BIBLIOGRAPHY


Cameron, Walter E. Wolfram. Molybdenite Mining in Queensland, Department of Mines, Brisbane, 1904.


Molybdenite Deposit of Turn Bow Lake, Quebec. Canadian Mining Journal, March 15, 1913, p. 190.

Ore Deposits Around Vancouver, B. C. Mining & Engineering Record, 1912, p. 262.

Moses, A. J. Descriptive Mineralogy.

Ohly, J. Rare Metals.
MOLYBDENUM

By P. E. Joseph

Introductory:—

Molybdenum was discovered by the Swedish chemist Scheele in 1778. In 1782, Hjelin, a chemist of the same school, succeeded in isolating it by using the trioxide for its production. The pure metal is very heavy, silver white in color, and very difficult to fuse. In the air it remains unchanged, and only combines with oxygen when heated to low redness. It takes up carbon, forming alloys, which are more easily fusible, but much harder than the pure metal.

Until recent years it was in little demand for industrial purposes, and very little search was made for deposits of molybdenum. At the present time, however, owing to its introduction into metallurgy, in the form of iron-molybdenum alloys, there is a considerable demand for such ores. They are produced, however, very irregularly and in small quantities. If a larger and more regular ore supply were assured, there is no doubt that new uses would be found for these alloys, and the demand for the ores would increase.

The use of molybdenum alloys in the United States has been relatively small, owing to the fact that production has been small. While it is true that molybdenum is more abundant in nature than tungsten, the impurities in tungsten have been less, and for this reason tungsten has been far more used in making toughened steels than has molybdenum. An industry has been built up manufacturing tungsten iron alloys, but there has been no distinct industry in the manufacture of ferro-molybdenum alloys, and even though the demand for the ferro-tungsten alloys has greatly increased, the manufacturers have attempted to get tungsten rather than substitute molybdenum. However, now that a steady supply of molybdenum ores seems to be assured by the opening of new mines and by improvements in the production of metallic molybdenum, there is little doubt that the molybdenum market will greatly improve.

What little molybdenum has been produced in the United States a few years back has been shipped to Germany, where the iron molybdenum alloys were made, and in many cases were shipped back to the United States. In the meantime, however, the American manufacturers of these alloys had acquired tungsten mines in order to assure themselves of regular supplies, and for this reason have not been particular-
ly anxious to push the production of molybdenum. It will be necessary to create a steady supply in order to make a consistent demand.

Another difficulty has been the fact that in the manufacture of iron molybdenum alloys, there was a tendency to oxidization on the part of the molybdenum, at a low heat, which prevented a true solution. Iron molybdenum alloys in their experimental stage have been uncertain and not always up to quality, which difficulty was not encountered with tungsten. It was found, however, that by the introduction of the molybdenum into nickel this oxidation did not occur, and that by the introduction of this alloy into steel much more satisfactory results were obtained than by the use of tungsten.

MOLYBDENUM ORES

Molybdenite:—The most common ore of molybdenum.
Composition:—Sulphide of molybdenum (MoS₂). When pure contains 60 per cent molybdenum and 40 per cent sulphur.

General Description:—A soft, bluish-gray mineral, having a metallic lustre and a greasy feel. It usually occurs in thin graphite-like scales or foliated masses, easily separated into flexible scales. These scales are not elastic, differing in this respect from mica. Some times found as tabular hexagonal crystals or in finely granular masses.

Physical Characteristics:—Hardness—scratched by finger nail.
Specific Gravity—Moderately heavy.
Lustre—Metallic. Opaque.
Streak—Greenish. Tenacity—May be cut by knife and is malleable.
Color—Bluish lead gray.

Molybdenite, although twice as heavy as graphite, is often confused with it. However, molybdenite may be easily distinguished by any of the following tests:

Quantitative Tests:—When heated in forceps is infusible. A little piece of molybdenite strongly heated by blow-pipe colors the flame greenish-yellow, while graphite shows no color and slowly burns up. Heated in an open tube, molybdenite gives off sulphurous fumes, and a sublimate of pale yellow oxide is formed on the sides of the tube. When powdered, molybdenite is heated on charcoal emitting a strong sulphurous odor and deposits a coating which is yellow when hot and white when cold; if the white coating is touched intermittently with the yellow flame, it becomes deep blue. Molybdenite decomposes in strong nitric acid, leaving a residue of white or grayish molybdic oxide. By looping a piece of platinum wire, and fusing on it some
of the powdered ore with a little borax, the head thus obtained is yellow when hot, colorless when cold in the oxidizing flame (O. F.); in the reducing flame, (R. F.) the bead is brown to black opaque. If, instead of borax, sodium ammonium phosphate is used, the bead is yellowish-green when hot, and colorless when cold, in the O. F. and emerald green in R. F.

Occurrence:—Molybdenite occurs usually in crystalline rocks and is not readily altered. It is found in many places in Arizona, notably in the Babaquivari mountains, Copper Basin district and in many other districts. It is found in the Gold Bullion mine, associated with a quartz vein on a granite contact.

Molybdite:—Is usually found along with molybdenite, from which it results by oxidation.

Composition:—Hydrated, iron molybdite, containing about 60\% MoO₃.

General Description:—Usually occurs as an earthy, yellow powder; rarely in tuffs and hair-like crystals of yellowish-white color.

Physical Characteristics:—Hardness—scratched by finger nail (1-2). Specific Gravity—moderately heavy (4-5).

Lustre—dull or silky. Opaque.

Color—yellow or yellowish-white.

Streak—yellowish-white.

Quantitive Tests:—If a little of the powdered ore is heated on charcoal it fuses, yielding crystals which are yellow when hot, white when cold, and made deep blue by the reducing flame. The bead test is the same as for molybdenite.

Occurrence:—Often found in small quantities along with molybdenite in the localities mentioned above.

Wulfenite:—Yellow lead ore.

Composition:—Molybdate of lead, PbMoO₄, sometimes containing calcium, chromium and vanadium. When pure, wulfenite contains 39.3 per cent MoO₃.

General Description:—Occurs usually in thin square tabular crystals of yellow, orange, or bright orange-red color and resinous lustre. Less frequently in granular masses or acute pyramidal crystals.

Physical Characteristics:—Hardness (3) easily scratched by knife. Specific Gravity—(6.7-7) Heavy.

Lustre—resinous or adamantine. Translucent.

Streak—white. Tenacity, brittle.

Color—wax yellow, bright red, brown, Cleavage, pyramidal.

rarely green.
Qualitative Tests:—If powdered ore is placed on charcoal and heated, it yields a yellow coating and finally fuses to a metallic glooblue. Partially soluble in strong hydraulic acid to a green liquid. If the solution is greatly diluted, cooled and a little metallic tin added, it becomes tin blue and finally brown. In sodium ammonium phosphate it dissolves to a bead, which is bright green in the reducing flame. In borax, it yields a colorless bead in O. F. which is made brown to black in R. F.

Wulfenite occurs with other lead minerals, especially vanadinite and pyromorphite. It is found with silver ores and occasionally with other lead ores in many localities in Arizona and New Mexico. It also occurs in the lead region of Wisconsin and Missouri, at Phoenixville, Penna., Inyo County, Calif., South Hampton, Mass., and in many other places, in each case associated with other ores of lead.

MODE OF OCCURRENCE

A. MOLYBDENITE

1. In view of pegmatite intersecting such rocks as gneiss, slate and quartzite. These veins have originated from material derived from large masses of granite, which are usually to be found in the vicinity and probably occur at no great depth beneath the pegmatite veins.

2. In quartz veins formed from filling of the fissures with material derived from underlying, deeply seated granitic rocks.

3. As irregular deposits, in association with fluorspar and quartz, in pegmatite dikes cutting across granite; the granite itself may be impregnated with scales and crystals of molybdenite.

4. In pyrosenite, in association with pyrite and pyrrhotite, near contact of intrusive granite or pegmatite with crystalline limestones.

B. WULFENITE

Almost always in veins in association with other lead minerals. Gold and silver often present.

MOLYBDENUM IN ARIZONA

Molybdenum, both as molybdenite and wulfenite is found in considerable quantities in many parts of Arizona. Most of the deposits in Arizona occur under geological conditions favorable for molybdenum, and while many deposits are already of commercial value, it is very likely that further developments will add many other deposits to the list of commercial producers. Arizona has a sufficiently large supply to create and supply a steady market, and with
the increased demand and increased prices, it seems assured that a steady supply will be ready.

MOLYBDENUM IN HELVETIA

Helvetia is situated 27 miles southeast of Tucson in the northern part of the Santa Rita Mountains on the west slope, at an elevation of about 4300 feet. Here molybdenite is found in the Leader and the Ridley mines. The Leader mine is situated east of the town at an elevation of about 7400 feet, near the contact of the altered Paleozoic limestone with underlying pre-Cambrian and post-Carboniferous granite. The molybdenite occurs in lenses, irregular bodies or in masses and crystal aggregate embedded in a dull-brownish and greenish to yellowish mineralized garnetiferous silicified limestone and quartz, which rock has resulted from contact metamorphism of the intrusive granite with the limestone. The molybdenite is mostly fine grained, but in places it is found in crystals ranging up to one-half inch and more in diameter.

RIDLEY MINE

In the Ridley mine, situated to the southwest of the town, at an elevation of about 4060 feet, some fine-grained molybdenite is found in the lower portion of the vein, in a band composed of sericite mica, quartz, pyrite, and varying in width of from one-eighth of an inch to 4 inches.

MADERO CANYON

Madero Canyon drains the northeastern part of the Old Baldy section of the Santa Rita Mountains, about 10 miles southwest of Helvetia and 35 miles south of Tucson. In the foothills part of its course, where the creek crosses the Pima-Santa Cruz County line, are found the McCleary prospects. The country rock is pre-Cambrian (?) granite. It has been fractured by dynamic disturbances, and along the resulting joints and fault fissures occur quartz veins. In these quartz veins molybdenum is found in heavy, thick masses, quite clean and pure.

MOLYBDENUM IN BABAQUIVARI MOUNTAINS

The Gold Bullion mine of this district, situated about 65 miles from Tucson in a southwest direction, is a producer of molybdenite. The ore occurs in quartz veins of various sizes, having an average ore tenor of about 3.6% molybdenite. The ore carries chalcopyrite in varying amounts, with some gold and silver. A 15-ton
concentrating experiment plant has been installed and the ore from
the dump is being treated. Experiments are under way to de-
termine the availability of oil flotation in the separation of the
molybdenite, both from the gangue and from the chalcopyrite, with
which it is associated in small quantities.

OTHER DEPOSITS.

A considerable tonnage of low grade molybdenite ore has been
marketed by the Leviathan Mines Corporation, near Copperville,
Mohave County.

In Duquesne and along the international border molybdenum does
not occur in sufficient quantities to be of commercial importance.

In the Mammoth gold mine, at Shultz, Pinal County, wulfenite
occurs abundantly, sometimes in aggregations of crystals, weighing
many pounds. For many years the Mammoth mine, which has been
a famous gold mine, has been accumulating tailings on the dump,
which has been picked over, and for three years has afforded the en-
tire output of wulfenite marketed in this country.

The ore is wulfenite, occurring in veins and associated with vanad-
inite, the veins being in granite and rhyolite. Other lead minerals
are found in the veins as well as quartz and calcite. The ore is
gold bearing, and was once a famous gold mine.

Wulfenite in association with vanadinite is found in the Old
Yuma mine, where considerable development work, including the
errection of a concentrating plant, has been recently done. This com-
pany is evidently preparing to supply regularly and consistently a
considerable portion of the wulfenite market.

The Troy Mountain Copper Co. has discovered sufficient wulf-
enite to warrant the erection of a 40-ton mill for concentration of the
molybenum ore and a plant for treating the concentrate.

Molybdenite is also found in disseminated ores of Miami, in copper
ores of Clifton-Morenci district, with copper in Hualpai mountain,
Maynard district, in Pinal county in ores at Ray-Kelvin mines as
original mineral.

Recent newspaper reports state the discovery of many molybdenum
deposits in various parts of the state. However, these have not yet
been sufficiently developed.

CONCENTRATION OF MOLYBDENITE.

The concentration of molybdenite is one of the most difficult
problems in ore dressing. The almost invariable association of moly-
bdenite with copper as chalcopyrite has been such as to hinder the marketability of the ore, as copper is an undesirable constituent. The mineral is very soft and largely occurs with a very hard gangue such as quartz and feldspar. In crushing the ore much of the molybdenite is finely divided and a large loss takes place by sliming. On the other hand, some of the larger flakes resist the action of the rolls and may be separated by means of sieves. Molybdenite is sufficiently heavy to be separated by washing, but its perfect cleavage gives rise to very thin scales and plates, and its natural greasy tendency causes it to readily float away and become lost.

**FLOTATION PROCESS**

Molybdenite has the property, common in a varying degree to most metallic sulphides, such as chalcopyrite, sphalerite, galena and pyrite, of not being wetted readily by water, and when dry and in small particles, of floating on a water surface. Moreover, like these sulphides it is easily wetted by most oils; further in the pulp of crushed ore and water oils have a preferential wetting action for particles of molybdenite, as against most particles of gangue minerals, such as quartz, and this selective wetting action is decidedly increased if the water is slightly acidified. Particles of molybdenite so wetted with oil are covered with a buoyant water-repelling coating that materially assists their flotation.

The reasons for many of these phenomena are not clearly understood, but they are the basis of all commercial flotation processes. In many of the oil processes the area of the effective surface of flotation is increased by the liberation of bubbles of gas or air in the liquid, the surface of each bubble acting in the same way as the horizontal surface of a liquid at rest. These bubbles may be of air, and may be produced by violent agitation of the pulp, or by releasing the air from solution in the liquid by a reduction of pressure, or they may be of carbonic acid gas formed by the action of sulphuric acid on limestone or other carbonates or by other means. No description of any particular flotation process will be given here. It suffices to say that flotation processes in general have a wider range of application in the concentration of molybdenite ores than either rolling and screening or electrostatic processes, and it is by means of flotation that the most successful work is being done at present in the concentration of molybdenite ores.
PREFERENTIAL FLOTATION OF MOLYBDENITE AND CHALCOPYRITE ORES*

"Selective" Flotation means the process of floating valuable minerals, usually in the form of sulphides, in the presence of the undesirable gangue-minerals. Thus, the floating of a mixture of galena and pyrite from a silica gangue is called "selective" flotation, and in such a case the concentrate contains both the galena and the pyrite. When, however, one of the ordinary selectively flotative sulphides is floated off in the presence of another such sulphide, the two sulphides are said to have been separated from one another by "preferential" flotation. Thus, when we have two or more substances present in any given ore, and these substances are all susceptible to flotation, it becomes possible, by means of "preferential flotation" to separate the one mineral from the other.

Molybdenite is extremely adaptable to the Flotation process, and gives even better results than a pure galena ore. It is on account of this property that it is possible, by just taking the least required amount of oil, to float the molybdenite and leave behind any impurity such as chalcopyrite.

In the Greenway and Lowry patent the following example is cited: A molybdenum ore containing 15% molybdenite and 25% iron pyrite was crushed to pass 100 mesh, and treated in a froth flotation with four times its weight of water, containing 0.25% sodium bichromate and heated to 120 degrees F. One pound of eucalyptus oil per ton of slime was used and the concentrate ran 95% MoS₂ and 4.9% iron pyrite.

In the above example sodium bichromate was used to stimulate a preferential action, but this becomes unnecessary when the correct kind and quantity of oil is used and the ore crushed to pass through a certain mesh, usually about 35 to 50. With a molybdenum ore, containing about 6.5% molybdenite and 3% chalcopyrite, we have obtained concentrates containing about 0.4% chalcopyrite and 67% molybdenite, with the use of only an oil.

It may be readily seen from the above that success has attended the efforts made in properly floating molybdenite ores, and it is very evident that oil flotation will be the coming process for molybdenite concentration.

In some cases ores are crushed and concentrated by ordinary washing methods; this is particularly true when it is not associated with copper, as it should be in more or less granular or massive form.

*H. J. Stander.
In some cases where molybdenite is flaky, so much so that the flakes are more flattened by the action of the rolls, the molybdenite has been separated by dry concentration and merely by separating in sieves.

Wulfenite may be concentrated by ordinary methods.

**TREATMENT OF ORES**

**CONCENTRATION**

Of the two commercial ores of molybdenum, namely, molybdenite and wulfenite ores, the first are not amendable to the ordinary processes of concentration by jigs, tables, vanners, etc., such as are usually employed in treating ores of copper, lead, zinc, gold and silver, as the grains or flakes of molybdenite, even when of considerable size, float readily on water, and therefore are lost if these methods are employed. On the other hand, little difficulty is experienced in the adaptation of the ordinary jig and table processes to wulfenite ores, as wulfenite is readily wetted, and because of its high specific gravity (6.7 to 7), it is much heavier than the gangue minerals which accompany it.

**CONCENTRATION OF MOLYBDENITE ORES**

The methods of concentration that have been used with success with molybdenite ores may be grouped into three general heads, as follows:

1. Rolling and screening processes.
2. Electrostatic methods.
3. Flotation processes.

**ROLLING AND SCREENING PROCESSES**

Rolling and screening processes consist of crushing the ore in rolls to flatten the molybdenite masses into flakes, the maximum diameters of which are in excess of those of the particles of the accompanying gangue mineral, and then separating them from the gangue by screening. The process is, of course, applicable only to ores in which the molybdenite occurs in fairly large masses and flakes, and even with this type of ore the fines are generally treated either by electrostatic or flotation methods.

**ELECTROSTATIC PROCESSES**

Electrostatic processes of separation depend upon the difference in conductivity between minerals which are relatively good conductors, such as molybdenite, chalcopyrite, pyrite, pyrrhotite, etc., and poor conductors, such as quartz, feldspar and most silicates, calcite, etc. For
the successful application of electrostatic methods a molybdenite ore
must be one in which the individual particles of molybdenite are of
fair size and in which the gangue and other principal associated min-
erals are nonconductors. The main requisite in the treatment of the
ore is that it be perfectly dry and warm. Ore as coarse as 6-mesh
and as fine as 200-mesh may be treated successfully, but the best re-
sults are usually obtained with coarse material.

CONCENTRATION OF WULFENITE ORES

As already stated, the treatment of wulfenite ores presents few
difficulties. As even the finest particles of wulfenite are readily
wetted, the sliming of the ore does not occasion the considerable
losses that would occur under similar circumstances in the treatment
of most metallic sulphides such as galena and calcopryite, as these
minerals float readily when finely divided. On account of the high
specific gravity of wulfenite, it is readily separated from all of the
gangue minerals with which it occurs. However, it is frequently
associated with vanadinite (specific gravity 6.66 to 7.23) from which
it cannot be separated by wet methods; also with cerussite (specific
gravity 6.46 to 6.57) and anglesite (specific gravity 6.12 to 6.39)
from which it can be only partly separated. Occasionally other lead
minerals of high specific gravity, such as galena, pyromorphite and
mimetite occur with wulfenite, and are recovered with it in the
concentrates. The pressure or absence of these other heavy minerals
in the ore determines largely the grade of wulfenite concentrates
that can be made.

PRICES AND MARKETS

PRICES

Under existing abnormal market conditions it is impossible to quote
exact prices for either molybdenite or wulfenite concentrates, sales of
even one or two ton lots being generally the subject of separate
negotiations and the prices received varying between wide limits.
Based on a content of 90% MoS₂, small lots of molybdenite in 1915
brought from $2,500 to $3,000 per short ton, or from $27.78 to
$33.33 per 20-pound unit of MoS₂. Probably from 100 to 200 tons,
of wulfenite concentrates of domestic origin were sold during the
year. Based on a content of 20% MoO₃, the price received was
reported to range from $216 to $300 per ton, or $10.80 to $15.00
per 20-pound unit of MoO₃.

At present (March, 1916), the prices offered for molybdenite are
about $20 per unit MoS₂, based on a content of 50% MoS₂. For
each per cent above or below this, 20 cents per unit may be added
or deducted from the price. For example, a concentrate containing
72% MoS₂ would be worth $20 + (22 × $20) or $24.40 per unit
and ore containing 31% MoS₂ would be worth $20 - (19 × $20)
or $16.20 per unit. Prices for wulfenite and molybdenite have more
than trebled in the last three years, and are at present altogether ex-
ceptional. In 1908 high-grade molybdenite concentrates containing
from 90% to 95% MoS₂ brought $6.50 to $7.60 per unit, and in
1909 the price was as low as $5.60 per unit. With increased pro-
duction and a more normal market the prices are sure to decline. In
the past they have been normal at $6 to $10 per unit for 90% MoS₂.
In September, 1915, the Australian government fixed by law the
maximum price for high-grade molybdenite concentrates at 105 shil-
lings per unit (22.4 pounds), which is equivalent to about $22.81
per unit (20 pounds). In March, 1916, English quotations on
ferro-molybdenum containing from 70% to 80% molybdenum were
about 15-6d., or $3.77, per pound.

HOW MOYBDENUM CONCENTRATES ARE BOUGHT AND SOLD

The basis upon which molybdenum ores and concentrates are
bought and sold varies according to whether the contained moly-
denum mineral is molybdenite or wulfenite. Molybdenite products
are invariably purchased on the basis of their molybdenum content,
reckoned as MoS₂, whereas wulfenite is bought either on the basis
of its content of metallic molybdenum, or as MoO₃.

One part by weight of MoS₂ is equivalent to 0.9 part of MoO₃
and 0.6 part of Mo; inversely, one part by weight of Mo is equiva-
 lent to 1.5 parts of MoO₃ and 1.67 parts of MoS₂.

In the United States the short ton of 2,000 pounds and the unit
of 20 pounds are used in buying and selling molybdenum ore, whereas
in Europe, the long ton of 2,240 pounds and a unit of 22.4 pounds
are generally used. Quotations are usually made on a sliding scale
to cover various grades of material. Specifications generally state
the minimum percentage of MoS₂, MoO₃ or Mo in the ore or con-
centrates that is acceptable, and also the maximum allowable per-
centage of objectionable elements, such as copper, tungsten, bismuth,
arsenic and antimony. Just what are objectionable elements de-
pends largely on the use to which the molybdenum product derived
from the material is destined, and the methods employed in treating
it. Copper is particularly undesirable, and more than 2% or 3%
of it usually renders even high-grade material unmarketable.
Up to 1914 it was difficult to sell molybdenite concentrates containing less than 80% MoS$_2$ or wulfenite concentrates with less than 25% MoO$_3$, but at present, March, 1916, it is reported that concentrates containing as low as 20% MoS$_2$ and 18% MoO$_3$ respectively, can be marketed.

USES OF MOLYBDENUM

Molybdenum forms one of the most remarkable compounds with steel, especially an alloy of molybdenum and nickel. It is far better than tungsten or any of the other combinations of steel hardening material. It not only hardens the steel, but gives it a great tensile strength. It is also a splendid lubricant and disinfectant. Since the first discovery of the metal, like tungsten, it has been used for coloring the finer grades of silk. It is also extensively used in the manufacture of chemicals, principally ammonium molybdate, which is much used in the determination of phosphoric acid. There is no doubt that if a larger and more regular ore supply were assured, new uses for molybdenum would be found.

Mines of molybdenum are well worth seeking for and developing. At the present time the market, although not regular, is high, the demand being large as ore is being imported from Europe. One of the most beneficial effects of the war upon the United States has been the forcing of the industries of this country to create and manufacture the materials necessary to carry on their work. This is particularly true of molybdenum, and while the demand is not large, the supply does not nearly equal the demand. With an increase in the supply, the demand will also increase, although it is doubtful whether the price will remain as high as at the present time.

In as much as molybdenum is only used as the alloys and in chemical manufacturing, the large industrial chemical companies are the purchasers of this material. Although its greatest use is in steel, the steel companies do not buy it direct, but purchase it from the chemical companies.

ARIZONA HAS A SUFFICIENT SUPPLY TO CREATE A STEADY MARKET FOR MOLYBDENUM ALLOYS, AND IT MERELY REMAINS TO HAVE THE SUPPLY DEVELOPED, SO THAT THE BUYERS MAY BE ASSURED THAT SHOULD THEY START MANUFACTURING THE NICKEL MOLYBDENUM ALLOY, THEY MAY DEPEND UPON A STEADY SUPPLY.
Some of the buyers of molybdenum ores are:
J. T. Baker Chemical Co., Phillipsburg, N. J.
Goldschmidt Thermit Co., 90 West St., New York City.
Primos Chemical Co., Primos, Pa.
Pfanstiehl Co., N. Chicago, Ill.
Grasselli Chemical Co., Cleveland, Ohio.
Henry E. Wood Co., Denver, Colo.
David Taylor, Boston, Bldg., Salt Lake City, Utah.