

Recovery of vanadium from alkaline leaching solution from roasted stone coal

Sisi Long^a, Qiming Feng^a, Guofan Zhang^{a,*}, Dongsheng He^b

^a School of Resources Processing and Bioengineering, Central South University, Changsha 410083 China

^b School of Environment and Civil Engineering, Wuhan Institute of Technology, Wuhan 430073 China

*Corresponding author, e-mail: zhangguofan2002@163.com

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ABSTRACT: A two-stage purification-extraction-stripping-NH₄NO₃ technology to precipitate V₂O₅ was developed based on the characteristics of the alkaline leaching solution produced from roasted stone coal. Factors influencing purification, extraction, stripping, and NH₄VO₃ precipitation were studied. Vanadium can be recovered effectively from alkaline leaching solutions using this technology. The purity of the V₂O₅ product was 99.6%, thereby meeting national standards. The overall vanadium recovery was 90.9%.

KEYWORDS: vanadium pentoxide, purification, extraction

INTRODUCTION

The classical technology for extracting vanadium from stone coal has two main problems, low vanadium recovery (< 50%) and the production of environmental pollutants^{1,2}, and is therefore being eliminated gradually. In recent years, researchers have developed new technologies^{3–8}, such as oxidizing roasting-acid leaching-salt production-extraction-deposition with ammonium-thermal decomposition, oxidizing roasting-acid leaching-extraction-deposition with ammonium-thermal decomposition, and oxidizing roasting-acid leaching and purification-deposition with ammonium-thermal decomposition. In contrast with the classical technology, these technologies have advantages of higher recovery, simpler flowsheet and lower cost. However, they require acid as a leaching agent and this causes problems such as high acid consumption, a requirement for acid-resistance equipment, and treatment of acidified wastewater and solid residues before discharge^{4,8}. To overcome the disadvantages of the acid leaching technology, we investigated an alkali leaching technology^{9,10}. In contrast with acid leaching technologies, the advantages of the alkali leaching technology are, reduced impurities in the leaching solution, which is better for subsequent processes; low requirements for corrosion resistance of equipment; direct discharge of wastewater and solid residues after simple treatment. Using our previous results from the development of an alkali leaching technology⁹, we present here a detailed report on the recovery of vanadium from alkali leaching solutions.

MATERIALS AND METHODS

Materials

The stone coal in this study is black and rock-like in appearance. This fuel with low calorific value can be treated as a polymetallic ore. It contains mostly quartz, illite, kaolinite, pyrite, and 18% organic matter with main chemical composition being 1% V₂O₅, 68% SiO₂, 6% Al₂O₃, and 5% Fe₂O₃. The vanadium distribution in the silicates is approximately 80%. The loss on burning of the organic matter in the stone coal is approximately 17%.

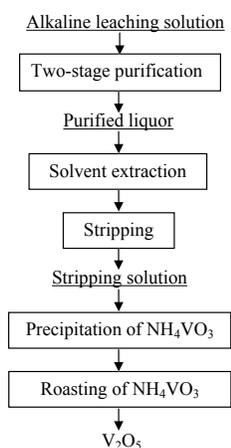
The raw stone coal was roasted at 850 °C for 3 h and then leached with NaOH solution at a certain temperature to obtain an alkaline leaching solution containing vanadium. Table 1 gives the chemical composition of the alkaline leaching solution where the main elements in solution are V, Si, and Na, with traces of Al and As. The Si concentration reaches 63.23 g/l. Si, Al and As are impurities which should be removed to ensure the final product purity.

Methods

The Si, Al, and As impurities in solution were removed through chemical precipitation in two steps (two-stage purification). After the two-stage purification, almost all impurities were removed, and a purified liquor was obtained. The impurities (Si and Al) in solution were removed by chemical precipitation by addition of H₂SO₄, Mg(NO₃)₂, and ammonia. After extracting vanadium from the purified liquor using an extractant (10 vol % N235, 20 vol % secondary

Table 1 Chemical composition of alkaline leaching solution.

| Constituent | V ₂ O ₅ | SiO ₂ | Al ₂ O ₃ | As | Na ₂ O |
|---------------------|-------------------------------|------------------|--------------------------------|-------|-------------------|
| Concentration (g/l) | 10.40 | 63.23 | 0.56 | 0.023 | 54.75 |

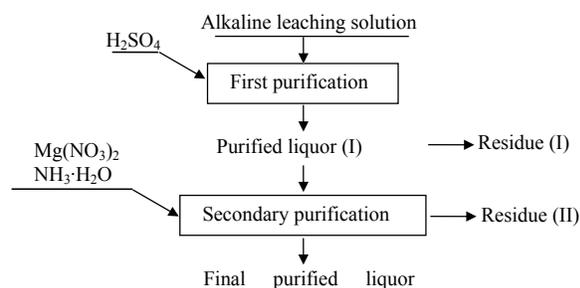
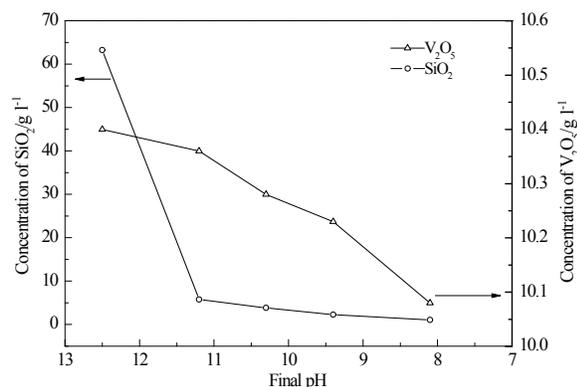
**Fig. 1** Principle flowsheet for extracting vanadium from alkaline leaching.

octyl alcohol and 70 vol % sulphonated kerosene), NaOH was used as vanadium stripping agent. N235 is a tertiary amine with structure N[C_nH_{2n+1}]₃ (n = 8–10). Ammonium metavanadate was crystallized from the stripping solution by NH₄NO₃ addition, and high quality V₂O₅ was obtained by calcination of ammonium metavanadate at high temperature. The principle flowsheet for extracting vanadium from alkaline leaching solution is shown in Fig. 1.

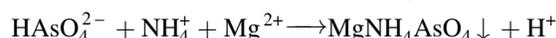
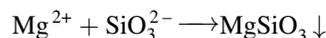
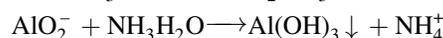
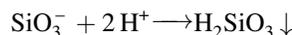
RESULTS AND DISCUSSION

Purification

The principle flowsheet for purification of the leaching solution in Fig. 2 consists of two steps. First, most

**Fig. 2** Principle flowsheet of the purification of alkaline leaching.**Fig. 3** Effect of final pH on purification efficiency.

Si and Al are removed by adjusting the solution pH to a suitable value with H₂SO₄. As and the remaining Si are removed by Mg(NO₃)₂ and ammonia addition and the chemical precipitation of low solubility MgSiO₃ and MgNH₄AsO₄. The corresponding reactions are^{11,12}:



Factors affecting the purification efficiency are the purification temperature, purification time, reagent dosage, stirring speed, and H₂SO₄ addition rate. For the first step, the final solution pH is the key influencing factor¹³. Suitable purification conditions acquired through a series of experiments are as follows: purification temperature at ambient temperature, purification time of 1 h, H₂SO₄ concentration of 50% (v/v), H₂SO₄ addition rate of 2 ml/min and stripping speed of 500 rpm. Under these conditions, the relationship between the final solution pH and desilication efficiency was studied. Fig. 3 shows the effect of final pH on Si and V concentration in the purified liquor. The Si and V concentration decreased with decrease in final pH. A certain amount of V was therefore lost in the desilication process. The optimal final pH should ensure maximum desilication efficiency and minimal V loss. From Fig. 3, it appears that the suitable final pH is 8–9.

Under the above conditions, the first purification experiments were carried out with results shown in Table 2. The desilication efficiency reached 97.9% with loss of efficiency of vanadium of 3.4%. After the first purification, there was a certain amount of Si and As in the purified liquor, which should be

Table 2 Purification results.

| Purification | Grade of purified liquid (g/l) | | Recovery of purification residue (%) | | Recovery of purified liquid (%) | |
|--------------|--------------------------------|------------------|--------------------------------------|------------------|---------------------------------|------------------|
| | V ₂ O ₅ | SiO ₂ | V ₂ O ₅ | SiO ₂ | V ₂ O ₅ | SiO ₂ |
| First | 10.25 | 1.35 | 3.4 | 97.9 | 96.6 | 2.1 |
| Second | 10.10 | 0.066 | 2.4 | 95.2 | 97.6 | 4.8 |

Table 3 Chemical compositions of final purified liquor.

| Constituent | V ₂ O ₅ | SiO ₂ | Al ₂ O ₃ | As | Na ₂ O |
|---------------------|-------------------------------|------------------|--------------------------------|--------|-------------------|
| Concentration (g/l) | 10.10 | 0.066 | 0.075 | 0.0013 | 54.35 |

removed through the second purification step. The experimental conditions of the second purification experiments were reagent dosage of 8 g Mg(NO₃)₂ and 10 ml ammonia per litre of solution, purification temperature of 60 °C, purification time of 1 h, stirring speed of 500 rpm. The result is shown in Table 2 with the concentration of impurities in the final purified liquor given in Table 3. After the second purification (Table 2), the desilication efficiency was 95.2%, and efficiency of vanadium loss was 2.4%. The desilication efficiency and efficiency of vanadium loss in the overall purification process were 99.9% and 5.8%, respectively. The impurity concentrations (Si:Al and As) in the final purified liquor were low, and these concentrations will not affect the subsequent processes.

Solvent extraction

Extraction and stripping processes were necessary to enrich vanadium. The composition of the chosen extractant was 10 vol % N235, 20 vol % secondary octyl alcohol and 70 vol % sulphonated kerosene. The N235 was acidified using 2 mol/l HCl (volume ratio 1:1) before use¹⁴. The extraction was performed at ambient temperature with organic/aqueous (O/A) ratio of 1:6, and 3 min equilibrium time. Table 4 shows that the pH had a significant effect on extraction efficiency with an optimal pH of approximately 3.5. NaOH was used as stripping agent with stripping experimental conditions as O/A ratio of 2:1, ambient temperature and equilibrium time of 4 min. Table 5 shows the effect of NaOH concentration on stripping efficiency. The stripping efficiency increased with increase in

Table 4 Effect of pH on extraction efficiency.

| Solution pH | 1.98 | 2.31 | 2.62 | 3.43 | 4.28 |
|---|------|------|------|-------|------|
| Concentration of V ₂ O ₅ in raffinate (g/l) | 0.84 | 0.33 | 0.17 | 0.033 | 0.25 |
| Extraction efficiency (%) | 89.3 | 95.8 | 97.8 | 99.7 | 96.8 |

Table 5 Effect of NaOH concentration on stripping efficiency.

| Concentration of NaOH (%) | 2 | 4 | 6 | 8 |
|--|------|------|------|------|
| Concentration of V ₂ O ₅ in stripping liquor (g/l) | 84.5 | 87.3 | 89.5 | 91.5 |
| Stripping efficiency (%) | 90.7 | 93.7 | 96.0 | 98.2 |

Table 6 Effect of pH on precipitation efficiency of ammonium metavanadate.

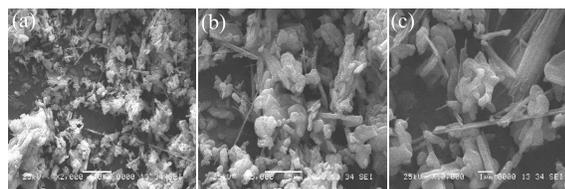
| pH | 6.1 | 7.3 | 8.2 | 9.5 |
|---|------|------|------|------|
| Concentration of V ₂ O ₅ in residual liquor (g/l) | 0.57 | 0.85 | 1.59 | 3.13 |
| Precipitation efficiency of vanadium (%) | 99.4 | 99.1 | 98.2 | 96.7 |

NaOH concentration. When the NaOH concentration was 6 and 8%, the stripping efficiency reached 96.02 and 98.2%, respectively. However, for the NaOH concentration of 8%, a crystalline phase forms, which is harmful to the stripping process. Thus a suitable NaOH concentration is 6%.

Precipitation of ammonium metavanadate and V₂O₅

After stripping, the vanadium was enriched, and the V₂O₅ concentration in the stripping liquor reached approximately 90 g/l. This concentration was sufficient for ammonium metavanadate precipitation¹⁵. As NH₄NO₃ was added to the stripping liquor at 35 °C, and ammonium metavanadate crystallized from solution. The NH₄NO₃ dosage was 80 g NH₄NO₃ per stripping liquor. The effect of pH on the precipitation efficiency of vanadium was investigated with results shown in Table 6. The vanadium precipitation efficiency decreases with increase in pH. When the pH is 6–7, the vanadium precipitation efficiency reaches 99% and this pH range is therefore suitable.

NH₄VO₃ was roasted in a muffle furnace at 500 °C for 1 h to obtain V₂O₅. The V₂O₅ purity reached 99.6%, meeting the standard specification. SEM images of the V₂O₅ formed are provided in Fig. 4.

**Fig. 4** SEM images of the vanadium pentoxide formed: (a) 2000 times magnification, (b) 5000 times magnification, and (c) 10000 times magnification.

CONCLUSIONS

The recovery of vanadium from the alkaline leaching solution of roasted stone coal was performed by two-stage purification, solvent extraction, stripping, precipitation of ammonium metavanadate and preparation of V_2O_5 . The overall vanadium recovery was 90.9% with V_2O_5 purity of 99.6%, thereby meeting the standard specification. This technology has advantages of higher recovery, production purity and environmental safety.

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