Towards the efficient flotation of monazite from silicate-rich tailings with fatty acids collectors using a lanthanum salt as a selective phosphate activator

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Towards the efficient flotation of monazite from silicate-rich tailings with fatty acids collectors using a lanthanum salt as a selective phosphate activator

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Highlights:

- The effect of $LaCl_3$ on the monazite flotation with a fatty acid was investigated.
- Sequential addition of $LaCl_3$ and sodium oleate improved the flotation performance.
- At low dosages (0.1-1 g t^{-1}), $LaCl_3$ selectively enhanced the floatability of phosphate minerals.
- At higher dosages, $LaCl_3$ also increased the floatability of Ti and Al-rich minerals.

Abbreviations: BSE: backscattered electron; EDX: energy disperse X-ray; HREE: heavy rare-earth elements; ICP-AES: inductively coupled plasma atomic emission spectroscopy; ICP-MS: inductively coupled plasma mass spectrometry; LREE: light rare-earth elements; MIBC: methyl isobutyl carbinol; MLA: mineral liberation analysis; REE: rare-earth elements; REM: rare-earth mineral; SEM: scanning electron microscope.

Abstract

The exploitation of massive rare-earth element (REE) deposits is frequently contested because of the pollution generated by the heavy mining operations and REE extractive metallurgy operations. In an effort to minimise the environmental footprint of the REE production and meet the increasing demand for these elements, mine wastes and extractive metallurgy tailings are attracting attention as alternative primary sources. However, these residues frequently contain small amounts of monazite [(Ce,La,Nd)PO_4] in silicate-rich gangues, rendering the efficient and selective recovery via current flotation routes difficult. Herein, we investigated the use of $LaCl_3$ as an activator to promote the selective adsorption of fatty acid collectors on the surface of phosphate minerals, thus improving the monazite flotation performance. Bench-scale flotation tests were performed on a low monazite-grade, silicate-rich residue and revealed that a low $LaCl_3$ dosage (about 1 g t^{-1}) selectively enhanced the floatability of monazite and gangue phosphate minerals. We found that the influence of $LaCl_3$ on the monazite flotation performance depends on the $LaCl_3$ dosage, collector dosage, and method of addition of these reagents to the pulp. The mineral composition of the flotation products was determined by mineral liberation analysis (MLA), which indicated that higher concentrations of lanthanum ions promote the adsorption of the collector on rutile and aluminium-rich minerals, thus reducing the selectivity of the monazite flotation separation. This study is a stepping stone towards the development of a new practice of monazite flotation with environmentally friendly collectors and may render low REE-grade residues a commodity.

Keywords: Rare earths, Monazite, Flotation, Phosphate mineral, Lanthanum chloride, Carboxylate collector.

1. Introduction

The transition to renewable energy sources and the development of electric vehicles prompted a significant growth in the demand for light rare-earth elements (LREEs). Currently, their production largely relies on the exploitation of a few massive carbonatite-related deposits in which bastnaesite [(Ce,La,Nd)CO_3F], the main rare-earth mineral (REM), and monazite [(Ce,La,Nd)PO_4] are associated with other semi-soluble salts such as calcite ($CaCO_3$), fluorite (CaF_2), and barite ($BaSO_4$). In recent years, the LREE production from monazite-dominated primary deposits significantly increased with the rise in the production capacity of the Mount Weld carbonatite laterite deposit operations in Australia. As the current LREE production is dominated by the exploitation of these two types of giant deposits which are not evenly distributed around the globe, the supply chain risk for importing countries (Keilhacker and Minner, 2017) and the environmental impact of the required mining and extractive metallurgy operations (Tian et al., 2018b; Wang et al., 2018, 2016) are frequently debated.

Over the last years, numerous alternative REE sources such as urban mining (Binnemans et al., 2013; Jowitt et al., 2018; Omodara et al., 2019; Tunsu et al., 2015), phosphate fertiliser production residues (Binnemans et al., 2015; Cánovas et al., 2019; Rychkov et al., 2018) and coal-related materials (Zhang et al., 2020) have been explored in order to minimise both the risk of LREE supply shortage and the environmental footprint of their production. Recent studies also examined the extraction of REM from mine wastes and extractive metallurgy tailings (Abaka-Wood et al., 2018b; Dehaine et al., 2019; Jyothi et al., 2020; Peelman et al., 2016; Tunsu et al., 2019). Many of these studies reported the presence of monazite as main REM but, apart from certain tailings of heavy mineral sand exploitations that contains from a few percent to a few dozen percent of monazite (Szamałek et al., 2013; Tranvik et al., 2017), its concentration is generally only between a few hundred ppm and several thousand ppm, this mineral being

frequently associated with silicate-rich gangues (Filippov et al., 2016; Purwadi et al., 2020; Tunsu et al., 2019).

In the case of these low monazite-grade, silicate-rich tailings, there is an economic interest in concentrating monazite before REEs are extracted in a hydrometallurgical plant. However, poor monazite flotation performance is reported, due probably to both the low monazite content in these specific tailings and the limited selectivity of collectors towards REM. The flotation separation of semi-soluble REE salt minerals such as bastnaesite, monazite, and xenotime (YPO_4) is generally achieved with carboxylates or hydroxamates, which are the deprotonated forms of carboxylic acids (e.g., fatty acids) and hydroxamic acids (Chelgani et al., 2015; Houot et al., 1991; Jordens et al., 2013; Marion et al., 2020). In past decades, REM flotation techniques have been developed and optimised for high-grade carbonatite deposits. In contrast to certain other minerals, such as calcium bearing minerals (Filippov et al., 2018; Foucaud et al., 2019; Wang et al., 2020), the development of new reagents to improve the REM selectivity of carboxylate and hydroxamate collectors has been rarely addressed. As mine wastes and extractive metallurgy tailings have generally lower REE content and feature more exotic mineral associations than primary REE ores, their exploitation by the current flotation methods seems economically non-sustainable. Therefore, it is crucial to develop new practices for monazite flotation, particularly from silicate-rich gangues, to transform these residues into commodities.

Based on bench scale flotation tests with samples from Mountain pass, a major rare-earth deposit in a carbonatitic context, Fuerstenau et al. (1982) and Pradip and Fuerstenau (1991) concluded that fatty acids are poorly selective towards rare earth minerals compared with alkyl hydroxamate collectors. The findings of these case studies have largely been taken-up by several authors and a significant part of the emerging fundamental and applied REM flotation studies involve hydroxamate collectors (Abaka-Wood et al., 2018a; Cui and Anderson, 2017; Cui et al.,

2012; Duan et al., 2020; Espiritu et al., 2018; Lee et al., 2014; Li et al., 2018; Qi et al., 2020; Ren et al., 2000; Sarvaramini et al., 2016; Zhang and Honaker, 2018; Zhang et al., 2014). Whereas fatty acids are affordable, non-toxic, bio-sourced compounds, notably obtained by distillation of crude tall oil, hydroxamic acids, which are conventionally synthesised by amidation of fatty acids or esters with hydroxylamines (Massaro et al., 2007), have variable production costs and toxicity. Among this class, certain mutagen compounds, such as benzohydroxamic acid (Ching Yung Wang, 1977; Skipper et al., 1980) were used as the collector of choice in most of the recent studies. Hence, the environmental footprint of some hydroxamate collectors can be significantly larger than that of carboxylate collectors, especially when the former are used along with high quantities of heavy metal salts, such as lead nitrate, to improve the REM flotation performance (Jordens et al., 2016; Lin et al., 2020; Marion et al., 2020; Xia et al., 2015b). Therefore, the development of high-performance REM flotation techniques with carboxylates would provide a more efficient, cheaper, and greener alternative to the joint use of toxic hydroxamate collectors and heavy metal salts.

Although the REM flotation performance with carboxylate collectors increases at higher temperatures (Bulatovic, 2010; Morrice and Wong, 1982; Pradip and Fuerstenau, 1991), the financial and environmental costs of this approach are certainly prohibitive at industrial scale. In contrast, the addition of soluble metal salts is a common method to tune the collector adsorption on a specific mineral surface. Although recent studies examined the use of lead nitrate/hydroxamate mixtures, the addition of metal salts to carboxylate or hydroxamate collectors for REM flotation remains relatively unexplored, as previous studies mainly addressed the release of alkaline earth metals, aluminium, and iron in the pulp by gangue minerals (Cao et al., 2018; Xia et al., 2015a).

In this preliminary case study, a novel approach to selectively increase the monazite flotation performance was developed by using $LaCl_3$ to activate the adsorption of carboxylates on the surface of phosphate minerals.

2. Material and methods

2.1. Material origin

A processing residue of the ore extracted from the Kankberg mine, a gold and tellurium underground mine located in the Boliden area (Skellefte mining district, Sweden) and operated by Boliden Mineral AB since 2012, was used in this study. The Kankberg mine ore underwent different mineral processing and hydrometallurgy steps at the Boliden concentrator to recover contained gold and tellurium. A simplified bloc-diagram of these operations is depicted in Figure 1. Tailings were collected as a pulp with process water after cyanide destruction using the INCO air/SO_2 process. After water removal by filtration, the material was dried at 40 °C, homogenised, riffled, and subsequently stored in the dark at -18°C to avoid material transformation.

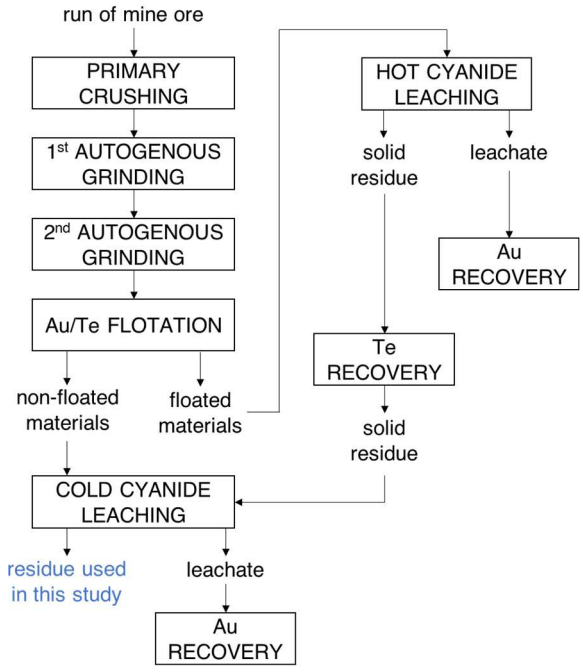

Figure 1: Gold and tellurium extractive metallurgy operations.

Importantly, this residue has been previously floated in the Boliden concentrator using potassium amyl xanthate as collector and polyglycol methyl ether as frother. In addition, it has been subjected to cyanide leaching operations using lime as a pH modifier with a subsequent cyanide-destruction process. Therefore, upon water removal and drying this material still contained non-negligible amounts of chemical reagents that may have affected the results of the performed flotation tests.

2.2. Modal mineral composition and mineral association analyses

Samples were prepared with graphite and epoxy resin to prepare polished grain mounts (Heinig et al., 2015) for scanning electron microscopy (SEM; FEI Quanta 650F) at the Helmholtz Institute Freiberg for Resource Technology. Furthermore, the FEI MLA software package for automation and data processing was used to acquire backscattered electron (BSE) images and energy-dispersive X-ray (EDX) spectra with semi-automated grain mount mapping (MLA; GXMAP) for modal composition and mineral association (Bachmann et al., 2017). The analyses were conducted at 25 kV acceleration voltage, 10 nA probe current, and 1 µm/pixel resolution for BSE with EDX-spectra acquired every 6 pixels.

2.3. Chemical analyses

Samples were riffled, pulverised in a planetary ball mill using tungsten grinding media, and subsequently assayed at the Service d'Analyse des Roches et des Minéraux (SARM-CNRS, Nancy, France). The concentrations of major and trace elements were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (ICP-MS), respectively, following the analytical procedure reported by Carignan et al. (2001).

2.4. Bench-scale flotation

Two series of bench-scale flotation kinetics tests were performed with collector dosages of 50 g t^{-1} and 100 g t^{-1} (grams per tonne of material) to assess the effect of lanthanum ions on the flotation of monazite and other phosphate minerals and determine the $LaCl_3$ dosage that results in the highest monazite flotation performance. Low collector dosages were preferred to ensure, in presence of a selective phosphate minerals activator, a proper monazite recovery with limited flotation of gangue minerals.

The flotation tests were conducted in a 1.5 L Agitair LA-500 flotation cell. The pulp treatment was performed at a rotor speed of 1000 rpm and solid content of 60 wt%, while flotation was performed at a rotor speed of 900 rpm, solid content of 30 wt%, and airflow of 4.5 L min^{-1}. After attrition of the mineral pulp for 5 min, a Na_2O:SiO_2 solution (0.3:1 ratio, 35.1 wt% Na_2O+SiO_2) was added at a dosage of 2850 g t^{-1} (dosage equivalent to 1000 g of Na_2O+SiO_2 per tonne of ore) to disperse fine particles and depress silicate gangue minerals.

The preliminary flotation tests indicated the presence of fast-floating particles, mainly of sphalerite and iron sulfides, which had been probably hydrophobised during the gold-tellurium processing route or cyanide destruction. To avoid the presence of these minerals in the floated product, after 8 min of treatment with the depressant, water is added to reach a solid content of 30 wt%, methyl isobutyl carbinol frother (MIBC) was added at a dosage of 5 g t^{-1} and these few highly hydrophobic particles were eliminated during a 2 min pre-flotation stage. The $LaCl_3$ solution at a concentration of 0.5 %, 0.05 %, or 0.005 % (g $LaCl_3$ per g of solution), produced by the dilution of a $LaCl_3$ precipitate provided by Alfa Aesar (99.9 % purity) and the sodium oleate solution at a concentration of 10^{-2} mol L^{-1}, produced by the dilution of a sodium oleate precipitate provided by Carl Roth (90 % purity), both at room temperature and with deionized water, were then added to the flotation cell either sequentially (2 min between the two additions) or as a

mixture. After 2 min, air is injected and floated products were collected after 30 s, 1 min, 2 min, 4 min, 8 min, and 15 min of flotation. Importantly, the initial pulp temperature was stabilised at 25 °C and the pH was maintained at 8.2–8.4 during pulp treatment and flotation using USP grade hydrochloric acid and sodium hydroxide.

3. Theory

Despite the high affinity of lanthanum ions for carboxylate and phosphate species (Hannah, 1970; Janicki et al., 2017; Lu and Wang, 2012; Mills, 2005), the influence of lanthanide salts on the phosphate flotation with carboxylate collectors has been seldom studied. Using a mixture of tributyl phosphate and saponified waste oil as collector for the flotation of phosphate from a low-grade tailing, Al-Thyabat and Zhang (2015) observed that the addition of a mixture of cerium compounds, lanthanum compounds, and soda ash was beneficial. They showed that an appropriate amount of this mixture may significantly improve phosphate recovery and the selectivity of the collector towards phosphate minerals. However, they highlighted that the activator dosage must be strictly controlled to avoid detrimental effects on the flotation performance. Furthermore, Sørensen and Lundgaard (1966) studied the recovery of monazite and streenstrupine from an agpaitic rock and reported an increase in the flotation rate without any tangible loss of selectivity when lanthanum nitrates were added before the sodium oleate collector. Recently, $LaCl_3$ was reported to promote the adsorption of carboxylate collectors on the monazite surface (Geneyton et al., 2020). Using thermodynamics calculation, X-ray photoelectron spectroscopy and density functional theory calculations, we found in this previous study that lanthanum ions adsorb in the form of $LaClCO_3$ on the monazite surface and act as highly attractive adsorption sites for carboxylate collectors. The significant increase in surface hydrophobicity resulting from the treatment of monazite with sodium oleate and $LaCl_3$, instead of sodium oleate alone, suggest that this reagent combination may improve the monazite flotation performance.

The use of soluble metal salts to specifically promote or limit the adsorption of collectors on the surface of certain minerals is a common practice in flotation research and numerous studies were conducted to understand the underlying mechanisms. Although the two proposed mechanisms differ in certain aspects, they both involve a configuration in which a cation plays the role of a chemical bridge between the mineral surface and the anionic collector. In the first mechanism, adsorption of a metal cation on the mineral surface either promotes or limits collector adsorption (Ren et al., 2000, 2017; Tian et al., 2018a; Xia et al., 2015b; Xiao et al., 2018). In contrast, the second mechanism postulates that reaction between a metal and the collector in the bulk forms a complex that adsorbs more or less efficiently on the mineral surface (Meng et al., 2018; Tian et al., 2018c, 2018a). As it is likely that both mechanisms coexist, pre-mixing the metal salt with the collector or adding first the metal salt in the pulp may favour one mechanism over the other. It is important to consider that stabilisation of the collector by the added metal species in the bulk may disfavour its adsorption on the mineral surface or lead to precipitation of a metal/collector salt. Hence, the effect of a metal salt on the monazite flotation performance depends on whether it is added to the pulp prior to introduction of the collector or pre-mixed with the collector. Given the strong affinity of lanthanum ions for carboxylate ligands and the low solubility of certain lanthanum carboxylates (Lu and Wang, 2012), this study examines the influence of the mode of addition of $LaCl_3$ on the monazite flotation performance, providing useful insight for further work.

4. Results

4.1. Material characterisation

4.1.1. *Modal mineralogy and overall chemical composition*

The concentrations of major and trace elements in the flotation feed material were determined by ICP-MS and ICP-AES and are summarised in Table 1. According to the modal mineralogy data

presented in Table 2, quartz, muscovite, topaz, andalusite, and corundum are the main gangue minerals amongst the 38 identified minerals, thus explaining the particularly high Al_2O_3 content of the material. This mineral association is consistent with the fact that gold and tellurium mineralisation zones in the Skellefte district (Sweden) mainly occur within or along a strong Si-Al alteration zone dominated by silica-rich rocks with abundant topaz, andalusite, and corundum (Wasström et al., 1999).

In this work, REE refers only to lanthanides, excluding scandium and yttrium. Every lanthanide content except promethium content was quantified by the ICP-AES analyses. The directly measured REE and P_2O_5 contents of the flotation feed material (Table 1) were similar to the values estimated by recombining the flotation products analyses. The flotation feed material assay indicated that LREE are more than 10 times more abundant than heavy REE (HREE). According to the MLA analyses, the main REM, monazite, accounted for 98.5–100 % of the total REE amount in the feed material (i.e., Ce/Gd/La/Nd/Pr/Sm). Furthermore, apatite was the main phosphate-bearing mineral, accounting for 88.6 % of the total phosphorus content in the feed material, whereas monazite accounted for 11.1 % of the total amount of phosphorus.

Table 1: Major and trace elements concentrations in the residue used as flotation feed material, determined by ICP-MS and ICP-AES analyses.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	P_2O_5
Content (wt%)	63.1	27.7	0.71	1.11	0.54	0.52	2.75	0.38	0.18
	Zn	*LREE*	*HREE*	*Y*	*Sc*	*Th*	*U*	*Nb*	
Content (ppm)	411	322	27	19	15	12	7	14	

Table 2: Modal mineralogy of the residue used as flotation feed material, determined by MLA measurements.

Mineral	*Formula*	*Content (wt%)*

Apatite	$Ca_5(PO4)_3(OH,F,Cl)$	0.4
Monazite	$(Ce,La,Nd,Th)PO_4$	0.1
Total phosphates		***0.5***
Pyrite	FeS_2	0.4
Sphalerite	ZnS	0.1
Total sulfides		***0.5***
Quartz	SiO_2	42.8
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	24.3
Topaz	$Al_2SiO_4(F,OH)_2$	16.0
Andalusite	Al_2SiO_5	4.7
Corundum	Al_2O_3	4.4
Rutile	TiO_2	1.2
Albite	$NaAlSi_3O_8$	0.9
Chlorite	$(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	0.9
Kaolinite	$Al_2(Si_4O_{10})(OH)_2$	0.7
Zoisite	$Ca_2Al_3Si_3O_{12}(OH)$	0.5
Plagioclase	$Na_{0.5}Ca_{0.5}Si_3Al_{O8}$	0.5
K-feldspar	$KAlSi_3O_8$	0.4
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$	0.3
Biotite	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,Cl)_2$	0.3
Dravite	$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$	0.3
Phlogopite	$KMg_3(Si_3Al)O_{10}(FOH)_2$	0.3
Tourmaline	$Na(Mg,Fe^{2+})_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$	0.2
Others		0.4
Total other gangue minerals		***99.0***

4.1.2. *Mineral liberation analysis*

Size-by-size chemical assays, presented in Table 3, revealed that approximately 50 % of the total REE amount was naturally concentrated in the <20 µm size class, which renders monazite concentration by conventional flotation technologies challenging due to the entrainment of gangue particles.

Table 3: Distribution of mass, P_2O_5, and REE by size fractions in the residue used as flotation feed material.

Size fraction	*Mass (%)*	*P_2O_5 (%)*	*REE (%)*
>100 µm	6.4	3.4	2.0
80-100 µm	4.3	3.8	1.9
63-80 µm	14.4	14.4	8.0
40-63 µm	17.4	17.4	13.4
20-40 µm	26.2	26.2	25.4
<20 µm	31.4	34.9	49.2

The association diagrams for phosphate minerals and main gangue minerals are presented in Figure 2 and indicate that monazite and apatite are rarely associated with each other or with other gangue minerals. Therefore, it was possible to study their behaviour during flotation by assessing the progress of REE and phosphorus recovery. In general, rutile, topaz, andalusite, corundum, quartz, and muscovite, whose flotation behaviours are discussed herein, also exhibit a high proportion of free surface.

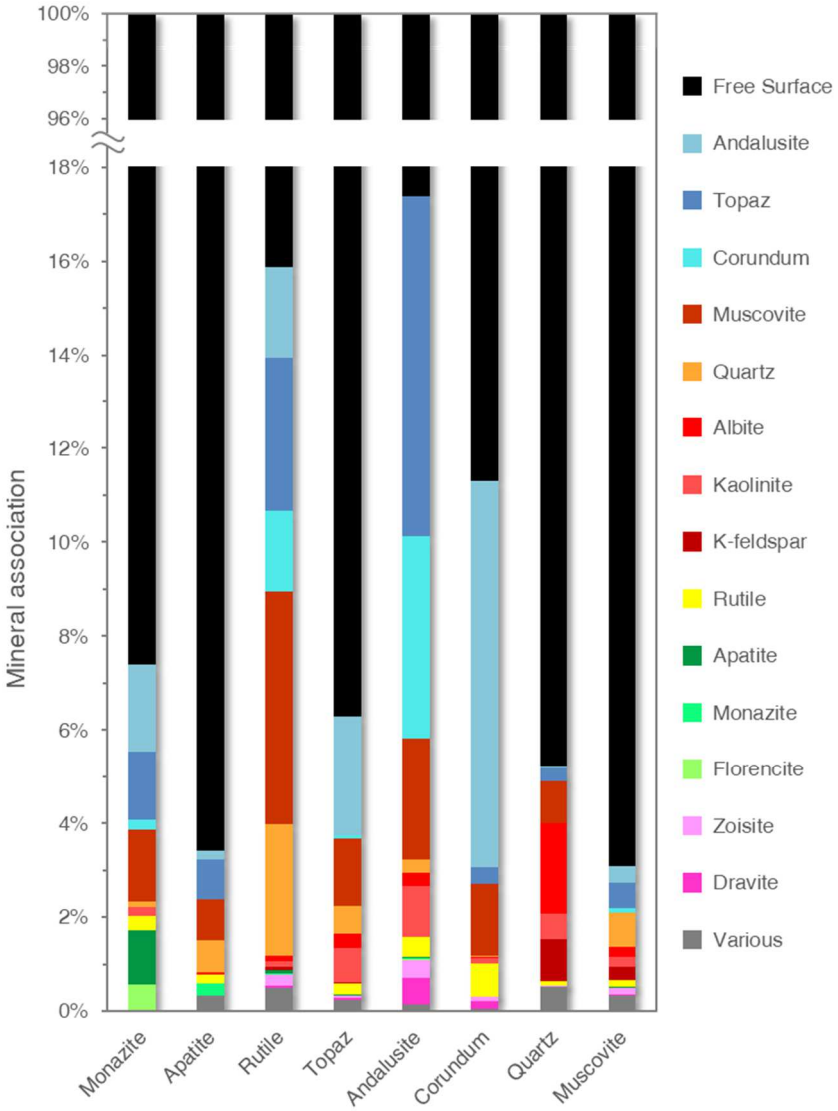

Figure 2: Association diagrams for monazite, apatite, rutile, topaz, andalusite, corundum, quartz, and muscovite in the residue used as flotation feed material, measured with an MLA instrument.

4.2. Flotation tests

4.2.1. *Influence of lanthanum ions on the monazite recovery*

The yield and REE recovery (based on the quantification of each lanthanide except promethium) during the flotation tests are presented in Figure 3. For a collector dosage of 50 g t^{-1}, the addition of $LaCl_3$ before sodium oleate increased monazite recovery (Figure 3-A_1). The enhancement of the monazite flotation performance is greater at a $LaCl_3$ dosage of 1 g t^{-1} than 0.1 g t^{-1} (Figure 4). At low lanthanum salt dosages (0.1–1 g t^{-1}), selectivity is enhanced, as shown by the improvement in REE recovery at a given mass yield (Figure 3-A_1) and the improvement in REE grade at a given REE recovery (Figure 4). Moreover, although higher $LaCl_3$ dosages (10 g t^{-1}) did not further improve the monazite recovery or its flotation kinetics, the significant increase in the yield suggests activation of gangue minerals (Figure 3-A_1). Therefore, the highest improvement of the monazite flotation performance was achieved at a $LaCl_3$ dosage of approximately 1 g t^{-1} (Figure 4).

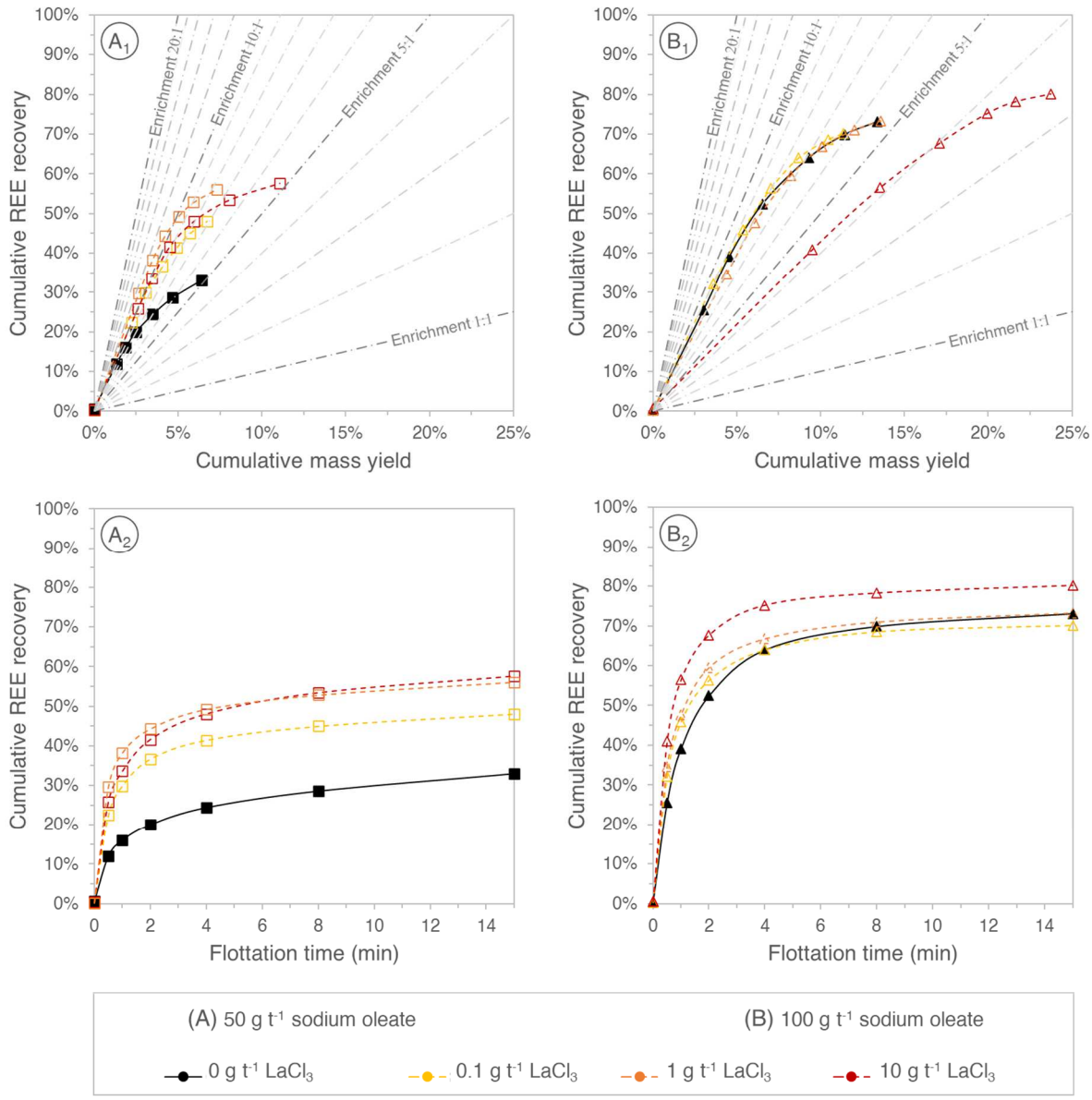

Figure 3: Influence of the sequential addition of $LaCl_3$ and sodium oleate on the progress of REE recovery and yield during flotation.

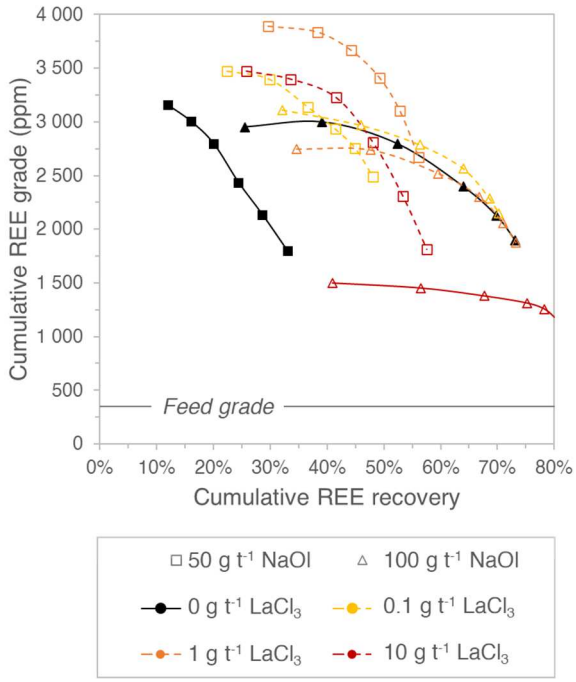

Figure 4: Influence of the sequential addition of $LaCl_3$ and sodium oleate (NaOl) on the progress of REE recovery and concentrate REE grade during flotation.

Although the influence of $LaCl_3$ on the monazite flotation kinetics is noticeable at a sodium oleate dosage of 100 g t^{-1} and a $LaCl_3$ dosage of 0.1-10 g t^{-1} (Figure 3-B_2), its influence on the monazite recovery was less pronounced (Figure 3-B_1). Indeed, $LaCl_3$ slightly improved monazite recovery only at a significant amount (10 g t^{-1}). Nonetheless, this high $LaCl_3$ dosage likely lead to a strong gangue mineral activation, as suggested by the yield increase (Figure 3-B_1) and the concentrate REE grade decrease (Figure 4).

Previously, we reported that the adsorption of lanthanum ions on the monazite surface facilitates the adsorption of the carboxylate collectors (Geneyton et al., 2020). This phenomenon explains the considerable increase in the monazite flotation performance at a collector dosage of 50 g t^{-1} (Figure 4). In contrast, at a collector dosage of 100 g t^{-1}, the collector alone ensures an efficient monazite recovery (Figure 3-B_1), low $LaCl_3$ dosages (0.1–1 g t^{-1}) slightly improve the monazite flotation kinetics, and only a high $LaCl_3$ dosage (10 g t^{-1}) improved monazite recovery as well as the yield (Figure 3-B_1), resulting in a decrease of the REE grade (Figure 4). Hence, we

postulated that, for the two collector dosages tested, at low dosages (0.1-1 g t^{-1}), lanthanum ions mostly adsorb on the monazite surface, limiting the collector adsorption on gangue mineral surfaces. In contrast, at higher dosages (such as 10 g t^{-1}), the lanthanum ions also adsorb on the surfaces of gangue minerals, thus activating the collector adsorption on these mineral surfaces.

4.2.2. *Influence of the lanthanum ions on the floatability of certain gangue minerals*

In order to compare the flotation performance of monazite and apatite, the P_2O_5 recovery values were expressed as a function of the REE recovery at each step of flotation kinetics tests. Figure 5 displays a correlation between the monazite recovery and the total phosphate minerals recovery. Given the strong relationship between the two, monazite and apatite, which account for 11.1 % and 88.6 %, respectively, of the phosphorus amount detected in the feed material, have similar flotation behaviour regardless of the collector or $LaCl_3$ dosages. These results suggest that lanthanum ions affect the surface of monazite and apatite similarly.

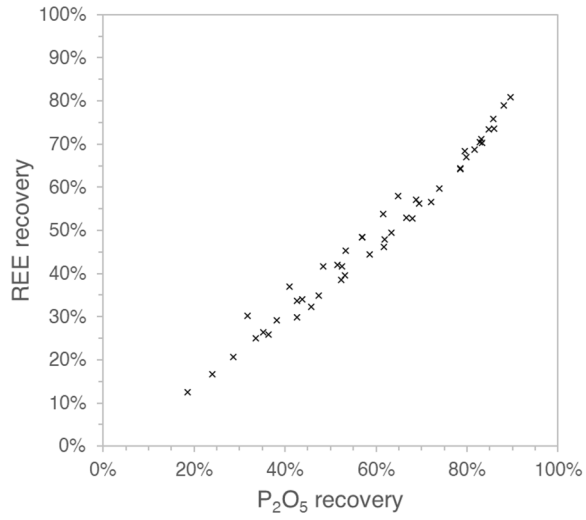

Figure 5: Correlation between REE and P_2O_5 recovery during the flotation.

The flotation tests also suggest that activation of gangue minerals occurs when $LaCl_3$ is employed at a dosage of 10 g t^{-1}. To evaluate whether certain major gangue minerals are selectively activated under these conditions, the cumulative SiO_2, Al_2O_3, K_2O, and TiO_2

enrichment in the floated products was calculated (Figure 6). The enrichment is obtained by dividing the grade of the floated product on the grade of the feed material. The results revealed that a sodium oleate dosage of 100 g t^{-1} and a $LaCl_3$ dosage of 10 g t^{-1} lead to a floated product that is remarkably more enriched in Al_2O_3 and in TiO_2 but also less enriched in K_2O (Figure 6-B_2, Figure 6-B_4, and Figure 6-B_3). This high $LaCl_3$ dosage also resulted in higher TiO_2 grades at a sodium oleate dosage of 50 g t^{-1} (Figure 6-A_4). Therefore, the floatability of rutile, which accounts for 98.8 % of titanium in the feed material, is influenced by high $LaCl_3$ concentrations.

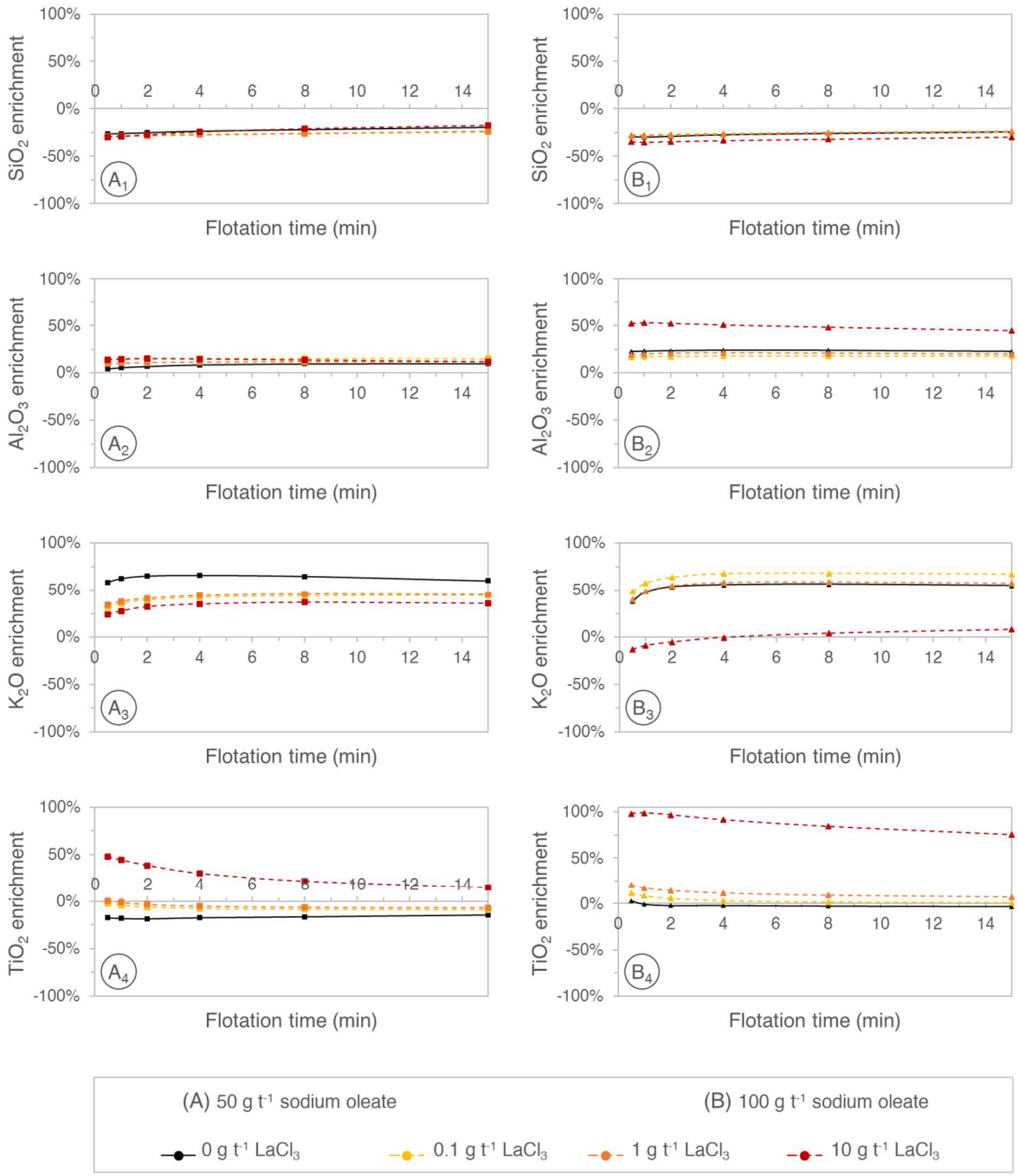

Figure 6: Influence of the sequential addition of $LaCl_3$ and sodium oleate on the cumulative TiO_2, SiO_2, Al_2O_3, and K_2O enrichment in the floated products. The (cumulative) enrichment is obtained by dividing the (cumulative) grade of the floated product on the grade of the feed material.

To identify the other main gangue minerals whose flotation behaviour may be affected by $LaCl_3$, MLA measurements were performed on the flotation products obtained at a collector dosage of 100 g t^{-1} and various $LaCl_3$ dosages. The back-calculated recoveries of main gangue minerals, presented in Figure 7, indicate that the flotation of rutile, topaz, and corundum, and that

of quartz and andalusite to a lesser extent, were activated by $LaCl_3$. The enhanced recovery of topaz, andalusite, and corundum, which account for 60.6 % of the total aluminium in the feed material, explain the higher Al_2O_3 enrichment visible in Figure 6-B_2. The relatively unaffected recovery of muscovite, which accounts for 95.4 % of the total potassium in the feed material, suggest that the K_2O grade decrease visible in Figure 6-B_3 results from the dilution of muscovite by aluminium-rich minerals.

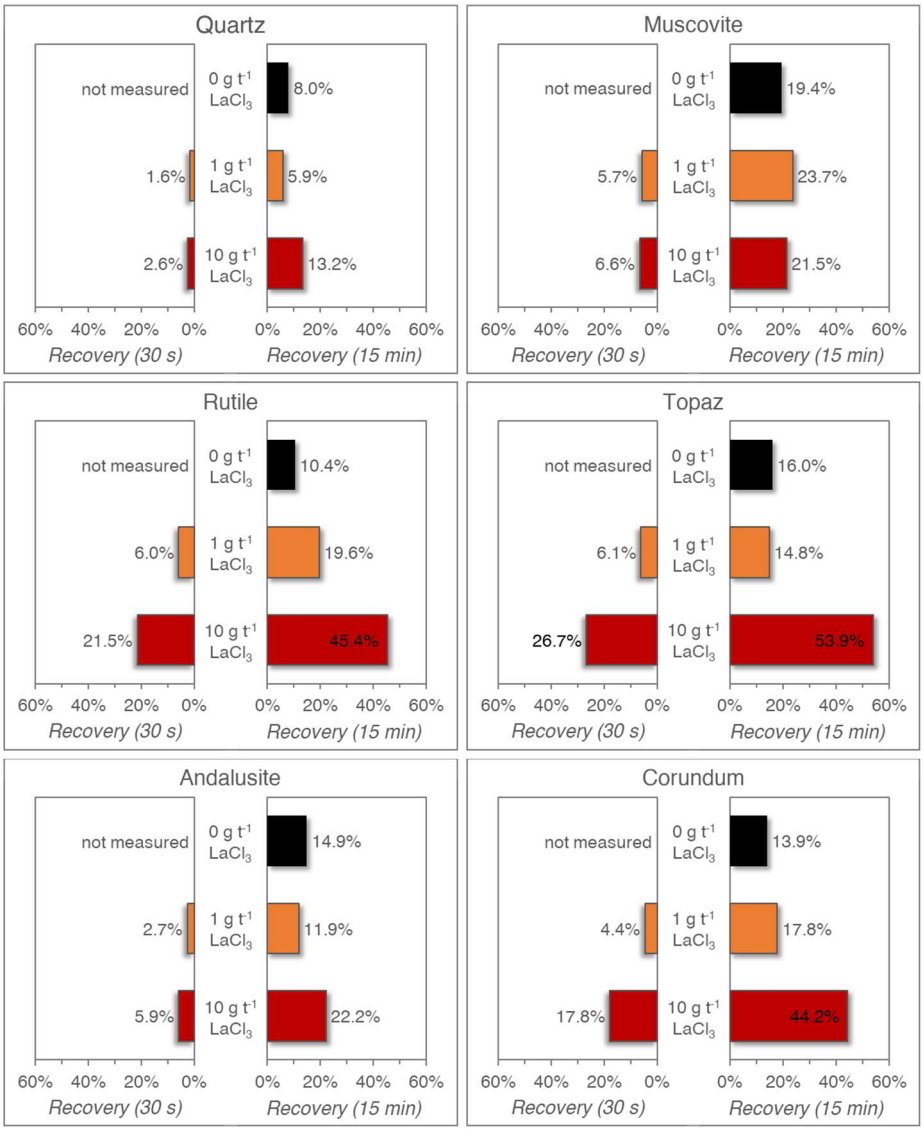

Figure 7: Cumulative recovery of main gangue minerals after 30 s and 15 min of flotation using a 100 g t^{-1} collector dosage. These results are based on the MLA measurements of the flotation feed material, the flotation products collected after 30s and the non-floated products collected after 15 min of flotation.

4.2.3. *Effect of the pre-mixing of $LaCl_3$ and sodium oleate*

The influence of the mode of addition of $LaCl_3$ was assessed by pre-mixing $LaCl_3$ with a sodium oleate solution for 5 min before addition to the flotation cell. During the pre-mixing, lanthanum oleate precipitation occurred (Figure 8). The similar precipitation of a mixture of $LaCl_3$ and potassium oleate salt in a water-alcohol medium had been previously reported [65] (Mehrotra and Upadhyaya, 1988).

	Sodium oleate			$LaCl_3$		
	Volume	Conc.	Cons.	Volume	Conc.	Cons.
(A)	16.4 mL	10^{-2} mol L^{-1}	100 g t^{-1}	/	/	/
(B)	16.4 mL	10^{-2} mol L^{-1}	100 g t^{-1}	1 mL	0.005 %	0.1 g t^{-1}
(C)	16.4 mL	10^{-2} mol L^{-1}	100 g t^{-1}	1 mL	0.05 %	1 g t^{-1}
(D)	16.4 mL	10^{-2} mol L^{-1}	100 g t^{-1}	1 mL	0.5 %	10 g t^{-1}

Figure 8: Mixed sodium oleate / $LaCl_3$ solutions before addition to the flotation cell. "conc" are the concentrations of the individual solutions before mixing and "cons" are the equivalent reagents consumptions for 500 g of material treated.

The precipitation of lanthanum oleate may reduce the collector availability and reduce the interaction between lanthanum ions and mineral surfaces. According to the stoichiometry, a sodium oleate dosage of 50 g t^{-1} and a $LaCl_3$ dosage of 10 g t^{-1} imply that nearly 75 % of the carboxylate anions may react to form lanthanum trioleate. Given the extremely low solubility of lanthanide oleate in water (Liu et al., 2009), the activity constant of lanthanum oleate has solely been measured in specific solvent media such as a benzene/methanol mixture (Mehrotra and

Upadhyaya, 1988). Thus, an estimation of the partitioning of oleate into sodium oleate, aqueous lanthanum oleate, and solid lanthanum oleate in aqueous medium is impossible.

In the conducted series of flotation tests using a mixture of sodium oleate and $LaCl_3$, a beneficial effect of the lanthanum ions on the monazite flotation performance may still be observed. Indeed, the monazite recovery and the concentrate REE grade increased when a $LaCl_3$ dosage of 0.1-1 g t^{-1} and a collector dosage of 50 g t^{-1} were used (Figure 9-A and Figure 10), suggesting that under these operational conditions not all the lanthanum ions was converted to non-reactive lanthanum oleate, the remaining available lanthanum ions having a beneficial effect on the monazite flotation selectivity. Conversely, a higher $LaCl_3$ dosage increased the yield and decreased the REE recovery (Figure 9-A), resulting in a significant decrease of the monazite flotation performance (Figure 10). The slightly improved TiO_2 and Al_2O_3 enrichment, observed with this specific $LaCl_3$ dosage (Figure 11-A_1/A_2), indicates that the surface of rutile and aluminium-rich minerals was activated by the lanthanum ions. Hence, we suggest that, with a $LaCl_3$ dosage of 10 g t^{-1}, the collector adsorption on certain activated gangue minerals surfaces and the formation of non-reactive lanthanum oleate limit the collector adsorption on monazite surface resulting in a limited monazite recovery.

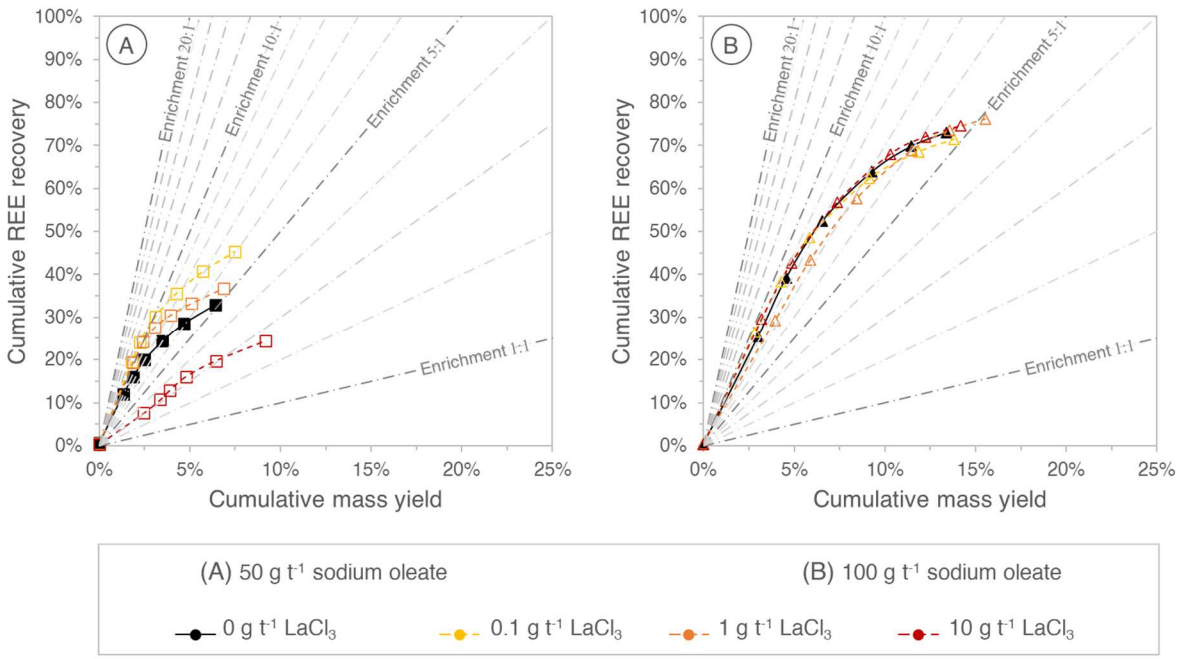

Figure 9: Influence of the addition of pre-mixed $LaCl_3$ and sodium oleate on the progress of REE recovery and yield during flotation.

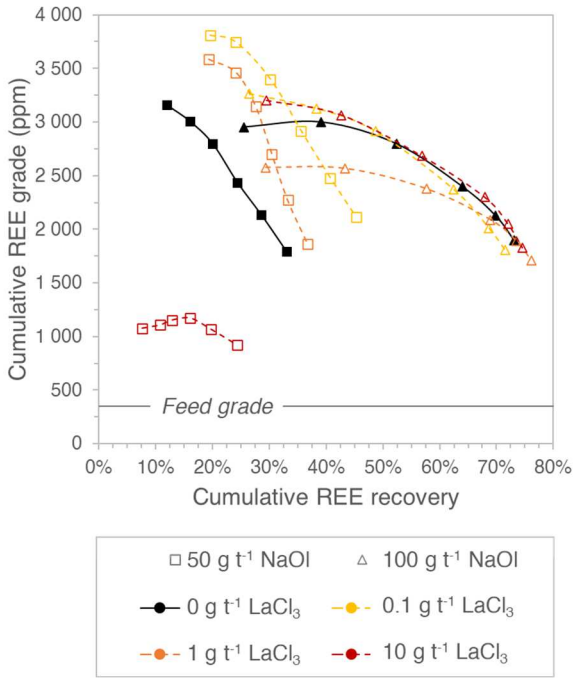

Figure 10: Influence of the addition of pre-mixed $LaCl_3$ and sodium oleate (NaOl) on the progress of REE recovery and concentrate REE grade during flotation.

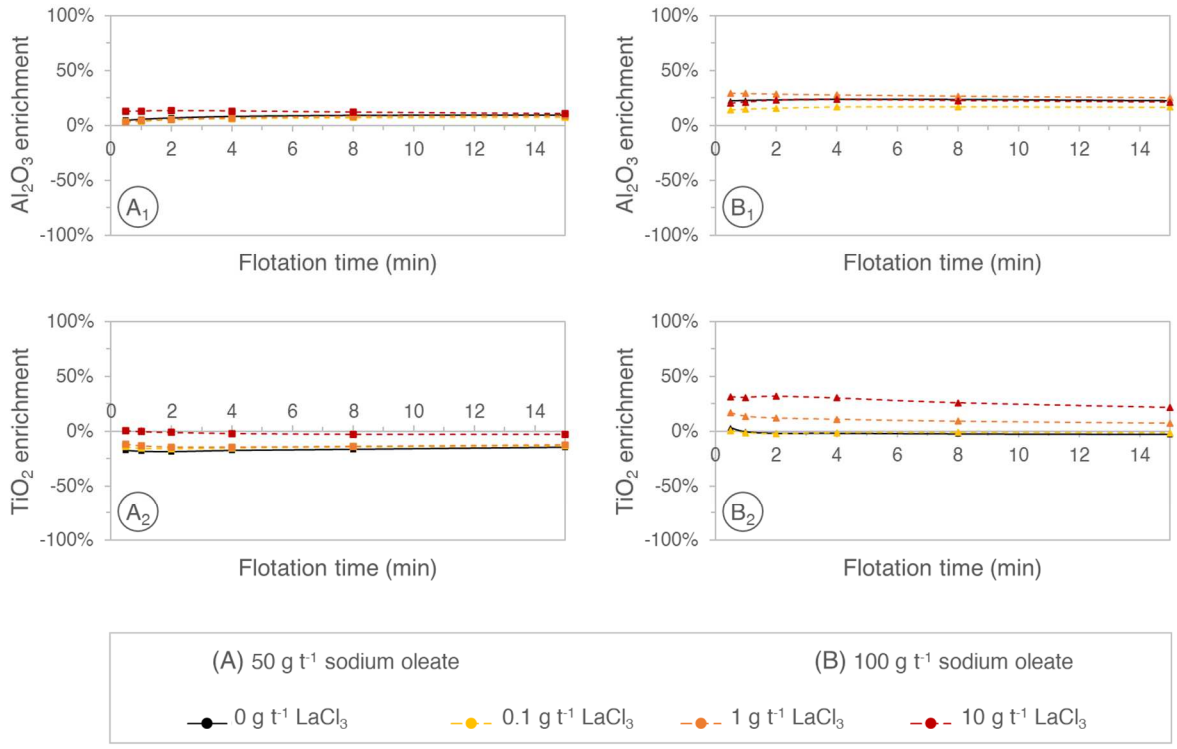

Figure 11: Influence of the addition of pre-mixed $LaCl_3$ and sodium oleate on the cumulative TiO_2 and Al_2O_3 enrichment of the floated product (enrichment over feed material).

At a collector dosage of 100 g t^{-1}, the addition of $LaCl_3$ has no remarkable effect on the monazite recovery and monazite flotation kinetics (Figure 9-B). Hence, we hypothesise that the collector availability in the pulp was sufficient to ensure an appropriate monazite flotation performance without $LaCl_3$. High $LaCl_3$ dosages (1 and 10 g t^{-1}) significantly increase the TiO_2 content of the floated products (Figure 11-B_2), suggesting that, despite the formation of non-reactive lanthanum oleate, the availability of the collector and lanthanum ions was sufficient to render the rutile surface more hydrophobic. Overall, the addition of $LaCl_3$ has limited effect on the monazite flotation performance (Figure 10). It only decreased the REE content in the floated product during the first minutes of the flotation test when a $LaCl_3$ dosage of 1 g t^{-1} was used. It probably stems from a temporarily slightly higher recovery of aluminium-rich minerals (Figure 11-B_1) suggesting that $LaCl_3$ affects the aluminium-rich minerals flotation kinetics without significantly affecting the final recovery of these minerals. Therefore, although the availability of the collector and lanthanum ions was sufficient to enhance the rutile flotation

performance, it was likely insufficient to activate enough the flotation of aluminium-rich minerals and cause the significant yield increase and loss of selectivity we observed with a $LaCl_3$ dosage of 10 g t^{-1} and a collector dosage of 100 g t-1 when these reagents were not pre-mixed (Figure 3-B_1 and Figure 4).

Importantly, similar conclusions are valid with regard to the overall phosphate mineral flotation performance, confirming that $LaCl_3$ affects the floatability of monazite and apatite likewise.

5. Discussion

In a previous study, we highlighted that lanthanum ions strongly adsorb on the monazite surface due to the under-coordinated phosphate groups, thus acting as highly attractive adsorption sites for carboxylate collectors (Geneyton et al., 2020). The observed higher hydrophobicity of the monazite surface upon treatment with $LaCl_3$ and sodium oleate, rather than sodium oleate alone, likely arises from this increase in the affinity of the carboxylate collectors towards the monazite surface. The aim of the present study was to confirm that these synergistic effects effectively improve the monazite flotation performance when monazite is associated with gangue minerals.

The flotation tests featuring the sequential addition of $LaCl_3$ and sodium oleate showed that very low $LaCl_3$ dosages (0.1–1 g t^{-1}) selectively enhance the flotation performance of monazite and apatite. At a collector dosage of 50 g t^{-1}, the addition of small amounts of $LaCl_3$ significantly increases the recovery of these minerals (Figure 3-A_2), whereas it only slightly increases the flotation kinetics at a collector dosage of 100 g t^{-1} (Figure 3-B_2). In the latter case, it is likely that the collector availability in the pulp was sufficient to ensure an appropriate extent of collector adsorption on the phosphate mineral surface and consequent recovery in the absence of $LaCl_3$. However, although it has no significant impact on the monazite flotation performance, the slight increase in the monazite and apatite flotation kinetics suggests that the addition of lanthanum ions can further increase the amount of collector adsorbed on the phosphate mineral surfaces.

The highest enhancement of the monazite and apatite flotation performance occurred with a $LaCl_3$ dosage of 1 g t^{-1} and a collector dosage of 50 g t^{-1}. In the case of this particular tailing, higher $LaCl_3$ dosages significantly increase the yield, especially with a collector dosage of 100 g t^{-1} (Figure 3-A_1 and Figure 3-B_1). MLA measurements performed on flotation products

obtained at sodium oleate and $LaCl_3$ dosages of 100 g t^{-1} and 10 g t^{-1}, respectively, reveal that the increase in the yield is associated with a higher recovery of rutile, topaz, andalusite, and corundum, suggesting that the lanthanum ions also activate the adsorption of carboxylate on the surfaces of these gangue minerals. Lanthanum ions are known to adsorb on rutile (Fendorf and Fendorf, 1996) and γ-Al_2O_3 (Wang et al., 2004), indicating their strong affinity for the titanate and aluminate groups present on the surface of these minerals. Therefore, we assume that although lanthanum ions mainly adsorb on the phosphate groups of the monazite and apatite surfaces, the adsorption of lanthanum ions on the surface titanate and aluminate groups above a critical $LaCl_3$ dosage becomes sufficient to activate the adsorption of the collector on the surface of rutile and aluminium-rich minerals, namely topaz, andalusite, and corundum. In the present case study, the use of $LaCl_3$ dosages higher than a few grams per tonne of material was found to be detrimental for the monazite flotation performance. Nonetheless, we cannot exclude that such $LaCl_3$ dosages further improve the monazite flotation performance in the case of silicate-rich tailings that contain lower amounts of these lanthanum-sensitive gangue minerals.

The comparison of the grade/recovery curves indicates that, with a collector dosage of 50 g t^{-1}, the sequential addition of $LaCl_3$ and sodium oleate gave better improvement of the monazite flotation performance than the pre-mixing of these reagents. We hypothesise that this pre-mixing reduces the collector availability and limits the interactions between the lanthanum ions and mineral surfaces due to the formation of non-reactive lanthanum oleate. In contrast, in the case of sequential $LaCl_3$ and sodium oleate addition, initial adsorption of the lanthanum ions on the mineral surfaces promotes the selective collector adsorption. The limited interactions between the mineral surfaces and both lanthanum ions and the collector, due to the formation of non-reactive lanthanum oleate, explained the limited activation of the flotation of rutile and the absence of significant activation of the flotation of aluminium-rich minerals with a collector dosage of 100 g t^{-1}.

The best monazite flotation performance was not sufficient to produce a marketable monazite concentrate (Figure 4 and Figure 10). However, the purpose of this study was not to develop an optimised flotation procedure for the Kankberg residues and, with an initial REE content of 349 ppm (Table 1), we did not expect to produce in a single flotation step a valuable concentrate. The present report, which highlights the effect of $LaCl_3$ on the monazite flotation performance and the importance of its dosage and mode of addition, is a promising step towards the efficient beneficiation of monazite of low monazite-grade, silicate-rich tailings. The technical relevance of this practice must be further studied, notably with tailings that do not contain high amounts of lanthanum-sensitive gangue minerals such as rutile and aluminium-rich minerals. The economic relevance and environmental sustainability of this practice must also be evaluated. Such assessments require consolidated data that may be obtained by identifying the optimal reagent dosage for the roughing and cleaning flotation of different types of silicate-rich tailings. The main assessment criteria are the $LaCl_3$ consumption to selectively promote monazite flotation, which is limited in the present case study, and the presence of lanthanum ions in the process water and non-floated product, which was not evaluated in this study.

6. Conclusion

Flotation tests performed on low monazite-grade, silicate-rich tailings indicated that the addition of $LaCl_3$ before that of the carboxylate collectors affects the flotation performance of the phosphate minerals monazite and apatite. At a low sodium oleate dosage (50 g t^{-1}), the addition of 0.1–1 g t^{-1} of $LaCl_3$ selectively enhanced the monazite and apatite recovery, suggesting that the collector adsorption on these minerals was improved. At a sodium oleate dosage that enables sufficient phosphate recovery (100 g t^{-1}), the addition of 0.1–1 g t^{-1} of $LaCl_3$ only slightly enhanced the phosphate mineral flotation kinetics. In the present case study, the use of higher $LaCl_3$ dosages was detrimental, as it led to recovery of gangue minerals. We highlighted that the

sequential addition of $LaCl_3$ and sodium oleate give better improvement of the monazite flotation performance than the pre-mixing of these reagents.

The flotation results presented herein confirm the previously reported synergistic effect of $LaCl_3$ and carboxylate collectors on the floatability of phosphate minerals. Moreover, the adsorption of lanthanum ions on the surface titanate and aluminate groups occurs at high $LaCl_3$ dosage, promoting collector adsorption on the surface of the rutile and aluminium-rich minerals topaz, andalusite, and corundum.

In this case study, we developed a new approach for the selective flotation of monazite using carboxylate collectors as inexpensive and environmentally friendly surfactants along with very small amounts of lanthanum salts to promote the selective collector adsorption on the monazite surface. Hence, this study may be regarded as a first step towards the promising development of new flotation practices for the exploitation of low monazite-grade, silicate-rich tailings as alternative REE sources.

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