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Effects of crystal chemistry on sodium oleate adsorption on fluorite surface investigated by molecular dynamics simulation

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ABSTRACT

The surface properties of minerals are governed by the crystal chemistry of their cleaved and exposed surfaces, which will vary with the reduction of particle size under mechanical crushing or grinding. Molecular dynamics (MD) simulations were used to study the adsorption conformations and interaction energies of sodium oleate (NaOL) on different fluorite (CaF_2) surfaces in an explicit solution system. Three fluorite crystal planes, namely, the (1 1 1) surface, the (1 1 0) surface and the (3 1 1) surface, were considered. Anisotropic surface energies and broken bond densities were calculated based on density function theory (DFT) to confirm the cleavage plane of fluorite and to investigate the crystal-chemical characteristics of fluorite crystal planes. It was demonstrated that NaOL preferentially combined in a bridged ring complex configuration with the most stable plane of fluorite, the (1 1 1) surface, which bears a Ca···F broken bond density of 100%. The exposure of the (1 1 0) surface of fluorite limited its flotation response to NaOL collectors, as this surface exhibited a lower affinity for NaOL, agreeing well with the results of the fluorite flotation experiments performed with different size distributions. The anisotropy of fluorite with different size fractions was further verified by X-ray diffraction (XRD) analyses. The findings in this work suggest that the flotability of fluorite could be further improved if a selective grinding process is applied to favour the exposure of the (1 1 1) surface.

1. Introduction

Fluorine (F) is known to be an indispensable chemical material that has been utilized in various fields of research, such as new energy, new materials, optoelectronics, and metallurgy (Gao et al., 2016). Fluorite (CaF_2), containing 48.67% fluorine, is by far the most important fluorine bearing mineral phase in the Earth's crust (Akgün et al., 2006; Garand and Mucci, 2004; Zhang and Song, 2003). In addition to the production of hydrofluoric acid, fluorite is also significant as an ultraviolet optical material for integrated circuit lithography, as well as being used to produce a semiconductor on insulator structures (Engelhardt et al., 2000; Free and Miller, 1997; Velichko et al., 2007).

To obtain high grade fluorite ($CaF_2 \geq 97\%$), flotation has been considered as the most commonly used beneficiation process for fluorite separation from gangue minerals, normally employing fatty acid collectors and sometimes associated with highly selective depressants. The flotation separation of fluorite from calcium bearing minerals, such as calcite and scheelite, is challenging, compared to all other gangue minerals, due to their similar solubility and having the same active Ca site that interacts with anionic collectors (Gao et al., 2015; Xu et al., 2016). Several researchers have investigated new flotation schemes, mixture collectors and novel depressants in fluorite flotation systems and have achieved excellent results (Gao et al., 2015; Ren et al., 2017; Zhang and Song, 2003). The long-chain fatty acids and their alkaline salts, especially oleic acid and sodium oleate (NaOL), are the most extensively used collectors for fluorite flotation. In addition, the interaction mechanisms of fatty acid adsorption on calcium minerals, such as physisorption, chemisorption and surface precipitation, have been previously reported in the literature (Chennakesavulu et al., 2009; Fa et al., 2006; Pugh and Stenius, 1985; Rao et al., 1988; Somasundaran, 1969; Young and Miller, 2000). Most of these findings revealed that the interaction between collectors and Ca sites on a mineral surface was mainly influenced by the solubility, surface species, surface charge and zeta potential, among other factors. It is worth noting that the surface properties of minerals, such as surface charge and surface free energy, are significantly determined by the crystal chemistry of the cleaved and exposed surface (Gupta and Miller, 2010; Yan et al., 2013; Yin et al., 2012). Moreover, the cleaved and exposed surface of a mineral can differ greatly under various crushing and grinding processes. Therefore, we investigate the properties of different

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Table 1
Chemical component of fluorite samples.

Sample	Mass fraction/%										
	F	Mg	Al	Si	P	S	Ca	Fe	Sr	Ba	L.O.I[a]
S1	48.11	0.02	0.02	0.02	–	0.13	50.33	–	0.02	0.84	0.50
S2	48.28	–	0.04	0.70	0.01	0.01	50.45	0.02	0.02	–	0.49
S3	48.43	–	0.15	0.96	0.01	0.01	49.65	0.07	0.02	–	0.72

[a] Loss on ignition.

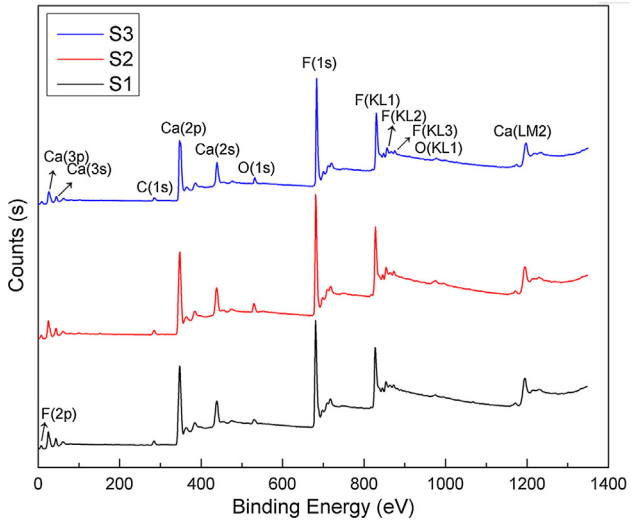

Fig. 1. XPS patterns of powdered fluorites.

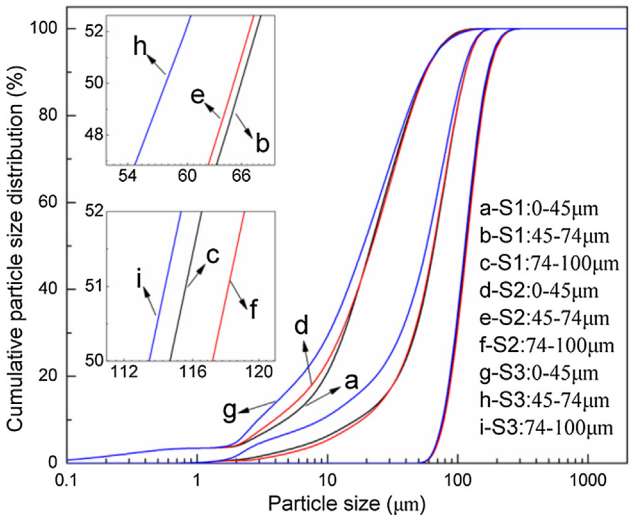

Fig. 2. Cumulative size distribution of fluorites.

fluorite cleaved planes and their adsorption behaviour for NaOL collectors in this work.

Recently, computational simulations have become a powerful tool and are widely applied to surface engineering, such as in the adsorption of reagents on mineral surfaces at an atomic level. For instance, Araghi et al. (2016) and Araghi and Zabihi (2013) investigated the interaction between Co_{55} nanoclusters and a Cu (0 0 1) substrate, and the growth of CdTe on a Si (1 0 0) surface with the help of computational simulations. These studies demonstrated the great importance of simulation results due to their guiding roles in the experiments. Maldonado et al. (2013) have successfully predicted the surface stability of fluorite utilizing first-principle simulations, indicating that the fluorite (1 1 1) surface

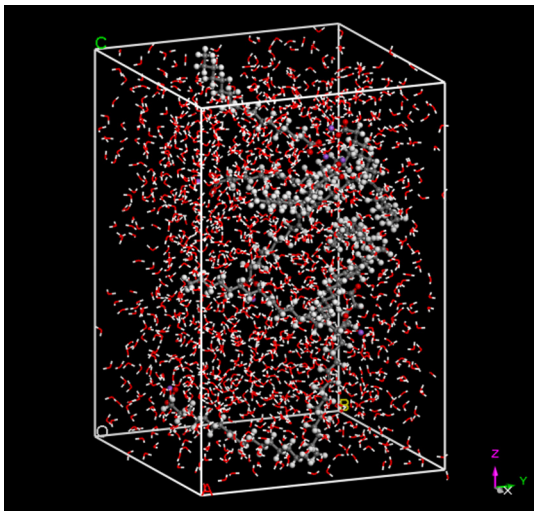

Fig. 3. Model of NaOL solution box.

was the most stable crystal plane since it had the lowest surface energy. Gao et al. (2012, 2014) calculated surface energies and surface broken bond densities of several fluorite crystal planes based on density function theory (DFT) and found a linear correlation between surface energy and the broken bond density of fluorite. Leeuw (1998) and Pradip et al. (2002a, 2002b) researched the interactions between calcium mineral surfaces and surfactants, including methanoic acid, alkyl hydroxamates and diphosphonic acid reagents, using an atomistic simulation technique and a molecular modelling approach. These researchers showed that the simulation results matched remarkably well with the experimental micro-flotation test results and proposed that such computational simulations should be capable of predicting adsorption behaviour and designing collector molecules, both of which are of central importance to the mineral processing technique of flotation.

Empirically, the flotation separation of minerals is usually conducted in a solution system, and water plays a significant role in both reagent hydrolysis and dissolution of mineral particles. However, in most simulation studies, the effects of a solution on the liquid-solid interface were simplified or ignored, and the simulations were undertaken in a vacuum system. In the present work, the surface crystal chemistry of normal cleaved and exposed planes of fluorite crystals, namely, the (1 1 1) surface, the (1 1 0) surface and the (3 1 1) surface were characterized by calculating their surface energies and broken bond densities based on DFT. Furthermore, the adsorption behaviours of NaOL on the three fluorite crystal planes, and the related adsorption conformations and interaction energies, were investigated by molecular dynamics (MD) simulations in an explicit solution system coupled with flotation experiments, collector adsorption measurements and X-ray diffraction (XRD) analyses with different particle sizes.