# Studies on the Flotation of Molybdenite. II : Some Experiments on the Kerosene Flotation



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# Studies on the Flotation of Molybdenite. II

## Some Experiments on the Kerosene Flotation*

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**Synopsis**

Some experiments were carried out on the flotative properties of kerosene which is commonly used for molybdenite ore. Two kinds of molybdenite ore from the Daito mine, Shimane Prefecture, were used as samples.

Kerosene shows the different flotation effects on the samples of ore differing in mineral composition and size distribution, though the samples were obtained from the same mine. But it may be worthwhile to note that kerosene has an effect of improving the flotation results of low grade ore. It may be considered that the conditioning time for sutiable period after adding kerosene promotes the selectivity of molybdenite and pyrite. The increase in the proportion of kerosene mixed with pine oil is also useful in obtaining higher selectivities. The distilled fractions of kerosene, having the intermediate boiling point range, are more effective than those having high and low boiling point range.

Generally, the use of emulsifying agents with kerosene increase the recovery of molybdenite. Non-ionic emulsifying agents, particularly polyglycolesters of fatty acids or alkylphenolpolyglycolethers, give good flotation results. Moreover, the use of emulsifying agents contributes to the improvement of the worse conditions of forths caused by the addition of kerosene.

## I. Introduction

The authors and their collaborators reported that the necessary quantity of oily collector, such as kerosene, for the flotation of molybdenite was much larger than that of xanthate for ordinary sulphide minerals(1): they further showed that the oily collectors mainly composed of paraffin-base hydrocarbon were widely used.(2)

The collecting action of oily collector on molybdenite has been investigated by Krokhin et al.,(3),(4) but many problems remain to be cleared in future.

The present article deals with the results obtained from some experiments on

* The 142 nd report of the Research Institute of Mineral Dressing and Metallurgy. The original report in Japanese was published in Bull. Res. Inst. Min. Dress. Met., Tohoku Univ., **18** (1962), 15-22.

(1) M. Wada, H. Majima, R. Takeda, S. Takeshita and K. Hirose, Bull. Res. Inst. Min. Dress. and Met., Tohoku Univ., **17** (1961), 69.

(2) M. Wada and H. Majima, Flotation, No. **17** (1962), 9.

(3) S.I. Krokhin, Sbornik Nauch., Trudov Severo-Kavkaz. Gorno-Met. Inst., No. **14** (1959), 105; C.A. **54**, 22,225.

(4) S.I. Krokhin and R.I. Chermkuhina, Izvest. Vysshikh Ucheb. Zavedenii, Tsvetnaya Met., **2**, No. 1 (1959), 26; C.A. **54**, 14,017.

the flotative properties of kerosene, particularly the behavior of kerosene to molybdentie flotation, the collecting effect of the distilled fractions of kerosene, and the improvement of flotation results by the use of emulsifying agents.

## II. Materials

Two kinds of molybdenite ores were obtained from the Daito mine, Shimane Prefecture, to be used in this investigation.

Hand-picked ore from the Daito mine was first crushed in a roll-jaw crusher and then ground in a sample grinder to all -65-mesh (Sample A). Crude ore from the same mine was crushed in the roll-jaw crusher to pass through 4-mesh screen; the product was screened wet on 325-mesh and the undersize was rejected; the -4+65-mesh fraction was further ground in a sample grinder to all -65-mesh; and these products were mixed (Sample B).

The chemical analyses and the size distributions of Samples A and B are presented in Tables 1 and 2 respectively. In this article, the results obtained on Sample A are mainly reported. Kanto Chemicals Co.'s Cica Brand kerosene was used as reagent. The fractions of kerosene distilled under the ordinary pressure, having sutiable boiling point range, were applied to the experiments on collecting effect.

Table 1. Chemical analyses of molybdenite ores.

| Sample | Grade (%) | | | | |
|---|---|---|---|---|---|
| | $MoS_2$ | Fe | S | $SiO_2$ | $Al_2O_3$ |
| A | 8.18 | 5.99 | 8.89 | 71.41 | 5.84 |
| B | 1.44 | 5.71 | 4.73 | 80.93 | 4.34 |

Table 2. Size distributions of ore samples.

| Size | Weight (%) | |
|---|---|---|
| (mesh) | Sample A | Sample B |
| +100 | 35.6 | 0.3 |
| 100-150 | 23.0 | 29.1 |
| 150-200 | 7.5 | 14.3 |
| 200-270 | 13.1 | 25.8 |
| 270-400 | 8.4 | 13.2 |
| -400 | 12.4 | 17.3 |

Table 3 shows the physical properties of distilled fractions of kerosene. The extra pure grade reagents of sodium lauryl sulphate and sodium alkylarylsulphonate from the Tokyo Kasei Co., and Monogen, Neogen, Noigen, and Turkey red oil from the Daiichi Kogyo Seiyaku Co. as emulsifying agents for kerosene, and Nikko No. 7 pine oil as frother were used.

Table 3. Physical properties of distilled fractions of kerosene.

| Boiling point range (°C, 1 atm.) | Weight (%) | Specific gravity $d_4^{20}$ | Refractive index $n_D^{19}$ |
|---|---|---|---|
| — | 100.00 | 0.789 | 1.4427 |
| <150 | 2.53 | 0.760 | 1.4300 |
| 150-180 | 13.62 | 0.770 | 1.4347 |
| 180-200 | 31.70 | 0.781 | 1.4390 |
| 200-220 | 43.92 | 0.794 | 1.4451 |
| 220-235 | 1.29 | 0.802 | 1.4488 |
| >235 | 6.95 | 0.809 | 1.4519 |

## III. Experimental prdocedure

In this study, the flotation tests were employed to evaluate the flotative properties of kerosene for molybdenite ores. 50 gram M.S. type flotation machine modified at Kyoto University was used under the constant conditions: periferal speed of the impeller, 104 m/min; pulp density, 20% solids; agitation of pulp, 5 min; and flotation, 5 min. One ml. of the solution of emulsifying agents, containing 1 g/l of their effective component, was added to the pulp one min. before adding kerosene-pine oil mixture.

## IV. Experimental results and discussions

1) Flotation effects of kerosene

It is important that the flotation effects of kerosene on molybdenite should be well understood when kerosene is added with frother.

A flotation test using 280 g/t pine oil alone on Sample A gave a concentrate assaying 46.48% $MoS_2$ and 9.39% Fe with recovery of 90.3% $MoS_2$ and 24.9% Fe. But, in the case where 1,400 g/t kerosene and 280 g/t pine oil, were used, a concentrate assaying 40.50% $MoS_2$ and 9.57% Fe was obtained with recovery of 90.6% $MoS_2$ and 28.9% Fe. From these results it was concluded that the flotation effect of kerosene on Sample A was not remarkable. On the contrary, the different flotation effect was expected for Sample B. In the flotation of Sample B with 140 g/t pine oil alone, a concentrate assaying 10.92% $MoS_2$ and 43.00% Fe was only obtained with recovery of 7.7% $MoS_2$ and 7.7% Fe. But a concentrate assaying 13.06% $MoS_2$ and 17.56% Fe was obtained with recovery of 27.0% $MoS_2$ and 9.2% Fe, when a flotation test was carried out by using 140 g/t pine oil after conditioning with 660g/t kerosene for 10 min. The use of kerosene resulted in the marked increase in $MoS_2$ recovery and the sharp drop in Fe grade of the froth product.

The above results show that kerosene improves the selectivity between molybdenite and pyrite in the ore. It is noticeable that the effect of kerosene improving the flotative properties of molybdenite is marked when low grade ore is treated.

Oily collectors, such as kerosene, are usually applied to low-grade molybdentie ores, and to lump ores assaying 80% $MoS_2$ in few cases to obtain high-purity concentrates.[(5)] From the present results, however, it is considered necessary to use

(5) V.A. Skorov and V.A. Kuleshov, Tsvetnye Metally, **33**, No. 3 (1960), 1.

kerosene after examining sufficiently the applicability of kerosene to the ore in question.

Fig. 1 shows the effect of conditioning period after adding kerosene. In these tests 1,100 g/t kerosene and 280 g/t pine oil were added, and the froths were taken for 5 min. At the end of flotation the temperatures of the pulp were 17.5–23.5°C and the pH values 6.4–6.6. With the increase in conditioning period, the $MoS_2$ grade of the froth product rose, while the Fe grade was hardly affected. The $MoS_2$ recovery attained its maximum at 5 min conditioning period, being nearly constant for further conditioning period. The Fe recovery attained its maximum at 15 min conditioning period. Therefore, it may be considered that the sutiable conditioning period after kerosene addition promotes the selectivity between molybdenite and pyrite.

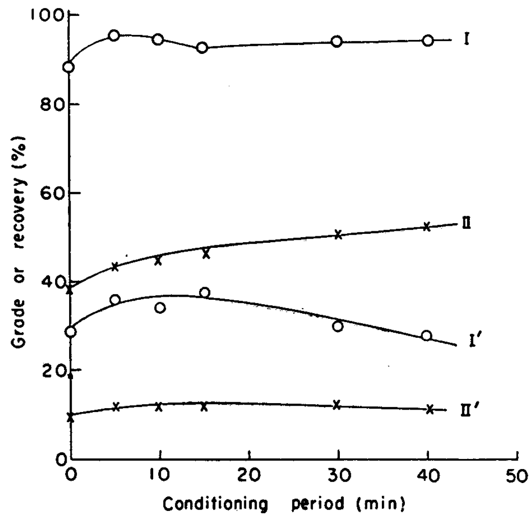


Fig. 1. Influence of the conditioning period after adding kerosene. I: $MoS_2$ recovery, I': Fe recovery, II: $MoS_2$ grade of froth product, II': Fe grade of froth product.

Kerosene is cheaper than ordinary frothing agents such as pine oil. So, even in the case where flotation is successful with frothing agent only, economical profit may be expected if kerosene can be used partially as substitute for frothing agent. Fig. 2 shows the flotation results obtained by using 1,400 g/t mixed oil prepared by mixing kerosene and pine oil in voluntary proportions. In these tests, the froths were taken for 5 min. After flotation the temperatures of pulps were 15.7–17.0°C and the pH values 6.4–6.6. The $MoS_2$ recovery decreased gradually with the increase in the proportion of kerosene in mixed oil, while the Fe recovery declined remarkably. For instance, the $MoS_2$ and Fe recoveries were 96.3% and 73.7% respectively without kerosene, while they were 86.2% and 7.5% respectively with the mixed oil containing 95% of kerosene. It is noteworthy that the Fe recovery dropped sharply when mixed oil of higher kerosene proportions was used. On the other hand, the $MoS_2$ grade of the froth product was raised from 30.17% to 62.89% by the use of mixed oil containing 95% of kerosene. These results serve to confirm the fact that the increase in the proportion of kerosene to pine oil is effective in improving the selectivity of molybdenite from pyrite. As seen in Fig. 2, in the range of over 80% proportion of kerosene, the improvement in the

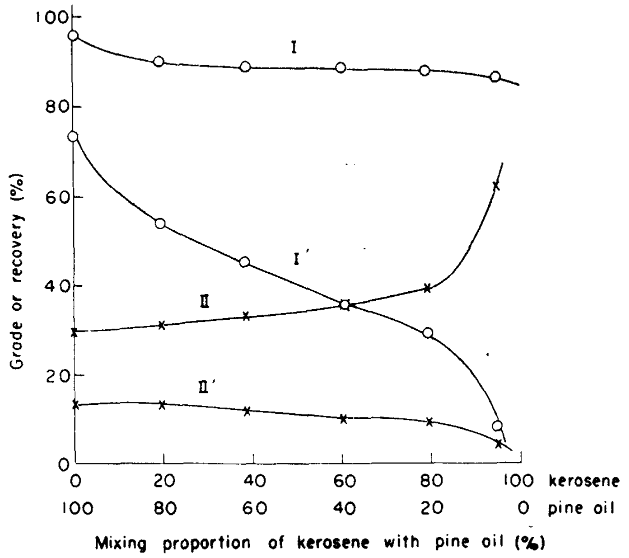


Fig. 2. Influence of the mixing proportion of kerosene with pine oil. Total quantities of mixed oil added 1,400g/t.
I: $MoS_2$ recovery, I': Fe recovery, II: $MoS_2$ grade of froth product, II': Fe grade of froth product.

$MoS_2$ grade and the lowering of the Fe grade of the concentrate were remarkable.

Undesirable froth conditions caused by adding a large quantity of kerosene, as pointed out by Cuthbertson,[(6)] were also observed in this study. But the froth condition can be modified markedly by the addition of a certain kind of emulsifying agents, as will be mentioned later.

It is important to mention especially that kerosene mixed with pine oil in suitable proportions was effective in obtaining a good flotation result on Sample A which responded with poor results to kerosene in the previous tests. The fact that a small amount of high grade concentrate is obtained by the use of mixed oil containing high proportion of kerosene may be of significance in the consideration of the cleaning process.

2) Collecting effects of distilled fractions of kerosene

As widely known, kerosene is a kind of petroleum products. It contains for the most part saturated hydrocarbons having a boiling point range of 150–250°C. So, it may not be hard to suppose that fractions of kerosene of different compositions will show different collecting effects.

(6) R.E. Cuthbertson, Am. Inst. Mining Met. Engrs., Tech. Publ. No. 1,675 (in Mining Technol., 8) (1944).

Figs. 3 and 4 illustrate the flotation results obtained by using 1,400 g/t of distilled fractions of kerosene, the physical properties of which are shown in Table 3.

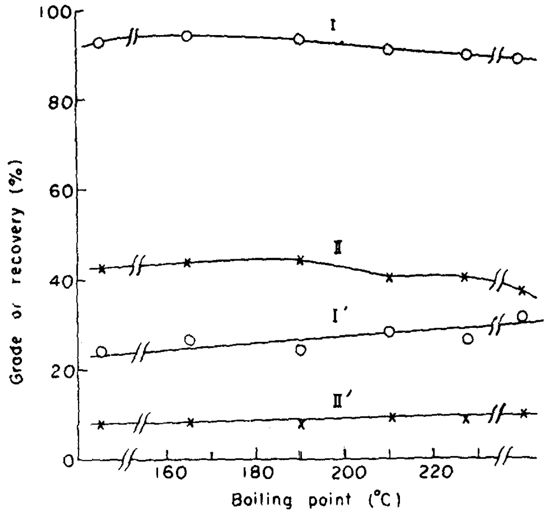


Fig. 3. Flotation effect of the distilled fractions of kerosene. (For SampleA)
I: $MoS_2$ recovery, I,: Fe recovery, II: $MoS_2$ grade of froth product, II': Fe grade of froth product.

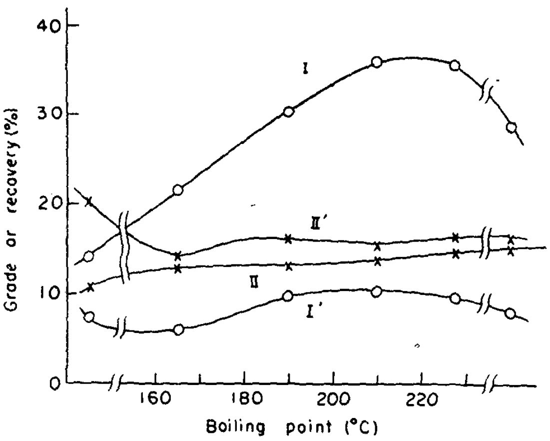


Fig. 4. Flotation effect of the distilled fractions of kerosene. (For Sample B)
I: $MoS_2$ recovery, I': Fe recovery, II: $MoS_2$ grade of froth product, II': Fe grade of froth product.

As shown in Fig. 3, the $MoS_2$ content could be recovered best from Sample A by the use of distilled fractions having the boiling point range of 150–180°C, but the variation in the $MoS_2$ recovery with the boiling point of distilled fractions was not so large. On the other hand, the Fe grade and recovery increased gradually with the rise in the temperature of distillation. Fig. 4 shows the experimental results obtained for Sample B. The amount of addition of distilled fractions of kerosene was fixed at about 660 g/t. The collecting effects of distilled fractions of kerosene for Sample B differ fairly from those for Sample A. That is, the distilled fractions of kerosene having boiling point ranges of 200–220°C and 220–235°C respectively gave the best results on the recovery of molybdenite. The collecting effect of distilled fractions of kerosene was previously studied by Krokhin,(3) by measuring the wettability of molybdenite by distilled fractions of kerosene. He stated that an appreciable amount of low boiling point fractions ($<$ 180°C) having no collecting properties was contained in the kerosene and high boiling point fractions (180–220°C and $>$220°C) were more effective collectors.

The present results, however, did not coincide with those of Krokhin. It may be supposed that the reason for such discrepancy in collecting properties is due to the difference between the presumption by measurements of wettability and the direct evaluation by flotation tests. At any rate, there may be no doubt about the fact that the distilled fractions of kerosene in the intermediate range of boiling points are more effective than those in the ranges of high and low boiling points for the present samples of ore, which is considered to be the most popular type of molybdenite ore associated with a small amount of pyrite.

3) Influence of emulsifying agents

Kerosene is dissolved in water with difficulty. Therefore, if kerosene is emulsified, its flotation effect will be intensified. At the Climax mine, Syntex M, composed mainly of sulphated monoglyceride, has been reported to be used as an emulsifying agent for hydrocarbon.(6)–(8) The use of such emulsifying agents was conceivable from the above reasoning. Even though sulphated monoglyceride was effective on pale blue neutral oil extracted from crude oil of paraffin series as in the case of the Climax mine, it may not necessarily be effective on kerosene. Therefore, flotation tests were carried out with various kinds of emulsifying agents tabulated in Table 4. The emulsifying agents was added to the pulp in a quantity corresponding to 20 g/t of its effective component, and the pulp was agitated for 1 min. The 1,400 g/t of mixed oil, prepared by mixing pine oil and kerosene in the proportion of 1: 4 in weight, was added and the froths were taken for 5 min. The temperature and the pH value of the pulp after flotation were 17.2–21.2°C and 6.5–6.9 respectively.

The flotation results with various emulsifying agents were presented in Table 4. Even if it is difficult to draw the conclusion on the flotation effects of emulsifying agents from the above results, a general trend of the flotation effects of these emulsifying agents may roughly be estimated. Thus, without emulsifying agents, the grades of froth products were 39.24% $MoS_2$ and 9.57% Fe, and the recoveries 88.3% $MoS_2$ and 29.4% Fe respectively. On the contrary, when emulsifying agents were used, the $MoS_2$ and Fe recoveries were higher. Above all, fatty alcohol sulphates as anionic emulsifying agents and polyglycolesters of fatty acids and

(7) E.J. Duggan, Am. Inst. Mining Met. Engrs., Tech. Publ. No. 1,456 (in Mining Technol., **6**) (1942).
(8) Mining Eng., **7** (1955), 742.

Table 4. Emulsifying agents and flotation results.

| Emulsifying agent | Formula | Name or trade name of reagent | Purity | Grade of rougher concentrate (%) | | Recovery (%) | |
|---|---|---|---|---|---|---|---|
| | | | | $MoS_2$ | Fe | $MoS_2$ | Fe |
| A. Anionic | | | | | | | |
| I. Sulphonic acid group | $R-S(=O)_2-OM$ | | | | | | |
| Alkylaryl-sulphonates | | Sodium alkylaryl-sulphonate | EP | 34.52 | 11.71 | 91.2 | 42.3 |
| | | Neogen powder | 35% | 32.52 | 11.74 | 93.0 | 45.9 |
| II. Fatty alcohol sulphates | $R-O-S(=O)_2-OM$ | | | | | | |
| Laurylsulphate | | Sodium lauryl sulphate | EP | 35.18 | 11.92 | 93.3 | 43.2 |
| | | Monogen powder | 35% | 32.24 | 11.83 | 94.6 | 47.4 |
| Oleylsulphate | | Monogen paste | 27% | 35.19 | 11.56 | 94.6 | 42.5 |
| III. Sulphated monoglyceride | $RCO_2CH_2CH\cdot(OH)CH_2OSO_3M$ | Turkey red oil | 40% | 30.29 | 12.83 | 91.1 | 52.7 |
| B. Non-ionic | | | | | | | |
| I. Polyglycolesters of fatty alcohols | $RO(C_2H_4O)_nH$ | Noigen ET 80 | 99% | 39.87 | 11.38 | 90.7 | 35.3 |
| | | Noigen ET 143 | 99% | 40.04 | 11.29 | 90.1 | 34.7 |
| | | Noigen ET 190 | 99% | 41.10 | 10.84 | 90.4 | 32.6 |
| II. Polyglycolesters of fatty acids | $RCOO(C_2H_4O)_nH$ | Noigen ES 90 | 99% | 41.46 | 11.38 | 92.8 | 35.9 |
| | | Noigen ES 120 | 99% | 41.22 | 11.13 | 93.2 | 33.7 |
| | | Noigen ES 160 | 99% | 39.70 | 11.56 | 95.1 | 37.9 |
| III. Alkylphenol-polyglycolethers | $R-C_6H_4-O(C_2H_4O)_nH$ | Noigen EA 80 | 99% | 45.44 | 11.71 | 93.3 | 32.8 |
| | | Noigen EA 120 | 99% | 38.40 | 12.65 | 95.3 | 42.9 |
| | | Noigen EA 160 | 99% | 39.01 | 12.65 | 94.0 | 41.6 |
| None | — | — | — | 39.24 | 9.57 | 88.3 | 29.4 |

alkylphenolpolyglycolethers as non-ionic emulsifying agents were effective in increasing the $MoS_2$ recovery. The Fe recovery increased more markedly with anionic emulsifying agents, than with non-ionic emulsifying agnets. The $MoS_2$ grade of froth product was lower with anionic emulsifying agents than with mixed oil alone, but was nearly the same with or even higher than non-ionic emulsifying agents. In particular, the $MoS_2$ grade of froth product was 45.44% with Noigen EA 80, composed mainly of alkylphenolpolyoxyethylenethers. In general, the Fe grade of froth product became higher with the addition of emulsifying agents. From these results, it seems preferable to use non-ionic emulsifying agents, particularly polyethylglycolesters of fatty acids or alkylphenolpolyglycolethers, to obtain froth products of high $MoS_2$ grade with high $MoS_2$ and low Fe recoveries.

As previously mentioned, the very undesirable froth conditions were caused by adding kerosene, but the addition of emulsifying agents contributed to the improvement of such conditions. The use of Turkey red oil having the same chief component as Syntex M used at the Climax mine, resulted in the lowering in the $MoS_2$ grade of froth products.

## Summary

Kerosene is commonly used for the flotation of molybdenite ore, but its flotative properties are not clarified so much. So, in the present study, some experiments were carried out to elucidate the flotative properties of kerosene for the molybdenite ore associated with a small amount of pyrite.

The essential results can be summarized as follows:

(1) Kerosene shows the different flotation effects on the samples of ore having the different mineral compositions and size distributions, though the samples were obtained from the same mine.

(2) The use of kerosene in the flotation of low grade ore shows an improving effect on both $MoS_2$ grade and recovery of the concentrate.

(3) The conditioning for sutiable period after adding kerosene promotes the selectivity of molybdenite from pyrite.

(4) The increase in the proportion of kerosene mixed with pine oil is useful for the improvement of the $MoS_2$ grade of the concentrate as well as the rejection of pyrite from the concentrate.

(5) The distilled fractions of kerosene, having the intermediate range of boiling points, are more effective than those of the ranges of high and low boiling points.

(6) The use of emulsifying agents with kerosene generally increases the $MoS_2$ recovery. Non-ionic emulsifying agents, particularly polyglycolesters of fatty acids or alkylphenolpolyglycolethers, give good flotation results.

(7) The use of emulsifying agents contributes to the improvement of the undesirable froth conditions caused by the addition of kerosene.

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