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A study of selective flotation recovery of rare earth oxides from hematite and quartz using hydroxamic acid as a collector

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ABSTRACT

Monazite is a major rare earth elements (REE)-bearing phosphate mineral predominantly found in association with hematite and quartz in some Australian rare earth deposits. The flotation of rare earth oxides (REO) in monazite from mixtures containing monazite, hematite, and quartz with hydroxamic acid as a collector has been investigated using an IMN microflotation cell and a 1.2 L Denver flotation cell. Maximum flotation recovery of both monazite and hematite was attained at pH 7, whereas that of quartz, at pH 3. The flotation kinetics data indicated the need for depressants to achieve selective REO recovery from hematite and quartz mixtures. Sodium silicate and starch were thus tested as depressants of both hematite and quartz. The separation efficiency of REO in the absence of depressants was low and averaged 6.42% at 99% REO recovery, but could be increased to 44.78% with corresponding 93% REO recovery when 4000 g/t starch was used. However, the efficiencies of REO separation obtained with sodium silicate were generally lower (<18%), due to higher gangue minerals content in the flotation concentrates. A blend of sodium silicate and starch showed a good performance for REO recovery, with enhanced selectivity against hematite and quartz through a rougher-cleaner flotation test. This study presents the feasibility of upgrading REO from iron-oxide rich tailings using hydroxamic acid, in the presence of sodium silicate and starch as depressants.

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1. Introduction

Recent literature have estimated the total rare earth oxides (REO) production worldwide averages 110 Mt, with not less than 80% of production from China [1–4]. Abaka-Wood et al. [3], Jordens et al. [5], Krishnamurthy and Gupta [6], and Zhang and Edwards [7] have reviewed froth flotation as a key beneficiation technique for rare earth elements (REE)-bearing minerals. This technique which exploits the differences in surface wettability of mineral particles has proven to be efficient and economical for REE deposits which were otherwise proven to be uneconomical to treat [3,8]. REE minerals are naturally hydrophilic thus require the use of collectors to aid in flotation recovery [3,5,9,10].

The versatility of froth flotation has paved way for many researchers to study the dynamics of flotation in terms of mineral particle size distribution, froth stability, pulp chemistry, and collector-mineral surface interactions. Flotation rate test measures flotation performance in terms of mass pull, recovery, and concentrate grade. The variation in recovery of mineral particles over time

is characterised as the flotation kinetics of the mineral [11,12]. The results obtained are used to describe the flotation performance of a mineral under flotation conditions at a time. Typically, flotation duration, the degree of mineral surface-collector interaction, pulp pH, collector type and dosage, and mineral species affect the flotation rate of the mineral [11,12]. Flotation duration is key in evaluating flotation performance, for example, lengthy flotation duration results in loss of mineral of interest to froth breakage, thus reducing selectivity of the operation [11]. The rate of flotation of mineral particles is characterised by chemical analogy where hydrophobic particles interact with bubbles to form mineralised froths. Methods for determining the flotation kinetics of minerals have been presented by Bulatovic [12]. The flotation recovery of mineral particles is generally described as a first order reaction with respect to mineral particle concentration, at constant froth concentration [13,14]. In a flotation cell, where all the operational parameters remain constant, the first order reaction of flotation model can be expressed as [12–14];

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

where $R(t)$ and R_{max} are the recovery at time t and maximum recovery, respectively, and k is the distributed rate constant. The

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distributed rate constant is defined as the rate constant of a single floatable mineral species [12–14]. However, a modified flotation rate constant called undistributed rate constant which considers both maximum recovery (R_{max}) and distributed rate constant has been proposed [13,15,16]. The undistributed rate constant, k^* is calculated using the expression [13–16];

$$k^* = \frac{kR_{max}}{100} \quad (2)$$

The undistributed rate constant was proposed to overcome the difficulties in comparing k and R_{max} values during flotation experiments, which have been discussed in the literature by Sriprya et al. [16]. Flotation rate as presented in this investigation represents the undistributed/modified rate constant (k^*).

Selectivity index which shows whether the selectivity of the valuable mineral over the gangue minerals remains unchanged, increased or decreased when flotation conditions are varied may be calculated based on the undistributed rate constant and is expressed as [16,17];

$$SI(A/B) = \frac{k^* \text{ of mineral A}}{k^* \text{ of mineral B}} \quad (3)$$

where, $SI(A/B)$ is the selectivity index of mineral A over B during flotation.

1.1. Flotation of REO using hydroxamates

Hydroxamates are N-alkyl derivatives of hydroxyl amine, which have a wide range of applications in the flotation of REE minerals [3,18–23], and other minerals such as malachite, ilmenite, cassiterite, and pyrochlore [12,18]. Though considered as a chelating agent, hydroxamates are used for floating REE minerals, because of high selectivity for REE ions in mild alkaline medium [12,20,24]. However, similar flotation response of gangue minerals in comparison with REE minerals necessitates the use of depressants to aid in selective flotation separation. For example, hydroxamates are known to form strong complexes with iron and niobium ions [18], hence depressants are required when such gangue metals/minerals are present.

A review of the literature [5–7,19,22,23,25–30] has revealed a knowledge gap on the flotation recovery of REO in monazite using hydroxamates, where hematite and quartz (in association) are the major gangue minerals. Most of the published works have REE minerals (bastnasite, monazite, florencite, and xenotime) being separated from heavy mineral sands (such as ilmenite, rutile, zircon), calcite, barite, dolomite, albite, K-feldspars, and quartz (see Table 1).

The flotation characteristics of monazite, zircon, and rutile were investigated by Pavez and Peres [31] with sodium oleate, a commercial hydroxamate, and a pure hydroxamate as collectors in a modified Hallimond tube. Sodium metasilicate and sodium sulphide were used as depressants for zircon and rutile. The best condition for selective recovery of monazite was achieved with either

oleate or commercial hydroxamate at pH 10, where depression of zircon and rutile was enhanced.

Espiritu and Waters [25] also studied the flotation response of monazite and dolomite using organic phosphoric acid (Flotator 1682), sodium oleate, and benzohydroxamic acid as collectors. Results presented by Espiritu and Waters [25] suggested that direct flotation of monazite from dolomite was achievable at pH 7 using benzohydroxamic acid, whereas reverse flotation was feasible at pH 4 using sodium oleate and with Flotator 1682, at pH 4 and 7. The importance of depressant usage for a more effective separation was suggested.

Numerous investigations have been conducted on the Nechalacho Project Thor Lake deposit (Canada) for which different forms of hydroxamates have been tested [19,22,29]. Mineralogical data on Nechalacho rare earth deposit presented by Jordens et al. [19] indicated allanite, bastnasite, columbite (Fe), fergusonite, monazite, synchysite, and zircon as the REE minerals, with quartz (11.82%), plagioclase (14.15%), K-feldspar (10.22%), and Fe-oxides (10.16%) being the gangue phases present. Jordens et al. [19] studied the flotation response of Nechalacho rare earth deposit using benzohydroxamic acid as a collector. Flotation kinetics results revealed that bastnasite was the fastest floating REE mineral, whilst zircon and allanite were the slowest. There was a notable increase in the recovery of the less floatable REE minerals (zircon and allanite) with a corresponding increase in the recovery of silicate gangue minerals when lead ions were added as an activator.

Xia et al. [22] also investigated the use of hydroxamates to simplify and improve flotation recoveries of REE minerals from Nechalacho REE deposit, which initially employed the use of alkyl phosphates and phosphoric acid ester as collectors to concentrate REE minerals. Microflotation of REE minerals using three forms of hydroxamates namely; salicylic, benzoyl, and naphthoyl was carried out. The results showed that de-sliming of flotation feed had negligible impact on flotation recovery of REE minerals, with higher recovery of light REE-bearing minerals from slime fraction relative to heavy REE minerals. Xia et al. [22] concluded that salicylic hydroxamate was more effective for recovery of light REE minerals, whilst benzoyl hydroxamate appeared to be more effective for heavy REE minerals. Hart et al. [29] also carried out a microflotation and surface chemistry study of REE minerals in the Nechalacho REE deposit using hydroxamates (naphthoyl, cyclohexyl, benzoyl, octyl, tetra-butyl benzoyl, and, salicylic) and citric acid. Octyl hydroxamate was identified as the best hydroxamate for REE minerals recovery.

Yang et al. [27] studied the beneficiation of REE minerals from a complex ore which had quartz (33.34%), albite (27.37%), and K-feldspar (26.61%) as the major gangue minerals, whereas hematite (0.72%) and other oxides were identified as the minor gangue minerals present. Sodium oleate was found to yield better REO upgrade and recovery in comparison with hydroxamic acid.

Previous investigations and the literature [3,5,7,19,22,29] present promising results and opportunities to study and exploit hydroxamates as collectors for differing REE-bearing minerals, paying attention to the gangue minerals in the ores, as well as the economics of the flowsheets to be developed. The challenges associated with flotation of REO are predominantly defined by the ore type being processed. Of interest to the present investigation is improving the selectivity of REO flotation over hematite and quartz using hydroxamic acid as a collector, in the presence of two conventional depressants; sodium silicate and starch.

This investigation is one of numerous model minerals studies aimed at identifying suitable processing methods to recover and upgrade REO from iron oxide-rich tailings from selected Australian mining operations, in which hematite and quartz are the main gangue minerals. This paper, through a comparative study, seeks to investigate the flotation kinetics and selectivity of monazite,

Table 1
Summary of major gangue minerals in flotation of monazite using hydroxamates.

Reference	Gangue minerals
Pavez and Peres [31]	Zircon and rutile
Liping [30]	Barite and fluorite
Pavez et al. [26]	Silicate and oxides
Jordens et al. [19], Xia et al. [22]	Quartz, plagioclase, K-feldspar, Fe-oxides (Nechalacho ore)
Nduwa-Mushidi and Anderson [32]	Apatite, ilmenite, quartz, rutile and zircon
Espiritu and Waters [25]	Dolomite

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