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Influence of montmorillonite hydration and delamination on coal flotation

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Abstract: In this study, the influence of montmorillonite (MT) hydration and delamination on coal flotation was investigated through flotation tests using coal-MT mixtures. MT particles were subjected to hydration at different time intervals. The Fuerstenau upgrading curve was plotted to evaluate the change in overall flotation selectivity. The zeta potential and particle size distribution were used to characterize the delamination behavior of MT in deionized water at natural pH level. Atomic force microscopy (AFM) (colloidal probe) was used to analyze the interaction force between coal and MT particles. It was found that smaller particles (individual silicate layers or thin packets of layers) with higher zeta potentials appeared gradually, and their volume proportion increased with increasing hydration time. AFM results showed that a monotonous repulsive force was detected consistently throughout the separation distance between coal and these emerging smaller MT particles. The decrease of these MT coating on coal surface was responsible for the higher flotation recovery and better selectivity. A jump-into-contact phenomenon was observed in coal and MT interaction when MT hydrated incompletely. It showed that heterocoagulation between coal and MT occurred and MT coating on the coal surface was responsible for the depression of flotation.

Keywords: coal flotation, montmorillonite, hydration, delamination, slime coating

1. Introduction

Flotation, which exploits the difference in wettability between valuable mineral and gangue mineral surfaces, is an important technology to concentrate fine and ultra-fine coal particles. Major components of gangue minerals in coal are believed to include various types of clays, such as kaolinite, illite, and montmorillonite (MT). On average, 60–80% of the total gangue minerals in raw coal are clays (Arnold and Aplan, 1986). Clay particles are ultrafine in size, usually less than 2 µm in the coal flotation pulp. And these ultrafine particles have an adverse effect on coal flotation, mainly through slime coating and mechanical entrainment, resulting in low flotation recovery and poor flotation selectivity (Oats et al., 2010; Zhao and Peng, 2012). Currently, with the increase in the degree of mechanization of coal mining operations and preparations, the proportion of clay minerals in raw coal increases, which presents more severe challenges to fine coal flotation.

Montmorillonite, with a 2:1 layered hierarchical structure connected by weak van der Waals forces, is a member of the family of anisotropic phyllosilicate minerals. The hierarchical structure comprises two silica tetrahedral sheets, between which lies an octahedral alumina sheet (Bailey, 1980). The tetrahedral and octahedral sheets couple together through hydrogen bonding. As the result of ion substitution in the sheets (e.g., Al^{3+} substituted by Mg^{2+} in octahedral alumina sheets), the basal faces of MT carry a permanent negative charge, which is balanced by exchangeable cations (e.g., Na^{+} and Ca^{2+}) from the interlayer space (Luckham and Possi, 1999). The spacing between individual layers is

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approximately 2.5 Å in the dry state. Upon immersion in an aqueous environment, the exchangeable cations are hydrated by water molecules which have penetrated the interlayer region. The weak van der Waals attraction can be overcome by the resulting high osmotic pressure, leading to the separation of the layers by 10–20 Å. When the exchangeable cations are alkali cations, such as Li^+ or Na^+, interlayer spacing can increase up to several hundred angstroms or even completely separate, generating thin packets of layers and individual silicate layers (Morris and Zbik, 2009).

Both the flotation concentrate grade and recovery can be greatly reduced by even small amounts of MT in coal (Oats et al., 2010; Xu et al., 2003). Based on zeta potential distribution, Xu et al. used coal and clay suspensions, individually and collectively, to investigate the observed reduction of coal flotation by MT, suggesting that the slime coating with MT is the main reason for the reduction of the coal flotation (Xu et al., 2003). Yaowen et al. has found a slight jump-into-contact phenomenon in the coal-MT interaction force in deionized water. Enhancing Ca^{2+} concentration, the electrostatic repulsive force was fully suppressed, thus aggravating MT coating and decreasing flotation recovery (Xing et al., 2017). Wang et al., using cryo-SEM, found that in deionized water, clay minerals coating on the coal particle surface were in a dispersed form, while in saline water, they emerged in either face-face, or edge-edge associated forms (Wang and Peng, 2014). With regards to previous studies, coal preparation considered MT as stable particles in aqueous solutions. Their hydration and delamination behaviours and the influence relative to their characteristics change were not taken into account. Theoretically, changes in size distribution and surface physicochemical characteristics will have an influence on coal flotation.

Through flotation studies on a coal-MT mixture, this paper aimed to investigate the impact of MT hydration and delamination on coal flotation. The Fuerstenau upgrading curve was adopted to evaluate overall flotation selectivity. The AFM colloidal probe technique was directly applied in the measurement of the interaction force between the MT particles and coal. Nonetheless, It should be noted that the inconsistent geometry and surface heterogeneity of the MT particles made it difficult to use this technique to get precise and reproducible force readings for quantitative analysis. As a result, our discussion is limited to qualitative speculations. This procedure has also been adopted by other researchers (Gui et al., 2016; Ozdemir et al., 2009). The findings of this study should give a more thorough and precise description of how MT hydration and delamination affect coal flotation.

2. Experimental

2.1. Materials

Fine coal samples containing 2.81% mineral matter with -45 μm particle size were supplied by Xingtai coal preparation plant in Hebei Province, China. A MT sample with an 80% passing of 20 μm (P_{80} = 20 μm) particle size was purchased from Sdu-chemic China Co., Ltd. Coal and MT samples were combined in the flotation test at a mass ratio of 3:1. Ultra-pure graphite substrate was used to represent the ultra-pure coal in the AFM test.

2.2. Methods

2.2.1. MT dispersion preparation and flotation kinetics experiments

To prepare MT suspensions with varying degrees of hydration and delamination, 13 g of MT was mixed with 700 mL of deionized water. The mixture was dispersed by shaking the container for 1 min, and then left for the required time for use. The standing times (hydration time) were 0, 1, 12, and 48 h, respectively.

The pre-prepared MT mixture was transferred to a 1.0 dm^3 XFD(III) laboratory flotation cell and the required amount of deionized water and coal sample was added to obtain flotation pulp with about 5.0% solid ratio. After the pulp was pre-wetted for 300 s at 950 rpm of impeller speed, 80 g/t of industrial-grade kerosene and 60 g/t of octanol were added as the collector and frother, respectively. Their conditioning periods were 180 and 60 s, respectivly. The flotation tests were carried out at an air flow rate of 0.1 m^3/h at which normal flotation was observed. During the flotation stage, five froth concentrates were collected after cumulative times of 30, 60, 120, 180, and 300 s, respectively. At last, flotation concentrates and tailing products were filtered, dried at 80°C and weighed for ash analysis.

2.2.2. Fuerstenau upgrading curves analysis

The overall coal flotation selectivity in the presence of MT particles was characterized, compared, and analyzed by Fuerstenau upgrading curves, which have been found to be useful in analyzing the results of coal flotation derived from de-ashing and desulfurization. (Xu et al., 2003; Bakalarz and Drzymala, 2013). The Fuerstenau upgrading curves are provided by the kinetic equation shown in Eq. (1), which is obtained by combining the two first-order flotation kinetics of both combustible and ash matters, as shown in Eqs. (2) and (3). Eqs. (2) and (3) relate the recovery of the combustibe and ash in concentrates to time, respectively.

$$\varepsilon = \varepsilon_\infty\left[1-\left(\frac{\varepsilon_{a\infty}-\varepsilon_a}{\varepsilon_{a\infty}}\right)^K\right], \tag{1}$$

$$\varepsilon = \varepsilon_\infty(1-e^{-k_1 t}), \tag{2}$$

$$\varepsilon_a = \varepsilon_{a\infty}(1-e^{-k_2 t}), \tag{3}$$

where ε and ε_a are the recoveries of combustible matter and ash in concentrates, respectively; ε_∞ and $\varepsilon_{a\infty}$ are the maximum values of combustible matter and ash recoveries, respectively; k_1 and k_2 are the first-order flotation rate constants of the combustible and ash materials, respectively; and K is the separation selectivity index, which is calculated as $K=\frac{k_1}{k_2}$.

2.2.3. Particle size and Zeta potential measurements

The particle size distribution of the MT was determined using a laser diffraction mastersizer (Malvern, UK) at time intervals of 0, 1, 12, and 48 h. This technique is based on the idea that when a particle enters a laser beam, it scatters light at an angle that is inversely proportional to the particle's size.

Zeta potential distribution measurements for MT samples were carried out using ZetaPALS (Brookhaven, USA) at 25°C. A fully dispersed suspension (20 cm^3) was transferred into a centrifuge tube using a pipette and allowed to settle for 10 min, after which a 1 cm^3 aliquot was transferred from the upper portion to ZetaPALS for measuring the zeta potential distribution of the samples. Each measurement was repeated 10 times, and average value was calculated. The natural pH of the suspension was 7.8.

2.2.4. AFM measurements and cryo-SEM analysis

An AFM instrument (Multimode 8, Bruker, Germany) was used in the contact mode for force measurement between MT particles and graphite substrate, representing the ultra-pure coal. MT particles were obtained from MT suspensions that underwent hydration and delamination for the required time. The prepared MT particles were glued to the apexes of the tipless cantilevers using a little epoxy resin under an optical microscope beforehand. The force measurement process has been described in the previous papers (Xing et al., 2017; Ducker et al., 1992; Bowem and Hilal, 2009). In brief, the graphite substrate was placed in a fluid cell filled with deionized water. Before force experiment, the system sensitivity and spring constant of the cantilever constant were determined using Bruker software. Interaction forces were obtained by recording the cantilever deflection via the optical lever technique. All experiments were carried out at a room temperature of 20 ± 1°C, and the average forces were calculated and presented.

Cryovitrification SEM (cryo-SEM) was used to observe the appearance of MT particles. The sample was obtained from pre-prepared MT dispersions fully dispersed using a large-aperture (>5mm) pipette. Firstly, it was transferred into a cryo-vitrification unit for vitrification using liquid nitrogen. Frozen samples were then fractured and coated with gold plasma for further examination. The detailed procedure for sample preparation has been previously described (Battersby et al., 1994). Finally, a PHILIPS XL30 field-emission gun scanning electron microscope was used to examine the particle shapes.

3. Results and discussion

3.1. Influence of MT hydration and delamination on coal flotation

Fig. 1 illustrates the influence of MT subjected different time of hydration on coal flotation in deionized water. For all systems, as the flotation time increased, both cumulative combustible recovery and ash recovery increased. These results are consistent with those obtained in literature (Xu et al., 2003; Xing et al., 2017). With MT subjected to hydration from 0 to 48 h, the cumulative combustible recovery gradually increased, and the cumulative ash recovery gradually decreased. After 48 h hydration, recoveries with flotation times up to 300 s were 69.3 and 5.7% for the combustible matter and ash, respectively. In contrast, only 50.5 and 8.3% recoveries were obtained for the system with 0 h hydration time. Also shown was the flotation kinetics increased with increasing hydration time. This indicates that the flotation process was improved and enhanced by MT hydration and delamination.

To better explore the MT hydration and delamination influence on coal flotation selectivity, the Fuerstenau upgrading curves of the flotation systems were plotted, as displayed in Fig. 2. Assuming that $\varepsilon_\infty = \varepsilon_{a\infty} = 100\%$, Eq.(1) can be simplified to Eq.(4).

$$\varepsilon = 100\left[1-\left(\frac{100-\varepsilon_a}{100}\right)^K\right] \tag{4}$$

Kinetic data was fitted using Eq.(4), and the fitting results were presented in Fig. 2. A larger separation selectivity index, K, was observed when the MT hydration time increased, from 7.54 at 0 h to 17.81 at 48 h. The significant improvement of flotation selectivity may be due to the decrease of the severe MT coating on the coal surface through MT hydration and delamination. The hydrophobicity of coal particles was recovered and bubble-particle attachment was promoted, leading to enhancement of coal recovery and flotation selectivity.

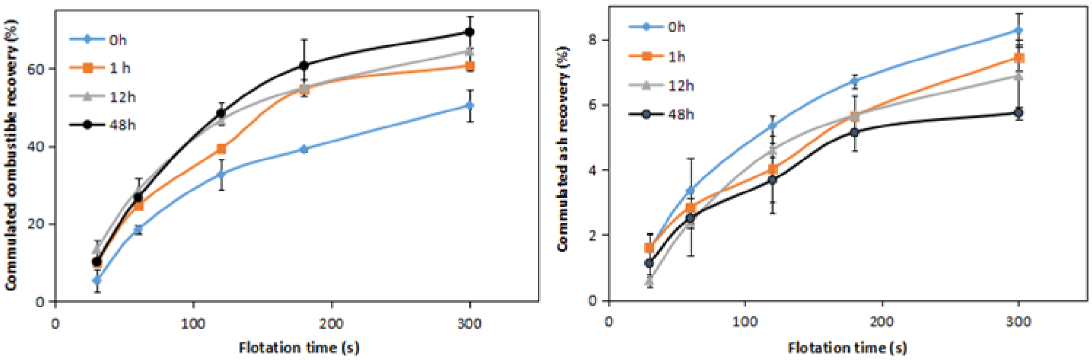

Fig. 1. Effect of montmorillonite subjected to various hydration time on fine coal flotation in deionized water

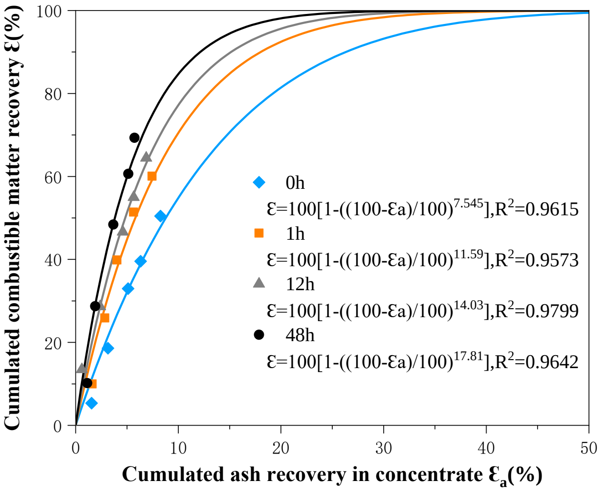

Fig. 2. Fuerstenau upgrading curves of coal-montmorillonite systems in deionized water

3.2. Influence of MT hydration on its size and zeta distribution

The particle size distribution *versus* the percentages of particle volume at varying hydration times are shown in Fig. 3. These curves show a bimodal size distribution. The size of the smaller particles shifted to lower values with increasing hydration time, decreasing from 415 to 209, 113, and 70 nm when the

MT samples were hydrated for 0, 1, 12, and 48 h, respectively. Meanwhile, the sizes of the larger particles shifted from 1710 to 581, 524, and 413 nm, respectively. Conversely, the size of the smallest particles remained at approximately 70 nm and no further decrease was observed, however its percentage particle volume increased with treatment time up to 48 h.

Fig. 4 shows the zeta potential analyses for MT particles in deionized water at natural pH. These curves all show a single peak that varied from the bimodal distribution of particle size. This was expected as the zeta potential measurements for each sample were carried out on the supernatant of settled dispersions with the coarse particles removed. The maximum shifted to −42.2, −43.5, −46.26, and −53.4 mV for the 0, 1, 12, and 48 h hydration time, respectively. The changes of particle size and zeta potential supplied a direct evidence about MT delamination and appearance of small particles with high zeta potential. The longer the hydration time, the stronger the electronegativity and the smaller the size of the generated particles.

Fig. 5 shows cryo-SEM images of the samples obtained after 0 h and 48 h of hydration. It showes that most particles exist as stacks of individual clay platelets aligned in a face-face orientation. After 48 h hydration and delamination, some of the particles break-up into single clay layers or thin packets of layers that have a flat sheet-like particle shape and high aspect ratio.

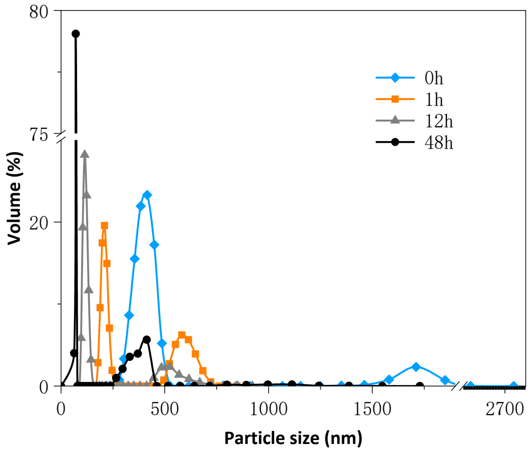

Fig. 3. Particle size distribution for MT subjected to various hydration time

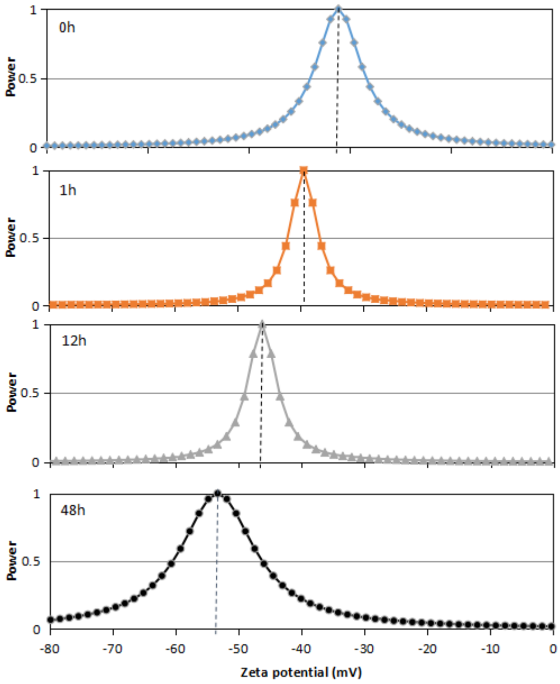

Fig. 4. Zeta potential distribution of MT subjected to various hydration time

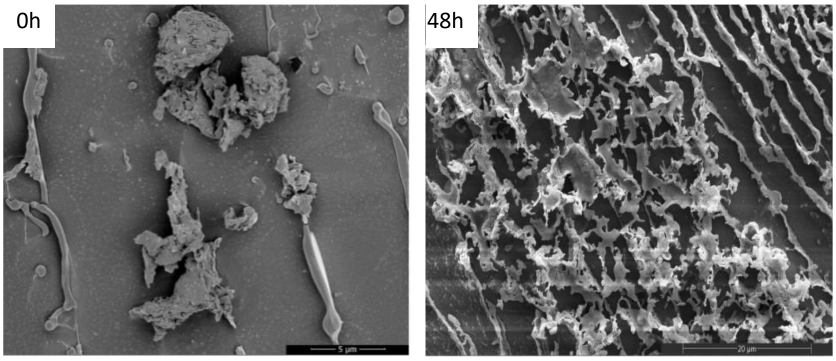

Fig. 5. Cryo-SEM images of montmorillonite after hydration and delamination

3.3. Interaction force between coal and MT particles

To provide direct insight into the influence of MT hydration and delamination on its coating behaviour on coal surface, AFM colloidal probe technique was used to measure the interaction force between coal and MT particles in the dispersion subjected to various hydration time. Fig. 6 shows the force curves between the graphite representing coal with ultra-low ash content, and MT particle. At large separation distances, no interaction forces were found for any of the coal-MT systems. In the coal-MT system not subjected to hydration (0 h curve), a slight jump-into-contact phenomenon with adhesion forces were observed at 18 nm, which is consistent with the results reported by Yaowen Xing (Xing et al., 2017). According to Derjguin-Landau-Verwey-Overbeek (DLVO) theory, the interaction between coal and MT particles is controlled by both attracting van der Waals force and electrostatic potential generated by electrical double layer. The jump-into-contact phenomenon indicates that the van der Waals force was sufficiently strong to overcome the repulsive electrostatic force, thus leading to the total DLVO interaction energy attraction. This result can be used to explain the coating behavior of MT, resulting in the significant depression of MT on coal flotation. As the hydration time increased, a monotonous repulsive force was observed and the slight jump-into-contact phenomenon gradually disappeared. This shows that the electrostatic repulsive force dominates the whole range profile and that the van der Waals force is insufficient to overcome it. As a result, the total DLVO interaction energy was positive, which means MT particles could not coat the coal surface, thereby dispersing in the flotation pulp. Hence, in this case, the flotation of coal was significantly improved.

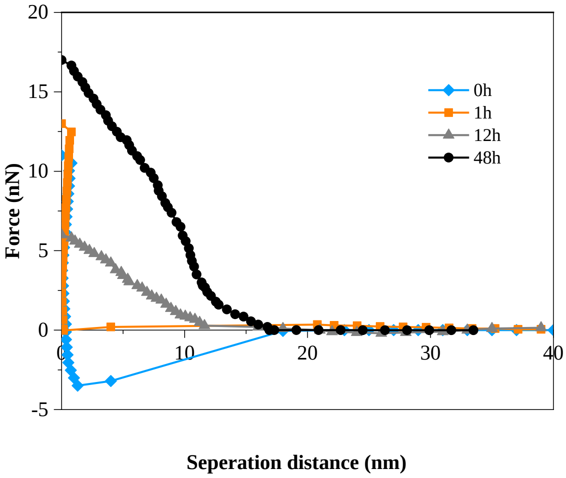

Fig. 6. Force curves between ultra-pure graphite and montmorillonite particles

Moreover, MT particles in solution tend to exit in association forms including edge-edge, edge-face and face-face. Clay association form is related to particle aspect ratio (ratio of particle diameter to thickness) (Gupta et al., 2011). According to Gupta et al., MT particles subjected to incompletely hydration and delamination, were with a low aspect ratio and would orient themselves dominantly in both edge-face and face-face manner. Bo wang et al. found that these two association units were strong enough to pass through the flotation process and transfer to the concentrate coating on coal particle surface (Wang and Peng, 2014). The emerging particles through thorough delamination had high aspect ratio, and would interact in face-face form or flow independently in aqueous solution (Battersby et al., 1994). The face-face interaction form was not strong. In coal flotation pulp, these clay particles may transfer to the flotation concentrate by entrainment more readily than by entrapment. As a result, flotation recovery and selectivity were improved.

4. Conclusions

The hydration and delamination of MT caused an obvious improvement in the coal flotation process in deionized water. When the MT hydration time was 48 h, 69.3% combustible matter recovery and 5.7% ash recovery were obtained, compared to only 50.5% combustible matter recovery and 8.3% ash recovery after 0 h of hydration. The improvements in flotation recovery and selectivity were attributed to the generation of smaller particles (individual silicate layers or thin packets of layers) with a higher zeta potential. According to AFM findings, there was a continuous repulsive force present in the coal-MT contact when MT was subjected to a high degree of hydration and delamination. The resulting particles dispersion was responsible for the high flotation recovery and better selectivity. A jump-into-contact phenomenon was observed as MT was not entirely hydrated, indicating that the slime coating of MT on the coal surface occured which was responsible for the depression of flotation under these circumstances. However, More research was needed to determine how the MT's surface charge and shape change affect flotation engineering.

Acknowledgements

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References

ARNOLD, B.J., APLAN, F.F., 1986. *The effect of clay slimes on coal flotation, part I: the nature of the clay*. Int. J. Miner. Process., 17, 225-242.

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, 413-9.

ZHAO, S., PENG, Y., 2012. *The oxidation of copper sulfide minerals during grinding and their interactions with clay particles*. Powder Technol., 230, 112-7.

BAILEY S.W., 1980. *Summary of recommendations of AIPEA Nomenclature Committee on clay minerals*. American Mineralogist, 65, 1-7.

LUCKHAM, P.F., ROSSI, S. 2009. *The colloidal and rheological properties of bentonite suspensions*. Adv. Colloid Interface. Sci., 82, 43-92.

MORRIS, G.E, ZBIK, M.S. 2009. *Smectite suspension structural behaviour*. Int. J. Miner. Process., 93(1), 20-25.

XU, Z., LIU, J., CHOUNG, J.W., ET AL. 2003. *Electrokinetic study of clay interactions with coal in flotation*. Int. J. Miner. Process., 68(1), 183-196.

XING, Y., XU, X., GUI, X., ET AL. 2017. *Effect of kaolinite and montmorillonite on fine coal flotation*. Fuel, 195, 284-289.

WANG B., PENG Y., 2014. *The interaction of clay minerals and saline water in coarse coal flotation.* Fuel, 134(9), 326-332.

GUI, X., XING, Y., RONG, G. 2016. *Interaction forces between coal and kaolinite particles measured by atomic force microscopy*. Powder Technol., 301, 349–55.

OZDEMIR, O., TARAN, E., HAMPTON, M.A., KARAKASHEV, S.I. NGUYEN, AV., 2009. *Surface chemistry aspects of coal flotation in bore water.* Int J Miner Process, 92, 177–83.

BAKALARZ, A., DRZYMALA, J., 2013. *Interrelation of the Fuerstenau upgrading curves with kinetics of separation*. Physicochem Probl Miner Process, 49, 443–51.

DUCKER, W.A., SENDEN, T.J., PASHLEY, R.M. 1992. *Measurement of forces in liquids using a force microscope*. Langmuir, 8, 1831-6.

BOWEN, W.R., NIDAL, H., 2009. *Atomic force microscopy in process engineering – an introduction to AFM for improved processes and product*s. Great Britain: Butterworth-Heinemann. p. 3-4.

BATTERSBY, B.J., SHARP, JCW, WEBB, R.I., ET AL., 1994, *Vitrification of aqueous suspensions from a controlled environment for electron microscopy: an improved plunge-cooling device*. J. Microsc., 176, 110-20

GUPTA, V., HAMPTON, M.A., STOKES, J.R., ET AL. 2011. *Particle interactions in kaolinite suspensions and corresponding aggregate structures.* J. Colloid Interface Sci., 359(1), 95-103.