SUPPLEMENTARY MATERIAL

Recovery of Rare Earth Elements from Coal Fly and Bottom Ashes by Ultrasonic Roasting Followed by Microwave Leaching

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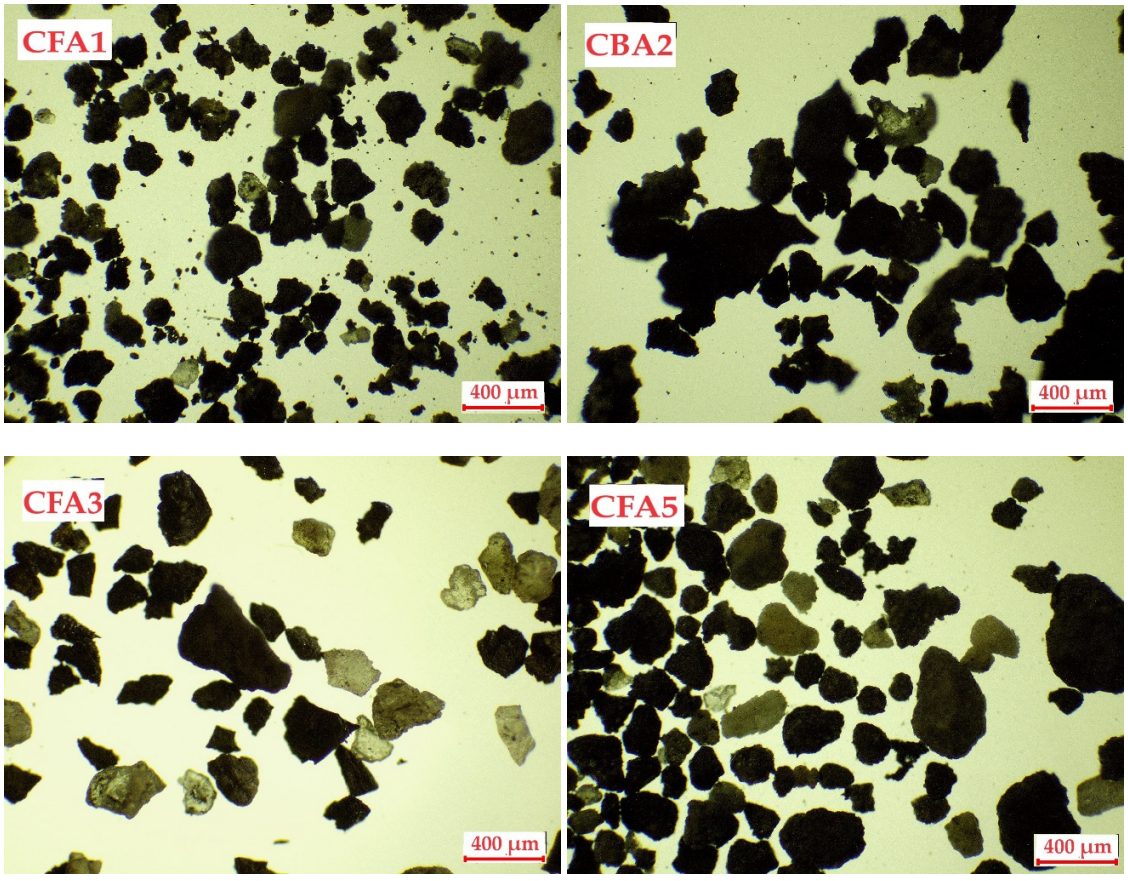
Table S1. Plackett–Burman design for screening set of experiments

No. of exp.	base	V_b, mL	T_b, °C	C_b, M	t_b, min	acid	V_a, mL	T_a, °C	Ca, M	t_a, min	H
1	NaOH	1	95	10	60	HCl	30	95	1	60	US
2	CaO	1	95	1	10	HCl	30	95	10	10	MW
3	CaO	5	25	10	60	HCl	30	25	1	10	MW
4	NaOH	5	25	1	10	HNO_3	30	95	1	60	MW
5	CaO	5	95	1	60	HNO_3	10	95	1	10	US
6	NaOH	1	25	10	60	HNO_3	10	95	10	10	MW
7	NaOH	5	95	1	60	HCl	10	25	10	60	MW
8	CaO	1	25	1	60	HNO_3	30	25	10	60	US
9	NaOH	5	95	10	10	HNO_3	30	25	10	10	US
10	NaOH	1	25	1	10	HCl	10	25	1	10	US
11	CaO	5	25	10	10	HCl	10	95	10	60	US
12	CaO	1	95	10	10	HNO_3	10	25	1	60	MW

Table S2. Box–Behnken design for response surface methodology set of experiments

No. of experiment	T, °C	t, min	acid*
1	90	10	0.5
2	90	30	0
3	140	50	0
4	140	30	0.5
5	140	50	1
6	140	30	0.5
7	90	50	0.5
8	190	50	0.5
9	190	30	0
10	140	10	1
11	190	10	0.5
12	140	30	0.5
13	190	30	1
14	140	10	0
15	90	30	1

* - acid is the share of HNO_3 in the HCl:HNO_3 mixture



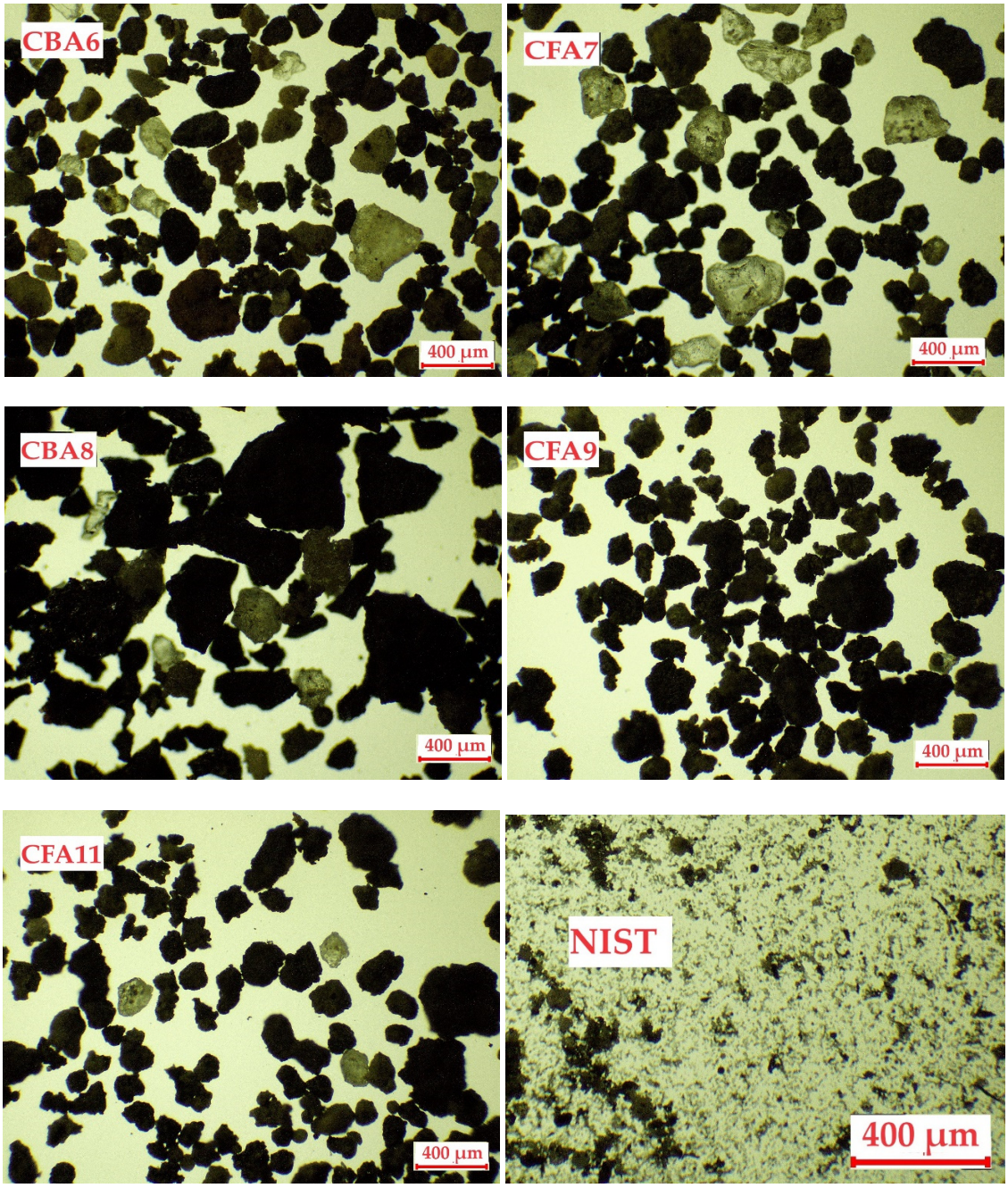


Figure S1. Microscopic images of coal fly and bottom ashes

Table S3. The D50 and D90 values for the studied coal ash samples (μm)

	CFA1	CBA2	CFA3	CFA4	CFA5	CBA6	CFA7	CBA8	CFA9	CBA10	CFA11
D50	114	209	164	232	164	190	190	282	209	232	171
D90	246	390	246	339	325	325	325	664	339	420	282

Table S4. Total REE content in studied fly and bottom coal ashes after alkaline fusion (mg kg^{-1})

	CFA1	CBA2	CFA3	CFA4	CFA5	CBA6	CFA7	CBA8	CFA9	CBA10	CFA11	NIST
Ce	56.7	37.9	31.0	105	71.3	64.0	100	53.1	88.4	61.3	79.1	139
Dy	2.8	2.2	2.0	6.0	3.4	2.7	4.8	2.5	5.2	2.5	3.4	11.2
Er	1.5	1.2	0.9	2.9	1.8	1.4	2.4	1.3	2.7	1.2	1.7	6.0
Eu	0.6	0.4	0.6	1.7	0.9	0.6	1.4	0.8	1.4	0.7	1.0	3.1
Gd	3.2	2.3	2.6	7.4	4.3	3.3	6.2	3.2	6.2	3.3	4.2	12.9
Ho	0.4	0.3	0.4	1.0	0.5	0.3	0.8	0.5	0.9	0.4	0.5	2.3
La	23.2	16.7	13.1	57.2	34.5	28.1	57.2	26.2	51.5	31.8	40.5	74.3
Lu	0.2	0.1	0.1	0.3	0.2	0.2	0.3	0.2	0.2	0.2	0.3	0.5
Nd	17.1	12.8	13.0	41.3	24.1	19.7	37.5	18.1	35.2	19.6	26.3	61.4
Pr	5.2	3.9	2.8	13.0	7.5	6.0	12.3	5.8	11.1	6.3	8.4	19.1
Sc	18.6	12.2	6.0	20.7	14.8	12.8	23.2	9.1	19.8	10.9	15.0	32.5
Sm	3.4	2.5	2.8	8.1	4.6	3.7	7.1	3.6	6.9	3.6	4.9	13.1
Tb	0.3	0.2	0.4	1.0	0.4	0.3	0.7	0.5	0.8	0.4	0.5	2.0
Tm	0.2	0.1	0.2	0.4	0.2	0.2	0.5	0.3	0.3	0.3	0.4	0.9
Y	16.8	13.4	7.2	31.9	19.7	16.5	25.9	12.2	29.2	12.7	18.8	65.1
Yb	1.3	1.1	0.5	2.4	1.5	1.2	2.0	1.1	2.2	0.9	1.4	4.9

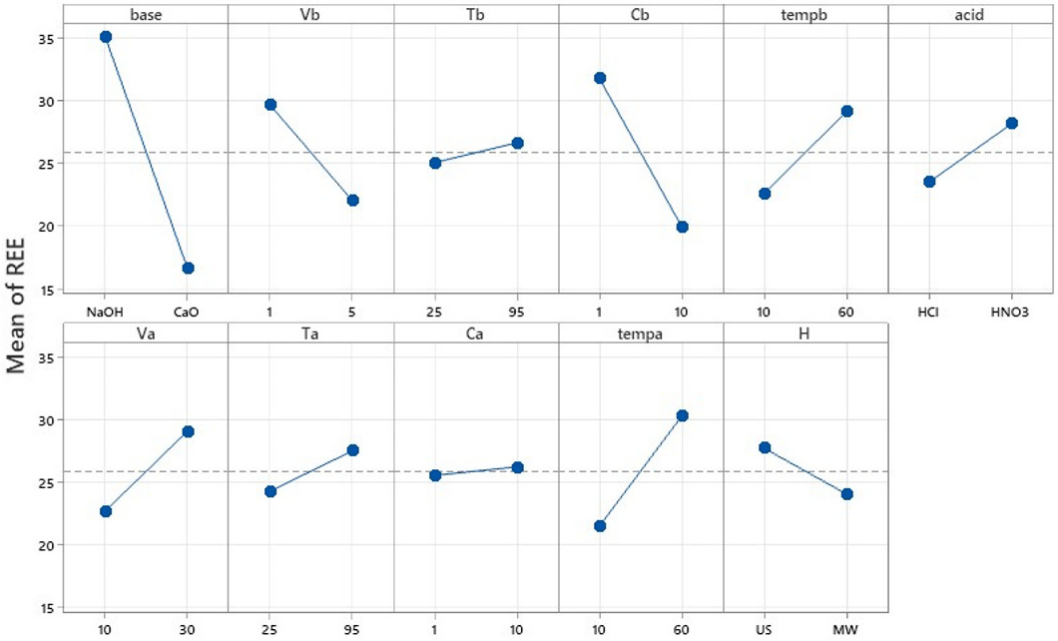


Figure S2. Main plot analyses for screening experiments (response is REE content, mg kg^{-1})

Table S5. REE content recovered from fly and bottom coal ashes (mg kg^{-1})

	CFA1	CBA2	CFA3	CFA4	CFA5	CBA6	CFA7	CBA8	CFA9	CBA10	CFA11	NIST
Ce	37.5	20	26.5	98.5	55.5	41.7	94.3	41.4	74.3	42.8	63.9	123
Dy	2.75	1.54	1.76	5.61	2.97	2.31	4.62	2.75	4.4	2.2	3.52	10.9
Er	1.44	0.81	0.81	2.43	1.44	1.08	2.16	1.26	2.07	0.99	1.62	5.13
Eu	0.64	0.41	0.39	1.52	0.96	0.64	1.28	0.72	1.12	0.64	0.96	2.48
Gd	3.15	1.71	2.07	7.65	3.87	2.97	6.3	3.51	5.49	3.15	4.59	12.0
Ho	0.41	0.24	0.24	0.80	0.42	0.32	0.64	0.40	0.64	0.32	0.49	1.6
La	16.1	8.58	12.1	44.9	25.1	19.0	42.9	18.7	34.5	20.3	29.8	50.0
Lu	0.18	0.09	0.09	0.27	0.18	0.18	0.27	0.18	0.21	0.09	0.18	0.56
Nd	15.7	8.28	10.5	39.6	22.5	16.7	37.3	16.8	30.3	16.6	25.7	56.2
Pr	3.96	2.16	2.79	10.5	5.85	4.41	10.1	4.41	7.92	4.5	6.93	13.8
Sc	14.8	7.65	5.49	19.6	13.3	11.3	19.8	8.82	16.5	9.0	14.2	21.1
Sm	3.33	1.8	2.16	8.01	4.41	3.33	7.38	3.33	6.12	3.24	5.13	13.0
Tb	0.35	0.16	0.24	0.8	0.4	0.32	0.64	0.4	0.64	0.32	0.48	1.44
Tm	0.18	0.09	0.09	0.36	0.18	0.18	0.27	0.18	0.27	0.18	0.27	0.72
Y	13.8	8.19	7.92	25.2	15.7	11.6	24.5	12.1	22.9	10.9	18.6	61.7
Yb	1.2	0.72	0.49	1.76	1.2	0.88	1.84	0.88	1.76	0.8	1.36	4.0

Table S6. Green metrics for initial (i) and final (f) sets of experiments

Sample	E-factor$_i$	Atom economy$_i$, %	Energy consumption$_i$, Wh	E-factor$_f$	Atom economy$_f$, %	Energy consumption$_f$, Wh
CFA1	54.9	1.82	785	66.2	1.49	963
CBA2	594	0.17	625	123	0.81	963
CFA3	2398	0.04	25	104	0.95	963
CFA4	72.7	1.37	1800	28.0	3.45	963
CFA5	92.6	1.08	468	49.3	1.99	963
CBA6	254	0.39	325	65.3	1.51	963
CFA7	131	0.76	1825	29.5	3.28	963
CBA8	508	0.20	385	65.9	1.50	963
CFA9	891	0.11	118	36.1	2.70	963
CBA10	48.1	2.18	85	65.9	1.50	963
CFA11	1706	0.06	435	42.6	2.29	963
NIST	185	0.54	325	19.5	4.87	963