

# A study of flotation characteristics of monazite, hematite, and quartz using anionic collectors



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## ABSTRACT

Rare earth element (REE) minerals found in most South Australian ore deposits are in complex association with gangue minerals, typically hematite and quartz. Monazite, a phosphate mineral containing mainly light REEs, is one of the principal minerals found in South Australian REE-bearing deposits. Froth flotation, which exploits the differences in the physicochemical properties of minerals, has proven to be effective in the beneficiation of REE minerals. The physicochemical properties of monazite, hematite, and quartz including zeta potential, contact angle, and floatability were determined in this investigation. Sodium oleate, sodium dodecyl sulphate, and hydroxamic acid were employed as collectors. Electroacoustic zeta potential measurements were used to identify the interaction between monazite, hematite, and quartz and the selected collectors. The capillary rise method was used to determine the contact angle of the three minerals. Single mineral flotation using Denver microflotation cell was carried out to confirm physicochemical properties measured. It is shown that the contact angle of the minerals is dependent on the collector type used. The isoelectric point (IEP) of monazite, hematite, and quartz occurred at pH of 6.5, 6.9, and 2.2, respectively. The zeta potential results also suggest that the collectors chemisorb onto monazite and hematite surfaces with a corresponding change in IEP values. Single mineral flotation results demonstrated that monazite and hematite could be floated by the selected collectors; however, low or no quartz flotation was observed in some cases. Results from electrokinetic and contact angle measurements are consistent with that of the floatability of monazite, hematite, and quartz.

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## 1. Introduction

The growing importance of REE's industrial and medical applications has resulted in greater demand for REE beneficiation and extraction. Bastnasite, monazite, xenotime, and loparite are considered as principal commercial sources of REE minerals. REE generally occur in deposits with other elements (such as copper, gold, uranium, phosphorus, and iron) and compounds as trivalent cations in carbonates, oxides, halides, phosphates, and silicates (Castor and Hedrick, 2006; Lusty and Walters, 2010).

Monazite is a phosphate mineral with the chemical formula [(Ce, La, Nd, Th)PO<sub>4</sub>]. Silica may also be present in monazite, replacing a small percentage of the phosphate groups, but this is not typically shown in its chemical formula. Uranium may also be found in a trace amount in some deposits. Monazite is usually found in igneous and metamorphic rocks such as granite, schist, and gneiss and are able to withstand weathering and end up concentrated in host rocks (Lusty and Walters, 2010). Monazite's REE, cerium (Ce), lanthanum (La), praseodymium

(Pr), and neodymium (Nd), are major constituents of many high-tech (eg. phosphors, glasses, lasers, magnets, and optics) and green energy sector products.

### 1.1. Froth flotation

Froth flotation is a multipurpose and versatile method of separating minerals by exploiting the differences in their physicochemical properties. Froth flotation has been vital for the beneficiation of low-grade and complex ores, which were otherwise classified as uneconomical to mine and process (Wills and Napier-Munn, 2006). Mineral particles may range between hydrophilic and hydrophobic in surface characteristics. The aid of surface modifying reagent molecules (typically, collectors) is imperative in controlling the relative hydrophobicity and maintaining proper froth flotation selectivity between mineral particles of different phases (Bulatovic, 2007). Collectors may adsorb either by physical forces (physisorption) or chemical bonding (chemisorption) and require a molecular structure having a polar head group and a non-polar hydrocarbon chain (Bulatovic, 2007). Zeta potential measurement is a key technique employed in studying the adsorption mechanism of collectors on mineral surfaces (Jordens et al., 2013, 2014a).

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## 1.2. Monazite flotation

Flotation of monazite has been reported extensively in the literature (Chelgani et al., 2015; Jordens et al., 2013). Sodium oleate and hydroxamic acid have been the most common and important collectors for monazite flotation. Other collectors that have been investigated include sodium dodecyl sulphate, sodium dodecyl amine, and citric acid (Abeidu, 1972; Zhou and Luo, 1989).

Hydroxamic acid is typically noted to adsorb chemically onto monazite surface, forming very stable complexes with rare earth (RE) cations (Bogdanov, 1977; Pavez et al., 1996). Pavez et al. (1996) reported that sodium oleate adsorbs physically onto monazite surfaces below its IEP. Chemisorption of sodium oleate onto monazite surface above IEP values was reported, as determined via infrared spectroscopy measurements. Furthermore, it was concluded that potassium octyl-hydroxamate chemisorbs onto monazite surface above the IEP and flotation recovery was pH-dependant (Pavez et al., 1996).

Cheng et al. (1993), in a comparative study of the flotation characteristics of monazite and xenotime, suggested that maximum floatability of both minerals occurs above pH 7, with that of monazite at pH 8.5–9.0. Experimental evidence presented in this investigation showed that sodium oleate was chemisorbed onto the monazite surface. High monazite recovery (~80%) in the pH range 5–10 also suggested that sodium oleate is chemisorbed onto the monazite surface. Poor monazite recoveries were expected at high pH values, on the assumption that sodium oleate is physically adsorbed onto monazite, but the opposite was realised hence, it was concluded that sodium oleate chemisorbs onto monazite surface (Cheng et al., 1993).

Xia et al. (2014) reported on the microflotation of REE minerals using salicylic, benzoyl, and naphthoyl hydroxamates as alternative collectors for alkyl phosphates and phosphoric acid ester. Experimental results showed that salicylic hydroxamate produced the highest grade of light REE (LREE). A similar recovery response was observed for both salicylic and naphthoyl hydroxamate, having affinity for LREE over heavy REE (HREE). It was also reported that elevated temperature promotes recovery of REE minerals.

### 1.2.1. Zeta potential

A major step in defining the physical chemistry of flotation system involves the reconciliation of the concepts of the electrical double layer and electrokinetic potentials. These concepts can be used in the elucidation of flotation phenomena in terms of collector adsorption mechanism on particle surfaces and particle-bubble interactions. Zeta potential measurements are used in determining the surface potential of a mineral under specified pH conditions. IEP is the pH at which the zeta potential of a mineral's surface is zero. Published data on the electrokinetic properties of monazite such as IEP, and electrokinetic potential vary markedly and are dependent on the sample origin, type of electrolyte background and the procedure employed (Chelgani et al., 2015; Jordens et al., 2013). A wide range of IEP values for monazite minerals have been reported in literature, as summarised in Table 1.

Collector adsorption is described as physisorption when there is essentially no adsorption at, or shift of, the IEP of the mineral. Physisorption may also be observed as simple ion exchange in the electrical double layer at the collector-mineral particle interface. Chemisorption, on the other hand, is characterised by adsorption at IEP and

a shift in the IEP value (Han et al., 1973). Abeidu (1972) reported that the IEP of monazite occurs at pH 5.5. It was demonstrated that sodium dodecyl sulphate displaced the IEP of monazite from pH 5.5 to 3.8. Similarly, it was reported that oleic acid displaced the IEP value to 4.5. Zeta potential curve of monazite as a function of pH, in the absence of collectors, were presented by Pavez et al. (1996), and showed the IEP occurring at pH 5.2. The presence of collectors, sodium oleate, and hydroxamate displaced the IEP of monazite to pH 3 and 4, respectively. The changes in the IEP values were attributed to chemisorption of the collectors onto the surface of the monazite samples.

### 1.2.2. Contact angle

The surface wettability of a particle is important, especially when considering the floatability of a mineral of interest and recovery from associated gangue mineral(s). In a flotation system, the interface where the mineral particle, water, and bubble co-exists is referred to as the three phase contact line. The intersection of the water-mineral particle interface and the water-bubble interface yields the contact angle, which defines the wettability of a mineral and its changes. In flotation, particles with contact angles  $<60^\circ$  may be classified as hydrophilic and may need the aid of a collector to be separated by flotation (Feurstenau and Somasundaran, 2003; Wills and Napier-Munn, 2006; Yuan and Lee, 2013).

Contact angle is determined by a combination of surface tension and external forces (typically gravity). External forces generally deform the shape of droplets of liquids. On the other hand, surface tension is the intermolecular force which contracts the surface of liquids (Yuan and Lee, 2013). The contact angle of a pulped mineral system is defined by the mechanical equilibrium between the interfacial surface tensions established as shown in Fig. 1.

The equilibrium setup at the three phase contact line is given by Young's equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \quad (1)$$

where  $\gamma_{SG}$ ,  $\gamma_{SL}$  and  $\gamma_{LG}$  are solid-gas, solid-liquid, and liquid-gas interfacial tensions, respectively, and  $\theta$  is the contact angle.

Yuan and Lee (2013) classified most of the techniques used in measuring contact angle into two types, the direct optical method and the indirect force method. Readers interested in learning more about contact angle and its measurement techniques should consult the following publications (Decker et al., 1999; Huang et al., 2010; Krishnan et al., 2005; Kwok and Neumann, 1999; Pyter et al., 1982; Shang et al., 2008; Siebold et al., 2000; Snoeijer and Andreotti, 2008; Teipel and Mikonsaari, 2004; Yuan and Lee, 2013).

The Washburn capillary rise (WCR) technique has been widely utilized for determining contact angles and surface free energy of powders or porous materials. In this method, powders or granules of a mineral sample are compacted into powder cakes, to which drops of liquid are applied and the contact angles measured by means of capillary penetration (Liao and Zatz, 1979; Steiner and Adam, 1984; Yuan and Lee, 2013). Results obtained from this technique may be influenced by surface roughness, porosity, and particle swelling. In this method, the rate at

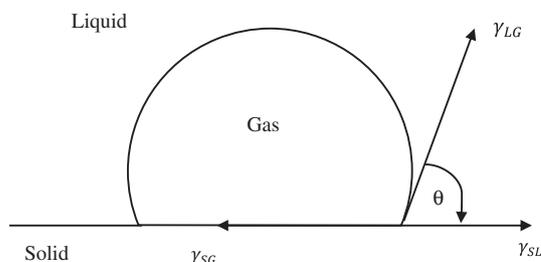


Fig. 1. Schematic representation of the equilibrium contact between an air bubble and solid immersed in liquid (Feurstenau and Somasundaran, 2003).

Table 1  
Summary of selected reported IEP values for monazite.

IEP	Reference
1.1–3.2	Houot et al. (1991)
3.4	Houot et al. (1991)
5.3	Cheng et al. (1993)
5.5	Abeidu (1972)
6.1	Houot et al. (1991)
9.0	Houot et al. (1991)

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