

Article

Reagent Formulations for Selective Flotation Under Challenging Complex Rare Earth Elements Ores

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Abstract

Rare earth elements (REEs) flotation from carbonatitic ores remains challenging due to the complex association between REE-bearing minerals and carbonate-rich gangue phases. Although previous studies have reported REE beneficiation from the Fen Deposit, the influence of depressant type, sodium silicate dosage, EDTA addition, and collector selection on flotation selectivity remains poorly understood. Therefore, this study presents a preliminary assessment of different reagent schemes for the flotation of REE-bearing minerals from the Fen Deposit. Chemical and mineralogical characterization confirmed the predominance of light REEs, mainly Ce and La, associated with monazite and fluorocarbonate minerals of the bastnäsite–parisite–synchysite group. Flotation screening tests revealed limited gangue rejection, particularly for Ca- and Ba-bearing minerals, indicating that mineralogical complexity strongly influences flotation selectivity. Among the depressants evaluated, sodium silicate and citric acid exhibited the most promising performance, while EDTA enhanced the total rare earth oxides (TREO) grade at higher sodium silicate dosages. Collector tests resulted in moderate REE enrichment in the overflow products, with NaOL yielding the highest recovery (~62%). However, TREO grades remained relatively low (~2.3–2.7%), suggesting that reagent selection alone is insufficient to overcome the flotation limitations imposed by the ore from the Fen Deposit. The results provide an exploratory evaluation of reagent schemes for Fen carbonatite ore and identify key challenges and opportunities for future process optimization.

Keywords: rare earth flotation; carbonatitic ore; depressant; EDTA; collector



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1. Introduction

Rare earth elements (REEs) are critical raw materials with strategic importance due to their extensive use in a wide range of industrial applications, including electronics, electric vehicles, high-performance magnets, information and communication technologies, renewable energy production and storage, aerospace systems, catalysis, medical imaging, advanced metallic alloys, and specialty ceramics and glasses [1–6]. Owing to their unique physicochemical properties, REEs are indispensable to modern technologies and play a central role in enabling the global energy transition.

In the European context, the transition toward a low-carbon and climate-neutral energy system has intensified the demand for REEs, particularly for applications related to wind turbines, electric mobility, and energy-efficient technologies. Ensuring a secure and sustainable supply of these elements has therefore become a strategic priority for Europe, highlighting the need to develop domestic and responsibly sourced REEs and to advance efficient mineral processing technologies [7].

The Fen Deposit, located in Nome, Telemark region, Norway, has recently emerged as a promising source of REEs in Europe. The Fen Complex comprises several carbonatite units, among which the ferruginous dolomite carbonatite (FDC) is considered the most economically attractive and Europe's largest known deposit of REEs. This unit hosts REE-bearing minerals such as bastnäsite ($(\text{Ce,Nd,Y})(\text{CO}_3)\text{F}$), parisite ($\text{Ca}(\text{Ce,La,Nd})_2(\text{CO}_3)_3\text{F}_2$), synchysite ($\text{Ca}(\text{Ce,Nd,Y})(\text{CO}_3)_2\text{F}$), and the phosphate mineral monazite ($(\text{REE})\text{PO}_4$) [8]. Despite its promising mineralogy, the complex and fine-grained nature of the ore poses significant challenges for mineral beneficiation.

In recent years, rare earth flotation technologies have progressed substantially, driven by the increasing need for more efficient, selective, and environmentally sustainable processing routes. Various reagent schemes have been proposed to improve the selective recovery of REE-bearing minerals, including the application of different collectors, depressants, and surface modifiers to ores [7]. Despite these advances, achieving high flotation selectivity remains challenging, particularly for ores containing significant amounts of carbonate gangue minerals.

Among the depressants investigated for REE flotation, sodium silicate (Na_2SiO_3) remains one of the most widely used reagents due to its ability to depress silicate and carbonate gangue minerals. However, its application may also unintentionally depress bastnäsite, particularly in the presence of dissolved Ca^{2+} ions [7]. To mitigate this effect, Hu et al. [9] reported that ethylenediaminetetraacetic acid (EDTA) can selectively complex Ca^{2+} ions and reduce the co-depressive effect of sodium silicate on bastnäsite. In addition to sodium silicate, several other depressants have shown promising performance in mineral flotation systems. Xanthan gum has demonstrated selective depression of calcite due to its strong interaction with calcium ions [10], whereas sodium alginate has been reported as an efficient and environmentally friendly depressant for fluorite when combined with hydroxamate collectors [11,12]. Similarly, phytic acid, owing to its strong chelating affinity for divalent metal ions, has been successfully applied in the flotation separation of scheelite and fluorite [13]. Citric acid, another biodegradable complexing agent, has also been reported as an effective depressant in mineral flotation systems [14].

Collectors play an equally important role in REE flotation by increasing the hydrophobicity of mineral surfaces and promoting particle attachment to air bubbles. Several classes of collectors have been investigated, including carboxylates, hydroxamates, and phosphoric acid esters [12]. Octanohydroxamic acid (OHA) is particularly attractive due to its ability to form stable chelates with REE ions such as Ce^{4+} and La^{3+} , often resulting in greater selectivity than fatty acid collectors [12,15]. Nevertheless, its relatively high cost and handling requirements may limit large-scale applications [16]. Sodium oleate (NaOL), a low-cost and widely available collector, has also been extensively used in REE flotation; however, its selectivity is often compromised by the simultaneous flotation of carbonate gangue minerals such as calcite and fluorite [12]. Other collectors, including benzohydroxamic acid (BHA) and commercial formulations such as AERO[®] 6493, have also been investigated to improve REE recovery from complex ores [7,8].

Despite significant advances in reagent development, selective flotation of REE-bearing minerals from carbonatite ores remains a major challenge. Although acceptable recoveries can often be achieved, concentrate grades frequently remain limited due to the complex mineralogical characteristics of these deposits. Previous studies have highlighted that mineralogical factors, including fine intergrowth between REE-bearing minerals and gangue phases, incomplete liberation, and similarities in surface chemistry between fluorocarbonates and carbonate gangue minerals, may substantially reduce flotation selectivity and promote gangue recovery into the concentrate [12,15,17]. Therefore, flotation performance in carbonatitic REE ores should not be interpreted solely in terms of reagent chemistry, as mineralogical constraints may also play a decisive role in controlling gangue rejection and REE enrichment.

In this context, although previous studies have investigated the flotation of REE-bearing minerals from the Fen Deposit [7,8], the factors contributing to the limited flotation selectivity observed during the beneficiation of Fen REE ores remain poorly understood. In particular, the combined influence of depressant type, sodium silicate dosage, EDTA addition, and collector selection has not been systematically evaluated for this mineralogically complex carbonatite ore. Therefore, this study aims to perform an exploratory assessment of different depressants, collector types, sodium silicate dosages, and EDTA additions for the flotation of REE-bearing minerals from the Fen Deposit. The main objective was to identify promising reagent schemes for REE enrichment and gangue rejection while discussing potential mineralogical factors that may contribute to the limited flotation selectivity observed in this type of ore.

2. Materials and Methods

2.1. Ore Sample and Reagents

The feed material used in this study was obtained from the Fen Deposit, classified as an iron–dolomite carbonatite ore containing REE-bearing minerals, including bastnäsite, parisite, synchysite, and monazite. The bulk sample was comminuted using a ring mill with a 200 mm diameter, aiming to achieve a particle size below 85 µm (Siebtechnik, Mülheim an der Ruhr, Germany), which is considered suitable for direct flotation tests.

Prior to the systematic flotation experiments, preliminary blank flotation tests were performed under the same operational conditions used in the subsequent tests, but without collector addition. These tests did not produce a froth or a measurable overflow product, suggesting negligible natural floatability of the feed material under the investigated conditions. Therefore, blank tests were not included in the final experimental matrix, and the available sample was prioritized for the evaluation of the selected reagent schemes.

All flotation tests were conducted under the same experimental protocol to ensure consistency among the different reagent conditions. Although replicate flotation tests were not performed for all conditions, the results were interpreted considering the expected experimental variability associated with bench-scale flotation tests. The test sequence was designed to provide continuity between the different experimental stages, beginning with depressant screening, followed by EDTA-assisted tests and collector comparison. This sequential approach allowed the results from each stage to guide the interpretation of the subsequent tests.

Hydroxamate-based collectors, particularly octanohydroxamic acid (OHA; >99.0% purity; Tokyo Chemical Industry Co., Ltd. [TCI], Tokyo, Japan), were selected due to their well-documented selectivity towards REE-bearing minerals when compared to other reagent classes such as carboxylates and phosphoric acid esters [3,12,18]. In this stage, the influence of different depressants on REE flotation and gangue mineral suppression was systematically evaluated. Five depressants were investigated (Table 1): sodium silicate

(SS; extra pure; Supelco/Merck KGaA, Darmstadt, Germany; $\text{SiO}_2/\text{Na}_2\text{O}$ ratio ≈ 3.48), phytic acid (PA; hydrate, purity not specified; Sigma-Aldrich, St. Louis, MO, USA, made in Switzerland), quinic acid (QA; 98% purity; Thermo Scientific, Heysham, UK, made in Germany), citric acid (CA; 99% purity; Sigma-Aldrich, St. Louis, MO, USA), and sodium alginate (SA; purity not specified; Sigma-Aldrich, St. Louis, MO, USA; made in China), all applied at a dosage of $0.5 \text{ g}\cdot\text{kg}^{-1}$, including the collector.

Table 1. Summary of reagent schemes and experimental conditions applied in flotation tests.

Stage	Test ID	Collector ($0.5 \text{ g}\cdot\text{kg}^{-1}$)	Depressant	Depressant Dosage ($\text{g}\cdot\text{kg}^{-1}$)	EDTA
Preliminary screening for depressant	S1	OHA	Sodium silicate	0.5	No
	S2	OHA	Phytic acid	0.5	No
	S3	OHA	Quinic acid	0.5	No
	S4	OHA	Citric acid	0.5	No
	S5	OHA	Sodium alginate	0.5	No
Depressant optimization	D1	OHA	Sodium silicate	1	No
	D2	OHA	Sodium silicate	0.5	No
	D3	OHA	Sodium silicate	0.25	No
	D4	OHA	Sodium silicate	1	Yes
	D5	OHA	Sodium silicate	0.5	Yes
	D6	OHA	Sodium silicate	0.25	Yes
Collector optimization	C1	OHA	Sodium silicate	1	No
	C2	NaOL	Sodium silicate	1	No
	C3	OA	Sodium silicate	1	No

Following this screening, particular attention was given to sodium silicate (Na_2SiO_3), as it has been widely reported as an effective gangue depressant, used to reduce the buoyancy of calcite in combined mineral flotation systems [15,19,20]. However, previous studies indicate that sodium silicate may also inadvertently depress bastnäsite, especially in the presence of dissolved Ca^{2+} ions [7]. To address this limitation, additional tests were conducted to evaluate the effect of sodium silicate dosage (1000, 500, and $250 \text{ mg}\cdot\text{kg}^{-1}$) under conditions with and without the addition of ethylenediaminetetraacetic acid (EDTA; analytical grade/for analysis; 99–101% purity; Merck KGaA, Merck KGaA, Darmstadt, Germany), which has been reported to mitigate the co-depression of bastnäsite by complexing calcium ions [9].

After establishing the most favorable depression conditions, different collectors were evaluated. In addition to OHA, sodium oleate (NaOL; >99% purity; Sigma-Aldrich, St. Louis, MO, USA) and oleic acid (OA; technical grade, 90% purity; Thermo Scientific, Kandel, Germany) were tested, all at a concentration of $0.5 \text{ g}\cdot\text{kg}^{-1}$. All reagents were used as received, without further purification. Aqueous reagent solutions were prepared using deionized water.

2.2. Flotation Tests

The flotation tests, including depressant screening, collector types, sodium silicate dosages, and EDTA addition, were conducted through a two-stage flotation approach (primary and secondary flotation), aiming to maximize the recovery of REEs. These experiments were performed using a laboratory-scale adapted flotation system, consisting of a 600 mL beaker operating as a flotation cell and immersed in a thermostatic water bath. This configuration allowed maintaining the pulp temperature at approximately 50°C .

The pulp was agitated at 400 rpm to ensure adequate suspension of particles and promote effective particle–bubble interactions. The pH was controlled under slightly alkaline conditions, around 8.3, which has been reported as optimal for REE flotation in carbonatitic systems [21,22]. The pulp pH was measured after reagent addition and adjusted, when necessary, using HCl to decrease the pH and NaOH to increase the pH. The natural pH of the feed pulp was approximately 8.5; however, the addition of flotation reagents modified the pulp pH. Sodium silicate increased the pH to approximately 9.1, whereas acidic depressants, including quinic, phytic, and citric acids, decreased the pH to approximately 8.1. Octanohydroxamic acid also caused a slight decrease in pH. Therefore, small additions of HCl or NaOH were made, when required, to maintain the pH close to the target value before flotation.

In the primary flotation stage, 180 g of feed material was used, corresponding to a solids concentration of approximately 25 wt%. The underflow obtained from this stage was subsequently subjected to a second flotation stage, in which 100 g of material was processed, resulting in a solids concentration of about 15 wt%. This two-step approach was designed to improve the recovery of REE-bearing minerals that were not recovered during the initial flotation stage.

2.3. Chemical Analysis and Characterization

After the crushing and grinding steps, the feed material was comprehensively characterized in terms of particle size distribution, chemical composition, and radiological properties. Particle size distribution was determined to ensure suitability for flotation conditions, using a Malvern Mastersize 2000 Particle Size Analyzer (Malvern Instruments, Malvern, UK). The semi-quantitative elemental composition was obtained by X-ray fluorescence (XRF) using a portable X-MET7500 analyzer (Oxford Instruments, High Wycombe, UK).

The concentration of REEs in the feed sample was quantitatively determined by inductively coupled plasma mass spectrometry (ICP-MS) using an iCAP TQ ICP-MS equipped with a triple-quadrupole mass filter (Thermo Fisher Scientific, Waltham, MA, USA), complemented by mineralogical and microstructural analyses using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). SEM-EDS was used only as a qualitative supporting technique to assess elemental associations and to assist in the tentative identification of REE-bearing phases.

All products obtained from flotation experiments were also analyzed for REE content using ICP-MS. Prior to analysis, the samples were subjected to microwave-assisted acid digestion using a 4-acid mixture composed of hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄), and hydrofluoric acid (HF), following standard protocols to ensure complete dissolution of silicate- and carbonate-rich mineral matrices. Approximately 0.25 g of each solid sample was digested using 10 mL of the acid mixture, consisting of 3 mL HCl, 3 mL HNO₃, 2 mL HF, and 2 mL HClO₄. The resulting solutions were subsequently diluted to appropriate concentrations and analyzed by ICP-MS for quantitative determination of REEs.

The elemental concentrations of rare earth elements determined by ICP-MS were converted to oxide-equivalent concentrations using stoichiometric conversion factors calculated from the molar masses of the corresponding oxides. The oxide concentration of each rare earth element was obtained by multiplying the elemental concentration by its respective conversion factor. Ce, Pr, and Tb were reported as CeO₂, Pr₆O₁₁, and Tb₄O₇, respectively, while La, Nd, Sm, Gd, Y, Eu, Dy, Sc, Er, Yb, Ho, Tm, and Lu were reported as their corresponding sesquioxides (REE₂O₃). TREO was calculated as the sum of the individual rare earth oxide concentrations. The conversion factors used were 1.228 for CeO₂, 1.173 for La₂O₃, 1.166 for Nd₂O₃, 1.208 for Pr₆O₁₁, 1.160 for Sm₂O₃, 1.153 for Gd₂O₃,

1.270 for Y_2O_3 , 1.158 for Eu_2O_3 , 1.148 for Dy_2O_3 , 1.533 for Sc_2O_3 , 1.176 for Tb_4O_7 , 1.143 for Er_2O_3 , 1.139 for Yb_2O_3 , 1.146 for Ho_2O_3 , 1.142 for Tm_2O_3 , and 1.137 for Lu_2O_3 .

Repeated chemical analyses were performed for the flotation products, and the standard deviations are included in the corresponding figures and table. These analytical deviations were used to assess the reliability of trends in TREO grade and recovery.

3. Results and Discussion

3.1. Chemical and Mineralogical Characterization of the Feed Material

The chemical composition of the feed material determined by ICP-MS is presented in Table 2. Cerium was identified as the most abundant rare earth element (REE), with a concentration of 6680 ppm, followed by La at 4600 ppm. Neodymium and Pr were detected at concentrations of 1900 and 625 ppm, respectively. The predominance of light rare earth elements (LREEs), particularly Ce and La, indicates a mineral assemblage characteristic of REE-bearing carbonatitic or hydrothermal systems. Consistent with previous studies conducted on the same deposit [7,8], the geochemical trends are similar; however, the concentrations observed in this feed material are slightly lower.

Table 2. Rare earth element concentrations in the feed material obtained by ICP-MS.

Element	Concentration (ppm)
Ce	6680 ± 164
La	4600 ± 290
Nd	1900 ± 103
Pr	625 ± 60
Sm	170 ± 72
Gd	71 ± 20
Y	76 ± 41
Eu	38 ± 15
Dy	23 ± 5.4
Sc	55 ± 22
Tb	6.1 ± 2.3
Er	5.9 ± 2.3
Yb	3.4 ± 1.2
Ho	2.9 ± 1.2
Tm	0.7 ± 0.2
Lu	0.4 ± 0.2
TREE	14,256 ± 447
TREO	17,121 ± 54.2

SEM-EDS analyses indicated the highly heterogeneous nature of the feed material used in the flotation experiments (Figure 1). Among the REE-bearing phases inferred from SEM-EDS elemental associations, region Z2 was associated with monazite, based on the association of REEs and P, with a composition compatible with $(\text{Nd,L a,Ce})\text{PO}_4$. Region Z3 was tentatively assigned to a REE fluorocarbonate phase, based on the association of REEs, Ca, F, C, and O in the EDS spectrum. Its composition is compatible with minerals of the bastnäsite–parisite–synchysite group. However, due to the qualitative nature of EDS and the analytical limitations associated with light elements such as C, O, and F, a definitive distinction among these minerals cannot be made based solely on SEM-EDS data. The intense Ca peak suggests a Ca-bearing fluorocarbonate phase, possibly closer to parisite, synchysite, or an intermediate parisite–synchysite composition, whereas bastnäsite is considered less likely due to its typically low or absent Ca content.

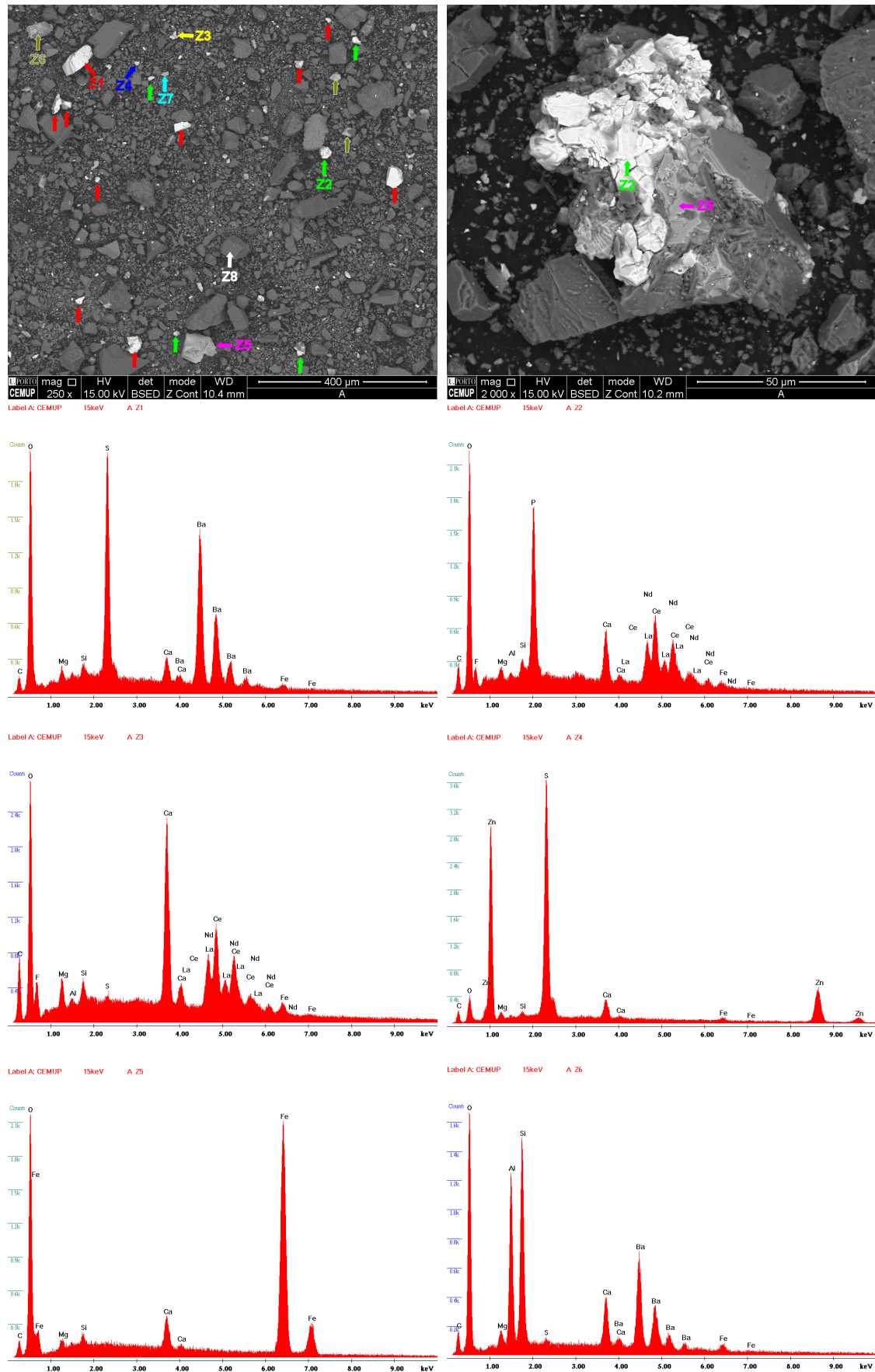


Figure 1. Cont.

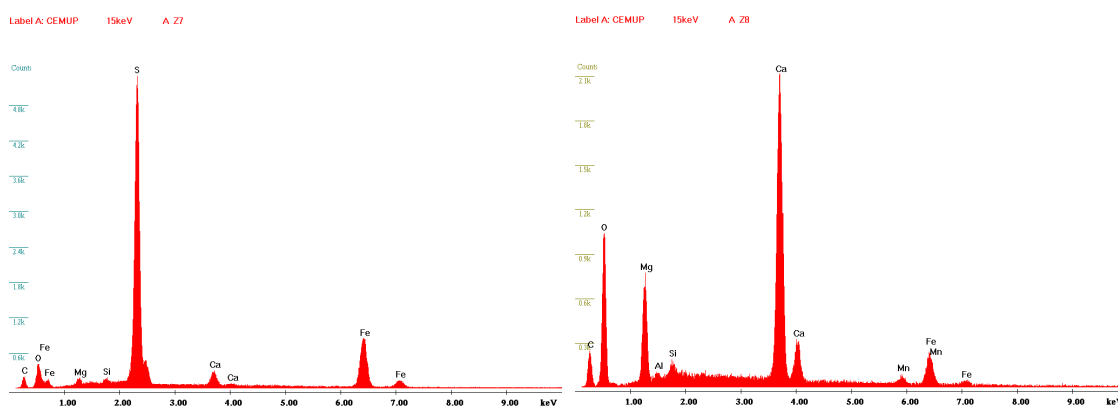


Figure 1. SEM micrographs and EDS spectra of mineral phases identified in the feed sample. Z1 (Barite- BaSO_4); Z2 (Monazite- $(\text{Nd}, \text{La}, \text{Ce})\text{PO}_4$); Z3 (Parisite- $\text{Ca}(\text{Ce}, \text{La}, \text{Nd})_2(\text{CO}_3)_3\text{F}_2$, Synchysite- $\text{Ca}(\text{Ce}, \text{La}, \text{Nd})(\text{CO}_3)_2\text{F}$ or Bastnäs site- $\text{Ce}, \text{La}, \text{Nd}, \text{Y}(\text{CO}_3)\text{F}$); Z4 (Sphalerite- $(\text{Zn}, \text{Fe})\text{S}$); Z5 (Magnetite- Fe_3O_4); Z6 (Barium silicate- BaSiO_3); Z7 (Pyrite- FeS_2); Z8 (Carbonate- CO_3^{-2}).

SEM–EDS observations of the feed sample provided qualitative evidence of textural differences among the REE-bearing minerals. Particles attributed to monazite, Z2, appeared to be relatively more liberated, as they were not commonly observed in association with other mineral phases in the analyzed images. In contrast, fluorocarbonate minerals of the bastnäs site–parisite–synchysite group, Z3, frequently occurred as composite particles associated with magnetite, Z5, as shown in Figure 1. Although the feed material had a relatively fine particle size distribution, with a D90 of approximately $86 \pm 5 \mu\text{m}$, these observations indicate that some REE-bearing fluorocarbonate particles remained associated with iron-bearing gangue minerals.

It should be noted, however, that SEM–EDS observations are qualitative and do not prove the extent of mineral liberation. The observed association between fluorocarbonates and magnetite only suggests that partial locking may have contributed to the limited flotation performance. In such composite particles, the flotation response may depend not only on the REE-bearing phase, but also on the gangue minerals exposed at the particle surface. This could reduce collector access to REE-bearing surfaces and contribute to lower selectivity and recovery. Quantitative liberation data obtained by Mineral Liberation Analysis (MLA) or a similar automated mineralogy technique would therefore be necessary to confirm the role of mineral locking in the flotation response of this ore.

This behavior agrees with recent literature. According to Choi [17], sufficiently fine grinding is often required to liberate bastnäs site from closely intergrown gangue minerals; however, the generation of fine and ultrafine particles can also reduce flotation efficiency. Similar observations were also reported by Akyildiz [7], who identified locked grains as the dominant occurrence form of parisite in the Fen Deposit ore. Nevertheless, the authors reported that, despite the higher degree of monazite liberation resulting in improved recoveries, the flotation performance of monazite remained comparable to that of bastnäs site and parisite. These findings indicate that, while mineral liberation strongly influences flotation response, reagent selectivity, particle surface chemistry, and the behavior of composite particles are also critical factors governing the final separation efficiency.

In addition to the REE-bearing minerals, several gangue and accessory mineral phases were identified. These included barite (BaSO_4) in region Z1, sphalerite ($(\text{Zn}, \text{Fe})\text{S}$) in Z4, magnetite (Fe_3O_4) in Z5, barium silicate (BaSiO_3) in Z6, and pyrite (FeS_2) in Z7. Carbonate phases were also observed in region Z8, likely corresponding to ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$), calcite ($\text{Ca}(\text{CO}_3)$), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and ferroan dolomite ($\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$). The occurrence of these carbonate minerals is consistent with the

mineralogical association commonly observed in REE-bearing deposits, particularly those related to carbonatitic environments.

The presence of these Ca- and Ba-bearing gangue phases is particularly relevant from a processing perspective, as their ineffective rejection can directly limit REE concentrate grade. Minerals such as calcite, dolomite, ankerite, fluorite, and barite may be recovered together with REE-bearing minerals, resulting in concentrate dilution and potentially increasing the complexity of downstream processing and residue management [15].

3.2. Screening Tests for Flotation Reagents

The elemental composition of the products obtained during the flotation tests, determined by XRF and ICP-MS analyses, is presented in Table 3. Calcium (Ca), iron (Fe), manganese (Mn), and barium (Ba) were identified as the dominant elements in both overflow and underflow products. These results are consistent with the complex mineralogical composition of the feed material, which is mainly composed of carbonate gangue minerals, including ankerite, calcite, and dolomite, together with quartz, barite, apatite, and sulfides such as pyrite [7,8].

A broadly similar elemental composition was observed between overflow and underflow products for most flotation conditions evaluated, suggesting limited selectivity in gangue mineral rejection. In particular, the persistence of Ca- and Ba-bearing phases in the overflow products suggests that the ineffective rejection of carbonate and barite-related gangue was one of the main limitations to concentrate upgrading during the reagent screening stage [15]. This poor rejection of Ca- and Ba-bearing phases likely contributed to concentrate dilution and restricted the improvement of REE grades.

These results indicate that the reagent schemes initially investigated were insufficient to promote an effective separation between REE-bearing minerals and carbonate-/barite-rich gangue phases. This limitation may be partly related to the high abundance of carbonate minerals in the ore and to possible similarities in surface response between carbonate gangue and REE-bearing fluorocarbonates under the tested flotation conditions. Furthermore, REE flotation is strongly influenced by dissolved species released from gangue minerals, such as calcite, fluorite, and barite [17]. The dissolved ions can affect reagent performance by modifying mineral surface charge, promoting surface complexation or precipitation reactions, and interfering with collector adsorption or depressant action.

Therefore, the following sub-sections evaluate the effect of depressants, sodium silicate dosage, EDTA, and collectors not only in terms of REE recovery, but also in terms of their ability to reject Ca- and Ba-bearing gangue phases. This difficulty may result from several interconnected interfacial phenomena, including the limited accessibility of exposed rare-earth surface sites, surface-state sensitivity to oxidation, dissolved-ion effects, variations in water chemistry, and competitive adsorption at mineral interfaces [17].

Table 3. Elemental composition of products obtained in the flotation tests.

Stage	Test ID	Ca	Mg	Fe	Ba	Mn	Al (mg/kg)	Sr	Th	Zn	K	Na	
	Feed	152,900	59,820	68,990	18,810	8807	2112	2237	271	169	351	617	
Preliminary screening for depressants	S1	1 ^a Stage_O	202,433	46,191	59,493	38,785	11,568	2798	4014	213	849	473	783
		1 ^a Stage_U	199,261	47,403	73,012	22,287	11,696	3464	3980	212	667	536	742
		2 ^a Stage_O	219,050	46,126	67,163	37,541	11,492	2419	4580	210	976	460	1113
		2 ^a Stage_U	206,300	46,280	72,360	16,864	11,270	4140	4276	167	573	576	1074
	S2	1 ^a Stage_O	128,589	64,408	60,740	11,140	8973	3093	2395	268	645	158	101
		1 ^a Stage_U	133,289	65,778	62,310	12,290	9341	3977	2442	248	235	251	88
		2 ^a Stage_O	113,789	57,958	72,880	7521	8584	4572	2118	221	1,284	276	63
		2 ^a Stage_U	130,689	66,668	62,630	16,190	9536	3583	2443	217	138	191	42
	S3	1 ^a Stage_O	132,189	62,798	67,920	10,400	9322	1778	2436	190	282	77	70
		1 ^a Stage_U	130,489	65,778	63,620	16,590	9121	3409	2466	245	265	194	78
		2 ^a Stage_O	126,489	60,148	65,150	22,700	8976	2020	2401	247	253	104	45
		2 ^a Stage_U	111,489	56,758	53,550	5931	8224	4045	1996	62	206	251	8
	S4	1 ^a Stage_O	158,222	36,144	69,897	18,735	8151	2144	1869	229	826	352	417
		1 ^a Stage_U	162,417	36,350	77,476	14,916	8177	1763	1785	151	280	341	392
		2 ^a Stage_O	156,029	35,683	94,293	16,601	8079	2453	1823	223	607	357	307
		2 ^a Stage_U	159,183	38,304	73,009	14,631	8483	2071	1891	184	189	351	298
	S5	1 ^a Stage_O	164,202	37,381	79,325	15,340	8360	2878	1821	211	1132	411	402
		1 ^a Stage_U	161,044	37,102	77,351	14,926	8297	1804	1842	172	333	344	400
		2 ^a Stage_O	128,758	15,093	69,926	9469	9092	708	484	469	1705	43	19
		2 ^a Stage_U	133,696	14,580	62,056	18,339	9529	474	486	441	313	41	18
Depressant optimization	D1	1 ^a Stage_O	142,389	69,618	46,180	23,820	9561	1651	2700	289	151	77	75
		1 ^a Stage_U	129,789	67,388	70,020	16,300	9412	3970	2435	277	198	232	96
		2 ^a Stage_O	129,689	60,698	49,270	21,540	8862	2149	2518	348	500	115	50
		2 ^a Stage_U	127,689	65,708	67,910	17,970	9454	5640	2365	283	226	265	102
	D2	1 ^a Stage_O	202,433	46,191	59,493	38,785	11,568	2798	4014	213	849	473	783
		1 ^a Stage_U	199,261	47,403	73,012	22,287	11,696	3464	3980	212	667	536	742
		2 ^a Stage_O	219,050	46,126	67,163	37,541	11,492	2419	4580	210	976	460	1113
		2 ^a Stage_U	206,300	46,280	72,360	16,864	11,270	4140	4276	167	573	576	1074

Table 3. Cont.

Stage	Test ID	Ca	Mg	Fe	Ba	Mn	Al (mg/kg)	Sr	Th	Zn	K	Na	
	Feed	152,900	59,820	68,990	18,810	8807	2112	2237	271	169	351	617	
Depressant optimization	D3	1 ^a Stage_O	206,058	44,809	59,008	38,813	11,250	2690	4771	178	1129	461	839
		1 ^a Stage_U	202,557	45,286	75,190	27,895	10,797	2972	4467	218	687	506	1017
		2 ^a Stage_O	216,580	45,471	65,692	34,797	10,944	2214	4693	181	788	424	818
		2 ^a Stage_U	203,437	45,584	70,604	17,595	11,051	4520	4315	174	566	602	774
	D4	1 ^a Stage_O	198,820	45,332	55,538	38,906	11,295	2539	4609	317	1080	450	809
		1 ^a Stage_U	198,982	47,684	73,263	24,475	11,661	3359	4136	280	671	497	798
		2 ^a Stage_O	205,859	45,048	62,236	37,598	11,519	2464	5139	220	1211	461	1136
		2 ^a Stage_U	206,539	46,132	71,581	20,097	11,364	4119	4503	193	576	570	1258
	D5	1 ^a Stage_O	191,863	44,755	55,225	37,313	10,959	2600	3911	196	960	468	813
		1 ^a Stage_U	207,534	47,592	76,978	27,534	11,781	3090	4705	200	744	538	883
		2 ^a Stage_O	202,157	43,917	65,072	42,193	10,787	2216	4610	164	1124	441	894
		2 ^a Stage_U	204,609	45,461	68,156	22,843	11,103	3801	5207	162	593	553	952
	D6	1 ^a Stage_O	172,825	39,109	78,968	20,717	8686	1483	2150	229	524	392	365
		1 ^a Stage_U	163,340	39,049	99,815	14,087	8461	3348	2028	241	628	402	326
		2 ^a Stage_O	170,828	38,490	101,113	18,371	8511	1651	2028	259	484	331	320
		2 ^a Stage_U	163,505	38,785	106,647	17,229	7974	3941	1867	232	292	468	315
Collector optimization	C1	1 ^a Stage_O	142,389	69,618	46,180	23,820	9561	1651	2700	289	151	77	75
		1 ^a Stage_U	129,789	67,388	70,020	16,300	9412	3970	2435	277	198	232	96
		2 ^a Stage_O	129,689	60,698	49,270	21,540	8862	2149	2518	348	500	115	50
		2 ^a Stage_U	127,689	65,708	67,910	17,970	9454	5640	2365	283	226	265	102
	C2	1 ^a Stage_O	204,255	44,676	55,853	31,801	11,237	2532	4123	346	520	438	655
		1 ^a Stage_U	208,134	47,518	71,411	20,173	11,932	3402	4217	263	774	482	731
		2 ^a Stage_O	205,853	44,656	52,357	30,487	10,857	1770	4743	308	765	438	1380
		2 ^a Stage_U	208,367	46,825	80,581	17,833	11,861	4631	4739	241	891	616	947
	C3	1 ^a Stage_O	189,324	44,532	51,689	26,899	10,876	2959	3947	353	513	458	1005
		1 ^a Stage_U	208,150	48,592	70,955	23,321	12,076	3494	4135	263	755	504	884
		2 ^a Stage_O	221,602	46,114	55,381	41,540	11,798	1453	5013	313	872	392	1044
		2 ^a Stage_U	223,321	47,332	77,758	16,042	11,631	4435	4505	222	824	554	1091

Note: Test IDs are defined in Table 2. S1–S5 correspond to preliminary depressant screening tests using sodium silicate, phytic acid, quinic acid, citric acid, and sodium alginate, respectively. D1–D3 correspond to sodium silicate optimization tests without EDTA, whereas D4–D6 correspond to sodium silicate optimization tests with EDTA. C1–C3 correspond to collector comparison tests using OHA, NaOL, and OA, respectively. The suffixes O and U denote overflow, floated product, and underflow, non-floated product, respectively.

3.2.1. Influence of Depressants on Gangue Rejection and REE Recovery

Among the depressants investigated, limited rejection of gangue-associated elements was achieved. Phytic acid promoted a slight reduction in Ba content in the concentrates from both flotation stages, together with minor decreases in Ca and Mg during the second stage (Table 3). This reduction, although limited, may be related to its chelating capacity toward divalent metal ions, particularly Ca^{2+} and Mg^{2+} , due to the presence of phosphate groups in its molecular structure, which can favor adsorption onto calcium-bearing mineral surfaces [13]. Sodium alginate also reduced Ba content in the overflow, mainly during the second stage, possibly reflecting a delayed depressant effect after the removal of readily floatable particles. This behavior is consistent with its anionic polymeric structure, rich in hydroxyl and carboxylate groups, which can complex multivalent metal ions and promote hydrophilization of calcium-bearing mineral surfaces [11]. However, neither phytic acid nor sodium alginate produced promising overall flotation performance, suggesting that its adsorption was either insufficiently selective or not strong enough to depress the dominant gangue phases present in this ore.

In contrast, sodium silicate promoted Ba enrichment in the overflow, while quinic acid reduced Ba content only during the first flotation stage. Both depressants were also associated with a decrease in Al concentration. Citric acid promoted reductions in Mg and Mn contents only during the second flotation stage but showed limited effectiveness in suppressing the other gangue-associated elements. This behavior differs from previous reports in scheelite–fluorite systems, where citric acid has been described as an efficient and selective depressant due to its ability to dissolve calcium species from gangue mineral surfaces [14]. The discrepancy may be related to differences in pH, depressant dosage, collector chemistry, and, more importantly, mineralogical composition. Scheelite is a tungstate mineral with surface properties substantially different from those of bastnäsite, parisite, synchysite, and monazite.

These results indicate that none of the depressants tested was able to achieve an effective rejection of the main gangue-associated elements, particularly Ca and Ba, which remained a key limitation for selective REE upgrading.

Cerium was the most abundant REE in the ore, followed by La, Nd, and Pr (Figure 2). Among the depressants tested, sodium silicate, citric acid, and quinic acid showed the most promising flotation responses. Citric acid produced the highest REE concentrations in the overflow during both flotation stages, with the first stage being the most promising (Figure 2a,b). Silva [8] also reported REE enrichment in carbonatitic ores from the Fen Deposit, with higher TREO grades obtained after the initial flotation stages when citric acid was used in combination with sodium silicate. Although the reagent scheme used in the present study was different, these results suggest that citric acid may perform more effectively when combined with complementary depressant systems, such as sodium silicate, thereby potentially improving selectivity through synergistic reagent interactions.

When both recovery and concentrate grade are considered, sodium silicate and citric acid showed the best overall performance, achieving recoveries of approximately 65% and 70% and TREO grades of 2.1% and 2.3%, respectively (Figure 2c). However, when comparing the two stages, the second stage was found to be essential for the overall recovery, showing TREO recovery efficiencies of 49% and 50% for sodium silicate and citric acid, respectively, compared with 41% and 35% in the first stage, in the same order. On the other hand, the TREO grade was higher in the first-stage concentrate than in the second-stage concentrate, as expected, since the feed to the second stage corresponded to the underflow from the first stage, that is, to a fraction further depleted in REEs.

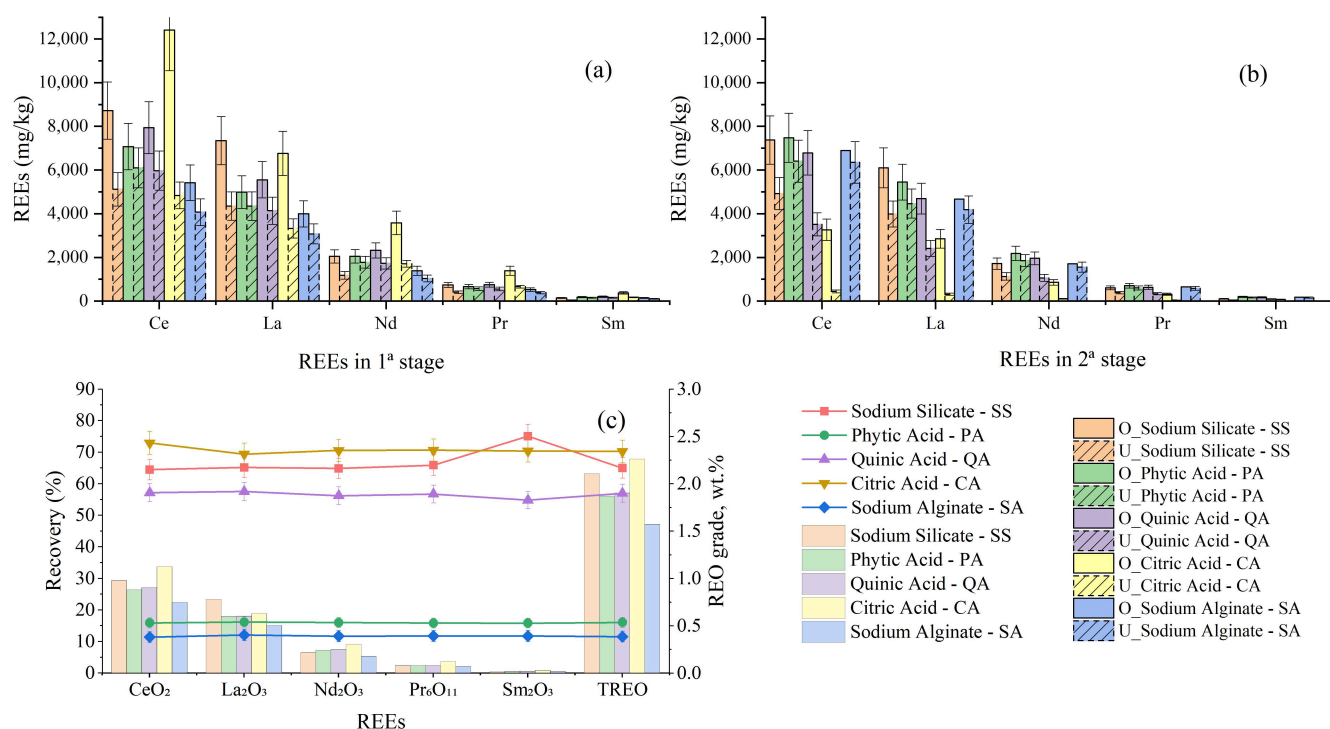


Figure 2. Distribution of rare earth elements (REEs) in the overflow (O, concentrate) and underflow (U) products obtained during the (a) first and (b) second stages of the flotation tests in the presence of different depressants and their corresponding (c) overall recovery and TREO grade of the main REOs.

Quinic acid resulted in a recovery of approximately 57% and a TREO grade of 1.9%. In contrast, phytic acid and sodium alginate produced the lowest recoveries, between 12% and 16%, and TREO grades between 1.6% and 1.9%. For these latter depressants, the second stage did not lead to a significant improvement in either overall recovery or concentrate grade. Overall, the results indicate that the tested depressants affected REE recovery and gangue rejection in different ways; however, none of the reagent schemes evaluated provided a sufficiently selective separation.

Overall, the depressant screening showed that none of the tested reagents achieved effective rejection of the main gangue-associated elements. Although some depressants produced partial reductions in selected gangue elements, these effects were limited and did not translate into substantial TREO upgrading. This indicates that the low concentrate grades were controlled not only by REE recovery, but also by the insufficient depression of carbonate-, fluoride-, and Ba-bearing gangue phases, which represents one of the major selectivity bottlenecks in the flotation of this ore [15].

The poor gangue rejection may be related to several interconnected factors, including mineral intergrowth, incomplete liberation, fine particle dissemination, competitive adsorption at mineral interfaces, and similarities in surface response between gangue minerals and REE-bearing fluorocarbonates [17]. In composite fluorocarbonate–magnetite particles, such similarities or differences in surface response may affect the apparent surface charge of the particles and, consequently, the adsorption selectivity of collectors and depressants. In addition, although dissolved ion concentrations were not measured, the abundance of Ca-, Mg-, and Fe-bearing minerals suggests that pulp chemistry may also have affected reagent performance. Previous studies have shown that dissolved multivalent ions can interfere with depressant adsorption, promote surface complexation or precipitation reactions, and reduce flotation selectivity [3,17,19,23,24]. Therefore, possible dissolved-ion effects should be considered as a plausible contributing factor in future studies.

These results demonstrate the need for further optimization focused not only on improving REE recovery, but also on enhancing the selective rejection of Ca- and Ba-bearing gangue phases. Future work should evaluate depressant dosage, pH, conditioning time, reagent combinations, collector–depressant interactions, and process water chemistry. Additional cleaning and regrinding stages may also be required to improve TREO recovery and grade in this complex carbonatitic ore, as suggested by [8].

3.2.2. Effect of Sodium Silicate Dosage and EDTA on REE Flotation

Sodium silicate was selected for further investigation at different concentrations, in the presence and absence of EDTA, owing to its well-established application as a gangue depressant in rare earth flotation systems, particularly for the suppression of carbonate minerals such as calcite [15,19,20]. In addition, as discussed in Section 3.2.1, sodium silicate exhibited one of the most promising flotation performances among the depressants evaluated, together with citric acid, resulting in higher REE recoveries and improved TREO grades.

The elemental chemical characterization of the flotation products indicated reductions in Fe, Al, and K concentrations in the overflow product even at low sodium silicate dosage, namely 0.25 g/kg SS, both in the absence and presence of EDTA (Table 3). These results suggest that, under the investigated conditions, the sodium silicate concentrations evaluated did not significantly alter the overall elemental distribution of the major gangue-associated elements in the flotation products. Similarly, the addition of EDTA did not appear to substantially affect the bulk distribution of these elements. This indicates that the main differences observed between the tests are more clearly reflected in the REE response than in the overall behavior of the major gangue-associated elements.

However, when considering the REEs, illustrated in Figure 3, a contrasting behavior was observed depending on the sodium silicate dosage employed. In general, REEs were concentrated under all tested conditions (Figure 3a,b), during both the first and second flotation stages, although with prominently different efficiencies.

As shown in Figure 3c, the addition of EDTA negatively affected REE recovery when sodium silicate concentrations were equal to or lower than 0.5 g/kg. Nevertheless, only the lowest sodium silicate dosage (0.25 g/kg) resulted in a reduction in TREO grade. In contrast, at the highest sodium silicate concentration investigated (1 g/kg), the use of EDTA did not significantly affect overall TREO recovery but improved the TREO grade of the concentrate, reaching approximately 2.7%, compared with the feed grade of approximately 1.7% TREO.

When comparing the performance between the first and second stages, a trend similar to that observed for the different depressants was identified. The second stage was important for increasing the overall process efficiency, generally showing TREO recoveries equal to or higher than those obtained in the first stage. Recoveries ranged from 33% to 47% in the first stage and from 33% to 49% in the second stage. On the other hand, the TREO grades were generally higher in the first-stage concentrate, except for the flotation test carried out with 1 g/kg sodium silicate without EDTA, in which the grade obtained in the second stage was higher, reaching 2.5%, compared with 2.2% in the first stage. At the same sodium silicate concentration, but with EDTA addition, the highest TREO grade was observed, approximately 2.9%.

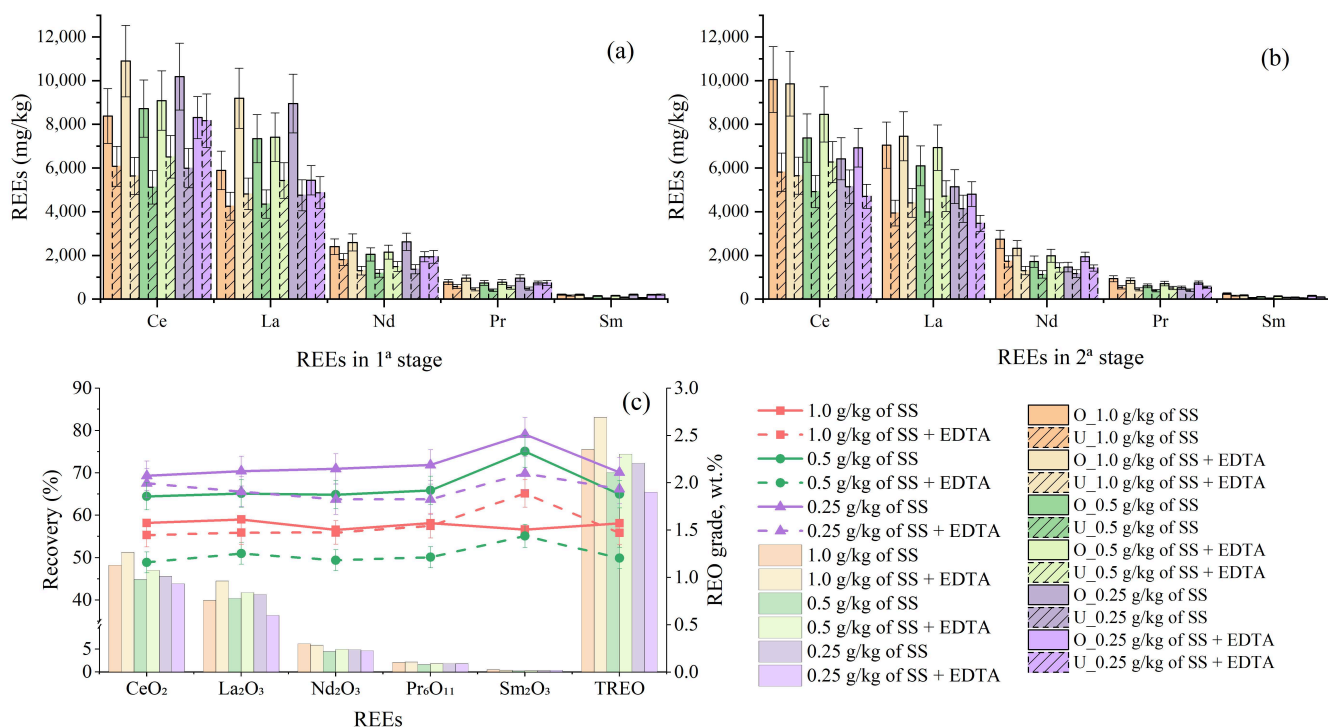


Figure 3. Distribution of rare earth elements (REEs) in the overflow (O, concentrate) and underflow (U) products obtained during the (a) first and (b) second stages of the flotation tests under different sodium silicate concentrations, in the presence and absence of EDTA, and their corresponding (c) overall recovery and TREO grade of the main REOs.

These results suggest that the effect of EDTA was strongly dependent on the sodium silicate concentration. At low sodium silicate dosages, EDTA addition was not sufficient to improve flotation selectivity and was associated with lower REE recovery. This behavior may reflect non-selective interactions involving EDTA, sodium silicate, dissolved species, and mineral surfaces, potentially leading to partial depression of both REE-bearing and gangue minerals. At higher sodium silicate dosages, the improved TREO grade observed in the presence of EDTA suggests that the interaction between sodium silicate, EDTA, and OHA may have favored a more selective flotation response. One possible explanation, supported by previous literature, is that EDTA can complex metallic ions that interfere with collector adsorption or depressant selectivity. In particular, Hu et al. (2024) [9] reported that EDTA can complex Ca^{2+} species associated with bastnäsite surfaces, weakening the co-depression effect between Ca^{2+} ions and sodium silicate and consequently improving octanohydroxamic acid adsorption onto bastnäsite. However, in the present study, dissolved ion concentrations and mineral surface properties were not directly measured. Therefore, the role of EDTA in complexing dissolved or surface-associated cations should be interpreted as a tentative mechanism rather than direct experimental evidence.

This limitation is particularly relevant in complex flotation systems, where several dissolved ions, residual reagents, and mineral surfaces may compete simultaneously [17]. In such systems, complexing agents such as EDTA may partially restore flotation performance by sequestering interfering cations, but their effectiveness may be reduced or modified when multiple ions and residual reagents are present in solution.

Therefore, the flotation tests conducted at different sodium silicate concentrations, in the presence and absence of EDTA, suggest that the combined use of EDTA and sodium silicate can improve REE upgrading under specific operating conditions. In particular, the improvement in TREO grade at the highest sodium silicate dosage is consistent with a possible enhancement in flotation selectivity. However, the proposed role of EDTA in complexing

competing metallic ions and modifying OHA adsorption should be regarded as a literature-supported hypothesis. Future work should include solution chemistry analyses, such as dissolved Ca, Ba, Sr, Fe, Al, and REE concentrations, as well as surface-characterization techniques, including zeta potential measurements and X-ray Photoelectron Spectroscopy (XPS), to verify whether dissolved-ion complexation and surface modification directly contributed to the observed flotation behavior.

3.2.3. Effect of Collectors on REE Flotation Performance

The influence of collector type on the elemental chemical composition of the flotation products is presented in Table 3. The collectors evaluated promoted reductions in the concentrations of several gangue-associated elements in the overflow products, particularly Mg, Fe, Mn, Al, and K, with a more pronounced depression of aluminum-bearing phases. This behavior was consistently observed during both flotation stages. The reduction in Fe concentration for all collectors tested suggests a partial rejection of Fe-bearing gangue minerals, likely associated with pyrite and magnetite.

In contrast, no significant depression of calcium (Ca) and barium (Ba) was observed. This behavior may have negatively affected flotation selectivity, since Ca- and Ba-bearing minerals are frequently associated with gangue phases that interfere with the selective flotation of rare earth-bearing minerals [7,12]. Such behavior is particularly relevant in complexly intergrown ores, where mineral associations can hinder gangue depression and reduce the flotation efficiency of valuable REE-bearing phases, while simultaneously increasing gangue recovery into the concentrate [25]. As already mentioned, if magnetite or gangue phases dominate the exposed surface, reagent adsorption may not reflect the presence of REE-bearing minerals in the particle interior, leading either to poor REE recovery or to non-selective gangue recovery. Consequently, the persistence of Ca and Ba in the overflow products suggests a limitation in the effectiveness of sodium silicate, at the dosage evaluated, to sufficiently suppress these specific gangue constituents, as well as a possible recovery of composite particles containing gangue phases along with the concentrate.

Figure 4 presents the distribution of the main REEs in the flotation products. All collectors evaluated promoted enrichment of REEs in the overflow products during both the first and second flotation stages (Figure 4a,b). However, despite the improvement in REE concentration, the TREO grades remained limited for all collectors tested, reaching approximately 2.4–2.3% (Figure 4c). These results indicate that, although the reagent scheme favored the concentration of REEs in the overflow fraction, a substantial portion of the valuable minerals remained in the underflow products.

The overall recoveries achieved were approximately 57%, 64%, and 59% for OHA, NaOL, and OA, respectively. Among the collectors evaluated, NaOL presented the highest overall recovery, while all collectors exhibited similar TREO grades.

As observed in the previous tests, the second flotation stage played an important role in increasing the overall TREO recovery. The TREO recovery in the second stage ranged from approximately 43% to 54%, whereas in the first stage it ranged from about 17% to 36%. However, the behavior of the TREO grades differed depending on the collector used. For NaOL, the second-stage concentrate presented a slightly lower TREO grade than the first-stage concentrate, with values of 2.3% and 2.4%, respectively. In contrast, for OHA and OA, the TREO grade increased in the second stage, from 2.2% in the first stage to 2.5% and 2.4%, respectively.

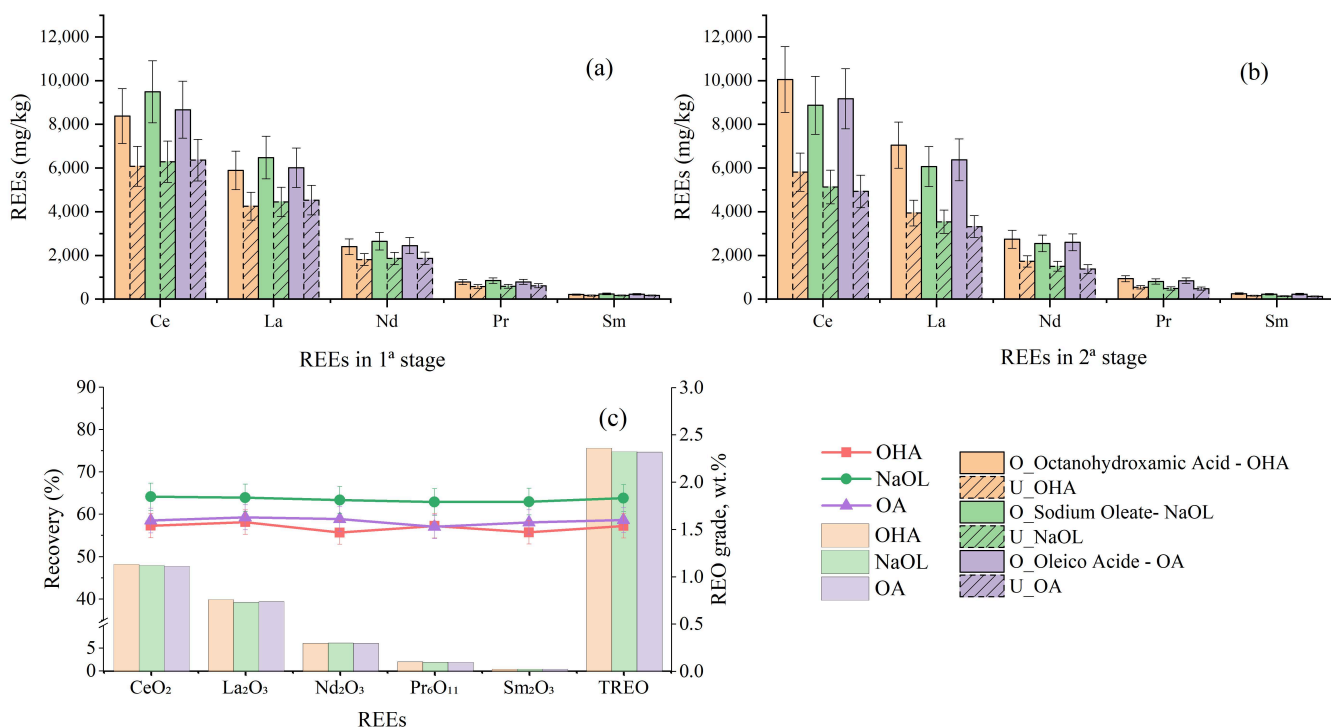


Figure 4. Distribution of rare earth elements (REEs) in the overflow (O, concentrate) and underflow (U) products obtained during the (a) first and (b) second stages of the flotation tests using different collectors, and their corresponding (c) overall recovery and TREO grade of the main REOs.

These findings highlight the need for further process optimization, particularly regarding reagent selection and dosage, as well as possible adjustments in operational parameters. The relatively low recoveries suggest that the current flotation strategy, although effective in promoting REE upgrading, remains insufficient to achieve the recovery levels required for efficient flotation of REE-bearing minerals.

3.3. Challenges and Future Directions for Improving REE Flotation Selectivity

The flotation results obtained in this study show that the beneficiation of REE-bearing minerals from the Fen carbonatite ore is limited by several interconnected factors. Although different depressants, collector systems, sodium silicate dosages, and EDTA addition were evaluated, only moderate TREO enrichment was achieved, and significant amounts of Ca- and Ba-bearing gangue minerals remained in the overflow products. This indicates that reagent modification alone was not sufficient to overcome the selectivity constraints imposed by the ore.

A major limitation may be related to mineral liberation. SEM-EDS observations suggested that REE-bearing fluorocarbonate minerals occur partly as locked or partially liberated particles associated with gangue phases, particularly magnetite. In contrast, particles tentatively attributed to monazite appeared to occur as more liberated grains. This difference is important because the flotation response of a particle is controlled mainly by its exposed surface, rather than by its bulk composition. Consequently, collector adsorption on composite particles is expected to depend on whether the exposed surface is dominated by REE fluorocarbonates, magnetite, or other gangue minerals. Since these phases may present different surface charges, hydroxylation behavior, and affinities for the collector under the flotation pH conditions, partially liberated fluorocarbonate–magnetite particles may exhibit a mixed or non-ideal flotation response. Therefore, poorly liberated fluorocarbonate particles may be lost to the underflow if REE-rich surfaces are not sufficiently exposed,

while composite particles containing gangue phases may report to the overflow by non-selective flotation or entrainment.

The poor rejection of Ca- and Ba-bearing minerals also represents a central bottleneck. The presence of calcite, dolomite, ankerite, fluorite, and barite can dilute the concentrate and reduce TREO grade, even when REE recovery is improved. Thus, the main challenge is not only to recover REE-bearing minerals but also to do so selectively against gangue phases with similar or competing flotation responses. Similar difficulties have been reported for complex REE deposits, where mineral intergrowth, fine dissemination, and surface-chemical similarities between REE minerals and carbonate gangue hinder selective separation and promote gangue recovery into the concentrate [7,25].

Surface and water chemistry may have further contributed to the limited selectivity. Although dissolved ions were not measured in this study, Ca-, Mg-, Ba-, Fe-, and Al-bearing minerals may release multivalent ions into the pulp, depending on pH, conditioning time, mineral solubility, and process water composition. These ions can potentially modify mineral surface charge, interfere with collector or depressant adsorption, and promote surface complexation or precipitation reactions. Previous studies have shown that multivalent ions can affect the flotation of REE minerals with hydroxamic collectors, particularly by modifying bastnäsite flotation behavior [3,23,24]. Therefore, dissolved-ion effects may be considered a plausible contributing factor, but they cannot be confirmed or quantified without solution chemistry data.

Overall, the moderate TREO grades obtained in this study should be interpreted as the result of combined mineralogical and chemical constraints, including possible incomplete liberation, fine particle dissemination, gangue co-recovery, surface-chemical similarities between REE-bearing minerals and Ca- and Ba-bearing gangue phases, and potential water chemistry effects. The SEM-EDS observations provided qualitative indications of mineral associations, particularly between REE-bearing fluorocarbonates and magnetite; however, quantitative liberation analysis would be required to confirm the extent to which mineral locking affected flotation performance.

Future work should therefore prioritize improved liberation, selective depression of Ca- and Ba-bearing gangue minerals, cleaning or regrinding stages, and detailed solution chemistry analyses to clarify the role of dissolved ions in flotation performance. In particular, measurements of dissolved Ca, Ba, Fe, and REE species by ICP-OES or ICP-MS would help evaluate the influence of metal ions on reagent adsorption, gangue activation, and EDTA complexation. These analyses should be combined with surface-characterization techniques such as zeta potential measurements, XPS, and FTIR to better understand surface modification, collector adsorption, and reagent–mineral interactions. In addition, MLA or a comparable automated mineralogy technique would be necessary to quantify mineral liberation, particle associations, and the exposure of REE-bearing phases in composite particles.

4. Conclusions

Overall, the reagent schemes evaluated showed limited selectivity in rare earth element recovery and gangue mineral rejection, reflecting the mineralogical complexity of the Fen carbonatite ore. This response may be associated with several limiting factors, including mineral intergrowth, incomplete liberation, fine particle dissemination, and competitive adsorption at mineral interfaces. However, these interpretations should be regarded as hypotheses based on comparisons with the literature, since their confirmation requires further studies.

Among the depressants tested, despite the limited rejection of gangue material, sodium silicate and citric acid stood out as the most promising reagents, achieving the highest overall TREO recoveries, in the range of approximately 65–70%. Regarding the evaluation of sodium silicate concentration and the use of EDTA, the highest sodium silicate dosage, 1 g/kg, was found to be more favorable for increasing the TREO grade. In addition, EDTA was effective in improving the TREO grade only at this highest sodium silicate concentration, indicating that depressant dosage has a significant influence on the flotation response. In this regard, future studies should consider testing higher sodium silicate dosages to determine whether gangue mineral rejection can be further improved.

The response observed with EDTA may be related to changes in the availability of interfering metallic species in solution. However, this mechanism could not be confirmed based on the experimental data obtained in this study. Therefore, additional investigations into solution chemistry are required to better understand the role of EDTA and its interaction with sodium silicate during flotation.

Finally, among the collectors evaluated, NaOL showed the highest overall TREO recovery, approximately 64%, although the values obtained with OHA and OA were also relatively close, approximately 57% and 59%, respectively. Moreover, all collectors produced similar TREO grades, between 2.3% and 2.4%, indicating that the increase in recovery was not accompanied by a substantial improvement in selectivity. One possible explanation is that incomplete liberation may have limited the exposure of fluorocarbonate mineral surfaces to the collectors, thereby reducing their flotation response and contributing to losses in selectivity. Competitive adsorption at mineral interfaces may also have contributed to this behavior. However, additional data are required to confirm these hypotheses. Therefore, future work should include MLA to quantify mineral liberation and mineral associations, together with surface-characterization techniques such as zeta potential measurements, XPS, and FTIR to better understand collector adsorption and reagent–mineral interactions.

Further, the reagent scheme selected in this study provides the basis for the development of a semi-pilot scale flotation flowsheet, which will be addressed in future work.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

REEs	Rare earth elements (REEs)
EDTA	Ethylenediaminetetraacetic acid
TREO	Total rare earth oxides
LREEs	Light rare earth elements
FDC	ferruginous dolomite carbonatite
OHA	Octanohydroxamic acid
NaOL	Sodium oleate
BHA	Benzohydroxamic acid
OA	Oleic acid
SS	Sodium silicate
PA	Phytic acid
QA	Quinic acid
CA	Citric acid
SA	Sodium alginate
XRF	X-ray fluorescence
ICP-MS	Inductively coupled plasma mass spectrometry
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
MLA	Mineral Liberation Analysis
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
HNO ₃	Nitric acid
HClO ₄	Perchloric acid
HF	Hydrofluoric acid

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