Process Flowsheet Development for Separation of Sm, Co, Cu, and Fe from Magnet Scrap

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ABSTRACT: A complete process flowsheet to recover metal values from Sm₂Co₁₇-type magnet scrap was investigated. The magnet scrap was leached in chloride medium at pulp density of 2% (w/v) under the optimum conditions of 15% (v/v) HCl and 5% (v/v) H₂O₂ at 70 °C for 3 h, which yielded 98.5% Sm and 99% Co extractions. The full factorial Design of Experiment technique was adopted for the optimization of leaching conditions. Sm was selectively separated from the leach liquor as precipitated double salt using Na₂SO₄. The precipitated double sulfate was later converted to Sm-oxalate, which was subsequently calcined to produce pure Sm₂O₃. Following Sm separation, Fe was removed through precipitation by adjusting the pH to 3.0. For Cu and Co recovery, solvent extraction techniques using LIX 84I and Na-CYNEX 302, respectively, were followed. The McCabe–Thiele diagrams for extraction as well as stripping were presented for both Cu and Co.

1. INTRODUCTION

With the growing demand for cleaner energy production technologies, applications of rare earth elements (REEs) as permanent magnets in wind turbines, energy-efficient lighting, electric vehicles, and so forth are proportionately on the rise. The most common permanent magnets are NdFeB magnets with the highest energy product (200–440 kJ/m³), which is much higher than ordinary ferrite magnets. The other less common magnets are SmCo alloy-based, which are of two types: SmCo₅ and Sm₂Co₁₇. SmCo alloy magnets possess high corrosion resistance, excellent thermal stability, and high coercivity in comparison to NdFeB magnets. Because of high demand for the REEs and limited availability of primary resources, recycling of waste resources appears to be a viable solution. As per a 2019 review, “around 12.5% of e-waste is currently being recycled for all metals.”

Several studies have been reported on processing of NdFeB magnets. Some of the studies involved recovery of REEs through solvent extraction using Na-CYNEX 302 from chloride leach liquor and D2EHPA in solvent 70 from citric acid + acetic acid leach liquor. Studies on the recovery of REEs from the chloride leach liquor of NdFeB magnets as mixed oxalates through the oxalate precipitation route were reported. Recently, hydrochloric acid pressure leaching of a roasted magnet with the addition of some NaNO₃ was carried out to get significant separation of REEs and boron from Fe₂O₃, leaving apart the hematite-rich residue. Sm is one of the 17 REEs which finds useful applications in optical lasers and electrodes, the major one being in the manufacture of SmCo (SmCo₅ and Sm₂Co₁₇) permanent magnets. During the processing of magnets for a specific shape, huge amounts of waste are generated. Commercially, Sm is recovered as mixed rare earth oxides from minerals such as monazite and bastnasite, and the processes are highly energy-intensive. There is a great opportunity and need for recycling of Sm from magnet scrap. Recycling of Sm is very low, despite the fact that a massive amount is wasted at the manufacturing site or else exported.

Zhong et al. reported the separation study of Sm and Co from SmCo alloy (SmCo₅) waste through H₂SO₄ leaching followed by precipitation. It was observed that 99.9% of Co and 24.1% of Sm could be leached under the conditions of L:S ratio 6:1, 75 min, and 4.0 M H₂SO₄. From the leach liquor, 93.4% of Sm was separated as double sulfate by using Na₂SO₄ at 80 °C, 60 min of precipitation time, and a Na₂SO₄:Sm ratio of 4:1. In another study, a mixture of rare earth double sulfates along with samarium was produced from a low-grade bastnasite by sulfuric acid baking, subsequent water leaching, and precipitation with sodium sulfate. The total rare earth double sulfate content was >90% with 0.7% of other impurities. Onoda and Kurioka rather used phosphoric acid while adjusting pH with NaOH to precipitate Sm from a
synthetic solution with a Co:Sm ratio of 9, which matches with ratio in the Sm₂Co₁₇ permanent magnet. They could separate 99% of Sm as samarium phosphate. As an extended study of the same work, instead of only Sm and Co solution, Sm-Co-Fe-Cu solution was used as the starting solution. Before mixing phosphoric acid, ascorbic acid was added to suppress the formation of iron phosphate. In another study, the mixed Sm and Gd oxides as well as cobalt oxide was prepared from sulfuric acid leach liquor of Co-based magnet waste. The Co and Fe values in the leach solution were first oxidized using sodium persulfate followed by sequential hydroxide precipitation of respective metals. Cobalt oxide was obtained by roasting Co(OH)₃. Sm and Gd were precipitated using ammonium oxalate, and 96% was recovered as mixed oxide after calcining the RE oxalate.

Besides precipitation, several studies on solvent extraction as an effective route for separation of Sm were reported. Processing of a SmCo magnet for recovery of Sm and Co, and separation of Sm using CYANEX 572 from chloride leach liquor, was reported. The authors demagnetized the waste magnet by roasting at 1123 K prior to leaching with 4 M HCl at 368 K under 100 g/L S:L. Precipitated Sm and Co oxalates were calcined to produce oxides of Sm and Co. In another study, Sm separation using 2-oxalylaminopyridine in xylene was reported. The stripping efficiencies with HNO₃, HCl, and CH₃COOH as well as the thermodynamic functions of extraction were established. In continuation of Sm extraction from synthetic solution, Lee et al. investigated the extraction of Sm from SmCl₃ solution using PC88A and saponified PC88A. The study involved estimation of equilibrium constants for both PC88A and saponified PC88A by analyzing ionic equilibria and prediction of distribution coefficients by developing a chemical model. Recently, the preparation of Sm²O₃ and Co₆O₁₄ from a SmCo₃ magnet swarf was reported. Although leaching in HCl and H₂SO₄ both resulted in more than 95% extraction, the chloride leach liquor was preferred for further processing because of the problem of in situ precipitation of Sm in sulfate medium. Sm extraction from leach liquor was carried out through solvent extraction using TOPS-99, followed by stripping with oxalic acid to get Sm-oxalate. The raffinate containing Co was precipitated as cobalt oxalate. The oxides of both Sm and Co were finally obtained by calcination of respective oxalates. In the case liquid–liquid extraction, investigation of the synergistic extraction is sought after by many researchers. In this aspect, the effects of various parameters on Sm extraction using CYANEX 301 alone and in combination with D2EHPA in nitrate medium were studied. The addition of D2EHPA to the CYANEX 301 extraction system increased the extraction efficiency of CYANEX 301 with better stripping in the low concentration range. In another study, a mixture of sec-octylphenoxyacetic acid and 1,10-phenanthroline was used for extraction of Sm and other REEs from a synthetic solution in nitrate medium. A comparative study on separation of Co (II) and Sm (III) by dissolving their chloride salts in water as well as in ethylene glycol (EG) in the presence of LiCl was studied. Aliquat 336 was used for extracting both Co and Sm from aqueous solution. Co was extracted more efficiently than Sm in EG solution, and Sm was left in the raffinate. As an alternative to the traditional hydrometallurgical route, an attempt had been made to use the solvometallurgical route in which water is replaced by organic solvent when carrying out leaching with 2 M HCl solution in EG. From the leach liquor, Co, Fe, and Cu were extracted with 37 wt % HCl-saturated Aliquat 336 (50 wt %) in toluene followed by consecutive stripping of Co and Cu with 0.5 mol L⁻¹ HCl and 5 vol % NH₃ solutions, respectively. Sm from the raffinate was extracted using 20 vol % CYANEX 272 in n-dodecane and subsequently recovered as Sm-oxalate by precipitation stripping with 0.2 mol L⁻¹ oxalic acid.

The use of ionic liquid in the metal extraction has recently drawn the attention of researchers. Recently, separation of Sm/Co/Cu present in a concentrated synthetic solution through split-anion extraction using ammonium ILs without the addition of molecular diluents was reported. The undiluted quaternary ammonium salt Aliquat 336, [A336][Cl], and its thiocyanate and nitrate analogues [A336][SCN] and [A336][NO₃] were used as the organic phase. Corresponding stripping studies were investigated. In another study, the selective precipitation of Sm and Cu based on [(triethyl(tetradecylphosphonium)][benzene-1,4-dioxydiacetate] ([P666,14][BDOAC]) from the simulated leach solution of SmCo waste magnets, leaving behind the Co-rich solution, was reported. Also, the dissolution of metals from a SmCo magnet using IL trihexyltetradeclphosphonium trichloride and [P666,14][Cl₃] as the oxidizing solvent was studied. The dissolution study involved the variation of mixtures of ILs [P666,14][Cl₃] and [P666,14][Cl], solid-to-liquid ratios, and temperature. Regeneration of ILs was reported by selectively stripping all metals consecutively with 3 M NaCl, twice with water and 3 M NH₃ solution.

Previous studies on the recovery of Sm mostly reported the recovery from the bastnasite, Sm₂O₃, magnet, and simulated or equivalent Sm₂Co₁₇ magnet scrap. The studies are either limited to leaching studies, and the downstream processing routes are through solvent extraction or solvometallurgical approach or by using ILs. The transition elements were not being addressed or left as such in the solution after the recovery of Sm. The present study involves complete flowsheet development with end-to-end processing of Sm₂Co₁₇ magnet scrap through the hydrometallurgical route to recover Sm as well as other co-existing transition metals. In the present investigation, leaching of the magnet was carried out without undergoing any high-temperature pretreatment process. The problem of Fe co-extraction is anticipated during the solvent extraction step for Sm, as both Sm and Fe are extracted at around the same pH range of 1.0–2.5. Hence, the selective double sulfate precipitation route was chosen to recover the Sm values bypassing the complexities of Sm and Fe separation. The high purity Sm₂(C₂O₄)₃ was produced from NaSm(SO₄)₂·H₂O through conversion—precipitation using oxalic acid. Subsequent calcination of the oxalate precipitate resulted in pure Sm₂O₃. The major interfering element, that is, Fe was separated through precipitation prior to the recovery of Cu and Co through solvent extraction. The high purity sulfate solutions of Cu and Co produced from the stripping unit can be further processed individually for the production of respective salt or metal based on the requirement. The parameters, such as pH, stirring time, concentration of precipitating reagents, and extractants, were optimized for each unit operation.

2. EXPERIMENTAL SECTION

2.1. Materials. The scrap magnets considered for the present study were collected from Defence Metallurgical Research Laboratory (DMRL), Hyderabad, India. Initially,
the scrap magnets were crushed to suitable sizes followed by grinding in a pulverizer. After sieving (−150 + 106), micrometer size fraction was collected and used for all leaching experiments.

2.2. Chemicals and Reagents. The commercial extractants TOPS-99 (di-2-ethylhexyl phosphoric acid), LIX 84I (2-hydroxy-5-nonylacetophenone oxime), and CYANEX 272 (bis (2, 4, 4-trimethyl pentyl) phosphinic acid) were supplied by Heavy Water Plant, Talcher, Odisha (India), Cognis Inc. (USA), and Cytec Inc. (USA), respectively. These extractants were used as such without any further purification. Distilled kerosene (b.p. 180−240 °C) was used as the diluent. D2EHPA and CYANEX 272 were 70% saponified using NaOH before use during solvent extraction. All other chemicals used in the experiments were of AR grade (Merck).

2.3. Procedure. 2.3.1. Leaching. Leaching experiments were carried out in a double-walled glass reactor of 500 mL capacity (Model KGW-Isotherm, Germany). The reactor contents were heated to the predetermined temperature through the circulation of hot water from the Julabo thermostatic water bath through the outside shell of the reactor. The contents were constantly agitated through a Teflon anchor agitator positioned at the center of the reactor. For each experiment, 400 mL of leach solution (deionized water + required amount of HCl) was used along with 8 g of the powdered sample, maintaining the S:L (w/v) ratio of 1:50. In all the leaching experiments, 5% H2O2 (v/v) was used along with 8 g of the powdered sample, maintaining the S:L (w/v) ratio of 1:50. In all the leaching experiments, 5% H2O2 (v/v) was used to ensure complete oxidation of Fe (II) to Fe (III) for easy precipitation of iron.

2.3.2. Solvent Extraction. For extraction and stripping studies, both aqueous and organic phases were taken in separatory funnels and equilibrated for 5 min with the help of a mechanical shaker. The pH of the aqueous phase was adjusted before each experiment by adding dilute NaOH or HCl. After a clear separation of both the phases, the equilibrium pH was measured by a digital HANA pH meter [Model L1 120]. The concentration of Sm in the aqueous phase was analyzed by inductively coupled plasma optical emission spectrometry (Thermo Scientific, Model: iCAP7600 Duo) and that of other metal ions by atomic absorption spectrophotometry, [Perkin Elmer, Model AA200] after suitable dilutions. The metal concentration in the organic phase was determined by two methods: (i) by analyzing after stripping with acid and (ii) by directly calculating from the difference of the metal concentrations in the aqueous phase before and after extraction. Before stripping, the organic phase was filtered through Whatman 1PS filter paper for avoiding any contamination in the aqueous phase.

2.3.3. Precipitation. The precipitation experiments were carried out in a beaker by adding the stoichiometric amount of salt at a particular temperature with continuous stirring. The pH of the solution was maintained by the addition of dilute NaOH or HCl. The temperature and stirring rate were regulated by a hot plate cum magnetic stirrer.

2.3.4. Design of Experiments. Design of Experiments (DoE) is a standard and very popular statistical technique, through which the parameters (factors) involved can be varied simultaneously at respective levels, and information can be obtained with the minimum number of experiments. When the effect of more than one factor on response is examined, such experiments are known as full factorial experiments. The most widely used experimental design is 2^k, where “k” is the number of factors at two levels. In the present work, 2^3 full factorial design was employed. The parameters chosen were HCl concentration, time, and temperature. The levels of the parameters are shown in Table 1.

| Table 1. Factors, Levels, and Extractions at Various Levels of Factors |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| HCl concentration (X1), % v/v | time (X2), h | temperature (X3), °C | Sm (%) | Co (%) |
| 10 | 4 | 80 | 86.72 | 85.81 |
| 20 | 4 | 80 | 88.59 | 99.96 |
| 10 | 8 | 50 | 40.50 | 53.13 |
| 10 | 2 | 50 | 61.17 | 61.17 |
| 2 | 4 | 80 | 18.19 | 17.54 |
| 2 | 4 | 80 | 42.36 | 42.48 |
| 2 | 4 | 50 | 15.61 | 16.39 |
| 2 | 4 | 50 | 31.48 | 25.65 |

3. RESULTS AND DISCUSSION

3.1. Characterization. The X-ray diffraction pattern of the ground sample obtained through PANalytical Empyrean Series 2 XRD equipment is shown in Figure 1. The major peaks match well with the Sm2Co17 phase as per the ICDD File no. 98-062-5217. Besides the Sm2Co17 phase, it also indicates the presence of CuO and Fe2O3 phases. The chemical analysis of the powdered sample indicated to contain 32.2% Sm, 47.6% Co, 14.2% Fe, and 4.2% Cu.

3.2. Full Factorial Design for Leaching. The extents of Sm and Co leaching obtained under different combinations as per the design matrix are presented in Table 1. Maximum metal extractions both for Sm and Co are found at +1 + 1 + 1 levels.

The percentage of extraction can be expressed by the full regression equation as given below:

\[ Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{123} X_1 X_2 X_3 \]

where Y denotes the % extraction; b1, b2, and b3 are linear coefficients; b12, b23, and b13 are two-way interaction coefficients; and b123 is a three-way interaction coefficient.

The leaching extents, that is, % extraction as responses were fed into the Minitab 17, and the regression equations for Sm and Co extractions were generated along with analysis of variance (ANOVA) tables.

The regression equation for Sm is as follows:

\[ Y_{Sm} = 27.4 - 8.06X_1 - 3.48X_2 - 0.445X_3 - 0.219X_1X_2 + 2.082X_1X_2 + 0.1675X_1X_2X_3 - 0.0376X_1X_2X_3 \]
In the same way, the regression equation for cobalt is as follows:

\[
Y_{\text{Co}} = 24.6 - 2.47X_1 - 6.62X_2 - 0.422X_3 + 0.143X_4 + X_5 + 0.495X_6 + 0.198X_7 + 0.012X_8
\]

(3)

The ANOVA table (Table S1) for Sm extraction indicates that factors HCl concentration, time, and temperature are statistically significant, and so are the two-way interaction term (acid*temperature) and three-way interaction terms because the \(P\) values are less than 0.05. The acid concentration is the most influencing parameter, followed by temperature and leaching time. Similarly, the ANOVA table for Co extraction (Table S2) indicates all the factors and two-way interaction terms \(X_1*X_3\) (acid*temperature) and \(X_2*X_3\) (time*temperature) are statistically significant.

The validity of the individual regression equation was tested by comparing the predicted versus experimental extraction values under some random conditions, which were not part of the design matrix. Table 2 presents a comparison between predicted and experimental results. The predicted and experimental values are within approximately ±5%, which indicates the model equations to be valid.

On analyzing all the experimental data, including those obtained under random conditions, it appears that 10% acid is not adequate for the complete recovery of metal values. Hence, it was decided to increase the acid concentration to 15%, while keeping the temperature at 70 °C, time as 3 h, and S/L liquid ratio 1:50 (w/v). The pH of the generated leach liquor under the above-optimized conditions was 0.25, and the composition was as follows: Sm 6.34 g/L; Co 9.42 g/L; Fe 2.8 g/L; and Cu 0.81 g/L.

### 3.3. Precipitation of Sm

#### 3.3.1. Na\(\text{Sm(SO}_4\text{)}_2\cdot\text{H}_2\text{O}\) Precipitation. The REEs precipitate as double sulfate with anhydrous Na\(\text{SO}_4\) and can be easily separated from the leach liquor by filtration.\(^{23}\) In the present leach liquor, Sm was first recovered through the double sulfate precipitation route using Na\(\text{SO}_4\). The effect of various parameters such as pH, Na\(\text{SO}_4\) concentration, and stirring time was examined in this precipitation study.

##### 3.3.1.1. Effect of pH

While keeping the temperature, stirring speed, and stirring time constant at 50 °C, 300 rpm, and 10 min, respectively, the pH of the solution was varied from 0.5 to 2.0 using dilute NaOH. The concentration of added Na\(\text{SO}_4\) was maintained at 5% (w/v). It was observed that precipitation of Sm increased from 0 to 94.19% with the increase in pH from 0.5 to 1.0, beyond which the effect of pH was nominal (Figure 2). It has been observed that rare earth sulfate precipitation is better at lower pH, specifically between pH 1 and 2.\(^{24}\) No coprecipitation of Cu and Co was observed in the studied pH range, but some coprecipitation of Fe (0.8 to 2.4%) was observed beyond pH 1.0. Hence, further experiments were conducted at pH 1.0.

##### 3.3.1.2. Effect of Na\(\text{SO}_4\) Concentration

Keeping the solution pH constant at 1.0, Na\(\text{SO}_4\) concentration was varied from 2.5 to 12.5% (w/v). The precipitation results are presented in Figure 3. The precipitation of Sm increased from 74.1 to 94.19% with the increase of the Na\(\text{SO}_4\) concentration from 2.5 to 5% (w/v). Beyond 5% (w/v) concentration, the increase in precipitation was nominal, which might be due to the higher amount of Na\(\text{SO}_4\) used. Because 5% (w/v) Na\(\text{SO}_4\) is approximately 8.33 times stoichiometric requirement for precipitation of Sm, further increase in

| acid conc., % v/v | temp, °C | time, h | Sm  | Co  |
|-------------------|---------|---------|-----|-----|
| 10                | 80      | 3       | 88.91 | 88.68 | 92.29 | 94.82 |
| 10                | 85      | 1       | 93.50 | 95.13 | 88.50 | 90.85 |
| 5                 | 70      | 2       | 46.19 | 43.73 | 41.89 | 43.97 |
| 15                | 70      | 3       | 98.5  | 100.00 | 99.00 | 100.00 |

The predicted result, that is, calculated values were beyond 100%, may be because acid concentration was well beyond the factorial level value; hence, it is taken as 100%.

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**Table 2. Predicted vs Experimental Extraction Values**

**Figure 1.** X-ray diffraction pattern of magnet scrap.

**Figure 2.** Precipitation behavior of Sm at different pH values.

**Figure 3.** Effect of Na\(\text{SO}_4\) concentration on the precipitation of Sm.
Na$_2$SO$_4$ concentration did not have any effect. This 5% (w/v) Na$_2$SO$_4$ was considered as the optimum concentration without coprecipitation of other metals.

### 3.3.1.3. Effect of Stirring and Ageing Time

The effect of stirring time on precipitation was conducted by varying stirring time from 5 to 40 min. The pH values of the leach liquor, temperature, and concentration of Na$_2$SO$_4$ were kept constant at 1.0, 50 °C, and 5% (w/v), respectively. The solution was filtered immediately, and the percentage of precipitation was calculated. There was no significant effect observed with the variation of stirring time.

Also, another set of experiments were carried out by keeping the experimental conditions constant as above. Additionally, the solution was allowed to remain for an ageing time of 5−15 min without stirring before filtration. In this case also, there was no effect of ageing time observed and the extent of precipitation remained at ~94%.

The concentrations of leach liquor after Sm separation were 368 mg/L Sm, 2.78 g/L Fe, 0.82 g/L Cu, and 9.40 g/L Co, which were further processed for recovery of Cu and Co.

#### 3.3.2. Sm$_2$(C$_2$O$_4$)$_3$ Precipitation

**Conversion**—precipitation of Sm-double sulfate to oxalate was carried out under the experimental conditions of 0.5 M oxalic acid solution, 5% (w/v) Sm-double sulfate salt, agitation time 1 h at room temperature, and 300 rpm. The XRD patterns of the thoroughly washed and oven-dried precipitate confirmed the phase as Sm-oxalate-only (Figure S1b).

#### 3.3.3. Sm$_2$O$_3$ Preparation

The precipitated Sm-oxalate was subjected to calcination at 800 °C for 1 h in a temperature-controlled Muffle furnace to produce pure Sm$_2$O$_3$. The X-ray diffraction patterns, as shown in Figure S1a, confirmed the presence of the pure Sm$_2$O$_3$ phase.

### 3.4. Precipitation of Fe

After separation of Sm, Fe content from the liquor was separated as ferric hydroxide by precipitation through pH adjustment with CaO. The pH of the Sm-depleted leach liquor was increased from 2.0 to 4.0 by using dilute NaOH slurry. The precipitation of Fe increased rapidly from 0.8 to 93.2% with the increase in pH from 2.0 to 3.0, as shown in Figure 4. Beyond pH 3.0, precipitation was relatively slow and increased to 99.5% at pH 4.0. There was no coprecipitation of Cu and Co up to pH 3.0, beyond which coprecipitation of Cu and Co was observed in the range of 2.4−20.16% and 2.16−2.81%, respectively. Hence, at the optimum pH of 3.0, all the liquor was processed for Fe precipitation. After precipitation of Fe, the leach liquor contained 190.0 mg/L Fe, 366 mg/L Sm, 0.80 g/L Cu, and 9.38 g/L Co.

### 3.5. Extraction of Cu

LIX series of extractants are widely used for Cu extraction because of its high selectivity.$^{25−29}$ Hence, LIX 84I was chosen as the extractant for the recovery of Cu. The concentration of LIX 84I was varied in the range of 1−4% (v/v), while the pH of the filtrate was increased to 3.5 using dilute NaOH. At increased pH, iron concentration further decreased to about 90 ppm because of precipitation. The extraction of Cu increased from 44.5 to 97.25% with an increase in the LIX 84I concentration from 1 to 4% (v/v) (Figure 5). However, no coextraction of Sm, Fe, and Co was observed. The number of stages and A:O ratio required for the quantitative extraction of a metal ion depends on the extraction percentage in a single stage, and the number of stages decreases with the increase in extraction. In this study, the extraction was 94.25% with 3% (v/v) LIX 84I. Therefore, this
concentration of LIX 84I was used to construct the McCabe–Thiele diagram.

The leach liquor (pH 3.5) was contacted with 3% (v/v) LIX 84I at different phase ratios starting from 1:5 to 5:1, and total aqueous+organic phase volume was kept constant throughout the experiment. The McCabe–Thiele diagram (Figure 6) indicated quantitative Cu extraction in two counter-current stages at the A:O ratio of 1:1. A two-stage counter-current simulation study carried out with A:O = 1:1 resulted in the second stage raffinate of 0.004 g/L Cu, indicating 99.5% of Cu extraction.

### 3.6. Stripping of Cu.

The Cu-loaded organic (0.79 g/L Cu) when stripped with 10% H2SO4 (v/v) at an O:A ratio of 1:1 resulted in 99% stripping in a single stage. For predicting the number of stages and A:O ratio for the quantitative stripping of Cu with higher concentration, the McCabe–Thiele plot was constructed with 10% H2SO4 (v/v). The respective metal concentrations of strip solutions were plotted against spent organic at different phase ratios of 1:5 to 5:1. The diagram shown in Figure 7 depicts quantitative stripping of Cu in two counter-current stages at an O:A ratio of 2:1. For validating the abovementioned findings, a two-stage counter-current simulation study was conducted with the optimum conditions. The second stage strip solution was analyzed to contain 1.56 g/L Cu, confirming 98.7% stripping.

### 3.7. Extraction of Co.

After separation of Sm, Fe, and Cu by precipitation and solvent extraction, the leach liquor contained 9.38 g/L Co. In order to generate pure Co solution, the abovementioned leach liquor was treated with Na-D2EHPA and Na-CYANEX 272 + 5% (v/v) TBP at different pH values in the range 2.0 to 4.5. The corresponding equilibrium pH for Na-D2EHPA was 2.5 to 4.72, and it was 2.8 to 6.38 for Na-CYANEX 272 + 5% (v/v) TBP (Figure 8).
The pH of the liquor was maintained by using dilute HCl or NaOH solution. For easy phase separation, 5% (v/v) TBP was added as a phase modifier to Na-CYANEX 272. The concentration of extractants and A:O ratio were kept constant at 0.5 M and 1:1, respectively. The percentage extraction of Co was increased from 3.0 to 69.6% by using Na-D2EHPA and from 25.0 to 98.42% using Na-CYANEX 272 + 5% (v/v) TBP (Figure 8). Therefore, Na-CYANEX 272 + 5% (v/v) TBP was found to be a more suitable extractant for Co recovery.

For optimization of the Na-CYANEX 272 concentration with 5% (v/v) TBP, its concentration was varied in the range of 0.3−0.7 M at pH 4.0. Here, pH 4.0 (Eq. pH 6.3) was chosen, as there was no significant difference in the extraction efficiency between pH 4.0 (Eq. pH 6.3) and pH 4.5 (Eq. pH 6.3), as per Figure 8. Figure 9 shows that by increasing Na-CYANEX 272 concentration from 0.3 to 0.6 M, the extraction of Co increased from 67.19 to 99.9%, beyond which there was a minimal increase.

At 0.4 M Na-CYANEX 272 with 5% (v/v) TBP, 81.5% extraction efficiency was obtained in a single stage. Hence, for the McCabe−Thiele diagram, the leach liquor was contacted with 0.4 M Na-CYANEX 272 + 5% (v/v) TBP at pH 4.0 with varying phase ratios from 1:5 to 5:1. The extraction isotherm plot (Figure 10) established the requirement of three counter-current stages at an A:O ratio of 1:1 for the quantitative extraction of Co.

A three-stage counter-current simulation experiment was conducted with the abovementioned optimum conditions at pH 4.0 and A:O of 1:1. The third stage raffinate analysis showed 0.006 g/L Co, indicating 99.94% extraction of Co. The generated raffinate basically contained sodium released from the Na-CYANEX 272, which could be discharged directly or recycled back to the leaching unit after recovering the salts.

3.8. Stripping of Co. The stripping study of the cobalt-loaded organic was carried out with different concentrations of H₂SO₄ ranging from 0.1 to 1.0%. The stripping efficiency of H₂SO₄ increased from 52.5 to 82.4% with an increase in its concentration from 0.1 to 1.0%. As the stripping of cobalt was maximum with 1% H₂SO₄, this concentration was chosen to construct the McCabe−Thiele diagram.

The McCabe−Thiele diagram was plotted by varying O:A between 1:5 and 5:1 for identifying the number of stages and O:A ratio. Figure 11 shows two-stage counter-current stripping of Co at the O:A ratio of 1:2. Subsequently, a two-stage counter-current simulation study was performed at the O:A ratio of 1:2. Analysis of the strip solution showed 4.67 g/L Co, indicating 99.7% stripping.

The schematic flowsheet for the recovery of Sm, Cu, and Co from Sm₂Co₁₇ magnet scrap is given in Figure 12. As per the flowsheet, the main REE Sm can be produced as pure Sm₂O₃. The other two valuable metals Cu and Co are recovered as pure CuSO₄ and CoSO₄ solutions, respectively, which can be recycled as feedstock for the leaching unit.

Figure 11. Stripping isotherm of Co with 1% H₂SO₄.

Figure 12. Schematic flowsheet for the recovery of Sm, Cu, and Co from Sm₂Co₁₇ magnet scrap.
further be processed to produce respective metal cathodes after required modification. The Fe content is separated as Fe(OH)₃, which may contain CaSO₄ also because of the use of CaO as a neutralizing agent during pH adjustment of a solution containing both Cl⁻ and SO₄²⁻ ions. Two liquid effluents are generated in the system. The first one is after Sm-oxalate precipitation, which can be recycled to the precipitation unit operation, thus reducing the requirement of fresh oxalic acid. The other liquid effluent is after coextraction, which is mainly a mixture of Na₂SO₄ and NaCl-containing solution, from which the salt content can be recovered after enrichment and suitable treatment before discharging.

The material balance for Sm is provided in Table S3.

4. CONCLUSIONS

Because of the presence of base metals like Fe and Cu, separation of Co and Sm from Sm₂Co₁₇-type scrap magnets is a challenging task. The aim of the present study was development of a complete flowsheet for the effective separation of Sm, Fe, Cu, and Co sequentially. The DoE was a very effective tool for leaching parameter optimization, and the predicted leaching efficiency of Sm and Co remained well within ±5% of the experimental values. Under the optimum conditions of 15% (v/v) HCl, 20 g/L solid loading, 1% (v/v) H₂O₂, 70 °C, and 3 h, more than 98% Co and Sm could be leached with a nearly equivalent amount of Cu and Fe. Double sulfate [NaSm(SO₄)₂·H₂O] precipitation of Sm directly from the leach liquor using 5% (w/v) Na₂SO₄ at pH 1.0 and 50 °C for 10 min agitation time is better option than the solvent extraction route, which requires Fe removal before Sm recovery. Sm-double sulfate salt could be easily converted to Sm-oxalate by precipitating with oxalic acid solution at room temperature. Production of pure Sm₂O₃ requires Sm-oxalate calcination at 800 °C for 1 h. After Sm separation, Fe can be removed by raising the pH to 3.0. About 98% extraction of Cu from Sm and Fe free leach liquor using 3% (v/v) LIX 84L in two stages with the A:O ratio of 1:1 is achievable. Finally, extraction of Co is achieved with 0.4 M Na-CYANEX 272 with 5% (v/v) TBP in three stages at the A:O ratio of 1:1. The pure sulfate solutions of Cu and Co generated through stripping of the loaded organics can be used for further for salt/metal production. We feel that the complete flowsheet developed for recovering all the valuable metals from Sm₂Co₁₇ scrap magnets will generate interest in the recycling of such waste.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04132.

ANOVA table for Sm, ANOVA table for Co, material balance of Sm, and XRD patterns of samarium oxalate and samarium oxide (PDF).

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Notes
The authors declare no competing financial interest.

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