Supplementary Information for

"Synergistic strategies for defluoridation from $RECl_3$-$AlCl_3$-F complex solution: pH regulation and hydrolysis coprecipitation of aluminum by $Ca_2Al(OH)_6Cl{\cdot}2H_2O$"

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Supporting Information: 19 Pages, 9 Figures, and 6 Tables.

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Part 1.1 Determination of fluorine concentration in solution [1,2]

Determination of the actual response slope S value of the electrode: After the reference electrode, fluoride electrode and ion meter were securely connected, the potential values of standard solutions were measured with varying fluorine concentrations at room temperature (see Table P1). The calibration curve for the actual response slope S value of the electrode was shown in Fig. P1, showing that -lg*c(F)* was directly proportional to the potential (*E*), and it can be seen from Nernst equation that S=58.232.

Measurement procedure: Prepare a known volume of test solution, add 20 ml of total ionic strength adjustment buffer (TISAB) and dilute with deionized water to 50 ml to form the test solution. Measure the initial potential and the potential after the addition of the standard solution. Substitute $\Delta E=E_x-E_1$ into the following formula of the standard addition method to determine the concentration of F in the test solution.

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$$c(F)_x = \frac{n\mathrm{V}_s\mathrm{c(F)_s}}{V_x(10^{\Delta E/S}-1)} \quad (1)$$

Where:

$c(F)_x$ represents the concentration of the test solution, mg/L;

$\mathrm{V_s}$ is the volume of the fluoride standard solution added, mL;

$\mathrm{c(F)_s}$ is the concentration of the fluorine standard solution, mg/L;

V_x is the volume of the test solution, mL;

ΔE is the potential difference, mV;

S is the electrode response slope;

n indicates the dilution ratio.

Table P1. Electrode potential measured at different mass concentrations of F.

C/(mg/L)	0.5	1	5	10	20	50
E/(mV)	254.7	238.1	197.3	180.2	162.6	139.2

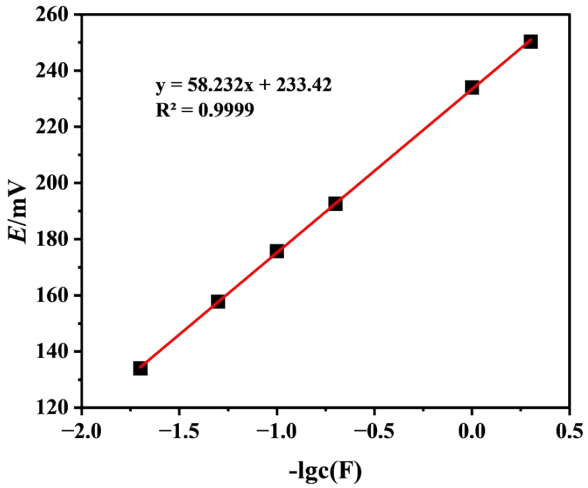

Fig. P1. Calibration curve of the actual response slope (S value) of the electrode.

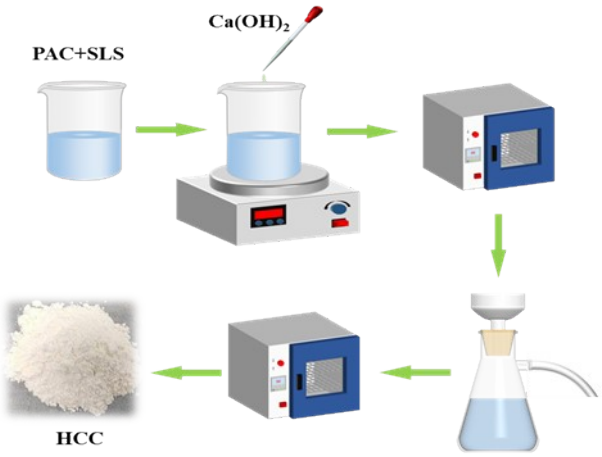

Fig. S1. Schematic flowchart of the synthesis route for HCC ($Ca_2Al(OH)_6Cl{\cdot}2H_2O$).

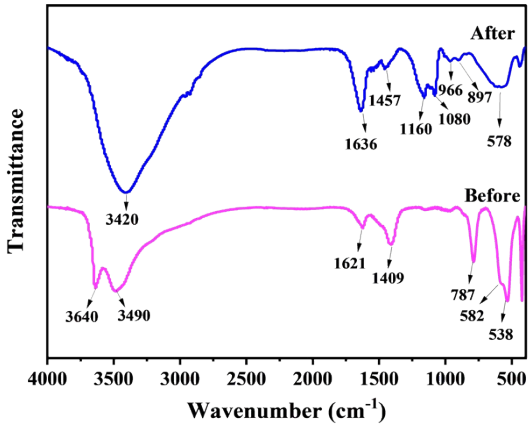

Fig. S2. FTIR spectrum of defluoridant before and after defluoridation.

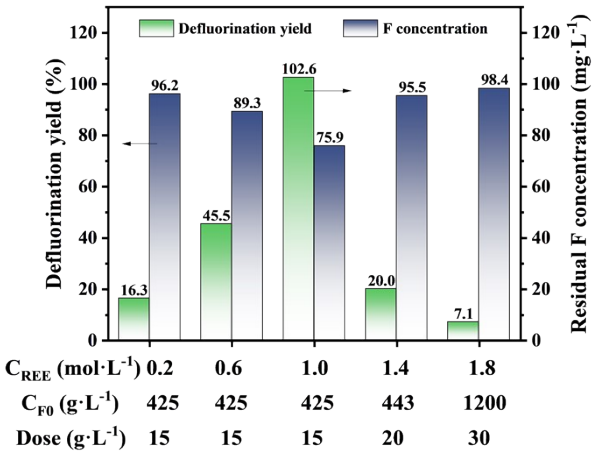

Fig. S3. Influence of REEs and F concentrations on defluoridation process.

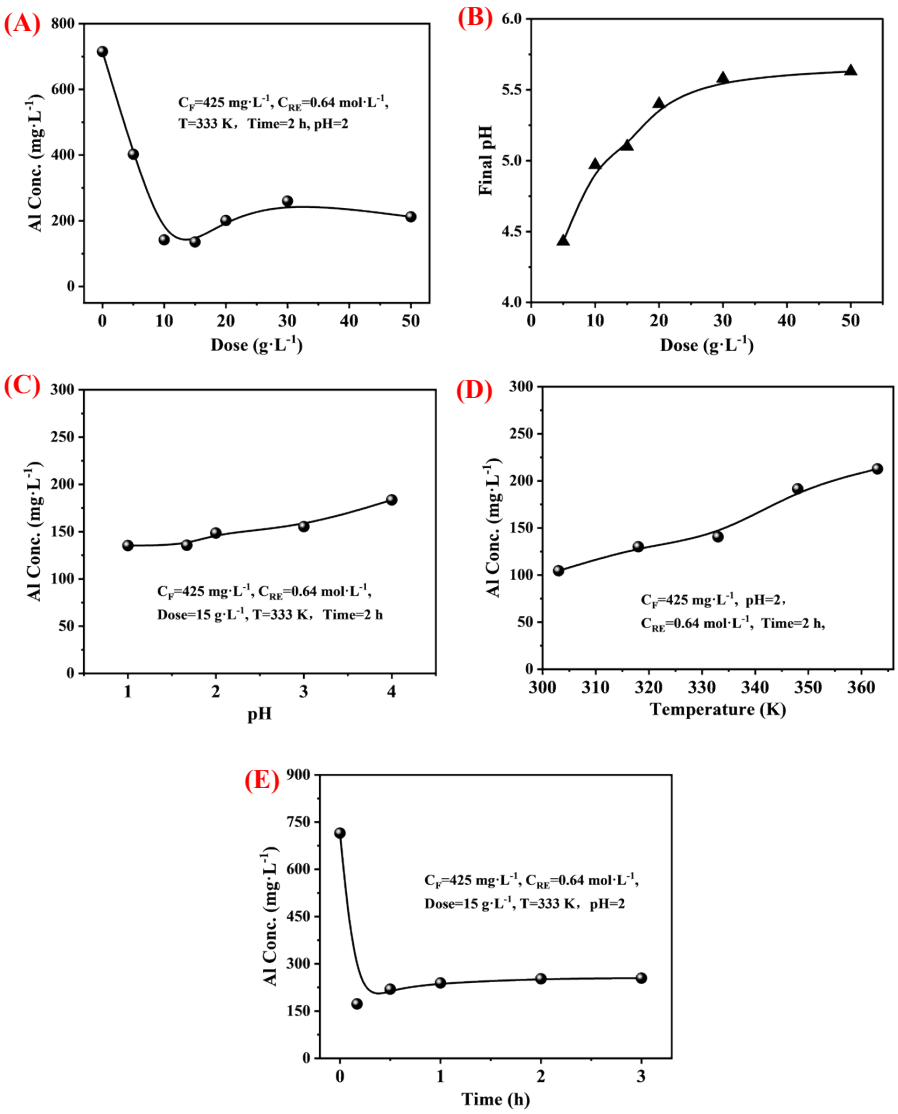

Fig. S4. Influence of factors on impurity Al, **(A)** Dose; **(B)** Dose for final pH; **(C)** Initial pH; **(D)** Temperature; and **(E)** Time.

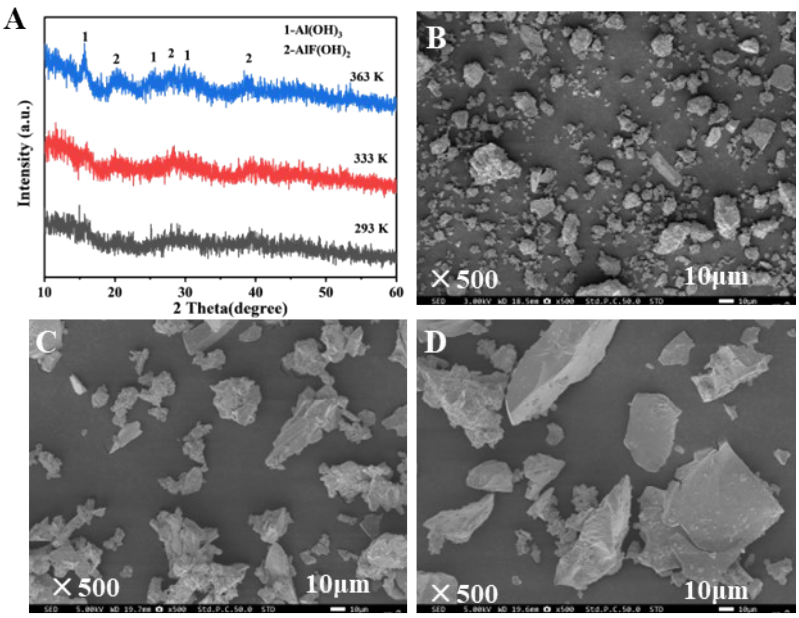

Fig. S5. Effect of temperature on defluoridation residue, **(A)** XRD spectrum. SEM, **(B)** 293K; **(C)** 333K; **(D)** 363K.

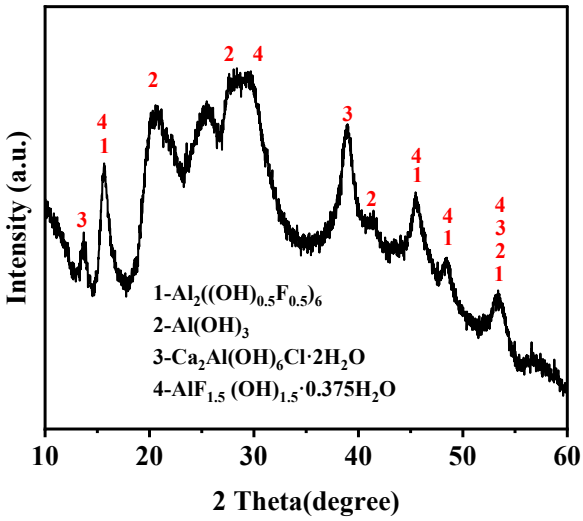

Fig. S6. XRD spectrum of defluorination residue.

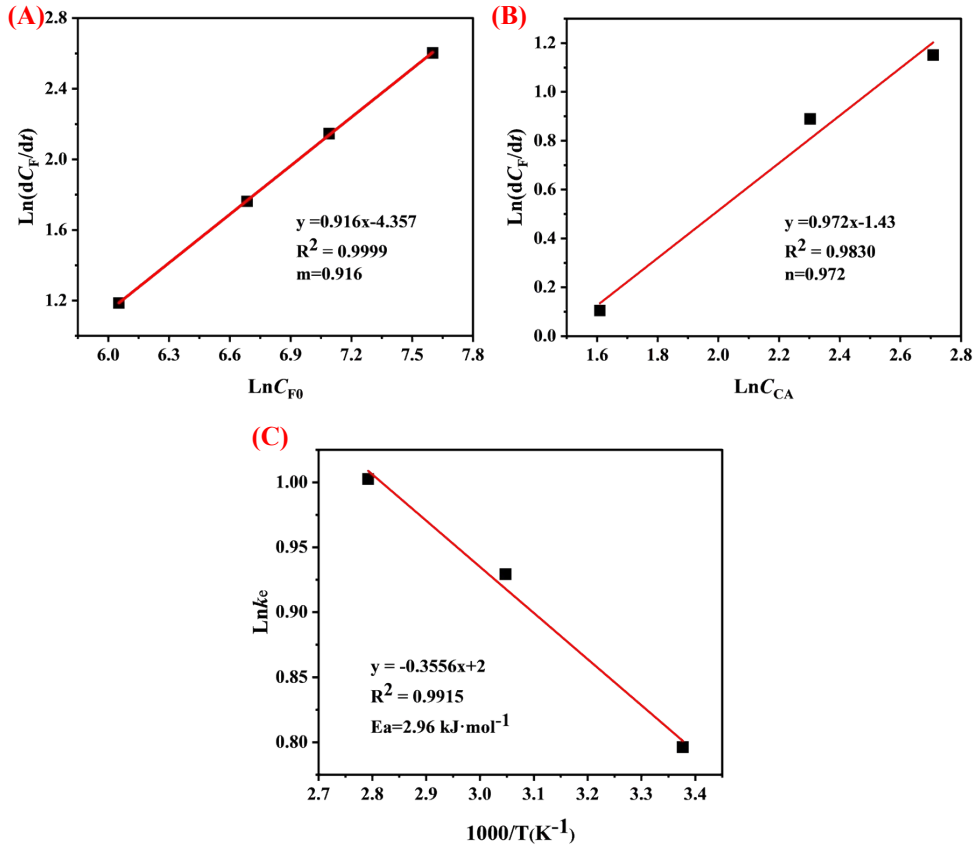

Fig. S7. Kinetic analysis of reaction orders, (A) m; (B) n; (C) lnke-1/T linear regression diagram.

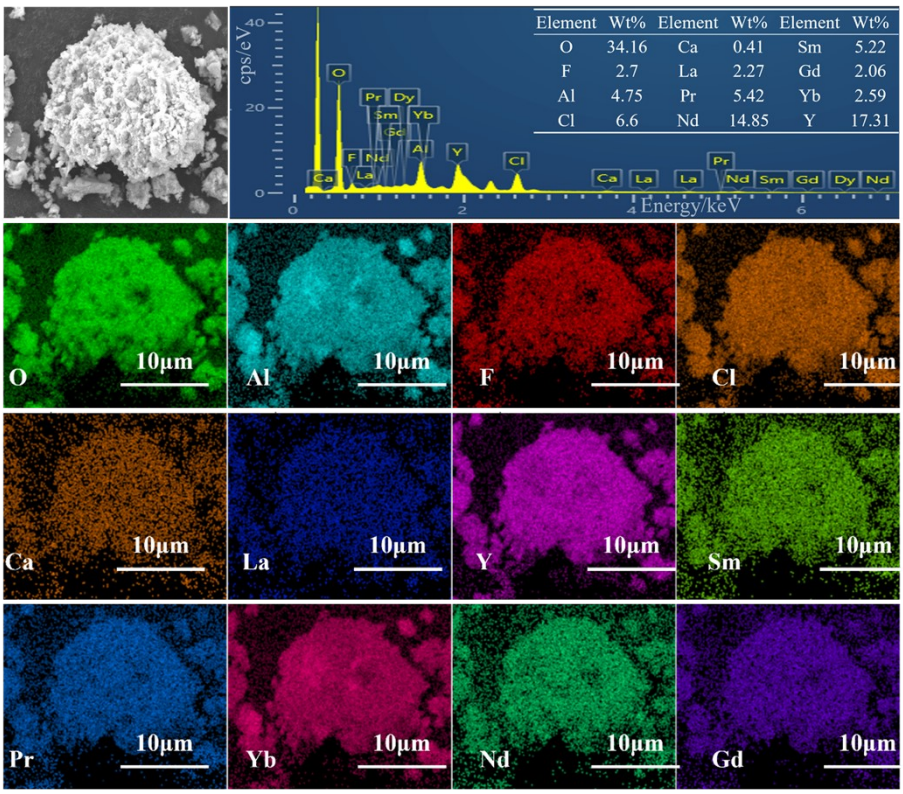

Fig. S8. SEM-EDS analysis of the defluoridation residue.

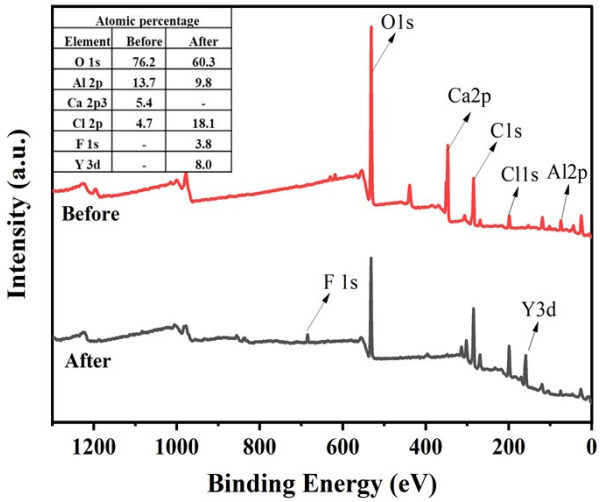

Fig. S9. XPS analysis of survey spectrum of the defluoridant before and after defluorination.

Table S1

XRF results of REO concentrate (TREO, total rare earths)

Components	Al_2O_3	CaO	CeO_2	Dy_2O_3	Er_2O_3	F	Fe_2O_3	Gd_2O_3	Ho_2O_3	K_2O	La_2O_3
Conc. %	1.03	1.31	1.75	4.76	2.64	0.42	0.08	4.37	0.76	0.12	18.76
Components	Nd_2O_3	NiO	Pr_6O_{11}	SiO_2	Sm_2O_3	SO_3	Tb_4O_7	Tm_2O_3	Yb_2O_3	Y_2O_3	TREO
Conc. %	15.67	0.22	4.1	0.07	3.57	2.91	0.83	0.31	2.14	34.09	93.75

Table S2

Major chemical compositions of the defluoridant by XRF.

Components	CaO	A_2O_3	Cl	SiO_2	Fe_2O_3	MgO	SO_3
%	61.60	22.62	11.36	2.61	0.87	0.48	0.28

Table S3

The characterization of the prepared defluoridant.

Defluoridant	BET surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)
$Ca_2Al(OH)_6Cl \cdot 2H_2O$	11.81	0.07	25.46

Table S4

EDS results of initial Al/F ratio on the Al/F ratio in defluoridation residue

Initial Al/F molar ratio		0.5			1.2			
EDS of points		point 1	point 2	point 3	point 4	point 5	point 6	point 7
Al/F molar ratio of defluoridation residue		**0.50**	**0.62**	**1.09**	**1.41**	**1.39**	**1.56**	**1.34**
EDS (wt%)	O	37.75	77.68	48.00	34.48	38.57	41.50	47.74
	F	10.74	2.16	6.24	3.72	3.93	3.91	4.54
	Al	7.69	1.89	9.68	7.48	7.78	8.68	8.66
	others	43.82	18.26	36.08	54.32	49.72	45.91	39.06
Initial Al/F molar ratio		2				3		
EDS of points		point 8	point 9	point 10	point 11	point 12	point 13	point 14	point 15
Al/F molar ratio of defluoridation residue		**1.82**	**1.70**	**2.01**	**2.14**	**2.62**	**3.33**	**4.26**	**8.07**
EDS (wt%)	O	40.78	45.54	50.58	43.44	44.18	41.86	26.97	25.64
	F	3.54	4.43	3.35	3.87	2.29	1.85	0.62	1.41
	Al	9.16	10.73	9.55	11.77	8.53	8.72	3.75	16.16
	others	46.52	39.31	36.53	40.91	45.0	47.57	68.66	56.79

Table S5

Assignments of main spectral bands based on the binding energy and the percentage of atomic.

Atomic species	Before leaching		After leaching		Assignments
	B.E. (eV)	Percent (%)	B.E. (eV)	Percent (%)	
Al2p	73.80	49.4	74.5	43.9	Al-O
	74.32	50.6	75.0	38.2	Al-OH
	-	-	75.7	17.9	Al-F
Total		100		100	
F1s	-	-	684.9	100	Al-F-OH
Total		-		100	
O1s	530.6	19.0	531.0	24.3	Me-O
	531.36	74.5	532.1	68.0	OH
	532.9	6.5	533.4	7.8	H_2O
Total		100		100	

Table S6

Comparative analysis of defluoridation performance of $Ca_2Al(OH)_6Cl{\cdot}2H_2O$ with other materials.

Defluoridant	Hyperhaline solution	Capacity (mg/g)	Conditions	References
$Ca_2Al(OH)_6Cl{\cdot}2H_2O$	$RECl_3$	96.4%*	C_0=425 mg/L, Time=2 h, Dosage=5 g/L, pH=2, T=333 K	This work
Lanthanum carbonate	$RECl_3$	21.2	C_0=570 mg/L, Time=2 h, Dosage=8 wt% (~27 g/L), pH=1, T=363 K	3
CO_2	$RECl_3$	98.9%*	CO_2 injection flow, 1000 L/h; 343 K; initial pH=1; Time=1.5 h	3
Aluminum-based composite	$ZnSO_4$	5.6	C_0=124 mg/L, Dosage=15 g/L, pH=5.1, 323 K, Time=2.5 h	4
Amorphous porous layered-Al_2O_3	$ZnSO_4$	12.1	C_0=120 mg/L, Dosage=10 g/L, pH=5.0, T=313 K, Time=2 h	5
Modified mayenite $Ca_{12}Al_{14}O_{33}$	$NaAlO_2$	36.86	C_0=300 mg/L, Caustic ratio: 1.6, Time=120 min, Dosage=20 g/L, T=353 K	2

* Defluoridation yield. (Since it is not an adsorption process, the adsorption isotherms cannot be obtained, so the fluoride removal yield is provided here.)

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