

Received October 25, 2011; reviewed; accepted January 3, 2012

IMPROVING FLOATABILITY OF TAI XI ANTHRACITE COAL OF MILD OXIDATION BY GRINDING

Wencheng XIA, Jianguo YANG, Yuemin ZHAO, Bin ZHU, Yuling WANG

School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu 221116, China, xiawencheng@cumt.edu.cn, scetyjg@126.com

Abstract. Grinding is widely used in ore size reduction. In this investigation, grinding is proved to be advantageous in improving the floatability of anthracite coal of mild oxidation. FTIR was used to explain changes in the main functional chemical groups of anthracite coal of mild oxidation upon grinding. Improvements of the floatability of four size fractions, namely, +0.25 mm, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm, were discussed respectively. The results show that the floatability of anthracite coal of mild oxidation can be improved by 30 minutes grinding. The anthracite coal of mild oxidation can obtain many fresh hydrophobic surfaces by scuffing. Besides, the anthracite coal of mild oxidation can be crushed and/or ground to form fines which also contain many fresh hydrophobic surfaces. Combustible matter recovery of anthracite coal of mild oxidation, ground by 30 minutes, can reach 72.14% with ash content of 8.63%, while combustible matter recovery of original coal is 56.65% with ash content of 9.90%.

keywords: anthracite; oxidation; grinding; floatability; FTIR

1. Introduction

Coal can be oxidized in air easily, i.e. underground, stored in coal bunkers, and even in the process of long distance transport (Huggins and Huffman, 1989). This oxidation process is known as weathering. Coal oxidation processes include three major aspects, i.e. oxygen adsorption, gas release, and heat release (Wang et al., 2003). The heat release causes coal to be oxidized to a further extent. All of these result in the formation of oxygen functional groups, such as carboxyl, phenolic and carbonyl functionalities on the coal surface, which reduce the hydrophobicity of the coal surface by increasing the number of sites that can form hydrogen bond with water molecules. Weathering processes make the coal more difficult to float with oily collectors (Aplan, 1988; Fuerstenau et al., 1992; Fuerstenau and Diao, 1990; Harris et al., 1995; Jia et al., 2000; Laskowski and Miller, 1984). Certainly, the oxidation processes also lead to many changes in the physical composition, besides chemical property, making coal porous and breakable.

Previous studies were focused on the oxidation mechanism by simulating the oxidation processes and show that the coal oxidation processes are concerned with oxidation temperature, coal particle size, and coal moisture (Chen, 1993; Coward, 1957; Sun, 1954). Oxidation rate decreases with the coal particle size and increases with the coal specific surface (Akgun and Arisoy, 1994; Carras and Young, 1994). The oxidation processes generally occur on the coal particle surface. Therefore, the physical composition and chemical property inside the coal particle change less (Somasundaran et al., 2000). It is generally acknowledged that the oxidation rate is inversely proportional to the degree of coalification (Diao and Fuerstenau, 1992; Schmal, 1989). Flotation tests of difficult-to-float oxidized coal were successfully accomplished by applying a direct coal and flotation reagents contact procedure with appropriate reagents (Ahmed and Drzymala, 2004). Coal stored at coarse size and then ground to fine size before flotation exhibits a higher flotation yield than that stored as fines (Fuerstenau et al., 1994). Recently, attrition has been used in improving the floatability of oxidized surface of anthracite waste coal (Sokolovic et al., 2012). Evidently, grinding generates sufficient fresh surface that minimizes the effects of the external oxidized surface, but grinding process may produce more ultra-fine coal particles, whose sizes are less than 10 micrometers, which are difficult to float (Forbes, 2011). Simultaneously, the ultra-fine coal particles need more flotation agent and the ultra-fine gangue particles adsorb on the coal surface leading to a more hydrophilic coal surface (Huynh et al., 2000; Oats et al., 2010). Optimal grinding time will be determined in this study. Coal particles of different sizes have different flotabilities which change through grinding. In this paper four size fractions, i.e. +0.25 mm, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm of flotation concentrates will be compared for ground and original coal. In this regard, the paper investigates the flotation behavior and hydrophobicity of anthracite coal of mild oxidation before and after grinding using flotation. In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analysis is used to explain the changes in the main functional chemical groups of anthracite coal of mild oxidation upon grinding.

2. Experimental method and procedure

In this investigation, dodecane was used as the oily collector and 2-octanol was used as the frother. Coal samples were provided by Taixi Coal Preparation Plant in China. Coal in this plant is stored outside and oxidizes mildly under the air, rain and sunshine. Coal samples were screened to pass 0.5 mm. The flotation tests were conducted in a 1.5 dm³ XFG flotation cell using 100 g of coal at a pulp density of 6.25% solids. The impeller speed of the flotation machine was 1910 rpm and the airflow rate was 2 dm³/min. Dodecane collector dose was 5 kg/Mg and 2-octanol frother 1 kg/Mg of coal. In each flotation test, the pulp was first agitated in the flotation cell for 3 min, after which dodecane collector (5 kg/Mg) was added and the pulp conditioned for an additional period of 3-min. 2-octanol frother (1 kg/Mg) was then added and the pulp was conditioned for an additional one minute.

The FTIR spectrum was obtained with KBr pellets prepared with 0.125-0.074 mm anthracite coal of mild oxidation samples (original coal) and the same anthracite coal of mild oxidation samples ground with KBr for an additional time in a mortar. For the FTIR analyses a Perkin Elmer Spectrum 2000 model spectrometer was used and the spectrum was obtained at 2 cm^{-1} resolution, between 4000 and 400 cm^{-1} . It is worth emphasizing that ash content influences the FTIR spectrum. The 0.125-0.074 mm anthracite coal of mild oxidation samples were separated by density separation using a centrifugal extractor with the density fraction of 1.4 kg/dm^3 .

Grinding was conducted in a laboratory dry rod mill. Grinding times were 5 min, 10 min, 20 min and 30 min, respectively. The grinding products and flotation concentrate were screened to get four size fractions: $+0.25\text{ mm}$, $0.25\text{-}0.125\text{ mm}$, $0.125\text{-}0.074\text{ mm}$ and $\text{-}0.074\text{ mm}$. Every size fraction was analyzed to determine parameters such as ash content, combustible matter recovery and yield. Eq. (1) was used to calculate the combustible matter recovery of the flotation experiments:

$$\text{Combustible matter recovery (\%)} = [M_c(100 - A_c) / M_F(100 - A_F)] \times 100, \quad (1)$$

where M_C is weight of the concentrate (%), M_F is weight of the feed (%), A_C is the ash content of the concentrate (%), and A_F is the ash content of the feed (%).

3. Results and discussion

3.1. FTIR spectrum

The FTIR spectra of original and ground coal are showed in Fig. 1. After grinding, the FTIR spectrum shows five main functional chemical groups more than the original coal. The five main functional chemical groups are: 3030 cm^{-1} , 2910 cm^{-1} , 867 cm^{-1} , 797 cm^{-1} and 736 cm^{-1} . Among the five functional chemical groups, 3030 cm^{-1} and 2910 cm^{-1} are aliphatic hydrocarbons which are hydrophobic. Another three functional chemical groups 867 cm^{-1} , 797 cm^{-1} and 736 cm^{-1} indicate the presence of benzene rings which also are more hydrophobic than the oxygen functional groups. Oxygen functional groups detected at 3440 cm^{-1} and 1630 cm^{-1} are shown in Fig. 1. The FTIR image shows that grinding leads to more fresh surface and hydrophobic functional chemical groups on the surface of anthracite coal of mild oxidation than that of original coal. The absorbances of functional chemical groups are widely used for quantitative analysis (Jena et al., 2008; Yuh and Wolt, 1983). The absorbance is concerned with the functional chemical groups' content. Low absorbance is considered as a result of low functional chemical group content. After grinding, the anthracite coal of mild oxidation has low absorbance of the oxygen functional groups (3440 cm^{-1} and 1630 cm^{-1}). Thus, grinding causes anthracite coal of mild oxidation to be more hydrophobic than the original coal.

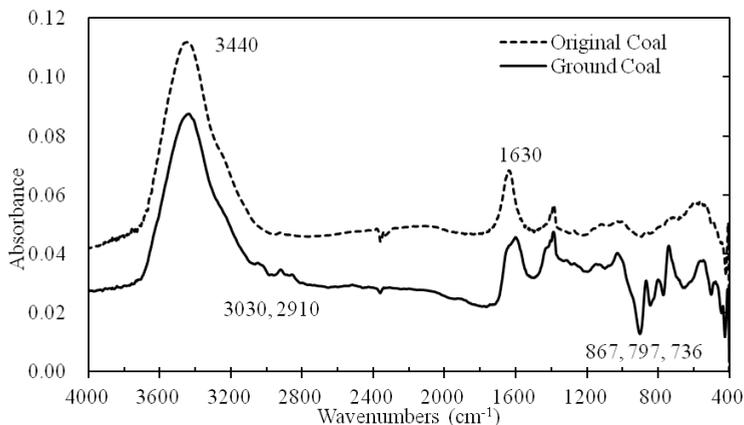


Fig. 1. FTIR spectrum of anthracite coal of mild oxidation before and after grinding

3.2. Size fractions changing

Figure 2 shows that the yield of the +0.25 mm fraction decreases and that of -0.074 mm increases with the grinding time. Middle size fractions (0.25-0.125 mm and 0.125-0.074 mm), should be crushed or ground to be fine, but the yield of the two size fractions increases with the increasing grinding time. It is so because the +0.25 mm size fraction during crushing and/or grinding forms three size fractions, namely, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm. As shown in Fig. 3, the +0.25 mm size fraction during crushing or grinding becomes 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm fractions. Coal particles can be also surface ground and their sizes are less changed, so the size fractions of the coal particles are not changed.

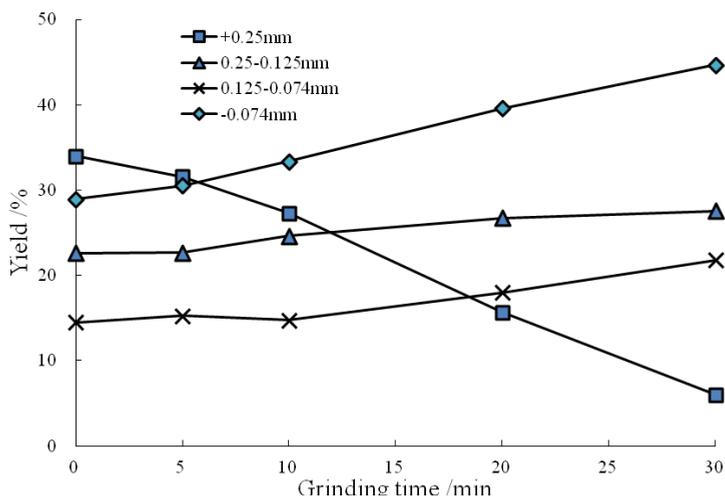


Fig. 2. Yields of size fractions before and after grinding

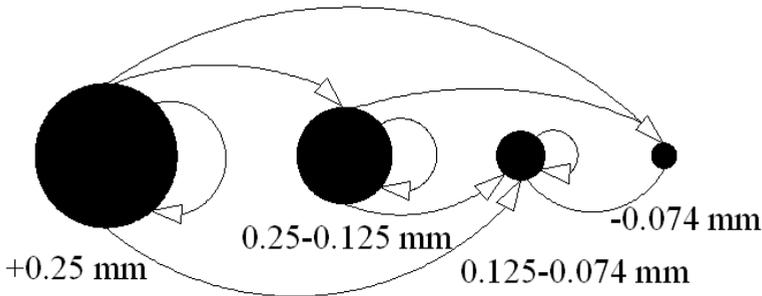


Fig.3. Size fractions changes due to grinding

As shown in Fig. 4, the ash content analysis of the four size fractions shows that the ash content of -0.074 mm decreases with the grinding time. Ash content of the $+0.25$ mm fraction reaches the highest after 5 min of grinding, and then decreases with the increasing of grinding time. Ash contents of the middle size fractions change less and in a random manner. Ash contents of the four size fractions of original coal decrease with the increasing of size, namely, $+0.25$ mm $<$ $0.25-0.125$ mm $<$ $0.125-0.074$ mm $<$ -0.074 mm. Because low ash content coarse coals are crushed and/or ground to be small particles or fines, these small particles or fines make up the loss of middle size fractions, so the middle size fractions and fines ash contents go down with the increasing grinding time.

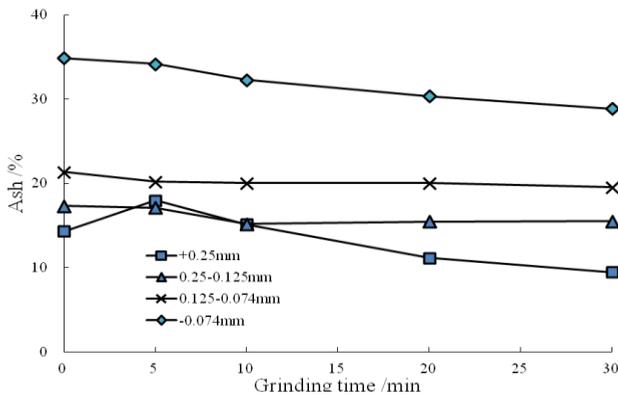


Fig. 4. Ash content of size fractions before and after grinding

3.3. Flotation tests

Figure 5 shows combustible matter recovery of anthracite coal of mild oxidation before and after grinding. The combustible matter recovery in concentrate increases

with the increasing grinding time for grinding time of 20 min and 30 min. The combustible matter recovery of +0.25 mm size fraction reaches the highest value after 20 min of grinding, and recovery after 30 min of grinding is smaller, but both are higher than these after 5 min or 10 min of grinding. The combustible matter recovery of different size fractions, namely, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm, increases with the grinding time and is similar when the grinding time is either 20 min or 30 min. From the original coal flotation results, it can be seen that the size fractions, namely, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm, have a similar combustible matter recovery, therefore, the size fraction has less effect on the floatability of anthracite coal of mild oxidation particles when the particles size is less than -0.25 mm. However, the combustible matter recovery of the 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm size fractions is different and becomes higher after grinding. All of these prove that grinding can improve floatability of anthracite coal of mild oxidation.

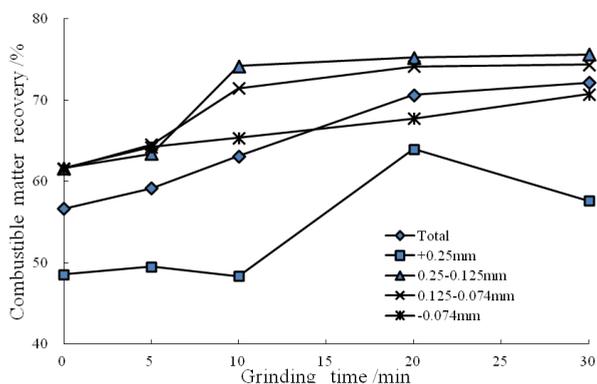


Fig. 5. Combustible matter recovery of size fractions before and after grinding

Figure 5 shows that anthracite coal of mild oxidation after 20 min or 30 min grinding time has higher combustible matter recovery and similar ash content. However, the combustible matter recovery of +0.25 mm size fraction decreases when the grinding time is more than 20 min. It may be explained that long time grinding produces many fines and ultra-fine coal particles which need more flotation agent dose. Ultra-fine gangue particles also adsorb on the coal surface causing the coal surface to be hydrophilic. Coarse coals need more hydrophobic surface for flotation than the middle size particles or fines because greater mass.

Figure 5 shows that the combustible matter recovery of different size fractions, namely, 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm, are higher than +0.25 mm. This phenomenon proves that the size fraction has a great effect on coal particles flotation, even though the coarse coals have been surface ground. In addition, the combustible matter recovery of size fractions, namely, 0.25-0.125 mm and 0.125-0.074 mm, is higher than -0.074 mm. It proves that fines from the surface of anthracite

coal of mild oxidation are more hydrophilic than small coal particles produced by surface grinding. Maybe the -0.074 mm anthracite coal fraction of mild oxidations is affected less by grinding as grinding has priority in coarse coals.

Figure 6 shows that ash contents of all size fractions first decrease with the increasing of grinding and then become similar when the grinding time is 20 min or 30 min. The ash content of the -0.074 mm size fraction reduces obviously from 19.03% to 13.63%. One of the reasons is that the low ash content of coarse coal particles (with the diameter between 0.5 mm and 0.125 mm) are crushed and/or ground to be fines (with the diameter less than 0.074 mm) which are easily floated.

Anthracite coal of mild oxidation surface has more oxygen functional groups causing the coal surface to be hydrophilic and prevents the coal surface from being covered by oily collectors, making coal difficult-to-float. Grinding is widely used to separate coal from gangue minerals. In addition, grinding can also produce fresh surface having higher hydrophobicity than the oxidized surface. As shown in Fig. 1, the FTIR spectrum indicates that grinding can produce fresh surface. The $+0.25$ mm coal particles have higher combustible matter recovery after grinding. It proves that grinding can improve the flotability of coarse coal particles. It appears that the floatability of other size fractions, such as 0.25-0.125 mm, 0.125-0.074 mm and -0.074 mm, are also improved by grinding.

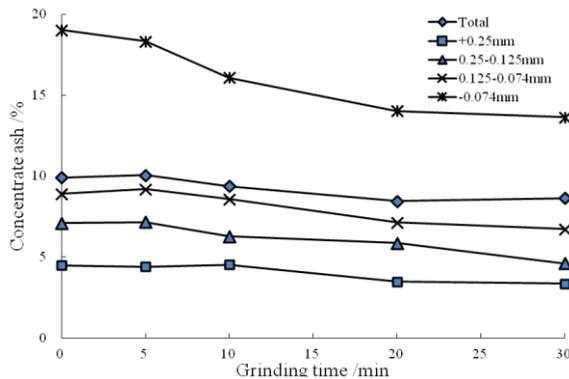


Fig. 6. Ash content of different size fractions of concentrate before and after

Grinding consists of two main processes: surface grinding and crushing, as shown in Fig. 7. Surface grinding changes the coal particle size not too much but has a great effect on the coal particle surface. Crushing changes the coal particle size more and also has the effect on the coal particle surface. Both the surface grinding and crushing produce many fresh hydrophobic areas on the coal surfaces of coal particles. Coal particles are crushed and/or ground to produce small particles and fines. The fines may also acquire many fresh spots as shown in Fig. 7. The original surfaces are more hydrophilic while the fresh surfaces, produced by crushing and/or grinding are more hydrophobic.

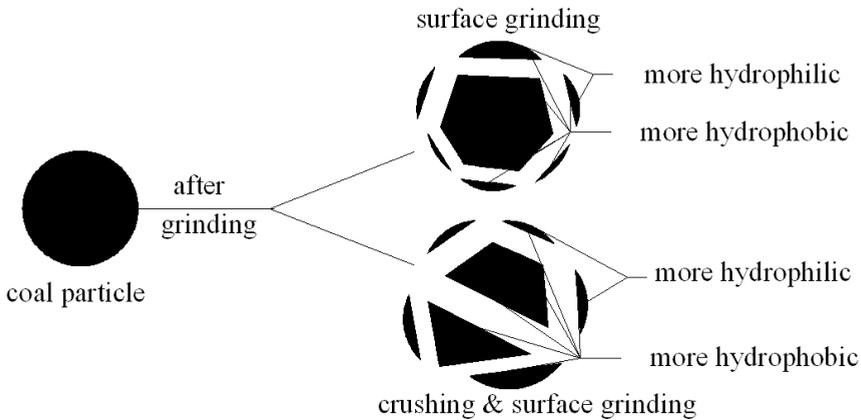


Fig.7. Surface properties changed by grinding

4. Conclusion

Oxidation processes occurring on the coal surface causes coal to be of low floatability. Grinding can be used to improve the floatability of anthracite coal of mild oxidation by producing many fresh surfaces areas. As shown in Fig. 7, grinding can be described as two main processes: surface grinding and crushing. Coal particles can be crushed and/or ground to form small particles or fines, some of which are formerly parts of the surfaces of anthracite coal of mild oxidation particles. These small particles or fines become more hydrophobic. Flotation tests show that the combustible matter recovery of anthracite coal of mild oxidation can reach 72.14% with ash content of 8.63% by 30 minutes grinding, while that of original coal recovery is 56.65% with ash content of 9.90%. It is evident that the floatability of anthracite coal of mild oxidation can be improved by grinding.

Acknowledgements

This work was supported by the Fund from the Natural Science Foundation of China for Innovative Research Group (Grant 50921002).

References

- AHMED, H.A.M., DRZYMALA, J., 2004, *Effect of flotation procedure and composition of reagents on yield of a difficult-to-float coal*. Physicochem. Probl. Miner. Process. 38, 53–63.
- APLAN, F.F., 1988, *How the nature of raw coal influences its cleaning*. In: Klimpel, R.R., Luckie, P.T. (Eds.), *Industrial Practice of Fine Coal Process*. SME, Littleton, CO:99–111.
- AKGUN, F., ARISOY, A., 1994, *Effect of particle size on the spontaneous heating of a coal stockpile*. Combust Flame 99, 137–46.
- COWARD, H.F., 1957, *Research on spontaneous combustion of coal in mines—a review*. Research Report 142, Great Britain: Safety in Mines Research Establishment.
- CHEN, X.D., STOTT, J.B., 1993, *The effect of moisture content on the oxidation rate of coal during near-equilibrium drying and wetting at 50°C*, Fuel 72, 787–792.

- CARRAS, J.N., YOUNG, B.C., 1994, *Self-heating of coal and related materials: models, application and test methods*. Prog. Energy Combust. Sci. 20, 1–15.
- DIAO, J., FUERSTENAU, D.W., 1992, *Characterization of coal oxidation and coal wetting behavior by film flotation*. Coal Preparation 10, 1–17.
- FORBES, E., 2011, *Shear, selective and temperature responsive flocculation: A comparison of fine particle flotation techniques*. Int. J. Miner. Process. 99, 1–10.
- FUERSTENAU, D.W., SASTRY, K.V.S., HANSON, J. S., NARAYANAN, K.S., SOTILLO, F., DIAO, J. et al., 1992, *Coal Surface Control for Advanced Fine Coal Flotation*, Final Report.
- FUERSTENAU, D.W., DIAO, J., 1990, *Surface Properties of Coal and Their Role in Coal Beneficiation*, Final Report.
- FUERSTENAU, D.W., DIAO, J., HANSON, J.S., SOTILLO, F., SOMASUNDARAN, P., 1994, *Effect of weathering on the wetting behavior and flotation response of coal*. In: Blaschke, W.S., Gordon, Breach (Eds.), *New Trends in Coal Preparation Technologies and Equipment*, 747–753.
- HUGGINS, F.E., HUFFMAN, G.P., 1989, *Coal weathering and oxidation: the early stages*. In: Nelson CR, editor. *Chemistry of coal weathering*, vol.14, 33–60. Elsevier, Amsterdam.
- HARRIS, G.H., DIAO, J., FUERSTENAU, D.W., 1995, *Coal flotation with nonionic surfactants*. Coal Preparation 16, 135–147.
- HUYNH, L., FEILER, A., MICHELMORE, A., RALSTON, J., JENKINS, P., 2000, *Control of slime coatings by the use of anionic phosphates: a fundamental study*. Miner. Eng. 13(10-11), 1059–1069.
- JIA, R., HARRIS, G.H., FUERSTENAU, D.W., 2000, *An improved class of universal collectors for the flotation of oxidized and/or low-rank coal*. Int. J. Miner. Process. 58, 99–118.
- JENA M.S., BISWAL S.K., RUDRAMUNIYAPPA M.V, 2008, *Study on flotation characteristics of oxidised Indian high ash sub-bituminous coal*. Int. J. Miner. Process. 87, 42–50.
- LASKOWSKI, J.S., MILLER, J.D., 1984, *New reagents in coal flotation*. In: Jones, M.J., Oblatt, R. (Eds.), *Reagents in the Mineral Industry*. The Institution of Mining and Metallurgy, 145–154.
- SOMASUNDARAN, P., ZHANG, L., FUERSTENAU, D.W., 2000, *The effect of environment, oxidation and dissolved metal species on the chemistry of coal flotation*. Int. J. Miner. Process. 58, 85–97.
- SUN, S.C., 1954, *Effects of oxidation of coals on their flotation properties*. Trans. Am. Inst. Min. Metall. Eng. April, 396–401.
- SCHMAL, D., 1989, *Spontaneous heating of stored coal*. In: Nelson C.R., (Ed.). *Chemistry of coal weathering*, 133–215. Elsevier, Amsterdam.
- SOKOLOVIC, J.M., STANOJLOVIC, R.D., MARKOVIC, Z.S., 2012, *Activation of oxidized surface of anthracite waste coal by attrition*. Physicochem. Probl. Miner. Process. 48(1), 5–18.
- WANG H. H., DLUGOGORSKI, B. Z., KENNEDY, E. M., 2003, *Coal Oxidation at Low Temperatures: Oxygen Consumption, Oxidation Products, Reaction Mechanism and Kinetic Modeling*, Progress in Energy and Combustion Science, 29, 487–513.
- OATS, W.J., OZDEMIR, O., NGUYEN, A.V., 2010, *Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation*. Miner. Eng. 23, 413–419.
- YUH, S.J., WOLT, E.E., 1983, *FTIR studies of potassium catalyst treated gasified coal chars and carbon*. Fuel 62, 252–255.

