Mineralogical Study of Rare Earth Minerals to Develop a Selective Flotation Process

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Abstract

The similarity in mineralogical properties between rare earth minerals (REM) and associated gangue minerals makes the enrichment process of rare earth oxides (REO) challenging. Although, extensive studies attempted to explain the interaction mechanism between these minerals, much uncertainty still exists about REM flotation. The focus of this study is to develop a selective flotation process while providing mineralogical information for the following targeted REM from the Fen carbonatite complex in Norway; parisite, bastnäsite, monazite and synchysite. The outputs were assessed by chemical analyses methods (i.e., portable X-ray fluorescence spectrometer-pXRF and inductively coupled plasma mass spectrometry-ICP-MS) besides mineralogical characterization via Scanning Electron Microscopy based Automated Mineralogy (SEM-AM). A recovery of 86% and grade of 45% REO were achieved in the final concentrate via a flotation process. In addition, SEM-AM data showed over 70% of each targeted REM were recovered in the final concentrate.

Keywords: Rare earth elements, physical separation, flotation, automated mineralogy

1. Introduction

The decarbonization of Europe is the aim of the Green Deal which is a set of policy initiatives by the European Commission (European Commission, 2020). In other words, the goal is to turn the European Union into a resource-efficient and competitive economy by 2050, with no net greenhouse gas emissions. This transition is expected to enhance the well-being and health of future generations through access to healthy and affordable food and water, cleaner energy sources, and sustainable products (Gregoir and Acker, 2022). The concept of cleaner energy involves its production and utilization. Shifting towards a low-carbon energy system requires scaling up production and international trade of energy transition materials that are essential for producing green energy components (International Energy Agency, 2022). Specifically, rare earth elements (REE) play a pivotal role in the green energy industry including electric vehicles, wind turbines, solar photovoltaic cells, high-efficiency lighting, and hydrogen storage. The worldwide consumption of these elements is projected to increase fivefold in the near future (Geng et al., 2023). The growing demand besides the uncertainties in supply of these strategic elements caused by the Chinese monopole has led to new research (Mancheri, 2015).

There are more than 250 different rare earth minerals; however, the ones which have been mostly focused on in terms of beneficiation are bastnäsite and monazite; the main REE minerals (REM) in Bayan Obo and Mountain Pass deposits (Zhang et al., 2013; Yang, et al., 2015). It is possible to process REM based on physical and/or chemical properties that differ from gangue minerals. Gravity concentration, magnetic and electrostatic separation and froth flotation are the methods used to beneficiate REM. Liberation by comminution is needed for almost all types of ores before beneficiation processes. Gravity, magnetic and electrostatic separation methods have been found feasible, however, neither of the techniques alone are sufficient to achieve the desired recovery and they should be combined with other methods (Jordens et al., 2013).

Froth flotation is the most promising method owing to its tailorable nature for different types of ore with a broad particle size range (Marion et al., 2020). The Fen carbonatite complex, located in southeastern part of Norway – Telemark County, is one of the largest REE deposits in Europe. The complex has an ongoing exploration drilling campaign by Rare Earths Norway and it hosts parisite ($Ca(Ce/La/Nd)_2(CO_3)_3F_2$), bastnäsite ($(Ce/Nd/Y)(CO_3)F$), monazite ($((REE)PO_4)$ and synchysite $Ca(Ce/Nd/Y)(CO_3)_2F$ as REE minerals (Silva et al., 2023; Coint and Dahlgren, 2019). The similarity in physical and chemical properties between REM and associated gangue minerals makes the enrichment process of rare earth oxides (REO) challenging. Although extensive studies attempted to explain the interaction mechanism between these minerals, much uncertainty still exists about REM flotation (Jordens, 2014). As shown in the study published by Silva et al (2023); 60% of recovery of TREO with 34 wt.% of grade is possible via rougher flotation in 50 – 100 µm particle size range.

In the current study, the ore from the Fen deposit with a particle size below 150 µm was used to conduct flotation tests with cleaner steps and define mineral behavior during process for developing a selective flotation process. The outputs were assessed by two chemical analyses methods: portable X-ray fluorescence spectrometer (pXRF), and inductively coupled plasma - mass spectrometry (ICP-MS). Mineralogical characterization via scanning electron microscopy based automated mineralogy (SEM-AM) was applied to characterize and quantify the minerals' phases, particle size and shape, as well as a degree of liberation.

2. Methodology

2.1 Material

The material utilized to conduct the beneficiation trials was collected from Tuftestollen, an historic niobium mine located in Ulefoss, Norway (Norwegian Mineral Directorate, 1957). The ore was crushed using a high-pressure grinding roll (HPGR), and then sieved in a close circuit to obtain a particle size below 150 µm. Flotation kinetics on the same material with a particle size fraction of 50 and 100 µm were previously presented by Silva et al. (2023), which revealed that REM showed a high degree of liberation within that size fraction and improvement in recovery was possible. In the current study the particles below 50 µm were not eliminated in order to study the effect of fine particles on the flotation performance.

2.2 Flotation trials

The flotation trials were conducted, at the Mineral Processing Laboratory at NTNU, following the procedure of 5 rougher and 2 cleaner steps (Fig. 1)

Based on preliminary experimental trials, the flotation tests were run using 1300 rpm and airflow of 200 l/h. Two kilograms of ore, with a particle size below 150 µm, was used for each test. The following chemicals were used: benzohydroxamic acid and Aero® 6493, Na-silicate, Na-carbonate, Brij 58 and citric acid.

At the beginning of each flotation step, pH values were measured and adjusted. Then, the flotation chemicals were added and conditioned with the material. The frother was added right before scrubbing. Both floated and non-floated products were filtered, dried at 80°C for 12 hours, weighed and analyzed.

Wet magnetic separation was applied to concentrate obtained from the second cleaning step to separate any magnetic mineral (e.g. magnetite).

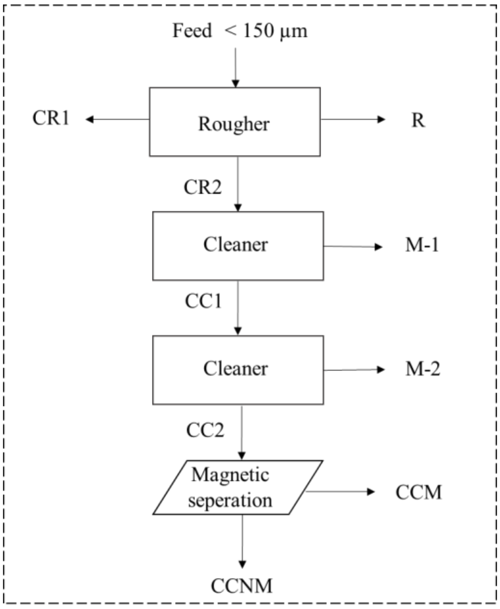


Figure 1. Flowsheet for trials.

2.3 Chemical and Mineralogical Analysis

2.3.1 Sample Preparation

The standard NTNU procedure for conducting ICP-MS analyses uses a HNO_3 solution to digest the samples at 85 °C for 20 hours. Each sample digests approximately 0.4 g of material.

Grain mounts were prepared as polished blocks of samples mixed with epoxy (Logitech 2 Part Epoxy Resin Type 301) in pucks of 25 mm diameter. As recommended by Røisi and Aasly (2018) the graphite powder was added prior to mixing with epoxy to reduce the amount of agglomeration of the fine fractions in the samples. After hardening, 25 mm pucks were cut into cross sections and remolded as 30 mm pucks, with the cross sections facing upwards to avoid density settling issues, and polished. Air bubbles were evacuated from the samples under vacuum before hardening at 30°C for 24 hours.

2.3.2 Chemical Analysis

All the products obtained from flotation trial (9) and feed material were analyzed via X-ray fluorescence hand-held spectrometer (pXRF) and inductively coupled plasma mass spectrometry (ICP-MS). The pXRF analyses were performed with a Niton XL3t X-ray fluorescence hand-held spectrometer using the Ta/Hf calibration from Thermo Scientific. The ICP-MS analyses were performed with a PerkinElmer SCIEX — ELAN DRC-II spectrometer with axial field technology. Both equipment was used at the Department of Geoscience and Petroleum (IGP), NTNU. Additionally, a second ICP-MS analyses round performed by an accredited laboratory (ALS Laboratory Group) was conducted to all the products from the flotation trials. The objective of the second analytical round was to verify the results acquired at IGP.

2.3.3 Mineralogical Analysis

Analyses were performed to further evaluate the flotation process and to have comprehensive information on the mineralogy and the behavior of minerals during the flotation processes. Scanning electron microscopy-based automated mineralogy (SEM-AM), was performed on polished sections of flotation products in the Norwegian Laboratory for Minerals and Materials Characterization (MiMaC). Automated mineralogy was acquired using a ZEISS Sigma 300VP Field Emission SEM equipped with two Bruker X-flash 6|60, 129 eV EDS detectors and ZEISS Mineralogic Software, Mining plug-in. The following microscope settings were used: 8.5 mm working distance (WD), 20kV acceleration voltage, and an aperture of 120 µm. The step size was set to 2 µm due to fine intergrowths of various minerals.

The list of REM and their formulae is presented in Table 1.

Table 1. Chemical formula of minerals (Webmineral, 2023)

Mineral	Chemical formula
Ankerite	$Ca(Fe^{2+},Mg,Mn^{2+})(CO_3)_2$
Apatite	$Ca_5(PO_4)_3(Cl,F,OH)$
Barite	$BaSO_4$
Bastnäsite	$(Ce,La,Nd,Y)(CO_3)F$
Calcite	$Ca(CO_3)$
Ferroan dolomite	$Ca(Mg,Fe)(CO_3)_2$
Magnetite	Fe_3O_4
Monazite	$(Nd,La,Ce)PO_4$
Parisite	$CaCe_2(CO_3)_3F_2$
Pyrite	FeS_2
Synchysite	$Ca(Nd,La)(CO_3)_2F$
Quartz	SiO_2

3. Results and Discussion

3.1 Chemical Analysis

The chemical analyses via ICP-MS for different products are displayed in Table 2 and Figure 2. Cerium oxide (Ce_2O_3), lanthanum oxide (La_2O_3), praseodymium oxide (Pr_2O_3), and neodymium oxide (Nd_2O_3) were used to calculate the total REO (TREO) with a conversion factor of 1.17.

The TREO grade of CC2 is 45 wt.% with a recovery of 72%. TREO grade of CC2 was slightly increased to 48 wt.% after wet magnetic separation and non-magnetic fraction CC2 (CCNM) shows the highest amount of TREO. Regarding cleaning steps, CR2 had a grade of 19 wt.% of TREO while CC1 had 39 wt.%. The maximum grade of sulfur was achieved in the first concentrate (CR1) with a grade of 12 wt.% and 21% of the recovery. The results show that cleaning steps are highly needed to attain a higher recovery of REM. The TREO content of M-1 (6 wt.%) and M-2 (11 wt.%) indicates that further processing is required to improve beneficiation performance.

The chemical analyses of the flotation products via pXRF are given in Appendix A.

The different analytical methodologies (pXRF and ICP-MS) report different compositional data: pXRF reports elemental data, ICP-MS reports oxide data. To compare the methodologies oxides were selected, thus elemental data was converted to oxide. The conversion was carried using trend equations between the different data sources. The data comparison, correlation coefficients and trend equations are given in Appendix B.

Table 2. Elemental concentration obtained from ICP-MS analyses of the feed material and flotation outputs.

Element	**Unit**	**Feed**	**CR1**	**CR2**	**CC1**	**CC2**	**CCNM**	**CCM**	**M-1**	**M-2**	**R**
Y	ppm	22.1	17.6	103.4	189.2	221.7	230.3	10.7	41.5	71.4	8.0
La	%	1.0	0.8	6.1	12.2	14.4	15.4	0.6	1.9	3.5	0.1
Ce	%	1.3	1.1	7.9	15.9	18.6	19.2	0.8	2.4	4.5	0.1
Pr	%	0.1	0.1	0.6	1.3	1.5	1.6	0.1	0.2	0.4	0.0
Nd	%	0.1	0.1	1.8	3.5	4.1	4.5	0.1	0.6	1.0	0.0
Sm	%	0.0	0.0	0.1	0.2	0.3	0.3	0.0	0.0	0.1	0.0
Eu	ppm	41.0	32.2	0.0	458.7	546.1	565.4	23.7	76.7	139.3	8.5
Gd	%	0.0	0.0	0.2	0.3	0.3	0.4	0.0	0.1	0.1	0.0
Tb	ppm	14.1	11.6	84.7	159.9	191.7	199.1	8.1	26.8	49.3	2.1
Dy	ppm	14.3	11.6	79.0	152.2	178.0	189.2	7.8	26.4	48.6	2.8
Ho	ppm	1.3	1.1	6.4	11.9	13.8	14.8	0.7	2.4	4.4	0.4
Er	ppm	13.9	11.4	79.2	153.2	180.6	184.8	8.0	26.1	48.5	2.4

Tm	ppm	0.2	0.2	0.7	1.2	1.3	1.4	0.1	0.4	0.6	0.1
Yb	ppm	1.8	1.4	7.3	12.8	14.8	15.0	0.9	3.1	5.2	0.8
Lu	ppm	< 0.4	< 0.4	0.8	1.4	1.6	1.6	< 0.4	0.4	0.6	<0.4
Th	%	0.0	0.0	0.1	0.2	0.2	0.2	0.0	0.0	0.1	0.0
S	%	0.5	11.7	0.4	0.6	0.5	0.5	0.5	0.5	0.5	0.5
TREE	%	2.5	2.1	16.4	32.9	38.6	40.7	1.5	5.0	9.4	0.3
TREO	%	2.9	2.4	19.2	38.5	45.2	47.6	1.7	5.9	11.0	0.3

(*) TREE = La + Ce + Pr + Nd.
(**) TREO = TREE ×1.17.

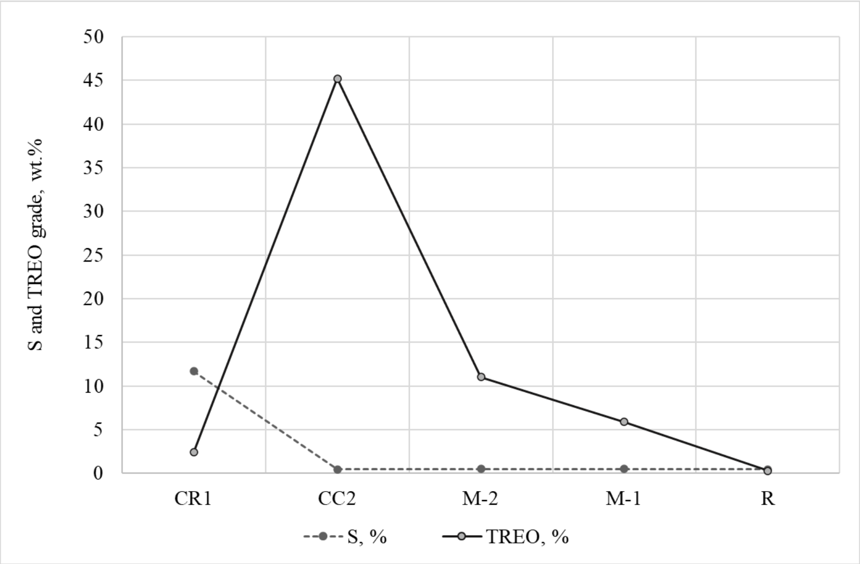


Figure 2. Flotation response by comparing the grade of TREO and S based on ICP-MS analyses.

3.2 Mineralogical Characterization

3.2.1 Modal Mineralogy

The modal mineralogy estimated that the main REM is parisite (1.6%), bastnäsite (0.3%), monazite (0.4%), and synchysite (0.1%). The main gangue minerals are ankerite, ferroan dolomite, calcite and quartz in the feed. REM amount in the flotation products after the first rougher step started to increase significantly. The amount of the main REM, parisite, increased to 30.4% from 1.6% in the final product. The product CCNM shows the highest content of REM with a 48%, while its magnetic counterpart, CCM, had 3% of REM. 3% of REM in the magnetic product and the difference in magnetite amount between CC2 and CCNM shows the magnetic separation step should be improved. The product R predominantly consists of gangue minerals, such as ankerite (50%), ferroan dolomite (18%), calcite (17%), and quartz (3%). Regarding rougher flotation, the CR1 product consisted to a great extent of sulfur-minerals such as pyrite with a 14%. On the other hand, the sulfur-mineral content drops below 1% in the other flotation products. The modal mineralogy of the samples is displayed in Table 3 and Figure 3. Mineral phases at minor concentrations in the products are grouped as 'others'.

Table 3. Modal mineralogy based on main mineral phases detected in outputs and feed from SEM-AM analyses.

Mineral Area %	CR1	CR2	CC1	CC2	CCNM	CCM	M-1	M-2	R	Feed
Ankerite	17.2	25.3	8.6	5.0	4.9	0.6	36.6	25.2	49.9	46.6
Ferroan dolomite	6.3	8.3	3.2	2.3	2.1	0.3	11.7	9.1	18.5	17.4
Calcite	16.3	19.1	14.8	12.5	13.3	1.7	18.7	23.0	17.6	18.1
Parisite	1.5	11.1	23.0	29.2	30.4	2.0	3.2	6.1	0.2	1.6

Monazite	0.3	1.7	3.9	4.7	4.8	0.2	0.5	0.6	0.0	0.4
Bastnäsite	0.3	3.0	6.5	9.3	9.7	0.6	0.8	1.6	0.1	0.3
Apatite	0.4	4.2	4.6	3.5	3.7	0.1	4.5	7.3	0.8	1.4
Quartz	11.4	6.6	8.7	8.8	8.0	1.3	6.9	10.5	3.1	3.6
Magnetite	0.4	1.5	1.8	2.3	0.9	82.5	1.7	1.3	0.1	0.4
Barite	0.7	1.6	1.2	1.3	1.5	0.4	2.0	2.8	2.0	1.7
Pyrite	14.0	0.1	0.4	0.4	0.6	0.0	0.1	0.2	0.0	0.3
Synchysite	0.1	1.1	2.6	3.1	3.0	0.1	0.3	0.5	0.0	0.1
Others	7.6	2.6	2.7	1.1	0.9	0.7	2.2	1.6	1.2	1.3

The flotation response of the minerals based on automated mineralogical data is shown in Figure 4. The total amount of pyrite, pyrrhotite, molybdenite and sphalerite in each product is provided under the category of sulfides (S-minerals). As shown by Silva et al. 2023, the data correlate with the chemical analysis results for CR1 showing a high amount of sulfides and a low amount of REM.

Only pyrite, which is the main sulfide in the ore, will be included in further mineralogical characterization studies within this paper. Results show that the product after second cleaning step - CC2 consists of ca. 29 wt.% of parisite, 9 wt.% of bastnäsite, 5 wt.% of monazite and 3 wt.% of synchysite.

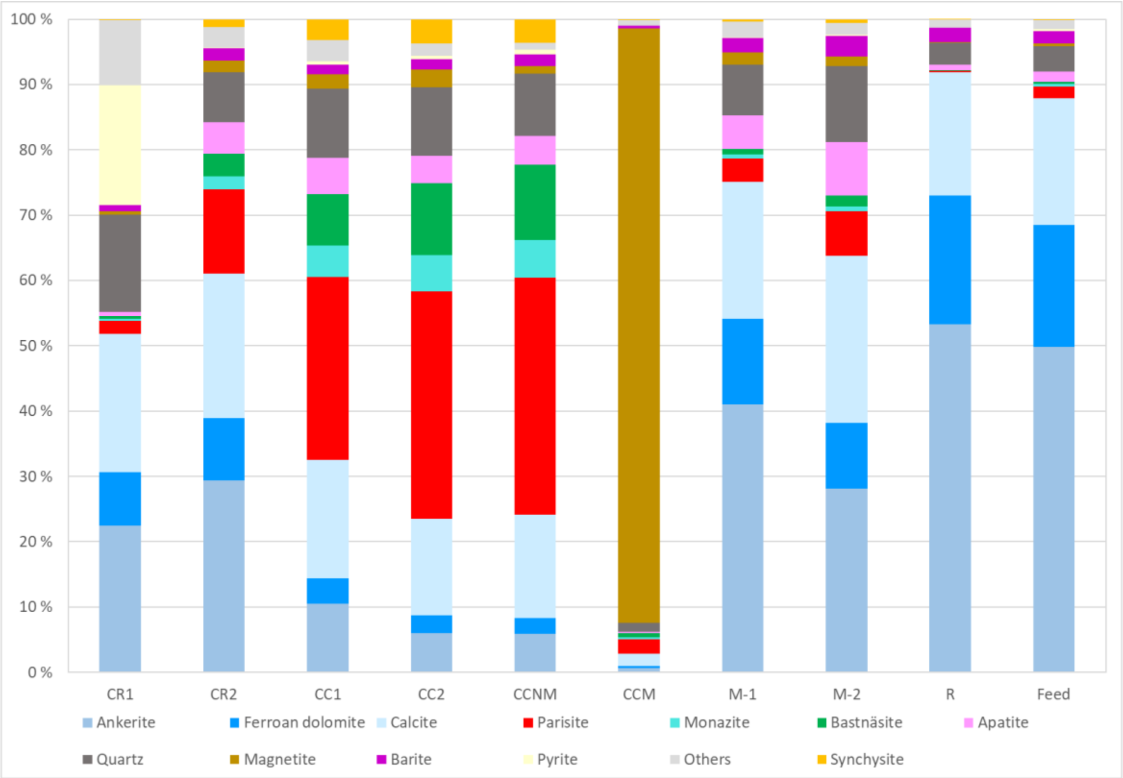


Figure 3. Modal mineralogy given in area % of the investigated samples gained by SEM-AM.

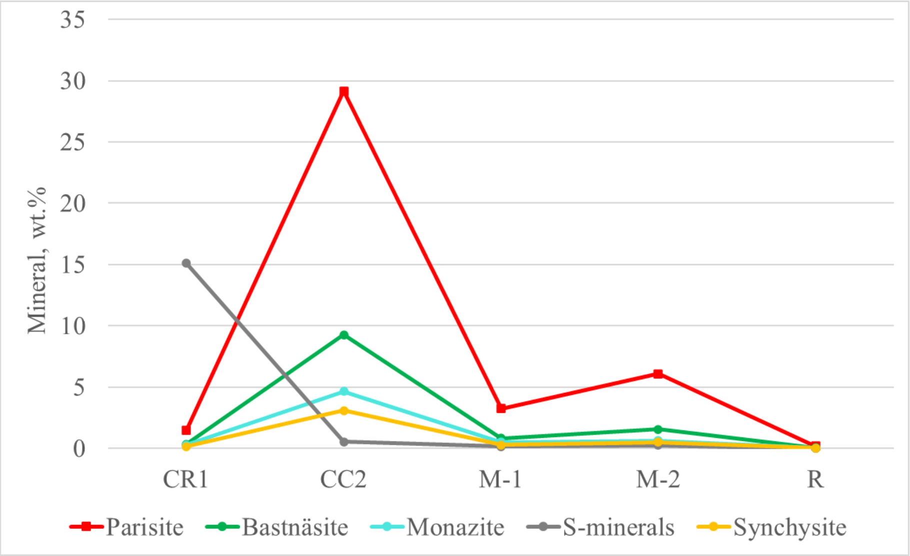


Figure 4. Flotation response of S-minerals and REE bearing minerals based on AM data.

3.2.2 Liberation Analysis

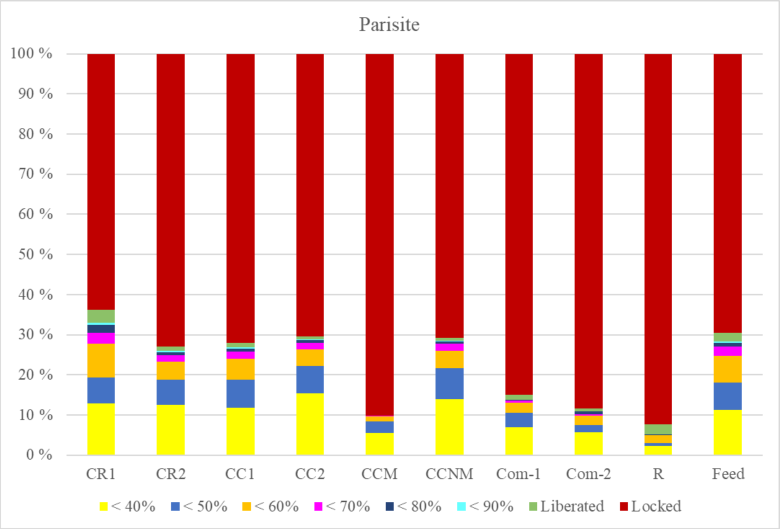
Exposed particle perimeters were used to assess the liberation degree of the minerals. The degree of liberation for REM and pyrite is shown in Table 4. Monazite exhibits the highest degree of liberation within all flotation products. Synchysite is the mineral with the lowest degree of liberation; 87% of the particles are locked in the product after second cleaning step (CC2). Over 60% of the REM in the flotation products and the feed are locked except monazite; nevertheless, it is mostly in the composite form indicating further grinding is needed. In Figure 5, different classes of liberation are displayed for each product. 98% of the bastnäsite particles in the non-floated material are locked while the ratio for parisite is 92%, for synchysite is 81% and for monazite is 78%. CCM had the second highest amount of locked REM particles after non-floated material which explains the amount of 5 wt.% TREO. Middlings (M-1 and M-2) follow non-floated material within the flotation products with the second highest number of locked particles which indicates further grinding steps are also needed for middlings. The first concentrate (CR1) had the lowest amount of the locked and highest amount of the liberated REM compared to the other products. Mineral liberation analysis shows that it is possible to enhance the recovery performance of the process by particle size reduction.

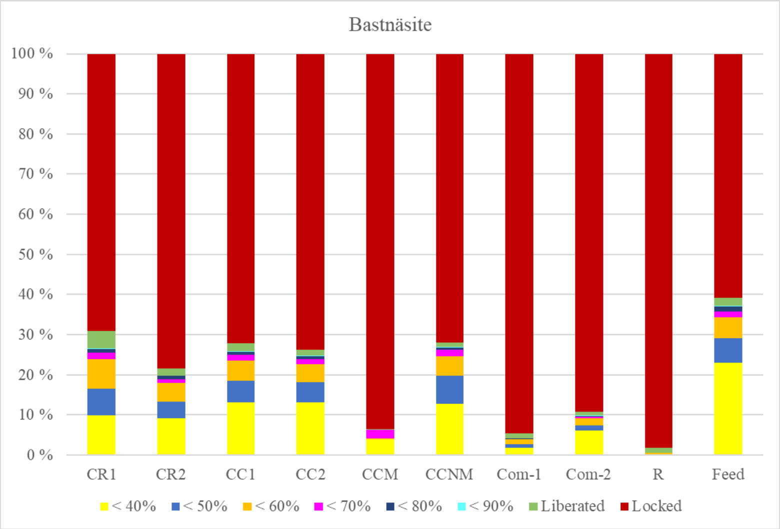
Table 4. Degree of liberation based on partial perimeter for REM based on partial perimeter per flotation output.

Product	Liberation class	Parisite (%)	Bastnäsite (%)	Monazite (%)	Synchysite (%)	Pyrite (%)
CR1	Liberated	3.3	4.2	6.9	6.5	1.5
	Composite	32.7	26.6	49.9	18.8	4.4
	Locked	64.0	69.2	43.1	74.6	94.1
CR2	Liberated	1.2	1.7	4.6	2.9	5.5
	Composite	25.9	72.3	72.3	10.6	21.9
	Locked	72.9	78.6	23.1	86.4	72.7
CC1	Liberated	1.2	2.0	4.1	2.7	3.3
	Composite	26.7	25.8	69.3	11.9	6.0
	Locked	72.1	72.3	26.6	85.4	90.7
CC2	Liberated	0.9	1.3	2.7	2.1	2.5
	Composite	28.7	24.8	75.7	10.6	5.1
	Locked	70.4	73.9	21.6	87.3	92.4
CCM	Liberated	0.1	0.6	0.4	0.5	0.0
	Composite	9.8	6.3	38.6	1.2	0.0

	Locked	90.1	93.1	61.0	98.4	100.0
	Liberated	0.8	1.1	2.6	1.9	0.6
CCNM	Composite	28.4	26.9	76.3	9.0	0.0
	Locked	70.8	71.9	21.1	89.1	97.5
	Liberated	1.2	1.3	3.9	4.4	3.0
M-1	Composite	13.8	4.1	41.0	6.5	16.1
	Locked	85.0	94.6	55.2	89.1	80.9
	Liberated	0.7	1.0	3.5	2.5	1.5
M-2	Composite	10.9	9.8	40.7	13.9	11.0
	Locked	88.4	89.2	55.8	83.7	87.5
	Liberated	2.5	1.2	7.7	3.4	6.9
R	Composite	5.1	0.5	13.6	15.6	10.3
	Locked	92.4	98.3	78.6	81.0	82.8

Liberation classes: Liberated = >90%; Composite = 90-30%; Locked = <30%.





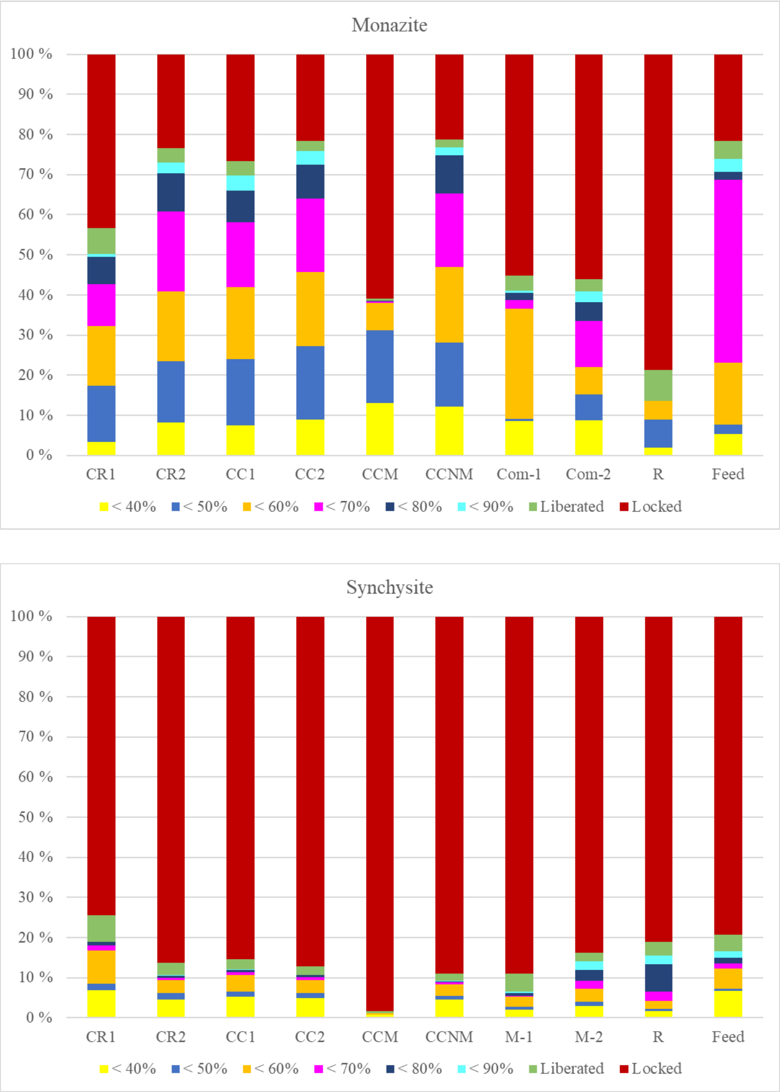


Figure 5. Degree of liberation for parisite, bastnäsite, monazite, synchysite based on partial perimeter for flotation products and feed material.

The selectivity curve (grade-recovery) based on the SEM-AM data of the flotation process is presented in Figure 7. A concentration of 29 wt.% parisite with a recovery of 74%, a concentration of 9 wt.% bastnäsite with a recovery of 77%, a concentration of 5 wt.% monazite with a recovery of 73% and a concentration of 3 wt.% synchysite with a recovery of 71% were achieved in CC2. Sulfide minerals (pyrite, pyrrhotite, molybdenite and sphalerite) were floated mostly in the first rougher step (CR1) with a concentration of 15wt.% and a recovery of 78%. At least 70% of all the REM are recovered in CC2 using the previously described flotation procedure.

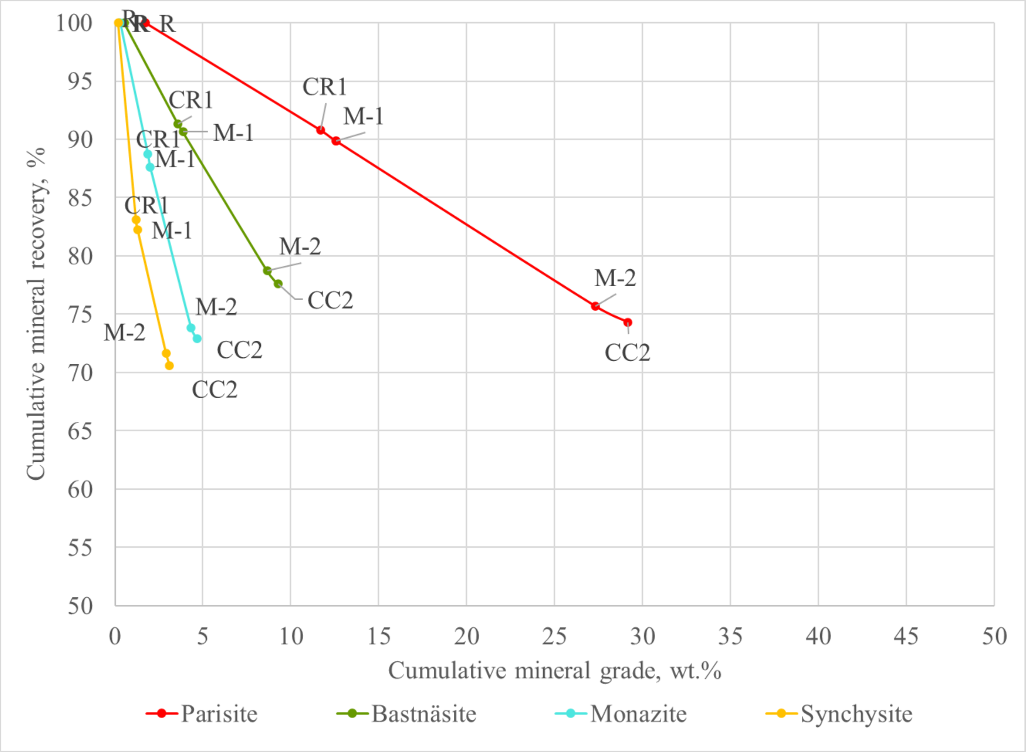


Figure 7. Selectivity curve of REE minerals based on AM data.

4. Conclusions

The flotation performance of three trials under the same conditions demonstrated consistent recovery of REO in CC2, indicating a high level of repeatability. Based on ICP-MS data, recovery of 86% and grade of 45% rare earth oxides were achieved in CC2 via a flotation process. In addition, SEM-AM data showed over 70% of each target REM was recovered in CC2. The grade and recovery values of CR2 and CC1 highlight that cleaning steps are crucial to achieving the desired recovery in the final product. The grade is slightly improved via wet magnetic separation of CC2. However, the necessity of this step should be determined in terms of next processing stages.

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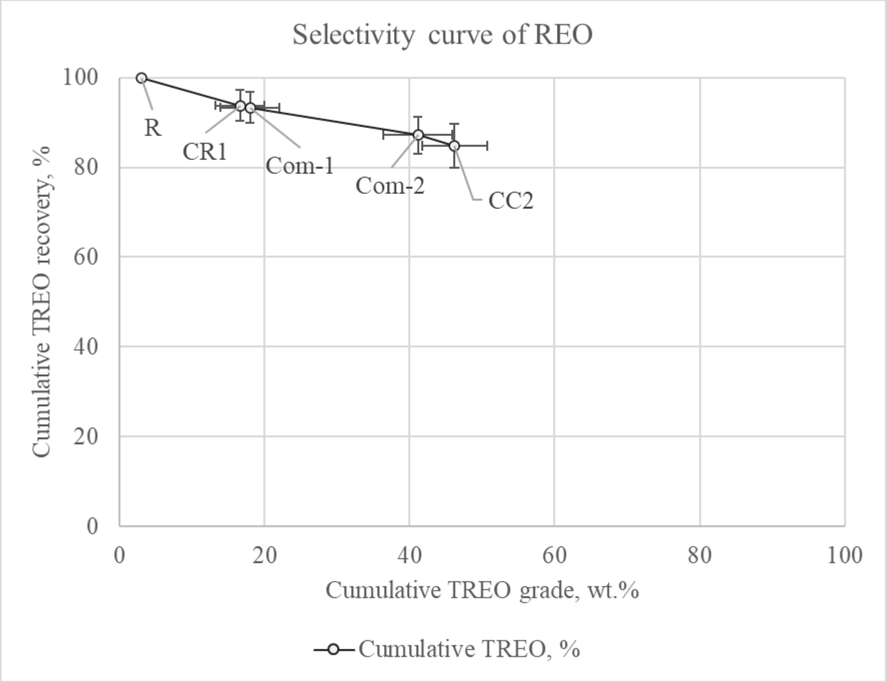
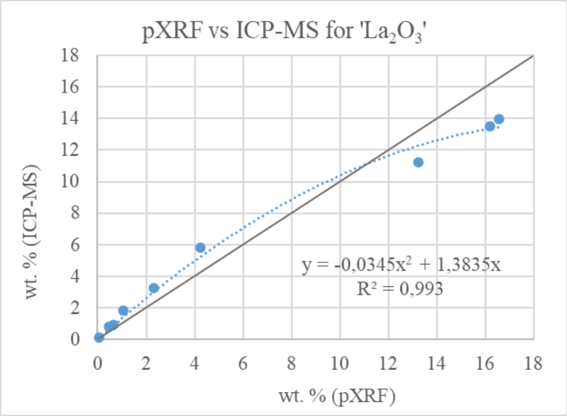
Appendix A.

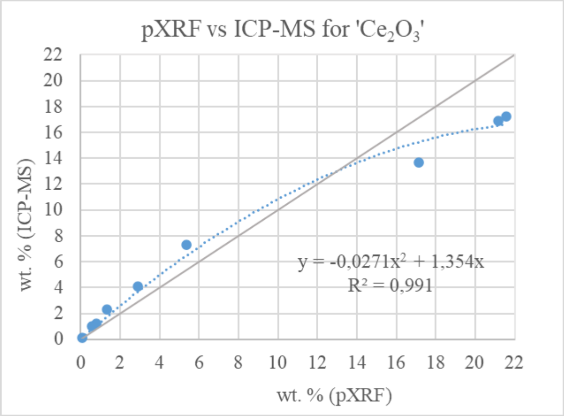
Flotation performance of multiple trials at same conditions, based on pXRF data (3 tests).

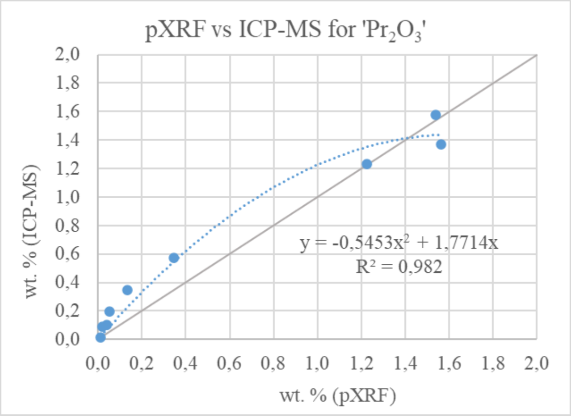


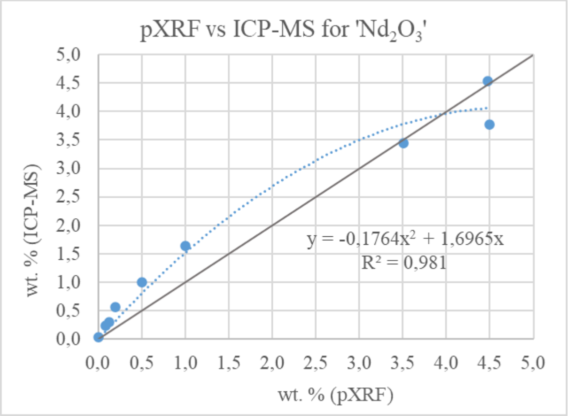
Appendix B.

The equations for calculation of the REO composition from pXRF data and the coefficients of the correlation with the calibration curves (between pXRF and ICP-MS).









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