Effect of Ammonium Salt on the Adsorption Behavior and Surface Characteristics of Sub-Bituminous Coal and Silica

Yonggai Li,* Qingmin Nie, Jianzhong Chen,† Lijuan Shen, and Jiawei Li

Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China

ABSTRACT: Ammonium salt is a common collector in coal reverse flotation. This study compared the difference of adsorption behavior on ammonium salt Lilaflot D817M between sub-bituminous coal and silica as well as the surface characteristic change after being processed by ammonium salt. The results indicate that the adsorption capacity of sub-bituminous coal is always higher than that of silica under different experimental conditions, such as different initial concentrations of ammonium salt, different adsorption times, different concentrations of the depressant dextrin, and different pH values. Ammonium salt could increase the isoelectric point of both silica and sub-bituminous coal greatly. However, the hydrophobicity of silica enhances much more significantly than that of sub-bituminous coal after being treated by Lilaflot D817M. This indicates that the surface wettability change degrees of sub-bituminous coal and silica after being treated by ammonium salt are not proportional to the adsorption capacity because of their different surface structures. The reverse flotation test result shows that 2 kg/t Lilaflot D817M dosage could help obtain relatively good flotation indexes.

1. INTRODUCTION

There are many different kinds of gangue minerals in raw coal, and the character of gangue minerals determines the choice of the collector in coal reverse flotation.1,2 Research shows that the main gangue minerals in coal are silica and clay minerals, such as kaolinite.2,3 Fuerstenau found that the isoelectric point of silica is between pH 1.3 and 3.7, indicating that the silica surface presents electronegativity when the solution pH is larger than its isoelectric point.3 Therefore, it is much easier for silica to adsorb cationic reagents, such as amines and ammonium salts, which have been applied in silica flotation successfully.4–11 Similarly, when pH is higher than the isoelectric point of kaolinite, amines or ammonium salts could also perform well in kaolinite flotation.12–16 Amine is one common cationic collector derived from ammonia after the hydrogen atom is replaced by aryl or alkyl.1 The most common cationic collector is a long-chain ammonium salt, such as laurylamine hydrochloride.1 Besides, the collecting behavior of the ammonium salt is to break the hydration layer of minerals by adsorbing on the negative ends of minerals with the positive ends, leading continuous unidirectional hydrocarbon chains to be distributed in aqueous solution and making the mineral surface become hydrophobic.1,2

Reverse flotation method has been widely used in the separation of metal minerals or nonmetal minerals, such as iron ore, bauxite, phosphate, etc.5–8 Also, it is also one feasible method to separate difficult-to-flot coal, such as low-rank coal or oxidized coal when ammonium salt is used as a collector.16–23 The previous research shows that the oxygen-containing functional groups on the surface of the low-rank coal or oxidized coal could make its surface present electronegativity and adsorb cationic ammonium salt in the solution under certain conditions.17,19,21,23 Thus, during coal reverse flotation, ammonium salt would be consumed both by coal and gangue minerals.17,21,23 Therefore, it is very necessary to study and compare the action difference of ammonium salt on coal and gangue minerals. In this research, sub-bituminous coal and silica were used to represent low-rank coal and one kind of gangue mineral in a coal sample, respectively. The difference of adsorption behavior of ammonium salt on sub-bituminous coal and silica as well as the surface characteristic change after being processed by ammonium salt were explored and explained. The research result would provide a certain theoretical direction for coal reverse flotation.

2. RESULTS AND DISCUSSION

2.1. Results of Scanning Electron Microscope Analysis. A field emission scanning electron microscope (HITACHITM, S-4300) was used to analyze the morphology and microstructure of sub-bituminous coal and silica. Figure 1 shows the form and microstructure of sub-bituminous coal under a scanning electron microscope. It can be known from the picture that the surface of this sub-bituminous coal sample is rough containing some cracks and pores, which could result in high porosity and specific surface area.24–26 The scanning electron microscope image of silica in Figure 2 indicates that the surface of silica is very smooth and there are no pores. The existence of the pores on the surface of sub-bituminous coal
and the high specific surface area would cause more adsorption of reagents.

2.2. Results of the Adsorption Test. During the adsorption test, both of the sub-bituminous coal and silica were the whole size range samples. The adsorption formula of sub-bituminous coal and silica on ammonium salt is as follows

$$q_c = \frac{(C_0 - C_c) \times V}{m}$$

(1)

where $q_c$ is the equilibrium adsorption capacity (mg/g), $C_0$ is the initial concentration of ammonium salt (mg/L), $C_c$ is the equilibrium concentration (mg/L), $V$ is the volume of the solution (L), and $m$ is the sample quality (g).

2.2.1. Standard Curve of Ammonium Salt Solution. The relationship between the total nitrogen content and the concentration of ammonium salt Lilaflot D817M solution could be obtained through measuring the total nitrogen content in ammonium salt solution with different concen-
trations, and the result is plotted in Figure 3. The standard curve of Lilaflot D817M is as follows

\[ y = 0.0752x + 0.2175 \]

where the correlation coefficient \( R^2 \) is 0.9996. The effective concentration range of ammonium salt is 10–300 mg/L.

2.2.2. Adsorption Properties under Different Initial Ammonium Salt Concentrations. The adsorption properties of ammonium salt on sub-bituminous coal and silica under different initial concentrations are illustrated in Figure 4. It can be seen that the adsorption capacity of sub-bituminous coal increases with the increase of the initial concentration of Lilaflot D817M. When the concentration of Lilaflot D817M is higher than 180 mg/L, the adsorption speed of silica decreases gradually and the equilibrium adsorption quantity (8.71 mg/g) reaches 200 mg/L. The adsorption capacity of ammonium salt on sub-bituminous coal under different initial concentrations is always higher than that on silica.

2.2.3. Adsorption Properties under Different Adsorption Times. The concentration of ammonium salt Lilaflot D817M was set at 180 mg/L, and the relationship between adsorption time and adsorption quantity was explored. It can be seen in Figure 5 that the adsorption speed of ammonium salt on sub-bituminous coal is faster relatively in the beginning 60 min. It is because that the concentration of ammonium salt is higher relatively at the beginning and the quantity of the adsorption active sites is larger. Later, the adsorption of ammonium salt on sub-bituminous coal decreases gradually and reaches equilibrium at about 90 min. The equilibrium adsorption capacity is 17.19 mg/g. The adsorption of ammonium salt on silica reaches equilibrium after 60 min, and the equilibrium adsorption capacity is 8.61 mg/g. Comparing the adsorption equilibrium curves of sub-bituminous coal and silica, we can see that the adsorption speed of ammonium salt on sub-bituminous coal is always higher than that on silica in the beginning 60 min. Also, during the whole process, the adsorption quantity of ammonium salt on sub-bituminous coal is also higher than that on silica. It might be because of the surface structure difference between sub-bituminous coal and silica.

2.2.4. Adsorption Properties under Different Dextrin Concentrations. During the process of coal reverse flotation, a depressant is usually added into the pulp before a collector after conditioning. Dextrin is one common depressant in coal reverse flotation. To explore the effect of depressant addition on the collector adsorption of minerals, the adsorption properties of Lilaflot D817M on the sub-bituminous coal and silica surfaces under different dextrin concentrations were explored. The result is reported in Figure 6. With the increase of dextrin concentration, the adsorption quantities of Lilaflot D817M on sub-bituminous coal and silica...
both decrease gradually, indicating that the existence of dextrin could depress the adsorption of Lilaflot D817M on both sub-bituminous coal and silica. As the goal minerals in coal reverse flotation are gangue minerals like silica, kaolinite, etc., excessive dextrin might deteriorate the collection of gangue minerals. Even with the addition of dextrin, the adsorption quantity of ammonium salt on sub-bituminous coal is still always higher than that on silica.

2.2.5. Adsorption Properties under Different pH Values.

The adsorption of ammonium salt on minerals could be influenced by solution chemistry in the pulp. Figure 7 shows the adsorption properties of Lilaflot D817M on sub-bituminous coal and silica under different pH values. Lilaflot D817M on the surface ζ-potential of silica. Within the whole tested pH range, the surface of silica always presents electronegativity and the isoelectric point of silica is at about pH 2. The isoelectric point of silica increases to pH 10.5 after being processed in 0.057 g/L Lilaflot D817M solution because of electrostatic adsorption, leading the surface electric potential to change from negative to positive. This indicates that Lilaflot D817M could affect the surface potential of silica significantly.

The ζ-potential of sub-bituminous coal after being treated by ammonium salt solution under different pH values is shown in Figure 9. It can be seen that the isoelectric point of sub-bituminous coal changes from about pH 3 to pH 9.8 after being processed in 0.057 g/L Lilaflot D817M solution. The surface positivity of sub-bituminous coal after being processed enhances when pH is lower than 3. Besides, it changes from negative to positive when the pH value is between 3 and 9.8. It turns out that Lilaflot D817M could also change the surface potential of sub-bituminous coal greatly by adsorbing on the negatively charged sites provided by the oxygen-containing functional groups, such as −OH, −COOH, etc. through electrostatic interaction.27

2.3. Influence of Ammonium Salt on the Surface Properties of Sub-Bituminous Coal and Silica. 2.3.1. ζ-Potential. Figure 8 illustrates the effect of ammonium salt
coal after adsorbing ammonium salt is 0.007 g^2/s when deionized water is used as the wetting liquid, which is lower than that before adsorption (0.009 g^2/s). We can see in Figure 11 that when the wetting liquid is changed to n-hexane the wetting rate of sub-bituminous coal after being treated by Lilafot D817M is 0.0035 g^2/s, which is higher than that before adsorbing ammonium salt (0.003 g^2/s). This indicates that the hydrophobicity of sub-bituminous coal after adsorbing ammonium salt enhances slightly.

Figures 12 and 13 show the wetting curves of silica before and after being treated by Lilafot D817M with deionized water and n-hexane, respectively. It could be seen in Figure 12 that the wetting rate of silica after adsorbing ammonium salt is 4 × 10^{-6} g^2/s when the wetting liquid is deionized water, which is much lower than that before adsorption (0.0045 g^2/s). When n-hexane is used as the wetting liquid, shown in Figure 13, the wetting rate of silica after adsorbing Lilafot D817M is 0.007 g^2/s, which is much higher than that before adsorbing ammonium salt (0.0021 g^2/s). This indicates that the hydrophobicity of silica after adsorbing ammonium salt improves significantly.

The wetting rate change results of sub-bituminous coal and silica before and after adsorbing Lilafot D817M are shown in Table 1. These illustrate that the wetting rate change degree of silica is larger than that of sub-bituminous coal after adsorbing Lilafot D817M, meaning that the surface of silica could become more hydrophobic than that of sub-bituminous coal after being processed by Lilafot D817M. This is consistent with the contact angle results in the previous research of minerals after adsorbing ammonium salt.21 This phenomenon is advantageous for coal reverse flotation. However, the surface wettability change degrees of sub-bituminous coal and silica after being treated by ammonium salt are not proportional to their adsorption quantity shown in the above study, which is consistent with the research of Pawlik et al.23 This might be because the surface of sub-bituminous coal is heterogeneous, which could lead both the hydrophobic and the polar groups of the ammonium salt to orient toward the solution and induce a lower hydrophobicity.28,29 Also, the high specific surface area hydrophobicity of silica after adsorbing ammonium salt improves significantly.

Figures 9, 10, 11, 12, and 13 show the wetting curves of silica before and after being treated by Lilafot D817M with deionized water and n-hexane, respectively.
caused by the cracks and pores on the surface of sub-bituminous coal might be also one reason for high adsorption of ammonium salt.

2.4. Results of the Reverse Flotation Test. Reverse flotation using ammonium salt Lilafot D817M as a collector was conducted. The flotation feed was prepared by mixing sub-bituminous coal and silica with the ratio of 7:3. The flotation process and the index calculation were performed referring to the previous research. The effect of collector dosage on reverse flotation performance is illustrated in Figure 14. When the collector dosage changes from 1 to 4 kg/t, the ash content of concentrates decreases gradually as more silica is mineralized and collected into the froth product. However, the combustible recovery in concentrates decreases with the increase of collector dosage. This might be because the excessive collector in the pulp could be adsorbed by sub-bituminous coal. The separation efficiency of reverse flotation decreases from 83 to 68.94% when the collector dosage changes from 1 to 2 kg/t and then it does not fluctuate much with more collector dosage. This indicates that 2 kg/t collector is appropriate in this coal reverse flotation to obtain relatively good flotation indexes.

3. CONCLUSIONS

(1) The adsorption quantity of sub-bituminous coal on ammonium salt Lilafot D817M is always higher than that of silica under different conditions.

(2) Lilafot D817M could change the surface ζ-potential of both sub-bituminous coal and silica from negative to positive through electrostatic adsorption.

(3) The surface of silica becomes more hydrophobic than that of sub-bituminous coal after being treated by Lilafot D817M.

(4) The surface wettability change degrees of sub-bituminous coal and silica after being treated by ammonium salt are not proportional to their adsorption quantities, which might be because of the different surface structures.

(5) 2 kg/t collector is appropriate in coal reverse flotation to obtain relatively good flotation indexes.

4. MATERIALS AND METHODS

4.1. Experimental Materials. The sub-bituminous coal sample used in this research was collected from the Powder River coal basin. The particle size composition of the representative sample after being crushed by a hammer mill is shown in Table 2. The proximate analysis of this sub-bituminous coal is as follows: Mad, 27.72%; Aad, 8.81%; Vad, 46.62%; FCad, 16.85%; and SAd, 0.72%. The particle size distribution of the silica (c-778, purchased from eBay) sample with purity 98.8% is as follows: 10%, 1.53 μm; 50%, 7.24 μm; 90%, 26.71 μm; mean size, 10.87 μm. Dextrin (Fisher Scientific) was used as the depressant in coal reverse flotation. The ammonium salt Lilafot D817M (AKZO NOBEL), was used in this study. The chemical composition of Lilafot D817M was shown in Table 3. Besides, the proximate analysis of Lilafot D817M was shown in Table 3.

Table 2. Particle Size Distribution of Sub-Bituminous Coal

| particle size/μm | yield/% | ash dry/% |
|------------------|--------|-----------|
| 150–200          | 15.71  | 6.42      |
| 120–150          | 12.92  | 6.96      |
| 74–120           | 15.3   | 7.05      |
| 53–74            | 10.52  | 7.3       |
| 38–53            | 3.51   | 8.7       |
| <38              | 42.04  | 11.3      |
| total            | 100.00 | 8.81      |
solution and dextrin solution were both used as a 1% solution made by diluting 1 g of as-received reagents to 100 mL with distilled water.

### 4.3. Experimental Methods

#### 4.3.1. Adsorption Test

Ammonium salt solution (1%) was diluted to 10–500 mg/L. A total of 20 mL of the diluent was taken into the total organic carbon (TOC) test tube. The linear relation curve between the concentration of ammonium salt solution and the nitrogen content, which would be taken as a standard curve, was obtained by measuring the total nitrogen content in different concentrations of ammonium salt solutions using a TOC analyzer. The adsorption quantity of ammonium salt on the sample was obtained by calculating the difference of the total nitrogen content in ammonium salt solution before and after being adsorbed by samples.

The process steps were as follows: First, 1 g of sub-bituminous coal or the silica sample was put into a beaker containing 100 mL of ammonium salt solution under different concentrations. The sample was agitated and wetted sufficiently using a glass bar. Next, the beaker was put on a magnetic stirrer with a medium speed for 5 min to disperse the sample sufficiently. When it reached the adsorption equilibrium after 3 h standing, the pulp was poured into a pressure filter to obtain the filtrate. Then, 20 mL of the filtrate was taken into a test tube and the content of total nitrogen was measured using a TOC analyzer. Last, the test result was compared with the standard curve and the value of the difference was calculated, which is the adsorbing quantity of the sample.

#### 4.3.2. ζ-Potential Test

Both coal sample and silica were ground to ~30 μm using an Agate pestle for the ζ-potential test. HCl (25.00% v/v) and NaOH (99.99% grade) were used for pH adjustment. The concentration of KCl used as the supporting electrolyte was 10−3 M. Distilled water was used in the whole process. The procedures were as follows: 0.2 g of sub-bituminous coal or silica was put into a 100 mL beaker, and the supporting electrolyte close to 100 mL was added. Then, the pH of the pulp was adjusted to different values after sufficient mixing. Afterward, the pulp was transferred into a 100 mL volumetric flask and 0.57 mL of 1% Lilafot D817M was added into the volumetric flask. The cap of the volumetric flask was tightened, and the flask was shaken up and down three times before putting it into an ultrasonic water bath for 15 min to diversify the pulp well. Last, the volumetric flask was taken out from the ultrasonic water bath and 1.5 mL of the supernatant was extracted for the ζ-potential test by a pipette after 15 min standing. The zeta potential analyzer used in this research is manufactured by Brookhaven Instruments Corporation. Every sample was tested 10 times, and the average values were taken.

#### 4.3.3. Surface Wetting Rate Test

The sub-bituminous coal and silica sample after being processed in 100 mL of 180 mg/L ammonium salt solution for 3 h were used to measure the surface wetting rate using surface tension apparatus (Tensiometer K100) after filtration and low-temperature drying. The principle of measurement is shown in Figure 15. In the picture, $F_1$ is the additional pressure, $\theta$ is the contact angle of a liquid on a solid, $F_2$ is the viscous resistance, $F_3$ is the gravity, and $h$ is the rising height of the liquid. When the additional pressure is higher than gravity and viscous resistance, the liquid will rise gradually.

The process steps were as follows:

1. The sample was ground to ~0.074 μm to guarantee the accuracy of the test.
2. A certain amount of the sample was measured and put into the test tube, and then the tube was tapped to make the sample compact. The height of the sample was about two-thirds that of the test tube.
3. The upper nut was tightened, the sample tube was fixed on the balance hook, and then the sample tube was put into the beaker with different wetting liquids.

### ACKNOWLEDGMENTS

The work was supported by “the Fundamental Research Funds for the Central Universities (2018QNA20)”. We also want to acknowledge the support of the Priority Academic Program Development of Jiangsu Higher Education Institutions.

### REFERENCES

1. Li, Y. Research on Particle Size Effect and Interface Interaction in Low Rank Coal Reverse Flotation; China University of Mining and Technology: Xuzhou, 2017; pp 8–10.
2. Jaiswal, S.; Tripathy, S. K.; Banerjee, P. K. An overview of reverse flotation process for coal. Int. J. Miner. Process. 2015, 134, 97–110.
3. Fuerstenau, D. Interfacial processes in mineral/water systems. Pure Appl. Chem. 1970, 24, 135–164.
4. Zhang, W.; Honaker, R.; Li, Y.; Chen, J. The importance of mechanical scrubbing in magnetite-concentrate reverse-flotation. Miner. Eng. 2014, 69, 133–136.
5. Yin, R. M.; Chen, L. Z.; Hou, Q. L.; Li, J.; Liu, T. R. Research on flotation mechanism of quartz using magnesium ion as activator. Adv. Mater. Res. 2013, 683, 621–625.

**Table 3. Proportion of Ingredients in Ammonium Salt Lilafot D817M**

| chemical name                        | concentration/% |
|-------------------------------------|-----------------|
| N-(3-(tridecyloxy)propyl)-1,3-propane diamine, acetate | 50–60           |
| N-(3-(tridecyloxy)propyl)-1,3-propane diamine          | 40–50           |
(6) Bada, S.; Afolabi, A.; Makhula, M. Effect of reverse flotation on magnetic separation concentrates. Int. J. Miner., Metall. Mater. 2012, 19, 669–674.

(7) Filippov, L.; Severov, V.; Filippova, I. An overview of the beneficiation of iron ores via reverse cationic flotation. Int. J. Miner. Process. 2014, 127, 62–69.

(8) Ata, S.; Yates, P. D. Stability and flotation behaviour of silica in the presence of a non-polar oil and cationic surfactant. Colloids Surf., A 2006, 277, 1–7.

(9) Wang, Y.; Hu, Y.; He, P.; Gu, G. Reverse flotation for removal of silicates from diasporic-bauxite. Miner. Eng. 2004, 17, 63–68.

(10) Vieira, A. M.; Peres, A. E. C. The effect of amine type, pH, and size range in the flotation of quartz. Miner. Eng. 2007, 20, 1008–1013.

(11) Fuerstenau, D. W.; Jia, R. The adsorption of alkylpyridinium chlorides and their effect on the interfacial behavior of quartz. Colloids Surf., A 2004, 250, 223–231.

(12) Yuehua, H.; Wei, S.; Haipu, L.; Xu, Z. Role of macromolecules in kaolinite flotation. Miner. Eng. 2004, 17, 1017–1022.

(13) Hu, Y.; Sun, W.; Hao, J.; Miller, J. D.; Fa, K. The anomalous behavior of kaolinite flotation with dodecyl amine collector as explained from crystal structure considerations. Int. J. Miner. Process. 2005, 76, 163–172.

(14) Liu, C.; Hu, Y.; Cao, X. Substituent effects in kaolinite flotation using dodecyl tertiary amines. Miner. Eng. 2009, 22, 849–852.

(15) Xia, L. Y.; Zhong, H.; Liu, G.; Li, X. G. Electron bandstructure of kaolinite and its mechanism of flotation using dodecylamine as collector. J. Cent. South Univ. Technol. 2009, 16, 73–79.

(16) Jiang, H.; Liu, G.; Hu, Y.; Xu, L.; Yu, Y.; Xie, Z.; Chen, H. Flotation and adsorption of quaternary ammonium salts collectors on kaolinite of different particle size. Int. J. Min. Sci. Technol. 2013, 23, 249–253.

(17) Li, Y.; Honaker, R.; Chen, J.; Shen, L. Effect of particle size on the reverse flotation of subbituminous coal. Powder Technol. 2016, 301, 323–330.

(18) Li, Y.; Chen, J.; Shen, L. Flotation behaviors of coal particles and mineral particles of different size ranges in coal reverse flotation. Energy Fuels 2016, 30, 9933–9938.

(19) Li, Y.; Chen, J.; Shen, L. Beneficiation of coal-silica mixture using reverse flotation. Energy Sources, Part A 2017, 39, 103–109.

(20) Xia, W.; Yang, J. Reverse flotation of Taixi oxidized coal. Energy Fuels 2013, 27, 7324–7329.

(21) Li, Y.; Li, J.; Chen, P.; Chen, J.; Shen, L.; Zhu, X.; Cheng, G. The effect of ultra-fine coal on the flotation behavior of silica in subbituminous coal reverse flotation. Powder Technol. 2019, 342, 457–463.

(22) Patil, D. P.; Laskowski, J. S. Development of zero conditioning procedure for coal reverse flotation. Miner. Eng. 2008, 21, 373–379.

(23) Pawlik, M.; Laskowski, J. S. Coal reverse flotation. Part I. Adsorption of dodecyltrimethyl ammonium bromide and humic acids onto coal and silica. Coal Prep. 2003, 23, 91–112.

(24) usu, H.; Tatsukawa, T.; Saeki, T.; Katagiri, K. Rheology of low rank coal slurries prepared by an upgrading process. Coal Prep. 1997, 18, 119–128.

(25) Qu, J.; Tao, X.; Tang, L.; Liang, K.; Zeng, W. Research on characterization of surface properties of Shendong low rank coal before and after flotation. China Coal 2014, 8, 88–92.

(26) Duan, X.; Qu, J.; Wang, Z. Pore structure of macerals from a low rank bituminous. J. China Univ. Min. Technol. 2009, 38, 224–228.

(27) Sarikaya, M.; Ozbayoglu, G. Electrokinetics of oxidized coal. Fuel Process. Technol. 1990, 24, 459–466.

(28) Eskilsson, K.; Yaminsky, V. V. Deposition of monolayers by retraction from solution: ellipsometric study of cetyltrimethylammonium bromide adsorption at silica-air and silica-water interfaces. Langmuir 1998, 14, 2444–2450.

(29) Li, Y. Effect of dextrin on the adsorption behavior and surface characteristics of sub-bituminous coal and silica. ACS Omega 2019, 4, 7231–7236.