

Review

Hydrometallurgical Recovery and Process Optimization of Rare Earth Fluorides from Recycled Magnets

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Abstract: Magnets containing substantial quantities of rare earth elements are currently one of the most sought-after commodities because of their strategic importance. Recycling these rare earth magnets after their life span has been identified to be a unique approach for mitigating environmental issues that originate from mining and also for sustaining natural resources. The approach is hydrometallurgical, with leaching and precipitation followed by separation and recovery of neodymium (Nd), praseodymium (Pr) and dysprosium (Dy) in the form of rare earth fluorides (REF) as the final product. The methodology is specifically comprised of sulfuric acid (H_2SO_4) leaching and ammonium hydroxide (NH_4OH) precipitation followed by reacting the filtrate with ammonium bifluoride ($\text{NH}_4\text{F}\cdot\text{HF}$) to yield the REF. Additional filtering also produces ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) as a byproduct fertilizer. Quantitative and qualitative evaluations by means of XRD, ICP and TGA-DSC to determine decomposition of ammonium jarosite, which is an impurity in the recovery process were performed. Additionally, conditional and response variables were used in a surface-response model to optimize REF production from end-of-life magnets. A REF recovery of 56.2% with a REF purity of 62.4% was found to be optimal.

Keywords: rare earth elements; magnets; recycling; recovery; fluorides; modelling

1. Introduction

Disquiet around the sustainability of rare-earth elements (REE) provisions has stimulated determination not only to recycle but also to improve the proficiency of the materials they are used to make [1]. With respect to the amount of REEs produced, neodymium (Nd) usage in the production of neodymium-Iron-Boron (NdFeB) magnets from mine output is about 13%. Out of that, 34% of the magnets produced are used in the manufacturing of actuator hard disk drives [1–3]. With their life span centered on their application, rare earth materials in hard disk drives are also applied in parts such as printed circuit boards (PCB), spindles, and so on [4].

In the production of these magnets, specific additions of elements are also used to adjust their properties [5,6]. For example, cobalt (Co) is used to substitute REE and iron (Fe) materials (up to over 5%) to increase the Curie temperature [7,8]. Dysprosium (Dy) addition increases the temperature characteristics such that the compound has a better stability against demagnetization. It also decreases the residual induction of the magnet, which leads to lower magnetic field properties [6,9]. To lower the production costs, Pr is now used as a substitute of Nd (up to 20–25%) in the production of magnets. Additionally, the magnet material is coated with a protective layer, such as copper (Cu), aluminum (Al), or nickel (Ni), as well as polymeric material to hold the magnet on the steel plate [4]. Although this shows that recycling of end-of-life magnets can help reduce the criticality of these REE in the near future, commercial recycling of REE is low, at less than 1%. This is mainly due to inefficient collection, technological difficulties, and high cost of processing [10–15].

Separation stage(s) have always been an important step in recycling. For rare earth magnets, since the element of interest is found with two or more others, they may require different extraction technology. Hydrometallurgical approaches have been shown to be a very efficient way to separate the REEs in which chemical separation by leaching is performed [16,17]. For REE leaching, lixiviants are directly added with or without heat treatment to dissolve the solid materials. Once the materials are in solution, various processes such as precipitation, solvent extraction, and ion exchange can be used to economically produce individual REE in the required form.

As a part of the impurities encountered in REE recovery, some of the leached Fe is also recovered as ammonium jarosite in the final REF product. To remove this impurity, the final product form is subjected to high temperature (250–500 °C) to decompose the ammonium jarosite [18–21]

For solvent extraction and ion exchange, different cationic, anionic and solvating extractants such as di (2-ethyl-hexyl) phosphoric acid (D2EHPA), dialkyl phosphonic acid (Cyanex 272), 2-ethyl-hexyl phosphonic acid mono-2-ethyl-hexyl ester (PC 88A), neodecanoic acid (Versatic 10), tributyl phosphate (TBP), and tricaprylmethylammonium chloride (Aliquat 336) have been reported for the separation of REEs from solution with D2EHPA being more commonly used with nitrate, sulfate, chloride and perchlorate solutions, PC 88A with chloride solutions, and TBP with nitrate solutions [22–35]. Interestingly, many of the same chemical types used as solvent extractants are also used in solid form as ion-exchange resins from the same type of leaching solutions [23,24,28,32]. For both solvent extraction and ion exchange, the REE-loaded material must then be selectively stripped. The resulting solutions are then predominantly processed to precipitate the individual REEs, often as REOs, but not always [36–39].

This paper presents the recycling Nd magnet scrap using a novel hydrometallurgical process involving H_2SO_4 leach, NH_4OH precipitation, and $\text{NH}_4\text{F}\cdot\text{HF}$ reaction. The latter step transforms the precipitate into rare earth fluorides (REF) which should be appropriate feedstock for subsequent pyrometallurgical processing into metal in molten fluoride electrolysis [39]. The application of hydrofluoric acid (HF) was completely avoided and the process was optimized through statistical analysis and modelling.

2. Experimental

2.1. Materials

Samples of scrap magnets were obtained from end-of-life computer hard drives from the IT Department of Montana Tech. Ammonium hydroxide (NH_4OH) dissolved in water at 28–30% concentration was obtained from VWR International LLC. Sulfuric acid (98% H_2SO_4) from Pharmco Products Inc. and ammonium bifluoride (98.8% $\text{NH}_4\text{F}\cdot\text{HF}$) manufactured by J.T. Baker were the other reagents used in the work.

2.2. Sample Preparation

2.2.1. Demagnetization

Nd magnets were obtained by disassembling the actuators in various hard drives. After loading in a ThermoScientific Lindberg/Blue M box furnace, the furnace was programmed to heat up to 500 °C at 5 °C per minute under ambient air. This was done in order to cause demagnetization and weaken the adhesive used to hold the magnet on the steel plate. The temperature was held at 500 °C for 60 min. Afterwards, the demagnetized magnets were air-cooled and sorted from the steel plates.

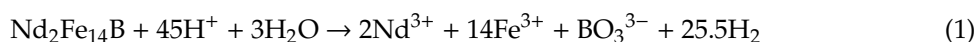
2.2.2. Comminution

Comminution was done to liberate the NdFeB part of the demagnetized sample so that ground mass could be easily leached with the lixiviant in view of the increased surface area of the material. Using a disc pulverizer from Bico Inc. (Burbank, CA, USA), the samples were initially comminuted

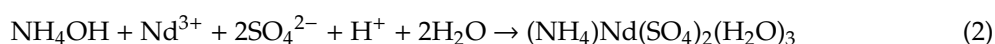
with a set of 3.1 mm. That product was further comminuted with a set of 0.3 mm. A sieve analysis was performed to determine the size distribution of the comminuted material and is discussed later.

2.3. Hydrometallurgical Processing

REEs were leached from the comminuted sample in a 2M H₂SO₄ acid solution with sample to solution ratio of 1g:10mL [4]. This process was done under a fume hood for 2 h with the acid solution being added in small amounts because of the aggressiveness of the reaction as shown in Equation (1).



Filtration was performed after leaching to separate the REE-acidic pregnant solution from the residue. NH₄OH was then added to the filtrate in a ratio of 1 mL NH₄OH to 20 mL rare earth rich pregnant solution to adjust the pH to 1.2, as shown in Equation (2).



Upon addition, the solution was stirred at 90 rpm to completely dissolve back into solution anything that formed when the NH₄OH was added. After that, the solution was allowed to sit for 12 h so the REE-rich precipitate could fully form and settle. Finally, filtration was performed so that the REE-rich residue could be collected and allowed to air dry. The dry REE-rich precipitate is then added into a mixture of NH₄F·HF and deionized water in a ratio of 1g:1.5g:10g and stirred for 45 min to enhance the formation of REF. The residue obtained after filtration was air dried and analyzed for REF content. The process flow sheet is shown in Figure 1. Various stages are also identified in the figure to facilitate further discussion later in this paper.

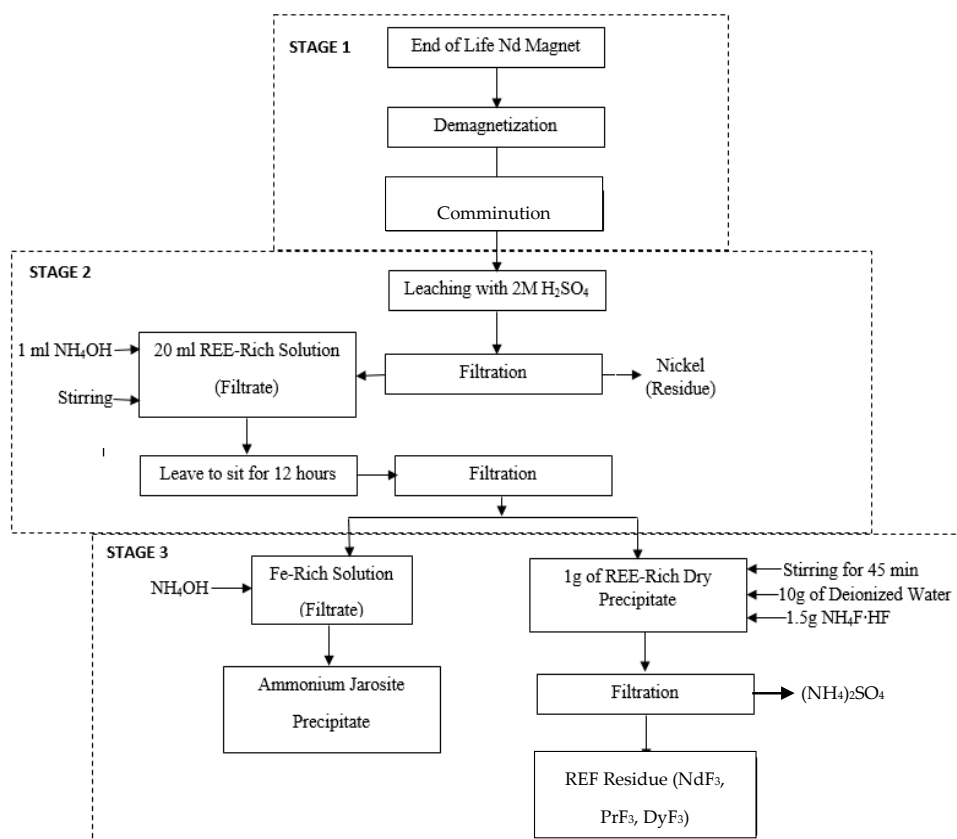


Figure 1. Flow sheet of Nd magnet recycling to produce REF.

Recovery of Fe in the form of ammonium jarosite, as shown in Equation (3), can also be done by the addition of more NH_4OH into the Fe-rich solution (as shown in Stage 3). With Equation (3) representing the reaction, the pH of the solution increased until a pH of 2 where maximum ammonium jarosite precipitated [17].



2.4. Modelling of REF Recovery

Stage 1 and Stage 2 of the flow sheet in Figure 1 were identified as less critical compared to Stage 3 of the process. Hence, it was decided to optimize Stage 3 in the present work. To optimize the REF recovery, Response Surface Methodology (RSM) was pragmatic in the analysis of the experiments. RSM is a mathematical and statistical technique that employs empirical models to fit the experimental data with reference to the Design of Experiments (DOE). With the process responses not following a linear model, the Box-Behnken design was employed for designing the experimental matrix to delineate the response surfaces generated by the condition variables [39–44]. This design selects points in the experimental domain for a three-level factorial arrangement in such a way that permits proficient approximation of the first and second order coefficients for the mathematical model [42]. The user identifies a high level and a low level of each condition variable and the mid-point is automatically identified for the point selection. Several experiments (usually 3 or 5) are conducted at the mid-point of all variables to estimate the inherent variability associated with the experimental technique.

In this work, the objectives were to maximize the amount of REF recovered from the precipitate along with their purity. This RSM was used at the point in the experiment where the REE-rich precipitate is added to $\text{NH}_4\text{F} \cdot \text{HF}$ to produce the REF in Stage 3. The experiments were performed as per the RSM design of experiments developed using the statistical software Design Expert 9 procured from Stat-Ease Inc., Minneapolis, MN, USA [43]. During the scoping tests, several condition variables were identified that affected the amount of REF recovered from the precipitate as well as its purity. To limit the number of experiments, the most important three condition variables were chosen, namely, the amount of deionized water (mL), amount of $\text{NH}_4\text{F} \cdot \text{HF}$ (g) and degree of stirring (min). Of course, the identified responses were the amount of REF recovered from the precipitate and the purity of the REF. The selected points in the experimental domain and the responses obtained are discussed later, along with the response surfaces, model equations, optimization and the interaction of the condition variables.

2.5. Material Characterization

After demagnification, the feed materials as well as intermediate and final products from this study were characterized using Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX), X-ray Diffractometry (XRD), Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES), and a thermal analyzer with thermogravimetric (TG) and differential scanning calorimetry (DSC) capabilities.

2.5.1. SEM/EDX

The SEM-EDX analyzer was employed to determine the chemical compositions of all phases in the demagnetized material. The SEM-EDX system uses a TESCAN TIMA with a tungsten filament and an EDAX Z2 analyzer (TESCAN ORSAY HOLDING, a.s., Kohoutovice, Czech Republic). Cross-sectioned sides of a representative sample were hand-separated and cold-mounted in epoxy using molds approximately 25 mm in diameter and 10 mm in thickness. Resulting mounts were ground and polished to a smooth finish and then conductively coated with carbon to obtain SEM images by backscattered electron (BSE) detection. EDX analyses helped determine the chemical compositions of all products.

2.5.2. XRD

X-ray diffraction was carried out with a Rigaku Ultima IV X-ray Diffractometer (XRD) (RIGAKU AMERICAS CORPORATION, Woodland, TX, USA) using Cu-K α radiation at 40 kV and 40 mA. This was used for quantitative analysis and also to determine the various phases of the precipitates and the products obtained after NH₄·HF addition.

2.5.3. ICP-OES

A ratio of 3:1 *v/v* HCl to HNO₃ was used to digest a representative sample of the final product obtained at the end of each experiment and resulting solutions were analyzed by ICP-OES to determine the elemental content of the sample (Thermo Electron Duo View iCAP 6500, Waltham, MA, USA).

2.5.4. TGA-DSC

Thermal decomposition of the ammonium jarosite, obtained in the final stage, was carried out in a TA Instruments SDT Q650 simultaneous thermal analyzer with thermogravimetric (TG) and differential scanning calorimetry (DSC) capabilities (TA Instruments, New Castle, DE, USA). Analyses were performed using 10 mg sample with a heating rate of 10 °C/min to 400 °C under argon atmosphere. The furnace temperature was regulated precisely to provide a uniform rate of decomposition.

3. Results and Discussions

3.1. Granulometry

Regarding Stage 1 of Figure 1 and using sieves ranging in aperture size from 0.149 to 4.699 mm, the size distribution of the comminuted sample is shown in Figure 2. It can be seen from this figure that nearly 50% of the material passed through the 0.6 mm sieve size. The 80% passing size (d₈₀) of the comminuted mass is about 1.7 mm.

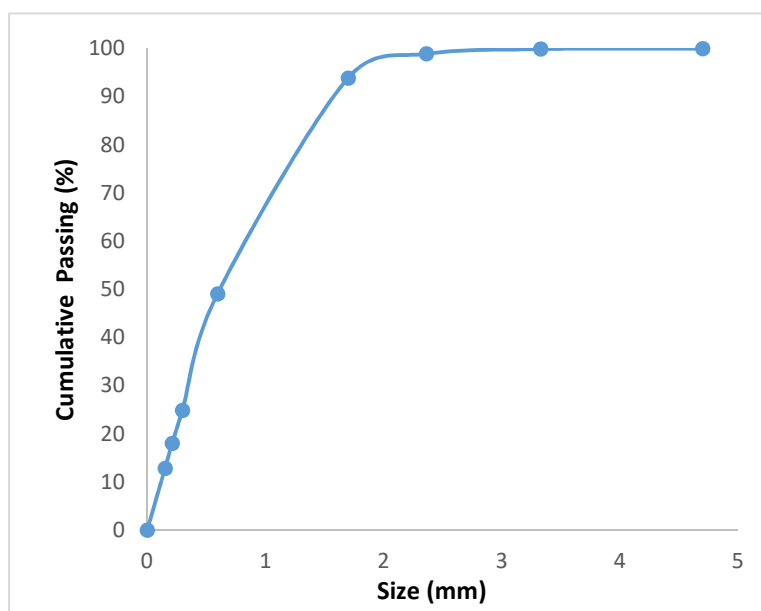


Figure 2. Cumulative particle size distribution of the demagnetized and comminuted sample.

3.2. SEM-EDX Analysis

Image from the Backscatter Electron (BSE) detector on the SEM-EDX demonstrate some dissimilar phases in the demagnetized and comminuted sample (see Stage 1 of Figure 1). “Three Dots” analysis was performed using the EDX. Of the three indicated points shown in Figure 3, each has a distinctive chemistry: point (a) appears to be Ni, which is the outer layer; point (b) is a combination of Pr, Nd and

Fe, where Pr is used to substitute Nd (up to 20–25%) to lower production costs; and point (c) shows a mixture of Nd and Fe. It is noted that boron (B) was not detected due to its low intensity, resulting from it being a light element (i.e., element #5 on the periodic table), as well as from the inherent disability of the BSE detector that was used [45].

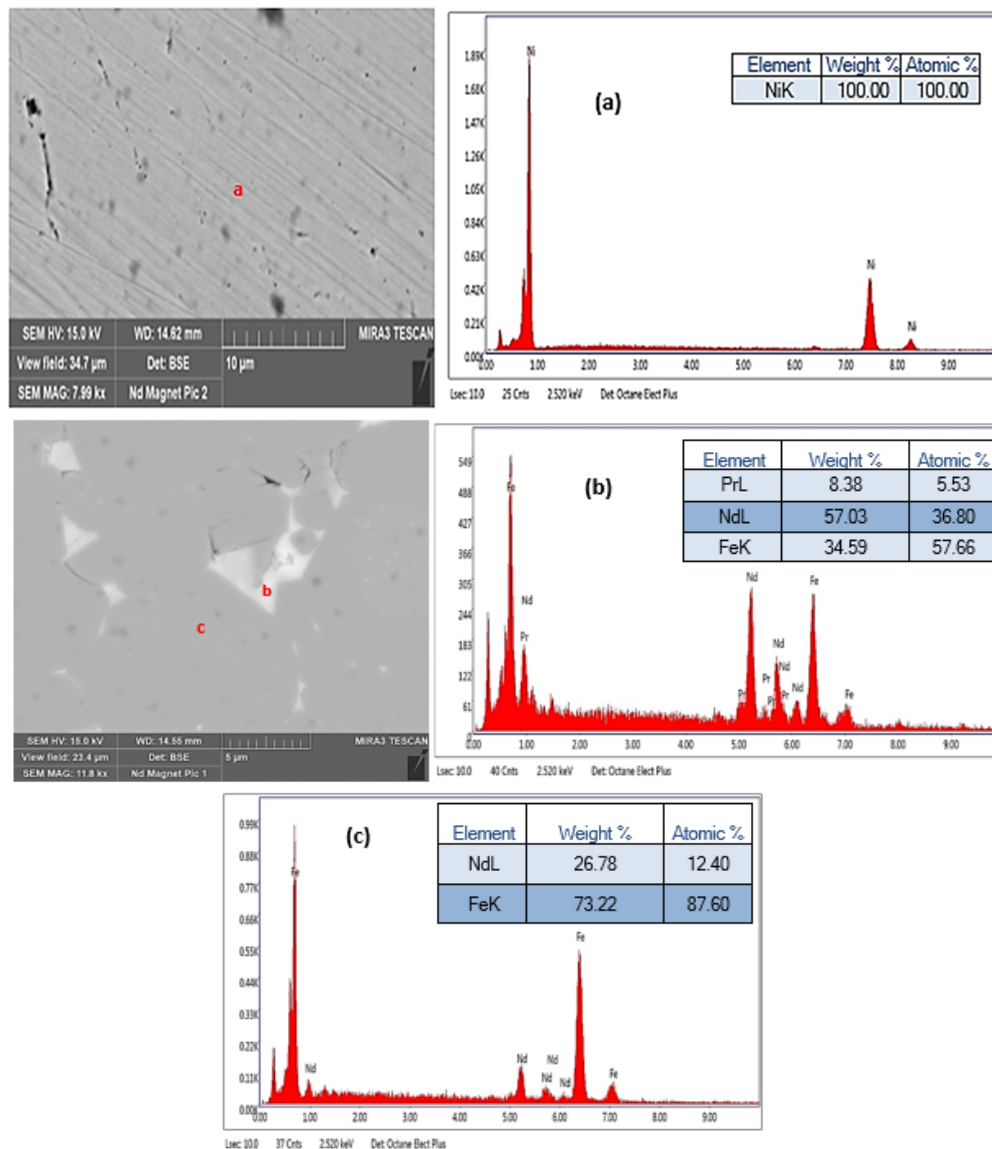
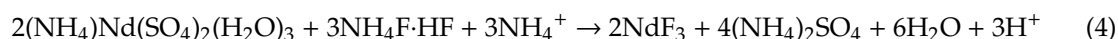


Figure 3. SEM image and EDX composition of the demagnetized and comminuted sample (see text for details). (a) Ni; (b) Pr, Nd, Fe; (c) Nd, Fe.

3.3. XRD Results

Figures 4 and 5 show the phase compositions of the precipitates (Stage 2 feed to Stage 3 rich, dry precipitate, as per Figure 1) and the final product (Stage 3 REF residue, as per Figure 1), respectively. From Figure 4, it can be said that most of the Fe remains in solution and that the dry precipitate is made up of mainly $(\text{NH}_4)\text{Nd}(\text{SO}_4)_2(\text{H}_2\text{O})_3$. This compound is an ammonium neodymium sulfate double salt and is noted to be similar to ammonium jarosite [17] with Nd substituting for Fe. Figure 5 also shows the phases of the product made after adding and stirring the dry precipitate in $\text{NH}_4\text{F}\cdot\text{HF}$ for 45 min, which is then heated under argon atmosphere to 400 °C and allowed to cool. Equation (4)

depicts a possible mechanism for REF formation with the REE being Nd assuming ammonium (NH_4^+) is in excess:



The product is clearly a REF containing REEs of Nd, Dy and Pr. It can therefore be concluded that REF can be produced by this process and the resulting fluorides can be used later as feedstock for pyrometallurgical metal production [39].

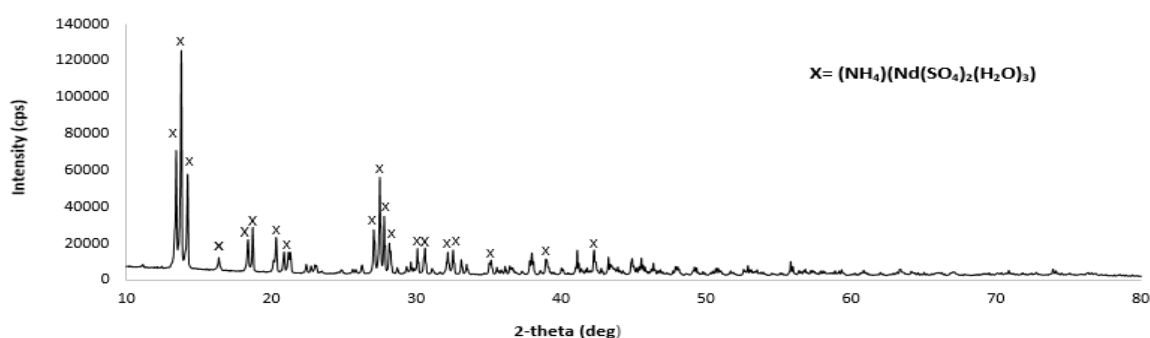


Figure 4. Crystal phases in the REE rich precipitate after adding NH_4OH .

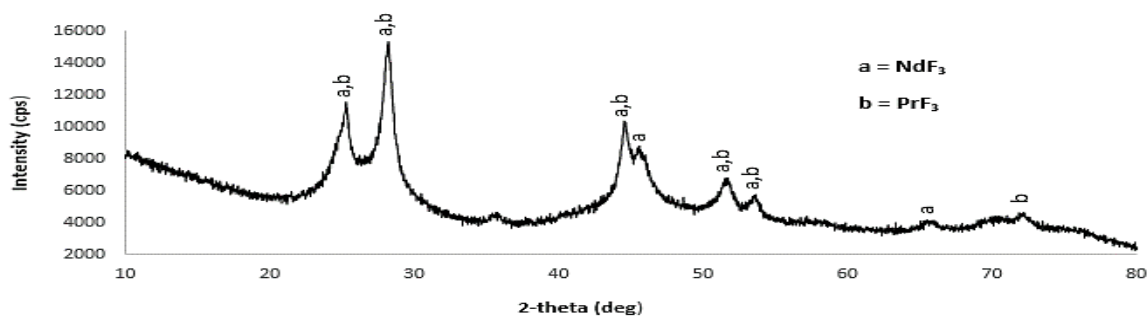


Figure 5. Crystal phases in the REF filtrate after 45 min in $\text{NH}_4\text{F} \cdot \text{HF}$ and heated to 400°C .

3.4. ICP Results

Table 1 shows the chemical composition of REEs in the final REF product indicating Dy and Fe are present, apparently in amounts below the XRD detection limit. Together, the total REE amount sums to 63.25%. Based on stoichiometry and assuming the REEs exist as REF (i.e., NdF_3 , PrF_3 and DyF_3), the F-content would be 24.94%. This leaves a balance of 10.59%, which is expected to be ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ and ammonium jarosite $[(\text{NH}_4)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$, as per Equation (4). Furthermore, based on the stoichiometry of the jarosite, the Fe content would equate to 3.44% of these other components, suggesting there is 7.15% ammonium sulfate. Both ammonium sulfate and ammonium jarosite can be monohydrated [46] which will thermally decompose at low temperature. In this regard, a TGA-DSC study was undertaken on the final REF residue from Stage 3. Because the product was heated to 400°C under argon, a subsequent TGA-DSC scan did not exceed 400°C . It is important to note that this REF residue, as discussed above, is not pure, and therefore contains some ammonium sulfate and ammonium jarosite.

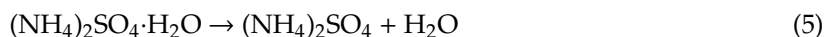
Table 1. The chemical composition of the final product.

Sample Composition	Dy	Fe	Nd	Pr	Others
Weight (%)	2.89	1.22	52.95	7.41	35.53

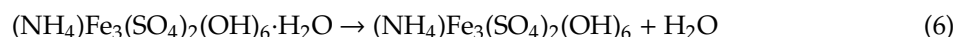
3.5. TGA-DSC Results

The TGA-DSC graphs of the REF residue are shown in Figure 6. The plot shows that mass loss occurs in five steps which agrees with the literature [46–49]. In this regard, the first two steps equate simply to crystalline water loss of the ammonium sulfate (Equation (5)) and ammonium jarosite (Equation (7)), respectively:

25–50 °C

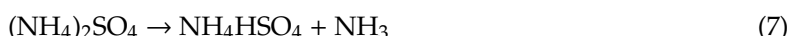


75–125 °C



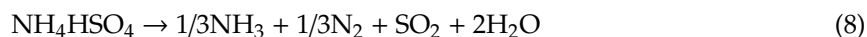
The third step corresponds to the decomposition of dehydrated ammonium sulfate to ammonium bisulfate:

140–210 °C



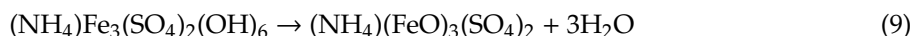
The fourth step is likely caused by complete thermal decomposition of the ammonium bisulfate:

220–250 °C



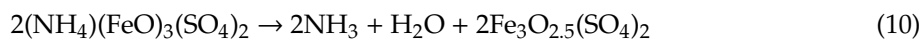
Finally, the fifth step appears to be the dehydroxylation of the dehydrated ammonium jarosite, thereby accounting for the continued loss in weight as the temperature increased to 380 °C:

>260 °C

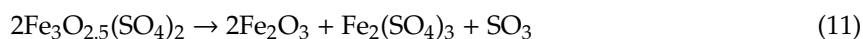


If the temperature had been increased to 600 °C, three additional steps involving the sequential reactions of the dehydroxylated ammonium jarosite would be observed such that all of the Fe ultimately becomes hematite [46–49]:

>385 °C



>510 °C



>540 °C



where $\text{Fe}_3\text{O}_{2.5}(\text{SO}_4)_2$ is essentially equivalent to a solid solution of $2/3 \text{Fe}_2(\text{SO}_4)_3$ and $5/6 \text{Fe}_2\text{O}_3$.

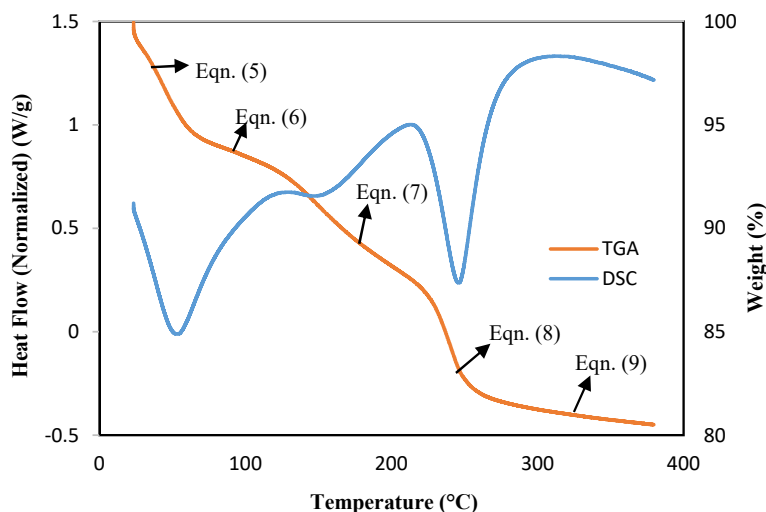


Figure 6. TGA-DSC curve for REF residue from Stage 3.

4. Model Development and Process Optimization Using RSM

Table 2 shows the Design of Experiments (DOE) along with the condition variables and responses for Stage 3 processing. In all, 17 experiments were performed, each using 2 g of REE-rich dry precipitate from Stage 2. The following ranges of the condition variables were employed: deionized water volume was 10–30 mL; 2–4 g of $\text{NH}_4\text{F}\cdot\text{HF}$ was added; the degree of stirring was 15–45 min. Responses were REE recovery and REF purity where recovery refers to the amount of REE from Stage 2 being converted to REF residue and purity refers to the quality of the REF residue based on ICP analysis.

Table 2. DOE conditions and their responses.

Standard	Run	Volume of Deionized Water (mL)	Amount of $\text{NH}_4\text{F}\cdot\text{HF}$ (g)	Degree of Stirring (mins)	REE Recovery (%)	Purity of REF Residue (%)
2	1	30	2	30	46.76	60.59
8	2	30	3	45	55.58	63.26
10	3	20	4	15	53.15	54.01
7	4	10	3	45	63.03	46.12
4	5	30	4	30	49.63	58.38
17	6	20	3	30	47.16	56.93
3	7	10	4	30	64.09	49.66
1	8	10	2	30	50.44	45.52
12	9	20	4	45	55.41	51.84
16	10	20	3	30	49.67	53.08
5	11	10	3	15	57.48	51.19
11	12	20	2	45	54.65	48.59
15	13	20	3	30	50.09	54.94
14	14	20	3	30	52.74	51.39
6	15	30	3	15	52.13	50.85
9	16	20	2	15	53.56	50.65
13	17	20	3	30	51.38	57.42

Furthermore, five experiments were completed with all condition variables being at their midpoints. The results were analyzed to develop a statistically significant model for the responses of the REE recovery and REF purity as shown in Equations (13) and (14):

$$\text{REE Recovery (\%)} = 50.14 - 3.87A + 0.087B + 0.84C - 2.70AB - 0.53AC + 2.68A^2 + 4.15C^2 + 4.04A^2B + 1.41A^2C \quad (13)$$

$$\text{REF Purity (\%)} = 54.75 + 4.20A + 1.65B - 1.06C - 1.59AB + 4.37AC + 0.18A^2 - 1.40B^2 - 2.08C^2 - 1.17A^2B + 2.89A^2C \quad (14)$$

where A denotes the volume of deionized water used, B denotes the amount of $\text{NH}_4\text{F}\cdot\text{HF}$ added, and C denotes the degree of stirring. In both cases, a cubic model represented the data best and the R^2 values were 0.94 and 0.93 for recovery and purity, respectively.

Using Equations (13) and (14), 3-D surface plots in Figures 7 and 8 were generated to illustrate the effects of the condition variables on the responses. From Figure 7a,b, it can be said that $\text{NH}_4\text{F}\cdot\text{HF}$ addition appears to have more prominent effect on the process efficiency. The impact of deionized water addition is more prominent at higher stirring rates and higher $\text{NH}_4\text{F}\cdot\text{HF}$ additions. With respect to stirring, it can be observed from Figure 7a that the amount of REF recovery increases with stirring time for both 10 and 30 mL of water used. However, recovery is higher for lower volumes of water than for higher ones, and this same pattern is observed with respect to $\text{NH}_4\text{F}\cdot\text{HF}$ addition as illustrated in Figure 7b when using Equation (13).

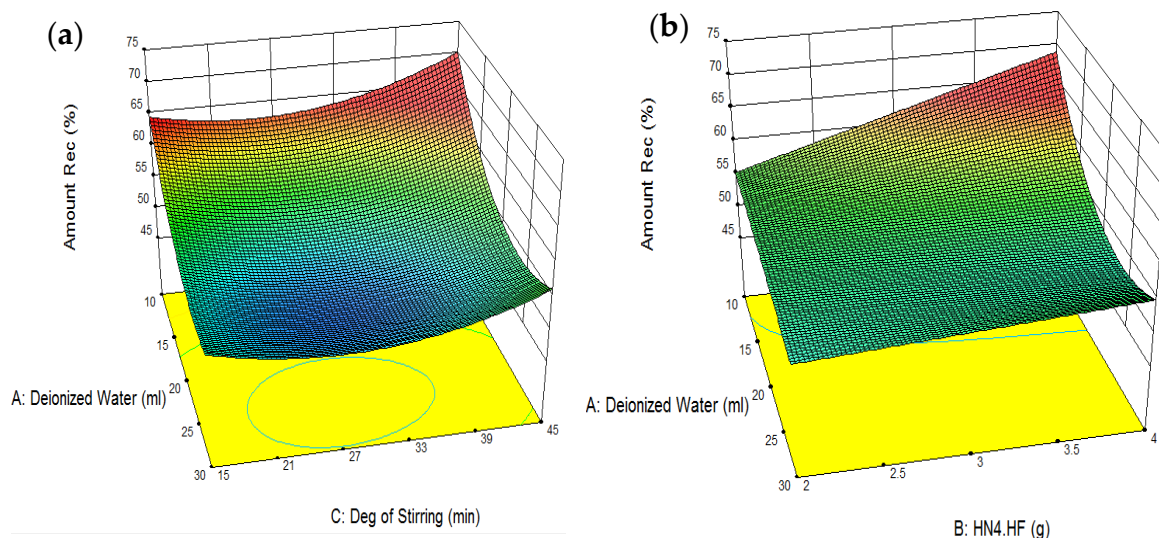


Figure 7. 3D plots of REF recovery with respect to process variables at (a) 4 g of $\text{NH}_4\text{F}\cdot\text{HF}$ and (b) 43 min for degree of stirring.

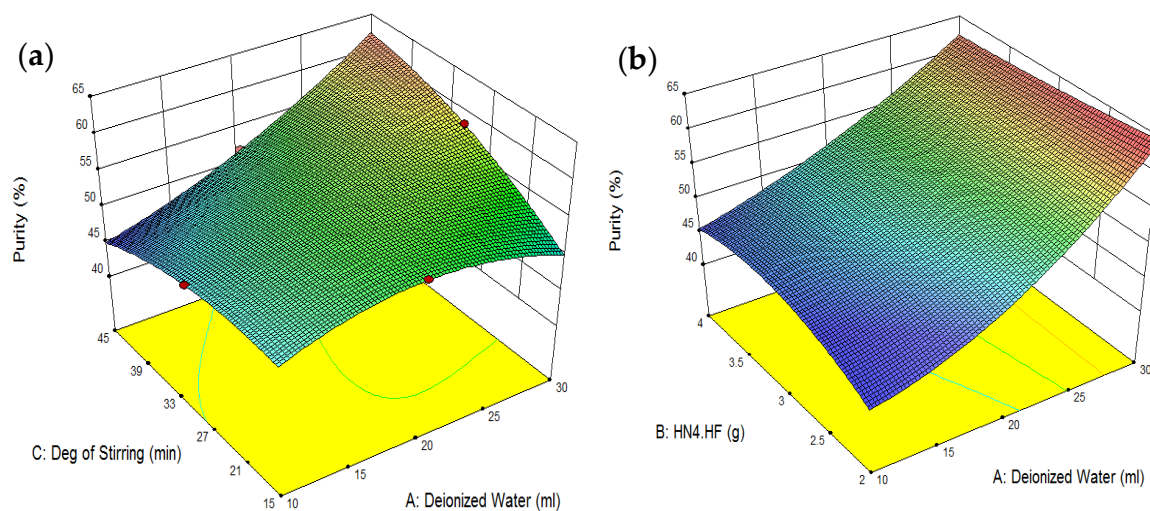


Figure 8. 3D plots of REF purity with respect to process variables at (a) 4 g of $\text{NH}_4\text{F}\cdot\text{HF}$ and (b) 44 min for degree of stirring.

Figure 8a,b were generated from Equation (14) and illustrates the response surfaces for REF purity in relations to the process variables. From these plots, it is observed that the amount of deionized water again did influence purity of REF recovery to a significant extent at all $\text{NH}_4\text{F}\cdot\text{HF}$ additions and also at higher stirring degrees. The degree of stirring, as observed in Figure 8a, seems to affect the REF insignificantly at low water additions. However, REF purity increased sharply with stirring time at a high volume of water addition. Figure 8b shows that $\text{NH}_4\text{F}\cdot\text{HF}$ addition has less impact on the purity of REF. Sharp increase in the purity of the REF is seen with increase in the volume of water.

It may also be noted that, in Equations (13) and (14), the process variables are all in terms of the coded values and differ in the range +1 to −1, with the mid-point having a value of zero. Thus, for B, the maximum amount of $\text{NH}_4\text{F}\cdot\text{HF}$ used (4 g) corresponds to +1 and the lowest (2 g) corresponds to −1, whereas the midpoint of 3 g corresponds to 0. To use these statistically significant equations, the actual variable value needs to be converted to the coded form lying between +1 and −1. Using the above model equations optimization was carried out to find the conditions that maximized both REF recovery

and REF purity. The identified conditions and their maximum corresponding responses are as follows:

Amount of Deionized Water Used: 30 mL

REF Recovery: 56.23%

NH₄F·HF Added: 4 g

REF Purity: 62.42%

Degree of Stirring: 45 min

5. Conclusions

From this study, it is established REF can be produced from end-of-life Nd magnet from hard disk drive by hydrometallurgical techniques using NH₄F·HF. The final product (REF) can also be used as part of the salt bath for molten salt electrolysis using fluoride salt [39]. This process is preferred over those reported in the literature because the use of hazardous HF was avoided. Employing statistical design of experiments (DOE), process parameters such as volume of deionized water, amount of NH₄F·HF and degree of stirring were defined in detail, and a conducive process regime for the recovery of the REFs was identified. It was established that at higher volumes of water, NH₄F·HF addition, and degree of stirring, optimum REF recovery with reasonably high purity can be achieved.

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