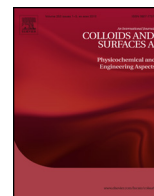




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Specific surface free energy component distributions and flotabilities of mineral microparticles in flotation—An inverse gas chromatography study

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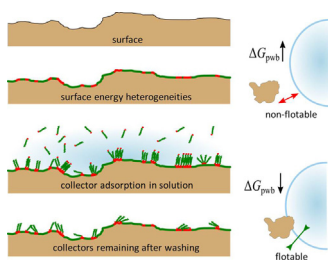
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HIGHLIGHTS

- Mineral microparticle surfaces exhibit heterogeneous surface free energies.
- Wettability heterogeneities are well characterized by inverse Gas Chromatography.
- Surfactants have most effect on and reduce the high energy sites of surfaces.
- Surface area fraction relevant to render a surface floatable is less than 1%.
- Energy-of-interaction vs. flotability correlate stronger at small fractional area.

GRAPHICAL ABSTRACT



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ABSTRACT

In fundamental flotation studies often the contact angle with water is used to describe wettability of a mineral surface and it is correlated with flotability. A more fundamental parameter however is the specific surface free energy related to the contact angle via Young's equation. Inverse gas chromatography (iGC) has recently been proven to be a suitable method to determine specific surface free energy components and their distributions of particulate surfaces. In this study the pure minerals quartz (SiO_2), fluoro-apatite ($\text{Ca}_5[\text{F}(\text{PO}_4)_3]$), and magnetite (Fe_3O_4) are examined for flotabilities and surface energy component distributions considering different methods of sample treatment and the effect of the collectors sodium oleate and dodecyl ammonium acetate. The parameter of specific net free energy of interaction between bubbles and particles immersed in water ΔG_{pwb} resulting from the complex surface energy analyses is introduced and used to evaluate the hydrophobicity of the mineral surface in correlation to microflotation recoveries. The results lead to the hypothesis that only small fractions of the surface and their change of wettability by flotation reagent adsorption will inherently define the flotability of minerals. Consequently, the main purpose of the amphiphilic collector molecules seems to be the reduction of high specific surface free energies of small fractions of the surface that lead to a strong attraction between particle surface sites and water molecules rather than the hydrophobization of the entire mineral surface, a new paradigm in flotation science.

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1. Introduction

Flotation is a well-established and widely used separation process in minerals engineering and recycling. Nevertheless, scien-

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tifically, the complex synergistic and antagonistic micro processes are underlying ongoing research and controversial discussions [1–7]. Since flotation is a separation method based on the different wettabilities of the particles to be separated, many researchers have been looking for functions of the flotation recovery and contact angles against water as a parameter to account for wettability [1,8–10]. However, the determination of particle wettability is not a straight forward task as classic sessile drop contact angle determinations or the captive bubble method should be avoided on powder samples for the porosity and roughness effects are typically not assessable and penetration methods like the Washburn method are very much structure dependent [11–13]. Furthermore does the sole determination of a contact angle between a surface and the polar solvent water not allow for the description of the surface wettability, as specific and aspecific interactions need to be distinguished [14–17]. Consequently, two surfaces with the same water contact angle can actually be very much different with respect to their hydrophobicity [18]. We apply the relatively new but established method of inverse gas chromatography iGC [19–23] which is capable of describing the wettability of solids by determination of the specific surface free energies of minerals in flotation as has been presented by Mohammadi-Jam [24] recently.

The total specific surface free energies of the interfaces (solid (s) or liquid (l) in gas) in a three phase contact γ^t are related to the contact angle by Young's equation in Eq. (1) [18]. The total specific surface free energy is by assumptions of additivity [14,25] a sum of the disperse interactions γ^d and the quadratic mean of the Lewis acid/base interactions γ^+/γ^- , respectively. Consequently, the contact angle is not the immanent physical parameter of wettability (i.e. hydrophobicity or hydrophilicity) as shown in Eqs. (1) and (2).

$$\gamma^t = \gamma^d + 2 \cdot \sqrt{\gamma^+ \cdot \gamma^-} \quad (1)$$

$$\gamma_{s,l}^t = \gamma_s^t + \gamma_l^t - 2 \left(\sqrt{\gamma_s^d \cdot \gamma_l^d} + \sqrt{\gamma_s^+ \cdot \gamma_l^-} + \sqrt{\gamma_l^+ \cdot \gamma_s^-} \right) \quad (2)$$

To thermodynamically evaluate whether the particle-bubble contact in water (pwb) is favorable, the specific free energy of interaction ΔG_{pwb} as introduced by van Oss is calculated following Eq. (3) [18].

$$\begin{aligned} \Delta G_{pwb} = & \left(\sqrt{\gamma_p^d} - \sqrt{\gamma_b^d} \right)^2 - \left(\sqrt{\gamma_p^d} - \sqrt{\gamma_w^d} \right)^2 \\ & - \left(\sqrt{\gamma_b^d} - \sqrt{\gamma_w^d} \right)^2 + 2 \cdot \left[\sqrt{\gamma_w^+} \left(\sqrt{\gamma_p^-} + \sqrt{\gamma_b^-} - \sqrt{\gamma_w^-} \right) \right. \\ & \left. + \sqrt{\gamma_w^-} \left(\sqrt{\gamma_p^+} + \sqrt{\gamma_b^+} - \sqrt{\gamma_w^+} \right) - \sqrt{\gamma_p^+ \gamma_b^-} - \sqrt{\gamma_p^- \gamma_b^+} \right] \quad (3) \end{aligned}$$

The more negative ΔG_{pwb} the stronger the hydrophobic effect and the more favorable for the particle to form a three phase contact with a hyper-hydrophobic gas bubble when dispersed in water as

depicted in Fig. 1. This approach is similar to the investigations of Holysz and Chibowski [16] where they used the parameter of work of water spreading onto the mineral surface.

Consequently, there should not be a search for the relation of flotation response (recovery of hydrophobic particles) based on the parameter of contact angle with water but rather the net energy of interaction between a bubble and a particle immersed in water taking the specific surface free energy components into account.

The iGC method not only allows for determining the specific surface free energy components of the entire powder surface but can also determine the heterogeneity of surface energies by detecting the specific surface free energy over the fraction of particle surface coverage [19,26]. Hence it can be investigated if e.g. the high energy surface sites at heterogeneities are responsible mainly for hydrophilicity/hydrophobicity because these sites will primarily be covered with collectors when conditioning with flotation reagents.

One drawback of iGC for flotation studies is that the measurement takes place on dried powders but flotation is characterized by particle bubble interactions in a pulp. Therefore we investigated how the preparation of the mineral particles, after collector conditioning to achieve a dry powder, influences both the flotation response after resuspending and the specific surface free energy results of iGC. We tested washing the collector covered minerals with water only and with water and subsequent acetone before drying in an oven at 50 °C. We furthermore look at collectors with chemical or physical adsorption mechanisms. The minerals chosen are pure minerals of fluoro apatite $\text{Ca}_5(\text{F},\text{PO}_4)_3$ (APA), magnetite Fe_3O_4 (MAG) and quartz SiO_2 (QRZ). The collectors are the anionic sodium oleate (NaOl) and the cationic dodecyl ammonium acetate (DDAA). It is well known that NaOl is chemisorbed by calcium-oleate precipitation on apatite under basic conditions whereas DDAA is physisorbed [27–29]. Chemisorption also takes place for NaOl and magnetite by covalent binding to ferric ions on the magnetite surface [30]. For quartz and DDAA physisorption of the cationic collector on the negatively charged surface at close to neutral pH is the presumed mechanism of interactions [31]. We have not found a reference in the literature testing the washing effect on the remaining particle surface wettability.

The direct comparison of iGC results and flotation has so far only been reported by the McGill group of Kristian Waters by Ali [19] and most recently by Mohammadi-Jam [21,24]. Mohammadi-Jam presented a conclusive study on the wettability of pyrite and a correlation of flotability and the work of adhesion, a similar parameter like the free energy of interaction ΔG_{pwb} used here. However they did not focus on the effect of the fractional coverage of the probe molecules of the iGC measurement, which would show surface energy distributions and thus changes in heterogeneity. The unique point of this work therefore is to shed light on the heterogeneity of surface energy components with respect to floatabilities of minerals.

As a result of this study of surface free energy components distributions we present the hypothesis that the collector molecules'

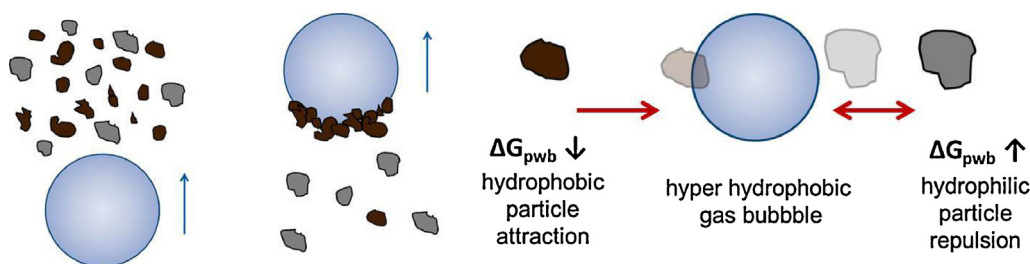


Fig. 1. (left) Schematic of a rising gas bubble picking up hydrophobic brown particles leaving behind the hydrophilic gray gangue, (right) schematic presentation of hydrophobic attraction and repulsion for negative and positive free energy of interaction, respectively, of a particle interacting with the hyperhydrophobic bubble in water.

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