

The enhanced extraction of rare earth elements from coal gangue and coal fly ash

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Abstract

Rare earth elements (REEs) are unrenowable, uneven distributed and less productive worldwide, but technological-critical and strategic important. Searching for alternative REEs resource has motivated many interests and technological advancement. The recent example was studies launched by U.S. on the recovery of REEs from coal and coal byproducts, since substantial REEs have been found in coal recourses despite in their lower occurrence. The extraction of REEs from coal and coal products face many technological challenges because REEs mainly exist in the inorganic lattice structure of coal and its byproducts, such as silicon-aluminum oxides. In this study, coal gangue and fly ash were selected as two representative coal by-products to extract REEs. The extraction of their REEs was alternative to the direct conventional acid leaching procedure. In this study, the realization of the CFA activation was initialized before moving-on to the conventional acid leaching. The activation of selected coal byproducts was subject to the calcination at the elevated temperatures using sodium carbonate (Na_2CO_3). Studies regarding effects of the temperature and the Na_2CO_3 dosage during the calcination as well as pH adjustment during leaching on the following-up maximize the extraction efficiency of REEs were intensively investigated. The results showed that the best practices achieved by 93.2% and 95.8% for coal fly ash and coal gangue in the extraction efficiency of REEs, upon the mixing molar ratio of silicon-aluminum oxides in coal byproducts and sodium carbonate at 1:1, the calcination temperature at 850°C and the acid leaching pH at 2.

1. Introduction

Rare Earth Elements (REEs) are a strategic source which is important in the future development of technologies and economics worldwide (Sangine 2020; Bauer et al. 2010; Guo et al. 2018; Ji et al. 2020). REEs are composed of 17 elements involving 15 lanthanide elements (La-Lu) and scandium (Sc) and yttrium (Y) (Hower et al. 2016). Their similar physical and chemical properties make their mining, extraction, purification and analysis great challenges. Their applications involve optics, lasers, renewable energy, energy storage, magnetism, catalysts, alloys, nuclear radiation and many other fields (Binnemans et al. 2013). Rare Earth Elements (REEs) known as the “industrial vitamin”, are indispensable elements in many modern industries, have become a crucial strategic resource for the 21st century (Xu et al. 2014). China once dominates its deposit, mining and supply, which is necessary to be such in the future. The increase of REEs supply can be achieved via the exploration and extraction of REEs in solid wastes (Yakaboylu et al. 2014; Lin et al. 2021). However, this new source of REEs challenges technically in respect of its lower concentration and available environmentally friendly process.

The mining and use of coal resources over the years result in the great accumulation of coal-based solid wastes which likely imposes threats to the environment and human society if they are not handled or used properly (Sun et al. 2020; Gao et al. 2021; Cao et al. 2015). Coal gangue (CG) and coal fly ash (CFA) are two representative coal-based solid wastes. The most recent effort has been made on the extraction of highly value-added rare earth elements (REEs) from CG and CFA. The recent example was studies launched by U.S. on the recovery of REEs from coal and coal byproducts (Huang et al. 2018; Learn et al.

2017; Zhang et al. 2020), since substantial REEs have been found in coal recourses despite in their lower occurrence (Ge et al. 2012; Sun et al. 2016). Although REEs are at their low-occurring contents in CFA, the total amount of REEs reserve is still greater and attractable compare to available REEs ore resources because of the great quantity of CFA. Therefore, CFA can be regarded as an alternative source of REEs. The successful and economic extraction of REEs from CFA can not only reduce the tension of the shortage of REEs, but also increase values of the CFA utilizations.

The conventional way to extract REEs is the enhanced acid or ammonia leaching (Wen et al. 2020; Tang et al. 2019; Pan et al. 2021). This method functions efficiently on REEs in their ionic status, but fails in many cases of CFA-like raw materials, where the occurrence of REEs is in silicon-aluminum structures of CFA which acids or ammonia can not be reachable (Wu et al. 2020). This also likely results in the increased use of acids or ammonia during the leaching step and additional energy consumption by reactions between the CFA silicon-aluminum and leaching acids. Moreover, the neutralization step is generally necessary to closed-up the extraction process. Thus, it's unavoidably complex and inefficient in operation as well as poor in economies.

In this study, coal gangue and fly ash were selected as two representative coal by-products to extract REEs. The extraction of their REEs was alternative to the direct conventional acid leaching procedure. In this study, the realization of the CFA activation was initialized before moving-on to the conventional acid leaching. The activation of selected coal byproducts was subject to the calcination at the elevated temperatures using sodium carbonate (Na_2CO_3). Studies regarding effects of the temperature and the Na_2CO_3 dosage during the calcination as well as pH adjustment during leaching on the following-up maximize the extraction efficiency of REEs were intensively investigated. The results showed that the best practices achieved by 93.2% and 95.8% for the coal ash and coal gangue in the extraction efficiency of REEs, upon the mixing molar ratio of silicon-aluminum oxides in coal byproducts and sodium carbonate at 1:1, the calcination temperature at 850°C and the acid leaching pH at 2. The success of this study provided a solid base to establish the technical-sound, environmentally-friendly, energy-saving and economical process on the extraction of trace REEs, and further contributed to the step-forward formation of the secondary sources of REEs.

2. Experimental Section

2.1 Materials, reagents and instruments

Coal fly ash and coal gangue were collected from Anhui province, China. The inductively coupled plasma mass spectrometer ICAP-Q (Thermo Fisher Scientific, USA) was applied in the determination of REEs; Applied reagents such as hydrochloric acid, sodium carbonate, hydrofluoric acid and perchloric acid are all in their analytical purity.

2.2 Experimental method

a. REEs analysis of fly ash and gangue. 0.2 gram of the involved coal waste samples was weighed and calcined in the muffle furnace 800 °C for 60 mins to burned off the carbon completely in the gangue sample. Then the carbon-free samples were transferred into a digestion tank (0.2 mL HF and 0.5 ml HNO₃) in a microwave digestion apparatus for its digestion. This was followed by driving-off the digestion acids in the digested solution and the addition of the pure water to the certain volume, and finally the determination of REE contents using the ICP-MS.

b. The complete procedure of REEs extraction. 0.5g of two involved coal waste samples were quantitatively weighed respectively. The alkali additives were weighed and mixed with fly ash and coal gangue samples at a desirable molar ratio. The mixtures were calcined in a muffle furnace to certain temperatures 800°C and 850°C and maintained for desirable times 120 mins. Then they were cooled to the ambient temperature, grind in agate mortar, water-washed. The separated liquid phase samples were subject to the acid leaching by adjusted pHs prior to the final REEs analysis using ICP.

c. The determination of REEs in 2 coal waste samples. The determination of rare earth elements in two selected coal waste samples showed that the total amount of rare earth elements in coal fly ash is 457.230 µg/g, while less in coal gangue in the total amount of rare earth elements of 281.121 µg/g. Among of them, the contents of Ce element in both coal gangue and coal fly ash is highest, to be 102.576 µg/g and 151.276 µg/g, respectively. Five valuable elements, such as Sc, La, Pr, Nd and Y are the secondly higher group. Light rare earths are the majority constituents in the total REEs in coal wastes, contrasting to heavy rare earth elements.

2.3 Characterizations of coal fly ash and gangue samples

The elemental and XRF analysis on the coal fly ash and coal gangue samples were conducted, and results were shown in Table 1 and 2. It was found that there is carbon element occurring in both samples despite in their lower contents. The major oxide components of both are silica and alumina, in a total content of over 83%. The XRD plots of samples, as shown in Figure 3, indicated that the main mineral compositions of fly ash is mullite and quartz, contrasting to those of coal gangue being kaolinite and quartz. Other mineral compositions of two are similar but less in the content.

Table 1. Elemental analysis of experimental samples

Components/%	C	H	N
Coal gangue	3.002	0.798	0.000
Fly ash	0.581	0.012	0.000

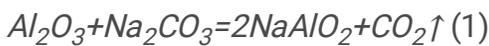
Table 2. The main components of the test sample

Components/%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO
Coal gangue	59.528	22.902	0.548	1.634	0.488	1.489	4.590
Fly ash	55.798	27.695	2.918	0.882	0.661	1.231	0.400

3. Results And Discussion

3.1 Experimental principle

Previous efforts failed to extract REEs in coal wastes since the occurrence of REEs in silicon-aluminum of coal wastes, which are not in extractable ionic status. In this study, prior to the regular acid leaching procedure, the calcination pretreatment of coal wastes using Na₂CO₃ under elevated temperatures was initialized. It's likely that the original silica-aluminate minerals may be decomposed to produce new silica-aluminate as well as silicate substances in their higher activity (Wen et al. 2020). The specific reactions are shown as follows:



This was a so-called the activation procedure for REEs extraction from coal wastes. The consequence of this activation resulted in the dissolvable silica-aluminate at least in acid environment. Simultaneously, REEs occurring in coal wastes could be also accessible in the acid leaching. The specific reactions are likely as follows



Fig. 4. shows the SEM images of coal fly ash and coal gangue before and after the activation procedure. Coal fly ash, which is from the higher temperature combustion process showed the melting trend in its regular round shape grains. The was not maintained and it showed a mixing status of melting grain in regular shape and irregular structures after the activation that was even still in a condition of the similar elevated temperatures, implying the somehow decomposition of silica-aluminate crystal structure during the activation. Coal gangue, from a natural deposition condition, showed its typical shape character in the irregular stacking structure. Under an elevated temperature calcination during of the activation, the regular melting contrastingly and clearly showed-up. Fig 5. and Fig. 6 shows comparison of XRD plots of coal fly ash and coal gangue. It was found that the original main mineral compositions of mullite and quartz in ash and kaolinite and quartz in coal gangue disappeared. Alternatively, the activation process changed them into crystals of sodium metasilicate and sodium silicate-aluminate, implying the completeness of the activation.

3.2 The REEs extraction of coal fly ash

Figure 7 shows the extraction efficiency of REEs after the pretreated calcination at 800°C and 850°C. Generally, a higher calcination temperature at 850°C seemed better to the enhanced extraction efficiency of REEs except for element Y, and as for elements La and Pr, the calcination at 800°C seemed enough for the desirable extraction efficiency. Noticeably, elements of Ce and Tb were two showing the significant different upon the change of the calcination temperature from 800°C to 850°C, while the extraction efficiency of the element Ce as very sensitive on the calcination temperature than that of the element of Tb. Fig. 8 shows the extraction efficiency of REEs upon the usage of the calcination additive of the sodium carbonate. The usage of the sodium carbonate was determined based on the theoretical molar ratio of chemical reactions, as shown in Eq (1) and (2), which is that between the actual silica-alumina mineral contents in the coal fly ash and coal gangue and the sodium carbonate. The molar ration was varied from 1:0.7 to 1:1.0 in this study. It's found the extraction efficiency of REEs gradually improved upon the increasing usage of sodium carbonate until a molar ratio at 1:1.0 when the extraction efficiency of REEs (pH=2) achieved its highest. The aforementioned investigations were true in views of the light REEs, heavy REEs and naturally the total REEs.

Fig. 9 shows the effect of pH in the aqueous extraction environment on the extraction of REEs (Zhang et al. 1987). The decrease of pH significantly increased the extraction efficiency of REEs. Studies also indicated an aqueous extraction environment at pH=4 seemed not effective on the REEs leaching. This was not true when pH dropped to 3 and further 2, the extraction efficiency of most REEs can be achieved by about 60% and further as high as 90% (pH=2). The acid extraction seemed not functional well on the element Ce during the acid extraction, especially at pH=4 and 3 where the extraction efficiency corresponded to only 23% and 30%, respectively. This was significantly changed to 86% in the extraction efficiency when pH=2. This study confirmed the optimal pH in the aqueous environment for the maximum extent of REEs leaching should be about 2. The aforementioned investigations were true in views of the light REEs, heavy REEs and naturally the total REEs.

3.3 The REEs extraction of coal gangue

Similar results can be obtained in the investigations on the REEs extraction of coal gangue. Figure 10 shows the extraction efficiency of REEs of coal gangue after the pretreated calcination at 800°C and 850°C, implying a higher temperature at 850°C for the calcination was necessary to enhance the extraction efficiency of REEs. Except for element elements La, Pr, and additionally Nd in the coal gangue case, the calcination at 800°C seemed enough for the desirable extraction efficiency of REEs. That the sensitive response of the extraction efficiency of the element Ce was again found on the calcination temperature, and insensitive for the Tb was similarly shown. Tb. Figure 11 shows the extraction efficiency of REEs in coal gangue upon the usage of the sodium carbonate. It was found that the extraction efficiency of REEs expectedly enhanced upon the increased usage of the sodium carbonate. A molar ratio of 1:1.0 during the calcination of the coal gangue can maintain the extraction efficiency by the later-on acid leaching achieved as high as 90-100%. The aforementioned investigations were true in views of the light REEs, heavy REEs and naturally the total REEs.

Fig. 12 shows the effect of pH in the aqueous extraction environment on the extraction of REEs in an alternative case of coal gangue. Similar to that of coal fly ash, the decreased pH of the acid leaching environment also significantly enhanced the extraction efficiency of REEs. Again for the coal gangue an aqueous extraction environment at pH=4 did not show expectedly effective on the REEs leaching. This can be significantly changed when pH dropped to 3 and further 2, the extraction efficiency of most REEs can be achieved by about 55% and further as high as 95% (pH=2). As for the element Ce, its similar lower extraction efficiency was found during the acid extraction at pH=4 and 3, but significant higher to be over 95% in the extraction efficiency upon pH of the acid leaching environment was adjusted to be 2. The aforementioned investigations were true in views of the light REEs, heavy REEs and naturally the total REEs.

4. Conclusion

(1) REEs in coal gangue and ash mainly occur in their original silica-alumina minerals, that prevents REEs accessible and also likely increases the acid usage during the following-up acid leaching. The alkali calcination at elevated temperatures works effectively on the decomposition of silica-alumina minerals in studied coal wastes, leading the following-up effective extraction of their REEs. Both XRD and SEM characterizations verified the decomposition of the original silica-alumina minerals.

(2) The optimal REEs extraction conditions were found to be the use of sodium carbonate as alkali calcination medium, a molar ratio of silica-alumina minerals in coal wastes and sodium carbonate at 1:1, a calcination temperature at 850°C, the following-up acid leaching at pH=2, when the REEs extraction efficiency conditions of coal fly ash and coal gangue were achieved as high as 93.2% and 95.8, respectively.

Declarations

Author contribution

Conceptualization: Yan Cao; Data analysis: Yan Cao, Rui Zhang and Chunming Zhang; Investigation & methodology: Yan Cao, Rui Zhang and Chunming Zhang; Project administration: Yan Cao; Writing—original draft: Yan Cao; writing—review and editing: all coauthors; all authors read and approved the final manuscript.

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Data Availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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Figures

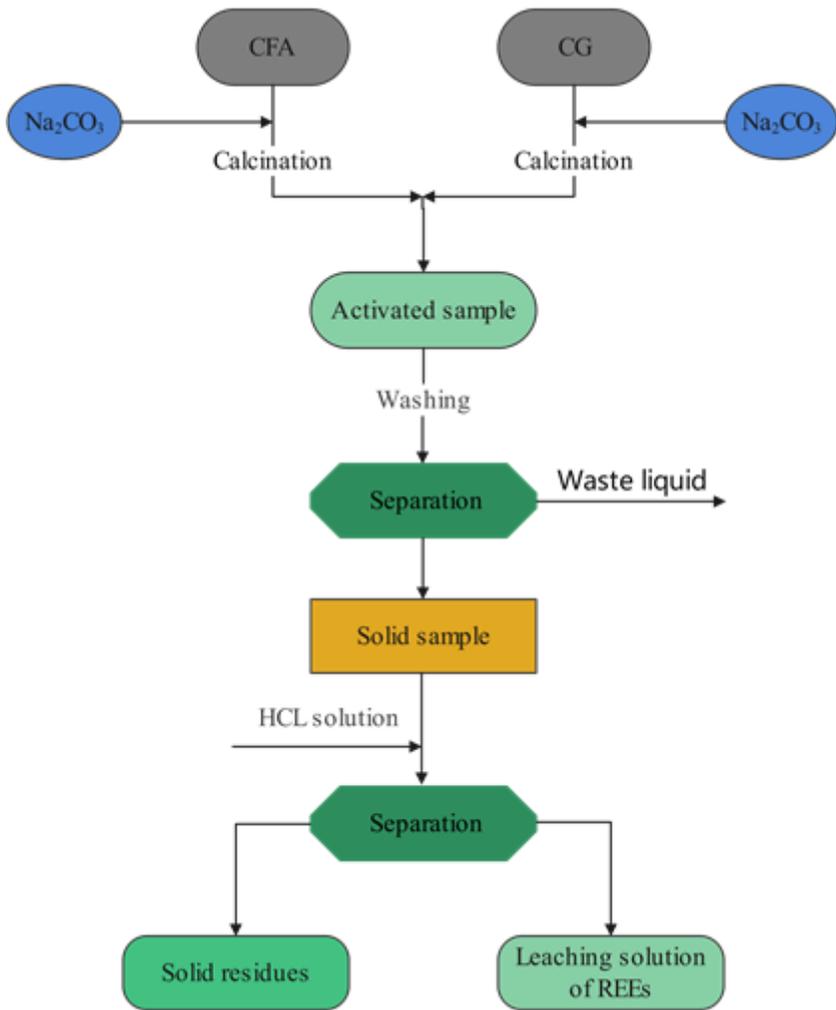


Figure 1

Experimental flow chart

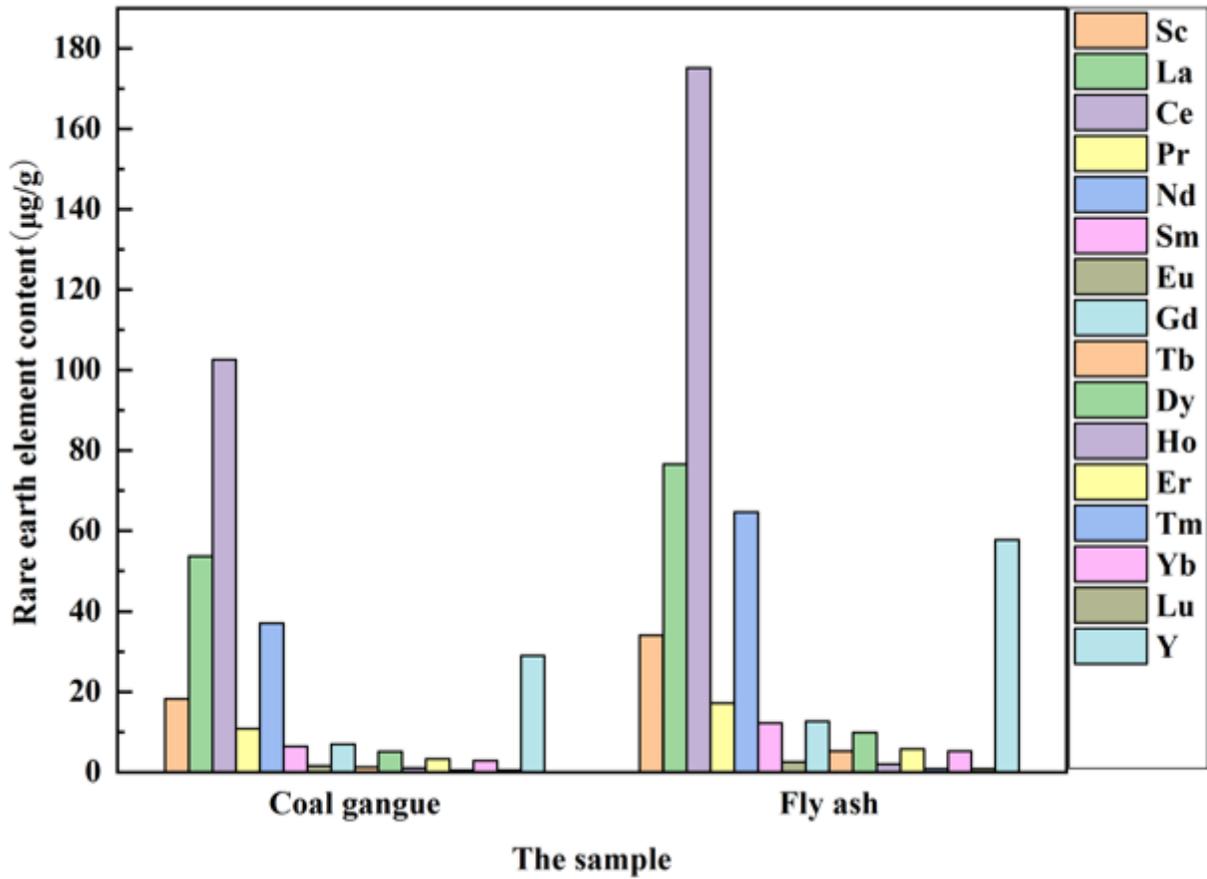


Figure 2

Contents of rare earth elements in coal fly ash and coal gangue samples

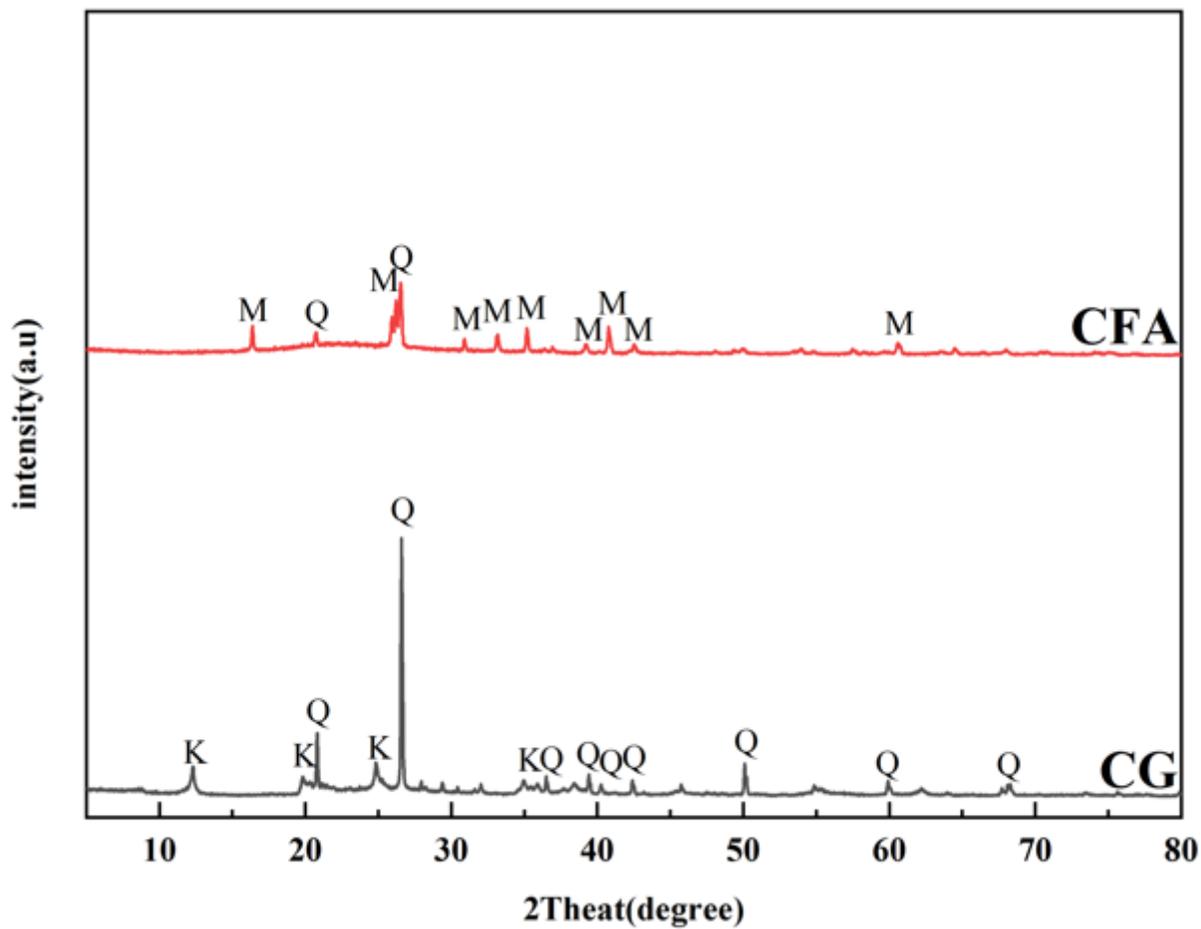


Figure 3

XRD patterns of raw samples (K-Kaolinite Q-Quartz M- Mullite)

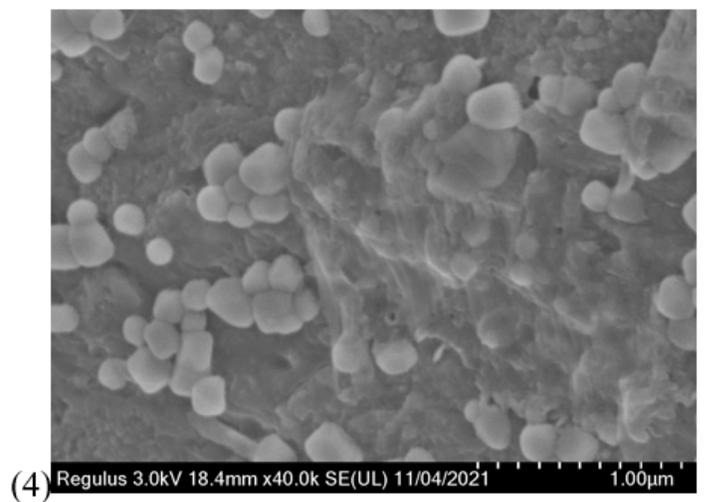
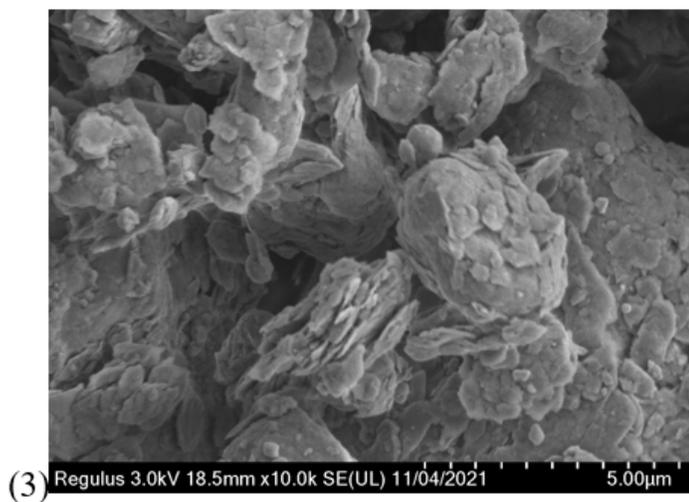
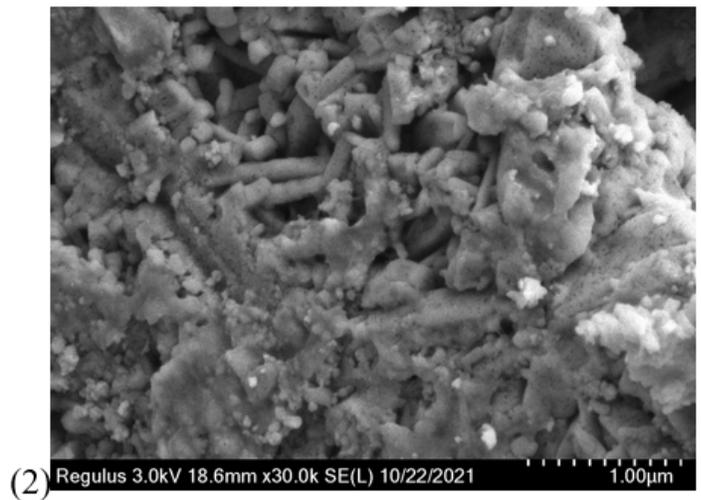
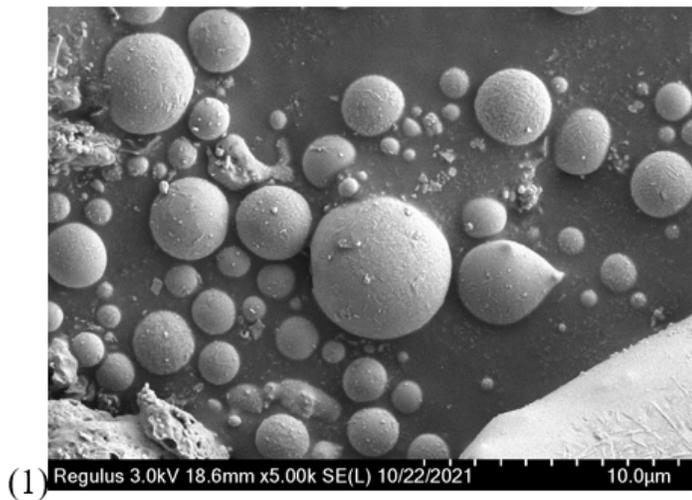


Figure 4

SEM of fly ash and coal gangue

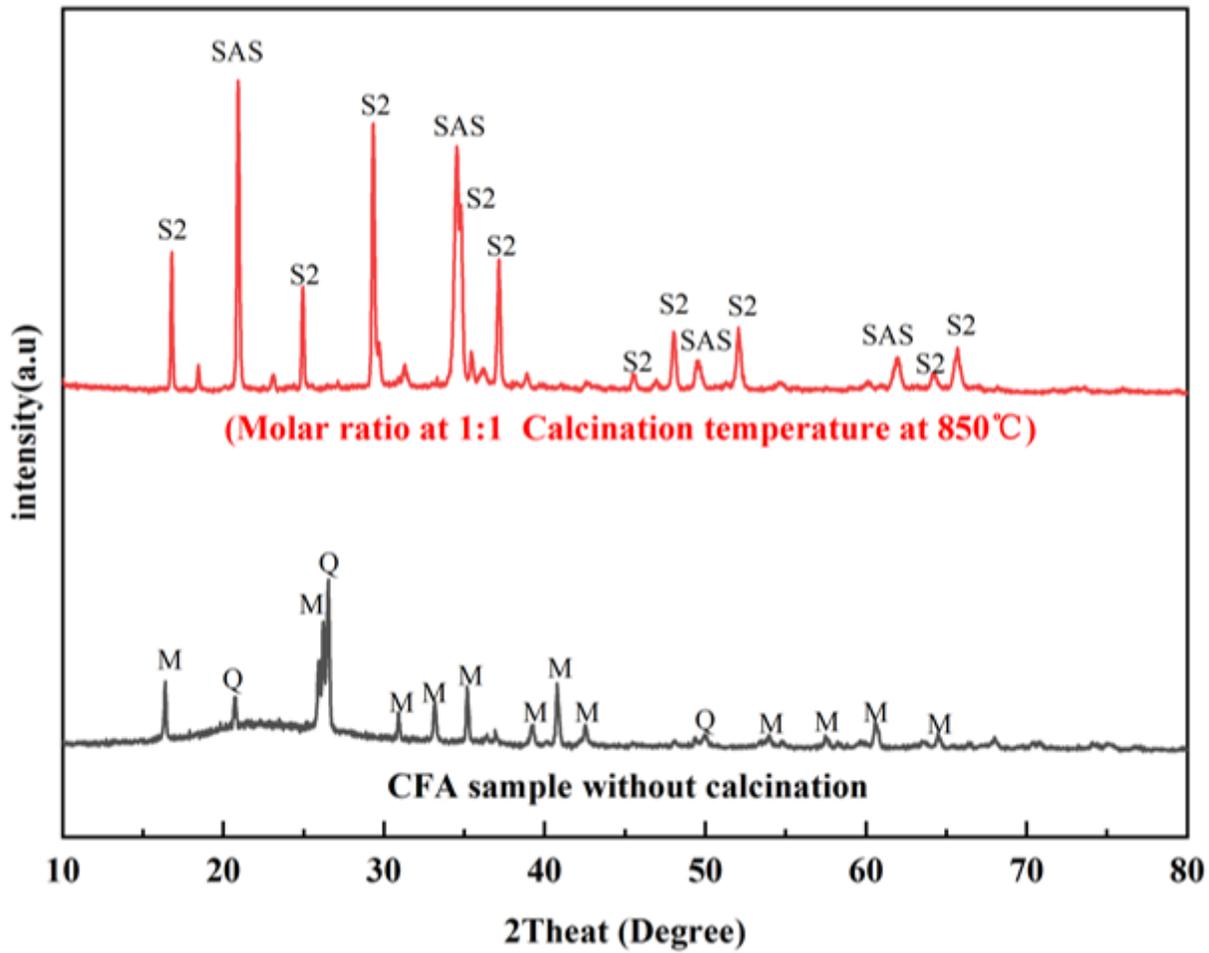


Figure 5

XRD diagram of fly ash before and after the activation

(M- Mullite Q-Quartz S2- Na_2SO_3 SAS- NaAlSiO_4)

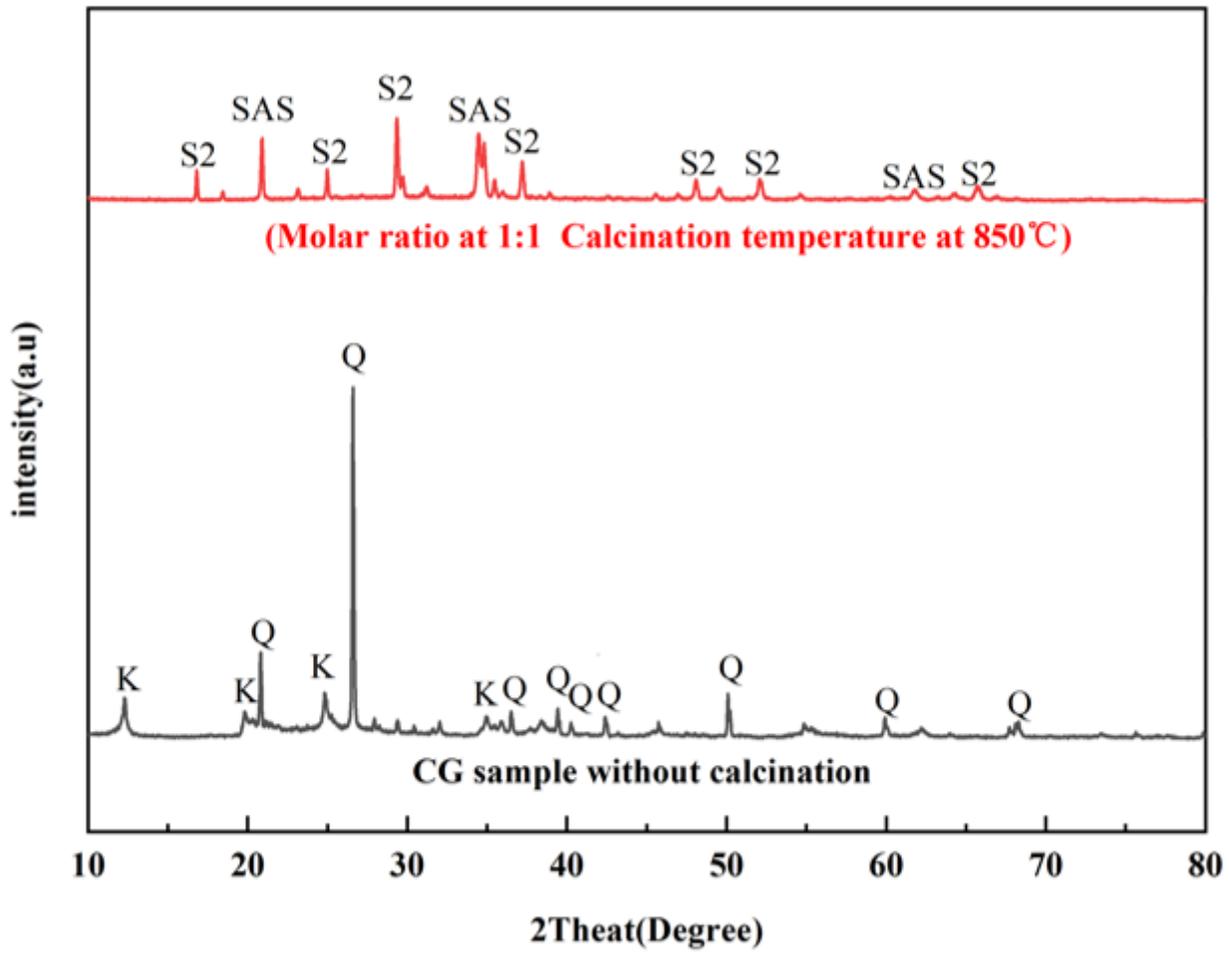


Figure 6

XRD diagram of Coal gangue before and after the activation

(K-Kaolinite Q-Quartz S2- Na_2SO_3 SAS- NaAlSiO_4)

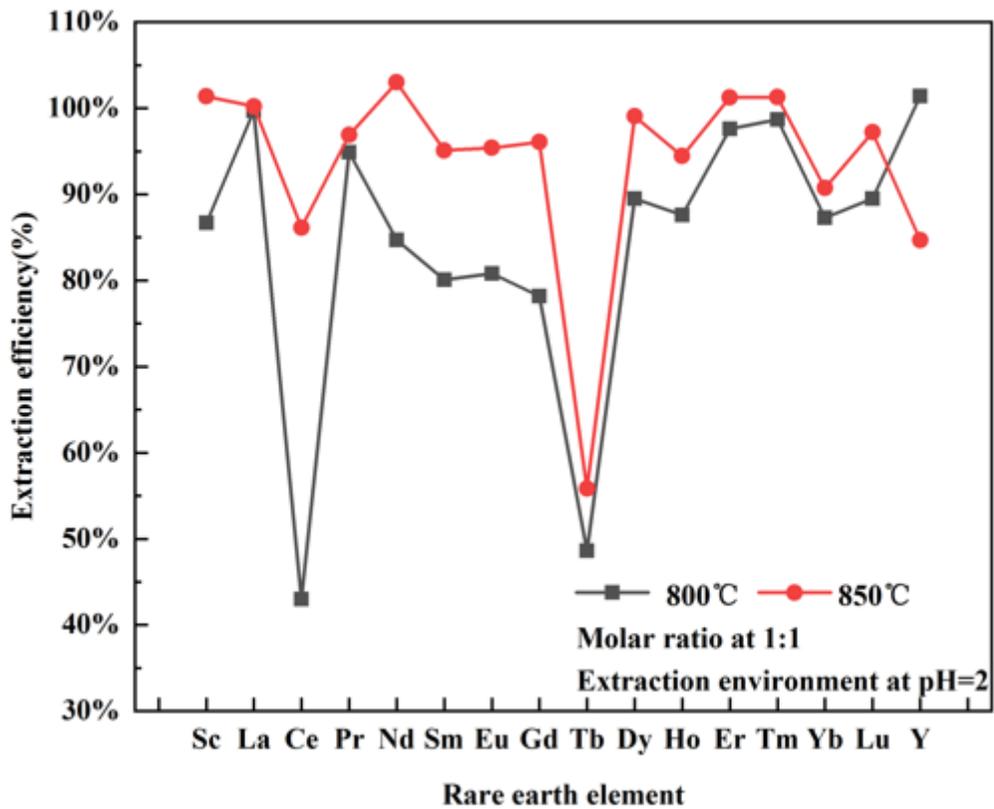


Figure 7

The extraction efficiency of in coal fly ash corresponding to calcination temperatures

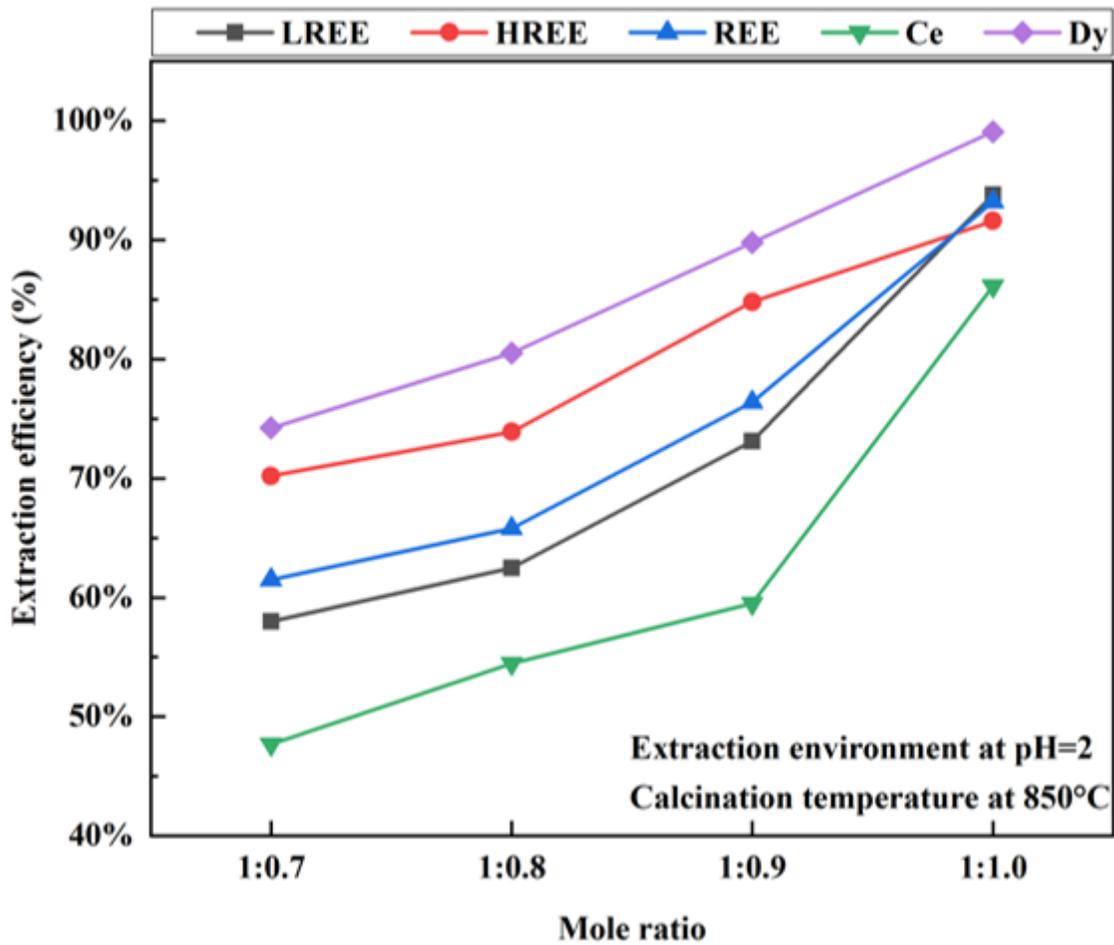


Figure 8

The extraction efficiency of REEs in coal fly ash corresponding to molar ratios of sodium carbonate and coal wastes

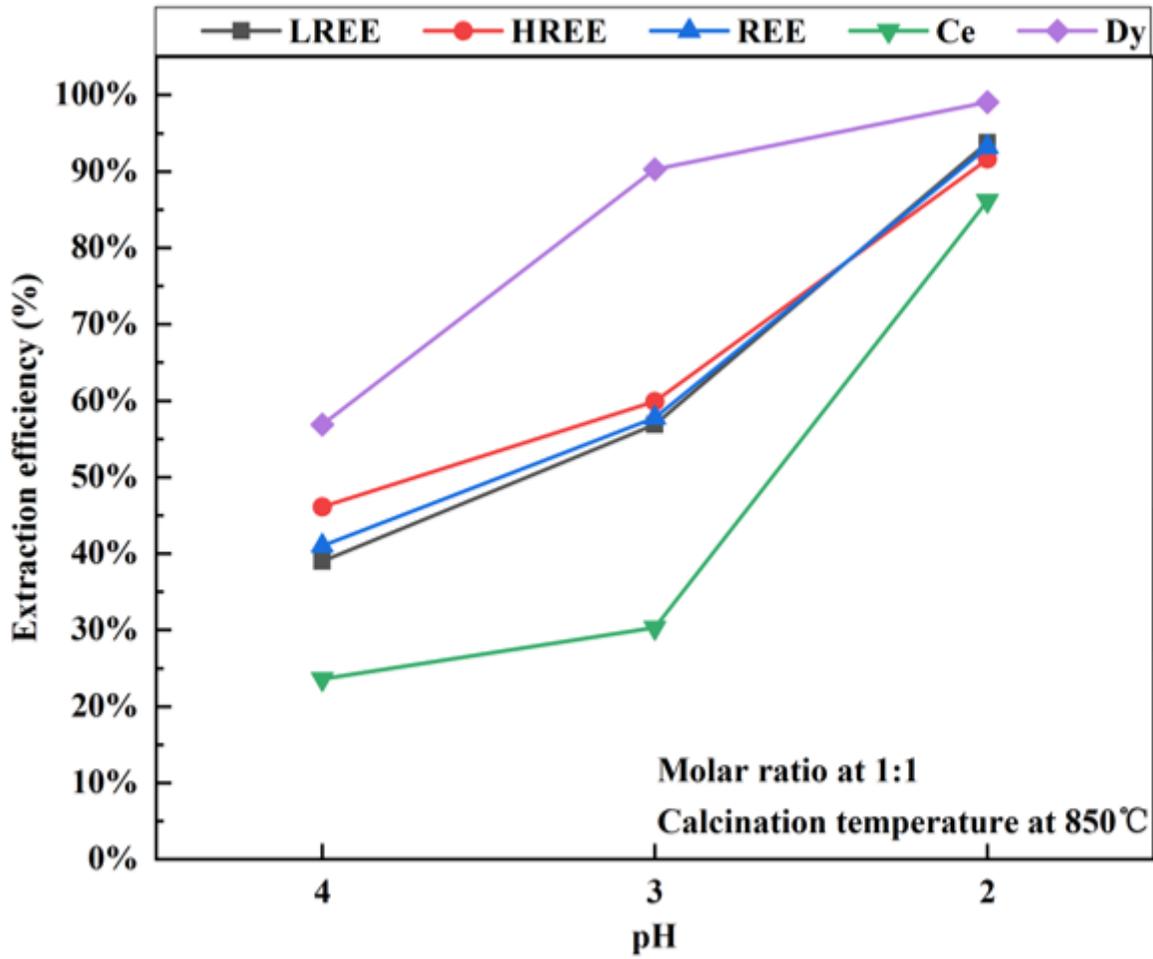


Figure 9

The extraction efficiency of REEs in coal fly ash corresponding to pH in the acid leaching

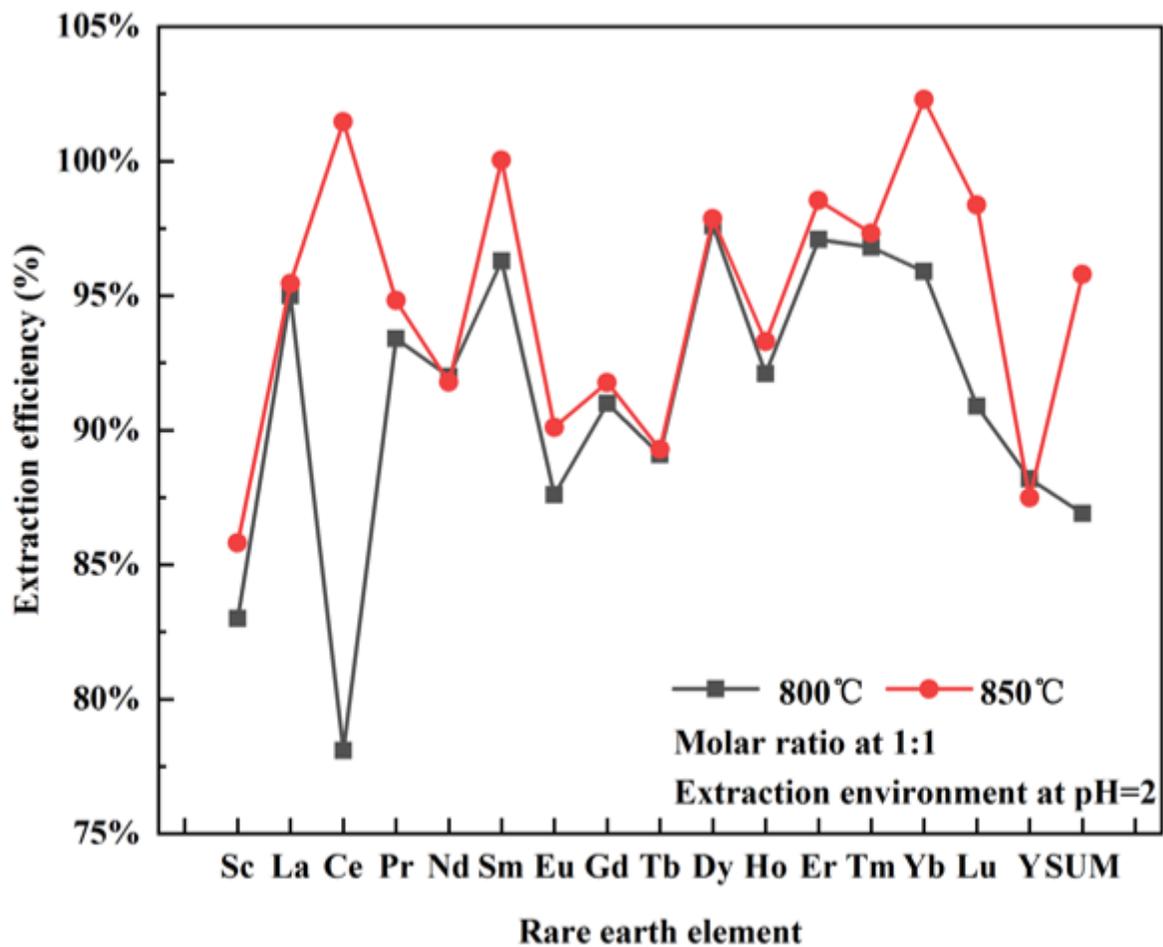


Figure 10

The extraction efficiency of REEs in coal gangue corresponding to calcination temperatures

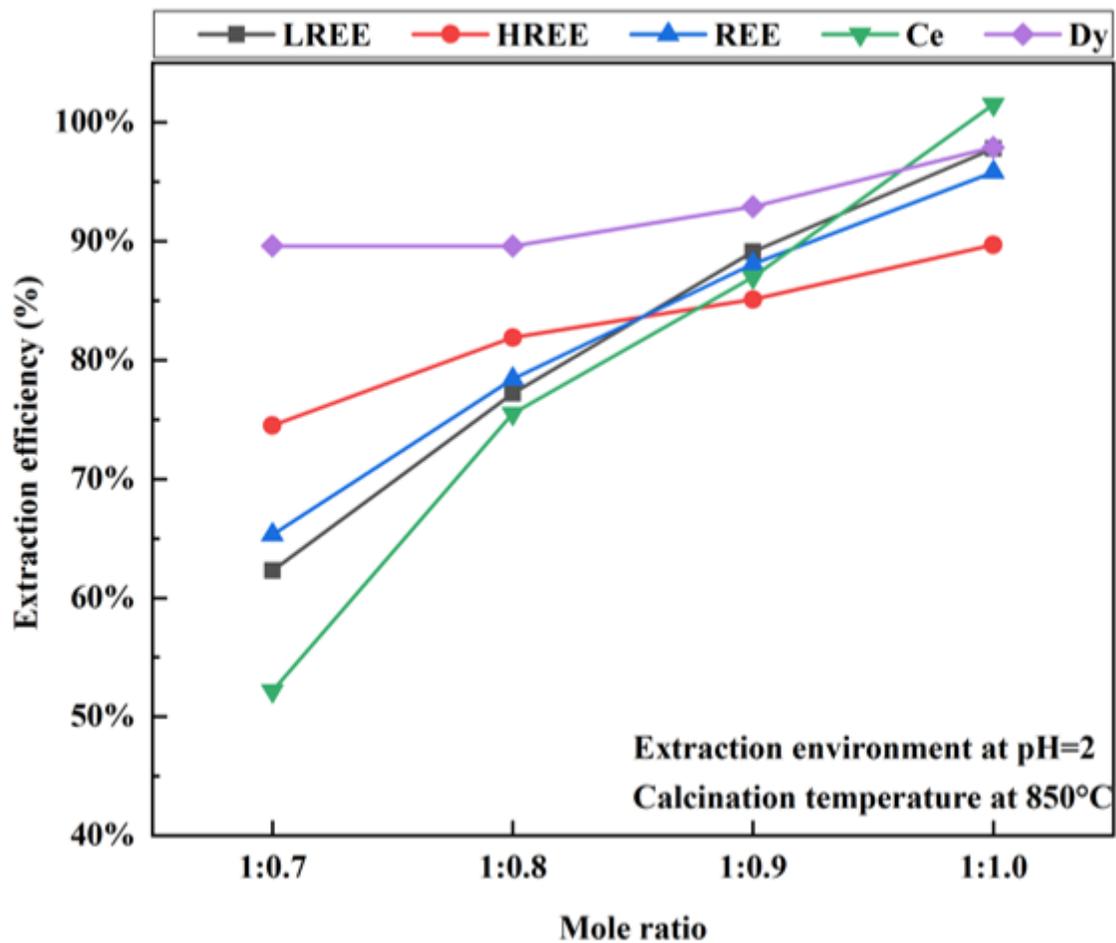


Figure 11

The extraction efficiency of REEs in coal gangue corresponding to molar ratios of sodium carbonate and coal wastes

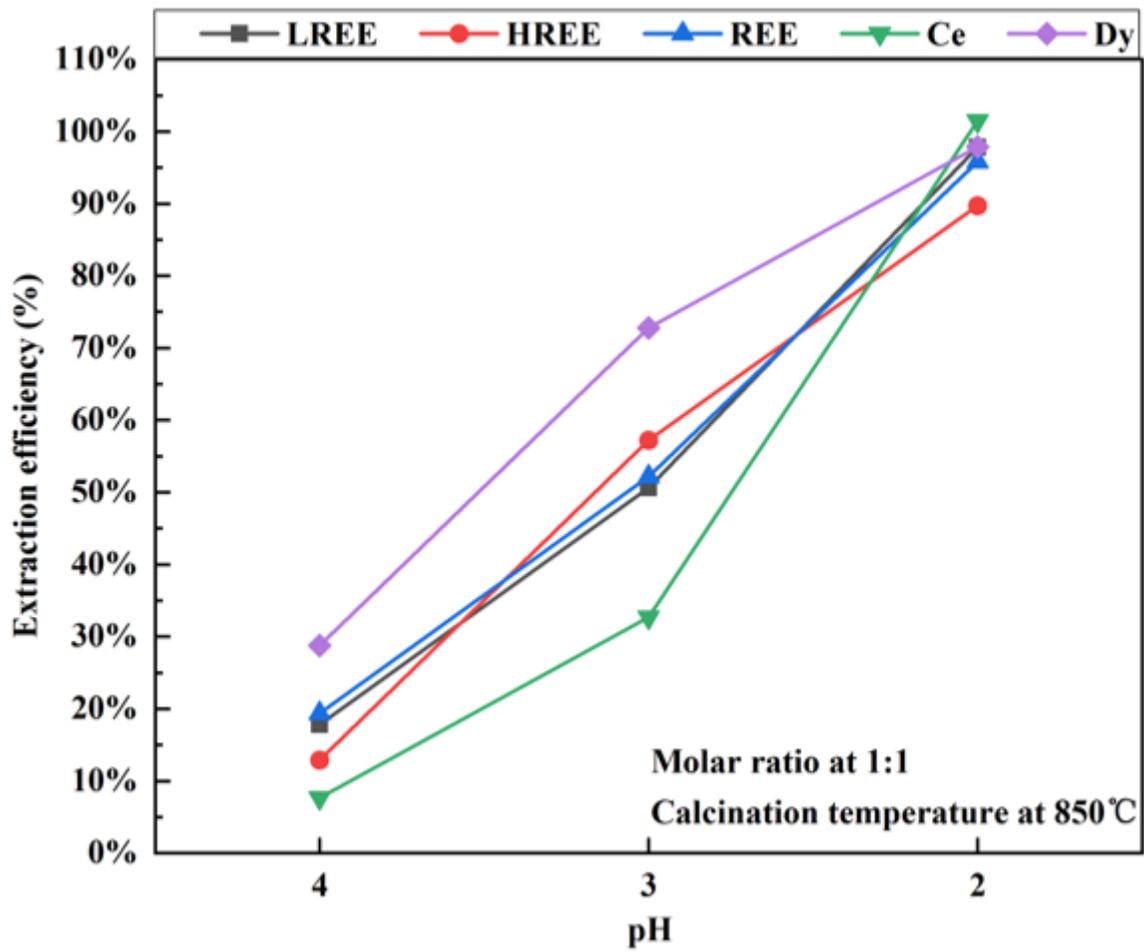


Figure 12

The extraction efficiency of REEs in coal gangue corresponding to pH in the acid leaching