Electronic Supplementary Information

Supercritical Carbon Dioxide/Nitrogen/Air Extraction with Multistage Stripping Enables Selective Recovery of Rare Earth Elements from Coal Fly Ashes

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Summary

13 pages, including 2 texts, 6 figures, and 8 tables.

S1. Determination of the optimal volume ratio of reacted TBP-HNO_3 and 1% HNO_3 in a multistage stripping process for concentrating REEs.

To determine the optimal volume ratios of reacted TBP-HNO_3 and 1% HNO_3 (1:10, 1:1, 10:1, or 100:1) stripping solution, we used neodymium (Nd) as a model REE. For this optimization, two criteria were used: One was the REE concentration, and the other was the stripping efficiency, calculated as in Eq. S1.

$$Stripping\ Efficiency = \frac{Concentration\ of\ REE\ in\ stripping\ solution \times stripping\ solution\ volume}{Amount\ of\ REE\ added\ into\ TBP{-}HNO_3} \times 100\% . \qquad \text{Eq. S1}$$

As Fig. S5 shows, the stripped Nd concentration and stripping efficiency show opposite trends at different volume ratios of TBP-HNO_3 and 1% HNO_3. The stripping efficiencies decrease as the volume ratios decrease, suggesting that the distribution of REEs is determined by the volume ratio. When the volume ratio is 1:10, the efficiency is about 90%. When the volume ratio is 10:1, the stripping efficiency decreases to about 30%, but Nd is significantly concentrated because of the small stripping solution volume. When the volume ratio is decreased to 100:1, the Nd concentration does not increase, and the efficiency drops to nearly zero. Thus, a volume ratio of 10:1 is optimal for concentrating REEs in this process. Further, the reacted TBP-HNO_3 can be stripped multiples times to collect the maximum amount of REEs from the stripping solution.

S2. The influence of the pressure and composition of supercritical fluids on the impurity amounts in the extraction product

Different from a pure substance (i.e., scCO_2 and scN_2), scAir is a mixture of 78% N_2, 21% O_2, 0.93% Ar, 0.04% CO_2, and small amounts of other gases. To investigate how the impurity concentrations in our multistage stripping process for scAir extraction products differ from those from scN_2 extraction, additional tests were conducted, including using 120 bar N_2 and using 120 bar N_2 with 30 bar CO_2 as SCFs for REEs extraction. We summed the concentrations of the collected major impurities (Ca, Fe, Mg, Al) in stripping solutions from all ten stages of the stripping process and listed them in Table S8. Comparing the 150 bar scN_2 and 150 bar scAir conditions, we notice that, in the 150 bar scAir condition, the Ca concentration is smaller, but the Al concentration is larger. The opposite trends of Ca and Al suggest that different components in the scAir have different influences on the impurity concentrations. Because 150 bar scAir can be considered as a mixture of approximately 120 bar N_2, 30 bar O_2, and trace amounts of CO_2 and other gases, we separately evaluated each component's effect on decreasing the impurity amounts. Under 120 bar scN_2, concentrations of most impurities increased compared to the concentration from 150 bar scN_2. The addition of CO_2 (120 bar N_2 with 30 bar CO_2), even when not in a supercritical state, can significantly decrease the concentrations of impurities, especially Al. Comparing the 150 bar scN_2 and 150 bar scAir results, the concentrations of impurities decreased except for Al. Therefore, adding oxygen decreases Al concentrations. Hence, different components in scAir indeed affect the extraction of impurities.

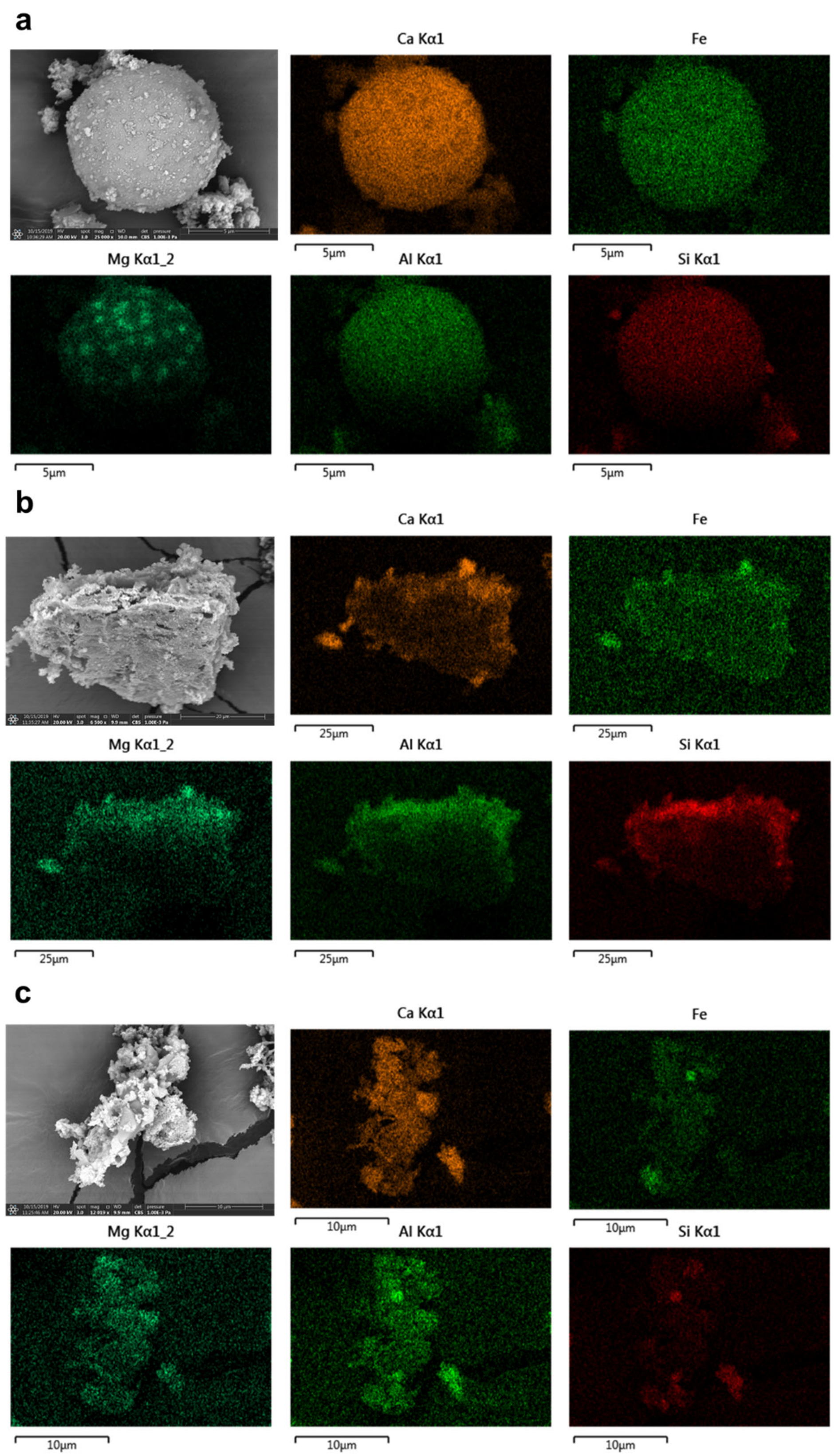

Fig. S1. SEM images and EDX elemental mappings of CFA particles.

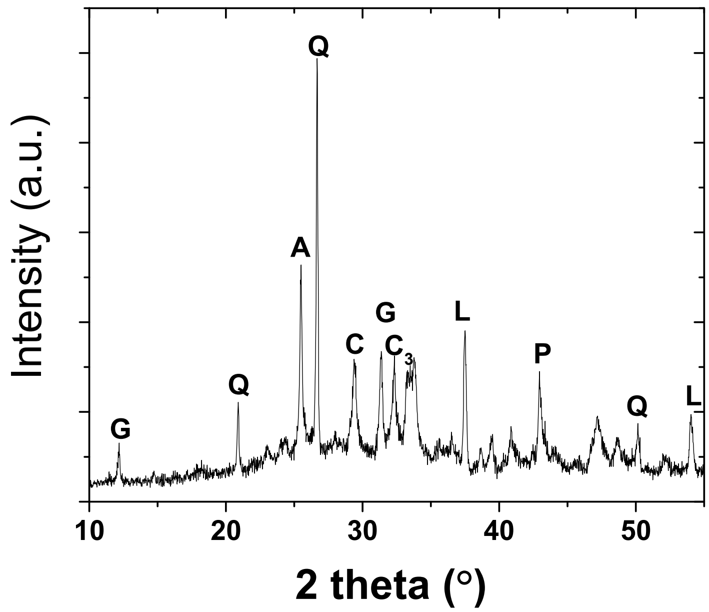

Fig. S2. XRD pattern of CFA. Q (quartz), G (gehlenite), A (anhydrite), P (periclase), L (lime), C_3 (tricalcium aluminate), G (gypsum), and C (calcite).

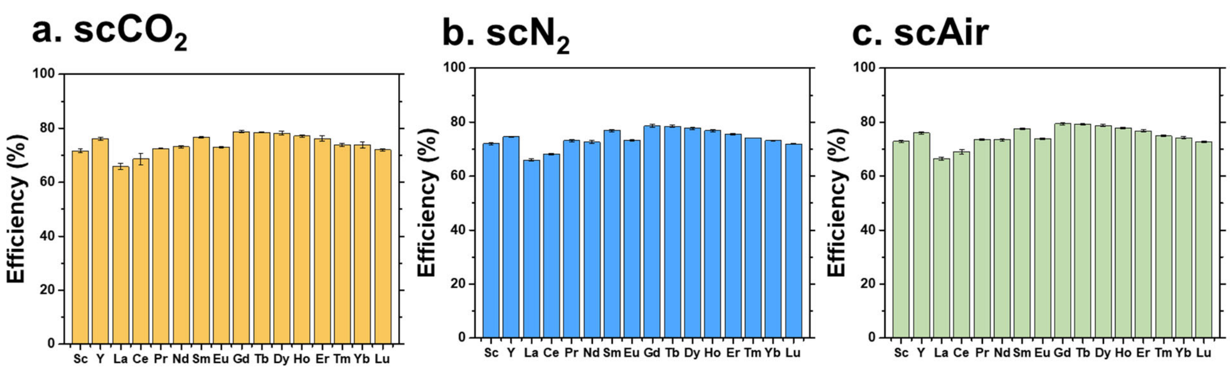

Fig. S3. Efficiency of REEs extraction from CFAs under different conditions, as calculated by Eq. 1. Error bars represent the standard errors from triplicate extraction experiments.

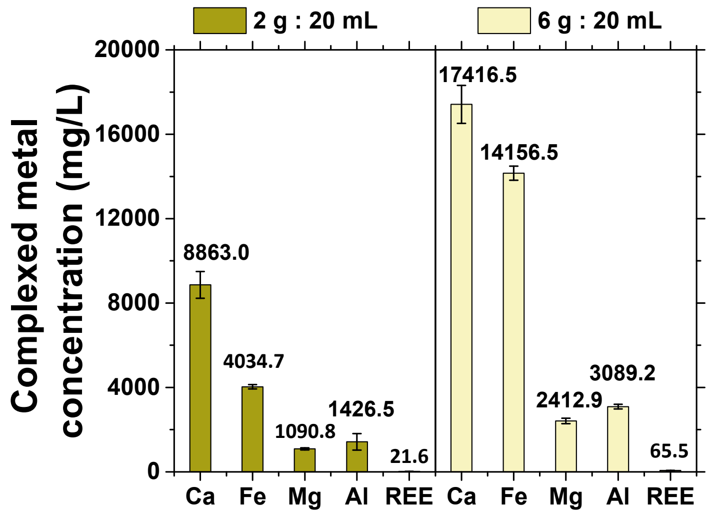

Fig. S4. TBP-complexed impurities under heating-only conditions (i.e., without supercritical fluids). The left plot shows results for 2 g of CFA and 20 mL of TBP-HNO_3. The right plot shows results for 6 g of CFA and 20 mL of TBP-HNO_3. We consider that increasing the CFA amounts decreases the effective concentrations of TBP.

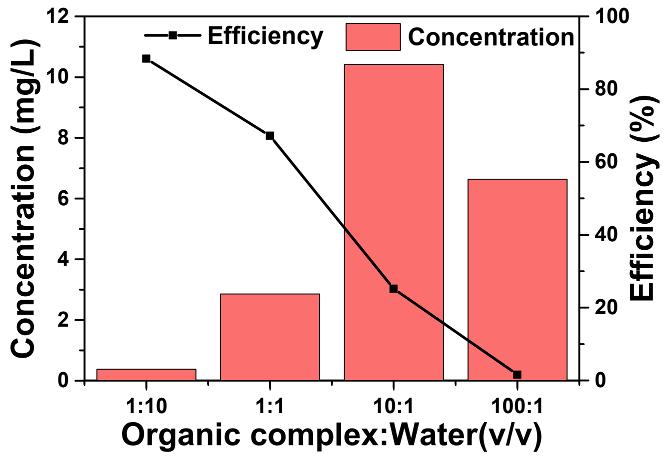

Fig. S5. Neodymium concentrations in stripping solutions, and stripping efficiency at different TBP-HNO_3: 1% HNO_3 volume ratios.

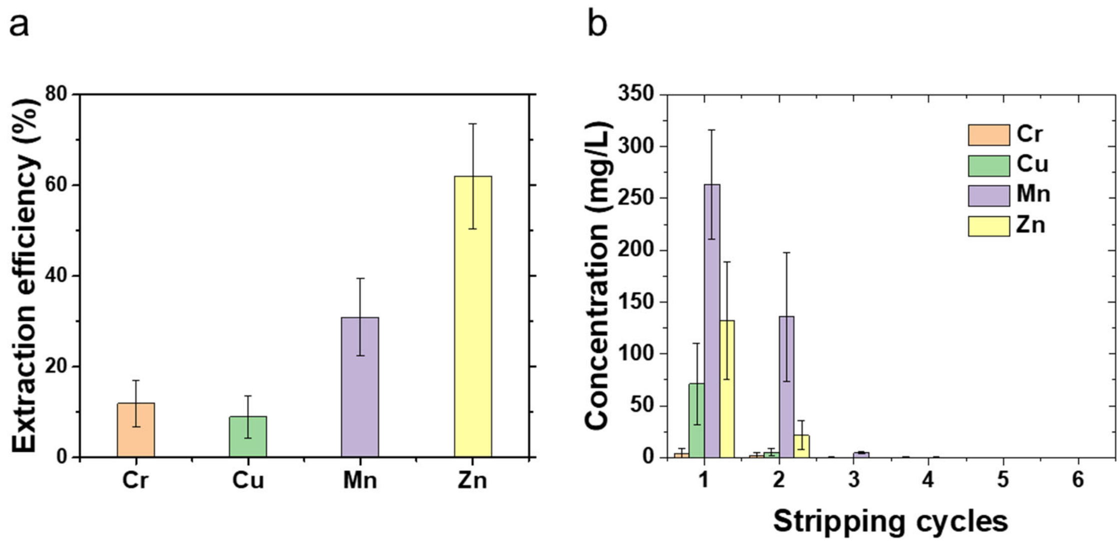

Fig. S6. Extraction and stripping results for representative heavy metals (Cr, Cu, Mn, and Zn) in CFA. **a**, Extraction efficiency of heavy metals from CFA using $scCO_2$ and TBP-HNO_3. **b,** Concentrations of heavy metals in stripping solutions from different stripping stages. Error bars represent the standard deviations of stripping results from triplicate experiments.

Table S1. Major element wt% compositions in CFAs, analyzed by X-ray fluorescence spectroscopy.

Major elements	wt%
K_2O	0.91
CaO	27.49
TiO_2	0.58
MnO	0.20
Fe_2O_3	7.15
Na_2O	0.4
MgO	6.7
Al_2O_3	12.2
SiO_2	23.6
P_2O_5	0.12
Loss on ignition	20.5

Table S2. Minor element concentrations in CFAs, analyzed by X-ray fluorescence spectroscopy.

Minor elements	$mg\cdot kg^{-1}$
Y	36
Sr	2113
Rb	53
Pb	248
Ce	113
Nd	42
La	54
Ba	5917

Table S3. Overview of studies on supercritical fluid extraction of REEs using TBP-HNO_3

Ref	REE source	Condition		Extraction efficiency (%)
		Temperature (°C)	Pressure (bar)	
Tomioka et al. (1998)	Nd_2O_3 Gd_2O_3	40	120, 150	Nd: 51, 45 Gd: 46, 28
Tomioka et al. (2002)	Nd_2O_3 Nd_2O_3–ZrO_2 Nd_2O_3–MoO_3 Nd_2O_3–RuO_2	40	120	Nd: 66.3 50.87 18.69 50.26
Fox et al. (2005)	$Ho(NO_3)_3 \cdot 5H_2O$	35	275-310	Ho: Log K_{ext} = 8.9
Shimizu et al. (2005)	Y, Eu, La, Ce, Tb containing simulated waste fluorescent lamp	60	150	Y: 99.7; Eu: 99.8; La, Ce, Tb < 7
Zhu et al. (2009)	Nd_2O_3	50	150-300	Nd:96
Vincent et al. (2009)	Nd_2O_3	50	350	Nd: 65
Wuhua et al. (2010)	Nd_2O_3 CeO_2	50 40-60	150 210	Nd: 95 Ce < 1
Baek et al. (2016)	Y, Ce, Eu, Tb, Dy oxides	65	345	Y: 99, Ce: 0.12, Eu: 99, Tb: 92.1, Dy: 98.5
Samsonov et al. (2016)	Phosphogypsum	45	203	La: 60.7, Ce: 28.7, Pr: 60.5, Nd, 62.4, Sm: 58.2, Eu: 88.0, Gd: 60.5, Tb: 57.5, Dy: 57.6, Ho: 59.5, Er: 52.7, Tm: 55.0, Yb: 45.9, Lu: 46.1
Sinclair et al. (2017)	Bastnaesite	65	340	La: 3, Ce: 100, Pr: 99, Nd: 100
Yao et al. (2018)	Nickel metal hydride battery	35-55	207-310	La: 30-86, Ce: 45-86, Pr: 56-88, Nd: 45-90
Zhang et al. (2018)	NdFeB magnet	35-55	207-310	Nd: 61.1-94.8, Dy: 74.8-100, Pr: 56.6-94.2
This work	Coal fly ash	50	150	Sc: 71.7, Y: 76.2, La: 65.8, Ce: 68.6, Pr: 72.5, Nd, 73.2, Sm: 76.8, Eu: 73.0, Gd: 78.7, Tb: 78.4, Dy: 78.2, Ho: 77.1, Er: 76.2, Tm: 73.9, Yb: 73.9, Lu: 72.0

Table S4. For $scCO_2$ extraction products, the concentrations of majority impurities (Ca, Fe, Mg, Al, Si) and total REEs in the stripping solutions collected from the first stage through the tenth stage of the stripping process. The REEs' purity was calculated by Eq. 2 in the main text for each collected stripping solution. (Triplicate experiments; standard errors were within 10%).

Stage	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
Ca ($mg \cdot L^{-1}$)	18890.8	9620.0	1206.0	246.6	138.6	74.2	33.4	18.9	14.9	8.3
Fe ($mg \cdot L^{-1}$)	20693.9	13136.6	492.5	313.8	200.2	132.6	34.5	27.8	25.9	20.9
Mg ($mg \cdot L^{-1}$)	626.2	83.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al ($mg \cdot L^{-1}$)	174.5	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Si ($mg \cdot L^{-1}$)	0	0	0	0	0	0	0	0	0	0
REEs ($mg \cdot L^{-1}$)	33.3	31.8	26.9	21.4	16.1	11.4	6.4	3.9	4.4	3.2
REEs purity (%)	0.1	0.2	1.4	3.4	6.5	6.3	7.2	5.7	7.0	6.0

Table S5. For heating only extraction products, the concentrations of majority impurities (Ca, Fe, Mg, Al, Si) and total REEs in the stripping solutions collected from the first stage through the tenth stage of the stripping process. The REEs' purity was calculated by Eq. 2 in the main text for each collected stripping solution. (Triplicate experiments; standard errors were within 10%).

Stage	***1***	***2***	***3***	***4***	***5***	***6***
Ca ($mg \cdot L^{-1}$)	52666.1	13242.9	3947.3	590.3	255.4	145.6
Fe ($mg \cdot L^{-1}$)	15752.6	11655.6	3786.0	734.1	428.3	604.3
Mg ($mg \cdot L^{-1}$)	15561.3	350.1	95.3	9.7	1.6	0.8
Al ($mg \cdot L^{-1}$)	8820.6	1781.8	611.8	152.8	80.8	77.2
Si ($mg \cdot L^{-1}$)	0.0	0.0	0.0	0.0	0.0	0.0
REEs ($mg \cdot L^{-1}$)	14.8	33.8	33.1	21.7	21.2	15.9
REEs purity (%)	0.0	0.1	0.3	1.1	1.9	1.3

Table S6. For the scN_2 extraction products, the concentrations of majority impurities (Ca, Fe, Mg, Al, Si) and total REEs in the stripping solutions collected from the first stage through the tenth stage of the stripping process. The REEs purity was calculated by Eq. 2 in the main text for each collected stripping solution. (Triplicate experiments; standard errors were within 10%).

Stage	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
Ca ($mg\cdot L^{-1}$)	45398.4	8056.2	1634.3	291.2	38.2	25.0	5.2	1.1	2.4	1.2
Fe ($mg\cdot L^{-1}$)	24101.3	7965.5	2187.6	400.2	151.1	92.3	43.8	16.4	25.2	17.5
Mg ($mg\cdot L^{-1}$)	5988.8	435.2	10.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al ($mg\cdot L^{-1}$)	1011.1	348.6	15.1	7.4	0.0	0.0	0.0	0.0	0.0	0.0
Si ($mg\cdot L^{-1}$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
REEs ($mg\cdot L^{-1}$)	23.8	35.4	33.8	25.2	16.7	11.7	6.4	2.2	4.7	2.8
REEs purity (%)	0.0	0.2	0.9	3.4	8.0	8.9	8.0	4.8	8.5	6.2

Table S7. For scAir extraction products, the concentrations of majority impurities (Ca, Fe, Mg, Al, Si) and total REEs in the stripping solutions collected from the first stage through the tenth stage of the stripping process. The REEs purity was calculated by Eq. 2 in the main text for each collected stripping solution. (Triplicate experiments; standard errors were within 10%).

Stage	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***
Ca ($mg\cdot L^{-1}$)	38356.7	7676.1	1901.3	149.0	104.5	96.7	2.4	0.0	0.0	0.0
Fe ($mg\cdot L^{-1}$)	20943.5	8224.8	1808.4	317.1	200.3	229.6	121.0	97.6	65.4	51.6
Mg ($mg\cdot L^{-1}$)	6272.0	280.1	6.1	1.0	0.0	0.0	0.0	0.0	0.0	0.0
Al ($mg\cdot L^{-1}$)	2294.6	188.5	23.7	2.1	0.5	0.3	0.0	0.0	0.0	0.0
Si ($mg\cdot L^{-1}$)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
REEs ($mg\cdot L^{-1}$)	23.0	29.1	25.3	13.9	13.4	9.9	5.3	5.6	3.5	2.3
REEs purity (%)	0.0	0.2	0.9	3.5	4.1	2.8	3.8	4.8	3.5	2.9

Table S8. Total impurity concentrations in the ten-stage stripping solution under different supercritical states of CO_2, N_2, air, and their mixtures and the heating-only condition. (Triplicate experiments; standard errors were within 10%).

Pressure (bar)	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	Al (mg/L)
150 N_2	55443.4	34897.9	6434.1	1382.1
120 N_2	55609.0	37960.6	9805.0	1847.0
150 Air	48286.8	32059.3	6559.2	2509.8
120 N_2 + 30 CO_2	41830.9	30338.4	5203.8	783.8
150 CO_2	30251.5	35603.8	709.3	177.56
Heat + 1 bar atmosphere	70847.6	32960.8	16018.8	11524.9