The Role of Surfactants in the Flotation of Molybdenite at Climax

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Abstract

The use of petroleum hydrocarbon as a collector for molybdenum sulfide improved metal recovery but necessitated the investigation of surfactants to produce a suitable froth for flotation at the Climax, Colorado mill of American Metal Climax, Inc. Up to December, 1958, 346 surfactants had been tested and evaluated. A sulfated monoglyceride of coconut oil is presently employed at Climax. The study of the role of surfactants for molybdenum sulfide flotation is continuing. One of the better materials evaluated in the last 10 years is ethoxylated, esterified and neutralized lauryl alcohol. Longer and shorter chain alcohols ethoxylated, esterified and neutralized have also been evaluated with encouraging results. Adsorption of iron hydrated complexes on molybdenite occurs which results in increased wettability of the molybdenite, an effect to strongly link the molybdenite to the water phase and reduce separability. Adsorption of ionic iron on montmorillonite and other clays occurs which activates the clays for adsorption onto the molybdenite particles. In fact, a cocoon-like coating has been found to surround molybdenite particles. This coating being highly water wettable, prevents particles of molybdenite from responding to flotation. Depression of molybdenite particulates may be caused by a "failure to collect" which is a descriptive term indicating the lack of a collector reaction at the molybdenite surfaces. For example, iron ionic complexes adsorbed at the molybdenite surface may not be reactive with the collector or the iron ions could reduce the collector concentrating by reaction in the fluid phase. Certain of the iron complexes upon adsorption onto the molybdenite may react on highly hydrated surfaces, firmly linking the particulates to the water phase. Actually, the depression of molybdenite is incompletely understood, but it is known that hydrated ionic complexes of ferrous and ferric iron are surface-active on molybdenite. In excessive concentrations these ions could be depressive. On the other hand, limited concentration of these ions could serve as activating ions.

Discussion

Before describing the role of surfactants in flotation at Climax Molybdenum Co., a brief history of the development of other flotation reagents is apropos.

Prior to 1937, in essence the only flotation reagent employed at Climax as a frother-promoter was pine oil. Sodium cyanide, however, was also added as a depressant primarily to control pyrite and chalcopyrite. The recovery of molybdenite was in the 80–85% range at a much finer grind than what is practiced today.

TABLE I

Influence on Hydrocarbon Type on MoS_2 Recovery

Hydrocarbon type	MoS_2 recovery, %	Middling index[a]
Laboratory tests with pine oil and hydrocarbon		
Kerosene	85.3	23.8
100 vis. raw distillate[b]	87.7	34.0
100 vis. pale neutral oil[c]	87.8	35.0
100 vis. white oil[d]	88.0	38.2
Laboratory tests with syntex, pine oil and hydrocarbon		
Kerosene	87.4	38.7
100 vis. raw distillate[b]	91.4	61.9
100 vis. pale neutral oil[c]	92.2	71.5
100 vis. white oil[d]	91.5	62.5

[a] Middling index, pounds of plus 100 mesh material floated in rougher froth from 1 ton of crude ore.
[b] Raw distillate contains approximately 26% unsaturates.
[c] Pale neutral oil contains approximately 10% unsaturates.
[d] White oil used in these tests contains approximately 3% unsaturates.

TABLE II

Influence of Hydrocarbon Viscosity on MoS_2 Recovery

Hydrocarbon viscosity	MoS_2 recovery, %	Middling index
100 vis. pale neutral oil	92.0	55.0
200 vis. pale neutral oil	92.4	60.4
300 vis. pale neutral oil	92.9	60.8

A small staff of metallurgical engineers and associates was organized by Climax under the direction of A. J. Weinig, at the Experimental Plant of the Colorado School of Mines, now known as the Colorado School of Mines Research Institute, to conduct studies in ways and means to improve the ore dressing metallurgy of molybdenite.

From microscopic studies of Climax ore it became evident that the molybdenite was finely disseminated and would require a considerably finer grind than minus 325 mesh to completely liberate the molybdenite from feldspar, quartz, sericite and associated minerals. Fortunately, Mother Nature made molybdenite one of the most floatable of all sulfide minerals.

The major portion of the early research program was conducted to study flotation reagents that would float fine specks of molybdenite that were attached to coarse grains of quartz, feldspar and associated minerals. This objective was necessary for economic reasons. The ore assayed between 0.45% and 0.75% MoS_2; today the feed is between 0.28% and 0.35% MoS_2. If a primary concentration, rougher flotation, of the molybdenite could be achieved at a coarse grind, like 44% retained on a 100 mesh screen versus minus 325 mesh for complete liberation of molybdenite, a considerable grinding cost could be eliminated.

During the latter part of 1937 it was discovered that an improvement in rougher recovery was obtained by adding a petroleum hydrocarbon as a promoter of molybdenite. Many types of hydrocarbons were tested. Some of the earlier ones were kerosene, gas oil, dark stove oil, mineral oil and refined lubricating oils to name a few.

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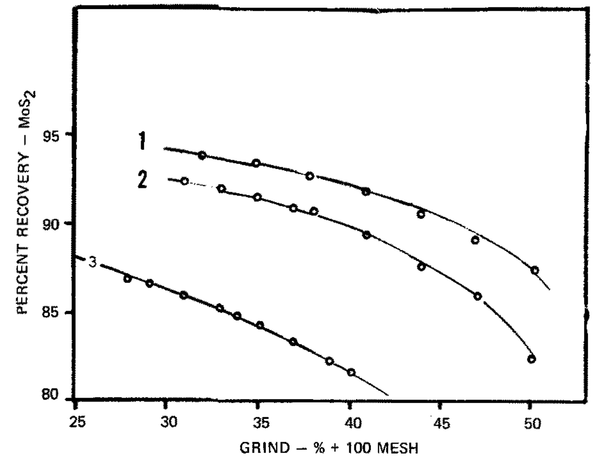

FIG. 1. Recovery, grind relationships employing Syntex, a surfactant with other reagents. 1, Flotation with Syntex, pine oil and hydrocarbon; 1, Flotation with pine oil and hydrocarbon; 3, Flotation with pine oil alone.

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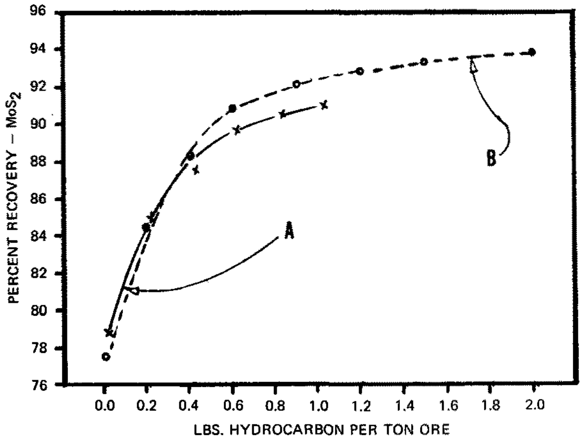

FIG. 2. Recovery curves with and without Syntex with varying amounts of hydrocarbon. A, Flotation with pine oil and hydrocarbon; B, Flotation with Syntex pine oil and hydrocarbon.

This improvement in recovery caused other problems. The froth was flat and did not overflow readily, and made the flotation operation quite difficult. Because of this problem, hydrocarbon addition was held at a minimum. The next study was directed at oil emulsification in the flotation pulp by mechanical or chemical means. Several types of homogenizers were tested without being very successful. It became apparent that a chemical means would be the more fruitful approach. Accordingly, surfactants of many types were studied. The early types of emulsifiers were: (a) gums, such as tragacanth, arabic and others; (b) sulfonated oils; (c) wetting agents such as aerosols; and (d) soaps of every type. These early ones, for some reason, wetted the oil-filmed molybdenite and practically destroyed the advantage of hydrocarbon as a promoter.

It was not until the sulfated alcohols, the neutralized esters of long chain, 10 to 14 carbon alcohols, and sulfuric acid were tested that encouraging results were obtained.

Fortunately, one of the first attempted surfactants of this type was sodium lauryl sulfate. This enabled the mill operators to add larger amounts of hydrocarbon effectively. However, the customary addition of a normal amount of pine oil, 0.2 lb/ton, as a frother was excessive in that the froth was wild and could not be handled in the launders, pump sumps and other equipment. When the amount of pine oil was lowered to 0.05 lb/ton the froth was controlled.

The surfactant employed at Climax today is Artic Syntex L, a sulfated monoglyceride made from coconut oil. In its manufacture two of the fatty acid groups are split off the glycerine, and the end alcohol group is esterified with sulfuric acid and neutralized with caustic soda.

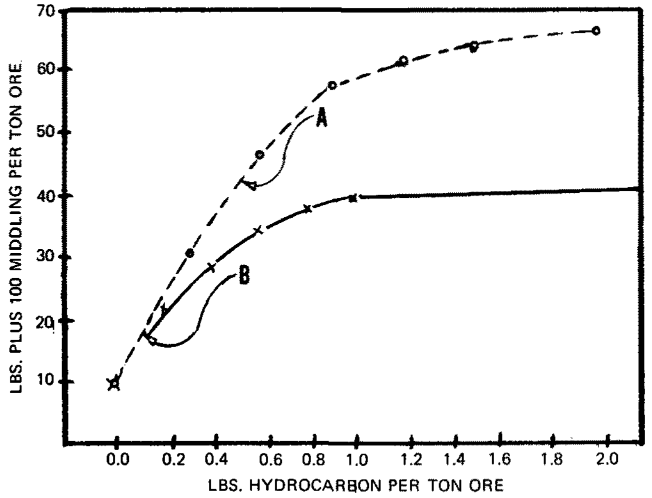

FIG. 3. Middling index curves with various reagent combinations. A, Flotation with Syntex pine oil and hydrocarbon; B, Flotation with pine oil and hydrocarbon.

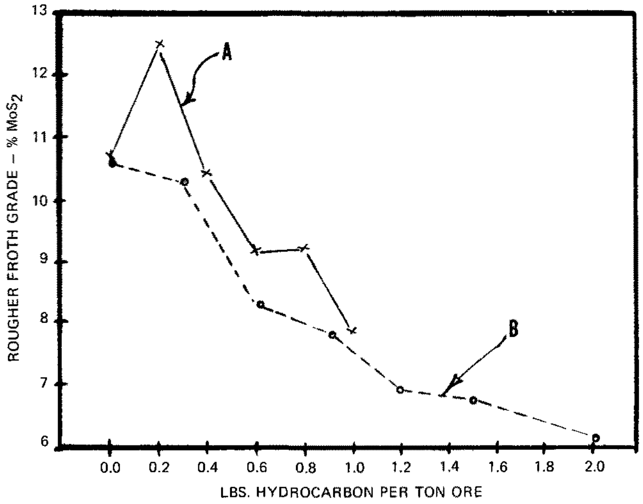

FIG. 4. Grade of rougher concentrate as a function of reagents and amount of hydrocarbon. A, Flotation with pine oil and hydrocarbon; B, Flotation with Syntex, pine oil and hydrocarbon.

This reagent proved to be somewhat more effective at Climax than the straight sodium lauryl sulfate because perhaps it did not precipitate with high calcium salts that are encountered in the recycled water at Climax, Colorado. In deionized water there was not and is not any difference in flotation characteristics.

Needless to say the study of the role of surfactants at Climax was and is a never ending task. Up to December of 1958, 346 surfactants were tested and evaluated.

In order that anyone concerned with surfactants in ore dressing applications could have our evaluation studies, R. E. Cuthbertson, Climax Director of Research at that time, published a booklet entitled, "Surfactants as Related to the Recovery of Molybdenite at Climax Molybdenum Co., Climax, Colorado."

We have just detailed the other 220 surfactants tested in the last 10 years, with a different format for evaluating results from the original compilation. This is the result of a new group of metallurgists with a more sophisticated viewpoint on calculating recoveries.

One of the best ones evaluated in the last decade is an ethoxylated lauryl alcohol. The source of the lauryl alcohol in this case is made from tetra propolene, a petroleum source. Approximately three molecules of ethylene oxide are added before the end alcohol is esterified with sulfuric acid and neutralized with caustic soda. Longer and shorter chain alcohols ethyoxylated, esterified and neutralized have also been evaluated with encouraging results. These surfactants are in a price structure much lower than from a vegetable oil source and hence will eventually take over the market.

The question is, what is the role of a surfactant? First, it lowers the surface tension of water and the solid as well as the interfacial tension between the two as is done in any window washing formulation. Most important, it emulsifies hydrocarbon to the precise degree that is necessary to have the oil enter the interstices of the mineral particles which lowers the overall specific gravity of the grains and in addition allows air bubbles to attach themselves to the molybdenite and bring them selectively to the surface.

It is this ability of surfactants to incorporate sufficient hydrocarbon onto minute specks of molybdenite that are attached to coarse grains of gangue that has made the Climax operation function economically.

(Continued on page 512A)

(Continued from page 508A)

The Surfactants Tested in the Last Decade at Climax Molybdenum Company's Extractive Metallurgical Laboratory

The reagents tested were based on the formula (Concentrate Index):

$$C_I = (\frac{C}{H} - 1) \times (\frac{1}{100T})$$

where C is the % MoS_2 (grade) of concentrate; H, the % MoS_2 in the feed or head; T, the % MoS_2 in the tailing. The reagents tested will be rated on this C_I until a better way of rating is worked out.

Surfactant Rating based on Concentrate Index (C_I): A plus = 0.4 C_I and more above normal or standard; A standard or normal C_I ± 0.4 range; B = 0.4 to −0.8 C_I range below normal or standard; C = 0.8 to −1.8 C_I range below normal or standard; D = 1.8 C_I or more range below normal or standard.

Symbols: G = Golden water, C = Climax water; NI = not identified; K = ratio of concentration; C_I = concentration index.

Part 1

List of surfactants that were substituted for Artic Syntex L that gave near equal results to the standard test rating of C_I with a rating of A+ or A:

Reagents	*Reagent Type*
Dupanol RF	N-dodecal-tetra-ethylene glycol sulfate
Molysulfier No. 4	Product from Van Waters and Rogers Co. no identification.
No. 328–97	Product from Stepan Chemical Co., not identified
Steol Ca 460	Lauryl ether sulfate
Steol Cs 460	Na lauryl ether sulfate
Stepanol WA Special	Na lauryl alkyl sulfate
Steol 4N	Na lauryl ether alcohol
288-43E	Product from Stepan, not identified
TLE 2433	Product from Dupont, not identified
Dow 250	60% Methoxy tetrapropylene glycol and polypropylene glycol
Sa 1263	50% Dow Froth 250 50% Butoxy-tetrapropylene glycol
Monad G	Product from Colgate-Palmolive Co., not identified
SA 8	Product from Amway Corporation, not identified
Aerosol Ay	Diamyl ester sodium sulfoccinic acid 3 Na Ni, 2 (dicarboxy ethyl) decylsulfosuccinamate
Cheelox B-13	Alkyldiamine polyacetic acids General Aniline & Film Corp., Dyestuft & Chem. Div.
Gantrez AN-139	Methylvinylether and maleic anhydride
NP-K90	Poly vinyl pyrrolidone (PVP)
NP-K60	Poly vinyl pyrrolidone (PVP)
Tergitol Anionic 08	Na-2-ethyl-hexyl-sulfate
Alfonic 1618–60	Normal primary alcohol high-mole-ethoxylated
Alfonic 1012–6	Normal primary alcohol high-mole-ethoxylated
Surfactant No. 1	1 Mole ethylene oxide C_8-C_{10} NH_4 straight chain sulfate
Surfactant No. 3	3 Mole ethylene oxide C_8-C_{10} NH_4 straight chain sulfate
Surfactant No. 4	3.5 Mole ethylene oxide C_8-C_{10} NH_4 straight chain sulfate
Surfactant No. 5	5.5 Mole ethylene oxide C_8-C_{10} NH_4 straight chain sulfate
Surfactant No. 6	2.5 Mole ethylene oxide C_8-C_{10} NH_4 straight chain sulfate
Surfactant No. 11	40% Ethylene oxide C_{12}-C_{15} straight chain alcohol sulfate
Surfactant No. 12	5.5 Mole ethylene oxide C_{12}-C_{15} ethylene oxide phosphate
BLO	N-vinyl 1–2 pyrrolidone butyrolactone
Foamer L-1	Product from Stepan Chemical Co., not identified
Methyl Oleate	As name indicates
Stepanol WA Special	Sodium lauryl sulfate
Na Salt Alpha Oletin Sulfate	As name indicates
Surf. 0348 Nonionic	Product by Stepan Chemical Co. not identified
Toximul AP	Ca anionic
Amidox C-f	Coconut amide
Biot A 8013	C_{13}-C_{18} alcohols Na sulfonate
DP 2431	Alcohol ether sulfate
NO 2432	Neutral alcohol ether sulfate
DP 2433	Neutral alcohol ether sulfate
DP 2434	Neutral alcohol ether sulfate
DP 2435	Neutral alcohol ether sulfate
Tergitol 15-S-3A	NH_4 salt ethyl alcohol sulfate
Tergitol 15-S-3S	Na salt ethox alcohol sulfate
Aero Promoter 3302	Xanthate
Reagent 5–3497	33.5% Active, product by American Cyanamid Co., not identified
Reagent 5–3498	35.0% Active, product by American Cyanamid Co., not identified
Reagent 5–3496	40.0% Active, product by American Cyanamid Co., not identified
Oronite 66R-5073	Alpha olefin sulfon C_{15}-C_{16}
Oronite 66R-7068	Alpha olefin sulfon C_{18}-C_{20}
Surf. AD400	Polyethylene glycolether and resen alcohol
SA 351	Sulfated fatty alcohol
GN 300	Product by American Gilsonite Co., not identified
Emsorl 6915	Sorbitan monolaurate
Prosol SA 3330	Coconut diethanol superamid

Part 2

List of reagents substituted for pine oil that gave near equal results to the standard test rating of C_I with a rating of A+ or A.

Reagent	*Reagent Type*
Dow ET 530	Produced by Dow Chemical Co., not identified
Olin No. 631744	Propoxylated methanol
No. 150 Improved Pine Oil	Tertiary and secondary alcohols
Glidco Terpenes	Tertiary and secondary alcohols
Methyl Isobutyl Carbinol	As name indicates
1,1,3 Triethoxybutane	As name indicates
Neoflex No. 7	Blend of alcohol C_8-C_{11}
Neoflex No. 61	Blend of alcohol C_6-C_{11}
Neoflex No. 71	Blend of alcohol C_6-C_{12}
Frother No. R1	Mixed C_6 alcohol
Frother No. R6	Mixed C_6 alcohol

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• *Flotation Surfactants at Climax . . .*

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Frother No. R15	C_8/C_6 alcohol
Frother No. R17	Product by Union Carbide, not identified
Alfol No. 6	Primary alcohol + 1 hexanol
Alfol No. 610	Primary alcohol C_6-C_{10}
Hercofroth 1565	Product by Hercules Powder Co., not identified
NCP Ethyl Accelerator	Product by National Products Co., not identified
Glidco Terpenes SW	Primary and secondary alcohols

Part 3

List of reagents substituted for hydrocarbon or vapor oil that gave near equal results to the standard test rating of C_I with a rating of A+ or A.

Reagent	*Reagent Type*
Napoleum 600	Product by Kerr-McGee, not identified
702 Conventional Neut.	Product by Kerr-McGee, not identified
1002 Conventional Neut.	Product by Kerr-McGee, not identified
Sinc Tech No. 6	Produced by Sinclair Refining Co., not identified
Sinc Tech No. 8	Produced by Sinclair Refining Co., not identified
Shellflex 210	Produced by Shell Oil Co., not identified
Shellflex 212	Produced by Shell Oil Co., not identified
Shell 61S Oil	Produced by Shell Oil Co., not identified
Heavy Cycle Oil	Produced by Shell Oil Co., not identified

Part 4

List of reagents substituted for more than one reagent that gave near equal results to the standard test rating of C_I with a rating of A+ or A.

50% CS 460 50% 328–97	Product by Stepan Chemical Co., not identified
Dow Froth 250	Product by Dow Chemical Co., not identified
Agent 328–97	Product by Stepan Chemical Co.

[Received August 25, 1969]

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Chemical Processing Equipment and Industrial Process Controls Exhibition in France

The French chemical industry has an 8.5% growth rate; its output has nearly doubled in the last six years; capital investment is expected to be $750 million in three years, and $400 million in export sales opportunities for over five years is forecast. The French chemical industry has $4 billion to spend in the next five years for plant modernization and construction. As one of the strongest sectors in the French industrial complex, the chemical industry leads the list consistently in annual growth and is now searching for the latest developments in plant automation and chemical processing equipment. Here is an opportunity to meet with French technicians and buyers in Europe's biggest chemical trade fair in 1971. For more information call 202–967–2434, U.S. Commercial Exhibition, Salon International de la Chimie, Paris, April 19–25, 1971.

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• *Local Section News . . .*

(Continued from page 511A)

understanding of hydrogenation flavor, deep fat frying and butter fat modification. He is currently studying the flavor chemistry of beef, butter, potato chips and onions.

Dr. Chang's service to the AOCS is well known to all of us. He has served as President of the Northeast Section, as Associate Editor of JAOCS, and is currently the President of the American Oil Chemists' Society.

It should be mentioned that Professor Chang is unique in his training program for oil chemists. His former post doctorates and graduate students are now working all over the world in both fat research and the fat and oil industry."

Left to right: D. S. Fritz, President of NEAOCS, Manny Eijadi, Vice President and Daniel Meshnick, Treasurer.

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Free Trade Zones Abroad Provide Useful Bases for U. S. Exporters

Customs-privileged areas overseas, such as free trade zones, can often provide U.S. exporters with bases at which they can process, sell, distribute and service their products, the U.S. Department of Commerce says in a new publication, "Free Trade Zones and Related Facilities Abroad."

Free trade zones, which offer exemption from customs duties under individual systems of regulation and control, are not new. However, as international trade operations have grown in volume and complexity, and as the pressure of competition has intensified, governments and traders alike have become increasingly interested in the potentialities of developing and using customs-privileged areas to facilitate the handling of export and import shipments.

Published as a service to U.S. businessmen, "Free Trade Zones and Related Facilities Abroad" presents data on facilities, administration, restrictions and controls for free trade zones in Europe, Latin America, the Caribbean, Asia and Africa.

Frequently, U.S. firms can save on transportation costs by shipping in bulk to free trade zones and repacking there, the publication notes.

Typically, customs duties become payable, and other import controls become operative, only if and when foreign goods are removed from a free trade zone or similar facility for use or consumption in the country in which it is located, the 128-page publication says.

"Free Trade Zones and Related Facilities Abroad" is available from the Sales and Distribution Branch, U.S. Department of Commerce, Washington, D.C. 20230.

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