

Flotation-Calcination-Magnetic Separation Hybrid Process for Concentration of Rare Earth Minerals Contained in a Carbonatite Ore

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Abstract

A hybrid process consisting of flotation and magnetic separation has been developed to concentrate multi-phase rare earth minerals associated with a carbonatite ore that contains a significant amount of niobium. The deposit is known to contain at least 15 different rare earth minerals identified as silico-carbonatite, magnesiocarbonatite, ferrocyanatites, calciocarbonatite, REE/Nb ferrocyanatite, phosphates and niobates. Although no collector exists to float all the different rare earth minerals, the hydroxamic acid-based collectors have shown adequate efficiency in floating most of these minerals. 92% recovery of total rare earth oxide (TREO) and niobium in 45% mass was possible at d_{80} of <65 microns grind size. It was also possible to reduce the mass pull to 28%, but TREO and Nb's recovery dropped to 85%. Calcination of the concentrate followed by quenching and fine grinding to <25 μm allowed upgrading the flotation concentrate by magnetic separation. It was demonstrated that at least 87% TREO and 85% Nb could be recovered in 16% of the feed mass. The paper discusses the overall concept of the flowsheet and the experimental strategies that led to this process.

Keywords

Flotation, Calcination of Rare Earth Flotation Concentrate, Magnetic Separation

1. Introduction

Rare earth elements (REEs) include the fifteen lanthanides, yttrium and scandium. They are found in more than 250 minerals, worldwide [1]. However, only about 60 of them contain REEs in significant amounts to warrant extracting.

Over 95% of the world's rare earth oxides (REOs) come in the form of three minerals [2] [3]), namely bastnaesite (Ce, La, Y)CO₃F, monazite (Ce, La, Nd, Th)PO₄ and xenotime Y(PO)₄. An estimated 51.4% of global REO resources are hosted by carbonatite deposits [4]. Any one of the REEs, or commonly all of them, can be found in these deposits. As the demand for REEs currently considered critical (Nd, Eu, Tb, Dy and Y) increases due to the ever-increasing applications in advanced technologies, many deposits containing other forms of REE minerals will have to be developed. REE minerals are extensively dispersed and intergrown with several oxides, silicates, carbonates, and phosphate minerals. Consequently, it is possible to liberate them only at fine grinding and is thus difficult to separate and produce high-grade rare earth mineral concentrates. Most of these minerals contain other important elements such as tantalum (Ta), niobium (Nb), uranium (U), and thorium (Th) in varying quantities. REE minerals in the same ore may exist as carbonates, fluorocarbonates, niobates, silicates, phosphates etc., in association with gangue minerals belonging to different mineralogical groups.

Classification of REE deposits based on their mineralogy is still a work in progress. The U.S. Geological Survey classification in 2013 consisted of 34 different mineral deposits [5]. The two most important subclasses of alkaline rocks concerning REE deposits are the carbonatites and peralkaline rocks. At present, mineral deposits related to carbonatites account for most REEs production [5]. The most famous examples of carbonatite REE deposits are the Bayan Obo deposit in Inner Mongolia (China), and the Sulphide Queen Carbonatite of the Mountain Pass district in California. The only two significant mines outside China: Mt. Weld and Mountain Pass (although production is currently on hold) are carbonatite-type deposits. The International Union of Geological Sciences (IUGS) system of igneous rock classification defines carbonatites as having more than 50% of primary carbonate minerals, such as calcite, dolomite, and ankerite, and less than 20% SiO₂. Carbonatite REE deposits are enormously enriched in light REEs, particularly lanthanum, cerium, and neodymium.

Understanding each class of the REE mineral deposits' mineralogical characteristics is critical for determining the most suitable processing and extraction options. It is not uncommon to have several different mineralogical compositions within one deposit. An excellent example of this case is the Montviel REE deposit located in Quebec, Canada, which is the subject of this research and paper. Unlike most precious metals and base metal ores, where separation involves only a few minerals, the beneficiation of rare earth ores requires selective separation of a host of REE-bearing minerals (**Table 1**), each of which occurs in small quantities.

The Montviel deposit belongs to the carbonatite class of deposits. Its complex mineralization consists of silicocarbonatite, magnesiocarbonatite, ferrocarnatites, calciocarbonatite, apatite-bearing and REE/Nb ferrocarnatite. A detailed mineralogical study by SGS-Lakefield identified the main REE-minerals as hua-

nghoite and cebaite, which belong to the bastnaesite-synchysite family of fluoro-carbonate minerals where pyrochlore is the main Nb-bearing mineral. A recent study by Nadeau *et al.* [6] did not identify any REE fluorocarbonate, bastnaesite-(Ce), at the Montviel deposit. They stated the identification of REE carbonates and fluorocarbonates was challenging. Nevertheless, the REE minerals positively identified are shown in **Table 1**.

Mineralogical analysis of the ore sample used in this investigation revealed that carbonate minerals shown in **Table 2** account for over 90% of the ore sample. Other minor gangue minerals present in the ore are listed in **Table 3**. The relative abundance of major minerals as determined by XRD and image analysis is shown in **Table 4**. The dominant gangue minerals are ankerite/dolomite (74.7%), siderite (9.10%), quartz (4.80%) and calcite (3.70%). The assay for the head sample is shown in **Table 5**.

The ore was selected for in-depth mineral processing research primarily for its complexity and inadequate response to standard beneficiation methods such as flotation, magnetic and gravity separations. It represents the most important class of primary RE deposit as a carbonatite ore, the only type producing rare earth elements to date.

Table 1. Minerals known to contain REEs and Nb in the Montviel ore deposit.

Mineral	Formula	S.G.
Allanite-(Ce)	$\text{Ca}_{1.26}\text{Ce}_{0.74}\text{Al}_{1.83}\text{Fe}_{1.17}(\text{SiO}_4)_5(\text{OH})$	3.3 - 4.2
Ancylite-(Ce)	$\text{Sr}(\text{Ce}, \text{La})(\text{CO}_3)_2(\text{O.H.})\cdot\text{H}_2\text{O}$	3.9
Burbankite	$(\text{Na}, \text{Ca})_3(\text{Sr}, \text{Ba}, \text{Ce})_3(\text{CO}_3)_5$	3.5
Carbocernite	$(\text{Na}, \text{Ca})(\text{Sr}, \text{REE}, \text{Ba})(\text{CO}_3)_2$	
Cebaite	$\text{Ba}_3\text{Ce}_2(\text{CO}_3)_5\text{F}_2$	4.8
Cordylite	$(\text{Na}, \text{Ca})\text{Ba}(\text{REE}, \text{Sr})(\text{CO}_3)_4\text{F}$	4.4
Ewaldite	$(\text{Ba}, \text{Sr})(\text{Ca}, \text{Na}, \text{REE}, \text{Y})(\text{CO}_3)_2$	3.3
Huanghoite	$\text{BaRE}(\text{CO}_3)_2\text{F}$	4.6
Kukhareenkoite-(Ce)	$\text{Ba}_2\text{REE}(\text{CO}_3)_3\text{F}$	4.6
Monazite-(Ce)	$(\text{Ce}, \text{La}, \text{Nd}, \text{Th})(\text{PO}_4)$	4.6 - 5.7
Qaqarssukite-(Ce)	$\text{Ba}(\text{Ce}, \text{REE})(\text{CO}_3)_2\text{F}$	4.6
Synchysite	$(\text{CaREE})(\text{CO}_3)_2\text{F}$	4.21
Xenotime-(Y)	YPO_4	4.4 - 5.1
Parisite	$\text{CaCe}_2(\text{CO}_3)_3\text{F}_2$	4.4
Petersenite (Ce)	$\text{Na}_4\text{Ce}_2(\text{CO}_3)_5$	3.9
Barium-Strontium	BaSrNaREE Phase REE	
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$	3.1
Pyrochlore	$(\text{Na}, \text{Ca})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})$	4.2 - 6.4
Fergusonite-(Y)	YNbO_4	5.1

Table 2. Ca, Sr, Mg and Ba gangue carbonates.

Mineral	Formula	S.G.
Calcite	CaCO ₃	2.7
Dolomite	CaMg(CO ₃) ₂	2.9
Siderite	FeCO ₃	3.8
Strontianite	SrCO ₃	3.8
Norsethite	BaMg(CO ₃) ₂	3.8
Barytocalcite	BaCa(CO ₃) ₂	3.7
Witherite	BaCO ₃	4.3
Ankerite	Ca(Fe ²⁺ , Mg, Mn)(CO ₃) ₂	3.1

Table 3. Other minor gangue minerals.

Mineral	Formula	S.G.	Magnetic Properties	Hardness
Quartz	SiO ₂	2.6	Diamagnetic	7
Chlorite	(Mg, Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	2.6 - 3.4		2 - 2.5
Pyrite	FeS ₂	4.9 - 5.0	Paramagnetic	6 - 6.5
Sphalerite	ZnS	3.9 - 4.2	Diamagnetic	3.5 - 4
Cancrinite	Na ₆ Ca ₂ Al ₆ Si ₆ O ₂₄ (CO ₃) ₂	2.5		
Microcline	KAlSi ₃ O ₈	2.6		
Nepheline	(Na, K)AlSi ₃ O ₄	2.7		
Sodalite	Na ₈ (Al ₆ Si ₆ O ₂₄)Cl ₂	2.2		

Table 4. X-ray diffraction analysis of the head sample.

Mineral	Quantity (%)	Mineral chemical formula
Ankerite/Dolomite (Mn)	74.70	Ca(Mg, Fe, Mn)CO ₃
Siderite	9.10	FeCO ₃
Quartz	4.80	SiO ₂
Calcite	3.70	CaCO ₃
Burbankite	3.40	(Na, Ca) ₃ (Sr, Ba, Ce) ₃ (CO ₃) ₅
Petersenite (Ce)	1.70	Na ₄ Ce ₂ (CO ₃) ₅
Allanite-(Ce)	1.10	Ca _{1.26} Ce _{0.74} Al _{1.83} Fe _{1.17} (SiO ₄) ₃ (OH)
Biotite	0.90	K(Mg, Fe ²⁺) ₃ [AlSi ₃ O ₁₀ (OH, F) ₂]
Chlorite	0.40	(Mg, Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈
Celestine-Ba	0.20	(Sr, Ba)SO ₄
Total	100.00	

Table 5. Head sample assay.

	Ce ₂ O ₃	Pr ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	Nd ₂ O ₃	Dy ₂ O ₃	TREO						LOI
	1.1	0.09	0.01	0.72	0.33	0.002	2.24						
Nb₂O₅	Al ₂ O ₃	Ba ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	31.01
0.31	0.98	4.87	17.87	0.01	20.62	0.75	7.65	2.1	1.66	0.2	5.91	0.8	

Yu *et al.* [7] conducted exploratory tests on this ore to compare the effects of collector type and dosage, grind fineness, and pulp temperature. They investigated several collectors such as: a fatty acid (Sylvat FA2), phosphoric acid ester (Clariant 1682), alkyl hydroxamate (Aero 6493), salicyl hydroxamic acid, and T610, another variant of salicyl hydroxamic acid manufactured in China. Despite the very good recovery of 73% Ce_2O_3 (comparable to TREO recovery) in 22% of the mass, the recovery of Nb_2O_5 was poor, only ~9%. Additional investigations that employed a combination of gravity separation and flotation at a grind size of 80%—72 μm did not achieve any benefit. Gravity separation alone yielded only 32% Nb_2O_5 and 27% Ce_2O_3 recovery in a concentrate accounting for 14% of the mass. Cleaning of the gravity concentrate using either gravity or magnetic separation was unsuccessful. Scavenging the gravity tailings by flotation, utilizing a combination of fatty acid and alkyl hydroxamate collectors and sodium silicate and carboxyl methylcellulose (CMC) depressants, resulted in 84% Nb_2O_5 and 74% Ce_2O_3 recovery in a combined gravity and flotation concentrate in 43% of the mass. The gravity concentration amenability tests conducted using Wilfley Table, Mozley Table, Falcon Enhanced Gravity Concentrator, and heavy media separations did not yield results comparable to those obtained by flotation.

The current investigation achieved higher than 92% TREO and Nb recoveries at 45% mass pull using flotation only. Re-grinding the concentrate before cleaning did result in significant upgrading but at reduced recoveries. The rougher and scavenger flotation concentrates were combined and submitted to SGS Lakefield for hydrometallurgical processing. Lixiviation of the concentrate using hydrochloric acid yielded REE extractions of ~99%. An overall (from ore in the ground to final precipitate) REE recovery of 80% was obtained through a series of selective precipitation steps.

This paper presents the advancements made in improving the physical separation conditions and upgrading the flotation concentrates by using magnetizing calcination followed by concentrate regrind and magnetic separation techniques.

2. Experimental

The effects of reagents, reagent addition points, pH, pulp de-sliming, conditioning intensity, particle size distributions and temperature were studied using a 1 kg sample wet ground to a d_{80} of 37 μm at 66% solids. Both pH and temperature were monitored and tightly controlled. After several reagent combinations were tested, alkyl hydroxamic acid (collector), Na-silicate (dispersant), and carboxymethyl cellulose (depressant) were found to have the right synergy to recover both the REE- and Nb-bearing minerals. The collector used was the Aero 6493 supplied by Cytec and the dispersant was the sodium metasilicate pentahydrate ($(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O})$). The depressant (CMC) used was $\text{C}_8\text{H}_{15}\text{NaO}_8$ (DS = 0.7) and supplied by Fisher Scientific. Although no collector exists synthesized to float all the different rare earth minerals and Nb-bearing minerals concurrently, the alkyl hydroxamic acid has shown adequate efficiency of floating most of these miner-

als. Due to the frothing characteristics of the collector, no additional frother was needed.

The flotation concentrate obtained under optimum grind size and flotation chemistry after multiple reagents and flotation investigations was calcined, re-ground to a d_{80} of 25 μm and magnetically upgraded.

Equipment

A modified flotation vessel (2.75 L volume) with a froth crowding dome and a forward froth deflecting plate was fitted to a Denver agitation system to allow unassisted and unrestricted concentrate froth flow (**Figure 1**). 0.5 L/min of air-flow and agitation speed of 1200 rpm was used throughout the experiment. Due to the new cell design, pulp level control was neither required nor desired as it dilutes the pulp unnecessarily. Timed flotation using this flotation system accurately predicts both metal recovery and mass pull when the well-known flotation kinetics model (Equation (1)) is used. R_t is a recovery or mass pull at time t , k is a flotation rate constant, and R_∞ is a recovery or mass pull at infinite time.

$$R_t = R_\infty (1 - e^{-kt}) \quad (1)$$

Calcination of flotation concentrate was carried in a small benchtop temperature-controlled furnace. The furnace was preheated to the set temperature before a sample loaded into a ceramic crucible was introduced. The furnace cavity was open to the atmosphere through a 2.5 cm diameter hole at the top of the furnace. The magnetic separator (**Figure 2**) consists of two sets of magnetic blocks separated by a canister with their north poles oriented towards each other. The canister was designed to take either a ferromagnetic wire-mesh pad or balls. The gap between the magnets was set using a crankshaft driven, left- and right-hand threaded long screw to which the two blocks of magnets are connected. It was possible to create the intensity and gradient suitable for the separation of this ore

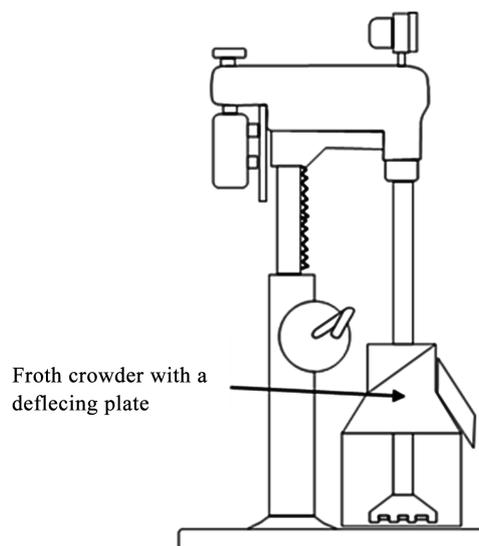


Figure 1. Modified Denver flotation cell.

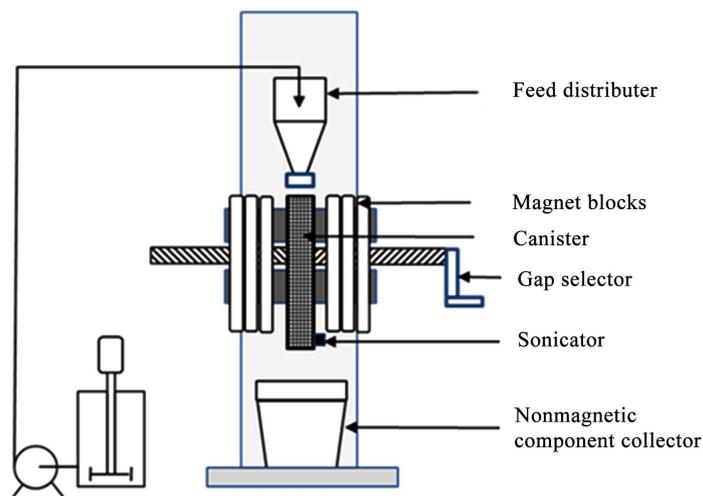


Figure 2. Low-intensity high-gradient magnetic separator.

in a manner that was not possible with commercial LIMS and HGMS laboratory equipment. The variable gap, the mesh size, and the ball size create continuous infinite intensity and gradient settings within the natural limit of the magnets' strength. At the narrowest gap (1.5 cm) between the two sets of magnets, the maximum magnetic flux density generated at the empty canister centre was 2.4 kGauss. The feed (50 to 60 g) was suspended in 250 mL of water and pumped to the matrix-filled canister at a rate of 100 mL/min. At the end of the separation, the canister was rinsed with 250 mL of water. To minimize particle entrapment within the voids in the magnetic particles bed, the canister was sonicated with a mechanical device.

3. Results and Discussions

3.1. Flotation

Since Ce's recovery was about the same as that of the total rare earth oxide (TREO) for this ore, only the recovery of Ce was plotted. This does not imply that the recovery of the individual REEs was equivalent to that of Ce.

3.1.1. Reagent Addition Sequence

Figure 3 and **Figure 4** show the effect of the reagent addition sequence; 1243 g/t Aero 6493, 850 g/t Na-silicate, and 430 g/t of CMC additions were used for these experiments. No frother was required. The pulp was conditioned for three minutes with a collector and two minutes each with Na-silicate and CMC. The total flotation time was 15 minutes. Besides the reagents themselves, the most critical parameter was the addition sequence. The pulp was normally first conditioned with depressants and then with the appropriate collector to achieve acceptable separation of valuable minerals from the gangue. In this case, however, such a strategy resulted in significantly less REE and Nb minerals separation, as shown in **Figure 3** and **Figure 4**. Hence, for this ore, the reagent addition sequences were reversed.

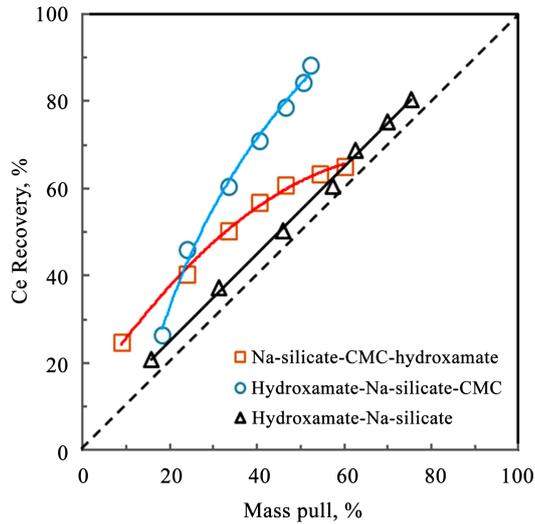


Figure 3. Effect of reagents addition sequence on Ce recovery.

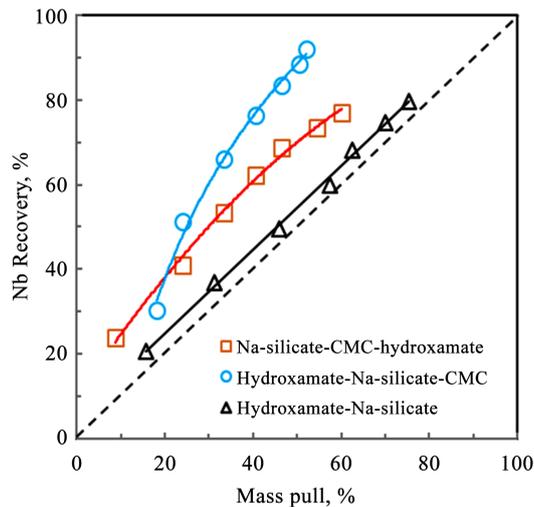


Figure 4. Effect of reagents addition sequence on Nb recovery.

In the absence of CMC, there is practically no REEs or Nb separation. At 50% mass pull, Ce and Nb recoveries were ~21% higher when the pulp was conditioned with collector first and then with depressants.

3.1.2. Effects of Na-Silicate and CMC

Figure 5 and **Figure 6** show the effects of Na-silicate and CMC when applied separately. In the absence of CMC, there was practically no separation of either REE or Nb minerals. However, in the absence of Na-silicate, both REE and Nb minerals' separation was significant, more so for Nb minerals. At 50% mass pull, REEs and Nb recoveries are about 62% and 75%, respectively. This implies that Na-silicate by itself had very little effect on the separation of the REE and Nb minerals from the gangue. Its primary role appears to enhance the effect of CMC shown in **Figure 5** and **Figure 6**. In the presence of both Na-silicate and CMC the Ce and Nb recoveries at 50% mass pull were 86% and 90%, respectively.

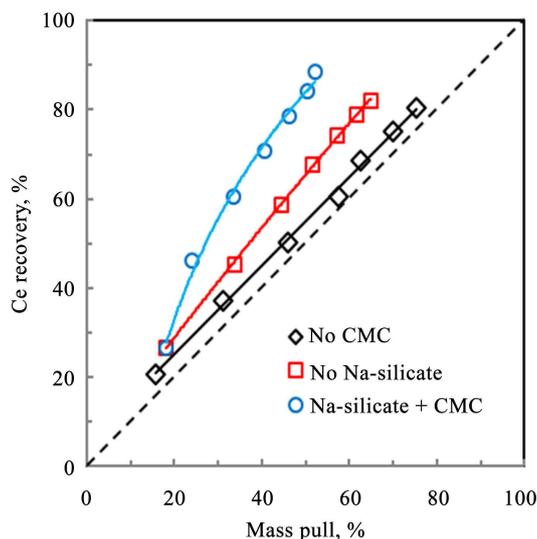


Figure 5. Synergetic effects of CMC and Na-silicate on Ce recovery.

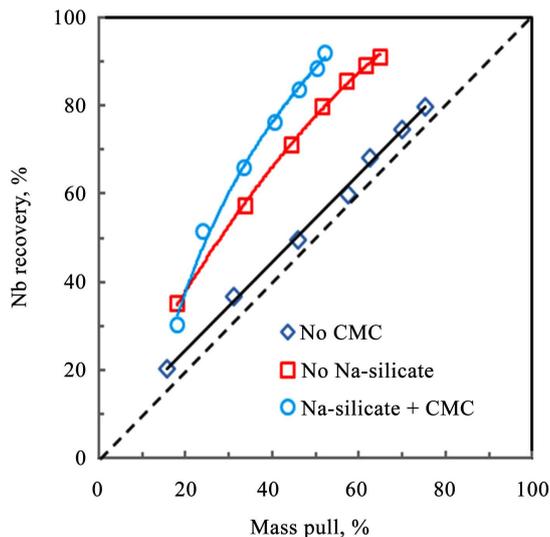


Figure 6. Synergetic effects of CMC and Na-silicate on Nb recovery.

3.1.3. Flotation Pulp De-Sliming

The flotation pulp was de-slimed before and after it was conditioned with reagents (*i.e.* before flotation) to improve separation performance. As shown in **Figure 7** and **Figure 8**, de-sliming of the pulp after grinding (*i.e.* before conditioning with reagents) significantly reduced the separation of REE and Nb minerals from the gangue minerals. At 50% mass pull, Ce and Nb recoveries dropped from 82% and 90% to 60% and 66%, respectively. Whereas it did not influence Ce recovery, de-sliming after conditioning with reagents improved Nb recovery significantly, as seen in **Figure 8**.

3.1.4. CMC Dosage

An increase in CMC addition from 430 g/t to 645 g/t decreased the Ce and Nb recoveries by 20% at 50% mass pull (**Figure 9** and **Figure 10**).

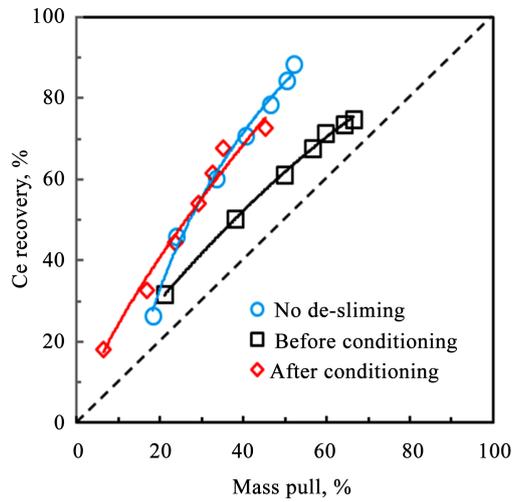


Figure 7. Effect of de-sliming on Ce recovery.

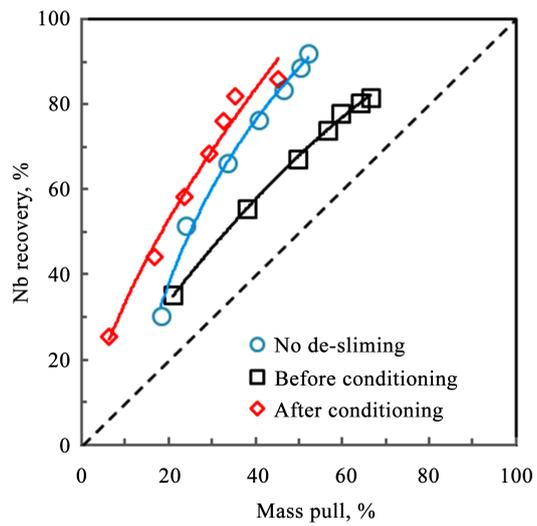


Figure 8. Effect of de-sliming on Nb recovery.

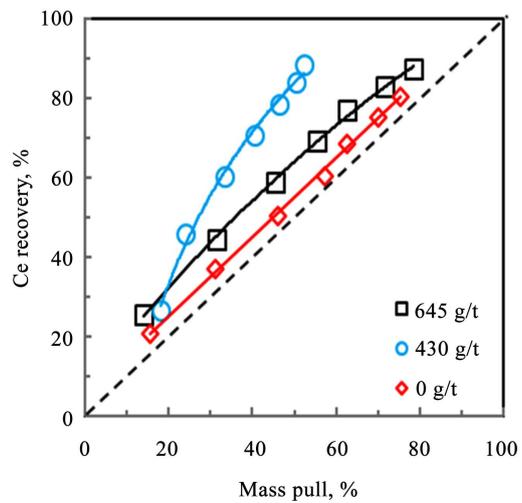


Figure 9. Effect of CMC dosage on Ce recovery.

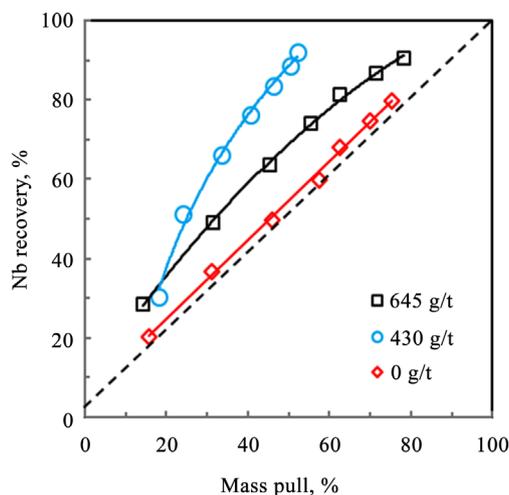


Figure 10. Effect of CMC dosage on Nb recovery.

3.1.5. Flotation Pulp Temperature

An increase in the pulp temperature had a negative effect on separation efficiency as shown in **Figure 11** and **Figure 12**. While it is apparent for this fine grind that the separation efficiency would be hampered with an increase in pulp temperature, increasing the temperature had a negligible effect for a coarser grind of $d_{80} \sim 63 \mu\text{m}$ (not plotted).

3.1.6. Conditioning Intensity

Whereas the effect of conditioning intensity on Ce recovery was only marginal (**Figure 13**), it did improve the separation of Nb significantly (**Figure 14**), lowering the mass pull for a given recovery.

3.1.7. Particle Size Distribution

At a coarser grind size of $d_{80} \sim 63 \mu\text{m}$, both Ce and Nb separation efficiencies dropped significantly under these flotation conditions (**Figure 15** and **Figure 16**).

3.1.8. Pulp pH

The recoveries of both Ce and Nb were strongly dependent on pH and sharply improved with an increase in pH as shown in **Figure 17**.

3.2. Distributed Addition of Reagents

A multi-step sequential collector-depressant conditioning was adopted (**Figure 18** and **Table 6**) to enhance REE and Nb minerals' recoveries. Under these conditions, it was possible to increase the grind size to $d_{80} \sim 63 \mu\text{m}$. The data plotted in **Figure 19** and **Figure 20** are the results of five 2-kg tests conducted to produce enough concentrate for further upgrading studies and verify the flotation process repeatability. This strategy made it possible to obtain precisely the same separation efficiencies and recoveries for both TREO and Nb, 92% recovery at 45% mass pull with excellent repeatability as indicated in **Figure 19** and **Figure 20**.

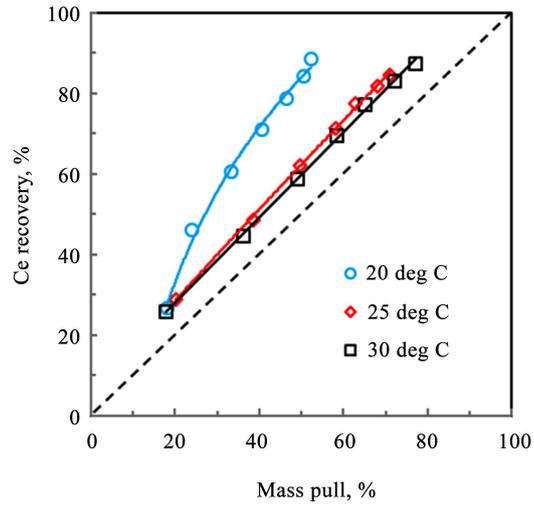


Figure 11. Effect of temperature on Ce recovery.

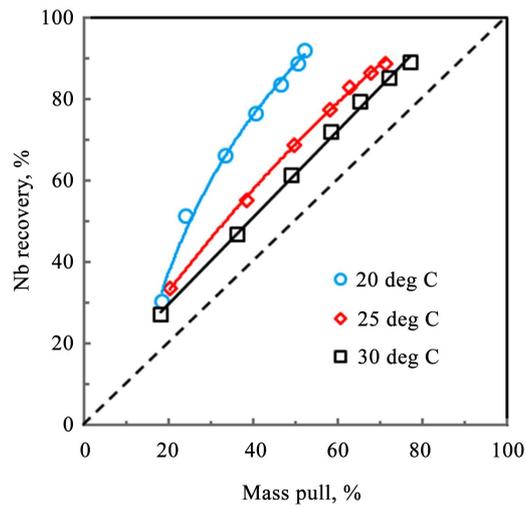


Figure 12. Effect of temperature on Nb recovery.

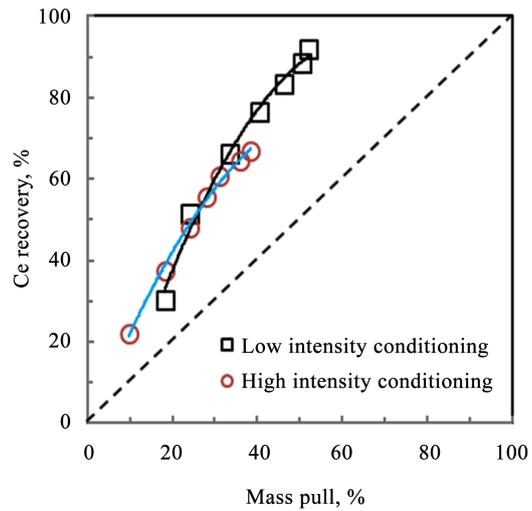


Figure 13. Effect of conditioning intensity on Ce recovery.

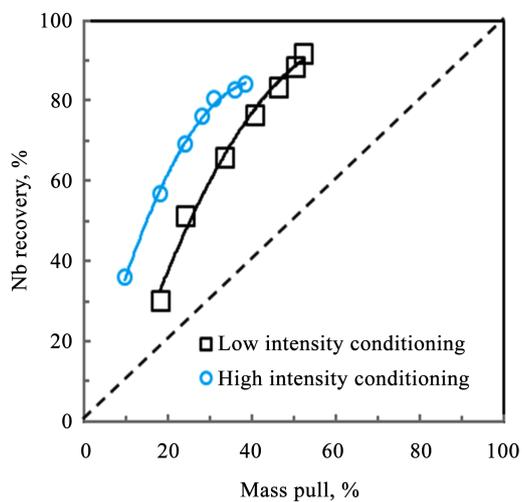


Figure 14. Effect of conditioning intensity on Nb recovery.

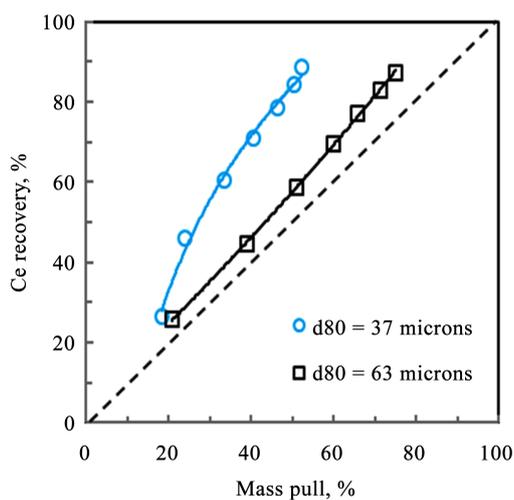


Figure 15. Effect of particle size distribution on Ce recovery.

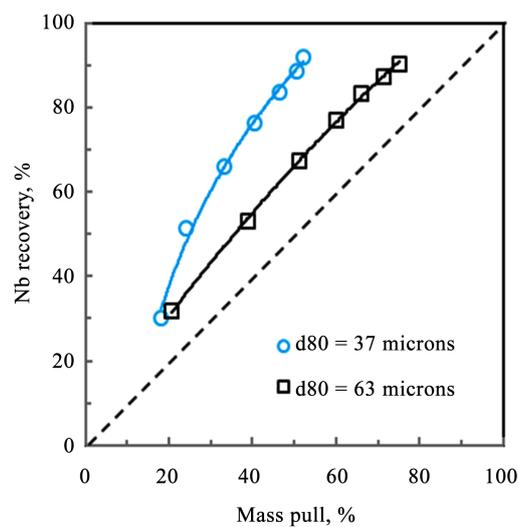


Figure 16. Effect of particle size distribution on Nb recovery.

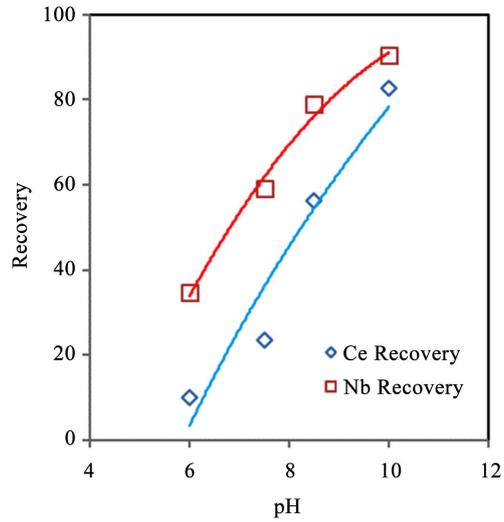


Figure 17. Effect of pH on Ce and Nb recovery.

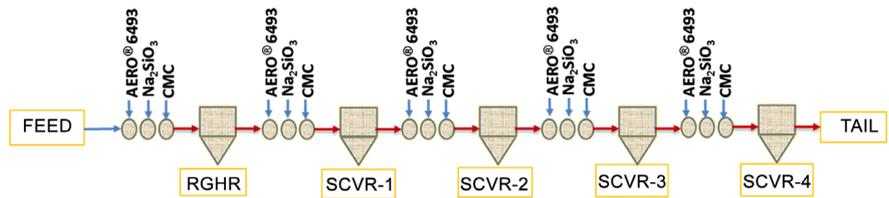


Figure 18. Reagent addition sequences and conditioning scheme.

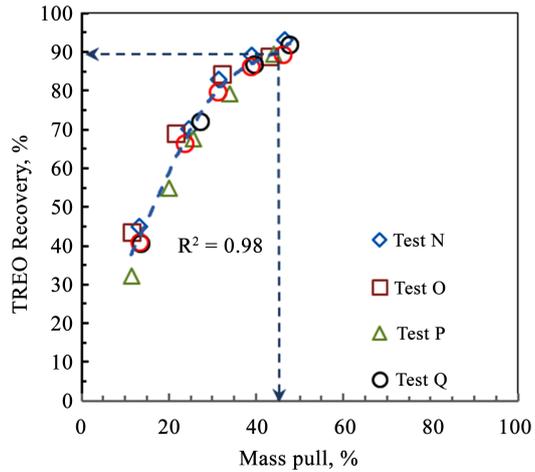


Figure 19. TREO recovery/separation enhancement with stage conditioning and flotation.

Table 6. Reagent conditions.

	Reagent, g/t				
	RGHR	SCVR-1	SCVR-2	SCVR-3	SCVR-4
Aero 6493	732	537	244	341	341
Na-silicate	675	289	289	96	675
CMC	341	146	98	98	49

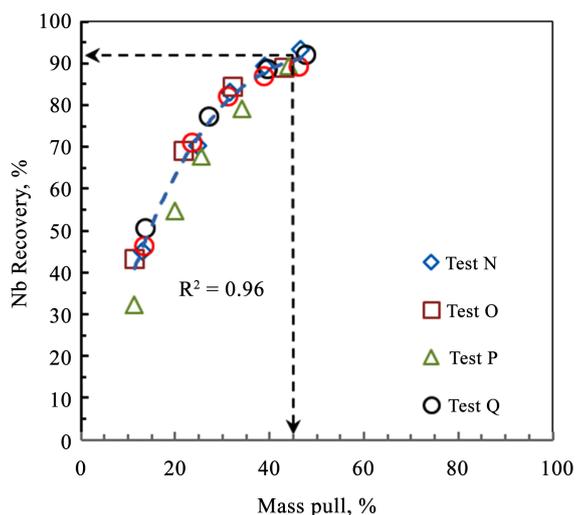


Figure 20. Nb recovery/separation enhancement with stage conditioning and flotation.

4. Flotation Concentrate Upgrading

Despite the successful enhancement of both the recovery and separation efficiency, the concentrate did not respond to cleaning by flotation due to the high level of reagent used. Up to 3-fold concentrate upgrading was possible using conventional gravity separation equipment such as the Mozley or the Gemini Tables, but the recovery loss remained high. Because of this, a systematic investigation was conducted to upgrade the concentrate with magnetic separation. Both conventional LIMS and HGMS resulted in significant separation but not satisfactory recovery.

Regrinding of the concentrate to d_{80} 37 μm improved the simultaneous separation of REE and Nb minerals from the gangue, but the recovery remained low. Subsequently, calcination of the flotation concentrates at temperatures varying from 750°C to 900°C for four hours was explored as shown in **Figure 21** and **Figure 22**. The results shown in both figures were obtained only after the calcined concentrate was reground to d_{80} of ~ 37 μm and magnetically upgraded. The recovery-mass pull profile was generated from the cumulative mass balance following separations at four inter-magnet pole gaps (*i.e.* four magnetic intensity levels). The concentrate was the non-magnetic component of the separator. The magnetic separation efficiency improved with increasing intensity at the cost of recovery. Within the calcination temperature range studied (750°C - 900°C), the separation efficiency improved with increasing calcination temperature. Since the flotation concentration obtained 45% mass pull and 92% recovery for both REEs and Nb (**Figure 19** and **Figure 20**), if a 35% mass pull of the magnetic separation was taken as the optimal cut-off (**Figure 21** and **Figure 22**), the overall recovery of REEs will be 87.4% at the overall mass pull of 15.8%. The overall recovery of Nb would be slightly lower at 84.7%. The hybrid flotation-calcination-regrind-magnetic separation flowsheet is shown in **Figure 23**. The average mass loss during calcination was about 30%.

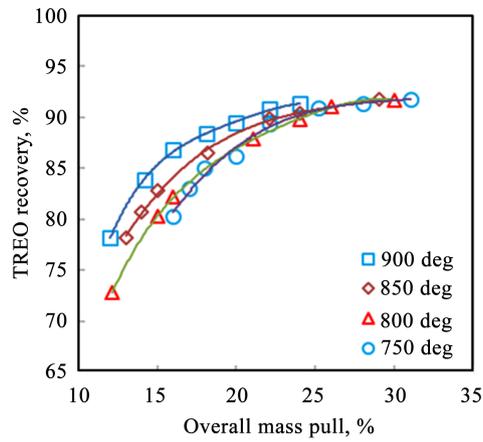


Figure 21. Effects of concentrate calcination temperature on magnetic separation of TREO.

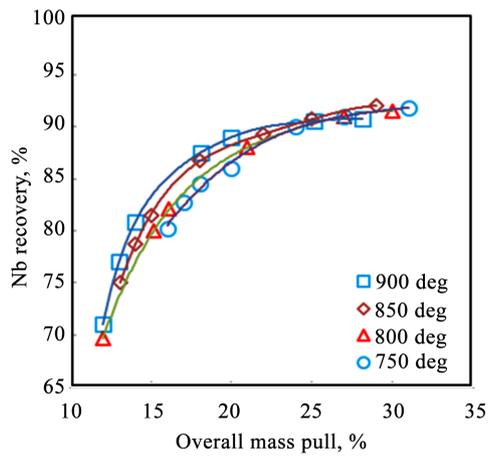


Figure 22. Effects of concentrate calcination temperature on magnetic separation of Nb.

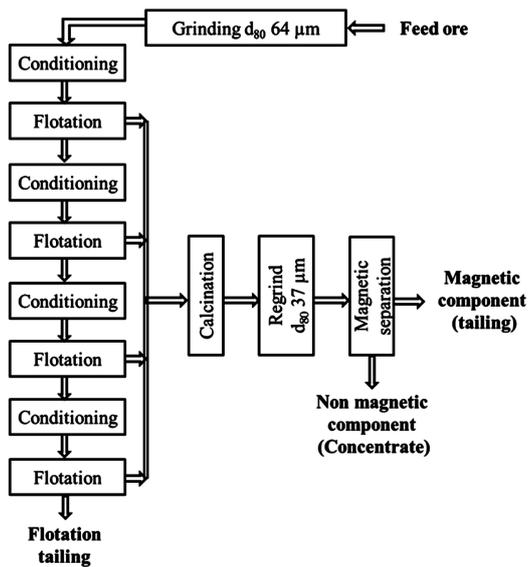


Figure 23. Grinding, conditioning, flotation, calcinations and magnetic separation flow-sheet.

5. Conclusions

Several reagents were tested separately and concurrently to separate the major REE-bearing minerals namely kukharonkite ($\text{Ba}_2\text{REE}(\text{CO}_3)_3\text{F}$), burbankite $[(\text{Na}, \text{Ca})_3(\text{Sr}, \text{Ba}, \text{Ce})_3(\text{CO}_3)_5]$ and cebaite $[\text{Ba}_3\text{Ce}_2(\text{CO}_3)_5\text{F}_2]$ as well as Nb-minerals (pyrochlore and fergusonite) from the predominantly carbonate gangue minerals. Although kukharonkite and cebaite belong to the same family as bastnaesite, they proved irresponsive to all collectors known to have been used for its flotation except the alkyl hydroxamate. There were several notably unique flotation characteristics of this ore as determined using the timed flotation technique:

1) The customary flotation process sequence of conditioning with depressants first and then with collectors did not result in any concentration of value minerals. Meaningful separation could only be obtained when the sequence was reversed despite high collector consumption.

2) Among several depressant-collector combinations tested, only alkyl hydroxamic acid, sodium silicate, and CMC proved to work.

3) The role of CMC, as expected, is depressing the gangue which has already been exposed to a collector.

4) Sodium silicate is commercially used as a depressant or dispersant. For this ore, CMC's depressing effect in the absence of prior conditioning of the pulp with sodium silicate was insignificant. Besides, in the absence of CMC, sodium silicate does not exhibit any characteristics of a depressant. This proves that sodium silicate in and of itself does not possess the ability to depress the gangue. Its role was most probably dispersing the fine particles, thus creating favourable conditions for CMC adsorption. Sodium silicate does also play a significant role in controlling the pH due to its buffering capacity.

5) For the fine grind of $d_{80} \sim 37 \mu\text{m}$, under the timed flotation scheme (single-stage sequential conditioning with sodium silicate followed by CMC) the effect of pulp temperature variation between 20°C and 30°C was very significant. The separation efficiency drops significantly with increasing pulp temperature. At the coarser grind of $d_{80} \sim 63 \mu\text{m}$ and multiple stage conditioning (with alkyl hydroxamate, sodium silicate, and CMC) and multiple stage scavenger flotation, the effect of temperature in this range became negligible.

6) Under the timed-flotation scheme, both REE and Nb minerals' separation efficiencies were superior for the fine grind of $d_{80} 37 \mu\text{m}$ compared to the coarser grind of $d_{80} 63 \mu\text{m}$. Interestingly, under the multi-stage conditioning and flotation, the coarser grind yielded the best separation, grades, and recoveries for both REE and Nb minerals. Of course, under this scheme, significantly more reagents were consumed.

7) De-sliming of the pulp before reagent additions reduced the separation efficiency. However, de-sliming of the pulp after conditioning favoured the increase in Nb recovery with no significant effect on REE minerals' recovery.

8) Similarly, high-intensity pulp conditioning positively affected Nb minerals recovery without significant effects on REE minerals.

9) The flotation recovery of both REE and Nb minerals was strongly dependent on pH. Within the pH range investigated (pH 6 to pH 10), the separation of REE and Nb minerals sharply improves with an increase in pH.

10) To enhance the bulk recovery of REE and Nb minerals, while at the same time decreasing the mass pull, a multi-step sequential collector-depressant conditioning was adopted. Under these conditions, it was possible to increase the grind size to $d_{80} \sim 63 \mu\text{m}$. This strategy made it possible to obtain precisely the same separation efficiencies and recoveries for both TREO and Nb, 92% recovery at 45% mass pull with excellent repeatability.

11) The hybrid flotation-calcination-regrind-magnetic separation flowsheet developed resulted in overall 87.4% and 84.7% recoveries of TREO and Nb, respectively, in 15.8% mass pull. This was only made possible by the magnetic separator suitable for selecting a variable range of magnetic field intensity and gradient to process a very fine ($d_{80} 25 \mu\text{m}$) mainly liberated mineral particles.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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