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Introducing inverse gas chromatography as a method of determining the surface heterogeneity of minerals for flotation

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ABSTRACT

Inverse gas chromatography has great potential in allowing an enhanced understanding of mineral surfaces, and the interactions between particles and air and water in mineral processing separations, such as flotation.
Two minerals of different degrees of natural hydrophobicity were investigated, namely galena and quartz. The surface energy was determined as a function of surface area, with the quartz sample displaying a higher work of adhesion, implying a higher degree of hydrophilicity. This was then compared to microflotation experiments. The higher work of adhesion to water for the quartz than galena (114.54 mJ m^{-2} compared to 101.71 mJ m^{-2} @ 5% coverage; 86.78 mJ m^{-2} compared to 71.69 mJ m^{-2} @ 38% coverage) was related to a lower recovery of quartz (6.94%) than galena (27.63%) through collectorless flotation.

1. Introduction

1.1. Flotation

Flotation is a separation process that utilizes the differences in the physico-chemical properties, such as wettability, of different minerals to facilitate their separation. It is one of the most widely used processes in the mining and mineral processing industry with hundreds of millions of tonnes of ore processed annually using flotation. The process is an important ore concentration step used to separate the valuable material in an ore from the waste material (gangue).

1.2. Wettability and surface energy

The wettability or wetting characteristic of a material is a measure of the interaction of the material surface with water. A wettable material is hydrophilic while a non-wettable material is hydrophobic. The most common method of characterising wettability is by the measurement of contact angles. The idea of observing a three phase contact angle created by a fluid sitting on a smooth surface in air was first proposed by Thomas Young in 1805 [1], leading to the well-known Young's Equation (Eq. (1)).

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}. \tag{1}$$

The γ values denote surface tension (or energy) [mJ m^{-2}] at an interface, and the subscript LV stands for liquid–vapour, SL is solid–liquid and SV is solid–vapour. The contact angle at the three phase contact point is θ.

The wettability of a particle surface is vital in the flotation process with the degree of wettability of a material being determined by its surface energy. However, as noted by Sun & Berg, the database of the surface energy of solids is extremely small, especially when compared to that of liquids [2]. Therefore, investigations into the surface energy of solids are of importance, especially in mineral processing.

The total solid surface energy (γ_S^t) is made up of two components: the dispersive surface energy (${\gamma^d}_s$); and the specific surface energy, or the Acid/Base component (γ_s^{AB}). The dispersive component represents the surface energy due to non-polar van der Waals interactions occurring at the surface, while the specific surface energy represents the surface energy due to polar/Acid–Base interactions (hydrogen bonds, ionic bonds, metallic interactions). The total surface energy is simply the sum of the dispersive and specific components [3]:

$$\gamma_s^t = \gamma_s^d + \gamma_s^{AB}. \tag{2}$$

Recent work on surface energy suggests that the specific surface energy (γ_S^{sp}) is best described in terms of acid/electron acceptor (γ_S^+) and base/electron donor terms (γ_S^-) [4], as shown in Eq. (3).

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+\gamma_s^-}. \tag{3}$$

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The work of adhesion, W_{adh}, is defined as the difference in interfacial energy between adhering and individual separated phases. Therefore, this parameter provides a direct indication of the wettability of a material (Eq. (4)).

$$W_{adh} = \gamma_{LV}(1 + \cos\theta). \tag{4}$$

W_{adh} is directly related to the surface energy of a solid and may be calculated from the surface energy using Eq. (5):

$$W_{adh} = 2\left[\sqrt{\left(\gamma_S^d \gamma_L^d\right)} + \sqrt{\left(\gamma_S^+ \gamma_L^-\right)} + \sqrt{\left(\gamma_S^- \gamma_L^+\right)}\right]. \tag{5}$$

As indicated by Eq. (4), there is a direct correlation between the work of adhesion and the surface energy of a solid material. In the case of flotation, where the interaction between a solid and an air bubble in an aqueous medium facilitates the separation, it is the work of adhesion to water that is of interest. As the surface energy increases (more hydrophilic), the work of adhesion increases and therefore the wettability of the material is higher. This work investigates the surface energy of two minerals (galena and quartz) using inverse gas chromatography, and compares this to small scale flotation.

1.3. Inverse gas chromatography

1.3.1. Theory

Conventional gas chromatography (GC) is used to determine the composition of an unknown volatile vapour mixture. The vapour is passed through a column containing a packed bed of a known solid, and the elution peaks of the components of the vapour detail what they are. In inverse gas chromatography (iGC), a known volume of a known vapour is passed through a column containing particles under investigation. The elution peak obtained gives information on the surface properties of the material. In order to determine the dispersive component of the surface energy, a series of non-polar probes must be used to obtain a linear relationship between the net retention volume (V_N) and the surface tension of the non-polar probe. In practice, the probes are a series of n-alkanes of an increasing carbon chain length.

The solid mineral sample under investigation is the stationary phase while a carrier gas, such as helium, acts as the mobile phase [5]. Various vapour probes are injected, one at a time, carried by the carrier gas into a chromatograph column containing the solid particles. The probe molecules adsorb onto, and then subsequently desorb from the solid. Following the desorption, the probe molecules travel to a Flame Ionization Detector (FID), which feeds data to a computer allowing the determination of the retention time curve for each probe on the solid.

The iGC technique is widely used in the study of polymers (both synthetic and biological), polymer blends, glass, pharmaceutical powders, carbon fibres and solid foods. Common properties measured include polymer crystallinity, phase transition temperatures, solid surface area, adsorption characteristics, diffusion parameters and Acid–Base characteristics. Gamble et al. used the iGC technique to investigate the surface energy characteristics of an active pharmaceutical ingredient [6], Menzel et al. studied the structural and chemical surface properties of carbon nanotubes using iGC [7], and Bardavid et al. used iGC to study the interaction parameters of anionic surfactants [8]. Dove et al. compared the dispersive and polar components of the surface energy as measured using two different contact angle measurement techniques (Wilhelmy Plate and a glass slide method) and inverse gas chromatography. It was noted that the dispersive components as measured by all three methods were identical, but the manipulation of the data led to the Acid/Base (polar) components not being directly comparable [9]. The iGC has a number of advantages compared to contact angle measurements; it is much more suitable for minerals used in flotation or similar processes where flat solid surfaces are not available. Additionally, the iGC technique requires only a small mineral sample for analysis (~1–4 g).

From Schultz et al. [4], Eq. (6) can be used to determine the dispersive component of the surface energy:

$$RT \ln V_N = 2Na_m\sqrt{\gamma_S^d \gamma_L^d} + C. \tag{6}$$

R is the gas constant (J mol^{-1} K^{-1}); T is the absolute temperature (K); V_N is the net retention volume (ml g^{-1}); N is Avogadro's Constant (mol^{-1}); a_m is the area of the probe molecule (m^2); and C is a constant. A plot of RT ln V_N against $a_m\sqrt{\gamma_L^d}$ yields a straight line, the gradient of which allows the calculation of $\gamma^d{}_s$. To determine the Acid/Base components, a mono-polar probe molecule is used, and the difference between the RT ln V_N and the line from Eq. (6) allows the calculation of the Gibbs Free Energy and then the Acid/Base components.

Dorris & Gray developed a technique to determine the dispersive surface energy using the carbon number on the alkane chain [10,11], however this technique does not allow the easy determination of the Acid/Base component. For a more detailed description of the equations used in determining the surface energy through iGC, please refer to Voelkel et al. [3], Jefferson et al. [12], and Ho and Heng [13].

1.3.2. Inverse gas chromatography investigations of minerals

Inverse gas chromatography has been used in limited studies of mineral surfaces, and as yet the wetting characteristics have not been investigated. Bandsoz et al. used iGC to investigate the surface properties of clays from a Wyoming bentonite sample, including the effect of adding polymers to the surface of the samples [14]. In the majority of cases, it has been plate-like minerals such as clays and talc that have been investigated using iGC [15–19].

There have been a few exceptions, including the effect of temperature on the free energy of adsorption of probes onto a hematite sample [20], and Milonjic who investigated the surface free (dispersive) energy of naturally occurring magnetite, as a function of temperature, as well as synthetic sulphides [21]. In addition, Sun and Berg investigated the effect of moisture on the surface free energy of oxides as well as the free energy of adsorption of polar molecules (ΔG^{AB}), but did not investigate the potential link with mineral processing [2].

2. Experimental

2.1. Materials preparation

2.1.1. Minerals

The two minerals investigated in this project were galena and quartz. These two materials were chosen because galena is a sulphide mineral with a certain degree of natural hydrophobicity (and a major mineral in lead production) while quartz is naturally hydrophilic. Therefore, a difference was expected in both the measured surface energies and flotation responses of these materials. Crystals of galena and quartz were obtained from Ward's Scientific (United States of America). The samples were in the form of large crystals and were crushed in a jaw crusher (Svedala Industries Inc.) and ground in a drum mill (Siebtechnik) to obtain a particle size of 100% passing a screen with a 106 μm aperture.

2.1.2. Analysis

The N_2 BET specific surface area was measured using the Tristar 3000 surface area and porosity analyser (Micromeritics, GA, USA).

2.2. Inverse gas chromatography

Inverse gas chromatography was carried out using the Surface Energy Analyser, SEA (Surface Measurement Systems Ltd., UK). The samples were placed in presilanised glass columns, with an internal diameter of 4 mm. The mass of mineral added was that which gave a total exposed