Thoughts on the Development of Molybdenum Beneficiation Technology

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ABSTRACT Currently, the speed of national economic development is accelerating, and the level of science and technology has also been significantly improved, and the demand for molybdenum in modern industrial production has increased accordingly. With the large-scale extraction of molybdenum resources, the amount of molybdenum resources stored is constantly decreasing. For this reason, the optimization and innovation of molybdenum ore beneficiation technology is very important to improve the utilization of molybdenum ore resources and provide necessary assistance for the sustainable development of the modern mineral industry. Based on this, the paper takes molybdenum ore as the main research topic with focus on the development of the beneficiation process in hope of helping related communities.

1. Introduction
Molybdenum is a rare metal and strategic reserve resource. It has a high melting point and high temperature resistance, and has good thermosetting characteristics. Therefore, it has been widely used in the fields of electronics, aerospace, steel, nuclear industry, machinery, weapons, and chemicals, and it has also promoted the rapid development of the Chinese national economy. Currently, the Chinese domestic reserves of molybdenum resources are relatively rich, ranking second in the world and accounting for 25% of the world's total reserves. The sources of molybdenum are: 1) primary molybdenum in the original molybdenum ore; 2) by-product of complex molybdenum- copper ore; 3) molybdenum recovered from molybdenum-containing catalyst waste. The first two sources account for the largest proportion in supply and the production cost of molybdenum from complex copper ore is not high compared to primary molybdenum. In this research, we will focus on the development of molybdenum ore beneficiation technology to further promote the progress of the mineral industry.

2. Overview of Molybdenum Resources
2.1. Distribution of Molybdenum Ore
According to the survey data released by the U.S. Geological Survey in 2015, the world reserve of molybdenum resources is 11 million tons, while the reserve in China, a country rich in molybdenum resources, is 4.3 million tons\(^{1}\). At the same time, according to data analysis provided by the Ministry of Land and Resources of China, 27 million tons of molybdenum ore reserves have been investigated as of 2014. In China, the central and southern regions are the main areas of molybdenum ores, accounting for 35% of the total reserves, followed by the Northeast, Northwest, Northern and Southwest regions.
2.2. Forms of Molybdenum Ores
Molybdenum does not occur as free metal in nature and is only found in complex ores with other metals in the form of compounds. There are not many types of molybdenum-containing minerals, with only 24 known types currently. These minerals are mainly divided into two categories, molybdenum sulphide (molybdenite) minerals and molybdenum oxide ore. Among them, molybdenite is mainly used. Molybdenite is a soft lead-gray mineral with metallic luster. It is a scaly or thin-plate-like crystal with a layered hexagonal crystal lattice. Molybdenite often contains isomorphic rhenium, which can have yield as high as 0.33%.

2.3. Categories of Molybdenum Ores
The molybdenum ores include molybdenum-containing polymetallic ores, single molybdenite and high-oxide molybdenum ores. There are significant differences in grade and properties between various types of molybdenum ores. Generally, molybdenum ore containing talc, high-oxide molybdenum ore, copper-molybdenum ore, and finely disseminated and ultrafine molybdenum ore, all of which with grades higher than 0.08%, are extremely difficult to beneficiate. Molybdenum ores with grades higher than 0.1% usually contain valuable metals such as lead, gold, and silver, so the practical extraction and utilization value is more significant.

3. Molybdenum Ore Beneficiation Technologies
Molybdenum ore resources are abundant in China, and the value of copper-molybdenum ore separation is especially significant. In order to obtain more molybdenum in copper-molybdenum ore, it is necessary to scientifically and rationally choose and use the beneficiation process to achieve copper and molybdenum separation.

3.1. Single Molybdenum Ore Beneficiation Technology
Molybdenum ore can be coarsely grounded. Therefore, non-polar oils are generally used as collectors when selecting floating reagents, and foaming agents and butyl xanthates are added to improve the recovery rate from molybdenite. Based on the use of hydrocarbon oil emulsification technology and butylene oxide and other technologies, the effect of improving the floatability of molybdenite is relatively prominent [2]. Although molybdenite floats easily, the real molybdenum content is not high, generally between 0.01-0.4%. Generally, a molybdenite ore is classified as rich ore if the known content exceeds 0.2%. Therefore, to ensure that the molybdenum content is between 45-47%, several beneficiation treatments are required.

3.2. Molybdenum-Copper Ore Beneficiation Technology
The most concentrated source of molybdenum is copper-molybdenum ore, and it accounts for 48% of global molybdenum production. Although the amount of copper-molybdenum ore reserve is phenomenal, the grade of such ores is not high, the embedded grain size is fine and the layered structure is relatively complicated[3]. In order to better separate the elements in the copper-molybdenum ore, two methods, namely the priority flotation and mixed flotation, can be used. Because copper sulfide and molybdenite float easily, it is easy to obtain their concentrates. In order to successfully separate copper and molybdenum minerals, the two methods mentioned above must be used. The application of mixed flotation is relatively common in practice. It is mainly used to separate the copper-molybdenum crude concentrate on the basis of roughing. Then the molybdenum and copper contained in the crude concentrate can be obtained and separated successfully. Because copper sulfide ore and molybdenite float easily, the acquisition of copper and molybdenum concentrate is relatively simple. But to separate copper and molybdenum in copper-molybdenum ore, pretreatments are required:

1st Heat treatment to separate copper and molybdenum. Through heat treatment, the water film of collectors on the surface of oxide minerals can decompose, evaporate or oxidize to achieve the target suppression. Globally, 40% of copper-ore concentrators have introduced heat treatment methods to achieve target separation. Meanwhile, heat treatment can further optimize the quality and efficiency of reclamation.

2nd Concentrated reagent removal. Foamed products can be obtained through the use of mixed
flotation methods. However, the xanthogenate contained in this category of products has a large amount of collectors. It is necessary to avoid the influence of residual chemicals on the floatability of chalcopyrite. Therefore, it is necessary to reduce the amount of chemicals used, or to perform concentrated reagent removal treatment before separating copper-molybdenum ore.

3rd Oxidation treatment. Addition of various types of strong oxidants can produce chlorine, hydrogen peroxide or ozone, etc., to achieve the oxidative decomposition treatment on the surface of copper sulfide minerals, and also enable the minerals to form an adsorptive oxide layer on the surface of the slurry, resulting in higher hydrophilicity.

4th The separation of copper and molybdenum can be carried out after the pretreatments, and the most commonly used methods include the following: 1) Conventional flotation. Under normal circumstances, the flotation method needs to be completed with inhibitors. During the flotation of molybdenum ore, non-polar oil is added to it to improve the grade of molybdenum concentrate. At the same time, a variety of inhibitory gangue minerals such as sodium hexametaphosphate and water glass should be added continuously to optimize the quality of the molybdenum concentrate. The latter mainly include cyanide, Knox and sodium sulfide reagents, which can be used alone or in combination, to enhance the separation effect of copper-molybdenum\(^4\). 2) High gradient magnetic separation. Although this flotation method has not been developed for a long time, it has a wide range of applications, mainly in the flotation separation of manganese ore, weak magnetite and wolframite. 3) Nitrogen filling flotation. Through the application of nitrogen-filled flotation technology, the use of inhibitors can be reasonably controlled.

4. Beneficiation Reagents for Molybdenum Ores

4.1.Collectors
Hydrocarbon oil is the most commonly used collector for molybdenite flotation separation. Among hydrocarbon oils, kerosene, diesel and aromatic hydrocarbons are the most commonly used. Most domestic molybdenum and copper-molybdenum beneficiation plants in China use kerosene, and some concentrators use diesel oil. In order to improve the effect of oil collectors, emulsifiers such as sintex and lauryl sulfate can be added to emulsify them.

4.2. Foaming Agents
The most commonly used foaming agent in the flotation separation of molybdenite is terpineol, and almost all Chinese molybdenum processing plants use this foaming agent. Most concentrators in other countries also use terpineol, while some molybdenum concentrators use methyl isobutyl carbinol (MIBC), Dow 250 (DOW250), or the combination of two. In recent years, some Chinese plants have used fusel instead of terpineol as a foaming agent in molybdenum concentrators to solve the problem of sticky foam formation.

4.3. Inhibitors
Mainly includes: Cyanides, sulfides, Knox reagents, ferricyanides, ferrocyanides, various organic compounds and oxidants.

5. New Molybdenum Beneficiation Technologies and Applications

5.1.Semi-automatic grinding process instead of conventional crushing and grinding process
Automatic /semi- automatic grinding technology has been explored for half a century and has gradually developed into a mature and reliable technology after much improvement and research. In various countries, automatic/semi-automatic grinding technology is heavily used in new plants, expanded plants and transformed old plants. In recent years, copper-molybdenum concentrators in China have gradually replaced the traditional "three-stage one closed-circuit crushing-ball mill" process with "coarse crushing semi-automatic grinding-ball mill" process, which not only simplifies
the process flow of the concentrator, but also improves the operation conditions and reduce labor intensity.

5.2. New breakthroughs in the research of high-grade molybdenum concentrate technology
The JDC Molybdenum Group placed the deep flotation separation process directly after the selection and increased the grade of molybdenum concentrate from 52% to more than 57%, setting precedence for molybdenum flotation separation in China. After much exploration, the combination of flotation column and flotation machine with vertical stirring and friction scrubbing technology was implemented for the first time, achieving the use of a single flotation method to produce high-quality molybdenum concentrate with grade greater than 57% without reducing recovery rate.

5.3. Technological innovation of complex refractory molybdenum ore beneficiation
Currently, the main refractory molybdenum ores in China generally include: high oxidation rate molybdenum ores, talc-containing molybdenum ores, talc-containing copper-molybdenum ores, carbon-containing, carbonaceous shale and organic molybdenum carbon-type molybdenum ores, polymetallic molybdenum ore with finer or ultrafine particle size, and molybdenum ores with complex structure. Molybdenum ores with high oxidation rate use water glass as sludge dispersant, kerosene as collector for sulfide ores, modified water glass as gangue inhibitor, and RT as collector for oxidized molybdenum ores to first extract molybdenite preferentially then molybdenum oxides. Talc-type molybdenum ores adopt a new process of "strong magnetic pre-separation of iron - spiral chute gravity separation and desliming molybdenum flotation separation". Carbon-containing nickel-molybdenum ores are burned for desulfurization at 600℃, and then leached with alkali and activated oxygen. The leaching rate of molybdenum is close to 100%. The sulfur dioxide flue gas released during the roasting process is used to produce sodium metabisulfite, which can greatly alleviate sulfur dioxide emissions and the associated environmental pollution problems.

5.4. New Breakthroughs in Reagent Application Research
In response to the increasingly tightening supply of kerosene, Golden Molybdenum Group has carried out experimental research on the application of new-type selective collectors, and has made some breakthroughs. The research has developed a method that simply uses hydrocarbon oil collectors (YC agents) to increase molybdenum separating flotation index. The research results broke the long history of using kerosene in molybdenum separation in China, and successfully solved the urgent issue of replacing kerosene in the molybdenum flotation separation process. It has important value as a reference for the development of theoretical research and application of molybdenum flotation separation.

6. CONCLUSIONS
In conclusion, the active development of molybdenum ore beneficiation technology and reagent analysis can continuously increase the utilization rate of molybdenum ore resources, effectively reduce resource wastage and significantly alleviate environmental pollution. With sustainable development and progress of mineral processing technology, it has promoted the development of modern mining to a certain extent. For this reason, it is necessary to use advanced technology flexibly to better innovate the mining and mineral processing technology and to accelerate the steady development of the mineral industry.

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