

Efficient Recovery of End-of-Life NdFeB Permanent Magnets by Selective Leaching with Deep Eutectic Solvents

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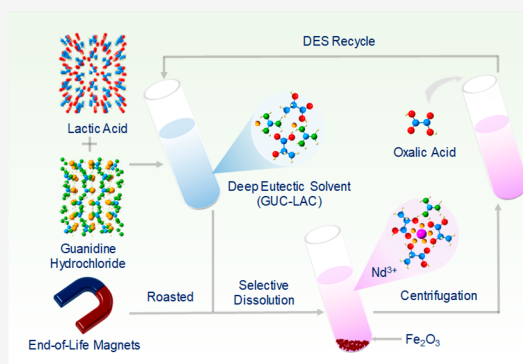


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Supporting Information

ABSTRACT: The NdFeB permanent magnet is a critical material in digital electronics and clean energy industry. Traditional recovery processes based on the solvent extraction technique would consume high energy and large amounts of chemicals as well as resulting in abundant secondary organic wastes. In this work, a green process using deep eutectic solvents (DESs) in the selective leaching technology was designed to recover NdFeB permanent magnets. Nine kinds of DESs composed of guanidine were prepared and screened as the leachants. The guanidine hydrochloride–lactic acid (GUC–LAC) combined DES achieved the highest separation factor (>1300) between neodymium and iron through simple dissolution of their corresponding oxide mixture. The mass concentration of Nd dissolved in the GUC–LAC DES could reach 6.7×10^4 ppm. The viscosity of this type of DES at 50 °C was 36 cP, which was comparable to many common organic solvents. In a practical recovery of roasted magnet powders, the Nd_2O_3 product with 99% purity was facilely obtained with only one dissolution step, followed by a stripping process with oxalic acid. Even after 3 cycles, the GUC–LAC DES kept the same dissolution property and chemical stability. With such superior performances in selective leaching of rare earth elements from transition metals, the GUC–LAC DES is greatly promising in the rare earth element recovery field.



INTRODUCTION

In modern society, rare earth elements (REEs) play an essential role in electric cars, wind turbines, electronics, photovoltaic films, catalysts, glass, ceramics, metallurgy/alloys, etc. These wide and critical applications are based on the unique magnetic, catalyst, and phosphorescent properties of REEs, leading to the high demand of raw REE materials, such as permanent magnets, hydrogen storage alloys, and phosphor powders.^{1–3} In these materials, a neodymium–iron–boron (NdFeB) magnet is essential in digital electronics and clean energy industry because of its higher maximum energy product than a traditional permanent magnet.^{4,5} In the leading REE production country, China,⁶ praseodymium and neodymium occupy less than 30% of the production but contribute to more than 70% of the benefits. The gap between the high industrial demand for REEs in magnets and their low relative abundance in carbonatite deposits requires new resources of these elements other than traditional REE ores.⁷ Recycling REEs from end-of-life materials generated from the production and consumption provides an option for closing the material flow loop, diversifying supply sources, and creating added economic value.⁸ However, less than 1% REEs used today are recycled, given the challenge of collecting and low efficiencies in the recycling processes.^{9,10}

Various technologies have been developed to recover REEs from end-of-life magnets, including hydrometallurgy, electrochemistry, gas-phase extraction, membrane separation, bio-

logical extraction, and pyrometallurgy.^{1,3,11–14} Among them, the solvent extraction technique, a typical hydrometallurgy technique applied in the rare earth ore processing, is widely considered to be more suitable for recovering REEs on a large scale.^{15–17} The solvent extraction has some advantages, such as high processing capacity, low cost, and continuous production, but it also generates severe environmental burden as a result of using high volumes of acid/base reagents and volatile organic solvents.^{2,9,18,19} Thus, some more environmentally friendly REE recycling processes are highly desirable.²⁰

One method is replacing the hazardous acids and organic solvents with ecologically friendly solvents, such as ionic liquids (ILs) or deep eutectic solvents (DESs), in the solvent extraction process.^{21–25} For example, Riano and Binnemans used a IL, trihexyl(tetradecyl)phosphonium nitrate, as the organic phase to extract REEs from iron-free leachate of a NdFeB permanent magnet.²⁶ In comparison to the traditional organic solvents, the ILs and DESs are green solvents with low volatility or biodegradable in nature, avoiding the large

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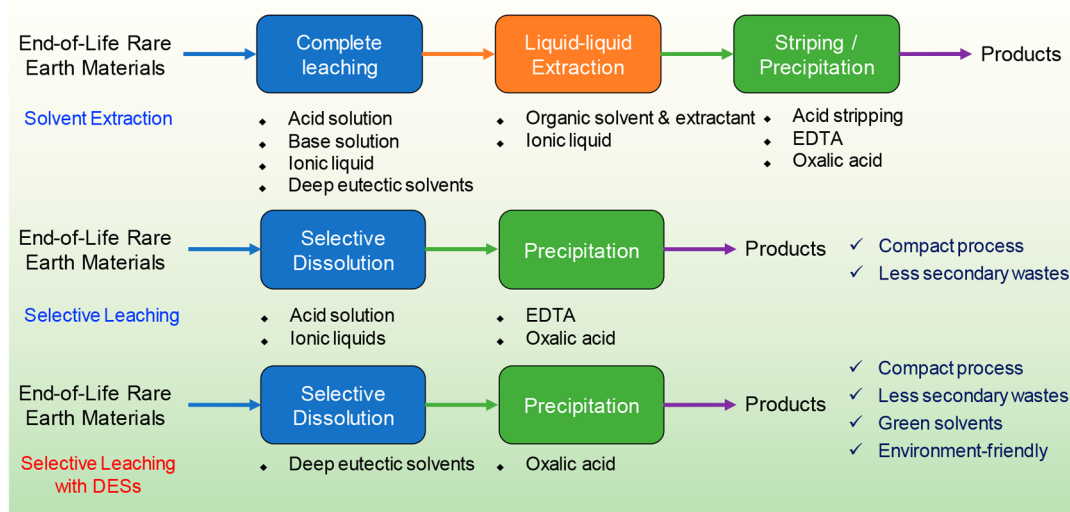
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Scheme 1. Flowcharts for Recovering End-of-Life REEs



secondary chemical wastes.^{27–29} The inorganic acid used in complete leaching could also be replaced by greener ILs or DESs to reduce the amounts of wastewaters.^{30,31} Another method to improve the separation process is a process optimization, which replaces complete leaching with selective leaching.^{32–34} Because the target metals are selectively leached from the solid materials, the solvent extraction procedure is not necessary for this method, which endows it with great strengths in compact and green processes.^{35,36} The flowcharts of the solvent extraction and selective leaching processes are comparatively shown in Scheme 1.

The DESs are solvents formed by the hydrogen-bond linking between hydrogen-bond acceptors (HBAs) and hydrogen-bond donors (HBDs).^{37,38} These solvents have melting points lower than any of their individual components. In comparison to ILs, as emerging types of green solvents, the DESs have advantages of low cost, easy preparation, and lower biotoxicity,^{39,40} making them more promising in the recovery and separation of valuable metals.^{41–44} Until now, the application of DESs in the recovery of end-of-life REE materials has still been focused on the complete leaching, followed by liquid/liquid extraction.³⁰ To the best of our knowledge, there has been no reports on the selective leaching of REEs from NdFeB permanent magnets by DESs thus far. Herein, we developed a simple selective leaching process for efficient recovery of REEs from end-of-life NdFeB permanent magnets based on some novel DESs composed of guanidines and organic acids.

MATERIALS AND METHODS

DES Preparations. The HBA and HBD used in this work were listed as follows: HBA, guanidine hydrochloride (GUC), 1-aminoguanidine hydrochloride (AGU), 1,3-diaminoguanidine hydrochloride (DAG), and choline chloride (CC); HBD, glycolic acid (GA), ethylene glycol (EG), malic acid (MA), L-lactic acid (LAC), and glycerol (GLY). The DESs were prepared according to the method mentioned in ref 37. The HBD was simply combined with the corresponding HBA in a flask at 70 °C under stirring conditions until a homogeneous transparent liquid was formed. After reaction, the formed liquid was naturally cooled to room temperature. In the cases of GUC–MA, AGU–GA, and DAG–GA, the reaction

temperature was 90 °C. The molar ratio of HBA/HBD was 1:2 in most DESs, except 1:3 for GUC–MA and GUC–GLY.

Metal Dissolution Experiments. The metal oxides and DESs were added to a 10 mL bottle with a solid/liquid ratio of 1:50 and sealed carefully. The mixture was then shaken in a water bath shaking table at 50 °C for 24 h, except for the time and temperature experiments. After dissolution, the liquid and undissolved solids were separated by centrifugation at 12 000 rpm. Finally, the DES containing metals was digested with concentrated nitric acid in a microwave digestion system, and the concentration of metals was analyzed by inductively coupled plasma optical emission spectrometry (ICP–OES).

In the practical recovery process, roasted NdFeB powders were dissolved in DES: GUC–LAC (1:2) with a solid/liquid ratio of 1:10 at 40 °C for 6 h. After phase separation by centrifugation, the solid oxalic acid was added to the Nd-loaded DESs with a solid/liquid ratio of 1:100 and reacted at the same conditions of dissolution. Nd was stripped from the DESs by oxalic acid during this reaction. After centrifugation, a white precipitation was obtained and calcinated at 900 °C for 3 h to obtain the Nd₂O₃ products, which was redissolved in hydrochloric acid solution to analyze the content. The recycle of GUC–LAC was achieved during the stripping of Nd. The residual contents of Nd and Fe of recycled GUC–LAC were listed in Table S3 of the Supporting Information. In the test of GUC–LAC recycling, GUC–LAC used in the practical recovery process of NdFeB powders was defined as cycle 0. GUC–LAC obtained via stripping Nd by oxalic acid was defined as cycle 1. Then, cycle 1 GUC–LAC was reacted with the roasted NdFeB powders in the same operation of the practical recovery process to test the dissolution and separation property of the recycled DES. This recycle of GUC–LAC was conducted 3 times in total. The following two GUC–LAC obtained by stripping were defined as cycles 2 and 3. The residual contents of Nd and Fe were also listed in Table S3 of the Supporting Information.

The dissolution ratio was calculated via dividing the total mass of metals dissolved in the DES by the mass of initial metal added to the dissolution reaction. The uncertainties were mainly caused by the analysis of the metal concentration in DES by ICP–OES; thus, it was calculated by the standard deviation of triplex analyzing values of the metal concentration

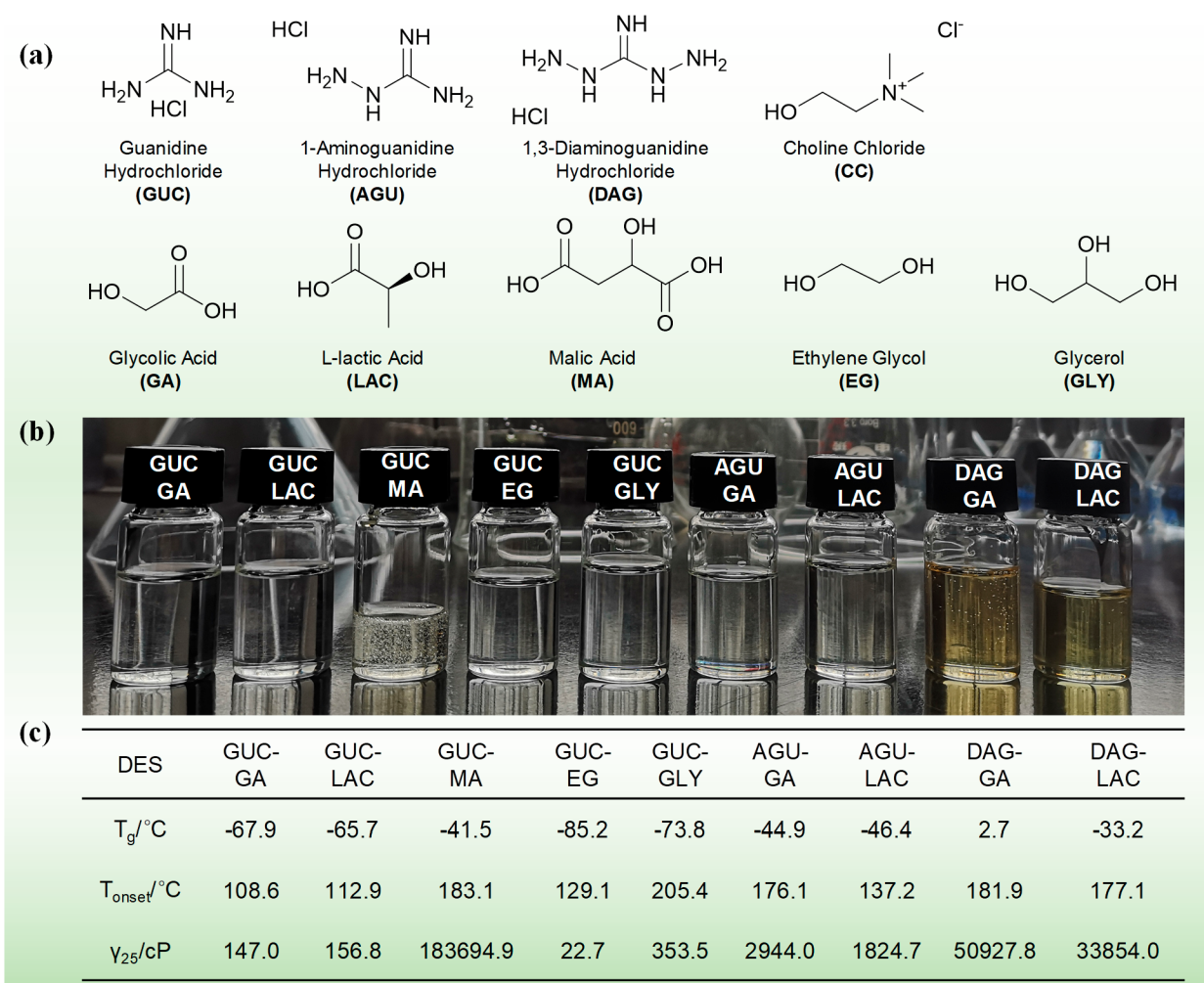


Figure 1. (a) Chemical structures of HBA and HBD molecules used in this work, (b) photograph of prepared DESs, and (c) glass transition temperature (T_g), onset decomposition temperature (T_{onset}), and viscosity (γ) at 25 °C of guanidine-based DESs.

in the DES. The uncertainties of dissolution ratios were listed in Table S1 of the Supporting Information. The dissolution ratio (D) and separation factor (SF) of metals were calculated by the following equations:

$$D = \frac{w_{M,d} m_{\text{DES}}}{m_{M,r}} \times 100\% \quad (1)$$

$$SF = \frac{D_{M,A}/(1 - D_{M,A})}{D_{M,B}/(1 - D_{M,B})} \quad (2)$$

where $w_{M,d}$ denotes the mass concentration of metal in DES with the unit of g g^{-1} , m_{DES} means the mass of DES after dissolution, $m_{M,r}$ is the original mass of metal before dissolution, and $D_{M,A}$ and $D_{M,B}$ represent the dissolution ratios of metals A and B, respectively.

RESULTS AND DISCUSSION

Preparation and Physical Properties of Guanidine-Based DESs. Selective leaching is an environmentally friendly process to recover end-of-life NdFeB permanent magnets. However, the DESs reported in the literature always showed similar dissolution properties toward both Nd and Fe metals.³⁰ To develop selective leaching reagents, we prepared nine novel DESs based on guanidines, including GUC-GA, GUC-LAC,

GUC-MA, GUC-EG, GUC-GLY, AGU-GA, AGU-LAC, DAG-GA, and DAG-LAC. In these DESs, all of the HBAs were guanidines, including GUC, AGU, and DAG, while GA, LAC, MA, EG, and GLY acted as HBDs. The molar ratio between HBA and HBD in GUC-MA and GUC-GLY was 1:3, and it was 1:2 in other DESs. The chemical structure of the component of these DESs is listed in Figure 1a. The photographs of these DESs are shown in Figure 1b. In our experiment, the DESs exhibited a glass transition rather than freezing and melting at low temperatures. The glass transition temperature of DESs was collected from differential scanning calorimetry (DSC) curves and shown in Figure 2a and Figures S1–S11 of the Supporting Information. The glass transition temperature of all of the DESs was lower than 0 °C, except DAG-GA, which was 2.7 °C (Figure 1c). These DESs had much lower T_g than the melting temperature of their individual components. When GUC-LAC DES is taken as an example (Figures 2b), its T_g dropped more than 100 °C from a HBA/HBD ratio of 1:2 to 1:8. The very close four points in Figure 2b did not exhibit an explicit eutectic point of GUC-LAC because it had a glass transition temperature rather than the melting point at a low temperature. These phenomena were very common in many other DES systems.^{42,45} According to the thermogravimetry–differential scanning calorimetry (TG–DSC) data, all of the DESs were not decomposed before 100

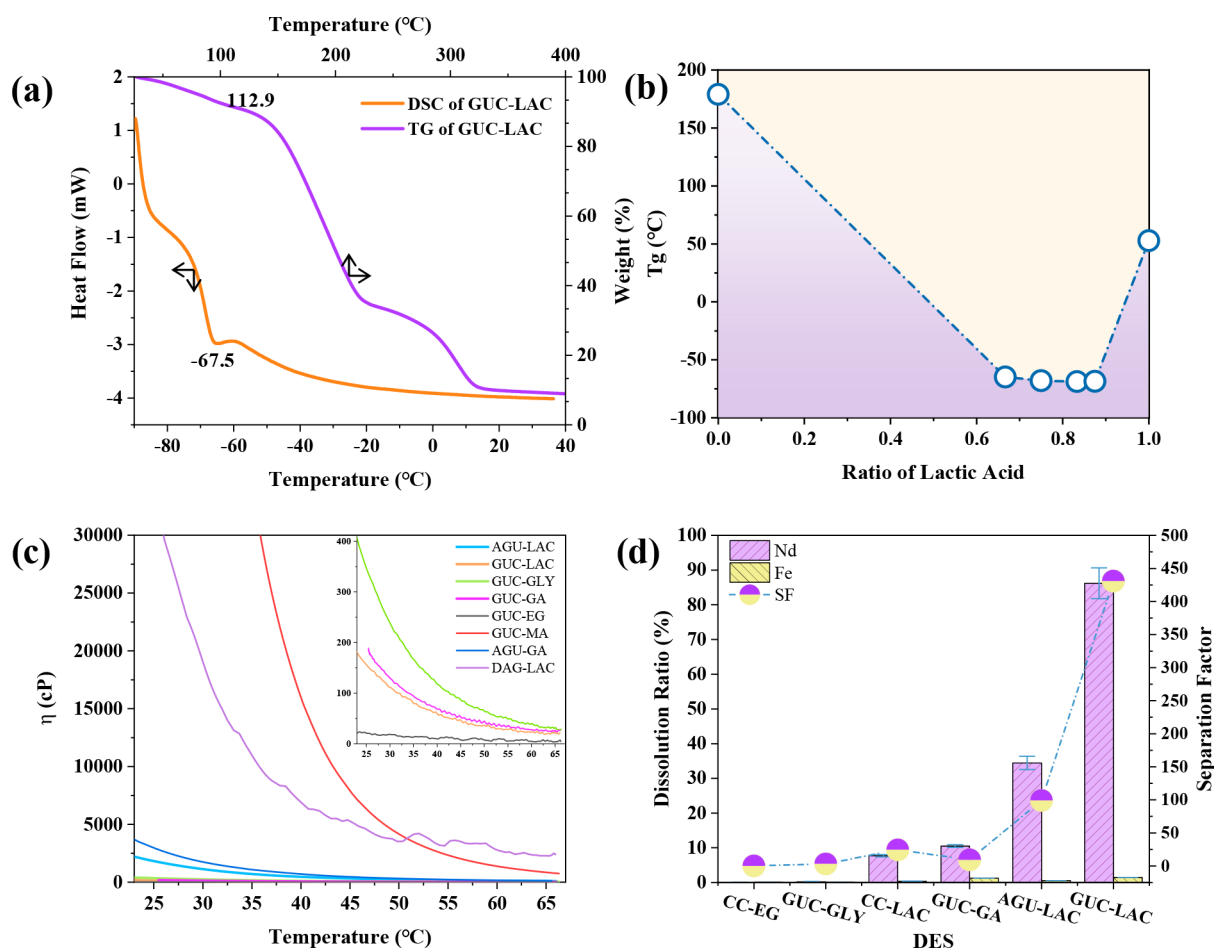


Figure 2. (a) TG and DSC curves of GUC-LAC, (b) phase diagram of GUC-LAC, (c) viscosity-temperature curves of guanidine-based DESs, and (d) initial dissolution results of Nd and Fe by different DESs.

°C, indicating that they were quite stable under our tested temperature.

The viscosity of these DESs was greatly associated with the HBAs. As shown in Figure 2c, the viscosity of DAG-based DESs was larger than 30 000 cP, whereas those of AGU and GUC DESs were 1 or 2 orders of magnitude smaller. DAG-GA exhibited an extremely high viscosity compared to other DESs, and the viscosity increased with the temperature after 37 °C because it formed a paste rather than a real fluid above this temperature. The viscosity of all of the other DESs decreased rapidly with the increasing temperature. At 50 °C, the temperature of dissolution experiments in this work, the viscosity of GUC-LAC was lower than 40 cP, which was comparable to many common organic solvents.

The forming of hydrogen bonds was characterized from the Fourier transform infrared (FTIR) spectra and nuclear magnetic resonance (NMR) spectra, which are shown in Figures 3 and 4 and Figures S12–S21 of the Supporting Information. The HBAs were guanidine-based hydrochloride, while the HBDs were three hydroxycarboxylic acids and two polyols in this work. It could be inferred that the hydrogen bonds were mainly formed between chloride of HBAs and hydrogen of HBDs. The change of spectra between the DESs and their individual components were similar. When GUC-GA was taken as an example, in the FTIR spectra, GUC, GA, and GUC-GA all exhibited abundant hydrogen bonds at the peaks around 3300 cm^{-1} . The C–O stretching vibration of GA

appeared at 1732 and 1434 cm^{-1} , both showing a red shift to 1667 and 1404 cm^{-1} after forming DES, indicative of the formation of new hydrogen bonds. The peaks of N–H bonds of GUC in the DES were influenced by the peaks of –COOH. Thus, it is difficult to judge whether it formed new hydrogen bonds. However, the N–H stretching vibration of $-\text{NH}_2^+$ in GUC at 2157 and 1537 cm^{-1} almost disappeared in the DES. This change clearly indicated that there was a strong interaction between the counter Cl^- and carboxylic acids. In the ^1H NMR spectra, the chemical shifts of –OH and –NH in GUC-GA also moved downfield in comparison to the individual compounds, giving an obvious sign of forming hydrogen bonds. In comparison to GUC, the AGU and DAG DESs with the same HBDs exhibited larger changes in the peak shapes of FTIR spectra and chemical shifts in NMR spectra. This tendency might indicate that stronger hydrogen bonds were formed with an increase of the amino group in the HBAs.

The application of DESs in the dissolution was mainly associated with the viscosity. A large viscosity always leads to high energy consumption in the industry.^{31,46} After screening, only the DESs with low viscosity tested the dissolution properties. The initial dissolution results of Nd_2O_3 and Fe_2O_3 by several screened guanidine DESs and two traditional CC DESs are depicted in Figure 2d. Only the DESs prepared from GA and LAC could efficiently dissolve Nd_2O_3 . GUC-GLY and CC-EG dissolved less than 1% Nd or Fe into the bulk solvents. Among all of the DESs, GUC-LAC had the highest

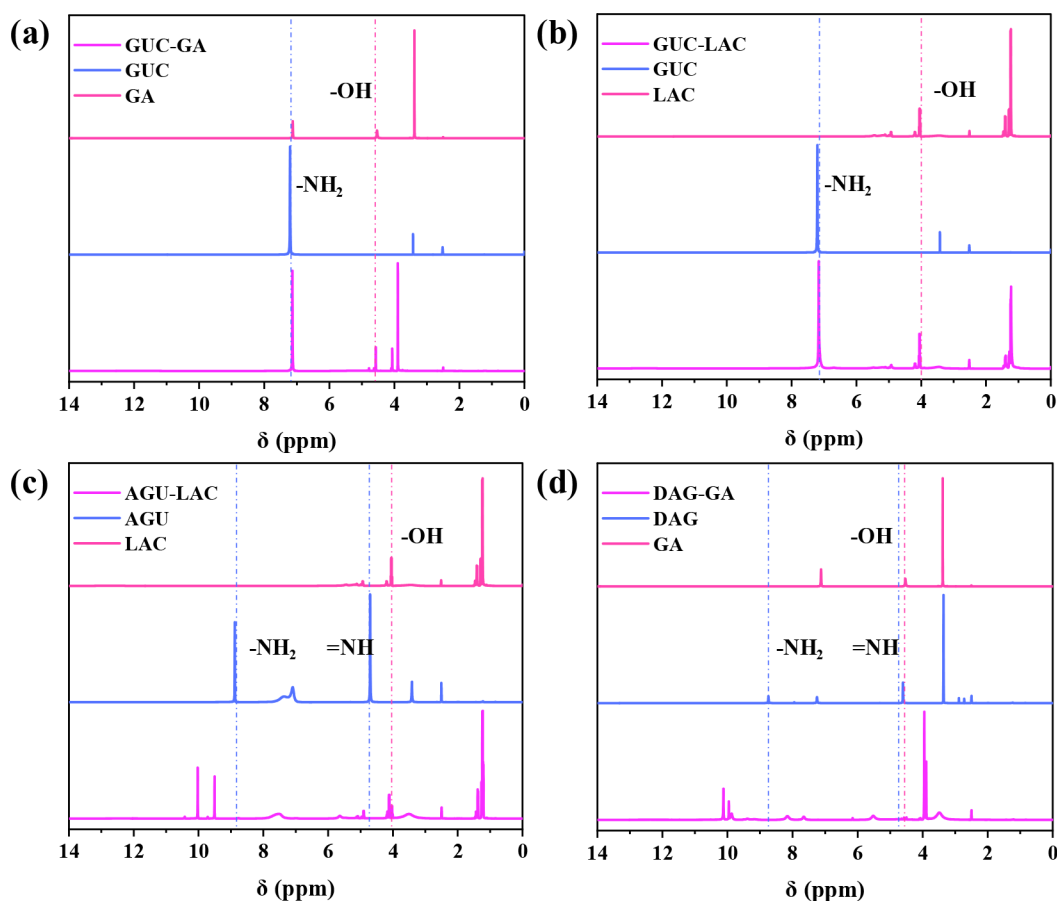


Figure 3. ^1H NMR spectra of DESs and their corresponding pure HBA and HBD components.

dissolution ratio of Nd and separation factor for Nd/Fe. Thus, this DES was screened out for the following dissolution and leaching experiments.

Dissolution of Nd and Fe. To obtain the optimal conditions of the selective leaching method, we investigated the effects of the HBD ratio, solid/liquid ratio, reaction time, and temperature on the dissolution ratios and separation factors, which were calculated from eqs 1 and 2. As shown in Figure 5a, the solid/liquid ratio in the experimental range has almost no effect on the dissolution ratio of Nd. However, the dissolution ratio of Fe decreased with the increase of the solid/liquid ratio. This phenomenon might be due to the different solubilities of Nd and Fe. The solubility of Nd ions in GUC–LAC reached 6.7×10^4 ppm at the solid/liquid ratio of 7:50, which was larger than the value in other DESs.⁴² However, for Fe, its solubility was only 727 ppm and the dissolution was close to the equilibrium at the solid/liquid ratio of 1:50. As the solid/liquid ratio increased, the dissolution ratios of Fe were decreased. However, a larger solid–liquid ratio also led to a high Nd concentration in the DESs, causing higher viscosity, which was unfavorable for the practical separation process.⁴⁶ To obtain the optimum separation factor between Nd and Fe, a solid–liquid ratio of 1:10 was suggested for the dissolution procedure.

As seen in Figure 5b, the dissolution ratios of Nd and Fe both increased with the increasing temperature. The dissolution ratio of Nd (D_{Nd}) reached 84% at 30 °C and then increased very slowly. On the contrary, D_{Fe} increased very slowly below 50 °C but multiplied after that. From Figure 5c, D_{Nd} increased rapidly with the reaction time before 6 h and

then reached equilibrium, while D_{Fe} kept increasing, even after 6 h. Considering a balance between the dissolution ratio and separation factor, a dissolution temperature of 40 °C and a reaction time of 6 h might be appropriate for the selective leaching process.

The HBD ratio also changed the dissolution ratio of metals, because GUC and LAC acted in different roles in the dissolution reaction. As shown in Figure 5d, although GUC was Brønsted acid, it was too weak to react with metal oxides. Both D_{Nd} and D_{Fe} were less than 1% by just using GUC. LAC was only strong enough to dissolve $\sim 10\%$ Nd, while D_{Fe} was still lower than 1%. Because Nd_2O_3 is more ionic compared to Fe_2O_3 , it exhibited a larger dissolution ratio.⁴¹ Another reason might be due to the smaller size of Fe^{3+} (0.69 Å compared to 1.12 Å of Nd^{3+}) having a stronger electrostatic attraction with O^{2-} , which resulted in a weaker chemical reactivity with acids.^{47,48} After the formation of DES, the hydrogen bond activated H^+ of lactic acid, largely increasing both D_{Nd} (7 times) and D_{Fe} (2 times). The larger increasing rate of D_{Nd} promised the possibility of selective separation between Nd and Fe. Keeping the increase of the HBD ratio would reduce the hydrogen bond numbers and lead to a decrease of both D_{Nd} and the separation factor. Thus, a 1:2 HBA/HBD ratio was selected as the working condition in this case.

The change of FTIR spectra (Figure 6a) after the dissolution of Nd and Fe confirmed the interaction between LAC and metal oxides. The vibrational band of $-\text{COOH}$ around 1731 cm^{-1} became weaker than that of $-\text{COO}^-$ around 1667 cm^{-1} . It should be noticed that the spectrum of Fe almost did not change compared to the original DES because dissolved Fe was

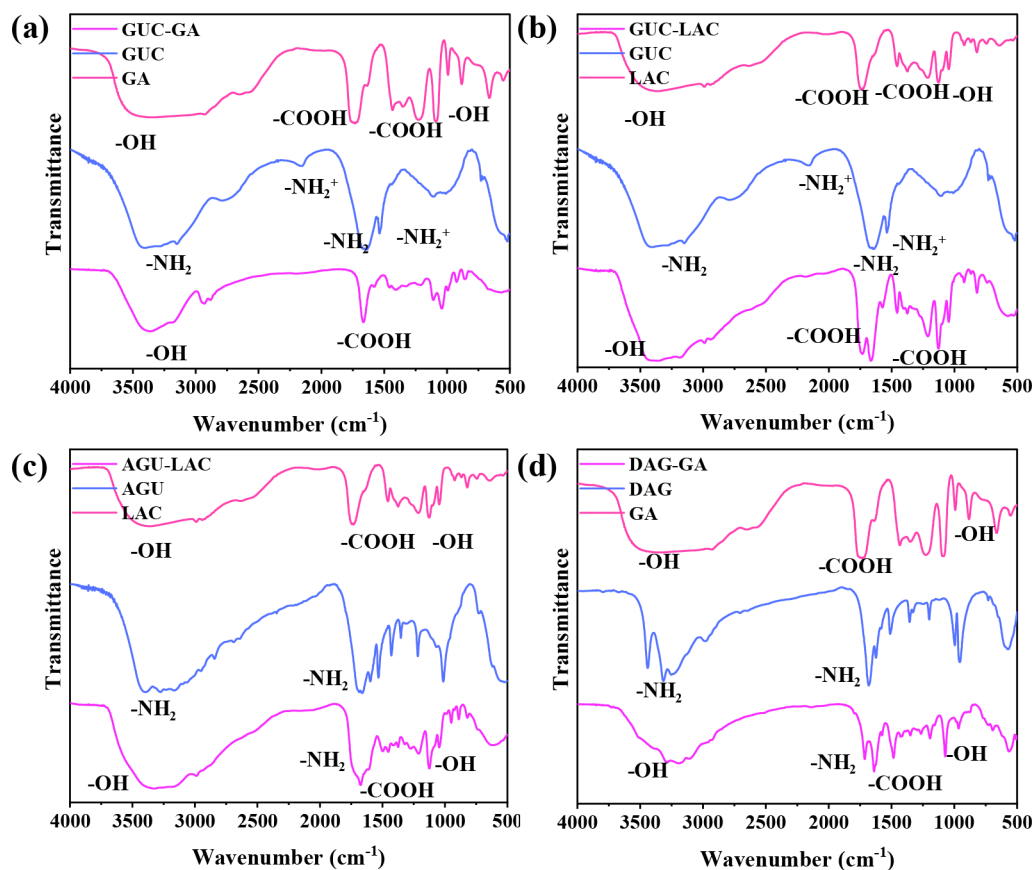


Figure 4. FTIR spectra of DESs and pure HBA and HBD components.

too small. Similar to the FTIR spectra, the NMR spectrum of Fe-loaded DES was also the same as the pristine DES. The dissolution of Nd caused the δ value of $-\text{NH}_2$ to move downfield (Figure 6b), which indicated that GUC not only acted as the HBA, but also participated in the dissolution reaction.

To verify this hypothesis, the ultraviolet–visible (UV–vis) spectra of Nd-loaded DES are collected and shown in Figure 6c. The absorption band of Nd(III) around 575 nm is sensitive to the coordination environment.⁴⁹ As the ligands changed from Cl^- to LAC^- (solutions 4 and 5) in aqueous solution, the absorption band changed from 575 to 577.6 nm. However, the difference among absorption bands of solutions 1 (Nd_2O_3 -dissolved GUC–LAC), 2 (NdCl_3 -dissolved GUC–GLY), and 3 (NdCl_3 -dissolved GUC–LAC) was only 0.6 nm, which indicated that they had a similar coordination environment of Nd(III) in these solutions, especially between solutions 2 and 3. Because the dissociation of hydroxy GLY could be ignored in this case, it was reasonable to infer that Nd(III) was only coordinated with Cl^- in solution 2. Thus, in GUC–LAC DES, Nd(III) was mainly coordinated with Cl^- besides trace LAC^- generated in the dissolution reaction, which caused this slight change. Some previous studies revealed that most metal cations were coordinated with Cl^- to form complex anions in ILs and DESs.^{30,41,50} In combination with the literature and our analysis, we can conclude that Nd(III) was dissolved in GUC–LAC DES in the form of anionic $[\text{NdCl}_x]^{3-x}$ species.

Selective Leaching and DES Recycle. A practical recovery process for the end-of-life NdFeB permanent magnets was proposed. The roasted NdFeB magnet powder was composed of a mixture of Nd_2O_3 and Fe_2O_3 with a mole

ratio of 1:7. This powder was dissolved in GUC–LAC with a solid/liquid ratio of 1:10 at 40 °C for 6 h. The liquid DES was then separated from the solid by centrifugation. The isolated solid was reddish brown, which might be mainly composed of Fe_2O_3 . Because most Nd was dissolved in the DESs, from a mass balance view, only a few Nd were left in the solid. Nd-loaded GUC–LAC was regenerated with the stripping by solid oxalic acid to yield a $\text{Nd}_2(\text{C}_2\text{O}_4)_3$ precipitate, which has an average particle size of 7.76 μm (Figure S24 of the Supporting Information). The energy-dispersive X-ray spectroscopy (EDS) result (Table S5 of the Supporting Information) indicated that this precipitate did not contain any Fe, and its structure was confirmed by the powder X-ray diffraction (PXRD) pattern (Figure S25 of the Supporting Information). $\text{Nd}_2(\text{C}_2\text{O}_4)_3$ was further calcinated to prepare the Nd_2O_3 product. Nd_2O_3 had an average particle size of 5.83 μm (Figure S29 of the Supporting Information), and also no Fe appeared in the EDS analysis (Table S6 of the Supporting Information). As shown in Figure S30 of the Supporting Information, the diffraction peaks of the obtained Nd_2O_3 product agreed well with the standard X-ray diffraction (XRD) patterns of Nd_2O_3 [Joint Committee on Powder Diffraction Standards (JCPDS) card number 75-2255]. The total recovery rate of Nd in the whole process was 83.1%. The purity of Nd was 99.56% (the detailed metal composition was listed in Table S4 of the Supporting Information) confirmed by ICP–OES, which was enough to be a raw material for the NdFeB magnet production. Regenerated GUC–LAC was retested for the dissolution property. After running for 3 cycles, the dissolution ratio and separation factor were almost the same as the original DES. In combination with the following

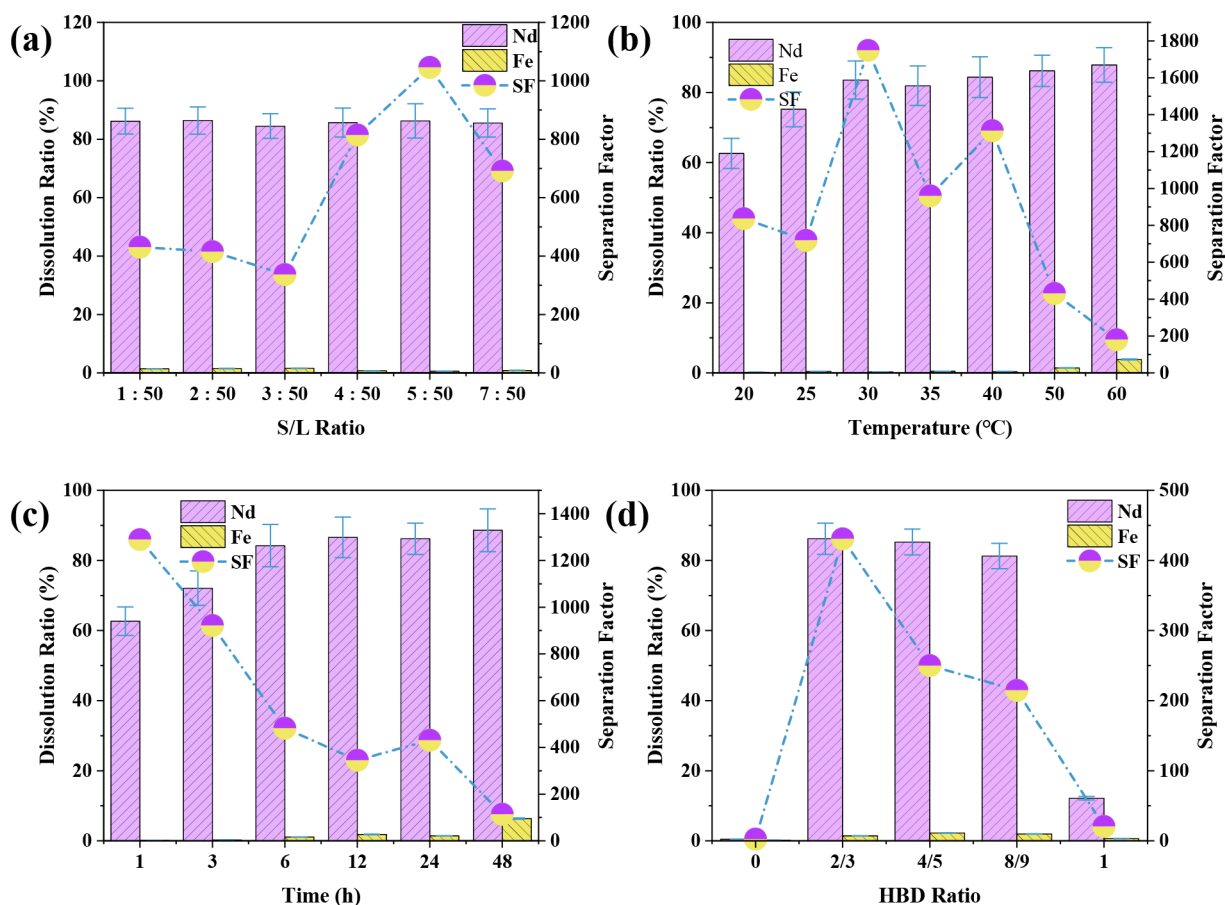


Figure 5. Effect of (a) solid/liquid ratio, (b) temperature, (c) reaction time, and (d) HBD ratio on the dissolution ratios and separation factors of Nd and Fe.

reasons, we could infer that the HBA/HBD ratio of this DES did not change after recycling. First, the boiling points of GUC and LAC were 173 and 122 °C, which were far from the working dissolution temperature. Second, the TG analysis in Figure 2a indicated that GUC–LAC was stable before 100 °C. Third, from Figures S22 and S23 of the Supporting Information, the chemical shift in ^1H NMR practically did not change and there were almost no differences in the FTIR spectra for each recycled DES.

Environmental Implications. The recovery of REEs from end-of life material is beneficial from both economic and environment aspects. However, the total recovery rate was low as a result of the lack of an efficient and clean recovery technique. The state-of-the-art recovery process based on hydrometallurgy methods, solvent extraction, is a heavy burden to the environment. Besides the emission of volatile solvents and ammonia waste gas, the inorganic acids adopted in the complete leaching and liquid–liquid extraction procedures contributed significantly to the ozone depletion, human toxicity potential, marine aquatic eco-toxicity potential, eutrophication, greenhouse gas emission, and material cost of the total hydrometallurgy process.^{20,51–53} The selective leaching process was regarded as an efficient technique to decrease the acid consumptions. In the recovery of a NdFeB permanent magnet, the acids needed in the selective leaching were only $1/8$ of the complete leaching theoretically (the calculation details were shown in the Supporting Information). If considering the acids and bases consumed in the solvent extraction, stripping, and pH adjustment of the solvent

extraction process, this gap would be much greater. Replacing the inorganic acids by green solvents would make this process friendly to the environment. The existing green solvents, including ILs, adopted in the leaching of a NdFeB permanent magnet exhibit not enough difference in the solubility between Nd and Fe, which made them improper to be applied in the selective leaching process.

According to this point, we prepared several novel DESs based on guanidine to establish a selective leaching process for the recovery of a NdFeB permanent magnet, aiming to achieve a green recycle process for this critical material. Only few guanidine-based DESs were reported before, and none of them was applied in the separation of metals.^{54–59} Criteria such as glass transition temperature, decomposition temperature, viscosity, solubility, and separation ratio were adopted to choose proper DESs to recover Nd. Among these nine DESs, GUC–LAC has low viscosity, low glass transition temperature, and high selectivity to dissolve Nd compared to Fe. In the dissolution of roasted NdFeB magnet powders, over 95% Nd was dissolved in GUC–LAC with less than 1% dissolution of Fe. In most cases, the separation factors between these two elements were larger than 400. This separation process could be achieved using a simple dissolution procedure and would not consume high energy and toxic chemicals, like the traditional solvent extraction process. Nd-loaded GUC–LAC could also be regenerated by stripping of Nd with oxalic acid, and the recycled DES kept the same dissolution performance. Nd_2O_3 produced in this recovery process had a purity larger than 99%, which was suitable for the direct NdFeB production.

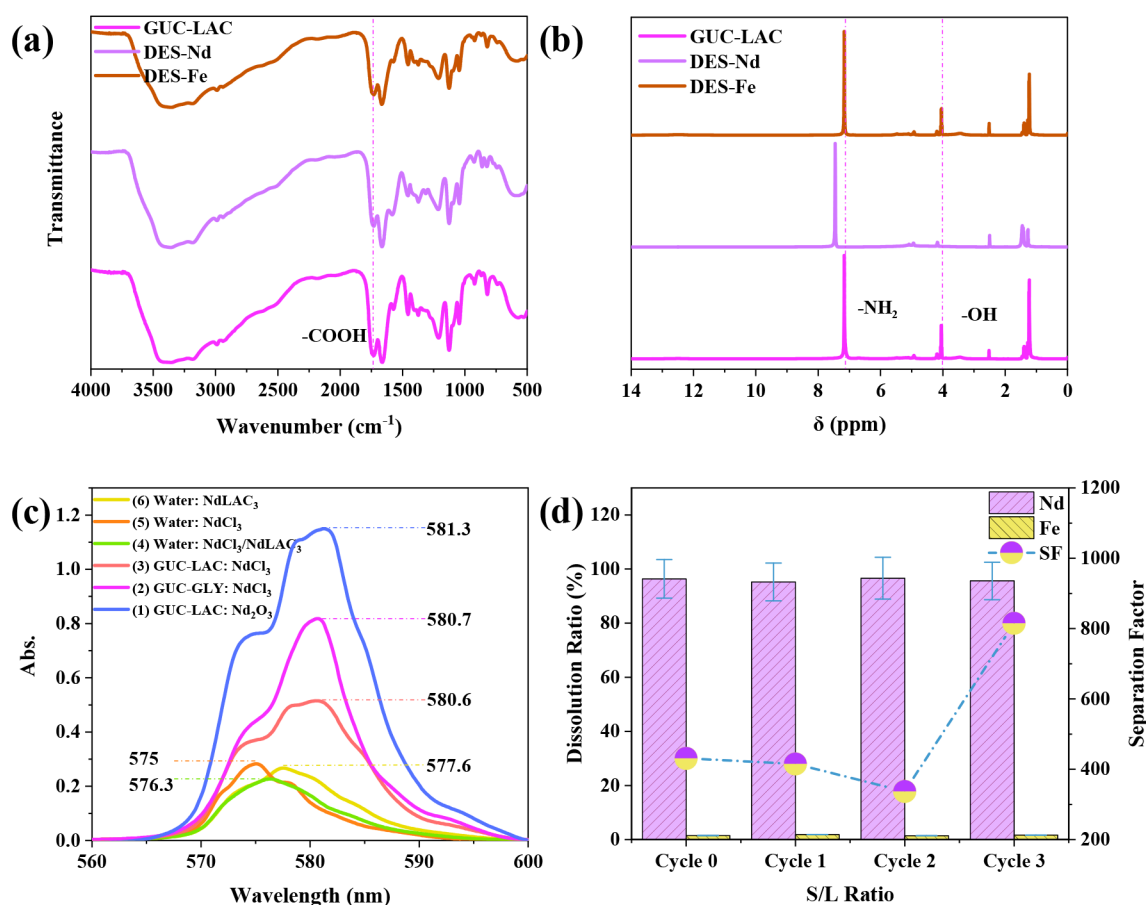


Figure 6. (a) FTIR, (b) ^1H NMR, and (c) UV-vis spectra of Nd- and Fe-loaded DESs and (d) dissolution results of recycled GUC-LAC.

The closed loop of both chemicals in the separation and life cycle of NdFeB materials could be achieved in this recovery process. The DESs, such as GUC-LAC and GUC-GA, also exhibited high dissolution toward transition oxides, such as V_2O_5 and CrO_3 , and rare earth oxides, such as La_2O_3 , which indicated that these DESs might be widely applied in the treatment of hazardous solid wastes and recovery of other valuable metal resources.

In addition, the DESs adopted in this work are facilely prepared from cheap as-obtained materials. For example, the reference prices of GUC and LAC were \$2500/ton⁶⁰ and \$1300/ton,⁴⁵ which were much cheaper than most ILs. The hydrogen ion in the DES was provided by lactic acid, which was produced by bacterial fermentation of sugar and starch, causing a lower environmental impact than inorganic acids.⁴⁵

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c03278>.

Additional chemicals and materials, characterization methods, TG-DSC, FTIR, ^1H NMR, metal concentration characterizations, calculation of the oxalic acid amount, and calculation of the acid consumption (PDF)

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Notes

The authors declare no competing financial interest.

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