

Investigations on flotation separation of scheelite from calcite by using a novel depressant: Sodium phytate

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ARTICLE INFO

Keywords:

Flotation
Sodium phytate
Scheelite
Calcite
Chelating adsorption

ABSTRACT

In this paper, sodium phytate, a phosphate ester salt rich in phosphate groups, was evaluated as a flotation depressant for selective separation of scheelite from calcite. Its adsorption mechanism on the mineral surface was also investigated through zeta potential and FTIR spectra analysis. The micro flotation results of both single and mixed binary minerals showed that sodium phytate exhibited strong depressant effect on calcite flotation while had little influence on scheelite flotation, when it was added before the collector sodium oleate. Using sodium phytate as depressant improved the flotation separation of scheelite from calcite in the pH range of 7–12. The results of zeta potential measurements and FTIR spectra analysis demonstrated that sodium phytate adsorbed on the calcite surface and hindered the subsequent chemisorption of sodium oleate. The chelating adsorption mainly consisted of the interactions between Ca^{2+} on calcite surface and the PO tetrahedron in sodium phytate. Sodium phytate did not adsorb on the surface of scheelite and did not hinder the subsequent coverage by the collector sodium oleate. Based on these findings, sodium phytate has the potential to act as an effective depressant in flotation separation of scheelite from calcite.

1. Introduction

Tungsten is an important rare metal and has wide application in modern industry. Scheelite, a typical tungsten-containing mineral (CaWO_4), is the main resource for producing tungsten from ore deposits in the field of mineral processing. Scheelite is usually associated with other calcium-containing minerals in deposits, such as calcite (CaCO_3), fluorite (CaF_2) and fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$]. Among these gangue minerals, calcite is often regarded as the least valuable one and must be removed (Castro and de Borrego, 1996). Flotation, a physico-chemical separation process that utilizes the difference in surface properties of the valuable minerals and the unwanted gangue minerals (Wills and Napier-Munn, 2005), is the main technique to recover scheelite from calcite and other gangue minerals at the present time (Hu et al., 2012).

In scheelite flotation, fatty acids and their derivatives are the most commonly used collectors. However, due to the same active Ca^{2+} species on the cleavage surfaces of scheelite and calcite, the two minerals often exhibit similar reactivity to these fatty acids collectors, which causes poor selectivity in flotation (Pradip et al., 2002). It has been widely recognized that the fatty acids collectors can collect both scheelite and calcite through chemisorption by forming calcium dicarboxylates on the mineral surfaces (Atademir et al., 1981; Ozcan and

Bulutcu, 1993; Rao et al., 1990; Rao and Forsberg, 1991). Therefore, it is almost impossible to separate scheelite and calcite without any depressant, when the fatty acids are used as collectors in flotation of calcitic scheelite ore.

Depressants, aiming at reducing the flotability of calcite under scheelite flotation conditions, are widely used in scheelite flotation plants to improve the flotation selectivity. The depressant effect is mostly realized through the selective interactions between the Ca^{2+} on calcite surface and the functional groups in the inhibitors. The most common functional groups are silicate, hydroxy, carboxyl and phosphate, corresponding to the reported inhibitors shown in Table 1. The depressants with functional groups including silicate, hydroxy and carboxyl, are reported to make calcite surface hydrophilic by adsorbing and forming new hydrophilic species on particle surface. However, these reagents often show limited selectivity in scheelite flotation practice because they also depress scheelite to a large extent.

Of all the reported depressants in Table 1, phosphates (see Fig. 1) are special kinds because their depressant effect on calcium minerals is not related to their adsorption and formation of new species on particle surface. It has been demonstrated that the phosphates depress the calcium minerals by dissolving and complexing the Ca^{2+} on mineral surfaces, which is intimately influenced by the pulp pH and phosphate

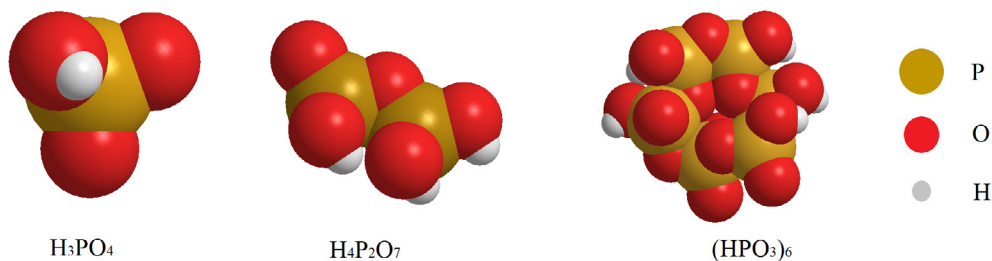
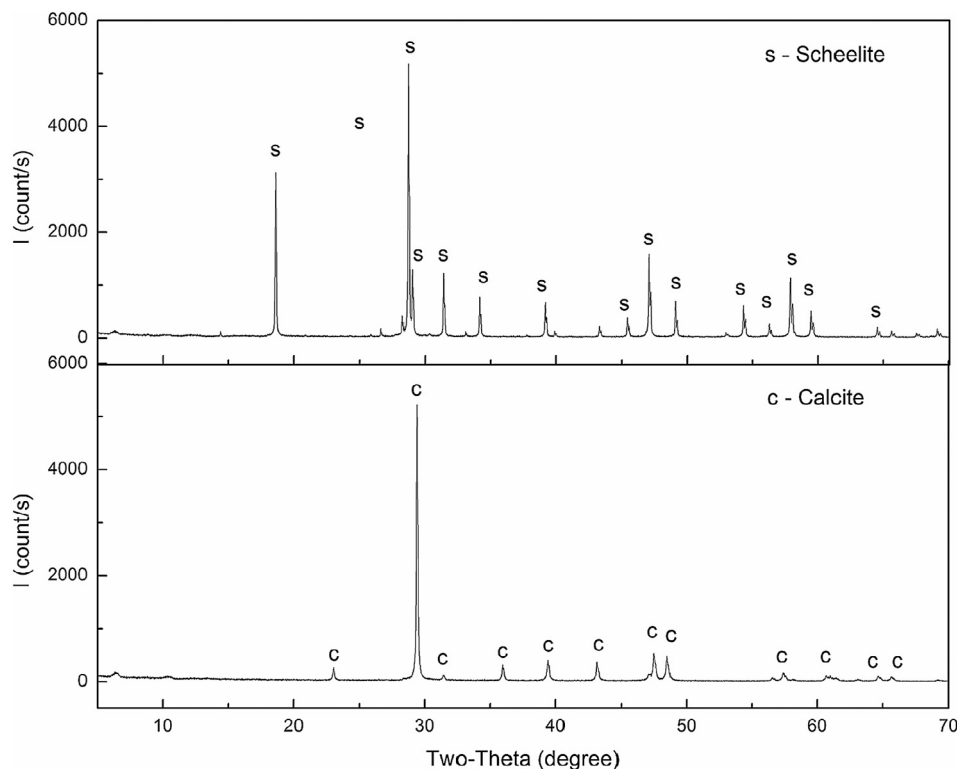
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Table 1

A classification of reported calcite depressants according to the functional groups.

Functional group	Depressants
Silicate	Water glass (Haisheng et al., 2017; Marinakis and Shergold, 1985), acidified water glass (Bo et al., 2015), salinized water glass (Bo et al., 2017)
Hydroxy	Quebracho (de Castro and de Hoces, 1993; Ozcan and Bulutcu, 1993), pyrogallol (Chen et al., 2017a), tannin (Liu et al., 2016)
Carboxyl	Sodium polyacrylate (Zhang et al., 2017), carboxymethyl cellulose (Tian et al., 2017), alginate (Chen et al., 2017b)
Phosphate	Sodium phosphate, sodium pyrophosphate, sodium hexametaphosphate (Yongxin and Changgen, 1983)

**Fig. 1.** 3-D space-filling model of some phosphates (represented by relative acids) used in flotation.**Fig. 2.** XRD spectra of the scheelite and calcite samples.

structure in solutions (Changgen and Yongxin, 1983). It has been found out that the preferential flotation separation of scheelite from calcite could be realized by using phosphates as flotation depressants, by control of pulp pH range of 9.0 for Na_3PO_4 , 8.0 for $\text{Na}_4\text{P}_2\text{O}_7$ and 9.5–10.5 for $(\text{NaPO}_3)_6$, respectively (Changgen and Yongxin, 1983; Gao et al., 2018). However, the best pH ranges that the phosphates work are too narrow to be precisely controlled in flotation plants. As a result, the depressant effect of phosphates in scheelite flotation is often discounted and the efficient separation of scheelite and calcite remains challenging.

Phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$) is a naturally occurring phosphate ester in legume seed, cereal grains and beans (Sandberg and Scheers, 2016). It is easily available from agricultural products and can exist in aqueous solution stably. As an organic macromolecule compound, phytic acid

has 12 free hydroxyl groups and 6 phosphate groups on its carbon ring in one molecule, hence exhibiting powerful chelating capability with many metal ions (Torres et al., 2005), as shown in Fig. 3. Phytic acid is generally used as the corrosion resistant inhibitor for the paint or pigment (Nan et al., 2015; Notoya et al., 1995). It is also reported to act as the reactant to form conversion coating in alloy materials (Cui et al., 2008; Pan et al., 2009). However, there are few published papers referring to utilizing its chelating capability in flotation field, especially in the separation of scheelite and calcite.

In this paper, a sodium salt of phytic acid named sodium phytate (SP) was evaluated as a novel phosphates depressant for calcite in scheelite flotation using sodium oleate (NaOl) as collector. The effects of SP on the flotation performance of scheelite and calcite were investigated. The adsorption mechanism of SP and NaOl on mineral

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