Thionocarbamates in Copper Slag Flotation

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Thionocarbamates are the group of collectors that are mostly used for flotation of sulphide copper minerals, alone or in combination with xanthates depending on a mineralogical composition of the ore. Collectors are a group of reagents used in flotation for enhancing hydrophobicity of wanted minerals. They are organic compounds which are being adsorbed on surfaces of desired minerals, thus making them hydrophobic, reducing the stability of the hydrated layer separating the mineral from the air bubble to such extent that attachment of the particle to the bubble can be made, i.e., collectors reduce the induction time. Another purpose of collectors is to provide selectivity of minerals with similar floatability properties.

Thionocarbamates

Collectors

Adsorption

copper slag

1. Introduction

The selection of collector in copper flotation is in close correlation with nature and appearance of copper minerals and other sulfides that are associated with them ^[1]. Xanthates are mostly used collectors in copper flotation and they can be applied alone or in combination with other collectors, such as dithiophosphates or thionocarbamates, which are normally used for flotation of secondary copper minerals or in the case when flotation is performed at lower pH ^[2].

Thionocarbamates are classified as chelating collectors, in which stabile complexes are formed by chelation with surface metal ions through the C=S and N-H groups ^[3]. Thionocarbamates are mostly used for copper sulphide minerals flotation, alone or in combination with xanthates depending on a mineralogical composition of the ore ^{[2][4]}. Thionocarbamates in combination with xantates represent an efficient collector mixture for flotation of two or more copper minerals, e.g., chalcocite, covellite, chalcopyrite, and bornite, present in the ore ^{[2][5]}. O-isobutyl-N-ethyl thionocarbamate (IPETC) can be used for the flotation of variety of copper minerals such as chalcocite, chalcopyrite, cubanite, and bornite ^{[6][2]}. Thionocarbamates are also well-known selective collectors used for selective flotation of sulfide copper minerals from other sulfides such as pyrite, arsenopyrite, galena, sphalerite, marmatite, etc., or selection of one sulfide mineral from other sulfides. Bu et al. ^[8] applied IPETC for selection of chalcopyrite from galena. The same collector, i.e., IPETC, was used by for decoupling pyrite and arsenopyrite, with the addition of CuSO₄ for activation of both oxidised pyrite and arsenopyrite ^[9]. The separation of Cu sulfide minerals (chalcopyrite, chalcocite, covellite, and bornite) from Fe sulfide minerals (pyrite and marcasite) by using dialkyl thionocarbamates and ethoxycarbonyl thionocarbamates was studied by Guang-yi et al. ^[10]. The results of the study showed that ethoxycarbonyl thionocarbamates (ECTC) had very good recovery rates for copper minerals, and they were also very selective against iron sulfide minerals at pH 8–9. Thionocarbamates can be also

used as secondary collectors for processing copper-zinc ores, in both copper and zinc flotation circuits. Their main role in copper flotation circuit is to increase copper recovery ^[4] and in zinc flotation circuit, when sulfide iron minerals are present, they are used for selection of zinc minerals (sphalerite or marmatite) from sulfide iron minerals (pyrite or pyrrhotite) ^{[2][3]}.

Copper slag represents a residue of pyro-metallurgical treatment of copper concentrates ^[11]. Since the concentrates are obtained from copper ores that differ in mineralogical composition and are being processed by different smelting technologies, large amounts of copper and other valuable metals can be present in the slag ^[12] ^{[13][14]}. In addition, quantities of slag that are being generated vary on applied technology and, according to some sources, approximately 2,2 t of slag are generated for production of 1 t of pure copper ^[12].

The main minerals present in the slag are fayalite and magnetite [14][15][16]. Copper can be present in the form of sulfide minerals, oxide minerals or as a native copper [17][18].

Copper and other valuable metals can be recovered from slag by flotation ^{[13][19][20][21]}, leaching ^{[22][23][24]}, roasting ^{[25][26]}, or their combination ^{[27][28][29]}. Some of these methods were briefly reviewed by Gorai et al. (2002) ^[12].

Copper slag and/or residues from slag' processing can be also used for various purposes such as cement production, construction of roads and buildings, etc. [30][31][32][33][34][35][36][37][38][39][40][41].

Flotation is the main process for processing slag for valorization of copper and other metals. In order to achieve the best copper recovery and quality of the concentrate, it is necessary to optimize the whole process starting from grinding, i.e., liberation of copper bearing minerals from gangue ^{[19][21][42]}, flotation parameters such as pulp' density, pH, conditioning and flotation time, etc. ^[13] and also types and dosages of applied flotation reagents: collectors, frothers and others ^[43]. Xanthates are most commonly used collectors for recovery of copper bearing minerals from slag. However, some recent research has shown that a combination of xantahes with some other secondary collectors can result in enhanced copper recovery ^{[21][43]}. Application of thionocarbamates as collectors for flotation of copper bearing minerals from slag was investigated by very few researchers, and the research conducted with this collector type on copper minerals from copper ores indicates the necessity for more thorough investigation since copper in slag mainly appears in correlation with sulfur, i.e., in sulfide form.

2. Adsorption Mechanism of Thionocarbamates

The mechanisms of the adsorption of collectors on sulfide mineral surfaces play an important role in the flotation process. A large number of studies have been conducted with a focus on the adsorption of thionocarbamates on sulfide copper minerals, but there are no studies dealing with adsorption of thionocarbamates on surfaces of copper bearing particles present in copper slag.

Ethoxycarbonyl thionocarbamates (ECTC) collectors are powerful for chalcopyrite and very selective against pyrite in alkaline and neutral pH conditions. The adsorption on chalcopyrite preferentially occurs at Cu atoms instead of Fe atoms ^[44].

The separation of Cu and Fe sulfide minerals by flotation can be achieved at pH 8.5 for ECTC. It was reported that ECTC collectors were powerful for copper minerals and very selective against iron sulfide minerals at pH 8–9 ^[10].

Flotation effect of O-isobutyl-N-ethyl thionocarbamates (IBET) on Cu minerals, at pH 10, is very good. IBET has the ability to collect most copper-bearing minerals in porphyry copper ores, especially chalcocite and chalcopyrite. IBET is primarily adsorbed by sulfur atoms combined with monovalent copper ions (Cu⁻) or divalent copper ions (Cu²⁺) on the surface of the chalcocite and chalcopyrite [7].

Flotation collector O-isopropyl N-ethylthionocarbamate (IPETC), often referred to as Z-200, is widely used for separation of sulfides ores, and numerous research studies were conducted on the adsorption of IPECT on the mineral surface [6][8][9][45][46].

IPETC interacts strongly with Cu atoms on the mineral surface of chalcopyrite. Most of the IPETC is strongly adsorbed on the chalcopyrite surface as HIPETC, with minor IPETC chemisorbed to Cu atoms ^[6].

IPETC adsorbs most strongly on chalcocite at pH 4–10, while on chalcopyrite and pyrite, adsorption continues to increase with decreasing pH. Adsorption on chalcocite is 3–20 times higher than on chalcopyrite and pyrite. IPETC chemisorbs on chalcocite through sulfur below pH 6 and through both sulfur and oxygen above pH 6 ^[45].

The floatability of chalcopyrite is better than that of galena in the presence of IPETC, and the recovery difference between chalcopyrite and galena is about 20% when IPETC is 7×10^{-4} mol/L at pH 9.5, while the floatability difference between the two minerals is significant. Competitive adsorption of OH- and IPETC on mineral surfaces leads to lower floatability of galena than that of chalcopyrite. IPETC is able to remove the hydration layer on mineral surfaces and then adsorb on active sites ^[8].

The adsorption of IPETC (Z-200) is more exothermic on chalcopyrite than on pyrite, which indicates the strong selectivity against pyrite ^[46].

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