Supporting Information for

Rare Earths Recovery from Calcium-Rich Coal Fly Ash: Secondary Phase Formation and Mitigation Approaches

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Table S1- Major cation composition of the fly ash samples used in this study, measured via ICP-MS analysis of full digestion samples. Concentrations shown here were converted from elemental ppm to oxide wt%, and represent the average values obtained from duplicate runs.

Sample	Na_2O (wt. %)	MgO (wt. %)	Al_2O_3 (wt. %)	K_2O (wt. %)	CaO (wt. %)	Fe_2O_3 (wt. %)	P_2O_5 (wt. %)	TiO_2 (wt. %)	SrO (wt. %)	BaO (wt. %)	SiO_2* (wt. %)
FA-1	0.5	1.0	19.0	2.3	2.6	20.7	0.1	0.9	0.0	0.0	52.9
FA-2	0.3	2.8	22.4	1.2	13.9	4.7	0.0	1.4	0.4	0.2	52.8
FA-3	8.4	3.0	17.0	1.1	19.9	5.5	0.5	1.2	0.7	1.1	41.6
FA-4	1.8	6.9	16.5	0.4	27.9	5.3	0.8	1.1	0.5	0.7	38.3

*Estimated via mass balance due to Si volatilization and loss during HF-HNO_3 sample digestion

Table S2- Average REEs concentrations in the fly ash samples used in this study. Concentrations were measured via ICP-MS analysis on duplicate runs of full digestion samples.

Sample	Sc (ppm)	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Total REEs (ppm)
FA-1	29.58	84.92	92.72	199.11	24.77	99.00	21.35	4.67	21.07	3.11	17.64	3.49	9.49	1.40	8.64	1.28	622.2
FA-2	24.7	54.6	74.3	144.5	16.5	60.9	11.9	3.1	12.6	1.9	11.0	2.4	6.9	1.0	6.3	1.0	433.5
FA-3	16.2	42.1	51.5	101.0	11.7	44.3	9.2	4.5	10.0	1.5	8.5	1.8	5.0	0.7	4.6	0.7	313.1
FA-4	23.5	65.1	81.8	159.4	19.2	73.5	15.0	4.1	15.5	2.3	12.9	2.6	7.2	1.0	6.5	1.0	490.7

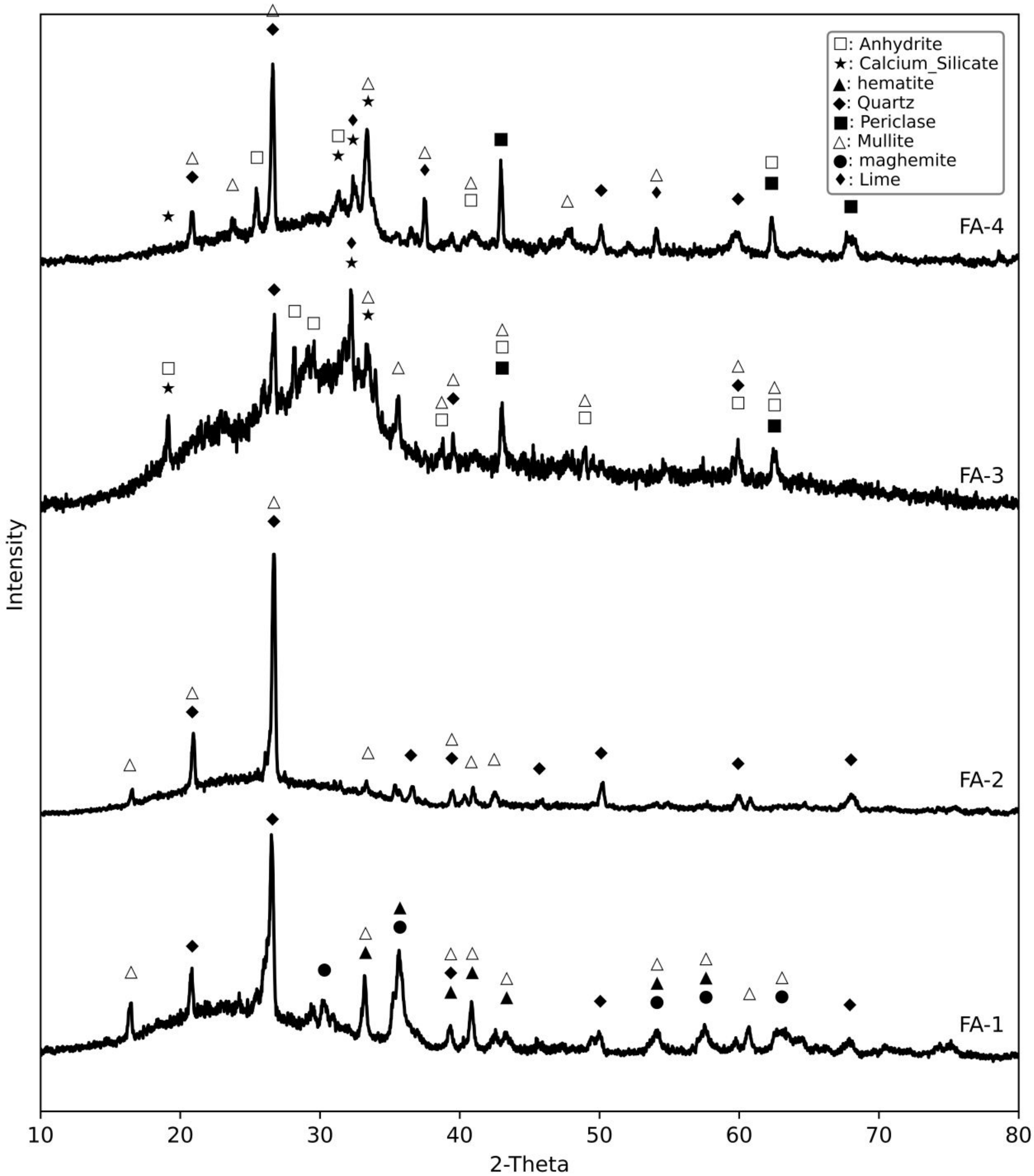

Figure S1- Initial mineralogy of ash samples used in this study characterized via XRD. The main phases found in fly ash include quartz, mullite, iron oxide phases (i.e., hematite, maghemite), and basic compounds and salts (i.e., anhydrite, lime, periclase, calcium silicate)

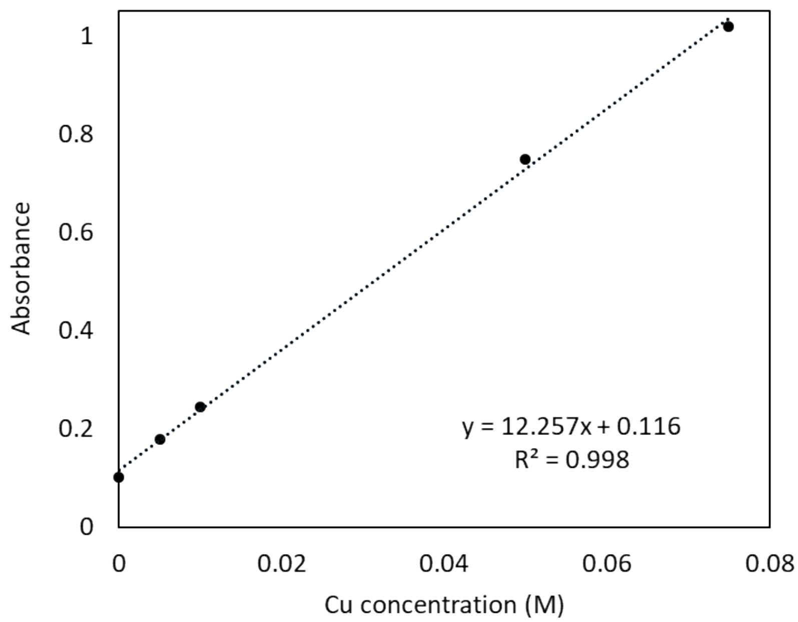

Figure S2- UV-Vis normal calibration curve for copper (II) nitrate solution, measured at λ_{abs}= 800 nm.

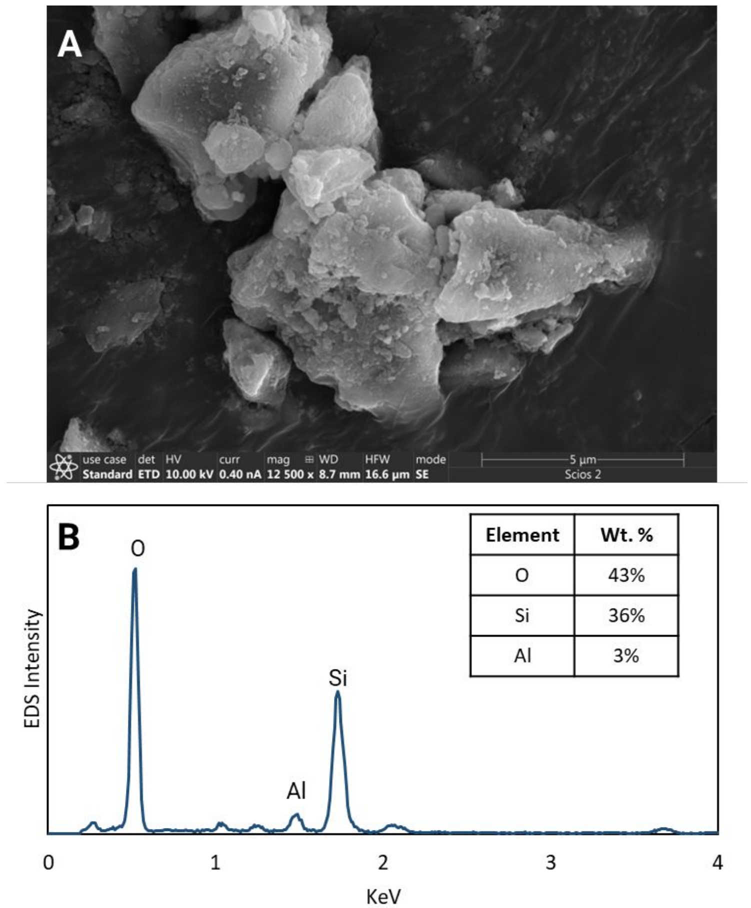

Figure S3- SEM-EDS compositional data for the solid residues obtained from 6M HNO_3 leaching conditions. (A) SEM micrograph of amorphous flocculants precipitated during leaching. (B) EDS spectrum and semi-quantitative elemental composition of the precipitates.

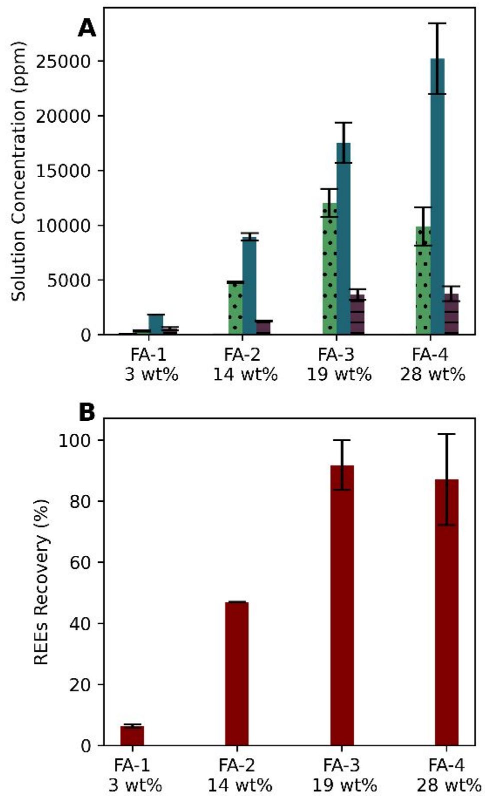

Figure S4- Major cation composition data of the leachates originated from 6M leaching of ash samples. Initial calcium concentrations (reported here as oxide equivalent wt.%) are shown below the ash sample labels and increase from left to right. (B) Average REEs recovery efficiencies for each ash sample, plotted as a function of calcium oxide concentration in the ash. Higher REEs recovery efficiencies are observed in ashes with greater calcium oxide content.

Table S3- Average elemental concentrations for 4-hour 6M leaching experiments using S:L ratio of 10.

ash type	Na	Mg	Al	Si	K	Ca	Fe	Sr	Ba	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
FA-1	-	39.7	343.4	86.2	74.7	1816.0	524.1	1.9	2.9	0.2	0.8	0.5	1.1	0.2	0.6	0.2	0.0
FA-2	104.3	1125.2	4775.1	13.5	164.9	8934.9	1258.5	248.0	117.9	1.7	3.7	3.5	6.6	0.8	3.0	0.6	0.2
FA-3	6668.0	3380.0	12022.6	14.0	756.2	17537.7	3664.9	648.4	57.3	2.7	5.0	5.6	10.5	1.3	5.0	1.0	0.3
FA-4	1241.0	4801.7	9903.4	9.4	200.0	25218.3	3745.9	480.8	64.0	2.4	6.8	8.5	16.8	2.1	7.9	1.6	0.4

Table S4- Average recovery efficiencies for 4-hour 6M leaching experiments using S:L ratio of 10.

ash type	Na	Mg	Al	Si	K	Ca	Fe	Sr	Ba	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
FA-1	-	5.9	3.0	-	3.5	84.5	3.1	12.0	7.1	6.1	8.1	4.8	4.9	5.4	5.6	6.4	7.0	6.9
FA-2	37.1	62.0	36.7	-	15.5	93.4	34.0	71.6	65.2	58.8	59.3	40.8	39.1	41.7	42.2	44.1	48.9	47.3
FA-3	91.0	152.8	114.9	-	73.1	105.8	80.0	93.5	4.8	149.7	101.3	93.8	89.1	96.7	97.0	96.3	49.8	92.7
FA-4	77.7	96.6	95.4	-	57.5	106.2	82.8	101.7	9.1	86.8	87.1	87.6	88.5	90.2	90.3	90.1	78.3	89.0

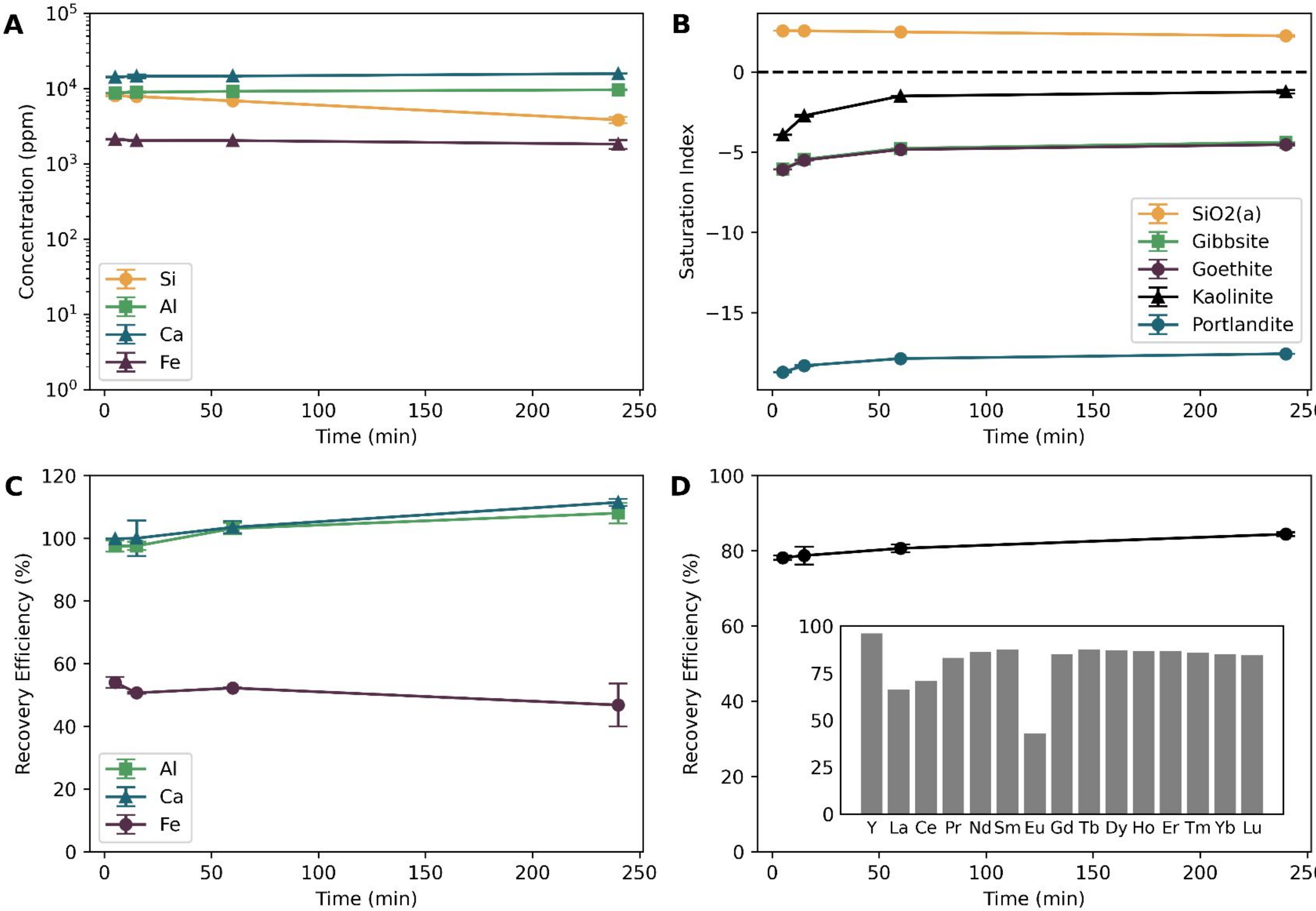

Figure S5- (A) Elemental concentration of Si, Al, Ca, and Fe, (B) Calculated saturation indices for amorphous silica, gibbsite, goethite, kaolinite, and portlandite. (C) recovery efficiency of Al, Ca, and Fe in fly ash. (D) REEs recovery efficiency, showcasing the REEs leaching kinetics profile to up to 4 hours.

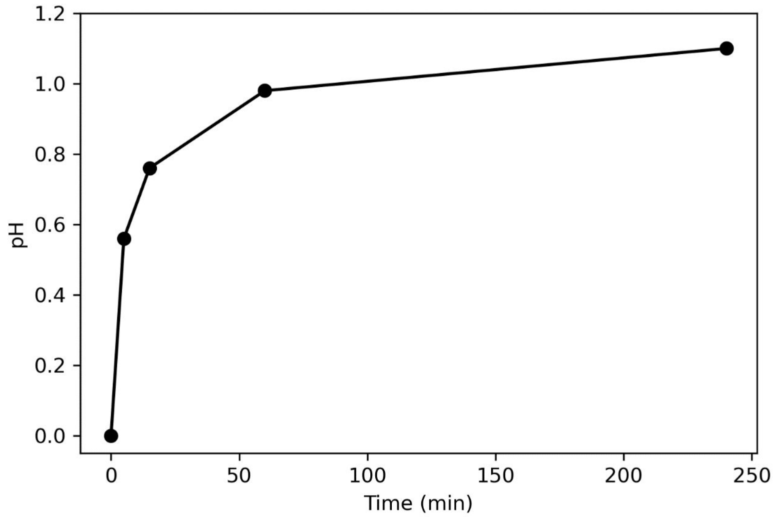

Figure S6- pH measurements for FA-3 ash sample during 2M HNO_3 leaching. The pH of the leachate increases from < 0 at initial time to 1.1 after 4 hours. Measurements were performed in duplicate samples and average values were used for plotting.

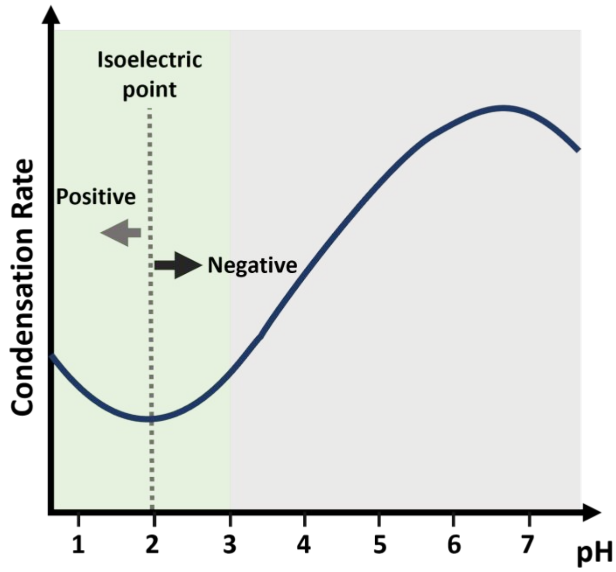

Figure S7- Silica condensation rate as a function of pH. At the isoelectric point of silica, silica surface is neutral and the condensation rate reaches a minimum. At pH values below the isoelectric point, silica surfaces are primarily positively charged ($[SiOH_2^+]/[SiOH]$ increases with pH decrease), and at pH values above the isoelectric point, silica surfaces are primarily negatively charged ($[SiO^-]/[SiOH]$ increases with pH increase). The green shaded region corresponds to the metastable region, whereas gray shaded region corresponds to the rapid aggregation region. Adapted from Iler (1979).

Table S5- Summary of relevant saturation indices calculated for ash samples FA-1, FA-2, FA-3, FA-4, after a 4-hour 6 M HNO_3 leaching.

Sample	$SiO_{2(a)}$	Gibbsite	Kaolinite	Goethite	Portlandite	$Nd(OH)_3$	$Dy(OH)_3$
FA-1	3.1	-10.6	-11.4	-9.3	-19.6	-6.9	-7.1
FA-2	2.6	-9.6	-10.3	-9.0	-18.6	-4.9	-5.1
FA-3	3.2	-9.5	-8.9	-8.8	-17.9	-2.2	-2.5
FA-4	3.0	-9.6	-9.5	-8.8	-17.8	-2.2	-2.5

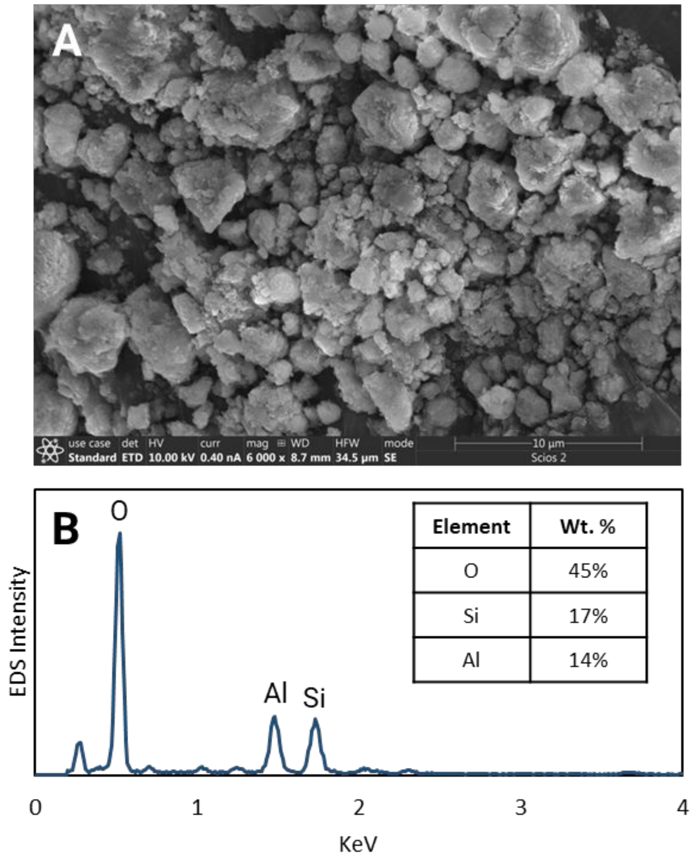

Figure S8- SEM-EDS compositional data for the solid residues obtained from 1M HNO_3 leaching conditions. (A) SEM micrograph of amorphous flocculants precipitated during leaching. (B) EDS spectrum and semi-quantitative elemental composition of the precipitates.

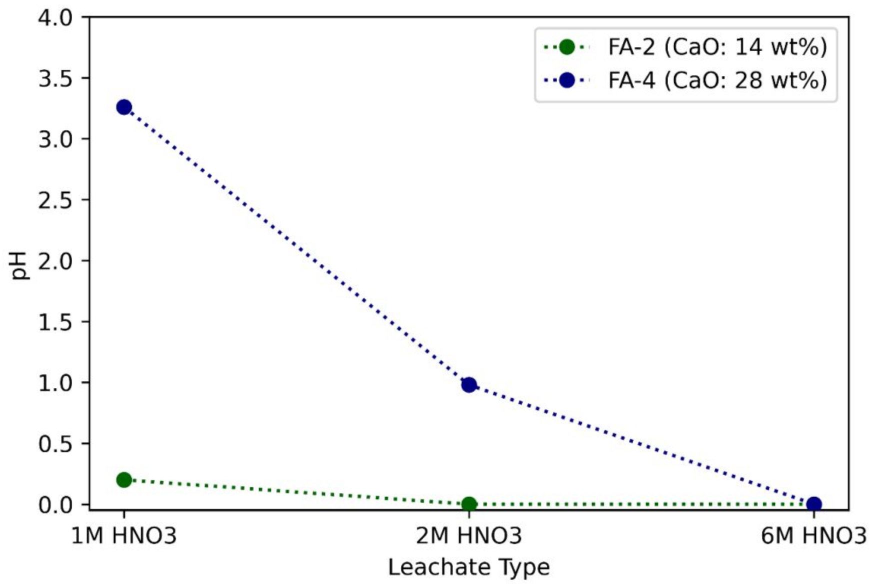

Figure S9- pH measurements for fly ash samples FA-2 and FA-4 after acid leaching for 4 hours at a temperature of 80^{o} C. Experiments were performed in duplicate and average values are reported in the plot.

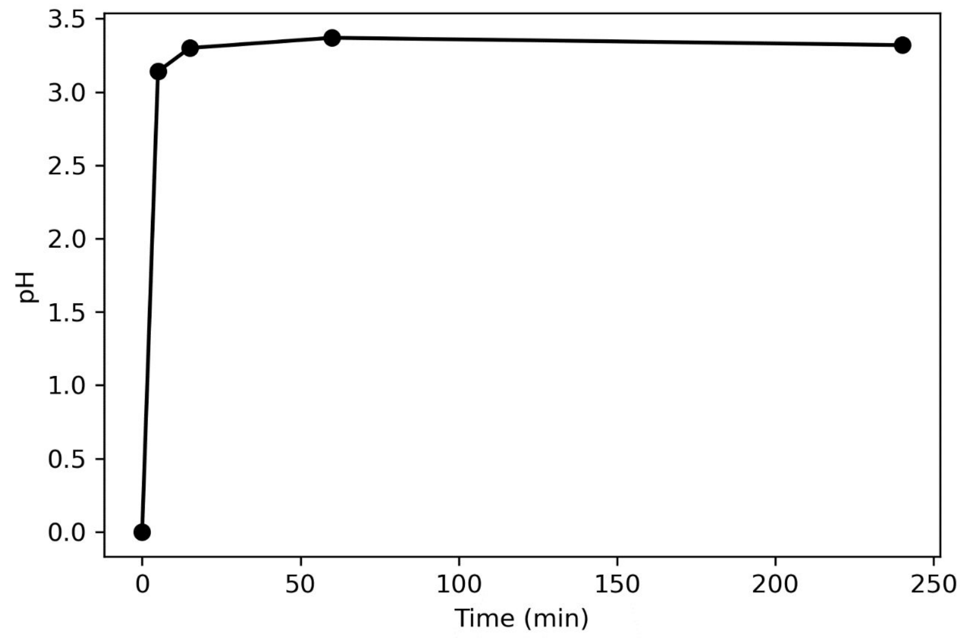

Figure S10- pH measurements for FA-3 ash sample during 1M HNO_3 leaching. The final pH of the solution after a 4-hour leaching was 3.4.

Table S6- Summary of relevant saturation indices calculated for ash samples FA-2, FA-3, FA-4, after a 4-hour 1M HNO_3 leaching.

Sample	SiO2(a)	Gibbsite	Kaolinite	Goethite	Portlandite	$Nd(OH)_3$	$Dy(OH)_3$
FA-3	0.0	1.4	5.8	-0.6	-13.8	-6.4	-6.7
FA-2	1.5	-7.4	-8.8	-7.4	-20.3	-15.6	-15.8
FA-4	0.1	0.4	4.1	0.0	-13.8	-6.7	-7.1