INFLUENCE OF COALIFICATION ON HYDROPHOBICITY OF BLACK COAL

Lukáš KOVAĽ, Lucia KOVAĽOVÁ*, Ján RUŠAJ*, Martin HALÍK**

Abstract
The Ostrava-Karviná coalfield represents the Czech part of the Upper Silesian Basin, which is one of the most important European coal deposits. The coal seams mainly comprise bituminous coal. The majority of coals are of a high quality and can be used for coke production.Hydrophobic/hydrophilic properties of coal influence significantly value of moisture which represents very important parameter from the point of utilization of coal in energy production. Hydrofobicity was studied by means of contact angle measurements. It was proved that for black coal the hydrofilic properties increase with coalification. Article is to assess the influence of coalification on wettability of black coal from Upper Silesia basin which influenced its humidity and therefore also effectiveness of its energy use.
Key words: Contact angle, coal, reflectance, vitrinite content

1. Introduction

Contact angles have been studied intensively for more than one century.[1,2,3] The contact angle concept is important in understanding many natural and industrial processes that are controlled or influenced by the interfacial properties of interacting systems. Characterization of surface wetability by measuring the contact angle formed by the surface of interest is attractive due to the apparent relative simplicity with which contact angle can be measured.[4] However, the precise measurement and prediction of contact angles for real mineral surfaces is extremly difficult due to the many factors that influence wetting phenomena, such as surface roughness and heterogenity of real systems. On such surfaces, there exist many metastabe states each of wich is characterized by a different contact angle. The contact angle is a very common measure of the hydrophobicity of a solid surface and is an important parameter in wet processing of minerals. The contact angle is frequently measured as the angle between the air-liquid interface and the solid-liquid interface at the three-phase contact point. A variety of contact angles has been defined to adress different situations and some of these are outlined below. [1,3,4]

* *Ph.D. eng. - Institute of Environmental Engineering, Faculty of Mining and Geology, VŠB – Technical University of Ostrava, Czech Republic*

2. The Young equation

The relationship between surface tension and contact angle was first recognised by Young. In principle, the contact angle of an air bubble on a solid surface in aqueos solution is determined by the mechanical equilibrium under the action of three interfacial tensions. The contact angle determined by balancing the surface tension forces is known as Young´s contact angle Θ_Y, and relationship describing the balance of surface forces is known as Young´s equation.

$$\gamma s/a = \gamma s/l + \gamma l/a \cos\Theta_Y$$

$\gamma_{s/a}$ – solid/air surface tension
$\gamma_{s/l}$ – solid/liquid interfacial tension
$\gamma_{l/a}$ – liquid/air surface tension
Θ_Y – Young´s contact angle

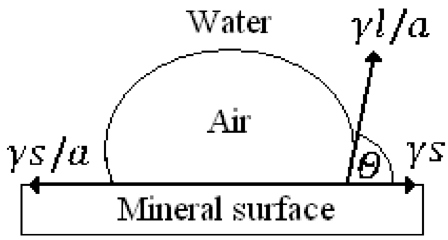

Fig. 1 *Contact angle between bubble and mineral solid surface in aqueous medium*

The validity of Young´s equation requires that the solid surface is smooth, flat, homogenous, inert, insoluble, non-reactive, non-porous, and non-deformable quality. These conditions are usually not met by real surfaces. Surface which meets all the requirements is referred as an ideal surface. However, most practical surfaces are non-ideal and the measurable contact values on such surfaces are referred to as apparent contact angles Θ_{ap}.

As a consequence, this value is not unique but falls into a mor or less wide interval between the advancing and the receding contact angle hysteresis. The three main contributing factor relating to non-ideal surfaces are: contamination of either the liquid or the soliud surface, surface roughness, and surface immobility on a macromolecular scale.

Over the years, many different techniques have been developed for measurements of contact angles. For real mineral systems, only few of the available techniques can offer precise, meaningful and realistic contact angle values without unreasonable requirements and/or assumptions.

Two procedures are available for studying contact angles at the three-phase contact line as shown on figure 2. The simplest method of contact angle determination relies on a direct measurement of an angle of bubble attachment to a mineral surface immersed in water. It is called the captive bubble method. When using this method it is important for an air bubble not to stick to particle edges because both different hydrophobicity of the edge and additional forces cause distortion of the results. [3,5] Second method is called sessile drop method. A drop of water can be placed on a solid surface.

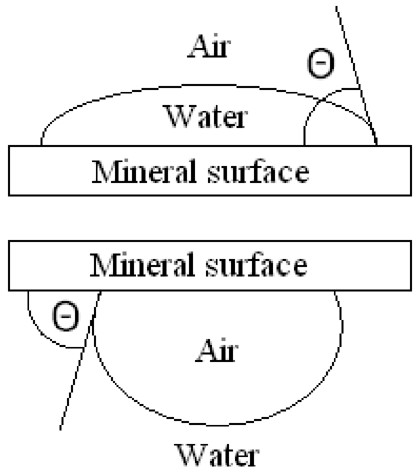

Fig. 2 *Sessile drop method (up) and captive bubble method (down)*

Both ways of expressing contact angle are equally valid, since the sum of contact angle measured trough the water phase, as well as the angle expressed trough a gas phase is 180°. So in principle, these two contact angles are the same. [3,5,6]

It is noted that surface roughness and chemical heterogeneity are present to some extent in all real mineral samples. As a result, the contact angle may change from one point to another along the contact line and will be differentiated into three definitions as shown on figure 3.

The intrinsic contact angle Θ_{in} is expected for an ideal solid surface. The usual optical methods for measuring contact angles. The apparent contact angle Θ_{ap} is yield by using usual optical methods for measuring contact angels. The apparent contact angle is the angle between solid the direction of the tangent to the smoothed solid surface and the direction of the tangent to the air-water interface.

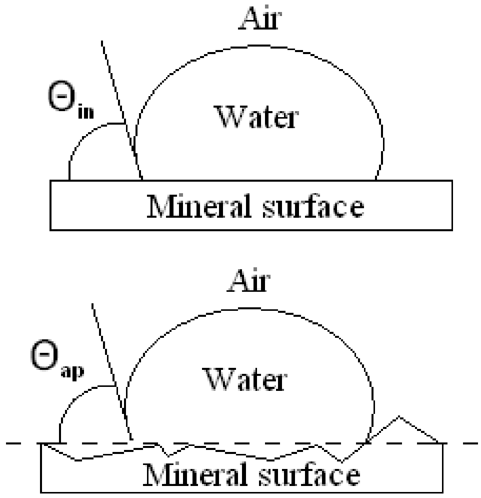

Fig. 3 *Differentiation between intrinsic contact angle (up) and apparent contact angle (down)*

On perfectly smooth solid surfaces, the apparent contact angle is identical with the actual contact angle. On real mineral surfaces, those two values may be very different. The apparent contact angle of a real surface is not unique, but falls into a more or less wide interval between the advancing and receding contact angle.

A low contact angle values means high wettability of the surface or low hydrophobicity and high contact angle values means poor wettability or high hydrophobicity. Difference between the maximum contact angle (advancing) and minimum contact angle (receding) is defined as contact angle hysteresis. [4,7]

Three main reasons that cause hysteresis are contamination of either the liquid or the solid surface, surface roughness, and surface immobility on a macromolecular scale. Unfortunately, there is no independent means of distiguishing the source of reasons that cause contact angle hysteresis. Therefore there is a particular interest in producing surfaces that are as close to perfect as possible so that there will be minimum and negligible contact angle hysteresis. [8]

To avoid hysteresis of contact angle resulting from surface roughness, the surface should be well polished. Occurrence of hysteresis of contact angle can be detected when contact angle, measured trough a water phase, after slight increase in bubble size, shows lower values than the angle after releasing the gas from a bubble. Minimum angle obtained during such measurements is called receding angle, while maximum one the advancing contact angle. The hysteresis of a contact angle can also take place due to other reasons, for instance surface energy heterogeneity. The contact angle can be also measured using the sessile drop method.

The contact angle depends not only on the method of measurement, physical or chemical heterogeneity of the surface, but also on such paramaters as drop and bubble size. The value of a contact angle can be also effected by the so-called line tension, which is an analogue of a surface tension, but characterizing the energy of contact line of phases. Therefore, each measuring system of contact angle is specific in some respect, which, if taken into account, can provide the equilibrium contact angle. Unfortunately, exact procedures for recalculating the measured contact angles into equilibrium contact angles is not known.

Hydrophobicity is a feature of material characterizing its ability to be wetted with the liquid in the presence of a gas phase. In mineral processing, solids which can be easily wetted with water are called hydrophilic, while solids with limited affinitiy for wetting are called hydrophobic. Substances can be hydrophobic to a different degree and the measure of their hydrophobicity is contact angle. [5]

Since coal, being a sedimentary substance coprised of organic matter (macerals) and inorganic matter (minerals), is very heterogenous, the contact angles reported for coal surfaces in the literature vary significantly. [4,7] Coal is intrinsically hydrophobic because of its chemical composition (surface aromatic aliphatic groups). The coal surface may be less hydrophobic because of oxidation resulting in the formation of hydrophilic carbonyl, carboxyl, and ester groups. The decrease of coal hydrophobicity can also be attributed to the slime coating of coal particle surfaces by hydrophilic fine clay particles. Coal is composed of a number of distinct organic etnities called macerals. Different maceral groups with different physical and chemical properties control the overall behavior of coal, including its hydrophobicities. The maceral groups in coal can be identified by petrographic analysis, which is conducted by observing the reflectance of polished coal surface under a microscope.

The difference in coal surface chemistry is caused by oxidation, different maceral groups, and the inclusion of mineral matter.[6,9]

3. Experiment

3.1 Material and Surface Preparation

Ten different black coal samples from Stařič and Chlebovice coal basin were selected for this investigation, which mean maximum reflectance of vitrinite R_{max} varied from 1,3 – 1,7. All samples were dried under laboratory conditions and then crushed using laboratory jaw crusher BB 200 (Retsch, Germany) with jaw gap set on 0,5 mm and after crushing sieved to nine (over 2 mm, 1,5–2 mm, 1–1,5 mm, 0,5–1 mm, 0,2–0,5 mm, 0,1–0,2 mm, 0,063–0,1 mm, 0,045–0,063 mm, under 0,045 mm) fractions using sieve analysis. After drying, crushing and sieving representative samples were prepared for petrographic analysis using ČSN ISO 7404/5 and ČSN ISO 7404/3 carried out at Institute of Geonics AS CR VSB – TU Ostrava.

3.2 Pellets with Real Surface

From each fraction of each sample 2,5 g of coal was used to made tablets with 35 mm diameter Tablets were made using manual laboratory press SPECAC (United Kingdom) under the pressure of $10t^{-1}$ for duration at least one minute with 3 repeatings for each tablet.

3.3 Pellets with Polished Surface

Black coal tablets with polished surface were made after contact angle measurments from tablets with the real surface. The real surface tablets were measured and after that set in polymer resin, wet polished with fine abrasive papers (abrasiveness 600, 800, 1200, 2500) followed by polishing with fine silica powder. Surface was then polished with a polishing cloth to a smooth surface. Samples were washed with a stream of water after each polishing step.

3.4 Contact angle measurement

Contact angles were measured using sessile drop method on each sample. For measuring fully computer controlled Attension Theta (Biolin Scientific, Finland) apparatus was used as shown on figure 4.

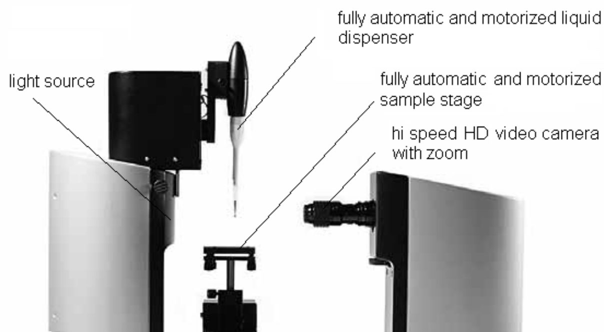

Fig. 4 *Attension Theta apparatus*

The experimental protocol was as follows: sample was placed on the sample stage and adjusted to obtain a level surface. A sessile drop of distilled water with a volume of 5 µl was formed at the end of the liquid dispenser tip and placed on the sample surface. The shapes of the sessile drops were digitized, analyzed off-line and fitted numerically using Attension Theta softwere to obtain a contact angle value. Measurements were carried out under laboratory conditions (23-25 °C) and repeated severel times.

3.5 Results and Discussion

The results of petrography analysis of coal and light reflectance (mean value of reflectance Rr) are shown in Table 1. From results shown in table 1 is obvious that samples of coal from Hrusov layers have lower degree of coalification, vitrinite content than samples from Upper Petrkovice layers.

Table 1 *Petrography analysis of coal*

Sample	Rr	Vitrinite	Inertinite	Liptinite
	(%)			
1215340	1,350	65,4	34,3	0,3
1125445	1,402	68,7	29,9	1,4
1125447	1,402	65,0	34,3	0,7
1124440	1,418	64,3	35,2	0,5
Average	1,393	65,8	33,4	0,7
0595342	1,509	67,5	32,2	0,3
063606	1,512	65,0	34,0	1,0
084273	1,591	70,0	29,8	0,2
0635350	1,655	68,6	31,6	0
0805251	1,664	68,0	32,0	0
0745357	1,772	70,3	29,7	0
Average	1,62	68,2	31,5	0,25

Notes: grey – Lower Hrusov layers,
white – Upper Petrkovice layers

Hydrophilic character of coal is increasing with the increase of degree of coalification (reflectance). Similar pattern occur between contact angle and the content of vitrinite in the sample. The linear relationships are statistically significant because condition of critical values of the correlation coefficient for 10 samples (r = 0.80) is met with significance level 0.005. Results are in good agreement with conclusions reported by Arnold et al. (1989).

4. Conclusion

In contrast to coal with a lower degree of coalification (brown coal, lignite) has been shown that with increasing degree of coalification of black coal its hydrophobicity is reduced. Statistically significant relationship between the contact angle and reflectance and the content of vitrinite was determined.

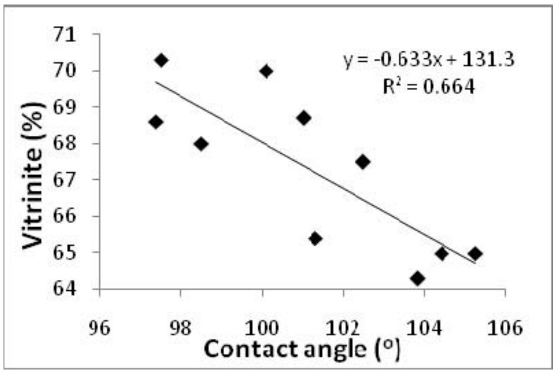

Fig. 5 *Relationship between contact angle and vitrinite content*

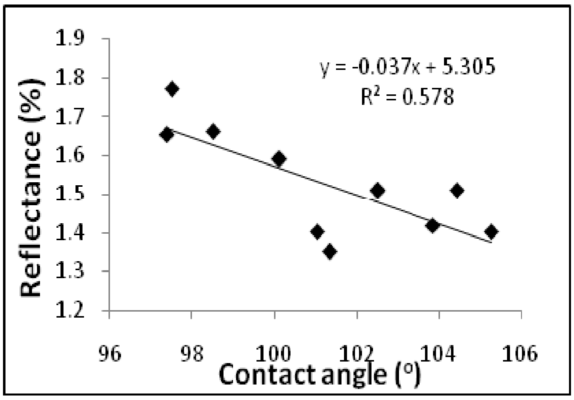

Fig. 6 *Relationship between contact angle and reflectance*

Acknowledgement

Support by the project OpVaVpi „Institute of Clean Technologies for Mining and Utilization of Raw Materials for Energy Use“ CZ.1.05 / 2.1.00 / 03.0082 is gratefully acknowledged.

References

1. **Kwok, D. Y., Neumann, A. W.**
Contact angle techniques and measurements. In: Milling AJ, editor. Surface Chracterization Methods: Principles, Techniques and Applications. New York: Marcel Dekker, Inc; 1999

2. **Chibowski, E., Perea-Caprio, R.,**
Adv Colloid Interface Sci 2002; 98:245-64.

3. **Chau, T.T., W.J. Bruckard, P.T.L. Koh, A.V. Nguyen**
A review of factors that affect contact angle and implications for flotation practice. Advances in Colloid and Interface Science. 2009, ISSN 00018686. DOI: 10.1016/j.cis.2009.07.003.

4. **Ofori, P., B. Firth, G. O`Brien, C. McNally, A.V. Nguyen**
Assessing the Hydrophobicity of Petrographically Heterogeneous Coal Surfaces. Energy. 2010, s. 5965-5971. ISSN 0887-0624. DOI: 10.1021/ef100793t.

5. **Drzymala, J.**
Mineral processing: foundations of theory and practice of minerallurgy. 1st eng. ed. Wroclaw: University of Technology, 2007. ISBN 978-837-4933-629.

6. **Ding, L.P., B. Firth, G. O`Brien, C. McNally, A.V. Nguyen**
Investigation of Bituminous Coal Hydrophobicity and its Influence on Flotation. Energy. 2009, ISSN 0887-0624. DOI: 10.1021/ef900589d.

7. **Gosiewska, A.; Drelich, J.; Laskowski, J.S.; Pawlik, M.J.**
Colloid Interface Sci. 2002, 247, 107-116

8. **Chau, T.T., B Firth, G. O`Brien, C. McNally, A.V. Nguyen.**
A review of techniques for measurement of contact angles and their applicability on mineral surfaces. Minerals Engineering. 2009, roč. 22, č. 3, s. 213-219. ISSN 08926875. DOI: 10.1016/j.mineng.2008.07.009.

9. **Xu, Z., Liu J., Choung, J.W.; Zhou, Z.**
Int. J. Miner. Process. 2003, 68,183-19