Tailored Oxidised Starch Derivatives for Enhanced Selectivity of Pyrrhotite Depression in Gold–Copper Flotation

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Unintended flotation of pyrrhotite remains a major challenge in processing complex sulphide ores [1-7]. Its recovery reduces concentrate grades and contributes to elevated sulphur dioxide (SO_2) emissions during smelting, making selective depression essential for both metallurgical and environmental performance. However, surface transformations under flotation conditions complicate this task. Partial oxidation at the pulp–solution interface produces elemental sulphur (S^0), which increases hydrophobicity, and iron-hydroxy-sulphide species (e.g., $Fe(OH)[S]^+$), which serve as active sites for xanthate adsorption [8]. Additionally, multivalent metal ions such as Cu^{2+}, introduced through mineral dissolution or recycled process water, can further activate pyrrhotite by forming additional collector-binding sites [9]. These concurrent oxidation and activation processes significantly enhance pyrrhotite floatability, often overriding conventional depressant schemes.

These challenges are further intensified by pyrrhotite's non-stoichiometric composition ($Fe_{1-x}S$, $0 < x \leqslant 0.125$), which gives rise to several crystallographic polytypes with distinct flotation responses. The 4C form is monoclinic and ferromagnetic, whereas the 5C and 6C (often referred to as NC or hexagonal pyrrhotite) are non-magnetic and exhibit hexagonal or orthorhombic symmetry [6]. These structural variations affect surface oxidation behaviour, redox activity, and interactions with flotation reagents. Under alkaline conditions, non-magnetic pyrrhotites tend to be more floatable [2,3,6,7] and less responsive to conventional methods such as magnetic separation or pulp potential (Eh) control [7]. Therefore, more selective reagent strategies are required to effectively target these non-magnetic forms, particularly by passivating redox-active iron sites and preventing the formation of hydrophobic surface species that promote unintended flotation.

Recent investigations have highlighted several promising strategies for selectively depressing pyrrhotite, particularly the more flotation-prone non-magnetic superstructures. These include, (i) nitrogen purging, which modulates pulp potential and inhibits pyrrhotite oxidation and flotation by maintaining reducing conditions [7,10], (ii) surface deactivation through reagent synergism, notably the combined use of sodium metabisulphite (SMBS) and polyamines such as diethylenetriamine (DETA) or triethylenetetramine (TETA), which target surface metal centres and suppress the formation of hydrophobic oxidation products [1,11,12], and (iii) collector-starvation techniques, which limit xanthate availability and thereby favour selective adsorption on valuable minerals like chalcopyrite and gold [13].

Among the various strategies for pyrrhotite depression in sulphide flotation, simple approaches such as xanthate starvation and lime addition have been widely adopted due to their low cost and ease of use. However, their effectiveness and selectivity, particularly against non-magnetic pyrrhotite, are often limited, especially in complex ore systems. In contrast, more selective systems such as the SMBS combined with polyamines like TETA or DETA have demonstrated improved performance [1,11,12]. Despite their technical advantages, industrial uptake of SMBS/polyamine systems remains limited due to environmental, hygiene, and operational challenges. Polyamines form strong complexes with metal ions such as Cu^{2+} and Fe^{2+}, disrupting metal precipitation during tailings treatment and complicating water recycling [14,15]. Previous findings have shown that TETA binds strongly to gold surfaces, causing surface passivation and reduced gold recovery in gold-bearing ores [11]. In addition, SMBS acts as a strong oxygen scavenger [16], rapidly reacting with dissolved oxygen in aerated flotation pulp, which depletes the active species and necessitates frequent dosing, increasing reagent consumption and circuit variability. As a result, there is growing interest in greener, more stable alternatives that combine selectivity with environmental compatibility.

Addressing the flotation challenges posed by pyrrhotite, particularly its non-magnetic polytypes, requires next-generation depressants that offer both selectivity and environmental compatibility. Natural polymers such as starch, guar gum, carboxymethyl cellulose, chitosan, and dextrin have emerged as promising green alternatives [17-20], with starch standing out due to its abundance, low cost, renewability, and biodegradability. Starch consists of D-glucose units arranged as linear amylose and branched amylopectin. However, its numerous hydroxyl groups form extensive hydrogen bonds, leading to poor solubility, high viscosity, and limited selectivity in flotation [21]. Chemical oxidation can overcome these limitations by introducing carbonyl and carboxyl groups at C2, C3, and C6 positions, enhancing polarity, adsorption capacity, and wettability. It also facilitates controlled depolymerisation, lowering viscosity while preserving structural integrity [22].

Hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaClO) are the most common oxidants for starch, but yield different functionalities. H_2O_2 oxidation primarily yields carbonyl groups with some carboxylation [23], whereas NaClO introduces both functionalities, typically resulting in a higher carboxyl content [24]. Since these functional groups govern the interaction of oxidised starch with mineral surfaces, the choice of oxidising agent and the resulting balance of carbonyl and carboxyl functionalities may significantly influence adsorption behaviour and depression performance, warranting further investigation.

Gonçalves et al. [14,25] evaluated starch-based depressants on pentlandite–hexagonal pyrrhotite mixtures but reported poor selectivity due to non-specific adsorption driven by acid-base interactions and metal ion bridging. To improve performance, oxidation of starch has been investigated. Khoso et al. [26] employed tricarboxylate sodium starch to selectively depress pyrite and pyrrhotite (unspecified superstructure), while Fletcher et al. [27] achieved improved depression of Cu^{2+}-activated pyrite using oxidised wheat starch, attributing the effect to introduced carbonyl and carboxyl groups. However, these studies were limited mainly to microflotation of single-mineral or artificial binary systems. While encouraging, the selectivity of oxidised starch must still be validated under more realistic flotation conditions, namely, complex multi-mineral ores with coexisting pyrrhotite superstructures and stricter collector dosage constraints that are more typical of current plant flowsheets, to assess its industrial applicability.

In this study, flotation tests, synchrotron XRD, and DFT simulations collectively showed that depressant performance is strongly governed by the chemistry and coordination behaviour of surface-active functional groups. Carboxyl-rich NaClO-OS provided the most effective and uniform depression across pyrrhotite superstructures, including the non-magnetic 5C and 6C forms that are typically the most difficult to suppress. In contrast, carbonyl-dominated H_2O_2-oxidised starch and native starch exhibited weaker, less selective suppression.

At the molecular level, NaClO-OS interacts with pyrrhotite surfaces through inner-sphere complexation between carboxylate groups and surface Fe atoms, forming stable hydrophilic films that displace xanthate collectors. This competitive adsorption mechanism explains its enhanced selectivity and stronger depression, particularly for non-magnetic pyrrhotite.

Overall, the results establish that functional-group tailoring of biodegradable polymers can deliver effective, selective, and sustainable pyrrhotite depression. Carboxylate functionalisation of starch transforms it from a weak, non-selective polymer into a targeted depressant suitable for modern gold–copper flotation systems. These insights provide a practical framework for designing next-generation bio-reagents that improve both metallurgical performance and environmental outcomes in complex sulphide processing.

References

[1] Multani RS, Waters KE. Pyrrhotite depression studies with DETA and SMBS on a Ni-Cu sulphide ore. The Canadian Journal of Chemical Engineering. 2019;97:2121-30.

[2] Multani RS, Williams H, Johnson B, Li R, Waters KE. The effect of superstructure on the zeta potential, xanthate adsorption, and flotation response of pyrrhotite. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2018;551:108-16.

[3] Rezvani A, Raji F, Fan R, Kappes R, Gao Z, Peng Y. Depression of pyrrhotite superstructures in copper flotation: A synchrotron X-ray powder diffraction and DFT study. International Journal of Mining Science and Technology. 2025.

[4] Rezvani A, Raji F, Fan R, Kappes R, Peng Y. Quantifying pyrrhotite superstructures in copper-gold ore flotation through synchrotron X-ray diffraction analysis. Minerals Engineering. 2024;216:108894.

[5] Rezvani A, Raji F, Liu Q, Peng Y. Unveiling different pyrrhotite superstructures in copper-gold ore samples: Insights from advanced spectroscopic and microscopic characterization. Minerals Engineering. 2024;206:108536.

[6] Rezvani A, Raji F, Liu Q, Peng Y. Identification and quantification of pyrrhotite superstructures in base metal sulfide ore samples: A critical review. Minerals Engineering. 2024;218:108975.

[7] Tang X, Chen Y. A review of flotation and selective separation of pyrrhotite: A perspective from crystal structures. International Journal of Mining Science and Technology. 2022;32:847-63.

[8] Wang H. A review on process-related characteristics of pyrrhotite. Mineral Processing and Extractive Metallurgy Review. 2007;29:1-41.

[9] Qi C, Liu J, Malainey J, Kormos LJ, Coffin J, Deredin C, et al. The role of Cu ion activation and surface oxidation for polymorphic pyrrhotite flotation performance in Strathcona Mill. Minerals Engineering. 2019;134:87-96.

[10] Rao S, Finch J. Adsorption of amyl xanthate at pyrrhotite in the presence of nitrogen and implications in flotation. Canadian metallurgical quarterly. 1991;30:1-6.

[11] Raji F, Kappes R, Peng Y. Deleterious impacts of triethylenetetramine and sodium metabisulphite on gold flotation during pyrrhotite depression. Minerals Engineering. 2024;216:108884.

[12] Kelebek S, Tukel C. The effect of sodium metabisulfite and triethylenetetramine system on pentlandite–pyrrhotite separation. International journal of mineral processing. 1999;57:135-52.

[13] Senior G, Shannon L, Trahar W. The flotation of pentlandite from pyrrhotite with particular reference to the effects of particle size. International journal of mineral processing. 1994;42:169-90.

[14] da Costa Gonçalves C, Liu Q. The effect of crosslinking additives and molecular weight of starch depressants on pyrrhotite and pentlandite floatabilities. Minerals Engineering. 2022;180:107489.

[15] Bai G, Huang C, Li Y, Zhang M. Selective Flotation Separation of Chalcopyrite from Copper-Activated Pyrite and Pyrrhotite Using Oxidized Starch as Depressant. Minerals. 2025;15:133.

[16] Tukel C, Kelebek S. Modulation of xanthate action by sulphite ions in pyrrhotite deactivation/depression. International Journal of Mineral Processing. 2010;95:47-52.

[17] Bogusz E, Brienne S, Butler I, Rao S, Finch J. Metal ions and dextrin adsorption on pyrite. Minerals Engineering. 1997;10:441-5.

[18] Laskowski J, Liu Q, O'connor C. Current understanding of the mechanism of polysaccharide adsorption at the mineral/aqueous solution interface. International Journal of Mineral Processing. 2007;84:59-68.

[19] Chimonyo W, Fletcher B, Peng Y. The effect of oxidized starches on chalcopyrite flotation. Minerals Engineering. 2021;165:106749.

[20] Liu Q, Zhang Y, Laskowski J. The adsorption of polysaccharides onto mineral surfaces: an acid/base interaction. International Journal of Mineral Processing. 2000;60:229-45.

[21] Zhang SD, Zhang YR, Wang XL, Wang YZ. High carbonyl content oxidized starch prepared by hydrogen peroxide and its thermoplastic application. Starch-Stärke. 2009;61:646-55.

[22] Chimonyo W, Fletcher B, Peng Y. Adsorption and morphology of oxidized starches on graphite. Minerals Engineering. 2021;168:106936.

[23] Dimri S, Aditi, Bist Y, Singh S. Oxidation of Starch. Starch: Advances in modifications, technologies and applications: Springer; 2023. p. 55-82.

[24] Chapagai MK, Fletcher B, Witt T, Dhital S, Flanagan BM, Gidley MJ. Multiple length scale structure-property relationships of wheat starch oxidized by sodium hypochlorite or hydrogen peroxide. Carbohydrate Polymer Technologies and Applications. 2021;2:100147.

[25] da Costa Gonçalves C, Bobicki ER, Liu Q. Insight on the mechanism of hexagonal pyrrhotite depression by starch during flotation. Minerals Engineering. 2023;203:108335.

[26] Khoso SA, Gao Z, Tian M, Hu Y, Sun W. Adsorption and depression mechanism of an environmentally friendly reagent in differential flotation of Cu–Fe sulphides. Journal of materials research and technology. 2019;8:5422-31.

[27] Fletcher B, Chimonyo W, Peng Y. The potential of modified starches as mineral flotation depressants. Mining, Metallurgy & Exploration. 2021;38:739-50.