at the selection of optimal leaching conditions were carried out on a sample of sludge No. 3 (Table 1). Figure 1 demonstrates the outcomes of H$_2$SO$_4$ concentration on the recovery rate of V$_2$O$_5$ into solution from the initial sludge at different temperatures and S/L = 1/5 (g/mL). The maximal recovery rate of V$_2$O$_5$ into solution (58%) is achieved at the leaching temperature of 80 $^\circ$C and concentration of 5% of H$_2$SO$_4$ solution, without heating, the recovery rate of V$_2$O$_5$ is $\approx$50%. The leaching process at the temperature of 80 $^\circ$C has such a disadvantage, as the need for constant monitoring of the level S/L due to significant evaporation of the leaching solution. As can be seen from Figure 1, heating has a small effect on the recovery rate of V$_2$O$_5$, thus it was decided to conduct the experiments without heating at 5% H$_2$SO$_4$ solution, while the concentration of V$_2$O$_5$ in the solution was $\approx$3 g/L. The optimal S/L ratio was found to be 1/2.5 (g/mL) (Figure 2). The maximum concentration of vanadium in the solution is reached 30 min after the start of the process (Figure 3).

![Figure 1](image_url)

**Figure 1.** Effects of H$_2$SO$_4$ concentration on the recovery rate of V$_2$O$_5$ into solution at leaching temperature 20 $^\circ$C (1), 60 $^\circ$C (2) and 80 $^\circ$C (3).
Figure 2. Effects of S/L on the recovery rate of V$_2$O$_5$ into solution.

Figure 3. Effects of leaching time on the recovery rate of V$_2$O$_5$ into solution.

The optimal conditions for two-stage counterflow leaching of roasted sludge with 1 wt% CaCO$_3$ additive were selected in [33]: H$_2$SO$_4$ concentration of the solution is 5–7%, the leaching time is 20 min at each stage of the process; S/L = 1/2.5. These data were used in this work for obtaining vanadium-concentrated solutions with its further precipitation by brucite and NH$_4$Cl.

3.2. Reducing Leaching

For studies of vanadium leaching with its further reduction by FeSO$_4$·7H$_2$O, sludges with V$_2$O$_5$ content of 2.25 wt% were used (Table 1, sample No. 1).

The test sample contains 0.94 wt% V$_2$O$_{5a.s.}$, i.e., this amount of V$_2$O$_5$ can be converted into a solution by leaching with a 7% H$_2$SO$_4$ solution [33]. Vanadium can be represented in the acid-soluble part in the form of salts: orthovanadates (Me$_3$VO$_4$), pyrovanadates (Me$_4$V$_2$O$_7$) and metavanadates (MeVO$_3$), where Me is a monovalent metal ion. Since the sludge under study is a product of vanadium converter slag processing roasted with limestone, the most possible acid-soluble phases in the sludge are Ca$_3$(VO$_4$)$_2$, Ca$_2$V$_2$O$_7$, Ca(VO$_3$)$_2$. As a result of the treatment of calcium vanadates with a solution of sulfuric acid, various vanadium ions can be formed depending on the pH of the solution and the concentration of vanadium, (Figure 4) [38].
When vanadium is leached with a 5% H$_2$SO$_4$ solution, at which the pH of the resulting solution was 0.6–0.8, and the vanadium concentration in the solution after leaching was ≈ 3 g/L, the formation of VO$_2^+$ ions is probable by the following reaction:

\[
\text{VO}_4^{3-} + 4\text{H}^+ \rightarrow \text{VO}_2^+ + 2\text{H}_2\text{O}. \tag{3}
\]

For example, the reaction could occur as followed:

\[
\text{Ca}_3(\text{VO}_4)_2 + 4\text{H}_2\text{SO}_4 \rightarrow 3\text{CaSO}_4 + (\text{VO}_2)_2\text{SO}_4 + 4\text{H}_2\text{O} \tag{4}
\]

In acidic medium at pH = 2–3 VO$_2^+$ is reduced to VO$_2^+$ by iron sulphate with the following reactions:

\[
\text{VO}_2^+ + 2\text{H}^+ + e^- \rightarrow \text{VO}_2^+ + \text{H}_2\text{O}, \tag{5}
\]

\[
\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+}. \tag{6}
\]

The leaching solution acquired a blue color after the addition of FeSO$_4$·7H$_2$O crystals indicating the predominance of V$^{4+}$ in solution.

It is known that VO$^{2+}$ ions in aqueous solutions are existing mainly in the form of [VO(H$_2$O)$_5$]$^{2+}$ when pH < 3.5 and as [VO(OH)]$^+$ at higher pH values (Figure 5) [40]. At pH > 4 precipitation of VO(OH)$_2$ occurs by reaction:

\[
\text{VO}^{2+} + 2\text{OH}^- \rightarrow \text{VO(OH)}_2\downarrow \tag{7}
\]

After precipitation by brucite and roasting of the residuum, a light brown concentrate was obtained. As one can see in Table 2, it was possible to obtain a concentrate with V$_2$O$_5$ content of ~22%. This concentrate contains a significant content of impurities, including phosphorus which is a harmful impurity for ferrous metallurgy. Thus, this concentrate requires further processing before obtaining vanadium alloys.
Investigations on reduction by metallic iron were carried out using sludge with V₂O₅ content of 2.78 wt%. (Table 1, sample No. 2). Optimizing the process, we added iron for vanadium reduction during the leaching process and heated the pulp to 80 °C immediately after iron powder addition. As the concentrate obtained by reduction with iron sulfate contains a significant amount of phosphorus, the pH value was increased to ≈1.6. Reduction of V⁵⁺ passing into solution by metallic iron can proceed by the following reactions:

\[
(\text{VO}_2)_2\text{SO}_4 + \text{Fe} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{VOSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O} \quad (8)
\]

\[
2\text{VOSO}_4 + \text{Fe} + 2\text{H}_2\text{SO}_4 \rightarrow \text{V}_2(\text{SO}_4)_3 + \text{FeSO}_4 + 2\text{H}_2\text{O} \quad (9)
\]

In this process, solutions with V₂O₅ content of ≈6.1 g/L were obtained, while the recovery rate of V₂O₅ into solution was 36.5 wt%. The final concentrate after roasting in the muffle furnace contained 26.5 wt% of V₂O₅. Thus, metallic iron as a reducing agent allowed to increase V₂O₅ content slightly and to reduce phosphorus content in the final concentrate (see Table 2).

Table 2. Chemical composition of initial sludges, products and wastes of reducing processes.

| Component | Content (wt%) with Using Reducing Agent |
|-----------|----------------------------------------|
|           | FeSO₄·7H₂O                               | Metallic Iron                     |
|           | Sludge Initial | Waste Sludge | Concentrate | Sludge Initial | Waste Sludge | Concentrate |
| V₂O₅      | 2.25          | 1.55         | 22.1        | 2.78          | 1.41         | 26.5        |
| V₂O₅ a.s. | 0.94          | 0.1          | n/d *       | 1.61          | 0.30         | n/d         |
| Mn total  | 6.50          | 4.54         | 1.82        | 5.20          | 4.33         | 4.58        |
| Fe total  | 40.9          | 28.4         | 9.3         | 27.3          | 30.1         | 15.7        |
| SiO₂      | 11.69         | 10.6         | 5.19        | 11.2          | 11.0         | 5.52        |
| Al₂O₃     | 2.28          | 2.12         | 4.23        | 2.20          | 2.14         | 4.51        |
| TiO₂      | 7.14          | 7.48         | 0.77        | 7.69          | 7.59         | 0.17        |
| K₂O       | 0.1           | 0.081        | n/d         | 0.11          | n/d          | n/d         |
| MgO       | 1.36          | 2.34         | 36.2        | 1.53          | 5.7          | 27.1        |
| CaO       | 12.2          | 10.76        | 5.50        | 11.4          | 8.56         | 1.7         |
| P₂O₅      | 0.03          | 0.005        | 0.52        | 0.03          | 0.014        | 0.16        |
| S total   | 5.8           | 6.12         | 5.02        | 5.70          | 6.0          | 2.43        |
| Cr₂O₃     | 3.13          | 3.24         | n/d         | 3.14          | n/d          | 0.25        |

* Not defined.
Methods of one-stage reduction leaching with followed precipitation by brucite are ineffective for processing sludge due to the low vanadium content and high content of harmful impurities in the resulting concentrates as shown by investigations.

The method of reducing leaching with of FeSO$_4$·7H$_2$O additive was investigated for the recovery of vanadium from solutions with a concentration of ~20 g/L obtained under optimal conditions from roasted sludge with 1% CaCO$_3$ additive by two-stage counterflow leaching. The process was carried out as previous studies with FeSO$_4$·7H$_2$O additive, and as a result, a concentrate with content V$_2$O$_5$ of 53.6 wt% was obtained (Table 3). This concentrate is characterized by a significant content of impurities, however, due to the high vanadium content, it may be suitable for smelting vanadium ligatures [40].

Table 3. Chemical composition of roasted sludge, product and waste of reducing process from solution with concentration V$_2$O$_5$ of ~20 g/L.

| Component | Roasting Sludge with 1 % CaCO$_3$ Additive | Waste Sludge | Concentrate |
|-----------|-------------------------------------------|--------------|-------------|
| V$_2$O$_5$ | 3.55                                      | 0.61         | 53.6        |
| V$_2$O$_{5x,x}$ | 3.50                               | n/d         | n/d         |
| Al$_2$O$_3$ | 1.54                                    | 1.91         | 0.64        |
| CaO       | 12.79                                   | 13.3         | 4.11        |
| Fe$_2$O$_3$ | 36.43                                  | 38.0         | 18.3        |
| K$_2$O    | 0.11                                    | n/d          | n/d         |
| MgO       | 1.03                                    | 1.42         | 13.3        |
| MnO       | 6.45                                    | 4.72         | 4.84        |
| P$_2$O$_5$ | 0.03                                    | n/d          | 0.45        |
| SO$_3$    | 15.84                                   | 17.44        | 0.54        |
| SiO$_2$   | 11.5                                    | 12.1         | 3.96        |
| TiO$_2$   | 7.23                                    | 6.91         | 0.26        |

Table 4 presents the technological parameters and consumption parameters of the considered processes of reducing leaching and subsequent precipitation in terms of 1 g of the resulting concentrate.

3.3. V$_2$O$_5$ Precipitation by Ammonium Salt

Investigations of vanadium concentrate production by precipitation with ammonium salt NH$_4$Cl from solutions with a content of V$_2$O$_5$ > 10 g/L were carried out using initial sludge (Table 1, Sample No. 3) and roasted sludge with 1% CaCO$_3$ additive.

A final solution with a concentration of 15 g/L V$_2$O$_5$ and pH = 0.65 was obtained from the initial sludge by three-stage counterflow leaching with 5% H$_2$SO$_4$ solution at the first stage. It is known that vanadium precipitates from an acidic solution at pH = 1.8–3 and at pH = 4–8 [12]. At pH = 1.8–3, vanadium can precipitate in the form of ammonium hexavanadate by reaction:

$$3\text{V}_{10}\text{O}_{28}^{6-} + 10\text{NH}_4^+ + 8\text{H}^+ = 5(\text{NH}_4)_2\text{V}_6\text{O}_{16} + 4\text{H}_2\text{O}$$

(10)

As a result of reaction with NH$_4$Cl ammonium metavanadate is formed from alkaline solutions:

$$\text{VO}_3^- + \text{NH}_4^+ \rightarrow \text{NH}_4\text{VO}_3$$

(11)

The influence of pH on the recovery rate of V$_2$O$_5$ into the concentrate is shown in Figure 6. Tests at pH < 3 were carried out heating solutions to 95 °C. The maximal recovery rate of 96% of V$_2$O$_5$ into the concentrate from the solution is achieved at pH = 2.4. An increase in NH$_4$Cl flow rate does not practically affect the yield of V$_2$O$_5$ (Figure 7).
Table 4. Parameters of reducing leaching.

| Parameter                        | Value at Using a Reducing Agent during Leaching |
|----------------------------------|-----------------------------------------------|
|                                  | One-Stage | Multistage |
|                                  | FeSO₄·7H₂O | Fe Metallic | FeSO₄·7H₂O |
| Leaching                         |           |            |
| Content V₂O₅ in solution, g/L    | 3.05      | 6.1        | 20.0      |
| Solution pH                      | 0.5       | 1.6        | 0.70      |
| Fe flow rate, g/g concentrate    | –         | 0.023      | –         |
| Precipitation                    |           |            |
| Mg₂(OH)₂ flow rate up to pH ≈ 3 | 1.33      | –          | 1.20      |
| g/g concentrate                  | 0.22      | –          | 0.55      |
| FeSO₄·7H₂O g/g concentrate       | 0.74      | 0.15       | 0.80      |
| Mg₂(OH)₂ flow rate to pH ≈ 5.5   | 0.2       | 0.45       | 1.97      |
| g/g concentrate                  |           |            |
| Content V₂O₅ after precipitation, g/L | 0.2    |            |           |

| Concentrate                      |           |            |
| Concentrate yield, g/kg sludge   | 42.3      | 29.2       | 27.4      |
| Recovery rate of V₂O₅ into the concentrate, wt. % | 29.3 | 33.4 | 56.0 |

Figure 6. Effect of pH value on the recovery of V₂O₅ into the concentrate (30 g/L NH₄Cl flow rate).

Figure 7. Effect of NH₄Cl flow rate on the recovery of V₂O₅ into the concentrate.

Compositions of concentrates at different pH values are presented in Table 5. With an increasing pH, the recovery rate of V₂O₅ into the concentrate decreases, and an increasing amount of impurities is also observed.
Table 5. Chemical composition of initial sludge and concentrates after precipitation at different pH values.

| Component | Content, wt% |
|-----------|-------------|
|           | Sludge Initial | Concentrate (pH = 2.4) | Concentrate (pH = 4) | Concentrate (pH = 8) |
| V₂O₅      | 3.59         | 78.0               | 60.4               | 45.0               |
| V₂O₅a.s.  | 1.4          | n/d                | n/d                | n/d                |
| Al₂O₃     | 1.56         | 0.81               | 1.03               | 1.34               |
| CaO       | 12.1         | 0.07               | 0.09               | 2.43               |
| Cr₂O₃     | 3.34         | n/d                | n/d                | n/d                |
| Fe₂O₃     | 36.8         | 16.92              | 14.92              | 9.01               |
| K₂O       | 0.11         | n/d                | 0.08               | 0.03               |
| MgO       | 1.04         | 0.13               | 0.12               | 8.21               |
| MnO       | 6.52         | 0.35               | 1.33               | 16.2               |
| Na₂O      | n/d          | 0.32               | 10.9               | 7.07               |
| P₂O₅      | 0.03         | 0.88               | 0.9                | 0.54               |
| SO₃       | 15.81        | 0.25               | 8.08               | 6.67               |
| SiO₂      | 11.8         | 0.38               | 0.59               | 1.14               |
| TiO₂      | 7.3          | 1.89               | 1.3                | 1.03               |
| Cl        | 0.0          | n/d                | 0.26               | 1.33               |

Let us consider the possibility of V₂O₅ precipitation from a solution with a concentration of V₂O₅ 23 g/L by ammonium salt obtained after two-stage counterflow leaching of roasted sludge with 1% CaCO₃ additive.

As a result of our studies, the following optimal parameters were selected: pH = 2.4, 40 g/L NH₄Cl flow rate (Figures 8 and 9). At optimal conditions, we obtained the concentrate with V₂O₅ content of 93.6 wt% (Table 6). However, higher purity vanadium pentoxide requires additional stages of concentrate processing.

Figure 8. Effect of pH value on the recovery of V₂O₅ into the concentrate (45 g/L NH₄Cl flow rate).
Reducing the content of impurities in concentrates obtained by precipitation from solutions with V$_2$O$_5$ concentration of 15 and 23 g/L at pH = 2.4 (Tables 5 and 6) was conducted on their washing by repulpation. Washing was carried out with 1% NH$_4$Cl solution at S/L = 1/10 at a temperature of 95 °C. In this process the removal of soluble sulfates of manganese, iron, titanium, and alkali metals takes place. Due to the low solubility of vanadium compounds in ammonium chloride solution, the losses of V$_2$O$_5$ into washing solutions were less than 0.5%. Washing of the concentrate obtained from the initial sludge allowed to increase V$_2$O$_5$ content to 84.94 wt% (Table 7), which is slightly lower than the requirements of the standard (≥90 wt%). Additionally, the concentrate has an increased phosphorus content unsuitable for smelting high-vanadium alloys, such as FeV60, FeV80. The concentrate obtained from the roasted sludge meeting to the grade of VNO-2 (Table 7). To obtain a cleaner vanadium pentoxide (pure, chemically pure), additional stages of washing from impurities will be required. The parameters of the considered processes are presented in Table 8.
Counterflow leaching method was considered to process the sludge. Roasting of the sludge, two-stage leaching of vanadium from the roasted sludge was conducted on their washing by repulpmation. Washing was carried out with 1% NH₄Cl solution at S/L = 1/10 at a temperature of 95 °C. In this process the removal of soluble sulfate of manganese, iron, titanium, and alkali metals takes place. Due to the low solubility of vanadium compounds in ammonium chloride solution, the losses of V₂O₅ into washing solutions were less than 0.5%. Washing of the concentrate obtained from the roasted sludge meeting to the grade of V NO-2 (Table 7). To obtain a cleaner vanadium pentoxide (pure, chemically pure), the additional stages of washing from impurities will be required. The parameters of the analyzed processes for obtaining vanadium concentrates from sludges are presented in Table 8. The most effective technology includes preliminary oxidation roasting of the sludge, two-stage leaching of vanadium from the roasted sludge with a sulfuric acid solution and its further precipitation by hydrolysis or ammonium salts.

Parameters of the analyzed processes for obtaining vanadium concentrates from sludges are presented in Table 9. The most effective technology includes preliminary oxidation roasting of the sludge, two-stage leaching of vanadium from the roasted sludge with a sulfuric acid solution and its further precipitation by hydrolysis or ammonium salts.

### Table 7. Chemical composition of washing concentrates obtained from initial and roasted sludges by counterflow leaching method.

| Component | Content (wt%) of Washing Concentrates, Obtained from Sludges |
|-----------|------------------------------------------------------------|
|           | Initial | Roasted          |
| V₂O₅     | 84.94   | 97.12            |
| Al₂O₃    | 0.5     | 0.7              |
| CaO      | 0.05    | 0.03             |
| Fe₂O₃    | 11.2    | 1.7              |
| MgO      | 0.09    | n/d              |
| MnO      | 0.1     | 0.1              |
| Na₂O     | 0.5     | 0.3              |
| P₂O₅     | 0.5     | 0.1              |
| SO₃      | 0.18    | 0.2              |
| SiO₂     | 0.38    | 0.17             |
| TiO₂     | 1.56    | 0.18             |
| Cl       | n/d     | 0.1              |

### Table 8. Parameters of counterflow leaching method.

| Parameter                  | Sludge   |                  |
|----------------------------|----------|------------------|
|                            | Initial  | Roasted          |
| **Leaching**               |          |                  |
| Content V₂O₅ in solution, g/L | 15       | 23               |
| Solution pH                | 0.65     | 0.70             |
| **Precipitation**          |          |                  |
| NaOH flow rate, g/L; pH = 2.4 | 60       | 60               |
| NH₄Cl flow rate, g/L       | 35       | 40               |
| Content V₂O₅ after precipitation, g/L | 0.8 | 3.1             |
| **Washing of Concentrates**|          |                  |
| NH₄Cl flow rate, g/g concentrate | 0.1 | 0.1            |
| **Concentrate after Washing**|          |                  |
| Concentrate yield, g/kg sludge | 14 | 21               |
| Recovery rate of V₂O₅ into the concentrate, wt% | 36.6 | 52              |

### Table 9. Comparative table of parameters of various hydrometallurgical processes of sludge processing.

| Method               | Material                        | Leaching Parameters                                      | V₂O₅ Precipitation                          | Concentrate                   |
|----------------------|---------------------------------|----------------------------------------------------------|--------------------------------------------|------------------------------|
|                      |                                 |                                                          |                                            | V₂O₅ Content, wt% | Recovery Rate V₂O₅ from Sludge, wt% |
| Counterflow leaching | Initial sludge (3.08 wt% V₂O₅) | 3 stages; 5% H₂SO₄ solution at 1 stage; S/L = 1/2.5 (g/mL) | Hydrolysis, 95–98 °C; pH = 1.4; 1 h | 71.2 | 35.0 |
|                      | Roasted sludge (3.75 wt% V₂O₅) | 2 stages; 5% H₂SO₄ solution at 1 stage; S/L = 1/2.5 (g/mL) | Hydrolysis, 95–98 °C; pH = 1.0; 1 h | 90 | 45 |
|                      | Initial sludge (3.59 wt% V₂O₅) | 3 stages; S/L = 1/2. g/mL; 5% H₂SO₄ solution at 1 stage | NH₄Cl 35 g/L; additional washing 1% NH₄Cl solution | 85 | 36.6 |
|                      | Roasted sludge (3.55 wt% V₂O₅) | 2 stages; S/L = 1/2.5 (g/mL); 5% H₂SO₄ solution at 1 stage | NH₄Cl 40 g/L; additional washing 1% NH₄Cl solution | 97 | 52 |
4. Conclusions

Waste from the production of vanadium pentoxide is undoubtedly a promising technogenic source of raw materials for vanadium production. The experimental analysis of various sulfuric acid methods of sludge processing has shown that the most effective method is an oxidation roasting of sludge with further two-stage counterflow leaching of vanadium with 5% H$_2$SO$_4$ solution in the first stage at S/L = 1/2.5 (g/mL). Precipitation from solutions with a high concentration of more than 20 g/L by hydrolysis or ammonium salts allows fabricating concentrates with >90 wt% V$_2$O$_5$ satisfying the requirements of the standard.

Technologies of counterflow leaching of vanadium from the initial sludges can also be used to obtain vanadium concentrates, but in this case, V$_2$O$_5$ content is significantly lower: 72–78 wt% V$_2$O$_5$. V$_2$O$_5$ content increases after additional purification to 85 wt%, at the same time a significant amount of vanadium remains in the waste sludge. In ferrous metallurgy, such concentrates can be used for the low vanadium ferroalloys (FeV40) and ligatures production.

Methods of reducing leaching with subsequent precipitation of vanadium with brucite have not proven their effectiveness due to the high content of impurities in obtaining concentrates.

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