Review of Molybdenum Recovery Processes

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SUMMARY
Our purpose in this paper is to review present molybdenum recovery processes from a historical viewpoint and to point out areas where research should be concentrated. As in many mineral deposits, ore grades of molybdenite are trending toward lower values and substantially different grade-recovery economics are likely to occur. We suggest that closer examination of the relationship between mineral beneficiation by physical means (gravity and flotation) and chemical means (roasting and leaching) might result in greater overall recovery of valuable materials at competitive economics. We hope to stimulate thinking along these lines.

INTRODUCTION
Molybdenite (MoS₂) is the most significant commercial source of molybdenum although small quantities of lead molybdate (PbMoO₄) are also mined. Molybdenite is found in host rock consisting mostly of quartz and feldspars or combined with other commercially mined minerals, the most common being chalcopyrite (copper ore).

The element molybdenum, Mo, is silver-gray; it is the forty-second element in the periodic table and has an atomic weight of 95.95. Elemental molybdenum was identified by the Swedish chemist Carl Wilhelm Scheele in 1778 and first used successfully in 1894, by the French, to toughen armor plate. In 1916, molybdenum production, stimulated by the war, reached 271,800 kg (600,000 lb). At that time, molybdenum provided an alternative to alloying with tungsten, chromium, nickel, and vanadium. By 1921 production had fallen to 9,500 kg (21,000 lb). In 1924, however, continuous production from the Climax Mine in Colorado began to provide assurance of a steady supply of molybdenum to stimulate research and applications in the steel and chemical industries. Today, the majority of world production comes from primary and by-product operations in North and South America, with about two-thirds produced in the United States. Steel and molybdenum metal consume about 90% of production and the balance goes to production of chemicals and lubricants.

Before the turn of the century, a bulk-oil flotation process was patented by Haynes.³ ¹ It was discovered that finely disseminated sulfide ore minerals with volumes of accompanying slimes could be selectively upgraded more successfully by a flotation process than by gravity separation methods.³ ⁴ The perfecting of flotation processes opened avenues for development of low-grade ore bodies containing valuable single- or multiple-ore minerals. As discussed later, molybdenite, being a sulfide mineral, floated readily although somewhat differently than other sulfide minerals. In fact, molybdenite flotation was so spontaneous that it was termed a natural floater, along with some other minerals such as talc, graphite, sulfur, coal, and the copper mineral, covellite (CuS), that exhibited natural floating properties. Talc and covellite are commonly associated with the ores we are discussing, and present particular problems in by-product copper-molybdenum separation.

An explanation of the natural floating characteristics of molybdenite has been established, since the basic sulfide flotation discovery, by studying the structure of broken (crushed and ground) molybdenite crystals. The broken crystals will form in two ways: either a covalent bond of sulfur and molybdenum, or weak Van der Waal's bonds of sulfur-sulfur. Fortunately, most crystal rupturing develops broken fragments forming along the Van der Waal bonds which readily float because this type of bond structure renders particles hydrophobic. Furthermore, molybdenite in aqueous media undergoes oxidation, forming soluble anions and exhibiting different floating characteristics than other nonferrous sulfides such as copper, lead, and zinc that produce cations and, upon hydrolysis, insoluble oxides and hydroxides. The difference in floating characteristics of molybdenite and other sulfide minerals is a benefit to upgrading concentrates of common ore bodies containing mixtures of basic nonferrous minerals. It is interesting to note that the weak Van der Waal's bonds of sulfur-sulfur easily cleave, giving molybdenum its special properties as a dry lubricant.

The penchant for natural flotability can be increased by adding a sulfhydrate collector, e.g., hydrocarbons and natural frotters such as pine oil or cresylic acid. The proper hydrocarbon selection can improve the selectivity of flotation for the specific mineral, as can other factors such as controlling the pH and pulp density. Application of the chemical reagents used to speed up flotability influences flotation plant design in that optimum flotation retention time must be provided. Also, particulate size must be considered when developing the flotation scheme. There is a pattern of flotation behavior quite dependent on particle size. A recovery plateau develops covering a range of particle sizes over which efficiency is maximum, and particle sizes larger or smaller than this range decrease efficiency.⁶ ⁷ A pattern or range can be established for all sulfide mineral flotation once the ore feed grade, metal value, and general plant operating conditions are known. There is also a maximum size above which most particles cannot be floated. Many factors then must be considered before an optimum flotation flowsheet is arrived at; even the specific gravity of the valuable mineral can change the shape of the recovery/size relationship.

Recovery becomes more complicated with multiple ore mineralization because secondary mineralization is usually not consistent with mineralization of the primary ore since it is usually deposited at a different geological time. Distribution of by-product molybdenum does not necessarily relate to areas of high copper concentration in the ore body. At this point, the similarity of molybdenum production from primary ore bodies begins to diverge from that of ore bodies containing other primary sulfides, such as copper, because grinding, particle size, reagent use, etc., are dictated by the necessity of recovering the primary mineral economically.
PRIMARY MOLYBDENUM RECOVERY

Today only about 40% of the world's molybdenum production originates from ore bodies where molybdenum is the primary material. The best known of these are the Climax, Henderson, and Questa mines in the United States, and the Endako Mine in Canada. Molybdenum concentration in these ore bodies ranges from <0.1% to about 0.25% in commercial deposits. Figure 1 illustrates a basic recovery flowsheet from a primary ore body. Climax now mines molybdenite ore averaging about 0.15% Mo; the Henderson ore averages 0.25% Mo.

The methods of comminution to an economical recovery size are quite different at the two mines. Climax uses primary, secondary, and tertiary crushing, with screening and rougher ball mills in closed circuit with spiral of hydrocyclone classification to produce a rougher feed to flotation. Henderson uses primary crushing and semiautogenous grinding in closed circuit with hydrocyclones to develop a rougher flotation feed. The objectives are the same, however—to break down the ore size to effect liberation for flotation. Before flotation the ore is milled to a size of -200 mesh and 40% 100 mesh and 40% +100 mesh. Coarse grinds are acceptable for primary molybdenum recovery to achieve economical liberation for flotation. An initial concentrate of 3-4% Mo is produced in rougher flotation. The concentrate is then upgraded by further steps of grinding and flotation in a cleaner process. This concept of upgrading progressively smaller volumes of concentrate was first adopted at Climax and has proven to be the most cost-effective means of handling large tonnages of low-grade molybdenum ores. Sufficient regrind steps follow to obtain the required liberation to achieve final concentrate grade. Five cleaner flotation steps are used at Climax and four at Henderson. The nonfloat from the last stage of cleaner flotation is circulated countercurrently through the previous cleaner stages. Molybdenite flotation is promoted and contaminant materials controlled in the rougher and regrinding steps by adding reagents for the pulp characteristics. A final concentrate of 48-56% Mo (80-93% MoS₂) is produced, with impurities of 0.50% Fe, 0.06% Cu, 0.03% Pb, 0.02% Bi, and 4% acid insoluble gangue consisting mostly of silica from the native quartzite host rock. Overall recovery is about 86% at Climax and 84% at Henderson.

Climax and Henderson use similar reagent programs established by successful application at Climax. But testing still continues as collector oils become more costly, new reagents are introduced, and the characteristics of flotation change with changes in the mined ore. Simple hydrocarbon collectors such as kerosene, stove oil, or some type of light oil can be used. The collector oil used at Climax and Henderson is a blend of high and low molecular weight oils of both napthenic and paraffinic stocks. Pine oil and Syntex VB, which have emulsifying and collecting properties, are used as frothers; lime is used to control pH to 8.5. Lime or calcium ions change the zeta potential rapidly, forming insoluble calcium molybdate and increasing the zeta potential above the optimum zero potential. The pH should be kept above a critical pH level to float molybdenite, but not other gangue minerals such as pyrite that float at a lower critical pH. In practice, Climax has found that these parameters are delicate to control. The natural pH of the ore feed can vary well above or below 8.5 pH in just a few minutes.

Sodium silicate is used to disperse slimes but has become less effective as the Climax since 1974 when open pit production began mining highly oxidized ore. Contaminant materials are controlled in the rougher and regrinding steps of flotation by adding depressing reagents and controlling pH. Lead and copper are common to both the Climax and Henderson ore bodies. Nokes reagent (P₂S₉, NaOH, H₂O) and sodium cyanide are used to depress these materials with the gangue.

The cleaner operations use Dowfroth 250 as the frother to develop a final concentrate in the final flotation steps. The collector oil is used also, but probably acts just as much as a controller to develop a consistent froth as it does a collector. Nokes reagent and cyanide are used in regrinding and are most effective here on the smaller pulp streams. Henderson proceeds a step further, using an HCl leach system to reduce the high lead content and produce a concentrate containing less than 0.06% Pb.

SECONDARY MOLYBDENUM RECOVERY

Almost all by-product molybdenum is associated with copper although there are economic molybdenum-bismuth mineralization deposits in northeastern Canada. The species of copper mineralization governs the method of copper-molybdenum separation. Ore feed averages between 0.6-1.6% Cu and 0.01-0.05% Mo. Of sixteen mines in the United States, the average head grade is 0.656% Cu and 0.05% to 0.25% Mo.