CHAPTER 12.24

Molybdenum

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Much of the following introductory text and history has been excerpted from *Extractive Metallurgy of Molybdenum*, C.K. Gupta's (1992) excellent and authoritative text on the subject.

"Molybdenum has an atomic number of 42, an average atomic weight of 95.95 [and] belongs to the sixth group of the periodic system of elements. It occurs between chromium and tungsten vertically and niobium and technetium horizontally" in the periodic table (Gupta 1992). The metal, first isolated in 1781 by Peter Jacob Hjelm, does not occur in nature in its metallic (native) form but can be found in a relatively small number of mineral species (12–14) of which only four are of industrial value. By far, the most important mineral for the economic production of molybdenum is molybdenite (MoS_2), which is a soft, metallic-gray mineral whose name is derived from the Greek word *molybdos*, meaning lead. The secondary minerals—powellite ($CaMoO_4$), ferrimolybdite ($Fe_2Mo_3O_{12}\cdot 8H_2O$), and wulfenite ($PbMoO_4$)—formed during the weathering of molybdenite are the other three molybdenum minerals of potential economic value (Sebenik 2005).

"In its pure state, molybdenum is a lustrous, gray, malleable metal, capable of being filed and polished. It can also be turned and milled without difficulty. Molybdenum is an important refractory metal with a very high melting point of 2,610°C" (only carbon, tungsten, rhenium, tantalum, and osmium possess higher melting points) and a relatively high density at 10.22 g/cm^3 at 20°C (Gupta 1992). Its coefficient of thermal expansion is significantly lower (one-third to one-half) than "that of most steels [and at] elevated temperatures, this low expansion provides dimensional stability and minimizes the danger of cracking" (Gupta 1992). Also, its "low specific heat allows molybdenum to be rapidly heated or cooled, with lower resultant thermal stresses than most other metals" (Gupta 1992). Additionally, molybdenum has one of the highest moduli of elasticity among commercial metals, and the value is not significantly affected by temperature (at 800°C, its modulus of elasticity substantially exceeds that of an ordinary steel at room temperature). Additionally, molybdenum's thermal conductivity exceeds that of all but a handful of elements, and together with its low electrical specific resistance, makes the metal suitable for use in electrical and coating applications.

HISTORY

The first documented mine production of molybdenum was around the end of the 18th century at the Knaben mine in southern Norway (Gupta 1992). However, without a significant commercial use and given the difficulty in extracting the pure metal, the metal remained a laboratory curiosity with little value until 1891, when it was first used in place of tungsten as an alloying element to produce armor-plated steel (Gupta 1992). The French Schneider Electric company was able to demonstrate that molybdenum, when alloyed in small quantities, created a substance that was remarkably tougher than steel alone and highly resistant to heat. Additionally, the material alloyed with molybdenum was lighter than materials created by alloying tungsten, as the atomic weight of molybdenum is approximately 57% that of tungsten.

In the early 20th century, development continued on both the processing of molybdenite ores (most significant were the advances in flotation technology) and the expansion of the commercial use of molybdenum, particularly in the production of high-speed steels and military armament applications. The demand for these alloyed steels increased during World War I because of the high demand for military armaments and shortages of tungsten; interest in molybdenum exploration and mining increased, and annual wartime production of molybdenum metal reached 816 t (metric tons) of contained metal by 1918 (Kelly et al. 2017).

Although the 1918 armistice following World War I almost entirely eliminated the demand for molybdenum, it

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also led to an unprecedented research program, driven largely by Climax Molybdenum Company, which created new applications and markets for the metal in the postwar period. Over the next 20 years, the valuable physical and mechanical properties that molybdenum imparts to alloys expanded, as it was used both alone and in conjunction with other alloying elements such as chromium, nickel, manganese, silicon, tungsten, copper, and vanadium. There was a notable increase in the production of alloy cast steels, with molybdenum often replacing both nickel and vanadium in many compositions, primarily associated with automotive structural parts and with railway and aircraft steels. Additionally, the use of molybdenum extended to general forgings and castings, and the substitution of molybdenum for tungsten in the tool steels continued to grow.

Before 1927, annual worldwide production of molybdenum never exceeded 1,000 t of contained metal. As research continued into new uses for molybdenum, demand for molybdenum increased, and increased molybdenum production followed. Worldwide production exceeded 10,000 t of contained molybdenum metal for the first time in 1937; 25,000 t first during the wartime production spike in 1942; 50,000 t first in 1966; and 100,000 t first in 1978. Production first exceeded 200,000 t of contained molybdenum in 2007 and is currently (2016) at about 226,000 t annually (Kelly et al. 2017)

A general timeline of world molybdenum production is as follows (based on statistics from Kelly et al. 2017 and Climax Molybdenum Company 1924–2017):

- **Prior to 1925.** World molybdenum production averaged <200 t/yr, except for the aforementioned wartime production spike in 1916 through 1919 that peaked at 816 t of molybdenum in 1918. Most molybdenum production in this period was outside the United States.
- **In 1924.** The Climax mine (Colorado) started producing continuously (there had been some earlier production during World War I). It was the largest U.S. producer for 1924 and provided 26% of world production in its first year of operation.
- **In 1933.** The first documented by-product molybdenite production through differential flotation from copper concentrate was carried out at Greene Cananea Consolidated Copper Company in Sonora, Mexico.
- **In 1936.** By-product molybdenum production was reported from the United States at Utah Copper Company's Bingham Canyon mine and Arizona's Miami Copper Company.
- **From 1924 to 2007.** The United States was the world's leading molybdenum producer.
- **From 1925 to 1981.** The United States produced more than 50% of the world's molybdenum production. From 1925 through 1957 and again from 1960 through 1965, the United States produced more than three-quarters of the world's production.
- **From 1924 to 1946, 1951–1970, and 1974–1977.** The Climax mine provided more than half of U.S. molybdenum production. In 1925 through 1965, the Climax mine alone produced on average 60% of the world's molybdenum production and 71% of the U.S. production.
- **The 1960s and later.** By-product molybdenum production from porphyry copper deposits, pioneered at Cananea, increased in importance as more porphyry copper deposits were brought into production. The shift with time from solution extraction/electrowinning (SX/EW) production from oxidized material to concentrator production from sulfide material also increased the trend toward greater by-product molybdenum production.
- **In 1983.** Climax shuts down for a full year for the first time since it began operating continuously in 1924. From 1984 through 1991, it operated sporadically with minor production relative to its early years before shutting down again in 1992. Molybdenum production restarted in 2012 and continues to the present. In 2014, Climax accounted for only 4% of the world's production—a dramatic drop relative to Climax's early years.
- **In 2008.** China unseated the United States as the world's leading molybdenum producer after 83 years. This was mainly driven by a sharp increase in production of molybdenum in China—from 46,000 t in 2007 to 81,000 t in 2008 and 93,500 t in 2009 (Blossom 2001–2017, 1994–2000).
- **In 2015.** Chile became the second largest molybdenum producer in the world after China, leaving the United States in third place (Blossom 2001–2017).

In summary, historic molybdenum production can be divided into three eras:

1. Prior to 1925, there was a period when molybdenum demand and supply was so low as to be negligible (relative to today's production), and what mining there was focused on small, high-grade deposits with ore sometimes concentrated through hand sorting.
2. From 1925 through 1965, world molybdenum production was dominated by a single mine—the Climax mine in Colorado.
3. From 1966 through the present, molybdenum production has been increasing, and there has been progressive diversification in molybdenum production both by country and by mine. By-product molybdenum production gained sharply in importance during this period.

GLOBAL PRODUCTION

As noted, as of 2016 the global molybdenum production (not including recycled molybdenum) was approximately 226,000 t annually (Kelly et al. 2017). The top producing countries in order of molybdenum production quantities were China, Chile, and the United States. Together they accounted for 77% of the world's production: 40% from China, 23% from Chile, and 14% from the United States (Blossom 2001–2017). The vast majority of the molybdenum produced by these countries comes from porphyry deposits, but there are differences in the details.

For China, detailed production data is scarce, but molybdenum reserves are estimated to be 78% in porphyry molybdenum deposits, with 13% in porphyry-skarns, 5% in skarns, and 4% in veins (Zeng et al. 2013).

Almost all of the molybdenum production in Chile is produced as a by-product from copper porphyries. For 2014, the U.S. Geological Survey (USGS) reported that 84% of Chile's molybdenum production came from the large deposits at Collahuasi, Chuquicamata, El Teniente, Los Bronces, Los Pelambres, and Radomiro Tomic (Wacaster 2017).

Based on the most recent USGS reporting (for 2016) for the United States, production from primary molybdenum mines (the Climax and Henderson mines, both in Colorado and both Climax-type porphyries) accounted for 59% of U.S. molybdenum production. Production of molybdenum as a by-product from seven copper mines accounted for the balance (Blossom 2001–2017; Climax Molybdenum Company 1924–2017). Primary mines are generally more sensitive to variations in the price of molybdenum, and production from these properties can swing significantly as the molybdenum price rises and falls.

GEOLOGY OF MOLYBDENUM ORE BODIES

Mines are developed around ore deposits, and ore is defined as a naturally occurring material which can be mined at a profit. What is ore now—based on present economics and use of current technologies—may not have been ore in the past. Conversely, some material that was mined as ore in the past—when labor was cheap—may not be ore now. And generally, higher grade deposits or deposits that are more economic for other reasons (mineralogy, proximity to the surface, etc.) are mined earlier.

A mineral deposit (a concentration of a particular mineral or element relative to the average concentration in rock) can become an ore deposit based on conditions prevalent at the time the deposit is evaluated for development. The type of ore deposits that were mined early in the 20th century are generally quite different from what we mine as ore deposits now. In the late 1800s and early 1900s, mining was focused on high-grade and generally lower tonnage targets such as veins. The development of mechanized open pit mining, underground block cave operations, and froth flotation in the early 1900s started to change what was regarded as an ore deposit. The development of the first by-product molybdenum recovery circuit at Cananea in Mexico in 1933 put in motion a step change in the economics of molybdenum production.

Metal deposits can be classified in many different ways. One of the most common classifications is based on the economics that make a deposit a mine. A molybdenum-producing mine may be one of the following:

- A primary molybdenum mine in which revenues are driven solely or primarily by molybdenum, possibly with lesser contributions by other commodities
- A by-product mine producing molybdenum where the primary revenue is from another commodity (usually copper in the case of molybdenum) with subordinate revenue provided by the production of molybdenum and possibly other by-products
- A co-product mine, which is uncommon, with the revenue from the production of multiple commodities required to make the mine profitable

Examples of primary molybdenum mines include the Climax and Henderson mines in Colorado, the Questa mine in New Mexico, and the Thompson Creek mine in Idaho (all in the United States). Examples of by-product molybdenum mines include the Bingham Canyon mine in Utah, the Bagdad mine in Arizona, and the Chuquicamata mine in Chile. An example of a co-product mine is the Sierrita mine in Arizona.

Another way to classify deposits is by their geologic *style* of mineralization. The following is a list of the most common types of molybdenum deposits:

- **Vein deposits.** These are generally planar deposits of minerals cutting wall rocks.
- **Pipe deposits.** These are cylindrical/pipe-like deposits of minerals cutting wall rocks.
- **Metasomatic/skarn deposits.** These are characterized by skarn (calc-silicate) minerals that develop due to the interaction of intrusives and (usually) sediments (commonly carbonates).
- **Pegmatites.** Very coarse-grained intrusive rocks, these are usually interpreted as products of very late-stage igneous differentiates with elevated water and incompatible element concentrations.
- **Porphyry deposits.** These are deposits where the minerals of interest are *disseminated* through a large volume of hydrothermally altered rock, usually concentrated along a stockwork of fractures and/or veinlets. Usually in or adjacent to a mass of intrusive rock, some of which commonly has a porphyritic texture, large-scale zoning of hypogene alteration (potassic, phyllic, silicic, argillic, and propylitic) is typical and varies with the type of porphyry deposit. These deposits are often amenable to mining through high-tonnage open pit operations.
- **Sedimentary/metasedimentary-related deposits.** Used here as a catchall category of deposits with elevated molybdenum contents, these deposits include roll-front uranium deposits (Bullock and Parnell 2017), Athabasca-type uranium (Ferguson 1984), Karoo Formation U-Mo deposits (Van der Merwe 1986), black shales (Smedley and Kinniburgh 2017), underwater hydrothermal vent deposits (Smedley and Kinniburgh 2017), and others. Ore-forming processes include the effects of diagenesis and supergene alteration on sedimentary rocks. Molybdenite can be the molybdenum-bearing mineral, particularly in the metasedimentary deposits, but a variety of molybdenum-containing oxide minerals are found in the sedimentary deposits (jordisite, ilsemannite, iron oxides, jarosite, etc.). So far, none of the deposits in this group has gained prominence as an important source of molybdenum.

The preceding list is representative, but not all inclusive—other deposit styles (e.g., greisens) can contain molybdenum mineralization.

Vein deposits and pipe deposits were important in the past, but as stand-alone deposits, they currently account for a minor portion of the world's molybdenum production. There has been some minor molybdenum production from pegmatites in the past. Metasomatic/skarn deposits containing molybdenum are sometimes of a sufficient size to be economic in today's conditions. Skarns sometimes occur in association with, and are mined with, porphyry deposits (e.g., at the Chino mine in New Mexico). Sedimentary- and metasedimentary-related deposits can contain anomalous concentrations of molybdenum, but to the authors' knowledge have not had any substantial molybdenum production to date. The vast majority of molybdenum currently produced, and that produced in the past, comes from porphyry deposits.

Porphyry deposits, which are the major source of molybdenum production, can be further divided by their mineralogy, chemistry, and the genetic models proposed to explain their origins. For molybdenum, the porphyry deposits have generally been divided into four types:

1. **Climax-type deposits.** Also known as high fluorine or alkali-feldspar rhyolite-granite porphyry molybdenum deposits, typical examples are the Climax and Henderson

mines in Colorado, the Mt. Hope deposit in Nevada (United States), and the Questa mine in New Mexico. This type of porphyry has higher molybdenum grades relative to the other two types—usually 0.10%–0.30% Mo. Molybdenum is the primary product. Associated intrusives are more silicic and potassic than the intrusives associated with porphyry coppers or low-F stockwork molybdenum deposits (generally granitic composition rather than monzonites, diorites, or granodiorites). They have high fluorine content (fluorite and/or topaz are common gangue minerals) and often anomalous tin (in cassiterite) and/or tungsten (in wolframite and/or scheelite), sometimes to the extent that tungsten and tin may be produced as by-products. Associated intrusives are generally classed as A-type granites and seem to have been generated when the tectonic regime was transitioning from compressional to extensional (Ludington and Plumlee 2009). The molybdenite concentrate produced from this type of deposit tends to be cleaner with higher Mo content and lower impurities (such as insolubles, which are generally silicate minerals, iron, copper, lead, and others) than that produced from the other two types of porphyries. Higher-value chemical- and lubricant-grade products are often produced from it. The Climax mine, the namesake of this deposit type, has produced more than 450 Mt (million metric tons) of $\geq$0.20% Mo ore and has reported minable reserves of 170 Mt at 0.15% Mo as of the end of 2016 (Climax Molybdenum Company 1924–2017).

2. **Porphyry copper deposits.** The economic driver for this porphyry type relies on the contained copper, but molybdenum can be present as a by-product. Typical examples include the Bingham Canyon mine in Utah, the Sierrita and Bagdad mines in Arizona, and the Cerro Verde mine in Peru. Molybdenum grades generally range from less than 0.010% (controlled mostly by the economics of the Mo recovery circuit) to 0.075% or so. Associated intrusives mostly range in composition from dioritic through monzonitic, though occasionally late-stage granites and/or rhyolites occur. Typical by-products (beyond the molybdenum) are gold and silver, often recovered during smelting/processing of the copper concentrate. Rhenium may be a by-product of processing of the molybdenum concentrate. Associated intrusives are generally classed as I-type granites and are thought to have been generated above subducting plates in a convergent plate margin boundary or island-arc environment (Berger et al. 2008).
3. **Low-fluorine stockwork molybdenum deposits.** Also known as arc-related porphyry molybdenum deposits and Endako-type deposits, typical examples include the Thompson Creek mine, Endako mine (British Columbia, Canada), and Quartz Hill deposit (Alaska). They are lithologically and tectonically very similar to the porphyry copper deposits. Molybdenum grades generally range from 0.05% to 0.20%, but economic copper is lacking (Ludington et al. 2009; Taylor et al. 2012).
4. **Dabie-type deposits.** These are porphyry molybdenum deposits formed in syn- to post-continental collisional tectonic settings. This is a relatively recent model based on deposits discovered and researched in China. The associated intrusives are high-potassium calc-alkaline to shoshonitic magmas. Examples include the Qian'echong and Yaochong deposits (Wu et al. 2017).

Molybdenum-bearing porphyry deposits in China seem to represent all four types. Shapinggou (Zhang et al. 2014) and Jinduicheng (Stein et al. 1997) appear to be good matches for the Climax-type model, Diyanqinamu and Chalukou are of the low-fluorine stockwork type (Wu et al. 2017), and Qian'echong and Yaochong are of the Dabie type (Wu et al. 2017). By-product molybdenum occurs in deposits in the Yulong porphyry copper belt.

In summary, although there are multiple mineral deposit types that may contain molybdenum, most current and past molybdenum production comes from porphyry deposits. There are at least four major types of molybdenum-producing porphyry deposits, which, although they share enough large-scale similarities to all be classed as porphyry deposits, also have distinct characteristics that permit classification as individual types of porphyries. These characteristics can affect the processing of the ore and the products produced from the deposits.

Molybdenum deposits have been formed throughout geologic time, from the Precambrian through the Cenozoic. Some types of deposits are distinct to certain periods (e.g., Athabasca- and Karoo-type deposits), and some deposit types are typically associated with a specific period in some regions (e.g., Laramide porphyry coppers in western North America).

MINERALOGY

Unlike many other metals, there are no known records of molybdenum usage in ancient times, and this is likely because molybdenum does not occur in nature in its free or native state (Gupta 1992). It is a relatively rare element and is only found in approximately two dozen known natural minerals, the most common of which are summarized next.

Molybdenum Minerals

For almost all production—current and past—the mineral carrying the recovered molybdenum values is molybdenite (molybdenum disulfide, MoS_2). There are other molybdenum-containing mineral species, but the relative abundance of molybdenite along with its amenability to concentration through froth flotation currently make it the predominant ore mineral for molybdenum. Supergene processes can cause the development of secondary molybdenum oxide minerals (e.g., molybdite, ferrimolybdite) and other oxide minerals that may contain molybdenum (iron oxides, jarosite, etc.) in any deposit that has molybdenite as the original molybdenum-containing mineral. In at least one case, a circuit was tested (at Climax, Colorado) for concentration of molybdenum from molybdenum oxide–mineralized material, but with only mixed results (Lane et al. 1972). In the early 20th century, particularly in the southwestern United States, some molybdenum was recovered from the secondary lead molybdate mineral wulfenite (Hess 1924; Kirkemo et al. 1965). Scheelite (calcium tungstate) and powellite (calcium molybdate) are the primary minerals and are usually found in skarns or veins; they form a solid solution series with each other, and tungsten and molybdenum substitute for each other. Scheelite is much more common than the molybdenum-bearing powellite, but scheelite can have some molybdenum content that can sometimes be recovered as a by-product from tungsten deposits. Table 1 shows the most common molybdenum minerals and some of their properties.

Rhenium

Copper-molybdenum porphyry deposits are the world's primary source of rhenium (Re), which occurs as solid substitution for molybdenum atoms on the MoS_2 lattice structure. While many other elements should be able to substitute for Mo, the trigonal arrangement of Mo^{+4} and the coordination number of 6 ensure that only tungsten (W) and Re satisfy the geometric conditions and electrical charge required for substitution, although W's affinity for oxygen means that generally only Re atoms are present with MoS_2 (Mo and Re also have nearly identical atomic radii of 1.39 and 1.37 Å, respectively). Note that Se and Te may also be present, caused by substitution of sulfur (S) (Gupta 1992). All three elements are often recovered from the flue gas of the roaster via hydrolyzation and subsequent extraction with tertiary amine ionic exchange processes.

Table 1 Molybdenite minerals and their properties

Mineral	Molecular Weight, g/mol	Specific Gravity, g/cm³	Molecular Formula
Bamfordite	412.76	3.64	$Fe^{3+}Mo_2O_6(OH)_3 \cdot H_2O$
Biehlite	426.07	5.24	$[(Sb,As)O]_2MoO_4$
Drysdallite	230.41	6.34	$Mo(Se,S)_2$
Ferrimolybdite	717.61	2.99	$Fe^{3+}{}_2(MoO_4)_3 \cdot n(H_2O)$
Hemusite	852.45	4.47	Cu_6SnMoS_8
Kamiokite	527.51	6.02	$Fe_2Mo_3O_8$
Lindgrenite	544.53	4.29	$Cu_3(MoO_4)_2(OH)_2$
Molybdenite	160.07	5.00	MoS_2
Molybdite	143.94	4.75	MoO_3
Monipite	185.60	8.93	MoNiP
Powellite	200.02	4.25	$CaMoO_4$
Tugarinovite	127.94	6.58	MoO_2
Wulfenite	367.14	6.82	$PbMoO_4$

Courtesy of Aminpro

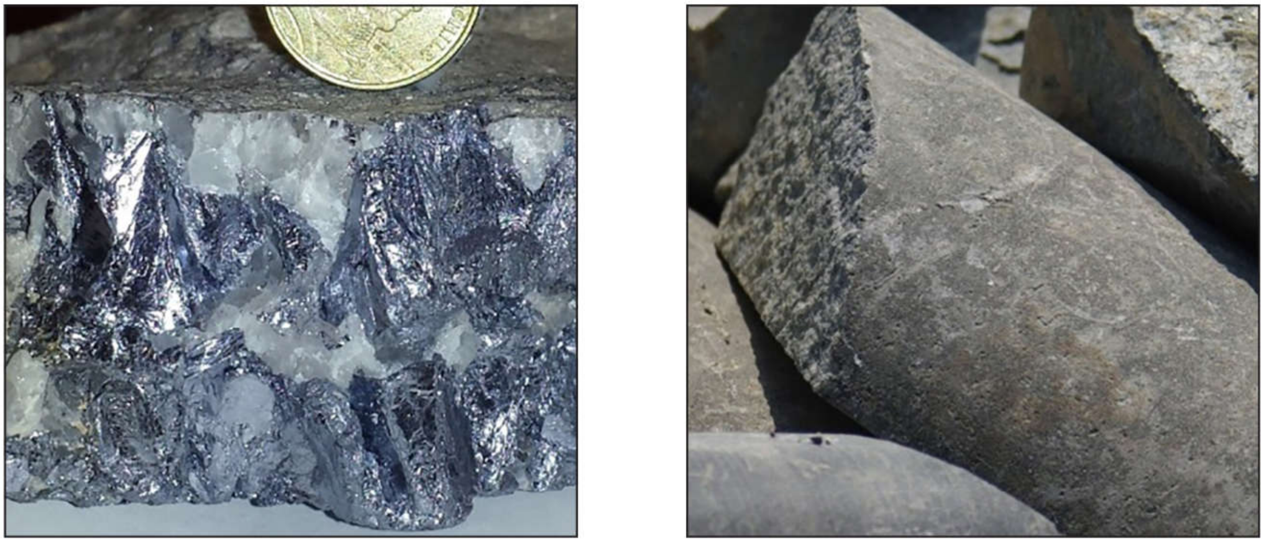
Mineralogical Factors Affecting Recovery

The mineralogy of the deposit is not the only important factor for molybdenite recovery. The grain size of the molybdenite crystals themselves also plays an important role in the selection of the processing equipment and circuit arrangement. For example, the following images in Figure 1 show samples of molybdenite-bearing copper ores from two different deposits. Figure 1A shows drill core from a coarse-grained porphyry deposit in the southwestern United States (Bagdad, Arizona). For this operation, the molybdenite presents primarily as coarse crystals that form as veinlets around fracture sets (average grain size = 35 µm, average grade = 0.02% Mo). Figure 1B is from a fine-grained porphyry in northern Chile (average grain = 6 µm, average grade = 0.04% Mo). For this operation, the molybdenite is finely disseminated and almost invisible to the naked eye, although the average grade is much higher. The coarse, North American operation can achieve higher recoveries at coarser grind sizes, higher pH, and with fewer cleaning stages. The fine-grained South American operation requires finer regrind sizes, much longer retention times, and active pH control to improve the separation kinetics.

In addition to molybdenum mineralogy and grain size, the presence of naturally hydrophobic gangue minerals can also be an important factor in the economics and/or design of the separation process. Many primary and by-product molybdenum deposits contain trace amounts of these minerals, which can include talc, elemental sulfur, carbon, pyrophyllite, or other floatable clays. The geological distribution and association of these minerals can vary greatly between deposits and even within deposits, and therefore significant characterization effort is required prior to process selection, particularly for greenfield projects where little historical information is available to guide the process development team.

ECONOMIC CONSIDERATIONS

Figure 2 shows the significant variations in realized price for technical-grade molybdenum trioxide and ferromolybdenum



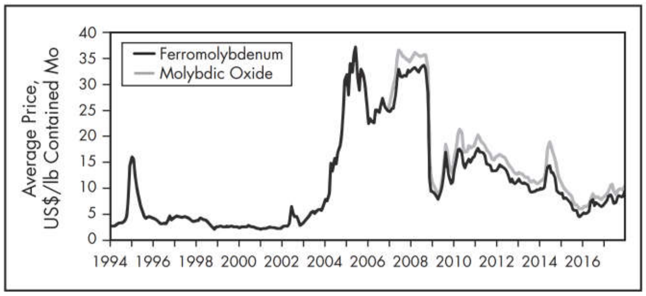
A. Coarse-grained molybdenite (Bagdad, AZ)

B. Fine-grained molybdenite (northern Chile)

Courtesy of Freeport-McMoRan

Courtesy of Aminpro

Figure 1 Coarse- and fine-grained molybdenite



Data from S&P Global Platts, n.d. (molybdic oxide); and CRU International, n.d. (ferromolybdenum)

Figure 2 Molybdic oxide and ferromolybdenum pricing history

over the past 20-plus years. Although the price of molybdenite is primarily driven by molybdenum supply and demand, much of the molybdenum supply is produced as a by-product of copper sulfide recovery processes; as a result, the price, and, therefore, the production rate, can be affected by the supply–demand equilibria of the copper market. For this reason, the supply curve of molybdenum is relatively inelastic with respect to molybdenum price. Other factors further complicate the economics:

- Molybdenum is a much smaller market than copper.
- The requirement of intermediate processing steps (roasting and/or oxidation) can sometimes create artificial or temporary production bottlenecks.
- A significant portion (40%) of the world production originates in China and is susceptible to state export quotas or controls.

The preceding factors cause a relatively high price volatility for molybdenum products, captured by Figure 2, which significantly impacts the sustainability of the primary molybdenum producers, for whom revenue and profitability are much more sensitive to commodity pricing. It is fundamentally for this reason that the primary molybdenum producers are often considered the *swing* producers, where operation is curtailed if market price gets too low.

RECOVERY OF MOLYBDENITE FROM PRIMARY MOLYBDENUM DEPOSITS

Molybdenite is one of the few sulfur-bearing minerals that exhibit natural hydrophobicity. It has been suggested that the native hydrophobicity of molybdenite is primarily caused by the crystal structure, in that a layer of molybdenum atoms is sandwiched between layers of sulfur atoms. The layers are held together by van der Waals bonds that give rise to a well-defined cleavage plane for molybdenite. The surface of molybdenite created by the cleavage plane is highly hydrophobic, and the plane perpendicular to it is only weakly hydrophobic (Chander and Fuerstenau 1972).

Primary molybdenum recovery and concentration relates to the flotation of molybdenite from molybdenum porphyries in which it is the only valuable component (in some cases, particularly in China, tungsten may also be economically recovered from the plant tails). The process is relatively simple and consists of the main processing steps common to most other hydrophobic mineral separation systems. They include comminution, multiple stages of froth flotation, regrind, and concentrate dewatering. In many cases, a chloride leach step is applied to the flotation concentrates to remove lead and other deleterious elements.

Comminution

The comminution circuit generally consists of crushing and grinding equipment (rod milling, autogenous milling, and ball milling), with the purpose of achieving economic liberation of the molybdenite mineral grains. The Henderson primary molybdenum concentrator in Colorado employs primary crushing followed by a single stage of semiautogenous grinding mills operating in closed-circuit configuration with hydrocyclones. The Climax, Endako, and Thompson Creek concentrators all use a combination of autogenous, semiautogenous, and ball milling to achieve liberation. Chinese operations, however, often use a combination of ball mills and rod mills, depending on the age and capacity of the process plant.

Flotation

Once the primary ore has been sufficiently ground, it is conditioned with a series of reagents to improve the selectivity of the separation process. Typical reagents include Calumet oil, pine oil, Syntex, and Nokes. Often, reagent addition occurs during the grinding step, as many of these oils are immiscible with water. After the ore has been properly conditioned, it is directed to a roughing froth flotation stage in which the hydrophobic, predominantly molybdenite minerals are removed. The process of regrinding, conditioning, and cleaner froth flotation is repeated until the desired liberation, concentration, and recovery is achieved.

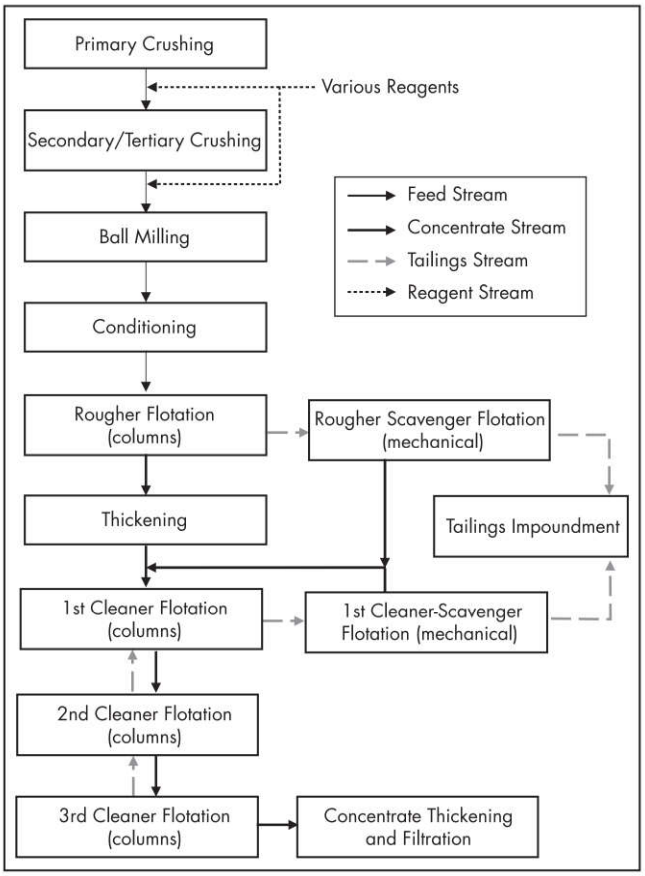
Flow-Sheet Configuration

Figures 3 and 4 show two typical flow-sheet configurations for primary molybdenum processing (one from a Chinese primary molybdenum processing plant and the other from a U.S. plant). The key difference between the two flow sheets is the use of column flotation cells in the roughing application in the case of the Chinese process configuration. The column cell is typically followed by a mechanical scavenging step with the concentrate advancing (as shown) or returning to the column (not shown). The use of the column cells with wash water in the roughing application eliminates hydraulic entrainment of fine gangue particles, allowing the size of the subsequent cleaning section to be significantly reduced.

Hydrochloric Acid Leaching

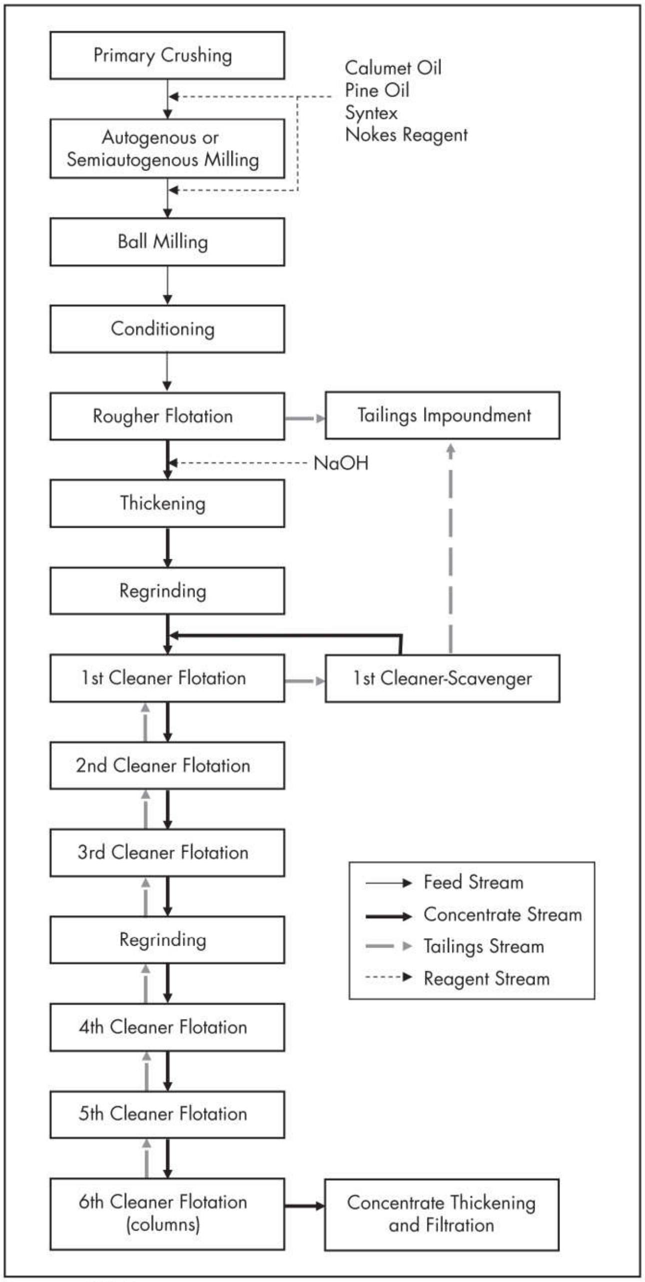
Primary concentrate is made into a slurry in a mixture of water and hydrochloric acid (HCl) to maintain approximately 40% solids and 2% acid strength. A surfactant is added to improve the solid/liquid contact and improve the kinetics of impurity removal. The leach tanks are kept at 79°C to support reaction kinetics and keep lead in solution. Leach slurry is filtered through drum filters followed by repulping with hot water to wash and remove the residual acid. The filter cake from the final filtration stage travels through a set of steam dryers to reduce moisture down to 2%–3% prior to storing in the final concentrate bins. Concentrate from the bins is packed and delivered to conversion sites. An example of typical feed and product assays before and after leaching is depicted in Table 2. Customer specifications vary, so lead content in final concentrate can vary.

In general, lead sulfide (PbS) leach kinetics in HCl solutions are quite fast, relative to ferric chloride leaching of copper (which will be discussed in the "Ferric Chloride Leaching"



Courtesy of Aminpro

Figure 3 Typical flow sheet for primary molybdenum concentration in China



Courtesy of Aminpro

Figure 4 Typical flow sheet for primary molybdenum concentration in the United States

section). Figure 5 shows laboratory-batch leach kinetics in HCl solutions of various strengths.

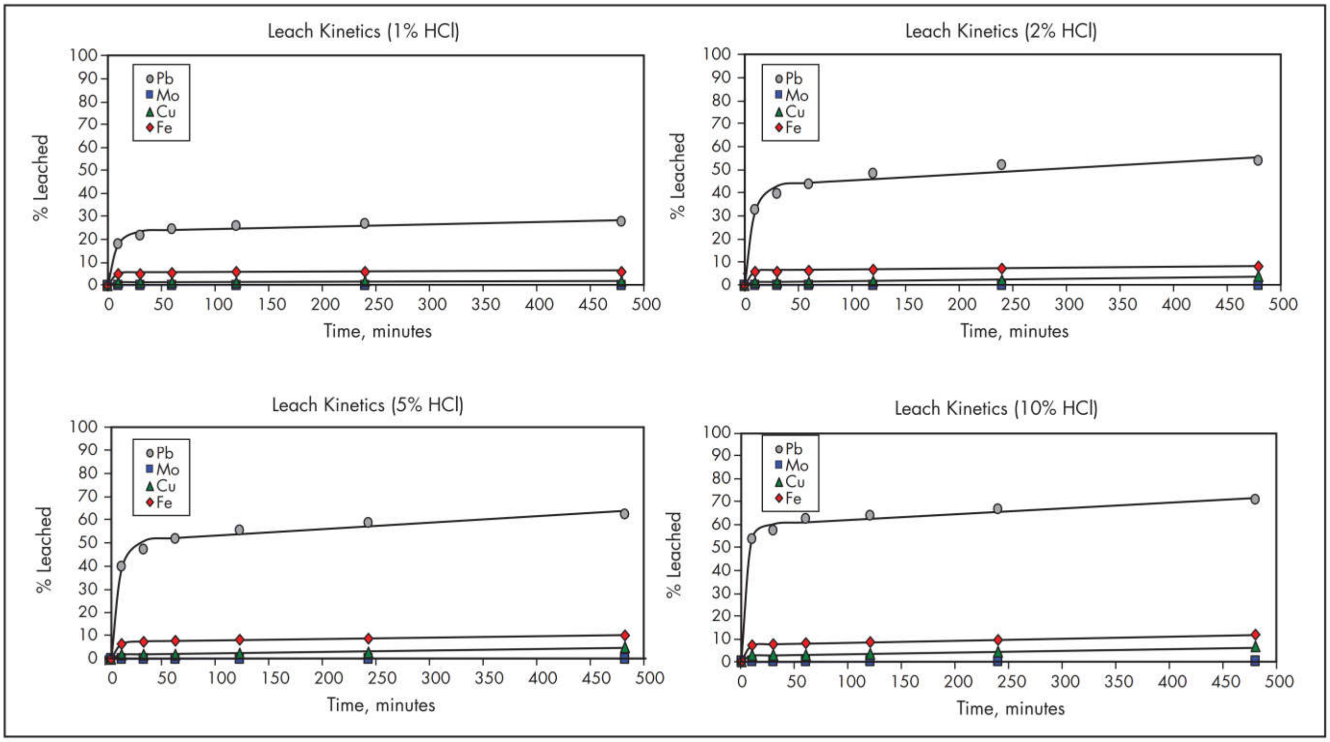
RECOVERY OF MOLYBDENITE FROM COPPER PORPHYRY ORES (BULK RECOVERY)

Molybdenite is recoverable from copper ores by froth flotation under much the same conditions as primary copper sulfide. Because molybdenite is naturally hydrophobic, it can be recovered readily without any collectors (although collectors are often used, as discussed in the next section). For economically exploitable molybdenum ore grades, the bulk of the molybdenum reports to the sulfide concentrate, together with the copper minerals, some of the pyrite, and any other hydrophobic minerals that may be present in the ore. The molybdenite is then separated from the bulk sulfides in a subsequent selective flotation processing step. The bulk sulfides, mainly Cu- and Fe-sulfide minerals, are depressed using a depressant—often sodium hydrosulfide (NaHS)—allowing the molybdenite to be recovered and concentrated. After one or more cleaning stages, the concentrated molybdenum is thickened, filtered, (sometimes) dried, and, if the conversion facilities are off-site, packaged and shipped to the customer. The tailings of the molybdenum separation circuit contain the copper concentrates, which are also thickened, filtered, and shipped to the downstream smelting or pressure leaching plant.

Table 2 Typical feed and product assays

	Slurry Concentrate A Prior to Leach, %	Dry Concentrate B Prior to Leach, %	Dry Concentrate After Leach, %
Molybdenum	58.9	58.6	58.9
Iron	0.15	0.16	0.14
Lead	0.047	0.047	0.010
Insolubles	1.12	1.22	1.26

Courtesy of Aminpro



Courtesy of Aminpro

Figure 5 Pb, Mo, Cu, and Fe leach kinetics in HCl leach solutions

In some cases, depending on the ratio of recovered copper to molybdenum, the molybdenum in the bulk concentrates can reach high enough concentrations to actually be considered a smelter penalty element if a molybdenum separation circuit is not implemented prior to smelting.

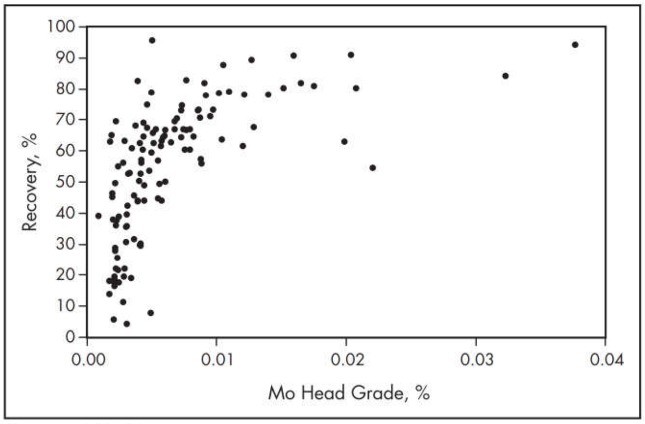
Factors Affecting Primary or Bulk Recovery

This section describes the four main factors affecting the *primary* or *bulk* molybdenite recovery step (i.e., the bulk sulfide flotation step), including a description of the main factors affecting the *secondary* molybdenite recovery step (i.e., the selective, molybdenite separation step).

Mineralogical Factors

The main mineralogical or geological factors affecting the recoverability of by-product molybdenite are head grade, mineral type, and liberation/association properties, including morphology (Triffett et al. 2008).

For many by-product porphyry properties, the maximum recovery of molybdenite in the bulk sulfide roughing stage decreases rapidly for head grades less than about 0.01% Mo, and this is one of the reasons why economic by-product molybdenum recovery is seldom achieved for lower head grades. Molybdenum recovery data from a South American Cu/Mo porphyry deposit are shown in Figure 6.



Courtesy of Aminpro

Figure 6 Molybdenum recovery in the bulk sulfide rougher flotation as a function of head grade

Most molybdenite-bearing porphyry ores contain only trace amounts of the nonfloatable molybdate mineral powellite, but in a few cases higher proportions of this mineral have been found. Like molybdenite, powellite is soluble in typical multi-acid solutions used for atomic absorption spectroscopy and is therefore not usually mineralogically identifiable by routine geochemical assaying. Furthermore, it can be difficult to detect using scanning electron microscopy because, when it occurs, it only does so in trace amounts that are often below the detection limits of current technologies. If powellite is detected or suspected in a deposit, the most common measurement approach is to use a separate weak acid digestion (such as dilute sulfuric acid solution) followed by atomic absorption spectroscopy. The results are then compared with molybdenum assayed with the standard multi-acid procedure, and the difference between the two is attributable to powellite (or other nonsulfide molybdenum species).

Pulp Conditions

Like all sulfide minerals, molybdenum flotation is affected by the characteristics of the pulp. In general, the flotation of molybdenite favors lower pH, and recoveries can drop significantly above pH of approximately 11.0. Molybdenite with finer natural grain sizes tend to be more sensitive to higher pH than those with coarser natural grain size. This phenomenon is not clearly understood and may vary from site to site, depending on operating conditions. This sensitivity to higher pH can often lead to very high (relative to copper sulfide) circulating loads of molybdenite in the bulk sulfide cleaning circuit.

Lower pulp density (percent solids) tends to favor molybdenite flotation kinetics. It is thought that the lower pulp viscosities of diluted slurries improve the particle collection kinetics of the molybdenite grains (relative to copper sulfides).

Collectors

Molybdenite is naturally hydrophobic, but kinetics can usually be increased with the use of insoluble nonpolar oily collectors, the most common of which is diesel or fuel oil. Typical collector dosages are between 5 and 25 g/t, although for some high-grade porphyry deposits dosages as high as 100 g/t have been seen in practice. The nature of the activation mechanism is not clearly understood, but two mechanisms have been proposed. In the first, it has been suggested (Born et al. 1976; Cuthebertson 1946) that the oily collectors coat the less hydrophobic grain facets and edges, creating a more compliant hydrophobic surface for bubble attachment and thereby increasing the hydrophobicity of the mineral as a whole. An alternative explanation stems from work done on molybdenite depression using lignosulfonate depressants (Ansari 2006). Lignosulfonate depressants—which work by creating hydrophilic precipitates on the hydrophobic molybdenite faces—can be rendered ineffective if the molybdenite is pretreated with an oily collector. The same phenomenon may be occurring in bulk flotation applications, but instead of preventing lignosulfonate precipitation, it is preventing calcium and other salt precipitates caused by lime saturation (probably calcium hydroxide, carbonate, sulfate, or molybdate).

Flotation Cells

Discussion of flotation equipment is reserved solely to aspects specific to molybdenum. For a broader discussion on flotation technology, see Chapter 7.4, "Froth Management."

The type of flotation cell can also impact the separation efficiency of molybdenite in the bulk circuit. It has been seen that columns, for example, tend to have a lower recovery of molybdenite than expected, compared with copper recovery and/or molybdenite recovery in conventional mechanical cells. It is thought that the reason for this is related to the higher pH at which columns typically operate (by virtue of application in cleaning circuits, where lime is added to depress pyrite). At higher pH, the molybdenite becomes less hydrophobic and the flotation kinetics drop. Froth crowding effects also play a role; that is, when the carry rate ($t/m^2/h$ of concentrate production) approaches the carrying capacity, the least hydrophobic minerals are the first ones that become dislodged in the froth or interface zone. Because copper sulfides are usually more hydrophobic, and because column cells often operate close to the carrying capacity, in this situation molybdenite recovery would suffer. This *crowding* effect has not been observed in molybdenite separation circuits, where there is no strongly hydrophobic specie to displace molybdenite.

SEPARATION OF MOLYBDENITE FROM BULK SULFIDE CONCENTRATES

As noted previously, much of the global supply of molybdenum is produced as a by-product (or a co-product) from copper mining. The molybdenum is recovered in the froth flotation process, together with copper and iron sulfide minerals, and is then separated from the so-called bulk concentrate through a secondary flotation circuit in which the copper and iron sulfides are depressed using chemical depressants, allowing the hydrophobic molybdenite to be selectively recovered and concentrated.

Principles of Molybdenite Separation

The selective froth flotation of molybdenite is based on several key principles. These include the nature and concentration of the depressant, the pH of the pulp, and the impact of hydraulic entrainment (and dispersants).

Depressants

Several depressants have been found to be effective for depressing copper and iron sulfide minerals, including sodium sulfide and sodium hydrosulfide, sodium cyanide, potassium ferri- and ferrocyanide, Nokes reagents, and Anamol-D. This chapter provides a selective overview of the use of sodium hydrosulfide and Nokes reagent, by the far the two most commonly used for by-product molybdenum production (Gupta 1992). Historically, sodium cyanide has been used to depress certain copper sulfide minerals, although this has fallen out of favor because of safety and cost disadvantages.

The Nokes reagent was invented by Charles Nokes at Kennecott (Utah) in the early 1940s. It is a reaction product of phosphorus pentasulfide and sodium hydroxide, which are usually mixed on-site. The reaction is highly exothermic and produces sodium sulfide or hydrogen sulfide (depending on the pH). The reaction equations are as follows (Gupta 1992):

$$6NaOH + P_2S_5 \leftrightarrow 2Na_3PO_2S_2 + 2H_2O + H_2S$$

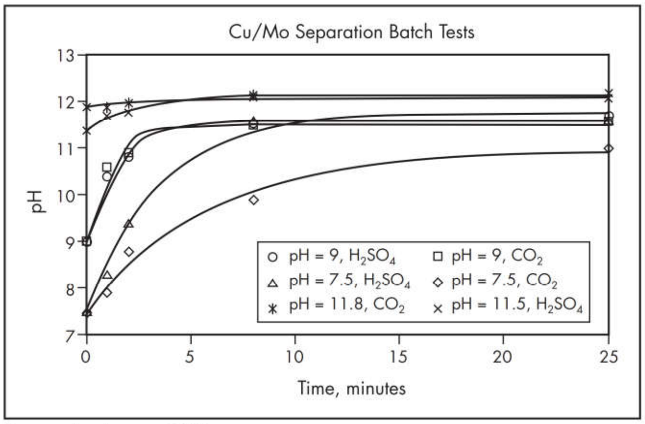
$$H_2S + NaOH \leftrightarrow NaHS + H_2O$$

$$P_2S_5 + 10NaOH \leftrightarrow Na_3PO_2S_2 + Na_3PO_3S + 2Na_2S + 5H_2O$$

Both the NaHS and the sodium sulfide (Na_2S) act as copper depressants in this chemical system (in solution, Na_2S hydrolyzes and then dissociates, forming HS^-).

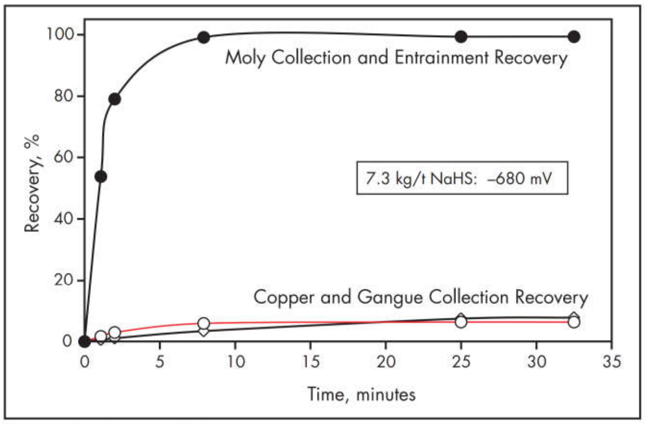
The depressing effect of Nokes reagent and NaHS is caused by the formation of hydrosulfide ion, which, at sufficient concentrations, reacts with the surface of the copper and iron sulfide minerals previously coated with cuprous xanthate and other collectors that were used in the upstream sulfide recovery circuit. The collectors desorb, rendering the minerals hydrophilic. Because hydrosulfide also reacts with any dissolved oxygen (or oxidized minerals), it usually has a limited life. Nokes reagent, therefore, has a longer life than NaHS because the complex thiosulfates can act as a reservoir for the sulfide ion, which reduces the oxidation rate and prolongs the time it remains available to play the role of depressant (Gupta 1992).

Another key difference relates to the sodium ion. For sodium hydrosulfide systems, the reaction product is sodium hydroxide. For Nokes systems, the reaction products are water and thiosulfates. Because the natural floatability of



Source: Amelunxen 2009

Figure 7 pH versus time in laboratory-batch flotation



Source: Amelunxen 2009

Figure 8 Collection recovery versus time for Cu/Mo separation

molybdenite is reduced at higher pulp pH levels, it is often necessary to use acidifying agents, such as sulfuric acid or carbon dioxide, to maintain pulp pH in hydrosulfide-based copper/molybdenum separation systems. This is discussed next.

Sodium hydrosulfide (NaHS) is, by far, the most commonly used copper and iron sulfide depressant in by-product molybdenum production. The following two basic reactions occur with NaHS in a Cu/Mo separation circuit:

1. NaHS dissociation to sodium ion and hydroxyl ion (HS^-), reduces the pulp potential and strips the xanthate from the surface of most metal sulfides, rendering them hydrophilic.
2. NaHS oxidation with O_2 to produce elemental polysulfur and sodium hydroxide (NaOH), rapidly driving the pH up. This is illustrated by Figure 7, which shows pH versus time for molybdenum (moly) rougher batch flotation tests using NaHS as the depressant.

The equations are as follows (Morales 1980):

$$NaHS + H_2O \leftrightarrow NaOH + H_2S$$

$$NaOH \leftrightarrow Na^+ + OH^-$$

$$H_2S \leftrightarrow H^+ + HS^-$$

$$HS^- \leftrightarrow H^+ + S^{2-}$$

$$H^+ + OH^- \leftrightarrow H_2O$$

$$\text{Overall: } NaHS + H_2O \leftrightarrow Na^+ + HS^-$$

$$2NaHS \leftrightarrow 2Na^+ + 2HS^-$$

$$2HS^- + O_2(aq) \leftrightarrow OH^- + S_n(s)$$

$$\text{Overall: } 2NaHS + O_2(aq) \leftrightarrow 2Na^+ + 2OH^- + 2S_n(s)$$

NaHS dosage is generally controlled by pulp potential, with moly plants typically operating between –600 mV and –400 mV (using an Ag/Ag-Cl reference electrode). In such an environment, the floatability of MoS_2 is relatively unaffected, but the floatability of copper and iron sulfides is so depressed that their collection recoveries are approximately equal to that of insoluble gangue (Figure 8). Adding NaHS to lower the pulp potential beyond this point does nothing further to improve the separation. Note that NaHS is a surface tension modifier and can act as a defoaming agent in some situations, thereby reducing copper recovery by entrainment (although the authors generally favor commercial defoamers for this application because they are less expensive and do not affect the process pH).

NaHS consumption can be reduced by eliminating process water from the moly plant feed prior to rougher flotation, such as by thickening to 65% and diluting with fresh water. Consumption can be further reduced by using the cleaner tails or copper thickener overflow waters, rather than fresh makeup water. Use of nitrogen and/or enclosed cells for oxygen-depleted air has been demonstrated at many plants to have reduced NaHS by 50% on average.

Table 3 shows some selected Cu/Mo by-product plants and the type of depressant used. Only one plant still uses sodium cyanide and arsenic Nokes, while another uses only Nokes (both are in South America).

Other Depressants

Because of safety concerns associated with the transport and use of NaHS, recent attention has been given to alternative depressants that can be used as a substitute or partial substitute for NaHS.

One such depressant, di-sodium carboxymethyl-tri-thiocarbonate, is marketed by Chevron Phillips under the commercial name Orfom D8 depressant. D8 is effective at depressing copper, iron, and lead sulfides at basic and acid pH ranges. It is applied at varying dosages depending on the application (Chevron Phillips 2000–2018).

Another depressant, calcium polysulfide (Tessenderlo Kerley 2016), marketed by Tessenderlo Kerley under the trade name TKI-330, is reported to provide virtually identical metallurgical recoveries relative to NaHS at similar dosages (Tessenderlo Kerley 2018). Unlike D8, however, TKI-330 still has a hydrogen sulfide (H_2S) vapor pressure, albeit significantly lower than that of NaHS solution. As a result, it reduces safety risks when operating at lower pH, but does not eliminate them. TKI-330 offers an additional advantage of being able to be manufactured from raw materials on-site, eliminating risks associated with the safe transport of the chemical (Tessenderlo Kerley 2018).

Table 3 Copper-molybdenum plants and reagents used

Site	Chalcopyrite, %	Covellite, %	Digenite, %	Chalcocite, %	Bomite, %	Floatable Gangue	Cu Collector	Mo Collector	Frother	Mo in Bulk, %	Bulk Mo Recovery, %
Plant 1, North America	33	33	25	8	<1		Thionocarbamate	MCO	X-133	0.70	70
Plant 2, North America	99						Xanthate	MCO	Nalco 9837/ X-133	3.00	80
Plant 3, North America	97.50	2.50		<1			Xanthate	Fuel oil	X-133	1.50	74
Plant 4, North America	95	1		3	1		Thionocarbamate/xanthate	MolyFlo	Methylisobutyl carbinol (MIBC)	0.70	90
Plant 5, North America	85	<1	<1	<1	14	Talc	Dithiophosphate/monothiophosphate	Fuel oil	X-237	1.40	80
Plant 6, North America	60				40		Xanthate	Fuel oil	Tennafroth 350	1.50	75
Plant 7, North America	100						Xanthate	Fuel oil	MIBC		
Plant 8, North America	100						Thionocarbamate/xanthate	Fuel oil	MIBC (F-2)	0.60	60
Plant 9, South America	98	1			1		Thionocarbamate	Fuel oil	MIBC	0.70	
Plant 10, South America	X	X	X	X	X						
Plant 11, South America	X			X							
Plant 12, South America	X				X						
Plant 13, South America	X				X						
Plant 14, South America	X	X		X	X						
Plant 15, South America	X				X		Dithiophosphate and xanthate	Fuel oil (diesel and kerosene)	MIBC	0.005	0.85

(continues)

Table 3 Copper-molybdenum plants and reagents used (continued)

Site	Mo Rougher, % Mo	Mo Rougher, % Cu	Depressant	Pretreatment	Pretreat Time	Particle Size	Depressant, kg/t	Roughers	Cleaners	pH, Rougher Condenser	eH, Rougher
Plant 1, North America	2.70	37	NaHS	High shear	1.5 hours	30% +325		Air	Air	10, CO_2	
Plant 2, North America	4.50	25	NaHS	High shear	0.5 hour	20% +325	15	N_2	Air	11.5	
Plant 3, North America	5.00	25	NaHS	Conditioning	19 minutes	26% +325	3.5	N_2	N_2	11.5	
Plant 4, North America	1.30	24	NaHS	Conditioning	15 minutes	45 µm	12.5	N_2	Air	10.3, CO_2	
Plant 5, North America	1.40	25	NaHS	Stock and conditioning	24 hours + 20 minutes	75 µm	9	N_2	Air	10.5	
Plant 6, North America	4.00	32	NaHS	Stock and conditioning		50 µm		N_2	N_2	8.8, CO_2	
Plant 7, North America			NaHS					Air, recirculated	Air, recirculated	8.5	
Plant 8, North America	1.20	28	NaHS	Stock and conditioning				N_2	N_2	9.2, H_2SO_4	
Plant 9, South America	1.20	30	NaHS		30 minutes	53 µm	4.4	Air, recirculated	Air	7.5, H_2SO_4 (CO_2 future)	
Plant 10, South America			NaHS				6	N_2	N_2	7.5, H_2SO_4	
Plant 11, South America			NaHS				4	N_2	N_2	10.5	
Plant 12, South America			NaHS				7.4	N_2	N_2		
Plant 13, South America			NaHS		Pipeline		4	Air, recirculated	Air, recirculated	7.5, H_2SO_4 (staged additional)	
Plant 14, South America			NaHS				4.6	N_2	N_2	7.5, H_2SO_4	
Plant 15, South America	0.007	0.0002	NaHS and pentasulfuros	Conditioning with acid	45 minutes	30% +325	4	N_2	First cleaners	9.3–9.5 (H_2SO_4 to pH 8.4 then CO_2 in first cells)	–450 mV

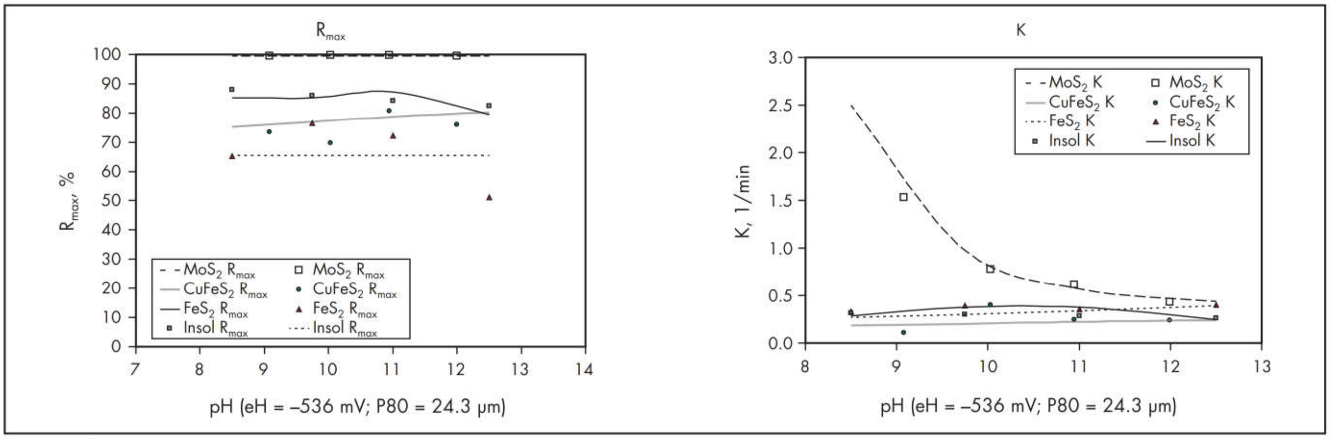
(continues)

Table 3 Copper-molybdenum plants and reagents used (continued)

Site	pH, Cleaners	Open Circuit Cleaner Tails	Cells Covered	Scrubbers	Regrind/Thickener	Cleaning Time, minutes	Column Cells	Mo Concentrate Grade, %	Cu Concentrate Grade, %	Selective Recovery, %	Overall Recovery, %
Plant 1, North America	10, CO_2	No	Yes	Yes	No/No	26	Yes	55	4	95	67
Plant 2, North America		No	Yes (ex cleaners)	No	Yes/No	26	No	48	2.5	95	76
Plant 3, North America		No	No	No	No/No	75	Yes	50	3	95	70
Plant 4, North America	12	No	Yes (ex columns)	No	No/Yes	198	Yes	51	2	91	82
Plant 5, North America	11.8	Sometimes	No	No	Yes/Yes	207	Yes	52	0.40	80	69
Plant 6, North America	9.5, CO_2	No	Yes	Yes	Yes/No		Yes	53	0.70	95	72
Plant 7, North America	10		Yes		Yes		Yes	52	2.50		
Plant 8, North America	11		Yes	No				48	2.50	60	36
Plant 9, South America	9.5, CO_2	No	Yes (ex columns)	No	No/No		Yes	50	3	89	60
Plant 10, South America			No								
Plant 11, South America	11.3		No								
Plant 12, South America			No								
Plant 13, South America	7.5, H_2SO_4 (staged)	No	Yes	Yes					92		
Plant 14, South America		No	Yes	Yes							
Plant 15, South America	9.1 (CO_2) in first cleaners	No	No	No	No/Yes		Yes	48	4 maximum	81	69

Courtesy of Aminpro Benchmarking

Note: Numeric values are from quantitative microscopy. Blank cells indicate that the mineral is not detectable. "X" means that the mineral is present in significant but unknown quantities, either because quantitative mineralogy is not available or because the mineralogy can change significantly between ore types.



Courtesy of Aminpro

Figure 9 R_{max} and collection zone rate constant as a function of pulp pH for a moly plant cleaner circuit

A third alternative, marketed by Solvay Group (formerly Cytec) under the trade name Aero 7260, has been shown to effectively depress copper sulfides when used as a partial replacement for NaHS (i.e., 50%–90% of the NaHS consumption is replaced). Dosages vary between 1.5 and 2.5 kg/t (Cytec 2013).

Currently, there is not an extensive usage history of these reagents in operating plants, but preliminary results indicate that they show promise. This area of research is expected to see rapid development soon.

pH Modifiers

As part of a previous study performed at a South American moly separation plant, moly cleaner separation kinetics were measured at different pH. The results are shown in Figure 9. It can be seen that at pH of approximately 12.0 and above, the kinetics of moly are virtually indistinguishable from those of chalcopyrite. For the high R_{max} values of the minerals, this means that it is virtually impossible to achieve a good moly separation without extremely high circulating loads. The solution, in this case, is to reduce the pH, thereby moving to the left along the x-axis of the right-hand graph. At pH ≤10, the kinetics become more favorable to moly separation.

Two different approaches to pH control are used in byproduct separation. The first, and most common, is passive pH control, in which the NaHS dosage, the use of nitrogen, and the use of natural pH makeup water are carefully controlled to maintain the pH in the appropriate range. In this case, pH is allowed to vary, albeit in a controlled manner. In some cases, with slow-floating molybdenum species or complex circuits (such as those involving talc, pyrophyllite, or other impurities), it may not be possible to control the pH using passive techniques. In these cases, active pH control may be more effective, which considers the use of acidifying agents to control the pH to a target setpoint, using instrumentation and process control strategies.

Sulfuric acid and carbon dioxide (CO_2) gas are the two most common acidifying agents used in active pH control strategies.

1. *Sulfuric acid* donates a hydrogen ion resulting in lower pH. Secondary hydrogen dissociation also occurs, yielding sulfate ion, which can form gypsum with dissolved calcium. The reactions are as follows:

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$

$$H^+ + OH^- \leftrightarrow H_2O$$

$$SO_4^{2-} + Ca^{2+} \leftrightarrow CaSO_4$$

2. *Carbon dioxide* acidifies the pulp through a series of reactions. The vast majority of dissolved CO_2 is not converted into carbonic acid and therefore is free to react directly with hydroxide ions. The reactions are as follows:

$$CO_2 + 2OH^- \leftrightarrow CO_3^{2-} + H_2O$$

$$CO_3^{2-} + CO_2 + H_2O \leftrightarrow 2HCO_3^-$$

$$2HCO_3^- \leftrightarrow 2H^+ + 2CO_3^{2-}$$

$$2H^+ + 2OH^- \leftrightarrow 2H_2O$$

$$2CO_3^{2-} + 2Ca^{2+} \leftrightarrow 2CaCO_3$$

Thus, each mole of CO_2 neutralizes two moles of hydroxide. The trace amounts of carbonic acid that are formed also reduce the pH:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$$

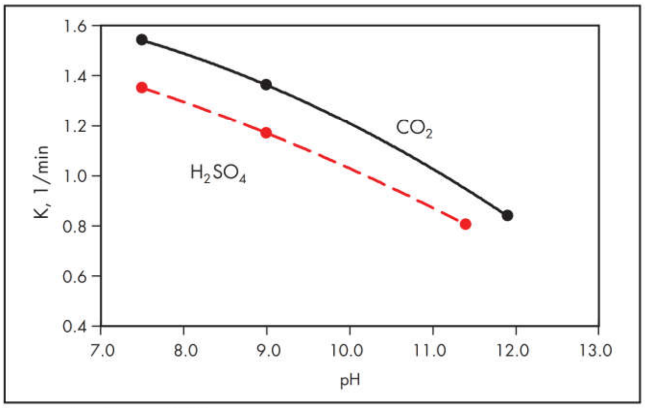
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$3H^+ + 3OH^- \leftrightarrow 3H_2O$$

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3$$

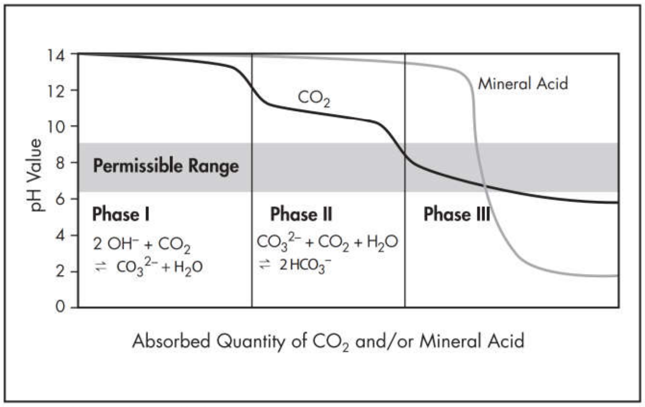
It has been found that CO_2 is metallurgically superior to sulfuric acid. For example, Figure 10 shows the relationship between pH and the rate constant (K) for a sample of bulk concentrate from El Teniente. One curve was generated using carbon dioxide as the pH modifier, and the other curve was produced with sulfuric acid as the pH modifier. It can be seen that the molybdenum flotation rate constant is significantly higher when using CO_2, rather than sulfuric acid, as the pH modifier.

It is thought that the improved floatability of molybdenite when using carbon dioxide as the pH modifier, rather than sulfuric acid (Figure 10), is caused by the difference between the



Source: Amelunxen 2009

Figure 10 Molybdenite rate constant versus pulp pH for CO_2 and H_2SO_4 neutralization



Source: Linde Group 2012

Figure 11 Example of basic neutralization curve for water solutions, mineral acid, and CO_2

equilibrium solubility of calcium carbonate ($CaCO_3$), which is 20 ppm on average at standard temperature and pressure in distilled water, and calcium sulfate (approximately 2,000 ppm) (Green and Maloney 1999). The solubility (Ksp) of $CaCO_3$ is a function of dissolved CO_2 content. At atmospheric CO_2 concentrations, the maximum equilibrium solubility in distilled water is approximately 50 ppm, but this increases as the concentration of carbonic acid in the pulp increases. Note that the presence of other ions will decrease the Ksp.

It has been recognized that calcium ion in solution can depress molybdenite, but the physicochemical explanation is not fully understood. Chander and Fuerstenau (1972) suggest that it forms calcium molybdate precipitate on the surface of MoS_2 crystals. Rhagavan and Hsu (1984) propose a heterocoagulation effect of silicon dioxide (SiO_2) and MoS_2 in the presence of calcium ion (the so-called slimes effect).

In addition to the metallurgical superiority of CO_2, there are other advantages to using CO_2, which include the following:

- It is environmentally benign, and therefore easier, to obtain permits for the transport and use of CO_2.
- It is safer, because there is less risk of mixing with NaHS-containing fluids during spillage. It is also less corrosive than sulfuric acid.
- It has a flatter neutralization curve, as can be seen in Figure 11. This makes it much easier to control the pulp pH and reduces the potential of overshooting.

By-product molybdenum separation plants that are currently employing active pH control include

- Highland Valley, British Columbia (CO_2-based, both roughers and cleaners);
- Antamina, Peru (roughers);
- Cerro Verde (roughers);
- Morenci Metcalf, Arizona (roughers, cleaners);
- Andina, Chile (sulfuric acid in the roughers, carbon dioxide in the cleaners);
- Los Pelambres (sulfuric acid rougher conditioning tank, undergoing CO_2 trials); and
- Los Bronces/Las Tortolas, Chile (sulfuric acid, roughers, and cleaners).

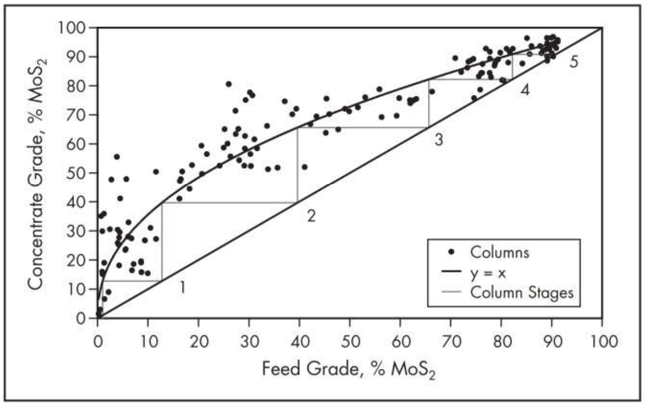
Dispersants

It has been shown that dispersants can be effective at increasing the recovery or separation kinetics of molybdenite in the separation circuit. It is thought that the dispersants help to reduce the heterocoagulation effect; that is, the tendency of excess calcium ion to coagulate with gangue and fine molybdenite particles creates a hydrophilic coating on the molybdenite grains. Water is by far the least expensive dispersant, but many molybdenum separation circuits employ sodium silicate in dosages between 20 and 200 g/t.

Flotation Equipment

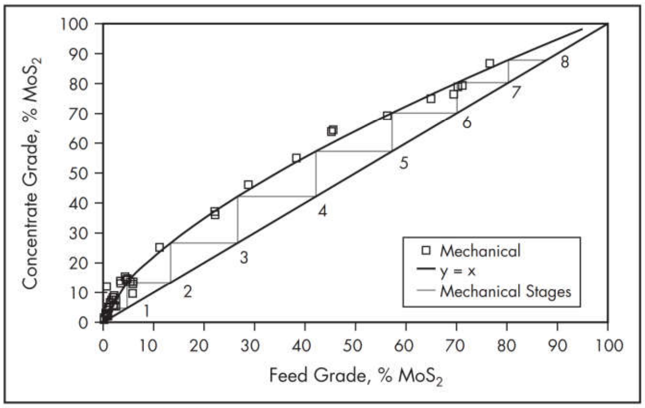
Most moly circuits run the roughing section with mechanical cells and run the cleaners with either fully mechanical cells, column cells, or a mixture of both columns and mechanical cells. Column roughers have only been seen in primary moly mines in mainland China.

Upgrading profiles using column flotation in by-product moly plants typically follow the curve shown in Figure 12. The profile indicates that at most five cleaning stages are required to achieve a high-purity product. A similar profile for mechanical cells is shown in Figure 13. For mechanical cells, at least eight stages are required to produce high-grade moly concentrates (i.e., >90% molybdenite in concentrate).



Source: Amelunxen 2009

Figure 12 Upgrading profile for column cells in by-product moly applications



Source: Amelunxen 2009

Figure 13 Upgrading curve for mechanical cells in by-product moly applications

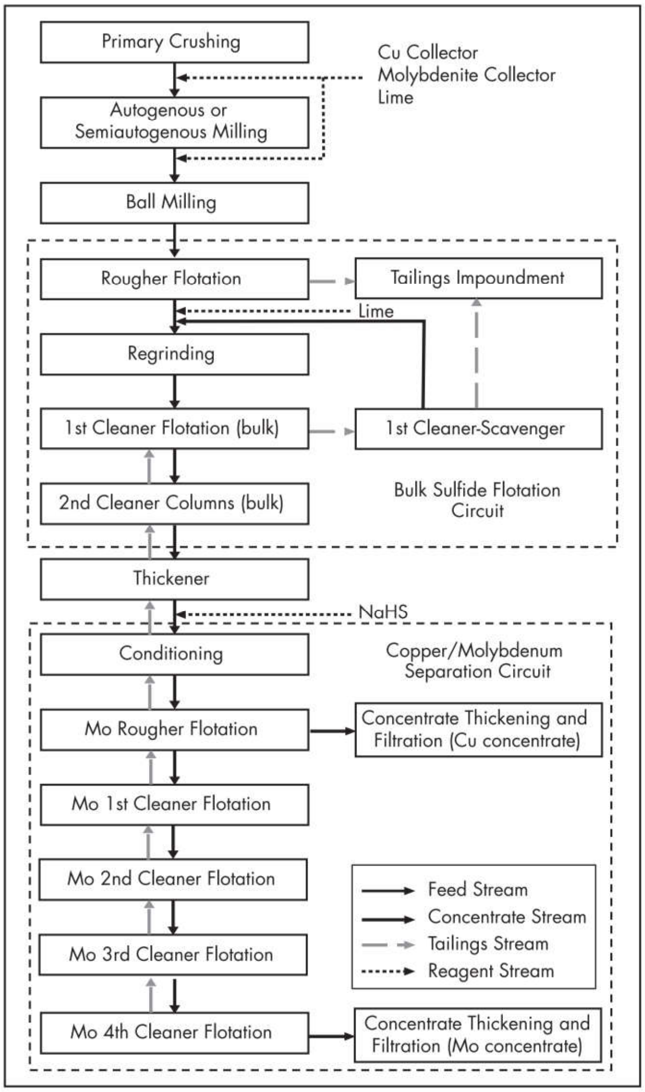
Design engineers generally favor mechanical roughers over column roughers in by-product moly circuits because of column's inability to attain high recoveries. The primary drawback with mechanical cells operating as roughers is that even in a well-operated circuit, at least one-third of the copper floated in the roughers does so through entrainment mechanisms, whereas with the column cell, most of this entrainment is avoided. If the operator is unaware of this, he or she may tend to increase the NaHS dosage when the copper levels are high in the roughers without paying attention to the more relevant parameters of froth bed depth, gas rate, and water recovery. Note that to reduce the entrainment recovery of solids, it is also necessary to reduce the froth recovery of MoS_2, and therefore the total recovery of moly will drop accordingly. It is primarily for this reason that the total rougher retention time is usually much longer in the moly plant than in the bulk circuit, where moly flotation is not affected by pulling rate constraints.

Flow-Sheet Configuration

A typical by-product molybdenum production flow sheet is shown in Figure 14. Depending on mineralogy, association, and molybdenite liberation, different properties have different flow-sheet concepts.

Ferric Chloride Leaching

By-product concentrate feed may contain 45%–48% molybdenum, 3% copper, and 0.3% lead. Leached by-product may contain 50% molybdenum, 0.15% copper, and 0.03% lead. Ferric chloride is often used to leach molybdenum concentrate. Many variables influence leaching: temperature, agitation, particle size, concentration, and oxygen-reduction potential. The chloride ion converts the lead into a form that is soluble. The copper dissolution, which occurs with the chloride ion, is recovered by ferric ion. The ferric ion is then regenerated by chlorination. A ferric digester keeps the total iron at the appropriate level and removes dissolved copper. This is a cementation process that exchanges cuprous for Fe^{+2} using scrap metal. The copper is then recycled at the smelter, and the ferrous solution is sent to the chlorinator to be regenerated to ferric. This reduces reagent costs by minimizing the need to bleed out ferric chloride because of high copper concentrations. An example of a by-product leach process is depicted in Figure 15.

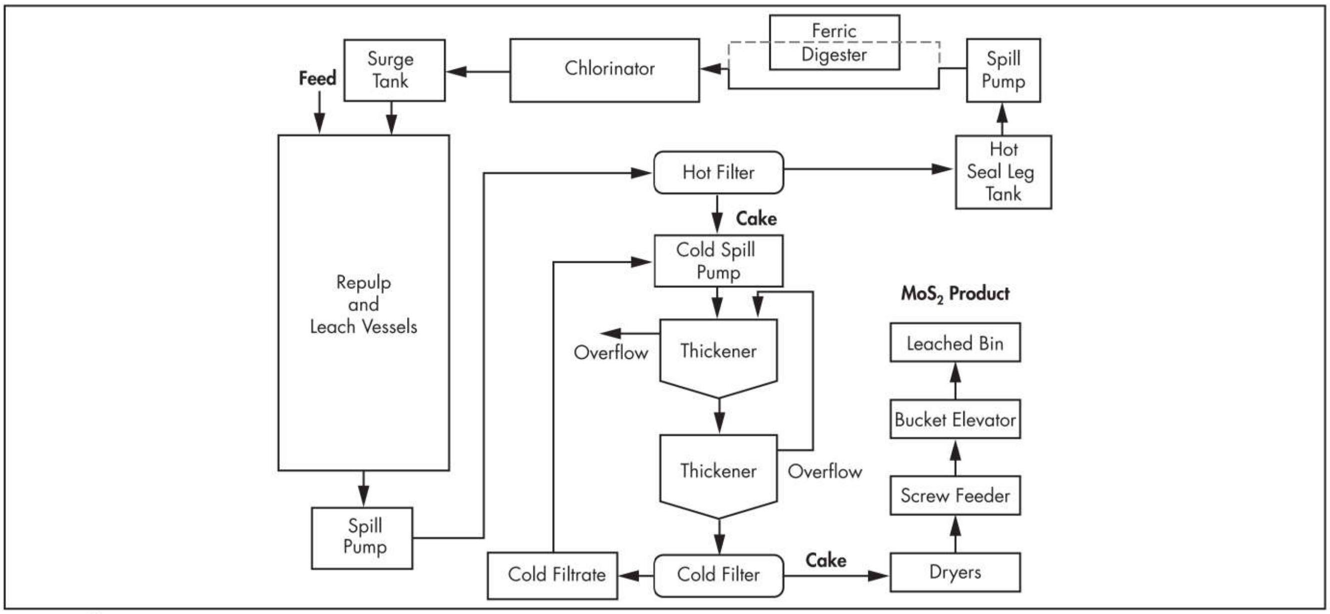


Courtesy of Aminpro

Figure 14 Typical by-product molybdenum flow sheet

Safety Considerations

The use of acidifying agents in combination with sodium hydrochloride can create serious safety concerns caused by the potential to generate lethal concentrations of H_2S gas. H_2S gas is naturally emanated from NaHS solutions in trace amounts, but as the pH drops and the pulp becomes more acidic, the evolution rate begins to increase dramatically. The following stability diagram shown in Figure 16 for HS^- in distilled water shows that below approximately pH 7.2 H_2S becomes the stable species, although in practice, pH of approximately 8.5 can lead to dangerous concentrations in poorly ventilated spaces. Active ventilation systems are therefore suggested for plants operating below pH of approximately 9.5. These systems consist of covered flotation cells that operate under negative pressure, with a NaOH-solution scrubber treating any process off-gas.



Courtesy of Freeport-McMoRan

Figure 15 By-product leach process

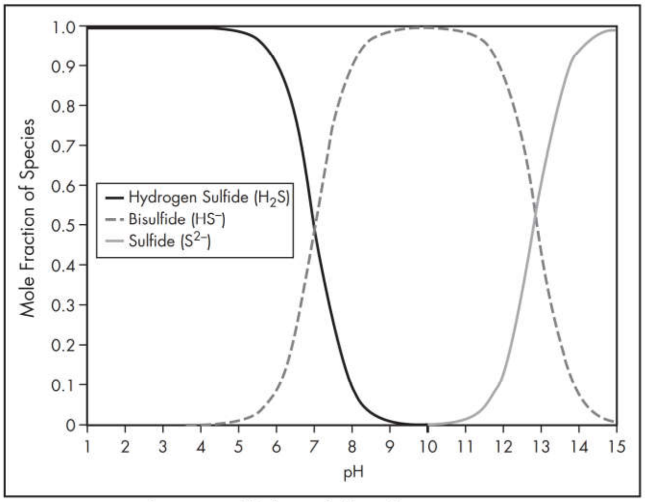


Figure 16 Hydrogen sulfide stability diagram

Table 4 Typical metallurgical-grade impurity limits

Impurity	No Penalties	Penalties	Rejected
Cu	<0.4%	0.4% < 3%	>3%
Moisture + oil	<6%	6% < 9%	>9%
Pb	<0.04%	0.04% < 0.1%	>0.1%
Cl	<500 ppm	500 < 2,000 ppm	>2,000 ppm
As	<200 ppm	200 < 1,000 ppm	>1,000 ppm

Courtesy of Aminpro

The use of covered cells is not ideal, as it obstructs visual inspection of the cells and hinders effective operation of the separation circuit. For this reason, it is desirable to maintain the pH above approximately 9.5 whenever possible, and in those cases with marginal separation kinetics, compensate with higher residence time.

Commercial Aspects

Saleable concentrate grades begin at around 44% Mo in the concentrate, although most by-product producers strive for higher grades to avoid penalties associated with copper and other contaminants. The penalties depend on whether the producer converts the molybdenite on-site or the concentrate is *tolled* through a third-party conversion facility. In the former case, the particular conversion facilities and costs dictate the required concentrate quality. In the latter, the tolling or sales contract will dictate the required concentrate quality.

Most conversion facilities use the pyrometallurgical route (i.e., roasting). Roasters generally charge toll fees ranging from US\$0.44/kg to US\$0.88/kg Mo for toll roasting, US\$0.22/kg to US\$0.44/kg for ferric chloride ($FeCl_3$) leaching, and US\$0.11/kg to US\$0.22/kg for packaging depending on market conditions. This amounts to tolling fees ranging from US\$0.77/kg to US\$1.54/kg, on top of which are added penalties for impurities.

Impurity limits depend on the roaster process and applicable environmental regulations; hence, they are usually roaster specific. Table 4 shows some typical values than can be used as a guideline for design purposes if a roaster contract is unavailable. Penalties generally range from US\$0.11/kg of Mo for relatively clean concentrates with minor amounts of a single impurity to as high as US\$1.10/kg for lower-grade concentrates that exceed all or almost all of the impurity level limits. Following is a brief discussion of some of the impurities.

Copper limits are generally a function of the copper removal process at the roaster or roasters treating the product. The most common options are chloride leach on the roaster feed or sulfuric acid leach of the roaster product, but many variants exist. Depending on the oxide consumer, tech oxide must contain less than 0.1%–0.5% Cu (0.09%–0.45% Cu in the roaster feed after accounting for mass reduction in the roaster); therefore, most commercial roasters treating predominantly by-product concentrate contain some kind of copper removal system. If the intended concentrate buyer does not, it may be necessary to include a copper leach facility (or extra regrind and/or cleaning stages) at the design stage of the moly plant.

Oil and water levels can be controlled with final concentrate dryers—approximately 50% of the typical diesel collector can be volatilized at 250°C and some 90% at 300°C (beyond which SO_2 emission can become a problem). The number one cause of excessive oil content, which refers strictly to hydrocarbon molybdenum collectors, is high moly collector dosage (leaking hydraulic fluid cables being a distant second). Diesel, by far the most common moly collector, would by virtue of its specific gravity float to the top of a flotation cell even if it was not naturally hydrophobic (and it is). Expect a large fraction of the total moly collector to report to the final concentrate.

Lead most often occurs as PbS (galena) and is difficult to depress under normal flotation condition. If Pb levels are excessive, consider HCl leach on the concentrate; the kinetics are fast, and the process is relatively benign from an environmental and safety standpoint.

Arsenic is often locked with copper sulfides, so reducing Cu levels will likely reduce the As levels.

Chlorine levels are only problematic when the concentrate will not be leached after it is sold (such as when the leach circuit is located on-site). It is usually only considered for design purposes when salty or briny water is used in the process.

Rhenium is generally found in solid solution with the MoS_2. Roasters recover anywhere from 50% to 90% but do not generally credit the producer for rhenium content, although this may change in the future as the new pressure oxidation methods (described in the following sections) offer significantly higher rhenium recoveries than traditional roasting. Relatively clean by-product concentrates with unusually high rhenium values (i.e., >800 ppm) may help reduce roaster premiums, but this is not generally seen at the design stage.

The authors have collected a database of primary and by-product concentrate grades; typical industrial impurity levels are shown in Table 5.

Table 5 Typical by-product concentrate quality

Impurity	No. of Mines	Database Statistics Minimum	Average	Maximum
H_2O, %	24	0.1	5.5	12
Oil, %	24	0.1	1.3	4.9
Mo, %	25	46.9	53.0	57.5
Cu, %	25	0.05	0.83	2.06
Pb, %	25	0.005	0.04	0.20
Fe, %	25	0.46	1.67	4.79
Cl, %	23	0.01	0.06	0.42
As, ppm	24	15	215	2,000
Se, ppm	24	100	250	700
Re, ppm	24	10	397	1,100

Courtesy of Aminpro

PLANT DESCRIPTIONS

There have been considerable changes in technology and industry safety culture since the development of the first molybdenum recovery circuit. Engineered safety systems, improved laboratory testing procedures, developments in flotation cell designs, and advancements in froth pumping, material handling, and dewatering systems have all led to significant improvements in plant performance and product quality.

Safety

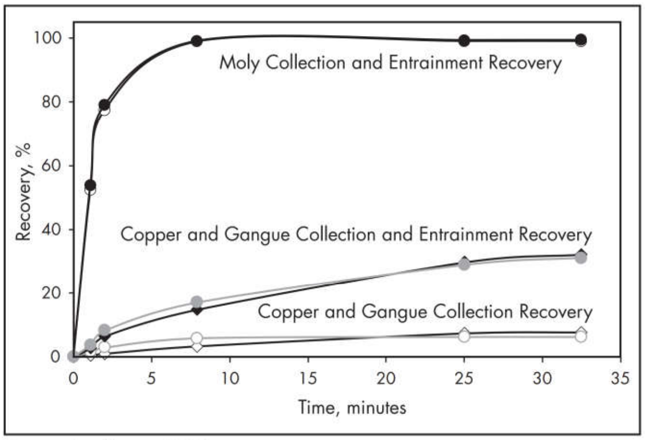
Safety should be the first and foremost consideration when designing and operating molybdenum plants. In general, molybdenum separation circuits are subject to the same safety risks and mitigation efforts as the rest of the plant (these are not discussed here). Of particular importance with molybdenum separation is the safety risk related to the use of sodium hydrosulfide as a copper depressant, which, as previously noted, has the potential to evolve H_2S gas in lethal quantities. Although safety risks can always be reduced to a negligible residual through application of engineering, equipment, and capital, it is always a good practice to eliminate the root cause rather than apply engineering and equipment fixes. This helps to eliminate risks that may arise as a result of unforeseen process modifications and upgrades. Although there are several promising alternatives to sodium hydrosulfide, these have not yet been proven in industrial applications and therefore, the overwhelming majority of molybdenum separation circuits rely on NaHS as the copper and iron sulfide depressant.

NaHS is usually purchased in the form of a liquid at 40%–45% strength and diluted to 20% strength in on-site solution storage tanks. In fewer cases, NaHS is purchased as a solid and dissolved on-site. The NaHS preparation station and/or offloading stations require special safety isolation equipment and protocols to ensure that concentrated H_2S fumes are safely contained.

If no acidifying agent is used in the molybdenum plant, NaHS solutions naturally trend to higher pH, as the NaOH present in the original NaHS, combined with the NaOH formed during the normal oxidation of solubilized NaHS, tends to increase pH. As a result, these moly plants are relatively safe and only require H_2S sensors in key locations.

If active pH control is used in combination with NaHS, then more safety considerations are required. These include online pH sensors (to ensure that line blockages and process upsets do not lead to lower pH conditions), a good pH meter maintenance and calibration procedure, H_2S gas sensors in key locations, specially designed spillage areas to ensure that spillage does not oxidize or acidify, and special interlock protection to automatically shut off the NaHS addition pumps when the pH is high or H_2S is detected.

In cases with active pH control and particularly difficult separation kinetics, it may be required to operate at quite low pH (i.e., in the 7.5-to-9.5 range). In these cases, in addition to those considerations noted earlier, the cells are likely to be hermetically sealed and operating at negative pressure with a scrubbing system. In addition to these engineered safety controls, it is advisable to install hazardous gas sensors and alarms and implement strict evacuation procedures to maintain a safe working environment and comply with regulatory agencies. Often these plants are required to be isolated from the main separation circuit, and access is strictly controlled.



Source: Amelunxen 2009

Figure 17 Collection and entrainment recovery from a batch flotation test

Laboratory Testing

Testing for moly flotation is notoriously difficult for a greenfield project, given the mass of sample required to produce enough bulk concentrate for moly rougher bench-scale flotation tests. As a result, many plants are designed in the absence of test work. This trend is not altogether absurd in that moly plant feed minerals may be divided into two categories: the floatables, consisting of molybdenite; and the non-floatables, made up of the rest of the minerals including copper. All that is needed from the test work is to verify the maximum recovery of molybdenite in the bulk (or Cu-Mo) concentrate and the rate constant in order to size the roughers properly. The remainder of the circuit may be designed using typical kinetics of other operating plants.

When sufficient sample is available for testing, care must be taken to discriminate between collection recovery and entrainment recovery in the batch test. Figure 17 shows the total recovery versus time (collection plus entrainment) for the same batch test shown in Figure 8. Because a batch test is operated with shallow froth and high pulling rates (i.e., high froth recovery), the entrainment recovery is very high, amounting to more than 80% of the total recovery of the non-floatables. Collection and entrainment need to be considered separately within the scale-up models to account for the previously mentioned long residence times and low pulling rates found in typical plant scale moly roughers.

Design Concepts

The process design of bulk sulfide circuits is usually driven by the economics of the primary copper sulfide minerals, although molybdenite considerations can play a role in the cleaning circuit, primarily if column cells are considered. As noted previously, these cells are susceptible to (what are thought to be) froth crowding effects caused by the higher pH and finer molybdenite grain size. As a result, in bulk circuits, column cells often function as inverse flotation stages for molybdenite, with higher molybdenite concentrations in the tails rather than the concentrate. The higher circulating loads are recovered with higher retention times in the cleaner-scavenging stage or stages, thereby recovering the molybdenite from the column tails and returning it to the column feed. The circuit eventually converges on an equilibrium circulating load that yields overall cleaner circuit recoveries slightly below those of copper sulfide minerals (95% for molybdenite vs. typically 97% for copper sulfides). The exception is when insufficient residence time is allowed for in the cleaner-scavengers, or if the column carry rate is already very high (because of undersized columns or high head grades). In these cases, minor process upsets are capable of causing high losses of molybdenum to the cleaner tails.

Unfortunately, there is no validated phenomenological model currently capable of modeling froth crowding and interface phenomena in industrial plants, and issues such as those just discussed are usually either ignored or dealt with through the use of ample safety margins or experience and heuristics.

Brownfields

Brownfield design programs are those in which a molybdenum separation circuit is added to an existing process plant. In this situation, it is usually the case that a large sample of bulk concentrate is available for detailed testing and, perhaps, piloting of the moly separation circuit. Suggested test matrices are shown in Tables 6 and 7 for roughers and cleaners, respectively.

Greenfields

Greenfield design applications—those in which there is no existing process infrastructure—present a significant problem in moly separation circuit design. Because of the typically low molybdenite concentrations in the ore, it is very difficult to procure sufficient sample of bulk concentrate on which to base the design of the molybdenite circuit. For example, each batch kinetics test for a molybdenite rougher separation requires at least 1,000 g of sample (assuming a 2-L cell). To procure this much sample, one would need between 50 and 100 kg of ore, depending on the head grades and mineralogy. This means that to obtain a basic test matrix of nine rougher tests (4 × P80, 3 × pH, 2 × % solids) one would need to convert approximately 1,000 kg of ore into bulk concentrate. This does not include the cleaner tests, of which a minimum of five are required for simulating cleaner circuit performance (3 × pH and 2 × % soils). It is suggested that the cleaner tests be performed with intermediate concentrate grading at least an order of magnitude (10×) higher than that of the bulk concentrate to ensure that any hydrophobic gangue minerals that may be present in trace quantities are sufficiently concentrated for detection. Assuming 10% mass recovery required to achieve a 10:1 upgrade ratio, a bare minimum of approximately 5 t of ore are required to perform a simple rougher and cleaner test matrix. Complex or difficult ores, such as those containing hydrophobic impurities such as talc, pyrophyllite, or carbon, will require much more sample.

It is primarily for this reason that molybdenite separation circuits are often designed with less-than-ideal information, and this is one reason they often require much longer ramp-up times post commissioning. It is not uncommon for molybdenite separation circuits to require up to two or more years, multiple configuration changes, and equipment upgrades to reach design capacity. In the opinion of the authors, modern flotation kinetics test methodologies and phenomenological models are sufficiently advanced and capable of mitigating most of the scale-up risks associated with by-product molybdenum flotation; project development teams are simply unable or unwilling to commit the core sample and funding required

Table 6 Typical test matrix for brownfield plant design—Molybdenum roughers

Test Number	Parameter Studied	% Mo Feed	% Solids	pH	P80	eH	Oily Collector	Dispersant
1	eH	Average/Composite	38	11	Nominal	Low	25	None
2	eH	Average/Composite	38	11	Nominal	Moderate	25	None
3	eH	Average/Composite	38	11	Nominal	High	25	None
4	Collector	Average/Composite	38	11	Nominal	Nominal	0	None
5	Collector	Average/Composite	38	11	Nominal	Nominal	25	None
6	Collector	Average/Composite	38	11	Nominal	Nominal	75	None
7	Collector	Average/Composite	38	11	Nominal	Nominal	150	None
8	pH	Average/Composite	38	8	Nominal	Nominal	Optimum	None
9	pH	Average/Composite	38	9.5	Nominal	Nominal	Optimum	None
10	pH	Average/Composite	38	11	Nominal	Nominal	Optimum	None
11	pH	Average/Composite	38	12.5	Nominal	Nominal	Optimum	Moderate
12	% Solids	Average/Composite	30	11	Nominal	Nominal	Optimum	None
13	% Solids	Average/Composite	38	11	Nominal	Nominal	Optimum	None
14	% Solids	Average/Composite	46	11	Nominal	Nominal	Optimum	None
15	P80	Average/Composite	38	11	2′ regrind	Nominal	Optimum	None
16	P80	Average/Composite	38	11	4′ regrind	Nominal	Optimum	None
17	P80	Average/Composite	38	11	8′ regrind	Nominal	Optimum	None
18	Dispersant	Average/Composite	38	11	Nominal	Nominal	Optimum	Moderate
19	Dispersant	Average/Composite	38	11	Nominal	Nominal	Optimum	High
20	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
21	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
22	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
23	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
24	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
25	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
26	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
27	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
28	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None
29	Variability—% Mo feed	Variable	38	11	Nominal	Nominal	Optimum	None

Courtesy of Aminpro

Table 7 Typical test matrix for brownfield plant design—Molybdenum cleaners

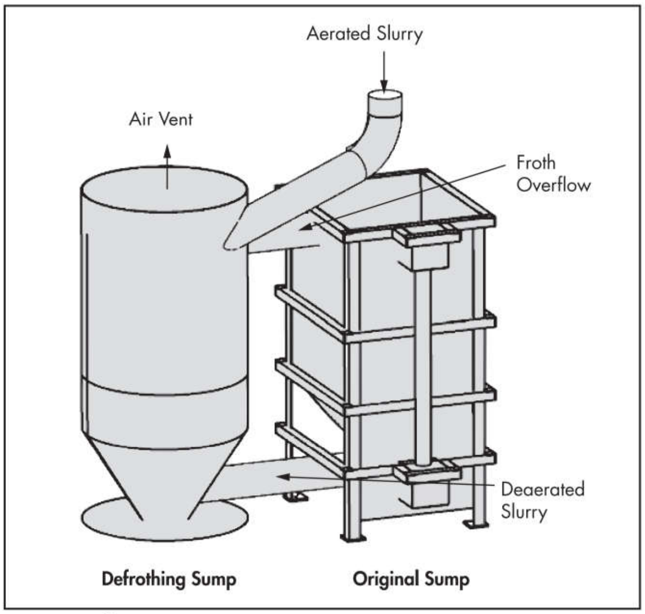
Test Number	Parameter Studied	% Mo Feed	% Solids	pH	P80	eH	Oily Collector	Dispersant
1	pH	Average/Composite	38	8	Nominal	Nominal	Optimum	None
2	pH	Average/Composite	38	9.5	Nominal	Nominal	Optimum	None
3	pH	Average/Composite	38	11	Nominal	Nominal	Optimum	None
4	pH	Average/Composite	38	12.5	Nominal	Nominal	Optimum	None
5	% Solids	Average/Composite	30	11	Nominal	Nominal	Optimum	None
6	% Solids	Average/Composite	38	11	Nominal	Nominal	Optimum	None
7	% Solids	Average/Composite	46	11	Nominal	Nominal	Optimum	None
8	P80	Average/Composite	38	11	2′ regrind	Nominal	Optimum	None
9	P80	Average/Composite	38	11	4′ regrind	Nominal	Optimum	None
10	P80	Average/Composite	38	11	8′ regrind	Nominal	Optimum	None
11	Dispersant	Average/Composite	38	11	Nominal	Nominal	Optimum	Moderate
12	Dispersant	Average/Composite	38	11	Nominal	Nominal	Optimum	High

Courtesy of Aminpro

for an adequate test program given the relatively minor portion of the overall revenue stream that molybdenite comprises. Indeed, many greenfield projects prefer to wait until after the primary sulfide concentrator is operational before collecting concentrate samples from the concentrator for subsequent moly separation testing and flow-sheet development.

Pumping and Froth Handling

Although overflowing pump boxes are usually the first indicator of a process upset, poor slurry pumping practice is usually a cause and seldom just a symptom. Moly plant froth can be very tenacious, particularly the concentrate streams, and



Source: Amelunxen 2009

Figure 18 Retrofitted defrothing sump

care must be taken to consider the implications of the bubbles when selecting the pump and sump configuration. Slurry froth factors can be as low as 1.1 at the pump intake line and as high as 4.5 at the top of the sump. (Slurry froth factor is the ratio of total slurry volume, including air, to slurry volume excluding air.) Any air entering the pump will cause air locking and lead to cavitation and failure of the pump to deliver the required flow. It generally leads the operator to design higher sump heights and add water sprays in an effort to break the froth down. One solution observed at several plants has been to install cyclonic defrothing sumps, such as the retrofit shown in Figure 18, that allow (or promote) the escape of air bubbles before the slurry reaches the pump sump.

Ferric Chloride Leach

In a ferric chloride leach circuit, the lead and copper react with the ferric chloride to form aqueous species. The aqueous species are then removed via filtration, and the ferric chloride is regenerated in a chlorinator by conversion of the ferrous to ferric chlorides using chlorine gas. The reaction equations are

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S^0$$

$$PbS + 2FeCl_3 \rightarrow PbCl_2 + 2FeCl_2 + S^0$$

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$

Ferric chloride leaching for purifying molybdenite concentrates has been practiced at Urad (Colorado), Henderson, Tonopah (Nevada), Sierrita, Brenda (British Columbia), Andina, Lornex (British Columbia), and other operations on and off for many years.

The impurity in Urad molybdenite concentrates is primarily PbS. The oxidizing ferric chloride leach is required mainly for leaching copper minerals. For leaching PbS from Urad's molybdenite concentrates, the more economic nonoxidative HCl solution is quite adequate. Thus, Urad abandoned ferric chloride leach in favor of HCl leach in the early 1970s. Later, the HCl leach for lead removal was also implemented at Climax's Henderson mine in Colorado. The HCl leach generates hydrogen sulfide.

$$PbS + 2HCl \rightarrow PbCl_2 + H_2S$$

In general, a caustic scrubbing unit is used for removal of the hydrogen sulfide.

The Tonopah plant in Nevada was built and operated by Anaconda Minerals Company in the early 1980s. The ferric chloride leach plant could process 50 t/d of molybdenite concentrates. For purifying its concentrate containing 1.5% Cu as chalcopyrite it used the following leaching conditions: 70°–80°C, 20% pulp density in five agitated tanks for a retention time of 24 hours. The lixiviant typically contains 9% $FeCl_3$ and some cupric chloride ($CuCl_2$). The addition of $CuCl_2$ accelerates the leach kinetics. The basic chemical reactions of chalcopyrite with cupric chloride and regeneration of cuprous to cupric chloride with ferric chloride can be described by the following equations:

$$CuFeS_2 + 3CuCl_2 \rightarrow 4CuCl + FeCl_2 + 2S^0$$

$$CuCl + FeCl_3 \rightarrow CuCl_2 + FeCl_2$$

The lower-temperature operation is to minimize the side reaction of sulfur to sulfate as shown:

$$6FeCl_3 + S^0 + 4H_2O \rightarrow 6FeCl_2 + 6HCl + H_2SO_4$$

At the Sierrita plant in Arizona, continuous atmospheric leaching conditions of molybdenite concentrates through the management of Duval, Cyprus Minerals, Cyprus Amax Minerals, and Phelps Dodge were similar. The plant can process about 100 t/d of concentrates. A 13% $FeCl_3$ solution is used to leach its concentrates containing about 2.5% Cu and 0.3% Pb at 88°C and 30% pulp density in five agitated tanks. After being acquired by Freeport-McMoRan, feed preparation and recycle of $FeCl_3$ leach solution has been optimized, and retention time has been reduced from 20–30 hours to ~10 hours. The improvement of the leaching rate can be attributed to the presence of cupric chloride in the recycled leach liquor. The purified concentrates contain about 0.08% Cu and 0.02% Pb.

Ancillary Operations

Suitably designed upstream and downstream support equipment and processes, proper reagent selection, and automated process controls are important considerations when developing a robust plant design.

Reagent Preparation

NaHS preparation is generally only required if handling NaHS in solid form. In this case, the technician requires protective clothing and an adequate ventilation mask. The NaHS usually arrives in super sacks, which are loaded and dumped in a dissolution tank that feeds a process storage tank.

Nitrogen and CO_2 are received as a liquid. The liquid is vaporized and injected as a gas at the required injection points. Mass flow meters and automatic valves are used to control the flow to each point.

Frothers and defoamers are often used in molybdenum separation circuits. Similar reagent handling protocols are used as in the bulk circuits. The defoamers, when necessary, are usually added to the stage feed (if froth control is

Table 8 Thickeners in separation circuits

Thickener	Unit Area, $m^2/t/d$	Specific Capacity, $t/m^2/d$
Cu/Mo	0.05–0.3	0.14–0.83
Intermediate Mo	0.05–0.15	0.28–0.83
Mo concentrate	0.2–0.5	0.08–0.21
Cu concentrate	0.05–0.3	0.14–0.83

Courtesy of Aminpro

required in the flotation cells) or the launders (if froth control is required to improve hydraulic transport).

Oily collectors are only rarely added in the molybdenite separation circuit, mainly because they are already present in sufficient concentrations because of upstream additions.

Flocculants are often used for dewatering in in-circuit thickeners and/or molybdenum concentrate filters. Similar preparation and injection practices are used as for any concentrate dewatering application. Low-molecular-weight flocculants and/or floccules are usually completely dispersed by a single centrifugal pump, and any surviving floccules are dispersed in the first cell of an agitated mechanical flotation cell. The authors are not aware of any convincing evidence that low-molecular-weight flocculants, in moderate dosages, negatively impact molybdenite flotation.

Dewatering

Molybdenite concentrates and intermediate concentrates are composed of particles that are significantly finer than those in normal copper concentrates, and, as such, higher unit areas are required for sizing thickeners. Flocculants and coagulants are almost always required because of the commonly occurring problem of molybdenum-bearing slimes in the thickener supernatant. Although thickeners should be designed based on settling tests, the ranges shown in Table 8 are typical of the various thickeners employed in moly separation circuits.

Modern molybdenum plants generally favor plate-and-frame pressure filters, although many older plants continue to operate vacuum drum filters. The filtration rate depends on many factors and should be evaluated based on test work.

Instrumentation and Process Control

Instrumentation costs for molybdenum separation circuits are usually between 3% and 5% of the total capital cost of the circuit. The instrumentation requirements are significantly higher for covered cells than for open cells, as they must be operated remotely without visual feedback to the operator. Modern molybdenum roughing stages are usually equipped with similar process control and instrumentation provisions as their counterparts in the bulk sulfide flotation circuit, including froth cameras, automatic level control, online pH meters, and air/nitrogen/CO_2 mass flow meters. Primary slurry streams, such as the rougher tailings, first cleaner tails, first cleaner-scavenger tails, and final concentrates are equipped with flow meters, density gauges, and online X-ray fluorescence analyzers.

MOLYBDENUM CONVERSION

Other than a small quantity that is upgraded for use in lubricant formulations, molybdenum disulfide is converted to technical-grade molybdenum trioxide, which is the starting material for a variety of products for the metallurgical and chemical industries. Typical concentrations in the analysis range of molybdenum disulfide are shown in Table 9. Analytical variations as shown in the table can be possible, depending on the nature and origin of the ore and the beneficiation procedure employed. If the molybdenum disulfide does not meet the specifications for the roasting process, it will have to be leached (as described in earlier sections) to remove impurities. The performance of the roaster component and the nature of the charge as it moves through the roasters are dependent on the impurity levels in addition to other operating parameters.

Table 9 Molybdenum disulfide sample analyses

MoS_2 Analysis	Weight %
Molybdenum	45–59
Sulfur	34.4–37.6
Insolubles	1.6–15.0
Lead	0.002–0.05
Phosphorus	0.002–0.04
Iron	0.3–1.0
Copper	0.006–2.0
Oil	0.5–8.3
Water	0.5–8.4

Courtesy of Freeport-McMoRan

Roasting

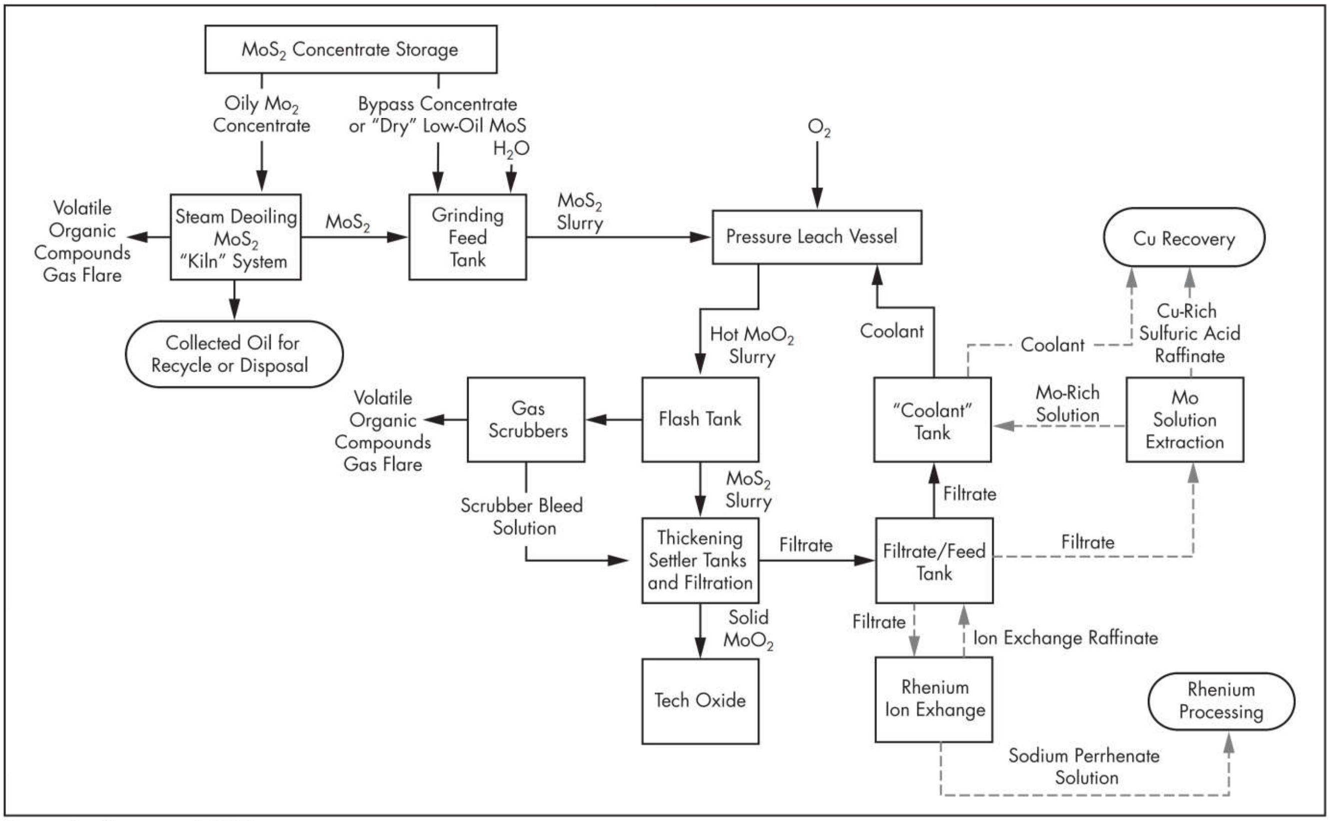
The pyrometallurgy conversion practice involves roasting the concentrate in a multiple-hearth roaster. Concentrate is moved from storage by a belt conveyer or other means to the roaster feeder and from there to the top hearth level of the roaster. Rabble arms extending from the central rotary shaft provide plowing action. Drop holes are located at the center or periphery so that the burden is gradually moved toward and through the drop holes on the succeeding lower hearth levels.

As the concentrate is fed at the top hearth level, the flotation oil burns and the concentrate ignites. The reaction, once started, is exothermic. Operating temperatures range between 538° and 816°C. By regulating the air flow to the individual hearths and the overall air inlet and gas outlet flows, these temperatures are maintained throughout the roaster. Most of the oxidation occurs on the upper hearths. Additional heat to complete the reaction is provided by fuel burners at the lower hearth levels. The overall chemical reaction is

$$MoS_2 + \frac{7}{2}O_2 \rightarrow MoO_3 + 2SO_2$$

Off-gas exiting the roaster is cooled either indirectly or by water sprayed directly into the flue gas. Efficient dust collectors, employing cyclones and electrostatic precipitators installed in the flue gas handling system, are utilized for improved product recovery. The off-gas exiting the electrostatic precipitators is treated with a lime slurry or processed in a sulfuric acid plant for sulfur dioxide recovery. For a lengthy and detailed discussion on pyrometallurgy of molybdenum, refer to chapter 4 in Gupta (1992).

Roasting temperatures higher than 815°C can lead to serious operating issues related to sublimation of molybdite (MoO_3) and because of partial melting and softening of the charge. Problems manifest themselves as excessive wear and corrosion of rabble teeth and plugging of drop holes in the upper hearths. Dust losses in the lower hearths can be



Source: Amelunxen et al. 2008

Figure 19 Molybdenum pressure leach vessel process

experienced because of volatilization as a result of temperatures of about 650°C.

Acid Pressure Oxidation

The roasting process has certain limitations based on the quality of the feed. For example, elevated copper levels can cause material handling issues within the roaster. These issues limit the type of feedstock a roaster can process, or require additional processing steps, such as leaching, prior to roasting. Another method for converting molybdenum disulfide to molybdenum trioxide is through a hydrometallurgical process of oxidation. This process involves the pressure oxidation of an aqueous slurry of molybdenum disulfide to form soluble and insoluble molybdenum species. Within the pressure leach vessel, the molybdenum disulfide is converted to molybdenum trioxide and sulfuric acid by the combination of heat, pressure, and oxygen:

$$2MoS_2 + 9O_2 + 4H_2O \rightarrow 2MoO_3 + 4H_2SO_4$$

The concept of using a pressure leach vessel to convert molybdenum disulfide to molybdenum trioxide has numerous patent holders. The method that is described here was developed, patented, and put into production by Freeport-McMoRan in 2009 and currently produces about 10,000 t of molybdenum trioxide each year. A pressure leach vessel includes a control system to regulate the process conditions including temperature, pressure, and feed rates of molybdenum disulfide concentrate, water, acidic coolant solution, and oxygen, as well as pressure leach vessel discharge and all necessary solution recycle and emission systems. Although some of the molybdenum trioxide enters the aqueous phase within the pressure leach vessel, the molybdenum trioxide compound has a low solubility limit. As such, only a fraction of the molybdenum is leached into the process slurry within the pressure leach vessel; the majority remains as a solid precipitate in the process slurry. Thus, the molybdenum disulfide is converted into partially soluble molybdenum trioxide within the slurry while other metallic elements (e.g., rhenium, copper, iron) that exist in the feedstock slurry are fully leached into solution because of the synthesis of sulfuric acid by the exothermic reaction within the pressure leach vessel. As such, within the pressure leach vessel, water and oxygen combine with the sulfides in the concentrate to generate an aqueous solution consisting largely of (1) sulfuric acid, (2) partially soluble molybdenum trioxide (most of which is a solid precipitate and some of which is in solution), (3) soluble rhenium, (4) soluble iron, and (5) soluble copper. As described next, the pressure leach vessel process incorporates subsystems that allow for the optional capture of these other soluble beneficial metals. When collected by filtration and washed free of the process solution, the solid product is (on a dry basis) generally 98% pure molybdenum trioxide with the remaining impurities composed of insoluble silicate minerals and unreacted molybdenum disulfide. An example of a molybdenum pressure leach vessel process is depicted in Figure 19.

Residual flotation reagents manifest themselves as an oily residue in some molybdenum mining concentrates. These reagent residues can interfere with the efficiency of the process that occurs in the pressure leach vessel. Therefore, concentrates with significant residual reagents are first fed into a de-oiling furnace wherein the agents contained in the flotation/reagent mix are volatilized. The molybdenum disulfide concentrate exiting the de-oiling unit is fed with other low-oil concentrate to a grinding process that ultimately feeds the pressure leach vessel.

As the feed stream is prepared and introduced to the pressure leach vessel, molybdenum disulfide is mixed with process water to create a process slurry. The mixing rates of slurry and oxygen within the pressure leach vessel maintain an oxygen overpressure within the vessel. The overall conditions inside the pressure leach vessel are maintained at a pressure between 3,102 and 3,447 kPa and a temperature of approximately 225°C. Heat in the pressure leach vessel results from exothermic reaction. Addition of water as part of the feed slurry and coolant helps to maintain the optimum operating temperature. The pressure leach vessel's temperature is below the melting or fusion point of the molybdenum concentrates. The chemical oxidation that occurs in the pressure leach vessel effectively converts the molybdenum disulfide contained in the feed stream into molybdenum trioxide, which is generally the same chemical reaction that occurs within a conventional roaster.

Slurry exiting the pressure leach vessel reports to a flash tank where the temperature and pressure of the hot process slurry are reduced to allow the mixture to continue forward into the thickening and filtration stage. At this point, the slurry contains precipitated molybdenum trioxide solids, minor insoluble mineral gangue, and an aqueous solution. This thickened slurry reports to a series of filters that remove solid molybdenum trioxide from the remaining aqueous solution and wash residual solution from it using water, a vacuum belt filter, and a pressure tube filter.

Solute from the pressure leach vessel is collected in a common tank to use for maintaining the process flow and/or additional beneficial metal recovery. Several options exist that may be used simultaneously or in combination. The filtrate can return to the pressure leach vessel as coolant through a coolant tank that also recycles the filtrate's metal and sulfuric acid content back through the process. Filtrate can be sent to a solution extraction (SX) circuit, which recovers soluble molybdenum and rhenium.

In the SX circuit, several extraction and stripping stages occur wherein the aqueous filtrate solution initially is mixed with an organic reagent to extract molybdenum and rhenium from the aqueous phase. Ultimately, after separation and return to an aqueous phase, the molybdenum- and rhenium-bearing solutions from SX are recycled back to the pressure leach vessel through the coolant system. The recycling of this first solution recovers molybdenum and rhenium that are soluble even after processing through the earlier thickener and filter systems. The raffinate solution from the SX contains sulfuric acid and additional metal values such as copper. These values may be recovered by electrowinning, cementation, or by utilizing the acid on a heap leach circuit.

To separate rhenium from the molybdenum an ion exchange (IX) circuit is employed using IX resins that bind selectively with soluble rhenium in the filtrate solution. When the resin is loaded with rhenium, the filtrate flow is stopped, and rhenium is stripped off the resin back into solution as sodium perrhenate. After the rhenium is removed, flow is started again, and the cycle repeats. The IX plant recovers the rhenium from the clear pressure leach vessel solutions, whereas the soluble molybdenum ultimately is returned to the pressure leach vessel for recycle. The rhenium recovery rate from the IX system varies based on the rhenium content present in the molybdenum concentrates that are fed into the pressure leach process. Therefore, the IX plant may operate only when a sufficient concentration of rhenium warrants.

Table 10 Technical-grade molybdenum trioxide sample analyses

MoO_3 Analysis	Weight %
Molybdenum	56–65
Sulfur	<0.1
Insolubles	2.00–11.00
Iron	0.30–1.00
Phosphorus	<0.05

Courtesy of Freeport-McMoRan

Molybdenum Products

Depending on the impurities that are present after conversion, molybdenum trioxide can either be marketed, or it can undergo further processing to meet specific customer or quality requirements.

Technical-Grade Molybdenum Trioxide

Roasted concentrate is discharged from the furnace and either marketed as technical-grade molybdenum trioxide or subjected to additional conversion operations to remove impurities. A typical analysis range of commercially available technical-grade molybdenum trioxide is shown in Table 10.

Technical-grade molybdenum trioxide is marketed either in bulk, drums, bags, or cans containing a predetermined amount of molybdenum. This is convenient to users in the steel industry. When added to molten steel, molybdenum trioxide is reduced to the metallic form and alloyed. The gangue minerals are removed with the slag.

Technical-Grade Molybdenum Trioxide Briquettes

Technical-grade molybdenum trioxide can be formed into briquettes, which facilitates additions of molybdenum in electric and foundry steelmaking processes. In the briquette form, losses experienced in blow-off when molybdenum trioxide is added to the furnace charge are minimized. Storage and handling are also simplified. To prepare the briquettes, technical-grade molybdenum trioxide is mixed with a carbon- or ammonia-based binder and formed into briquettes in a hydraulic press.

Molybdenum Processing for Ammonium Molybdates

Depending on the purity, the molybdenum trioxide feedstock may be leached with hot water and filtered to remove water-soluble impurities. The molybdenum trioxide is further leached in an aqueous-ammonia solution to put the molybdenum into solution as a monomolybdate:

$$MoO_3 + H_2O + 2NH_3 \rightarrow (NH_4)_2MoO_4$$

The ammoniated slurry is filtered to recover the ammoniated molybdate solution. The remaining insoluble material is reprocessed for molybdenum recovery. Solution impurities can be removed by selective precipitation, IX, SX, and/or an impurity bleed from the circuit. The molybdate solution is then evaporated in a continuous crystallizer to form ammonium dimolybdate crystals in equilibrium with ammoniated molybdate solution:

$$2(NH_4)_2MoO_4 \rightarrow (NH_4)_2Mo_2O_7 + H_2O\uparrow + 2NH_3\uparrow$$

The ammonium dimolybdate crystals are allowed to grow within a continuous crystallizer and are recovered by centrifuging. Depending on solution impurities, the liquid centrifuged out of the crystals may be put back into the crystallizer or removed from the crystallization circuit. The ammonium dimolybdate crystals from the centrifuge can either be dried and sold as final product or used as a feedstock for the manufacture of additional products. Ammonium dimolybdate can be completely thermally decomposed to form a calcined molybdenum trioxide or partially thermally decomposed to form ammonium octamolybdate:

$$(NH_4)2Mo_2O_7 \rightarrow 2MoO_3 + 2NH_3\uparrow + H_2O\uparrow$$

$$4(NH_4)2Mo_2O_7 \rightarrow (NH_4)_4Mo_8O_{26} + 4NH_3\uparrow + 2H_2O\uparrow$$

Additionally, calcined molybdenum trioxide that has been dissolved in aqua-ammonia at a 0.86 NH_4:Mo molar ratio can be crystallized to form ammonium heptamolybdate:

$$MoO_3 + NH_4OH + H_2O \rightarrow (NH_4)_6Mo_7O_{24}\cdot 4H_2O$$

Sodium molybdate crystalline is prepared by dissolving molybdenum trioxide in sodium hydroxide followed by filtration to remove gangue elements. After filtration, sodium molybdate is crystallized out of the filtrate:

$$2NaOH + MoO_3 + H_2O \rightarrow Na_2MoO_4\cdot 2H_2O$$

Pure Molybdenum Trioxide Sublimed Process

Sublimed molybdenum trioxide is a pure form of roasted molybdenum disulfide concentrate prepared by purification by sublimation:

$$MoO_3(s) \rightarrow MoO_3(g) \rightarrow MoO_3(s)$$

Sublimation is a thermal process in which molybdenum trioxide undergoes a phase transition directly from a solid to gaseous form, or vapor, without passing through a liquid phase. The pure form of molybdenum trioxide is achieved not by the rejection of impurities as much as by the concentrating of molybdenum trioxide.

ACKNOWLEDGMENT

The authors acknowledge the contributions to this chapter by John Hollow and Ross Edwards.

REFERENCES

Amelunxen, P.A. 2009. Moly plant design considerations. SME Preprint No. 09-136. Littleton, CO: SME.

Ansari, A. 2006. The effect of lignosulfonates on the floatability of molybdenite and chalcopyrite M.Sc. thesis, University of British Columbia, Vancouver, BC.

Berger, B.R., Ayyuso, R.A., Wynn, J.C., and Seals, R.R. 2008. *Preliminary Model of Porphyry Copper Deposits*. Open-File Report 1321. Reston, VA: U.S. Geological Survey.

Blossom, J. 1994–2000. Molybdenum. In *Minerals Yearbook*. Reston, VA: U.S. Geological Survey.

Blossom, J. 2001–2017. Molybdenum. In *Mineral Commodity Summaries*. Reston, VA: U.S. Geological Survey.

Born, C.A., Bender, F.N., and Kiehn, O.A. 1976. Molybdenite flotation reagent development at Climax, Colorado. In *Flotation: A.M. Gaudin Memorial Volume II*. Edited by D.W. Fuerstenau. New York: AIME. pp. 1147–1184.

Bullock, L.A., and Parnell, J. 2017. Selenium and molybdenum enrichment in uranium roll-front deposits of Wyoming and Colorado, USA. *J. Geochem. Explor.* 180(September):101–112.

Chander, S., and Fuerstenau, M. 1972. On the natural floatability of molybdenite. *Trans. AIME* 252:62–69.

Chevron Phillips. 2000–2018. Orfom D8 Depressant. www.cpchem.com/bl/specchem/en-us/Pages/OrfomD8Depressant.aspx. Accessed May 2018.

Climax Molybdenum Company. 1924–2017. Summary of Annual and Life-of-Mine Production from Climax Mine, Phoenix, AZ. Unpublished report.

CRU International. n.d. Ryan's Notes Weekly Commodity Pricing. London, UK. CRU International. www.crugroup.com.

Cuthebertson, R.E. 1946. Unusual reagent combination improves flotation at Climax. *Trans. AIME* 169:505–524.

Cytec. 2013. Aero 7260 HFP depressant: Novel, safe and sustainable alternative to traditional hazardous modifiers—NaSH, Nokes, Na_2S, and cyanide. In *Cytec Solutions for Solvent Extraction, Mineral Processing, and Alumina Processing*. Vol. 17. Woodland Park, NJ: Cytec Industries. www.cytec.com/sites/default/files/files/Cytec%20Solutions%20V17%202013.pdf.

Ferguson, J., ed. 1984. *Proterozoic Unconformity and Stratabound Uranium Deposits*. Report of the Working Group on Uranium Geology Organized by the International Atomic Energy Agency. IAEA-TecDoc-315. Vienna, Austria: International Atomic Energy Agency.

Green, D.W., and Maloney, J.O., eds. 1999. *Perry's Chemical Engineers' Handbook*, 7th ed. New York: McGraw-Hill. pp. 2–122.

Gupta, C.K. 1992. *Extractive Metallurgy of Molybdenum*. Boca Raton, FL: CRC Press.

Hess, F. 1924. *Molybdenum Deposits, A Short Review*. Bulletin 761. Washington, DC: U.S. Geological Survey.

Kelly, T.D., Magyar, M.J., and Polyak, D.E. 2017. Molybdenum. In *Historical Statistics for Mineral and Material Commodities in the United States*. Data series 140. Reston, VA: U.S. Geological Survey.

Kirkemo, H., Anderson, C.A., and Creasey, S.C. 1965. *Investigations of Molybdenum Deposits in the Conterminous United States 1942–1960*. Bulletin 1182-E. Washington, DC: U.S. Geological Survey.

Lane, J.W., Bender, F.N., and Ronzio, R.A. 1972. Recovery of molybdenum from oxidized ore at Climax, Colorado. *Trans. AIME* 255:77–82.

Linde Group. 2012. *When Being Green Matters: Solvocarb Neutralizes Alkaline Waters Quickly and Easily with* CO_2. Murray Hill, NJ: Linde North America. www.lindewatertreatment.com.

Ludington, S., and Plumlee, G.S. 2009. *Climax-Type Porphyry Molybdenum Deposits*. Open-File Report 1215. Reston, VA: U.S. Geological Survey.

Ludington, S., Hammarstrom, J., and Piatak, N. 2009. *Low-Fluorine Stockwork Molybdenite Deposits*. Open-File Report 1211. Reston, VA: U.S. Geological Survey.

Morales, J. 1980. Use of nitrogen in the separation of copper and molybdenum. M.S. thesis, University of Chile, Santiago.

Rhagavan, S., and Hsu, L. 1984. Factors affecting the flotation recovery of molybdenite from porphyry copper ores. *Int. J. Miner. Process*. 12(1-3):145–162.

S&P Global Platts. n.d. Metals (Steel, Copper, Aluminum) Prices, News, and Analysis. London, UK. www.platts.com.

Sebenik, R. 2005. Molybdenum and molybdenum compounds. In *Ulmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH.

Smedley, P.S., and Kinniburgh, D.G. 2017. Molybdenum in natural waters: A review of occurrence, distributions and controls. *Appl. Geochem*. 84:387–432.

Stein, H.J., Markey, R.J., Morgan, J.W., Du, A., and Sun, Y. 1997. Highly precise and accurate Re-Os ages for molybdenum from the East Quinling molybdenum belt, Shaanxi Province, China. *Econ. Geol*. 92(7):827–835.

Taylor, R.D., Hammarstrom, J.M., Piatak, N.M., and Seal, R.R. II. 2012. Arc-related porphyry molybdenum deposit model. In *Mineral Deposit Models for Resource Assessment*. Scientific Investigations Report 5070-D. Reston, VA: U.S. Geological Survey.

Tessenderlo Kerley. 2016. Safety data sheet: TKI-330. Revised June 10. Phoenix, AZ: Tessenderlo Kerley.

Tessenderlo Kerley. 2018. TKI-330 for Depression of Iron and Copper Sulfide [marketing brochure]. Phoenix, AZ: Tessenderlo Kerly.

Triffett, B., Veloo, C., Adair, B.J.I., and Bradshaw, D. 2008. An investigation of the factors affecting the recovery of molybdenite in the Kennecott Utah Copper bulk flotation circuit. *Miner. Eng*. 21(12-14):832–840.

Van der Merwe, P.J. 1986. *Uranium Prospecting in the Main Karoo Basin in Retrospect* (3 vols.). Pretoria: Atomic Energy Corporation of South Africa.

Wacaster, S. 2017. The mineral industry of Chile. In *2014 Minerals Yearbook: Chile [Advance Release]*. Reston, VA: U.S. Geological Survey. pp. 7.1–7.19.

Wu, Y-S., Chen, Y-J., and Zhou, K-F. 2017. Mo deposits in northwest China: Geology, geochemistry, geochronology, and tectonic setting. *Ore Geol. Rev.* 81(pt 2):641–671.

Zeng, Q.D., Liu, J.M., Qin, K.Z., Fan, H.R., Chu, S.X., Wang, Y.B., and Zhou, L. 2013. Types, characteristics, and time-space distribution of molybdenum deposits in China. *Int. Geol. Rev*. 55(11):1311–1358.

Zhang, H., Li, C-Y., Yang, X-Y., Sun, Y-L., Deng, J-H., Liang, H-Y., Wang, R-L., Wang, B-H., Wang, Y-X., and Sun, W-D. 2014. Shapinggou: The largest Climax-type porphyry Mo deposit in China. *Int. Geol. Rev.* 56(3):313–331.