Recovery of vanadium from black shale

LI Cun-xiong(   ), WEI Chang(   ), DENG Zhi-gan(   ), LI Min-ting(   ),
LI Xing-bin(   ), FAN Gang(   )

College of Metallurgical and Energy Engineering, Kunming University of Science and Technology,
Kunming 650093, China

Abstract: The recovery of vanadium from a black shale from Guizhou Province of China was performed using a three-step process, which consists of a leaching step in the H_2SO_4-HF-NaClO system under atmospheric pressure, the vanadium separation from leachate by solvent extraction and stripping, followed by precipitation of ammonium vanadate and thermal decomposition. Under the optimum leaching conditions of 100 g/L sulfuric, 15 g/L hydrofluoric acid, 1.5 g/L NaClO, 6 h leaching at 90 and oxygen partial pressure of 1 200 kPa, and the liquid-to-solid ratio of 2, about 91% vanadium extraction is achieved. The vanadium extraction yields of solvent and stripping are 99.83% and 97.66% when using 10% (volume fraction) P204, 5% TBP and 85% sulfonated berosene as organic phase and 15% (mass fraction) sulphuric acid as stripping agent. After thermal decomposition the purity of powder vanadium pentoxide products is 99.18% and the overall vanadium recovery is over 81% in the whole process.

Key words: black shale; vanadium extraction; H_2SO_4-HF-NaClO system; solvent extraction; precipitation; thermal decomposition

1 Introduction

Vanadium is an essential trace element in the earth. With specific physiological functions, it is used extensively as an alloying element in steel and iron and titanium alloys, and as catalysts[1]. Even if vanadium widely distributes throughout the lithosphere, it is not present in high concentrations in minerals and the highest concentration of vanadium is found in shales and clays[2]. Usually, vanadium exists in the combination with various minerals which include carnotite, roscoelite, vanadinite, mottramite and patronite as important sources of the metal. Because of the low grade of vanadium in the processed ores and the depletion of concentrated ore deposits in the world, many industrial sub-products, including the converter and smelter slag[3−5], spent catalysts[6], and oil fly ash[7−14], are becoming interesting sources for the recovery of vanadium in industry.

In China, vanadium is mostly recovered from the converter and smelter slag produced by the treatment of titanomagnetites in iron and steel industry and black shale. Black shale is carbonaceous shale with several valuable metals, such as vanadium, nickel, molybdenum and silver. The common grade of vanadium in this ore is usually less than 2%. Black shale is the most important resource for vanadium extraction in China, which accounts for more than 87% of the domestic reserve of vanadium[15−16]. Conventionally, the recovery of vanadium from black shale was performed containing a preliminary roasting process, which emits serious poisonous gases of HCl and Cl_2. With the increasing concerning of environment protection, the application of conventional technologies has been limited in China[17−20], and the classical process for vanadium recovery from black shale is gradually replaced by some environment friendly technologies[21−22].

The present work focuses on the design of integrated process for vanadium recovery from black shale. Firstly, the process is to systematically investigate the optimum conditions of vanadium extraction from one black shale in H_2SO_4-HF-NaClO system under atmospheric pressure, which gives the best yield of leaching and less pollution to environment. Secondly, to recover metal from the leachate, pretreatment of leach liquid and solvent extraction is involved. At last, purified vanadium pentoxide is prepared by precipitating the

vanadium as ammonium vanadate and thermal decomposition.

2 Experimental

2.1 Materials

The experimental study was carried out using black shale from Guizhou Province of China. The composition of the black shale used in this study is listed in Table 1. Table 2 lists the mineralogical composition of the concentrate and valence distribution of vanadium in the sample. As listed in Table 1, the black shale sample has a relatively high vanadium content of 1.987% and high quartz concentration of over 53.03% by mass, and the concentrate is also characterized by high alumina fraction.

Table 1 Chemical composition of black shale (mass fraction, %)

V	C	SiO_2	Fe	P_2O_5	Al_2O_3
1.978	5.62	53.03	3.74	0.19	16.62

S	CaO	MgO	Na_2O	K_2O
0.70	0.49	1.22	0.59	3.36

Table 2 Mineralogical composition of black shale

V-containing mineral	Mass fraction of mineral/%	w(V)/%
Iron oxide-clay	17.68	0.35
Micaceous insoluble	80.30	1.59
Silicoaluminate	2.02	0.04

It can be seen from Table 2 that the main composition of the black shale are ferric oxides, kaoline, roscoelite and garnet. It is reported that V( ) is substituted isomorphously with Al^{3+} in the roscoelite and garnet structure. V( ) or V(V) compounds are weakly adsorbed to the ferric oxides and kaoline[16]. It can be seen from Table 3 that the distribution rate of V( ) in the sample is about 34% and V( ) is undissolvable in acid or alkaloid solution. So, NaClO is used as an oxidant in the present study to oxidize V( ) into its dissolvable forms of V( ) or V(V).

Table 3 Valence distribution of vanadium in black shale

Valence	Mass fraction/%	Distribution/%
V( )	0.627	34.34
V( )	0.527	28.86
V( )	0.672	36.80
Total V	1.826	100.00

The particles less than 0.074 mm in the mineral sample used in this study account for 85%. The chemical agents, sulfuric acid, hydrofluoric acid, NaClO, NaOH, Na_2SO_3, $NaClO_3$ and ammonia used in the present study are all of analytical grade. In all the leaching experiments we employed sulfuric acid and hydrofluoric acid as leaching agents and NaClO as the vanadium oxidating agents.

2.2 Procedures

The leaching and oxidation process were conducted at atmospheric pressure in a pyrex stirred reactor, equipped with a reflux condenser and placed in a heated water bath. The various solutions derived from leaching the black shale concentrate, precipitation of the ammonium vanadate, and washings of the cakes were separated by vacuum filtration. The leaching slurry was agitated at 550 r/min.

3 Results and discussion

3.1 Leaching

The main variables studied are the concentration of sulfuric acid and hydrofluoric acid in the leaching solution, the amount of NaClO oxidant to be employed, the liquid-to-solid ratio of the slurry, time, and the temperature of the reaction. The results obtained are shown in Figs.1−6.

It can be concluded from Figs.1−6 that the optimum conditions of the vanadium extraction from the black shale concentrate in the H_2SO_4-HF-NaClO system under atmospheric pressure are that the concentrations of leaching agent of sulfuric acid and hydrofluoric acid in the leaching solution are 100 g/L and 15 g/L, respectively, the amount of NaClO oxidant to be employed is 1.5 g/L, the liquid-to-solid ratio of the slurry is 2, leaching time is
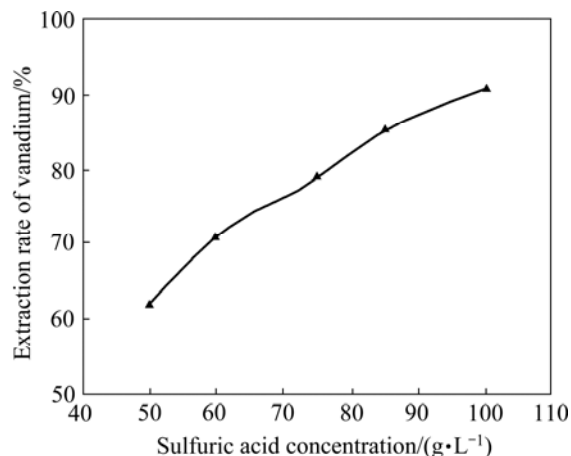

Fig.1 Effect of sulfuric acid concentration on vanadium extraction (20 g/L hydrofluoric acid, 1 g/L NaClO, liquid-to-solid ratio 2, leaching time 6 h, temperature 90)
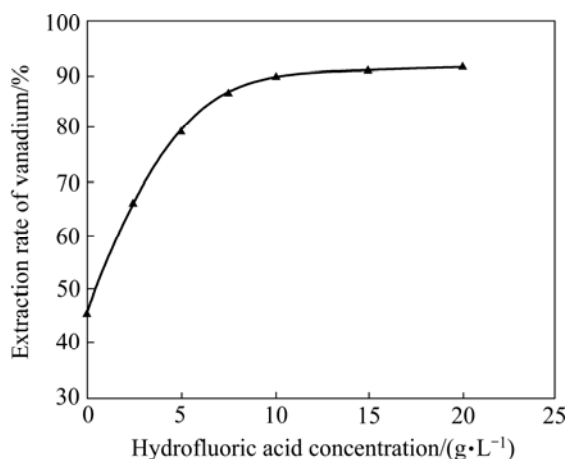
Fig.2 Effect of hydrofluoric acid concentration on vanadium extraction (100 g/L sulfuric acid, 1.0 g/L NaClO, liquid-to-solid ratio 2, leaching time 6 h, temperature 90   )
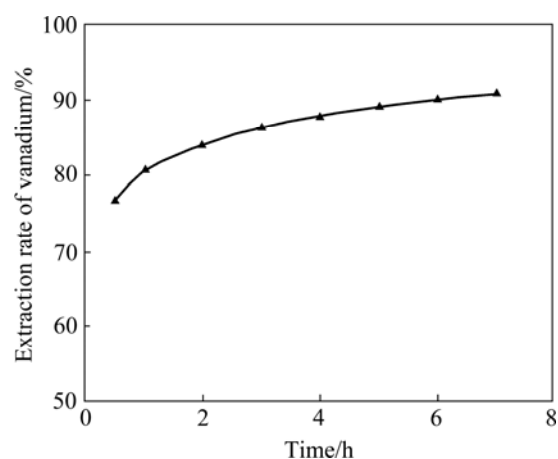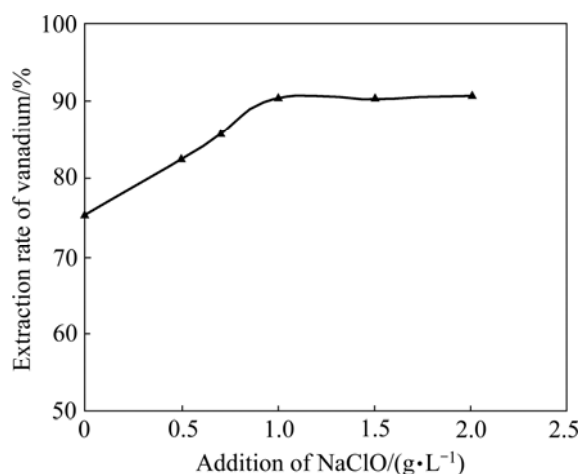

Fig.3 Effect of addition of NaClO on vanadium extraction (100 g/L sulfuric acid, 15 g/L hydrofluoric acid, liquid-to-solid ratio 2, leaching time of 6 h, temperature 90   )
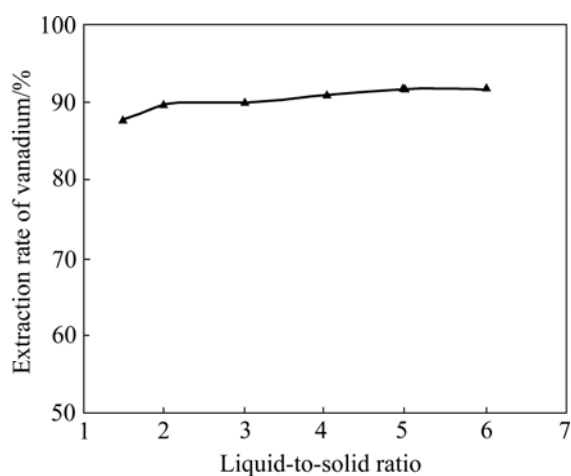

Fig.4 Effect of liquid-to-solid ratio on vanadium extraction (100 g/L sulfuric acid, 15 g/L hydrofluoric acid, 1.5 g/L NaClO, leaching time 6 h, temperature 90   )
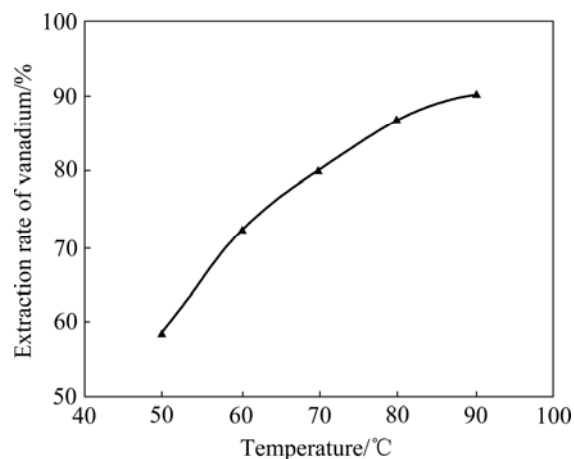

Fig.5 Effect of time on vanadium extraction (100 g/L sulfuric acid, 15 g/L hydrofluoric acid, 1.5 g/L NaClO, liquid-to-solid ratio 2, temperature 90   )

Fig.6 Effect of temperature on vanadium extraction (100 g/L sulfuric acid, 15 g/L hydrofluoric acid, 1.5 g/L NaClO, liquid-to-solid ratio 2, leaching time 6 h)

6 h, and the temperature of reaction is 90   . The experiments were carried out under the optimum conditions, the extraction rate of vanadium reaches about 91.2% and the composition of the leaching solution is shown in Table 4.

3.2 Solvent extraction and stripping

A series of experiments were carried out to determine the optimum extractants and extraction conditions, and di(2-ethylhexly)phosphoric acid (P204) and tributylphosphate (TBP) were chosen as extractants.

Table 4 Composition of leaching solution (g·L^{-1})

V	SiO$_2$	Fe	P	As	Al
9.02	1.49	10.03	0.75	0.083	6.78

Mg	Na$_2$O	K$_2$O	Cr	CaO
3.64	2.67	6.21	0.132	1.01

The organic phase was made up of 10% (volume fraction) P204, 5% TBP and 85% sulfonated kerosene. Before solvent extraction the leachate was adjusted to a suitable pH value of 2.0−2.5 using sodium hydroxide as neutralizing agent, and then followed by oxidizing any fraction of Fe( ) to Fe( ). An excess of 5% Na_2SO_3 was added compared to the total amount of Fe( ).

After the pre-treatment, the leachate is free of Fe( ). The organic phase, consisting of 10% P204, 5% TBP and 85% sulfonated kerosene, was used to extract vanadium in leaching liquor under the optimum conditions (obtained by our series of experiments) of pH 3.5, O/A ratio 1:6, ambient temperature for 10 min by six stages extraction. Stripping was performed by contacting the organic and 15% (mass fraction) sulfuric acid (O/A=6:1) at atmospheric temperature for 15 min. The results show that the solvent extraction and stripping of the vanadium are about 99.83% and 97.66%, respectively.

3.3 Precipitation and thermal decomposition

Whichever method (Ion exchange resins or solvent extraction) is used in separation of vanadium from leaching solution, the vanadium is finally precipitated as ammonium vanadate or vanadium pentoxide by ammonia or ammonium. The precipitation of the vanadium from the stripping solution was performed under the conditions that an excess of 25% $NaClO_3$ was added compared to the total amount of vanadium as the vanadium oxidating agent (oxidation of V( ) to V( )) at the boiling temperature of the solution, after 1 h of oxidation, 18% ammonia was added to keep the pH at 2. Under these conditions vanadium in stripping solution was gradually crystallized into ammonium vanadate. After solid liquid separation the red cake of ammonium vanadate was thermal decomposited at 550   for 2 h to produce qualified powder vanadium pentoxide. The precipitation yield of vanadium into ammonium vanadate reaches 98.36%, and the composition of the powder vanadium pentoxide is shown Table 5.

Table 5 Composition of powder vanadium pentoxide products (mass fraction, %)

V_2O_5	SiO_2	Fe	P	Mg	Na_2O	K_2O	CaO	Al_2O_3
99.18	0.101	0.023	0.007	0.123	0.049	0.166	0.013	0.018

4 Conclusions

1) The optimum conditions of vanadium extraction from the black shale concentrate in H_2SO_4-HF-NaClO system under atmospheric pressure are that the concentration of sulfuric acid is 100 g/L, the concentration

of hydrofluoric acid is 15 g/L, the amount of NaClO oxidant employed is 1.5 g/L, the liquid-to-solid ratio of the slurry is 2, the leaching time is 6 h, and the temperature of reaction is 90   . The extraction rate of vanadium is 91.2% under these conditions.

2) Vanadium can be effectively separated from leachate by solvent extraction with di(2-ethylhexly) phosphoric acid(P204) and tri-butyl-phosphate(TBP) as extractants, the solvent extraction yield and stripping yield are 99.83%, and 97.66%, respectively.

3) The purity of the powder vanadium pentoxide product is 99.18% and the overall vanadium recovery is above 81% in the whole process.

4) The proposed leaching, solvent extraction, precipitation and thermal decomposition steps give a feasible alternative for the processing of black shale concentrate with different vanadium contents.

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