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Separation of rare earth elements from waste NdFeB magnets: The influence of hematite seeds and agents on the hematite precipitation in nitric acid medium

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ABSTRACT

Nowadays with the evolution of technology and rare earth elements (REE) are raw materials for a multitude of products, especially in technological applications. Large amounts of electronic waste rich in REE are produced, and this can be utilized as a valuable resource. For these reasons, efforts and research are focusing on secondary production, which is recycling and recovery of REE and specifically neodymium (Nd) from end-of-life components. In this study, the recovery of REE from NdFeB was investigated based on Box-Behnken experimental design technique. The effect of the experimental parameters in the hydrolysis of Fe^{3+} to hematite in a nitric acid medium in the hydrothermal reactor was examined in detail. Afterwards, the influence of the temperature, time, and hematite precipitation agents including starch $(C_6H_{10}O_5)_n$, sucrose $(C_{12}H_{22}O_{11})$, and hematite seeds (Fe_2O_3) on the recovery of REE, and hematite precipitation were analyzed by statistical analyses. The optimal parameters for maximum REE recovery and iron removal under pressure and temperature were determined to be a process temperature of approximately 145°C, a process time of approximately 6 hours with the starch addition. The optimum parameters are in harmony with the validation experiments.

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KEYWORDS
NdFeB recycling; rare earth elements; hematite precipitation; Box-Behnken design; statistical investigation

Introduction

Nowadays, by using recycled materials in the manufacturing process, considerably lower amount of energy is necessary than that required for producing products from primary raw materials. The reason is that more energy is required for the processes of extraction, transportation, refining and processing of raw materials compared to providing industry-ready materials after recycling. Moreover, with the continuous development and evolution of technology, a constant material supply is necessary for products manufacturing. Materials utilized for high-tech and complex applications, such as rare earth elements (REE) for the production of NdFeB magnets are necessary to cover the increasing global demand in various electrical device applications. These magnets have become one of the most important type of magnets because of their higher strength, smaller size as well as their lower price compared to cobalt magnets. Although when the electric and electronic equipment has reached its end-of-life (EoL) period, they often end up on landfill sites.[1–7] Furthermore, the domination of the REE production by China, their export quotas and the consequent classification of REE as critical could lead to a bottleneck the production processes. Hence, the necessity of efficient recycling processing is evident, in order to protect the environment as well as transform the electronic waste materials to valuable metals as salable by-products.[8–10]

In the literature, there has been an abundance of research on the recovery of REE based on pyrometallurgy and hydrometallurgy.[11–19] Hydrometallurgy is the widely preferred technique for the extraction of REEs from scrap materials. As hydrometallurgical processes have usually lower investment and operational costs than pyrometallurgy, although it is susceptible to small changes and a careful waste management is essential. The challenges for the hydrometallurgical processes are to recover the REE from the end-of-life permanent magnets and separate them from other compounds like iron. For example, in NdFeB magnets contain a high amount of iron, on average 72 wt%, which is difficult to separate from the REE.[20–25] Moreover, high amount of chemicals is used with many separation steps.

The initial step in dissolving the REE from the magnet scrap by leaching. Usually, the EoL demagnetized magnets are crushed, milled and sieved to obtain a fine powder. Prior to leaching a roasting process may or may not be

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used in order to oxidize the iron to Fe^{+3} state which will precipitate at pH value around 3.[26] Then the magnet powder is added to an acid solution, stirred and/or heated to dissolve. Different acid solutions can be utilized, such as hydrochloric acid (HCl), sulfuric (H_2SO_4) or nitric acid (HNO_3) on various concentrations to achieve the desired leaching efficiency. Two distinct approaches can be utilized, the complete leaching and the selective leaching approach. In the first one, all components of the magnets scrap will be dissolved. Although a significant proportion of Fe dissolved in the solution must be separated, the solution can be treated with different agents like oxalic acid to precipitate the REE as oxalates.[27] The second approach is the selective leaching process, where Nd is extracted from the magnets without dissolving Fe and B. Firstly the powder is roasted or baked with acid and then leached. The recovery of REE is achieved by selectively interacting with these elements and not with Fe and B, since Nd is selectively precipitated as $Nd_2(SO_4)_3$ on the basis of the solubility difference from Fe. Thus, it is controlled by adjusting the pH value or by adding a precipitating agent like oxalic acid or sodium sulfate. REE were precipitated by oxalic acid at the pH range of 2–2.5, after the dissolution of scrap in hydrochloric acid. However, iron ions reacted with oxalate acid to form precipitates of iron-oxalate, which added impurity into the rare earth precipitates.[28] The REE-rich leaching solution must be purified from before it can be further utilized.[29] In another study, iron can be removed as iron hydroxide at a pH level of 3–3.5[26] and because REE do not form any hydroxide compounds when the pH value is lower than 5. However, the negative side-effect of utilizing such reagents is the co-precipitation of REE, which will result in considerable losses. If the pH value is increased above 5, then the REE losses rise significantly even more than 40%.[26] In addition, the iron precipitation in the hydrothermal reactor was investigated to effectively separate it from the NdFeB magnet scrap. They presented that after the material dissolution in the three mineral acids, the amount of dissolved Nd, Pr, Dy, and Fe were quite similar however the iron can be precipitated in HNO_3 not in HCl and H_2SO_4.[30]

This study aims to investigate a method to minimize the REE losses during iron precipitation. Particularly, to minimize the REE loses during the precipitation process, a hydrothermal reactor is used in a 2-step process, with the usage of sucrose, starch and hematite seed in the second step to boost the iron precipitation. The effects of three different parameters on the REE recovery ratio and the iron removal rate were investigated. Through 15 experiments the target was to obtain the experimental data to create a model to maximize the Fe removal ratio and the REE recovery ratio via Box-Behnken design, and which would reveal the optimal conditions to achieve them. Contour plots for time, temperature and precipitation agents were obtained and by employing the analysis of variance (ANOVA) results of the two models, the optimal conditions for these parameters were revealed for the maximization of the REE recovery ratio and the Fe removal rate.

Materials and methods

Design of experiment

In this study, 15 experiments were conducted with different parameters, in order to fulfill the necessary requirements of Box-Behnken design and finally obtain data for the response surface curves. Statistical experimental planning is used for more efficient planning and evaluation of tests. The DOE can be characterized by easy handling, efficiency, stability and clear presentation of the results. In the hydrothermal reactor three different parameters were investigated, time in furnace, temperature of furnace and addition of agents. Various values of the parameters were tested, in order to obtain the optimal conditions from the Box-Behnken design. Table 1 presents the experimental parameters for the hydrothermal treatment.

NdFeB magnet powder preparation

EoL demagnetized NdFeB magnets were supplied in bulk form, as rectangles and utilized to obtain magnet powder. Nitric acid (65%) from Sigma Aldrich was used for the leaching experiments, as well as deionized water to form aqueous solutions of the before mentioned compounds. Sucrose and starch (commercially available) were utilized for boosting iron precipitation in the hydrothermal reactor experiments.

The bulk magnet pieces were brittle, and they were crushed by the jaw crusher Retsch BB51. This process was repeated many times, in order to achieve the desired powder size. After crushing the magnet powders, the

Table 1. The experimental parameters for the hydrothermal treatment.

Parameter	1	2	3
Temperature (° C)	140	160	180
Time in furnace (hours)	4	5	6
Additive agents	Sucrose + Hematite seeds	Starch + Hematite seeds	Hematite seeds

obtained non-oxidized powder was sieved by a vibratory sieve shaker (Retsch, AS200), to acquire fine powder (powder size ≤ app. 90 µm).

Characterization of NdFeB magnet powders

The chemical composition of the non-oxidized magnet powders was determined using X-ray fluorescence (XRF) spectroscopy (Panalytical, wavelength dispersive WDXRF spectrometer from Malvern Panalytical B.V.) The phase analysis of NdFeB magnet powder and hematite precipitate were conducted by X-ray diffractometer (Empyrean, Malvern Panalytical).

Leaching of NdFeB magnet powders

For each leaching experiment, approximately 6.69 grams of the magnet powder was dissolved in 200 ml of 2 mol/L nitric acid solution. The leaching solution was prepared by mixing 172 ml water and 27.9 ml of nitric acid (65%), to obtain the desired acid concentration. Afterwards, a heat-controlled mantle was utilized with a 3-necked quartz reactor with constant overhead stirring at 450 revolutions per minute. In addition, a condenser with constant water throughput was used. The experimental setup for the leaching experiments can be found in elsewhere.[25] Firstly, the water quantity was introduced to the reactor, followed by the acid and stirred for 5 seconds to mix them. Afterwards, the powder was introduced and stirred for a few seconds and allowed to cool, since mineral acid leaching is an exothermic process. Then the stirring continued, with duration of each leaching experiment being 30 minutes at room temperature (~25°C), hence NdFeB magnet powder was allowed to dissolve almost completely into solution. The pH value of the leaching solution was recorded −0.15. Afterwards, the leach residue and the pregnant solution were separated via a vacuum filtration system. The pregnant solution was easily filtered and had a water-like viscosity. The Fe^{2+} concentration in the leaching solution was measured through potentiometric titration using cerium (IV) sulfate (Metrohm Dosimat 655, Titrosampler 855).

Hematite precipitation under pressure and temperature

In this study, the precipitation under pressure and temperature approach was investigated for the hematite precipitation. In order to remove the iron from the leaching solution, a hydrothermal reactor system was employed. A volume of 20 ml of the leaching solution was placed inside the reactor for a two-step process. By utilizing the Box-Behnken design, 15 different two-step experiments in the hydrothermal reactor were conducted. Three different parameters were investigated, including time in the furnace, temperature, and precipitation agent, in order to obtain the optimal conditions for the iron removal and REE recovery. In the first step, only the solution was placed into the hydrothermal reactor and then it was placed inside a preheated oven. In the second step, the solution in the hydrothermal reactor was cooled and then again placed in the preheated oven with or without the addition of reagents, in order to boost the iron precipitation. For the first time, the obtained hematite in the first step were used as precipitation seeds to boost the hematite precipitation in the second step. In this study, sucrose and starch (commercially available) were utilized to boost hematite precipitation under pressure and temperature. The quantities of sucrose and starch were determined based on Equations 1 and 2, resulting in an approximate sucrose-to-total Fe molar ratio of 0.62 and starch-to-total Fe molar ratio of 0.32.

$$\begin{aligned} C_6H_{10}O_5 + 4.8NO_3^- + 4.8H^+ \\ = 6CO_2 + 7.4H_2O + 2.4N_2 \end{aligned} \tag{1}$$

$$\begin{aligned} C_{12}H_{22}O_{11} + 9.6NO_3^- + 9.6H^+ \\ = 12CO_2 + 15.8H_2O + 4.8N_2 \end{aligned} \tag{2}$$

Starch and sucrose are saccharide polymers, and initially, they must be decomposed into their monomers for these reactions to occur. In that case, glycosidic bond in the polymer must be broken. Glycosidic bond can be broken with different mechanism including hydrolysis, temperature, and chemical cleavage. Glycosidic bonds may start to break down at temperatures ranging from 150°C to 300°C, depending on the specific structure and composition of the molecules. As well as it can be broken by the addition of water and acids.

Structural studies of hematite particles were conducted by X-Ray Diffractometer – PANanlytical EMPYREAN. Morphological investigation of hematite particles was performed by Scanning Electron Microscope, Thermo Fisher Quattro S.

Results and discussion

NdFeB magnet characterization

After crushing the EoL demagnetized NdFeB magnets into fine powder, an XRF analysis was conducted to determine their chemical composition. Table 2 shows chemical phase of NdFeB magnet powder determined by XRF analysis. High amounts of iron, neodymium and

Table 2. Chemical phase of NdFeB magnet powder determined by XRF analysis.

Component	Na_2O	Al_2O_3	SiO_2	MnO	Fe_2O_3
Composition (%)	0.34	0.42	0.24	1.97	68.1
Component	**Co_3O_4**	**CuO**	**Ga_2O_3**	**As_2O_3**	**Nb_2O_5**
Composition (%)	0.7	0.14	0.2	0.21	0.12
Component	**PdO**	**Pr_2O_3**	**Nd_2O_3**	**Tb_4O_7**	**Other**
Composition (%)	0.24	5.72	20.4	0.7	0.5

praseodymium as oxides are observed, with the addition of small amounts of Dy, Si, Al, Co, Mn and Pd.

In Figure 1, the SEM image of the NdFeB particles is presented (top), while on Figure 1 (bottom) the energy dispersive X-ray analysis is exhibited. This is an x-ray technique used to identify the elemental composition of materials. The peak analysis confirmed the presence of oxygen, iron, neodymium and praseodymium. This is because the higher the counts of a particular element, the higher will be its presence at that point or area of interest.

Moreover, the phase analysis of NdFeB magnet powder were performed by XRD analysis. Figure 2 depicts the XRD pattern of the magnet powders.

The XRD peaks in the pattern of NdFeB magnet powders correspond to tetragonal structure of the $Nd_2Fe_{14}B$ compound, which belongs to the space group of P_{42}/mnm, as reported elsewhere.[31]

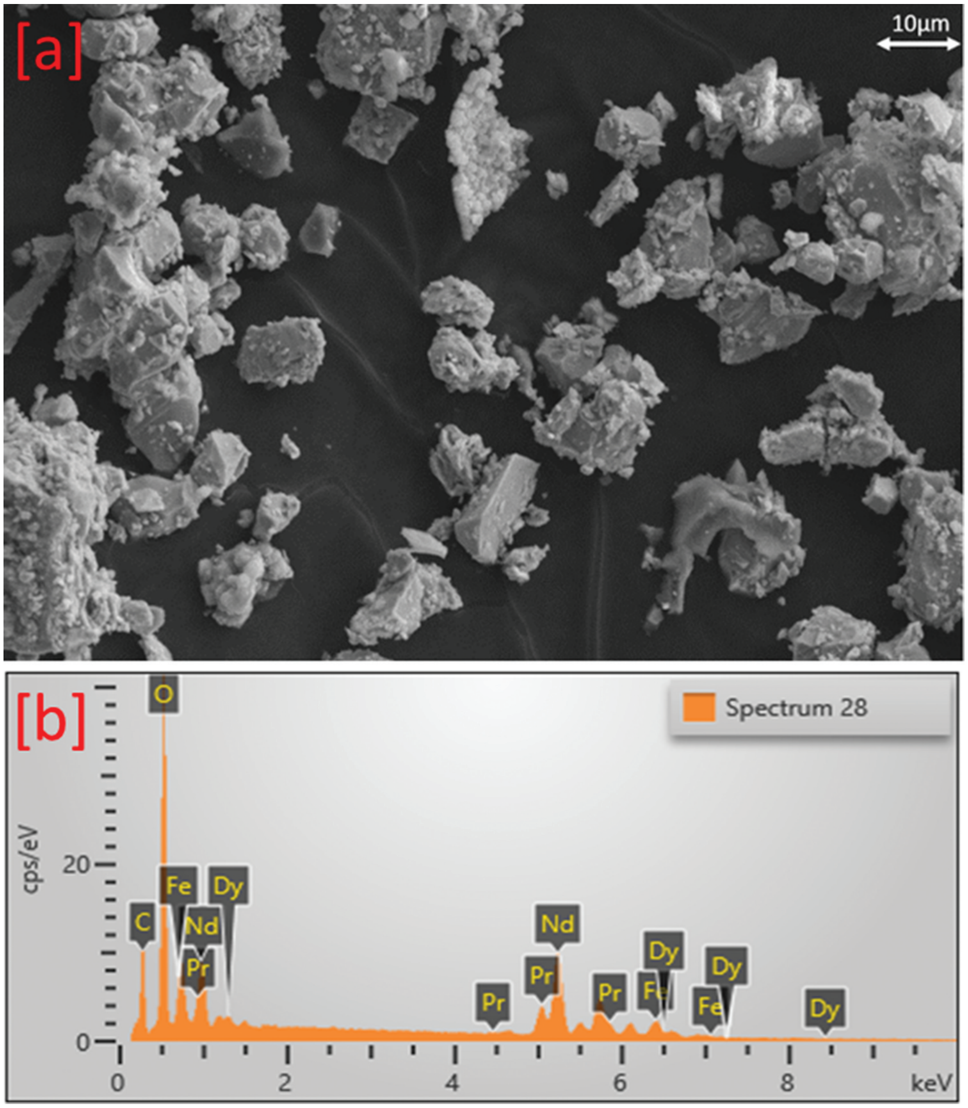


Figure 1. [a] SEM image of the NdFeB powder via 15 kV [b] energy dispersive X-ray analysis.

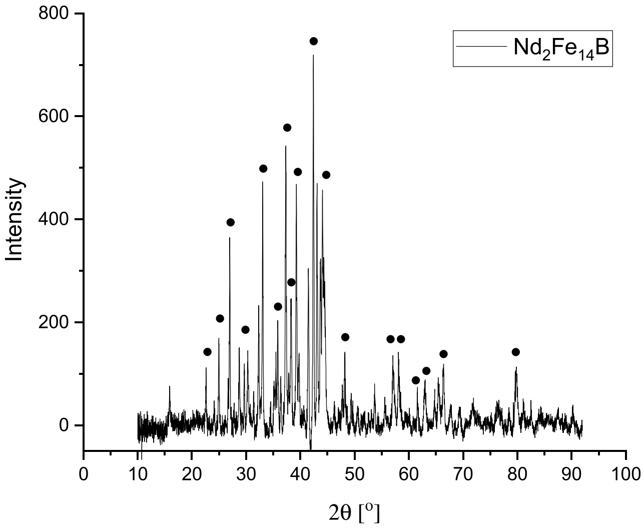


Figure 2. XRD analysis of NdFeB magnet powder.

Leaching experiment

Initially, screening leaching experiments were conducted over a 120-minute duration, with samples collected for chemical analysis every 15 minutes. As no substantial increase in metal dissolution was observed beyond the initial 30 minutes, the leaching period was determined to be 30 minutes. Furthermore, Rabatha et al. reported that upon selecting an HNO_3 concentration of 3 mol/L, the dissolution of Nd, Dy, and B exceeded 95% within the initial 5 minutes of leaching.[32]

The use of a nitric acid medium offers several advantages, including its capability to generate highly oxidizing conditions and to directly utilize oxygen from the air. This medium demonstrates unique properties specifically in relation to iron oxidation, it facilitates the oxidation of Fe^{2+} to Fe^{3+}. The Fe^{2+} concentration in the leaching solution was measured through potentiometric titration, the Fe^{2+} concentration was calculated less than %1 of the iron concentration in the solution.

Mineral acid leaching is an exothermic process and allows REE as well as the impurities to dissolve into solution. Here, the neodymium contained in the magnet was dissolved as well as the other elements. Iron was dissolved into the solution as Fe^{+3} ions. Overall, the leaching efficiency was almost 100%. Table 3 shows the chemical composition of the leaching solution.

Hematite precipitation in the hydrothermal reactor and statistical investigation

In the hydrothermal reactor, three different parameters were investigated, time in furnace, temperature of furnace and addition of agents and hematite seeds. The hematite precipitation reaction (Eq.6) is not occurred at atmospheric conditions, this reaction only happens in an autoclave under pressure, if the temperature is high, the hematite particles might dissolve. Thus, it is important to find optimum process temperature.

Various values of the parameters were tested, in order to obtain the optimal conditions from the Box-Behnken design. Table 4 illustrates the REE recovery rate and iron removal ratio after the precipitation in the hydrothermal reactor. From the results of the ICP-OES analysis in Table 4, it is observed that the maximum REE recovery rate was 99.95%, obtained at 160°C, 6 hours in furnace and starch addition. Moreover, the maximum iron ratio was detected at 180°C, 6 hours in furnace and with the addition of sucrose. Since elevated temperatures leads to the dissolution of hematite particles.

Figure 3 presents the contour plots for the relationship between temperature, time, and the addition of water on the removal of iron. Figure 3 (a), (c), (e) and 4.27 (b), (d), (f)represent the response surface plots for iron precipitation and REE, respectively.

Moreover, through the analysis of variance (ANOVA) of the results, a model is proposed for the optimal conditions for the experiments to maximize the iron removal ratio. Table 5 shows ANOVA result for the Fe removal. The established boundary conditions are a process temperature ranging from 140 to 180°C and a time in furnace between 4 and 6 hours.

The equation for this model is presented in Equation 3.

$$\begin{aligned}\text{Fe removal ratio}(\%) = {} & -579 + 7,00 * \mathrm{T} \\ & + 108,4 * \mathrm{PA} - 0,0165\mathrm{T} * \mathrm{T} \\ & - 12,87 * \mathrm{PA} * \mathrm{PA}\end{aligned} \tag{3}$$

where T is the temperature of the preheated furnace (°C), t is the time in furnace (hours), PA are the precipitation agents. PA has three possible values, −1 for no addition of any agent, 0 for sucrose addition and 1 for starch addition. Statistical analysis revealed that,

Table 3. Chemical composition of the leach solution.

Composition	Fe	Nd	Pr	B	Co
Concentration (mg/L)	2150	753	222	33.8	27.9
Composition	**Dy**	**Cu**	**Mo**	**Cr**	**Ni**
Concentration (mg/L)	16.9	<0.1	<0.1	<0.1	<0.1

Table 4. The REE recovery rate and iron removal ratio after the precipitation in the hydrothermal reactor.

Temperature (°)	Time (hours)	Fe precipitation agents	REE recovery rate (%)	Iron removal ratio (%)
160	4	starch	90.87	92.5
180	4	sucrose	89.17	97.72
140	4	sucrose	97.26	76.18
160	4	-	97.1	68.04
140	5	starch	96.65	81.67
180	5	-	95.92	93.25
180	5	starch	92.58	98.68
140	5	-	97	34.88
160	5	starch	94.19	93.72
160	5	sucrose	94.76	88.46
180	6	sucrose	92.39	98.92
160	6	starch	99.95	97.4
140	6	sucrose	99.31	94.74
160	6	-	93.13	84.55
160	6	sucrose	99.15	91.9

temperature and precipitation agents are important parameters for the Fe removal.

The optimal conditions for the Fe removal are presented in Figure 4.

They are noted in the red line and are 170.7°C, 6 hours in furnace and the addition of sucrose. Table 6 presents the chemical composition of the validation experiment for the optimized conditions for iron removal.

Afterwards, the ANOVA of the results was conducted for the REE, to obtain a model for the optimal experimental process to maximize the REE recovery rate. Table 7 presents ANOVA results for the REE recovery.

This model is presented in the following equation:

$$\text{REE recovery rate}(\%) = 124,5 - 0,302 * \text{T} \qquad (4)$$

where T is the temperature of the preheated furnace (°C), t is the time in furnace (hours), PA are the precipitation agents. Based on statistical analysis, temperature is the most important parameters for the recovery of REE. The addition of sucrose and starch aimed to promote hematite precipitation, resulting in a slight alteration of the pH value of the leach liquor. This change does not affect the precipitation of REEs, as they precipitate at higher pH values. As expected, this variable is statistically insignificant in Equation 4. The optimal conditions the maximum REE recovery is exhibited in Figure 5.

They are presented in the red line and are 140°C, 6 hours in furnace and the addition of starch. Table 8 shows the chemical composition of the validation experiment for the optimized conditions for the maximum REE recovery.

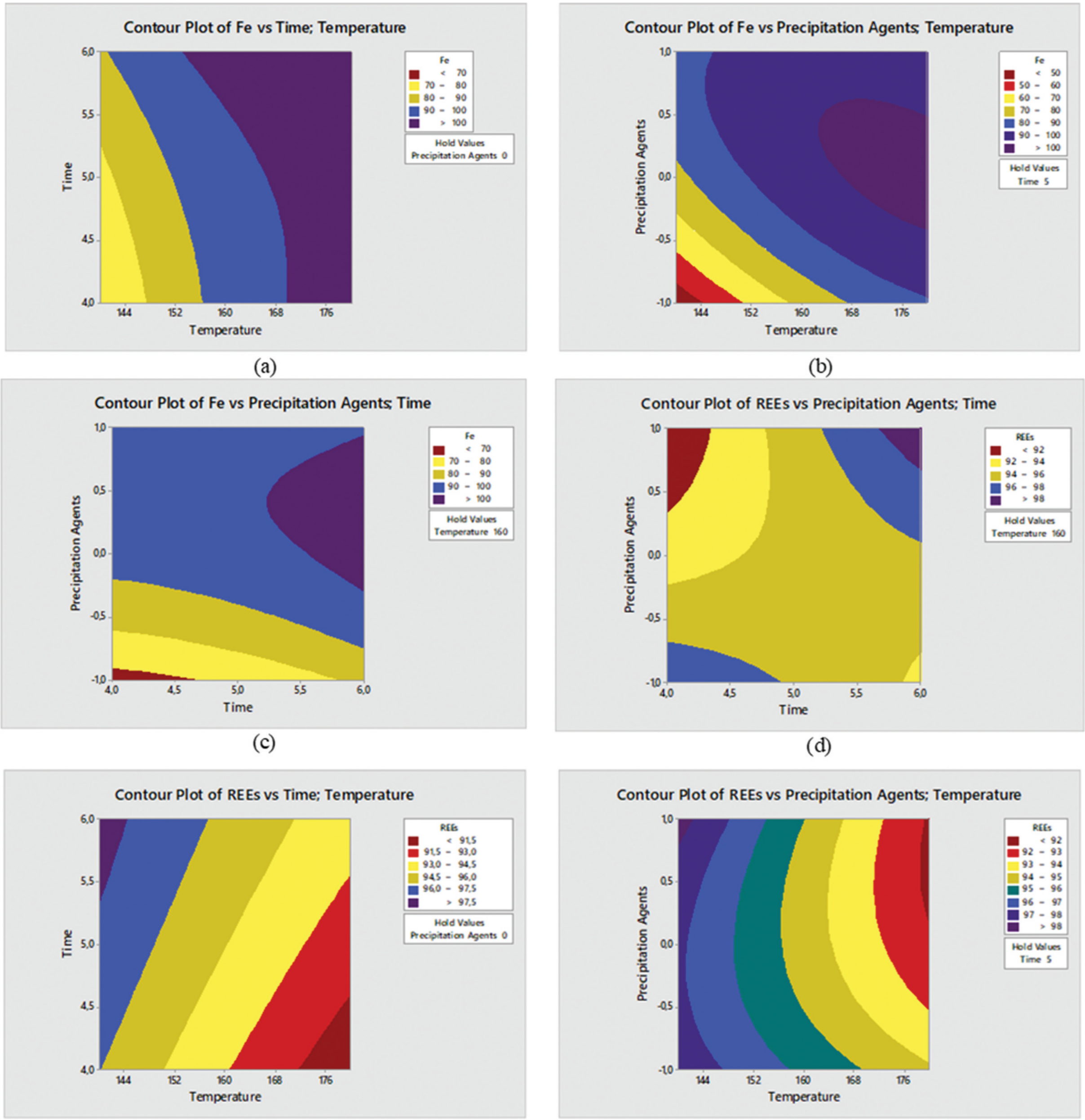
The obtained model for the system was acquired, for the combined target of maximizing the REE recovery ratio as well as maximizing the Fe removal ratio. The optimal condition for maximizing both REE recovery and Fe removal is exhibited in Figure 6.

Table 9 shows the chemical composition of the validation experiment for the optimized conditions for both the maximum REE recovery and iron removal.

The temperature range was 140–180°C, the range for time was 4/5/6 hours and the possible choices for additives are sucrose/starch/no additives used. The optimal conditions were presented as the 145°C, 6 hours in furnace and the addition of starch.

The precipitation of iron in a 2-step process in the hydrothermal reactor was investigated. The iron is dissolved iron as iron(III)-ions in the leaching solution. This can be precipitated as iron(III)-hydroxide which is unstable and then hydrolyzed to either iron oxide-hematite (Fe_2O_3) or ferric oxyhydroxide (FeOOH, also referred as iron(III) oxide-hydroxide). The governing factors for controlling which of these two compounds is primarily formed are the pH value, high temperature and the presence additives. After the first step in the hydrothermal reactor, where an amount of leaching solution was heated in the furnace, iron was precipitated as iron oxide-hematite. This is in agreement with the study of Cornell et. al,[33] where heating of acid ferric solutions above 80°C produced hematite. Then, the precipitated iron as iron oxide (hematite) which was formed in the first step was added to the second step. The addition of hematite into the saturated solution acts as a promoting agent for the formation of ordered regions, hence, acts as a nucleation agent for the formation of hematite from the iron content which was not precipitated in the solution.[34,35] Moreover, sucrose, starch or no addition of agent were used in the second step of this process, before introducing again the hydrothermal reactor to the preheated furnace. The target was to further reduce the iron content of the solution.

Glucose was hydrothermally oxidized by nitrate resulting in the production of levulinic acid ($C_5H_8O_3$), and 5-hydroxymethylfurfural ($C_6H_6O_3$).


Contour Plot of Fe vs Time; Temperature

Contour Plot of Fe vs Precipitation Agents; Temperature

Contour Plot of Fe vs Precipitation Agents; Time

Contour Plot of REEs vs Precipitation Agents; Time

Contour Plot of REEs vs Time; Temperature

Contour Plot of REEs vs Precipitation Agents; Temperature

(a) (b) (c) (d) (e) (f)

Figure 3. Contour plots obtain from MINITAB a) Fe-time and temperature, b) Fe-precipitation agents and temperature, c) Fe-precipitation agents and time, d) REE-precipitation agents and time, e) REE-time and temperature, f) REE-precipitation agents and temperature.

These products were subsequently subjected to further oxidation, leading to the formation of CO_2 and H_2O in accordance with Equation (5). As glucose underwent oxidation, nitrate underwent hydrothermal reduction to yield N_2, resulting in a noticeable decrease in its concentration. This reduction in nitrate concentration played a role in promoting the hydrolysis of Fe^{3+}. Furthermore, the redox reaction between glucose and nitrate, as described by Equation (5), also involved the participation of H^+ ions.[36]

$$5/3C_6H_{12}O_6 + 8NO_3^- + 8H^+ = CO_2 + N_2 + 14H_2O \tag{5}$$

Consequently, the increase in the solution's pH catalyzed the accelerated formation of hematite in the hydrothermal reactor, as indicated in Equation 6.

$$2Fe^{3+} + 6NO^{3-} + 3H_2O = Fe_2O_3 + 6HNO_3 \tag{6}$$

As an alternative the glucose, sucrose and starch were investigated for hematite precipitation. Starch, depending on the type and source, can be relatively cost-

Table 5. ANOVA result for the Fe removal.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	3797.05	421.89	6.27	0.029
Linear	3	2491.47	830.49	12.34	0.010
Temperature	1	1277.65	1277.65	18.99	0.007
Time	1	211.87	211.87	3.15	0.136
Precipitation Agents	1	1001.95	1001.95	14.89	0.012
Square	3	768.87	256.29	3.81	0.092
Temperature*Temperature	1	160.90	160.90	2.39	0.183
Time*Time	1	13.35	13.35	0.20	0.675
Precipitation Agents*Precipitation Agents	1	611.46	611.46	9.09	0.030
2-Way Interaction	3	536.70	178.90	2.66	0.160
Temperature*Time	1	75.34	75.34	1.12	0.338
Temperature*Precipitation Agents	1	427.66	427.66	6.36	0.053
Time*Precipitation Agents	1	33.70	33.70	0.50	0.511
Error	5	336.39	67.28		
Lack-of-Fit	3	336.39	112.13		
Pure Error	2	0.00	0.00		
Total	14	4133.45			

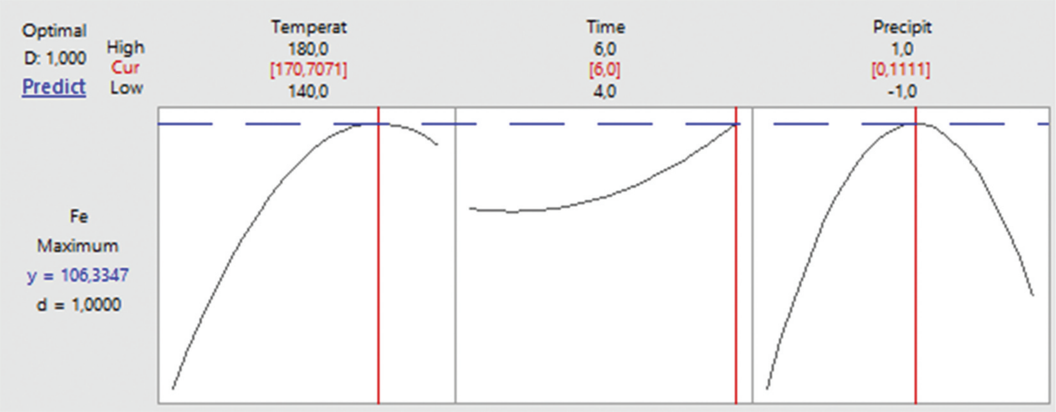


Figure 4. The optimal conditions for the Fe removal.

Table 6. The chemical composition of the validation experiment for the optimized conditions for iron removal.

B	Co	Fe	Dy	Nd	Pr
%3.275	%2.82	%1,69	%1,78	%69,67	%20,75

Table 7. ANOVA result for the REE recovery.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	113.538	26.154	4.37	0.060
Linear	3	65.473	218.242	7.55	0.026
Temperature	1	50.803	508.032	17.58	0.009
Time	1	13.468	134.680	4.66	0.083
Precipitation Agents	1	1.201	12.013	0.42	0.547
Square	3	2.913	0.9710	0.34	0.801
Temperature*Temperature	1	0.061	0.0612	0.02	0.890
Time*Time	1	0.079	0.0790	0.03	0.875
Precipitation Agents*Precipitation Agents	1	2.723	27.229	0.94	0.376
2-Way Interaction	3	45.153	150.510	5.21	0.054
Temperature*Time	1	0.342	0.3422	0.12	0.745
Temperature*Precipitation Agents	1	2.235	22.350	0.77	0.419
Time*Precipitation Agents	1	42.576	425.756	14.74	0.012
Error	5	14.445	28.891		
Lack-of-Fit	3	14.445	4.8152		
Pure Error	2	0.000	0.0000		
Total	14	127.984			

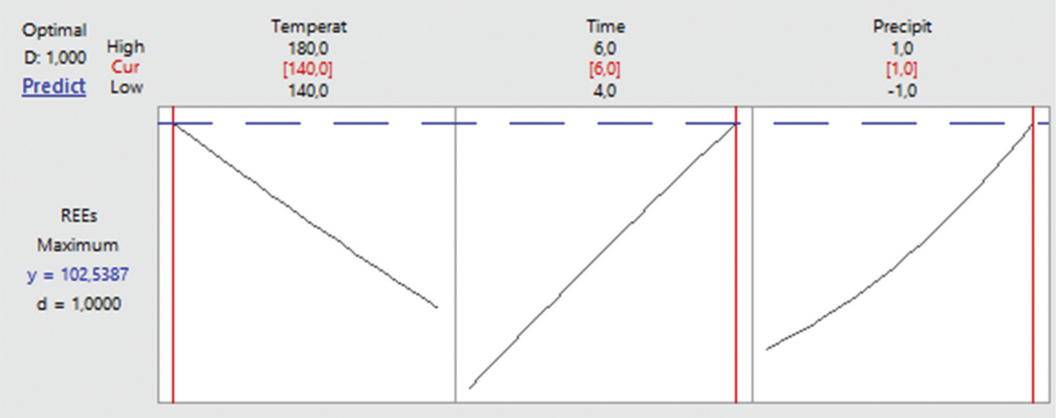


Figure 5. The optimal conditions for the maximum REE recovery.

Table 8. The chemical composition of the validation experiment for the optimized conditions for the maximum REE recovery.

B	Co	Fe	Dy	Nd	Pr
%3	%2.69	%4.92	%1.57	%67.32	%20.45

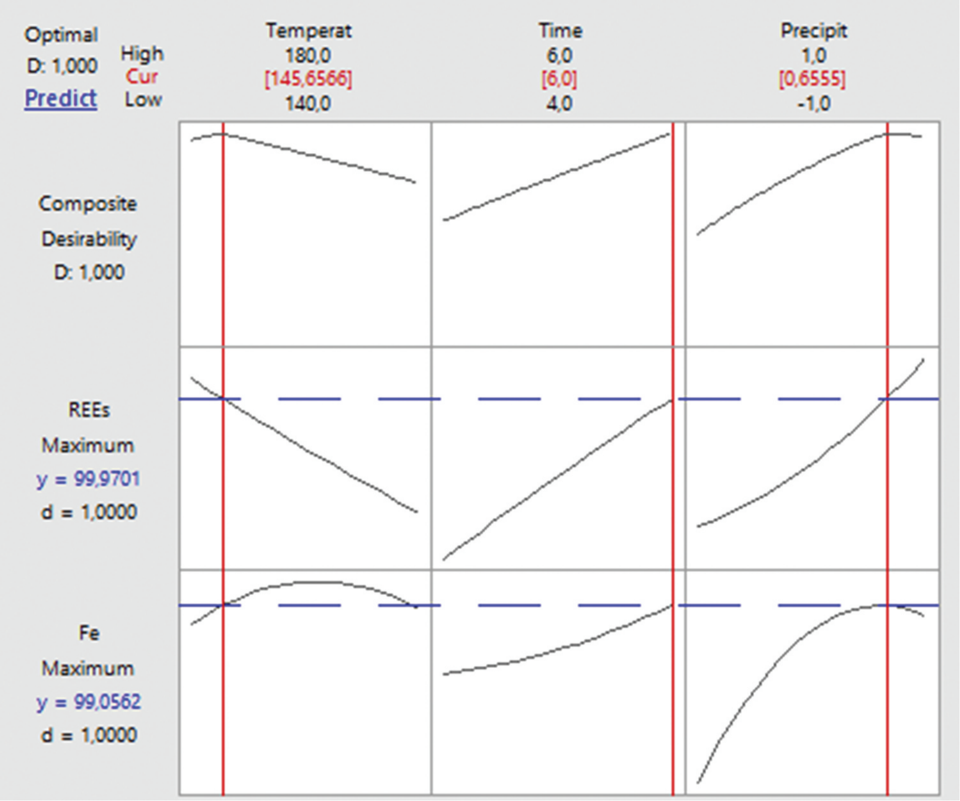


Figure 6. The optimal condition for maximizing both REE recovery and Fe removal ratio.

Table 9. The chemical composition of the validation experiment for the optimized conditions for both the maximum REE recovery and iron removal.

B	Co	Fe	Dy	Nd	Pr
%3	%2.59	%1.85	%1.75	%71.26	%19.52

effective compared to both glucose and sucrose. Moreover, the waste of sucrose and starch can be utilized to facilitate hematite precipitation within the industrial processes. Since an addition 7–30% increase in the iron removal ratio was observed when starch and sucrose were introduced. By comparing different experiments at the same temperature and time in furnace, the addition of sucrose and starch greatly benefited from the iron removal ratio in contrast with the experiments where no additive agent were used. It is assumed sucrose was hydrothermally oxidized by nitrate ions to produce CO_2, H_2O and nitrate. Then nitrate was hydrothermally reduced to nitrogen gas hence its concentration decreased, and the pH value was increased, from −0.15 of the leached solution to 0.55 after the hydrothermal treatments.

For the results of this process, from Table 5, the parameters with P-value smaller than 0.05 are statistically significant, hence the parameters that affect greatly the iron removal ratio are the temperature, the precipitation agents and from the square model the square of precipitation agents. The optimized conditions from the model were similar to the experimental results with the highest Fe removal ratio. The only variation observed was only in the parameter, the temperature where the model revealed a 10°C lower optimal conditions, 170°C instead of 180°C. Therefore, a minimum amount of iron will remain in the solution (<1.5%). From Table 7, the parameters that are statistically significant and affect greatly the REE recovery rate are the temperature and from the 2-way interaction model the precipitation agent-time in furnace. The optimized conditions from the model were similar to the experimental results with the highest REE recovery rate, although not identical. The difference observed was only in one parameter, the temperature, which experimentally was noticed to be 160°C while the model revealed the optimal of 140°C. The other two parameters revealed the same optimal conditions, hence a very small amount of REE will be lost in this process (<0.05%) and this model presented an accurate optimization process. Then the combined process model presented the most favorable conditions in order to achieve the simultaneous maximization of REE recovery and Fe removal. To sum up, very high REE recovery rate and very high Fe removal ratio were achieved through the processes in the hydrothermal reactor.

Characterization of the precipitate obtained by the validation experiments

The precipitation of hematite was performed under the specified conditions from the optimization studies. The precipitate obtained by the validation experiments were characterized by SEM and XRD analysis. Figure 7 exhibits the XRD patterns of the precipitate obtained by validation experiments. N1, N2 and N3 described the validation experiments conducted at 170.7°C for 6 hours with the addition of sucrose, at 140°C for 6 hours with the addition of starch, and at 145°C for 6 hours with the addition of starch, respectively.

The XRD peaks were indexed by rhombohedral phase of Fe_2O_3 with standard pattern from (JCPDS) file no 84–0307. Due to the high amount of iron in the system, the iron recycled from the system should be proposed for the usage in industrial applications.

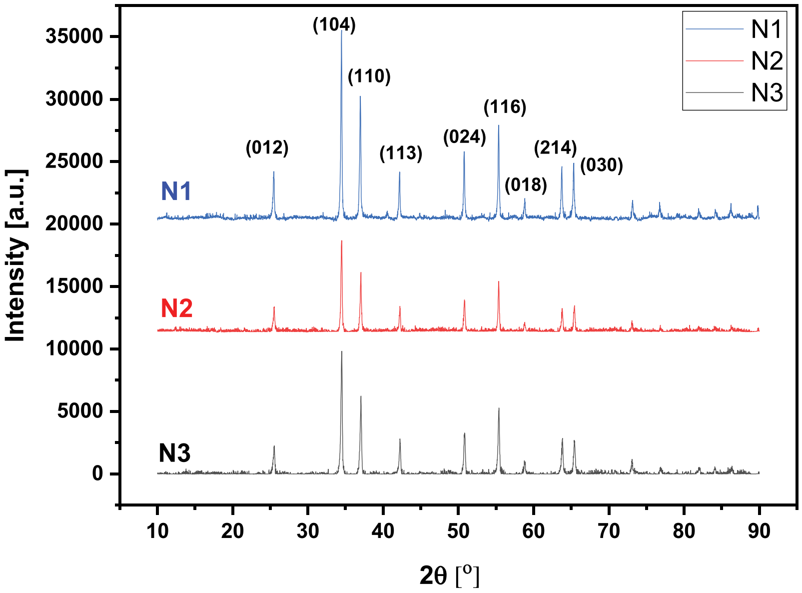


Figure 7. XRD patterns of the precipitate obtained by the validation experiments.

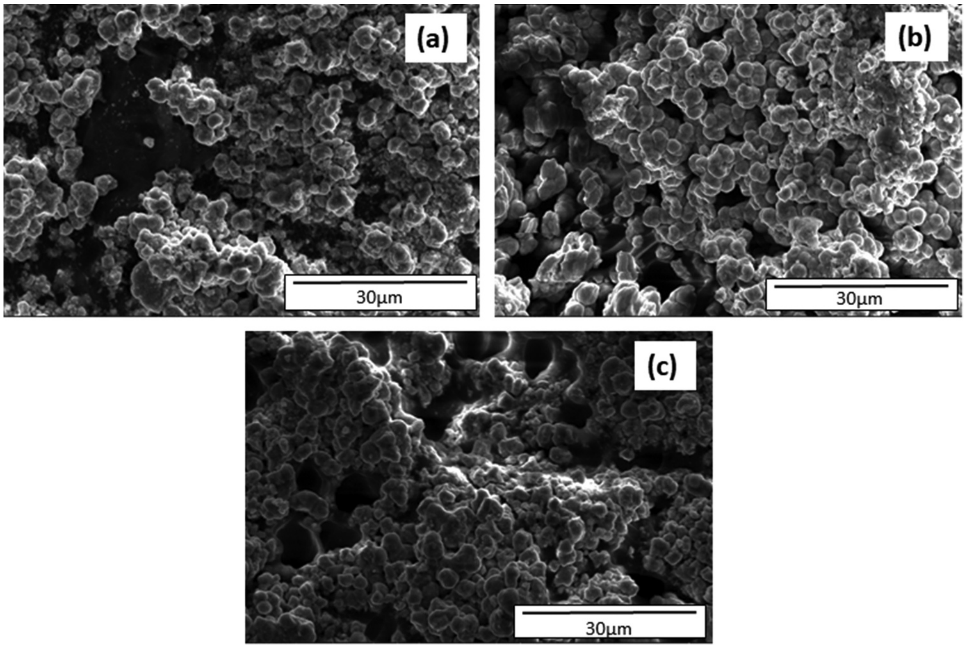


Figure 8. SEM analysis of the precipitate obtained from the validation experiments.

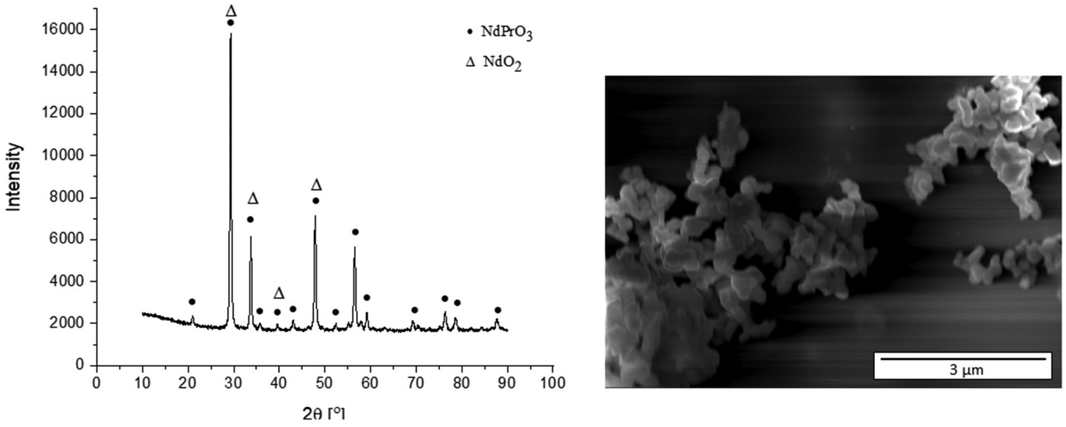
Hematite is one of the usable products of iron compounds in industrial applications. Figure 8 illustrates the SEM micrographs of the hematite obtained from the validation experiments.

SEM micrograph of the hematite precipitate showed that the morphology of powders was compact and spherical morphology with narrow size distribution. As can be seen in SEM micrographs, particles were agglomerated.

Production of mixed rare earth oxide by oxalate precipitation

For the production of high purity rare earth oxide, the solution obtained from the optimized conditions for maximizing both REE recovery and Fe removal ratio was selected. After the oxalate precipitation and calcination process, the XRD analysis was employed for the phase analysis of the final product. Figure 9 illustrates [a] XRD analysis of mixed rare earth oxide [b] SEM micrographs of mixed rare earth oxide.

The X-ray diffraction peaks were indexed by cubic phases of $NdPrO_3$, and NdO_2 with standard patterns from (JCPDS) files no 00-052-1438 and 00-046-1074, respectively. As can be observed in SEM micrograph, the precipitated and calcined at 800°C mixed rare earth oxide had a nearly spherical morphology.



[a] [b]

Figure 9. [a] XRD analysis of mixed rare earth oxide [b] SEM micrographs of mixed rare earth oxide.

Conclusion

In this study, high purity rare earth oxide and hematite powders were recovered from NdFeB magnets. The significant results observed in this study are listed below.

- During the leaching process in the nitric acid solution almost all the quantity of magnet powder was dissolved. Hence, the leaching in a 2 mol/L nitric acid solution is an efficient method to dissolve EoL NdFeB powder.
- In the second stage of the proposed process, the precipitation of iron in a 2-step process in the hydrothermal reactor was investigated. The iron is dissolved iron as iron(III)-ions in the leaching solution. This was precipitated as hematite under pressure and temperature. The precipitated iron as iron oxide (hematite) which was formed in the first step was added to the second step. Moreover, sucrose, starch or no addition of agent were used in the second step of this process, and they promoted the formation of hematite.
- The optimized conditions were determined by statistical analyses, the optimized conditions from the model were similar to the validation experiments.
- High REE recovery rate and high Fe removal ratio were achieved through hematite precipitation under pressure and temperature.
- The typical elemental composition of NdFeB magnets comprises approximately 29–32% neodymium, 63–68% iron, and around 1–1.2% boron. These percentages can vary based on the magnet's grade and the manufacturer, and additional elements like Dy and Pr might also be included in small amounts to alter the magnet's properties for specific applications. The variations in these compositions do not significantly impact the effectiveness of our process. Similar results can be achieved even when using various types of waste NdFeB magnet, therefore, the proposed method has the potential to be employed with various types of magnet waste.

Disclosure statement

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

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