

Monazite and Kaolinite Flotation Using Sodium Oleate as a Collector

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Abstract

Recently, the flotation of major rare earth elements (REE) minerals including bastnasite, monazite, and xenotime has been attracting high level of attention. Anionic collectors such as oleates and hydroxamates have been widely used in the flotation of valuable REE minerals. One of the key gangue minerals in REE deposits is kaolinite. Although there has already been previous research investigating kaolinite flotation from bauxite, there is limited data in the literature focused on flotation of REE minerals from kaolinite rich deposits. Since minerals in different ores may demonstrate differing flotation response, it is imperative to investigate their respective flotation behaviours. This work presents a fundamental study involving zeta potential and microflotation experiments with pure samples of monazite and kaolinite using sodium oleate as a collector. In this study, the floatability of monazite is high at pH 5–9, where kaolinite had comparatively lower flotation response. Complementary zeta potential measurements confirmed that sodium oleate interacts with REE ions on monazite surface resulting in the excellent flotation response, whereas minimal interaction was observed for kaolinite, hence the poor performance.

Keywords: monazite, flotation, kaolinite, sodium oleate, zeta potential

1 Introduction

Rare earth elements (REE) have been growing in importance due to their pivotal role in technological and industrial applications in the 21st century global economy. There is a Japanese metaphor which says "...rare earths are the vitamins of a modern economy". This group of elements are also often referred to as "seeds of technology". Elsewhere they have been tagged as the engines of electrification. There are no easy substitutes for REE in most of their applications, which has contributed to their increased global demand (Abaka-Wood *et al.*, 2016; Abaka-Wood *et al.*, 2021; Binnemans *et al.*, 2013; Charalampides *et al.*, 2015; Dushyantha *et al.*, 2020; Jordens *et al.*, 2013; Klinger, 2018).

This group of elements are a major constituent of many advanced materials, especially in the high-

tech and green energy sectors where robust performance, durability and low carbon emissions are so important. They find their applications in the manufacture of batteries of hybrid and electric cars, the screens of smart phones, computers, and flat panel televisions. For example, in the petroleum industry, lanthanum-based catalysts are employed in refinery processes. Cerium is largely used for polishing glass, jewels, silicon chips, television screens, and monitors. Also, large wind turbines use generators that contain strong permanent magnets composed of neodymium. The applications of REE are numerous and this has been well documented, and the reader is referred to a number of classic references and reviews (Balaram, 2019; Binnemans *et al.*, 2015; Charalampides *et al.*, 2015; Jordens *et al.*, 2013; Krishnamurthy and Gupta, 2015)

1.1 Flotation of monazite

Bastnasite and monazite are considered as the most important sources of REE because they contain significant amount of critical light REE such neodymium which is used in the manufacture of permanent magnets. In recovering and upgrading these important REE minerals from differing ores, froth flotation, which exploits the differences in the physicochemical properties of REE and gangue minerals, has been instrumental (Abaka-Wood *et al.*, 2018; Abaka-Wood *et al.*, 2019; Anderson *et al.*, 2016; Boulanger *et al.*, 2019; Keller, 2020; Marion *et al.*, 2020; Sarvaramini *et al.*, 2016; Shetty *et al.*, 2020).

The type of collector used in flotation process plays a crucial role in producing selective REE minerals recovery from differing gangue minerals. Fatty acids and hydroxamates have been identified as key collectors in the flotation of most REE minerals (Abaka-Wood *et al.*, 2018; Chelgani *et al.*, 2015; Espiritu *et al.*, 2018; Liu *et al.*, 2019; Yu *et al.*, 2020). It is worth mentioning that hydroxamate collectors are strongly chemisorbed onto REE minerals thus promoting high recoveries. However, some significant limitations persist, typically poor selectivity and high consumption rate (Abaka-Wood *et al.*, 2022).

Flotation of monazite has been well-studied and widely published in the literature. However, it is also important to study the flotation response of key gangue minerals in different ores hosting monazite. Particularly, studies comparing the relative response of monazite and gangue minerals are desirable as these aid in understanding the mineral-collector interactions at different pulp conditions (Abaka-Wood *et al.*, 2018; Chelgani *et al.*, 2015; Fan *et al.*, 2021; Jordens *et al.*, 2013; Karataşa *et al.*, 2017).

As part of an ongoing investigation to assess the technical feasibility of recovering REE minerals in a complex low grade saprolite ore, a series of model minerals studies were carried out to compare the flotation response of monazite, a key REE mineral, and kaolinite, a dominant gangue mineral in the saprolite ore. Specifically, the electrokinetic characteristics of monazite and kaolinite were studied in tandem with their flotation response as a function of pulp pH. The results of this research work are of practical significance for understanding

the flotation response of monazite and kaolinite in the saprolite ores.

2 Materials and Methods Used

2.1 Materials

Pure monazite was employed as a model REE mineral and kaolinite was used as a model gangue mineral. The particle size distribution of the model minerals has been shown in Figure 1. In this study ultrafine kaolinite was selected as preliminary characterization study has suggested that up to 85% of the kaolinite gangue mineral report within the slime fraction ($< 10\mu\text{m}$) of the ore, with the REE minerals mainly found within the $10\text{-}53\mu\text{m}$ size range. Table 1 shows the chemical composition of monazite and kaolinite model minerals obtained via Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results show that the total REE (TREE) content is 44.14%, with significantly low impurity elements (Al, Ca, Fe, and Si). As expected, the kaolinite mineral contained mainly Si and Al, with no REE content.

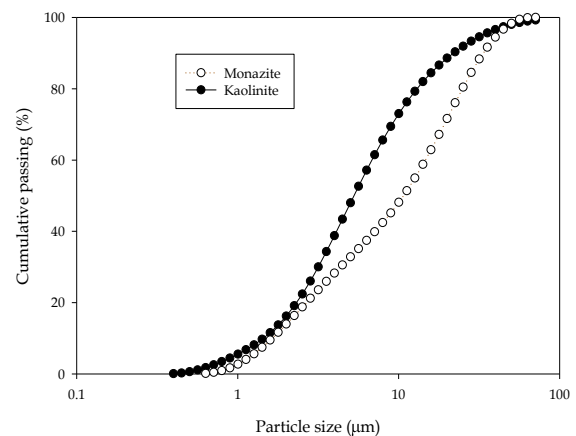


Fig. 1. Particle size distribution of monazite and kaolinite model minerals.

Sodium oleate (Sun Ace, Australia) was used as collector in all zeta potential and microflotation experiments. Dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust pH of the respective feed pulp. Adelaide (Australia) tap water was used for all the experiments.

Table 1. Chemical composition and particle characteristics of monazite and kaolinite mineral samples.

Chemical species	Monazite	Kaolinite
La (%)	9.66	<0.001
Ce (%)	19.6	<0.001
Pr (%)	2.38	<0.001
Nd (%)	8.94	<0.001
Y (%)	0.82	<0.001
Other REE (%)	2.74	<0.001
Total REE = TREE (%)	44.14	<0.001
Al (%)	<0.01	19.3
Ca (%)	<0.001	1.78
Fe (%)	0.62	0.82
Si (%)	0.12	24.1
P ₁₀	1.6	1.5
P ₅₀	10.7	5.7
P ₈₀	33.5	25.5

2.2 Methodology

2.2.1 Microflotation

Microflotation experiments were carried out in IMN Polish flotation cell using 10 g of the respective model minerals mixed with 250 mL tap water. The pulp pH was adjusted by HCl or NaOH for 5 min. Subsequently, sodium oleate was added and agitated for 5 min. Pulp agitation and air flow rates were maintained at 720 rpm and 1 L/min, respectively in both the conditioning and flotation stages. Flotation was conducted for 10 min, where concentrates were recovered at cumulative times of 1, 3, 6, and 10 min. The flotation products were weighed after drying and the recoveries were calculated.

2.2.2 Zeta Potential

Zeta potential measurements were carried out using a Malvern Zetasizer Nano Series. In this test, about 0.5 g <38 μm mineral sample was dispersed in 1×10^{-3} M KNO_3 and mixed for about 10 min on a magnetic stirrer, after which, the supernatant of the mixture was obtained for zeta potential measurements. The zeta potential was measured thrice, the average value was reported, and relative error estimated at 95% confidence level.

3 Results and Discussions

3.1 Single Minerals Flotation

Fig. 2 shows the flotation recoveries for monazite and kaolinite as a function of pulp pH in the

presence of sodium oleate. It can be seen from Fig. 2 that the flotation recovery of monazite increased with pH and reached maximum value around pH 9, where about 74% recovery was obtained. A further increase in pulp pH to 11 saw a sharp decrease in recovery to 27%.

The results in Fig. 2 clearly show that the flotation recovery of kaolinite was very low across the entire pH range tested. However, the kaolinite floatability increased slightly with increase in pulp pH where maximum recovery of 15% was obtained at pH 11. From the results, the best selectivity was observed at pH 9 where the difference in recoveries was highest and was selected for subsequent mixed minerals separation test.

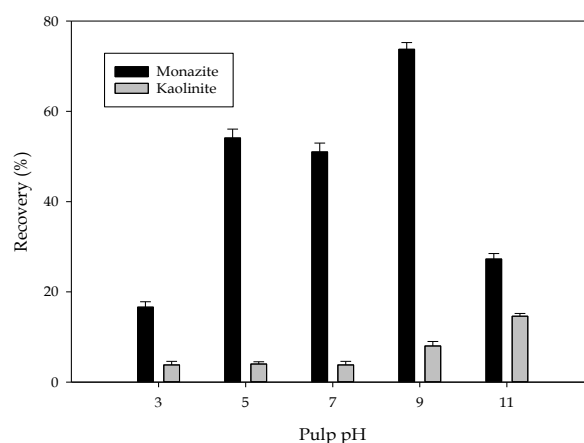


Figure 2. Flotation recoveries of monazite and kaolinite as a function of pulp pH [sodium oleate dosage = 1000 g/t].

3.2 Binary Minerals Flotation

Since minerals are expected to be mixed in an ore, flotation of monazite and kaolinite mixture (1:9 ratio) was carried out at pH 9 using 1000 g/t sodium oleate and the results have been shown in Table 2. As shown in Table 2, 68% TREE was recovered at a 7.95% concentrate grade along with 40% Al and 37% Si (kaolinite metal species). The results in Table 2 suggested that separation of monazite from kaolinite can be achieved when using sodium oleate as a collector.

Table 2. Flotation results of mixed monazite and kaolinite using 1000 g/t sodium oleate

Product	TREE		Si Rec. (%)	Al Rec. (%)
	Grade (%)	Rec. (%)		
Conc.	7.95	68	37	40
Tail	3.15	32	63	60
Feed	4.42	100	100	100

Ideally, kaolinite was not expected to report into the flotation concentrate when considering results from the single minerals flotation tests. The “high” kaolinite recovery could be attributed to entrainment. From the particle size distribution data, the kaolinite mineral has $P_{50} = 5.7 \mu\text{m}$, which makes it prone to recovery via entrainment. It has been reported in the literature that gangue mineral particles finer than $50 \mu\text{m}$ are easily recovered by entrainment (Wang *et al.*, 2020; Wang and Liu, 2021). This is exacerbated by dissolved Fe and REE ion species, which have been shown to activate silicate minerals thus promoting their recoveries (Fuerstenau and Somasundaran, 2003).

3.3 Zeta Potential Measurements

Fig. 3 and 4 show the zeta potential of monazite and kaolinite as a function of pH in the absence and presence of 1000 g/t sodium oleate. The isoelectric point (IEP) of monazite occurred at approximately pH 6.5, similar to the result presented by Zhang and Honaker (2017), Geneyton *et al.* (2019), and Cao *et al.* (2022). In the presence of sodium oleate, there was a significant change in the zeta potential of monazite which is demonstrated by the increased negative charge at all the pH tested. From Fig. 3, monazite was positively charged at $\text{pH} < 6.5$, but changed dramatically when sodium oleate was introduced resulting in monazite surface remaining negatively charged at all the pH conditions, thus resulting in no IEP value. These observations could be caused by sodium oleate being adsorbed onto the monazite surface.

On the other hand, there was statistically marginal or no interaction between kaolinite and sodium oleate at $\text{pH} \leq 5$. However, the surface charge of kaolinite became comparatively “more” negative when contacted with sodium oleate at $\text{pH} > 6$, with identical changes in zeta potential values. Overall, the somewhat benign increase in negative surface charge of kaolinite could be an indication of

surface activation by low but important cation species including Fe^{3+} , Ca^{2+} , and Al^{3+} .

Notably, monazite and kaolinite floatabilities correlate with the changes in zeta potential, and IEP. For example, kaolinite displayed poor floatability in the presence of sodium oleate in the single minerals flotation tests, which is confirmed by the marginal changes in zeta potential when contacted with sodium oleate. The significant changes in zeta potential of monazite in the presence sodium oleate is consistent with the high flotation recoveries obtained in the flotation tests.

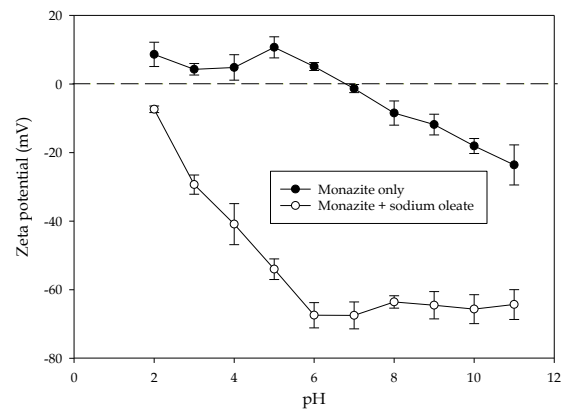


Fig. 3. Effect of sodium oleate dosage on the zeta potential of monazite as a function of pH.

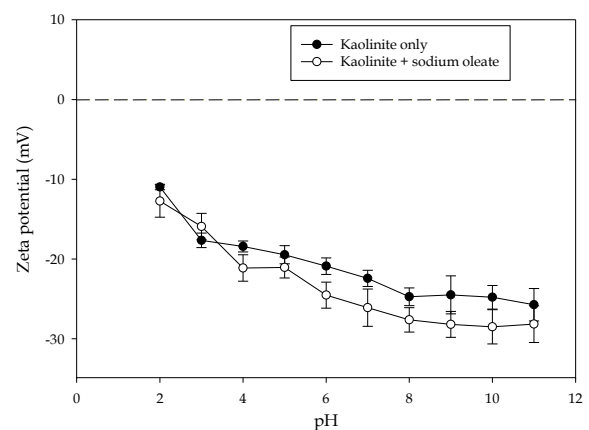


Fig. 4. Effect of sodium oleate dosage on the zeta potential of kaolinite as a function of pH.

4 Conclusions

The results of microflotation experiments using sodium oleate as a collector indicate that monazite exhibits good floatability around pH 5–9. On the other hand, kaolinite demonstrated significantly low floatabilities ($< 20\%$) across the whole pH range used in the experiments. This has

demonstrated potential conditions for monazite and kaolinite separation. When monazite was mixed with kaolinite, recovery of kaolinite was enhanced via entrainment and surface activation of by soluble cations.

The changes in zeta potential of monazite, can be attributed to the adsorption of oleate anions, which appears to selectively interact with the monazite surface than kaolinite surface. Overall, the electrokinetic measurements corroborate with the flotation behaviour of monazite and kaolinite, which confirms the importance of zeta potential measurements in the elucidation of flotation phenomena in terms of collector adsorption mechanism on mineral particle surfaces.

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