Review

Recovery of Rare Earth Elements Minerals from Iron-Oxide-Silicate-Rich Tailings: Research Review

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Abstract: The rapid depletion of high-grade rare earth elements (REE) resources implies that future supplies may be augmented with low-grade ores, tailings, and other unconventional resources to meet cut-off grades and, subsequently, supply demands. This paper presents an amalgamation of studies conducted on selected complex low-grade iron-oxide-silicate-rich tailings, with the overall aim of developing efficacious methods and associated process mineralogy characterization for enhanced REE minerals recovery and upgrade. To this end, a summary of the overarching key results from froth flotation, magnetic separation, and gravity separation studies of the tailings and their implications are presented in this review. Reconciliation of all the findings reveals lucid links between feed ore properties, mainly mineralogy and particle size distribution, as the key influential factors that affect the beneficiation of real complex low-grade tailings, although distinct differences in physicochemical properties of the valuable and gangue minerals may exist. It is clearly established that the unliberated association between REE and gangue minerals within the ore can lead to either synergistic or antagonistic effects on the quality of concentrates produced. Furthermore, the limitations presented by the poorly liberated minerals are exacerbated by their “fine” nature. With appreciable recoveries obtained using such readily available conventional separation methods, the tailings provide additional REE value to the primary commodities; hence, such material could be considered a potential resource for REE beneficiation. The learnings from the respective beneficiation studies are significantly important as they provide the knowledge base and greater understanding of the mineralogical characteristics and beneficiation response of REE minerals in typical complex, low-grade tailings.

Keywords: rare earth elements; magnetic separation; flotation; gravity separation; monazite; bastnäsite

1. Introduction

The criticality of rare earth elements (REE) supply as a result of their growing market demand and limited reserves has necessitated increased global attention. China has, over the years, dominated the production and supply of REE, accounting for not less than 80% of the global REE demand [1–5]. Over the years, China has been faced with the difficulty of sustaining the global REE demand due to its ever-increasing local demand and mining-related issues, including illegal mining and environmental destruction. This has highlighted the crucial need for the rest of the world to develop their REE resources into new, economically competitive industries. The establishment of new projects in other countries has been forecasted to contribute significantly to the global demand and supply. However, the rapid depletion of high-grade REE ores suggests that low-grade ores, landfills, mining tailings, and other unconventional resources such as permanent magnets, electronic

wastes, and fluorescent lamps may be exploited to meet cut-off grades and subsequently supply demands [6–8].

The ever-growing demand for materials and energy resources has given rise to a significant build-up of natural resources in waste deposits. The accumulation of such massive quantities of industrial, metallurgical, and mining waste could result in the geological storage of a significant quantity of valuable resources such as metals, minerals, and energy or biomass [9–12]. It is paramount that such wastes are exploited for their valuable contents through cost-effective and eco-friendly means. For example, valuable metals/minerals such as gold, copper, cobalt, iron, and lead may be recovered from tailings generated over a mine life [9,13–16].

Typically, REE-bearing minerals occur in complex association with primary commodities and gangue minerals in low-grade values; hence, they are mostly lost to the tailings during processing. Where REE minerals occur in high-grade values, historic processing methods have been reported to be ineffective, resulting in a large amount of REE minerals lost to the tailings [7,17,18]. The volume of tailings generated over a mining period increases significantly, with a corresponding increase in the amount REE lost to the tailings. In some instances, the amount of REE accumulated over time in the tailings becomes almost identical to an in situ REE deposit.

A typical example is the waste generated at the Mount Pass mine (USA), where about 3–5% REE is locked in the mining tailings. Furthermore, over 53 Mt REE has been accumulated from the extraction of copper, gold, and uranium in South Australian ores [6,19,20]. According to Zhang et al. [21], a significant proportion of REE in the Bayan Obo ore deposit (China) is lost to tailings as a result of ineffective methods used in recovering them. Binnemans et al. [18] also pointed out that the inefficient processing of a monazite-rich ore at the Rhodia Solvay processing plant located at La Rochelle (France) has resulted in the build-up of a significant amount of REE-rich tailings.

Elsewhere, studies conducted on waste and tailings piles generated at the Pea Ridge iron ore mine by Grauch et al. [22] suggested elevated concentrations of REE. The results obtained by Grauch et al. [22] were in agreement with an earlier study conducted by Vierrether and Cornell [23], where significant concentrations of REE, including samarium (Sm), neodymium (Nd), and dysprosium (Dy), were reported in the Pea Ridge tailings. The work of Vierrether and Cornell [23] identified that the REE were mineralized as apatite, monazite, xenotime, and britholite. Based on the data obtained from the characterization and separation studies, Vierrether and Cornell [23] proposed that the tailings at Pea Ridge iron ore mine could be considered for REE beneficiation.

2. Review Objectives

Binnemans et al. [18] outlined a three-fold approach to tackle REE supply challenges. The first component of this approach is to substitute critical REE with less critical metals. The second strategy is to invest in sustainable primary mining from old or new REE deposits, and the last one being investment in technospheric mining. With the growing interest in exploiting waste repositories as one of the key strategies in meeting the global REE demand, the beneficiation of REE minerals from tailings is receiving increased attention. This review paper gives a one-stop overview of REE recovery from iron-oxide-silicate-rich tailings within a conceptual framework that seeks to:

(i) Explain the rationale for reprocessing tailings for their REE content;
(ii) Reconcile and discuss all the key findings emerging from the comprehensive fundamental investigations carried out on complex low-grade tailings;
(iii) Summarize the response of valuable REE and gangue minerals in the real plant tailings during froth flotation, magnetic, and gravity separation methods;
(iv) Discuss the identified challenges and opportunities in the use of tailings as a secondary resource for REE minerals beneficiation.

Though the results from the various tests may not be generalized across all REE ores, this paper could serve as reference material for assessing potential beneficiation strategies.
prudent for the recovery and upgrade of REE minerals, as there is limited knowledge in
the literature focused on REE minerals beneficiation from complex low-grade iron-oxide-
silicate-rich tailings. Typically, most REE minerals may be contained in silicates or iron oxide
ores, respectively. It is rare to encounter studies involving ores containing a mixture of both
phases in almost similar proportion, occupying more than 80% (iron oxides + silicates) mass
of the ore. To this effect, this review will highlight the application of the new knowledge and
findings garnered in designing effective ore-specific beneficiation methods for enhanced
REE minerals recovery and upgrade from selected iron-oxide-silicate-rich tailings and other
secondary resources of similar mineralogical composition.

3. Beneficiation Studies

This review provides a summary of the overarching key results and their implications,
together with the key findings and the links between each of the already published research
articles by the authors. The primary objective of the project was to develop efficacious
methods and associated process mineralogy characterization for enhanced REE minerals
recovery and upgrade from tailings of complex mineralogy.

3.1. Rationale

There are several economic and environmental benefits associated with the extraction
of elements, metals, or minerals from the technosphere or mining tailings. Efficient and
successful recovery of commodities from such materials will present possible solutions to
ongoing global fears about the long-term availability and sustainability of mineral resources,
especially for REE and other critical minerals. This is because the recovery of commodities
from tailings contributes significantly to materials recycling and recirculation, with its
associated benefits, especially where global leaders aim toward a green economy [24,25].
Although it is well reported that secondary resources such as tailings contain low and
anomalous REE content, massive quantities of waste repositories are generated over time;
thus, the total REE content consequently increases. The treatment of such tailings for
their REE content could present a huge economic boost and enhance diversification of REE
resources, which in turn minimizes issues of REE market, prices, and export monopoly [18].

Processing of tailings has been identified to have significant environmental benefits [26,27].
In principle, tailings have been tagged as key pollutants and are associated with different
risk levels, thus requiring a high level of monitoring and remediation strategies [28–31].
To this end, successful REE recovery from tailings repositories and other historic storage
facilities provides an additional economic advantage compared to other operations that
may be solely established for primary commodities or REE beneficiation [27]. Further to
this, some researchers have identified simple conventional techniques that could be easily
installed to process such historic tailings [27,32,33]. Notwithstanding, there are also studies
being carried out by researchers to assess economically viable novel processes that could
be considered in ongoing efforts to recover REE minerals [34]. It is worth noting that the
extent of the economic advantage may vary as this depends on the quality of concentrate
generated from such tailings. REE preconcentrates produced as a by-product may be sold to
REE extraction operations for further hydrometallurgical or pyrometallurgical treatments.

Also, tailings have a particle size range, which is ideal for various beneficiation
methods. This is desirable compared to the processing of fresh in situ ores, which would
normally require detailed comminution and classification processes to attain a suitable
particle size range for subsequent beneficiation. Comminution, which is the progressive
disintegration of ore using crushers and grinding mills, has been reported to consume more
than half of processing and operating costs [35–38].

3.2. Physicochemical and Mineralogical Characteristics of the Tailings

In an attempt to recover REE minerals, there are some key questions that need to be
addressed before significant progress can be made.

• What are the REE-bearing minerals in the tailings?
What are the gangue minerals present in the tailings, and what are their physical and chemical characteristics?

What REE–gangue mineralization and associations are present in the tailings?

Answers to these questions play a crucial role in developing cost-effective methods for recovering REE minerals. Comprehensive physicochemical and mineralogical analyses of the tailings were carried out using conventional characterization tools. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted on representative samples to identify the distribution of elemental species to foster mineral phase identification via quantitative X-ray diffraction (QXRD, Panalytical Empyrean XRD, Malvern Panalytical, Australia) and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN, QEMSCAN 430, Zeiss Australia, Australia). Particle size analysis via laser diffractometer indicated that the material is polydispersed, with particles ranging from 0.2 to 720 \( \mu \text{m} \). The bulk chemistry data indicated that the tailings contained 1.07% total rare earth oxides (TREO), 26.2% Fe, and 18.6% Si (Table 1).

<table>
<thead>
<tr>
<th>Rare Earth Oxides</th>
<th>Content (%)</th>
<th>Gangue Elements</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_2\text{O}_3 )</td>
<td>0.35</td>
<td>Al</td>
<td>3.9</td>
</tr>
<tr>
<td>( \text{CeO} )</td>
<td>0.52</td>
<td>Ca</td>
<td>1.71</td>
</tr>
<tr>
<td>( \text{Pr}<em>6\text{O}</em>{11} )</td>
<td>0.05</td>
<td>Fe</td>
<td>26.2</td>
</tr>
<tr>
<td>( \text{Nd}_2\text{O}_3 )</td>
<td>0.13</td>
<td>Mg</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3 )</td>
<td>0.02</td>
<td>P</td>
<td>0.15</td>
</tr>
<tr>
<td>TREO</td>
<td>1.07</td>
<td>Si</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Mineralogical analysis data presented in Table 2 confirmed that the tailings are complex and principally consisted of iron oxides (hematite–magnetite associations, goethite–limonite associations) and silicate (typically quartz, muscovite, and annite, illite, and feldspar) minerals. Of key interest to the investigation, the data obtained also suggested that there was a rather low (1.11 wt.%) but important concentration of REE in the tailings mineralized as bastnäsite, monazite, florencite, and other minor REE phases. Specifically, hematite and quartz were identified as the dominant iron oxide and silicate minerals, respectively. With hematite and quartz identified as the major gangue minerals, a key challenge in processing the tailings for their REE content is the selective removal of iron oxides and silicates, which have been shown to host the REE minerals.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Relative Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REE minerals (bastnäsite, monazite, florencite, and others)</td>
<td>1.11</td>
</tr>
<tr>
<td>Iron oxide (hematite, goethite)</td>
<td>40.15</td>
</tr>
<tr>
<td>Quartz</td>
<td>29.53</td>
</tr>
<tr>
<td>Muscovite</td>
<td>8.82</td>
</tr>
<tr>
<td>Annite</td>
<td>4.76</td>
</tr>
<tr>
<td>Other silicates</td>
<td>8.84</td>
</tr>
<tr>
<td>Other oxides</td>
<td>6.79</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

In addition, the QEMSCAN investigation revealed that the REE minerals were fine-grained (average 4.5 \( \mu \text{m} \)) and disseminated among both the major and minor gangue minerals. Liberation and locking statistics data from the QEMSCAN analysis showed that only <5% of bastnäsite mineral particles were completely liberated. The remaining REE minerals formed complex middling composite particles with the gangue minerals. These observations suggested major beneficiation challenges.
3.3. Froth Flotation

To mimic a typical complex, low-grade REE-bearing iron-oxide-silicate-rich tailings, low-grade mixtures (0.83% TREO grade) were tested with the fatty acids (oleic acid and sodium oleate) and hydroxamic acid in the absence and presence of sodium silicate and starch as depressants [6]. Both depressants were effective in selectively decreasing the recoveries of both hematite and quartz. Based on the outcome of the model minerals mixture studies, sodium oleate and hydroxamic acid were selected as suitable collectors for recovering and upgrading REE minerals in the tailings.

In the flotation studies, the relative effects of pulp pH, collector type and dosage, and depressants dosage on the recovery and upgrade of REE minerals were investigated. The results showed that the flotation recovery of REE minerals from the tailings was pulp pH-dependent, with pH 9 identified as most suitable for recovering REE minerals with both collectors (sodium oleate and hydroxamic acid) [1]. As expected, REE and gangue minerals recoveries increased with increasing sodium oleate and hydroxamic acid dosage, respectively. This led to a corresponding decrease in REE upgrade in the respective flotation concentrates. In an attempt to achieve selective REE recovery, two different multistage flotation methods (Figure 1) were considered, where sodium oleate was used in the first method (A) whereas hydroxamic acid was used in the second (B), in the presence of the sodium silicate and starch as depressants. Table 3 summarizes the results obtained from the two processes. The test results demonstrated that the flotation performance of the collectors was improved by depressing the gangue minerals and subsequent cleaning/scavenging of the concentrates [1].

![Figure 1. Schematic flowsheets for flotation of REE from the tailings using (A) sodium oleate and (B) hydroxamic acid, respectively, in the presence of sodium silicate (SS) and starch (ST), adopted from Abaka-Wood et al. [1].](image)

<table>
<thead>
<tr>
<th>Flowsheet</th>
<th>TREO Dist. (%)</th>
<th>TREO Grade (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>100</td>
<td>1.07</td>
</tr>
<tr>
<td>A (sodium oleate + sodium silicate + starch)</td>
<td>63</td>
<td>2.25</td>
</tr>
<tr>
<td>B (hydroxamic acid + sodium silicate + starch)</td>
<td>60</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table 3. Comparison of TREO content in concentrates obtained from the flowsheets in Figure 1 [1].

Mineralogical characterization results of the final concentrate from Flowsheet A in Figure 2 revealed that iron oxides and silicates made up the bulk of the flotation concentrate, suggesting entrainment and incomplete liberation instigated the low TREO upgrade, although high recoveries were obtained. Indeed, QEMSCAN analysis conducted on the flotation concentrate confirmed that the REE minerals were fine-grained and in unliberated associations with the gangue minerals (Figure 3). The flotation studies on the tailings produced some important findings; paramount among them was that preconcentration
methods (such as gravity separation and magnetic separation) could be investigated prior to froth flotation to remove a significant amount of barren gangue minerals. This has profound advantages, including enhancing REE minerals selectivity and reducing reagents consumption during flotation and leaching processes [32,39,40].

![Figure 2.](image)

Figure 2. Mineral mass abundance of TREE and gangue minerals in the flotation feed and concentrate from Flowsheet A in Figure 1 [1].

3.4. Gravity Separation

Although froth flotation demonstrated promising results in the recovery of REE minerals (typically bastnäsite, monazite, and florencite), generally, poor upgrades were observed. Mineralogical analysis of the flotation concentrates confirmed the upgrade of REE minerals, with iron oxides and silicate minerals occupying the bulk of the concentrates, although depressants were used. It was suggested that physical preconcentration methods...
could be exploited to ascertain the feasibility of rejecting some iron oxides and silicates prior to froth flotation separation.

Physical preconcentration methods (including gravity, magnetic, and electrostatic) are employed mainly to reject a significant amount of gangue minerals to provide comparatively higher feed grade and lower throughput to subsequent processes [39,41]. To this end, the technical feasibility of exploiting the differences in the specific gravities of valuable minerals in the tailings to produce REE minerals preconcentrates was investigated. A study was thus conducted to compare the performance of a conventional (Wilfley shaking table) and advanced gravity concentration (Knelson Concentrator (KC)) processes to identify opportunities and challenges associated with REE minerals recovery from the tailings [42].

Typically, REE minerals were expected to report into the gravity preconcentrates along with the iron oxides, as both groups of minerals have a similar range of specific gravities (4–6), while the silicates (specific gravities <3.5) were expected to make up the bulk of the gravity tailings. QEMSCAN data on both KC and tabling concentrates suggested that both units could produce a split between the light and heavy minerals. However, the shaking table was superior in terms of selectivity, achieving an overall REE and iron oxide minerals upgrade ratios of 3.33 and 1.80, respectively, at 29% REE recovery compared with 1.57 and 1.22, respectively, at 59% REE recovery when the KC was used. Figure 4 compares the mineral mass abundance of REE and gangue minerals in the respective concentrates obtained from the gravity concentration processes. Mineralogical analysis of the concentrates revealed that gravity concentration processes upgraded both bastnäsite and monazite. The shaking table effectively rejected the silicate gangue minerals even though they were generally unliberated. In addition, tests conducted on different size fractions of the tailings revealed that particle size distribution had a significant impact on the performance of both the KC and shaking table, with their performances deteriorating with decreasing ore particle size.

![Figure 4. Mineral mass abundance of TREE and gangue minerals in the feed and gravity (KC and tabling) concentrates.](image)

A major observation made during the gravity separation processes was that up to 58% of iron oxides reported to the tabling tailings, and about 65% of silicate minerals misreported to the KC concentrates. This was an indication that mineralogical characteristics, including minerals liberation and association, have a significant impact on gravity separation, even when distinct differences in specific gravities exist [42]. Furthermore, it was deduced from this study that the sole reliance on the concentration criterion to predict
the feasibility of separation may be misleading. A major limitation identified with the conventional concentration criterion expression was that it did not consider the liberation and association characteristics of minerals, which may result in improper prediction of separation feasibility [42]. A modified concentration criterion that considers the liberation and association characteristics of minerals was proposed [42]. Indeed, with the depletion of easy-to-process ores, the modified concentration criterion will be a more helpful tool in predicting the feasibility of gravity concentration of complex low-grade ores. This criterion could also provide an idea of the extent of comminution required to attain an optimum/desired level of mineral liberation for enhanced separation [42].

Overall, the study indicated that the performance of both gravity separation units was significantly affected by the mineralogical characteristics and particle size distribution of the tailings. Essentially, tabling was identified as the preferred gravity preconcentration method due to its better selectivity. However, desliming of the tailings to remove <38 µm is crucial to achieving any selective split between the light and heavy minerals via tabling. Furthermore, the investigation also demonstrated that the differences in the specific gravities of the valuable minerals could be exploited to some extent to preconcentrate REE minerals. However, the efficiency of the process is limited by mineralogical characteristics and particle size distribution [42].

3.5. Magnetic Separation

In cognizance of the advantages attributed to magnetic separation in REE minerals beneficiation, the promising outcome during the magnetic separation of mixed minerals [43], and there being no reported data on the use of magnetic separation in the beneficiation of the tailings, magnetic separation was tested as a potential preconcentration method for REE minerals recovery. A wet high-intensity magnetic separator (WHIMS) was selected to remove iron oxides at low magnetic field intensities while concentrating the REE minerals at higher magnetic field intensities, with the silicates reporting into the nonmagnetic tailings [44]. Test parameters and procedures from a previous work by Abaka-Wood et al. [43] were modified and employed during the magnetic separation tests, where the applied magnetic field intensity was varied from 0.11 T to 2 T.

The experimental data from this study revealed that as the magnetic field intensity was increased, more magnetic particles, including the weakly magnetic particles (REE and some silicate minerals), reported to the concentrate along with the iron oxides, as depicted in Figure 5. The results suggested that the iron oxides could be selectively concentrated at 0.11 T, even though they were poorly liberated. However, separation selectivity was compromised when higher magnetic field intensities were tested (>0.56 T).

Figure 5. (a,b) Effect of applied magnetic field intensity on TREO, Fe, and Si recovery from the tailings modified after Abaka-Wood et al. [44].
Subsequently, a multistage magnetic process (Figure 6) was developed to selectively reject iron oxides and to preconcentrate the REE minerals for subsequent froth flotation recovery and upgrade. The process was successful by selectively removing 25% iron oxides at Fe grade of 55.6% and 8% TREO assaying a grade of 0.68% at 0.11 T. Subsequently, the REE minerals were split between the high intensity (1.74 T) concentrate and the corresponding nonmagnetic tailings. It was also observed that up to 60% of iron oxides assaying 39% Fe and about 29% of silicate minerals reported to the high-intensity concentrate along with the REE minerals (51% recovery at 1.25% TREO grade) because of insufficient liberation, their ferro-/paramagnetic nature (i.e., iron oxides and muscovite, respectively), and entrainment recovery of silicate minerals. Overall, two magnetic REE ‘rich’ products (high-intensity magnetic concentrate and nonmagnetic tails) for subsequent processing by froth flotation were produced.

![Figure 6. Flowsheet configuration using WHIMS to remove iron oxides prior to REE minerals upgrade [44].](image)

QXRD analysis on the low-intensity concentrate (FMC) showed that hematite (70%) occupied the bulk fraction of the concentrate, with no REE minerals detected. QEMSCAN analysis conducted on the high-intensity preconcentrate (PMC) revealed an overall REE and iron oxide minerals upgrade ratios of 1.82 and 1.37, respectively, compared with 1.36 and 0.14, respectively, in the nonmagnetic tailings (Figure 7). The results corroborate with the varying magnetic properties of REE minerals, where bastnäsite, monazite, pyrochlore, and xenotime are known to be paramagnetic, whereas florencite, perovskite, zircon are examples of diamagnetic REE-bearing minerals [17]. As expected, the multistage separation process concentrated the silicate minerals in the nonmagnetic tailings. Overall, the study indicated that the differences in magnetic properties of the minerals in the tailings can be exploited to preconcentrate REE minerals for subsequent processing.

### 3.6. Flotation of Magnetic Separation Products

Owing to the successes associated with the combination of magnetic and froth flotation separation in the beneficiation of differing REE ores [32,45–47], a decision was made to subject the magnetic preconcentrates to froth flotation separation [48]. The feasibility of further recovering and upgrading REE minerals in the magnetic preconcentrates and nonmagnetic tailings was carried out using the reagents schemes from previous studies by Abaka-Wood et al. [1]. Specifically, the performances of sodium oleate and hydroxamic acid were compared in the presence of sodium silicate and starch.
QEMSCAN analysis conducted on the final concentrates from a three-stage hydroxamic acid flotation cleaning of the magnetic preconcentrates (PMC) and nonmagnetic tailings presented variable outputs as shown in Figures 8 and 9. The bulk of flotation concentrates from the high magnetic intensity concentrate was occupied by iron oxides, where 40% REE minerals recovery at ~1.1 upgrade ratio was obtained. On the other hand, comparatively lower REE minerals recovery (32%) at a higher upgrade ratio (1.84) was observed for flotation tests conducted on the nonmagnetic tailings.

**Figure 7.** Mineral mass abundance of TREE and gangue minerals in the feed and magnetic (PMC and nonmagnetic tailings) products.

**Figure 8.** Mineral mass abundance of TREE and gangue minerals in the feed, magnetic preconcentrate (PMC), and flotation concentrate from PMC using hydroxamic acid.
Figure 9. Mineral mass abundance of TREE and gangue minerals in the feed, non-magnetic tailings, and flotation concentrate from non-magnetic tailings using hydroxamic acid.

3.7. REE Minerals Grade–Recovery Relationship

Figure 10 illustrates the grade–recovery relationship in selected separation products obtained from the various beneficiation tests. The best concentrate grade (3.7%) was obtained during the tabling process, where REE minerals recovery (29%) was the lowest. The corresponding silicate content in the tabling concentrate was significantly low; however, the high iron oxide content (Table 4) is undesirable. On the other hand, where REE minerals recoveries were higher (≥30%), the corresponding concentrate grades were comparatively lower. In terms of recovery, the best result was achieved during the multistage flotation process in the presence of hydroxamic acid and depressants, but a number of challenges have been identified with the process. For example, hydroxamates are expensive and characterized by a high consumption rate. Furthermore, the high silicate content (62.13%) in the flotation concentrate would need to be reduced, possibly by introducing a desliming stage, to remove fine/ultrafine silicates, which are easily recovered via entrainment. In addition, regrinding of the feed or selected flotation products to promote REE–gangue minerals liberation may be considered.
Table 4. Summary of the mineralogical composition of selected separation products.

<table>
<thead>
<tr>
<th>Product</th>
<th>REE Minerals</th>
<th>Iron Oxides</th>
<th>Silicates</th>
<th>Others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1.11</td>
<td>40.15</td>
<td>51.95</td>
<td>6.79</td>
<td>100</td>
</tr>
<tr>
<td>KC conc</td>
<td>1.74</td>
<td>48.92</td>
<td>43.93</td>
<td>5.42</td>
<td>100</td>
</tr>
<tr>
<td>Tabling conc</td>
<td>3.70</td>
<td>72.23</td>
<td>19.62</td>
<td>4.45</td>
<td>100</td>
</tr>
<tr>
<td>Flotation conc. (hydroxamic acid)</td>
<td>2.00</td>
<td>23.46</td>
<td>62.13</td>
<td>12.41</td>
<td>100</td>
</tr>
<tr>
<td>WHIMS concentrate (PMC)</td>
<td>2.02</td>
<td>55.01</td>
<td>39.29</td>
<td>3.68</td>
<td>100</td>
</tr>
<tr>
<td>Nonmagnetic tails (NMT)</td>
<td>1.51</td>
<td>5.69</td>
<td>83.07</td>
<td>9.74</td>
<td>100</td>
</tr>
<tr>
<td>Flotation conc from PMC</td>
<td>2.14</td>
<td>77.01</td>
<td>15.86</td>
<td>4.99</td>
<td>100</td>
</tr>
<tr>
<td>Flotation conc from NMT</td>
<td>2.78</td>
<td>8.82</td>
<td>72.17</td>
<td>16.23</td>
<td>100</td>
</tr>
</tbody>
</table>

Notably, flotation of magnetic separation products enhanced REE concentrate upgrade (PMC = 2.02%–2.14% and NMT = 1.51%–2.78%), where an average of 20% REE minerals was lost to the tailings during the processes. It may be preempted that any attempt to further clean the tabling concentrates by flotation may improve the concentrate grade but at the expense of recovery. In effect, for this kind of material, there ought to be a trade-off between grade and recovery, where the preference will be determined by the downstream processes and their economics. The results from these studies are encouraging and potentially significant in view of the gigantic REE-bearing tailings generated from the processing of primary commodities. It is worth noting that such tailings are expected to yield variable processing responses as dictated by their mineralogy and particle size distribution.

4. Discussion

4.1. Identified Challenges and Limitations

The primary aim of the various beneficiation processes was to assess the technical feasibility of producing rich REE preconcentrates for subsequent hydrometallurgical or pyrometallurgical processes. The parallel aim of selectively rejecting significant fractions of key gangue minerals, namely silicates and iron oxides, was assessed. Some specific gains were achieved in all the tests conducted, which are mainly characterized by high REE recoveries and appreciable upgrade ratios. However, some challenges and limitations were encountered, which serve as motivation for further studies to be carried out to enhance our understanding of the processing behavior and opportunities associated with tailings as a secondary resource for REE beneficiation.

For instance, in the flotation studies [1], although high REE recoveries were achieved with both sodium oleate and hydroxamic acid, the extents of the upgrade were generally low. A key factor responsible for this observation is ore particle size distribution. Detailed particle size analysis via wet screening and laser diffraction method revealed that close to 70% of the total feed mass was finer than 40 μm. It has been well documented in the literature that ore particles finer than 50 μm promote gangue minerals recovery by mechanical entrainment [49–52]. Recovery by entrainment is characterized by poor flotation selectivity, usually with high gangue minerals recovery, as demonstrated in previous studies [1,48,53–55].

The deleterious effect of particle size distribution was also observed during magnetic separation, where an increase in magnetic field intensity up to 2 T was not enough to recover fine-grained paramagnetic iron oxides and REE minerals. This was attributed to the dominance of hydrodynamic drag force, which is unselective, thus misplacing fine iron oxides and REE minerals into the nonmagnetic fraction [44]. In wet magnetic separation, fine magnetic (paramagnetic or ferromagnetic) particles are usually lost to tailings due to the pronounced effect of hydrodynamic drag force [44,56]. This is exacerbated by feed flow and wash water, which may carry away ultrafine iron oxides and REE minerals from the matrix fitted in the WHIMS, as observed in similar investigations carried out on ultrafine wolframite [57,58]. Although magnetic separation was most selective compared to the other beneficiation methods, the fractions of iron oxides and REE minerals, which reported
with the nonmagnetic fraction, could have been reduced if the tailings “feed” was not dominated by fine-grained iron oxides and REE minerals particles.

Furthermore, the high content of gangue minerals in the separation (flotation, magnetic, and gravity) concentrates may also be attributed to incomplete REE minerals liberation from the gangue minerals. Strategic basic studies involving single and mixed model minerals performed provided fundamental, benchmarking understanding and knowledge of the feasibility of selectively recovering REE from hematite–quartz mixtures via froth flotation, magnetic and gravity separation methods [6,43,59–61]. The particle and mineralogical characteristics of the real tailings were major challenges associated with the recovery and upgrade of REE minerals. The tailings material used in this investigation is a complex ore system with over 40 fine-grained minerals in intimate associations with each other. These characteristics were absent in the model minerals mixtures, which account for some of the differing and, in most cases, significantly lower REE minerals upgrade from the tailings even though high recoveries were obtained.

The unliberated associations between REE silicates and iron oxide silicates within fine-grained particles promoted the flotation recovery of silicate minerals (typically quartz, annite, and illite), which may float poorly in the presence of anionic collectors [62]. Furthermore, the genuine interaction of iron oxides with anionic collectors coupled with their intimate associations with REE minerals limited the potency of depressants in preventing their recoveries. Again, the fine-grained nature and poor liberation between the minerals limited the performance of gravity separation units, although marked differences in specific gravities existed.

Furthermore, similar flotation response, specific gravity, and magnetic properties of REE minerals and iron oxides (typically, hematite and goethite) intensified the separation selectivity challenges. It is expected that when the REE minerals are well liberated, higher REE minerals recovery and upgrade at lower iron oxides and silicate recoveries can be achieved with the flotation, WHIMS, and gravity (KC and shaking table) methods. Overall, the series of beneficiation studies conducted demonstrated that the limitations presented by the poorly liberated REE minerals are exacerbated by their fine-grained nature.

4.2. Future Considerations

With the bulk of the material being fine/ultrafine, it is desirable that further studies will be conducted to ascertain the influential role of desliming on the recovery and upgrade of REE minerals. Furthermore, it is known that magnetic separation and froth flotation performance deteriorates with decreasing particle size distribution; however, it is imperative to carry out diagnostic grind–magnetic separation or diagnostic grind–flotation separation tests on the material to ascertain the effects of ultrafine particle sizes and enhanced mineral liberation on REE minerals recovery and upgrade. Prior to that, grind–mineral liberation relationship should be ascertained to identify any chance of enhancing REE minerals liberation from the gangue minerals. Studies involving magnetization roasting processes should be carried out to assess any chance of enhancing iron oxides rejection prior to REE upgrade. Previous studies by other researchers have demonstrated that magnetization roasting pretreatment has significant positive effects on the magnetic properties of hematite ores. Reduction roasting has been shown to enhance the magnetic susceptibility and magnetism saturation of hematite particles through the conversion of hematite to magnetite [63–67].

The prospect of leaching REE from the tailings may be considered in future studies. This may involve direct leaching (with acids, base, and in some cases water) of the raw tailings “feed”, which may be compared to leaching studies conducted on REE preconcentrates obtained from froth flotation, magnetic separation, and gravity concentration. This will inform stakeholders about the relevance of the various preconcentration processes. For example, previous studies have identified major processing challenges with high iron content in hydrometallurgical (leach) feed [68–70]. Elsewhere, leaching has been employed on differing (low and high-grade) resources, with varying outcomes. It is important to note that the selection of lixiviant is ore-specific, with major advances in hydrometallurgical
processes paving the way for enhanced REE recovery from unconventional resources with \( \leq 1\% \) TREO \[71–75\], although this may be associated with co-leaching of gangue minerals, expensive pretreatments, and high reagents consumption \[68,76,77\]. This suggests that the concentrates generated from this work could be considered for further processing as appreciable fractions of gangue species such as iron oxides and silicates were removed during the preconcentration processes.

Also, the prospect of using modern simulation tools to test different possible combinations of gravity, magnetic separation, and flotation to evaluate and confirm the potentials and limitations of the already tested unit operations and their combinations may be considered in future studies.

5. Summary

A review of various beneficiation studies conducted on low-grade tailings has been presented. There are distinct differences in the beneficiation response of REE and gangue minerals in the tailings. Gravity, wet magnetic, and froth flotation separation methods produced significantly varying REE recoveries and upgrades. Tabling presented a better potential for REE minerals upgrade compared to the KC. However, wet magnetic separation produced two REE “rich” preconcentrates. The two REE preconcentrates were subsequently upgraded via froth flotation. In terms of recovery, the best result was achieved during the multistage flotation process carried out on the tailings “feed” in the presence of hydroxamic acid and depressants. With high recoveries obtained using such readily available conventional separation methods, the tailings provide additional REE value to the primary commodities; hence, such tailings as used in this investigation could be considered a potential resource for REE beneficiation. The opportunity to enhance REE minerals recovery and upgrade through magnetic roasting, desliming flotation, diagnostic grind–magnetic separation, and diagnostic grind–froth flotation has been proposed for consideration in future studies to obtain a value chain that could serve as hydrometallurgical or pyrometallurgical process feed.

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