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Recovery of valuable metals from SmCo magnets through sulfation, selective oxidation, and water leaching

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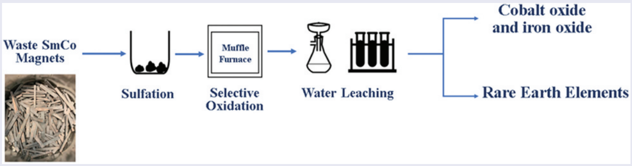
ABSTRACT
Samarium-cobalt (SmCo) magnets, comprised of rare earth elements (REE), and cobalt (Co) are widely employed in diverse sectors such as aerospace, medical, defense, automotive, and more due to their unique properties such as outstanding high-temperature resistance, superior corrosion resistance, a higher Curie temperature, and high energy density. REE and Co are on the critical metals list for many years, along with increased production costs and challenges. With the increasing amount of waste SmCo, the recycling of these magnets has gained importance. This study investigates the recycling of SmCo magnet scraps through sulfation, selective oxidation, and water leaching. The effect of experimental parameters, such as powder/acid concentration, selective oxidation temperature, selective oxidation time, solid/liquid ratio and leaching time for water leaching are studied in detail. The optimal parameters are determined: 800°C selective oxidation temperature, 1-h selective oxidation time, 1/3 g/ml magnet: acid ratio, 2-h water leaching time and 1/20 water leaching s/l ratio. Under the optimum conditions the extraction efficiency of Sm reached approximately 65%, The solubility of Fe, Co, and Cu metals in the solution is negligible.



The proposed process of recycling of SmCo magnets

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Recycling; separation; Hydrometallurgy; critical metals

Introduction

REE are one of the most important raw materials since they are used in the production of high technological applications such as electronic devices, catalysts, hybrid vehicles, wind turbines, solar panels, electronic circuits. According to the 2023 EU report, 16 out of 17 REE are listed as critical raw materials.[1] The other element found in this list, Co, plays a crucial role in various applications such as rechargeable batteries, catalysts, pigments, coatings, alloys and magnets.[2] Due to the presence of both Co and REE, recycling of SmCo magnets have gained significant importance in recent years.

The recycling processes of NdFeB magnets is well-documented in the literature, studies on SmCo magnets are relatively new and limited. However, compared to NdFeB magnets, SmCo magnets are much more suitable for specialized applications such as automotive transmissions, military equipments and aircraft engines due to their higher magnetic coercivity and better temperature resistance.[3,4] There are two different SmCo permanent magnets, SmCo$_5$ and Sm$_2$Co$_{17}$. SmCo$_5$ consists of only Sm and Co. A typical Sm$_2$Co$_{17}$ magnet consists of approximately %30–40 Sm and %50–60 Co, with the rest of the composition comprising other metals, including Fe, copper (Cu), nickel (Ni) and zirconium (Zr).[5] It has been reported that approximately 150 tons of waste were generated from 500 tons of SmCo magnets produced in the year 2008, which contained 40 tons of REE, 85 tons of Co, 1 ton of Cu, and 4 tons of Zr.[6] The demand for SmCo have also led to an increase in the amount of SmCo waste.

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Hydrometallurgical processes, which commonly include acid leaching, solvent extraction, ion exchange, and selective precipitation, often result in higher chemical consumption and increased costs due to the elevated usage of solvents.[5,7–10] Certain investigations have explored recycling using organic solvents and ionic liquids; however, these methods necessitate the use of different types and a broader range of chemicals.[11–14] Conducting these studies in multiple stages further extends the process and complicates the achieve of desired yields. There are few studies on SmCo through pyrometallurgical methods. However, pyrometallurgical methods in metal recycling face challenges such as high energy requirements and the generation of a significant amount of solid waste.[15] In recent times, combination of pyro-hydrometallurgical methods has emerged in the literature with the aim of minimizing the disadvantages of both methods and capitalizing on their advantages.

Lorenz and Bertau[16] applied the solid-state chlorination method to recovery of SmCo magnets for the first time, achieving a recycling efficiency of approximately 97% for Sm from $SmCo_5$ magnet waste. The decomposition of ammonium chloride (NH_4Cl) during roasting at 225–325°C, converts the magnets into water-soluble chlorides. The metal chlorides are subsequently dissolved in an acetate buffer solution to obtain REE in a solution, and the resulting solution is regenerated for reuse.

In the literature, numerous studies on recycling have utilized the sulfate-roasting-leaching method as a pyro-hydrometallurgical approach.[17–21] Önal et al.[21] applied this method to recovery of NdFeB magnet powders through sulfation, followed by selective roasting at temperatures ranging from 650 to 850°C. They study subsequently investigated water leaching for extraction of REE. The extraction efficiency was approximately 95% for the recovery of Nd, Pr, and Dy. Ponou et al.[22] employed this method for the recycling of REE from bottom ash, Borra,[23] and Rivera[24] from bauxite. Li et al.[25] also utilized this approach for the recovery of REE from florencite-rich ores.

In this article, a simple and controllable alternative pyro-hydrometallurgical approach is proposed for recovery of REE, Co, Cu and Fe from the SmCo magnets, investigating the effect of selective oxidation temperature, oxidation time, solid/liquid ratio and water leaching time on extraction efficiency of Sm. In comparison to other works in the literature, our approach exclusively utilizes water and H_2SO_4 for the extraction and separation of REE from Fe and Co oxides from SmCo. The proposed route contributes the circularity of critical metals, including Co and REE. Additionally, it has substantial potential to improve resource efficiency for spent SmCo magnets.

Theoretical background

The sulfation – selective oxidation – leaching process consists of three different steps: the first step involves mixing the magnet powders with concentrated sulfuric acid (e.g., sulfation); the second is selective oxidation at a muffle furnace, and the last step is water leaching. During acid mixing, most of the oxides convert to their respective sulfates. During the selective oxidation, sulfates decompose to give their respective water-insoluble oxides due to their low thermal stability.[23] When iron sulfate compounds are heated above 550°C, initially, FeO decomposes; however, it oxidizes to Fe_2O_3 either through reaction with oxygen in the air or through the slow decomposition of SO_3, as indicated in Equation (1).[21]

$$2\mathrm{FeSO_4} \rightarrow 2\mathrm{Fe_2O_3}+\mathrm{SO_2(g)}+\mathrm{SO_3(g)} \tag{1}$$

The thermal decomposition behavior of $Fe_2(SO_4)_3$ is as a simple process, directly yielding hematite and releasing SO_3 gas. In the literature, temperatures ranging from 500–600°C, 550–625°C, 500–545°C, and 575–600°C have been reported for the thermal decomposition of $Fe_2(SO_4)_3$.[21] Tagawa reported the decomposition of Co sulfate ($CoSO_4$) in air at 690°C and proposed two reactions for the decomposition of $CoSO_4$, which are given in Equations 2 and 3.[26]

$$\mathrm{CoSO_4} \rightarrow \mathrm{CoO} + \mathrm{SO_3} \tag{2}$$

$$\mathrm{CoSO_4} \rightarrow 13\ \mathrm{Co3O_4} + 13\ \mathrm{SO_4} + 13\ \mathrm{SO_3} \tag{3}$$

The decomposition of REE sulfates, similar to the thermal decomposition of metal sulfates, is represented by reactions 3.6 and 3.7, where REE is represented as R.[27]

$$\mathrm{R_2(SO_4)_3} \rightarrow \mathrm{R_2O_2(SO_4)}+2\mathrm{SO_3(g)} \tag{4}$$

$$\mathrm{R_2O_2(SO_4)} \rightarrow \mathrm{R_2O_3}+\mathrm{SO_3(g)} \tag{5}$$

In the study conducted by Poston et al., they indicated that the dehydration of Sm sulfate occurred between 100 and 300°C, followed by the decomposition of Sm sulfate starting at approximately 700°C.[28] However, through thermogravimetric analysis (TGA), they observed a rapid decrease in material weight at 800°C, followed by a milder weight loss between 800 and 890°C. The transformation of Sm sulfate to oxy-sulfate ($R_2O_2(SO_4)$) was reported to occur around 900°C, with the oxy-sulfates converting to Sm oxide at 1210°C. Nathans and Wendlandt, in their investigation of the thermal decomposition of rare earth sulfates, noted a distinct range of

855–946°C for the decomposition of Nd and Pr metal sulfates.[29] The resulting metal oxides in the R_2O_3 structure from thermal decompositions are generally insoluble in water, with few exceptions for certain metal oxides.

The water-soluble rare-earth sulfates exhibit stability within distinct temperature ranges, and they readily dissolve during water leaching, thereby leaving behind iron oxides in the residue.[23]

Based on studies in the literature, the experimental temperatures in the range of 650–800°C have been selected in this paper to preserve the sulfate form of REE (Sm, Nd, and Pr) while allowing other metals (Co, Cu, Fe, Zr) to take on their oxide forms. The formation of these compounds relies on the differences in the thermal stabilities of Co, Cu, Fe and REE sulfates.

Materials and methods

Materials

The SmCo magnet samples were collected from Vacuumschmelze GmbH & Co. KG, located in Germany. The SmCo magnet samples are scrap residues from magnet production and do not require demagnetization. All the chemicals used in this study are of analytical grades. H_2SO_4 was kindly provided by Honeywell, % 96 and was utilized for all following experiments.

Methodology and procedures

The magnets were initially crushed to approximately 90 µm by a jaw crusher (Retsch BB51). Then, the obtained powders were sieved using a vibrating sieve shaker (Retsch, AS200) to obtain powder samples with particle sizes smaller than 90 µm. The magnet powders were exposed to a high concentration of H_2SO_4 to establish the desired sulfation of REE. Subsequently, the mixture is selectively calcined in a muffle furnace to obtain soluble REE (Sm, Nd, Pr) sulfates, and insoluble Co and Fe oxides. The mixture is then leached with water and filtered to obtain a leaching solution including REE (Sm, Nd, Pr) and the leaching residue including, Co an Fe oxide particles. The experimental procedures can be grouped into three subheadings: sulfation of SmCo magnet powders, selective oxidation, and water leaching. Table 1 illustrates the experimental parameters.

Sulfation of SmCo magnet powder

After grinding and sieving, the initial magnet powders were taken in 3-gram and moistened with 2–3 drops of deionized water to facilitate ionization of the powders. The powders were mixed in a cylindrical alumina crucible with the H_2SO_4 (96%) drop by drop by magnet: acid ratio (g/ml) of 1/2, 1/3, 1/4 and 1/5. After intensive bubbling was achieved by mixturing, the mixture was left for 1 hour to facilitate sulfate formation. Continuous bubbling was noted due to the ongoing structure of the acid-magnet reaction. All sulfation experiments were performed at the fume hood due to gas formation.

Selective oxidation

After the powders have been left for 1 hour, the sulfate mixture was transferred to the furnace crucibles and then placed in the muffle furnace (Heraeus Brand, M104 Model) and the furnace was heated to 650, 700, 750 and 800°C based on the desired experimental conditions. The furnace experiments lasted approximately 5–8 hours depending on the temperature. Once the desired temperature was reached, the furnace was held at the desired experimental conditions for a selective oxidation period of 1 or 2 hours. After the furnace had cooled down, the obtained products were quantitatively scraped off from the crucibles by a scraper. The calcines were transformed into a powder form by grinding to obtain a homogeneous mixture. Figure 1 illustrates the schematic representation of sulfation and selective oxidation processes.

Table 1. Experimental parameters.

		Sulfation		Selective Oxidation		Water Leaching	
	Experiment Code	Magnet Powder (g)	Magnet Powder/acid (g/ml)	Temperature (°C)	Time (hour)	Solid/liquid ratio (g./ml)	Time (hour)
1	S15–2	3	1/5	650	2	1/20	2
2	S25–2	3	1/5	700	2	1/20	2
3	S35–2	3	1/5	750	2	1/20	2
4	S45–2	3	1/5	800	2	1/20	2
5	S45–1	3	1/5	800	1	1/20	2
6	S35–3	3	1/5	750	3	1/20	2
7	S44–1	3	1/4	800	1	1/20	2
8	S44–2	3	1/4	800	2	1/20	2
9	S42–2	3	1/2	800	2	1/20	2
10	S43–2	3	1/3	800	2	1/20	2
11	S43-2A	3	1/3	800	2	1/10	2
12	S43–1	3	1/3	800	1	1/20	2
13	S43-1A	3	1/3	800	1	1/10	2

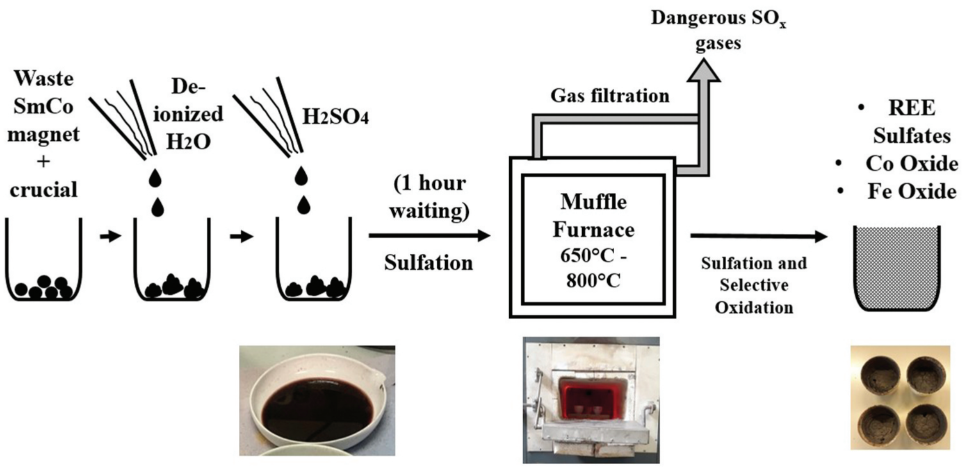


Figure 1. Schematic representation of sulfation and selective oxidation processes.

Water leaching

Leaching experiments were conducted in a three-necked flask with a mechanical stirrer, which had a capacity of 500 mL. Five grams of calcine samples were leached with deionized water at powder-to-acid ratios (g/ml) of 1/10 and1/20 for 2 hours at 350 rpm. For ICP-OES analysis, solutions were prepared by subjecting the leached sludge to filtration using a syringe filter. Solid residues for analyses were obtained by filtering the sludge under vacuum through a Buchner funnel with the filter paper. The filter cake was dried at 80°C.

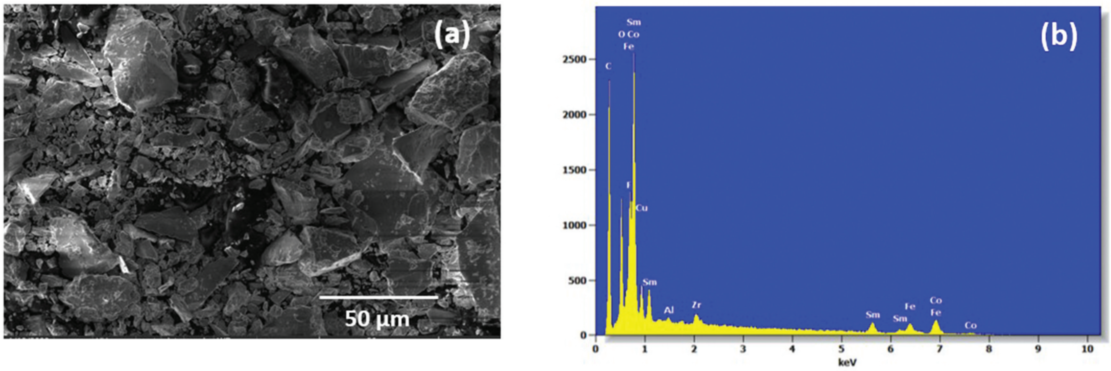
Materials characterization

The composition of the magnet samples and the metal concentration in the leaching solution were determined through ICP-OES analysis (SPECTRO ARCOS), the particle sizes were determined via a dynamic particle analyzer M5 lens (SympaTech Quick Pick Oasis). The phase analyses of selectively oxidized powders and leach residues were investigated by X-ray diffractometer using monochromatic CuK$_\alpha$ radiation (XRD, PANanalytical EMPYREAN). The elemental mapping analyses were conducted using FE-SEM coupled with EDX analysis. (Scanning Electron Microscope, Thermo Fisher Quattro S).

Results and discussion

Characterization of the SmCo magnet powders

Before starting the experiments, a comprehensive characterization study was carried out. Figure 2 illustrates (a) SEM micrograph of SmCo magnets and (b) EDX spectrum of the magnet powders and (c) table of chemical composition of the magnet powders.



(c)

C	O	F	Al	Fe	Co	Cu	Zr	Sm	Total (%)
5.843	4.563	0	0.22	13.063	30.782	3.959	1.891	39.68	100.001

Figure 2. (a) SEM micrograph (b) EDX spectrum and (c) chemical composition of SmCo Magnets.

Table 2. Chemical analysis of the leach solution.

Elements	Co	Sm	Fe	Nd	Cu	Zr
wt.%	55	21	15.2	0.8	5.1	2.7

The presences of Co, Sm, Fe, Cu, Zr, C and O are proved with the EDX analysis of the SmCo magnet. Additionally, the presence of aluminum (Al) may have appeared due to the aluminum substrate during the SEM analysis.

To ensure the accuracy and reliability of the EDX results, chemical analysis was performed on SmCo magnets. The solution samples obtained after dissolution of SmCo magnet powders with HNO_3 were analyzed using ICP-OES, and the results is presented in Table 2. As shown in the table, the main components of the magnet powders are Co, Sm, and Fe.

As a result of EDX analysis and ICP-OES analysis, the presence of Co, Sm, Fe, Nd, Cu and Zr elements was cross checked.

Phase analyses of the selectively oxidized powders

Phase analysis of the selectively oxidized powders was performed to confirm the presence of sulfate and oxide phases after the selective oxidation. Table 1 illustrates the coding of all samples and their experimental conditions.

Figure 3 represents the XRD spectra of 1/5 g/mL powder/acid constant variable samples after selective oxidation at 650, 700, 750, and 800°C for investigating the temperature effect. The presence of Fe oxide (Fe_2O_3, Fe_3O_4), Co oxide (Co_3O_4), REE sulfate ($REESO_4$) and Sm oxy sulfates ($Sm_2O_2SO_4$) was observed in the sample (S45–2) at 800°C. It confirms the successful selective oxidation of Fe/Co oxides. However, some amount of REE does not remain in sulfate form and some of it turns into oxy sulfates in samples up to 750°C (S15–2, S25–2, S35–2). The temperatures between 650°C and 750°C are not sufficient for the completion of selective oxidation.

Figure 4 represents the XRD analyses of the samples after selective oxidation. The selective oxidation was successful in these samples because of the presence of Fe_2O_3, Fe_3O_4, Co_3O_4, $REESO_4$ ($SmSO_4$, $Sm_2(SO_4)_3$, $NdSO_4$) and $Sm_2O_2SO_4$, although some REE sulfates were abundant, however, some of the sulfates turned into oxy sulfates. S43–1 and S43–2 samples after selective oxidation also represent the S43-1A and S43-2A samples after water leaching.

The references and card numbers used to determine XRD phases are as follows: Fe_2O_3 (79–0007 JCPDS), Fe_3O_4 (01-075-0033 ICDD), Co_3O_4 (01-073-1701 ICDD), $Sm_2O_2SO_4$ (00-041-0681 ICDD), $FeSO_4$,[21,30] $CoSO_4$,[31] $SmSO_4$,[32] $Sm_2(SO_4)_3$,[33] $NdSO_4$.[21]

Effects on the selective oxidation

Effect of selective oxidation temperature on extraction efficiency

Selective oxidation temperature is crucial for the formation of REE sulfates and the oxidation of other metals. Therefore, it was first aimed to find the optimum oxidation temperature. Selective oxidation was carried out at

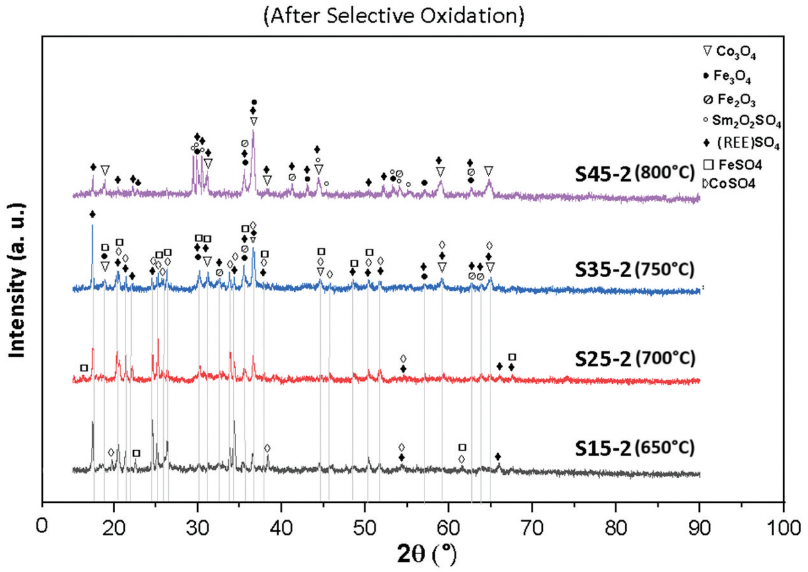


Figure 3. XRD analyses of the samples after selective oxidation (fixed parameters: sulfation (1/5 g/ml powder/acid ratio), selective oxidation (2-h time), leaching (2-h time, 1/20 s/l ratio)).

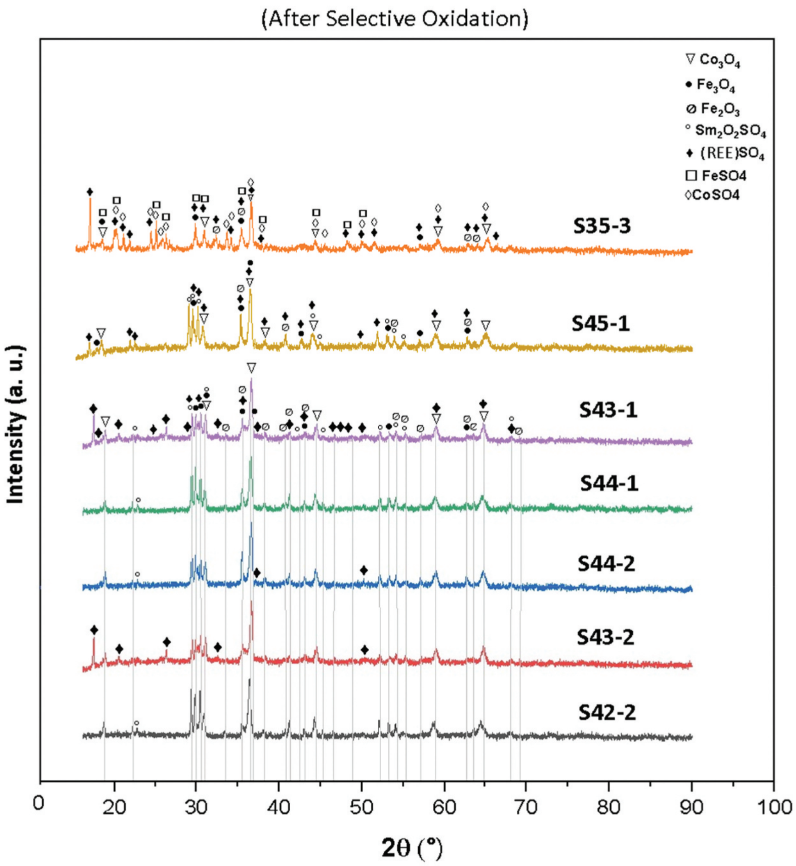


Figure 4. XRD analyses of the samples after selective oxidation.

temperatures of 650°C, 700°C, 750°C and 800°C to preserve the sulfate forms of REE and to decompose other metal sulfates to take their oxide forms. The effects of these temperatures, chosen considering the thermal stability of metal sulfates, on the extraction efficiency of metals are shown in Fig. 5. The fixed parameters include: a powder/acid ratio of 1/5 g/ml in the sulfation step; a 2-hour duration for the selective oxidation step; and a 2-hour duration and a solid/liquid ratio of 1/20 in the leaching step. The codes of the samples at these temperatures are S15–2, S25–2, S35–2, S45–2, respectively. Other parameters except temperature were kept constant and are all included in Table 1.

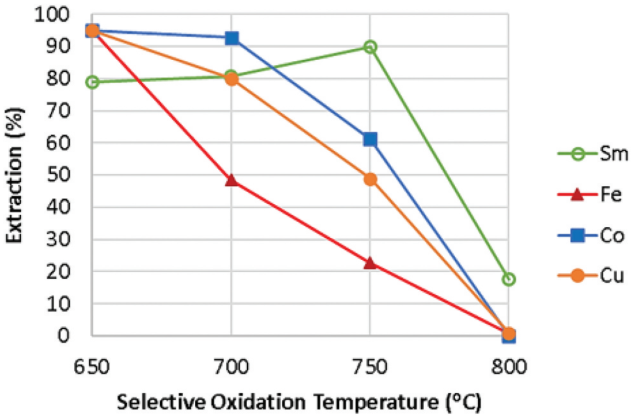


Figure 5. Effect of selective oxidation temperature on metal extractions (fixed parameters: sulfation (1/5 g/ml powder/acid ratio), selective oxidation (2-h time), leaching (2-h time, 1/20 s/l ratio)).

In the Fig. 5, between 650°C and 750°C, the Sm extraction efficiency gradually increased reaching 90%, but at 800°C, there was a sudden decrease to 20%. It is seen that the highest quantity of Sm sulfates is formed during the selective oxidation stage at 750°C and subsequently taken into solution during the leaching stage. This significant difference, which is only present in the 800°C sample, is also confirmed by the difference in the XRD peaks in Fig. 3. The low extraction efficiency in this sample (S45–2) is due to formation of Sm oxy sulfates during selective oxidation. This may be attributed to the high selective oxidation temperature. It is seen that Co, Cu and Fe metals are taken into solution in very high amounts in the 650°C sample. As the temperature increases, the extraction efficiencies for these metals have gradually decreased. This phenomenon can be attributed to the fact that 650°C temperature is insufficient for the oxidation of these metals. The decomposition of metal sulfates started after 650°C and continued to form as the temperature increased. At 800°C, the decomposition of metal sulfates is complete, resulting in the formation of oxides, as confirmed by the presence of Co_3O_4 and Fe_2O_3 in the phase analysis.

Effect of selective oxidation time on extraction efficiency

Based on the previous experimental parameters, the effect of selective oxidation time at 750°C and 800°C was examined in detail. It was aimed to complete the formation of Sm sulfates by increasing the selective oxidation time at 750°C, and to prevent the formation of oxysulfates by reducing the selective oxidation time at 800°C. To ensure optimization, samples with powder/acid ratios of 1/5 g/ml evaluated for both parameters and 2-h leaching time and 1/20 leaching s/l ratios.

When the selective oxidation time is prolonged to 3 hours at 750°C, a decrease of about 5% is observed for Sm in Fig. 6(a). Since the aim is to enhance Sm extraction, a longer selective oxidation time at this temperature has only a minor negative effect on Sm extraction. For other metals such as Co, Cu, and Fe, whose extraction into the solution is undesired, extending the selective oxidation time to 3 hours at 750°C resulted in only approximately a 10% decrease in Fig. 5(a). Since these metals remain in solution at levels between 20% to 50%, extending the selective oxidation time at 750°C did not lead to the desired extraction efficiencies for Co, Cu, and Fe.

In Fig. 6(b), it is observed that while the extraction efficiencies of Sm, Co, Cu, Fe (~1%) did not change during the 1- and 2-hours selective oxidation periods. The small difference of Sm extraction efficiency at 800°C indicates that Sm oxysulfates can form in minor amounts at this temperature, and their amount in the leaching residue increases with the increasing selective oxidation temperature.

Effect of selective oxidation time at the optimum temperature

Based on the findings from previous results, the effect of selective oxidation times at different selective temperatures was examined at 800°C, 1/3 of magnet powder/acid ratio, leaching time of 2 hours, and s/l ratio of 1/20, and the graphs are given in Fig. 7. The longer selective oxidation time has not demonstrated a positive effect on the extraction of Sm, it decreased from 65% to 45% from 1-hour to 2-hours. In both the 1-hour and 2-hours selective oxidation times, no transition of Fe into the solution observed. This temperature proves to be highly efficient for the complete oxidation of Fe. The metals Co and Cu have exhibited a minimal transition into the solution, at rates as low as 2%.

Effects on the sulfation

Effect of acid concentration on extraction efficiency

Since undesired Co, Cu and Fe extractions from the solution were at very low rates at 800°C, different magnet powder/acid ratios (1/3, 1/4, 1/5) were examined for 1 and 2 hours of selective oxidation time at 800°C. When the effects of powder/acid ratios for 2-h selective oxidation time are examined in Fig. 8(a), it is seen that the highest Sm extraction was achieved with a value of 45% at a 1/3 powder/acid ratio and the 1/4 and 1/5 ratios provide very low extractions such as 17–22%. These low extraction efficiencies are not sufficient for the recycling of SmCo magnets. Co, Cu, and Fe leach into the solution at levels approximately ranging from 0% to 2% at all powder/acid ratios.

The extraction efficiencies of a 1-hour selective oxidation time in Fig. 8(b) have similar results to the 2-hours sample. While Sm had the highest efficiency at 1/3 magnet/acid ratio, it showed a decrease at 1/4 rate and continues with a slight increase at 1/5 rate. Co, Cu and Fe metal extractions also indicate similar effects

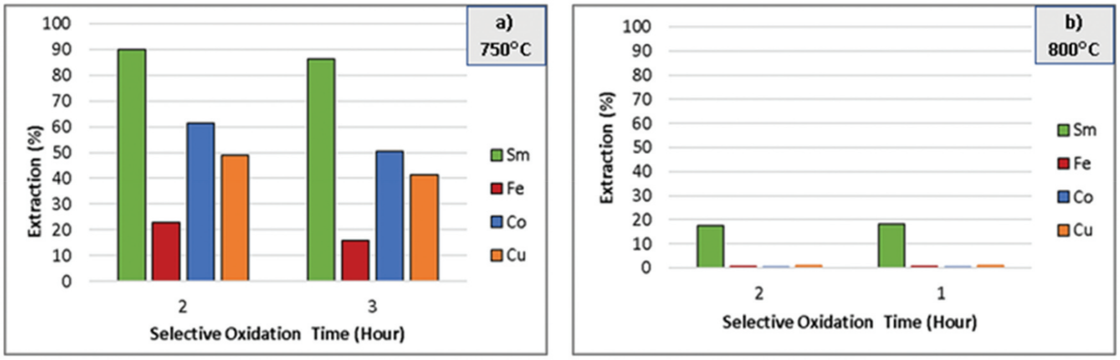


Figure 6. Effect of selective oxidation time on metal extractions (a) 750°C (b) 800°C (fixed parameters: sulfation (1/5 g/ml powder/acid ratio), selective oxidation (2-h time), leaching (2-h time, 1/20 s/l ratio)).

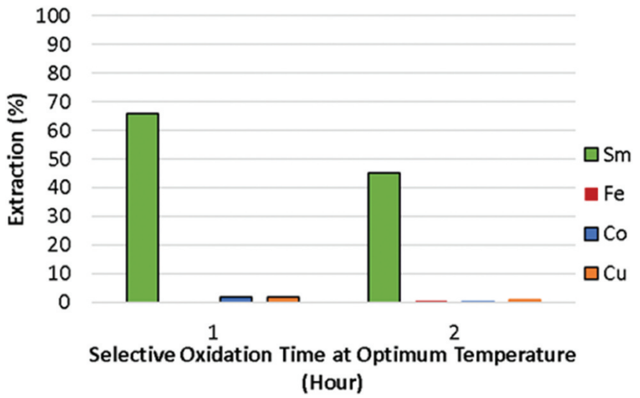


Figure 7. Effect of selective oxidation time on metal extraction at optimum temperature (fixed parameters: sulfation (1/3 g/ml powder/acid ratio), selective oxidation (800°C temperature), leaching (2-h time, 1/20 s/l ratio)).

with the 2-hour. This low efficiency at 1/4 may be due to different conditions in the furnace and sampling and it is predicted that water-insoluble Sm oxysulfate is continues to form during selective oxidation at 1/4 and 1/5 powder/acid ratios. When the effects of magnet/acid ratios on extraction efficiencies were compared at both 2-hour and 1-hour selective oxidation times, the highest Sm and the lowest Co, Cu, Fe extraction efficiencies were achieved at 1/3 magnet ratio.

Increasing the amount of acid during sulfation results in the formation of REE sulfates, as well as REE oxides and oxysulfates species during selective oxidation, as can been in Figs. 4 and 3. The formation of REE oxides and oxysulfates species contributes to a decrease in extraction efficiency. Thus, the optimum magnet to acid ratio is 1/3.

Effects on the water leaching

Effect of solid/liquid ratio on extraction efficiency

After the optimization of selective oxidation, leaching experiments were conducted for both 1-hour and 2-hour selective oxidation durations at solid/liquid (s/l) ratios of 1/10 and 1/20 with the aim of optimizing the solid/liquid ratio from leaching conditions. The fixed experimental conditions are as follows: 1/3 magnet powder/acid ratio, 800°C selective oxidation temperature, 2-hour leaching time.

In Fig. 9(a, b), the 1/10 solid-to-liquid (s/l) ratio is inadequate for both 1-hour and 2-hour selective oxidation times. For both selective oxidation times, the highest extractions occur at the 1/20 of s/l ratio. The extractions of Co, Cu, and Fe are all within the 0–2% range. These extractions are acceptable as they are low enough to be subsequently removed by precipitation. The highest Sm extraction was achieved at the 1/20 s/l ratio at 1-hour selective oxidation time.

Effect of leaching time on extraction efficiency

The leaching time was optimized based on parameters including an 800°C selective oxidation temperature, 1-hour selective oxidation duration, 1/3 powders/acid ratio, and 1/20 solid/liquid ratio, with leaching times of 30, 60, and 120 minutes.

Approximately 57% of Sm was extracted into the solution at 30 minutes, gradually increasing to a maximum extraction efficiency of 65% at 120 minutes. Fe and Co oxides remain in the leach residue. Moreover, approximately 2% of Co and Cu were extracted into the solution by 120 minutes. Figure 10 illustrates the extraction efficiency of the optimum sample and its parallels at different times.

To investigate the repeatability and reliability of the experiments, the optimum conditions were repeated. The closely matching extraction efficiencies confirm the reliability of the experiments.

Phase analyses of the leach residues

Figure 11 shows the XRD spectrum of 1/5 g/mL powder/acid constant variable samples at 650°C, 700°C,

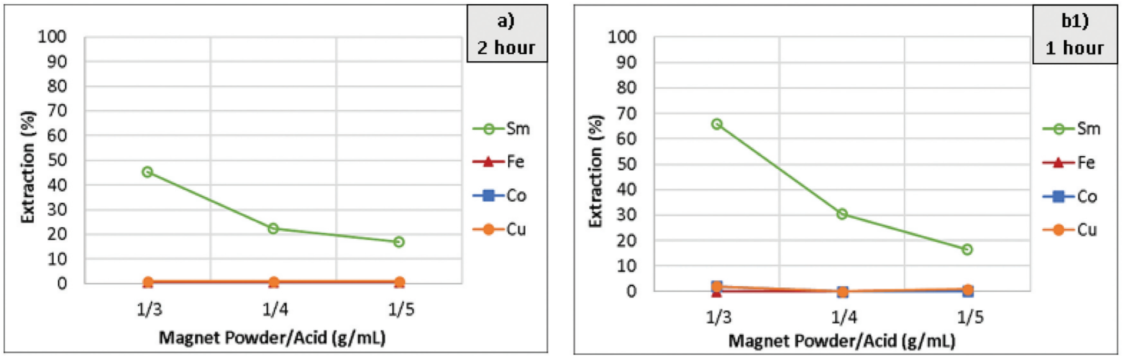


Figure 8. Effect of magnet powder/acid ratio on metal extraction (a) 2-hour (b) 1-hour selective oxidation time (fixed parameters: selective oxidation (800°C temperature), leaching (2-h time, 1/20 s/l ratio)).

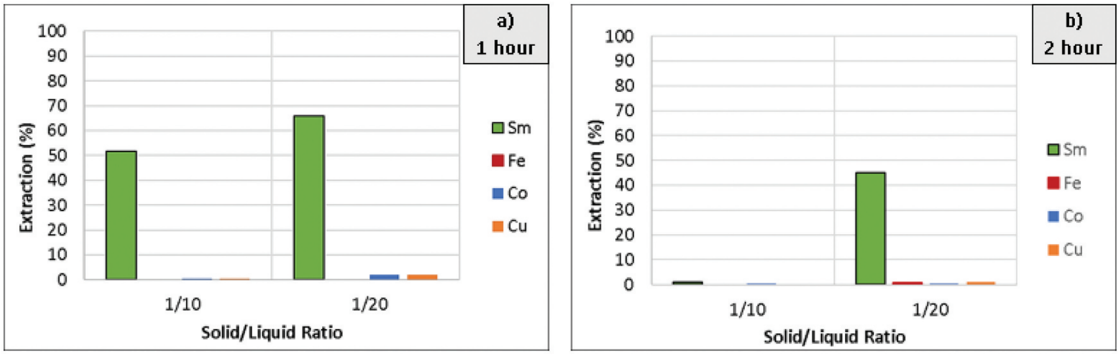
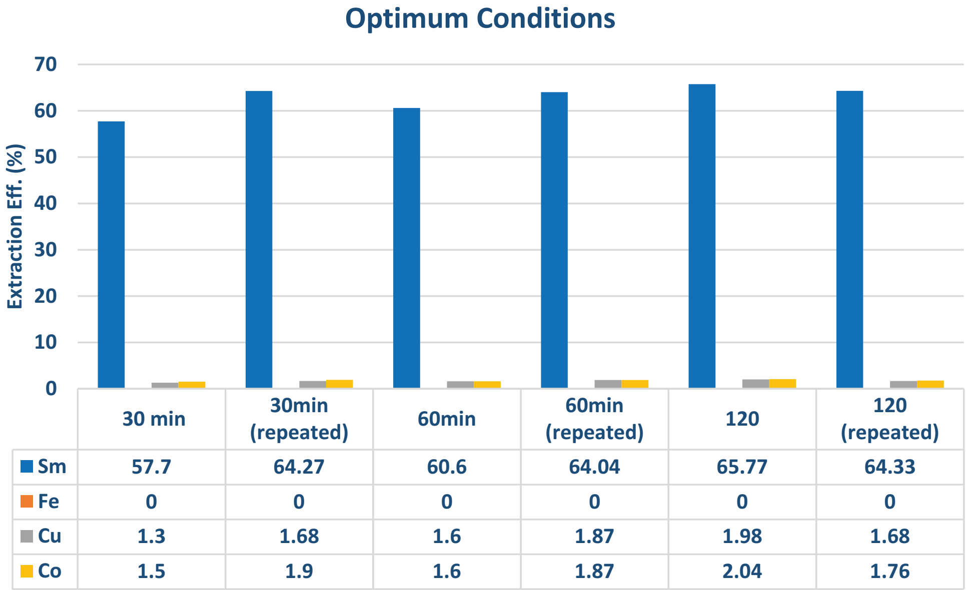


Figure 9. Effect of leaching solid/liquid ratio on metal extraction (a) 1-hour (b) 2-hour selective oxidation time (fixed parameters: sulfation (1/3 g/ml powder/acid ratio), selective oxidation (800°C temperature), leaching (2-h time)).



	30 min	30min (repeated)	60min	60min (repeated)	120	120 (repeated)
🟦 Sm	57.7	64.27	60.6	64.04	65.77	64.33
🟧 Fe	0	0	0	0	0	0
⬜ Cu	1.3	1.68	1.6	1.87	1.98	1.68
🟨 Co	1.5	1.9	1.6	1.87	2.04	1.76

Figure 10. Effect of leaching time on metal extraction with comparison of the parallels (fixed parameters: sulfation (1/3 g/ml powder/acid ratio), selective oxidation (800°C temperature, 1-h time), leaching (1/20 s/l ratio)).

750°C, and 800°C, aiming to compare the effect of selective oxidation temperature. The XRD analysis of the samples oxidized at 800°C (S45–1 and S45–2) shows the presence of Fe_2O_3, Fe_3O_4, Co_3O_4, and $Sm_2O_2SO_4$ in the leach residue. It is notable that Fe and Co oxides remain in the leach residue after water leaching. In contrast, for samples oxidized at 650°C, 700°C, and 750°C (S15, S25, S35), a significant amount of Fe and Co sulfates are leached into the solution, resulting in only small amounts of Fe_2O_3, Fe_3O_4, and Co_3O_4 observed in the leach residue.

Figure 12 depicts the XRD analyses of the leach residue obtained from water leaching. The XRD spectrum of the leach residue reveals the presence of Fe_2O_3, Fe_3O_4, Co_3O_4, and $Sm_2O_2SO_4$.

Optimization of the extraction process

An optimal combination for the high Sm extraction was selected: 800°C selective oxidation temperature, 1-h selective oxidation time, 1/3 g/ml magnet: acid ratio, 2-h water leaching time and 1/20 water leaching s/l ratio. Figure 13 shows the flowsheet with optimum conditions. Approximately 65% extraction efficiency of Sm were achieved with and very high selectivity to undesired other initial metals, including Fe, Co and Cu.

Table 3 illustrates the chemical composition analysis of leaching solution obtained from optimum conditions. A small amount of Co and Cu is observed in the leaching solution, along with the extraction of Sm, Nd and Pr.

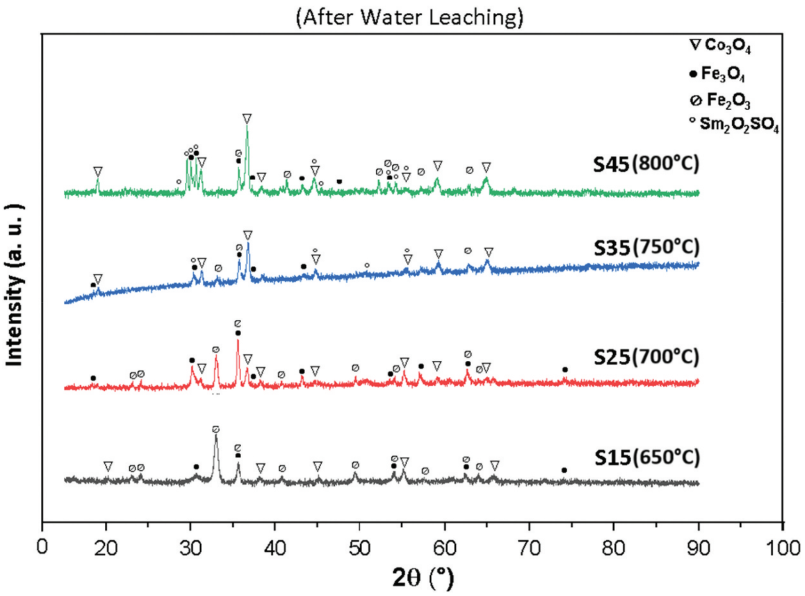


Figure 11. XRD analyses of the samples at various calcination temperatures following water leaching.

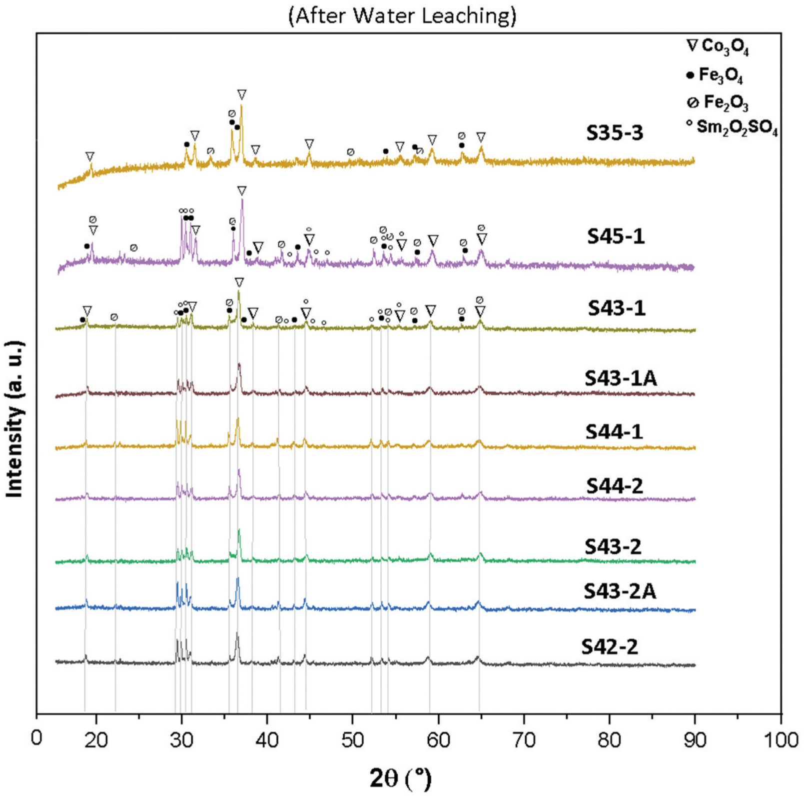


Figure 12. XRD analyses of the leach residue obtained from water leaching.

Table 4 illustrates the chemical composition analysis of the leach residue obtained under optimum conditions.

The leach residue consists of approximately 38% Co, 12% Fe, and 8% Sm. Considering the chemical composition of the leaching solution, this confirms that a significant portion of Co and Fe transferred to the leach residue. The presence of 8.8% Sm in the leach residue is attributed to the formation of Sm-oxysulfate, a phosphorescent material component usable in X-ray computed tomography and the detection of radioactive radiation.[34]

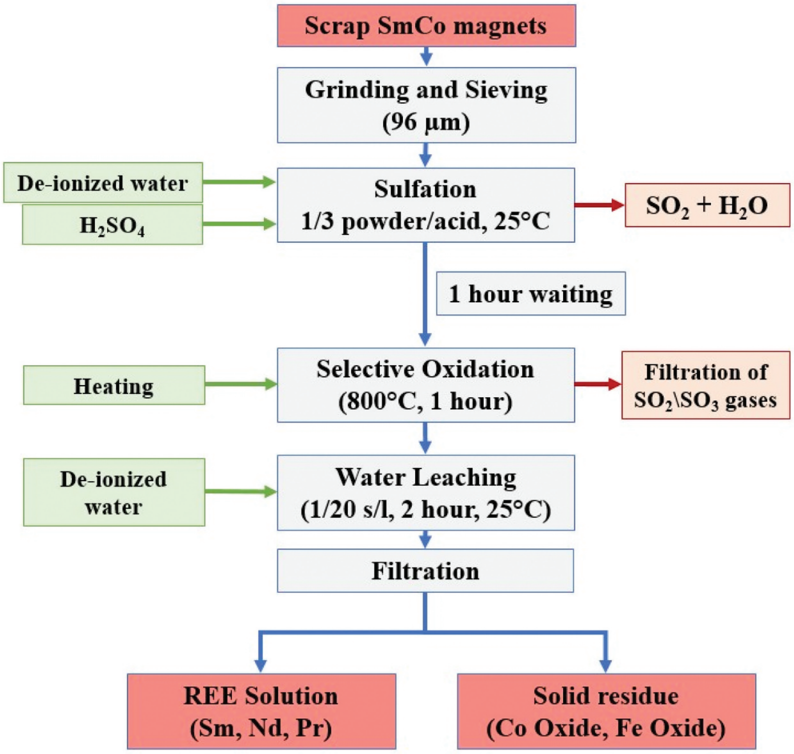


Figure 13. Flowsheet of recycling of the SmCo magnet samples with highest extraction.

Table 3. Chemical composition analysis of leaching solution obtained from optimum conditions.

Elements	Co	Cu	Fe	Nd	Pr	Sm
S43–1 wt. (mg/L)	22.6	2.23	<0,1	1.39	2.19	342

Table 4. Chemical analysis of leaching residue obtained from optimum conditions.

Elements	Co %	Cu %	Fe %	Nd (ppm)	Pr (ppm)	Sm %
S43–1 wt.	38,2	3,76	11,8	<50	394	8,81

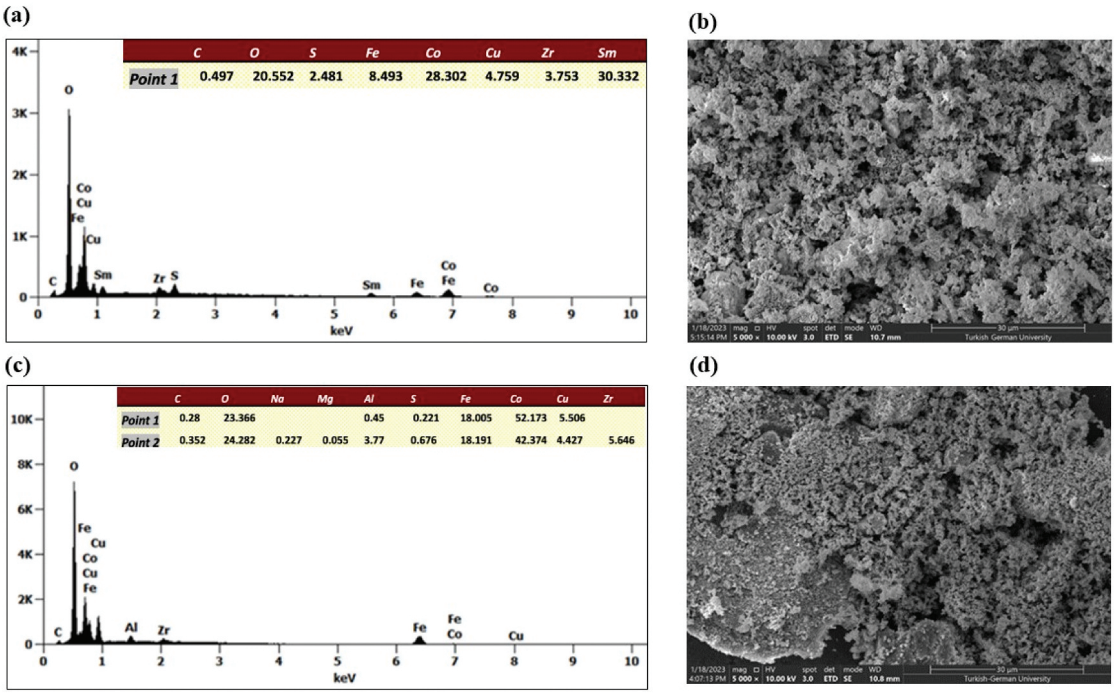
Comparison of selectively oxidized powders and leaching residues obtained from optimum conditions

For comparison of the selectively oxidized powders and leaching residues belonging to the optimum condition, SEM, EDS, and elemental mapping analyses were conducted. When comparing the chemical compositions of powders after selective oxidation (Fig. 14 (a)) and after leaching (Fig. 14 (c)), the absence of Sm and S elements in the leach residue confirms the dissolution of Sm sulfate compounds into the leaching solution. Other metals present in SmCo magnets, such as Fe, Co, Cu, Zr, and their oxide compounds are in the leach residue. Al may have originated from the substrate. When comparing SEM micrographs, it is evident from Fig. 14 (b, d) that the particle size decreases after water leaching. The particle sizes in both samples are approximately smaller than 5 µm.

After selective oxidation, the presence of Sm, Fe, Co, Cu, Zr, S, C and O elements was observed in the calcined product in Fig. 15(a). The high presence of Sm, Fe, Co, O and S confirms the existence of sulfate and oxide compounds. The absence of sulfur in the residue after leaching, as observed in Fig. 15(b), confirms that sulfate compounds have dissolved into the leach solution. Due to the formation of Sm oxide sulfates, a small amount of Sm persists in the leach residue and Fe, Co, Cu and Zr remain in the leach residue.

Conclusions

Recycling of REE and Co/Fe oxides from waste SmCo magnets was achieved through sulfation, selective oxidation, and water leaching. The most critical aspect of this study is preventing the formation of Sm-oxysulfate to increase Sm extraction efficiency. Although the formation of SmOxy cannot be prevented, this compound can be used as a luminescent material. Therefore, Sm-oxysulfate should be separated from Co and Fe oxides. When the selective oxidation temperature is raised



	C	O	S	Fe	Co	Cu	Zr	Sm
Point 1	0.497	20.552	2.481	8.493	28.302	4.759	3.753	30.332

	C	O	Na	Mg	Al	S	Fe	Co	Cu	Zr
Point 1	0.28	23.366			0.45	0.221	18.005	52.173	5.506	
Point 2	0.352	24.282	0.227	0.055	3.77	0.676	18.191	42.374	4.427	5.646

Figure 14. (a) Chemical composition the powders obtained from selective oxidation and (b) SEM micrograph of the powders obtained from selective oxidation; (c) chemical composition of the water leach residue and (d) SEM micrograph of water leach residue obtained from optimum condition.

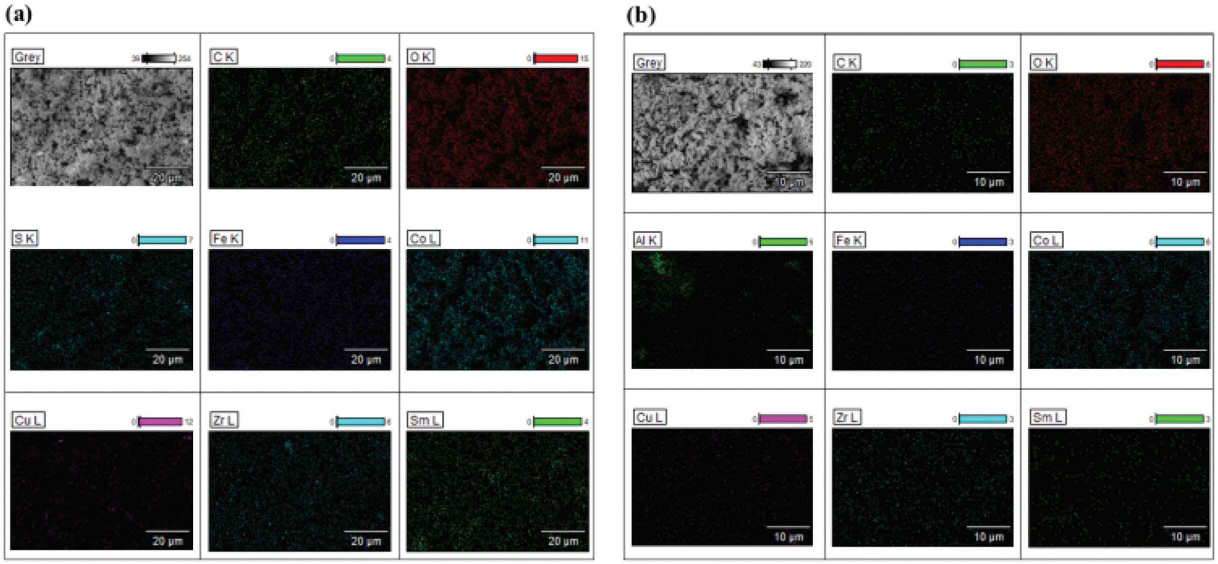


Figure 15. Elemental mapping of the samples obtained from optimum condition; (a) after selective oxidation and (b) after water leaching.

above ~ 800°C, depending on other experimental parameters, the thermal decomposition of REE sulfates can initiate, leading to the formation of REE-oxysulfates. Another critical point is the acid molarity in the initial stage; insufficient or excessive sulfation negatively affects the entire process from the beginning. The optimal parameters were 800°C selective oxidation temperature, 1-h selective oxidation time, 1/3 g/ml magnet: acid ratio, 2-h leaching time and 1/20 leaching s/l ratio. Under the optimized conditions, Co/Fe oxides were effectively separated from REE, remaining in the solid leach residue. The solubility of Fe, Co, and Cu metals in the solution was minimal, accounting for approximately 2%, while the extraction efficiency of

Sm is approximately 65%. In this process, the combination of H_2SO_4, heating, and water was employed to extract and separate Sm from Co and Fe oxides. In contrast to literature, which involves the use of ammonium chloride, capable of releasing chlorine gas and ammonia during decomposition, posing potential environmental hazards, our method relies on a single, cost-effective chemical suitable for industrial use. This chemical reaction produces SOx gas, which can be utilized in the production of H_2SO_4.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

Author contributions

Conceptualization E.E.K., Experiments, M.P, Data curation E.E.K and M.P. formal analysis M.P, E.E.K. Funding acquisition S.S, S.G, B.F., Investigation M.P., Methodology M.P. Project Administration S.S, S.G, B.F., Resources S.S, S.G, B. F., Supervision E.E.K. S.G. and B.F., Validation M.P. Writing-original draft M.P, E.E.K writing-review % editing E.E.K., M.P.

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