


## Article

# Insights into Selection of the Auxiliary Collector and Its Applicability Analysis for Improving Molybdenite Flotation

Hui Li <sup>1,2,\*</sup> , Tingshu He <sup>3</sup>, He Wan <sup>3,\*</sup>, Yuexin Han <sup>1,2</sup>, Yufeng Guo <sup>3</sup> and Jianping Jin <sup>3,4</sup>

<sup>1</sup> College of Resource and Civil Engineering, Northeastern University, Shenyang 110819, China; dongdafulong@mail.neu.edu.cn

<sup>2</sup> National-Local Joint Engineering Research Center of High-Efficient Exploitation Technology for Refractory Iron Ore Resources, Shenyang 110819, China

<sup>3</sup> School of Resources Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China; hetingshu@xauat.edu.cn (T.H.); 2010741@stu.neu.edu.cn (Y.G.); jinjianping@mail.neu.edu.cn (J.J.)

<sup>4</sup> China Molybdenum Co. Ltd., Luanchuan 471500, China

\* Correspondence: lih@mail.neu.edu.cn (H.L.); Wanhe@xauat.edu.cn (H.W.); Tel.: +86-159-9167-4357 (H.L.)

**Abstract:** In this study, two auxiliary collectors (methyl naphthalene and naphthalene) of molybdenite and the traditional collector (kerosene) were mixed for molybdenite flotation, respectively. According to the selection and analysis of the auxiliary collector, it was found that the surface energy ( $\gamma_C = 44.50 \text{ mJ/m}^2$ ) of the polycyclic aromatic hydrocarbons is very close to that ( $\gamma_S = 42.55 \text{ mJ/m}^2$ ) of the molybdenite {100} surface. Therefore, it can be physically adsorbed onto the molybdenite {100} surface according to the principle of similar compatibility. Batch flotation was conducted on actual ore with the mixed collector, compared with kerosene alone. Batch flotation results showed that the mixed collector at a mass ratio of 95:5 of main collector to auxiliary collector at pH 11.0 improved molybdenite flotation, that is, the Mo recovery was increased by 3–4%. The practical application feasibility of the auxiliary collector was analyzed by the filtration speed of the flotation concentrate and the crystal resolution characteristics of the auxiliary collector. The results show that solid naphthalene (Nap) is easy to crystallize at low temperature and adhere to the surface of the flotation concentrate, resulting in a decrease of filtration velocity, while liquid methylnaphthalene (MNap) does not crystallize at low temperature. These results imply that the mixed collector Kerosene/MNap can generate a superior synergistic effect and achieve better collecting capacity than kerosene alone, resulting in the increase of flotation recovery by 3–4 percentage points. Moreover, the addition of MNap has little negative impact on the subsequent treatment of the product.

**Keywords:** auxiliary collector; molybdenite flotation; selection basis; filtration velocity; crystallization characteristics



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## 1. Introduction

Molybdenite is an anisotropic sulfide mineral with a layered structure and exhibits two types of surfaces, namely “face” and “edge” [1–3]. The breakage of covalent bonds between molybdenum and sulfur produces a high-energy surface, called the “edge”. The rupture of weak van der Waals forces between S–Mo–S layers exposes a low-energy surface, the basal plane or “face”. These edge and face surfaces display different surface properties, especially wettability [4].

As is well known, nonpolar hydrocarbon oils (saturated hydrocarbons) such as kerosene, diesel oil, transformer oil, and solar oil are normally used as molybdenite flotation collectors [5–8]. Nevertheless, they only adsorb on the nonpolar “face” of molybdenite to improve its hydrophobicity by hydrophobic interactions and van der Waals forces [9–14], because the surface energy of nonpolar hydrocarbon oils is similar to that of the molybdenite “face”. Thus, the hydrophobicity of the molybdenite edges cannot be improved by nonpolar hydrocarbon oils [15,16].

Fine molybdenite particles have a low “face/edge” ratio with a high exposure of edges [17]. With the increase of molybdenite fineness, the quantity ratio of “face/edge” gradually decreases. It can be seen that the properties of the “edge” affect the floatability of molybdenite. Therefore, enhancing the hydrophobicity of molybdenite particles is the key to improve its floatability. Some studies have shown that the surfactant or xanthate can be mixed with a nonpolar hydrocarbon oil to improve the molybdenite flotation [1,18–22]. The adsorption form is similar to that of butyl xanthate and other sulfide minerals. The surfactant or xanthate could be absorbed on the molybdenite edges to improve their hydrophobicity. Thus, when the non-polar hydrocarbon oil and polar collector are used together, the recovery of molybdenite can be obviously increased. However, the combination of flotation reagents has a significant effect on the flotation of single molybdenite, but it is poor for molybdenite associated with other non-molybdenum sulfide ores [23]. Therefore, it is key to overcome the negative effect of the molybdenite particle “edge” on its floatability for improving molybdenum recovery of fine molybdenite.

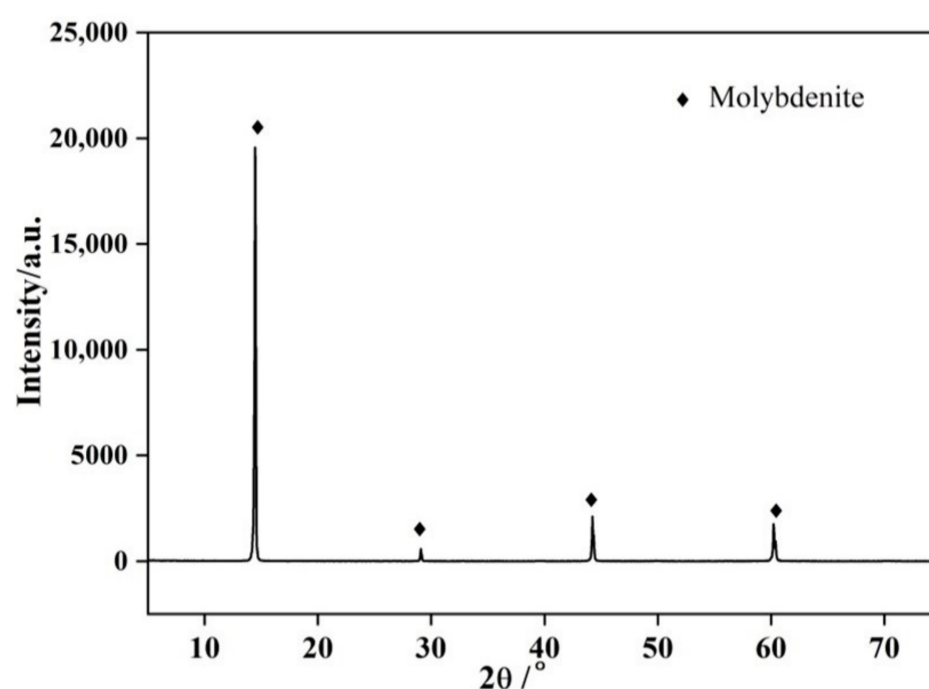
The author’s team is committed to the research of molybdenum ore separation technology and theory, and has achieved many useful research results. In the early stage, the mixed collectors of hydrocarbon oil and the appropriate amount of solid polycyclic aromatic hydrocarbons can improve the floatability of molybdenite [3], while their mixing ratio needs to be appropriate. If the amount of polycyclic aromatic hydrocarbons is too much, the collecting ability of kerosene on molybdenite will be weakened, affecting the molybdenite floatability. Laboratory and field tests have shown that solid polycyclic aromatic hydrocarbons can improve the flotation effect of molybdenite, especially for fine molybdenite. However, when the temperature is low in winter, solid polycyclic aromatic hydrocarbons have poor compatibility with hydrocarbon oil, namely the ease to crystallize and precipitate, slow filtration velocity of flotation concentrate etc. Guo Yufeng [24] also conducted a preliminary exploration and carried out relevant work on the research of a liquid auxiliary collector, while the mechanism was also studied [25]. We reported research on improving fine molybdenite flotation using a combination of aliphatic hydrocarbon oil and liquid polycyclic aromatic hydrocarbon [25]. This composite collector was examined in the flotation of molybdenite particles from different size fractions. It was found that this composite collector improved the flotation of molybdenite particles especially for finer size fractions. Based on the above analysis and previous studies, it is considered very important to undergo more research and develop new collectors, but even more important is the applicability. The collector should not only improve the effect, but also be easy to store and transport, and have strong adaptability to temperature, as well as little negative influence on the subsequent product treatment process. Therefore, only by fully studying the applicability of the new collector can it be applied in industry. However, there have been few studies on the applicability of new collectors.

The purpose of this work was to reveal the selection basis of auxiliary collectors. The effects of liquid auxiliary collector and solid auxiliary collector were carried out by flotation tests. Furthermore, their applicability was also studied by analyzing the crystallization characteristics and filtration velocity of the flotation concentrate. The results aimed to provide new ideas for the research of a new molybdenite collector and its practicability.

## 2. Materials and Methods

### 2.1. Materials

Molybdenum single mineral originated from Guangxi province. The high purity minerals were first collected by handpicking, and then ground in a ceramic ball mill. After dry sieving, the fractions with particle size between 38 µm and 74 µm were collected for the micro-flotation experiments. The mineral samples were then sealed in polyethylene bags and stored in a freezer for later tests and analysis. The processed samples were analyzed by EDTA-complexometric titration and quantitative XRD (Figure 1), and showed a purity of more than 98% molybdenite.



**Figure 1.** X-ray diffraction (XRD) analysis of molybdenum single mineral sample.

The actual ore used in this study was collected from the China Molybdenum Co., Ltd., Luoyang, Henan Province. The chemical composition analysis of the Mo ore was conducted using inductively coupled plasma mass spectrometry (ICP-MS), and the results are shown in Table 1. The results revealed 0.12 wt% Mo and 0.11 wt%  $\text{WO}_3$  in the ore sample. The mineralogical composition of the Mo ore (Figure 2) was analyzed by the application of X-ray diffraction analysis, which indicated that silicate minerals were the predominant gangue mineral in this ore sample. The actual Mo ore and molybdenum single mineral prepared in this study represented the natural molybdenite entering the flotation process without any chemical contamination.

**Table 1.** The elements composition of the actual ore.

Compositions	Mo	S	$\text{SiO}_2$	Cu	$\text{WO}_3$	TFe	Pb	Zn	$\text{Al}_2\text{O}_3$	MgO
Content/%	0.12	1.853	47.81	0.018	0.11	9.50	0.020	0.012	7.85	2.83

Methylnaphthalene (MNap), naphthalene (Nap) and kerosene of industrial grade were used as collectors without any emulsification process.

An aromatic hydrocarbon refers to a hydrocarbon with a benzene ring in the molecule, which has a little polarity. Aromatic hydrocarbons are not necessarily sensually aromatic. For example, naphthalene as an aromatic hydrocarbon has a pungent taste. If two benzene rings share one side in the hydrocarbon, they are named polycyclic aromatic hydrocarbons. In this study, we selected two kinds of polycyclic aromatic hydrocarbons, one a liquid polycyclic aromatic hydrocarbon, and the other a solid polycyclic aromatic hydrocarbon.

The liquid one was industrial methylnaphthalene (MNap), which has a wide range of sources, and its price is slightly higher than that of kerosene. Methylnaphthalene is a colorless to yellowish brown oil-like liquid, with a naphthalene-like smell. It is volatile with steam, flammable, insoluble in water, and soluble in ether and ethanol, mainly as  $\alpha$ -naphthalene and  $\beta$ -naphthalene mixture. Figure 3 shows the molecular structure of  $\alpha$ -naphthalene and  $\beta$ -Methylnaphthalene. Solid naphthalene (Nap) is the simplest polycyclic aromatic hydrocarbon with the molecular formula of  $\text{C}_{10}\text{H}_8$ . It is composed of two benzene rings sharing two adjacent carbon atoms, which is colorless, toxic, and easy to sublime and has a special smell of flake crystal. Figure 4 shows the molecular structure of Nap.

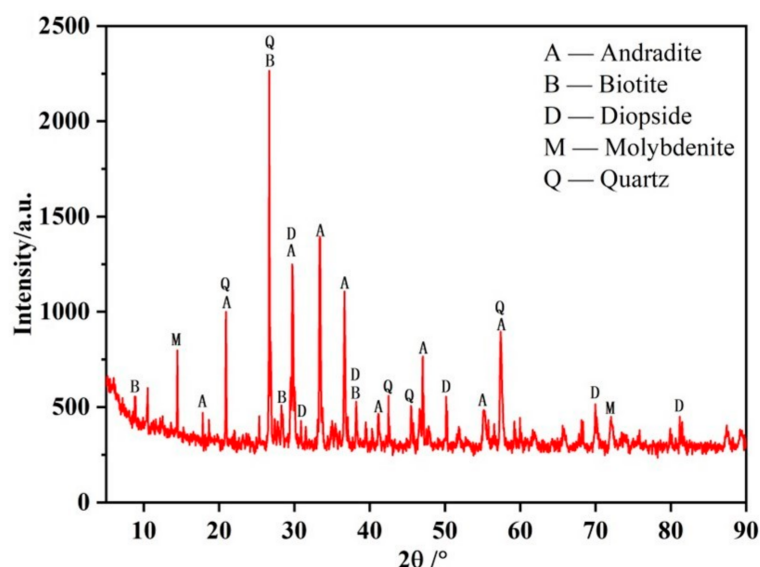


Figure 2. X-ray diffraction (XRD) analysis of raw ore.



Figure 3. Molecular structure of  $\alpha$ -Methylnaphthalene (a) and  $\beta$ -Methylnaphthalene (b).

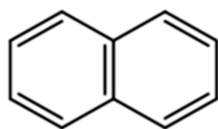


Figure 4. Molecular structure of naphthalene.

Industry grade pine oil was used as the frother. The total dosage of collector used in actual ore flotation is 170 g/t with frother 90 g/t, which were all divided into rougher, scavenging I, and scavenging II according to the mass ratio of 7:2:1, respectively. Calcium oxide,  $\text{H}_2\text{SO}_4$ , and NaOH were used to adjust pH. Tap water was used in the actual ore flotation. Distilled water was used in the micro-flotation tests.

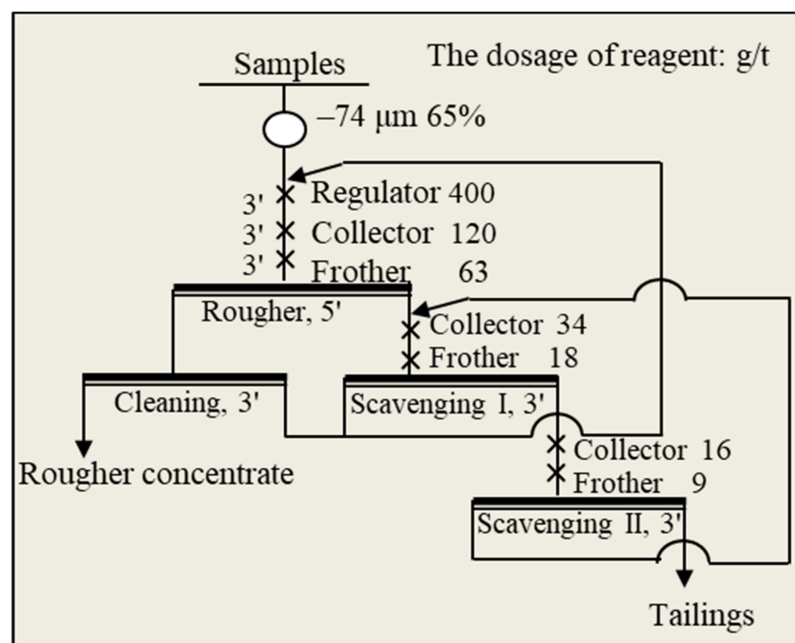
## 2.2. Flotation Tests

Micro-flotation tests were conducted in a 40 mL XFG trough-type flotation machine with an impeller rotation speed of 1760 r/min. Then, 2.0 g molybdenite samples were added to the flotation cell with 40 mL distilled water. After conditioning for 2 min, the pH value of the slurry was adjusted using  $\text{H}_2\text{SO}_4$  or NaOH. The collector was then added to the slurry, and conditioning was performed for 3 min. Subsequently, the frother was added with a conditioning time of 3 min. The flotation process was carried out by manual scraping, and the flotation time was 5 min. The concentrates and tailings were collected, filtered, dried, and analyzed to evaluate the mass recovery of molybdenite.

Actual ore flotation experiments were carried out in an XFD laboratory flotation machine with a 3.0 L flotation cell, manufactured by Jilin Exploration Machinery Plant (China). The feeding pulp concentration was controlled to be around 33.3%. An amount of 1 kg molybdenite sample was transferred into the flotation cell after grinding. The proportion of the particle size fractions of less than 74  $\mu\text{m}$  in the grinding products was approximately 65.0%, maintaining the same fineness as the mineral processing plant. Before



the flotation, the pH of the slurry was adjusted for 3 min in the range of around pH 11 using calcium oxide (CaO), based on field application. Furthermore, the appropriate dosages of collector and frother were introduced into the pulp and conditioned for 3 min in turn. Then the rougher test was carried out for 5 min following pulp aeration for 2 min. Thereafter, the froth products were collected. Subsequently, scavenging I and scavenging II were conducted according to the process shown in Figure 5. The froth products from three separations were combined as concentrate. The concentrate and the product in the tank were filtered, dried, weighed, and assayed.



**Figure 5.** Closed-circuit flowsheets of molybdenite flotation with three types of collectors.

A closed circuit flotation test was also conducted with a 3.0 L flotation cell. The closed-circuit flowsheets of the molybdenite sample flotation are shown in Figure 5 with the types and dosage of reagents.

### 2.3. Filtration Characteristic Tests of Flotation Concentrate

The flotation tests of actual molybdenite ore were carried out conditioned with three types of collectors under the condition of pulp temperatures of 25 °C and 3 °C, respectively. The obtained concentrate pulp was placed at 25 °C or 3 °C for 3.0 h. The supernatant of the pulp was then poured out and 20 mL of the precipitated concentrate in each beaker was retained. Then the supernatant was added which had just been poured out into the beaker until the pulp volume reached 150 mL. Finally, 150 mL pulp was filtered under the designated pressure, and the time for filtration was recorded.

### 2.4. Crystallization Characteristics Analysis of Collectors

Three types of collectors were prepared: 50 g kerosene, 40 g kerosene and 5 g MNap, 40 g kerosene and 5 g Nap, and stored in three beakers, respectively. Then three different collectors were placed in different temperature environments for 2.0 h. After the temperature was stable, collectors were photographed and their state changes were observed. The temperatures were 25 °C, 3 °C, −10 °C, and −15 °C, respectively.

### 2.5. Crystallization Characteristic Measurements of Collectors on the Surface of Flotation Concentrate

An amount of 2.0 g molybdenite single mineral was put into the beaker with 50 mL distilled water and a certain amount of collector, and the mixture was stirred for 10 min

with a magnetic stirrer. Then the beaker was placed at a certain temperature for 2.0 h and the solution was filtered under a certain pressure to obtain molybdenite single mineral. The surface of the molybdenite single mineral was observed by optical microscopy and photographs taken. The temperatures were 25 °C, 3 °C, −10 °C, and −15 °C, respectively.

### 3. Results

#### 3.1. Analysis on the Selection Principle of the Main Collector and Auxiliary Collector

The aliphatic hydrocarbons and molybdenite faces have similar surface force properties and surface energy. Therefore, aliphatic hydrocarbon collectors can adsorb on the faces of molybdenite particles through a dispersion force to improve their hydrophobicity to collect molybdenite, but they cannot adsorb on the edges of molybdenite particles. As is well known, aliphatic hydrocarbons are hydrocarbons with the basic properties of aliphatic compounds. Usually, the main representative of the hydrocarbon oils used in the flotation of molybdenite is kerosene and diesel oil. Kerosene and diesel oil have good collecting ability at room temperature and are widely used in the field. However, the dispersion of diesel oil in pulp at low temperature is poor, resulting in a poor flotation effect of the molybdenite. As a result, kerosene was selected as the main collector in this study.

In this case, the key was to find a type of collector as an auxiliary collector mixed with kerosene which could adsorb on the “edge” of the molybdenite particle and improve its hydrophobicity, so as to improve the flotation effect of molybdenite. Because molybdenite edges possess a certain polarity, a kind of polar non-polar oil collector is required to selectively adsorb on the particle edges to improve their hydrophobicity. It has been shown [18–22] that polar collector, syntax emulsifier, and kerosene can be mixed to improve the separation index of molybdenite, but at the same time, other non-molybdenum sulfide minerals can also be collected which increases the difficulty of flotation separation from molybdenite. Hence, the addition of polar reagents with low selectivity is only suitable for single molybdenite, but not for molybdenite with other complex minerals. In order to achieve this goal, the selection of an auxiliary collector is a strict procedure. The principle of selection is that the auxiliary collector has a certain polarity, which is not too high, and a good selectivity. What is more, it should have no collecting effect on the other non-molybdenum sulfide minerals. Aromatic hydrocarbons with benzene ring are especially suitable for this requirement.

#### 3.2. Surface Energy Analysis of Collectors

The surface force properties and surface energy are similar between aliphatic hydrocarbon and molybdenite particles. Therefore, aliphatic hydrocarbon collectors can improve the hydrophobicity of molybdenite particles by dispersive force adsorption. Similarly, we can calculate and compare the surface energy of polycyclic aromatic hydrocarbons and the molybdenite “edge”. The surface free energy of molybdenite was calculated secondhand by Young’s equation according to the relationship between the contact angles of the three liquids on the “face” and “edge” [26,27]. The surface energy of the polycyclic aromatic hydrocarbons was determined by measuring the contact angle of the three liquids on the solid surface treated by the polycyclic aromatic hydrocarbons.

Young’s equation is shown as follows:

$$\gamma_L \times \cos\theta = \gamma_s - \gamma_{SL} \quad (1)$$

where  $\gamma_L$  is the surface tension of the liquid ( $\text{mJ}/\text{m}^2$ );  $\theta$  is the contact angle in degrees ( $^\circ$ );  $\gamma_s$  is the surface free energy of the solid ( $\text{mJ}/\text{m}^2$ );  $\gamma_{SL}$  is the free energy of solid–liquid interface ( $\text{mJ}/\text{m}^2$ ).

According to the viewpoint of van Oss, Fowkes, and Chaudhury [28–30], the surface free energy of a solid can be explained by the acid base theoretical model, i.e.,  $\gamma_s$  is composed of Lifshitz van der Waals  $\gamma_s^{LW}$  and the component electron donor acceptor  $\gamma_s^{AB}$  (also known as acid base interaction), which can be described as follows:

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} \quad (2)$$

where  $\gamma_s^{AB}$  can be divided into the electron acceptor component  $\gamma_s^+$  and electron donor component  $\gamma_s^-$ . The relationship is shown in Equation (3).

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \times \gamma_s^-} \quad (3)$$

By introducing Equation (3) into Equation (2), another expression of surface free energy of the solid can be obtained as follows:

$$\gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \times \gamma_s^-} \quad (4)$$

Similarly, the surface free energy of the liquid can be expressed as:

$$\gamma_L = \gamma_L^{LW} + 2\sqrt{\gamma_L^+ \times \gamma_L^-} \quad (5)$$

The free energy of the solid–liquid interface can also be expressed as a function of the geometric average of components  $\gamma_{SL}^{LW}$  and  $\gamma_{SL}^{AB}$ , and can be described as follows:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\left(\sqrt{\gamma_s^{LW} \times \gamma_L^{LW}} + \sqrt{\gamma_s^+ \times \gamma_L^-} + \sqrt{\gamma_s^- \times \gamma_L^+}\right) \quad (6)$$

By combining Equations (4)–(6) with Young's equation, the following results are obtained:

$$\gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_s^{LW} \times \gamma_L^{LW}} + \sqrt{\gamma_s^+ \times \gamma_L^-} + \sqrt{\gamma_s^- \times \gamma_L^+}\right) \quad (7)$$

In this study, distilled water (polar liquid), formamide (polar liquid), and di-iodomethane (nonpolar liquid) were selected. The contact angle of the common exposed surface of the molybdenite crystal under the action of three liquids is shown in Table 2. The surface tension and component parameters of the three liquids are shown in Table 3 [31,32]. The contact angle was measured by the sessile drop method [33]. According to Equation (7), the surface energy of molybdenite “face” and “edge” can be calculated. The results are shown in Table 4. Similarly, the surface free energy of MNap was calculated, but not for Nap. The results are shown in Table 5.

**Table 2.** Average contact angle values measured by the droplet of three liquids on each commonly exposed surface of molybdenite.

Surface	Contact Angle/°		
	Distilled Water	Formamide	Di-Iodomethane
{001}	85.3	48.7	37.5
{100}	13.5	8.2	76.8

**Table 3.** Surface tension  $\gamma$  of each probe liquid and its components (mJ/m<sup>2</sup>).

Liquid for Detection	$\gamma_L$	$\gamma_L^{LW}$	$\gamma_L^+$	$\gamma_L^-$	$\gamma_L^{AB}$
Distilled water	72.8	21.8	25.5	25.5	51.0
Formamide	58.0	39.0	2.28	39.6	19.0
Di-iodomethane	50.8	50.8	0.0	0.0	0.0

**Table 4.** Surface free energy and its components of the common exposed surfaces of molybdenite (mJ/m<sup>2</sup>).

Surface	$\gamma_S$	$\gamma_S^{LW}$	$\gamma_S^+$	$\gamma_S^-$	$\gamma_S^{AB}$
{001}	42.55	40.84	1.28	0.57	1.71
{100}	195.18	19.16	39.72	195.01	176.02

**Table 5.** Surface free energy parameters of collectors (mJ/m<sup>2</sup>).

Surface	$\gamma_C$	$\gamma_C^{LW}$	$\gamma_C^+$	$\gamma_C^-$	$\gamma_C^{AB}$
Surface treated with kerosene	44.50	41.97	0.12	4.62	2.53
Surface treated with MNap	198.53	18.38	41.46	195.69	180.15

The results in Table 5 show that the surface energy value of kerosene is  $\gamma_C = 44.50$  mJ/m<sup>2</sup> close to that ( $\gamma_S = 42.55$  mJ/m<sup>2</sup>) of the molybdenite {001} surface shown in Table 4, which is consistent with the results of previous studies [34,35]. The  $\gamma_C^+$  and  $\gamma_C^-$  of kerosene are low, which indicates that kerosene does not adsorb on the molybdenite surface by chemical reaction, but by physical adsorption on the {001} surface of molybdenite according to the principle of similar compatibility. For fine-grained molybdenite, it is not enough to collect molybdenite particles by kerosene adsorption on the “face”. As a result, the floatability of fine-grained molybdenite in the kerosene system is lower than that of coarse-grained molybdenite. To solve this problem, the effect of auxiliary collector adsorption on molybdenite “edge” needs to be studied in a scientific way.

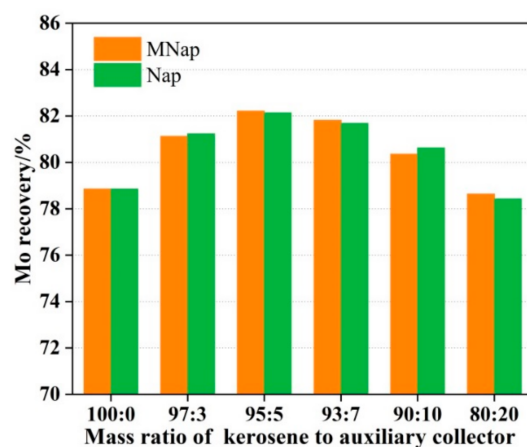
Table 5 shows the surface energy value (198.53 mJ/m<sup>2</sup>) of MNap as being also extraordinarily close to that (195.18 mJ/m<sup>2</sup>) of {100} surface of molybdenite, and  $\gamma_C^+$  and  $\gamma_C^-$  of MNap are relatively high and close to that of the {100} surface of molybdenite. Thus, MNap can adsorb on the {100} surface of molybdenite. In conclusion, the adsorption of polycyclic aromatic hydrocarbons on the molybdenite “edge” to enhance its hydrophobicity can be studied in a scientific way.

### 3.3. The Effect of Auxiliary Collector on Molybdenite Flotation

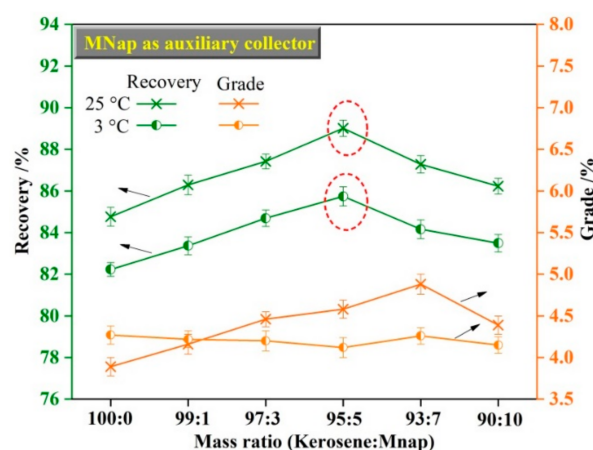
In this study, MNap and Nap were selected as auxiliary collector mixed with kerosene in the proper proportion in the flotation experiments, respectively. Micro-flotation experiments were conducted under the conditions of different mass ratios of kerosene to auxiliary collector and the results are shown in Figure 6. As can be seen, molybdenum recovery remained about 78.85% with kerosene as collector alone. It is obvious that molybdenum recovery first increased and then decreased with increasing mass ratio of kerosene to auxiliary collector and reached a maximum of 82.21% and 82.13% when MNap and Nap were auxiliary collectors, respectively, with the mass ratio of kerosene to auxiliary collector being 95:5.

The results of micro flotation experiments illustrate that the addition of auxiliary collector is helpful to improve the flotation recovery. In order to further verify the improvement effect of auxiliary collector on actual ore flotation, the flotation experiments of molybdenite were carried out under the conditions of pulp temperature of 25 °C and 3 °C, to find the best mixing ratio of auxiliary collector and kerosene. Figure 7 shows the effect of mass ratio of kerosene to MNap on molybdenite flotation, with the mass ratios of 100:0, 99:1, 97:3, 95:5, and 93:7, respectively. The total dosage of collector is 170 g/t, and the total dosage of frother is 90 g/t, which are distributed to rougher, scavenging I, and scavenging II in the proportion of 7:2:1. As shown in Figure 7, under the conditions of pulp temperature of 25 °C, the Mo recovery rate of molybdenite concentrate first gradually increased and then decreased with the increase of the proportion of MNap, while the grade also increased. The optimum mass ratio of kerosene to MNap was 95:5 corresponding to 89.01% molybdenite recovery, which was increased by 4.25% compared with the use of kerosene as the collector alone. Obviously, when the content of auxiliary collector is

above 5 wt%, the flotation recovery of molybdenite began to decrease. Under the condition of pulp temperature of 3 °C, the recovery curve of molybdenite concentrate is similar to that of pulp temperature of 25 °C. The optimum mass ratio of kerosene to MNaP was 95:5 corresponding to 85.37% molybdenite recovery, which was increased by 3.51% compared with the use of kerosene as the collector alone.



**Figure 6.** The effect of mass ratio of kerosene to MNaP on molybdenite flotation (collector 170 g/t, frother 90 g/t).



**Figure 7.** The effect of mass ratio of kerosene to MNaP on molybdenite flotation (collector 170 g/t, frother 90 g/t).

Figure 8 shows the effect of mass ratio of kerosene to Nap on molybdenite flotation, with the mass ratios also of 100:0, 99:1, 97:3, 95:5 and 93:7, respectively. When the auxiliary collector was Nap, the change in the trend of the flotation test results was similar to that of auxiliary collector MNaP. As well, the optimum mass ratio of kerosene to Nap was 95:5, and the recovery was increased by 3.47% and 3.70% under the condition of pulp temperature of 25 °C and 3 °C, respectively.

In order to more clearly express the effect of the optimal auxiliary collector dosage on the improvement of the molybdenite flotation recovery rate, the data comparison is shown in Figure 9. We can draw the conclusion that MNaP and Nap as auxiliary collector can improve the flotation recovery of molybdenite both at room temperature and low temperature.

According to the above data and the analysis of the selection basis of the auxiliary collector, the auxiliary collector may be adsorbed onto the molybdenite particles to improve their hydrophobicity. The combined use of auxiliary collector and kerosene as molybdenite collector can effectively improve the flotation index of molybdenite at the mass ratio of 95:5 kerosene to MNaP or Nap. Furthermore, the degree of improvement of the molybdenite

flotation index is very close. On the basis of condition tests, closed circuit experiments were carried out according to the process shown in Figure 5. The results are shown in Table 6.

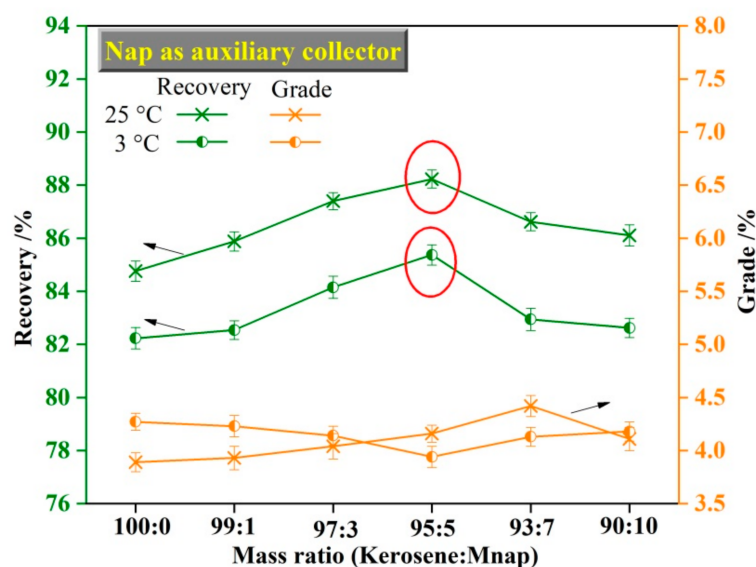


Figure 8. The effect of mass ratio of kerosene to Nap on molybdenite flotation (collector 170 g/t, frother 90 g/t).

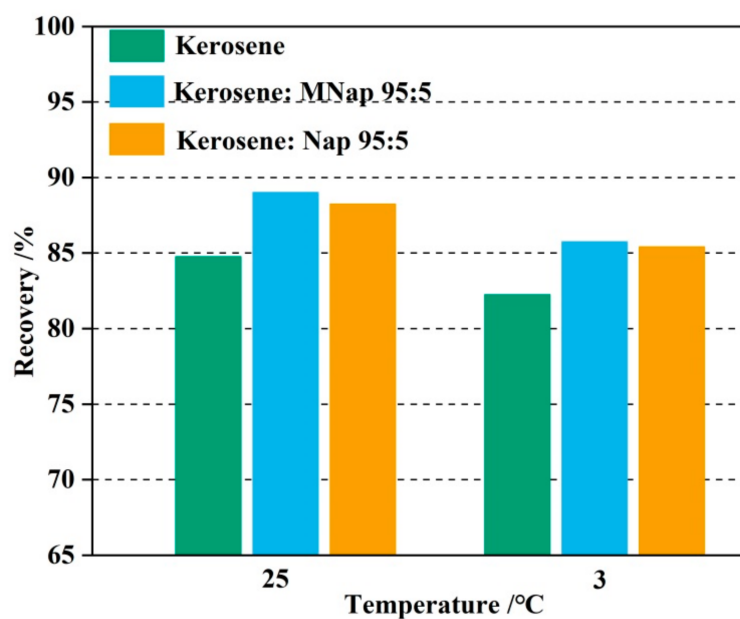


Figure 9. Recovery of molybdenite flotation concentrates with and without auxiliary collector.

Table 6. Results of closed-circuit flow sheets.

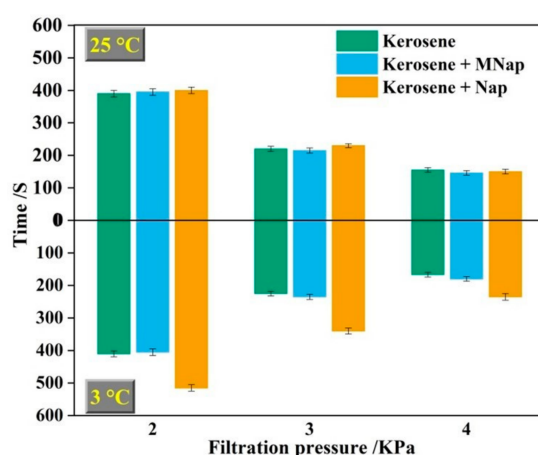
Type of Collectors	Product	Rate (%)	Grade (%)	Recovery (%)
Kerosene	Concentrate	1.17	8.74	83.14
	Tailings	98.83	0.021	16.86
	Feed	100.00	0.123	100.00
Kerosene:MNap 95:5	Concentrate	1.06	10.11	86.42
	Tailings	98.94	0.017	13.58
	Feed	100.00	0.124	100.00
Kerosene:Nap 95:5	Concentrate	1.13	9.40	86.35
	Tailings	98.87	0.017	13.65
	Feed	98.87	0.123	13.65



According to the results of the closed-circuit test in Table 6, the flotation indexes with “kerosene + MNap” and “kerosene + Nap” as collectors were better than those with kerosene as collector. Compared with kerosene as collector alone, the recoveries were increased by 3.28% and 3.21%, while “kerosene + MNap” and “kerosene + Nap” as collectors, respectively. Therefore, the closed-circuit test shows that the recovery of molybdenite can be effectively improved by the combination of two kinds of polycyclic aromatic hydrocarbons and kerosene, respectively.

### 3.4. Filtration Characteristics of Flotation Concentrate with Different Collectors

The flotation results demonstrated that the MNap and Nap could improve the flotation recovery under the condition of pulp temperatures of 25 °C and 3 °C. In the field application, it was found that the filtration velocities of these three collectors were different at low temperature in winter. To investigate the influence of the three collectors (kerosene, kerosene + MNap and kerosene + Nap) on the filtration velocity of flotation concentrate in winter, the filtration time of flotation concentrate with different collectors was determined. The results are shown in Figure 10.



**Figure 10.** Filtration time of flotation concentrate with three collectors at different pressures and temperatures.

It is evident from the results in Figure 10, that the filtration time of the same quality concentrate obtained respectively by the three collectors shows little difference to room temperature of 25 °C. This shows that the addition of the two auxiliary collectors has little negative effect on the filtration velocity of the concentrate at room temperature. It is to be noted that in Figure 10, the filtration time of the concentrate with “kerosene + Nap” as the collector was much longer than that of the other two collectors at different filtration pressures at the low temperature of 3 °C.

By comparison of the filtration times at 25 °C and 3 °C, under the same filtration pressure, for the concentrates with “kerosene” and “kerosene + MNap” as collectors, the filtration time at room temperature was similar to that at low temperature. However, when “kerosene + Nap” is used as collector, the filtration time of concentrate at low temperature was longer than that at room temperature. This shows that the auxiliary collector “Nap” may be only suitable for use at relatively high temperature, but not in winter. As such, it can be considered that MNap added into kerosene as auxiliary collector of molybdenite has little effect on the filtration speed of flotation concentrate at low temperature in winter. MNap not only improves the recovery, but also has little negative influence on the subsequent treatment of concentrate.

### 3.5. Crystallization Characteristics of Different Collectors

Due to the low temperature in winter in the northern part of our country, the ambient temperature may have a negative impact on the collectors, thus affecting collecting perfor-

mance. Consequently, in order to study the existing state of collectors (Kerosene, Kerosene + MNap, Kerosene + Nap) at different temperatures, three collectors were observed and pictures taken with a camera. The results are shown in Figure 7.

It is clear that in Figure 11, the three collectors all existed in the form of liquid at 25 °C. When the temperature was reduced to 3 °C, there was no change in “kerosene” and “kerosene + MNap”, but a small amount of white crystals began to precipitate in “kerosene + Nap”. When the temperature dropped to −10 °C, there was still no change in “kerosene” and “kerosene + MNap”, while the white crystals precipitated from “kerosene + Nap” gradually increased with more at −15 °C. These results demonstrated that Nap crystallized readily in liquid at low temperature. Although the indoor temperature is above 0 °C in winter in northern China, the outdoor temperature is generally below 0 °C, which is not conducive to the transportation, storage, and use under the conditions of low temperature in northern winter.

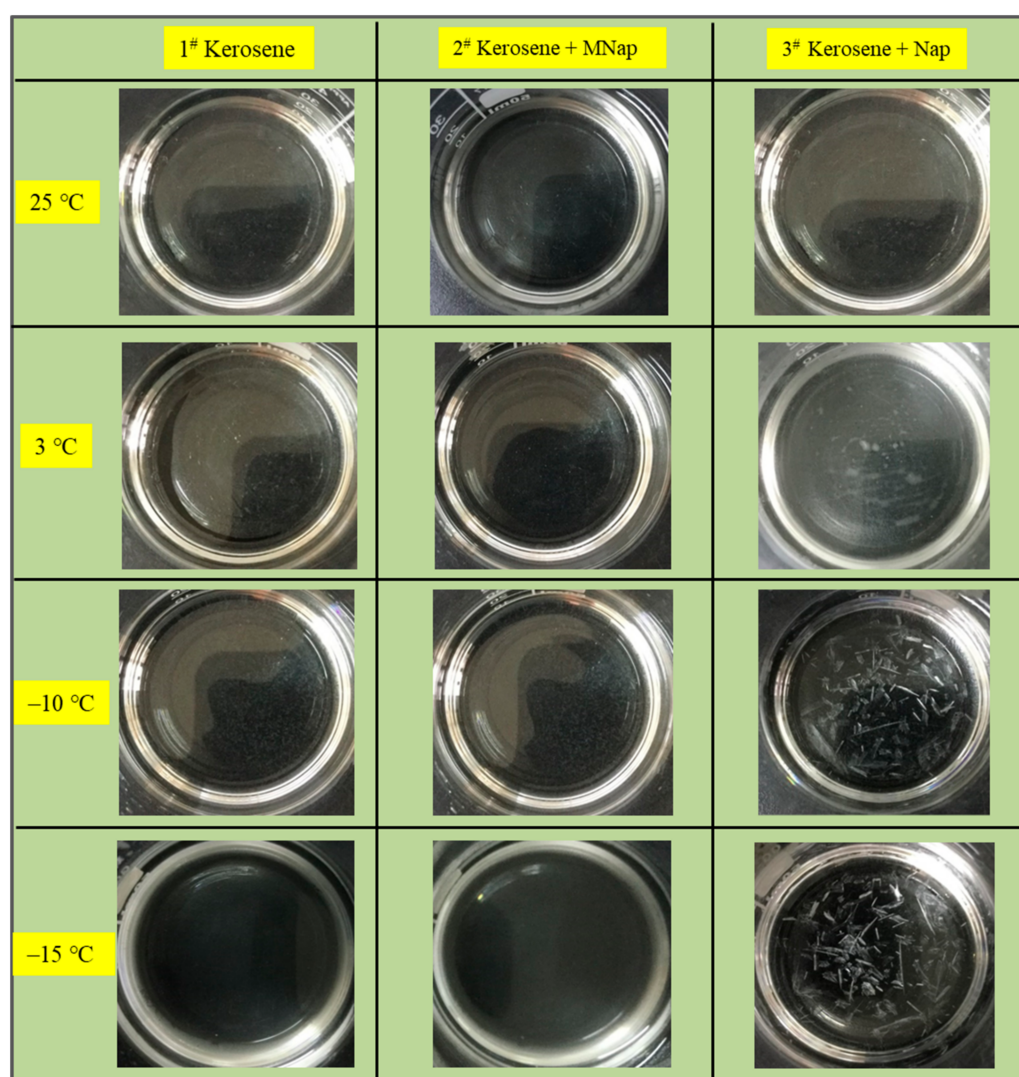
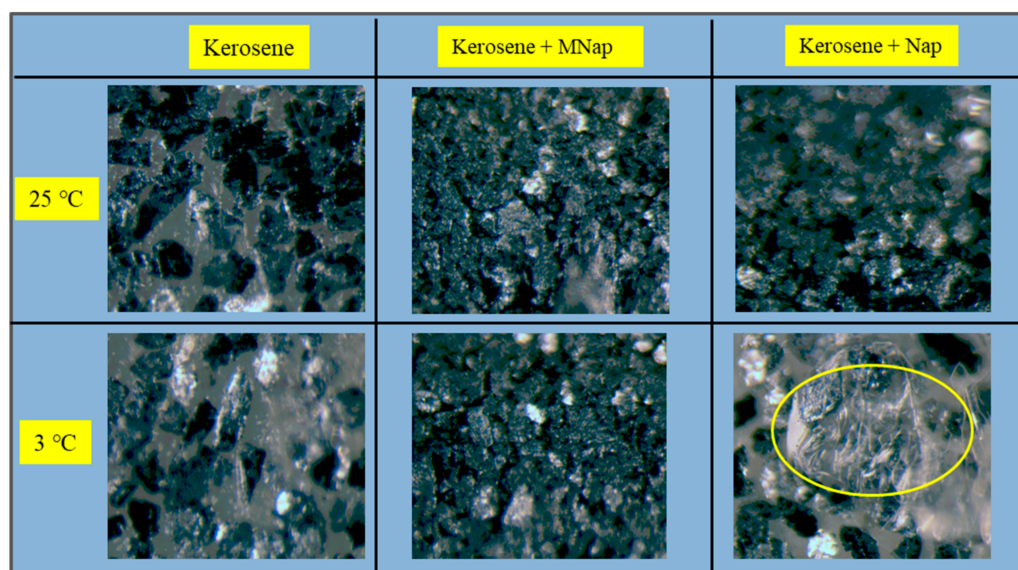


Figure 11. Crystallization characteristics of the three collectors at different temperatures.

Therefore, it can be concluded that although “kerosene + Nap” can improve the flotation index of molybdenite, it is not suitable for molybdenite flotation in the northern cold winter area. However, the existing state of MNap at room temperature and low temperature shows no change. As a result, MNap can be used as auxiliary collector and mixed with kerosene to improve molybdenite flotation.

### 3.6. Crystallization Characteristics of the Collectors on the Flotation Concentrate Surface at Different Temperatures

Based on the above experimental results, Nap can precipitate from kerosene at low temperature. In the field application tests, it was also found that the filtration time of flotation concentrate was longer when “kerosene + Nap” was used as collector. Therefore, to find out the reason affecting the filtration time, the molybdenite single mineral flotation experiments with different collectors were carried out at low temperature (3 °C) and normal temperature (25 °C), and then flotation concentrates were observed and compared under the ordinary optical microscope respectively. The benefit was to more intuitively watch the changes on the surface of the molybdenite with the different collectors, affecting the filtration velocity at low and room temperature. Figure 12 presents the results.



**Figure 12.** Surface changes of flotation concentrate at different temperatures.

It is obvious in Figure 12 that at room temperature of 25 °C, there was no crystal precipitation on the surface of the flotation concentrate with the three collectors after filtration respectively, indicating that the addition of the two auxiliary collectors has no effect on the filtration of the concentrate. At low temperature of 3 °C, crystal precipitation cannot be observed on the surface of the concentrate after filtration with “kerosene” and “kerosene + MNap” as collectors, but there were white crystals on the surface of the concentrate obtained by “kerosene + Nap” as collector after filtration, leading to the slow filtration speed. This is mainly due to the addition of auxiliary collector “Nap”. Nap is a solid lamellar crystal that can be dissolved in kerosene at room temperature. It can be seen from Figure 12 that it was precipitated from kerosene at low temperature. The precipitation of Nap at low temperature was the fundamental reason that affected the filtration velocity of concentrate, which led to the longer filtration time in winter. Furthermore, this effect will be more obvious when nap is applied in industrial experiments.

Based on these findings, it can be inferred that using “kerosene + MNap” as the collector for molybdenite separation, white crystals were not precipitated from the surface of the flotation concentrate at room and low temperature, thus MNap did not have adverse impact on the filtration velocity of concentrate and had strong adaptability to the environmental temperature. Furthermore, when MNap was added as an auxiliary collector of molybdenite, we noted that the recovery rate of molybdenite can be improved at room temperature and at low temperature. Based on these considerations, we considered MNap to be a good auxiliary collector to improve the flotation index of molybdenite.

## 4. Conclusions

Based on the results of this investigation, the following conclusions can be drawn:

- (1) The mixed (kerosene/MNap or kerosene/Nap) collectors display a stronger collecting ability for molybdenite than the individual kerosene. We obtained a maximum recovery of 89.01% and 85.74% using the kerosene/MNap as the collector at temperatures of 25 °C and 3 °C, while using the kerosene/Nap as the collector at the temperature of 25 °C and 3 °C we obtained 88.23% and 85.41%. The molybdenum recovery was also increased by 3–4% both at room temperature and low temperature.
- (2) The surface energy ( $\gamma_C = 44.50 \text{ mJ/m}^2$ ) of polycyclic aromatic hydrocarbons was very close to that ( $\gamma_S = 42.55 \text{ mJ/m}^2$ ) of the molybdenite {100} surface. Therefore, it can physically be adsorbed on the molybdenite {100} surface according to the principle of similar compatibility. The filtration velocity of flotation concentrate with kerosene mixed with auxiliary collector MNap as collector was basically the same as that obtained by using kerosene alone, and there was no crystallization phenomenon on the surface of flotation concentrate. This shows that MNap is suitable at various temperatures and its addition has no adverse effect for the use in industrial production in cold winter weather.

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