Applying an atomic force microscopy in the study of mineral flotation

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An atomic force microscopy (AFM) has been applied to study in situ the adsorption of chemicals on minerals, i.e. chalcopyrite and molybdenite, in aqueous solution. The AFM images showed that some absorbate in patches was detected on the chalcopyrite surface, after the mineral sample was soaked in $5 \times 10^{-4}$ M potassium ethyl xanthate (KEX) solution at pH 11 for 10 minutes. The absorbate can be removed from the chalcopyrite surface by rinsing with ethanol. On the other hand, the AFM images obtained with molybdenite in solutions showed that the absorbed chemicals on molybdenite surface were very sparse.

The findings clarify that, in industrial flotation practice, KEX and its homologues are widely applied for chalcopyrite flotation; on the other hand, hydrocarbon oil, rather than KEX, is generally used as the promoter of molybdenite flotation. The results also show that an AFM can be a powerful tool for the fundamental study of the adsorption of chemicals on mineral surface in froth flotation.

Keywords AFM; flotation; chalcopyrite; molybdenite; adsorption

1. Introduction

In mining industry, valuable sulfide minerals, such as chalcopyrite and molybdenite, are usually separated selectively from non-valuable gangue by froth flotation, which treats the highest throughput and produces the maximum economic outcome of any surface chemistry process. In flotation, collectors are added into the pulp (mixture of water and fine-grained minerals) to selectively adsorb onto the target mineral and render its surface with high hydrophobicity, which is generally beneficial for a strong mineral-bubble attachment and thus a high flotation recovery.

The adsorption of collector on mineral surface, therefore, is vital for a successful flotation process and it has been studied by applying various surface analysis techniques, such as IR and XPS. [1, 2] These studies have revealed a lot of information, such as reaction, product and mechanism, of chemicals adsorption on mineral surface. However, it is also of great interest to directly obtain the image of adsorbed chemicals/collectors on mineral surface changing with pulp chemistry, such as pH, redox potential, ionic strength and chemical’s dosage.

More than 50 years ago, Polkin et al. [3] and Plaksin et al. [4] started applying the autoradiography technique to collect images and study the adsorption of xanthate radioactive isotopes on sulfide minerals. Their results revealed the mosaic distribution of xanthate chemicals on mineral surface and suggested that the adsorbed chemicals occupied only a small part of the total mineral surface.

Kim et al. [5] and Smart et al. [6] applied scanning tunneling microscopy (STM) to study the change, i.e. oxidation, reaction and absorption, of galena surface under flotation-related conditions. The in-situ obtained STM images showed that the pulp chemistry, such as pH and chemical’s dosage, impacts the reaction and its products on galena surface. The reported results clearly suggest that a surface imaging technique, for example, the STM, is beneficial for the study of the chemicals adsorption on mineral surface.

The AFM imaging technique has been widely applied in surface characterization of various materials. It can also be used to study the adsorption of chemicals on mineral surfaces. [7] In addition, it has some advantages over other surface characterization techniques. First, by employing an AFM fluid cell, one can study the in-situ absorption of chemicals on solid in solution, which closely resembles an actual flotation condition. On the other hand, some other analysis techniques, such as XPS, with the prerequisite of taking solid sample out of solution may not collect the actual adsorption information because the adsorption can change when the sample is removed from solution. Second, a high vacuum is not required for an AFM measurement. Some chemicals such as dixanthogen, an important reaction product on sulfide surface to increase the mineral’s hydrophobicity, are usually in a liquid form at room temperature. Thus, it is extremely hard, under a high vacuum, to detect these chemicals without cooling the measuring system to a low temperature. [2]

In present investigation, an AFM will be applied to study the chemicals adsorption on the surface of sulfide mineral, i.e. chalcopyrite and molybdenite, in solutions by comparing the images obtained under different conditions. The finding of present work will help understand the reaction and adsorption of xanthate on sulfide minerals. The findings can also be applied for the development of collector for a better flotation practice.
2. Experimental

2.1 Materials
The research grade chalcopyrite (CuFeS₂) and Molybdenite (MoS₂) were obtained from Wards Natural Science Establishment Inc. The samples were finely polished and further cleaned by rinsing thoroughly with ethanol and water. A 1.2 cm ×1.2 cm freshly prepared clean mineral sample was used for the surface characterization experiments. The nanopure water used in present work has a conductivity of 18.2 MΩ-cm at 25°C and a surface tension of 72.5 mN/m at 22°C. The water was used without purposely removing the dissolved atmospheric CO₂. Thus, the pH of the water used was in the range of 5.8–6.0. Potassium ethyl xanthate (KEX) (>98%) was obtained from Alfa Aesar and used without further purification. The KEX surfactant solution was freshly prepared each time right before the experiment of surface characterization was carried out.

2.2 AFM surface image measurement
Surface forces between the AFM probe and the mineral sample were measured using a Digital Instrument Nanoscope IIIa AFM at room temperature (25±1°C). The separation distance (H) between the probe and the substrate (molybdenite or chalcopyrite plate) was measured by monitoring the deflection of the cantilever. Silicon nitride NPO20 cantilevers were obtained from Veeco, CA. Triangular cantilevers with nominal spring constant of 0.12~0.58 N/m were used for surface image measurement. For the study of mineral surface in water, an AFM surface image measurement was carried out right after the nanopure water was injected into an AFM fluid cell. After the surface images were collected in pristine water, 10 ml 5×10⁻⁴ M potassium ethyl xanthate solution was flushed through the liquid cell and the AFM image measurement was commenced after a specific time after the exposure of the mineral plate to the xanthate solution.

The AFM images reported in this communication include both height and deflection images obtained in the contact mode. They are processed by no image modification other than being flattened. The same silicon nitride probe was applied to obtain the AFM image of the mineral plate at different conditions.

3. Results and Discussion

3.1 AFM surface image of chalcopyrite surface in solutions
Fig. 1A) shows the AFM deflection image of the bare chalcopyrite surface, which has been soaked in nanopure water in an AFM liquid cell for 30 minutes. No detectable changes in surface morphology were observed from the image of a 10 µm × 10 µm scan area after water was injected into the cell. Some scratch lines due to surface polishing are clearly shown on the sample. Therefore, in present investigation, we specifically used deflection images to study the change in surface morphology. As shown in Fig. 1A), the left part is chalcopyrite, while the right part is silicate, which is the impurity of the sample. Image was purposefully scanned including the boundary of the two minerals to show the difference of the adsorption of chemicals on different minerals. Fig. 1B) shows the AFM deflection image of the chalcopyrite surface soaked in 5×10⁻⁴ M potassium ethyl xanthate (KEX) in an AFM liquid cell for 30 minutes. A big lump, as indicated by the white arrow, appeared on the surface of the chalcopyrite (the left part of the image). However, the surface of silicate (the right part) remains exactly the same as obtained in water. As shown by Figure 1B), some species absorbed on chalcopyrite surface when the surface contacted xanthate solution; however, the absorbate had no affinity for silicate surface.
Figure 2 shows 10 µm × 10 µm AFM images of a chalcopyrite surface obtained after the sample was soaked in 5×10⁻⁶ M KEX for 10 minutes. Fig. 2A) is the AFM height image with a 200 nm data scale. One can clearly see that quite a lot small patches appeared on chalcopyrite surface. During the imaging experiments, we found that these patches are relatively deformable under the scanning AFM probe at room temperature; therefore, a minimal scan force was applied in order not to disturb the absorbate. Fig. 2B) is the AFM deflection image with a data scale of 50 nm, from which one can see the shape and morphology of the patches of absorbate clearly.

Figure 3 shows 10 µm × 10 µm AFM images of a chalcopyrite surface obtained after the sample was soaked in 5×10⁻⁶ M KEX for 30 minutes. Fig. 3A) is the AFM height image with an 800 nm data scale. A much larger data scale was chosen in Fig. 3, because the height of these patch-like absorbate is much larger than that obtained in Fig. 2. In addition, the sizes of some patches are also much larger. Fig. 3B) is the AFM deflection image with a data scale of 200 nm. The image clearly shows that the absorbate is now in quite good spherical shape. It is interesting to mention that these dots are also deformable. As shown by Fig. 3B), for example, some patches on the top part of the image are “cut off” a little bit by the scanning AFM probe. Therefore, as mention in previous section, a minimal scan force was also applied when the chalcopyrite surface of interest was scanned. By comparing Fig. 2 and Fig. 3, one can see that both the size and the height of the absorbate increase when the soaking time increases from 10 minutes to 30 minutes. It means that the size of the patches increases with soaking time lapsing.
After the chalcopyrite sample was soaked in \(5 \times 10^{-4}\) M KEX solution for 1 hour, it was further rinsed with 20 ml ethanol alcohol. An AFM height image of the substrate was sequentially taken and shown as Figure 4. From the image, one can see that the patches of the adsorbate have been removed and the chalcopyrite surface becomes "clean". The solid surface obtained after ethanol rising is comparable to the bare surface as shown by the left part of Fig. 1A) and it is much smoother than the one obtained in \(5 \times 10^{-7}\) M KEX solution.

3.2 AFM surface image of molybdenite surface in solutions

Figure 5A) shows the AFM image of the bare molybdenite surface obtained in air just before the injection of water into the AFM liquid cell. The solid surface is very smooth in a 10 µm × 10 µm scan area. In addition, no evident cracks or particles were detected on the solid surface. A smooth substrate is usually beneficial for a study of the adsorption of chemicals on solid surface because of the minimum interference arising from the background morphology. The obtained smooth surface also suggested that the freshly cleaved molybdenite surface studied in present investigation was mainly the basal surface and the portion of edge surface was extremely small.

Fig. 3 AFM images of chalcopyrite surface soaked in \(5 \times 10^{-4}\) M KEX for 30 minutes. A) the height image with a data scale of 800 nm and B) the deflection image with a data scale of 200 nm.

Fig. 4 AFM image of a chalcopyrite surface after the sample was soaked in \(5 \times 10^{-4}\) M KEX solution for 1 hour and further rinsed with ethanol. The size of the scan area is 10 µm × 10 µm with a data scale of 200 nm. The surface is smooth with only several polishing lines.
Figure 5B) shows the AFM image of bare molybdenite surface soaked in nanopure water for 1 hour in an AFM liquid cell. Once again, the image shows a very smooth mineral surface with no cracks and particles. One thing worthy of being mentioned is that no evident change in surface morphology was observed even after the solid surface contacted water for 1 hour. It suggests that, being different from galena and other sulfide minerals, the basal surface of molybdenite is quite inert and the possible oxidation of mineral surface in the presence of O₂ in water must be very slow on the basal surface.

Figure 6 shows the surface image of the molybdenite plate soaked in an aqueous 1×10⁻⁴ M KEX solution for 1 hour. Compared to the image of bare molybdenite surface as shown in Figure 5, the solid surface becomes a little bit rougher; however, the fact that the change in surface morphology is not evident suggests that the adsorption of KEX on molybdenite basal surface is minor.

After the molybdenite sample was soaked in 1×10⁻⁴ M KEX solution for 1 hour, it was further rinsed with ethanol and then dried in air. An AFM image of the substrate was sequentially taken and shown as Figure 7. From the image, one can clearly see that the molybdenite surface after ethanol rising is very similar to the bare surface.

3.3 Implications of mineral flotation using KEX as a collector

Because the adsorption of xanthate on sulfide minerals is vital in froth flotation, a lot of works have since been carried out to clarify the adsorption mechanism. [8-14] In spite of the fact that there are still a lot of debates, as reviewed by
Leja [15], the deposition of low solubility metal xanthate on sulfide mineral and the oxidization of xanthate into dixanthogen are the two main mechanisms for the increase of hydrophobicity of sulfide minerals in flotation.

Concerning the adsorption of xanthate on chalcopyrite surface, Kuhn [11] reported the existence of both dixanthogen and curpous xanthate on chalcopyrite surface through an infrared spectroscopic study by directly adding dixanthogen onto chalcopyrite. On the other hand, Allison et al. [12, 13] claimed that dixanthogen was the product on a chalcopyrite electrode in a 6.25×10⁻⁴ M KEX solution.

As shown by Fig. 2 and Fig. 3, the AFM images obtained with chalcopyrite in 5×10⁻⁴ M KEX solution showed that some patch-like chemicals were adsorbed on chalcopyrite surface. The change of surface morphology can’t be attributed to the oxidization of chalcopyrite in water, because in present investigation we noticed that the mineral surface remained the same, as shown in Figure 1 A), even after the sample was soaked in water for 30 minutes.

It is well known that xanthate can be oxidized into dixanthogen in the presence of oxygen in solution. According to Allison [12, 13], when chalcopyrite is soaked in KEX solution, xanthate will be oxidized into diethyl dixanthogen, of which the melting point is close to 32°[16-18], under ambient conditions, i.e. room temperature and normal pressure. The low melting point suggests that diethyl dixanthogen is a “soft” solid at room temperature and it is usually an oily substance, according to Rao [16], when extracted at room temperature. The obtained AFM images showed a patch-like morphology and it fits well with the appearance of an oily substance in water. That is, the absorbate is very likely the dixanthogen, an oily oxidation product of KEX to render mineral surface more hydrophobic.

As shown by the AFM images obtained in present work, few other evident changes in surface morphology were detected, except for the reported patches. It means that even though there may be some other species absorbed on chalcopyrite surface; however, the absorption must be quite sparse. A practical meaning for this is that the absorbed patches should have a predominating impact on chalcopyrite flotation, because in flotation practice, a bubble, of which the size is much larger than that of mineral particles, usually contacts the patches first because of their relatively “high” morphology.

As to the adsorption of xanthate on molybdenite, in general, no insoluble metal xanthate was reported to exist on the basal surface of molybdenite. Allison et al. [12, 13] claimed the existence of dixanthogen and another not-identified product on molybdenite in xanthate solution without the detection of metallic xanthate. Chander and Fuerstenau [19, 20] studied the adsorption of potassium diethyldithiophosphate on the surface of molybdenite and attributed the slight increase in contact angle only to the physical adsorption of the oxidation product of KDTP, i.e. (DTP)₂.

In present work, the AFM image obtained with molybdenite in 1×10⁻⁷ M KEX solution shows a sparse adsorption of chemicals on molybdenite surface. Especially, the absorbate is much less than the one observed on chalcopyrite surface in KEX solution. The obtained AFM images suggest that KEX is not an efficient collector for molybdenite because of the minor adsorption of chemicals on mineral surface. The findings explain very well the fact that, in industrial flotation practice, KEX and its homologues are widely applied for chalcopyrite flotation; on the other hand, hydrocarbon oil, rather than KEX, is generally used as the promoter of molybdenite flotation.

4. Conclusions

An AFM has been applied to study in situ the surface image and surface force of minerals, i.e. chalcopyrite and molybdenite, in aqueous solution. The AFM images showed that chemicals absorbed on mineral surface in patches after the chalcopyrite sample was soaked in 5×10⁻⁴ M potassium ethyl xanthate (KEX) solution at pH 11 for 10 minutes. The patches were found to increase in size with time elapsing. The absorbate is very likely to be dixanthogen, which is in the morphology of oily substance at room temperature. The absorption increases the surface hydrophobicity of chalcopyrite mineral and therefore facilitates its flotation.

On the other hand, minor adsorption of chemicals on molybdenite surface was observed from the obtained AFM images. The findings clarify that KEX and its homologues are efficient collectors for chalcopyrite flotation; while they break down in the case of molybdenite flotation, in which hydrocarbon oil is generally used as a promoter.

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Reference


