

SUPPLEMENTARY INFORMATION

Bifluoride ($[\text{HF}_2]^-$) formation at the fluoridated aluminium hydroxide/water interface

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Table S1. Peak binding energies at the gibbsite/water interface.

mL ^a	pH	Na 1s ₁	Na 1s ₂	F 1s ₁	F 1s ₂	O 1s OH	O 1s H ₂ O	Al 2p
Gibbsite in 50 mM NaF + HF								
0	8.65	1071.6(1.7)		684.9(2.0)		532.1(1.6)	533.4(1.8)	74.5(1.5)
0.3	7.92	1071.5(1.5)	1073.3(3.3)	684.9(2.1)	687.6(2.7)	532.0(1.6)	533.3(1.8)	74.5(1.6)
0.64	8.41	1071.6(1.6)	1073.2(3.3)	685.0(2.0)	687.1(3.2)	532.2(1.6)	533.4(1.8)	74.6(1.5)
1.3	8.51	1071.6(1.6)	1073.8(2.9)	685.1(2.1)	687.5(2.7)	532.0(1.6)	533.3(1.8)	74.5(1.5)
0.04 ^b	9.74	1071.4(1.6)		684.8(1.9)		532.2(1.6)	533.4(1.8)	74.6(1.6)
Gibbsite in 50 mM NaF + 1.2 mL (HClO₄ + NaClO₄)^c								
0	7.80	1071.7(1.7)		685.0(2.1)		532.1(1.6)	533.4(1.8)	74.6(1.5)
0.3	8.16	1071.7(1.6)	1073.0(3.0)	685.0(2.0)	687.0(3.6)	532.0(1.6)	533.3(1.8)	74.5(1.4)
0.6	8.07	1071.7(1.6)	1073.6(3.5)	685.1(2.1)	687.9(3.0)	532.2(1.6)	533.5(1.8)	74.6(1.5)
0.9	7.58	1071.7(1.7)	1073.8(3.4)	685.2(2.2)	687.8(3.0)	532.1(1.6)	533.4(1.8)	74.6(1.5)
1.2	7.67	1071.8(1.6)	1073.9(2.6)	685.2(2.0)	687.7(2.5)	532.0(1.6)	533.4(1.8)	74.5(1.3)

Procedure (cf. Section 2.2 of paper): Aqueous suspensions of gibbsite (4.5 g/L) in 50 mM NaF and NaClO₄ were prepared at least two days prior cryogenic XPS measurements. HF, HClO₄ or NaOH were added to 5 mL aliquots of the gibbsite suspension and equilibrated overnight under an atmosphere of water-saturated N₂(g).

Peak binding energies referred to the C 1s peak at 285.0 eV. The peak binding energies of Cl 2p of [ClO₄], 208.8 ± 0.1 eV, are excluded from the table.

Numbers in parentheses indicate the full width at half maximum.

^a volume of acid added.

^b 50 mM NaOH was added instead of the acid.

^d sum of the volumes of HClO₄ and NaClO₄ added are constant at 1.2 mL

Table S2. Peak binding energy of elements in reference materials.

	Na 1s	F 1s ₁	F 1s ₂	C 1s CH	O 1s OH	O 1s H ₂ O	Al 2p
Gibbsite (solid)				285.0(1.7)	531.7(1.6)	533.1(1.8)	74.2(1.5)
Gibbsite (wet) ^a				285.0(1.7)	532.1(1.6)	533.4(1.8)	74.6(1.5)
NaF (140 mM) ^a		684.8(1.7)	686.3(2.3)	285.0(1.2)		533.1(1.4)	
HF ^{a,b}		685.3	686.6				
NaF (solid)	1071.4(1.8)	684.6(1.6)		285.0(1.7)			
Cryolite (solid)	1071.8(1.6)	685.2(1.4)		285.0(1.4)			75.2(1.4)
Na[HF ₂] ^a	1071.5(1.9)	684.3(1.6)	685.7(2.9)	285.0(1.7)			

The peak binding energies are referred to C 1s at 285.0 eV

Numbers in parentheses indicate the full width at half maximum.

^a Gibbsite centrifuged wet (ultrapure water) paste.

^b From Shimizu et al.¹

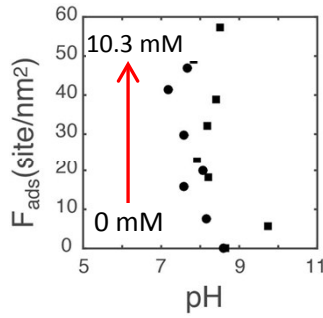


Figure S1. Fluoride removal from aqueous suspensions of gibbsite (4.5 g/L) in 50 mM NaF.

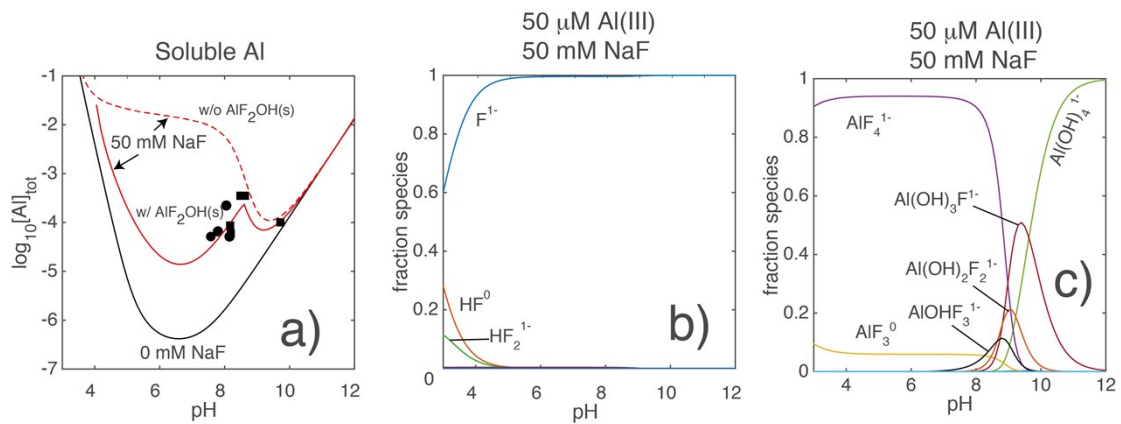


Figure S2. Gibbsite solubility in 0 and 50 mM NaF (a). Fluoride (b) and aluminum (c) speciation in a solution containing 50 μM dissolved Al(III) in 50 mM NaF, showing that F^{1-} is the predominant fluoride species under the conditions of this study. Thermodynamic speciation calculations of the Al(III)-F(I)- H_2O system (298 K, $I=0$), using equations and constants listed in Bodor *et al.*². Values for $\text{Na}_3\text{AlF}_6(\text{s})$ and $\text{AlF}_3(\text{s})$ solubility are taken from Nordin *et al.*³, and the one for $\text{AlF}_2(\text{OH})(\text{s})$ from Ntuk *et al.*⁴. Soluble Al (a) and F (b) show mismatch between classical models and measurements.

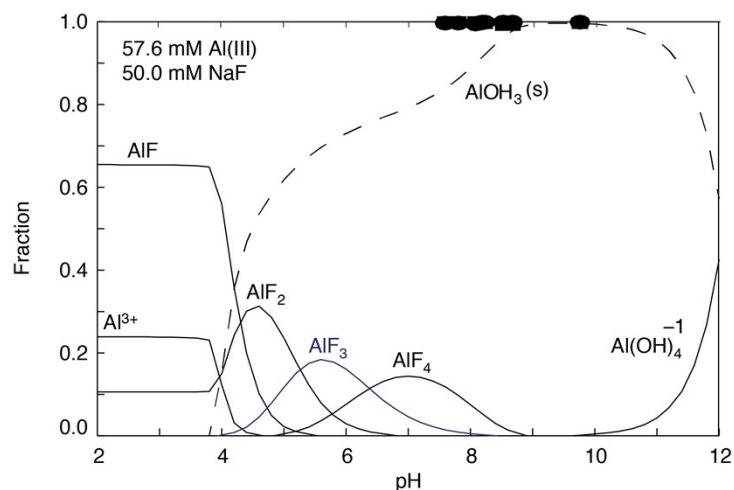


Figure S3. Data points in the pH 7.6-9.7 range correspond to the total insoluble Al in the samples under study. Thermodynamic speciation calculations of the Al(III)-F(I)-H₂O system (298 K, I=0), using equations and constants listed in Bodor *et al.*². Values for Na₃AlF₆(s) and AlF₃(s) solubility are taken from Nordin *et al.*³

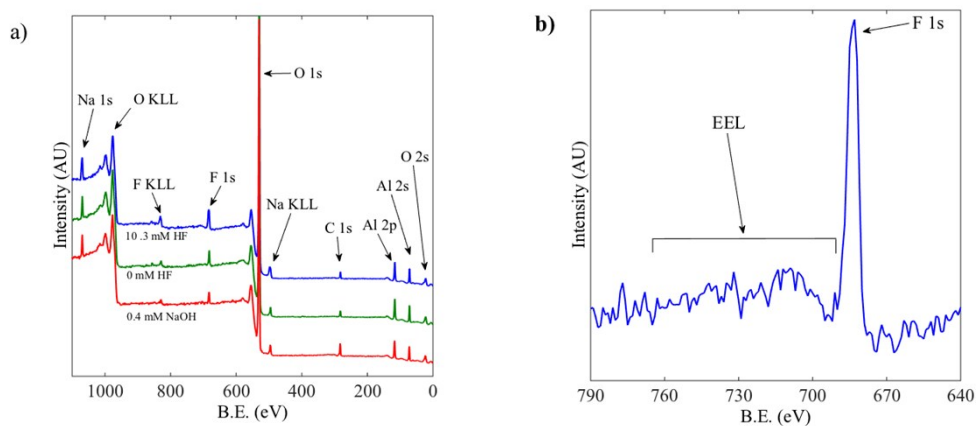


Figure S4. Wide XPS spectra over the entire binding energy range (a) and in the F 1s region of wet gibbsite particles reacted in NaF solutions containing 10.3 mM HF (blue), 0 mM HF (red) and 0.4 mM NaOH (green), and under a constant total ionic strength of 50 mM (Na)F.

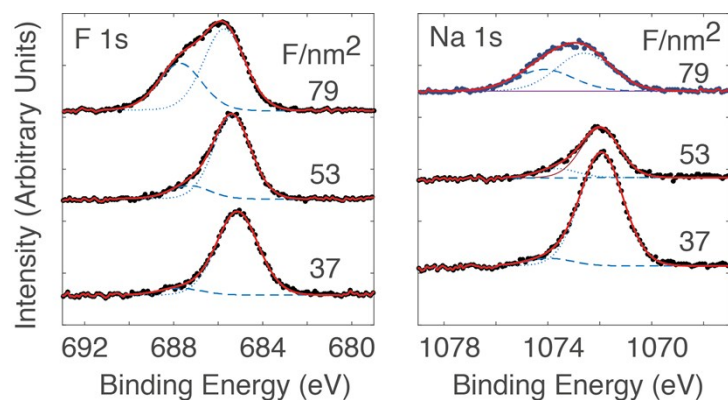


Figure S5. Narrow (left) F 1s and (right) Na 1s regions of wet bayerite particles reacted in NaF solutions at various HF and under a constant total ionic strength of 50 mM (Na)F. Fluoride loadings were derived from ISE measurements. Blue dashed lines are component fits and red full lines total fits to experimental data.

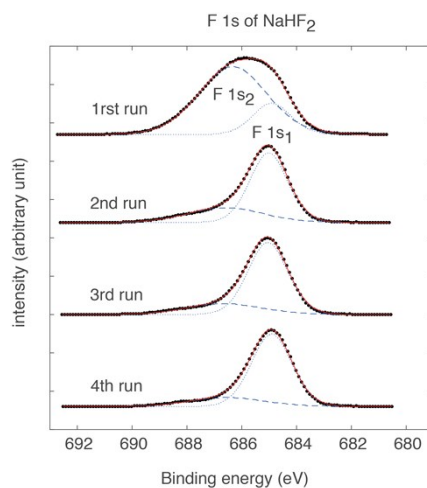


Figure S6. Room temperature XPS spectra of the F 1s region of sodium bifluoride. Four consecutive runs of measurements *in vacuo* show the progressive decomposition of the bifluoride anion (F 1s₂ at 687 eV) to that of fluoride (F 1s₁ at 685 eV).

References

- (1) Shimizu, K.; Shchukarev, A.; Kozin, P. A.; Boily, J. F. *Langmuir* **2013**, *29*, 2623.
- (2) Bodor, A.; Toth, I.; Banyai, I.; Zekany, L. S.; Sjoberg, S. *Geochim. Cosmochim. Acta* **2003**, *67*, 2793.
- (3) Nordin, J. P.; Sullivan, D. J.; Phillips, B. L.; Casey, W. H. *Geochim. Cosmochim. Acta* **1999**, *63*, 3513.
- (4) Ntuk, U.; Tait, S.; White, E. T.; Steel, K. M. *Hydrometallurgy* **2015**, *155*, 79.