Supplementary Information

Mitigating heavy metals leachability from CO_2 carbonated coal-based solid waste backfill in high-salinity environments via biochar-clay-nanomaterial synergistic modification

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Table S1. Quality Control parameters and limits of detection/quantification for target elements analyzed by ICP-MS

Element	Calibration Range (µg/L)	Standard Series (µg/L)	Calibration Linearity (R^2)	LOD (µg/L)	LOQ (µg/L)	Internal Standard	IS Recovery Range (%)
Cr	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.11	0.44	^{103}Rh	100.8 - 106.7
Ni	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.06	0.24	^{103}Rh	100.8 - 106.7
Cu	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.08	0.32	^{103}Rh	100.8 - 106.7
Zn	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.67	2.68	^{103}Rh	100.8 - 106.7
As	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.12	0.48	^{103}Rh	100.8 - 106.7
Cd	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.05	0.20	^{185}Re	85.0 - 102.3
Pb	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.09	0.36	^{185}Re	85.0 - 102.3
Be	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.04	0.16	^{103}Rh	100.8 - 106.7
Ag	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.04	0.16	^{185}Re	85.0 - 102.3
Mn	0 - 500	0, 5, 10, 20, 50, 100, 200, 500	> 0.999	0.12	0.48	^{103}Rh	100.8 - 106.7

Table S2. Comparison of TCLP leaching results for the raw materials and modified CCB with III-GQS and IV-GQS

Sample	Heavy metals	Concentration (μg/L)	III-GQS (μg/L)	Results	Met?	IV-GQS (μg/L)	Results	Met?
FA	Cr	1002.57	50	↑	No	100	↑	No
	Ni	151.07	20	↑	No	100	↑	No
	Cu	529.61	1000	↓	Yes	1500	↓	Yes
	Zn	796.85	1000	↓	Yes	5000	↓	Yes
	As	181.16	10	↑	No	50	↑	No
	Cd	2.88	5	↓	Yes	10	↓	Yes
	Pb	30.17	10	↑	No	100	↓	Yes
	Be	22.43	2	↑	No	60	↓	Yes
	Ag	1.19	50	↓	Yes	100	↓	Yes
	Mn	1910.14	100	↑	No	1500	↑	No
SG	Cr	14.98	50	↓	Yes	100	↓	Yes
	Ni	4.32	20	↓	Yes	100	↓	Yes
	Cu	14.23	1000	↓	Yes	1500	↓	Yes
	Zn	19.84	1000	↓	Yes	5000	↓	Yes
	As	2.46	10	↓	Yes	50	↓	Yes
	Cd	0	5	↓	Yes	10	↓	Yes
	Pb	6.26	10	↓	Yes	100	↓	Yes
	Be	0.16	2	↓	Yes	60	↓	Yes
	Ag	2239.39	50	↑	No	100	↑	No
	Mn	7613.53	100	↑	No	1500	↑	No
CCB	Cr	144.47	50	↑	No	100	↑	No
	Ni	93.22	20	↑	No	100	↓	Yes
	Cu	59.49	1000	↓	Yes	1500	↓	Yes
	Zn	81.00	1000	↓	Yes	5000	↓	Yes
	As	27.80	10	↑	No	50	↓	Yes
	Cd	1.61	5	↓	Yes	10	↓	Yes
	Pb	18.46	10	↑	No	100	↓	Yes
	Be	5.11	2	↑	No	60	↓	Yes
	Ag	24.74	50	↓	Yes	100	↓	Yes
	Mn	2726.46	100	↑	No	1500	↑	No
CCB-R	Cr	33.07	50	↓	Yes	100	↓	Yes
	Ni	59.18	20	↑	No	100	↓	Yes
	Cu	31.72	1000	↓	Yes	1500	↓	Yes
	Zn	72.89	1000	↓	Yes	5000	↓	Yes
	As	34.42	10	↑	No	50	↓	Yes
	Cd	1.33	5	↓	Yes	10	↓	Yes
	Pb	14.73	10	↑	No	100	↓	Yes

	Be	4.41	2	↑	No	60	↓	Yes
	Ag	0.81	50	↓	Yes	100	↓	Yes
	Mn	2030.73	100	↑	No	1500	↑	No
CCB-N	Cr	17.81	50	↓	Yes	100	↓	Yes
	Ni	60.67	20	↑	No	100	↓	Yes
	Cu	18.76	1000	↓	Yes	1500	↓	Yes
	Zn	51.74	1000	↓	Yes	5000	↓	Yes
	As	20.10	10	↑	No	50	↓	Yes
	Cd	1.12	5	↓	Yes	10	↓	Yes
	Pb	10.94	10	↑	No	100	↓	Yes
	Be	3.74	2	↑	No	60	↓	Yes
	Ag	10.09	50	↓	Yes	100	↓	Yes
	Mn	1232.00	100	↑	No	1500	↓	Yes
CCB-S	Cr	101.22	50	↑	No	100	↑	No
	Ni	23.97	20	↑	No	100	↓	Yes
	Cu	9.39	1000	↓	Yes	1500	↓	Yes
	Zn	8.26	1000	↓	Yes	5000	↓	Yes
	As	18.05	10	↑	No	50	↓	Yes
	Cd	0.03	5	↓	Yes	10	↓	Yes
	Pb	3.38	10	↓	Yes	100	↓	Yes
	Be	0	2	↓	Yes	60	↓	Yes
	Ag	2.93	50	↓	Yes	100	↓	Yes
	Mn	635.95	100	↑	No	1500	↓	Yes
CCB-RN	Cr	21.00	50	↓	Yes	100	↓	Yes
	Ni	57.67	20	↑	No	100	↓	Yes
	Cu	19.52	1000	↓	Yes	1500	↓	Yes
	Zn	49.91	1000	↓	Yes	5000	↓	Yes
	As	21.63	10	↑	No	50	↓	Yes
	Cd	1.08	5	↓	Yes	10	↓	Yes
	Pb	11.10	10	↑	No	100	↓	Yes
	Be	1.53	2	↓	Yes	60	↓	Yes
	Ag	0.82	50	↓	Yes	100	↓	Yes
	Mn	1289.49	100	↑	No	1500	↓	Yes
CCB-RS	Cr	17.03	50	↓	Yes	100	↓	Yes
	Ni	50.46	20	↑	No	100	↓	Yes
	Cu	12.77	1000	↓	Yes	1500	↓	Yes
	Zn	37.56	1000	↓	Yes	5000	↓	Yes
	As	22.66	10	↑	No	50	↓	Yes
	Cd	1.02	5	↓	Yes	10	↓	Yes
	Pb	10.82	10	↑	No	100	↓	Yes
	Be	0.77	2	↓	Yes	60	↓	Yes
	Ag	1.23	50	↓	Yes	100	↓	Yes
	Mn	957.99	100	↑	No	1500	↓	Yes

CCB-Rn	Cr	15.75	50	↓	Yes	100	↓	Yes
	Ni	59.38	20	↑	No	100	↓	Yes
	Cu	12.95	1000	↓	Yes	1500	↓	Yes
	Zn	40.29	1000	↓	Yes	5000	↓	Yes
	As	26.85	10	↑	No	50	↓	Yes
	Cd	1.22	5	↓	Yes	10	↓	Yes
	Pb	10.58	10	↑	No	100	↓	Yes
	Be	0.44	2	↓	Yes	60	↓	Yes
	Ag	1.22	50	↓	Yes	100	↓	Yes
	Mn	1451.47	100	↑	No	1500	↓	Yes
CCB-RNn	Cr	28.13	50	↓	Yes	100	↓	Yes
	Ni	61.94	20	↑	No	100	↓	Yes
	Cu	17.77	1000	↓	Yes	1500	↓	Yes
	Zn	65.93	1000	↓	Yes	5000	↓	Yes
	As	23.95	10	↑	No	50	↓	Yes
	Cd	1.35	5	↓	Yes	10	↓	Yes
	Pb	14.12	10	↑	No	100	↓	Yes
	Be	1.82	2	↓	Yes	60	↓	Yes
	Ag	5.27	50	↓	Yes	100	↓	Yes
	Mn	1437.35	100	↑	No	1500	↓	Yes
CCB-RSn	Cr	21.70	50	↓	Yes	100	↓	Yes
	Ni	52.65	20	↑	No	100	↓	Yes
	Cu	12.47	1000	↓	Yes	1500	↓	Yes
	Zn	36.01	1000	↓	Yes	5000	↓	Yes
	As	20.73	10	↑	No	50	↓	Yes
	Cd	1.13	5	↓	Yes	10	↓	Yes
	Pb	12.63	10	↑	No	100	↓	Yes
	Be	1.45	2	↓	Yes	60	↓	Yes
	Ag	2.55	50	↓	Yes	100	↓	Yes
	Mn	1058.61	100	↑	No	1500	↓	Yes

*Note: The concentrations of Cd in SG, and Cd and Be in CCB-S, were below the limit of detection (LOD).

Table S3. UCS of the modified samples

	CCB	CCB-R	CCB-N	CCB-S	CCB-RN	CCB-RS	CCB-Rn	CCB-RNn	CCB-RSn
Dried	5.70	5.41	5.01	8.64	6.03	6.52	6.27	5.99	7.48
Immer-1	5.08	4.80	4.60	7.32	5.31	5.90	5.76	5.74	6.82
Immer-3	5.62	5.20	5.10	9.03	5.74	6.37	5.83	5.97	7.65
Immer-7	6.44	5.78	5.48	9.17	6.15	6.63	6.47	6.38	7.68
Immer-14	6.65	5.65	5.64	9.79	6.30	6.63	6.53	6.41	7.90
Immer-30	6.80	6.28	6.38	9.99	6.75	6.94	6.75	6.65	7.99
Immer-60	6.01	6.68	5.88	10.07	6.89	7.45	7.26	6.92	8.34

Table S4. Porosity of the modified samples

	CCB	CCB-R	CCB-N	CCB-S	CCB-RN	CCB-RS	CCB-Rn	CCB-RNn	CCB-RSn
Dried	27.16	30.17	30.57	30.97	30.29	30.37	29.80	29.93	30.05
Immer-1	27.62	31.85	32.88	33.25	32.12	32.47	31.55	31.58	31.66
Immer-3	27.36	30.80	31.90	31.96	31.29	31.83	30.38	30.54	30.71
Immer-7	26.24	29.57	29.90	30.20	29.78	29.83	29.31	29.41	29.46
Immer-14	26.01	29.23	29.50	29.83	29.29	29.33	28.57	28.84	29.14
Immer-30	25.23	27.95	28.56	28.80	27.95	27.99	27.19	27.36	27.66
Immer-60	24.68	27.04	27.54	28.09	27.16	27.48	26.72	26.83	26.89

Table S5. The pH change of the solution

	CCB	CCB-R	CCB-N	CCB-S	CCB-RN	CCB-RS	CCB-Rn	CCB-RNn	CCB-RSn	FA	SG
Initial	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.33
Immer-1	9.31	9.23	8.81	9.20	9.36	9.10	9.11	8.83	8.75	9.12	8.65
Immer-3	10.41	10.18	9.87	10.37	10.40	10.40	10.46	10.33	9.89	9.08	9.34
Immer-7	10.67	10.59	10.69	10.66	10.61	10.67	10.64	10.67	10.68	8.74	10.59
Immer-14	9.51	9.45	9.77	9.54	9.64	9.65	9.86	9.51	9.58	8.30	10.76
Immer-30	9.28	9.13	9.35	9.30	9.22	9.32	9.50	9.19	9.20	8.18	10.74
Immer-60	8.70	8.63	8.76	8.79	8.68	8.80	8.82	8.76	8.74	8.12	10.68

Table S6. Percentage reduction in heavy metal leaching across different modified CCB groups

Sample	Results	Cr	Ni	Cu	Zn	As	Cd	Pb	Be	Ag	Mn	Average rate of change
CCB	Concentration (μg/L)	144.47	93.22	59.49	81.00	27.80	1.61	18.46	5.11	24.74	2726.46	/
CCB-R	Concentration (μg/L)	33.07	59.18	31.72	72.89	34.42	1.33	14.73	4.41	0.81	2030.73	/
	Rate of change	-77.11%	-36.51%	-46.68%	-10.01%	23.78%	-17.79%	-20.19%	-13.83%	-96.71%	-25.52%	-32.06%
CCB-N	Concentration (μg/L)	17.81	60.67	18.76	51.74	20.10	1.12	10.94	3.74	10.09	1232.00	/
	Rate of change	-87.68%	-34.92%	-68.46%	-36.13%	-27.69%	-30.72%	-40.74%	-26.95%	-59.20%	-54.81%	-46.73%
CCB-S	Concentration (μg/L)	101.22	23.97	9.39	8.26	18.05	0.03	3.38	0	2.93	635.95	/
	Rate of change	-29.94%	-74.29%	-84.21%	-89.80%	-35.09%	-97.95%	-81.67%	-100.00%	-88.17%	-76.68%	-75.78%
CCB-RN	Concentration (μg/L)	21.00	57.67	19.52	49.91	21.63	1.08	11.10	1.53	0.82	1289.49	/
	Rate of change	-85.46%	-38.13%	-67.19%	-38.37%	-22.21%	-33.15%	-39.84%	-70.03%	-96.69%	-52.70%	-54.38%
CCB-RS	Concentration (μg/L)	17.03	50.46	12.77	37.56	22.66	1.02	10.82	0.77	1.23	957.99	/
	Rate of change	-88.21%	-45.87%	-78.53%	-53.70%	-18.49%	-36.56%	-41.38%	-84.89%	-95.01%	-64.86%	-60.75%
CCB-Rn	Concentration (μg/L)	15.75	59.38	12.95	40.29	26.85	1.22	10.58	0.44	1.22	1451.47	/
	Rate of change	-89.10%	-36.30%	-78.23%	-50.25%	-3.43%	-24.33%	-42.68%	-91.49%	-95.06%	-46.76%	-55.76%
CCB-RNn	Concentration (μg/L)	28.13	61.94	17.77	65.93	23.95	1.35	14.12	1.82	5.27	1437.35	/
	Rate of change	-80.53%	-33.55%	-70.13%	-18.60%	-13.85%	-16.08%	-23.51%	-64.35%	-78.69%	-47.28%	-44.66%
CCB-RSn	Concentration (μg/L)	21.70	52.65	12.47	36.01	20.73	1.13	12.63	1.45	2.55	1058.61	/
	Rate of change	-84.98%	-43.52%	-79.03%	-55.54%	-25.45%	-29.96%	-31.60%	-71.58%	-89.70%	-61.17%	-57.25%

Table S7. Comparison of heavy metal immobilization efficiency with previous works

Application Field	Main Modifiers/ Materials	Target Heavy Metals	Matrix/ Environment	Immobilization / Removal Efficiency	Reference
Soil Remediation	nano-CaO (11.9% mass ratio)	As(III), Cd(II), Pb(II)	Agricultural soil	95% - 99%	[1]
Soil Remediation	nano-$CaCO_3$ (1.48% - 1.88% mass ratio)	Cd(II), Pb(II)	Acidic soils	97% - 100%	[2]
Soil Remediation	Sepiolite (20% dosage)	Pb, Cd	Alkaline soils	35% - 54%	[3, 4]
Soil Remediation	BC-nZVI (100 mg/kg)	As, Cd, Cr(VI)	High-organic soils	95.6% - 99.8%	[5, 6]
Soil Remediation	nZVI (10% mass ratio)	Cr(VI), Pb(II)	Neutral/weakly acidic soils	95% - 95.6%	[7-9]
Soil Remediation	Organic-inorganic composite of chitosan, nanoclay, and biochar (10 mg/mL)	Cu, Pb, Zn	Acidic soils	Cu(II) (100%), Zn(II) (100%), Pb(II) (52.29%)	[10]
Wastewater Treatment	Al_2O_3-supported nano-FeS (30% mass ratio of FeS to Al_2O_3)	Hg(II)	mercury-contaminated water	313 mg/g	[11]
Wastewater Treatment	Sepiolite (25 mg dosage)	Pb(II)	Aqueous solution	105.57 mg/g	[12]
Wastewater Treatment	magnetic halloysite/coconut shell biochar composites (HNTs:CS:Fe_3O_4 = 1:2:9)	Pb(II)	Aqueous solution	833.33 ± 16.71 mg/g	[13]
Wastewater Treatment	Clinoptilolite (0.3g/g-phosphoric acid)	Pb(II)	phosphoric acid medium	91.70%	[14]
Wastewater Treatment	Bismuth-impregnated straw biochar (2 mg/mL)	As(III), Cr(VI)	wastewater pollution	As(III) (16.21 mg/g), Cr(VI) (12.23 mg/g)	[15]
Wastewater Treatment	ZnO/ZnS-modified corn stover biochar (2 mg/mL)	Pb(II), Cu(II), Cr(VI)	heavy metal solution	Pb(II) (135.8 mg/g), Cu(II) (91.2 mg/g), Cr(VI) (24.5 mg/g)	[16]
Wastewater Treatment	$Fe_2O_3 – Al_2O_3$ nanocomposite fiber (2.5 mg/mL)	Cu(II), Ni(II), Pb(II), Hg(II)	heavy metal solution	Cu(II) (21%), Pb(II) (52%), Ni(II) (67%), Hg(II) (89%)	[17]
Solid Waste Backfill	nano-Al_2O_3 (1% mass ratio)	Zn, Pb, Ba, Cr	Backfill	complied with the Class III groundwater standard	[18]

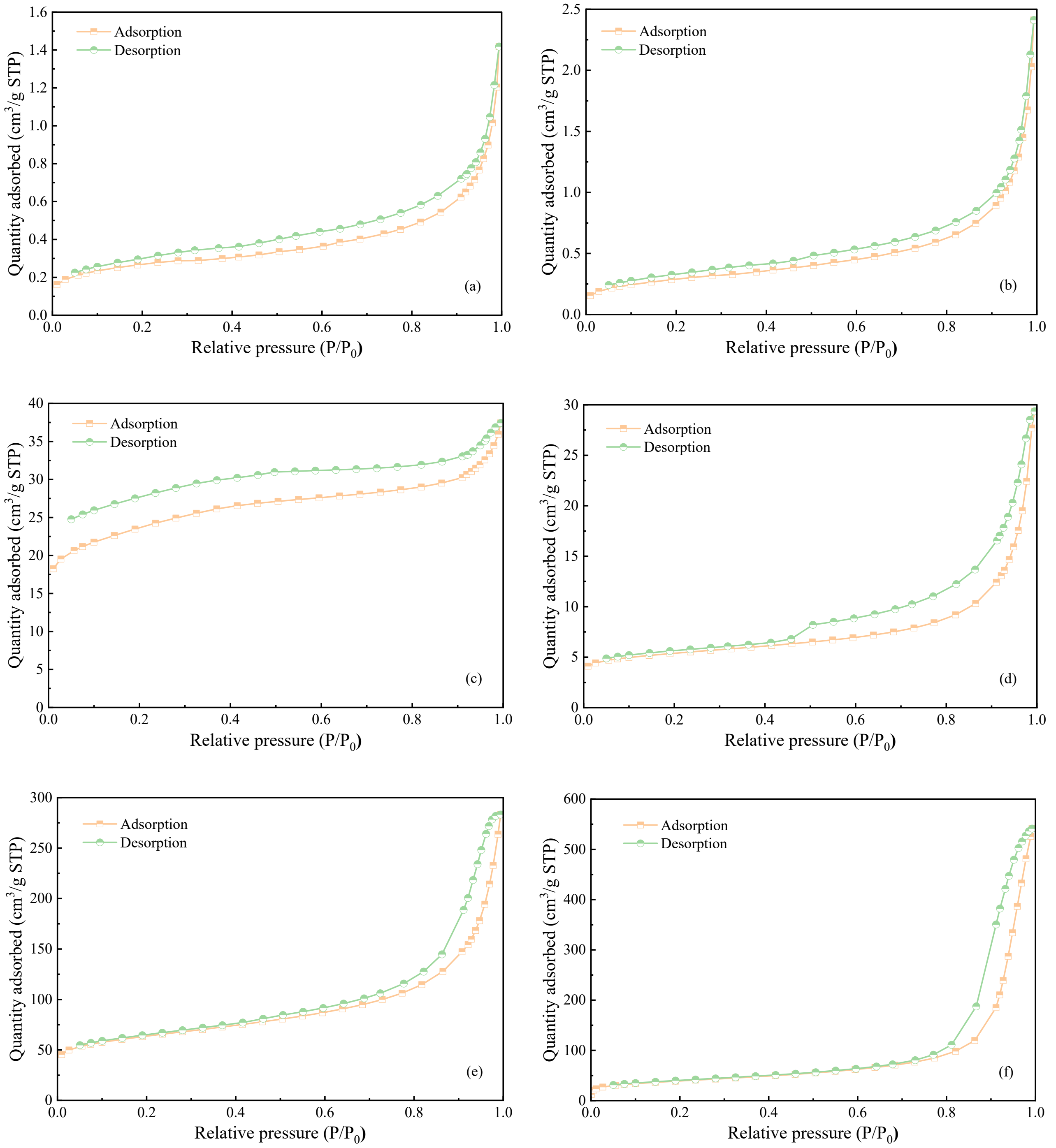

Fig. S1. N_2 adsorption-desorption isotherms of the different materials: (a) FA, (b) SG, (c) RHB, (d) NCP, (e) SEP, and (f) NA

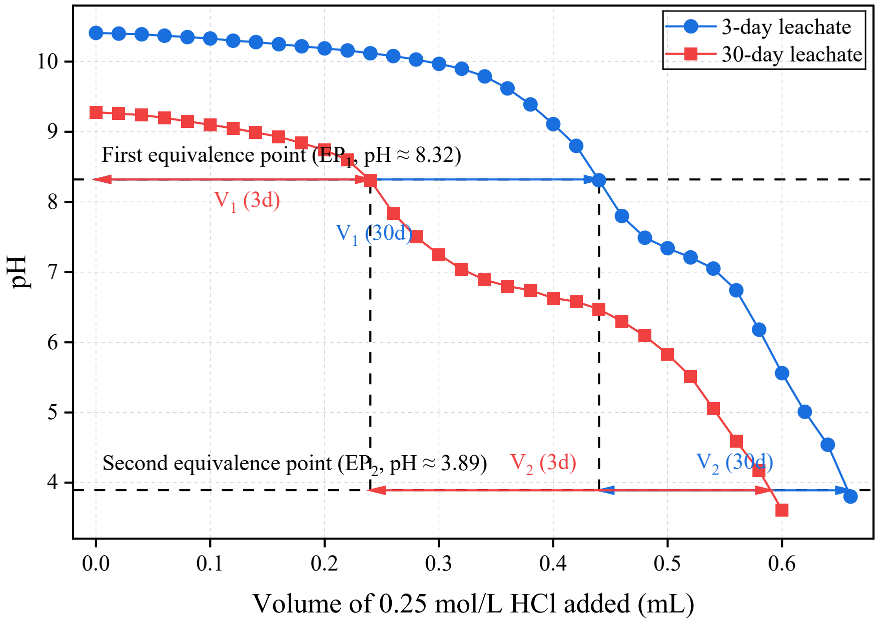

Fig. S2. Acid-base titration curve

Acid-base Titration Experiment and Analysis:

1. Experimental procedure

Acid-base titration experiments were conducted on the CCB leachates after 3 days (initial pH = 10.41) and 30 days (initial pH = 9.28) of soaking. For each group, 100 mL of the leachate was extracted and titrated using a 0.25 mol/L standard HCl solution. The titration was performed in precise increments of 20 μL.

2. Results and analysis

(1) V_1 and the consumption of OH^-: The volume of HCl required to reach the first equivalence point (EP1, pH ≈ 8.32), denoted as V_1, decreased from 0.44 mL (3-day) to 0.24 mL (30-day). This significant decrease in V_1 (approximately 45%) quantitatively demonstrates that the free OH^- in the solution was consumed by the continuous internal hydration and pozzolanic reactions within the matrix.

(2) V_2 and the variation of carbonates: With prolonged soaking time, V_2, which represents the total carbonate content, exhibited only a marginal increase. The volume of HCl consumed increased from 0.22 mL (3-day, corresponding to a carbonate concentration of 0.55 mmol/L) to 0.36 mL (30-day, corresponding to a carbonate concentration of 0.90 mmol/L). If the substantial pH drop from 10.41 to 9.28 were primarily caused by a massive dissolution of external atmospheric CO_2, the increase in V_2 would have been significantly larger. Furthermore, since the slight increase in V_2 could

also be attributed to the weak dissolution of inherent carbonates within the solid material, the actual impact of external CO_2 ingress should be considered more modest.

Based on the physical sealing measures implemented during the experiment and the newly supplemented acid-base titration data, it can be concluded that the decline in pH is primarily attributed to the consumption of OH^- by ongoing hydration reactions, rather than interference from atmospheric CO_2.

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