Recycle of vanadium from aluminum slag of ferrovanadium

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Abstract. Vanadium is a rare chemical element and it primarily comes from the by-product of other minerals. In this study, the material source mainly comes from vanadium-rich aluminum slag. This experiment aims to separate vanadium and other impurities, such as aluminum and zirconium. First, the slag was dissolved in the sodium hydroxide solution at pH value 13, and part of the alumina was precipitated. After removing the precipitation, the strong acid cation exchange resin, Dowex® G26, was added to eliminate the remaining impurities. In this procedure, the parameter of reaction time, the mass of ion exchange resin and pH value were supplied. Moreover, the adsorption isotherms described by means of the Langmuir and Freundlich isotherms were used to investigate the ion-exchange behaviors of vanadium. To sum up, this study will provide the best conditions of ion exchange to get high purity about 95% of vanadate.

Keywords: vanadium; ion exchange; aluminum slag; purify

1. Introduction

The compounds of vanadium have a wide range of applications such as steel industry, catalysts, automobiles, shipyard, fertilizers, ceramics, pigments and vanadium redox battery. 85% of all vanadium is used to create alloys such as ferrovanadium. Ferrovanadium contains 35% to 80% vanadium.

It can obtain ferrovanadium by silicon reduction, and the process is used commercially. In the process of producing ferrovanadium, scrap iron is melted, and a mixture of V₂O₅, aluminum and some flux is added. After the reaction, the aluminum is converted to alumina, and form the slag in the surface. The chemical composition of the slag varies depending on the raw materials, and it might contain some valuable metal, such as Vanadium and Gallium. The slag formed after producing ferrovanadium contained aluminum oxide (Al₂O₃), high percent of vanadium pentoxide (V₂O₅) which is used in the further processing of the metal and amount of Zirconium dioxide (ZrO₂). Ferrovanadium can be used in carbon steel, alloy steel high strength steel, and HSLA (High Strength Low Alloy) steel.

The first period of silicon reduction process is to restore vanadium from the fusion products of the third period of the previous heat. After the first period, the metal contains 25% to 30% V, 20% to 24% Si, and 0.3% to 0.5% C and V₂O₅ content 0.25% to 0.35% in the slag. In the second period,
the operations are to restore additional V₂O₅ with silicon and aluminum to increase vanadium content in the metal. At this period, the slag contains 8% to 10% V₂O₅. The second period ends when the metal composition reaches 35% to 40% V, 9% to 12% Si, and 0.4% to 0.6% C. The V₂O₅ content in the slag drops to <0.35% V₂O₅. In the third period more lime and vanadium pentoxide are added, and the purpose is to utilize reaming silicon in the metal to reduce more vanadium. The slag from the third period contains 12% to 16% V₂O₅. Ferrovanadium can be also prepared by the thermite reaction. In the process, vanadium and iron oxides are co-reduced by aluminum granules.⁸⁻⁹

Sodium carbonate roasting technology is used to extract vanadium from the vanadium-bearing slag. In this process, Na₂CO₃ is used as a calcining additive, and MgSO₄ is added as a conversion agent. By using this process, vanadium could be extracted, but leaching rate is low, only about 65% to 75%, and the aluminum can’t be recovered effectively.¹¹

Finding a way to separate the vanadium from the vanadium-rich slag is the main goal in this experiment. After leaching the slag with NaOH solution, it can obtain vanadium-contained solution. Compared with the methods mentioned above, the ion exchange method has the advantages of, such as high purification efficiency, less pollution, short reaction time, and the reusability of the resin. In the purification process, the cation ion-exchange resin is chosen to remove the impurities. Dowex G26, a strongly acidic cation exchange resin, has a great adsorption efficiency on the impurities, aluminum and zirconium. Because the colorless vanadate VO₃⁻ ions in alkaline medium. To sum up, the leaching method and the Dowex G26 resin were used to get a high purity of the vanadium.

2. Materials and experiments

2.1. Materials

The aluminum slag which is used in this study comes from the production of ferrovanadium. The slag is composed of 49.67% Al₂O₃, 49.31% V₂O₅ and 0.82% ZrO₂. The content of the slag detected by XRF analysis is shown in Table.1.

| Element | V₂O₅ | Al₂O₃ | ZrO₂ |
|---------|------|-------|------|
| Concentration (%) | 49.31% | 49.67% | 0.82% |

Sodium hydroxide (NaOH) was purchased from Sigma-Aldrich (St. Louis, MO, USA) (NaOH ≥ 98%), for the leaching step. Hydrogen chloride (HCl) and sulfuric acid (H₂SO₄) were purchased from Sigma-Aldrich (St. Louis, MO, USA) (HCl ≥ 36.5%)( H₂SO₄ ≥ 98%) to adjust the pH value. Dowex G26 was obtained from Sigma-Aldrich (St. Louis, MO, USA) and was used as a strong acidic cation exchange resin, to remove the impurities. Multi-elements ICP standard solutions were acquired from AccuStandard, New Haven, Connecticut State, USA. The nitric acid (HNO₃) were acquired from Sigma-Aldrich (St. Louis, MO, USA) (HNO₃ ≥ 65%). Ammonium hydroxide (NH₄OH) and Ammonium chloride (NH₄Cl) were obtained from Honeywell and Sigma-Aldrich (St. Louis, MO, USA) respectively (NH₄OH, 30-33%) (NH₄Cl ≥ 95%). (Table.2 and Table.3 show the information of the materials)

| Chemical Composition | Purity | Label |
|----------------------|--------|-------|
| NaOH                 | 98% ≥  | Applichem Panreac |
| HCl                  | ≥ 36.5%| Sigma-Aldrich    |
| HNO₃                 | 65% ≥  | Sigma-Aldrich    |
| NH₄OH                | 30-33% | Honeywell       |
| H₂SO₄                | 98% ≥  | Sigma-Aldrich    |
| NH₄Cl                | 99.5% ≥| Sigma-Aldrich    |
ICP multi-element standard solution IV --- Merck

Table 3. The information of Dowex G26

| Physical form       | Brown opaque spherical beads |
|---------------------|------------------------------|
| Matrix              | styrene-divinylbenzene(gel ) |
| pH group            | 0-14                         |
| Function groups     | Sulfuric acid                |
| Moisture holding capacity | 45-52%                |
| Particle size       | 0.6-0.7mm                    |
| Total exchange capacity | 2.0 meq/mL             |

2.2. Equipment
The materials were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX, PerkinElmer, Waltham, MA, USA).

2.3. Experimental Procedures

2.3.1. Leaching
This process is aims to leaching the vanadium from the slag. Figure 1 is the Eh–pH diagram of vanadium. According to the figure, vanadium pentoxide would turn into the colorless vanadate VO$_3^-$ ions in alkaline solution (The reaction is shown in Eq. 1).

$$V_2O_5 + NaOH \rightarrow Na_3VO_4 + H_2O \quad \text{Eq. 1}$$
2.3.2. Ion-Exchange

Dowex G26 is a strongly acidic resin which was used to exchange cations ions efficiently. In this study, we use Dowex G26 to remove the Aluminum and Zirconium ion which are the most two impurities in the solution. First, we use the adsorption isotherms described by means of the Langmuir and Freundlich isotherms to investigate the ion-exchange behaviors of Aluminum ion. Moreover, we compare the Aluminum and Zirconium ion adsorption efficiency at pH value from 12.5 to 14 to find the best parameter. With the parameters of pH value, we also compare the efficiency with the mass of ion exchange resin and reaction time (from 2 minutes to 1024 minutes). After removing the impurities, the content of the vanadium solutions was investigated in this study. The whole experiment process is shown in figure 2.

3. Result

3.1. Leaching

In this process, the 0.2 grams slag was dissolved in 100 milliliter Sodium Hydroxide solution, and part of the aluminium oxide (Al₂O₃) would be residue as the solid phase. In the experience, the lower the pH value is, the more the aluminium oxide (Al₂O₃), would be found at the bottom. As Figure 3 shows that the leaching of vanadium is 98.1%, the leaching of aluminium is 8.66% and the leaching of Zirconium is about 28.51% with the pH value is 12.5. At this condition, the maximum residues of aluminium oxide (Al₂O₃) is 0.0785g.
3.2. Ion-Exchange

3.2.1. Isothermal Adsorption Models

In this experiment, the varies initial concentrations of aluminium (10, 20, 50, 100, 200, 300 to 500 ppm) and the relationship between $C_e$ and $q_e$ were used to create the isothermal adsorption curve. ($C_e$: the equilibrium concentration of adsorbate (mg/Lc), $q_e$: the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)) Figure 4 shows the isothermal adsorption curve of aluminum. The saturated adsorption amount was about 208 milligram per gram.

To get the adsorption behavior of Dowex G26, Langmuir and Freundlich isothermal adsorption model were used and the regression coefficients were compared. Equation 2 show the Langmuir equation \[11\]. Figure 5 is the Langmuir isothermal adsorption curve. Equation 3 show the Freundlich equation \[11\]. Figure 6 is the Freundlich isothermal adsorption curve. By comparing the R square in figure 5 and 6, the adsorption behavior of Dowex G26 more fits with the Langmuir adsorption model.
It means that the adsorption of the Dowex G26 is uniform and no transmigration of adsorbate in the plane of the surface.

\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K_L}
\]

Eq. 2

Where:

\( C_e \): the equilibrium concentration of adsorbate (mg/L)
\( q_e \): the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)
\( q_m \): maximum monolayer coverage capacity (mg/g)
\( K_L \): Langmuir isotherm constant (L/mg)

\[
ln q_e = ln K_F + \frac{1}{n} ln C_e
\]

Eq. 3

Where:

\( C_e \): the equilibrium concentration of adsorbate (mg/L-1)
\( q_e \): the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)
\( n \): adsorption intensity
\( K_F \): Freundlich isotherm constant (mg/g)

Figure 5. Langmuir isothermal adsorption curve
3.2.2. Effect of pH value

The solution after leaching is used to investigate the effect of pH value with a range from 12.5 to 14. Figure 7 shows the relationship between the pH value and the adsorption efficiency of Aluminum and Zirconium ion. As seen in the figure, pH value 13 has the greatest adsorption efficiency of Zirconium ion, about 99.89%. The adsorption efficiency of Aluminum has the best parameter at pH 12.5 (90.94%) and the adsorption efficiency is 89.59% at pH 13. Due to this condition, pH 13 was chosen to be the best parameter.

3.2.3. Effect of Reaction Time

The reaction time was investigated from 2 to 1024 minute. Figure 8 shows the result of adsorption efficiency. In the figure, at 4 minutes the adsorption efficiency on zirconium was 100%. The adsorption efficiencies on aluminum from 2 minutes to 1024 minutes were almost the same (89.54%-92.95%). 4 minutes was chosen to be the best reaction time parameter.
3.2.4. Effect of the mass of ion exchange resin

Figure 9 shows the adsorption efficiency with the mass of ion exchange resin from 0.1 g to 1.5 g. According to this graph, when the mass of resin was 0.2 g, the adsorption efficiency of Zr approached 100%. With the mass of resin was 1.2 g and 1.5 g, the adsorption efficiencies of Al were almost the same (90.84% and 92.58% respectively). Due to this condition, 1.2 g resin was chosen to be the best parameter.

After getting the optimum parameters of reaction time, the mass of ion exchange resin and pH value, the vanadium solution were purified, and the content detected by ICP is shown in table 4.

![Figure 8. The adsorption efficiency with reaction time](image)

![Figure 9. The adsorption efficiency with the mass of ion exchange resin](image)

| Element | V   | Al  | Zr  |
|---------|-----|-----|-----|
| Content (%) | 99.76% | 0.24% | N.D. |

Table 4. The content of vanadium solution
4. Conclusion

1. The leaching efficiency of vanadium is 98.1% at the optimum condition of pH 12.5.

2. pH value 13.5, 4 minutes reaction time, 1.2g resin were the optimum parameter of Dowex G26 in ion-exchange step to purify the impurity.

3. The purity and recovery rate of vanadium product is 99.758% and 96.83%.

4. The process in this study can provide a method to purify vanadium effectively.

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