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## Wettability of quartz particles at varying conditions on the basis of the measurement of relative wetting contact angles and their flotation behaviour

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**Abstract:** In this paper, on the basis of a modified Washburn equation, the squared incremental pressure due to liquid rising vs. time were measured instead of wicking distances before reaching equilibrium, and the relative wetting contact angles (RWCA) were applied to characterize the surface wettability of quartz particles conditioned at different concentrations of flotation reagents. Combined with the flotation experiments on quartz particles at corresponding conditions, the relationship between flotation recoveries and RWCA was analysed, which proves that RWCA can characterize the surface wettability of quartz particles accurately. The results also showed that the best reagent conditions for floating quartz are pH 12.0, a  $\text{Ca}^{2+}$  concentration of  $1 \times 10^{-3} \text{ mol/dm}^3$  and a sodium oleate concentration of  $0.75 \times 10^{-3} \text{ mol/dm}^3$ , where the recovery of quartz is 86%. The surface tension of the filtrate of the pulp was determined by a fully-automatic tensiometer as well. Based on the measured values of RWCA and surface tension, the free energy changes ( $\Delta G$ ) before and after the adhesion of bubbles and particles per unit area at corresponding situations were calculated, respectively. The trends of  $\Delta G$  varying with the concentrations of reagents were in close accordance with those of RWCA and the flotation recoveries, proving that it is more likely for particles having bigger contact angles to adhere to bubbles, resulting in a higher flotation recovery. These results give a more feasible and accurate approach to analysing the surface wettability and floatability of fine particles.

**Keywords:** relative wetting contact angle, Washburn technique, surface free energy, flotation behaviour, sodium oleate

### 1. Introduction

Wettability of a particle surface is of fundamental significance for flotation and is usually evaluated by the measurement of contact angle (Wei, 2015; Gao et al, 2017), which is considered primary data to describe the degree of wetting and to determine surface free energy (Gao et al, 2018a). Contact angle is of utmost importance in modern technological applications and material science, however, its measurement and interpretation still suffer from deficient experimental and theoretical protocols. Several key terms including advancing, receding, equilibrium and most stable contact angles, or simply contact angle are defined precisely based the accumulative knowledge from the surface chemistry community over the last decades (Marmur et al, 2017). It's very meaningful and should help to make data interpretation and comparison easier for researchers (Gao et al, 2017).

Although there are several theories and approaches to measuring the contact angle of a solid, the most well-developed of them are standard for flat surfaces of bulk solids, such as the optical method and the Wilhelmy technique (Chau, 2009; Budziak and Neumann, 1990; Rodriguez et al, 2002). In contrast, there are less developed direct methods to determine contact angles of powder solids; however, the pressing plate method and capillary penetration method are available.

While the pressing plate method is adopted, powders are pressed to a plate to prepare a smooth surface at first, and then the contact angle measurement methods suitable for bulk solid are applied to

the plate (Fort and Patterson, 1963; Zdziennicka et al, 2016). However, the results would always be unstable due to the difficulty of pressing samples to the plate with a perfectly flat surface as well as the intractable determination of a contact point for three phases. Hence, the pressing plate method introduces error during the measurement of contact angles on powder materials.

Regarding flotation practice, it cannot be ignored that the mineral particles conditioned in flotation pulp are on the micron scale, so they are undoubtedly typical powders (Gao et al, 2018b). In addition, by the action of flotation reagents, the surface tension of the filtrate of the pulp and the surface wettability of mineral particles are both changed, resulting in the varying contact angles of particles as well as their flotation behaviours. Undoubtedly, it is necessary to explore the varying trend of surface wettability of mineral particles conditioned in different flotation pulps systematically.

The capillary penetration method is another practical approach to measuring the contact angles on powdered solids developed by Washburn (1921). The measurement was achieved by recording the depth of the liquid front intrusion as a function of time, and then the contact angle can be calculated according to Washburn theory:

$$h^2 = \frac{(CR)\gamma\cos\theta}{2\eta}t \quad (1)$$

where C, R,  $\gamma$  and  $\eta$  are the capillary factor, effective capillary radius of powder column, surface tension of the liquid and viscosity of the liquid, respectively. As equation 1 shows, at a constant temperature, as well as assuming R to be constant, the squared depth of the liquid front intrusion (namely, the wicking distances) should be a linear function of time; indeed, the relationship between them has been thoroughly observed.

Burtell and Whitney (1932) along with Eley and Pepper (1946) were among the first to employ the Washburn equation for contact angle determinations in porous columns. Later, van Oss et al. developed a method called 'thin layer wicking' (1992), in which a thin layer of solid powder, instead of a particle column, was deposited on glass slides. This facilitates the penetration of the liquid into the layer, and a sharp visible progressing contact line can usually be seen.

In 1992, Emil Chibowski proposed an approach and wicking procedure to verify different forms of Washburn equations to describe four cases which were distinguished by the liquid and energetic states of a solid surface. His research showed that the linear relationship between  $h^2$  and  $t$  was valid only in a limited range, and the solid surface free energy from the contact angle values were similar to those obtained via contact angles measured on a smooth solid surface. Later, Lucyna (1998) used thin layer wicking to determine energy change for a bare surface,  $\Delta G_b$  and that for a surface covered with a film (pre-contacted),  $\Delta G_p$ , finding their difference was equal to the difference in the works of adhesion. Lucyna's study also illustrated that the determined values of energy change were not influenced by the thickness of the layer and were similar to those measured on a smooth solid surface.

Based on the overview by Emil Chibowski in his paper published in 2002, formulation and determination of surface free energy is still a very debatable issue; however, as long as no method for the determination of its real quantities is known, even relative values charged with many simplified assumptions are very beneficial to understanding the wetting processes.

Another problem in the measurement of wicking distances is that the liquid does not always rise horizontally in the testing procedure due to the inequality of the packing density at different positions in the powders bed. So, it is difficult to measure the liquid rising height accurately, which might generate greater error. Some studies recorded the weight gained by the porous layer vs. time (Holysz, 1996; Siebold, 1997) instead of the wicking distances, applying a modified Washburn equation:

$$w^2 = c \frac{\rho^2 t}{\eta} \gamma_1 \cos\theta \quad (2)$$

As we can understand, when the wetting liquid penetrates upward vertically through a compressed powder cake, the pressure will increase continuously until the capillary pressure balances the weight of the liquid in the column. The static capillary pressure technique (SCPT) for contact angle measurement applies the relationship between the sum of the Laplace pressure,  $\Delta p$ , and the contact angle of the liquid against the solid:

$$\Delta P = \frac{2\gamma_{lv}}{r} \cos\theta \quad (3)$$

where  $\Delta P$  is the pressure difference,  $\gamma_{lv}$  is the surface tension of liquid,  $\theta$  is the contact angle, and  $r$  is the effective capillary radius. This technique was originally proposed by Bartell and co-workers (1932), and has been elegantly extended by White (1982), yielding the Laplace-White equation, which is a strict expression for  $\Delta P$  in porous media, given as:

$$(\Delta P)^2 = \frac{\gamma_{lv} \cos \theta \Phi A}{(1-\Phi)} \quad (4)$$

Later, the capillary pressure method was well applied by David Diggins, John Ralston and co-workers, illustrated as follows. In 1990, they set up a simple experimental apparatus to determine the contact angle as well as the specific surface area of angular quartz particles, covering a wide range of wetting situations: hydrophilic and hydrophobic particles wetted by water and a variety of organic liquids. Their research results show that the values for contact angle obtained from the proposed equipment are reliable and reproducible. Moreover, in 2009, Nate Stevens and John Ralston et al. performed capillary pressure measurements with advancing as well as receding liquids, proposing a new methodology to derive advancing and receding contact angles, respectively, and applied it successfully to various real particulate systems, such as hydrophobic chalcopyrite particles and hydrophilic quartz particles.

The successful application of SCPT to determine the contact angle of crushed irregular mineral particles motivates us to utilize this kind of method to characterize the wettability of mineral particles conditioned in a real flotation pulp, because the wetting liquids reported in related documents are not various enough to represent the wetting situations for a real flotation process.

There is another phenomenon worth noting for researchers, that is, the pressure during the dynamic measuring process of liquid penetrating through the powdered bed can similarly be measured dynamically, provided that the top of tube in which powders are packed is sealed and connected to a pressure sensor. The incremental pressure,  $\Delta p$ , is linearly related to  $h$  by the equation:

$$\Delta p = \rho gh \quad (5)$$

Combining equation 1 and equation 5 obtains another modified Washburn equation:

$$(\Delta p)^2 = \frac{\beta \gamma \cos \theta}{\eta} t \quad (6)$$

where  $\beta = \frac{CR(\rho g)^2}{2}$ , and it is related to  $C$ ,  $R$  and  $\rho$  (the density of the wetting liquid).

In light of the fact that  $CR$  can be considered a constant when the packing density of the powders is the same,  $\beta$  is also invariable when the wetting liquid is maintained the same throughout the whole measuring procedure. Therefore,  $\beta$  is also a constant, accordingly. Similarly,  $\gamma$  and  $\eta$  are also invariable when the same wetting liquid is adopted. Therefore, there is a linear correlation between  $(\Delta p)^2$  and  $t$ , and the slope  $K$  can be calculated by:

$$K = \beta \gamma \cos \theta / \eta \quad (7)$$

Obviously, the wettability differences of powders with various surface properties could be indicated by the differences in the slopes when an identical liquid is adopted for wetting. Accordingly,  $K$  and  $\cos \theta$  for different surfaces can be related by:

$$\frac{K_0}{K_i} = \frac{\cos \theta_0}{\cos \theta_i} \quad (8)$$

As equation 8 shows, the actual value of contact angle can be calculated on the basis that there is a kind of liquid that can make one of the surfaces of the powders wet entirely. Thus, it could be assumed that the contact angle is  $0^\circ$  at this case. However, in practice and research work, it is an intractable problem to find a liquid that could wet a solid completely.

Relative wetting contact angle (RWCA) was first mentioned by Ai et al. (2001), as there is no necessity to determine the absolute values of contact angles of solid particles in many situations. The contact angle of powders that have the maximum slope  $K_0$  can be assumed as  $0^\circ$ . The relative wetting contact angles of other powers can be calculated by the equation:

$$\theta_i = \arccos \left( \frac{K_i}{K_0} \right) \quad (9)$$

According to our expectation, the relative wetting contact angles of particles conditioned at varying concentrations of flotation reagents can be calculated from equation 9 to compare the differences in

surface wettability of particles, which would be undoubtedly meaningful for research on mineral flotation.

Generally, the measurement of contact angles based on Washburn's theory has been widely used in the fields of material modification (Yang et al., 2014) and water pollution (Wei, 2005), where RWCA values of many materials and sediments can be determined to characterize their surface properties more objectively and accurately. The measurement method of RWCA makes it possible to characterize the varying of surface wettability of mineral particles which would be conditioned in the flotation pulp with different concentrations of reagents.

For various ores, quartz is the main gangue which needs to be separated by flotation from objective minerals, such as iron, phosphate, and bauxite, etc. Therefore, it is of fundamental significance to investigate its wettability as well as its flotation behaviours. In addition to traditional flotation reagents, there are great numbers of researchers (Liu et al., 2018) focus on developing efficient reagents to improve the flotation effect.

The main purpose of the present study is to apply capillary pressure measurements to derive RWCA values of quartz particles conditioned in different situations for judging whether it can be applied to illustrate the wettability of mineral particles more intuitively. So, flotation experiments on quartz were conducted systematically in the corresponding situations. Moreover, the free energy changes before and after the adhesion of particles and bubbles were calculated from RWCA, as well as the surface tension of the filtrate of the pulp, to reveal the differences in the surface properties of quartz particles in various situations as well as the influence on the flotation behaviours of quartz from the thermodynamic point of view.

## 2. Materials and methods

### 2.1. Minerals and reagents

The quartz samples were provided by Anshan Steel, China. First, the samples were broken to -2 mm by a jaw crusher, and then were ground to -0.1 mm by a ceramic ball mill. After grinding, the particles were dehydrated, and then were soaked three times with 5% hydrochloric acid solution, for which the liquid-solid ratio is 3:1, lasting 24 h each time. Finally, the pure quartz particles were prepared after being washed until neutral by distilled water. The elemental analysis and X-ray Diffraction (XRD) results of the quartz samples are shown in Table 1 and Fig. 1, respectively.

Table 1 Elemental analysis of quartz

Components	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe	Mg	MgO
Content (%)	99.5	0.33	<0.001	0.001	---

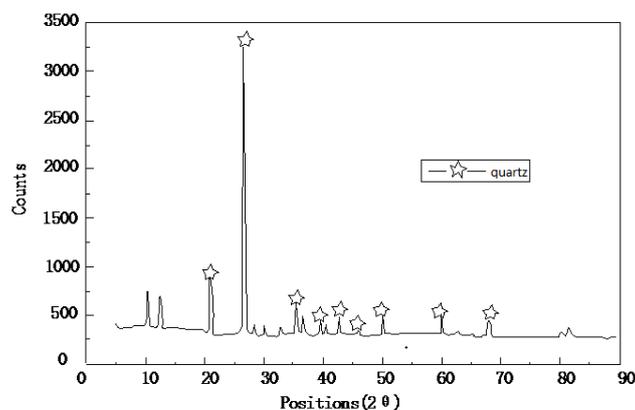


Fig. 1. XRD analysis of quartz sample

The content of SiO<sub>2</sub> is 99.5%, which meets the requirements of the flotation experiment for a single mineral.

The prepared quartz samples were further screened to the range of  $-0.074+0.045$  mm for carrying out the flotation experiment and determining the relative wetting contact angle. Analytical reagents, including deionized water, sodium hydroxide, calcium chloride and chemically pure sodium oleate, were used in the flotation experiments with quartz.

## 2.2. Experimental method

### 2.2.1. The measurement of the relative wetting contact angle of quartz

A commercial contact angle measuring instrument (JF99A) with a special powder column preparation device was used to determine the relative wetting contact angle. The instability of the measurement value caused by the difference of the powder column property can be effectively avoided.

Quartz particles were conditioned at varying flotation pulps, except aeration, and then the pulps were filtered and dried, preparing samples for the measurement of the relative wetting contact angle. Meanwhile, the filtrate of the pulp was placed in an incubator at a constant temperature of  $35\text{ }^{\circ}\text{C}$  for the determination of surface tension.

The measurement of relative wetting contact angle comprised the following steps: 2.5 g samples were loaded into the quartz tube and then compacted by the sampling machine, followed by pressing the tube by a seal cap which is loaded with a pressure sensor. A beaker with deionized water was placed beneath the quartz tube, and a syringe was carefully used to remove some tiny bubbles generated between the quartz tube and water to avoid it affecting measurement results. Finally, the instrument and computer programme were opened, and the option was chosen to connect them. So far, the differential pressure,  $\Delta p$ , could be derived with the continuous recording of a sample for 800 seconds.

### 2.2.2. The flotation experiment with quartz

The flotation experiment with quartz was carried out in a 5-35 g XFGCII aeration flotation cell, with 5 g samples and 250 mL of deionized water at  $35\text{ }^{\circ}\text{C}$ . The cell was mechanically agitated, and the rotation speed of the impellers was adjusted to 996 r/min. The required volume of sodium hydroxide (used as a pH modifier), calcium chloride (activator) and sodium oleate (collector) were added to the pulp in sequence with agitation for 2 minutes after each addition. The aeration rate was chosen at  $0.15\text{ dm}^3/\text{min}$ , and froth was collected for 4 minutes. Finally, the froth was dried and weighed to calculate the flotation recovery of the quartz.

### 2.2.3. The measurement of surface tension of the filtrate of the pulp

The surface tension of filtrate was determined by a fully-automatic tensiometer (JK99A). First, corresponding parameters were set that were appropriate for the measurement. The filtrates of flotation pulps were poured into beakers, and a platinum plate loaded with a sensor was controlled to drop vertically until immersed in the filtrate. So far, the measurement of surface tension could be carried out.

### 2.2.4. Calculation of free energy change based on relative wetting contact angle and surface tension

When the particles and bubbles adhere to each other per unit area, providing the bubble remains spherical, the change of free energy,  $\Delta G$ , is related to the surface tension at the liquid-gas interface,  $\gamma_{l-g}$ , and the contact angle,  $\theta$ , by:

$$-\Delta G = \gamma_{l-g}(1 - \cos \theta) \quad (10)$$

Here,  $\gamma_{l-g}$  is equal to the surface tension of the liquid, so  $\Delta G$  can be calculated from the values of surface tension and relative wetting contact angle measured before.

## 3. Results and discussion

### 3.1. RWCA and flotation behaviours of quartz at different pH values

The flotation tests were carried out on quartz samples at six pH values, 8, 9, 10, 11, 12 and 13, by adding different amounts of sodium hydroxide. It has been proven by many studies that quartz has almost no floatability in acidic conditions containing  $\text{Ca}^{2+}$ . Only in alkaline solution, especially when the value of

pH is from 10 to 12,  $\text{Ca}^{2+}$  can adsorb on a quartz surface in the form of a hydroxyl complex or hydroxide precipitation, which makes it possible for sodium oleate to be adsorbed on the quartz surface correspondingly.

During the investigation of the effect of pH value on the RWCA of quartz, the concentrations of calcium chloride and sodium oleate were both  $1 \times 10^{-3}$  mol/dm<sup>3</sup>. Fig.2 shows how the squared incremental pressure varied with time.

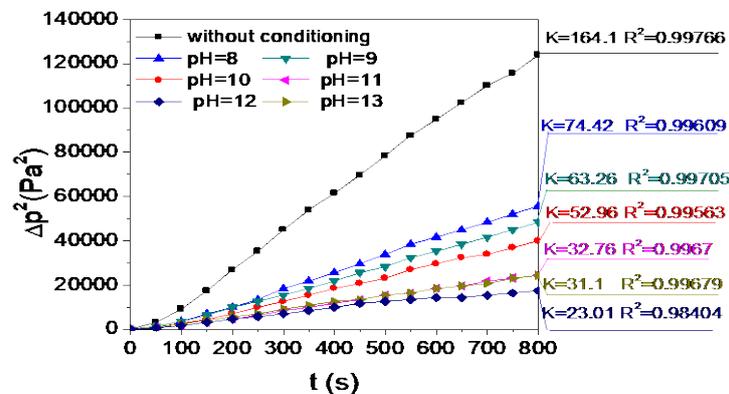


Fig. 2. Relationship between  $(\Delta p)^2$  and  $t$  at different pH values

Fig. 2 shows that the larger the pH value, the slower the squared incremental pressure changes, reflecting the slower the penetration speed of the liquid through the powder column. In other words, when the pH varies, there are remarkable differences in the seepage velocities of deionized water through the corresponding quartz particle column. Specifically, it is fairly fast when the pH of the flotation pulp is lower, and the linear relationship is significant. While the pH value increases to 11, it decreases distinctly, and the uniform variation of  $(\Delta p)^2$  with time is obvious only within 400 s, after which, it slows down, especially when pH value increases to 12. Thus, with invariable concentrations of the activator and collector, the action between the quartz surface and this activator and collector could be enhanced by increasing the pH value, resulting in the increased hydrophobicity of the quartz particles.

According to the results above, assuming that the relative wetting contact angle of quartz samples without conditioning is  $0^\circ$ , for the seepage velocity of the liquid at this situation is the fastest that can be found in Fig. 2. Thus, those of other samples can be calculated by equation 9. The RWCA and flotation recoveries in corresponding situations are depicted in Fig. 3.

As illustrated clearly in Fig. 3, the relative wetting contact angles of quartz particles increase with the increasing pH value from 8 to 12, which is highly consistent with the change rule of flotation recoveries of particles, proving that the surface wettability of quartz particles can be adjusted by the pH of the pulp and affect flotation behaviours correspondingly. The pH value of the pulp has a significant influence on flotation behaviours of quartz. In the pH range from 8 to 9, recoveries of quartz are very slow. However, the recovery rises rapidly with increasing of pH and reaches a peak at 12, followed by a decrease at pH 13. Therefore, the interaction between the surface of quartz particles and sodium oleate does reach the strongest in the pH range from 10 to 12, as reported by relevant studies.

### 3.2. RWCA and floatation behaviours of quartz at different concentrations of $\text{Ca}^{2+}$

For the sake of investigating the effects of the concentration of  $\text{Ca}^{2+}$  on RWCA and the flotation behaviours of quartz, the concentration of calcium chloride in the pulp was varied from 0 to  $1.25 \times 10^{-3}$  mol/dm<sup>3</sup>, at a constant pH value (12) and invariable concentration of sodium oleate ( $1 \times 10^{-3}$  mol/dm<sup>3</sup>). Fig. 4 shows how the squared incremental pressure changes with time at different concentrations of  $\text{Ca}^{2+}$ .

As shown in Fig. 4, the concentration of  $\text{Ca}^{2+}$  also has a significant influence on the penetration speed of the liquid. The higher the concentration of  $\text{Ca}^{2+}$ , the slower the squared incremental pressure changes as well as the penetration speed of liquid. This reflects that the concentration of  $\text{Ca}^{2+}$  does affect the surface wettability of quartz powders strongly with the action of sodium oleate. When the concentration

is higher than  $0.5 \times 10^{-3} \text{ mol/dm}^3$ , the penetration speed of the liquid declines continuously, and the uniform linear variation trend of  $(\Delta p)^2$  with time is obvious only within 500 s; after that, it levels out.

Similarly, the RWCA of quartz particles at varying conditions combined with flotation recoveries are shown in Fig. 5. The varying trend of relative wetting contact angles of quartz powders with concentration of  $\text{Ca}^{2+}$  is also consistent with the change rule of recovery, showing that the concentration of  $\text{Ca}^{2+}$  in the pulp benefits the adjustment of the surface properties of quartz particles and affects their flotation behaviours as well. The flotation recovery of quartz is low when the concentration of  $\text{Ca}^{2+}$  is less than  $0.25 \times 10^{-3} \text{ mol/dm}^3$ , but increases rapidly and reaches a peak at  $1 \times 10^{-3} \text{ mol/dm}^3$ . Therefore, it can be concluded that high recovery could be achieved at a suitable concentration of  $\text{Ca}^{2+}$  when sodium oleate is used to collect quartz.

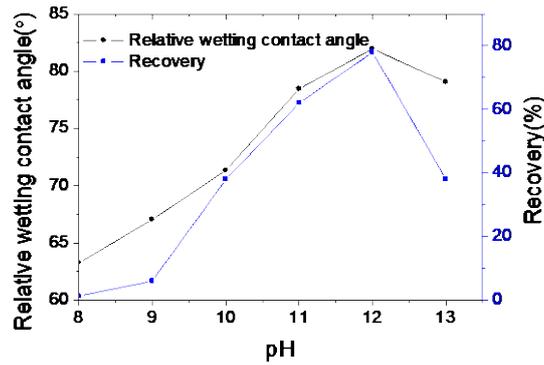


Fig. 3. Relative contact angles and recoveries of quartz at different pH values

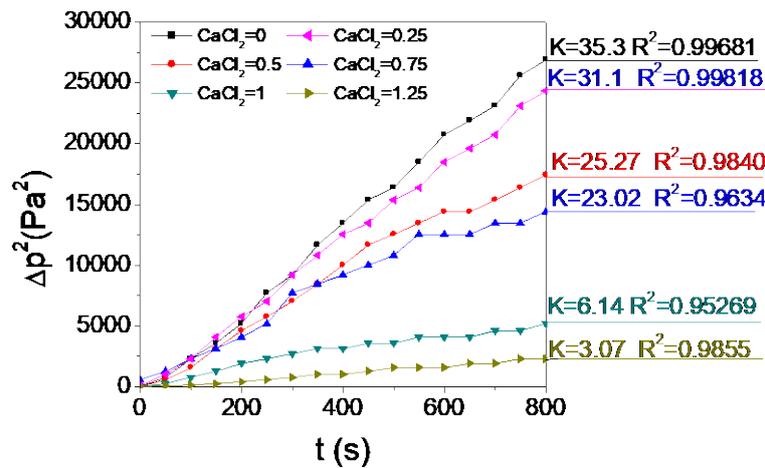


Fig. 4. Change of  $(\Delta p)^2$  with time at different concentrations of  $\text{Ca}^{2+}$

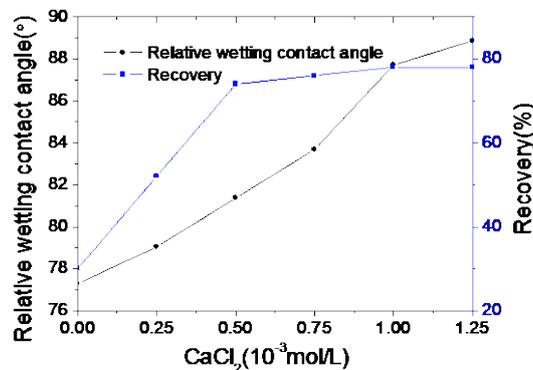


Fig. 5. Relative wetting contact angles and recoveries of quartz at different  $\text{Ca}^{2+}$  concentrations

Regarding the mechanisms of the interaction between  $\text{Ca}^{2+}$  and the quartz surface, Fuerstenau (1965) indicated that  $\text{Ca}(\text{OH})^+$  could be adsorbed on the surface of quartz. However, Wang and Hu (1988) assumed that  $\text{Ca}(\text{OH})_2$  was the more active ingredient according to the calculation of flotation solution chemistry at the pH values at which quartz particles can float. Lately the Zeta potentials of quartz conditioned at different concentrations of  $\text{Ca}^{2+}$  were determined by Kou et al. (2015), showing that the Zeta potential of quartz shifted to positive with the addition of  $\text{Ca}^{2+}$ . So, the anionic sodium oleate was more easily adsorbed on the quartz surface. In short, the greater the concentration of  $\text{Ca}^{2+}$ , the more obvious the increase of Zeta potential and the higher the flotation recovery obtained, correspondingly.

**3.3. RWCA and floatation behaviours of quartz at different concentrations of sodium oleate**

To investigate the effects of the concentration of sodium oleate on RWCA as well as the flotation behaviours of quartz, different amounts of sodium oleate were added to the pulp at a constant pH value (12) and invariable concentration of  $\text{Ca}^{2+}$  ( $1 \times 10^{-3} \text{ mol/dm}^3$ ). The relationship between the squared incremental pressure and time at varying concentrations of sodium oleate is presented in Fig. 6.

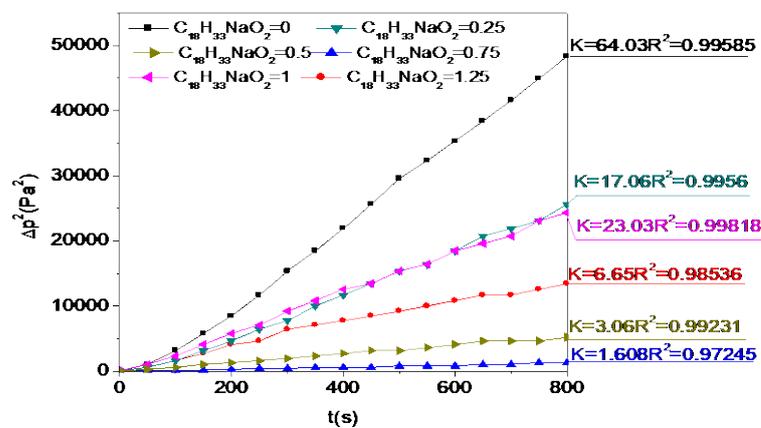


Fig. 6. Change of  $(\Delta p)^2$  with time at different concentrations of sodium oleate

Fig. 6 shows that the squared incremental pressure without adding sodium oleate rises more quickly than those of other situations. That is, the seepage velocity of liquid at this situation is the highest. By adding some amount of sodium oleate, seepage velocity drops evidently, but, when the concentration of sodium oleate exceeds  $0.75 \times 10^{-3} \text{ mol/dm}^3$ , it increases again and levels out with time slowly. This phenomenon indicates that the wettability of the quartz surface declines with the increasing concentration of sodium oleate until it reaches a certain value, followed by a fluctuation.

The relative wetting contact angles of quartz samples conditioned at different concentrations of sodium oleate can be calculated accordingly, with a contrast to flotation recoveries also given in Fig. 7.

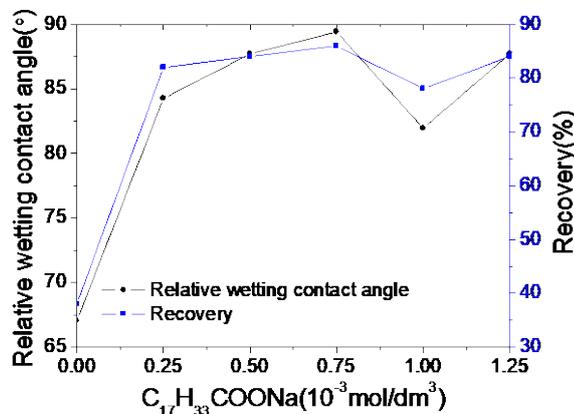


Fig. 7. Relative contact angles and recoveries of quartz at different concentrations of sodium oleate

The varying trend of relative wetting contact angles of quartz particles with changing concentrations of sodium oleate were almost consistent with the change rule of recoveries, as shown in Fig. 7, showing that the concentration of this kind of anionic collector has a remarkable influence on the floating quartz particles as well as regulating their surface properties. That is, when the concentration of sodium oleate changes from 0 to  $0.25 \times 10^{-3}$  mol/dm<sup>3</sup>, the flotation recovery and relative wetting contact angle of quartz surges, then climbs slowly with its increase until it reaches  $0.75 \times 10^{-3}$  mol/dm<sup>3</sup>; later, the recovery of quartz decreases as these values increase.

A few decades ago, Qiu and Guo concluded that the solubility product of calcium oleate was much smaller than that of calcium hydroxide. So, the excessive addition of sodium oleate was likely to result in lower content of calcium oleate being adsorbed on the quartz surface, contributing to the decrease of recovery (1965). In contrast, Shi et al. considered that it was the semi micelle reverse adsorption of sodium oleate that leads to the decrease of flotation recovery of quartz, as the concentration of sodium oleate was too high (2001).

Generally, it can be found through Fig. 2, Fig. 4 and Fig. 6 that there is a significant linear relationship between  $(\Delta p)^2$  and  $t$  measured by capillary pressure measurements. There are remarkable differences between the seepage speeds of liquid through the quartz particles column conditioned in different situations as well, showing corresponding differences in surface wettability.

According to the RWCA of quartz particles and the corresponding flotation recoveries in varying situations (as shown in Fig. 3, Fig. 5 and Fig. 7), it can be concluded that the bigger the RWCA of quartz particles, the higher their flotation recovery, indicating that RWCA measured by the capillary pressure technique can characterize the surface wettability of powders accurately and make it more convenient to compare the differences in wettability of particles in varying situations.

These figures mentioned above also show that the surface of quartz particles are more easily activated by Ca<sup>2+</sup> at pH 12, with a Ca<sup>2+</sup> concentration of  $1 \times 10^{-3}$  mol/dm<sup>3</sup> and a sodium oleate concentration of  $0.75 \times 10^{-3}$  mol/dm<sup>3</sup>; the RWCA of quartz in this situation is the largest, its floatability is the strongest, and its flotation recovery is the highest.

### 3.4. The surface tension of the filtrate of flotation pulp and relative free energy change in different situations

The relative free energy change ( $\Delta G$ ) of the flotation system is always used to measure the degree of adhesion between bubbles and particles. The surface tension of the filtrate,  $\gamma$ , and the values of  $\Delta G$  computed correspondingly are shown in Figs. 8 - 10.

As these figures show, the value of  $\Delta G$  rises with the increase of pH, and reaches a maximum at pH 12, and then declines. It also rises with the increase of the concentration of Ca<sup>2+</sup> similarly at a constant pH value and invariable concentration of sodium oleate. When pH and the concentration of Ca<sup>2+</sup> are constant, it increases first with the increasing concentration of sodium oleate but declines when it exceeds  $0.75 \times 10^{-3}$  mol/dm<sup>3</sup>. Undoubtedly, the varying of the value of  $\Delta G$  is in good accordance with the changes of RWCA of quartz particles as well as their flotation recoveries.

According to our understanding, the contact angle is positively related to the change of free energy before and after the adhesion of bubbles and particles and is related to the flotation recovery. According to the second law of thermodynamics, particles with strong hydrophobicity more easily adhere to bubbles and float with them, so their flotation results improve, explaining how the surface wettability of particles influences flotation behaviours.

As illustrated above, the surface tension of the filtrate increases first and then decreases with the varying of pH when the concentrations of Ca<sup>2+</sup> and sodium oleate are constant, but it rises with the increase of the concentration of Ca<sup>2+</sup> at an invariable pH value and concentration of sodium oleate. However, it decreases first and then increases with the rising of the concentration of sodium oleate when the other factors are constant.

The relationship between surface tension of the filtrate and the recovery of particles is complicated. On one hand, the greater the surface tension, the greater the change of free energy of the whole system and the more liable the adhesion of particles and bubbles may be, judging by equation 10. On the other hand, the surface tension affects the size of bubbles generated in the pulp as well as their stability remarkably, just as some findings that reduced surface tension restrains bubbles from merging to keep

small bubbles stable (Deng, 2014). Further investigations need to be conducted systemically to determine the whole effect of surface tension on flotation performance as well as bubble conditions.

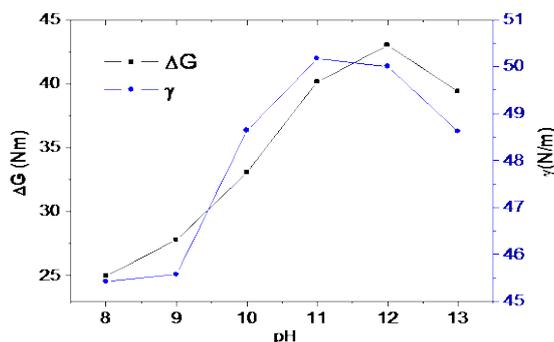


Fig. 8. Surface tension of the filtrate and ΔG at different pH values

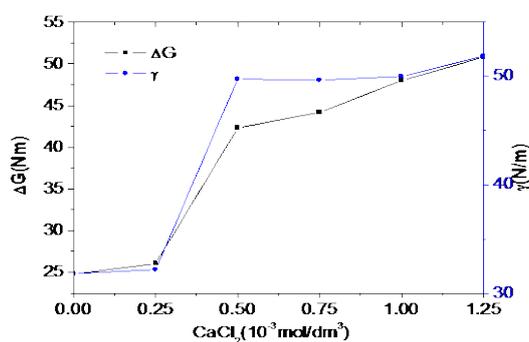


Fig. 9. Surface tension of the filtrate and ΔG at different concentrations of Ca<sup>2+</sup>

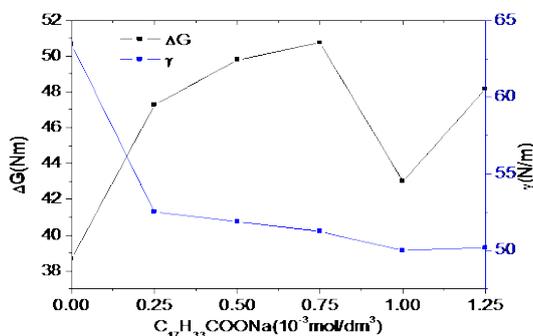


Fig. 10. Surface tension of the filtrate and ΔG at different concentrations of sodium oleate

A point worth noting is that when the concentrations of Ca<sup>2+</sup> and sodium oleate are 1.25 × 10<sup>-3</sup> mol/dm<sup>3</sup> and 1 × 10<sup>-3</sup> mol/dm<sup>3</sup>, respectively, the relative wetting contact angle of quartz is 87.89°, which is greater than that of quartz conditioned at 1 × 10<sup>-3</sup> mol/dm<sup>3</sup> Ca<sup>2+</sup> and 1.25 × 10<sup>-3</sup> mol/dm<sup>3</sup> sodium oleate. However, their corresponding recoveries are 78% and 84%. This phenomenon is possibly caused by the fact that the solution property affects the action status between bubbles and particles, indicating that the role of bubbles should not be ignored, although the surface wettability of particles plays a fairly marked role in the floating process.

#### 4. Conclusions

(1) The relative wetting contact angles (RWCA) based on a modified Washburn technique were validated to characterize the surface wettability of quartz particles ranging from 0.045 mm to 0.074 mm accurately, as the flotation recovery of quartz had markedly positive correspondence to them.

(2) The changes of the value of  $\Delta G$  calculated from RWCA and the surface tension are also in accordance with those of RWCA and flotation recoveries, proving that particles with larger contact angles are more inclined to adhere to bubbles, resulting in a higher flotation recovery. However, it should be kept in mind that neither RWCA nor the value of  $\Delta G$  are absolute values, so the present simplified method is qualitatively useful.

(3) The surface tension of the filtrate of the flotation pulp influences the free energy change as well as the status of bubbles, leading to a comprehensive variance of flotation recoveries of quartz particles. Further tests to investigate its influence on flotation performance as well as bubbles should be carried out more thoroughly by reliable methods.

(4) The suitable concentrations of flotation reagents were determined by flotation experiments with quartz particles  $-0.074+0.045$  mm in size, providing a reference for the reverse flotation practice for ores, in which the gangue minerals are mainly quartz and sodium oleate is adopted as the collector.

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