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Froth flotation of scheelite – A review

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ABSTRACT

Froth flotation of scheelite has regained new focus since the 2010s and research regarding floatability and reagents has made great progress over the years. The main objective was and remains the selective flotation of scheelite from other calcium-bearing minerals, in particular calcite, fluorite and apatite. Due to similar properties, most attempts have limited success or only specific application (linked to a type of ore or a location). This article aims at reviewing all general physical-chemical information on froth flotation of scheelite, including electrokinetic properties, influence of pH and already existing reagents as well as ones still under examination. It appears that chelating or mixed collectors and modified versions of sodium silicate and quebracho hold great promise for scheelite flotation, while the use of said depressants and/or promoters seems inevitable.

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1. Introduction

Scheelite (CaWO₄) is one of the main sources of tungsten, alongside with the other monotungstates stolzite (PbWO₄) and wolframite (a solid solution of ferberite (FeWO₄) and hübnerite (MnWO₄)). Scheelite is however more common and is found in approximately 65% of known tungsten deposits [1]. Pale white to brown-orange, scheelite's main characteristic is its blue color under UV, which changes to orange with increasing molybdenum content. Tungsten itself is used in the production of hard wear-resistant tungsten carbides used especially in the tool industry, but also in alloys, steels and chemical compounds [2].

When coarse, scheelite can be concentrated by gravity separation. However, as a brittle mineral (hardness of 4.5–5 on Mohs scale), it tends to slime easily during comminution. Finely grained scheelite is usually processed with froth flotation [3], which has only been the way to go since the 1970s [4]. This explains the increased interest in scheelite flotation in the 1970s (Fig. 1) whereas the renewed focus on scheelite flotation since the 2010s is linked to the depletion of wolframite resources in China [5].

This article aims at reviewing the research conducted on solubility and electrokinetic properties of scheelite as well as establishing a landscape of flotation reagents developed by researchers for its flotation. Most of said reagents look at the separation of scheelite from calcium minerals, especially calcite. It will be shown how this task is and has been complicating scheelite flotation for over 50 years [4,6–10], even though relative successes are to be reported.

2. Solubility and electrokinetic properties of scheelite

Scheelite is considered as a polar salt type mineral, similarly to apatite, bornite, fluorite and carbonates such as calcite, magnesite

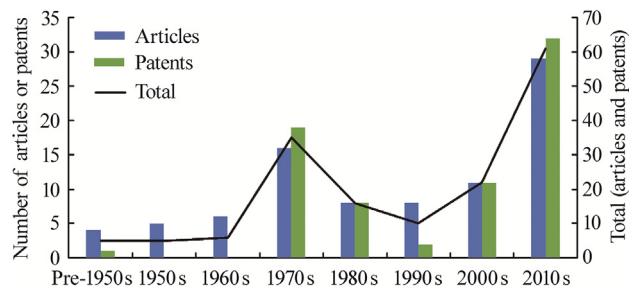


Fig. 1. Articles and patents related to scheelite flotation over the last 80 years.

and dolomite [11]. As a polar mineral, it exhibits relatively strong ionic surface bonding with high free energy values at its surface, allowing it to react with water molecules, making it hydrophilic [12]. It is therefore also semi-soluble.

The solubility product of scheelite in water at 25 °C remains constant at pH > 6 with a mean value of 8.87×10^{-9} [13] or 4.9×10^{-10} [14], $\log(K_{sp})$ varies between -8.05 and -9.31 . Scheelite solubility increases greatly below pH 6. Above pH 6, the molar concentration of WO₄²⁻ ions is much greater than Ca²⁺, exhibiting therefore a differentiated dissolution theoretically incompatible with the structure of the lattice ions [13,14].

When electrostatic interactions drive the adsorption of the collector, the surface charge information becomes crucial [15]. Having an ionic crystal structure, the surface charge of scheelite is determined by the Ca²⁺ and WO₄²⁻ ions in aqueous solutions [16,17]. The free energy of hydration of the calcium ions (Ca²⁺) is -1.50 MJ/mol while that of the tungstate ions (WO₄²⁻) is -0.68 MJ/mol, therefore tungstate ions will end up in light stoichiometric excess in the near-surface region as the calcium ions are preferentially removed [15]. Furthermore, Neiman has shown that the mean length of W–O and Ca–O bonds is of 1.777 Å and 2.458 Å in scheelite respectively, calculating corresponding bond energies of 610 kJ/mol and 130 kJ/mol [18]. This means that during breakage of scheelite, W–O covalent bonds will remain intact whereas Ca–O ionic bonds will break, generating an ionic surface.

As a consequence, scheelite is negatively charged almost over the whole pH range [14–16,19] but will tend towards its isoelectric point when Ca²⁺ ions are highly concentrated in the solution [16,17]. Hu and Xu are the only authors to report an isoelectric point of scheelite at pH 2 [9].

In the classical sense, scheelite should always exhibit a negative charge in flotation pulps except in potentially very hard waters. Yet, recent research has shown that the surface charge of minerals is not uniform over the whole mineral surface [20–22]. This had also been looked at before [23].

Scheelite occurs in the tetragonal system, mostly in the dipyrmidal form 4/m. Hu et al. [24] and Gao et al. [15,25] have made significant contributions in building the links between anisotropic surface broken bonds, cleavage, surface charge, surface energy and wettability of scheelite crystal. The most commonly exposed surfaces of scheelite particles are {112}, {101} and {001} [15,26], with cleavage being interrupted, distinct and indistinct respectively (Fig. 2).

When a specific scheelite surface is created, oxygen atoms lose bonds to calcium ions or are under-coordinated with the tungstate groups, resulting in dangling bonds and a reactive and unstable

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