Current Situation of Flotation Process and Reagents of Cu-Mo Sulphide Ores

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Abstract. This paper summarizes several flotation methods of copper and molybdenum ore, introduces the research progress of flotation collector and inhibitor of copper and molybdenum ore, and points out that the research and development of new efficient collector and copper and molybdenum beneficiation inhibitor is the key to comprehensive recovery of copper molybdenum ore resources.

Introduction

Many types of copper in the world contain molybdenum, although the molybdenum grade is very low (0.01% to 0.1%), but comprehensive recovery of molybdenum ore is of great economic value. About 20% of China's molybdenum is recovered from the copper and molybdenum ore. China's copper and molybdenum is rich in resources, widely distributed, but the average grade is low, the cost of mining is high, and the selection is difficult.[1] Copper-molybdenum deposits, which are mainly composed of copper and associated molybdenum, are usually existed in nature in the form of porphyry copper deposits. Because of the large reserves, porphyry copper deposits is an important resource for extracting copper and molybdenum at present. Most of the copper minerals in the porphyry copper deposit are mainly chalcopyrite (CuFeS2), the second is chalcocite (Cu2S) and other copper minerals are less. The molybdenum minerals associated with porphyry copper are generally molybenite (MoS2).

Research Progress of Flotation Process of Cu-Mo Mineral

Preferential Flotation

Preferential flotation mainly adopts the following two methods: the first method is preferential flotation of molybdenum, and then the re-flotation of copper; the second method is preferential flotation of copper, and then the re-flotation of molybdenum. These two methods have the same shortcomings that the depressed copper or molybdenum is hard to be activated. The industry rarely use the preferred flotation process because of the complicated process, high cost of process, poor flotation index.

Partial Bulk Flotation

The partial bulk flotation process is usually adopted, when the grade of molybdenum in copper molybdenum ore is high. The process uses the molybdenum ore collector to float part of the molybdenum with excellent floatability, getting part of the molybdenum concentrate. Then bulk flotation of copper and molybdenum can be used to get copper-molybdenum bulk concentrate with the action of sulfide ore collector. Finally, copper molybdenum beneficiation is carried out on copper molybdenum concentrates. The process can effectively reduce the difficulty of beneficiation of copper and molybdenum.

Bulk Flotation and re-beneficiation

The general method to deal with low-grade porphyry copper molybdenum sulfide ore is using sulfide
ore collector to float copper and molybdenum. Then copper molybdenum beneficiation is carried out. The preferred flotation process and the re-grinding process are rarely adopted. Try to completely float as much as possible copper by bulk flotation, and molybdenum is also floated into copper concentrate. When the molybdenum in the copper molybdenum ore content is too low, the concentrator usually only produces copper and molybdenum bulk concentrates because of the difficulty and high cost of separating copper molybdenum concentrates with bulk flotation. The advantages of the bulk flotation and re-beneficiation process: low grinding cost, less middling cycle consumption, easy operation and control of the process, and the site is easy to implement. Therefore, the process can effectively reduce the cost of copper molybdenum ore flotation process. However, when bulk flotation is carried out, the bulk concentrate contains excess reagents, which leads to the difficulty of separating the concentrate. Therefore, the process of copper and molybdenum beneficiation is usually first carried out to remove reagent to improve the beneficiation effect.

Research Progress of Flotation Reagents for Cu-Mo Ore

Flotation Collector for Copper Sulfide Ore

Xanthate. Xanthate which contains xanthate, xanthate esters and xanthate anionic collectors are effective collectors for sulfide ores. It is widely used as flotation collector for sulfide ores because it is cheap and easy to manufacture. The stability of xanthate is poor. When the xanthate meeting heat, water and acid, it will decompose. The lower pulp pH, xanthate decomposes faster. On the contrary, it is sufficiently stable in the alkaline pulp. There are two kinds of xanthate: potassium xanthate and sodium xanthate. Both of them have basically the same collecting performance. Potassium xanthate is stable, and sodium xanthate cost is slightly lower. Sodium ethyl xanthate and butyl sodium xanthate are the most widely used in China. Isopropyl xanthate and amyl xanthate have been used more widely abroad. The strength of xanthate’s collecting performance is largely dependent on the length of the hydrocarbon chain. The general rule is that the collecting performance increases with the increase of hydrocarbon chain, while the selectivity is opposite. The long hydrocarbon chain xanthate’s selectivity is better than the short hydrocarbon chain xanthate. Therefore, the collecting performance of butyl xanthate is stronger than that of ethyl xanthate, but the selectivity is relatively poor. For xanthate, the common hydrocarbon used in practice is C$_2$~C$_5$.

Aerofloat. Aerofloat and xanthate are combined by divalent sulfur atom and metal ions on the mineral lattice surface, so that the minerals can collected by xanthate can also be collected by aerofloat. Aerofloat’s collecting performance is weaker than xanthate’s, but it has a certain degree of foaming. The dosage of foaming agent can be reduced when using aerofloat. It is stable than xanthate. It’s not easy to decompose in acidic pulp. Meanwhile, it has week collecting performance to iron sulfide and has strong selectivity. Therefore, aerofloat is a sulfide ore collector which is widely used only after xanthate in practice. The frequently-used aerofloat in China are aerofloat 25; ammonium butyl aerofloat; aniline aerofloat and so on. The frequently-used aerofloat abroad are aerofloat242 (cresol aerofloat + thiourea); aerofloat238(sodium butyl aerofloat); aerofloat208 (sodium ethide aerofloat + sodium butyl aerofloat).

Flotation reagent of Molybdenite

Molybdenite is one of the minerals with excellent floatability. It belongs to non-polar mineral and can be easily selected by non polar hydrocarbon oil. Among them, non polar hydrocarbon oil such as kerosene, diesel oil and lubricating oil are usually used as collectors for molybdenite flotation. Kerosene is one of the most widely used non-polar hydrocarbon oil collectors in molybdenite flotation. The main component of kerosene is C$_{11}$~C$_{16}$alkane. It is basically insoluble in water and only has collecting performance. When the content of aromatic hydrocarbon is large, It has a certain foaming performance. In addition, when the amount of kerosene is too large, it has significant defoaming performance. Non-polar hydrocarbon oil which is frequently used in foreign countries is syntex (emulsifier), aromaticoil etc.
Advances in Flotation Depressant of Copper Molybdenum Ore

Inorganic Depressant.
1) Sulfur-containing compounds
   Sulfur compounds are mainly Na$_2$S; NaHS; sodium thiocarbonate (Na$_2$CS$_3$); P-Nokes(P$_2$S$_5$+NaOH); As-Nokes(As$_2$O$_3$+Na$_2$S);Na$_2$S$_2$O$_3$;Na$_2$SO$_3$.
   Na$_2$S has the advantages of low price, wide source and can effectively depress other sulfide minerals other than molybdenum ore. It can also make the hydrophobic film adsorbed on the surface of copper sulfide reduced and dissociated, thus having the effect of reagent removal and widely used in industry. However, Na$_2$S is a strong reducing substance, which is easily oxidized and lost effect in flotation process, so its high dosage leads to high cost. It has been reported that the oxidation rate of sodium sulfide can be reduced by steam or nitrogen flotation, sodium sulfide in batches, or by appropriately increasing the flotation concentration. These methods can reduce the oxidation rate of sodium sulfide, so that it can play a full depressing effect and can effectively reduce its amount.

2) Nitrogen-containing compound
   Nitrogen-containing compound are mainly NaCN; Na$_4$Fe(CN)$_6$;Na$_3$Fe(CN)$_6$;KCN;Zn(CN)$_2$;Ca(CN)$_2$ and so on. Cyanide is an effective depressant in the separation of nonferrous metal sulfide minerals. The depressing mechanism is CN$^-$ forms a hydrophilic insoluble cyanide or complex with metallic minerals. Cyanide has the advantages of low dosage and great depressing, but its toxicity is strong and harmful to the environment, limiting its application in production.

Organic Depressant
1) Synthetic organic depressant
   There are mainly alkyl dithiocarbamate; hydroxyl alkyl dithiocarbamate; benzene sulfonic acid; glycolic acid xanthate; mercapto acetic acid(Aero666,667); ethyl mercaptan; thiourea pyrimidine; dipicolinic acid; dicyandiamide and so on. Among them, mercapto acetic acid has the advantages of low toxicity, short reaction time, high selectivity, good water solubility, wide pH range. It can also improve the recovery rate of gold, silver and other rare and precious metals associated with ores, and it has shown a bright trend in the field of copper molybdenum separation industry. As early as 1948, the United States Cyanamide company applied for a patent for mercapto acetic acid they developed and used it in a large copper mine. Gordon study showed that Aero 666 was added at 0.05g/kg, and the best depressing effect was obtained. The grade of molybdenum concentrate was 57.2% and the recovery rate was 96.1%. Due to pure or high concentrations of mercapto acetic acid prone to oxidation and self-esterification reaction, resulting in loss of active ingredients, and the price is more expensive, it is difficult to reduce the cost of mineral processing agents, resulting in the use of copper molybdenum ore beneficiation process is limited.

2) Natural organic depressant
   Natural organic inhibitors mainly include modified starch; tannin; sodium humic acid and dextrin. These hydrophilic polymers can be used as depressants of molybdenite in the beneficiation of Cu-Mo ore. The results show that the adsorption of dextrin onto the surface of molybdenite is based on the physical adsorption and the formation of hydrophilic bonds. When dextrin adsorbed, it can depress molybdenite with collectorless flotation. But the existence of oil collector will weaken the depression effect of maltodextrin. Because of the strong floatability of molybdenite, it is difficult to oxidize and depress, and the depressed molybdenite is difficult to be activated. So, this kind of depressant is seldom used in beneficiation of copper and molybdenum.

Research Progress of New Depressants
   New single depressant
   HXM is a new depressant for the beneficiation of copper and molybdenum developed by Lingmin Guo and others. In the beneficiation process of Dexing copper molybdenum ore, its depression performance is similar to that of sodium sulfide. The qualified molybdenum concentrates with molybdenum grade of 48.86% and copper content of 1.64% were obtained.
Compared with Na₂S process, 30% of the reagent cost was effectively reduced. It is reported\[11\] that copper and molybdenum separation index can be obtained in low-grade porphyry copper-molybdenum flotation at low alkalinity (pH = 8 ~ 9) with the new depressant BK510. It is a low consumption and high efficiency depressant for separating molybdenum from copper and molybdenum.

**Conclusion**

The characteristics of copper molybdenum ore resources in China is that there are many lean ore and few rich ore. With the depletion of mineral resources, copper-molybdenum ore efficient recycling has become the key. Based on the comprehensive utilization of copper and molybdenum resources, the following conclusions are drawn:

1) The selection of low consumption and high efficiency copper molybdenum flotation process, such as bulk flotation re-separation process, is more common because it can effectively reduce the cost of copper molybdenum ore flotation process. In the future research work need to improve the shortcomings of the process to increase the comprehensive recovery of copper molybdenum ore.

2) The flotation reagents of copper molybdenum ore mainly include the collectors in the bulk flotation of copper and molybdenum, and the depressants in the beneficiation of copper and molybdenum. The choice of suitable collectors and depressants is related to the flotation efficiency of copper molybdenum ore.

3) At present, there are many defects in the beneficiation of copper molybdenum ore, such as large dosage, serious environmental pollution and high cost. Therefore, it is still of far-reaching significance to develop economic and environmental friendly depressant for the separation of copper-molybdenum, collectors for the flotation of copper molybdenum and new process and new equipment for separating copper molybdenum bulk concentrate.

**References**


