Influence of Mineral Surface Reactivity on Thionocarbamate and Dithiophosphate Adsorption Mechanisms and Copper Sulphide Flotation Performance

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Abstracts

Thionocarbamate and dithiophosphate collectors are widely recognized for their enhanced selectivity in copper sulphide flotation, especially in pyrite-rich systems where conventional xanthates often underperform. The flotation selectivity of thionocarbamate and dithiophosphate collectors, particularly in copper sulphide systems, is critically governed by the pre-flotation surface chemical conditions of the mineral particles. This study systematically investigates how mineral surface reactivity modulated by water-mediated surface alteration during wet grinding versus its absence under dry grinding conditions governs the adsorption behaviour of thionocarbamates and dithiophosphates and subsequent flotation response in copper sulphide systems using complementary electrokinetic and spectroscopic techniques, including ultraviolet–visible spectroscopy (UV-Vis), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and X-ray photoelectron spectroscopy (XPS). Both wet and dry grinding produced comparable particle size distributions achieved after 31 min at 28 rpm (wet) and 37 rpm (dry), and, in model mineral calibration, after 45 min at 10 rpm for both conditions. This consistency ensured that observed differences in downstream performance arose from grinding environment and chemistry rather than particle size variations.

Introduction

The efficiency of sulphide mineral flotation is fundamentally governed by the interfacial interactions between mineral surfaces and collector molecules. Among copper sulphide minerals, chalcopyrite, bornite, and chalcocite constitute the principal sources of copper production globally, and their selective recovery remains central to sustainable mineral beneficiation. However, the physicochemical condition of the mineral surface dictated by factors such as oxidation, grinding environment, and pulp chemistry strongly influences collector adsorption behaviour and, consequently, flotation performance (Forson et al., 2021c, Forson et al., 2022b, Wali et al., 2024). Understanding the interplay between mineral surface reactivity and collector adsorption mechanisms is therefore essential for the rational design and optimization of flotation processes.

Mineral surface reactivity refers to the tendency of a mineral surface to undergo oxidation, reduction, or other chemical transformations when exposed to aqueous and gaseous species during comminution and conditioning ore (Huang and Grano, 2005, Mu et al., 2018, Xu et al., 2021, Asamoah et al., 2021). In sulphide systems, these reactions generate surface oxidation products such as hydroxides, sulphates, or polysulphides, which can alter surface charge, hydrophobicity, and adsorption sites for collectors. The nature and composition of these surface layers are highly sensitive to grinding media, pH, oxygen potential, and solution chemistry, thereby influencing collector–mineral interactions at the molecular scale (Amankwaa-Kyeremeh et al., 2021, Amankwaa-Kyeremeh et al., 2023). Recent studies have shown that surface reactivity differences between dry and wet grinding environments can modify the oxidation state of copper species and consequently affect collector adsorption kinetics and flotation response.

Thionocarbamate and dithiophosphate collectors are among the most widely used reagents in the flotation of copper sulphide minerals. Both possess thiol functional groups that enable chemisorption onto metal sites on the mineral surface, but they differ in molecular structure, electron-donating capacity, and selectivity towards partially oxidized sulphide surfaces. Thionocarbamates exhibit a balanced hydrophobic–hydrophilic character, enabling efficient adsorption on moderately oxidized chalcopyrite and chalcocite surfaces, whereas dithiophosphates exhibit stronger metal affinity but are more sensitive to oxidation and pulp redox potential (Forson et al., 2021b, Forson et al., 2021a, Forson et al., 2022a). Despite their industrial importance, the adsorption mechanisms of these collectors under varying mineral surface reactivity conditions remain incompletely understood. Previous work has predominantly focused on collector adsorption under idealized, freshly ground conditions, often neglecting the impact of surface oxidation and reactivity states induced during grinding (Koleini et al., 2012, Liu et al., 2018) . Moreover, comparative studies assessing thionocarbamate and dithiophosphate adsorption on differently reactivated or pre-oxidized sulphide surfaces remain scarce. This knowledge gap limits our ability to establish mechanistic correlations between surface chemistry, collector adsorption thermodynamics, and flotation response particularly under environmentally diverse and complex plant conditions.

Accordingly, this study investigates the influence of mineral surface reactivity on the adsorption mechanisms of thionocarbamate and dithiophosphate collectors and their subsequent impact on the flotation performance of copper sulphide minerals. By integrating advanced surface characterization techniques including ultraviolet-visible (UV–Vis) spectroscopy, zeta potential, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS); the work elucidates the collector interactions of each collector as a function of surface oxidation and grinding environment. The findings provide fundamental insights into the physicochemical basis of collector–mineral interactions and propose mechanistic pathways that link surface reactivity with flotation selectivity and recovery, contributing to the development of more predictable and sustainable flotation reagent regimes.

2.0 Materials and methods

2.1 Materials and sample preparation obtained

Pure chalcopyrite was used as a model mineral, and a copper-bearing chalcopyrite ore was used as the real mineral in this study. A representative sample of the real mineral was analysed using ICP-AES for chemical composition, while the model mineral's mineralogical composition was determined via X-ray diffraction. Potassium amyl xanthate (PAX) from Interchem Pty Ltd was prepared at 1 wt.% for flotation, with methyl isobutyl carbinol (MIBC) as the frother. Sodium hydroxide, hydrochloric acid, and lime were used for pH adjustment, and potassium nitrate (KNO_3) was used for zeta potential measurements. Elemental composition of the chalcopyrite ore used is shown in Table 1. Grinding experiments were conducted using a Magomill® (Greet et al., 2004) with 2 kg batches of crushed Cadia ore (-2000 μm) for both dry and wet grinding. For wet grinding, 2 kg of roll-crushed ore was mixed with 1.2 dm³ demineralized water and ground with 20 kg of steel balls at 45 rpm, aiming for 80% passing 250 μm. The same procedure was used for dry grinding. Calibration studies were performed to ensure similar particle size distributions between dry and wet samples, allowing direct comparison during the experiment.

Table 1. Elemental composition of real chalcopyrite ore (%).

Elements (mass%)							
Al	Fe	S	Ca	Cu	Si	Mg	K
7.69	4.61	0.91	2.05	0.4	21.1	2.88	2.62

Table 2. Mineralogical composition of real chalcopyrite ore (%).

Mineral	Weight (%)
Native copper	0.14
Chalcopyrite	1.06
Bornite	0.08
Pyrite	1.76
Titanium Minerals	1.5

Fe Oxides	1.92
Fluorite	0.02
Quartz	19.5
Mica group	12.39
Albite	20.05
K Feldspar	29
Apatite	0.76
Carbonates	2.99
Clays	2.7
Other silicates	5.51
Others	0.62

Table 3. Elemental composition of model chalcopyrite ore (%).

Element	Aluminium	Iron	Sodium	Copper	Sulphur	silicon	Magnessium	Potassium	Calcium
Mass (%)	1.15	26.6	0.14	25.53	27.7	7.85	0.33	0.12	0.26

Table 4. Mineralogical composition of model chalcopyrite ore (%).

Element	Mass (%)
Pyrite	8
Chalcopyrite	74
Quartz	17
Talc group	1
Portlandite	1

2.2 Flotation

The effect of comminution environment on collector adsorption and flotation response of dry and wet ground particles was studied using a 4.5 L Denver flotation cell. Thionocarabamate, dithiophosphate and methyl isobutyl carbinol were used as collectors and frother respectively, in this test with hydrated lime ($Ca(OH)_2$ being used to adjust the pH during flotation. The test used 36 % pulp density, 900 rpm agitator speed, and 5-7 L/min air flow. Two kilograms of ore was added to 3.45 L water, and pH adjusted to 9 before adding collector (25 g/t) and frother (40 g/t). Air was introduced, and concentrates were collected at 1, 3, 6, and 10 min intervals, filtered, dried, weighed, and analysed.

3.0 Results and Discussions

3.1 Flotation

To evaluate the effect of mineral surface reactivity induced by different grinding environments on the flotation behaviour of copper sulphides, flotation tests were conducted on chalcopyrite ore using 25 g/t of dithiophosphate and thionocarbamate collectors. The results are presented in Figure 1. Both grinding environments produced good chalcopyrite recoveries; however, the dry grinding environment achieved the highest copper recovery compared to the wet grinding environment across both collectors tested. Specifically, copper recoveries were 79.6% (dry) and 76.6% (wet) for dithiophosphate, and 78.7% (dry) and 73.5% (wet) for thionocarbamate. The slightly lower recoveries observed under wet grinding may be attributed to galvanic interactions between the steel media and chalcopyrite, which modify mineral surface properties and promote surface passivation through the formation of galvanically derived oxidation products. This passivation decreases mineral reactivity, leading to reduced flotation performance. In contrast, dry grinding minimizes galvanic coupling, thereby preserving the mineral's reactive surface sites and may possibly enhance collector attachment and recovery (Bruckard et al., 2011, Koleini et al., 2012).

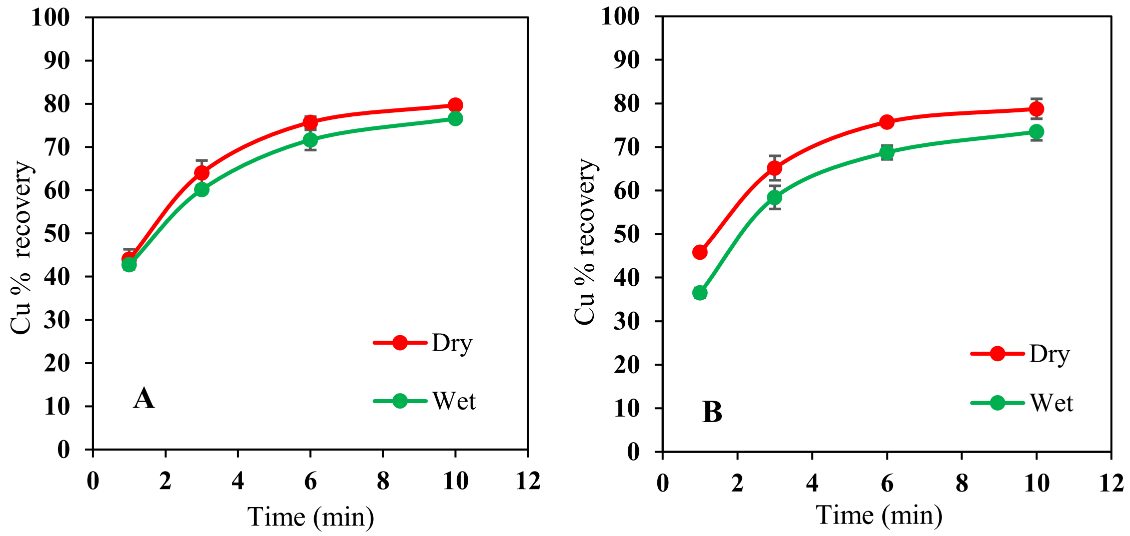

Figure 1. Flotation recovery of chalcopyrite ore ground under dry and wet conditions using (A) Dithiophosphate and (B) Thionocarbamate collectors.

4.0 Conclusion

This study establishes a framework for understanding how the grinding environment influences mineral surface reactivity, collector adsorption, and flotation performance of copper sulphides. Flotation results show that dry grinding consistently achieved higher chalcopyrite recoveries than wet grinding; 79.6% (dry) and 76.6% (wet) for and 78.7% (dry) and 73.5% (wet) for dithiophosphate and thionocarbamate collectors respectively. The reduced recovery under wet conditions is attributed to galvanic interactions that promote surface passivation and hinder collector adsorption, whereas dry grinding preserves surface reactivity and enhances flotation response. This study demonstrates that surface reactivity is a key determinant of collector performance. Further surface analysis will be conducted to elucidate these findings, and the results will be presented at the upcoming conference.

5.0. Refernces

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