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Interfacial characterisation for flotation: 1. Solid-liquid interface

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Understanding mineral-chemical interactions at the solid-liquid interface is an aim for all scientists and engineers that focus on mineral flotation, a process of mineral beneficiation. This article highlights some recent results and publications that have made use of advanced tools of physical chemistry, materials science, and colloid/interface chemistry, to gain insight into the properties of the solid-liquid interface of relevance for one of the most dominant processing techniques used in the mining industry. The focus is entirely on methods of interfacial characterisation that can probe the adsorption of flotation chemicals (termed reagents), and the effect of that adsorption, while the system is immersed in solution, thus maximising the relevance of the studies to a complex aqueous colloidal system. Both theoretical and experimental methodologies are addressed.

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1. Introduction

Flotation of minerals is one of the dominant methods of processing used by the mining industry to separate wanted (value) from unwanted (gangue) minerals [1]. The process involves the crushing and grinding of value-containing ore to physically disconnect minerals from each other (to liberate), followed by creating a suspension of minerals in a mixture of chemicals (slurry), and then bubbling air into the mixture. Bubbles rise and collect hydrophobic particles, creating a froth that is collected, while the hydrophilic particles remain in the suspension, and undergo further processing (to recover more value material or to recover water for re-use). It is a complex multi-phase system that involves interfacial chemistry at both solid-liquid and liquid-air interfaces. This article focuses on the former.

Mineral surface properties underpin all separations in flotation [2]. They control whether particles will attach to bubbles or whether they won't, and other than exploiting natural chemical variation or the reactivity of minerals exposed to aqueous solutions, the way that industry influences mineral surface properties is *via* adsorption of chemicals [3]. For the majority of the existence of flotation as an industrial separation process, the influence of adsorbed chemicals has been inferred (either from the study of depletion isotherms when one has an interest in quantifying adsorption, or from the correlation of dosage with flotation outcomes) or studied in a manner that is not representative of the flotation environment (such as removing mineral particles from a slurry and drying prior to analysis).

The most significant advances in understanding and controlling the modification of mineral surface properties has come from pushing against both of these trends, through the direct study of adsorbing molecules on mineral surfaces, with techniques capable of probing the solid-liquid interface (experimentally and theoretically). It is these techniques of physical and interfacial chemistry that are the focus of this review. Specifically, we will look at a collection of techniques that have provided key insights into flotation reagent adsorption (and subsequent impact on bubble-particle attachment) over the last 5–10 years. The literature covered will extend from computational methods to study adsorption, through chemical and physical characterisation of adsorption in experimental studies, and end with a description of the latest work on determining mineral surface hydrophobicity, in a manner that lends itself to understanding and predicting flotation outcomes.

2. Theory and simulation of adsorption

Theoretical and computational techniques have become a valuable tool in fundamental chemical research, particularly in the past decade or so. In 2003, Pradip and Rai [4] predicted that rapid advances in molecular modelling would facilitate a major breakthrough in the design of reagents and collectors for flotation. This prediction has come to pass, with the number of articles published on this topic per year increasing substantially in the past 5–7 years.

Simulation of the interactions between collectors and reagents can provide deep insight into physical and chemical phenomena, facilitating an understanding of the chemical reactivity and adsorption mechanisms, even without detailed experiments [5, 6, 7, 8, 9•, 10]. It provides an important tool to explore water/water and water/mineral interactions in order to gain detailed information and a fundamental understanding of mineral surface potential, surfactant/macromolecule adsorption and mineral floatability [11]. Simulation is particularly useful in cases where more than one mineral surface is exposed, or where the interaction mechanisms are hidden and cannot be easily probed using experimental techniques.

A number of different simulation techniques exist, however two of the most commonly used methods are molecular dynamics (MD) simulations and density functional theory (DFT). MD simulations use a classical potential based on the relevant van der Waals and electrostatic forces to determine the interactions between molecules, and can thereby explore the physicochemical properties of surfactants in solution and the structure of collectors on a metal surface [12]. The knowledge gained from these models can provide information on quantities such as the interaction energies, surface potential, and interfacial reaction, as well as probe the dynamic and thermodynamic characteristics of the adsorption process.

While MD simulations are less computationally expensive than DFT and can provide information about how a system evolves in time, they do not take into account other effects such as electron densities and quantum effects. In addition, an accurate classical potential may be difficult to define and some system properties may be overlooked. Nevertheless, many common collectors adsorb by van der Waals or electrostatic forces so that MD is still a valuable tool, despite its neglect of specific interactions *via* covalent or coordinate bonds, or electron transfer or orbital overlap. Indeed, there are many reported cases where the predicted interaction energy from these methods has been shown to accurately reflect experimental results (see for example Rai [6, 13], Xu et al. [14•]).

In situations where quantum effects are important, the electron density differs widely, or where non-covalent interactions are important (hydrogen-bonds, dispersion forces), DFT provides a reliable and versatile alternative [12]. DFT takes into account chemical interactions in addition to the interactions described above and as a result can provide chemical information about the energetics structure, the properties of atoms and molecules, chemical reactivity, interface chemistry reaction, and the relationship between structure and activity [7]. The interaction energies calculated by DFT can be used to evaluate the affinity and selectivity of a collector to a mineral, and thereby aid in the selection and design of new flotation collectors [12]. DFT can provide more information than MD simulation; however it is comparatively more computationally expensive. Published results show that the theoretical predictions of DFT are consistent with experimental flotation tests, FTIR spectra studies and zeta potential measurements (see for example Huang [15•]).

In the past, most commercially successful flotation reagents have been discovered by trial and error, or guesswork based on previous experience. With decreasing quality of ore, the high demands of cost, efficiency, and selectivity, and increasing environmental concerns, highly customised and selective reagents that are tailor made for specific applications are required [6]. This is the area in which simulation can be instrumental. Synthesising and testing all possible molecules is not possible, however simulation can provide convenient and efficient screening to facilitate the creation of a short list of candidate reagents that can then be extensively tested experimentally. In addition, if a specific molecular recognition mechanism can be identified, more selective and efficient reagents can be designed, where a specific molecular architecture can be targeted based on the calculated interaction energies [6].

3. Particle film ATR FTIR

FTIR spectroscopy is heavily used in flotation research, as it is in many fields of science that require an understanding of adsorption phenomena. Peaks due to the absorption of infrared radiation are indicative of the presence of particular molecules and bonds within those molecules. In addition, the versatility in sampling for particulate systems makes the technique amenable to the study of reagent adsorption on mineral particles. KBr disc preparation of