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WATER CONTACT ANGLE ON CORRESPONDING SURFACES OF FRESHLY FRACTURED FLUORITE, CALCITE AND MICA

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Abstract: Advancing and receding contact angles of water with corresponding surfaces of freshly fractured calcite, fluorite and mica were measured. The corresponding surfaces were obtained by mechanical splitting of a small lump of each mineral into two pieces. Theoretical considerations revealed that depending on the mineral cleaving plane, surfaces created by splitting into halves can be either identical or entirely different as far as their surface chemical composition is concerned. It was experimentally established that receding and advancing contact angles measured on the corresponding surfaces of fluorite, calcite and mica were identical for the sessile drop method. When the contact angle was measured by the captive bubble approach, there were small differences in the contact angles measured on the corresponding surfaces of fluorite. It was most probably due to surface irregularities and roughness, and therefore different times needed to rupture the liquid film between the bubble and solid surface.

Keywords: *contact angle; surface properties; cleaving plane; surface composition; corresponding halves; fluorite; calcite; mica*

Introduction

Wetting of a mineral surface can be characterized by the so-called contact angle. The contact angle, measured for solid/water/gas systems, is a very important parameter which is highly useful in wide areas such as chemistry, biotechnology, pharmacy and mineral processing, including flotation and oil agglomeration. Due to many forces involved in the flotation process, particularly in the bubble-particle aggregate formation and stability, there are several distinctive contact angles including static, dynamic, advancing, receding, equilibrium, rest, Young etc. (Drelich et al., 1996; Kowalczuk et al., 2011). All the contact angles have a meaning and play a role. In

flotation, for instance, the receding contact angle is responsible for formation of a bubble-particle aggregate, while the advancing contact angle for stability of the aggregate (Fig. 1). For flotation systems, that is for the particle-bubble aggregate and the solid at the liquid/gas interface, the advancing contact angle can be easily recalculated to the so-called rest contact angle (Drzymala, 1994a; Kowalczyk and Drzymala, 2012).

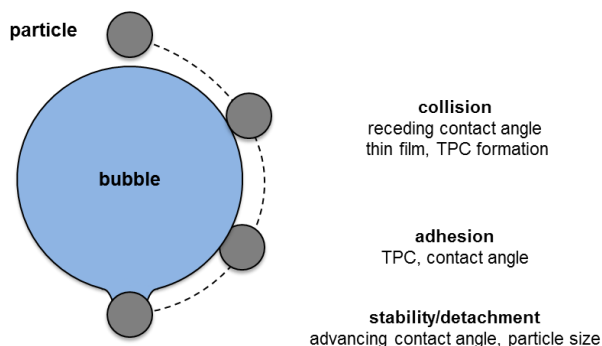


Fig. 1. Importance of receding and advancing contact angles in flotation (TPC means three-phase contact)

The water contact angle is affected by many factors including temperature, relative humidity, solid surface roughness, heterogeneity, surfaces preparation, sample pretreatment, gravity and many others. It is therefore not surprising that a large variation of contact angles for minerals is reported in literature (Shang et al., 2008; Chau, 2009). For an ideal surface, that is smooth, flat, homogeneous, insoluble, non-reactive and non-porous interface, which is attached to either a bubble or a drop in the absence of additional forces, there is a unique inclination of contact called the Young contact angle (Young, 1804; Adamson, 1990). However, the Young contact angle is valid only for limited situations, mostly when only excess pressure and capillary forces are present in the system. In typical flotation the solid phase is in a particulate form, which is attached to a bubble, both travelling to the froth phase. The surface of particle is usually rough. The shape and roughness of particles are determined by the way of crushing and grinding and also depend on the crystal inner structure as well as the cleavage planes of the solid.

Theoretical considerations of the physicochemical structure of materials and their cleavage planes indicate that either splitting, fracturing or cleavage a piece of mineral into halves provide two new surfaces, which can be identical, as in the case of the (001) mica plane (Oswald and Pieranski, 2005) or unequal, as for instance for the (110) cleavage plane of fluorite (Tasker, 1979; Janicki et al., 2016). Therefore, the aim of this research was to determine the advancing and receding contact angles measured by the sessile drop and captive bubble techniques, for fresh surfaces obtained by mechanical splitting of selected materials into halves. The measurements were

conducted for minerals which theoretically provide halves with either identical or different corresponding surfaces. The investigated minerals were fluorite, calcite and mica.

Materials and methods

To determine the water advancing and receding contact angles of corresponding surfaces of minerals, samples of pure fluorite, calcite and mica were used in the experiments. A representative pieces of the each mineral, obtained from the Laboratory of Mineral Processing (Wroclaw University of Science and Technology), were selected manually. The investigated minerals were checked by the XRD analysis which showed that they were of high purity. A lump of mineral was fractured into two pieces (halves) by applying a screwdriver and next pounding with a hammer. In this way two different (corresponding) surfaces of each mineral were obtained, and then they were immediately subjected to contact angle measurements. Since the measurements of contact angle on flat polished surfaces do not represent properties of mineral particles in industrial flotation (Chau, 2009) the contact angle measurements were conducted on fresh and unmodified surfaces of the investigated minerals. For each sample the receding and advancing contact angles were determined for the corresponding halves of each sample by means of the sessile drop and captive bubble techniques (Fig. 2). The contact angles were measured and expressed through the water phase. For the solid/liquid/gas system the contact angles formed by expanding and contracting liquid are referred to as the advancing and receding contact angles, respectively.

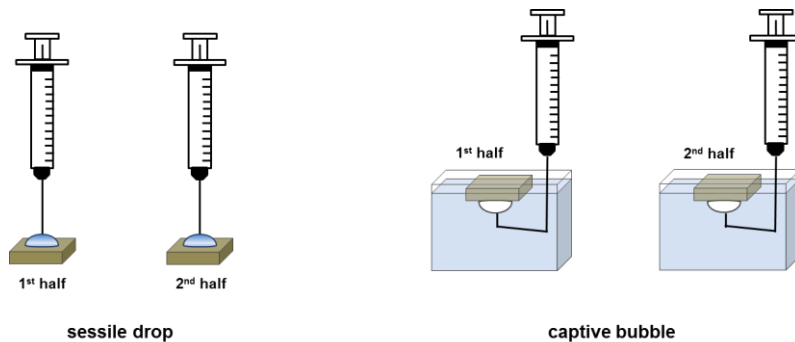


Fig. 2. Contact angle measurements arrangement

First, the sessile drop measurements were conducted for freshly cleaved minerals. In the measurements by means of the sessile drop method the mineral surface was held horizontally on a glass plate (Fig. 2). In the case of the measurements by means of the captive bubble method the mineral halves were immersed in distilled water in a rectangular, 44x28x46 mm in size, glass container (Fig. 2). The air bubble was formed

with a needle having 413 μm in the inner diameter and attached to the mineral surface. The immersion time was enough to record the advancing and receding contact angles. It allows to avoid the solubility of minerals. Before and after each experiment the minerals were dried by using compressed air. The experiments were recorded using a CCD camera connected to a PC (model Phoenix-300). Image XP and Image J software products were utilized for the particle/bubble/liquid contact angle determination. The experiments were conducted at ambient temperature of 23 $^{\circ}\text{C}$. Distilled water of $\text{pH} = 5.8 \pm 0.2$ and specific conductivity of 10^{-6} S/cm was used in cleaning and contact angle measurements. Each experiment was repeated 15 times, and the results were presented as average values.

Results and discussion

The surface structure of corresponding two surfaces obtained by either fracturing or splitting a piece of mineral along selected planes for many minerals has been described in various papers. In the case of fluorite, the perfect octahedral cleavage on (111) plane is well known (Schulz et al., 1994). Other fluorite planes, such as (110) and (100), are not the cleaving planes because in the sense of ionic charge distribution they are non-neutral planes (Schulz et al., 1994). On the other hand, Palache et al. (1951) showed that either parting or “cleavage” along the (110) fluorite plane can also occur. The bulk and surface structures of fluorite fractured along the (111), (110) and (100) planes are given in Fig. 3. Reorganization of the surface F and Ca ions for all of the considered cleavage planes after splitting was taken into account. It should be noted that the relaxation, as demonstrated elsewhere (Janicki et al., 2016), is insignificant (less than 3.5%) for the octahedral planes of fluorite.

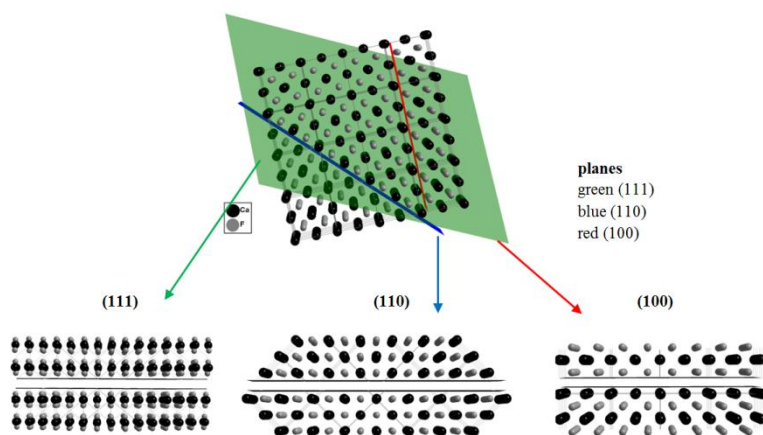


Fig. 3. Fluorite surface composition of corresponding halves depending on the splitting plane (based on Janicki et al., 2016)

It results from Fig. 3 that cleaving fluorite along the (111) and (100) planes provide identical surfaces, while splitting along the (110) plane produces unequal surfaces. In this case the surface of one half consists of Ca ions, while the second one with the F ions. These planes can be denoted as (110)^{Ca} and (100)^F, respectively. Therefore, it can be expected that the surface properties of both (110) halves, including their contact angle with water, are different, while the same for the (111) and (100) planes.

The presented in Table 1 results of contact angle measurements show that in the case of sessile drop method, there is no difference in the receding (1st half 26±4°, 2nd half 27±4°) and advancing (1st half 90±3°, 2nd half 90±2°) contact angles for the corresponding surfaces of fluorite obtained by splitting a piece of the mineral into halves. However, when the contact angle is measured by the captive bubble method, there is a small difference between advancing contact angles of corresponding halves of fluorite (1st half 76±5°, 2nd half 56±5°), while the receding contact angles are the same (1st half 28±5°, 2nd half 31±2°). When the hydrophobicity is measured by the captive bubble technique the additional parameter such as interfacial water film occurs. It determines the three-phase contact (TPC) formation. Therefore, the difference between advancing contact angles measured by the captive bubble technique is most probably due to surface irregularities and roughness, and therefore different times of TPC formation. The surface roughness and irregularities are of crucial importance in rupture the liquid film and formation of contact angle. The roughness influences the kinetics of the three-phase contact formation between bubble and solid surface both immersed in water. The time of three-phase contact formation at the surface of natural piece of fluorite ranges from 5 to 45 ms (Zawala et al., 2008). It especially happens when not a mono-crystal but a massive piece of mineral is subjected to splitting. More systematic studies are needed to confirm the existence of this effect.

Table 1. Mean advancing and receding contact angles of the investigated minerals

	Captive bubble				Sessile drop			
	1 st half		2 nd (corresponding) half		1 st half		2 nd (corresponding) half	
	Adv. °	Rec. °	Adv. °	Rec. °	Adv. °	Rec. °	Adv. °	Rec. °
Fluorite	76±5	28±5	56±5	31±2	90±3	26±4	90±2	27±4
Calcite	80±4	61±6	78±3	53±8	77±3	27±5	78±3	29±6
Mica	65±3	32±5	67±3	38±3	46±3	17±2	50±3	18±2

Table 1 also shows that fluorite is a naturally hydrophobic mineral since its advancing and receding contact angles, measured by both sessile drop and captive bubble techniques, are greater than zero. The natural hydrophobicity, and therefore flotation of fluorite depend on its origin, color and pH. Depending on the surface structure of mineral, pH and measurement method used, the contact angle of fluorite can be from 0 to 90° (Bakakin, 1960; Busscher et al., 1987; Janczuk et al., 1993;

Drzymala, 1994b; Zawala et al., 2007; Kowalczyk and Drzymala, 2011; Gao et al., 2012; Zhang et al., 2014; Table 1 of this work).

The second investigated in this work mineral was calcite. Calcite is a very common component of rocks. Its bulk structure and unit cell can be shown using either hexagonal or rhombohedral system (Muller et al., 2001). The hexagonal approach is preferred when atoms arrangement in the bulk is considered, while the rhombohedral crystal symmetry is used to emphasize perfect cleaving of calcite leading to rhombohedral pieces. Calcite has three perfect cleavage planes occurring along the three directions parallel to the rhombohedron form resulting in six-sided polyhedrons with diamond-shaped faces. The C and O atoms of the CO_3^{2-} groups form a stable carbonate ion, which does not split during cleaving. As a result of using either hexagonal or rhombohedral unit cell the planes and surfaces of calcite in literature are characterized by different Milliken-Bravais indices. For the same perfect cleaving leading to the rhombohedric piece of calcite, the cleaving planes have symbols: (10T1) (trigonal of hexagonal unit cell, acute rhombohedron) (Muller et al., 2001) (10T4), (trigonal lattice, cleavage rhombohedron) (de Leeuw and Parker, 1998; Mielczarski et al., 2006), (101) (hexagonal lattice – morphological unit cell) (Hazen, 2004), and (104) (hexagonal lattice – structural unit cell) (Hazen, 2004). Also the unit cells are different. Therefore, data presented in many scientific and popular publications, if not precisely explained, are to a great extent confusing.

The (10T4) surface of calcite contains both Ca^{2+} and CO_3^{2-} ions in the same layer (Fricke and Volmer, 2007). The surface consists of a closed-packed, non-polar arrangement of calcium and carbonate ions. Thus, a piece of calcite split along its perfect cleaving plane provides two identical (10T4) surfaces (Fig. 4). According to Fricke and Volkmer (2007), splitting calcite along other planes, especially the (00T1) and (01T2) planes (cleavage rhombohedron) (Fig. 4), is not likely because it would provide two highly polar and energetically unfavorable different surfaces. One surface would contain Ca^{2+} and the other CO_3^{2-} ions. Therefore, it is expected that the hydrophobicity of both calcite halves will be the same.

The data presented in Table 1 show that irrespective of the contact angle measurement technique, there is no difference in the advancing and receding contact angles on corresponding surfaces of calcite after splitting. It proves that splitting of calcite along its perfect cleaving plane provides two identical (10T4) surfaces.

Calcite, similarly to quartz, can be considered as either hydrophilic (Okayama et al., 1997) or hydrophobic mineral (Wu et al., 1996; Kowalczyk and Drzymala, 2011; Table 1 of this work). The value of water contact angle of calcite depends on the surface preparation prior experiment and method used. Wu et al. (1996) showed that the contact angle on the smooth and flat surface of calcite was 6° , while for ground calcite was 66° .

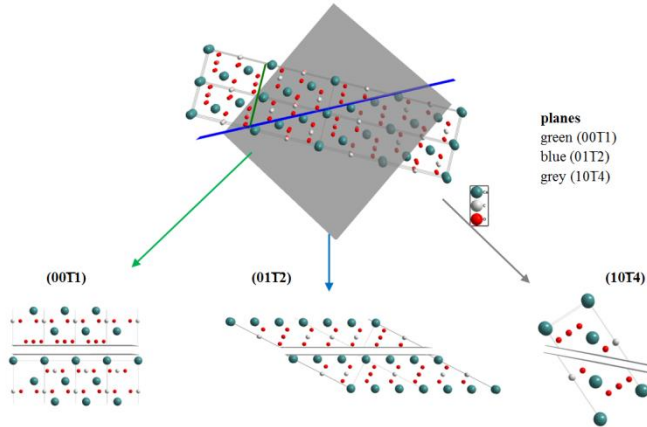


Fig. 4. Surfaces of calcite after cleaving along different planes. Splitting along (10T4) plane provides two identical surfaces, while cleaving along (00T1) and (01T2) gives different halves (one with Ca^{2+} ions and the other with CO_3^{2-} ions) (after Fricke and Volmer, 2007)

Mica is a phyllosilicate containing K, Na, Ca, Al, Mg, Fe, Mn etc., or shortly AB, with a general formula of $\text{AB}_{2-3}(\text{OH},\text{F})_2(\text{Si},\text{Al}_4\text{O}_{10})$. There are many types of mica with similar structures. The bulk and surface structure of micas are well known (Kuwahara, 2001). The structure of mica after Herder et al. (1988-1989) is shown in Fig. 5. Two surfaces obtained by cleaving mica along the (001) plane, which is the perfect cleaving plane, are always identical. It is proved by the contact angle measurements, because there is no difference between the advancing and receding contact angles on the corresponding surfaces of mica after cleavage (Table 1).

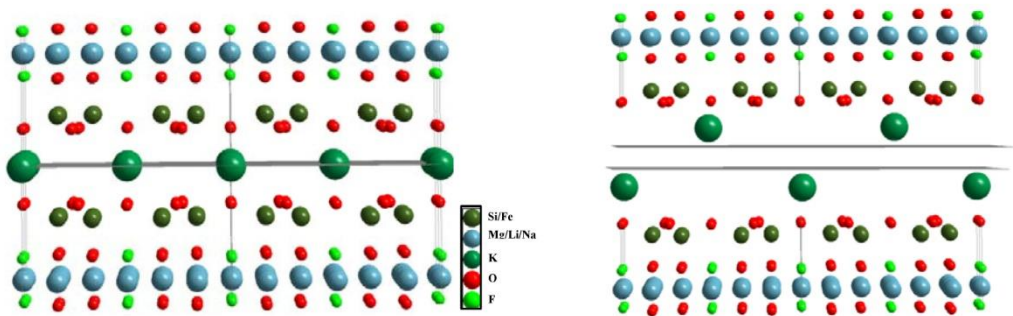


Fig. 5. Structure of mica (a) and two corresponding surfaces of mica after cleaving along the (001) plane (both halves are identical) (based on Herder et al., 1988-1989)

According to Zawala et al. (2008), in distilled water, there is no formation of the three-phase contact and attachment of bubble to the mica surface. It is caused by the electrostatic repulsion between negatively charged surfaces of mica and bubble

(Nishimura et al., 1992; Yang et al., 2001; Bueno-Tokunaga et al., 2015). It suggests that in distilled water mica is a hydrophilic mineral with zero contact angle. The obtained in this work values of both advancing and receding contact angles on corresponding surfaces (Table 1) indicate that the freshly produced halves of mica exhibit hydrophobic properties with the advancing and receding contact angles greater than zero (Table 1). The non-zero water contact angle of mica was also observed elsewhere (Bryant et al., 2006; Kowalczyk and Drzymala, 2011). Shang et al. (2008) showed that the water equilibrium and advancing contact angles measured by the sessile drop and Wilhelmy plate methods of the phyllosilicate minerals are greater than zero and vary from $41.9 \pm 2.5^\circ$ to $57.1 \pm 2.5^\circ$ for Ca-smectite, from $26.2 \pm 2.0^\circ$ to $29.3 \pm 2.2^\circ$ for Ca-kaolinite and from $24 \pm 3.2^\circ$ to $56.8 \pm 3.4^\circ$ for Ca-illite.

Table 1 also indicates, that irrespective of the contact angle measurements, there is a difference between advancing and receding contact angles for all used in this work minerals. It is not surprising since it is well known that the difference between contact angles, also called hysteresis, depends on many parameters including the method of measurement (Drelich et al., 1996; Montes Ruiz-Cabello et al., 2011; Eral et al., 2013; Kowalczyk and Drzymala, 2016).

Conclusions

Hydrophobicity of materials and their contact angles with water depend on many parameters including the solid surface composition. Theoretical considerations revealed that depending on the mineral crystallographic plane achieved by splitting a mineral into halves, the hydrophobicity of surfaces can be either identical or different due to the same or different chemical compositions of the surfaces. In the case of some minerals splitting along certain planes can provide different halves. It was experimentally shown that receding and advancing contact angles measured on the corresponding surfaces of fluorite, calcite and mica were identical for the sessile drop method. When the contact angle was measured by the captive bubble approach, there were small differences in the contact angles measured on the corresponding surfaces of fluorite. It was most probably due to surface irregularities and roughness, and therefore different times needed to rupture the liquid film between the bubble and solid surface.

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