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THE SiO_2-H_2O INTERFACE AND EFFECTS ON QUARTZ ACTIVATION IN FLOTATION SYSTEM①

Sun, Zhongxi, Willis, Forsling
Luleå University of Technology, S−951 87 Luleå, Sweden
Chen, Jin
Central South University of Technology, Changsha 410083, China

ABSTRACT

The correlation between surface complexation at the SiO_2-H_2O interface and quartz flotation behavior was studied. Computer assisted calculations, using the programs SOLGASWATER, were adapted in order to construct distribution diagrams of surface speciation in the SiO_2-metal ion-H^+ system in aqueous solutions. Equilibrium constants for both surface and solution reactions were introduced in the composition matrix. Surface complexation, surface charge as well as flotation results were compared and a good agreement was obtained. Furthermore, flotation mechanisms of quartz activation by common metal ions like Ca^{2+}, Mg^{2+}, Fe^{3+} are quantitatively discussed based on the surface reaction equilibrium constants.

Key words: surface complexation Sio_2−H_2O interface quartz flotation

1 INTRODUCTION

It is well known that quartz is a typical gangue mineral in many flotation systems. Although it possesses hydrophilic surface properties in nature, hydrophobicity can be induced either by adding multivalent metal ions and anion collectors or cation collectors to the system. The study of quartz activation by metal ions in flotation system is an important subject due to its influence on the quality of industrial minerals. Although many research papers[1−8] have been devoted to this topic in the past decades, the explanation of activation mechanisms is not clear yet. It is found that the activation behavior of quartz, by various metal ions, is pH dependent and the optimum activation corresponds to the pH interval of metal ion hydrolysis. Based on these findings the activation mechanisms have been explained by some researchers as a result of metal ion hydrolysis in solution. However, solution and surface reactions are different and the action of surface complexation in this system remains to be investigated.

On the other hand, the complexation of amorphous silica and silica gel in aqueous solution have been widely studied, and the acid-base properties of amorphous silica with related equilibrium constants have been determined. The reactive part of the aqueous quartz mineral is the hydrated surface functional group. Thus, the reaction mechanism of quartz resembles to that of amorphous silica,

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as the functional groups of quartz and amorphous silica are the same. The aim of this study is to apply the knowledge of surface complexation for amorphous silica to provide a quantitative interpretation of the activation behavior of quartz by common metal ions like the ferric, calcium and magnesium ions in a flotation system and elucidate their mechanisms.

2 BACKGROUND

In aqueous solutions, there is a disturbed layer on the quartz surface which resembles to the properties of amorphous silica. In the case of the amorphous silica surface, it has been shown that protonation and deprotonation of surface hydroxyl groups take place. The reactions are expressed as follows:

$$\equiv SiOH_2^+ \rightleftharpoons SiOH + H^+ \quad (1)$$

$$\equiv SiOH \rightleftharpoons SiO^- + H^+ \quad (2)$$

The surface group $\equiv$ SiOH acts as a base when it adsorbs protons from aqueous solutions but it may also act as a Bronsted acid by proton release. In addition, surface charge is developed by protonation and deprotonation of amphoteric surface sites, $\equiv$ SiOH, through the above reactions. Protons released from the surface are distinguished from H^+ (aq) due to the inequality in elecrical potential between surface and solution. Ψo, which results in a difference in chemical potential of the proton and hence in its activity. This amounts to the work required to move the proton through the potential gradient from bulk solution to the surface, thus

$$k_1 = [\equiv SiOH] \cdot [H^+] \cdot e^{(F\Psi_0/RT)} / [\equiv SiOH^+] \quad (3)$$

$$k_2 = [\equiv SiO^-] \cdot [H^+] \cdot e^{(-F\Psi_0/RT)} / [\equiv SiOH] \quad (4)$$

where F denotes the Faraday constant, and R is the gas constant. Acidity constants of amorphous silica can be found in references [9] and [10].

In the presence of metal ions, metal-surface complexes can be formed on the surface in a similar way as metal silica to complexes in the bulk solution. Stability constants of some metal-amorphous silica surface complexes have been determined by Schindler et al[11]

In the absence of metal ions, the quartz surface is charged at $pH > 2^{[1]}$. Owing to the repulsive force of the electric double layer at the quartz surface, an anion collector like oleate can not be absorbed at the surface. However, in the presence of certain amount of metal ions, the quartz surface may become neutral or even positively charged by the formation of metal ion-surface complexes. In that case the obstacle for anion collector adsorption is removed. The metal-surface binary and metal-surface-collector ternary complexes are certainly involved in the quartzs activation flotation system.

Surface charge is an important parameter in quartz flotation. Multivalent metal ions can be specifically absorbed on quartz surface, i. e. enter the inner Helmholtz layer and form surface complexes. Therefore the surface electtrokinetic properties are dramatically changed due to surface charge neutralization. It is well known that in quartz flotation, cation collectors are adsorbed on negatively charged surface and anion collectors are adsorbed on a positively charged surface activated by metal ions. Both the surface proton reaction and metal ion speciation are known to be pH dependent, leading to various surface charges. Thus the surface charge is controlled by the surface complexation.

Surface hydrophobicity is the key condition for mineral floatability. Due to the natural hydrophobicity of quartz, hydrophobic substances like cation or anion collectors have to be introduced to create the condition of quartz surface hydrophobicity. Oleate is a typical anion collector in quartz flotation. The pH value of oleate is about 5, which means that oleate anions are the dominating species in the neutral and alkaline pH regions. The behavior of oleate reactions with quartz surfaces can be attributed to surface complexation, where the activated quartz surface acts as a Lewis acid and oleate as a ligand or Lewis base.

3 EXPERIMENTAL

Pure quartz samples were prepared by grinding quartz crystals in a porcelain ball mill. After grinding, $-75+45$ μm was screened out for acid treatment. The boiling 6 mol / L HCl was used to rinse the quartz sample for 30 min. After acid treatment, the sample was washed repeatedly by doubly distilled water until the solution pH, and conductance did not change and no chloride ions could be detected by addition of $AgNO_3$. The sample was then dried naturally. This sample contains impurities less than 0. 02% . The specific surface area is 0. 027 m^2 / g, as determined by the B. E. T. method.

All chemicals were reagent grade and used without further purification. Doubly distilled water was used to prepare the required solutions throughout the entire study dilute HCl or NaOH was used to adjust the solution pH.

The flotation cell (type XFG–63) volume was 100 mL, 1,700 r / min speed was maintained during the experiments. 5 g sample was used for each test. The conditioning time after adding each reagent was 5 min. Pulp pH was measured by a pH meter. After flotation the concentrates were dried and weighed, and the flotation recovery of quartz was calculated by the weight percentage of the concentrates.

Zeta potential was determined using electro-osmosis equipment. A salt bridge was made of saturated potassium chloride and condensed agar solution with a concentation of 30 g / L. The sample was put into a U type glass test tube and centrifuged for 20 min at 2,500 r / min. Before centrifuging the conductance and pH of the solution were measured using conductivty and pH meters respectively. Each sample was 2. 5 g.

The temperature in all experiments was maintained at around 20 ℃.

The quantity of surface binding sites of the quartz sample was calculated with reference to the concentration of surface hydroxyl groups at the amorphous silica surface [11, 12] (5 / 100 A), and was found to be 1.11×10^{-5} mol / L (50 g / L and 0. 027 m^2 / g).

All the surface and solution species with equilibrium constants were defined and introduced in a composition matrix, at conditions similar to the flotation experiments. Using the computer program SOLGASWATER[13,14] the concentrations of all the solution and surface species were calculated. The theoretical distribution of species at optimum flotation conditions was used to evaluate activation mechanisms for metal ions.

In the composition matrix of SOLGASWATER, solutes are divided into components and complexes, the components being the smallest number of pure substances required for a rigorous description of the composition of the system. Every species in the system is defined before the calculations. A formation constant, K_f, is tested for each species together with its component included in the system. The quantity can be expressed as the total phases. Although sometimes it may be advantageous to state the activity of a free component, instead of the total concentration, e. g. pH. When the equilibrium composition of the system has been calculated at the specified points, the results can be extracted in the form of tables and graphs. When the results are calculated, one can select either ± lg (a) or ± lg (T_c) as axes for graphical presentation.

The distribution diagram used here is the fraction of different surface species plotted against pH of the suspension. Information about the change of species fraction with varying solution pH is clearly exhibited. Surface characteristics such as acid-base and ion exchange properties are also reflected in the distribution diagram. By accounting for all the reactions taking place in the system, including those occurring both at the surface and in the bulk solution, the distribution diagram can be specifically used in applied fields like flotation to interpret the phenomena involved. From the distribution of surface species, the surface charge can also be estimated, as it originates from surface reactions.

4 RESULTS AND DISCUSSION

4. 1 *Activation Conditions of Quartz by Metal Ions in the Flotation System*

In the absence of metal ions, quartz exhibits no floatability at all when oleate is used as collector. However, metal ions can connect the quartz surface and oleate collector and create the desired activation conditions. The optimum activation pH of quartz by metal ions depends on metal ion concentration. In the presence of 1×10^{-3} mol / L Ca^{2+}, 1×10^{-3} mol / L Mg^{2+} or 5×10^{-5} mol / L Fe^{3+} , the best flotation recovery was obtained at pH 12. 5, 11. 0 and 6 respectively [1]. Furthermore, a relationship between solution pH and activator concentration C at the condition of incipient activated quartz flotation was found to be

pH / C = Constant.[1]

In order to interpret the activation behavior of metal ions in the quartz system, Fuerstenau and Palmer[4] compared the activation pH with the metal ion hydrolysis, and concluded that the metal hydrolysis complexes are responsible for activation, since good agreement was obtained. Ahemed and Van Cleave [5] regarded metal ions as activators, suggesting that an alkaline pH makes the quartz surface more negative and consequently attracts positively charged metal ions. Clark and Cook[6] however, found that the optimum activation pH of Mg^{2+} corresponds to the area of insoluble metal hydroxide formation. Activation of quartz by metal ions is a surface modification process, thus surface complexation is involved. The activation may also be regarded as a stepwise surface complexation process. If so , the surface reactions can be quantified by the introduction of a series of surface equilibrium constants. The activation process brings the surface, metal ions and collector together, and thus the ternary system metal ion-surface-collector complexation may be responsible for quartz activation.

4. 2 *Surface Complexation*

The surface reactions in the quartz flotation system can be considered as follows

In the absence of metal ions:

$$\equiv SiOH = \equiv SiO^- + H^+ \qquad (5)$$

here $\lg K = -6.8$[15]

$$\mathrm{RCOOH} = \mathrm{RCOO^- + H^+} \qquad (6)$$

here $\lg K = -4.95 - -6.0$[16];

However, in the presence of metal ions, surface reactions like

$$\equiv \mathrm{SiOH + Me^{2+}} = \equiv \mathrm{SiMe^{(2-1)+} + H^+} \qquad (7)$$

$$\equiv \mathrm{SiOH + Me^{2+} + RCOO^- + H_2O} = \mathrm{2H^+} + \equiv \mathrm{SiOMeOHRCOO^-} \qquad (8)$$

or

$$\begin{matrix} \equiv \mathrm{SiOH} \\ \equiv \mathrm{SiOH} \end{matrix} + \mathrm{Me^{2+} + RCOO^- + H_2O} = \begin{matrix} \equiv \mathrm{SiO} \\ \equiv \mathrm{SiO} \end{matrix} \mathrm{MeOHRCOO^- + 3H^+} \qquad (9)$$

which could take place surface hydrophobicity.

In the presence of calcium or magnesium ion, calcium or magnesium ions can activate the quartz surface, and reduce the surface negative charge. It is also noticed that at optimum flotation conditions the quartz surface activated by calcium or magnesium ions is nearly neutrally charged. Flotation is a process, in which the combination of quartz surface activator and collector contribute to the floatability. Both activators, like metal ions, and collectors, like oleate, have to affect the quartz surface. Their mutual contact is a prerequisite for quartz activation. Thus, it is reasonable to assume that activation is a stepwise process, where the first step is neutralizing the surface charge according to the reaction:

$$\equiv \mathrm{SiO^- + Me^{2+} + H_2O} = \equiv \mathrm{SiOMeOH + H^+} \qquad (10)$$

whereafter the surface $\equiv$ SiOMeOH complex reacts with oleate and forms a surface metal hydrous-oleate complex, which is responsible for quartz flotation, i. e.

$$\equiv \mathrm{SiOMeOH + RCOO^-} = \equiv \mathrm{SiOMeOHRCOO^-}$$

The validity of reaction (11) for calcium and magnesium ions was tested by computer assisted calculations where an estimated equilibrium constant for reaction (11) was entered into the composition matrix. The surface reaction constants were collected from those for amorphous silica, and equilibrium constants for solution reactions were taken from reference[17]. Various combinations of components form different reaction products. At equilibrium conditions, using the computer program SOLGASWATER, the reactions were handled simultaneously. The distribution diagrams in $\equiv \mathrm{SiOH{-}Ca^{2+}{-}H_2O{-}O1{-}CO_3^{2-}}$ and $\equiv \mathrm{SiOH{-}Mg^{2+}{-}H_2O{-}O1{-}CO_3^{2-}}$ systems are presented in Fig.1 and 2, respectively. The component concentrations were chosen according to flotation experiments and the carbonate concentration was also taken into account, since the flotation takes place in an open atmosphere.

From Fig. 1 and 2, it is obvious that the peak of flotation recovery corresponds to the maximum fraction of surface complex. Good agreement was obtained between the flotation recoveries and the predominance of the surface species $\equiv \mathrm{SiOCaOHO1^-}$ and $\equiv \mathrm{SiOCaMgOHO1^-}$, respectively. It may be concluded that the proposed reaction (11) very likely exists and the surface ternary species are possibly responsible for the activated quartz flotation.

In the presence of ferric ions, in contrast to calcium and magnesium ions, quartz is activated in a slightly acidic pH region. After trial and error test using computer simulations, the best estimated model was found to be surface reaction (9). In this case, two surface sites are needed for the surface complexation leading to quartz flotation. The composition matrix for the $\equiv \mathrm{SiOH{-}Fe^{3+}{-}H_2O{-}O1{-}CO_3^{2-}}$ system is listed in Table 3. As can be seen the possible surface species and soluble ferric hydroxy complexes and insoluble precipitates were taken into account as well.

The distribution diagram is presented in Fig.3. The corresponding maximum in the formation of the surface complex described by reaction (9) and the flotation recovery clearly indicates good agreement.

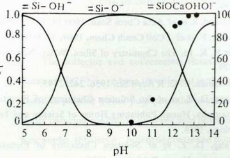

Fig. 1 Correlation between surface species distribution F_i and flotation recovery R_F of quartz activated by calcium ions

The solid curved line represents the theoretical distribution of surface species calculated from the assumed reaction model ($\equiv SiOCa_2OHRCOO$-) and known equilibrium constants for other surface and solution species filled dots (·) denote the flotation recoveries.

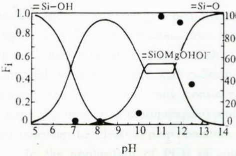

Fig. 2 Correlation between surface species distribution F_i and flotation recovery R_F of quartz activated by calcium ions

The solid line represents the theoretical distribution of surface species calculated from the assumed reaction model ($\equiv SiOMgOHRCOO^-$) and known equilibrium constants for other surface and solution species: filled dots (·) denote the flotation recoveries

5 CONCLUSIONS

The following conclusions can be drawn from the results of the computer assisted calculations and experimental observations on the metal ion activated quartz flotation systems:

(1) Activated quartz flotation phenonmena can be interpreted by the surface complexation model. Surface complextion leads to changes in the surface charge and hydrophobicity.

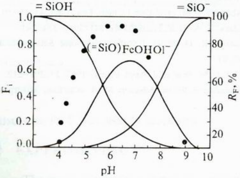

Fig. 3 Correlation between surface species distribution F_i and flotation recovery R_F of quartz activated by ferric ions

The solid line represents the theoretical distribution of surface species calculated from the assumed reaction model ($(\equiv SiO)_2FeOHRCOO^-$) and known equilibrium constants for other surface and solution species: filled dots denote the flotation recoveries

(2) At alkaline pH, quartz can be activated by calcium and magnesium ions. The surface complex $\equiv SiOMeOHRCOO^-$ is possibly responsible for the activated quartz floatability. The flotation can be satisfactorily explained by the estimated reaction models and constants. Observation of flotation recoveries and surface species distributions are in good agreement.

(3) In slightly acidic pH, quartz can be activated by ferric ions, The surface complex $\begin{matrix}\equiv SiO\\ \equiv SiO\end{matrix}FeOHRCOO^-$ seems to be responsible for quartz flotation, and the theoretical distribution of the surface species calculated from

the assumed model and equilibrium constant can be used to interpret the corresponding experimental flotation results.

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