A Novel Strategy for Sylvite Flotation through Controlled Crystallization

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RESUMEN

As one of the most valuable treasures on our planet, soluble or semi-soluble minerals such as phosphogypsum, calcium carbonate, fluorite, and another important type-inorganic salt like sylvite-are significant. Froth flotation has been widely recognized as a powerful method for recovering various minerals. Numerous efforts have been dedicated to improving flotation recovery through methods such as exploring new types of collectors, using different grinding media, and adjusting mineral surface properties. However, most of these methods focus on fine-tuning the end stages rather than addressing the mineral properties that hinder the flotation process, such as exposed faces and shapes, which could potentially enhance mineral recovery. Here, taking sylvite as an example, the crystal growth of its component crystal KCl was carefully controlled to produce samples with varied shapes and structures. The flotation behaviors of these samples were then described. The crystallization-controlled methodology was applied to help modulate KCl samples with various exposing faces and particle shapes. Further, their growing mechanism, properties as well as flotation behaviors were well researched to yield a better understanding of improved flotation recovery.

PALABRAS CLAVE: *Sylvite flotation; controlled crystalization; facets and morphologies*

ANTECEDENTES

Sylvite (KCl) a key water-soluble mineral, has been extensively mined and processed for the production of potassium compounds used in agriculture, as well as in various other industries such as medicine, batteries, ceramics, and plastics. Since the 1940s, most potash ore extraction has relied on flotation methods in the potash industry. With increasing demand for potassium and declining ore grades, there is a growing global need for potassium supply. Therefore, improving flotation recovery remains essential for optimizing industrial flotation systems.

Improving the recovery of potash ores during flotation primarily involves adjusting the hydrophobicity of crystal surfaces and enhancing the selectivity of bubble-crystal interactions. Over the decades, research has focused on developing a variety of surfactants, known as collectors, which consist of a hydrophilic group and a hydrophobic chain, to optimize flotation selectivity and performance. Early examples include primary alkylamines (RNH_2), followed by sodium alkylsulfites ($R\text{-}SO_3Na$), sodium alkylsulfates ($R\text{-}OSO_3Na$), and fatty acids (R-COOH). Despite the wide application of these collectors in the industry, further improvements in flotation recovery are still necessary.

Most minerals are crystalline in nature, characterized by standard repeating units and distinct crystallographic planes. These crystal samples exhibit varied physical and chemical properties depending on which faces are exposed. To achieve desired effects, the specific morphology and exposed faces must be carefully targeted. Typically, natural crystallographic habits are minimally affected under normal conditions due to thermodynamic equilibrium during crystallization. However, crystal structure, morphology, and surface properties can vary based on crystallization kinetics.

Investigating methods to design crystals without the use of additives holds significant scientific and technological importance, as it can lead to more environmentally friendly approaches for industrial crystal applications. The tendency of crystals to grow in clusters offers new insights into the controllable design of crystals by adjusting general parameters such as crystallization rate, supersaturation, and temperature. In this study, potassium chloride (KCl), one of the most important naturally occurring crystals, was used as an example to explore strategies for the controlled formation of crystals.

METODOLOGIA EXPERIMENTAL

Experimental design

A designed vertical cylindrical jacketed crystallizer with 250 mL capacity combined with mechanical stirring machine and a double blade parallel stir bar with length of 2 cm was performed, where warm water bath was provided by a constant speed programmable thermostatic bath to realize an accurate modulation with minimal configuration of 0.01 ◦C. By means of modulating cooling range, cooling rate and reaction period of water bath, the KCl crystals with different morphology were grown in the crystallizer.

RESULTADOS Y DISCUSIÓN

Various morphologies of KCl crystals were successfully prepared, including hollow cubic, smooth cubic, hopper, and spherical forms, as shown in the inserted images in Figure 1. The corresponding XRD results confirmed that all samples exhibited high purity and crystallinity. It was evident that the smooth cubic structure had a high percentage of (200) faces, while the hollow cubic crystals displayed relatively more (220) faces, likely due to inner beveling. The hopper crystals, with their complex exposed surface areas, revealed additional (222) faces. In contrast, the spherical crystals exhibited limited (200) and (400) faces due to their isotropic nature. In conclusion, the distinct shapes and specific exposed crystal faces contribute to varying face intensities, indicating potential applications based on the properties of these exposed surfaces.

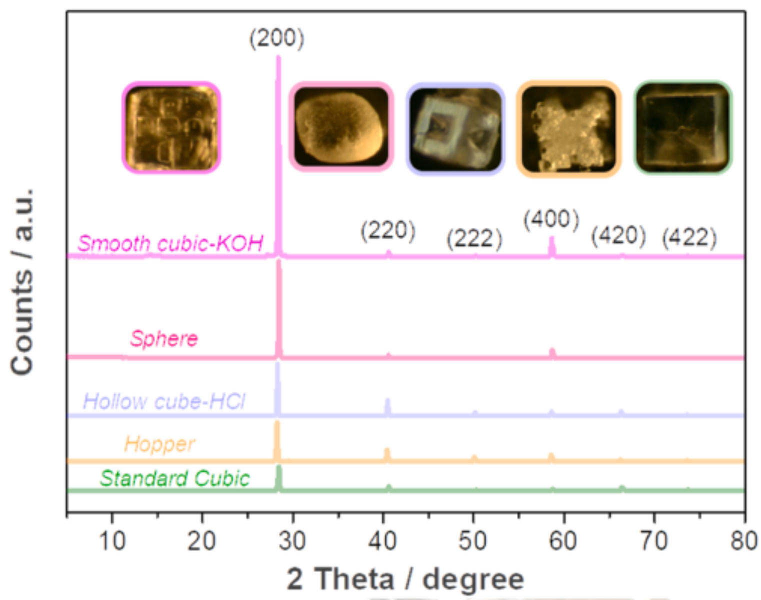

Figure 1. XRD results of smooth cubic with KOH, sphere, hollow cube with HCl, hopper and standard cubic KCl structure, and corresponding stereoscopic results.

The flotation experiments of two types of crystals with (200) and (222) exposing faces with size range at 178–250 μm using ODA (Octadecylamine hydrochloride) as collector were conducted, and the flotation kinetics results were shown as Figure 2. Both flotation recovery in the process were highly coincident with classical first-order model. The flotation rate of KCl (200) was higher than that of KCl(222). The KCl(200) samples achieved a recovery at 83.35%, while recovery of KCl(222) was about 53.42%, demonstrating a better interaction between cubic KCl crystals with bubbles under collector as ODA.

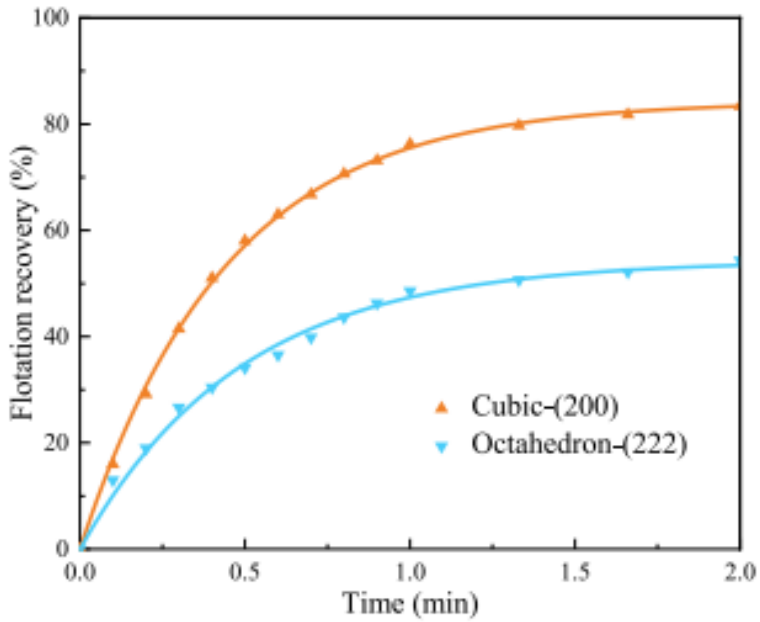

Figure 2. Flotation kinetics results of KCl(200) and KCl(222) crystals using ODA.

CONCLUSIONES

A green and controllable method was developed for the preparation of KCl crystals with various structures and morphologies through supersaturation modulation. In this study, hopper-, sphere-, and hollow cube-like crystals were successfully obtained. Key parameters such as stirring speed, seed additives, pH conditions, and cooling range and rate were thoroughly investigated and explained within the context of supersaturation modulation. Under specific conditions, the crystals grew uniformly, while under others, they formed smaller pieces or experienced crystal abrasion. The resulting products were analyzed in terms of structure, morphology, and surface properties. The KCl crystals with exposed (200) and (222) faces demonstrated flotation recoveries of 83.35% and 53.42%, respectively.

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