

EFFICIENT EXTRACTING VANADIUM FROM STONE COAL BY CO-ROASTING WITH SODIUM CHLORIDE AND BIOMASS

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In this paper, biomass was selected to replace coal as additives during vanadium extraction. Roasting experiments were performed to characterize the effects of biomass on extracting vanadium of stone coal. The results indicated that kalium in biomass catalyzed the formation of potash feldspar but inhibited the generation of insoluble anorthite selectively, and effectively improved the vanadium leaching rate. The optimal roasting conditions were determined when 30 % biomass was added into stone coal, roasting at about 820 °C for 2 hours with 6 % sodium chloride. Under the optimal condition the vanadium leaching rate was 44,6 %.

Key words: vanadium, extraction, stone coal, biomass, sodium roasting

INTRODUCTION

Stone coal is an important vanadium resource, accounting for more than 87 % of Chinese vanadium storage [1]. Therefore, much attentions were recently focused on efficient extracting vanadium from stone coal [2]. Vanadium generally was known in the state of $V(III)$ (trivalent vanadium) and $V(IV)$ (quadrivalent vanadium) and embedded in the crystal lattice of the aluminosilicate minerals in stone coal. Hence, vanadium was difficultly extracted from stone coal [3,4].

High sodium chloride roasting-water leaching technique was the earliest technique and widely adopted by small-scale factories in chinese [5]. However, a quantity of harmful gases made up of HCl and Cl_2 in the roasting process of sodium chloride also cause environmental pollution and ultra-high salinity wastewater. Thus, it is of essential to develop a new roasting technology to increase the vanadium leaching rate and decrease the dosage of sodium chloride.

MATERIALS AND METHODS

The stone coal as raw materials was collected from Hubei province in China. The sample of milled stone coal was preroasted to remove organic carbon for 45 minutes at 700 °C. The ash was grinded to less than 0,15 mm in size. Anthracite and sawdust were milled to less than 0,18mm and then dried for 24 hours at 70 °C and 105 °C, respectively. The particle size of the sodium chloride was less than 0,15 mm. Table1, 2 show the proximate and ultimate analyses of the two auxiliary fuels and the stone coal.

Table1 Proximate analyses of tested samples

Samples	M_{ad}	A_d	V_{daf}	FC_{daf}
Stone coal	0,53	63,72	6,21	29,54
Anthracite	1,31	2,52	7,03	89,14
Sawdust	5,19	0,71	83,23	16,77

Table 2 Ultimate analyses of tested samples

Samples	C	H	N	$S_{t,d}$	O*
Stone coal	29,20	0,38	3,13	0,01	2,83
Anthracite	93,77	3,72	0,73	0,21	1,57
Sawdust	46,63	8,10	0,11	0,08	45,08

^aad= air dried basis, d= dry basis, daf= dry and ash free. * Calculated by difference.

The stone coal ash was mixed with a given amount of the auxiliary fuel and sodium chloride. The oxidation roasts was carried out in an electrothermal furnace. The heating rate was at 8 °C/min. The samples were roasted in high-temperature resistance furnaces for 2 hours. The oxygen flow rate was 0,5 L/min. For measuring $V(V)$ of the aqueous solution, method of redox potentiometric titration was based on this paper [7]. Standard solution of $(NH_4)_2SO_4$ was adopted for redox titration.

RESULTS AND DISCUSSION

Effects of biomass on the roasting of stone coal

The mixture of stone coal and anthracite was 95/5. While the ratios of stone coal and sawdust were 90/10, 80/20, 70/30 and 60/40 as samples. Each sample weight was 10 g. The results of the vanadium extraction from the stone coal by the water leach were given in Figure1. It was noted that the vanadium leaching rate increased remarkably with the raising of temperature and obtained its maximum at around 820 °C for biomass, roughly

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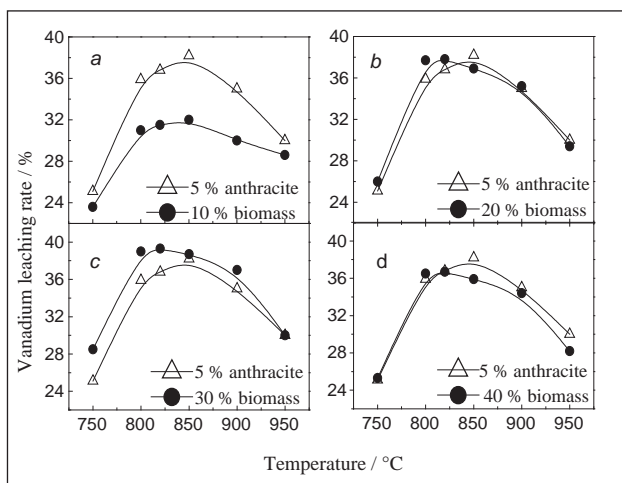


Figure 1 Variation of vanadium leaching rate with different proportions of biomass in different temperature

30 °C lower than the optimum roasting temperature required for 5 % anthracite sample (Figure 1 - b, Figure 1 - c, Figure 1 - d). And 30 % biomass tended to be the most effective proportion.

The results determined that a proper amount of biomass not only played a role in providing heat, but also reduced the optimal roasting temperature of stone coal. The difference might depend on the lower burning of the biomass. A plurality of combustible gas produced by roasting biomass was provided for the oxidation of the organic and pyrite in stone coal within a short time, promoting the sufficient reaction of the stone coal. Meanwhile, the heat transfer from biomass to stone coal by point-to-point contact accelerated the oxidation reaction of the organic and pyrite without affecting the oxidizing atmosphere required for vanadium oxidation.

Thermogravimetric(TG)-Differential Scanning Calorimetric(DSC) analysis

Figure 2 shows that there were two mass loss stages for stone coal. The first stage (600 °C – 740 °C) was 22,7 %. The calorific requirement was mainly used for the removal of structural water and the oxidation of the

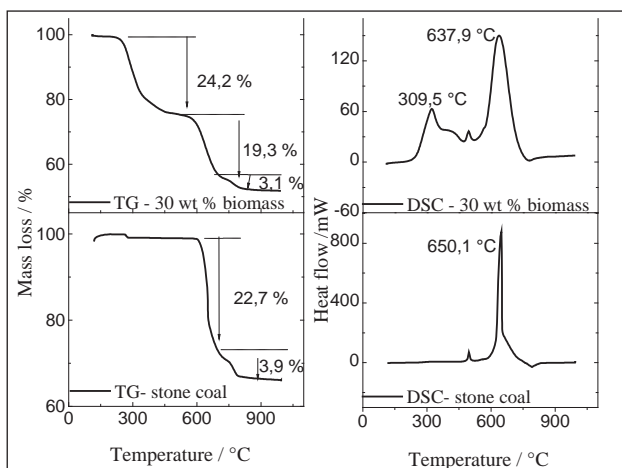


Figure 2 TG and DSC profiles of stone coal and stone coal mixed with 30 % biomass at 10 °C/min

organic matter in stone coal. The second stage (740 °C – 810 °C) was 3,9 %. The calorific requirement was attributed to the removal of hydroxide from silicate minerals and the decomposition of calcite [6].

The stone coal mixed with 30 % biomass presented three mass loss stages. The first stage (110 °C – 460 °C) was 24,2 %. The calorific requirement was mainly due to the removal of structural water and the oxidation of the organic matters in biomass. The second stage (550 °C – 720 °C) was 19,3 %. The calorific requirement was mainly due to the oxidation of the organic matter in the stone coal, the oxidation of pyrite into ferric oxide. The third stage (720 °C – 830 °C) was 3,1 %. The calorific requirement was mainly due to the removal of hydroxide from silicate minerals and the decomposition of calcite.

It is found that the exothermic reactions of organic matter and pyrite in stone coal began at 600 °C for the stone coal sample, while 550 °C for the 30 % biomass sample. Hydroxide was eliminated from silicate minerals and calcite was decomposed in stone coal, leading to the second mass loss stage of the stone coal sample and the third mass loss stage of the 30 % biomass sample, and the reaction temperature was advanced about 20 °C for the latter sample. Thus, biomass is effective in reducing reaction temperature and shortening reaction time for the roasting of stone coal.

Effects of biomass on sodium chloride roasting of stone coal

Figure 3 illustrates the vanadium leaching rates for the stone coal added with 30 % biomass and 5 % anthracite under the same proportion of sodium chloride. Samples were roasted at 820 °C for 2 hours. As can be observed, the vanadium leaching rate increased with the ratio of sodium chloride raising and then reached plateaus at around 8 % sodium chloride for the sample of stone coal mixed with 5 % anthracite. The result is consistent with the conclusion of the literature [6]. At the same content of sodium chloride, the samples of 30 % biomass resulted in obviously higher vanadium leaching rate in comparison with the samples of 5 % . In terms

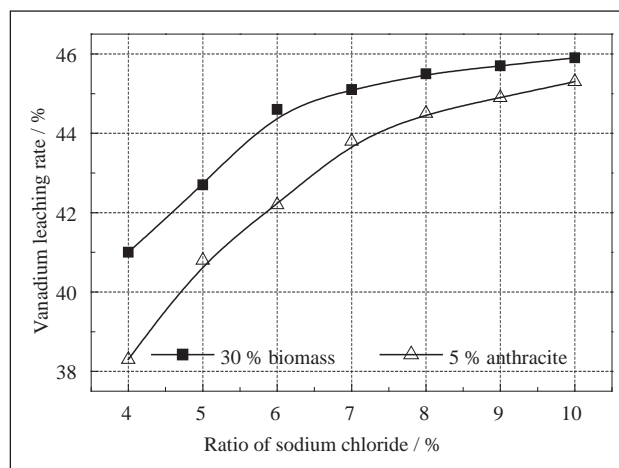


Figure 3 Variations of vanadium leaching rate with different ratios of sodium chloride at 820 °C for 2 hours

of reaching the possibly highest leaching rate, the optimal sodium chloride amount was about at 6 % for the 30 % biomass but 8 % for the anthracite.

X-ray diffraction (XRD)

Figure 4 presents the XRD analyses for raw stone coal and the roasting residue with or without biomass. There are mainly four crystalline mineral phases, quartz, pyrite, calcite and mica in the raw stone coal (Figure 4(a)). Compared with XRD patterns of raw stone coal, after roasted at 820 °C for 2 hours (without biomass), the peak intensities of pyrite, calcite and mica had obvious changes (Figure 4(c)), indicating that the roasting had destroyed the crystal lattice structure of such mineral phases. Nonetheless, the peak intensity of anorthite much increased. The raw stone coal mixed with biomass and sodium chloride greatly varied the XRD patterns and intensities of the minerals in stone coal (Figure 4(b)). The peak intensities of anorthite sharply decreased and even unable to detect. Meanwhile, a new mineral phase of potash feldspar was formed sharply increased.

X-ray fluorescence (XRF)

To investigate the reason biomass decreases the usage of sodium chloride and improves the vanadium leaching rate, we roasted biomass separately under the same condition, and analyzed the roasted samples.

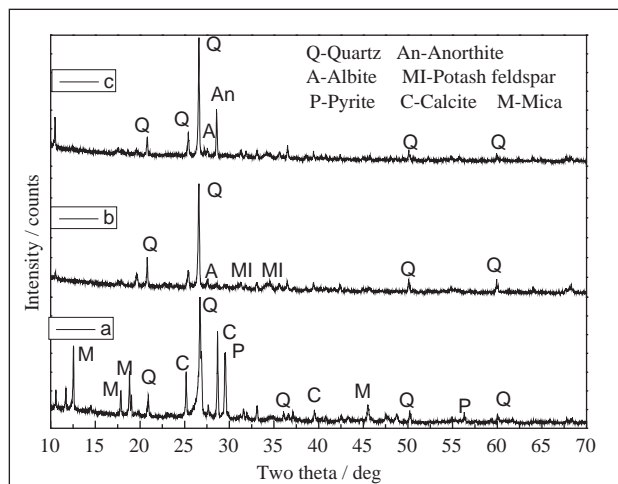
Literature[6] revealed that CaO, a decomposed product of the high-content calcite in stone coal, reacted with Al_2O_3 , SiO_2 and V_2O_5 generating anorthite and $Ca(VO_3)_2$. The water leaching rate of V was lowered since the $Ca(VO_3)_2$ is insoluble in water. However, the addition of biomass improved this problem. We found that the roasted biomass ash contained 28,36 % K_2O (Table3) which participated in reaction and generated potash feldspar, inhibited the formation of anorthite, promoted the generation of water-soluble KVO_3 , thus effectively improved the vanadium leaching rate.

Table 3 XRF results of sawdust ash /%

Component	K_2O	CaO	MgO	SiO_2
Content /%	28,36	21,04	10,63	10,20
Component	P_2O_5	Na_2O	Al_2O_3	Fe_2O_3
Content /%	8,64	4,86	2,36	1,81

CONCLUSION

This study investigated the effects of biomass on stone coal roasting process. The results showed that biomass not only increased the vanadium leaching rate but also reduced the necessarily required amount of additive and the roasting temperature. The optimal condi-



(a) raw stone coal, (b) roasting with 30 % and 6 % additives at 820 °C for 2 hours, (c) roasting with 5 % anthracite and 6 % additives at 820 °C for 2 hours.

Figure 4 XRD spectra of different samples

tions were shown to be adding 30 % biomass into stone coal, roasting at about 820 °C for about 2 hours and with 6 % sodium chloride as additive. Under these conditions the available vanadium leaching rate reached 44,6 %. In contrast to other date, roughly 2 % sodium chloride was reduced. The factor reducing the usage of sodium chloride is the large amount of K_2O produced by roasting biomass (sawdust). The K_2O of biomass ash promoted the generation of water-soluble KVO_3 and inhibited the generation of anorthite.

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Note: The responsible for English language is the Lector from University, LiaoNing, China.