A methodology for the heat of immersion as a measure of wettability of mineral mixtures

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Abstract

The measure of the extent to which a mineral interacts with water is called wettability and this is important in flotation processes. This is because the interactions between solid particles and liquid molecules (water) are important in understanding the flotation mechanism and achieving high recoveries. Contact angles and work of adhesion can be used to determine the physical properties of a given solid-liquid system, but there are drawbacks to these techniques. The advancement of microcalorimetry instrumentation has led to the use of heat of immersion to determine the surface wettability of solid surfaces.

Several calorimetric studies have proven that the heat of immersion can be used to determine the surface wettability of minerals. Previous research within the Centre for Minerals Research (CMR) has shown that the heat of immersion can provide a reliable measure of mineral surface wettability when it is measured by precision solution calorimetry. However, this was done only for single mineral systems and its application to real ores has not been investigated in depth. In this study, the heat of immersion as a measure of wettability is applied to a simple binary mineral mixture representative of a real ore. The binary mineral mixture consists of a hydrophobic sulphide mineral, galena and a hydrophilic silicate mineral, albite.

The results in this study have shown that the heat of immersion measurements present challenges such as an unexpected endothermic response. This endothermic response is attributed to the dissolution of the mineral in water. This dissolution is due to the surface ions on the mineral being exposed to the wetting liquid. In order to predict flotation response through measuring wettability, the aim is to measure only the heat of wetting, which is an exothermic response. Therefore, the dissolution process needs to be suppressed. Alternative techniques such as a solution saturated with the mineral sample, using organic liquids as the wetting liquids, and pre-coating of the mineral particles with collector were explored.

From the various approaches explored to suppress the dissolution, it was observed that the saturated solution approach was an effective technique for certain minerals such as albite but was ineffective at suppressing the dissolution process across a range of mineral types. It is, therefore, an ineffective technique for exploring the heat of immersion of binary mineral mixtures. Secondly, it was observed that the collector coating approach was effective for suppressing dissolution at surface coverages above 75%. The collector coating approach is not feasible for conducting the heat of immersion measurements for the binary mineral mixtures because it only successfully suppresses dissolution at excess surface coverages that are not necessarily those at which one would choose to do the experimental work. Additionally, collector coating does not allow for the natural wettability of the uncoated minerals to be measured. Thirdly, hexane was found as a good wetting liquid for suppressing dissolution but

there were some experimental difficulties that led to this liquid not being used for the binary mineral mixtures. These experimental difficulties include a premature immersion of the mineral into the wetting liquid due to the beeswax used to seal the ampoule dissolving in the hexane. Finally, hexanol was found to be a good wetting liquid in suppressing dissolution, had no associated experimental difficulties and was able to distinguish relative hydrophobicities between different mineral surfaces. It can, therefore, be used as an effective wetting liquid for mineral dissolution suppression and hydrophobicity determination.

Preliminary experimental work into the feasibility of using a binary mineral mixture as a simple model ore system was performed. A linear relationship was found between the heat of immersion and the fraction of pure mineral A in a binary A + B mineral mixture. The heat of immersion could be presented in various ways depending on what data is required and desired. The surface area fraction or mass composition can be used to create the linear relationship between the heat of immersion and the composition of the binary mineral mixture. It was shown that there is a linear relationship between the heat of immersion and mass composition or surface area fraction of the binary mineral mixture. From this linear relationship, the heat of immersion of the pure minerals comprising the mixture can be extrapolated. The linear relationship based on composition provides a simple and convenient way to estimate hydrophobicity of a floatable mineral in an ore where only the mass and mineral composition of the sample is known. This could be used in flotation modelling, where valuable mineral floatability is a required input parameter. To determine the relative hydrophobicity of a binary mineral mixture in hexanol where the mass composition is unknown, the heat of immersion or heat released by the binary mineral mixture is measured and this is correlated with the mixture's mineral weight composition. This linear relationship can then be extrapolated to zero and 100% respectively to obtain the heat of immersion of the pure minerals. These values can be read off a calibration curve such as that obtained by Taguta et al. (2018) to obtain a flotation rate constant.

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List of Abbreviations

Abbreviation	Description
SIBX	Sodium Isobutyl Xanthate

List of Symbols

Symbol	Description
ΔG_i^0	Standard free energy change
ΔG_γ^0	The contribution to the total free energy of immersion due to changes in the interfaces when the solid-gas interface is replaced by the solid-liquid interface during immersion
ΔG_{el}^0	The contribution due to the formation of an electrical double layer at the solid-liquid interface
ΔH_{imm}	Heat of immersion
h_i^d	Dispersion forces
h_i^μ	Polarising forces
h_i^α	Electrostatic forces
Σ	Surface area
e_{SL}	Energy of the solid – liquid interface
e_{S^0}	Energy of the solid surface
q_1	Heat of immersion of hydroxylated surface
q_2	Heat of immersion of dehydroxylated
S_1	Surface area fraction of hydroxylated surface
S_2	Surface area fraction of dehydroxylated
θ_c	Apparent contact angle
θ_{Y1}	Young contact angle for material 1
θ_{Y2}	Young contact angle for material 2
f_1	Surface area fraction of material 1
f_2	Surface area fraction of material 2
Ksp	Solubility product constant

1 Introduction

1.1 Background

Froth flotation is a widely used separation method in the minerals processing industry (Rao, 2013). It is important in the beneficiation of many economical and environmentally viable metals. This process separates minerals based on the differences in surface hydrophobicity. The hydrophobic metal-rich particles are contacted with air bubbles, and they attach to these bubbles and report to the concentrate stream while the hydrophilic gangue particles sink and report to the tailings stream.

The extent to which a mineral can interact with water is important to the flotation process. The measure of this extent of interaction is defined as wettability, where a wettable mineral is hydrophilic, and a non-wettable mineral is hydrophobic. Because flotation depends on the extent to which particles are removed from the water phase and attach to bubbles, it is crucial to understand these interactions for better recoveries and better understanding of the flotation mechanism. Understanding the wettability of surfaces is important, not only for flotation but for numerous practical processes in the minerals processing, pharmaceutical and oil recovery industries (Denoyel et al., 2004; Trabelsi et al., 1992). In predicting the wettability of any system, the knowledge of the solid-liquid interface would be enough; however, the solid-liquid interface is not directly measurable (Denoyel et al., 2004).

A variety of experimental methods and techniques have been used to explain the physical chemistry of solid-water interfacial interactions. These include contact angles, electrokinetic potentials, suspension stability, measurements of adsorption isotherms, and flotation behaviour. These techniques have provided ground-breaking information and have proven to be invaluable in the understanding of wetting behaviour, flotation behaviour, and the adsorption of reagents. All these methods are indirect measurements of the system energetics, and this has led to the development of the approach for the present study to directly measure the system energetics in a microcalorimeter to measure wettability. There are limitations with the current techniques such as the contact angle hysteresis, experimental difficulties etc. This led to the development of new techniques such as solution calorimetry to determine wettability.

This study aims to add knowledge to the minerals industry about an alternative technique to measure surface wettability of mineral mixtures focusing on the solution calorimetry technique which measures wettability using the heat of immersion. It will contribute to the development and innovation of new techniques for measuring wettability ultimately improving the beneficiation of mineral ores.

1.2 Problem Statement

In flotation, the hydrophobicity or wettability of the mineral particles is important since a critical hydrophobicity is required before flotation can occur. Various techniques have been used to quantify wettability, of which the most well-known is the measurement of contact angles, but all these techniques have drawbacks unique to the method. Previous research within the Centre for Minerals Research (CMR) has shown that the heat of immersion can provide a reliable measure of mineral surface wettability when it is measured by precision solution calorimetry. Heat of immersion is known to be a good indicator of both natural mineral hydrophobicity and the extent to which collectors render a mineral hydrophobic. The current state of art in immersion calorimetry has shown that the heat of immersion is a valuable indicator of mineral surface wettability for single mineral systems. However, real ores are composed of a combination of minerals, which would provide an additive heat of immersion. It is, therefore, necessary to expand or explore the heat of immersion technique as a measure of wettability for mineral mixtures.

As will become apparent in the results and accompanying discussion, the presence of an unexpected endothermic response from the interaction between certain minerals and water has led to the necessity of developing a methodology that is capable of decoupling the heat of immersion of the wetting interactions from any other interactions that may be taking place upon immersing a mineral in a liquid.

1.3 Scope and Limitations

Understanding the wettability of mineral surfaces is a crucial component in the flotation process in the minerals processing industry as it affects bubble-particle attachment and froth stability. The scope of the thesis is to develop a methodology for the measurement of heat of immersion as a wettability measuring technique for use in flotation. The focus is on the ability to decouple various reactions that may occur when a dry mineral is placed into a liquid and to be able to use the heat of immersion to measure and characterise the wettability of binary mineral mixtures comprising of both a hydrophobic and hydrophilic mineral component in different compositions. The assumption made for the binary mineral mixture is that the mineral mixture which serves as a synthetic ore is fully liberated. This is because the binary mineral mixture used is made up of two minerals mixed to form a homogenous mixture. The hydrophobic mineral will be a sulphide mineral and the hydrophilic mineral will be a silicate mineral; namely, galena and albite, respectively. The wetting liquid, that is, the medium used to measure the wettability will be explored to find a liquid that only interacts with the minerals in a manner that allows only for the wetting of the solid (mineral) without dissolution. The reasoning is based on the heat of immersion definition that states that the heat measured should be that of a solid immersed in a wetting liquid that does not react with it. However, it is well known that wettability, or rather, hydrophobicity is impacted by the addition of reagents such as collectors. This study will be focusing on collectors to understand wettability and in turn the dissolution of the mineral into the wetting liquid, water. The surface of one of the minerals will be modified to different degrees of hydrophobicity using a sodium isobutyl xanthate (SIBX). The effect of different collectors will not be reviewed; however, collector surface coverage will be varied to alter mineral surface hydrophobicity. The wetting liquid will be varied amongst polar and nonpolar liquids to investigate the interactions behind the wetting and the dissolution process. The scope of the work is schematically presented in Figure 1-1.

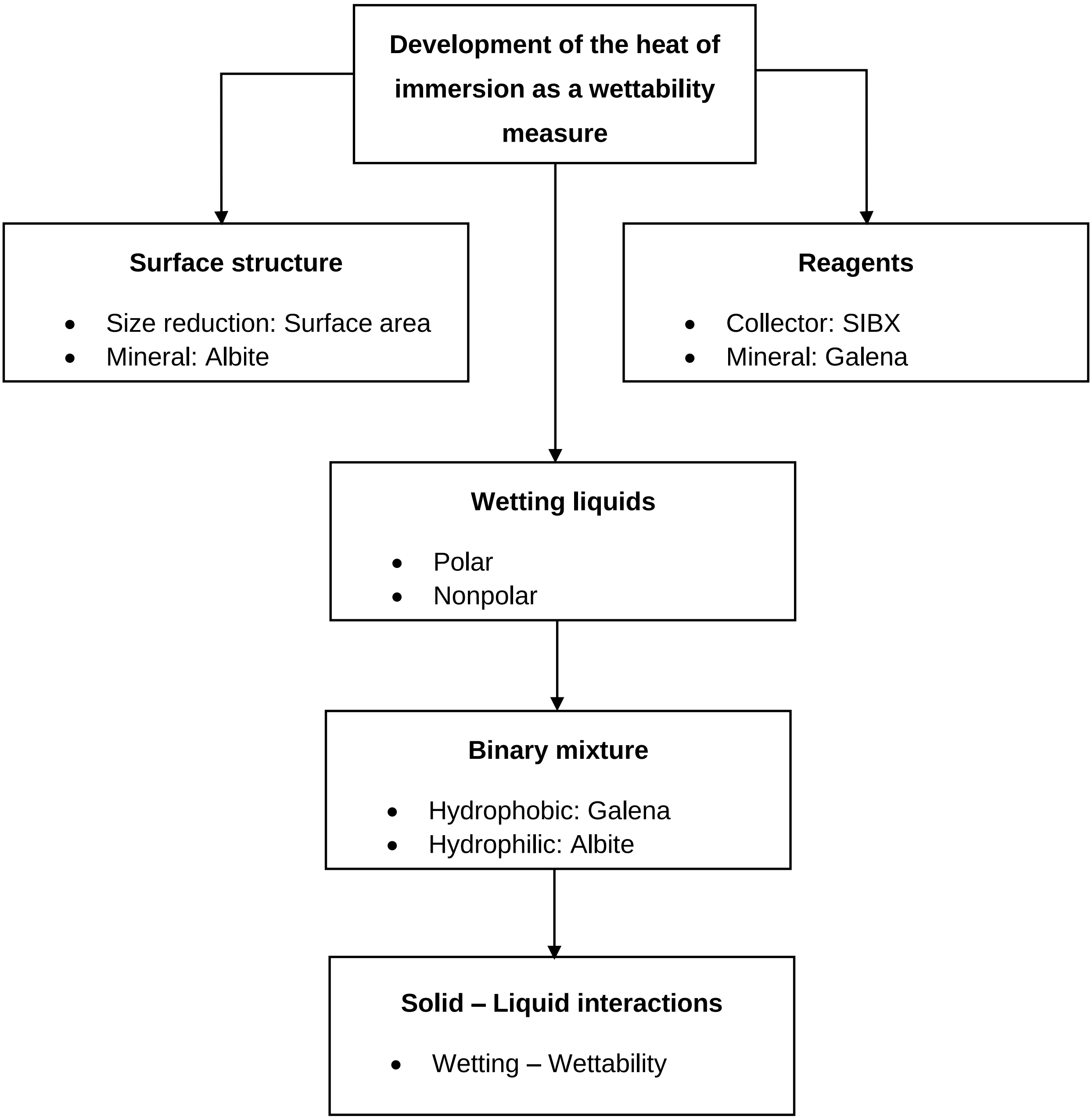


Figure 1-1: Schematic presentation of the scope.

1.4 Project Objectives

The main objective of this study is to develop a methodology that will demonstrate that the heat of immersion can be used to measure the wettability (hydrophobicity) of mineral mixtures using solution calorimetry and further explore or offer approaches to overcome the endothermic response associated with the measuring of wettability. The simplified aims are to:

- Develop a methodology to decouple the various reactions occurring simultaneously during the immersion of a dry solid into a liquid.
- Determine the effect of collector surface coverage as a dissolution suppression technique and on surface wettability.
- Determine the total heat of immersion of the binary mineral mixture as a function of the mineral mixture’s composition.

2 Literature Review

2.1 The Theory of the Flotation Mechanism

Ores which are classified as heterogeneous mixtures require efficient methods of separating the minerals when they are in a finely subdivided solid phase. The separation of these solids exploits physical and chemical characteristics. Froth flotation focuses more on exploiting the surface properties of the solids. It exploits surface energy and surface potential differences between minerals of different types. The difference in interfacial tensions results in hydrophobic or non-wetted solids to be separated to the froth phase when these hydrophobic solids are in contact with air bubbles. Minerals report to the froth phase in various ways, either by selective attachment of the hydrophobic mineral particles to the air bubbles and then transported to the froth, via entrainment with the pulp water that is carried to the froth phase by a swarm of bubbles, or via entrapment between particles in the froth attached to air bubbles. For bubble-particle attachment to occur, an effective contact is required, and this occurs when the mineral surface is sufficiently hydrophobic. In general, the difference in natural surface hydrophobicity of the target mineral and the gangue mineral is not sufficient for selective bubble-particle attachment. In this case, specific chemical reagents are used so that the target solids can acquire the required hydrophobic characteristics (Rao, 2013). Therefore, chemical reagents such as collectors can be added to a flotation system to increase the hydrophobicity and floatability of the target mineral (Melkus et al., 1989; Xing et al., 2017). Collectors selectively adsorb onto the particles to be floated, rendering them hydrophobic (Melkus et al*.,* 1989). There are many types of chemical reagents such as frothers, that play a role in stabilising air-water interfaces, and collectors, depressants, and activators, that act at the solid-liquid interface.

The recovery and selectivity of the flotation process is not only dependent on the operational and chemistry components of the cell, but also the equipment components i.e., hydrodynamics of the cell. All these conditions facilitate the attachment of air bubbles to the hydrophobic mineral and transport it to the froth phase. The contribution of each component to the process depends on the development of relationships between the metallurgical performance of flotation, and the cell geometry and hydrodynamics. The components of the flotation process are presented in Figure 2-1.

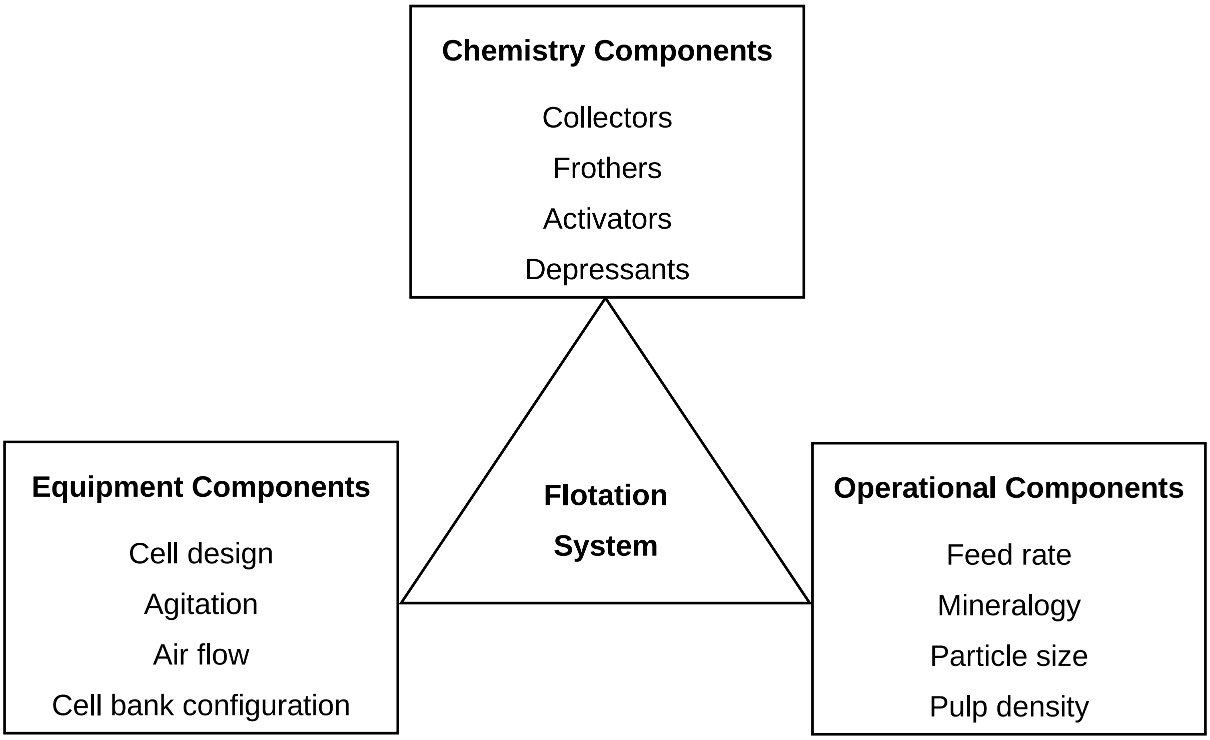


Figure 2-1: Froth flotation overview.

2.2 Mineral Types

The nature of the mineral influences the wettability of the mineral surface and in turn the flotation process. Therefore, different minerals were reviewed and tested for the binary mineral mixture that will be used in this research. The structure of each of these minerals is discussed briefly in this section.

2.2.1 Pyrite

Pyrite is an iron sulphide (FeS_2) with an isometric crystal structure that usually appear as cubes. The Fe atoms presented in grey in Figure 2-2 are octahedrally bonded to six S atoms and are at the corners and face centres of the cubic unit cell. The S atoms, indicated in yellow, are tetrahedrally bonded to three Fe atoms and one other S atom.

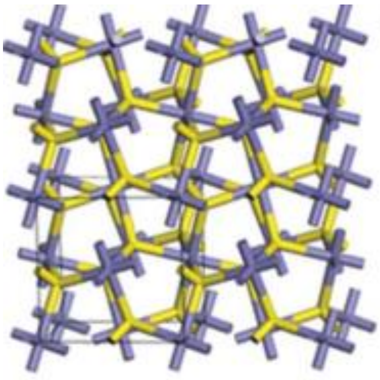


Figure 2-2: Crystal structure of pyrite (Zhu et al., 2012). Fe atoms = grey; S atoms = yellow.

2.2.2 Chalcopyrite

Chalcopyrite ($CuFeS_2$) belongs to the tetragonal crystal system as shown in Figure 2-3. Its structure is closely related to that of sphalerite (ZnS). The metal ions, Fe and Cu, are each bonded to four S atoms in a tetrahedral nature. Each S atom is bonded to two Cu and two Fe atoms.

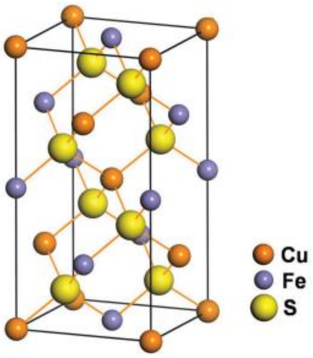


Figure 2-3: Crystal structure of $CuFeS_2$ (Xie et al., 2017).

2.2.3 Pyrrhotite

Pyrrhotite is an iron sulphide with the chemical formula $Fe_{(1-x)}S$ with x varying from 0 – 0.2. It is a nonstoichiometric variant of FeS. It can exist as a hexagonal or monoclinic crystal with the monoclinic crystal structure shown in Figure 2-4.

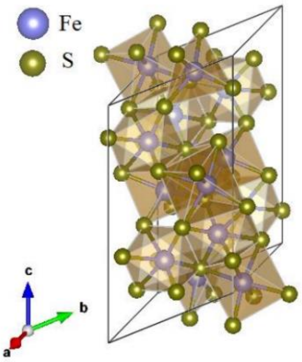


Figure 2-4: Crystal structure of a monoclinic pyrrhotite Fe_7S_8 (Benyoussef et al., 2020).

2.2.4 Galena

Galena (PbS) is a lead sulphide that belongs to the octahedral sulphide mineral group with its metal and S ions indicated in yellow, located in the octahedral position as shown in Figure 2-5. Divalent lead ions (Pb^{2+}) indicated in grey and S ions form a compact cubic unit.

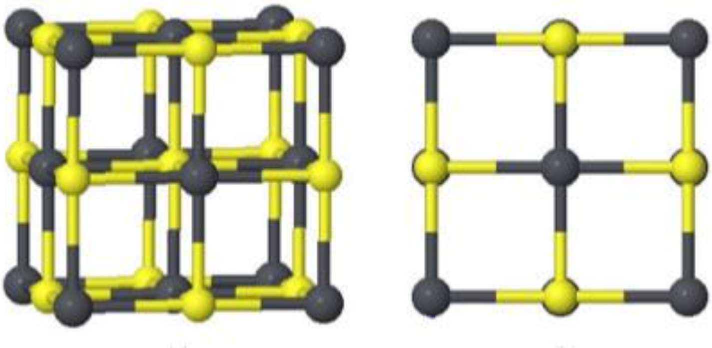


Figure 2-5: Side (left) and top (right) view of the crystal structure of galena (Hu et al., 2020). Lead atoms = grey; S atoms = yellow.

2.2.5 Quartz

Quartz is the mineral form of SiO_2 that is stable at low temperatures and pressures. The structure of quartz consists of corner-sharing SiO_4 tetrahedra so that each Si atom (black) is bonded to four oxygens (white), and each oxygen is bonded to two Si atoms. Quartz is classified as a tectosilicate or framework silicate since its structure forms an open three-dimensional framework. The typical structure of quartz is shown in Figure 2-6.

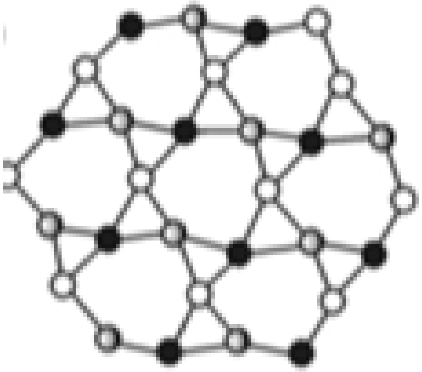


Figure 2-6: Typical crystal structure of quartz (Götze, 2009). Si atoms = black; O atoms = white.

2.2.6 Talc

Talc is a natural mineral with its elementary sheets composed of a layer of magnesium-oxygen/hydroxyl octahedra sandwiched between two layers of tetrahedra silica. The basal surfaces which are the main surfaces of the elementary sheets contain no hydroxyl groups or active ions thus making talc hydrophobic and inert. It is a phyllosilicate mineral that cleaves into thin sheets similar to that of micas. These sheets are held together by secondary van der Waals forces. Figure 2-7 shows the crystal structure of this mineral.

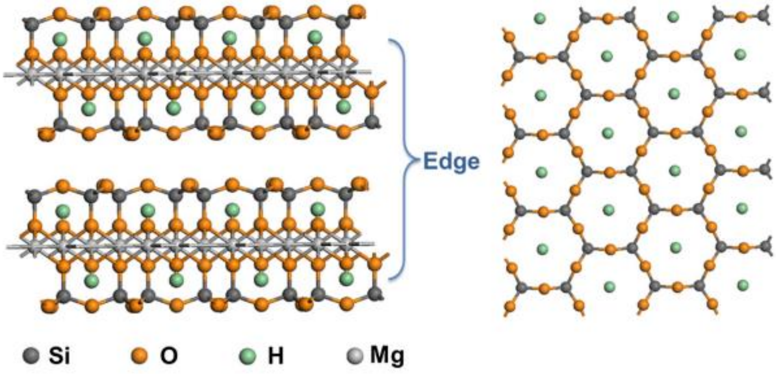


Figure 2-7: Crystal structure of talc. (left) side view of the basal plane (right) top view (Yuan et al., 2019).

2.2.7 Albite

Albite is a plagioclase feldspar of the sodium endmember with the formula $NaAlSi_3O_8$. It is a tectosilicate and is hydrophilic. It is comprised of a series of an interconnected framework of three SiO_4 and AlO_4 tetrahedra with all the oxygens shared between the tetrahedra. The remaining negative charge is balanced by the sodium ion, Na^+, which fills large voids in the structure. The structure is given in Figure 2-8.

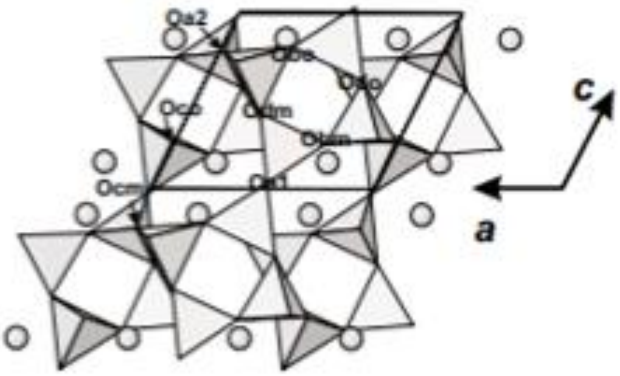


Figure 2-8: Polyhedral presentation of the albite structure at room temperature projected down the [010] axis (Benusa et al., 2005).

2.3 The Origin of the Heat of Immersion

The physical chemistry of the solid-liquid interface has been studied from two separate points of view. Methods such as the immersion calorimetry have been used to understand the basic thermodynamics of the solid-liquid interface. The data from calorimetry gives insight on the quantity of heat or strictly the enthalpy liberated when minerals or oxides are immersed in a liquid. The structure of the solid must first be characterised before understanding surface adsorption. Various types of adsorptions may occur on the surface of a solid when it is contacted with different compounds.

The physical quantities such as the contact angle, reversible work of adhesion and the heat of wetting are all connected with a particular wetting property of a given solid-liquid system. These have limitations in their application and are sometimes difficult to obtain experimentally. When the contact angle is zero, it is difficult to make a distinction between the solid-liquid interactions while the work of adhesion requires adsorption data which is difficult to obtain with precision at certain equilibrium conditions. Traditionally, contact angles have been used as an indicator of hydrophobicity of mineral particles. However, there are still reservations about the validity of using contact angles as a proxy for hydrophobicity (Rao, 2013). This technique allows for relationships between hydrophobicity and surface coverage, reagent requirements and flotation recovery to be developed.

Leja & Poling (1960) in analysing the process of bubble attachment to a flat solid surface stated that the contact angle is simply an indication of the extent to which a given solid-liquid-air system is utilising the available free energy of interfaces in the bubble deformation process. Moreover, the heterogeneity of surfaces of a real ore being treated in the flotation process complicates any determination of contact angles. Contact angles in single mineral systems have been correlated with mineral flotation; however, they are a poor predictor of flotation outcome in real systems with complex mineralogy (Nagaraj & Ravishanker, 2007). The advancement of calorimeters that have accurate and reliable measurements has resulted in their use to measure the heat of immersion. Heat of immersion has high sensitivity, and it can be used to determine the difference in wetting for solids reported to have contact angle values of zero (Taguta et al*.,* 2018). The calorimetry technique studies the interactions between fluids and solid surfaces (Denoyel et al*.,* 2004). It has been shown that immersion calorimetry is useful in investigating the wetting tendency of solid surfaces, surface polarity and site energy distribution (Melkus et al., 1989). This can help reveal the chemical nature of the solid surface and its interactions with liquid molecules in the solid surface surroundings.

The advantage of determining wettability of solid surfaces using heat of immersion is that the preparation method is simple compared to that of contact angle, it is not susceptible to contact angle hysteresis problems, and the surface roughness does not play a role (Spagnolo et al*.,* 1996). However, the disadvantage with the heat of immersion is that the solid surfaces are required to have high specific surface areas (Chessick & Zettlemoyer, 1959; Spagnolo et al., 1996). This is because, if the specific surface area of the solid is small, the resulting heat of immersion will be small. This is dependent on the surface energy of the solid, for example, hydrophobic solids have low surface energy and thus if they have a low specific surface area it is necessary to use larger sample mass. Additionally, chemisorption of the wetting liquid, structural changes or sintering during sample preparation are factors that need to be considered when the heat of immersion is compared across different solids.

Several calorimetric studies focusing on the heat of immersion have been done, but very few have been within the context of minerals processing. Studies have shown that the heat of immersion can be used to determine the wetting tendency of different single minerals typically found in mineral ores (Taguta et al., 2018). Therefore, in this study, a methodology for determining the heat of immersion for mineral mixtures will be developed, while taking into account the challenge of dissolution of the mineral (indicated by an endothermic response from the measurements).

2.3.1 Introduction to the Heat of Immersion

The heat of immersion is defined as the heat released when a clean solid is immersed in liquid (Melkus et al., 1989; Spagnolo et al., 1996). This was substantiated by Denoyel et al. (2004) and Emami et al*.* (2014) who defined heat of immersion as the energy or enthalpy released when clean, vacuum-dried solid particles are immersed in water. Glaser & Weitkamp (2008) and Silvestre-Albero et al*.* (2001) added the important caveat that the heat of immersion is the enthalpy change at constant temperature *where the immersion liquid is a non-reacting liquid*. The standard free energy accompanying the process of immersion is given by Equation 1 where ΔG_i^0 is the standard free energy change, ΔG_γ^0 is the contribution to the total free energy of immersion due to changes in the interfaces when the solid-gas interface is replaced by the solid-liquid interface during immersion, and ΔG_{el}^0 is the contribution due to the formation of an electrical double layer at the solid-liquid interface.

$$\Delta G_i^0 = \Delta G_\gamma^0 + \Delta G_{el}^0$$ Equation 1

Calorimetric studies have shown that for minerals such as alumina, silica, titania, and other inorganic oxides, heat of immersion can be characterised by the quantity of heat liberated when the oxide is immersed in a liquid given that the surface of the solid has been outgassed to remove the physically adsorbed surface water (Healy & Fuerstenau, 1965).

The heat of immersion (ΔH_{imm}) is the sum of dispersion forces (h_i^d), polarising forces (h_i^μ), and electrostatic forces (h_i^α) between the permanent dipole moment of the wetting liquid and the static electric field of the solid surface (Morita & Takami, 2004). This can be represented as shown in Equation 2.

Equation 2
$$\Delta H_{imm} = h_i^d + h_i^\mu + h_i^\alpha$$

During immersion, the replacement of the solid-gas interface with the solid-liquid interface causes a change in enthalpy which result in a decrease in free energy (Skwarek et al., 2018). This process is accompanied by a release of heat whose value is determined by the intensity of interactions between the liquid molecules and the solid surfaces, and the value of the interaction area (Goncharuk, 2015).

Heat of immersion is exothermic and for a known surface area of the solid, the heat of immersion can be represented on a unit area basis as shown in Equation 3, where ΔH_{imm} is the heat of immersion, $\sum$ is the surface area of the solid, and e_{SL} and e_{S^0} are the energies of the solid-liquid interface and the solid surface, respectively (Chessick & Zettlemoyer, 1959). This heat is exothermic because in the viewpoint of thermodynamics, the changes of the solid-gas interface to the solid-liquid interface result in a decrease in Gibbs free energy (Goncharuk, 2015).

$$\frac{\Delta H_{imm}}{\Sigma} = e_{SL} - e_{S^0}$$ Equation 3

2.4 Interactions Behind the Wetting Process

The heat of immersion does not only relate the surface of the solid available to the liquid but also the specific interactions between the solid and the immersion liquid resulting from the presence of polar sites on the solid surface (Barton & Harrison, 1976). Surface forces are of importance in determining whether or not a liquid will wet the solid surface. These surface forces are inclusive of van der Waals forces and electrostatic forces. Van der Waals are responsible for the way fluids spread over solid surfaces and for the equilibrium thickness of the wetting film (Barton & Harrison, 1976). The van der Waals interaction forces are inclusive of the dipole – dipole, dipole – induced dipole and induced dipole – induced dipole interactions. The heat of immersion per unit area is found to be a direct measure of the adsorptive forces interacting during the immersion of the solid into the liquid (Barton et al., 1973).

The wetting process takes into consideration a variety of intermolecular forces ranging from universal non-specific intermolecular interactions, which occur in all cases, to specific interactions such as hydrogen bonding, electrostatic interactions, and the formation of charge-transfer complexes (Goncharuk, 2015). Wetting and adsorption processes display dispersion interactions which are the simplest form of intermolecular interactions (Goncharuk, 2015). Dispersion interactions are universal non-specific intermolecular interactions caused by electron density fluctuations in the interacting systems (Goncharuk, 2015). However, the energy from the other polar interactions is much higher than the energy due to the dispersion interactions thus making the polar interactions more crucial in differences in the heat of immersion (Goncharuk, 2015; Young & Bursh, 1960). According to the molecular theory of wetting, the dispersive and polar (non-dispersive) intermolecular interactions have an additive contribution to the interfacial energy (Goncharuk, 2015). The strength of the interaction between water molecules and the solid surfaces can be directly measured or estimated using the heat of immersion technique.

A solid surface is considered hydrophobic if the attractive interactions between the solid surface and the wetting liquid are only due to dispersion forces (Glaser & Weitkamp, 2008). A solid surface is considered hydrophilic when there is contribution from the electrostatic and the dipolar attractions (Glaser & Weitkamp, 2008). Dipolar attraction are dipole-dipole forces that are attractive forces between the positive end of one polar molecule and the negative end of another polar molecule. Zettlemoyer et al. (1958) stated that for a heteropolar surface interacting with a polar molecule, a significant contribution to the interaction energy comes from the polar van der Waals forces.

The distinction between hydrophobic and hydrophilic is the competition between the free energy of cohesion of the water and the interfacial free energy of cohesion of the solid immersed in water (Van Oss & Giese, 1995). Chatterjee et al. (2017) stated that the interplay between the cohesive and adhesive intermolecular forces is a result of wettability. The degree of wettability is determined by the particles' surface energies (Ali et al., 2013). Fuji et al. (1999) added that the wetting behaviour of a liquid molecule on a solid surface is determined by the differences in adhesive interactions between the solid and the liquid, and the cohesive interactions between the liquid molecules themselves.

2.5 Previous Studies Using the Heat of Immersion to Establish Wettability

Many studies on the heat of immersion of various oxides have been conducted because the heat of immersion is a convenient way to estimate the strength of the interactions of water molecules and the solid surfaces (Takei & Chikazawa, 1998). Takei et al*.* (1998) mentioned that the heat of immersion in water is expected to be related to the interactions between water molecules and the solid surfaces. Immersion calorimetry is sometimes used in characterising the surface properties such as the surface area and pore size distribution. Silvestre-Albero et al. (2001) stated that measuring the heat of immersion in liquids of different molecular sizes allows for the assessment of micropore size distribution in coals. Additionally, Taraba and Zelenka (2017) showed that using calorimetry and the Stoeckli Kraehenbuehl equation has proven calorimetry to be an independent experimental method to complement the basic gas/vapour adsorption measurements as a way to qualitatively characterise micropore systems of activated carbons. Furthermore, the heat of immersion can be used to assess the site energy distribution of solid surfaces when it is measured for solid surfaces that are partially or totally pre-covered by a liquid film prior to the measurement (Silvestre-Albero et al., 2001).

Fuller (1980) used calorimetric studies to analyse the structure and chemistry of coals due to the importance of coals to energy and chemical feedstock. They stated that the heat evolution due to the wetting process is a result of two factors, namely, the capacity factor and intensity factor. The capacity factor is due to the pore size of the carbon surface induced by the absorbed liquid while the intensity factor is due to polarity.

In the mineral studies context, heat of immersion has been used to rank coal and study their wetting characteristics. Melkus et al*.* (1989) and Menendez (1998) stated that immersion calorimetry can be useful in determining and quantifying the hydrophobic and hydrophilic nature of carbons. The heat of immersion has been used to determine the structure and chemistry of coals and it has been demonstrated that it is a good technique for this purpose (Fuller, 1980). Silvestre-Albero et al. (2001) used the heat of immersion of activated carbon and graphite in water to understand the hydrophobic nature of the carbon surface. The heat of immersion has also been used to determine surface properties of zircon powders which are used in the ceramic industry (Chan et al., 1997). Chan et al*.* (1997) found that the heat of immersion increases with an increase in fineness of the powder, that is, increasing surface area.

Silica surface properties have been studied intensively because of the practical uses of silica as a catalyst support, adsorbent, and in fillers (Takei & Chikazawa, 1998). The heat of immersion in water has been used to determine the surface properties of various silicas and characterise their surface bonds (Young & Bursh, 1960). Heat of immersion has been used to understand how crystallinity affects the interaction of silica surfaces with water (Takei et al., 1998). Kondo et al. (1978) studied the effect of heat treatment of silica gels on the heat of immersion in water under different conditions. The relationship between the heat of immersion of silica gel has been explored by Takei et al. (1998) where the heat of immersion is related to the degree of surface hydroxylation as shown in Equation 4, where q_1 and q_2 are the heat of immersion of the perfectly hydroxylated and dehydroxylated silica while S_1 and S_2 are the fractions of the hydroxylated and dehydroxylated surface areas, respectively. This concept is similar to the concept of determining the heat of immersion for binary mineral mixtures as shown by a model provided by Taguta et al. (2019).

$$\Delta H_{imm} = q_1 S_1 + q_2 S_2 \qquad \text{Equation 4}$$

Despite the successful use of microcalorimetry in different industries, calorimetry has hardly been employed in the minerals processing industry as a measure of wettability.

2.6 Differences in the Heat of Immersion

It has been observed across various authors that the reported values of the heat of immersion of different oxides in water are different. This variation is because of the difference in structural changes of the solid surface, the presence and type of functional groups in the solid surface, and crystallinity. Other factors that influence the outcome of the heat of immersion are the mass of the sample, the surface area of the solid, outgassing temperature, and the chemical nature of both the immersion liquid and the solid surface. Outgassing temperature is the temperature at which the sample is vacuum dried or prepared before the immersion.

Heat of immersion has been measured for different solids such as silica, alumina, and titania in both polar and non-polar liquids. Most of the solids used in immersion calorimetry are polar solids of metal oxides and silicates. The heat of immersion has been reported as a function of outgassing temperature, surface area and particle size. There have been complex observations when solids are immersed in water; however, these have not been discussed in the minerals processing context except in the pharmaceutical and food industries.

2.6.1 The Effect of Outgassing Temperature on the Heat of Immersion

The temperature that the sample is vacuum dried at before the heat of immersion measurements can be conducted is referred to as the outgassing or degassing temperature. This temperature is recommended to be high so as to remove all the physically adsorbed water on the surface of the solid or mineral. However, there are limitations to the temperatures that some minerals can be exposed to. For example, galena oxidises at temperatures of approximately 60°C while hematite reduces at temperatures of approximately 250°C, therefore lower temperatures are chosen for such minerals.

In a study conducted by Rootare & Craig (1974), the heats of immersion for silica, alumina, and titania were observed to be increasing with an increase in outgassing temperature. This was related to the increasing loss of surface-adsorbed water as the outgassing temperatures were increased. The increase in outgassing temperatures causes the strongly bound water to dehydrate or desorb. Large amounts of energy are required for rehydration and adsorption thus in turn increasing the heat of immersion (Rootare & Craig, 1974). The results obtained by Watanabe & Seto (1988) agree with those obtained by Rootare & Craig (1974) where the former also observed that the heat of immersion of hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) increases with outgassing temperature as shown in Figure 2-9.

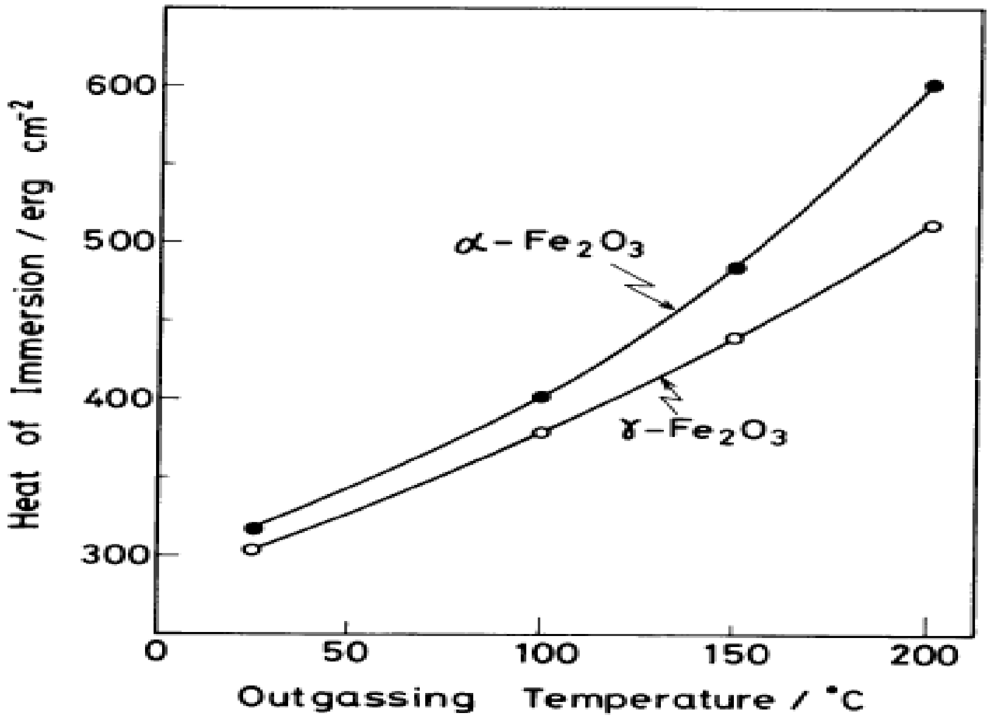


Figure 2-9: Heat of immersion of hematite and maghemite in water as a function of outgassing temperature (Watanabe & Seto, 1988).

If the outgassing process only removed the physisorbed water on the surface, then there should not be any physically bound or adsorbed water on the surface after outgassing, meaning that the heat of immersion would be independent of the outgassing temperature (Rootare & Craig, 1974). For the study conducted by Rootare & Craig (1974) on the immersion of hydroxyapatite (HAP) in water, it was observed that the heat of immersion increased steadily even when the surface area remained constant at outgassing temperatures between 100°C and 300°C. An explanation for this phenomenon as described by Rootare & Craig (1974) is that at high outgassing temperatures, physisorbed water that is strongly bound to the HAP surface is progressively removed. Therefore, when the HAP sample is immersed in liquid or water, the re-physisorbed water results in a larger net heat of adsorption or heat of immersion. An explanation by Barton & Harrison (1976) as to why the heat of immersion increases with an increase in outgassing temperature has been given to be the removal of physisorbed water on the solid surface, and the rehydration during immersion. This explanation aligns with that given by Rootare & Craig (1974).

2.6.2 Effect of Surface Area on the Heat of Immersion

Silvestre-Albero et al. (2001) assumed that for microporous carbons, there is a direct relationship between the heat of immersion and the total area of the solid accessible to the wetting liquid irrespective of the solid's external or internal microporous structure, size, and shape of the micropores. Chessick & Zettlemoyer (1959) and Spagnolo et al. (1996) added that because the heat of immersion is dependent on the surface energy of the solid, the required surface area is high especially for hydrophobic solids since their surface energy is low. This is because if the specific surface area of the solid is low, the measured heat of immersion will be small. Alternatively, larger mass of the solid can be used for the hydrophobic solids. Silvestre-Albero et al. (2001) found that for a given solid-liquid system, the heat of immersion increases with an increase in available surface area.

Terada & Yonemochi (2004) studied the effect of grinding on the physicochemical characteristics of talc and they found that the specific surface area increased proportional to the particle size reduction. They found that from the microcalorimetry experiments, the heat of immersion per unit area increased with increasing grinding time or increasing surface area (Tarada & Yonemochi, 2004). Holmes et al. (1972) who studied the heat of immersion of zirconium oxide concluded that the heat of immersion decreases with a decrease in surface area. This is in support of the findings by Rootare & Craig (1974) who studied the heat of immersion of hydroxyapatites. Donnet et al. (2008) who studied the influence of surface area on the heat of immersion for pyrogenic silicas also found consistent results with the above where the heat of immersion in water of these silicas was linearly proportional to the surface area. The notion of heat of immersion being linearly proportional to the surface area is supported by Chan et al. (1997) who stated that the heat of immersion increases with an increase in fineness of the powder or solid.

2.7 Dissolution

Many dissolution reactions reported in literature are exothermic. However, there is very little in the literature regarding the problematic endothermic response observed for certain minerals when immersed in water and this is an issue worthy of further investigation. This is not only to understand the fundamentals and thermodynamics behind this response but to reveal properties of the minerals that are not yet understood or easily interpretable. This is because it is well known that the heat of immersion is sensitive to the properties of the solid surface.

The output of a calorimetric experiment is a composite of the wetting process, liquid penetration for porous solids, and the dissolution process (Marabi et al., 2007). The detected heat in immersion calorimetry is the sum of individual reaction heats as described by Equation 5 where the total heat detected (Q_{exp}) is the sum of the heat of adsorption (or wetting) of the wetting liquid on a mineral surface and the heat of dissolution due to the dissolution of the mineral surface (Wierer & Dobiáš, 1988). In immersion calorimetry using water as a wetting liquid, the heat of adsorption can be expected to be negative while the heat of dissolution is positive (Wierer & Dobiáš, 1988).

$$Q_{exp} = H_{adsorption} + H_{dissolution} \qquad \text{Equation 5}$$

Dissolution, crystallisation, hydrolysis, and the formation of complex ions in solutions are the processes that the chemistry of crystalline solids in solution relates to (Voigt, 2011). When these solids are dissolved in water, it is required that the lattice energy is overcome by the ionic hydration process. The solubility of crystalline solids in water or solutions with other ions depends on the interactions such as the ion-water interactions and the ion-ion interactions. This is besides the intrinsic properties of the solid such as the entropy and lattice enthalpy. In addition, these interactions are sensitive to temperature, concentration, and composition (Voigt, 2011).

The enthalpy of dissolution in aqueous solutions that characterise the dissociation of crystalline solids in water can be presented as shown in Equation 6. The enthalpy of dissolution characterises the nature of the process as to whether it will be endothermic or exothermic. Craig & Newton (1991) added that the heat of solution represents the sum of all the enthalpies for each stage occurring during the dissolution process. Quantifying these individual processes is fairly difficult.

$$\Delta H_{dissolution} = \Delta H_{lattice\ dissociation} + \Delta H_{hydration} \qquad \text{Equation 6}$$

During dissolution, energy is required to break the intermolecular attractions of the solute to form new bonds. This energy is supplied by the new interactions that form in the solution. For a successful dissolution, the solute-solute and solvent-solvent interactions must be disrupted. The lattice dissociation enthalpy is a result of the breakage of the strong Coulombic interactions in the solid lattice when the separated ions are being formed. This energy is always positive. Conversely, the enthalpy of hydration results from the formation of the strong charge dipole and hydrogen bonding interactions with water molecules in the aqueous environment. This enthalpy is always negative. Therefore, the net effect which is the enthalpy of dissolution is a balance between the magnitudes of these two enthalpic contributions. If the lattice dissociation enthalpy is greater than the enthalpy of hydration then the process will be endothermic while if the inverse is true, then the process will be exothermic.

The energetics of dissolution occur in three discrete steps. The overall enthalpy of solution is the sum of the enthalpies in the three steps. Step 1 and step 2 are both endothermic since energy is required to overcome the intermolecular interactions between the solvent (solvent-solvent interactions) and the solute (solute-solute interactions). Step 3 which is the solute-solvent interactions must be stronger than both solute-solute and solvent-solvent interactions for the dissolution to be exothermic (negative). When the solute is an ionic solid, the solute-solute interactions represented by step 2 corresponds to lattice energy that must be overcome to form a solution. Solids that have higher lattice energy generally have low solubility in all solvents.

2.7.1 Previous Studies Using Calorimetry to Establish Heat of Dissolution

There are various fields where dissolution calorimetry has been applied, but none is in the minerals processing industry. The dissolution behaviour of crystalline and amorphous saccharides has been studied, where it was found that the crystalline saccharides presented an endothermic response while all the amorphous saccharides presented exothermic responses ranging from 17 to 90 J/g and -30 to -80 J/g, respectively (Marabi et al., 2007). The difference in these responses is attributed to the higher internal free energy and entropy of the metastable amorphous material which results in enhanced dissolution rate and chemical reactivity compared to the stable crystalline state which is thermodynamically favourable (Marabi et al., 2007). For the amorphous material, the solid interactions are said to be weaker resulting in a more spontaneous dissolution characterised by a release in energy**.** For the crystalline material, it is said that crystallisation possibly leads to impaired rehydration properties due to the change in physical structure or properties during the process. This is because the bonding energy plays a role in these differences since the crystalline and amorphous states do not have the same bonding energy.

In a study conducted by Gao & Rytting (1997) to determine the extent of crystallinity of drugs and excipients using solution calorimetry, it was found that the dissolution of crystalline sucrose in water at 25°C was endothermic. They stated that this may be because of the crystalline material being at its lowest energy state together with stronger interactions within the crystalline structure compared to the hydration process thus resulting in an overall endothermic response. They further measured the heat of solution of dry amorphous sucrose and obtained an exothermic response. The results from Marabi et al. (2007) and Gao & Rytting (1997) are in agreement in their observations.

Kayaert et al. (2010) studied solution calorimetry as an approach to study the dissolution of nanosuspensions in the drug industry. Conti et al. (2006) used solution calorimetry in their study as a technique to measure or monitor the swelling and dissolution of polymers. Their results showed that the responses of the 3 different polymers used were different and this is an indication of the level of sensitivity that the solution calorimetry offers and can subsequently be used to discriminate or compare between polymer grades.

Kayaert et al. (2010) demonstrated the contributions due to different processes occurring during immersion using solution calorimetry by monitoring the dissolution of compound A. Compound A did not only contain the pure compound but other reagents such as sodium carboxymethylcellulose, sodium deoxycholate, and polysorbate 20. During the dissolution of this compound in 0.05 M borate buffer at pH 10, the temperature decreased after the ampoule break, immediately followed by a temperature increase. This indicates that at least two phenomena or processes were occurring simultaneously. One of the phenomena is endothermic while the other is exothermic. The authors argued that in this case, the endothermic response is due to the dissolution process while the exothermic response is due to heat of immersion (Kayaert et al., 2010).

2.7.2 Remedies to the Dissolution Challenge

Results from experimental work conducted by Taguta et al. (2018) showed that the heat of immersion is greatly affected by the dissolution of the mineral surface ions. This dissolution of the mineral surface was explained to be observed as an endothermic peak that was then followed by an exothermic peak. The heat measured by the calorimetric equipment was then attributed as both the dissolution of the mineral surface ions and the interaction between the mineral surface and water molecules (Taguta et al., 2018). To overcome this, Taguta et al. (2018) suggested that the wetting liquid be a saturated solution containing ions of the mineral of interest. This was done to drive the dissolution reaction in the reverse direction during the heat of immersion measurements. This assumes that the wetting liquid is in equilibrium with the solid state of the mineral at all times and thus suppressing the contribution from the dissolution process. The endotherms (endothermic peak) disappeared when this technique was followed.

Zimmermann et al*.* (1987) conducted heat of immersion experiments of various minerals in a saturated solution as the wetting liquid to eliminate the contributions from the dissolution process. Taraba & Zelenka (2017) also conducted heat of immersion experiments in a saturated solution of butanol instead of water as used by other authors. The endotherm was not observed in both cases.

These were the only references to a suppression of the dissolution reaction that could be found in literature, and, in most studies, the dissolution reaction appears to have been ignored.

2.8 Various Wetting Liquids

The extent of the decrease in Gibbs free energy when a solid is immersed in a liquid is determined by the intensity of the interactions of the solid and liquid molecules. This has led to an exploration of various liquids to measure the heat of immersion without the solid reacting with the wetting liquid.

Kraus (1955) found that the heat of immersion depends on the chemical constitution of both the wetting liquid and the solid. They found that the heat of immersion is higher for inorganic solids containing oxygen when immersed in polar, hydrogen bonding liquids while the inverse is true for nonpolar liquids (Kraus, 1955).

Kraus (1955) studied the heat of immersion of carbon black in various liquids such as water, methanol, and n-hexane. They found that the heat of immersion remained fairly constant for the carbon blacks in hexane and their reasoning was that there is no possibility of hydrogen bonding between the carbon black and hexane and that the interaction forces involved are probably dispersion forces. Wade & Hackerman (1962) studied the heat of immersion of various solids in hexane as a function of outgassing temperature and particle size and they found that the heat of immersion in hexane is lower than that in water and this is because the only significant attractive forces acting during the interactions of hexane and solid surfaces arise from the van der Waals forces. During the interaction between the solids tested and water, the interaction energy or forces at play are the hydrogen bonding and these increase the heat of immersion. However, with hexane, the hydrogen bonding does not contribute. Goncharuk (2015) found that the heat of immersion in polar liquids was higher than in nonpolar liquids and this was attributed to the differences in intermolecular interactions between the solid and the wetting liquid (Goncharuk, 2015). The interaction of the solid surface with nonpolar wetting liquids is limited to van der Waals interactions. This is in support of the results obtained by Wade & Hackerman (1962). This ultimately leads to the heat of immersion in nonpolar liquids such as hexane and decane being low due to the low energy of interaction and the independence on the concentration of hydroxyl groups (OH).

Taraba & Zelenka (2017) studied different coal samples under different immersion liquids. Heats of immersion in methanol and ethanol were seen to strongly correspond with the hydrophobic and hydrophilic nature of the sample. Specifically for the hydrophilic coal sample, they observed that the heat of immersion in methanol and ethanol follow the same trend as that in water. Thus the specific interactions between the hydroxyl groups of the immersion liquid and the polar sites of the sample surface contribute mainly to the immersion heat effect (Taraba & Zelenka, 2017). Inversely, the heat of immersion values of the activated coal sample (hydrophobic coal sample) in methanol and ethanol are similar to that of benzene providing evidence that non-specific interactions between the alkyl chain of the alcohol and the hydrophobic carbonaceous surface is prevailing or dominant. Interestingly, the low rank sub-bituminous coal sample had heat of immersion values in methanol and ethanol that were equivalent to the sum of the heat of immersion values in water and benzene indicating that both the alkyl chain and hydroxyl group take part in immersion of this sample. It was mentioned by Goncharuk (2015) that the heat of immersion of hydrated amorphous silica in alcohol was higher than in alkanes (saturated hydrocarbons) because of the presence of the OH group for the alcohols. The interactions of the polar liquids with solid surfaces such as silica is complex as there is now an additional effect due to dispersive interactions and other interaction energies larger than that of dispersive interactions (Goncharuk, 2015).

2.9 Wettability of Heterogenous Surfaces and Mixtures

In reality, solid surfaces are never homogeneous, but chemically heterogenous because of the different materials in their structure. The heterogeneity may be a result of impurities in the mineral, different crystal faces being exposed, oxidation for sulphide minerals (Ali et al., 2013), shape, chemistry or roughness (Muganda et al., 2011), and unbalanced ratio of cations and anions. This heterogeneity then results in different wettabilities for the mineral particles. Since wettability is understood to be an important surface property that is related to the surface energy of the solid, it is believed to contain useful information about surface heterogeneity (Chatterjee et al., 2017). Heterogeneity can either be physical or chemical, where physical heterogeneity is a mixture of minerals whereas chemical heterogeneity is due to different surface sites of a single mineral. Microcalorimetry has been seldomly used in determining the hydrophobic and hydrophilic nature of minerals in minerals processing except in the few instances of oxides, but perhaps it could play a role in determining the surface heterogeneity of minerals.

The Cassie-Baxter (CB) model theoretically characterises the wetting of chemically heterogenous flat surfaces by an apparent contact angle (Nguyen et al., 2018). For binary mixtures, those containing only two different materials, the Cassie-Baxter model can be written as shown in Equation 7, where θ_C is the apparent contact angle, θ_{Y1} and θ_{Y2} are the equilibrium Young contact angle for material 1 and 2, and $f_1$and f_2 are the surface fractions of material 1 and 2, respectively.

$$cos\theta_C = f_1 cos\theta_{Y1} + f_2 cos\theta_{Y2} \qquad \text{Equation 7}$$

The Cassie-Baxter model is a generalised Young equation for composite materials, and it assumes a linear additivity of the wetting free energies of the comprising materials (Nguyen et al., 2018). The Cassie-Baxter model is widely used for smooth, chemically heterogenous surfaces by defining an average contact angle from the weighted mean of the contact angles of the pure solids.

It has been shown by Taguta et al*.* (2019) that there is a relationship between the heat of immersion and the composition of the hydrophilic mineral in a binary mineral mixture. It is clear from Figure 2-10 that the heat of immersion in water becomes more exothermic as the composition of the hydrophilic mineral increases. This means that an increase in the heat of immersion in water denotes an increase in hydrophilicity. This is a demonstration that the overall hydrophobicity of a synthetic ore decreases when the composition of the hydrophilic mineral is increased.

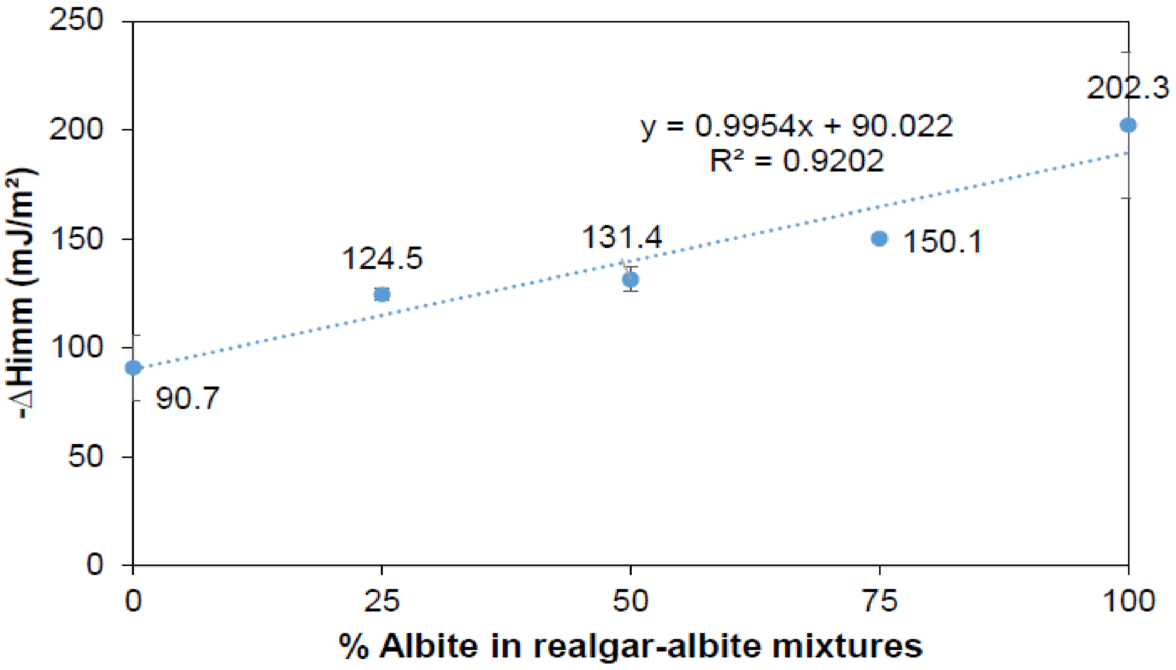


Figure 2-10: Heat of immersion as a function of mineral composition for binary mineral mixtures extracted from (Taguta et al., 2019).

Taguta et al. (2019) stated that the heat of immersion is additive in nature, and this aligns with the Cassie-Baxter model. This means that the heat of immersion of a synthetic ore can be calculated as the weighted sum of the heat of immersion per mass of the individual minerals constituting the ore. Gao & Rytting (1997) also found a linear relationship between the heat of dissolution measured by solution calorimetry and the composition of the crystalline material in the mixture. They further added that the heat of solution of non-reacting binary systems is the weighted sum of the heat of solution of the individual components of the binary system as shown by Equation 8 where X and ΔH are the weight fractions and the heat of solution respectively.

$$\Delta H_{imm} = X_a \Delta H_a + X_b \Delta H_b \qquad \text{Equation 8}$$

2.10 Heat of Immersion in Flotation

There is limited work that correlates the heat of immersion to floatability or flotation response. The heat of immersion has shown sensitivity to distinguish the wettability of different pure minerals (Taguta et al., 2018). The heat of immersion has been used to measure the wettability of mineral surfaces; however, this was done for pure minerals and that could limit the applicability of the results obtained (Taguta et al*.,* 2018). Taguta et al. (2019) demonstrated that there is a relationship between the heat of immersion and the flotation response as presented by the first order flotation rate constant and this relationship is shown in Figure 2-11. Additionally, Melkus et al*.* (1989) found that the flotation response is inversely proportional to the heat of immersion and that the heat of immersion significantly varies with coal ranks. This means that the coal that has low floatability has the highest heat of immersion.

Taguta et al*.* (2019) observed that the flotation rate constant decreases with an increase in the heat of immersion for the floatable minerals and this was supported by Melkus et al. (1989) who stated that the heat of immersion in water for coals is inversely proportional to the flotation response or floatability. This relationship was sustained even in the presence of a xanthate collector for both realgar and galena minerals (Taguta et al., 2019).

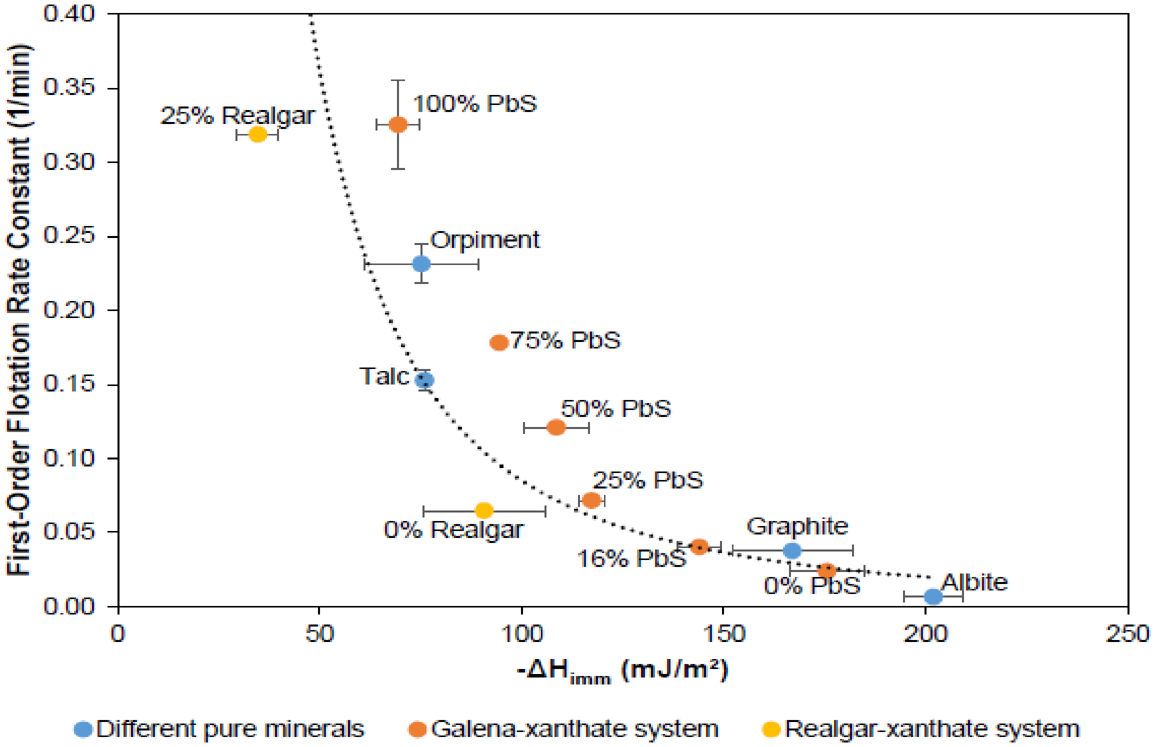


Figure 2-11: The relationship between heat of immersion and the flotation response (floatability) for galena-amyl xanthate system, realgar-xanthate system and different pure minerals extracted from (Taguta et al*.*, 2019).

2.10.1 Heat of Immersion with Addition of Reagents

Chemical reagents such as collectors are added to a flotation system to render the target mineral surface hydrophobic and increase its chances of reporting to the concentrate. Taguta et al*.* (2019) demonstrated that the heat of immersion in water is inversely proportional to the collector surface coverage. This is an indication that a collector increases the hydrophobicity of the mineral surface. They pointed out that the decrease in heat of immersion with increasing collector surface coverage is not mineral specific (Taguta et al., 2019). This demonstrates that the heat of immersion is able to assess changes in mineral surfaces due to collector coverage.

Melkus et al. (1989) used microcalorimetry studies to investigate the heat of immersion of coals in various liquids. The effects of chemical additives were also investigated using the heat of immersion technique. The results from the heat of immersion measurements were then compared with flotation experiments since the heat of immersion provides a relative measure of hydrophobicity. Melkus et al. (1989) found that the heat of immersion decreased with an increase in collector dosage. This means that the coals which were used in their investigation were more hydrophobic with increasing collector dosage. This aligned with their flotation results where the recovery increased with an increase in collector dosage. Based on this, the heat of immersion measurements of the coals with collector will be a result of the heat released when the solid is immersed in liquid and the heat due to the adsorption of the collector onto the mineral surface (Melkus et al., 1989). It was assumed that the adsorption of the collector occurs on specific sites of the coal surface blocking other sites from the water molecules resulting in an overall decrease of the heat of immersion (Melkus et al., 1989). Fuji et al*.* (1999) and Barton et al*.* (1973) conducted similar studies of precovering the solid sample with a liquid prior to heat of immersion experiments. Fuji et al. (1999) pre-covered silica samples with various alcohols and measured the heat in water. They found that the heat of immersion in water decreased with an increase in covering ratio. This alcohol covering technique was similar to covering with reagents and the results follow the same trend as that of covering with reagents. What will be of interest is knowing the interactions between the water and the alcohols in comparison to the interactions between water and collectors as it seems that covering with alcohol increases the hydrophobicity of the solid samples similar as covering with collectors as indicated by a decrease in the heat of immersion.

2.11 Detailed Objectives

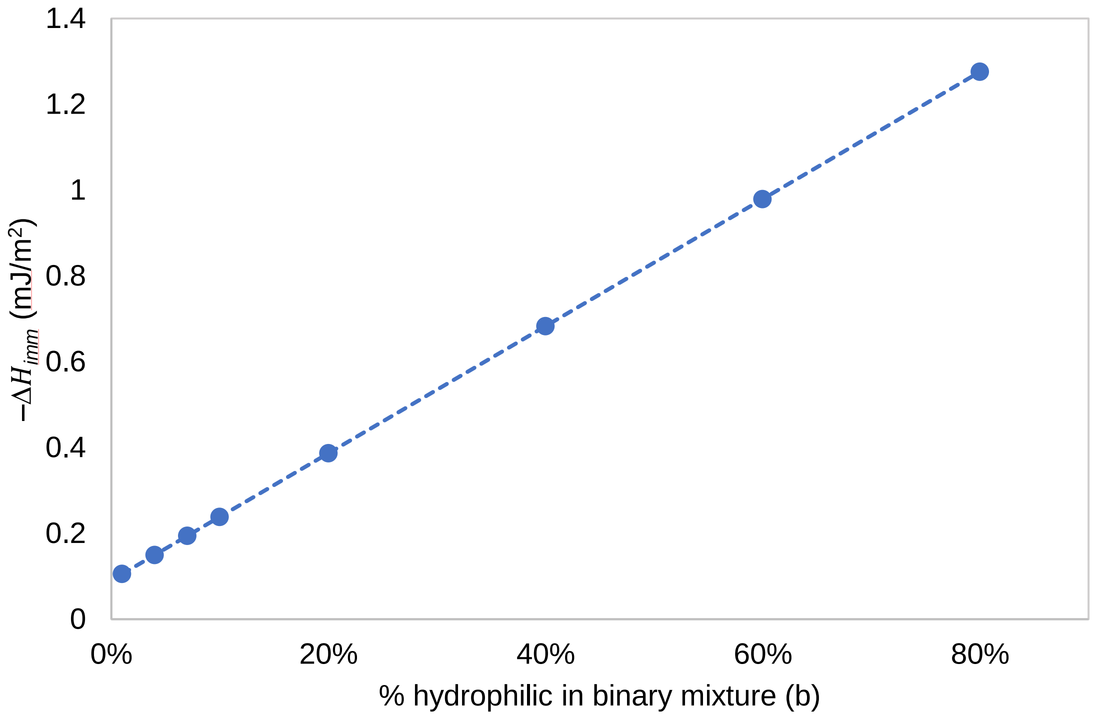
The outcome of this research project is to develop a methodology that will demonstrate that the heat of immersion can be used to measure the wettability of mineral mixtures using solution calorimetry. The elaborate project aims are as follows:

- To explore wetting liquids of different polarity to understand the heat of immersion response of minerals that simultaneously involves the dissolution process and the wetting process.
- To determine the effect of collector surface coverage on the heat of immersion as a dissolution suppression method.
- To determine the surface wettability of a binary mineral mixture. Establish a relationship between the total heat of immersion and the composition of the mineral mixture that can

be used to determine the heat of immersion for the pure minerals comprising of the binary mineral mixture.

2.12 Hypotheses

- The endothermic response observed during the heat of immersion measurements for some minerals is indicative of the dissolution of the mineral into water occurring simultaneously with the wetting process because it has been shown that the wetting process is exothermic while the dissolution process may be endothermic or exothermic depending on the lattice and hydration energy.
- The dissolution of the mineral into water can be suppressed by several techniques. It is hypothesized that:
    a. A saturated solution will promote the reverse of the dissolution reaction and hence reduce the extent to which the mineral dissolves into the immersion liquid.
    b. Mineral surface coverage by a collector will reduce dissolution by covering the mineral active surface sites and reduce their exposure to the wetting liquid.
    c. Using wetting liquids in which the mineral is not soluble will reduce the dissolution process
- The heat of immersion for the pure minerals comprising the binary mineral mixture will equate to the intercepts at 0 and 100% in the linear relationship between the heat of immersion and the composition of the binary mineral mixture as shown in Figure 2-12. The intercepts are representative of the pure minerals making the binary mineral mixture. This



is because the Cassie Baxter model for determining wettability of binary mixtures assumes linear additivity of the wetting free energies of the comprising materials.

Figure 2-12: The total heat of immersion of the binary mineral mixture as a function of surface composition.

2.13 Key Questions

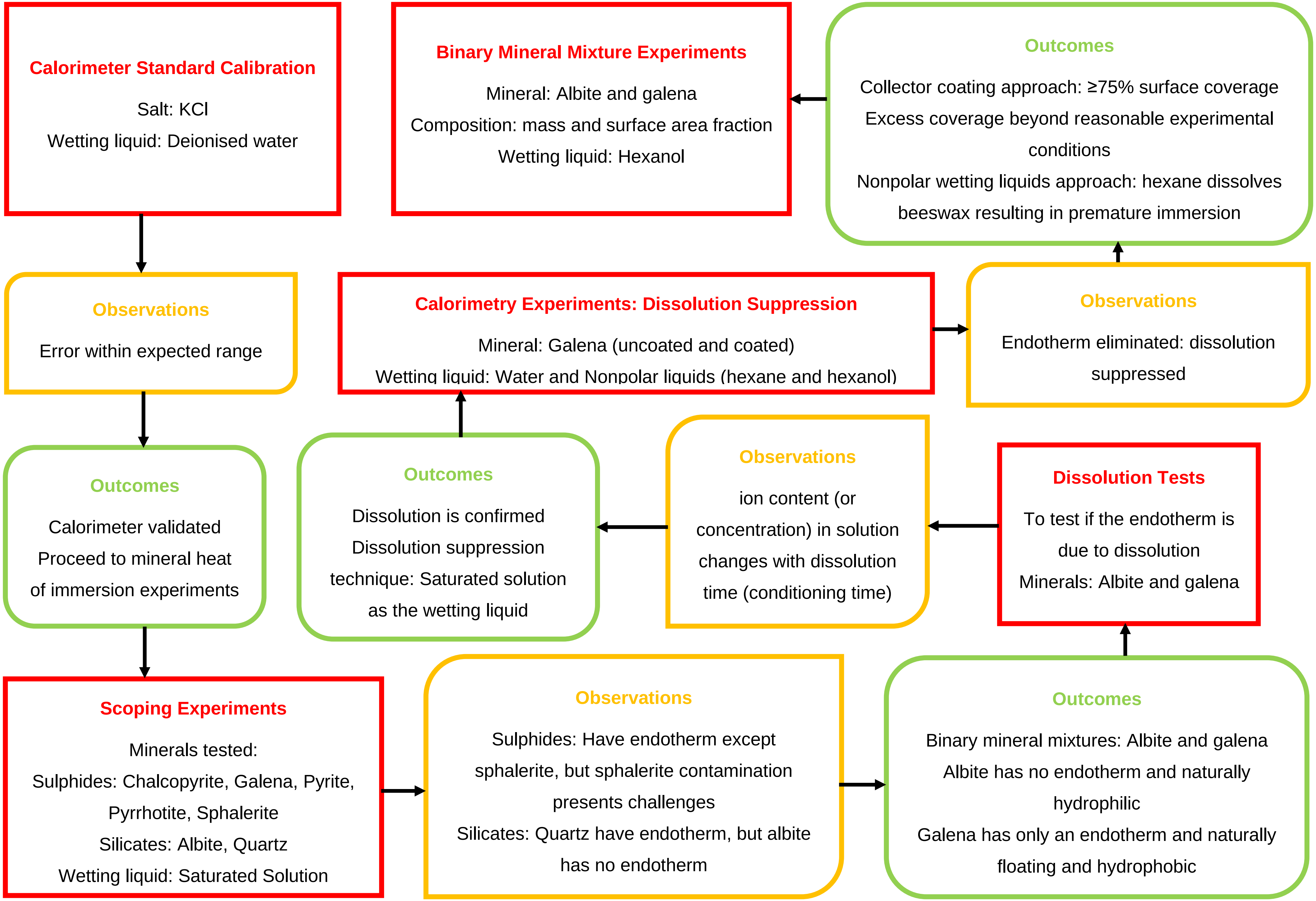
This section will identify the key questions that will be addressed in this research project to meet the objectives and validate the hypotheses.

- Can the dissolution process be suppressed by using a saturated solution as the wetting liquid to measure the heat of immersion?
- Can the dissolution process be suppressed by using other wetting liquids such as nonpolar liquids to measure the heat of immersion?
- At what collector surface coverage does the dissolution process get suppressed and how does increasing the collector surface coverage affect the heat of immersion?
- Is there a linear relationship between the heat of immersion and the composition of the binary mineral mixture?
- Does the extrapolated heat of immersion values for the pure minerals comprising the binary mineral mixture correspond with the experimentally measured values?

3 Experimental Methodology

The general aim of the project was two-folds: firstly, to address the challenges identified with the calorimetry technique for minerals, and secondly to extend the use of the technique to binary mineral mixtures. Taguta et al. (2018) highlighted concerns regarding dissolution of the mineral influencing the heat of immersion measurements. This will be explored in more detail within this project. Albite and galena were chosen as minerals to be studied for both the methodology and the binary mineral mixture. Due to the differences in hydrophilicities of these minerals, a difference in measured surface energies or wettability was expected. Albite was chosen because it had no endothermic response and is naturally hydrophilic whereas galena had an endothermic response and is naturally floatable. An endothermic response is proposed to be indicative of the dissolution of the mineral into the wetting liquid during the immersion measurements. Numerous methods were trialled to address dissolution, namely: saturated solutions, collector coating, and non-polar wetting liquids. The results will then inform a set of experimental conditions where dissolution is suppressed, and this will be applied in the investigation of a binary mineral mixture of albite and galena. A graphical representation of the project's experimental approach is displayed in Figure 3-1.

During the scoping tests on various minerals, sphalerite was initially a hydrophobic mineral of interest. However, characterisation of the mineral using XRD revealed that the mineral was only 74 wt.% sphalerite with galena being the main impurity at 24 wt.% and mica being the minor impurity at 2 wt.%. Moreover, the sphalerite purity changed as a function of the particle size. For this reason, sphalerite was excluded from further experimentations to avoid variation in the heat of immersion measurements as a function of surface area.



Calorimeter Standard Calibration

Salt: KCl

Wetting liquid: Deionised water

Observations

Error within expected range

Outcomes

Calorimeter validated

Proceed to mineral heat of immersion experiments

Scoping Experiments

Minerals tested:

Sulphides: Chalcopyrite, Galena, Pyrite, Pyrrhotite, Sphalerite

Silicates: Albite, Quartz

Wetting liquid: Saturated Solution

Observations

Sulphides: Have endotherm except sphalerite, but sphalerite contamination presents challenges

Silicates: Quartz have endotherm, but albite has no endotherm

Outcomes

Binary mineral mixtures: Albite and galena

Albite has no endotherm and naturally hydrophilic

Galena has only an endotherm and naturally floating and hydrophobic

Dissolution Tests

To test if the endotherm is due to dissolution

Minerals: Albite and galena

Observations

ion content (or concentration) in solution changes with dissolution time (conditioning time)

Outcomes

Dissolution is confirmed

Dissolution suppression technique: Saturated solution as the wetting liquid

Calorimetry Experiments: Dissolution Suppression

Mineral: Galena (uncoated and coated)

Wetting liquid: Water and Nonpolar liquids (hexane and hexanol)

Observations

Endotherm eliminated: dissolution suppressed

Outcomes

Collector coating approach: ≥75% surface coverage

Excess coverage beyond reasonable experimental conditions

Nonpolar wetting liquids approach: hexane dissolves beeswax resulting in premature immersion

Binary Mineral Mixture Experiments

Mineral: Albite and galena

Composition: mass and surface area fraction

Wetting liquid: Hexanol

Figure 3-1: Schematic representation of the experimental method.

3.1 Materials

3.1.1 Minerals

i. Albite and Galena

10 kg and 5 kg of albite and galena were received as chunks of rocks from the Ward's Natural Science Establishment and Top Stones, respectively. Primary size reduction of the minerals to -3 mm was performed by manual crushing using a hammer (hammering), followed by pulverising. Manual crushing was preferred over jaw crushing to avoid possible oxidation of the sulphide mineral surface due to exposure to steel or iron together with oxygen. After primary size reduction, the minerals were further ground in a Sieb Mill from the Ferguson Industrial Group to obtain a product size of 100% passing -106 µm. The minerals were then sieved to obtain a discrete size fraction of -25 µm. The -25 µm material was split using a rotary splitter to homogenise the sample and was stored under cold and dry conditions for the galena mineral and at laboratory 'room temperature' conditions for the albite mineral.

Mineral purity and surface area are crucial factors in the understanding of the heat of immersion response. Mineral purity was determined by the X-ray Diffraction (XRD) using the Rietveld method. Albite was found to be 96 wt.% pure with mica as the major impurity at around 4 wt.%. Galena was found to be 82 wt.% pure with cerussite and anglesite as the major impurities at 8 wt.% each. Galena had minor impurity such as biotite and smythite at 2 wt.% and <0.5 wt.% respectively. The galena major impurities, cerussite and anglesite, are also Pb minerals, shown in Table 3-1, and therefore can be assumed to be benign, meaning that the results will not be impacted adversely by their presence. The specific surface area of the minerals given in Table 3-2 was characterised using the Brunauer Emmett Teller (BET) technique using the Tristar II 3020.

Table 3-1: XRD results of albite and galena samples.

	Mineral	**Chemical formula**	**Composition (wt.%)**
Galena sample	Galena	PbS	82
	Cerussite	$PbCO_3$	8
	Anglesite	$PbSO_4$	8
	Biotite	$K_3AlSi_3O_{10}$	2
	Smythite	$(Fe,Ni)_9S_{11}$	<0.5
Albite sample	Albite	$NaAlSi_3O_8$	96
	Mica	-	4

Table 3-2: The specific surface area of albite and galena.

	Specific surface area (m^2/g)
Galena sample	0.551
Albite sample	1.63

ii. *Other Minerals*

Other minerals were initially also scoped in this study for the binary mineral mixture. Moreover, this was done to evaluate the presence of the endothermic response in various minerals of the same group. The minerals scoped are given in Table 3-3 and were all sourced from the Ward's Natural Science Establishment. The preparation method was similar to that outlined for albite and galena. However, mineral purity and specific surface area of these minerals was not determined.

Table 3-3: Different scoped minerals for the heat of immersion.

Mineral	**Chemical formula**	**Type**
Chalcopyrite	$CuFeS_2$	Copper Iron Sulphide
Pyrite	FeS_2	Iron sulphide
Pyrrhotite	$Fe_{(1-x)}S$	Iron sulphide
Sphalerite	ZnS	Zinc sulphide
Quartz	SiO_4	Silicate

3.1.2 Reagents

This section gives a brief outline on the reagents used to address the dissolution of the minerals.

i. *Saturated Solution*

The occurrence of the endothermic response was attributed to the dissolution of the mineral into the wetting liquid, deionised water. To mitigate this occurrence, a saturated solution as an alternative wetting liquid was explored in the heat of immersion measurements. The presence of the ions within the saturated solution will drive the dissolution reaction in reverse, closer to the equilibrium thus minimising the occurrence of the dissolution during the heat of immersion measurements.

The saturated solution was created using the mineral of interest in deionised water at 10 wt.%. The suspension was filtered, and the clear liquid was used in the experimental work. The pH of the saturated solution was found to be 8.6 for albite and 5.4 for galena. A fresh saturated solution was created prior to every experiment. A detailed experimental methodology for the preparation of the saturated solution is given in Section 3.3.3.

ii. Collector

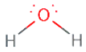
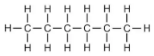
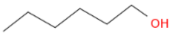
A second approach to suppressing dissolution and thus the endothermic response is covering the surface-active sites of the mineral to prevent the mineral surface ions from dissolving into the wetting liquid.

Sodium Isobutyl Xanthate (SIBX) was used for the experimental work in this study. It was supplied by AECI mining chemicals as granules at a reagent grade. It was prepared daily in deionised water as a stock solution of weight by volume percentage depending on the dosage requirements. The dosage was based on a theoretical monolayer coverage of the mineral surface based on the molecular footprint of xanthates of 28.8 Å^2 (Grano et al., 1997).

iii. Nonpolar Wetting Liquids

As part of the objectives of this study, wetting liquids comprised of organic hydrocarbons were tested to supress dissolution. The hydrocarbon liquids tested in this study were hexane and hexanol. The hydrocarbon liquids were explored because they have been used by other authors to measure the heat of immersion of various solids and no dissolution was observed or reported in the results (Goncharuk, 2015; Kraus, 1955). Hexane was supplied by Sigma Aldrich with a purity of 95% and hexanol was supplied by Merck, Schuchardt with a purity of 98%. Table 3-4 gives the characteristics of the various wetting liquids. The saturated solution and deionised water are included for comparison. The boiling point of the saturated solution was not experimentally determined but rather assumed to be approximately close to that of water at 100°C since the concentration of the ions in the solution is not significantly large.

Table 3-4: Characteristics of the wetting liquid.

	Water	**Saturated solution**	**Hexane**	**Hexanol**
Polarity	Polar	Polar	Nonpolar	Nonpolar
Boiling point (°C)	100	≈ 100	68	157
Intermolecular attractions	Hydrogen bonding	Hydrogen bonding and electrostatic interactions	Van der Waals	Van der Waals and hydrogen bonding
Structure		-		

3.2 Experimental Set-Up

3.2.1 Calorimetry

In almost every process, chemical or physical, there is a release of heat (exothermic) or absorption of heat (endothermic). This heat change can be measured by calorimetry, and it is observed as a change in temperature of the calorimeter. When the process is exothermic, the heat released is adsorbed by the solution and this increases the temperature of the calorimeter. But, when the process is endothermic, the heat required for the process is absorbed from the thermal energy of the solution and this decreases the temperature of the calorimeter.

In this study, the heat change when a solid is immersed in liquid was measured using a calorimeter. This heat change is referred as the heat of immersion. A Precision Solution Calorimeter shown in Figure 3-2 was used to quantitatively measure the heat involved in the immersion process. This calorimeter is sensitive to all heat changes and therefore the measured heat may contain heat contributions from all the process occurring in the reaction or immersion process. Section 3.3.1 will present a detailed set up and procedure for the calorimeter.

Figure 3-2: Isothermal Microcalorimeter, Thermal Adiabatic Thermostat III used for the Precision Solution Calorimetry.

3.2.2 Mineral Dissolution Tests

The endothermic response during the heat of immersion measurements for some minerals is thought to be due to mineral dissolution. To confirm that dissolution of the mineral was indeed occurring, further dissolution tests were performed. A slurry was created using 1 g of the target mineral with a size fraction of -25 µm in 100 mL deionised water. The slurry was stirred for different conditioning times of 5, 10, 20, 60 minutes and 20 hours. These conditioning times will later be referred to as dissolution times in the results sections. The stirring was done using a water bath as shown in Figure 3-3, at a shaking rate of 20 rpm. The shaking rate refers to the stirring or conditioning of the slurry samples. The water bath cannot be left unattended (stirring or conditioning) overnight due to safety concerns; therefore, for the conditioning time of 20 hours, a magnetic stirrer system was used at 400 rpm. The stirring rate was chosen to ensure that the solids do not settle. The slurry was then filtered, and the clear liquid was sent for elemental analysis by MP-AES. This analysis was used based on the detection limit as the quantities of the tested elements were very dilute.

The water bath was not used for temperature regulation of the slurry sample because of the controlled ambient laboratory temperatures.

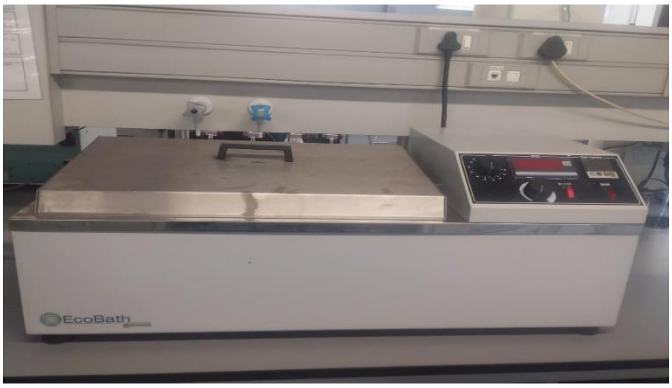


Figure 3-3: Water bath used for the conditioning of the slurry.

3.3 Experimental Methodology

3.3.1 Solution Calorimetry

i. Calibration and Validation

Before the heat of immersion measurements for the samples can be conducted, validation or calibration of the equipment was conducted using a standard test. The standard test involves performing a chemical calibration test of dissolving potassium chloride (KCl) in deionised water (Wadso & Goldberg, 2001). The dissolution of KCl in deionised water is an endothermic process that has been widely used to calibrate microcalorimeters. Numerous authors such as

Goncharuk (2015) and Takei & Chikazawa (1998) have used this reaction as a standard to calibrate their microcalorimeters. 232 mg of KCl was used in a 100 mL reaction vessel to perform the calibration test. The measurements are done at these conditions to avoid uncertainties that might result due to inaccuracies in values of the relative apparent molar enthalpy (Wadso & Goldberg, 2001). Duplicate experiments were conducted at a temperature of 25˚C.

ii. Blank Measurements

Blank test experiments are usually conducted to determine the energy or heat associated with the breaking of the ampoule during the heat of immersion measurements and to account for the vaporization of the calorimetric fluid due to incompletely filled ampoule. Sealed ampoules with no mineral present are used and the heat of breaking is measured. The heat of breaking the ampoule was neglected in the experimental work in this study.

iii. Mineral Measurement Procedure

Prior to the heat of immersion measurements, the samples were outgassed by drying in a vacuum oven that utilises the conventional vacuum system of oil diffusion pump and liquid nitrogen trap. The samples were dried for a period of 4 nights, approximately 96 ± 6 hours, to obtain samples with surfaces that are free of adsorbed water. The completion of drying within the stipulated time of 4 nights was confirmed by measuring the sample mass which showed no change over a 3-night period. The 4-night drying period was chosen to allow for complete drying even for samples with relatively large variation in the moisture content. The vacuum oven was operated at 150 mbar and a temperature of 40˚C for all the experiments. The pressure of 150 mbar within the vacuum oven was chosen as the vacuum pump could not achieve a lower pressure.

Outgassing the mineral samples before the heat of immersion measurements is recommended to remove the physically adsorbed water on the surface of the sample. Higher temperatures are usually preferred for outgassing; however, sulphide minerals tend to oxidise at relatively low temperatures of 50°C and are unstable at high temperatures. Higher temperatures may also decompose the xanthate collector used in this study. Therefore, a lower temperature of 40°C was used in our experiments to prevent oxidation of the sulphide mineral.

iv. Step-by-Step Method of Sample Loading

The detailed procedure followed during the heat of immersion measurements is outlined below.

Step 1: An empty ampoule with an approximate volume of 1.1 mL, together with a rubber seal were weighed using a microbalance. A known amount of mineral sample was added into the ampoule and the ampoule was closed using a rubber seal and the mass of the filled ampoule was recorded. The ampoule was sealed with melted beeswax using a hand-held burner. A filled and sealed ampoule is shown in Figure 3-4.

Figure 3-4: Sample ampoule filled with KCl and sealed with beeswax.

Step 2: The ampoule was placed into the stirrer system cautiously to avoid breaking the fragile ends of the ampoule. The ampoule was locked into place using the locking screw attached to the stirrer system.

Step 3: The reaction vessel was cleaned using deionised water by rinsing it 2 or 3 times. Any leftover pieces of glass left from previous experiments were removed during this cleaning process. The cleaning was performed by using a vacuum pump to suck out all the contents in the vessel from previous experiments, no disassembling of the vessel was done. The reaction vessel as shown in Figure 3-5, was filled with the wetting liquid using a volumetric pipette. The inside walls of the vessel or stirrer system were dried to avoid any liquid that might affect the results. The stirrer system from step 2 was inserted into the reaction vessel. Two reaction vessels sized 25 mL and 100 mL were used in the experimental work conducted in this study.

Figure 3-5: 100 mL reaction vessel.

Step 4: With the stirrer turned on at a recommended rate of 500 rpm, the temperature of the reaction vessel was adjusted by either cooling or heating to a temperature offset between -400 mK and -300 mK. The stirrer system shown in Figure 3-6 with the reaction vessel was inserted into the thermostat shown in Figure 3-2. Once the temperature offset had reached -250 mK, the resolution was changed to a high resolution. Low resolution is usually chosen for equilibrating the system or for experiments or reactions with relatively large heat outputs. The temperature offset can be adjusted or fine-tuned to -250 mK by using the heater option where the heater is turned to a power of 500 mW to achieve the required temperature offset.

Figure 3-6: The 100 mL reaction vessel with the sample ampoule attached and ready to be inserted into the thermostat.

The Pause section was then initiated, and all the experimental conditions set. The recommended heating power of 100 mW is preferred to further adjust the temperature offset to -220 mK. After this, the SolCal is left to equilibrate while watching the fit status. The experiment should only be started when the exponential fit shows a decay status, and a standard deviation of less than 10 uK. It is also recommended that all experiments be started at the same temperature of approximately -190 mK.

Step 5: The experiment was initiated, and the ampoule was broken when prompted. All the heat of immersion measurements were conducted at 25°C.

3.3.2 Scoping Experiments

Preliminary experiments, also referred to as the scoping experiments, were conducted to determine the exact minerals that will be used for the binary mineral mixture. The minerals scoped were silicate and sulphide minerals as given in Table 3-3. The binary mineral mixture has to consist of a hydrophobic sulphide mineral and a hydrophilic mineral representative of valuable and gangue minerals in real ores, respectively.

The size fraction suitable for the heat of immersion measurements, which determines the surface area of the mineral was determined during this stage together with the conditioning time for the saturated solution. The mineral samples were sized in three different size categories (size fractions) with different surface areas. The heat of immersion was measured for the different sizes to investigate the relationship between the heat of immersion and surface area. Albite was used for this purpose as it had no endothermic response. It is understood that the surface area affects the heat of immersion as minerals with higher surface area exhibit higher heat of immersion values due to increased intermolecular interactions. Secondly, the drying temperature used for outgassing was tested as this is known to influence the heat of immersion.

3.3.3 Saturated Solution

Results from the experimental work conducted in this study and that conducted by Taguta et al. (2018) showed that the heat of immersion is greatly affected by the dissolution of the mineral surface ions. This dissolution of mineral surface was explained to be observed as an endothermic response. To overcome this, Taguta et al. (2018) suggested that the wetting liquid be a saturated solution containing the mineral of interest. This was done to drive the dissolution reaction before the heat of immersion measurements can be conducted. This assumes that the wetting liquid is in equilibrium with the solid state of the mineral at all times and thus neglecting the contribution from the dissolution process. This saturated solution was prepared by adding 10 g of the mineral into 100 mL of deionised water (i.e., 10 wt.%) and stirred overnight; approximately 20 hours at laboratory conditions. The set-up is shown in Figure 3-7. The deionised water used to create the saturated solution was at a natural pH of 7.4. The slurry was filtered using millipore filter paper with a size of 0.22 µm and the clear liquid/solution was then used as the wetting liquid. The decision to use a saturated solution made from the target solid at the given conditions as a wetting liquid was reviewed and supported by Zimmermann et al. (1987) and Taraba & Zelenka (2017).

Figure 3-7: Slurry at 10 g solids in 100 mL of deionised water for the saturated solution.

3.3.4 Collector Coating

An alternative to the saturated solution in suppressing the dissolution is covering or coating the surface-active sites of the mineral with a collector to minimise the interactions between the mineral surface and water. From the two minerals that will be used for the binary mineral mixture, only galena still had an endothermic response after the saturated solution approach. Therefore, it was used in the collector coating approach. The galena surface was covered with a collector in different surface coverages ranging from 25% - 700%. The surface coverages beyond the 1 monolayer were tested initially to excessively cover the mineral surface and ensure that all the surface-active sites were covered.

4 g of the galena mineral that had been previously prepared and stored was weighed and prepared into a 60 mL slurry that was ultrasonicated for 5 minutes. The collector was prepared on a weight by volume percent based on the required surface coverage. The desired volume of collector was pipetted into the mineral slurry and conditioning was allowed for 10 minutes at a stirring rate of 500 rpm. After conditioning, the slurry was filtered allowing the liquid to be separated from the solids. The mineral was then excessively washed out with deionised water to remove any collector molecules that may not have adsorbed. The wet mineral was then dried (outgassed) in a vacuum oven for 4 days at 40°C to drive off the moisture and adsorbed water. The heat of immersion measurements were then performed as outlined in Section 3.3.1.

3.4 Data Analysis

3.4.1 Calorimetry Data

The output data from the precision solution calorimeter is a graph of temperature offset as a function of time. The experimental sequence and data output is shown in Figure 3-8. A drop in the temperature offset after the break indicates an endothermic response while an increase in the temperature offset indicates an exothermic reaction as shown in Figure 3-9. The heat change is determined by alterations in the SolCal software using the calibration and baseline before and after the break.

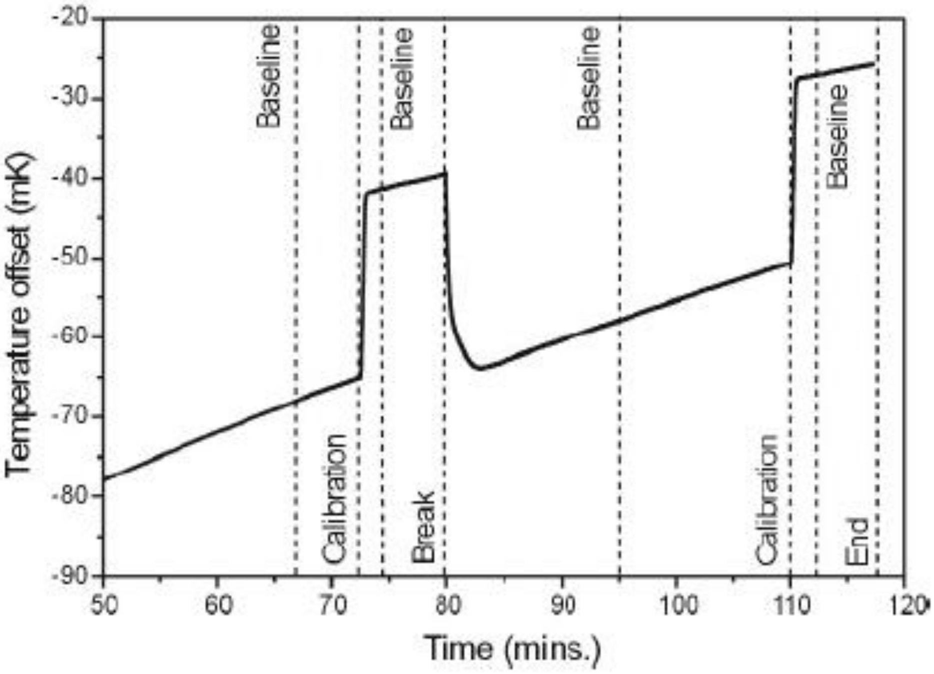


Figure 3-8: Typical response of the microcalorimeter showing the temperature offset as a function of time during the dissolution of KCl in water

Figure 3-9 shows the experimental graph for the immersion of a mineral in a wetting liquid. The calibration heats are provided by the equipment and are set at 1 J. There is a baseline prior to the calibration and immediately after the calibration, just before the break happens. This is to ensure that the equipment has properly equilibrated and all the conditions for the experiment are met. The break shows the response of breaking the ampoule, immersing the mineral into the wetting liquid. To determine the energy or heat change from the process, the area under the peak is integrated by the microcalorimeter software. This energy or heat can be normalised either relative to the mass or to the surface area of the mineral.

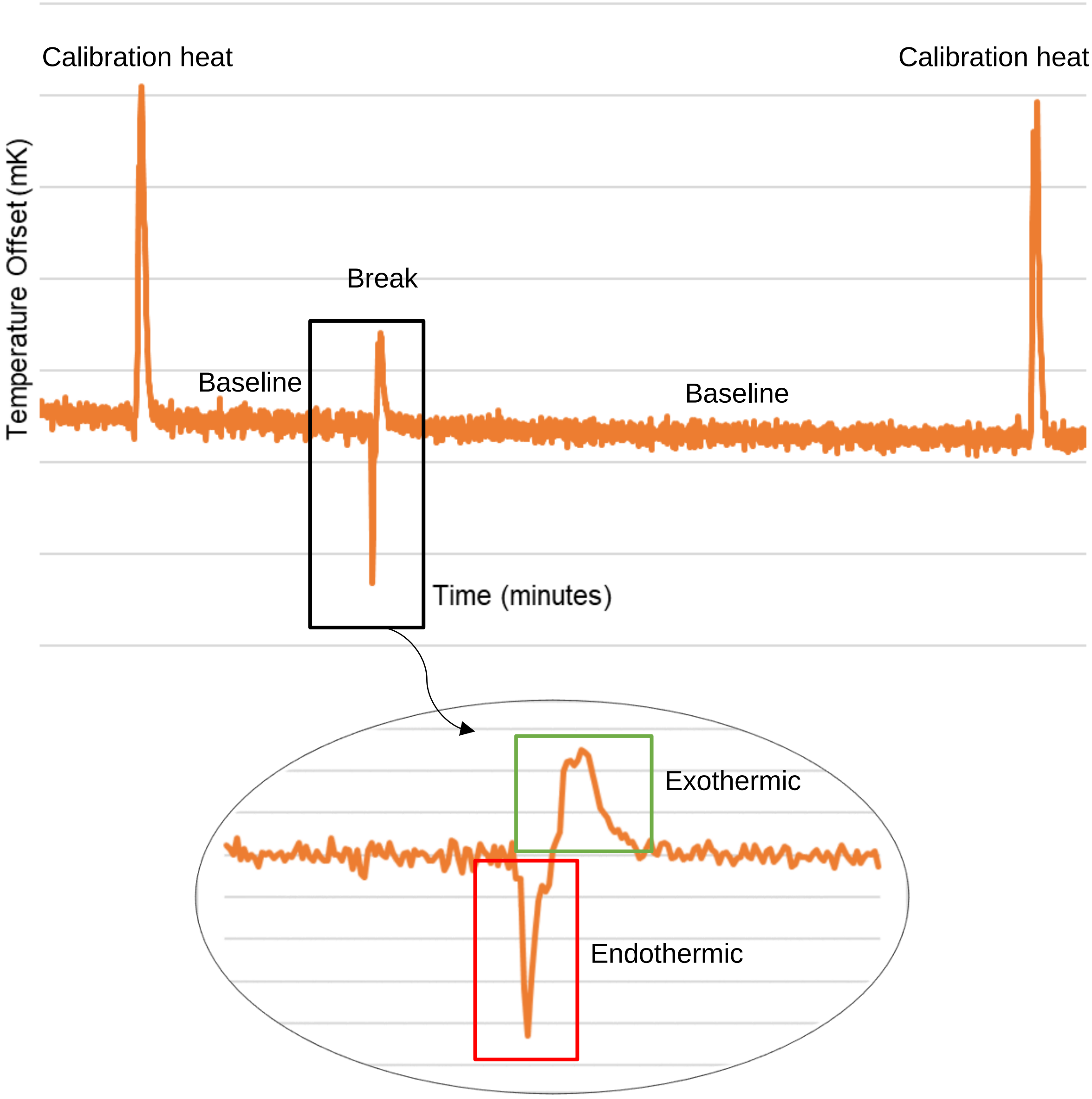


Figure 3-9: The heat of immersion response with both endothermic and exothermic response.

4 Results

This chapter will present the heat of immersion data that demonstrate various ways of suppressing dissolution such as using wetting liquids of different polarity and collector coating. It will also present heat of immersion data for mineral mixtures as a measure of wettability and look at the relationship between the heat of immersion and composition of the mixture. Results that are not directly related to the objectives of the research are presented in Section 9.

The outline of this chapter will start on the reproducibility of the measurements obtained using the microcalorimeter equipment and the validation of the results obtained, and further look at the differences in the measured responses from different reaction vessels for the heat of immersion measurements. Following that, results are presented relating to the factors that affect the heat of immersion, in which the focus is on the surface area of the mineral sample and the outgassing temperature. Furthermore, the results from the different approaches that were implemented to suppress the dissolution will be presented together with those of the binary mineral mixtures.

4.1 Reproducibility and Validation

The dissolution of potassium chloride (KCl) in water has been widely and extensively used as a standard validation test for solution calorimetry (Wadso & Goldberg, 2001). This dissolution reaction was performed to determine the precision and accuracy of the microcalorimeter. The heat of dissolution was found to be 17.01 ± 0.36 kJ/mol with a relative error of 2.12%. The value given by Wadso & Goldberg (2001) is 17.58 ± 0.017 kJ/mol. This gives a percentage difference of 3.3% between the literature value and the measured heat of dissolution value. This was considered sufficiently accurate and reproducible to validate the reliability of the equipment.

Reproducibility was found to be poor for the mineral immersion tests. In this case, there were two options available to obtain an increased response and, therefore, improve reproducibility. Firstly, increase the mineral surface area, which is discussed in more detail in Section 4.3. Secondly, there was an option to use a smaller (25 mL) reaction vessel to the standard 100 mL vessel. The response from these vessels was compared and the graphical representation is given in Figure 4-1. The response for the heat of immersion was found to be higher for the smaller 25 mL reaction vessel compared to the larger 100 mL reaction vessel. The comparison is presented by temperature offset against time shown in Figure 4-1 and in Table 4-1. The same sample was used in both the reaction vessels and a solid to immersion liquid ratio of approximately 2.6 wt.% was maintained for each vessel, viz. 2.8 g was used for the 100 mL vessel and 0.65 g used for the 25 mL vessel. However, the heat of immersion per unit surface area as seen in Table 4-1 was found to have a percentage difference of 14% between the two tests. This difference is deemed to be significant meaning that using the 25 mL reaction vessel will increase the observed response when the solid to immersion liquid ratio is kept constant and, therefore, improve the reproducibility of the measurements.

Figure 4-1 shows all the sections during the immersion measurements; however, in the subsequent sections the calibration heats will not be presented but only the point at which the vial was broken (“Break”) and some part of the baseline.

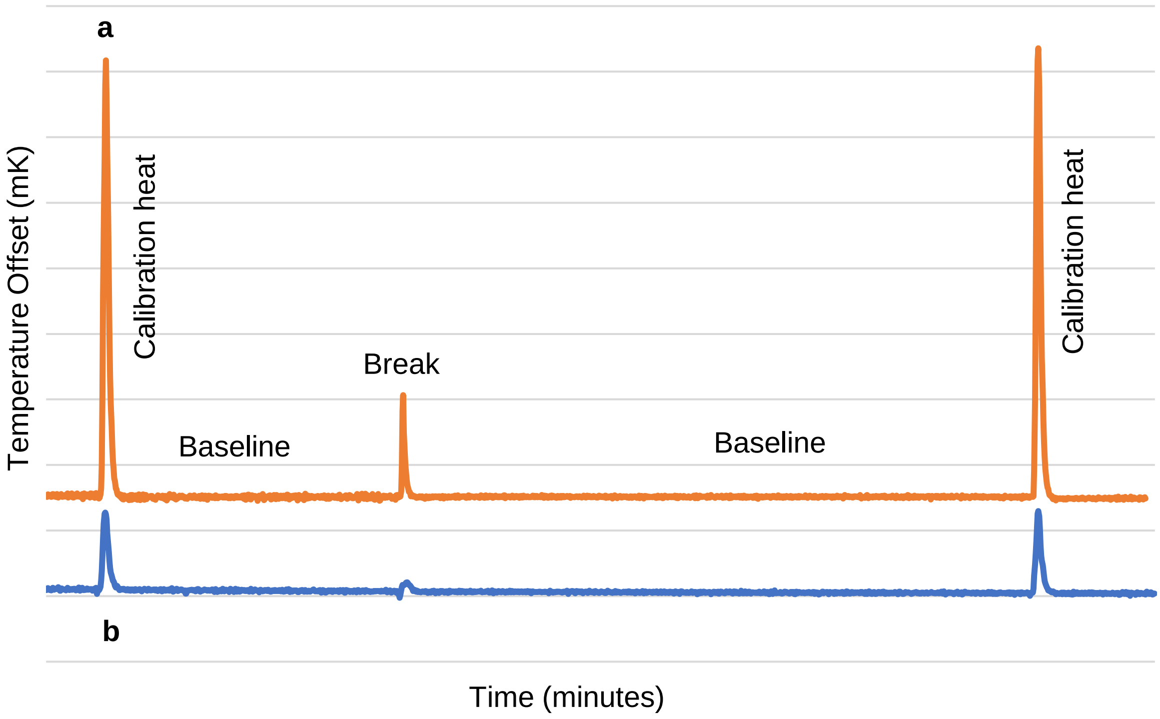


Figure 4-1: Comparison of the heat of immersion response in different vessels: a) 25 mL vessel b) 100 mL vessel.

Table 4-1: The heat of immersion per unit surface area of galena measured in different reaction vessel sizes.

Vessel size (mL)	**mass (g)**	**ΔH (mJ/m^2)**
25	0.65	-296
100	2.8	-257

4.2 The Heat of Immersion in Water

The heat of immersion as a measure of wettability of minerals and mineral mixtures is based on the immersion measurements being conducted in water, i.e., water as the wetting liquid.

This is because in the minerals processing context, water is used as a measure of wettability for processes such as flotation.

It was observed, as shown in Figure 4-2, that there is an endothermic response for the immersion of galena in deionised water. This unexpected response indicated that other phenomena were occurring alongside the exothermic wetting response. This will be addressed in more detail in Section 4.4.

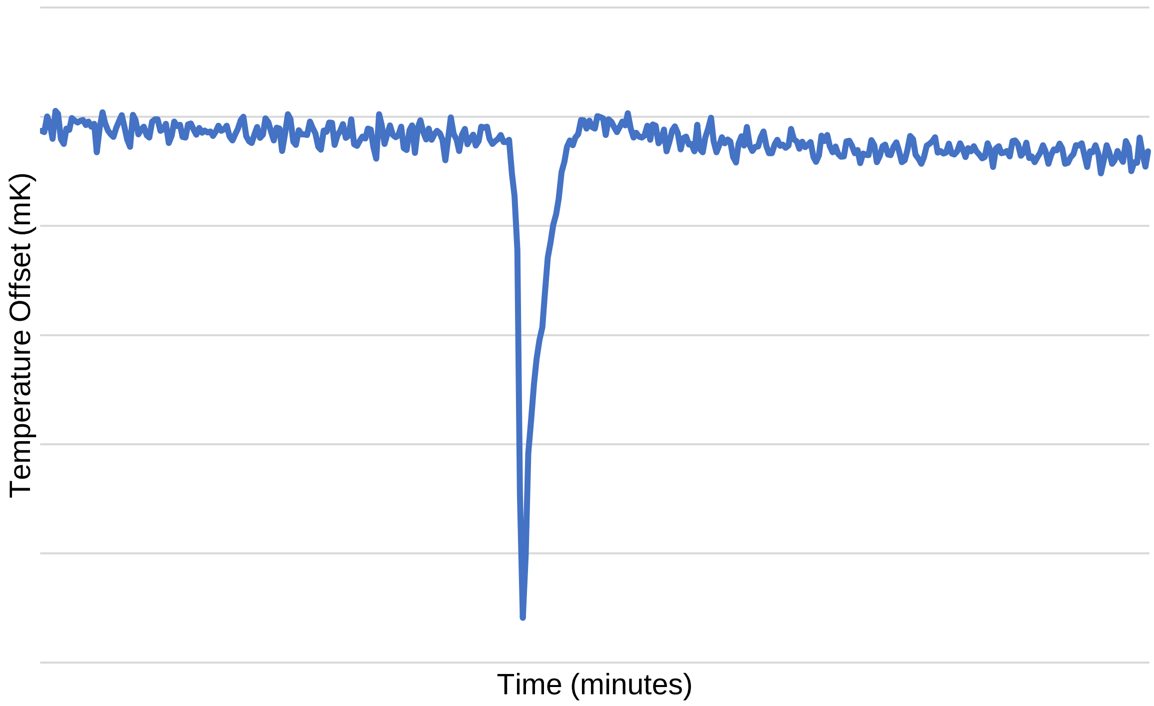


Figure 4-2: The heat of immersion response of galena in deionised water.

4.3 The Effect of Surface Area and Outgassing Temperature

The heat of immersion is affected by various factors such as the surface area, mass of the solid sample, outgassing temperature, properties of the solids etc. For minerals that have low surface energy, high surface area is required, and this is obtained by grinding the mineral finer. However, fine grinding may produce structural and crystallographic changes.

Figure 4-3 shows the heat of immersion response of quartz of different specific surface areas where the surface area is represented as that of a particular size fraction. The heat of immersion response of quartz for the -25 µm fraction is so small that it is almost undetectable. The response with the full baseline and all other experimental sections is given in the Supplementary Results, Figure 9-1a to clearly show how small the heat of immersion response is compared to the calibration heats. To improve the response, a much finer size fraction of -

5 µm was used, but it was observed that even though the heat of immersion response increased, there was now an endothermic response in addition to the expected exothermic response. This supports the assumption that other phenomena are occurring alongside the expected exothermic wetting response as mentioned in Section 4.2.

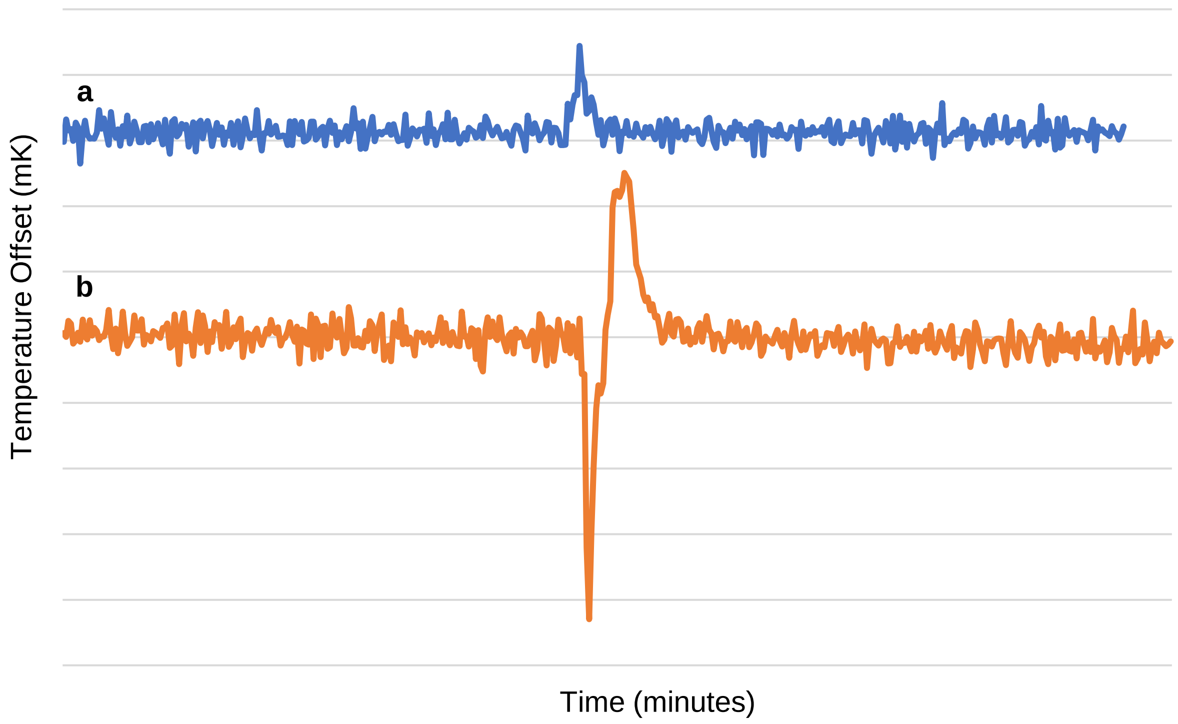


Figure 4-3: a) The heat of immersion response of quartz (-25 µm) in saturated solution b) The heat of immersion response of finely grinded quartz (-5 µm) in saturated solution.

In the case of albite, the heat released was observed to increase with an increase in surface area as shown in Figure 4-4, with no associated endothermic response. Theoretically, the response should be linear with the slope equal to the heat of immersion in mJ/m^2 and passing through the origin. However, this is not the case and may be due to the well-known problem of measuring relatively small surface areas using the BET method. The surface area of albite was measured to be 1.63 m^2/g. However, at 40°C, the temperature at which most heat of immersion measurements were performed, the slope of the line was 188 mJ/m^2, which was a good average representation of the energy released as a function of surface area. It should be noted that the intercept was set to zero as it is known that the heat of immersion of a solid with zero surface area will be zero.

At the same time, as presented in Figure 4-4, it was observed that the heat released increases with an increase in outgassing temperature due to the removal of physically adsorbed water on the surface of the mineral. The relationship between the heat released and the surface area was also maintained at higher outgassing temperatures. It can be seen from Figure 4-4 that the energy released per unit surface area (gradient of the curve with intercept set to zero since there is no heat of immersion for zero surface area) at 100°C is higher than that released at 40°C (336 mJ/m^2 versus 188 mJ/m^2). This is indicative of the slightly more hydrophilic nature of the albite surface when some of the physically adsorbed water had been removed at higher temperatures. This is because the actual surface of the albite mineral is exposed when the physically adsorbed water is removed. More physically adsorbed water is removed at higher outgassing temperatures.

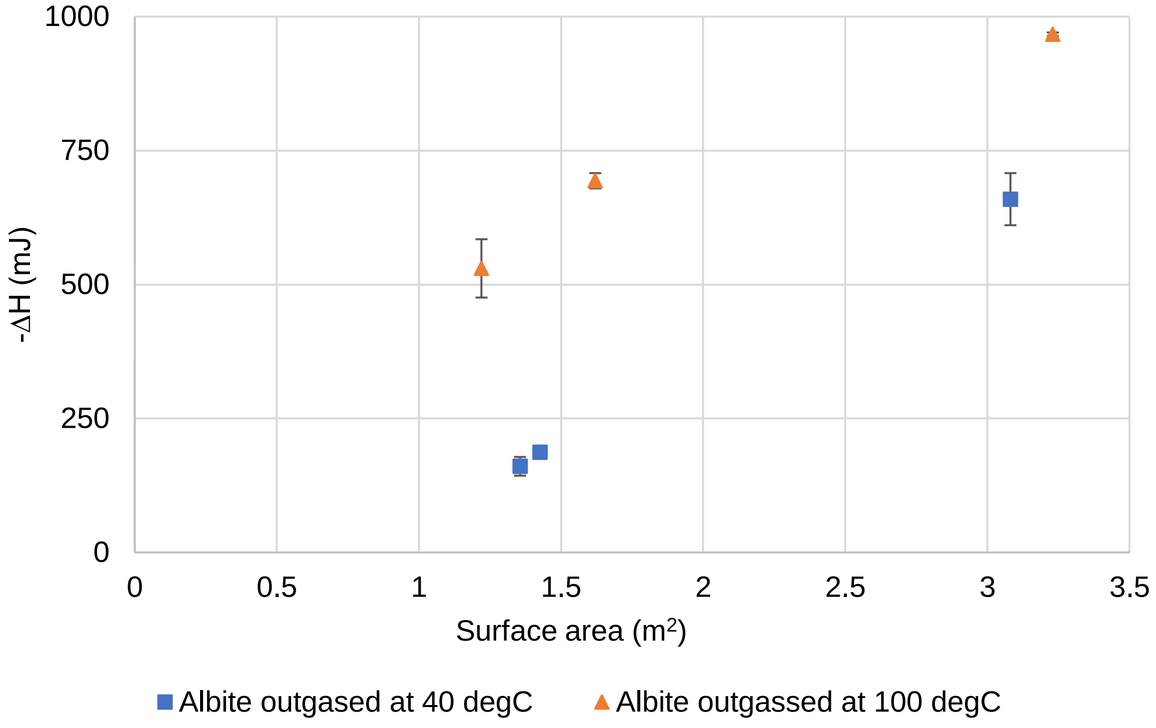


Figure 4-4: The effect of surface area and outgassing temperature on the heat of immersion.

4.4 Eliminating the Heat of Dissolution from the Heat of Wetting

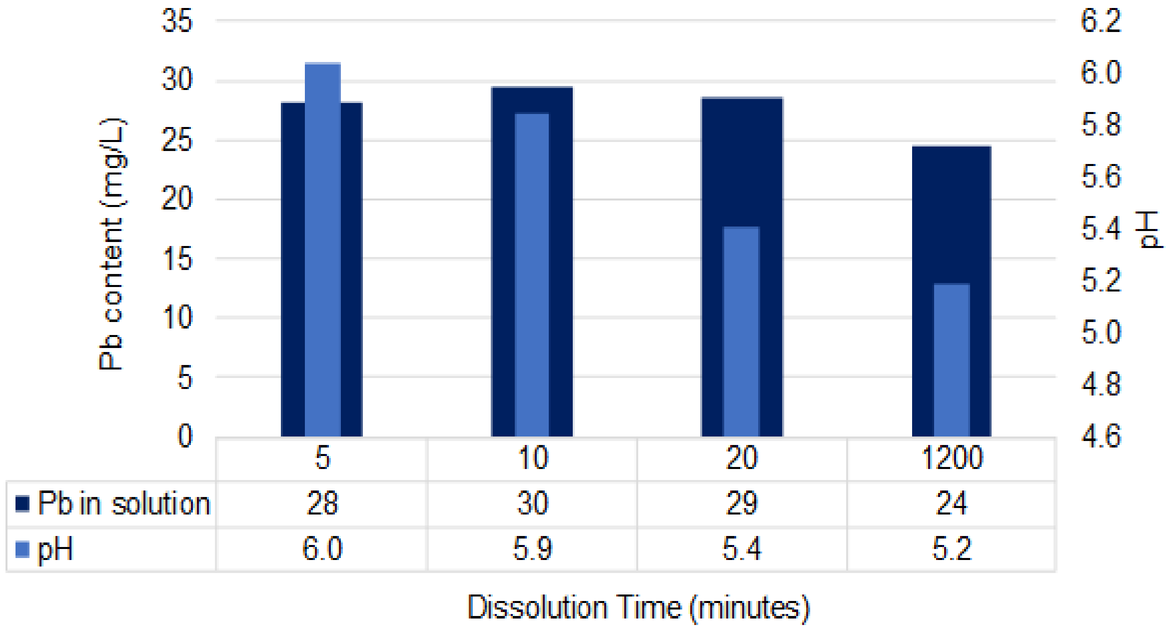
The presence of an endothermic response during the wetting of certain minerals by immersion was shown in Figure 4-2. As was highlighted in the literature review, the wetting response is an exothermic response and the endothermic response that was identified in the observed response was as a result of an unknown parallel reaction. Initially, the origin of the endotherm was not understood since there is no mention of this phenomenon in the minerals processing literature. However, it was suspected to be as a result of dissolution of the mineral into the water and initial tests were conducted to test this hypothesis. It could then suggest that various methodologies could be explored to suppress the dissolution reaction.

4.4.1 Confirmation of Dissolution of Mineral

As indicated above, the endothermic response in the heat of immersion measurements was assumed to be indicative of the dissolution of the mineral into water. Experimental tests were firstly conducted using galena and albite to confirm whether indeed the dissolution was occurring. Galena was chosen as the test mineral since the endothermic reaction was prominent during calorimetric wetting experiments. A suspension was created and analysed as mentioned in Section 3.2.2 of the Experimental Methodology. Different conditioning times were tested to supplement the data on the saturated solution covered in Section 4.4.3. This was to determine the amount of ions present in the solution during the immersion.

i. Galena

From the results presented in Figure 4-5, the dissolution of galena was confirmed to occur when the mineral was immersed in deionised water. The Lead (Pb) dissolved within the first 5 minutes to a level of approximately 30 mg/L and was then relatively constant up to 20 hours dissolution time. The slight reduction at 20 hours may represent Pb ions reprecipitating on the mineral surface during the conditioning. The Pb dissolved into the solution at a dissolution time of 10 minutes was found to represent about 0.39% of the total lead initially present in the galena sample. Additionally, the pH of the solution was observed to be decreasing as the dissolution time increased. The initial pH of the deionised water used for the dissolution was at 7.4 and this decreased to 6.0 within the first 5 minutes. The final pH after 20 hours was 5.2. The addition of galena to the deionised water decreased the overall pH from 6 to 5.2. The pH of the solution was tested because it is well known that pH is affected by dissolution. According to El Alaoui & Dekayir (2018), the dissolution of galena is controlled by pH, and this is why the pH was measured in this research study. However, although investigating the impact of pH on dissolution (or why the solution was acidic) was not part or focus of the project, pH was measured as it was known to influence the dissolution rate. Additionally, the rate of dissolution of feldspars is dependent on the pH of the solution (Crundwell, 2015a).



	5	10	20	1200
■ Pb in solution	28	30	29	24
■ pH	6.0	5.9	5.4	5.2

Figure 4-5: The dissolution of galena in deionised water at different conditioning times.

ii. Albite

Figure 4-6 gives the results of dissolution of albite in deionised water at different dissolution times. The results are presented in mg/L, but it is important to note that the molar (mol/L) presentation will result in similar trends obtained. Similarly, it was observed that there is dissolution of albite when it is immersed in deionised water. Sodium (Na) dissolution was the greatest, with much less aluminium (Al) and silicon (Si) dissolution. The aluminium content in solution was observed to decrease while the sodium content increased when the dissolution times were longer. There was no correlation observed for the silicon content, with the silicon dissolved at 10 minutes and 20 hours being roughly similar at 0.64 and 0.65 mg/L, respectively. After 20 hours dissolution time, the sodium dissolved into the solution was found to be approximately 10% of the total sodium initially present in the albite sample. Meanwhile the aluminium dissolved in the solution was about 0.92% at 10 minutes dissolution time. Lastly, the silicon dissolved into the solution was found to represent an equal percentage of about 0.19% at 10 minutes and 20 hours dissolution time. Additionally, the pH of the solution was observed to be constant ranging between 7.6 and 8.0.

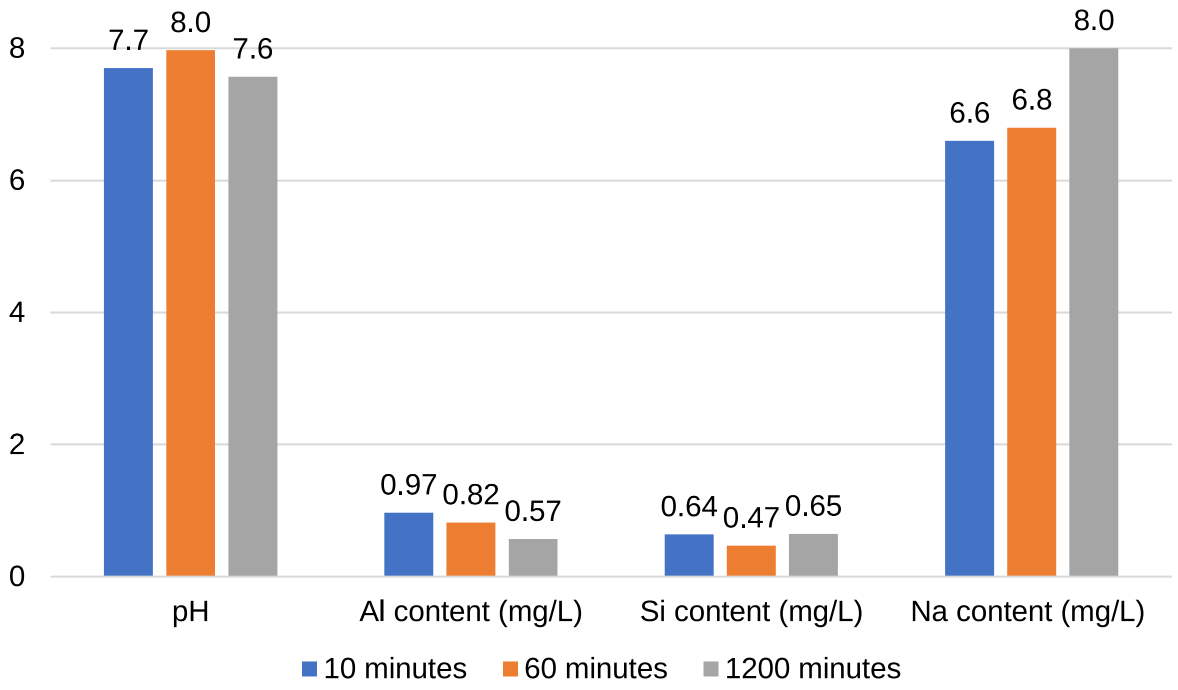


Figure 4-6: The dissolution of albite in deionised water at different conditioning times.

The 10 minutes dissolution time has an aluminium content of 0.97 mg/L, silicon content of 0.64 mg/L, sodium content of 6.6 mg/L and a pH of 7.7 while the 20 hours dissolution time has an aluminium content of 0.57 mg/L, silicon content of 0.65 mg/L, sodium content of 8.0 mg/L and a pH of 7.6. The dissolved elements of these two dissolution times are somewhat similar with noticeable differences (percentage differences) in aluminium content and sodium content of 52% and 19% respectively. The Na ions are dominant in the solution and thus expected to have a greater effect during the immersion, therefore a conditioning time of 20 hours was chosen for the saturated solution discussed in the Experimental Methodology.

The suspension used to analyse for the dissolved elements (dissolution) in both albite and galena was created under the same conditions with an initial mass of 1 g of mineral in 100 mL of deionised water. The extent of dissolution was calculated for both the minerals where this is based on the dissolved amount of metal (or element) over the initial amount of element in the solid sample. It was found that at 20 hours dissolution time, there was a higher extent of dissolution of sodium at 10%, followed by aluminium at 0.54%, lead at 0.33% and lastly silicon at 0.19%. Even though albite contains a significant amount of elemental silicon at about 32%, it is observed that silicon is the least dissolved element. Table 4-2 show the extent of dissolution of albite and galena. Galena is represented by the lead element while albite is represented by aluminium, silicon, and sodium. It can be observed that there is a greater extent of dissolution of albite than galena.

Table 4-2: The extent of dissolution of albite (Al, Si, Na) and galena (Pb) in deionised water.

Dissolution time (minutes)	Al % dissolution	Si % dissolution	Na % dissolution	Pb % dissolution
10	0.095	0.020	0.76	0.34
60	0.080	0.015	0.78	0.19
1200	0.056	0.020	0.92	0.28

This work has shown that dissolution of galena does occur in deionized water. The presence of ions in the solution due to dissolution would result in the development of surface charge, which will have an impact on the heat measured. This dissolution process is measured simultaneously with the wetting process during immersion experiments. Therefore, some remedy to this occurrence must be developed for immersion calorimetry to be a useful technique for mineral processing applications.

4.4.2 Heat of Dissolution of Salts in Water

The heat of dissolution of various salts was measured as a way to understand the interactions behind the dissolution process and the endothermic or exothermic processes involved. Table 4-3 shows the list of salts that were used and whether, by observation and solubility table found in literature, they appeared to be soluble, insoluble or partially soluble. Figure 4-7 shows the heat of dissolution of soluble salts in water and it can be observed that the heat of dissolution given in kJ/mol, is endothermic with the exception for $FeCl_2$ which has an exothermic energy. On the other hand, the heat of dissolution of insoluble salts in water as shown in Figure 4-8 is observed to be exothermic with the exception of $PbSO_4$. The heat of dissolution of the soluble salts is observed to be higher than that of insoluble salts.

Table 4-3: The heat of dissolution of various salts.

Salts	**Formula**	**Solubility**	**$\Delta H_{dissolution}$ (kJ/mol)**
Zinc sulphate heptahydrate	$ZnSO_4.7H_2O$	Soluble	18
Iron sulphate heptahydrate	$FeSO_4.7H_2O$	Soluble	20
Lead nitrate	$Pb(NO3)_2$	Soluble	9,7
Iron chloride tetrahydrate	$FeCl_2$	Soluble	-13
Iron oxide	Fe_2O_3	Insoluble	-0,16
Fe metal	Fe	Insoluble	-0,070
Lead sulphate	$PbSO_4$	Insoluble	0,084

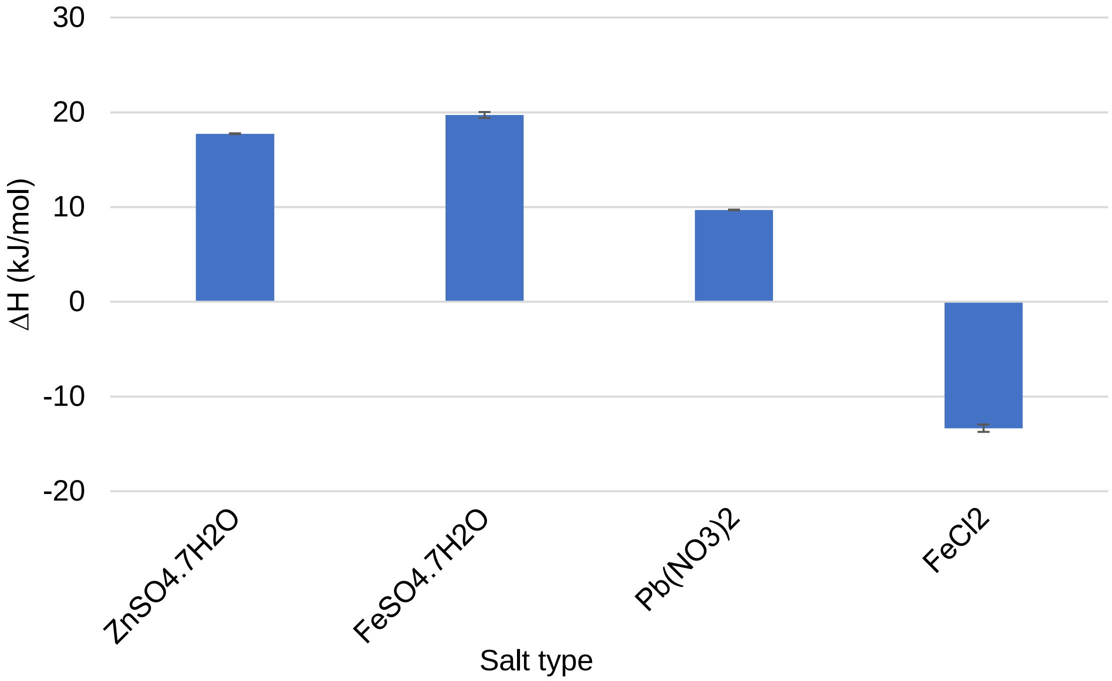


Figure 4-7: The heat of dissolution of soluble salts in deionised water. Error bars are based on the standard error of duplicate experiments.

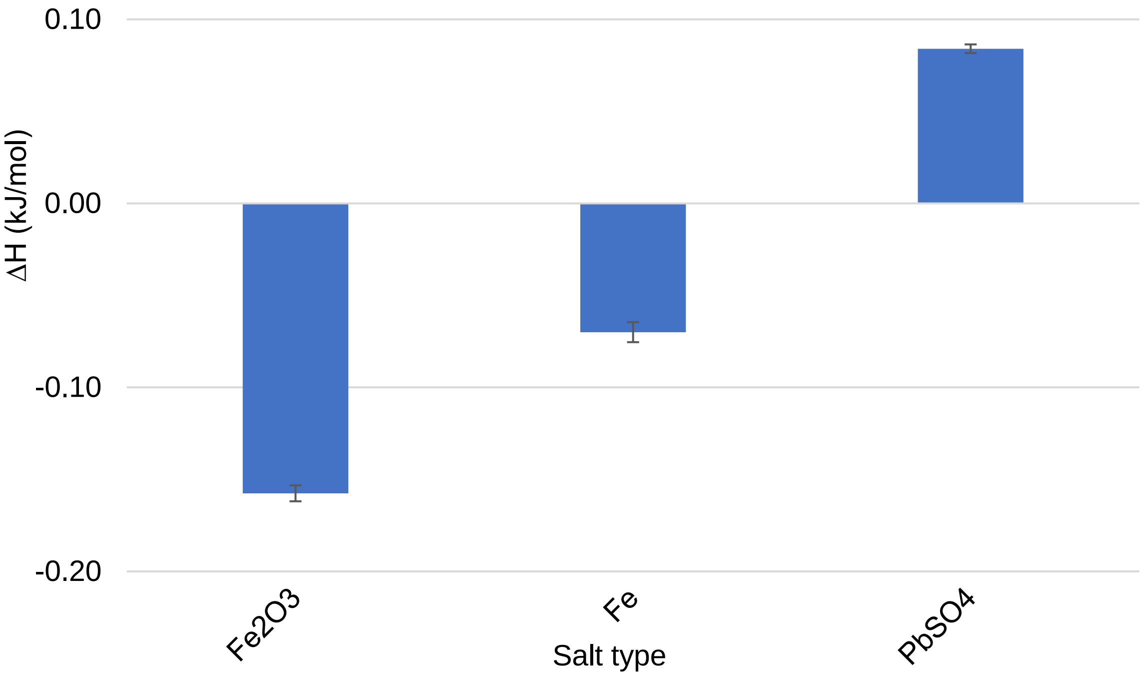


Figure 4-8: The heat of dissolution of insoluble salts in deionised water. Error bars are based on the standard error of duplicate experiments.

4.4.3 Saturated Solution Approach

Since it was confirmed in Section 4.4.1 that dissolution of the mineral was occurring during the immersion process in deionised water, various dissolution suppression methods were tested. The first such method involved the use of a saturated solution in which to measure the heat of wetting, i.e heat of immersion. The theory behind this is that the dissolution process will be driven in the reverse direction due to the presence of dissolved ions in solution. This is because there will be ions of interest in the immersion liquid and these ions will be at a saturation point preventing further dissolution from occurring.

Following the results obtained in Section 4.4.1, on the confirmation of dissolution, 20 hours was decided upon as the conditioning time for the saturated solution. This is because it was found that at this dissolution time, there was an overall higher amount of ions in the solution increasing the chances of suppressing the dissolution by driving the dissolution reaction in the reverse direction.

Figure 4-9 shows the heat of immersion response of various minerals conducted in a saturated solution as the wetting liquid, i.e., immersion liquid. It can be observed that there was an endothermic response for most sulphide minerals except for sphalerite. Only two silicate minerals were tested, and quartz had an endothermic response while albite had an exothermic response when the saturated solution was used as the wetting liquid.

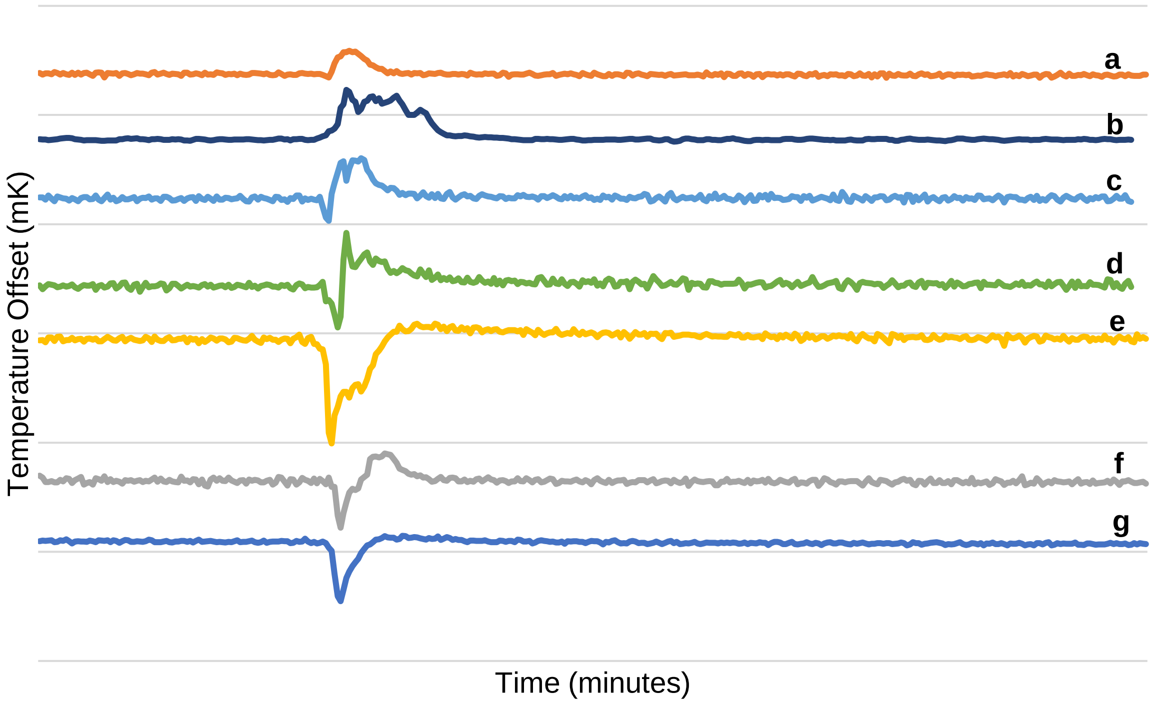


Figure 4-9: Heat of immersion response of various minerals in saturated solution: a) albite. b) sphalerite. c) chalcopyrite. d) pyrrhotite. e) pyrite. f) quartz. g) galena.

Table 4-4 summarises the results of various tested minerals using the saturated solution as the wetting liquid and presents their chemical formulas. It was observed that the dissolution was not suppressed for most minerals when using the saturated solution as the wetting liquid.

Table 4-4: The heat of immersion of various minerals in saturated solution.

Mineral	**Chemical formula**	**Presence of endotherm in saturated solution**
Chalcopyrite	$CuFeS_2$	Yes
Pyrite	FeS_2	Yes
Pyrrhotite	$Fe_{(1-x)}S$	Yes
Galena	PbS	Yes
Sphalerite	ZnS	No
Quartz	SiO_2	Yes
Albite	$NaAlSi_3O_8$	No

4.4.4 Collector Coating Approach

With the results for the saturated solution approach showing that the dissolution process was not suppressed for most minerals, another approach was explored where the mineral was coated with a xanthate collector to essentially cover the active sites before immersing the mineral in deionised water. The minerals of interest in this project were galena and albite, and since the dissolution of albite was suppressed using the saturated solution approach, only galena was used in the collector coating approach.

i. Water

The surface of galena was coated with a xanthate collector, SIBX, at different surface coverages, vacuum dried to remove the water and then immersed in deionised water to measure the heat of immersion. The surface coverages indicate pseudo-monolayer coverages where 100% surface coverage is 1 pseudo-monolayer. It was observed as shown in Figure 4-10 that the dissolution process was suppressed at surface coverages greater or equal to 75%. This is confirmed by only exothermic responses being observed at these surface coverages.

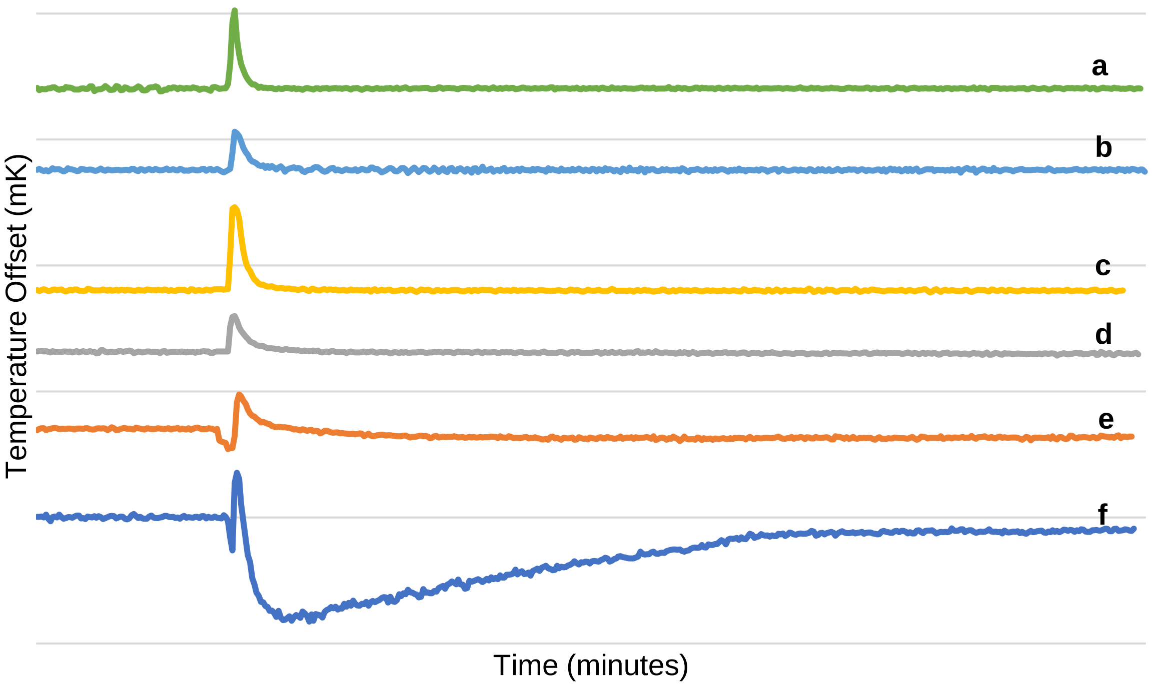


Figure 4-10: The heat of immersion response of collector coated galena at different ‘pseudo’ monolayers in water: a) 7 monolayers. b) 3 monolayers. c) 1 monolayer. d) 0.75 monolayers. e) 0.5 monolayers. f) 0.25 monolayers.

The results of the heat of immersion against the surface coverage are presented in Figure 4-11 and it was observed that the heat of immersion decreases exponentially with an increase in surface coverage, which is to be expected as the hydrophobicity of the mineral increases. It appears that at 300% surface coverage, complete hydrophobicity has been achieved and the addition of a further 4 monolayers does not add any further hydrophobicity to the mineral surface since the heat of immersion remains relatively constant.

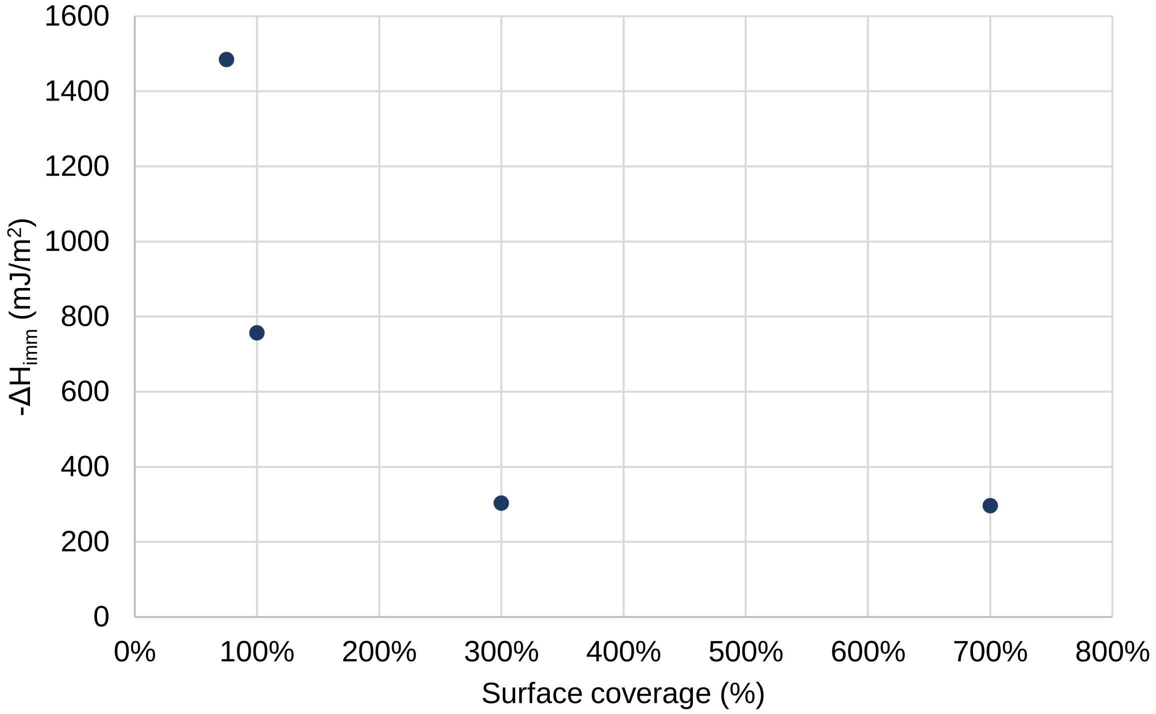


Figure 4-11: The heat of immersion of collector coated galena in deionised water.

ii. Hexane

As it will be discussed in Section 4.4.5, hexane was tested as a wetting liquid to suppress dissolution. It will be shown that the dissolution did not occur when hexane was used and therefore, the collector coating approach was tested in hexane by conducting heat of immersion measurements of collector coated galena in hexane. This is because it has been established that collector coating at certain surface coverages suppresses dissolution in water. Therefore, the aim was to determine the effects of collector on hydrophobicity when hexane is used as a wetting liquid.

It was observed as shown in Figure 4-12 that there was an endothermic response when the collector coated galena was immersed in hexane. This probably is as a result of the collector dissolving in the hexane and giving an endothermic response. Due to the dissolution, the effect of collector on hydrophobicity when hexane is used as the wetting liquid cannot be determined.

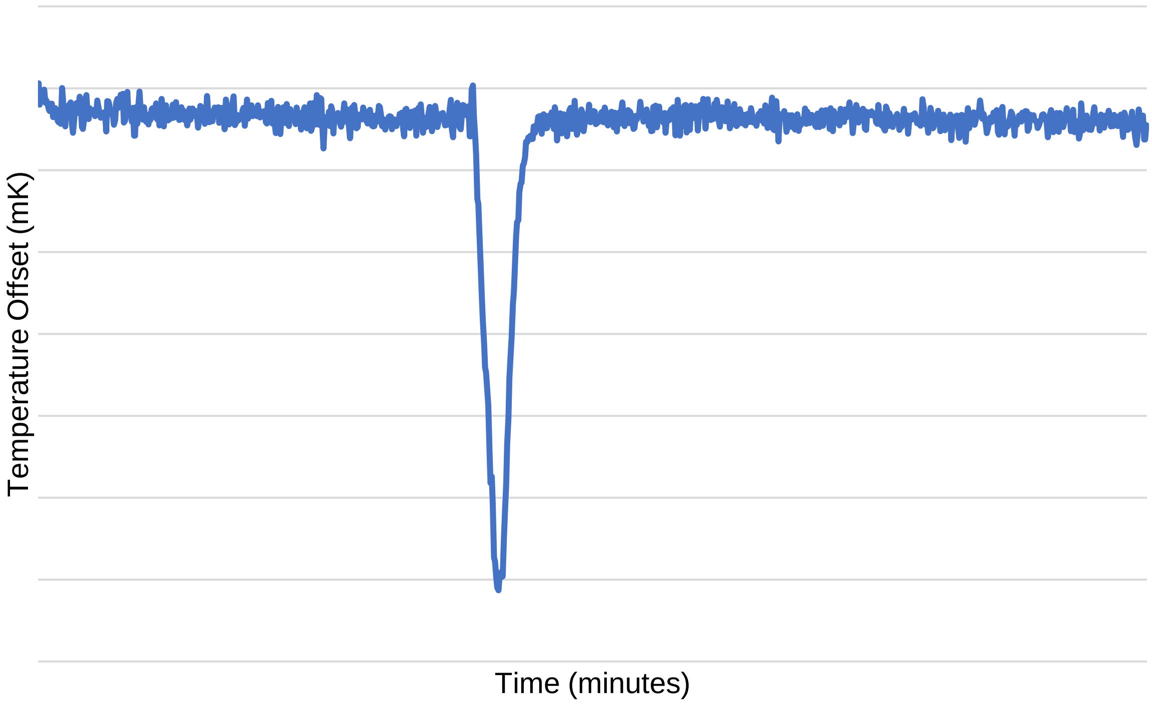


Figure 4-12: The heat of immersion response of collector coated galena in hexane.

4.4.5 Alternative Wetting Liquids Approach

A third dissolution suppression approach was explored where the heat of immersion was measured in nonpolar wetting liquids. These wetting liquids are organic compounds of different polarity. The reasoning behind this approach is that the heat of immersion is based on the surface energies or surface interactions between the liquid and the solid where the liquid and the solid are non-reacting. It is expected that dissolution will not occur in a liquid more non-polar than water.

i. Hexane

Figure 4-13 shows the heat of immersion response of galena in deionised water and in hexane and it was observed that the heat of immersion response of galena in water has an endothermic response indicative of the dissolution of galena into the wetting liquid while the heat of immersion response of galena in hexane is purely exothermic indicating that there is no dissolution of galena into hexane. Therefore, it was found that the endothermic dissolution response could be effectively suppressed in a non-polar wetting liquid.

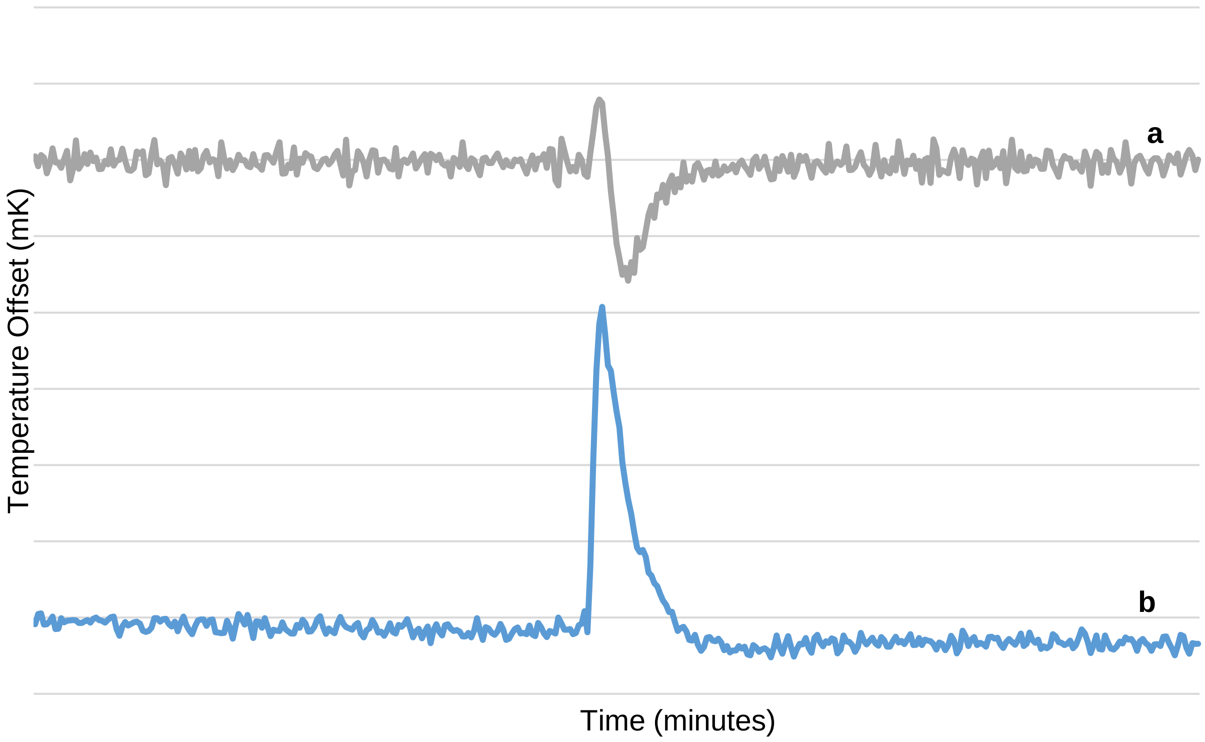


Figure 4-13: The heat of immersion response of galena in a) water and b) hexane.

The heat of immersion of various minerals in hexane was measured to investigate the relationship between the heat of immersion and hydrophobicity when hexane was used as a wetting liquid. Water is a widely used wetting liquid and there is an established relationship between the heat of immersion and hydrophobicity when it is used as a wetting liquid. However, there have been relatively few studies on the heat of immersion in hexane as a measure of hydrophobicity. In any event, the use of hexane is acceptable in terms of developing a relative scale of hydrophobicity or hydrophilicity since values in hexane would essentially be the inverse of those in water. Figure 4-14 shows the heat of immersion of various minerals in hexane. It was observed that heat of immersion is higher for hydrophilic minerals than for minerals that are known to be hydrophobic. Therefore, it was found that the heats of immersion of the two naturally hydrophobic minerals, galena and talc, are relatively similar at about -200 mJ/m^2, while that of the relatively hydrophilic mineral, albite, was found to be about -350 mJ/m^2. This is a similar trend, but with different absolute values, to that observed in water.

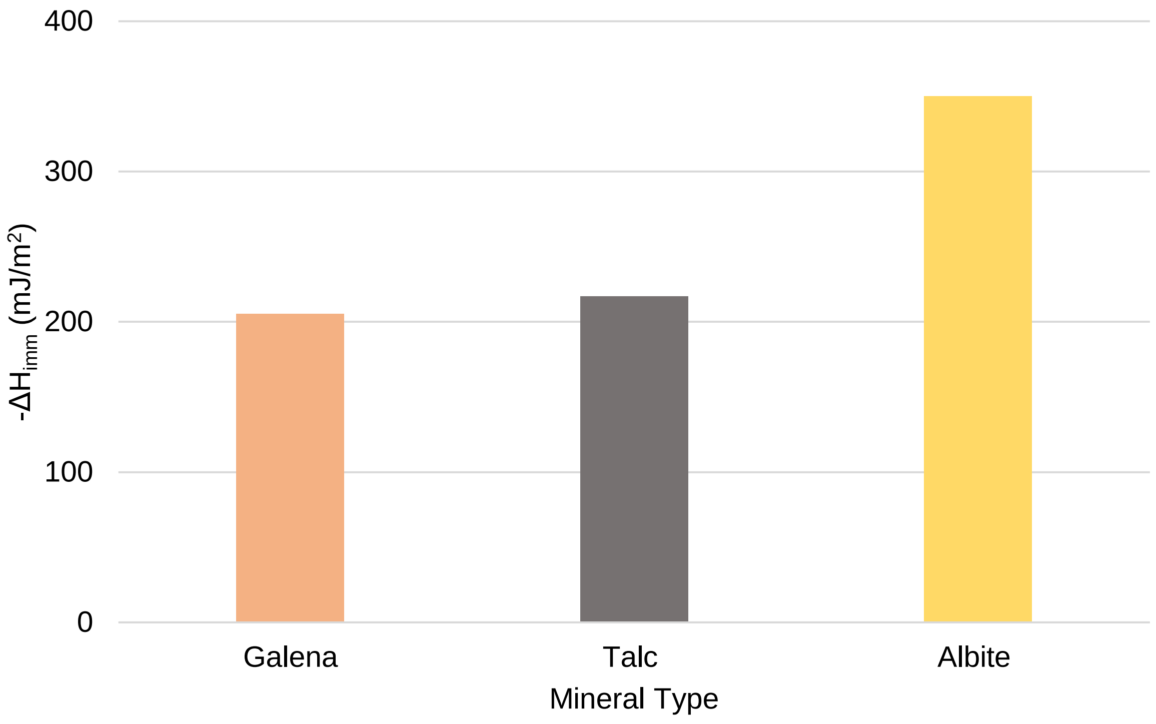


Figure 4-14: The heat of immersion response of various minerals in hexane.

iii. Hexanol

Due to experimental difficulties encountered with the hexane as discussed in the Experimental Methodology, hexanol was tested as a second nonpolar wetting liquid to suppress dissolution.

Figure 4-15 shows the heat of immersion response of galena and albite in hexanol. It was observed that the response for both the minerals was exothermic indicating that dissolution had been suppressed. The heat of immersion response of galena was found to be -97 mJ/m^2 while that of albite was found to be -15 mJ/m^2. In support of the findings from hexane as a wetting liquid, this work has shown that nonpolar liquids can be used to effectively suppress dissolution of the mineral and obtain relative hydrophobicity values for different mineral surfaces.

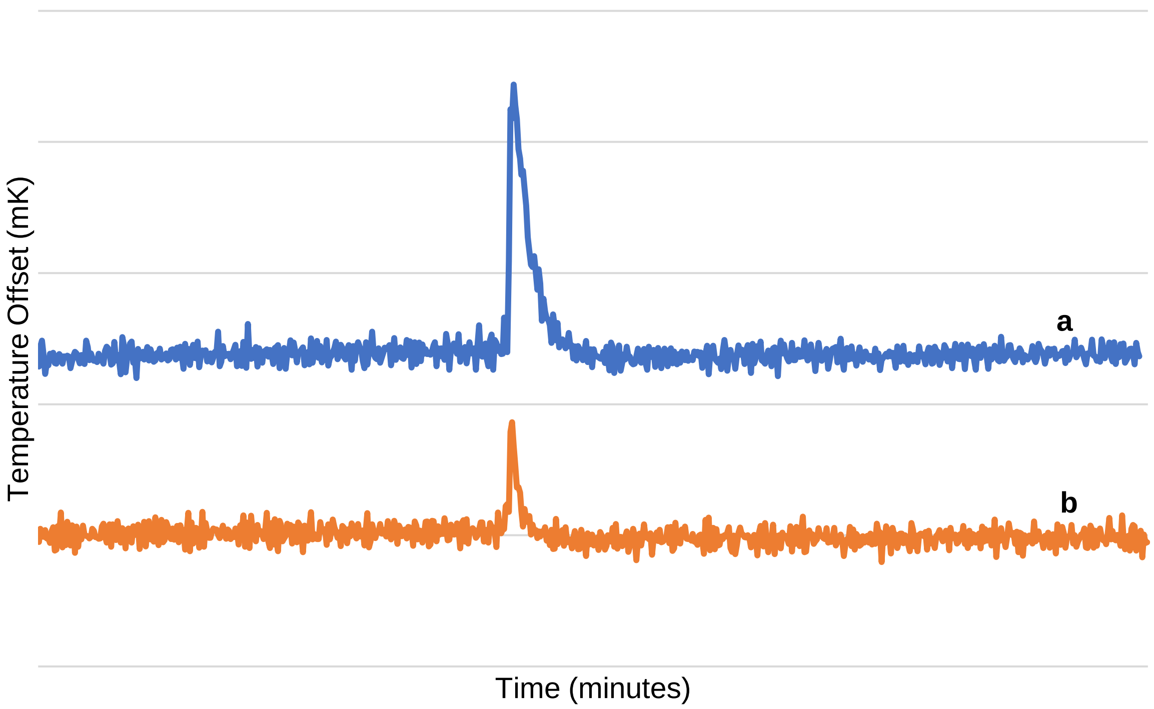


Figure 4-15: The heat of immersion response of a) galena and b) albite in hexanol.

4.4.6 Summary on Suppression of Dissolution Process

From the various approaches explored to suppress the dissolution, it was observed that the saturated solution approach was an effective technique for certain minerals such as albite but was not effective at suppressing the dissolution process for the galena mineral. It is, therefore, an ineffective technique for exploring the heat of immersion of binary mineral mixtures. Secondly, it was observed that the collector coating approach was effective for suppressing dissolution at surface coverages above 75%. The collector coating approach is not feasible for conducting the heat of immersion experiments for the binary mineral mixtures because it only successfully suppresses dissolution at excess surface coverages that are not necessarily those at which one would choose to do the experimental work. Additionally, collector coating does not allow for the natural wettability of the uncoated minerals to be measured. Thirdly, the hexane was found as a good wetting liquid for suppressing dissolution but there were some experimental difficulties that led to this liquid not being used for the binary mineral mixtures. These experimental difficulties include a premature immersion of the mineral into the wetting liquid due to the beeswax used to seal the ampoule dissolving in the hexane. Finally, hexanol was found to be a good wetting liquid in suppressing dissolution, had no associated experimental difficulties and was able to distinguish relative hydrophobicities between different mineral surfaces. It can, therefore, be used as an effective wetting liquid for suppressing mineral dissolution and hydrophobicity determination.

4.5 Heat of Immersion of Binary Mineral Mixtures

Having established a wetting liquid that was both practical and suppressed the dissolution of the mineral, synthetic mixtures of the minerals were prepared, and the heat of immersion was measured. There are different graphical forms of data analysis that are possible, which are shown from Figure 4-16 to Figure 4-19. These include plotting the total heat released on the y-axis, or the heat released per unit surface area of the sample. It should be borne in mind that, under practical conditions where no pure sample is available, the objective is to extrapolate to the pure galena and pure albite samples. The best measure of the heat released would be when it is normalized with respect to the specific surface area of the sample, since these values are comparable across different studies. In addition, since surface area can affect the heat released, it is best to normalise the heat with respect to the surface area. If one reports on total heat only, this is not an easily comparable value. Both options are shown in Figure 4-16 and Figure 4-18 for the heat released and in Figure 4-17 and Figure 4-19 for the heat released per unit surface area. On the x-axis, options are the percentage galena in the sample by weight percent, or by surface area percent. Since the interaction between the wetting liquid and the mineral takes place according to the amount of available surface area, then the surface area value is a better measure of the interaction. However, difficulties in measuring very small surface areas using BET analysis have been discussed in the Experimental Methodology and, for this reason both a surface area percent and mass percent binary mineral composition are shown in Figure 4-16 and Figure 4-17 for the mass percent, and Figure 4-18 and Figure 4-19 for the surface area percent.

Figure 4-16 and Figure 4-17 plots the heat released in mJ and heat released per unit surface area against the mass composition of the binary mineral mixture. From Figure 4-16, the slope of the experimental data points shows that for every 1% increase in the galena mass in the binary mineral mixture, there is 0.68 mJ increase in the exothermic heat released. The y-axis value is the heat released of the pure albite where the mass of galena is 0. This value is estimated or extrapolated to be 7.3 mJ and can be compared to the measured heat released of 12 mJ for pure albite. At x equal 100 where the mixture only consists of galena; the heat released is obtained as 76 mJ. In comparison, the measured heat released for pure galena was 78 mJ. Also shown in Figure 4-16 is the predicted heat released calculated from the weighted sum of the measured values for the pure minerals. The R^2 value between the predicted and experimentally measured values was calculated as 0.98. The R^2, the coefficient of determination, is a statistical measure that gives the proportion of the variation in the dependent variable that is predicted from an independent variable.

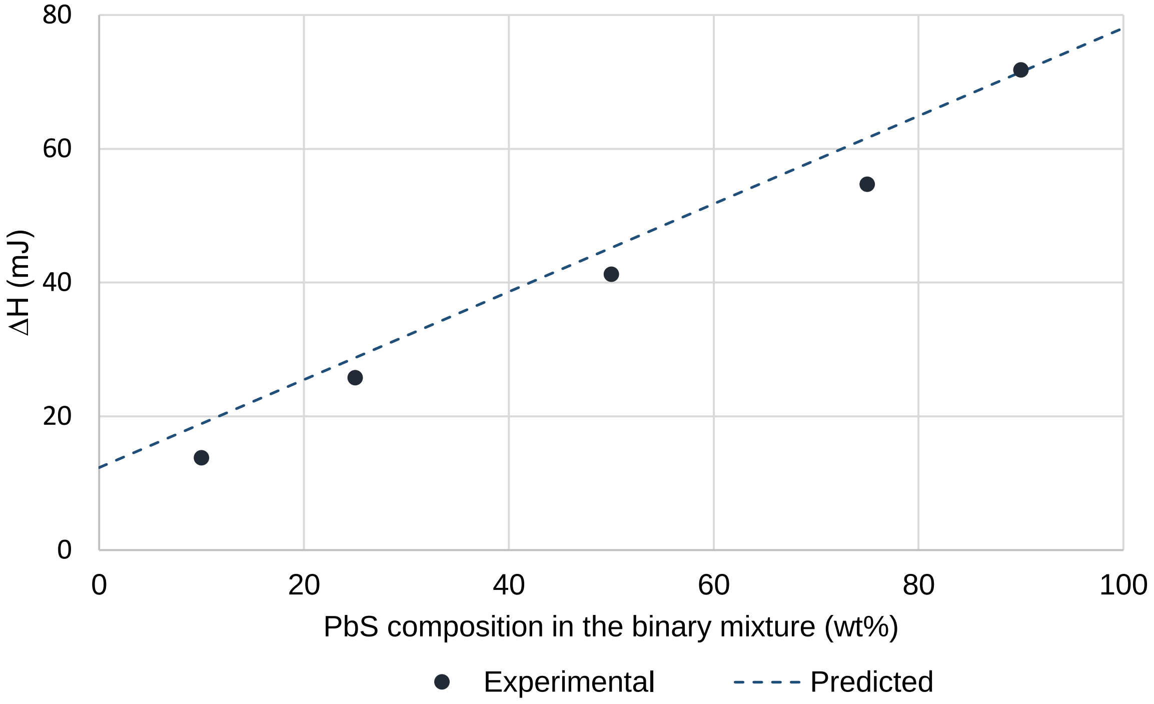


Figure 4-16: The relationship between the heat released in mJ and the mass composition of galena in the binary mineral mixture.

In a similar way, the slope of the experimental data shown in Figure 4-17 shows that for every 1% increase in the galena mass in the binary mineral mixture, there is a 0.80 mJ/m^2 increase in the exothermic heat released, i.e., the heat of immersion. The y-intercept gives the heat of immersion of the pure albite per unit surface area. This value is found to be 10 mJ/m^2 and can be compared to the experimentally measured value of 15 mJ/m^2. At x equal 100 where the mixture only consists of galena; the heat of immersion was determined or extrapolated to be 91 mJ/m^2 compared to an experimentally measured value of 97 mJ/m^2. Figure 4-17 also shows the predicted heat of immersion per unit surface area against the mass composition of the binary mineral mixture. This is calculated as the weighted sum of the heat of immersion values of the pure minerals comprising the mixture. The R^2 value between the predicted and the experimentally measured values was determined to be 0.99.

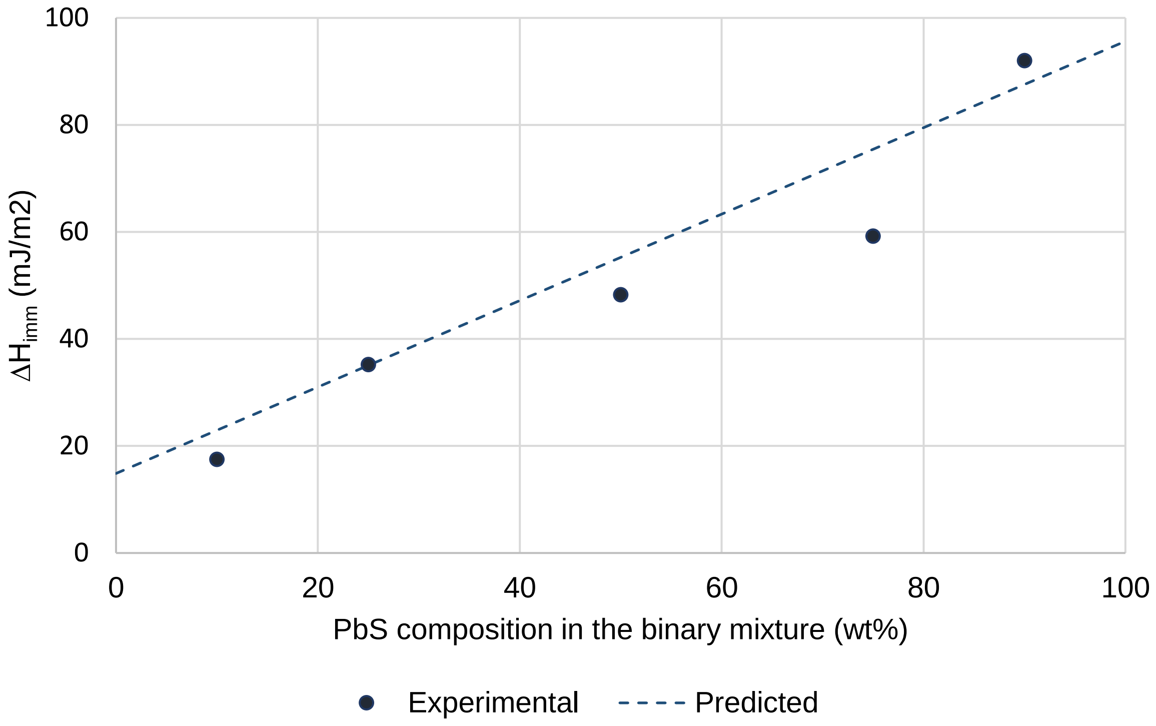


Figure 4-17: The relationship between the heat of immersion per square metre and the mass composition of galena in the binary mineral mixture.

Figure 4-18 and Figure 4-19 show the heat released in mJ and heat released per unit surface area against the surface area fraction of the binary mineral mixture. The experimental data in Figure 4-18 shows that a 1% change in the surface fraction of the binary mineral mixture will result in a 0.76 mJ increase in the exothermic heat released. As per the previous plots, the y-intercept gives the heat released for the pure albite in the mixture. This was found to be 17 mJ and can be compared to the experimentally measured heat released of 12 mJ. When the surface fraction as given in the x-axis is 100, the heat released will be for the pure galena and this is extrapolated to be 93 mJ. In comparison, the experimentally measured value for galena was found to be 78 mJ. Similarly, Figure 4-19 shows that for the experimental data, a change of 1% in the surface fraction would result in an increase of 0.92 mJ/m^2 in the heat of immersion per unit surface area. The y-intercept gives a heat of immersion value of 20 mJ/m^2 in comparison to the experimentally measured value of 15 mJ/m^2. For the galena, the heat of immersion was found to be approximately 110 mJ/m^2 as compared to the experimentally measured value of 97 mJ/m^2.

Figure 4-18 also shows the predicted heat released against the surface fraction of galena while Figure 4-19 shows the predicted heat of immersion per unit surface area against the surface fraction of galena. These were calculated as the weighted sum of the heat released (or heat of immersion per unit surface area as per Figure 4-19) of the pure minerals of the binary mineral mixture taking into account their surface fraction instead of the mass composition as done in Figure 4-16 and Figure 4-17. The R^2 between the predicted and experimentally measured values was found to be 0.98 in Figure 4-18 and 0.99 in Figure 4-19.

Figure 4-19 is best suited to represent the data as it plots the heat released per unit surface area and this will allow for comparison across different studies. Secondly, it plots the heat released per unit surface area against the surface area fraction. Plotting the surface area fraction takes into consideration that the heat released is due to the extent of the surface area that is available for interactions between the minerals and the wetting liquid.

When plotting the surface area fraction, it is essential to note that the surface areas used are based on the BET analysis which presents difficulties in measurement for surface areas less than 1 m^2/g. The surface areas used in this project are approximately 1 m^2/g and therefore this may cause deviation between the experimentally measured and predicted heat released data.

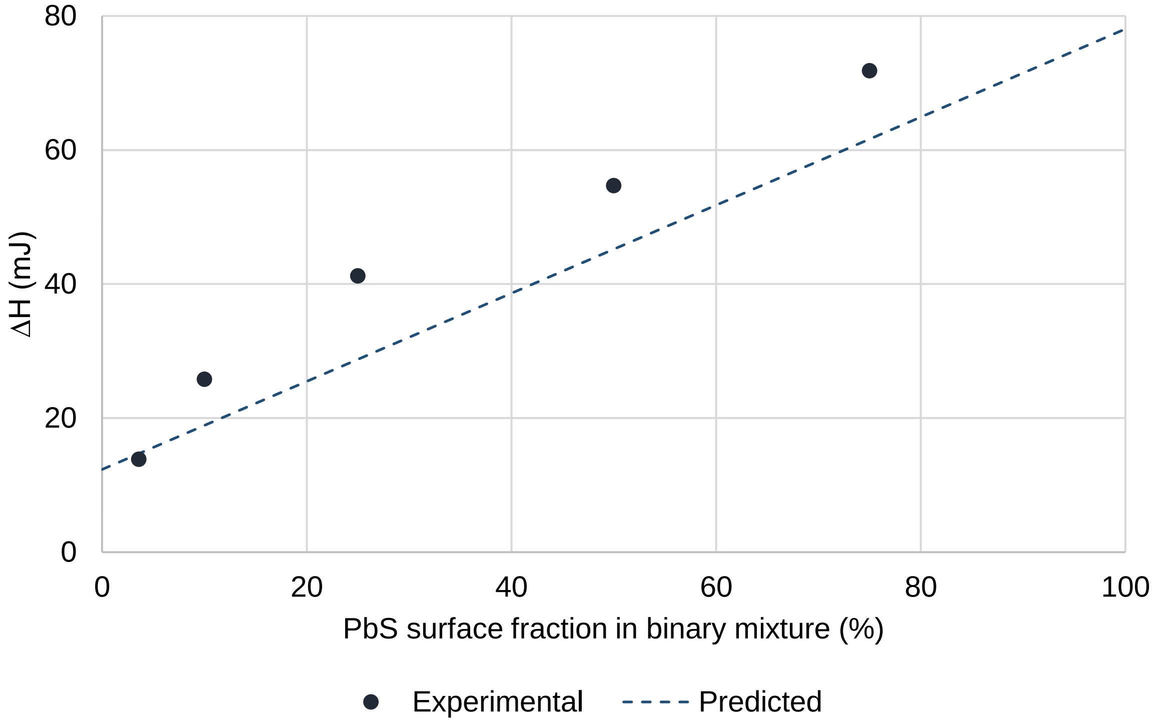


Figure 4-18: The relationship between the heat released in mJ and the surface area fraction of galena in the binary mineral mixture.

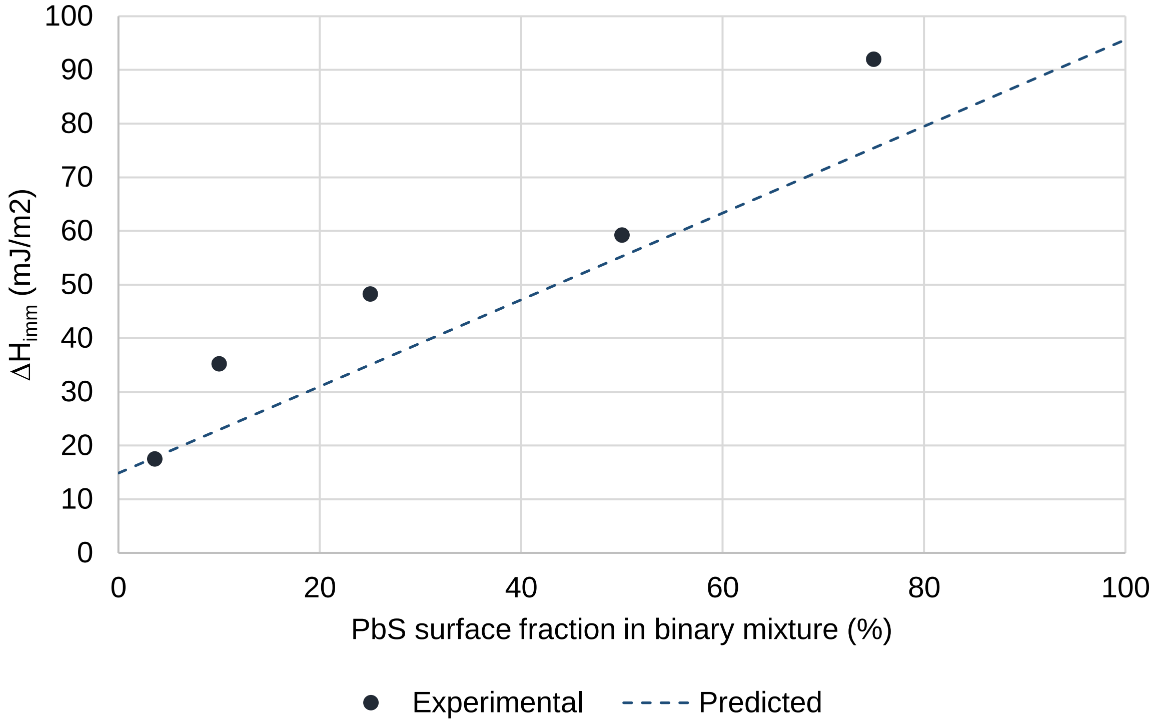


Figure 4-19: The relationship between the heat of immersion per square metre and the surface area fraction of galena in the binary mineral mixture.

There may be arguments to be made for any of the representations from Figure 4-16 to Figure 4-19, depending on how the data is received (as a weight percent assay and whether surface area is known) and how it will be used.

4.5.1 Extrapolated Heat of Immersion Values for the Pure Minerals

In an industrial context with a real ore, access to the pure minerals will practically be impossible. Therefore, it will be difficult to produce the heat of immersion against composition data that will allow one to predict the wettability of the mixture. However, there will be ample ore mixtures with different compositions, and this will allow for the heat of immersion against composition to be determined. From this relationship, the heat of immersion of the pure minerals comprising the mineral mixture can be determined by extrapolation. The extrapolation of the heat of immersion of the pure minerals will allow the determination or modelling of the mineral response.

The experimentally measured heat of immersion values for the pure minerals are compared with the predicted heat of immersion values in Table 4-5 and Table 4-6. The predicted heat of immersion values were extrapolated from the linear relationship between the heat released and the mass composition or surface area fraction of the mixture as shown in Section 4.5.

Table 4-5 shows the results of the experimentally measured and extrapolated heat released based on the mass composition of galena in the mixture and Table 4-6 shows the results based on the surface area fraction of galena in the mixture. The percentage difference between the experimentally measured and extrapolated heat released was calculated as shown in Equation 9. The percentage difference for albite was found to be 49% for the heat released in mJ and 40% for the heat of immersion per unit surface area. For galena, the percentage difference was found to be 2.6% for the heat released in mJ and 6.4% for the heat of immersion per unit surface area. These were based on the mass composition of galena in the binary mineral mixture.

Similarly, as shown in Table 4-6, the percentage difference between the experimentally measured and extrapolated heat released was determined when the surface area fraction was used. The percentage difference for albite was found to be 34% for the heat released in mJ and 29% for the heat of immersion per unit surface area. For the galena mineral, the percentage difference was found to be 18% for the heat released in mJ and 13% for the heat of immersion per unit surface area.

$$Percentage\ difference = \frac{Extrapolated - Experimentally\ measured}{(Extrapolated + Experimentally\ measured) \div 2}$$ Equation 9

For the galena mineral, the percentage difference is below 10% thus extrapolating for the heat released from the relationship between the heat released and mass composition of galena is acceptable. The heat released can either be in mJ or mJ/m^2. However, for the relationship between the heat released and surface area fraction, the percentage difference is above 10% for galena and thus extrapolating to obtain the heat released for the pure mineral is likely to be inaccurate.

For the albite, the percentage difference is ranging between 29% and 49% for the heat released. These values imply significant difference between the experimentally measured and extrapolated heat released. However, when the actual heat of immersion values are evaluated, the difference is not significant.

Overall, the heat of immersion values for the pure minerals comprising the mixture can be determined by extrapolation from the linear relationship between the heat released and mass composition of the binary mineral mixture. The heat released can be presented in mJ or mJ/m^2.

Table 4-5: The comparison of the experimentally measured and extrapolated heat released values of albite and galena in hexanol based on the mass composition of galena in the binary mineral mixture.

	Mineral	Albite	Galena	Figure
Experimental	**Heat released (mJ)**	-12	-78	Figure 4-16
	Heat of immersion (mJ/m^2)	-15	-97	Figure 4-17
Extrapolated	**Heat released (mJ)**	-7.3	-76	Figure 4-16
	Heat of immersion (mJ/m2)	-10	-91	Figure 4-17
Percentage difference	**Heat released (mJ)**	49	2.6	-
	Heat of immersion (mJ/m2)	40	6.4	-

Table 4-6: The comparison of the experimentally measured and extrapolated heat released values of albite and galena in hexanol based on the surface area fraction of galena in the binary mineral mixture.

	Mineral	Albite	Galena	Figure
Experimental	**Heat released (mJ)**	-12	-78	Figure 4-18
	Heat of immersion (mJ/m^2)	-15	-97	Figure 4-19
Extrapolated	**Heat released (mJ)**	-17	-93	Figure 4-18
	Heat of immersion (mJ/m2)	-20	-110	Figure 4-19
Percentage difference	**Heat released (mJ)**	34	18	-
	Heat of immersion (mJ/m2)	29	13	-

As stated previously, the heat of immersion is due to the extent of the surface area of the solid and the wetting liquid. The surface areas used for the measurement of the heat released for the graphs presented from Figure 4-16 to Figure 4-19 are 0.83 m^2 for albite and 0.82 m^2 for galena. These surface areas are based on the specific surface area measured by BET and the mass used for the heat of immersion measurements. Therefore, they are regarded as the experimentally measured surface areas. From the extrapolated heat released in mJ, the predicted or calculated surface areas are 0.73 m^2 for albite and 0.84 m^2 for galena. This is based on the heat released against the mass composition of the galena in the binary mineral mixture. The percentage difference for the surface area for albite is 13% while it is 2.4% for galena. This supports the use of the relationship between the heat released and mass composition in the binary mineral mixture to determine by extrapolation the heat of immersion of the pure minerals.

From the relationship between the heat released and the surface area fraction, the predicted surface areas from the extrapolated heat released is 0.85 m^2 for both albite and galena. The experimentally measured surface areas of the pure minerals comprising the mixture were almost similar at 0.83 m^2 and 0.82 m^2 for albite and galena, respectively. In addition, the predicted surface areas are similar with the percentage difference of 2.4% and 3.6% for albite and galena, respectively. The percentage difference is between the experimentally measured and predicted surface areas for each mineral. This supports the notion that any of the approaches used to represent the data as shown from Figure 4-16 to Figure 4-19, is relevant depending on how the data is obtained and how it will be used.

5 Discussion

This chapter discusses the results presented in Chapter 4 in relation to the objectives of the study which is to develop methodologies to suppress the dissolution of the mineral under investigation during immersion and wetting. It will discuss how the mineral and wetting liquid respond to the different dissolution suppression methods investigated with a view to explain why some methods were successful and others were not. It will further discuss the various observations made of the heat of immersion of binary mineral mixtures.

It has been shown in previous research that the heat of immersion can provide a reliable measure of mineral surface wettability by measuring the heat of wetting. The heat of wetting is observed as an exothermic response in the heat of immersion measurements. However, in the measurements conducted in this study, an endothermic response was observed, and this has not been previously explained or discussed in literature. The only explanation proposed in literature is with respect to salts or crystalline solids where the response of the heat of immersion is dependent on the lattice energy and ionic hydration energy which determine whether the heat released will be exothermic or endothermic.

5.1 Effects of Surface Area and Outgassing Temperature

The reproducibility of the heat of immersion was initially found to be poor for the minerals and to improve this, the surface area of the mineral was increased to increase the heat of immersion response. Quartz was used in these investigations and was ground finer to increase the heat of immersion response. However, it is well known that grinding produces structural and crystallographic changes, and this may expose ions on the surface of the mineral which may dissolve into the water upon exposure.

The desired structural changes during grinding for the heat of immersion are the specific surface area, but other changes such as the shape, polymorphism, and catalytic activities on the surface of the mineral can occur. Grinding results in surfaces with unoccupied valence sites due to the rupture of bonds. Some minerals such as sulphides may also undergo oxidation.

Figure 4-3 showed that, upon moving from a particle size distribution of less than 25 µm to less than 5 µm, an endothermic peak appeared during the immersion of quartz. Grinding quartz to smaller size fractions may introduce an amorphous phase (Takei et al., 1998). It is known that amorphous quartz dissolves in water and this could be the reason for the endothermic heat of immersion response observed at finer size fraction. During the grinding of quartz, the Si – O bonds break, leaving unstable bonds at the surface of the mineral.

Chapter 5: Discussion

The dissolution of quartz in water is given by Equation 10 (Krauskopf, 1956) and it is affected by pH, with the rate lower at acidic conditions and higher at basic or alkaline conditions (Krauskopf, 1956). The rate also varies depending on whether amorphous silica or crystalline quartz is used but the mechanism does not change.

$$SiO_{2(s)} + 2H_2O_{(l)} \leftrightarrow H_4SiO_{4(aq)} \qquad \text{Equation 10}$$

An increase in specific surface area is accompanied by an increase in solubility (Parks, 1984). This increase in solubility can also be used to estimate the surface free energies of solids immersed in liquids through the Freundlich-Ostwald equation (Parks, 1984).

Unlike silica, an increase in surface area through grinding in the case of albite did not introduce an endothermic response, but rather resulted in a relatively linear increase in the exothermic heat of immersion as a function of surface area (Figure 4-4). The results obtained for albite in this study are in agreement with those obtained by other authors (Chan et al., 1997; Donnet et al., 2008; Terada & Yonemochi, 2004) where the heat of immersion increases with an increase in the available surface area. This also indicates that there is no substantial change in the crystal structure of albite since the increase in the heat released is only due to the increase in surface area.

The preparation of the mineral sample prior to the heat of immersion measurements requires outgassing of the sample at certain temperatures. Outgassing at increasing temperatures, viz 40°C and 100°C, resulted in an increase in the heat of immersion for albite, because of the removal of the physically adsorbed water on the surface of the mineral. Other authors such as Rootare & Craig (1974) observed a similar response of an increase in the heat of immersion with increasing outgassing temperature.

This study has shown that the surface area has an effect on the heat of immersion with some minerals susceptible to structural changes that result in increased dissolution of the mineral at very fine particle sizes. Even though dissolution was confirmed for all the minerals, it was observed that sphalerite and albite do not appear to be susceptible to dissolution during immersion calorimetry. Therefore, for the purpose of determining wettability in mineral processing applications, the surface area or particle size distribution to which certain minerals may be ground for the heat of immersion measurements will be limited. This is because the surface area is increased by grinding and grinding produces structural and crystallographic changes which result in dissolution. In addition, there is simply more surface area available for the dissolution reaction to occur, which increases its contribution to the total heat measured. For minerals which are relatively insensitive to structural changes resulting in dissolution, the heat of immersion increases with an increase in available surface area. In the present investigation, albite was such a mineral. Secondly, the heat of immersion for albite increased from 188 mJ/m^2 to 336 mJ/m^2 with an increase in outgassing temperature from 40°C to 100°C due to the removal of physically adsorbed surface water.

5.2 Confirmation of Dissolution

It was hypothesised in the present investigation that the endothermic response observed for some minerals in the heat of immersion measurements is due to the dissolution of the mineral into the wetting liquid. Dissolution tests were thus conducted to determine whether dissolution occurs in either deionised water or solutions saturated with ions from the original mineral. It was found that there were elements present in the solution originating from the mineral under investigation indicating that dissolution of the mineral occured.

Even though the dissolution of the minerals processed by flotation is usually deemed less impactful on flotation due to low solubility of these minerals in water, it is important to note that grinding of these minerals to achieve certain specific sizes will expose the ions on the mineral surface resulting in some dissolution. Due to the sensitivity of the microcalorimeter used to measure the heat of immersion, the heat of dissolution will be measured upon immersion of a mineral in water. Makrides & Hackerman (1959) stated that the heat of immersion in water is a sum of the heat of wetting and the heat of dissolution. This confirms that during immersion, dissolution may occur, and the heat of dissolution can be measured by a microcalorimeter.

5.2.1 Galena Dissolution

As presented in Figure 4-5, galena was found to be slightly soluble in water, with approximately 0.4% of the total lead present in the sample dissolving into solution within 10 minutes. The dissolution of galena in water occurs as shown in Equation 11 (El Alaoui & Dekayir, 2018). The theoretical solubility product (Ksp) of galena is given as 10$^{-28.3}$. This implies that galena has very low solubility in water. Fine particle sizes of less than -25 µm were used in the dissolution studies of galena and these will have larger surface areas and therefore their dissolution will be increased in comparison to the bulk sample (Paugh & Bergstrom, 1986).

$$PbS + 2H^{+} \leftrightarrow Pb^{2+} + H_2S \qquad \text{Equation 11}$$

Lead sulphide, i.e., galena, becomes unstable upon exposure to oxidising environments leading to the oxidation of the sulphide to higher oxidation states or to the sulphate ion thus releasing the lead into the solution as shown in Equation 12 (Hsieh & Huang, 1989). This happens spontaneously. This implies that there will be a release of lead ions into the solution when the galena sample is immersed in deionised water.

$$PbS_{(s)} + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-} \qquad \text{Equation 12}$$

At the surface, galena has unsaturated bonds which result in surface oxidation. The immersion of galena with these unsaturated or broken bonds in water is accompanied by the surface dissolution. This can possibly be followed by interfacial precipitation or re-adsorption of lead hydroxy species at the surface of galena at pH above 8 (Hsieh & Huang, 1989). Rao (2013) added that while Pb ions may dissolve from the surface of galena into water, they may later precipitate or adsorb on the surface of galena as specific species. The decrease in dissolved Pb ions after 20 hours may be attributed to adsorption of Pb as specific species such as $PbOH^+$.

This work has shown that dissolution of galena does occur in deionised water. This dissolution process is measured simultaneously with the wetting process during immersion experiments. Therefore, some remedy to this occurrence must be developed for immersion calorimetry to be a useful technique for mineral processing applications.

5.2.2 Albite Dissolution

In the study of dissolution of albite, the rate of dissolution was determined by studying three of the component elements of albite: namely, sodium, aluminium, and silicon. It was observed that sodium dissolution was the greatest with lesser aluminium and silicon ion concentrations. The sodium ions increased with dissolution time while the aluminium ions decreased, and there was no correlation with the silicon ions. Additionally, it was observed that approximately 10% of the total initial sodium present dissolved within 20 hours dissolution time. This was observed to be a maximum dissolution for sodium ions, while the maximum achieved for aluminium ions was 0.92% at 10 minutes dissolution time, and 0.19% for silicon both at 10 minutes and 20 hours. These results are presented in Figure 4-6.

The mechanism of the dissolution of albite in water follows a trajectory where a residual layer forms on the surface of the mineral during dissolution (Blum & Stillings, 1995). The dissolution of albite in water is shown by Equation 13 given by Blum & Stillings, (1995). The dissolution of albite in water involves the first step reaction where the alkali or alkali earth ions exchange with the hydrogen ions forming hydrogen feldspar on the surface (Crundwell, 2015a; Crundwell, 2015b). They added that the first step in the formation of this layer involves the exchange of sodium ions with the hydrogen ions followed by the release of aluminium and silicon in smaller amounts. It is accepted that this exchange step is fast enough to reach equilibrium (Blum & Stillings, 1995). Other authors added that under natural conditions, the major energy involved during the dissolution of feldspars is the displacement of the sodium cations by hydrogen ions. Eventually, a steady state is reached when the ions in solution have reached the same stoichiometric values as that in the solid phase. A steady state dissolution phase is when the release of all the three elements has reached an approximate constant value. From the results in this study, it was observed that the silicon released to the solution was approximately constant while the aluminium content decreased. The decrease in aluminium content can be attributed to the precipitation of the secondary phases back to the mineral surface (Blum & Stillings, 1995). The sodium ions were at their highest concentration after 20 hours. This is because these ions are the first to exchange with the hydrogen ions during the dissolution and as found by Chou & Wollast (1985) and Crundwell (2015b), they are the most ions to be released during the dissolution. Since it is observed that there are some elements of albite in the solution, it can be confirmed that indeed there is dissolution of the mineral into the deionised water. Secondly, it can be said that the dissolution has not reached steady state as the ions in solution continue to increase with an increase in dissolution time and stoichiometry has not been established. Stoichiometry is established when the elements in solution are in the same ratio as the elements or abundance in the original mineral.

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_{4(aq)} + 2Na^+ \qquad \text{Equation 13}$$

This work has shown that there is dissolution of albite into the deionised water at laboratory conditions. This dissolution process is hypothesised to be indicated by the endothermic response in the heat of immersion measurements as shown in Figure 4-2 in Section 4.2. Similarly, a remedy to this occurrence must be established for immersion calorimetry to be a useful technique for mineral processing applications. The dissolution process occurred on both the hydrophilic and hydrophobic minerals used in this study.

5.2.3 Dissolution of Salts

In the confirmation of the dissolution process where the mineral dissolves into the wetting liquid, it was observed that the heat of dissolution of salts was either endothermic or exothermic depending on the difference between the lattice energy and the hydration energy. The results are presented in Section 4.4.2, Figure 4-7 and Figure 4-8.

When salts dissolve in water, the lattice energy is overcome by the ionic energy, that is, lattice dissociation is overcome by hydration. These energies determine the overall heat of dissolution of salts. Lattice dissociation is always positive while hydration is always negative.

Depending on which energy is larger, then the overall heat of solution is indicative of the larger energy. The lattice energy depends on the sum of the anionic and cationic radii while the hydration energy has separate anionic and cationic terms (LibreTexts, 2021). Solvation of small ions, especially cations, dominate the hydration energy. Lattice energy is the energy required to break the ionic solid apart and separate the ions into the gas phase and hydration energy is the energy released when the ions are surrounded by water after separation.

Increasing the size mismatch, that is, increasing the difference in size between the anion and cation increases the solubility in water (LibreTexts, 2021). Therefore, for the sulphate salts, the lead sulphate salt will have low solubility due to Pb ions having a larger radius compared to Zn and Fe ions. The atomic radii of the cations are presented in Table 5-1. $PbSO_4$, $ZnSO_4$, and $FeSO_4$ are all salts of sulphate with a common anion SO_4^{2-}. SO_4^{2-} has a larger radius than the cations. In terms of the radii of the cations for the sulphate salts used in this study, $Pb^{2+} > Fe^{2+} > Zn^{2+}$. In a periodic table, atomic radii decrease from left to right in a row, thus Zn is smaller than Fe. Similarly, the atomic radii increase from the top to bottom in column. Increasing the cationic radius, decreases the size mismatch. In this case, the lattice energy will exceed the hydration enthalpy and results in insoluble salts like $PbSO_4$ (LibreTexts, 2021). When the lattice energy is greater than the hydration energy, the heat of dissolution is endothermic (positive). $PbSO_4$ has the lowest heat of dissolution at 0.084 kJ/mol indicating that this has low solubility in comparison to $FeSO_4$ and $ZnSO_4$ with respective heats of dissolution of 20 and 18 kJ/mol. Secondly, the heat of dissolution is endothermic indicating that the lattice energy is greater than the hydration energy for these salts.

Table 5-1: Atomic radii (pm) of the cations for the sulphate salts extracted from Web Elements (1993). The coordination number represents the number of ions that immediately surround an ion of the opposite charge (sulphate anion) within a crystal lattice.

	Pb^{2+}	Fe^{2+}	Zn^{2+}
6 coordination	133	92	88
8 coordination	143	106	104

5.3 Dissolution Suppression Techniques

Since it was found in this work, and in the Ksp values from literature, that most minerals undergo a certain small amount of dissolution in water, procedures are needed to suppress the dissolution such that only the heat released due to wetting is measured in immersion experiments.

5.3.1 Saturated Solution

Since it was confirmed that there is dissolution of the mineral in water, a saturated solution was explored as a wetting liquid to suppress dissolution. A saturated solution is defined as a solution that is at equilibrium with the ions of the target mineral. In this case, a saturated solution was prepared as a 10 wt.% of the target mineral in deionised water. It is assumed that when a mineral is dissolved in a saturated solution of its own ions, the dissolution reaction will be driven in the reverse direction, viz. dissolution will be inhibited.

The results are presented in Table 4-4 and it was observed that the endothermic response indicative of the dissolution process was not eliminated or suppressed for most minerals with the use of a saturated solution as a wetting liquid. However, there was an exception with sphalerite, a sulphide mineral, and albite, a silicate mineral. The reason that the dissolution of the other minerals was not suppressed is possibly due to the solution not being fully saturated with the relevant ions.

The Ksp values of the tested minerals given in Table 5-2 have shown that most of the sulphides being investigated have low solubility in water. The dissolution of metal sulphides in water can occur due to oxidation of the sulphide to sulfoxyl compounds, promoted by the presence of oxygen (Rao, 2013). The presence of these oxidation compounds results in the dissolution process of the mineral. From the Ksp values from literature, sphalerite is said to have a relatively high solubility compared to the other sulphide minerals. This means that the saturated solution for sphalerite will have a high number of dissolved ions in solution thus having a high chance or probability of reaching equilibrium. A saturated solution with a high dissolution rate (high number of ions in solution) has a better chance of suppressing dissolution. When the saturated solution containing ions from the dissolved sphalerite was used as the wetting liquid, the dissolution process was suppressed due to the relative solubility of sphalerite.

Table 5-2: Ksp values extracted from Vaughan & Craig (1978).

Mineral	**Ksp**
Chalcopyrite	$1x10^{-49.3}$
Galena	$1x10^{-28.3}$
Pyrite	$1x10^{-26.9}$
Pyrrhotite	$1x10^{-17.9}$
Sphalerite	$1x10^{-20.6}$
Albite	-
Quartz	$1x10^{-3.98}$

Galena had a maximum amount of dissolved Pb ions at a dissolution time of 10 minutes. As the dissolution time increased to about 20 hours, the dissolved Pb ions decreased indicating that the dissolution process was not saturated or in equilibrium at this dissolution time. It is possible that precipitation of the surface ions was occurring. In performing the heat of immersion measurements, the saturated solutions for albite and galena were generated using a dissolution time of 20 hours. Since the Pb ions dissolved in solution for galena at 20 hours were not at equilibrium, this means that the dissolution process still occurred upon immersion of the dry galena into the saturated solution. However, for albite and sphalerite, it can be concluded that the saturated solution was at a saturation point with the ions as no further dissolution was observed during the heat of immersion measurements.

The 20 hours dissolution time for the saturated solution was chosen based on the dissolution results of albite as shown in Figure 4-6. This is because of the Na^+ ions that were observed to be dominant in the dissolution of albite and were the most dissolved at 20 hours. The sodium ions were still increasing with an increase in dissolution time meaning that equilibrium had not been reached within the tested dissolution times. However, albite does not oxidise upon exposure to oxygen or water thus the ions in solution remain the same as those on the mineral surface. Therefore, it is speculated that for most of the sulphide minerals, the ions in the saturated solution transformed to an oxidised species that may have then taken part in other reactions, eliciting an endothermic response.

Endothermic responses due to quartz dissolution may have been due to an alternative mechanism. Upon grinding quartz to very fine sizes, an amorphous layer is introduced, and this layer is more soluble. The dissolution or endothermic response of quartz is discussed in detail in Section 5.1.

Therefore, it was found that the saturated solution does not suppress dissolution for all minerals; however, there are exceptions where it managed to reduce the extent to which a mineral dissolved in water by reversing the dissolution process. This was also the procedure used by Taguta et al. (2018) for a range of minerals in which only exothermic reactions were observed. The saturated solution may, therefore, have more widespread application than that demonstrated by the minerals used in this study.

5.3.2 Collector Surface Coverage

Heat of immersion is known to be a good indicator of hydrophobicity for natural minerals (uncoated) and those coated with collector. The effect of collector surface coverage was studied as an alternative dissolution suppression technique since the collector will cover the surface-active sites of the mineral preventing further dissolution from happening since the mineral surface will have minimal exposure to water. The interactions that occur will be between the collector molecules and the wetting liquid.

Chapter 5: Discussion

At the solid-liquid interface, the adsorption behaviour of collectors or surfactants is determined by various forces such as the electrostatic force, hydrogen bonding etc. These forces will determine the adsorption heat between the collector and the mineral. A collector was used in this research to suppress the dissolution of the mineral into the wetting liquid. This is because collector molecules modify the surface of the mineral (Liu et al., 2020) and are believed to have a dual action of surface cleaning by removing oxidised material on the surface of the mineral and subsequently providing a hydrophobic surface (Smart et al., 2003). This mechanism is believed to be occurring on the galena surface when it is coated by the xanthate collector. In the case of coals, Melkus et al. (1989) stated that the adsorption of collector occurs on specific surface sites of the coal surface thus blocking other sites from the wetting liquid, water.

It was observed as shown in Figure 4-10 that using a xanthate collector to cover the surface-active sites of the mineral will result in dissolution being suppressed. However, a certain percentage of surface coverage has to be obtained and this was found to be at 75% surface coverage. The 75% surface coverage can be deemed as a minimum coverage required to coat the mineral surface to suppress the dissolution. Any coverage below 75% resulted in an endotherm appearing, which was assumed to be the result of dissolution occurring. The magnitude of this endotherm increased as the collector coverage decreased, and further mineral dissolution occurred.

At surface coverages below 75%, the specific surface sites are not all covered due to insufficient collector amount available for adsorption. Since the adsorption of collector on the surface of galena is not uniform, with the likelihood of it occurring on oxygen rich areas with face specificity (Smart et al., 2003), partial or incomplete coverage will still result in dissolution from the uncovered surfaces. Therefore, enough collector concentration or surface coverage is required to cover the whole of galena active surface sites to prevent dissolution from occurring.

The relationship between the collector surface coverage (above 75%, where no endothermic response observed) and the heat of immersion, i.e., wettability in water, was observed to be inversely proportional (Figure 4-11). This is because collector addition to minerals enhances the hydrophobicity of the minerals. Smart et al. (2003) added that collectors provide a hydrophobic surface to the mineral. Since the heat of immersion in water is lower for hydrophobic surfaces, the observed relationship between the collector surface coverage and the heat of immersion is expected where the heat of immersion decreases with an increase in collector surface coverage. Harkins & Jura (1944) observed similar results of an exponential decrease in the heat of immersion with an increase in surface coverage. Taguta et al. (2019) obtained a similar response of an inverse relationship between the heat of immersion as a measure of wettability and the flotation response. The relationship obtained was an inverse exponential response. A similar response was obtained by Melkus et al. (1989) and Blake & Ralston (1985). The inverse response was obtained because collectors render the mineral surface hydrophobic.

The observed relationship was an exponential inverse because at excess surface coverages, greater than 1 monolayer, the mineral surface will be fully covered and any further increase in collector dosage does not result in a significant increase in hydrophobicity. This is demonstrated clearly in Figure 4-11 where an increase of 400% collector surface coverage, from 300% coverage to 700% coverage, barely changes the heat of immersion response.

In summary, the collector coating can suppress dissolution and give meaningful immersion data about wettability in water. This is because the collector covers the surface-active sites of the mineral and reduces their exposure to water. However, there is a minimum surface coverage required before the dissolution can be suppressed. Increasing the collector surface coverages decreases the heat of immersion until a plateau has been reached where excess coverage results in no further increases in the hydrophobicity of the mineral.

5.3.3 Organic (Nonpolar) Wetting Liquids

The heat of immersion does not only relate the surface of the solid available to the liquid but also the specific interactions between the solid and the immersion liquid resulting from the presence of polar sites on the solid surface (Barton & Harrison, 1976). These surface forces determine whether the liquid will wet the solid. Wetting liquids, predominately nonpolar were explored to understand the heat of immersion response of minerals that simultaneously involves the dissolution and the wetting process in water. The nonpolar wetting liquids were explored to suppress dissolution because they will not solvate ‘dissolved’ ions. Secondly, it is known that the heat of immersion measurements are based on the surface energies and/or surface interactions between a solid and a non-reacting liquid. Ruiz et al. (1998) found that aliphatic compounds such as hexane have the weakest adsorption compared to polar and aromatic compounds. This means that there is little interaction between hexane and the mineral surface.

The heat of immersion in hexane as presented in Figure 4-13 was purely exothermic indicating that the dissolution had been suppressed. Possibly, because of very few acid-base properties of the organic liquids resulting in no significant proton transfer (Garnier et al., 1995). During the immersion of the minerals into the organic wetting liquids, the interactions involving the polarisation of the non-polar molecule restrict the dispersive effects (Garnier et al., 1995). Chessick et al. (1955) added that the total energy of adsorption for hydrophobic minerals is due to dispersive forces only. Dispersive effects, i.e., London dispersion forces, are temporary attractive forces that result when electrons on the nonpolar liquid and mineral surface occupy positions that make the atoms form temporary dipoles. These are the weakest intermolecular forces. The heat of wetting of hydrophobic surfaces is independent of the dipole moment of the wetting liquid (Chessick et al., 1955). For dissolution to occur, the solute-solute and solvent-solvent interactions must be disrupted, and the solvent must solvate or hydrate the ions. However, this process does not occur with hexane.

The heat of immersion in hexane was observed to be higher for the hydrophilic mineral, albite, compared to the hydrophobic minerals, galena and talc. This is because the interactions between nonpolar liquid and hydrophilic mineral is repulsive while the interaction between hydrophobic and nonpolar minerals is governed by the hydrophobic force. It is possible that during the immersion experiments, the hydrophobic forces are at play together with the dispersion and electrostatic forces and therefore will be measured in the heat of immersion (Xu & Yoon, 1990). The hydrophobic force is a non-DLVO force that exists beside the dispersion and electrostatic forces (Xu & Yoon, 1990). Metal sulphides such as galena have chemically altered surface layers particularly as oxides or hydroxides after exposure to air or aqueous solutions (Smart et al., 2003). This means that the galena sample used had oxygen or oxygenated surfaces due to exposure in air that led to oxidation. Samples that contain less oxygenated groups have increased interactions with nonpolar organic compounds, hexane (Hernandez-Monje et al., 2020). Galena has more oxygenated groups on the surface from grinding, thus it has less interactions with the hexane resulting in lower heat of immersion. Talc and albite as silicate minerals also have oxygen in their surfaces. However, it is surmised that galena and talc will have more oxygenated groups in the surface compared to albite. Therefore, the interactions between albite and hexane will be increased resulting in higher heat of immersion. An interesting point to note is that the heat of immersion of known hydrophobic minerals was approximately the same in hexane possibly meaning that the interactions between the hydrophobic minerals and the hexane were similar. The conjecture is that these minerals interact with hexane with similar intermolecular forces; namely, dispersion forces. Secondly, it can be said that the strength of the dispersion forces is equal due to equal number of oxygenated groups in the mineral surfaces. Or it can be said that the number of oxygenated groups on the surface of the hydrophobic minerals is similar with talc having more oxygenated groups because of it being a silicate mineral; having oxygen in its surface structure.

The heat of immersion in hexane was observed to be more exothermic for hydrophilic minerals, meaning that, the heat of immersion increases with hydrophilicity. This observation is similar to that of water where the heat of immersion is more exothermic for hydrophilic solids or minerals. Melkus et al. (1989) observed that the heat of immersion in water for the least floatable coal was more exothermic. This means that hydrophilic coals have a higher heat of immersion. Goncharuk (2015); Kondo et al., (1978); Taguta et al. (2018) also observed that the heat of immersion in water increases (more exothermic) for hydrophilic surfaces. The heat of immersion is more exothermic for hydrophilic solid surfaces in water due to electrostatic and dipolar attractions (Glaser & Weitkamp, 2008). However, the heat of immersion in hexane is due to dispersion forces and the oxygenated groups on the surface of the mineral.

Lastly, the heat of immersion of collector coated galena in hexane was observed to be endothermic due to hexane interacting or dissolving the collector molecules. Hexane has been used to extract surfactants such as dixanthogen (Rao et al., 2013).

The heat of immersion in hexanol was observed to be exothermic indicating that the dissolution had been suppressed. This is because hexanol interacts with the mineral surface in repulsive forces and dispersion forces. The heat of immersion of galena in hexanol was observed to be more exothermic than that of albite. This is because the interactions between hexanol and hydrophilic minerals are repulsive resulting in less heat of immersion due to less interactions (Xia et al., 2022). It is difficult for the hydrocarbon, hexanol, to adsorb onto the albite.

The heat of immersion of albite and galena were respectively found to be -75 mJ/m^2 and -485 mJ/m^2 in hexanol and -350 mJ/m^2 and -205 mJ/m^2 in hexane. From this, it can be seen that the heat of immersion of albite is more exothermic in hexane while for galena, it is more exothermic in hexanol. The more exothermic heat of immersion of albite in hexane than in hexanol is because alkanes have a higher repulsion force than alcohols when interacting with hydrophilic mineral surfaces due to the high electrostatic repulsion forces (Xia et al., 2022). Secondly, hexanol is more polar than hexane and will have less repulsion for hydrophilic minerals.

This study has shown that using hexane and hexanol as wetting liquids is a viable methodology for supressing the dissolution process in the heat of immersion measurements.

5.4 Heat of immersion of binary mixtures

The ultimate objective of the study was to measure the heat of immersion of binary mineral mixtures. In this study the binary mineral mixture used consisted of albite as the hydrophilic mineral and galena as the hydrophobic mineral which is more typical of a real ore comprising of hydrophobic and hydrophilic minerals.

The heat of immersion can be presented in various ways depending on what data is required and desired. Relating the value to the surface area fraction or mass composition results in a linear relationship being observed between the heat of immersion and the composition of the binary mineral mixture (Figure 4-16 to Figure 4-19). In all cases, a linear relationship was obtained with relatively good correlation coefficients. This validates the hypothesis that there is a linear relationship between the heat of immersion and the mass composition or surface area fraction of the binary mineral mixture. Tyler et al. (1971) stated that the heat of immersion as a measure of wettability (heat of wetting) cannot be reliably expressed per unit surface area for microporous surfaces when the surface area has been determined by the BET method. This is because in microporous materials, the micropores account for a very large part of the surface area. The BET method was the technique applied in this study to determine the specific surface areas of the mineral samples and this may have contributed to the deviation where the surface area fraction was used. Tyler et al. (1971) added that the gas adsorption isotherms of porous solids may be used to provide more precise information about the solids surface instead of the BET method using nitrogen. Alternatively, molecules much larger than nitrogen can be used in the determination of the external surface area using BET.

Gao & Rytting (1997) have shown that there is a linear relationship between the heat of immersion and the mass composition of the non-reacting binary mixture in support of the results obtained in Figure 4-16 and Figure 4-17. They further stated that the heat of immersion of the non-reacting binary mixture is based on the energy differences between the two interacting solids. Takei et al. (1998) demonstrated that there is a linear relationship between the heat of immersion and the surface area fraction of the binary mixture, and this supports the results presented in Figure 4-18 and Figure 4-19.

5.4.1 Extrapolated values

A linear relationship between the heat of immersion of a binary mineral mixture and the composition of the mixture was established and the heat of immersion of the pure minerals comprising the mixture was extrapolated from this relationship. This was then compared to the measured heat of immersion of the pure minerals. This methodology is proposed to be a technique that could be used to determine the heat of immersion of the mineral components of a simple ore, which could then be related, via an empirical relationship, to the mineral floatability for modelling purposes.

In a study by Takei et al. (1998) where they attempted to study the effect of crystallinity on the heat of immersion of silica in water, they employed the method of extrapolation to determine the heat of immersion values at a surface fraction of 0 and 1. The extrapolation was done from a linear relationship between the heat of immersion per unit surface area and the surface area fraction where the surface area fraction was defined as the ratio between the surface area calculated from water adsorption and that from nitrogen adsorption. At 0, the silica surface only had siloxane groups and at 1, it was fully hydroxylated. This shows that the extrapolation approach has been previously used to determine the heat of immersion of the components making up the binary mineral mixture.

In the case of albite used in this study, the measured value was -15 mJ/m^2 compared to the predicted value of -10 mJ/m^2. In the case of galena these values were -97 mJ/m^2 and -91 mJ/m^2, respectively. The difference between the measured and predicted heat of immersion values is not significantly large. This means that the linear relationship between the heat of immersion and the mass composition or surface area fraction can be used to determine the heat of immersion of the pure minerals comprising the mixture. Despite the difference in the heat of immersion values, the predicted heat of immersion values of the pure minerals would fall within the region of empirical floatability curve given in Figure 5-1 (c) which would still be useful for predicting floatability. It is suspected that the contributing factor to this difference is the surface area measured by the BET since the measured surface areas were small, below the detection limit.

The linear relationship based on composition provides a simple and convenient way to estimate hydrophobicity of an ore where only the mass and mineral composition of the sample is known. To determine the relative hydrophobicity of a binary mineral mixture in hexanol where the mass composition is unknown, the heat of immersion or heat released by the binary mineral mixture is measured and this is correlated with the mixture's mineral weight composition. This linear relationship can then be extrapolated to zero and 100% to obtain the heat of immersion of the pure minerals. These values can be read off a calibration curve such as that obtained by Taguta et al. (2019) to obtain a flotation rate constant. The procedure has been shown in Figure 5-1.

The detailed procedure leading to the extrapolation involves the sample preparation where binary mineral mixtures of various compositions will be obtained. These samples could comprise of a feed, concentrate and/or tails samples or just feed samples with different compositions. The heat released when the samples are immersed in hexanol will be measured following the procedure given in the Experimental Methodology. Based on the elemental mass composition and the mass-corrected heat of immersion, the relationship between the mass composition and the heat of immersion will be established (Figure 5-1 (b)). This linear relationship will be used in determining the heat of immersion of the pure components of a binary mineral mixture. The floatability of these pure components can then be determined from the empirical curve as shown in Figure 5-1 (c) and used in modelling of the flotation response.

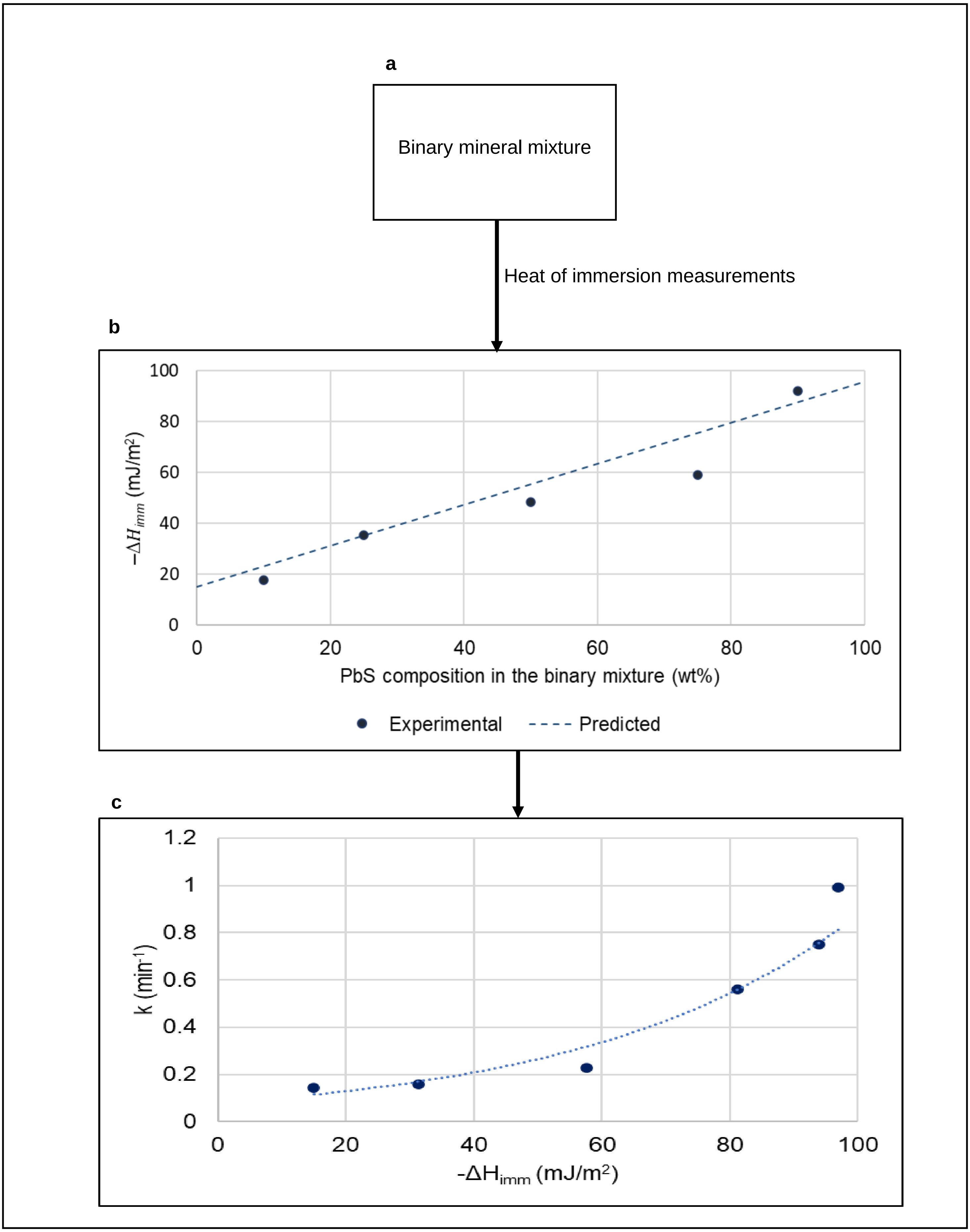


Figure 5-1: Heat of immersion extrapolation procedure for the pure minerals comprising the mixture. a) Binary mixture. b) Heat of immersion per unit surface area of the binary mixture. c) Modelling of the floatability for the binary mixture based on the heat of immersion.

6 Conclusions

This section highlights the main conclusions from the experimental work of this study and the subsequent results obtained. It will be divided into two parts, the methodology to conduct the heat of immersion measurements and the approach to binary mineral mixture heat of immersion measurements.

6.1 Factors Affecting the Heat of Immersion

The effect of surface area on the heat of immersion was observed to increase the heat of immersion response for minerals that are not susceptible to structural changes. The minerals that are susceptible to structural changes such as quartz resulted in the dissolution in water. Minerals such as albite and sphalerite were found not to be susceptible to structural changes that result in dissolution and albite revealed that the heat of immersion increased with an increase in available surface area. The surface area to which certain minerals must be ground for the heat of immersion measurements is therefore limited. Another observation was made on the factors that affect the heat of immersion where the heat of immersion increased with an increase in outgassing temperature. However, higher outgassing temperatures cannot be used as these will oxidise the sulphide minerals.

6.2 Dissolution Suppression Techniques

Immersing some minerals in deionised water resulted in the dissolution process that was simultaneously measured with the wetting process during the heat of immersion measurements. The dissolution process was observed as an endothermic response while the wetting process was observed as an exothermic response. The dissolution process occurred in both sulphide and silicate minerals. For the heat of immersion to be useful or applicable in minerals processing, the dissolution has to be suppressed. Methodologies were explored to suppress the dissolution by altering the mineral surface or using alternative wetting liquids. The first dissolution suppression method was using the saturated solution as the wetting liquid, and this was not successful for most minerals used in this study, except for albite and sphalerite. However, it was successfully applied to a range of minerals in the study by Taguta et al. 2018. Therefore, the use of a saturated solution cannot be said to be universally successful in suppressing the dissolution process.

The second approach in suppressing dissolution was the collector coating which successfully covered the surface-active sites of the mineral. Collector coating successfully suppressed dissolution and gave meaningful heat of immersion data about wettability in water. However, a minimum surface coverage of 75% is required for dissolution to be suppressed. Collector coating supresses dissolution at surface coverages beyond those applicable in laboratory scale and even plant scale. Therefore, this is not a viable approach for dissolution suppression. Secondly, collector coating does not allow for the natural hydrophobicity of the mineral to be measured. In addition, collector coating increased the hydrophobicity of the mineral, and this was revealed by the heat of immersion measurements in water where the heat of immersion decreased with an increase in collector surface coverage.

The last approach in the dissolution suppression was using nonpolar liquids, hexane and hexanol, as wetting liquids. These were shown to be viable in suppressing dissolution as there was no endothermic response in the heat of immersion response. For hexane, it was observed that the heat of immersion was more exothermic for hydrophilic minerals and less exothermic for hydrophobic minerals. For hexanol, the heat of immersion was more exothermic for hydrophobic minerals and less exothermic for hydrophilic minerals. Hexane presented an experimental challenge where the heat of immersion experiments were unsuccessful due to the beeswax dissolving in hexane resulting in premature wetting of the mineral by the hexane. Hexanol presented no difficulties in the experimental procedure and can be used in the binary mineral mixture measurements.

6.3 Binary Mineral Mixture Heat of Immersion

A methodology has been developed to measure heat of immersion using solution calorimetry as a wettability parameter for binary mineral mixtures. The methodology involves suppressing the dissolution of the mineral by conducting the heat of immersion measurements in hexanol.

The heat of immersion of the binary mineral mixture in hexanol was observed to increase with an increase in the content of the hydrophobic mineral in the mixture. Secondly, there is a linear relationship between the heat of immersion and the mass composition or surface area fraction of the binary mineral mixture. This linear relationship can be presented in various ways depending on what data is available or desired. When using the surface area to relate the heat of immersion of the binary mineral mixture, the method used to determine the specific surface area has to be evaluated and deviations arising from the method have to be accounted for.

To determine the heat of immersion of the pure minerals making up the mixture, extrapolation can be used as the method. The linear relationship established between the heat of immersion and mass composition, or surface area fraction is used for extrapolation where the heats of immersion of the pure minerals making up the mixture are equated to the intercepts at 0 and 100%. The flotation response of the binary mineral mixture can then be determined using a calibration curve to obtain a flotation rate constant. Being able to predict the flotation response of the binary mineral mixture will assist with predicting the processing of the binary mineral mixture.

7 Recommendations

The preparation of the sample for the heat of immersion measurements needs to be specified thoroughly especially if comparison across various authors is to be made. Factors such as the surface area and the outgassing temperature have an impact on the heat of immersion and therefore, special attention has to be taken in their determination. The minerals to be studied and the wetting liquid have to be carefully selected depending on the purpose and nature of the study.

The method used in determining the surface area of the minerals is crucial as the surface area has significant impact on the heat of immersion. Methods such as gas adsorption isotherms can be used to determine the surface area or the BET method using molecules larger than nitrogen.

For the saturated solution, various factors such as temperature, concentration, and pH need to be taken into consideration when creating the saturated solution. This is because these affect the number of dissolved ions in the solution. The saturated solution can also be created using salts containing the target ions. The heat contribution to the overall heat of immersion due to the surface charge can be considered in depth. Alternatively, water as the wetting liquid can be deoxygenated to avoid oxidation due to the presence of oxygen in water, and the immersion calorimetry measurements can be performed in an N2 atmosphere.

Other hydrocarbon solvents can be tested as wetting liquids in the heat of immersion measurements, varying the chain length, functional groups, or polarity to determine how these affect the heat of immersion. Similarly, different collector types and collector chain length can be tested to determine their effect on dissolution suppression.

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9 Supplementary Results

9.1.1 The Effect of Surface Area on the Heat of Immersion

Figure 9-1 shows the effect of increasing the surface area of the mineral through grinding as referenced in Section 4.3.

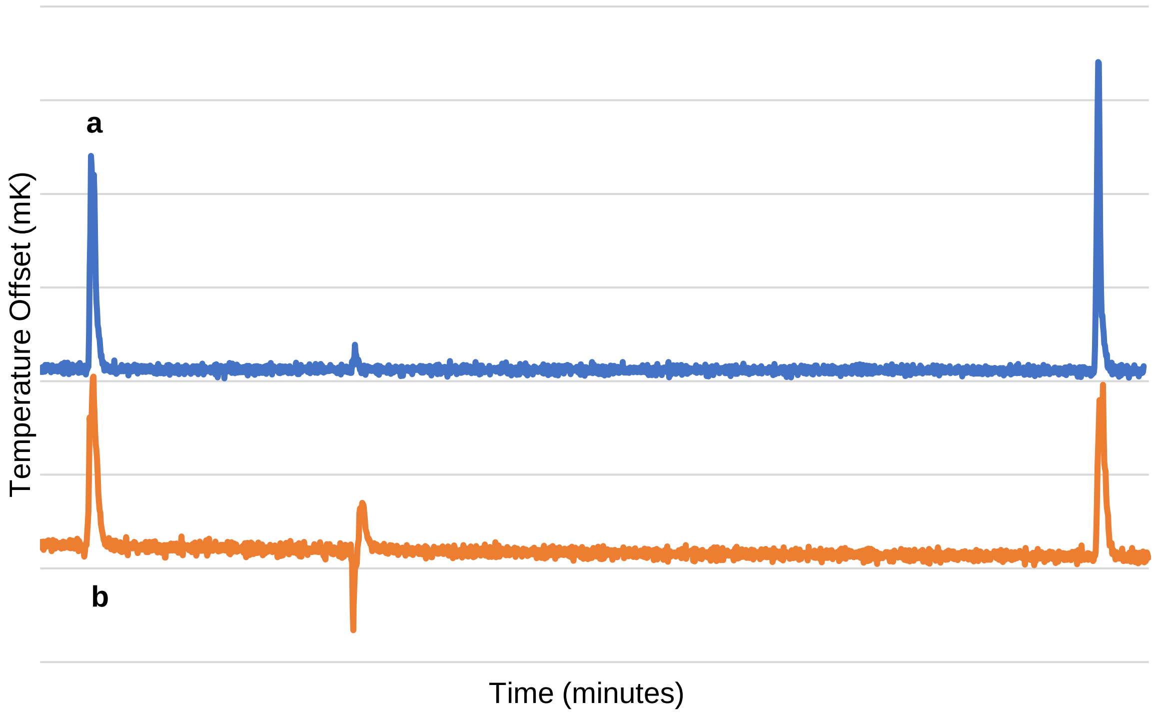

Figure 9-1: a) The heat of immersion of quartz (-25 µm) in saturated solution. b) The heat of immersion of finely grinded quartz (-5 µm) in saturated solution.