Table S1. Concentration of elements (mg/kg) in bulk underclay powders used for citrate and pH leaching experiments.

	UC-01 bulk	UC-02 bulk	UC-03 bulk	UC-06 bulk
Ca	3160.0	5755.8	4679.0	38533.0
Na	1983.1	2655.6	4637.1	3324.3
Ti	5794.7	8705.3	5825.1	7893.9
Mg	9458.2	3142.4	7078.8	2521.8
Al	96416.8	143976.6	100081.7	129906.0
Si	293678.7	296002.9	319937.7	305085.0
P	530.9	460.7	140.6	1610.6
K	29165.0	23975.9	31967.4	31631.2
Fe	68223.6	13319.2	35371.1	18111.1
Sc	20.0	33.6	19.2	18.1
Co	41.3	21.4	13.6	10.8
Ni	41.6	51.4	25.1	32.3
Cu	31.5	94.7	57.4	36.2
Zn	101.9	44.5	60.8	69.1
Ga	26.4	45.3	29.2	37.0
Zr	200.2	233.6	209.1	207.5
Ba	518.6	426.0	214.2	1160.1
La	99.2	116.9	72.4	129.2
Ce	12.4	13.1	8.4	12.0
Pr	47.3	44.2	30.6	39.5
Nd	10.1	9.4	6.7	9.4
Sm	2.1	2.5	2.3	2.3
Eu	9.8	9.5	6.7	7.4
Gd	1.6	1.4	1.1	0.8
Dy	9.1	8.8	7.3	5.5
Y	43.2	94.2	52.0	33.7
Er	4.8	4.7	4.2	3.3
Pb	29.0	44.3	22.0	35.8
Th	14.3	22.8	15.1	20.0
U	3.2	10.8	2.8	4.1
***SUM REE**	239.5	304.6	191.9	243.1

*Tb, Yb, Tm, Lu not determined

Table S2. Semiquantitative XRD results from random and oriented powder mounts.

	UC-01	**UC-02**	**UC-03**	**UC-06**
Mineral Phase				
Quartz	9.1	11.9	11.1	14.2
Kspar (ordered Microcline)	0.3	1.5	1.4	1.2
Plagioclase (labradorite)	1.4	1.1	2.1	1.2
Calcite	0.8	0.0	1.2	0.0
Calcite (Mg-rich)	13.2	26.1	22.8	25.4
Ilmenite	9.4	2.2	5.5	2.8
Total non-clays	**34.3**	**42.7**	**44.1**	**44.8**
Halloysite	5.7	7.4	0.0	5.2
Kaolinite (disordered)	0.0	9.4	0.0	0.0
Kaolinite (ordered)	0.0	0.0	0.0	0.0
Smectite (Saponite)	41.5	18.0	32.5	22.8
Illite (EP-10-66)	18.5	22.5	23.5	27.2
Total clays	**65.7**	**57.3**	**55.9**	**55.2**

*Samples were spiked with a zincite (NIST) internal standard on the order of ~ 10 wt%. Peak identification and Basic Rietveld fitting was performed using the PANalytical HighScore Plus software.

Table S3. Results of sequential digest of powdered underclay samples. Values reported in mg/kg.

		Na	Mg	Al	Si	K	Ca	Fe
	Detection limit	*0.1*	*0.0*	*0.4*	*0.1*	*0.0*	*0.1*	*0.1*
UC-1	$(NH_4)_2(SO_4)$	679.8	430.9	4.7	127.3	2098.9	793.8	1.2
	HCl	94.7	641.4	5522.9	3500.6	833.4	973.6	5686.3
	H_2SO_4	62.4	2828.2	9042.6	6410.2	1255.9	71.2	16474.9
	$LiBO_2$ Fusion	1109.3	5344.7	93265.4	273784.3	29226.3	728.7	44283.8
UC-02	$(NH_4)_2(SO_4)$	1214.4	76.9	0.5	132.0	1062.4	577.5	<DL
	HCl	59.3	34.9	1502.9	866.9	436.7	140.1	1354.5
	H2SO4	43.0	59.2	2169.5	1996.6	905.5	104.6	3923.3
	$LiBO_2$ Fusion	1063.5	3360.1	151090.1	250117.6	22452.4	3134.6	9942.0
UC-03	$(NH_4)_2(SO_4)$	3427.1	270.4	0.9	153.4	1378.6	2137.5	<DL
	HCl	124.4	196.0	1484.9	1417.0	504.0	462.6	995.4
	H2SO4	44.8	330.5	2078.7	1953.8	790.2	86.1	2512.1
	$LiBO_2$ Fusion	662.3	6797.0	102569.2	291378.8	31009.7	405.3	34427.5
UC-06	$(NH_4)_2(SO_4)$	1141.9	92.5	0.4	143.7	1039.3	911.1	<DL
	HCl	62.5	170.4	1044.3	704.6	431.8	573.1	2736.2
	H2SO4	52.9	182.2	1552.1	1246.4	935.0	483.7	3269.9
	$LiBO_2$ Fusion	1788.7	1997.0	128618.3	280111.1	29263.6	11647.6	11718.8

Table S4. Concentration of trace elements in sequential digest PLS. Values are in μg/L.

	P	Sc	Ti	V	Cr	Mn	Co	Ni	Ga	Ge	Zr	Nb	Sn	Sb	Ba
Detection limit	*82.3*	*2.3*	*0.9*	*0.2*	*0.8*	*0.5*	*0.3*	*1.1*	*0.1*	*0.1*	*0.1*	*0.0*	*0.5*	*0.3*	*0.1*
UC-01															
$(NH_4)_2(SO_4)$	<DL	<DL	9.1	1.0	1.3	968.7	91.9	92.3	0.3	<DL	23.2	<DL	<DL	3.7	44.0
HCl	6814.4	38.2	862.1	338.9	110.3	890.1	520.9	147.7	34.8	1.0	53.7	0.1	60.2	4.6	956.7
H_2SO_4	440.7	20.2	1785.7	169.0	1285.0	1528.3	114.4	802.0	51.4	1.3	139.3	5.1	51.3	1.8	58.1
UC-02															
$(NH_4)_2(SO_4)$	46.0	<DL	6.9	1.1	<DL	50.8	103.0	81.2	<DL	<DL	1.5	<DL	<DL	2.2	62.0
HCl	<DL	45.6	127.8	146.1	37.3	264.6	99.0	83.6	8.7	0.1	75.8	0.0	41.5	5.8	594.2
H_2SO_4	111.8	26.2	88.8	76.2	4514.2	600.5	95.7	2362.2	9.5	0.7	145.2	7.3	14.9	1.4	57.2
UC-03															
$(NH_4)_2(SO_4)$	<DL	2.5	7.2	6.3	1.2	148.1	23.7	13.9	<DL	<DL	1.3	<DL	<DL	0.5	62.4
HCl	149.7	49.9	119.4	258.1	25.9	327.8	119.4	34.9	12.4	0.9	88.5	<DL	27.2	1.1	612.6
H_2SO_4	204.5	22.8	95.1	56.1	1825.9	308.1	56.4	1025.8	9.9	1.0	128.9	3.3	9.0	0.6	57.7
UC-06															
$(NH_4)_2(SO_4)$	<DL	<DL	4.8	0.8	<DL	155.1	83.4	194.4	<DL	0.1	1.3	<DL	<DL	1.2	23.9
HCl	313.2	22.9	99.1	132.2	27.9	833.9	76.8	76.0	5.7	0.2	51.3	<DL	65.1	3.5	4387.7
H_2SO_4	300.9	10.1	61.9	44.3	29.3	379.7	18.3	72.4	6.6	0.4	148.7	0.4	5.7	0.6	69.3

Table S4 (continued) Concentration of trace elements in sequential digest PLS. Values are in μg/L.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th
Detection limit	*0.01*	*0.001*	*0.01*	*0.03*	*0.01*	*0.005*	*0.01*	*0.005*	*0.01*	*0.02*	*0.007*	*0.01*	*0.01*	*0.01*	*0.02*	*0.02*	*0.12*	*0.06*
UC-01																		
$(NH_4)_2(SO_4)$	17.9	5.0	0.7	2.2	0.6	0.2	0.9	0.1	0.5	8.6	0.1	0.1	0.0	0.1	0.0	0.5	0.3	<DL
HCl	73.0	134.9	21.7	111.4	43.0	10.6	49.8	6.3	31.0	158.5	4.5	10.9	1.2	6.7	1.0	1.5	250.3	80.7
H_2SO_4	29.2	77.8	9.9	43.3	10.0	2.2	8.6	1.1	5.9	25.0	0.9	2.6	0.3	1.9	0.3	3.1	10.1	14.7
UC-02																		
$(NH_4)_2(SO_4)$	421.6	3.0	1.3	1.1	0.3	11.9	1.0	0.2	2.3	593.3	0.2	0.5	0.1	0.4	0.1	0.0	0.8	<DL
HCl	420.4	12.8	3.3	5.9	3.3	38.7	6.8	1.1	10.0	615.2	1.2	3.4	0.5	3.3	0.4	2.4	443.2	14.7
H_2SO_4	77.2	16.7	1.0	4.7	2.7	2.6	5.8	1.0	6.3	58.9	1.1	3.2	0.4	2.5	0.3	3.4	29.7	13.7
UC-03																		
$(NH_4)_2(SO_4)$	370.8	2.3	0.9	0.9	0.2	1.8	0.3	0.0	1.0	113.7	0.1	0.1	0.0	0.1	0.0	<DL	4.5	<DL

HCl	445.1	230.2	34.5	136.8	34.4	18.5	24.1	2.4	15.1	422.2	1.2	2.9	0.4	2.6	0.4	3.3	226.0	69.8
H_2SO_4	70.3	153.2	19.8	85.4	19.4	4.1	14.0	1.4	7.8	41.7	0.9	2.2	0.3	1.7	0.2	2.9	15.3	32.8
<u>UC-06</u>																		
$(NH_4)_2(SO_4)$	17.5	1.7	0.5	0.9	0.1	0.9	0.3	0.0	1.2	115.4	0.1	0.3	0.0	0.2	0.0	<DL	0.2	<DL
HCl	204.9	19.2	4.1	6.1	1.5	8.9	2.1	0.4	7.6	196.4	0.5	1.4	0.2	1.4	0.2	1.9	105.8	9.4
H_2SO_4	25.6	11.6	1.0	3.1	0.8	0.7	1.7	0.4	3.5	30.3	0.6	1.9	0.2	1.4	0.2	3.1	4.3	3.9

Table S5. Concentration of elements in PLS from leaching of UC-02 (1 and 10% solids) with 0.1 mol/L citrate and 0.5 mol/L NaCl (Leaching solution RS-2). Values are in μg/L.

	Na	**Mg**	**Al**	**Si**	**K**	**Ca**	**P**	**Sc**	**Ti**	**V**
Detection Limit	*30.0*	*19.3*	*5.4*	*360*	*135*	*385*	*82.3*	*2.3*	*0.9*	*0.2*
UC-02 (1% solids)	13087847	1641	21230	13491	25086	16226	302	28	49	29
UC-02 (10% solids)	4166230	8634	145049	94984	74450	55153	3300	153	1965	268

	Cr	**Mn**	**Fe**	**Co**	**Ni**	**Ga**	**Ge**	**Y**	**Zr**	**Nb**	**Sn**	**Sb**
Detection Limit	*0.79*	*0.46*	*17.40*	*0.26*	*1.06*	*0.07*	*0.07*	*0.02*	*0.13*	*0.02*	*0.53*	*0.34*
UC-02 (1% solids)	20	33	3546	65	57	4.5	0.4	336	100	0.4	5.8	2.8
UC-02 (10% solids)	109	163	21427	3690	407	41.8	3.8	805	609	3.5	22.6	39.9

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**
Detection Limit	*0.005*	*0.003*	*0.001*	*0.028*	*0.008*	*0.002*	*0.000*	*0.003*	*0.013*	*0.002*	*0.006*	*0.001*
UC-02 (1% solids)	579	6.8	2.3	2.4	1.2	5.8	3.1	0.5	5.8	0.5	1.4	0.2
UC-02 (10% solids)	855	49.0	9.0	23.7	9.7	43.7	28.0	4.6	29.3	4.4	12.0	1.7

Table S6. Concentration of elements (μg/g) leached into PLS from underclay samples using citrate solution (RS-2).

	UC-01 Na-Citrate + NaCl (RS-2)	UC-02 Na-Citrate + NaCl (RS-2)	UC-03 Na-Citrate + NaCl (RS-2)	UC-06 Na-Citrate + NaCl (RS-2)
Sc	2.6	2.5	1.8	2.2
Co	29.1	5.7	6.1	20.9
Ni	7.8	5.0	1.7	5.2
Cu	0.6	48.0	32.9	10.3
Ga	1.2	0.4	0.3	0.3
Y	5.8	29.4	16.8	4.9
Zr	11.5	8.8	8.9	4.9
Ba	40.8	17.9	31.2	209.0
La	3.5	50.5	28.2	8.6
Ce	5.1	0.6	1.0	1.5
Pr	0.9	0.2	0.3	0.2
Nd	4.9	0.2	0.5	0.5
Sm	2.2	0.1	0.2	0.2
Eu	0.5	3.1	0.9	0.3
Gd	2.7	0.3	0.2	0.3
Dy	1.8	0.5	0.5	0.4
Er	0.6	0.1	0.1	0.1
Pb	11.6	13.4	8.5	5.2
Th	4.9	0.7	0.7	0.8
U	0.2	0.7	0.4	0.5
Ca	2385.7	1417.6	1909.3	10715.7
Na	584779.7	1143376.2	589257.4	609900.0
Ti	29.3	4.2	14.4	5.3
Mg	1289.5	143.3	567.2	483.2
Al	5506.6	1854.7	1538.1	1434.9
Si	4030.7	1178.6	2185.9	1570.7
P	246.8	26.3	4.7	356.5
K	3141.4	2191.5	2249.9	1901.0
Fe	4618.0	309.8	800.8	5120.7
SUM REE recovered	28.0	85.0	48.5	17.1
REE original solids	239.5	304.6	191.9	243.1
% recovery REE	11.7	27.9	25.3	7.0

Table S7. Concentration of elements (μg/g) leached from underclay samples UC-02 and UC-03 using citrate solutions buffered to pH 3, 4, 5, and 6.

	UC-02 Citrate pH 3	**UC-02 Citrate pH 4**	**UC-02 Citrate pH 5**	**UC-02 Citrate pH 6**	**UC-03 Citrate pH 3**	**UC-03 Citrate pH 4**	**UC-03 Citrate pH 5**	**UC-03 Citrate pH 6**
Sc	4.5	4.0	3.5	2.6	1.9	2.4	1.5	1.2
Co	10.4	13.5	13.1	11.3	4.5	6.3	5.6	5.0
Ni	2.9	4.7	3.2	2.4	2.2	2.2	1.3	1.1
Cu	78.1	81.4	87.9	74.4	17.4	22.5	20.7	19.2
Ga	0.7	0.7	0.6	0.4	0.4	0.7	0.3	0.3
Y	16.7	15.6	14.2	12.5	15.6	16.5	15.8	14.9
Zr	10.9	10.3	9.8	7.0	11.3	10.9	8.2	6.6
Ba	26.0	45.4	53.2	58.4	11.7	21.7	24.6	28.9
La	9.3	10.2	10.4	10.5	20.8	27.3	26.6	24.5
Ce	46.3	49.5	50.2	49.9	0.7	1.1	0.8	1.0
Pr	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.3
Nd	0.6	0.4	0.3	0.3	0.4	0.6	0.4	0.5
Sm	0.4	0.2	0.2	0.2	0.1	0.2	0.1	0.2
Eu	0.2	0.1	0.1	0.1	0.8	0.8	0.8	0.7
Gd	0.7	0.5	0.4	0.4	0.2	0.2	0.2	0.2
Dy	0.7	0.5	0.4	0.4	0.5	0.5	0.5	0.5
Er	0.4	0.2	0.2	0.2	0.1	0.1	0.1	0.1
Pb	10.5	15.9	17.6	16.2	6.1	6.6	6.3	5.8
Th	1.7	1.7	1.4	1.0	0.7	0.8	0.6	0.6
U	1.0	1.0	1.0	0.8	0.3	0.4	0.3	0.3
Ca	368.3	544.9	750.2	634.9	1117.9	1745.8	1981.2	1962.4
Na	39305.1	88755.3	122069.4	171127.2	42606.4	102383.8	138255.7	178318.7
Ti	6.2	5.7	4.6	2.5	6.1	19.1	6.2	9.3
Mg	94.5	140.2	141.8	130.4	281.6	512.7	443.9	459.3
Al	2762.3	2720.5	2410.7	1711.6	1830.6	2536.1	1293.9	1398.0
Si	2243.5	1881.8	1619.1	1313.1	2260.1	3631.8	1733.8	2185.9
P	bd	bd	bd	171.4	bd	1.7	bd	2.3
K	1052.7	1185.2	1249.4	1232.3	1162.0	1641.2	1300.3	1594.5
Fe	1094.9	873.7	354.9	172.4	1712.6	1537.6	668.5	554.7
REE recovered	75.3	77.4	76.5	74.5	39.5	47.7	45.5	42.8
REE original solids	304.6	304.6	304.6	304.6	191.9	191.9	191.9	191.9
% recovery REE	**24.7**	**25.4**	**25.1**	**24.5**	**20.6**	**24.8**	**23.7**	**22.3**

Grain Size Distribution of Solids.

Particle size distributions (as volume percentages) for the unreacted (initial) underclay samples UC-01, UC-02, UC-03, and UC-06. Particle size analyses performed on -100 mesh size fraction using ~5.5 g/L sodium hexametaphosphate as a dispersant and sonicating for 60 seconds on a Malvern Mastersizer2000.

Table S8. Tabulated parameters for particle size distributions of unreacted (initial) underclay samples UC-01, UC-02, UC-03, and UC-06

	D[4,3] vol. wt. mean	D[3,2] surf. wt. mean	Specific surface area	D(0.1)	D(0.5)	D(0.9)
	μm	μm	m^2/g	μm	μm	μm
UC-01-100	1.0	0.4	6.7	0.2	0.4	2.8
UC-02-100	11.8	5.4	0.5	2.5	7.2	27.2
UC-03-100	9.8	0.5	5.0	0.1	4.6	27.1
UC-06-100	21.6	0.7	3.4	0.2	6.4	62.4

Flow-through experiments

Powdered samples were prepared by crushing and grinding core samples using a Braun chipmunk jaw crusher and a Microne micronizing mill. Size fractions were separated through metal sieves. For flow-through reactions, the size fractions used were -20 mesh, -100 mesh, and -230 mesh. Approximately 5 g of powdered underclay samples were packed into 3/8" in diameter Swagelock reaction vessels (see below). At either end of the sample, quartz sand and glass wool were emplaced to keep the sample in place during pressurized flow.

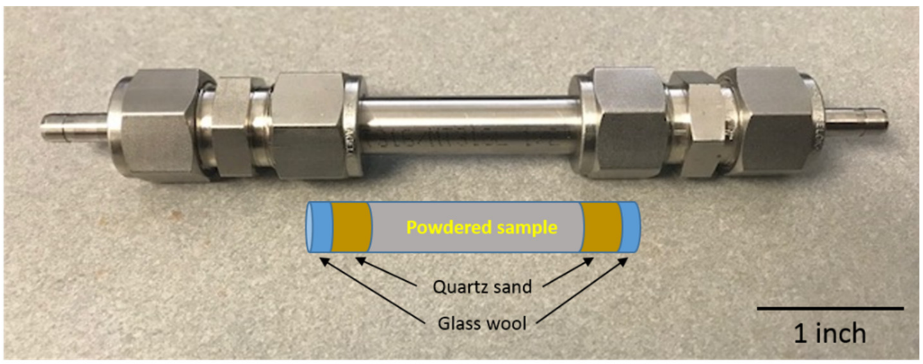

Figure S1. Photograph of powder reaction vessel constructed of thick walled stainless steel cylinder and Swagelok fittings, inset schematic shows orientation of materials in final packed vessel.

Core samples were drilled using a ½" diameter drill bit, with the length of the cores varying from ~2 to 5 mm. Prior to reaction, the cores were fractured along the longitudinal axis in a hydraulic press to allow fluid flow. Teflon tape was wrapped around the core to ensure a tight seal between the sides of the core and the walls of the core holder. The leachate used was a sodium citrate buffer at pH 5 created by combining 350 mL 0.1 M citric acid and 650 mL 0.1 M trisodium citrate. Sodium chloride was added to the solution in a final concentration of 0.5 M NaCl.

Flow-through operation

Flow-through experiments were conducted at the NETL Morgantown facilities and consisted of a network of stainless-steel tubing connected to a Quizix QX series syringe pump and pressure valves on the up- and down- stream sides of a Swagelok reaction vessel (Figures S1 and S2). In-line 60 µm nylon filters were attached downstream from the reaction vessel. Initial flow at 0.3 - 1 mL/min was established at atmospheric pressures before confining pressures were gradually increased to operating pressures of ~1600 - 1800 psi. Once operating pressures were established, the fluid flow rate was set to 0.3 mL/min. Underclay powder samples were also subjected to extended shut-in times of 5 days where the powders were saturated with the leachate and held at operating pressures of ~1600 - 1800 psi. Powders previously reacted through the 24-hour experiments schemes were re-run with extended shut-in times as well as fresh powder material that did not go through the 24-hour reactions. At the end of the 5-day shut-in times, fluid flow was established at 0.3 mL/min and samples collected over 20-

minute intervals for 1 hour. For the fractured core experiments, the cores were saturated with leachate and held in at pressure for 24 hours. After the 24-hour shut-in period, fluid flow was established at 0.3 mL/min and samples collected over 20-minute intervals for 1 hour.

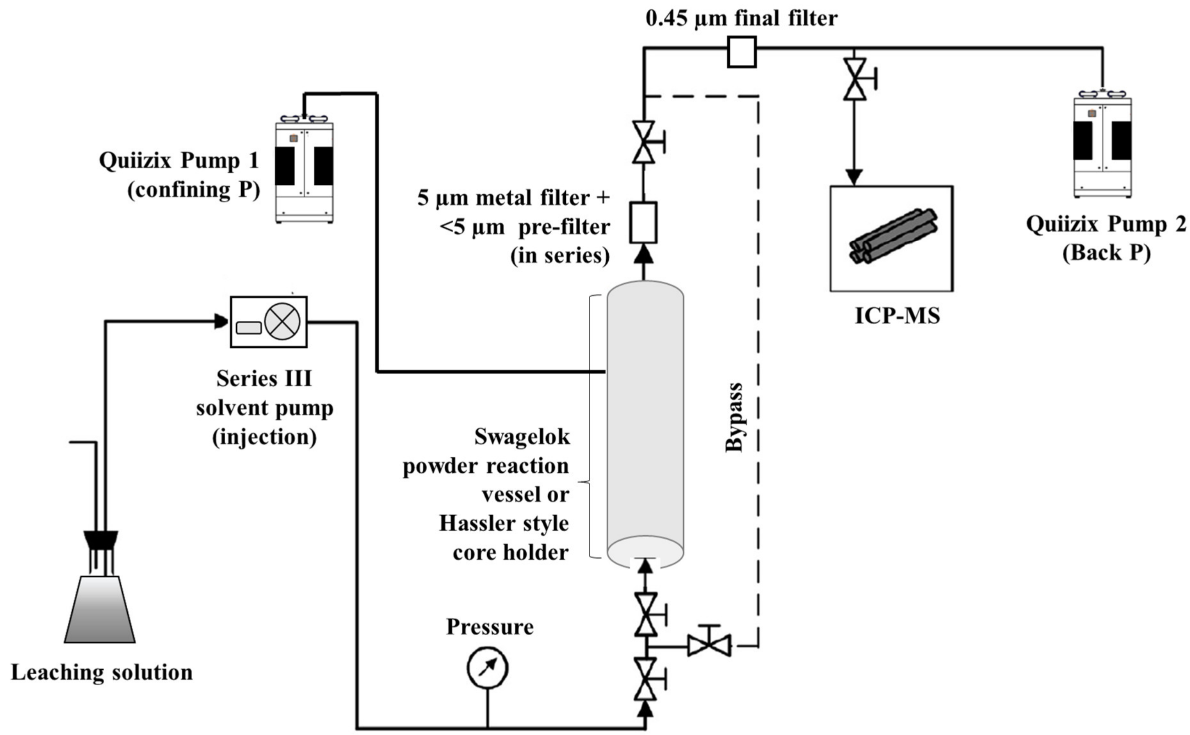

Figure S2. Schematic drawing of flow-through apparatus used for underclay powder leaching.

ICP-MS Analysis of flow through leachates

Solutions were analyzed on an Agilent 7500 ICP-MS at NETL Morgantown for the rare earth elements including yttrium. The Agilent 7500 was equipped with a Scott-type expansion chamber and concentric glass Seaspray nebulizer. Trace metal grade Optima nitric acid (HNO_3) was used to create all reagents, calibration standards, and external verification standards. Calibration standards were created from a multi-element stock solution. External verification standards from Inorganic Ventures and SPEX were monitored to assess accuracy of the calibration standards. Indium at a mass of 115 amu was used as an internal standard and added in concentrations of 10 ppb to the calibration standards and samples. Matrix corrections were performed on the signal of ^{115}In between the calibration standards and samples. All samples were diluted in 2% HNO_3 by a factor of 20.