Rare Metal Technology 2015
Edited by: Neale R. Neelameggham, Shafiq Alam, Harald Oosterhof, Animesh Jha, David Dreisinger, and Shijie Wang
TMS (The Minerals, Metals & Materials Society), 2015

A NOVEL TECHNOLOGY OF VANADIUM EXTRACTION FROM STONE COAL

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Abstract

A novel technology characterized by higher extraction of vanadium and recovery of valuable elements was developed to recover vanadium from stone coal. The brief flow of the novel technology mainly includes low temperature sulphation roasting, water leaching, recovering potassium, aluminum, copper and selenium, solvent extraction enrichment vanadium, precipitation of red vanadium, removal sodium from red vanadium and calcinations. The total recovery of vanadium reached 78.3%, which was higher than the current applied technology. The novel technology was environmentally-friendly and could extraction vanadium from the stone coal, in which the content of V_2O_5 was less than 0.8%.

Keywords: Stone coal; Vanadium; Comprehensive utilization

Introduction

Vanadium is an important by-product that is used almost exclusively in ferrous and non-ferrous alloys due to its physical properties such as tensile strength, hardness, and fatigue resistance. China, as a major player in the global supply of vanadium bearing products has two important vanadium sources, one is vanadium-titanium magnetite ore, and the other is vanadium bearing stone coal. With the rapid growth of demand of vanadium products, the study on the extraction of V_2O_5 from stone coal attracts more and more attentions.

From 1970s on, some companies began to extract vanadium from stone coal by the classical NaCl roasting technology. However, the released exhaust gas containing Cl_2 and HCl during roasting pollutes the environment seriously. In the recent years, many technologies, such as oxygen pressure acid leaching [1], roasting-alkaline leaching [2,3], calcium salt roasting-sulfuric acid leaching [4] and sulfuric acid with villiaumite leaching [5], have been used to extract vanadium from stone coal. The vanadium leaching percentage of these methods is high, but the operations are high costs or high water pollution for treating stone coal. A productive process of V_2O_5 from stone coal was proposed in 1996, which included grinding, two-step counter-current sulfuric acid leaching, solvent extraction, precipitation and pyrolysis [6]. This technology avoids waste gas pollution and the product V_2O_5 met the standard specification, however, it only can be used in partial stone coal, in which the vanadium mainly existed in amorphous phase form. This process was only successfully applied to commercial production in the south region of Shanxi province. In these stone coals, the vanadium existed in amorphous phase form accounts for about 66%, and the rest of vanadium existed in vanadium bearing minerals. All the above technologies were only used for stone coal, in which the content of V_2O_5 was more than 0.8%. In China, stone coal containing more than 0.8% V_2O_5 accounts for about 10% of the total stone coal reserve. Furthermore, all the above technologies were only used for extracting vanadium from stone coal. In fact, stone coal is complex ore, in which many other elemental also can be extracted.

Combining the advantages of the two processes of direct leaching and pressure leaching with sulfuric acid, a novel technology, named as low temperature sulphation roasting-water leaching was developed, which characterized by higher recovery of vanadium, low production costs, no pollution to environment as well as comprehensive recovery of copper, selenium, potassium and aluminum.

Materials and methods

Materials

The raw stone coal used in this study was taken from Xiangxi district, Hunan province in China and the main composition of stone coal is shown in Table 1.

Table 1 Main chemical composition of stone coal, wt%

V_2O_5	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
0.65	73.22	6.51	0.26	2.57	0.32
K_2O	C	S	Cu	Se	
0.86	12.81	1.82	0.058	0.027	

Methods

After crushed and ground, the particle size of stone coal is less than 0.18 mm. Prior to roasting process, 85 Kg ground stone coal was mixed with sulfuric acid solution in a desired ratio. After mixing, there is no flow dynamic solution in sample. The mixture was put in a stainless steel crucible, which can be heated by oil bath. After the mixture was roasted at a desired temperature and time, the calcine was taken out for leaching by water at room temperature to extract vanadium. After filtering, potassium and aluminum were recovered from solution by cooling to obtain the crystal of potassium aluminum sulfate.

Iron shavings was subsequently employed to reduce Fe^{3+} and recovery copper and selenium in the solution, then the pH of the solution was adjusted to about 2.0 by adding potassium carbonate before enriching vanadium. After enriching vanadium with P204 from the solution, H_2SO_4 solution was used as the stripping agent to strip vanadium from the loaded organic phase.

The oxidative of vanadium from the stripping solution was performed by using $NaClO_3$ as the oxidation agent at 60 ℃ for 1 h, and then 4 mol/l NaOH was added to adjust the pH to about 2.0 for the precipitating of red vanadium. After removing sodium, high quality V_2O_5 was acquired by calcining the red vanadium at 530 ℃ for 3h. Fig. 1 is the flow sheet of vanadium extraction from stone coal.

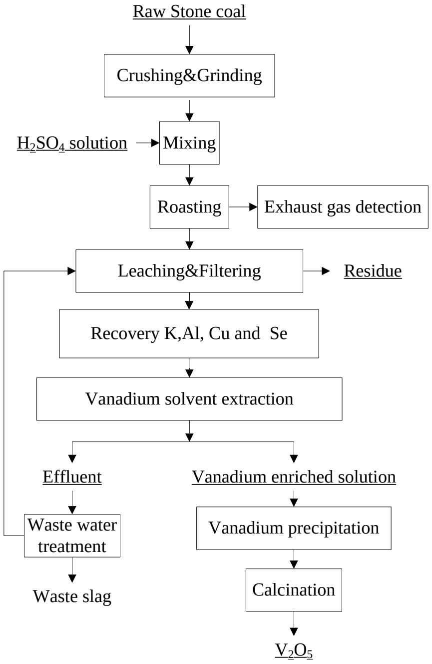

Fig.1 Flow sheet of vanadium extraction from stone coal

Results and discussion

Roasting

During sulphation roasting，the main chemical reactions of vanadium can be expressed by the following equations:

$$V_2O_3 + 3H_2SO_4 = V_2(SO_4)_3 + 3H_2O \quad (1)$$

$$VO_2 + H_2SO_4 = VOSO_4 + H_2O \quad (2)$$

One can see from the equations, the vanadium in stone coal will produce vanadium sulphate, which is easy to be dissolved in water. The purpose of the roasting was to improve the reaction temperature of Eq.(1) and Eq.(2), so as to improve its reaction rate. In this process, roasting temperature was very important. Too high roasting temperature will lead to the decomposition of sulfuric acid, as the decomposition temperature of sulfuric acid is only 330 ℃ [7]. Combined with the vanadium leaching percentage, the proper roasting condition was determined: roasting temperature 140 ℃, 3 h, and the addition of sulfuric acid was 20wt%.

For the extraction of vanadium, environmental is very important. The reason of many former process cannot be applied, is environmental pollution relatively large, particularly air pollution. The composition of roasting exhaust gas during low temperature sulphation roasting was illustrated in Table 2 (The composition was measured by Changsha Institute of Environmental Science).

Table 2 Composition of roasting exhaust gas, mg/Nm^3

SO_2	HF	HCl	Sulfuric acid mist	As	Hg	Pb
4.21	4.06	3.46	2,041	6.63×10^{-3}	7.80×10^{-5}	0.020

As can be seen from Table 2, in the roasting exhaust gas, the contents of harmful components were very low except sulfuric acid mist. Therefore, after water spray, the exhaust gas can be discharged.

Leaching

After sulphation roasting, the calcine was leached in a reaction kettle with water. In this process, $VOSO_4$, $V_2(SO_4)_3$ and others soluble sulfate were dissolved by water. The effects of liquid to solid ratio, leaching temperature and leaching time on vanadium leaching percentage, were studied. The suitable leaching condition was obtained by a series of experiments. The proper leaching condition was: room temperature leaching for 2 h with liquid to solid ratio of 1.6 ml/g. Under this condition, the leaching percentage of vanadium reached 78.3%. The concentrations of the main metal components of the leach solution are shown in Table 3, and pH of leaching solution is 1.1

Usually, only the stone coal in which the content of V_2O_5 was more than 0.8% can be used. It can be seen from Table 1, in this study the content of V_2O_5 is only 0.65%, which is far below 0.8%. That is to say, the novel technology can extraction vanadium from the stone coal, in which the content of V_2O_5 is less than 0.8% and also can get a high leaching rate.

Table 3 Composition of the leach solution of stone coal, g/L

V_2O_5	TFe	Al	P	Ti	Ca	Mg	K
2.81	9.61	13.16	2.43	0.11	0.54	0.31	2.51
Na	Cu	Se	Ni	Zn	Mo		
0.08	0.24	0.21	0.15	0.32	0.04		

Recovery potassium, aluminum, copper and selenium

During leaching, K, Al and Fe in the calcine were dissolved along with vanadium into water. In order to avoid the accumulation of Al and K in water circulating system, they were recovered by cooling crystallizing process for precipitating potassium aluminum sulfate, and the optimum cooling temperature was chosen as 10 ℃, based on the whole process requirements.

$$K^+ + Al^{3+} + 2SO_4^{2-} + 12H_2O = KAl(SO_4)_2 \cdot 12H_2O\downarrow \tag{3}$$

In order to recovered Cu and Se, Iron shavings were employed as the reductant. The suitable pretreatment condition was obtained by a series of experiments and the proper condition was: 0.5% iron shavings addition. In reduction process, Cu, Se et al also were employed and precipitated.

$$Fe + Fe^{3+} = 2Fe^{2+} \tag{4}$$

$$Fe + Cu^{2+} = Fe^{2+} + Cu \tag{5}$$

$$2Fe + 6H^+ + SeO_3^{2-} = Se + 2Fe^{2+} + 3H_2O \tag{6}$$

560 g dry precipitate can be obtained per 1 m^3 leach solution is reduced. After drying, the XRF analysis (X-Ray Fluorescence) of the precipitate is shown in Table 4. As can be seen, the main component of the precipitate is copper. The content of oxygen is high, which may be caused by drying process. The grains of the precipitate are fine, which is easy oxidized.

Table 4 XRF analysis of the precipitate, wt%

O	Mg	Al	Si	P	S	Cl	K	Ca
18.8	0.38	3.29	3.90	1.57	1.87	0.18	0.22	1.30
Ti	V	Cr	Mn	Fe	Ni	Cu	As	Se
0.29	0.41	0.75	1.88	2.65	0.016	49.27	4.51	2.6
Zr	Mo	Ag	Pb					
0.05	0.19	0.03	0.49					

Enrichment of vanadium

The concentration of vanadium in leach solution (2.81 g/L) was too low to precipitate red vanadium. Therefore, it was necessary to enrich the vanadium. According to the literature and our former work [8], 10 vol% P204 (D2EHPA), 5 vol% TBP (tributyl phosphate) and 85 vol% sulfonated kerosene were chosen as organic phase of solvent extraction. During the extraction, P204 (D2EHPA) reaction with vanadium can be expressed as follows:

$$VO^{2+} + 2\,(HR_2PO_4)_{(o)} \rightarrow VO\cdot(R_2PO_4)_{2(o)} + 2H^{2+} \tag{7}$$

Where R is C_8H_{17}. The optimum operating condition for the extraction was: pH 2.0 with the addition of potassium carbonate, O/A ratio 1.5:1, ambient temperature and extraction time 7 min. The extraction of vanadium was 98.92% by eight counter-current extraction stages using the optimum conditions.

1.5 mol/L H_2SO_4 solutions was used as stripping agent, and the optimum operating condition for stripping was: O/A ratio 2:1, stripping time 5min, flow ratio 10:1, ambient temperature. The stripping yield of vanadium was above 99.14% by five countercurrent stripping stages. The reaction of stripping between the P204 (D2EHPA) and the vanadium ions is shown as follows:

$$VO\cdot(R_2PO_4)_{2(o)} + H_2SO_4 \rightarrow 2\,(HR_2PO_4)_{(o)} + VOSO_4 \tag{8}$$

Production of V_2O_5

After stripping, the enriched vanadium solution was oxidized by 200g/L $NaClO_3$ solution at 50-60 ℃ for 1 h. After that, red vanadium was precipitated with the addition of 4 mol/l NaOH solutions at 90℃ for 3h and the end pH was 1-2. In order to removal the effect of sodium, the red vanadium was rinsed with the mixed solution of Ammonium chloride and ammonia [9]. After roasting the rinsed red vanadium at 530 ℃ for 3 h, the purity of V_2O_5 was 99.2%, meeting the standard specification.

Conclusions

It is proved from the experiments that it is an effective technique to recover vanadium from stone by sulphation roasting, water leaching, solvent extraction enrichment vanadium, precipitation of vanadium and calcinations. After sulphation roasting the generating electricity product at 140 ℃ for 3 h with 20wt% sulfuric acid addition, vanadium in which can be leached with water at room temperature and the vanadium leaching percentage reached 78.3%. The technology can extract vanadium from the stone coal, in which the content of V_2O_5 was less than 0.8%. In addition, K, Al , Cu and Se in stone coal can also be recovered.

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