

*Received May 29, 2014; reviewed; accepted June 3, 2014*

## KINETICS OF HYDROPHOBIC AGGLOMERATION OF MOLYBDENITE FINES IN AQUEOUS SUSPENSIONS

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**Abstract:** The kinetics of hydrophobic agglomeration of molybdenite fines in aqueous suspensions has been studied in this work. This study was performed on minus 5  $\mu\text{m}$  molybdenite particles through turbidity measurements and imaging. The results have showed that stirring strength and kerosene addition greatly affected the agglomeration rate of molybdenite fines in aqueous suspensions. The higher was the stirring strength, the larger the agglomeration rate was. Kerosene addition enhanced not only the agglomeration rate, but also the agglomerates structure. It was recommended to use radial impeller for the formation of hydrophobic agglomeration, because it produced a stronger shear field in impeller zone.

**Keywords:** *Agglomeration rate; molybdenite fines; hydrophobic agglomeration.*

### Introduction

Molybdenite ( $\text{MoS}_2$ ) is the primary natural source for the extraction of molybdenum. It consists of hexagonal layer of molybdenum atoms between two layers of sulfur atoms, in which strong covalent bonds act within S-Mo-S layers and weak van der Waal forces exist between adjacent S-S sheets. This strong anisotropy causes preferential cleavage of molybdenite along the adjacent S-S sheet, producing platelet shape fragment (Lince et al., 2001). Therefore, ground molybdenite particles show two kinds of surfaces, namely face and edge. The face is hydrophobic because of the weak unsaturated band, while the edge is hydrophilic due to the strong band. Molybdenite is generally considered as a naturally hydrophobic mineral and is generally concentrated by froth flotation. However, as the reduction of particle size, the face/edge ratio decreased and thus the hydrophobicity of the molybdenite surfaces decreased (Castro et al., 1994; Yang et al., 2014), leading to sharp declining of flotation efficiency (Chander et al., 1994; Ornela-Tabares et al., 2006). On the other hand, it is generally accepted that

froth flotation is not effective to respond fine particles, because of the lower collision and adhesion probability between particles and air bubbles (Zeng et al., 2004; Liu et al., 2006). Thus, conventional flotation fails in beneficiating molybdenite fines from ores.

Increasing particle size through the formation of hydrophobic agglomerates is an effective method to improve the poor flotation response of mineral fines (Song et al., 2012). This process is termed as floc-flotation, and has been commercially used for the flotation of fine scheelite (Coleman et al., 1995) and anatase (Greene et al., 1962). Hydrophobic agglomeration arises as a result of hydrophobic interaction between particles in aqueous suspensions, and is realized by means of mechanical agitation (Cebe-ci, 2003; Duzyola et al., 2010; Lu et al., 1991; Spicer et al., 1998). In the agitation, the formation and disruption of agglomerates occurred simultaneously (Lu et al., 1998). The stronger is the agitation, the stronger the disruption effect is. A lumped population balance model was used for studying agglomerate coalescence and breakage in the hydrophobic agglomeration of scheelite particles, showing that the breakage rate was approximately proportional to the 0.70 power of the agglomerates volume (Patil et al., 2001).

Although numerous researches have been performed on the fundamental aspects of hydrophobic agglomeration of mineral fines in aqueous suspensions, few reports have concerned the kinetics of hydrophobic agglomeration, especially for molybdenite fines. In this work, an attempt has been made to study the kinetics of hydrophobic agglomeration of molybdenite fines in aqueous suspensions. The objective is to obtain the understandings of the agglomeration rate of molybdenite fines in aqueous suspensions as affected by several parameters, such as stirring speed, kerosene and impeller type.

## **Experimental**

### **Material**

The molybdenite sample used in this work was natural molybdenite powder ( $<5\mu\text{m}$ ) from Yiji chemical agent Co. Ltd., Shanghai, China. The purity was 96.41%  $\text{MoS}_2$ . It was first washed by  $\text{CS}_2$  to remove kerosene and other organics on the surfaces, followed by thermal drying in a vacuum oven at  $40\text{ }^\circ\text{C}$ . The X-ray diffraction (XRD) pattern of the samples is shown in Fig. 1. All of the peaks belonged to molybdenite, indicating that there was no impurity over 5% in the sample. scanning electron microscope (SEM) image as shown in Fig. 2 reveals that the particle size was less than  $5\mu\text{m}$ , and the shape was plate-like. SEM-EDX analysis showed that the impurities in the sample were silica and pyrite.

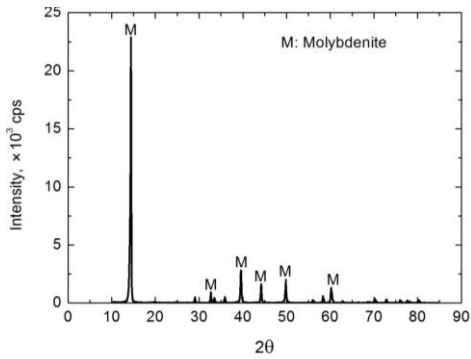


Fig. 1. XRD pattern of the molybdenite sample

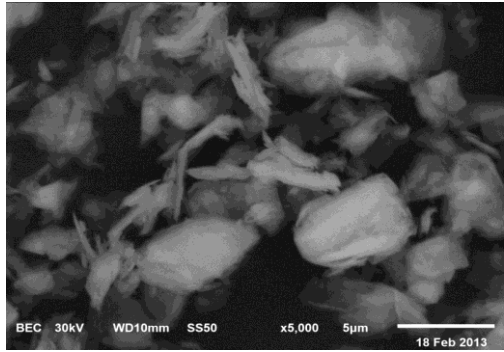


Fig. 2. SEM image of the molybdenite sample

Kerosene ( $50 \text{ mg/cm}^3$  hexane) from the Fisher Scientific without further purification was used. It was added into molybdenite suspensions in the form of oil emulsion. Prior to contact with molybdenite suspension, the mixture of kerosene and water (1.23% w/w) was first prepared by mechanically conditioning at 14000 rev/min for 10 min with a high speed mixer and then by ultrasonic treating for 15 minutes. The emulsified kerosene was imaged by Leica DMLP optical microscope, as shown in Fig. 3.

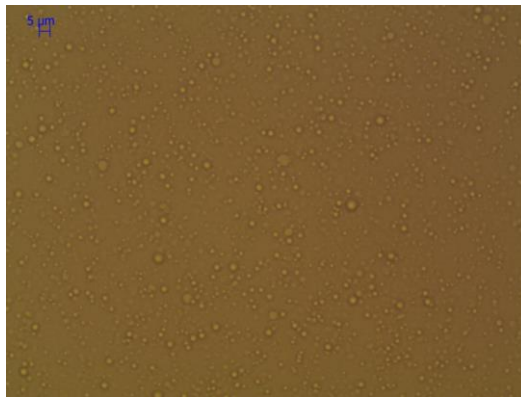


Fig. 3. Emulsified kerosene imaged with an optical microscopy

Potassium butyl xanthate that was originally from the Industria Quimica de Mexico and purified in our laboratory with the method described elsewhere (Song et al., 2001). The analytical grade hydrochloric acid and sodium hydroxide were used to adjust the pH of aqueous suspensions. The water used was distilled first, and then treated by passing through resin beds and a 0.2 mm filter.

### Determination of agglomeration rate

The hydrophobic agglomeration of molybdenite fines in aqueous suspensions was realized in a standard four-baffle stirred tank with 9.5 cm of height and diameter. The baffle is 8.2×0.95 in length and width. A Servodyne mixing head with a digital Servodyne mixer controller was used for slurry stirring.

Molybdenite sample with amount of 1.12 g with 620 cm<sup>3</sup> water was first conditioned with magnetic stirrer for 5 min. During the conditioning, hydrochloric acid or sodium hydroxide solution was added to adjust pH. Then, the suspension was dispersed by a Branson 2510 ultrasonic cleaner for 15 min. After that, the molybdenite suspensions were transferred into the stirred tank to be stirred at a given speed for a given time, while a given dosage of emulsified kerosene was added. During the stirring, 3 cm<sup>3</sup> of suspension was carefully sampled from the tank at given time intervals using a 5 mm diameter of Eppendorf research plus pipette. The samples were diluted by adding 60 ml distilled water. Finally, the diluted sample was determined for the turbidity by using a MicroTOL turbidimeter. It was reported that the pipette didn't modify the agglomerate size if the pipette openings were more than 2 mm (Gibbs and Konwar, 1982). In addition, hydrophobic agglomerates are very strong against rupture. Therefore, it is reasonable to presume that the sampling would not cause a significant disruption of the agglomerates.

The dispersion and agglomeration of the molybdenite fines is evaluated by agglomeration degree ( $E$ ), given by:

$$E = \frac{\tau_o - \tau_E}{\tau_o} \quad (1)$$

where  $\tau_o$  and  $\tau_E$  are the turbidities of the well-dispersed suspensions and of agglomerated suspensions at a given time of stirring. The agglomeration rate ( $dE/dt$ ) was obtained by differentiating  $E$  over  $t$  at the stirring time of 20 seconds:

$$K = \left. \frac{dE}{dt} \right|_{t \rightarrow 20s} \quad (2)$$

### Observation of hydrophobic agglomerates

A Leica DMLP optical microscope equipped with digital camera was used to observe hydrophobic agglomerates in aqueous suspensions. The samples were prepared by dropping molybdenite suspensions on a glass plate, followed by putting a thin glass slide on the drop to fix the suspensions. Some of agglomerates were photographed.

## Results and discussions

### Effect of stirring strength on agglomeration rate

The strength of the shear field closely correlated with stirring speed in a mechanical agitation. Figure 4 illustrates the effect of stirring speed on the agglomeration rate of molybdenite fines in aqueous suspensions. As it is shown, the agglomeration rate increased with the increase of stirring speed. The increase was sharp in the low speeds, and became mild at the critical speed, 1900 rev/min. The results indicated that the hydrophobic agglomerates of molybdenite could withstand great floc-rupture forces and keep growing at high stirring strengths. This observation might be due to the strong coalescence between the hydrophobic particles in aqueous solutions, because the agglomerate disruption process was dominated mainly by the fragmentation mechanism (Lu et al., 1998).

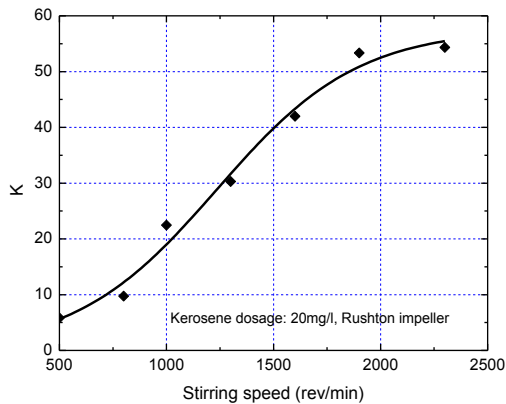


Fig. 4. Agglomeration rate of molybdenite fines in aqueous suspensions as a function of stirring speed

### Influence of kerosene dosage on agglomeration rate

The agglomeration rate of molybdenite fines in aqueous suspensions as a function of kerosene dosage is shown in Fig. 5. As the kerosene dosage increases, the agglomeration rate increases substantially and then flattens out, indicating that non-polar oil enhances the hydrophobic agglomeration of molybdenite fines. The enhancement was due to the increase of surface hydrophobicity and agglomerate strength through spreading oil droplets on molybdenite faces and forming oil bridges between the agglomerated particles, resulting in a high ability against rupture force from turbulence flows (Song et al., 1999). At the kerosene dosage above  $60 \text{ mg/dm}^3$ , the agglomeration rate reached a plateau.

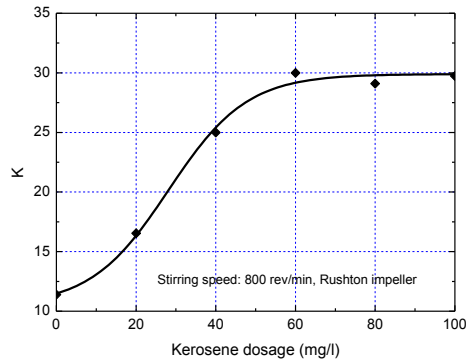


Fig. 5. Agglomeration rate of molybdenite fines in aqueous suspensions at 20 s as a function of kerosene dosage

Figure 6 shows the microscopy images of the hydrophobic agglomerates of molybdenite fines at the kerosene addition of  $20 \text{ mg/dm}^3$  and  $60 \text{ mg/dm}^3$ . It can be observed that at the  $20 \text{ mg/dm}^3$  kerosene, the agglomerates consisted of small compact agglomerates with big space between them, indicating a loose structure. At the  $60 \text{ mg/dm}^3$  kerosene, the agglomerates became more compact and there were no obvious spaces. The results suggested that kerosene could intensify hydrophobic agglomeration of molybdenite fines through compacting the agglomerate structure.

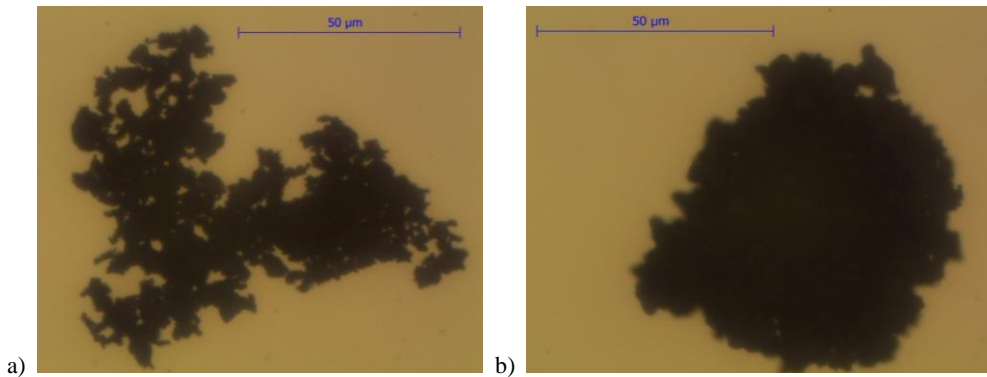


Fig. 6. Optical microscopy images of hydrophobic agglomerates of molybdenite fines at kerosene dosage  $20 \text{ mg/dm}^3$  (a) and  $60 \text{ mg/dm}^3$  (b)

### Effect of butyl xanthate on agglomeration rate

The effect of butyl xanthate on the agglomeration kinetics of molybdenite fines is shown in Fig. 7. The agglomeration degree greatly increased in the presence of butyl xanthate at the same time, suggesting that the xanthate could enhance the hydrophobic agglomeration. The enhancement might be attributed to the increase of hydrophobicity

of the edges of molybdenite upon the adsorption of xanthate. Moreover, at the same butyl xanthate dosage, the agglomeration was enhanced with the addition of 20 mg/dm<sup>3</sup> kerosene.

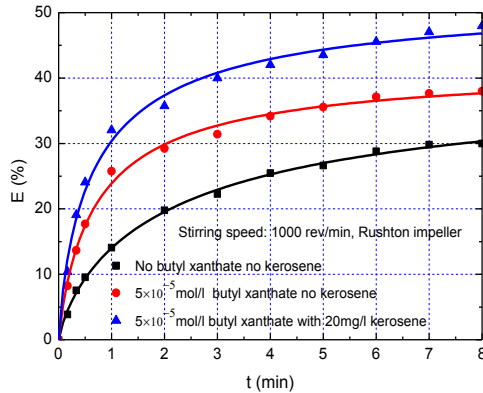


Fig. 7. Agglomeration degree of molybdenite fines in aqueous suspensions as a function of stirring time in the absence and presence of butyl xanthate

### Effect of impeller type on agglomeration rate

The flow characteristic (circulation time and strength) in the stirred tank is very important in hydrophobic agglomeration, which is closely related to the impeller type. Figure 8 shows the top view of three different impellers in this work. The impeller 1 and 2 produce an axial flow and radial flow, respectively, while impeller 3 produces a combined axial and radial flow. Impeller 1 produces flows toward the bottom of the tank followed by circulation to the top and a relatively rapid return to the impeller zone. Impeller 2 radiates fluid flow outward from the impeller and back to the impeller zone. Impeller 3 produces the flow downward at a certain angle from the vertical axis (Spicer et al., 1996).



Impeller 1



Impeller 2 (Rushton)



Impeller 3

Fig. 8. Top views of different impellers

The effect of impeller type on the agglomeration kinetics of molybdenite fines is illustrated in Fig. 9. Impeller 2 produced the best agglomeration, followed by impeller 3 and impeller 1. The results indicated that the radial flow achieved by impeller 2 was better for the formation of hydrophobic agglomerates than the axial flow. It might be attributed to that a greater shear field might exist in a radial flow than in an axial flow, because it produced flow perpendicular to the original direction of the approaching agglomerates (Spicer et al., 1996).

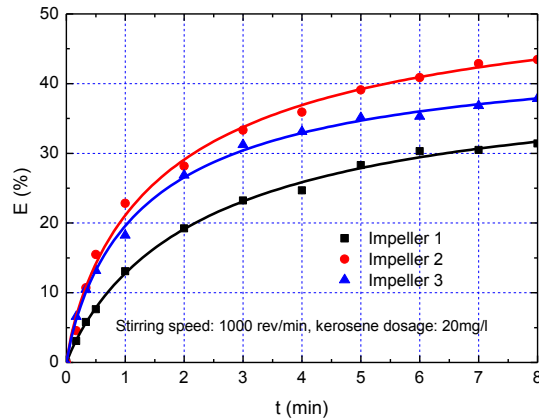


Fig. 9. Agglomeration degree of molybdenite fines in aqueous suspensions as a function of stirring time by different impellers

## Conclusions

The agglomeration rate of molybdenite fine in aqueous suspensions was closely correlated with the stirring strength in agitation. The higher was the stirring strength, the larger the agglomeration rate was. Kerosene played an important role in the hydrophobic agglomeration of molybdenite fines. It not only increased the agglomeration rate, but also enhanced the agglomerate structure. It was better to use radial impeller to generate hydrophobic agglomeration, because it produced a stronger shear field in impeller zone.

## Acknowledgments

The financial supports for this work from the Consejo Nacional de Ciencia y Tecnología (CONACyT) of Mexico under the Grant Nos. 123487 and 155148 are gratefully acknowledged. Also, B. Yang would like to thank the CONACyT of Mexico for offering him the scholarship under the grant No 416789 during his Ph.D. studying.

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