The enthalpy of immersion as an indicator of mineral surface wettability.

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ABSTRACT

The enthalpy of immersion is a very sensitive measure of the enthalpy produced when a liquid, such as water, interacts with a dry mineral surface. The extent of the interaction is dependent on the polarity (or wettability) of the mineral surface. This technique has had little application in the mineral processing literature and is introduced here as a potentially useful tool in characterising mineral surfaces with relation to their wettability and hence floatability since usually contact angle is used as an indicator of wettability. Enthalpies of immersion for different minerals were compared with their powder contact angles and these then related to their microflotation recoveries since microflotation is a good indicator of the hydrophobicity of a mineral particle.

It has been shown that the enthalpy of immersion technique was capable of distinguishing differences in wettabilities of different minerals and these differences are explained in terms of the solid state properties of the minerals. A critical enthalpy of immersion has been established to be in the region of -200mJ/m². When values are more negative than this value minimal flotation occurs. At values more positive that this value, the flotation rate constant was found to be inversely related to the magnitude of the enthalpy of immersion.Moreover it was found that the enthalpy of immersion is a more reproducible and sensitive indicator of wettability than the contact angle.

KEY WORDS

Enthalpy of immersion, solution calorimetry, microflotation, contact angle

1. Introduction

Wettability, defined as a measure of the extent of interaction of a given mineral with water, is central to the flotation process. A wettable mineral is hydrophilic while a non-wettable mineral is hydrophobic. In the flotation process, sufficiently hydrophobic particles attach to air bubbles forming stable bubble-particle agglomerates which report to the froth phase. For a given particle size, a critical hydrophobicity is required before flotation occurs (Blake & Ralston 1985; Crawford & Ralston 1988; Prestidge & Ralston 1996). Above the critical hydrophobicity, the flotation response increases significantly.

Key sub-processes in the collection of particles by bubbles in the pulp are bubble-particle collision, attachment and detachment (Dai et al. 1998; Duan et al. 2003). Collection efficiency, E_{coll} is a product of the efficiencies of the three sub-processes:

$$E_{coll} = E_c . E_a . E_s \qquad 1$$

where E_c, E_a and E_s are the collision, attachment and stability efficiencies respectively (Ralston 1999). Collision efficiency depends on hydrodynamic factors e.g. bubble size, superficial gas rate, energy input. Attachment efficiency depends on particle hydrophobicity. Stability of bubble-particle agglomerates depends on both the particle hydrophobicity and hydrodynamic factors against detachment forces in the pulp.

Some of the conventional methods used to characterise mineral surface wettability are inverse gas chromatography (IGC), time of flight secondary ion mass spectrometry (ToF-SIMS) and the contact angle. A number of researchers have employed the IGC to characterise the surface energies of mineral particle surfaces (Mohammadi-Jam et al. 2014; Mohammadi-Jam & Waters 2014; Ali et al. 2013). However, the IGC technique is a gas phase technique where measurement takes place on dried powders but flotation is characterized by particle bubble interactions in a pulp. A number of researchers have studied a possible correlation between the contact angle and the surface analysis by ToF-SIMS (Brito E Abreu & Skinner 2011b; Brito E Abreu & Skinner 2011a; Duan et al. 2003). However, ToF-SIMS is a high vacuum technique and the question arises of the state of the particle under high vacuum compared to an aqueous environment encountered in real flotation systems. The measurement of powder contact angle is not as simple, straight forward and well-described as that on flat, smooth and ideal surfaces (Buckton 1990). The Washburn and Bartell methods are the oldest direct techniques used to determine the contact angles on powders (Washburn 1921; Bartell & Merrill 1931). The deriving theory of the Washburn and Bartell techniques assumes a bundle of parallel capillaries with constant radius. This, however, is an over-simplification of the tortuous path travelled by the liquid in the bed (Spagnolo et al. 1996). This assumption demands that the bed is, and remains, homogenous throughout the wetting process. However, this is difficult to achieve in practice since wetting changes the surface properties of the particles, thereby altering the particle-particle interactions. Furthermore, it is difficult to obtain meaningful and reproducible contact angle values for real ores. This is because there are a number of parameters that are difficult to control – surface roughness, chemical heterogeneity, particle size & shape (Denoyel et al. 2004; Gharabaghi & Aghazadeh 2014).It is also difficult to prove that the contact angle induced by the completely wetting liquid is actually zero (Spagnolo et al. 1996).

This study proposes the use of the enthalpy of immersion as a tool to characterise the wettability of mineral surfaces.Theenthalpy of immersion is the enthalpy released or gained when the solid-gas interface is replaced with the solid-liquid interface during the immersion process. The immersion process is accompanied by the decrease in interfacial Gibbs surface energy and this process is associated with heat gain or heat loss. The enthalpy of immersion is a direct measure of the interfacial surface energy of the minerals as opposed to the contact angle which is inferred from the rate of liquid penetration into the packed bed. Theenthalpyof immersion is readily measurable using solution calorimetry at ambient conditions, typical of those prevailing in flotation concentrators. The magnitude of the enthalpy of immersion depends on the area of interaction at the interface and the intensity of interaction between the liquid molecules and the surface of the solid (Goncharuk 2015). The enthalpy of immersion is an established method for characterising the wettability of various materials, for example teflon, graphon, graphite and griseofulvin (Chessick et al. 1956; Young et al. 1954; Hansford et al. 1980). The enthalpy of immersion has been extensively used in studying various solid-fluid interactions (Groszek 1958; Templer 1972; Groszek 1998). The surface properties of silica have been extensively investigated because of its widespread use as a catalyst support and adsorbent (Yan et al. 2000; Goncharuk 2015; Young & Bursh 1960; Makrides & Hackerman 1952). Zeolites, mainly used as commercial adsorbents and catalysts, have also been widely characterised using the enthalpies of immersion (Nakamoto & Takahashi 1982; Tsutsumi & Takahashi 1969). The enthalpies of immersion has also been employed in carbon black and charcoal studies (Kraus 1955; Puri et al. 1953) as well as coal studies (Melkus et al. 1987; Wang et al. 1998). Despite the enthalpy of immersion being an established technique to characterise the surface properties of solids, it has seldom been applied in the field of mineral processing. Melkus et al. (1987) distinguished or ranked different types of coals using the enthalpy of immersion and their trends in the enthalpy of immersion coincided with trends reported for the floatability of different coals. This work was successful only in as far as distinguishing or ranking the different types of coal was concerned. However, the authors did not explicitly establish the relationship between the enthalpy of immersion and floatability. All minerals are classified as either polar or non-polar depending on their surface characteristics (Wills & Napier-munn 2006). If the interaction of the mineral surface with water is hydrophilic, the measured enthalpy of immersion is more exothermic and the opposite is also true. Malandrini et al. (1997) reported the enthalpies of immersion of quartz and Teflon to be -365mJ/m^2 and -6 mJ/m^2 respectively. This is intuitively correct since quartz is hydrophilic while teflon is hydrophobic. The relative values of the enthalpies of immersion indicate the relative wettabilities of mineral surfaces.

In this study, the enthalpies of immersion of different minerals in water were measured using a precision solution calorimeter.The Washburn method was employed to determine the contact angles of the minerals while microflotation was used to characterise the flotation response and hence hydrophobicity of the minerals. The relationships between the enthalpies of immersion, contact angles and flotation response are compared and the inter-relationships between the three measured parametersare proposed.

2. Methodology

2.1 Materials and Reagents

Table 1 shows different minerals which were chosen for this study. The minerals were received from Wadso Natural Resources, New York as chunks of up to 150 mm diameter. Double deionised water was used as medium in all experiments.

Table 1: XRD results and BET specific surface areas for different minerals.

Sample	Expected Mineral	BET Specific Surface Area (m^2/g)
1	Galena	0.7747
2	Talc	19.5136
3	Sulphur	0.2273
4	Graphite	7.1236
5	Albite	5.7863
6	Diopside	4.7511
7	Wollastonite	4.2762
8	Mica	24.0038

2.2 Mineral Preparation and handling

A ceramic mortar and pestle was used to grind the minerals into powder. Preliminary experiments showed that a very high specific surface area wasrequired to ensure a high thermal effect for enthalpy of immersion measurements. The material was split using a rotary splitter into 10 samples to obtain representative samples. The Brunauer–Emmett–Teller (BET) method was used to determine the surface areas of the mineral powders and the results are shown in

Table 1. After grinding, the mineral samples were purged immediately under nitrogen in a desiccator to exclude moisture that would affect the enthalpy of immersion measurements. The galena samples were immediately stored under N_2at -30 °C to minimise surface oxidation.Prior to the enthalpy of immersion measurements, the mineral samples were evacuated in a vacuum oven at a pressure of 100 mBar and temperature of 40°C over a period of 4 days to drive off moisture until a constant mass was achieved. The same method of preparation was used by Douillard et al. (2002) and Douillard et al. (2007) where talc and chlorite were stored under a vacuum of 10^{-3}Torr ($1.333 * 10^{-3}$mBar) at 150°C.

2.3 Solution Calorimetry

The Precision Solution Calorimeter supplied by TA instruments was used to determine the enthalpies of immersion at 25°C. It has a liquid bath controlled to within 0.0001°C. The instrument waselectrically calibrated against a known power input to determine the specific heat capacity of the calorimetric system. Additionally, the calorimeter was chemically calibrated using the dissolution of KCl (NBS 1655) as a test reaction at 298.15 K (Wadso & Goldberg 2001). The enthalpy of dissolution ascribed to this test reaction is +17.584 ± 0.017 kJ/mol and the one determined in this studywas 17.402 ± 0.028 kJ/mol. It is clear that equipmentwas reproducible and suitable to measure the enthalpies of immersion in this study.

A glass ampoule of known weightwasloaded with dry mineral powder taken straight from the vacuum oven. The loaded ampoule was then weighed and the mass of powder loaded was calculated.The glass ampoule was sealed using a silicon rubber and melted beeswax. The sealed ampoule was inserted into the ampoule holder which also doubles as a stirrer. The reaction vessel was filled with double deionised water using a 100 mL pipette. A stirrer speed of 300 rpm was set in all calorimetric experiments. Once thermal equilibrium was achieved, the reaction was initiated by breaking the glass ampoule.The duration of the immersion process was 10 mins. To suppress any contribution from the dissolution of mineral surface ions, all enthalpies of immersion experiments were conducted using water saturated with mineral solids as the wetting liquid.In this case, the wetting liquid is always in equilibrium with a small amount of solid mineral phase, and hence the contribution of the enthalpy of dissolution of the solidneglected. The same approach was employed by Zimmerman et al. (1987) and Douillard et al. (2002). The enthalpy measured in blank experiments (breaking of empty ampoules with no mineral present) was independently determined as-62.9mJ.The enthalpies of immersion values reported in this study were corrected for the blanks.

2.4 Contact Angle Measurements

The Krauss contact angle equipment which employs the Washburn method was used to determine the contact angles of different mineral powders. The method is based on comparing the liquid penetration rates of a perfectly wetting liquid to that of the wetting liquid of interest.The equation used is

$$cos\,\theta = \left(\frac{gradient\ of\ the\ water\ line}{gradient\ of\ the\ hexane\ line}\right) * \frac{\Upsilon_{hexane}}{\Upsilon_{water}} * \frac{\eta_{water}}{\eta_{hexane}} \qquad 2$$

where θ is the contact angle (°); Y is surface tension (Nm-1); η is viscosity (Pas).

Cyclohexane was used as a perfect wetting liquid. A reproducible packing of the bed of particles was obtained by centrifuging the loaded capillary tube at 4000 rpm for 10 minutes. A narrow particle size range of 38-53μm was chosen to maintain an essentially consistent particle size.Experiments were conducted in duplicates and average contact angles are reported in this paper.

2.5 Microflotation

A microflotation rig was used to measure the relative hydrophobicity of the different minerals using the first-order flotation rate constant as an indicator. The experimental procedure for the microflotation tests has been described previously (Taguta et al. 2017).Feed to the cell was 3 g; air flow rate was maintained at 10ml/min and a narrow particle size range of 38-53 μm was chosen to maintain the particle size constant. Concentrates are collected at 2, 4, 6, 8 minutes intervals. Experiments were conducted in duplicates and the averages are reported in this paper. All other parameters such as particle size, bubble size and energy input being constant, any changes in the microflotation response are attributed to the changes in the surface chemistry of the minerals. The first-order flotation rate constants, *k,* were obtained by least squares non-linear regression analysis using the first order rate model shown in Equation 3. The Excel Solver function was used for curve fitting.

$$R = R_{max}(1 - e^{-kt}) \quad 3$$

where*t* = flotation time (min); *R* = recovery at time *t* and R_{max} = maximum possible recovery of the mineral at infinite time

3 RESULTS AND DISCUSSION

The enthalpies of immersion, contact angle and first-order flotation rate constants for both the model system and different minerals are presented in this section. The enthalpies of immersion were normalised to 1 m² of the mineral surface area. Double deionised water was used in all the enthalpy of immersion, contact angle and microflotation experiments.

3.1 DIFFERENT MINERALS

3.1.1 Enthalpies of immersion of different minerals in water

The enthalpies of immersion of different minerals were measured and the results are shown in Figure 1.

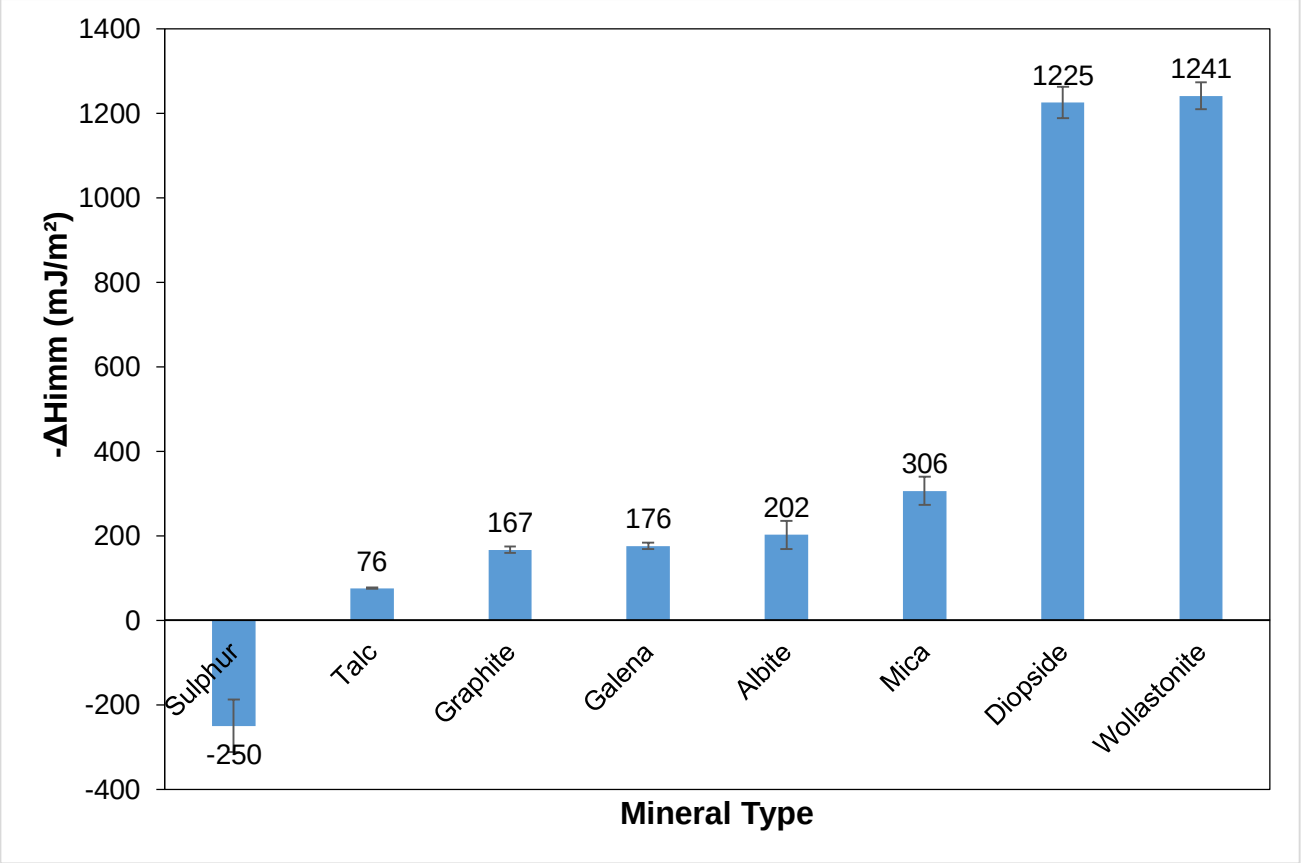


Figure 1: Enthalpy of immersion of different minerals in water

Error! Reference source not found.shows that the wetting process of all the minerals except sulphur in water was exothermic. It is clear that all the minerals produced different enthalpies of immersion, and thus all the minerals showed different extents of wetting. This is not surprising since the minerals have different surface properties which will affect their wettability. The enthalpies of immersion became more exothermic in the following order: Sulphur < Talc < Graphite < Galena < Albite < Mica <Diopside< Wollastonite. It follows that the magnitude of interaction

of the different minerals with water increased in the same order, with wollastonite being the most wettable while sulphur was least wettable. It is clear that the enthalpy of immersion technique was capable of distinguishing different mineral properties according to their wettabilities which is due to differences in their surface properties. The very small error bars show that the enthalpies of immersion measurements were reproducible.

Sulphur produced an endothermic enthalpy of immersion. Sulphur is known to be a very hydrophobic material (Wills & Napier-munn 2006). Sulphur exists as S_8 molecules with molecules joined together by van der Waals forces and thus minimal interaction with water is expected. Spagnolo et al. (1996) found the enthalpy of immersion of highly fluorinated carbons in water to be endothermic. They attributed this to forced flow of water onto the hydrophobic surface sites. This is an interesting result since it has been proposed by Woods and Gardner (1973) that elemental sulphur formed during oxidation accounts for collectorless flotation of sulphide minerals. Hence if hydrophobicity is inversely related to the enthalpy of immersion, then when S is present there should be high hydrophobicity. Talc is known to be a naturally floatable gangue mineral and this is consistent with the relatively low enthalpy of immersion. Graphite (carbon) is also known to be hydrophobic (Morcos, 1970). Graphite is an allotrope of carbon in which each carbon atom is covalently bonded to three other carbon atoms and these atoms are arranged in layers that can slide past one another. These layers are held together by very weak van der Waals forces, thus graphite is hydrophobic and is expected not to readily interact with water.Galena, a sulphide mineral classified as moderately hydrophobic (Wills & Napier-Munn 2006). Thus for these three minerals low exothermic enthalpies of immersion in wateris consistent with their known hydrophobic properties or their low degree of wettability.

The interaction of the silicate minerals with water is related to their structure. Figure 2shows the crystalline structures of talc and mica.

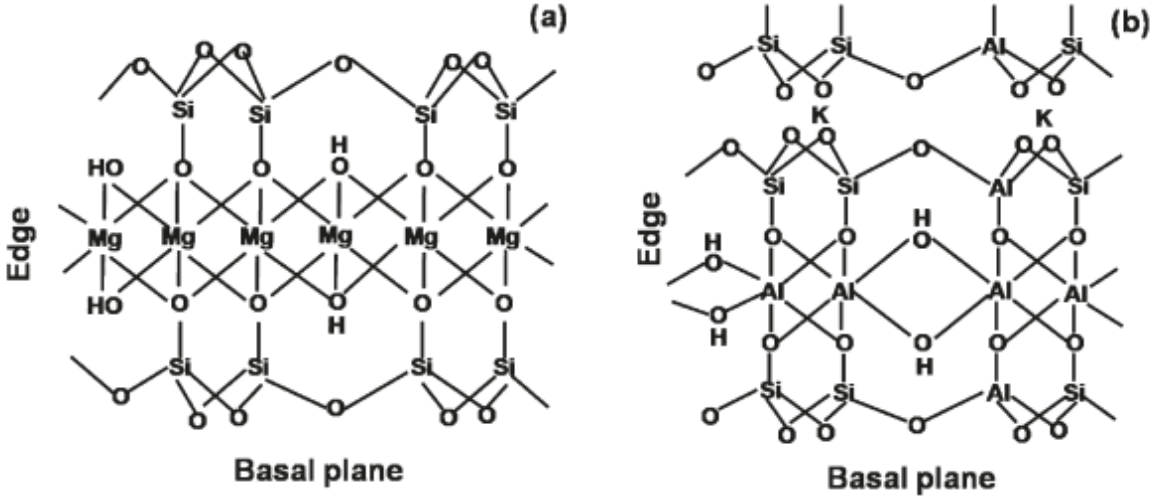


Figure 2:The structures of talc (a) and mica (b).

Talc is a trilayer silicate mineral with a structure of an octahedral layer (brucite or gibbsite layer) sandwiched by two silica tetrahedral layers as shown in Figure 2. The

two silica tetrahedral layers have negative charges and the octahedral gibbsite layer has a neutralising positive charge. Each sheet of talc has neutral net charge and van der Waals forces hold the trilayer sheets together. There is no tetrahedral substitution of silicon by aluminiun or magnesium which could affect the polarity of the talc. Because of the low substitution and low polarity, talc is naturally hydrophobic (Yan et al, 2011; Yin et al, 2012). Thus talc reacts with water via weak van der Waals forces and this is consistent with the relatively low exothermic enthalpy of immersion obtained for talc in this study.

Mica (shown in Figure 2), although a trilayer silicate mineral similar to talc, undergoes various degrees of lattice substitution whereby Al^{3+} substitute for the Si^{4+} in the tetrahedral layers. The result is a negative charge on the tetrahedral layer which is usually neutralised by potassium ions. However, the ion exchange capacity of mica is low as the potassium ions are fixed. When mica is cleaved during grinding, it is assumed that the surface carries a constant negative charge whose magnitude depends on the degree of lattice substitution (Yin et al 2012). It follows that mica sheets are held together by ionic inter-layer bonds which render it hydrophilic. It thus readily interacts with water producing a relatively more negative enthalpy of immersion than talc as seen in Figure 1.

Wollastonite is a calcium meta-silicate in which the Si-O tetrahedra groups into chains. Dissolution tests on wollastonite showed that slurry pH changes quickly in the initial stages before reaching equilibrium at pH 9.5 (Prabhakar et al, 2005). The same phenomenon was observed by other researchers (Bailey and Reesman, 1971; Rimstidt and Dove, 1986). This was attributed to the exchange of protons from the aqeous media with calcium ions on the wollastonite surface. The release of calcium was found to be higher than that of silicon, thus wollastonite undergoes incongruent dissolution. Dissolution was more pronounced for finer size fractions. Calcium dissolution leaves behind a negative lattice and active SiOH and SiO^- sites. Auger electron spectroscopic analysis has shown that the exposed atoms on the cleavage surfaces of wollastonite are mainly Si and O and few calcium atoms. The resultant silica rich surface is very hydrophilic, interacting strongly with water and hence the observed very highly exothermic enthalpies of immersion. Incongruent initial dissolution was also reported for albite and diopside (Blum and Lagasar, 1991; Wollast and Chou, 1992; Chou and Wollast, 1984; Shmulovich et al, 2001).This is consistent with the highly exothermic enthalpies of albite and diopside in water.The values of the enthalpies of immersion of the silicates in water obtained in this study are comparable to the work conducted by other researchers. Douillard et al. (2007) measured the enthalpies of immersion of green and black chlorite in water to be -900 mJ/m² and -700 mJ/m² respectively. Salles et al. (2006)reported the enthalpy of immersion of kaolinite to be -422 mJ/m². It is clearly evident that the enthalpy of immersion technique was able to classify all the different minerals according to their wettability.

3.1.2 Contact angle of different minerals with water

In order to compare the relative effectiveness of contact angle and enthalpy of immersion as indicators of hydrophobicity, contact angles were determined for three of the minerals studied in section 3.1.1. The contact angles (as measured by the Washburn method) of three of the minerals with water are shown in Table 2. Also shown are the enthalpies of immersion of these minerals.

Table 3: The contact angles of different minerals with water

Mineral	Contact angle (°)	Enthalpy of immersion (mJ/m²)
Talc	73	-76
Graphite	54	-167
Galena	41	-176

Cyclohexane was used as the perfectly wetting liquid in all water contact angle experiments. The contact angle of sulphur particles could not be measured because it was difficult for water to rise in the bed of sulphur particles. This is due to the very high hydrophobicity of sulphur. On the contrary, the enthalpy of immersion was able to characterise the wettability of sulphur.Furthermore, the contact angles of the silicate gangue minerals were difficult to measure as they could not be perfectly wetted using cyclohexane. The interaction of the silicate minerals with water have been extensively discussed in Section 3.1.1. Cleaved mica sheets are held together by ionic inter-layer bonds which readily interact with water and not cyclohexane which is classically used as wetting liquid when determining contact angle using the Washburn method. Bryant et al (2006), using the captive drop method determined the contact angle of freshly cleaved mica surfaces to be 10°. As already mentioned wollastonite, albite and diopside are reported to undergo incongruent dissolution (Prabhakar et al, 2005; Wollast and Chou, 1984; Shmulovich et al, 2001). This leaves a silica rich surface which interacts readily with water and not cyclohexane.Although the Washburn method could not differentiate between the wettabilities of the silicate gangue minerals, the enthalpy of immersion measurements were sensitive enough to do so. .

Table 3 shows that contact angle decreased in the order talc > graphite > galena. Hydrophobic surfaces are characterised by high contact angles with water and thus talc, graphite and galena are generally considered to be relatively hydrophobic. It can again be seen that the enthalpies of immersion are good indicators of contact angle for those minerals where it was possible to determine the latter values.

3.1.3 Flotation response of different minerals in water

Microflotation tests were performed to investigate the collectorless flotation response of the different minerals and the results are shown in Figure 3.

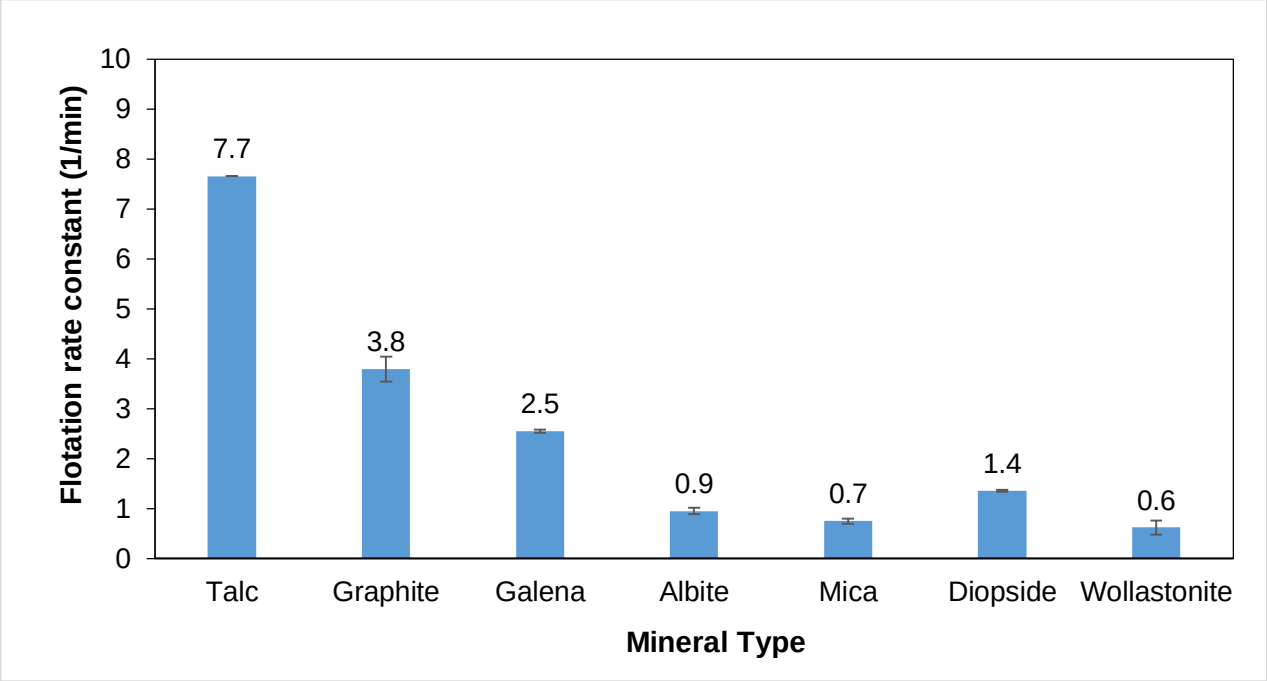


Figure 3 : Microflotation recoveries of different minerals in water

Figure 3 shows that different minerals produced different flotation responses. This was expected since the minerals have different surface properties, which dictate the wettability of the mineral surfaces. Sulphur particles could not be dispersed into a fine slurry amenable to flotation since it settled at the air-water interface. Figure 3shows that the microflotation recoveries decreased in the following order: Talc > Graphite > Galena > Albite ≈ Mica ≈Diopside≈ Wollastonite.Since the system hydrodynamics (energy, air flow rate, bubble size) as well as physical properties of the particles (particle size and shape) were maintained constant in the microflotation experiments, any changes in flotation response are attributed to the changes in the hydrophobicities of the minerals in the pulp. The trends in the flotation rate constant coincided with the trends in the contact angle (**Error! Reference source not found.** and Figure 3) for talc, graphite and galena. As already explained each sheet of talc has neutral net charge and van der Waals forces hold the trilayer sheets togetherand hence it is relatively very hydrophobic (Section 3.1.1). Thus as expected, talc showed fast flotation response. Similiarly, carbon layers in graphite are held together by weak van der Waals forces, and again, as is well known, is hydrophobic with little interaction with water. This is consistent with relatively fast flotation kinetics shown by graphite.The low flotation response obtained for the silicate gangue minerals (albite, diopside, wollastonite and mica) could be attributed to entrainment since these minerals are known not to be floatable. It is also worth noting that wollastonite has been shown to be readily entrained as a result of the needle-like shape of the particles (Wiese & O'Connor, 2016)

Despite having significantly different enthalpies of immersion, the silicate gangue minerals showed similar slow flotation responses. That the minerals are not floatable does not necessarily mean that their wettabilities are the same.Although the wettabilities of the silicate gangue minerals are significantly different, they are all

lower than the critical hydrophobicity required before flotation takes place (Blake & Ralston 1985; Crawford & Ralston 1988; Prestidge & Ralston 1996).The fact that the flotation rate constants of the silicates were similar while enthalpies of immersion of the same minerals were significantly different shows that the enthalpy of immersion is a more sensitive tool to characterise the wettability of mineral surface as opposed to the microflotation technique. The major limitation of the microflotation technique as far as characterising mineral surface wettability is that a certain critical contact angle (hydrophobicity) has to be achieved before mineral powders can float. This means that a non-floating particle does not necessarily have a zero contact angle and hence contact angle is insensitive for mineral samples having contact angles below the critical contact angle.

3.2 Relationship between the enthalpy of immersion and flotation rate constant

Figure 7 is presented to highlight the relationship between the enthalpy of immersion and flotation rate constant.

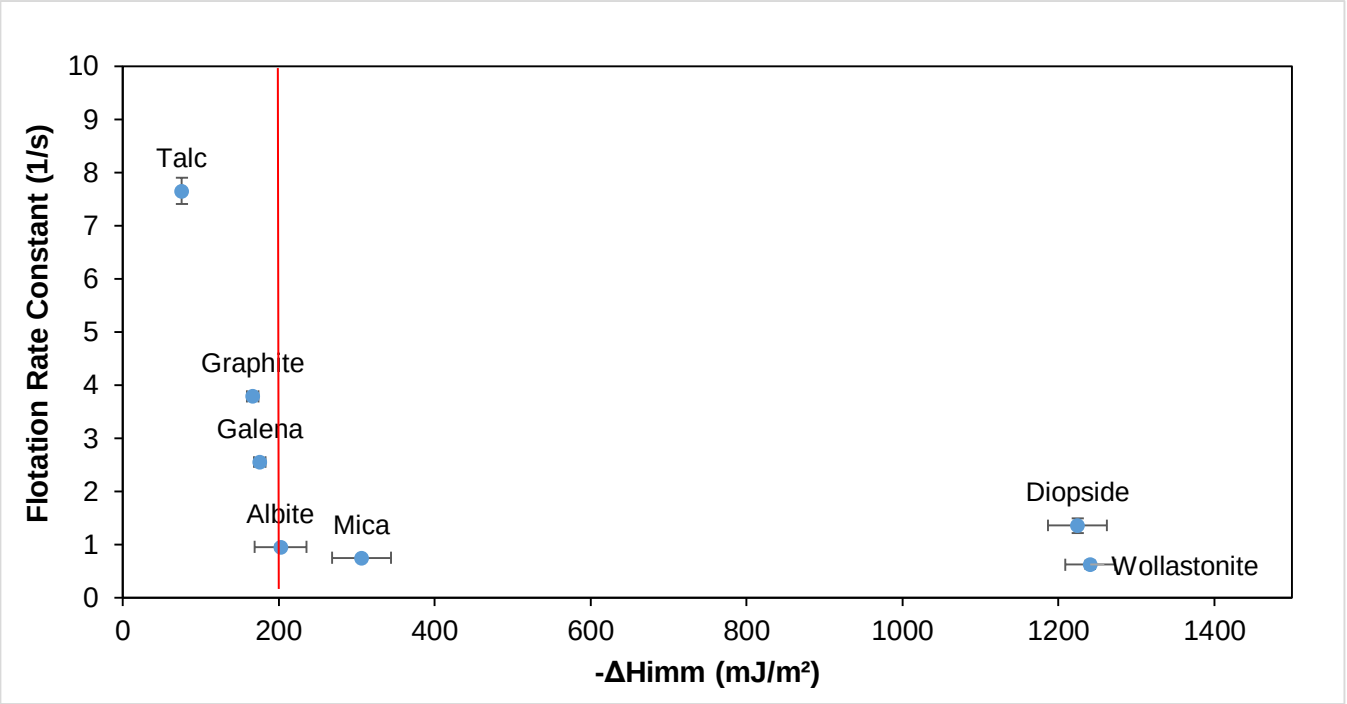


Figure 4: The enthalpy of immersion vs first-order flotation rate constant for different minerals.

It is clear from Figure 4 that there are 2 distinct regions namely the floatable region (hydrophobic) and the non-floatable (hydrophilic) region. In the floatable region, the flotation rate constant decreases with the increasing magnitude of the enthalpy of immersion.The results agree with Melkus et al. (1987) who reported that the trend in the enthalpies of immersion coincided with trends of the floatability of different coal, concluding that the floatability is inversely related to the enthalpy of immersion.The non-floatable region is characterised by very low or no flotation response, independent of the enthalpy of immersion.Thus, the minerals do not have sufficient hydrophobicity to attach to the air bubbles in the pulp zone.

The enthalpy of immersion value demarcating the floatable region from the non-floatable region is the critical enthalpy of immersion. Similar to the phenomenon of the critical contact angle proposed previously by Blake & Ralston (1985b), Crawford & Ralston (1988) and Prestidge & Ralston (1996), the critical enthalpy of immersion is the value of the enthalpy of immersion below which no flotation occurs. The critical enthalpy of immersion is in the region of - 200mJ/m².All minerals producing enthalpies of immersion more negative than -200mJ/m²are non-floatable while those producing enthalpies of immersion less exothermic than -200mJ/m² are floatable. This means that the minerals which produce enthalpies of immersion more exothermic than -200mJ/m² have not attained the critical hydrophobicity required to necessitate floatability. This value makes sense in that the enthalpies of immersion measured for oxides and silicates by other researchers are more exothermic than -200mJ/m². A preliminary literature survey for the values of enthalpies of immersion of different silicate minerals and oxides in water is summarised in Table 4.

Table 4: Values of the enthalpies of immersion of different silicate minerals in water surveyed in literature

Mineral Type	Enthalpy of immersion (mJ/m²)	Reference
Kaolinites	-422	Salles et al. (2006)
Serpentine	-300	Douillard (1997)
Green chlorite	-360	Salles et al. (2006)
Black chlorite	-900	Douillard et al. (2007)
Alumina	-775	Douillard et al. (2007)
Illite	-700	Douillard (1997)
Quartz	-400	Douillard (1997)
Silica	-400	Douillard (1997)

All the minerals in Table 4 are known to be hydrophilic, and hence not floatable. Their enthalpies of immersion are more exothermic than the critical enthalpy of immersion of -200mJ/m² obtained in in this study. Thus the value of the critical enthalpy of immersion obtained in this study is consistent with independent studies conducted by other researchers.

4 Conclusion

Immersion calorimetry has been shown be able to determine reproducibly the wetting characteristics of different minerals. It was found that there is a critical enthalpy of immersion of -200 mJ/m² and at values more negative than this no flotation occurs. The significance of this finding is that for any mineral whose flotation behaviour is unknown, the measurement of the enthalpy of immersion appears to be able to predict the flotation response of the mineral. The validity of the above findings was determined by investigating the relationship between the enthalpies of immersion for various minerals, their contact angle where it was possible to determine this value, and their flotation response using microflotation. It is therefore concluded that the enthalpy of immersion is a most useful indicator of the extent to which minerals are hydrophobic or hydrophilic in their natural form.

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