

Article

Recovery of Samarium from Waste SmCo Magnets via Selective Precipitation with Ammonium Bicarbonate: Optimization of Process Efficiency

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Abstract: SmCo magnets are a common material utilized in advanced technological applications. These magnets contain elevated concentrations of Sm and Co within their structural compositions. Given that both Sm and Co are classified as critical metals, the recycling of these magnets after their operational lifespan is of significant economic and environmental importance. Hydrometallurgical recycling processes represent an effective method for the recycling of these magnets. In this study, a pH-controlled selective precipitation method was developed using two HNO₃ solutions with distinct oxidizing properties for the recovery of Sm and Co from end-of-life (EoL) SmCo magnets. In the initial stage of the process, the magnets were leached in a low-oxidizing 2M HNO₃ solution, with a 1:30 (*w/v*) solid-to-liquid ratio at 20 °C. This step was undertaken to ensure the dissolution of Fe, thereby creating an environment conducive to its removal from the solution. The leaching experiments resulted in dissolution efficiencies of 95%, 96%, and 96% for Sm, Co, and Fe, respectively. In the second stage, a leaching experiment was performed using 3M HNO₃ with a 1:10 solid-to-liquid ratio at 60 °C. Under these conditions, Sm and Co achieved dissolution efficiencies of 99%, while Fe remained undissolved in the solid phase due to hydrolysis at the high temperature, thus increasing the solution purity. In the precipitation process, the pH of both leachates was initially adjusted to 4 to precipitate impurities such as Fe ions. As a result of precipitation at pH 4 in the 2M HNO₃ leachate, Fe ions were almost completely removed. This was followed by selective Sm precipitation in the pH range of 5–6.5 using NH₄HCO₃. The highest purity of Sm precipitation was achieved when the pH reached 6.5. An increase in Sm precipitation efficiency was observed with increasing pH, with an efficiency of 12.75% at pH 5, which rose to 82.37% at pH 6.5. Furthermore, although the precipitation efficiency of Co increased from 6.25% to 10% within this pH range, no significant difference in the extent of this increase was observed. In the case of the 3M HNO₃ leachate, the Sm precipitation efficiency at pH 5 was 44.28%, while at pH 6.5, nearly all of the Sm ions were precipitated. The co-precipitation efficiency at pH 5 was 1.89%, increasing to 36.43% at pH 6.5. This increase in co-precipitation was attributed to the system's Eh value, which reflects the enhanced oxidizing properties of the 3M HNO₃ leach solution. The results of the study indicate that as the oxidizing strength of the solution increased, the co-precipitation rate also increased with rising pH.

Keywords: SmCo magnets; recycling; selective precipitation; hydrometallurgy



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1. Introduction

Rare earth elements (REEs) and Co are among the critical raw materials, which are metals with high economic value and supply risk but nevertheless indispensable for use in many advanced technological applications [1]. SmCo magnets, developed by Alden Ray and Karl Strnat in the 1970s, are categorized into two distinct types: SmCo₅ and Sm₂Co₁₇ [2]. For several decades, SmCo has been recognized as the most thermally durable and energy-dense permanent magnet utilized in various applications. However, during the 1980s, the advent of NdFeB magnets developed by Japanese and American companies, distinguished by their economic efficiency and superior performance, led to a rapid transition from SmCo to NdFeB, particularly because of the challenges associated with cobalt supply at the time. NdFeB magnets have become the alternative in many electronic applications, such as hard disk drives, mobile phones, and electric vehicle motors, due to their lower cost and reduced susceptibility to price fluctuations [3]. Nevertheless, SmCo magnets exhibit distinctive performance characteristics that differentiate them from other types of magnets [4]. Their higher magnetic coercivity and superior temperature resistance make them particularly well-suited for specialized applications, such as vehicle powertrains and aircraft engines [3,4]. Recent research endeavors aim to enhance the performance of SmCo magnets while reducing their cost, with projections indicating an increase in global production in the coming years [5].

The recycling of Sm, Co, and other precious metals contained in end-of-life SmCo (EoL-SmCo) magnets is of significant importance for economic and environmental reasons, particularly in light of the economic importance of these metals and the environmental impact associated with ore production [6]. Hydrometallurgy is a frequently utilized method in the literature for the recycling of SmCo magnets [7–9]. The hydrometallurgical recycling processes of SmCo magnets consist of two steps: (1) leaching and (2) precipitation. Moreover, Sm, Co, and other metals are dissolved; solvent extraction is also used for the separation of metals [10]. Although solvent extraction provides high-efficiency metal separation, it has many disadvantages in terms of the environment and the economy [11]. The selective precipitation method has the potential to effectively separate Sm and Co [12], while simultaneously reducing the economic input of the process and requiring less chemical use. In the study conducted by Wang et al. (2022), waste SmCo magnets were leached with sulfuric acid, and then Fe and Cu ions were removed from the solution with ion resin [12]. Sm and Co remained in the solution; they proposed a process for the separation of Sm and Co from this solution via selective precipitation. In the samarium precipitation process, 98.7% efficiency was obtained by using Na₂SO₄ at 80 °C, a 4:1 molar ratio, and 90 min of processing time. The high temperature was determined as an important factor that increased Sm precipitation efficiency. While Sm was selectively precipitated, Co remained in the solution. In another study by Xu et al. (2010), ammonium oxalate was used to precipitate REEs from waste SmCo magnets following sequential leaching with sulfuric acid and sodium persulfate [13]. Initially, sulfuric acid leaching was performed to separate Sm and Co. Subsequent leaching with sodium persulfate was conducted to oxidize Co and Fe, resulting in increased concentrations of Fe and Co in solution and leading to the formation of Co-hydroxide (Co(OH)₃) and Fe-hydroxide (Fe(OH)₃). After filtration, Co, Fe, and rare earth elements (REEs) were separated. For REE precipitation, ammonium oxalate solution was applied, and REE oxides were obtained through drying and roasting following precipitation. REEs can be precipitated in the form of carbonates at relatively high pH values [14]. Although a variety of carbonate-containing compounds are employed as carbonate precipitating agents, ammonium bicarbonate (NH₄HCO₃) has garnered particular attention as an effective precipitating agent, exhibiting both precipitating and pH-increasing effects. In a recent publication, Anawati and Azimi (2022) detailed the stepwise precipitation method and the precipitating effect of ammonium bicarbonate for the separation of REEs from ionic clays originating from South America [15]. In the process, ammonium bicarbonate initially serves as a pH adjuster, selectively removing impurities that precipitate in the form of hydroxide at pH 6. Subsequently, it was reported

that ammonium bicarbonate acts as both a carbonate ion source and a pH adjuster in the pH range of 6–7.5, precipitating REEs in the form of carbonate. Ammonium bicarbonate is the preferred precipitating agent in the precipitation stage due to its low cost and environmentally friendly structure. The selective precipitation of Sm with NH_4HCO_3 after leaching of SmCo magnets has not, to the best of our knowledge, been attempted previously. NH_4HCO_3 has the potential to separate Co and Sm from solution, offering an alternative to ionic liquid or solvent extraction. It has the capacity to reduce process costs and is suitable for large-scale recovery processes. Furthermore, this study demonstrates the impact of solution oxidation degree on precipitation.

This study introduces a pH-controlled selective precipitation method for the recovery of Sm and Co from EoL SmCo magnets using HNO_3 solutions with distinct oxidizing properties. By tailoring leaching conditions and employing NH_4HCO_3 as both a pH adjuster and carbonate source, the method achieves high Sm precipitation efficiency at pH 6.5 while minimizing Co co-precipitation, offering an innovative, environmentally friendly approach to rare earth element recycling.

2. Materials and Methods

2.1. Materials

$\text{Sm}_2\text{Co}_{17}$ -type EoL-SmCo magnets were supplied by Vacuumschmelze GmbH & Co. KG (Hanau, Germany). HNO_3 (65%, Merck, Darmstadt, Germany) was used for the leaching process of EoL-SmCo magnets. The precipitation processes were conducted using NaOH pellets (Merck, Darmstadt Germany) and NH_4HCO_3 (Sigma Aldrich, St. Louis, MO, USA) while Milli-Q water was employed in the leaching, precipitation, and sample preparation procedures. Ethanol and acetone were used at various stages of the process.

2.2. Leaching of SmCo Magnets

The leaching process was conducted in a manner consistent with that employed in our previous study [7]. Two distinct leaching procedures were performed. The leaching parameters of both processes are presented in Table 1. The E1 leaching process was conducted with a solution of 2M HNO_3 , a solid-to-liquid ratio of 1/30 (g/L), a temperature of 20 °C, and a duration of 60 min. The E1 leaching process was carried out using a 2M HNO_3 solution with a solid-to-liquid ratio of 1/30 (g/L), at a temperature of 20 °C, and for a duration of 60 min. In contrast, the E2 leaching process was performed with a solution of 3M HNO_3 , a solid-to-liquid ratio of 1/10 (g/L), a temperature of 60 °C, and 60 min. The impact of the parameters was previously elucidated in our research study. E2 leaching provides a more oxidative solution; therefore, Fe remains in the leach residue. In the precipitation step, it is necessary to remove Fe ions before the precipitation of Sm ions. Otherwise, the presence of Fe ions affects the purity of the obtained precipitate. These two leaching solutions were used to investigate the effect of the removal of Fe ions during the pre-step on the Sm precipitation efficiency and to investigate the selective Sm precipitation behavior in the solution with more oxidizing conditions. Leaching efficiencies were calculated using Equation (1).

$$\text{The leaching efficiencies (\%)} = \frac{\text{Metal ion concentration } \left(\frac{\text{g}}{\text{L}}\right) \times \text{Leach volume (L)}}{\text{Metal amount of specific metal (\%)} \times \text{Initial metal amount (g)}} \times 100 \quad (1)$$

Table 1. Parameters of the experiments.

	HNO_3 Concentration (M)	Leaching Solid-to-Liquid Ratio (g/L)	Temperature (°C)	Time (min.)
E1	2	1/30	20	60
E2	3	1/10	60	60

Table 1. Cont.

	Precipitation	
	Initial pH	Precipitation pH
E1P1	4	5
E1P2	4	5.5
E1P3	4	6
E1P4	4	6.5
E2P1	4	5
E2P2	4	5.5
E2P3	4	6
E2P4	4	6.5

2.3. Precipitation

The pH of E1 and E2 leachates was adjusted to 4 using the required 2M NaOH solution. The pH was adjusted to 4 before precipitation, which was employed to remove Fe ions from the E1 solution. This same process was also used to provide a controlled pH increase during the Sm precipitation process with NH_4HCO_3 from the E1 and E2 solutions. The precipitation parameters with NH_4HCO_3 from solutions adjusted to pH 4 are presented in Table 1. E1P1–E1P4 and E1P1–E2P4 refer to the precipitation tests conducted with E1 and E2 leachates, specifying the pH conditions used in these tests. The initial pH for all tests was 4, while P1, P2, P3, and P4 correspond to pH values of 5, 5.5, 6, and 6.5, respectively. In addition to being a precipitating agent, NH_4HCO_3 also increases the pH of the solution. The requisite quantity of 2M NH_4HCO_3 was added to the solutions to precipitate the Sm complex within the pH range of 5–6.5, from both solutions. The obtained precipitates were washed 5 times with de-ionized water and dried in a vacuum oven at 50 °C. The experimental scheme of the study is presented in Figure 1. The precipitation efficiencies were calculated using Equation (2).

$$\text{The precipitation efficiencies (\%)} = \frac{(\text{Initial Metal ion concentration } (\frac{\text{g}}{\text{L}}) - \text{Metal ion concentration after precipitation } (\frac{\text{g}}{\text{L}}))}{\text{Initial Metal ion concentration } (\frac{\text{g}}{\text{L}})} \times 100 \quad (2)$$

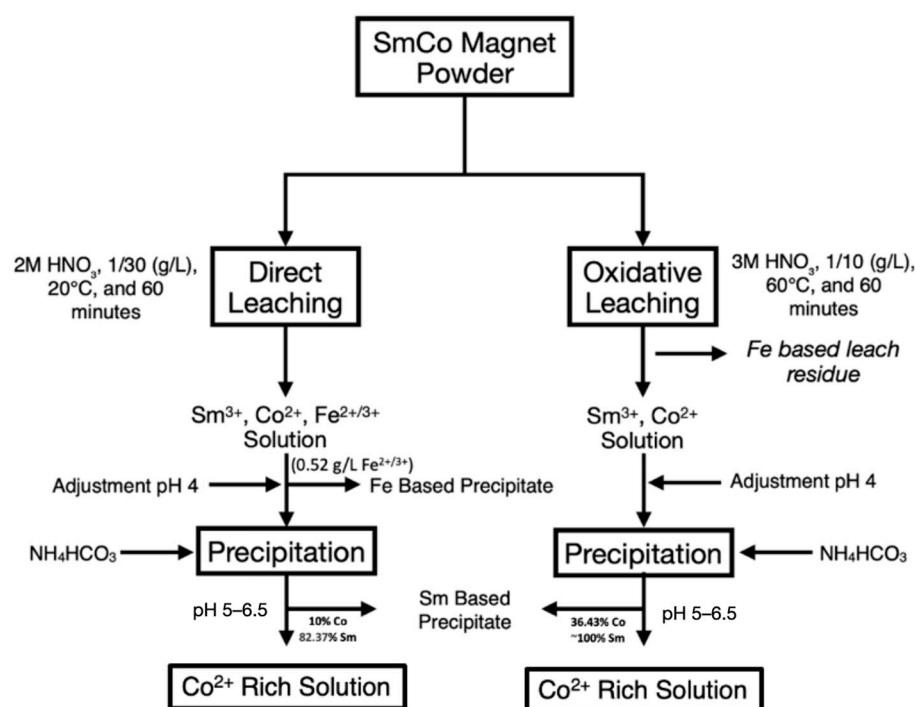


Figure 1. Experimental scheme of the study.

2.4. Characterization

The precipitation efficiencies of Sm, Co, and Fe were then calculated based on the metal concentrations obtained from the ICP-OES (SPECTRO ARCOS) analysis. SEM/EDS (Scanning Electron Microscope, Thermo Fisher Quattro S, Thermo Fisher Scientific, Brno, Czech Republic) analysis was performed to analyze of precipitates' morphology and elemental distribution.

3. Results and Discussion

3.1. Characterization of EoL SmCo Magnets

A detailed characterization of waste $\text{Sm}_2\text{Co}_{17}$ magnets was performed in our previous studies [7,16,17]. The SEM-EDS analysis results indicated that the $\text{Sm}_2\text{Co}_{17}$ magnet particle distribution was heterogeneous and non-uniform; the particles are primarily composed of Sm (39.68% *w/w*), Co (30.78% *w/w*), and Fe (13.06% *w/w*) metals [16]. Additionally, the EDS results showed the presence of Cu (3.95% *w/w*) and Zr (1.8% *w/w*) [16]. The $\text{Sm}_2\text{Co}_{17}$ alloy magnets used in high-temperature applications are also $\text{Sm}(\text{CoFeCuZr})_z$ ($z = 6.0\text{--}9.0$) quinary alloys [18], which explains the presence of impurities such as Fe, Cu, and Zr alongside Sm and Co in the characterization results. Furthermore, the chemical composition of the magnets was determined using ICP-OES, and the results are presented in Table 2.

Table 2. Chemical composition of the magnets.

Elements	Co	Sm	Fe	Cu	Zr	Nd
Weight, %	55	21	15.2	5.1	2.7	0.8

The XRD analysis showed that $\text{Sm}_2\text{Co}_{17}$ was the dominant phase in the structure of the magnets and the FeCo phase was also present, while dynamic particle analysis revealed that 90.3% of the particles were smaller than $96.25\text{ }\mu\text{m}$ [17].

3.2. Leaching Reactions

In a previous study involving oxidative leaching of SmCo magnets to remove Fe, leaching reactions were carried out, and the results were examined in detail [7]. As a result of testing numerous parameters, the optimal oxidative leaching conditions were determined through Taguchi plots and ANOVA analysis to be a 3M HNO_3 , a solid-to-liquid ratio of 1/10, and a process temperature of $60\text{ }^\circ\text{C}$. Leaching efficiencies obtained with E1 and E2 reactions are presented in Figure 2a; also, the metal ion concentrations of leachate solutions are given in Figure 2b. The leaching reaction was performed in 2 M HNO_3 at a 1/30 (*w/v*) solid–liquid ratio and $20\text{ }^\circ\text{C}$ (E1). The final solution pH was 0.2. In the leaching reaction with 3 M HNO_3 , a 1/10 solid–liquid ratio, and $60\text{ }^\circ\text{C}$ (E2), Sm and Co were efficiently leached (99%), while Fe remained in the residue due to hydrolysis at higher temperatures [7]. The final solution pH was ~ 2.67 , influenced by the high solid–liquid ratio. It is thought that the increase in pH may have favored the transfer of Fe^{3+} ions into the precipitate phase as goethite. The Pourbaix diagram of Sm, Co, and Fe is shown in Figure 3a. In addition, the heat map plotted according to the stability of the FeHO_2 structure is shown in Figure 3b. It was observed that after pH around 2, Fe transforms from ionic form to solid form, while Sm^{2+} and Co^{2+} remain in the solution. In addition, the heat map showed that the ΔG_{pbx} (Gibbs free energy) value (eV/atom) for FeHO_2 was 0.13 eV/atom at around pH 2 under oxidizing conditions. This shows that the structure maintains stability under these conditions and Fe remains in the residue.

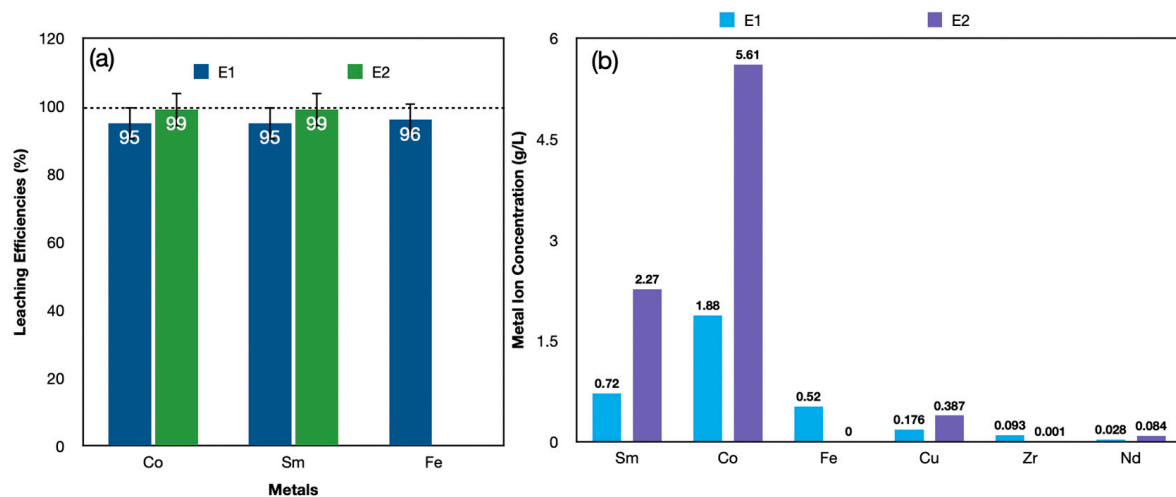


Figure 2. Leaching efficiencies (a) and metal ion concentration of leachates (b).

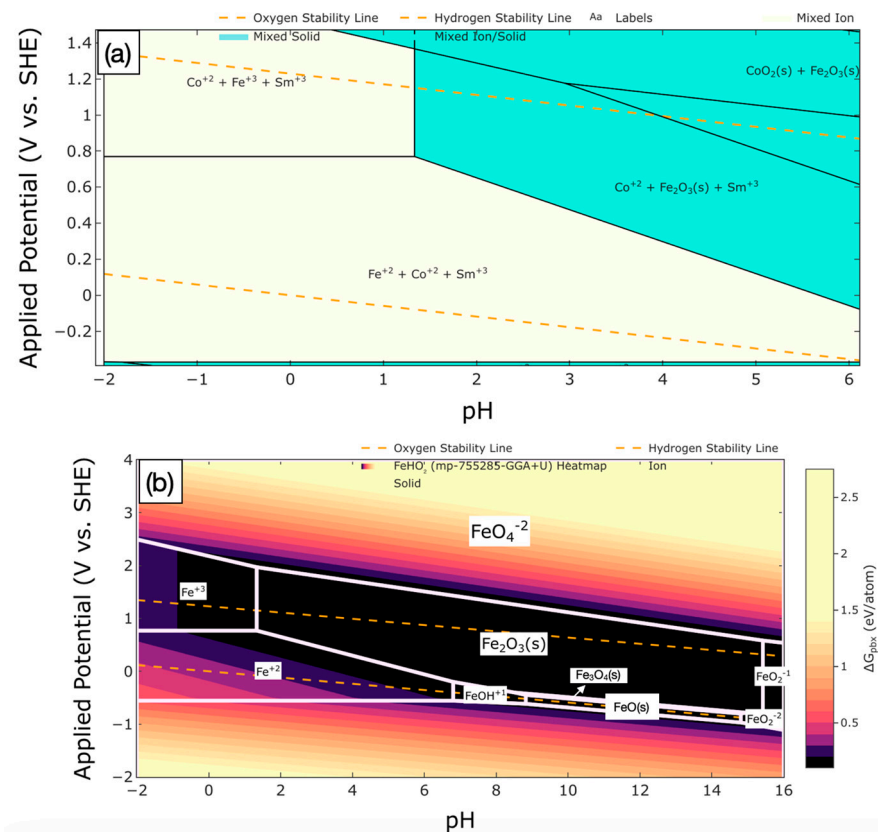


Figure 3. The Pourbaix diagram of Sm, Co, and Fe (a) and the heat map of FeHO₂ GGA + U (b) (drawn with The Materials Project) (Adapt from [19–21]).

3.3. Precipitation

The presence of Fe ions in the solution has an impact on the purity of the resulting precipitate. The precipitation of impurity ions, including Fe^{3+} , Al^{3+} , and Ca^{2+} , at pH values greater than 3–4 facilitates the purification of the leach solution from impurities [22]. In this study, to remove impurity ions in the solution, the pH value of the leaching solutions was increased to 4 before selective REE precipitation with NH_4HCO_3 , and in particular, the high concentration of Fe ions, obtained after the E1 leaching reaction, was removed from the solution via precipitation. In Figure 4, the precipitation efficiencies of Sm, Co, and Fe ions at pH 4 from the E1 leaching solution are presented. At a pH of 4, the Fe ions were

almost completely removed from the solution, while the loss of Sm and Co was calculated to be 0.44% and 3.94%, respectively. While Fe ions and other impurity ions precipitate, even if the pH range of the precipitation does not correspond to that of the REEs ions, these ions precipitate together with the impurities or can adsorb onto the surface of precipitated impurity complexes [23].

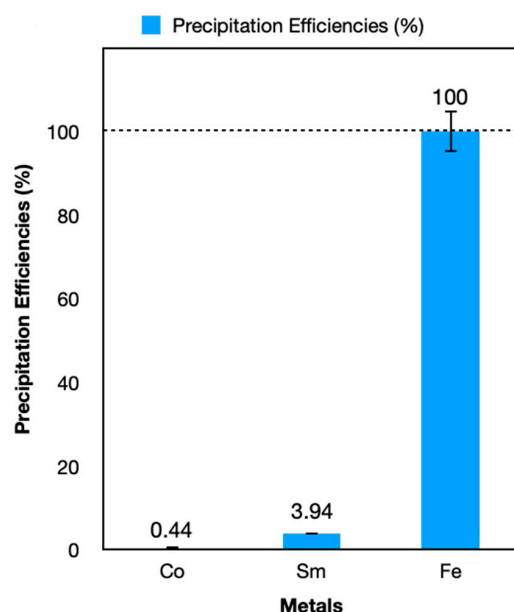


Figure 4. Precipitation efficiencies from E1 leachate at pH 4.

REEs can be easily precipitated by carbonate at high pH values, and carbonates are ideal precipitants due to their easy availability, low cost, and easy dissolution in mild acids for subsequent purification; however, since precipitation is difficult in acidic environments, a neutralization process is applied to the leach solution before REE precipitation, and during this process, impurities such as Fe^{3+} and Ca^{2+} are primarily precipitated, which may lead to the loss of REEs through adsorption and co-precipitation with oxides or complexes [14]. To precipitate REE carbonate complexes under mild acid conditions and remove impurities, the pH value in both solutions was adjusted to 4 and then precipitated with NH_4HCO_3 . It is appropriate to utilize NH_4HCO_3 as a precipitating agent for REEs. In addition to providing a carbonate source for complexation with REEs, it serves as a pH adjuster compared to other agents that offer carbonate sources [15,24]. REEs precipitate as REE carbonates ($\text{RE}_2(\text{CO}_3)_3$) with Equation (3) in the pH range of 7–8 [15]. However, the cobalt carbonate precipitate formation reaction occurs in the pH range of 6.5–8 [24]. To achieve selective precipitation of Co and Sm, precipitation was conducted within a pH range of 5–6.5. Sm and Co precipitation efficiencies from solution E1 in the pH range of 5–6.5 are given in Figure 5a. An increase in pH value from 5 to 6.5 resulted in a notable enhancement in the precipitation efficiency of Sm, with a significant rise from 12.75% to 82.37%. Nevertheless, during the selective precipitation process, some Co was also precipitated via co-precipitation or the adsorption of the formed Sm complex precipitates. Increasing the pH from 5 to 6.5 in solution E1 increased the Co-precipitation rate from 6.25% to 10%. Although this increase was attributable to the approach of the precipitation pH range of Co, no notable distinction was discerned between pH 5 and 6.5. Sm and Co precipitation efficiencies with NH_4HCO_3 from E2 solution (in the pH 5–6.5 range) are given in Figure 5b. The precipitation efficiency of the Sm carbonate was found to be 44.28% at pH 5, with the precipitation of all Sm ions in the solution occurring at pH 6.5. The Co-precipitation rate was observed to be 1.89% at pH 5 and 36.43% at pH 6.5. This considerable enhancement in the rate of Co-precipitation is contingent upon the Eh value of the system. At elevated temperatures, the solution obtained through leaching with HNO_3 (E2) exhibits

enhanced oxidizing properties [7]. It was observed that increasing the oxidizing properties of the solution increased the Co-precipitation rate with increasing pH.

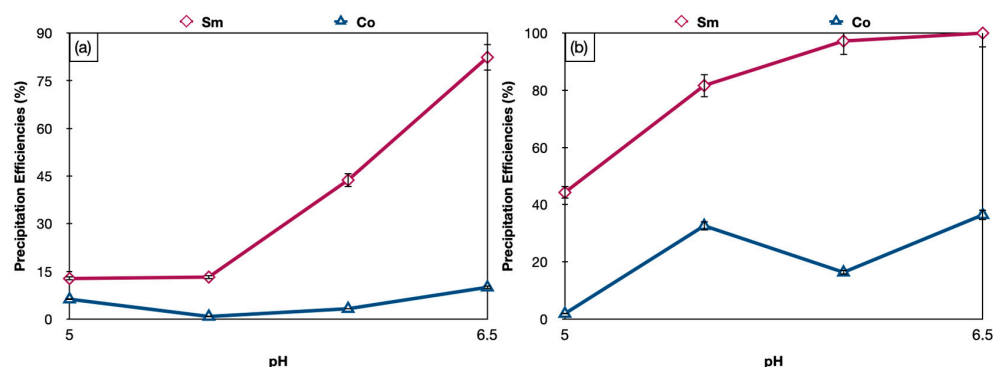
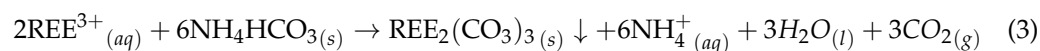


Figure 5. Precipitation efficiencies from E1 (a) and E2 (b) leachate solutions with NH_4HCO_3 in the 5–6.5 pH range.

Figure 6 illustrates the SEM images of the precipitates that were formed from the E1 and E2 solutions at pH values of 5 and 6.5, respectively. It was observed that the precipitates exhibited an irregular shape and agglomeration, similar to that observed in the particles obtained as a result of REE precipitation with NH_4HCO_3 in the literature. It was observed that the precipitates obtained from the solution with more oxidative conditions exhibited a particle size distribution that was smaller.

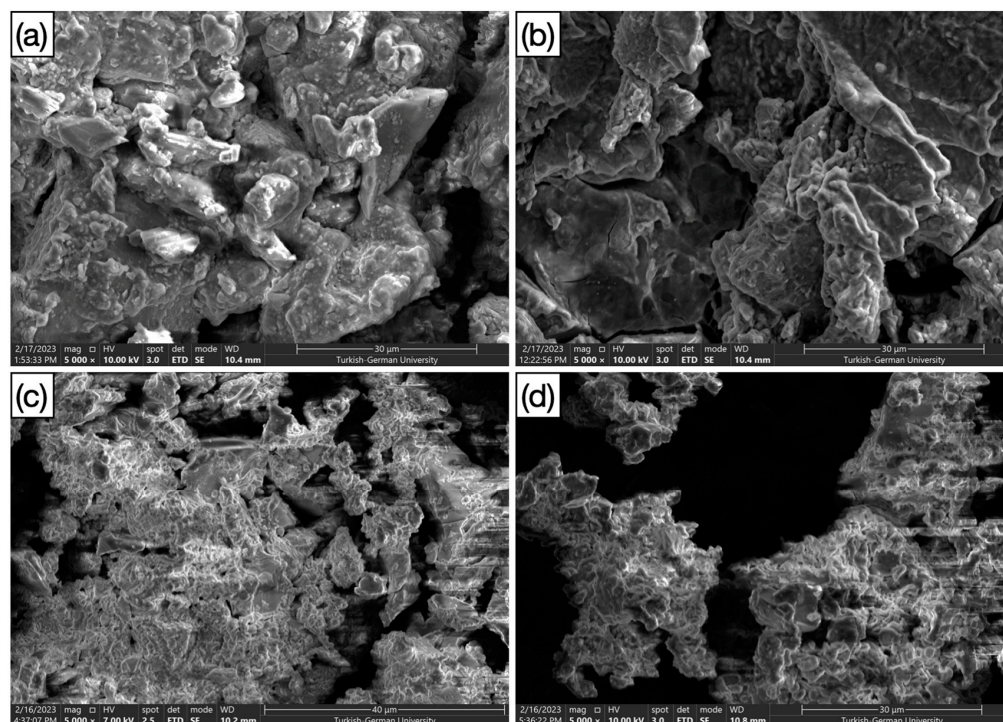


Figure 6. SEM images of the precipitate: from E1 solution at pH 5 (a) and pH 6.5 (b) and E2 solution at pH 5 (c) and pH 6.5 (d).

EDS maps of the precipitate obtained as a result of precipitation from solution E1 at pH 6.5 are given in Figure 7. It was observed that the distribution of Sm, Co, C, and O in the precipitate was homogeneous, occurring in the same regions. This indicates that Co

may either co-precipitate during the precipitation of Sm with carbonate or precipitate by adsorption on the surface of the formed Sm carbonate complexes.

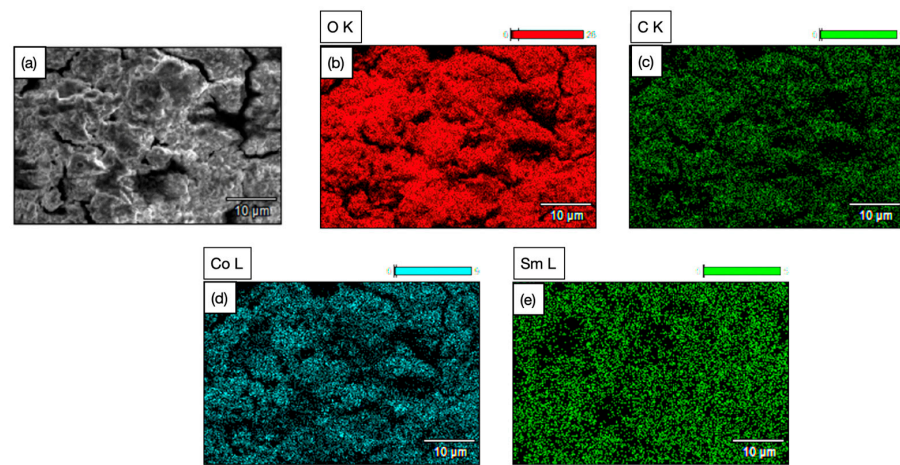


Figure 7. SEM images of the precipitate obtained at pH 6.5 from E1 (a), and EDS maps of O (b), C (c), Sm (d), and Co (e).

EDS results of 3 different points of the precipitate obtained from the E1 solution at pH 6.5 are given in Figure 8. It was observed that three distinct points exhibited a Sm concentration exceeding 60% by weight, with the predominant element in the precipitate being Sm. Furthermore, it was established that the concentration of Co remained below 3% by weight at three distinct points. Additionally, it was determined that Co co-precipitated or adsorbed to Sm complexes during precipitation. It is postulated that the observed Cu concentration (average 3.7% by weight) is derived from the SEM-EDS substrate. Moreover, no Fe was detected in the precipitate, and it was observed that the Fe was effectively removed before carbonate precipitation.

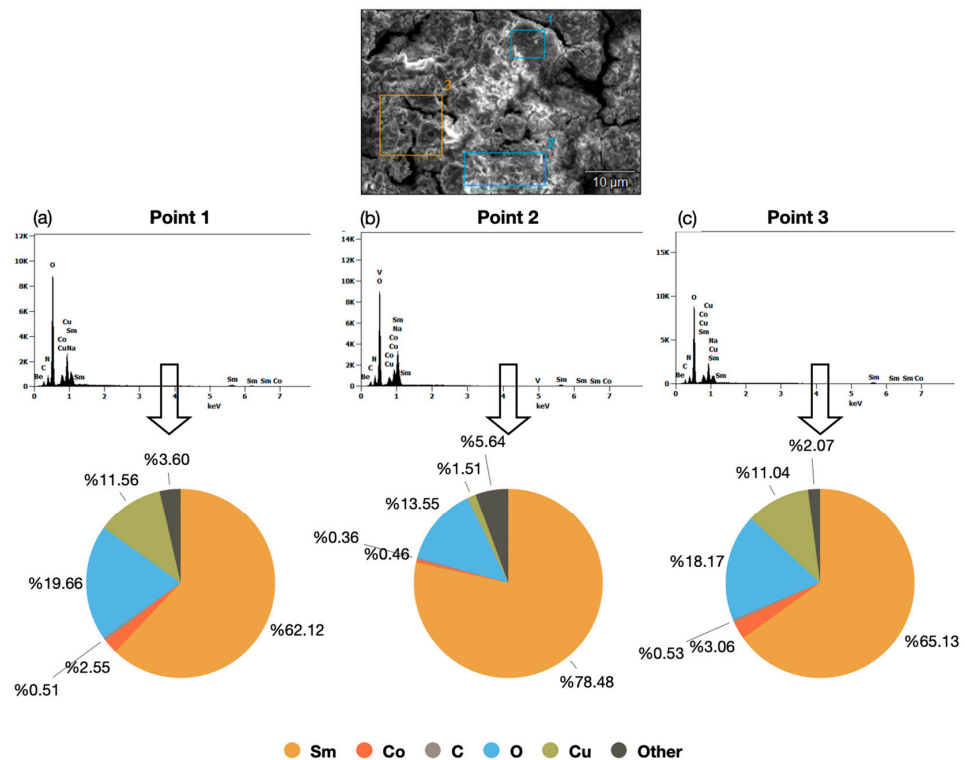


Figure 8. EDS results of 3 different points: point 1 (a), 2 (b), and 3 (c).

3.4. Comparison of Different Routes

This study was compared with our previous research in terms of process efficiency, the number of steps, environmental impact, advantages, and challenges. In the first route, acid baking with HNO_3 was carried out, followed by the separation of REEs through water leaching [17]. In the second route, acid baking with H_2SO_4 was performed, followed by REE separation via water leaching [16]. Table 3 presents a comparison of three different routes.

Table 3. Comparison of the three different routes.

Aspect	Acid Baking with HNO_3 and Water Leaching	Acid Baking with H_2SO_4 and Water Leaching	Oxidative Leaching and Selective Precipitation
Process Step	1. Mixture with HNO_3 , 2. Selective oxidation at 250 °C 3. Water leaching	1. Mixture with H_2SO_4 , 2. Selective oxidation at 800 °C 3. Water leaching	1. Oxidative leaching 2. Iron precipitation 3. Selective REE precipitation
Efficiency	>95% Sm extraction, <1% Co/Fe dissolution, and 99.4% purity of REEs in leach liquor	65% Sm extraction; Co/Fe oxides separated; minimal solubility of Fe, Co, and Cu (~2%).	99% Sm/Co dissolution at 60 °C; selective Sm precipitation (82.37–100%) at pH 6.5 with minimal Co co-precipitation (10–36%).
Environmental Impact	NO_x gas emission during acid baking; proposed reactor to address emissions. Lower selective oxidation temperature	SO_x gas emissions recycled for H_2SO_4 production. Higher selective oxidation temperature	Lower-temperature leaching reduces energy demands; careful pH control minimizes reagent use and impurity loss
Advantages	High Sm purity and low impurity dissolution; scalable with improved reactor design	Cost-effective, industrially scalable process	High dissolution and purification efficiencies; selective Sm recovery with minimal Co loss; scalable and versatile
Challenges	NO_x management and reactor scalability	Sm-oxysulfate formation limits extraction efficiency but offers reuse potential	Co co-precipitation increases at higher pH; small amounts of Sm loss in iron precipitation

4. Conclusions

This study demonstrates the effectiveness of an optimized hydrometallurgical process for selectively recovering Sm and Co from EoL SmCo magnets with high dissolution and purification efficiencies. Using 2M HNO_3 at 20 °C with a 1:30 (*w/v*) solid–liquid ratio, dissolution efficiencies of 95% for Sm, 96% for Co, and 96% for Fe were achieved. In contrast, leaching with 3M HNO_3 at 60 °C and a 1:10 ratio resulted in 99% dissolution efficiency for Sm and Co, while Fe remained undissolved due to hydrolysis, enabling effective impurity removal during purification. In the E1 solution, at pH 4, nearly all Fe was removed, minimizing Sm (0.44%) and Co (3.94%) losses. The use of NH_4HCO_3 in the pH 5–6.5 range enabled selective precipitation from the purified leach solution, achieving 82.37% Sm precipitation at pH 6.5 while limiting Co precipitation to 10%. In the E2 solution, the selective precipitation efficiency of Sm increased from 44.28% at pH 5 to 100% at pH 6.5, while Co co-precipitation increased from 1.89% to 36.43%. These results indicate that despite the increased oxidative conditions in E2, high-purity Sm recovery is achievable with controlled pH adjustment. This scalable method offers an efficient and selective approach to rare earth element recovery from waste materials. Further optimization of selective precipitation parameters may extend its applicability to other REEs, advancing sustainable recycling solutions.

Author Contributions: E.U.: validation, investigation, formal analysis, writing—original draft, writing—review and editing, and visualization. E.E.-K.: methodology, validation, investigation, formal analysis, writing—original draft, writing—review and editing, and conceptualization. H.N.D.: validation, formal analysis, writing—original draft, and writing—review and editing. M.P.: validation,

methodology, and investigation. S.G.: validation, resources, and supervision. B.F.: validation, resources, supervision, and project administration. All authors have read and agreed to the published version of the manuscript.

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