Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 52 (4) 249-253, 2010

FLOAT-SINK DESULFURIZATION OF HIGH-SULPHUR COAL FROM PUAN COUNTY, GUIZHOU PROVINCE, PRC

Tian Yingzhong[1,2], *Zhang Qin*[1,2*], *Tang Yun*[1,2,3] *Qiu Yueqin*[1.2.3] Liu Zhihong [1.2.3] *He Tin*[1.2], *Zhao Peiliang*[1,2] *Huang Xiaofen* [1,2], *Shi Ren* [1,2]
Tiancun XIAO [3, 4*]

[1] Mining and Mineral College of Guizhou University, Guiyang, Guizhou, PRC. 550003;[2]Key Laboratory of Comprehensive Utilization of Nonmetal Mineral Resources, Guiyang, Guizhou, PRC. 550003, 3.CSCST-Guizhou Clean Energy Centre, Guizhou University, Caijiaguan Campus, Guiyang City, 550003, Guizhou, China
[4]Inorganic Chemistry Laboratory, Oxford University, South Parks Road, OX1 3QR, UK, Email: xiao.tiancun@chem.ox.ac.uk

Received July 14, 2010, Accepted October 15, 2010

Abstract

Guizhou Province has very big coal reserves, which has middle to high sulphur content. It is of significance to study the feasibility of the desulphurization of high sulphur coal through float-and-sink test . Our washability study results showed that when using the media density below 1.5 g/cm^3 to float the coal, the total sulphur can be reduced to 1.53%, with coal recovery of 83.80%, the desulphurization ratio is up to 39.89%.

Key words: middle-high-sulphur coal; float-and-sink test; desulphurization.

1. Introduction

Guizhou Province is abundant in coal reserves. The proved minable coal reserve is 49,830,170,000 tons and forecast reserves (reliable level) 86.4 billion tons [1, 2]. The increasing coal mining leads to continuing deteriorating of coal quality. Thus, there needs an urgent solution to coal desulphurization thanks to the fact that most of coal in Guizhou province is of middle and high sulphur coal. The sulphur in coal can be divided into organic sulphur and inorganic sulphur, while inorganic sulphur has two sulphur forms: sulfate sulphur and sulphide sulphur. The main form of mineral in sulfate sulphur is gypsum, while the main form of mineral in sulfide is pyrite. Physical desulphurization mainly removes sulfide, namely pyrite. It has shown that physical desulphurization can remove up to 80% pyritic sulphur in form of inorganic sulphur in coal [3-5]. Mostly organic sulphur can be removed by chemical desulphurization and biodesulphurization. Physical desulphurization method is not efficient enough to remove sulfate sulphur in organic sulphur and inorganic sulphur, but it is widely used because of its simple processing, lower cost and more economical than chemical desulphurization [4, 6, 7].

Guizhou Province has the biggest coal reserve in South China, it is therefore a power base to transport electricity to East China. However, the coal in Guizhou has high ash content of ash and sulphur. The new national regulations require the coal must have less than 2wt% of sulphur for using as fuel for power generation [8-10]. This paper mainly deals with sieve and sink-float experiment, followed by the analysis on the result. Based on the analysis, the feasibility of high sulphur coal desulphurization has been studied.

2. Raw coal analysis

2.1 Proximate analysis of raw coal

It can be seen from table 1 that the water content of coal sample is 3.00%, ash content 9.03 %, volatile material 11.73%, fixed carbon 76.24% and calorific capacity 31.87 MJ/Kg. According to the data, the raw coal is of low ash coal type; the volatile material is 11.73%, which is meager coal, with higher content of fixed carbon. Therefore, to maximize resource utilization efficiency, recycling and comprehensive utilization of carbon should be taken into consideration. The calorific capacity of this coal is 31.87 MJ/Kg, a special high heat value coal.

Table 1 Proximate analysis of coal sample

	Mad/%	Aad/%	Vad/%	FCad /%	Qgr , ad MJ/Kg
Raw Coal Sample	3.00	9.03	11.73	76.24	31.87

2.2 Analysis of sulphur status in the raw coal

Table 1 shows that the ash content of raw coal sample is low, with high calorific capacity, but relatively high content of sulphur. It is necessary to analyze the mode of occurrence of sulphur; the result is shown in Table 2.

Table 2 Sulphur status analysis

Sulphur Forms	Content/%	Distribution Ratio /%
Organic sulphur	0.95	32.34
Sulphate sulphur	0.06	1.94
Sulphide sulphur (mineral)	1.94	65.72
Total sulphur	2.95	100.00

According to Table 2, the total sulphur content in the raw coal is 2.95%, suggesting that this coal could be classified as middle to high sulphur coals. The organic and sulfate sulphur contents are 0.95% and 0.06 % respectively, which in all accounts for 34.82% of the total sulphur content. It is well known that the organic sulphur and sulfate sulphur can’t be processed by gravity separation. Therefore, it’s difficult to deep removal the sulphur for these coal samples.

The content of sulphide sulphur in the coal sample is 1.94%, accounting for 65.72% of the total sulphur in the sample. The sulfide sulphur is normally bond to mineral namely sulphur pyrite, which can be removed using gravity separation. The physical desulphurization can remove 80% pyritic sulphur in form of inorganic sulphur in coal [2]. As a result, it is possible to reduce the total sulphur to 1.5% by physical methods in this coal sample

2.3 The composition of the raw coal sample

The coal was analyzed using CHNSO method, and the results are given in Table 3.

Table 3 The composition of the coal sample

	Cdaf/ %	Hdaf/ %	Ndaf/ %	Odaf/ %	Sdaf/ %
Raw coal sample	92.00	3.28	1.26	0.51	2.95

It can be seen in Table 3, the C of raw coal is 92%, H 3.28%, N 1.26%, O 0.51%, and S 2.95%. Those suggest that the raw coal is mature coal, high coalification rank. The "Coal Chemistry", edited by Shuang-Quan Zhang [5], illustrates that the basic structural units of low coalification rank coal are mainly of benzene, naphthalene and phenanthrene ring; middle coalification rank bituminous coal are mainly of phenanthrene, anthracene and the pyridine ring; the basic structural units of high coalification rank coal, whose aromatic of the basic structural nucleus increases rapidly, and gradually change into graphite. Therefore, it is desirable to further study the degree of graphitization of the coal so as to find a better value of the coal.

3. Experimental results and analysis

3.1 Screening test

Based on national standards of sampling and GB/T 478—2008 [9], a specific amount of coal sample has been collected, screening the raw coal into 6 fraction size, which are 50mm ~ 25mm, 25mm ~ 13mm, 13mm ~ 6mm, 6mm ~ 3 mm, 3mm ~ 0.5mm, 0.5 mm ~ 0mm, the results of coal screening are shown in Table 4.

Table 4 Coal screening results

Size /mm	Weight /%	Weight of Oversize/%	Ad/%	Sulphur /%	ε(s)/%
50～25	44.91	44.91	9.82	3.32	50.83
25～13	23.23	68.14	8.66	2.93	23.16
13～6	13.47	81.61	8.40	2.43	11.17
6～3	7.64	89.25	7.36	2.19	5.69
3～0.5	8.03	97.28	8.54	2.54	6.96
0.5～0	2.72	100.00	13.67	2.37	2.20
In Summary	100.00		9.17	2.94	100.00

According to Table 4, 50mm~25 mm ranged size sample accounts for the most proportion of the sample, which is 44.91%; the one with size range of 25 mm~13mm accounts for a fair proportion of the sample, which is 23.23%; and the one with size range of 13 mm~6mm for 13.47%; while the rest three sized accounts for less than 10 % of the entire sample account.

The ash content of each size ranged sample is not different significantly. The ash content in the sample with size range of 0.5 mm ~0 mm is the highest, 13.67%, because of its high sediment percentage. The ash content of in the coal sized range of 50mm~25 mm is 9.82%, while the ash content of the sample with size range of 6 mm~3 mm is 7.36%, which is lowest. The rest sample portions with different size range are close to each other. For the whole fraction, the trend changes are that with fraction size increasing, the ash content decreases first and then increases gradually

The sulphur content in the sample with the size range of 50mm~25 mm is the highest, 3.32%; the sulphur in the sample of 25 mm~13mm is close to that in the raw coal, 2.93%; the sample with size range of 13 mm~6mm has sulphur content of 2.43%; the one with size range of 6 mm~3 mm has 2.19% of sulphur, sulphur in the sample with size ranging 3 mm~0.5 mm is 2.54%; and the one in 0.5 mm ~0 mm is 2.37%. The distribution ratio of sulphur shows that the sample with size ranging of 50mm~25 mm has the highest sulphur content, 50.83%; the sample size ranging 25 mm~13mm has sulphur of 23.16%, the one in the size range of 13 mm~6mm is 11.17%, while the rest three fractions of the samples account for less than 10%. Therefore, it's very important to study the desulphurization of large particle size coal.

3.2 Float-and-sink test

Floatation liquid media used in the test is made of zinc chloride aqueous solution. As required in the test, the floatation liquid media is divided into 6 density level, <1.4g/cm^3 、 1.4g/cm^3~1.5g/cm^3 、 1.5g/cm^3~1.6g/cm^3 、 1.6g/cm^3~1.7g/cm^3 、 1.7g/cm^3~1.8g/cm^3、>1.8g/c m^3. Each of the above mentioned coal sized fractions are soaked into the different density level heavy liquid for the float and sink test. The results of the floatation test are discussed as follows.

3.2.1 Float-and-sink test of the coal sample size ranging 50～0.5mm

The float and sink test results of this sized coal are given in Table 5.

Table 5. Float-sink test results of 50mm~ 0.5mm range coal

Density Level / g/cm3	Weight /%	Ad /%	Total sulphur /%	Summary				δ±0.1	
				float		Sink		Density/ g·cm-3	Product Yield /%
				Weight /%	Sulfur /%	Weight /%	Sulphur /%		
<1.4	37.16	4.03	0.93	37.16	0.93	100.00	2.93	1.40	83.80
1.40~1.50	46.64	8.48	2.01	83.80	1.53	62.84	4.12	1.50	55.84
1.50~1.60	9.20	14.92	5.99	92.99	1.97	16.20	10.18	1.60	11.52
1.60~1.70	2.32	19.56	9.54	95.32	2.16	7.01	15.68	1.70	3.69
1.70~1.80	1.37	24.46	11.18	96.69	2.28	4.68	18.72	1.80	4.68
>1.8	3.32	38.74	21.84	100.00	2.93	3.32	21.84		
Subtotal	100.00	8.89	2.93						
Subtotal percent	99.20	8.89	2.93						
Slime	0.80	28.93	2.00						
Summary	100.00	9.05	2.92						

It can be seen from Table 5 that with the increase of floatation media density level, both ash content and sulphur increase, changing in the same trend. In the floatation media density below 1.4 g/cm^3, the ash content and sulphur are 4.03% and 0.93% respectively, both of which are of the lowest. The desulphurization in this floatation media density is the most complete, and the desulphurization rate is up to 25.32%. The coal content with the density of 1.40 g/cm^3~1.50 g/cm^3 is 46.64% in the total coal sample, which is the highest, with the ash content being 8.48%. Sulphur is reduced to 1.53% ,and desulphurization ratio is 14.54%. When coal sample density is greater than 1.6 g/cm^3, the ash content and sulphur in this coal portion are obviously higher than raw coal. When the density is greater than 1.8 g/cm^3, the ash content and sulphur reach the highest, with 38.74% and 21.84% respectively. According to the data in Table 5, the ash content and sulphur goes in the same trend. In the other words, the sulphur increases with the ash content rising, indicating that the sulphur (mainly pyrite) in the coal is accompanied by gangue. This provides theoretical practicability to desulphurization and ash fall.

3.3 Washability curve of sulphur

The main purpose of this study is desulphurization of the coal. Therefore, sulphur washability curve is drawn out of the above research findings, as shown in figure 1.

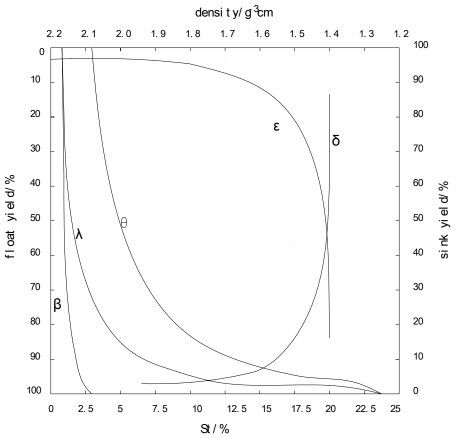

Figure 1 sulphur coal washability curve

It can be seen in Figure 1, when sulphur content is reduced to 1.5%, the clean coal recovery ratio is 83% and δ ± 0.1 content 21.8%, the coal belongs to refractory type. When sulphur content required to be less than 2.0%, the clean coal recovery ratio is up to 93.48% and δ ± 0.1 content 10.85%, the coal belongs to secondary optional, with fairly washability. When sulphur is required to be 2.035%, the clean coal recovery ratio is up to 94.03% and δ ± 0.1 content below 10%, the coal belongs to good wash ability. However, when sulphur requirement is 1.2625%, the clean coal weight is only 75.28% of the total coal sample and δ ± 0.1 content above 30%, the coal belongs to hard floatability.

4. Conclusions

(1) The coal float and sink test shows that with coal portion with density below 1.5 g/cm3 , a favorable desulphurization result can be achieved, with the total sulphur being 1.53%, the coal recovery ratio of 83.80%, and desulphurization rate up to 39.89%

(2) It's easy to find the heterogeneity of sulphur and ash content according to float and sink test.

(3) The desulphurization of coal portion with density below 1.4 g/cm3 is the most complete through floatation. Using the floatation media with density of of 1.40g/cm3 ~ 1.50 g/cm3 , tmost sulphur can be removed from the lightest coal portion (density<1.4). The ash content of coal portion with density below 1.5 g/cm3 is fairly low, and decreasing more significantly with the coal density. Both sulphur and ash content gradually increase in the coal with density of above 1.6 g/cm3.

(4) In the case of float -and -sink slime, the ash content is much higher and sulphur lower than raw coal because of high slime sediment percentage.

In summary, desulphurization and ash reduction can be achieved through float and sink test, therefore it is possible to desulphurize this coal to some extent with fair coal recovery rate.

Acknowledgements

This work was supported by China-UK Clean Energy Research Program. TXiao is grateful for the financial support from the "Chunhui Project", Ministry of Education of China.

Abbreviations

M	moisture (%)
A	ash (%)
MM	mineral matter (%)

Definition of subscripts

Ar	as received basis	Fcad	fixed carbon on air dried basis is:
ad	air dried basis	B	floated fraction profile
d	dry basis	Λ	ash characteristic profile
Mad	moisture on air dried basis.	Θ	the sink fraction profile
Vad	volatiles on air dried basis is:	E	sulphur content profile in the fraction
Aad	ash on air dried basis is:	Δ	density curve

References

[1] Zhu, B.-z., Y.-l. Sun, and C.-w. Xie: Spectroscopy research on the Guizhou Xingyi gangue of different calcined temperatures. Meitan Xuebao, 2008. 33(9): p. 1049-1052.
[2] Zhuang, X., et al.: Mineralogy and geochemistry of coal from the Liupanshui mining district, Guizhou, South China. Inter. J. of Coal Geology, 2000. 45(1): p. 21-37.
[3] Aplan, F.F.: Use of the flotation process for desulfurization of coal. ACS Symp. Ser., 1977. 64(Coal Desulfurization): p. 70-82.
[4] Atkins, A.S., et al.: A study of the suppression of pyritic sulfur in coal froth flotation by Thiobacillus ferrooxidans. Coal Prep. (Gordon & Breach), 1987. 5(1-2): p. 1-13.
[5] Ayhan, F.D., H. Abakay, and A. Saydut: Desulfurization and Deashing of Hazro Coal via a Flotation Method. Energy Fuels, 2005. 19(3): p. 1003-1007.
[6] Kawatra, S.K., T.C. Eisele, and H. Johnson: Recovery of liberated pyrite in coal flotation: entrainment or hydrophobicity, Coal Sci. Technol., 1991. 18(Process. Util. High-Sulfur Coals 4): p. 255-77.
[7] Laskowski, J., et al.: Desulfurizing flotation of eastern Canadian high-sulfur coal. Coal Sci. Technol., 1985. 9(Process. Util. High Sulfur Coals): p. 247-66.
[8] Cai, H., M. Du, and S. Wang: Floating and sinking tests for sieving high sulfur coal. Meitan Zhuanhua, 2007. 30(1): p. 57-59, 77.
[9] Cai, H. and M.-l. Du, Density Separation of Chinese High Sulfur Coal with Different Intervals of Particle Size. Sekitan Kagaku Kaigi Happyo Ronbunshu, 2006. 43rd: p. 21-22.
[10] Fan, W. and Y. Zhang: Chinese coal industry - gearing up for the 21st century. Journal of Mines, Metals and Fuels, 1997. 45(11&12): p. 321-325.