SUPPORTING INFORMATION

Manuscript Title: Recovery of Rare Earth Elements and Yttrium from Passive Remediation Systems of Acid Mine Drainage

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progression of reactions fronts in Almagrera calcite column (B) is faster than in Monte Romero (A) due to the higher acidity of the Almagrera inflow water.

Figure S14-S2. NASC normalized REE pattern of pore water from the Monte Romero (a) and Almagrera (b) treatment lines. The numbers indicate the depth with respect to the calcite column water-solid interface, D1 and D3 are the first decantation vessels and C2 and C5 the first 2 cm of the MgO columns.

Figure S15-S3. Distribution of element concentration in the solid phase from Monte Romero (a) and Almagrera (b) columns. The numbers of the vertical axes indicate the depth (cm) of the center of each solid slice, D1 and D3 indicate the first decantation vessels and C2-1 and C2-5 correspond to the first 2 cm slice of the MgO column. The different steps of sequential extraction are shown as bars.

Figure S17-S4. DRX diagram of a D1 sample. Legend: G = gypsum; B = bechererite; F = fluorite

Figure S18-S5 Distribution of fluorine aqueous species with pH along the treatment of the Monte Romero (a) and Almagrera (b) AMD. Vertical scale is the fraction of the total concentration. Calculations were made using the PHREEQC code and the LLNL thermodynamic database.[S3]

Figure S19-S6. A) View of the Mina Esperanza passive remediation systems after 15 months of functioning. B) Detail of the vertical zonation: 1) calcite-gypsum; 2) basaluminite; 3) schwertmannite zones.

DETAILS ON AQUEOUS PHASE ANALYSIS

Aqueous solution samples were collected from the input container, from the supernatant water, and from the drainpipe, and the leachates resulting from sequential extractions and total digestion of the solid samples.

Measurement of pH was made with a Crison® glass electrode calibrated with buffer solutions of pH 7 and 2. Redox potential was measured using a Pt combination electrode (ThermoOrionSureFlow®) that was calibrated with standard buffer solutions of 220 and 468 mV. Measurements were corrected to the Standard Hydrogen Electrode to calculate pE. Total (gross) alkalinity was measured by acid titration using an Alkalinity Test from Aquamerck® (limit of detection 0.1 mmol $H^{+}\cdot L^{-1}$, analytical error of 0.1 mmol $H^{+}\cdot L^{-1}$). The analysis of fluorine was performed by specific electrode Thermo Scientific Orion®, after stabilization of the sample with TISAB III. Filtered samples (0.1 µm) were acidified with HNO_3 for analysis of major and trace elements. Major cations (Ca, Mg, Zn, Fe, Mn, Si) and total S were measured by ICP-AES (Perkin-Elmer® Optima 3200 RL) and trace metals (Ni, Cd, Co, Pb) with ICP-MS (Perkin-Elmer®SciexElan 6000). Detection limits were 0.1 mg/L for S; 0.05 mg/L for Ca, Mg, Si; 0.02 mg/L for Fe, Zn, Mn; 5 µg/L for Al; 1.5 µg/L for Cu, Ni; 0.5 µg/L for Pb; 0.2 µg/L for Cd, Co and REY. The analytical precision error was estimated to be approximately 6% for ICP-AES and 4% for ICP-MS measurements. Two AMD laboratory standards supplied by P. Verplank (USGS), were also analyzed for REE accuracy, giving deviations lower than 5% of the recommended values[S1], with the exception of Eu, giving values 25% below the recommended value. Assuming all S to be sulfate, the charge balance error was usually less than 5%.

DETAILS ON SOLID PHASE ANALYSIS

The major mineral phases forming the solid samples were identified by X-ray diffraction (XRD) using a Bruker® D5005 X-Ray Diffractometer (XRD) with Cu Lα radiation. The samples were scanned from 0 to 60 degrees 2θ with a continuous scan at a rate of 0.025°/18 s. Granular material was also observed under a JEOL® JSM840 Field Emission Scanning Electron Microscope with Oxford Link® Energy Dispersive System (SEM-EDS).

To study in detail the partitioning of Al, Fe, and trace elements into the solid phase, a sequential extraction procedure adapted from Torres and Auleda[S2] was applied to the samples of solid residues to obtain the following fractions:

1) Water soluble fraction: 0.5 g of dry sample is treated with 50 mL of O2-free deionized water in a centrifuge tube. The water must be O2-free to prevent oxidation of reduced species and is obtained by bubbling N2 through the water after boiling. The sample is then shaken for 1 h in a rotator tumbler at 30 rpm at room temperature (RT) after which the suspension is centrifuged at 3000 rpm for 15 minutes and the supernatant water is separated by decantation. The supernatant is subsequently passed through 0.22 µm nylon syringe filters, diluted, acidified to below pH 2 and stored at 4°C until analysis.

2) Basaluminite and calcite: 20 mL of 1 M ammonium acetate at pH 4.5 is added to the residual solid of the previous step. The sample is then shaken for 2 h at RT, after which it is centrifuged, separated, filtered, acidified and stored as in the previous step.

3) Low crystalline Fe(III)-oxyhydroxides: 20 ml of 0.2 M ammonium oxalate at pH 3 are added to the residual solid of the previous step. The sample is then shaken for 1 h at RT in the dark, after which it is centrifuged, separated, filtered, acidified and stored as described in the previous step.

4) Crystalline Fe(III)-oxides: 20 mL of 0.2 M ammonium oxalate at pH 3 is added to the residual solid of the previous step. The sample is then stirred in a water bath at 80°C for 2 h, after which it is centrifuged, separated, filtered, acidified and stored as described in the previous step.

5) The residual fraction was transferred to a teflon reactor and 10 ml of concentrated HNO3 and 10 mL of concentrated HClO4 were added. Note that HF was not used as commonly in these procedures as no detrital silicates were expected in the samples. The sample was then heated at 135°C until all of the acids have evaporated and condensed in the elbows. Next, 3 mL of concentrated HNO3 were added and the sample was heated at 135°C to dissolve the salts. Finally, the solution was filtered through 0.22 µm nylon syringe filters, diluted and stored at 4°C until analysis.

All the solutions resulting from the different extraction steps were filtered through 0.22 µm nylon syringe filters, diluted and stored at 4°C until analysis. Duplicates were carried out to 10% of the total samples and the reproducibility was 93%.

To provide a general overview of the geochemical composition of the residues and to validate the sum of masses obtained from all the extraction steps, total digestions (as in step 5 of the protocol) of all the samples were conducted. The sequential-extraction element recovery rates were then compared with the totals from the digestion analyses and found to be between 80% and 120%.

DETAILS ON BASALUMINITE SYNTHESIS

Basaluminite was obtained following Prietzel et al.[S3] Thus, 30 mL of a 0.05 M solution of Al2(SO4)3·18H2O was prepared in a beaker and stirred magnetically. Then, 214 mL of 0.015 M Ca(OH)2 was added, and the mixture was stirred for a few minutes until a white homogeneous solution was obtained. The mixture was centrifuged for 10 minutes at 3900 rpm and the supernatant removed. The solid was washed at least three times with MilliQ-water and centrifuged to remove residual CaSO4·2H2O. The solid was dried at 40°C for three days

Table S5-S1. Pore water composition of the Monte Romero treatment system after 18 weeks of functioning: Distance= depth from the water-reactive interface in the calcite column; D1= decantation vessel after the calcite column; C2= 2 cm depth in the MgO column; D2= decantation vessel after the MgO column.

	C1-0	C1-1	C1-2	C1-3	C1-4	C1-5	C1-6	D1	C2-1	D2
depth (cm)	**0**	**4**	**8**	**12**	**16**	**20**	**25**	**D1**	**C2**	**D2**
O2 (mg/L)	7.86	1.63	1.43	2.32	1.82	1.94			2.37	
Eh (mV)	548	282	247	240	230	228	445	430	216	349
pH	2.8	4.7	5.6	5.8	5.7	5.8	5.8	6.4	9.2	6.8
EC (mS/cm)	4620							4930		5540
Alk (mmol/L)		1.1	1.8	1.8	2.4	3.2	3.4	3.3		4.9
mmol/L										
Al	4.76	2.97	0.59	0.28	0.23	0.22	0.28	0.15	0.00	0.01
Ca	5.44	13.27	16.36	18.63	18.63	18.46	18.79	13.27	13.96	12.20
F	0.47	0.48	0.51	0.50	0.49	0.49	0.48	0.59	0.19	0.23
Fe	2.88	0.01	0.00	0.00	0.00	0.01	0.01	0.05	0.00	0.00
K	0.04	0.04	0.04	0.02	0.05	0.05	0.05	0.06	0.06	0.07
Mg	10.80	11.56	11.41	11.27	11.41	11.47	11.29	14.47	23.29	24.32
Na	0.84	0.91	0.88	0.84	0.90	0.90	0.87	1.13	1.33	1.38
P	0.03	0.02	0.02	0.03	0.03	0.01	0.02	0.02	0.01	0.01
S	35.26	35.33	34.49	34.88	35.90	35.55	35.89	35.79	37.02	37.42
Si	1.44	1.30	0.88	0.71	0.92	0.90	0.88	0.59	0.00	0.02
mmol/L										
Li	43.78	41.96	43.88	45.25	44.09	45.73	46.30	59.36	73.32	74.86
Co	11.02	10.74	11.16	11.31	11.56	11.76	11.70	14.71	0.08	0.24
Cu	111.97	100.77	69.55	65.27	72.64	64.39	59.04	9.60	0.14	0.51
Mn	314.17	294.71	305.44	310.53	313.08	319.82	330.92	427.03	31.18	6.16
Ni	6.42	6.35	6.63	6.54	6.78	6.92	6.93	7.92	0.10	0.22
Zn	6585	6306	6366	5918	6418	6569	6780	7556	5.72	120.65
Cd	6.27	6.32	6.26	5.91	6.62	6.53	6.51	8.24	0.11	0.12
Th	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U	0.39	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sc	0.18	0.20	0.07	0.07	0.08	0.08	0.07	0.02	<0.01	<0.01
Y	10.80	11.67	6.79	7.19	8.18	7.52	7.58	1.56	<0.01	<0.01
La	8.31	8.87	5.24	5.27	5.60	4.81	4.87	1.02	<0.01	0.02
Ce	21.18	22.96	13.45	13.52	12.78	10.23	9.67	1.90	<0.01	0.04
Pr	2.44	2.79	1.58	1.57	1.42	1.09	0.95	0.20	<0.01	<0.01
Nd	8.80	9.97	5.75	5.67	5.13	3.94	3.38	0.72	<0.01	0.02
Sm	2.07	2.38	1.34	1.28	1.11	0.83	0.66	0.15	<0.01	<0.01
Eu	0.28	0.32	0.18	0.18	0.16	0.13	0.10	0.02	<0.01	<0.01
Gd	2.08	2.33	1.34	1.36	1.37	1.14	1.03	0.24	<0.01	<0.01
Tb	0.29	0.33	0.18	0.19	0.19	0.16	0.14	0.03	<0.01	<0.01
Dy	1.44	1.59	0.90	0.91	0.98	0.83	0.74	0.17	<0.01	<0.01
Ho	0.23	0.25	0.14	0.15	0.16	0.14	0.13	0.03	<0.01	<0.01
Er	0.53	0.58	0.33	0.33	0.36	0.31	0.28	0.06	<0.01	<0.01
Tm	0.06	0.06	0.04	0.04	0.04	0.03	0.03	<0.01	<0.01	<0.01
Yb	0.34	0.36	0.19	0.19	0.19	0.15	0.11	0.02	<0.01	<0.01
Lu	0.04	0.04	0.02	0.02	0.02	0.02	0.01	<0.01	<0.01	<0.01
ΣREY	58.89	64.52	37.49	37.85	37.69	31.33	29.67	6.11	0.01	0.12

Table S6-S2. Pore water composition of the Almagrera treatment system after 18 weeks of functioning: Distance= depth from the water-reactive interface in the calcite column; D3= decantation vessel after the calcite column; C5= 2 cm depth in the MgO column; D5= decantation vessel after the MgO column.

	C3-0	**C3-1**	**C3-2**	**C3-3**	**C3-4**	**C3-5**	**C3-6**	**D3**	**C5-1**	**D5**
depth (cm)	**0**	**4**	**8**	**12**	**16**	**20**	**25**	**D3**	**C5**	**D5**
O2 (mg/L)		1.99	1.86	1.36	1.71	1.1				
Eh (mV)	456	486	470	426	174	131	260	2.87	185	200
pH	2.6	2.7	2.8	3.2	5.1	5.6	5.5	6.3	9.2	7.5
EC (mS/cm)	12230							12610	14920	16060
Alk (mmol/L)					5.3	4.7	3.4	1.7		12.4
mmol/L										
Al	9.30	12.68	13.10	15.12	3.56	1.38	0.22	0.03	0.01	0.00
Ca	11.01	12.39	12.29	11.96	15.02	14.46	12.15	11.79	8.57	9.84
F	0.12	0.14	0.13	0.13	0.12	0.11	0.13	0.20	0.19	0.22
Fe	13.32	9.60	8.67	4.68	2.13	0.59	0.26	0.00	0.00	0.00
K	0.05	0.02	0.05	0.04	0.06	0.04	0.06	0.06	2.39	3.68
Mg	45.42	54.12	54.49	53.26	54.78	54.10	48.96	79.82	123.85	129.67
Na	4.56	5.77	5.69	5.55	5.66	5.51	5.11	8.29	12.46	14.85
P	0.06	0.07	0.08	0.08	0.06	0.06	0.04	0.04	0.01	0.00
S	117.07	135.35	133.77	125.63	106.80	94.79	87.70	131.90	138.84	150.13
Si	1.44	1.83	1.84	1.59	0.49	0.49	0.53	0.54	0.01	0.01
µmol/L										
Li	87.25	103.93	102.38	102.09	104.09	107.29	95.74	162.51	210.4	235.1
Co	163.91	192.76	187.67	187.84	192.76	195.82	178.34	317.14	0.08	0.43
Cu	2282.8	2651.6	2612.2	2634.3	2324.3	1225.7	940.7	121.2	0.56	0.91
Mn	7923.5	9301.39	9093.89	9099.35	9237.69	9445.19	8442.24	14145.0	486. 8	264.4
Ni	19.49	23.38	23.14	22.86	23.50	23.51	20.82	36.77	0.30	0.50
Zn	13557	15782	15415	15253	16210	15491	14064	21042	5.07	26.72
Cd	11.76	13.98	14.06	13.64	14.22	12.67	10.13	20.10	<0.01	0.03
Th	0.02	0.02	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
U	0.05	0.06	0.06	0.07	0.06	0.02	<0.01	<0.01	<0.01	<0.01
Sc	0.75	0.76	0.78	0.91	0.16	0.05	0.05	0.04	<0.01	<0.01
Y	9.92	11.30	11.13	11.21	9.65	6.18	4.82	3.05	<0.01	<0.01
La	1.99	2.26	2.25	2.21	1.76	1.02	0.67	0.54	<0.01	<0.01
Ce	6.62	7.33	7.23	7.17	5.20	2.48	1.38	0.75	<0.01	<0.01
Pr	0.90	1.02	1.02	1.00	0.69	0.30	0.17	0.07	<0.01	<0.01
Nd	3.78	4.32	4.33	4.22	2.91	1.19	0.68	0.26	<0.01	<0.01
Sm	1.04	1.20	1.21	1.19	0.83	0.31	0.18	0.05	<0.01	<0.01
Eu	0.20	0.23	0.23	0.23	0.16	0.07	0.04	<0.01	<0.01	<0.01
Gd	1.20	1.36	1.36	1.36	1.05	0.51	0.33	0.13	<0.01	<0.01
Tb	0.19	0.22	0.22	0.22	0.17	0.08	0.05	0.02	<0.01	<0.01
Dy	1.09	1.25	1.26	1.26	1.00	0.50	0.33	0.13	<0.01	<0.01
Ho	0.19	0.22	0.22	0.23	0.18	0.09	0.06	0.03	<0.01	<0.01
Er	0.51	0.59	0.60	0.60	0.49	0.25	0.17	0.07	<0.01	<0.01
Tm	0.06	0.07	0.08	0.08	0.06	0.03	0.02	<0.01	<0.01	<0.01
Yb	0.40	0.47	0.48	0.49	0.37	0.16	0.11	0.03	<0.01	<0.01
Lu	0.06	0.07	0.07	0.07	0.05	0.02	0.02	<0.01	<0.01	<0.01
ΣREY	28.16	31.93	31.71	31.55	24.56	13.19	9.03	2.14	0.01	0.01

Table S7-S3. Solid phase composition (µmol/g) of the Monte Romero column after 30 weeks of functioning extracted with the different the sequential steps: C1-x _ where x is the depth from the water-reactive interface in the calcite column; D1= decantation vessel after the calcite column; C2= 2 cm depth in the MgO column; HBA= synthetic basaluminite.

	Al	**Fe**	**Cu**	**Zn**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**	**ΣREY**
STEP I																						
C1-1	0.99	<0.01	0.013	1.539	0.009	0.006	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.004	0.085
C1-3	6.65	<0.02	0.012	0.323	0.009	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.003	0.081
C1-5	2.49	<0.03	0.013	0.059	0.009	0.006	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.004	0.085
C1-7	12.70	<0.04	0.013	0.013	0.009	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.084
C1-12	6.09	<0.05	0.013	0.013	0.009	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.084
C1-17	0.34	<0.06	0.013	0.012	0.009	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.083
D1	0.77	<0.07	0.051	63.295	0.009	0.065	0.063	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.199
C2	0.14	0.01	0.041	0.151	0.006	0.006	0.005	0.005	0.003	0.004	0.004	0.010	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.003	0.003	0.071
HBA	38.60																					
STEP II																						
C1-1	23.83	48.94	0.217	1.628	0.027	0.028	0.072	0.002	0.044	0.010	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.201
C1-3	347.23	5.51	0.731	3.183	0.102	0.080	0.256	0.034	0.154	0.038	0.002	0.029	0.002	0.021	0.002	0.008	0.002	0.002	0.002	0.001	0.015	0.734
C1-5	358.02	1.05	1.374	7.613	0.174	0.123	0.393	0.053	0.236	0.061	0.002	0.046	0.002	0.034	0.002	0.012	0.002	0.012	0.002	0.001	0.020	1.154
C1-7	198.07	0.62	3.216	15.506	0.323	0.245	0.836	0.109	0.488	0.121	0.015	0.091	0.012	0.062	0.009	0.022	0.002	0.019	0.002	0.001	0.026	2.356
C1-10	26.30	0.60	4.188	13.110	0.409	0.466	1.657	0.185	0.773	0.170	0.021	0.127	0.017	0.078	0.011	0.026	0.002	0.019	0.002	0.001	0.014	3.963
C1-13	16.69	0.39	5.155	14.395	0.356	0.338	1.031	0.122	0.511	0.111	0.014	0.095	0.012	0.062	0.009	0.022	0.002	0.014	0.002	0.001	0.008	2.701
D1	159.71	4.38	19.614	53.838	2.920	1.912	3.974	0.391	1.613	0.280	0.043	0.396	0.053	0.274	0.045	0.099	0.009	0.042	0.002	0.001	0.063	12.053
C2	0.89	3.41	1.455	148.189	0.059	0.057	0.049	0.005	0.032	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.224
HBA	983.15																					
STEP III																						
C1-1	20.36	306.23	0.450	2.573	0.004	0.011	0.016	0.002	0.010	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.064
C1-3	312.97	89.05	0.647	3.204	0.068	0.015	0.036	0.002	0.024	0.002	0.002	0.008	0.002	0.012	0.002	0.002	0.002	0.002	0.002	0.001	0.011	0.181

C1-5	385.89	3.89	1.026	9.384	0.100	0.016	0.039	0.002	0.027	0.010	0.002	0.010	0.002	0.016	0.002	0.002	0.002	0.009	0.002	0.001	0.019	0.242
C1-7	83.39	0.39	0.728	5.896	0.035	0.002	0.013	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.009	0.076
C1-10	3.32	0.28	0.540	0.997	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C1-13	1.66	0.06	0.502	0.985	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
D1	7.89	-0.01	0.631	11.288	0.285	0.041	0.077	0.002	0.030	0.002	0.002	0.019	0.002	0.024	0.002	0.010	0.002	0.002	0.002	0.001	0.001	0.502
C2	0.62	0.61	0.141	4.631	0.026	0.005	0.043	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.098
HBA	226.27																					
STEP IV																						
C1-1	24.92	1025.63	2.597	9.823	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
C1-3	62.03	125.16	0.785	4.180	0.004	0.002	0.013	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.043
C1-5	43.41	2.74	0.109	1.309	0.020	0.002	0.017	0.002	0.012	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.073
C1-7	10.85	1.13	0.102	1.058	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
C1-10	1.75	0.82	0.109	0.779	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
C1-13	2.19	0.81	0.101	0.515	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
D1	1.16	0.02	0.046	0.880	0.038	0.002	0.015	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.079
C2	0.62	0.61	0.030	0.214	0.007	0.002	0.005	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.038
HBA	51.42																					
STEP V																						
C1-1	3.87	15.52	0.229	0.844	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.016
C1-3	5.96	2.28	0.085	0.295	0.029	0.041	0.133	0.019	0.090	0.024	0.003	0.014	0.002	0.007	0.001	0.002	0.001	0.002	0.001	0.001	0.000	0.369
C1-5	3.68	0.34	0.021	0.115	0.047	0.056	0.186	0.027	0.131	0.036	0.005	0.022	0.003	0.012	0.001	0.003	0.001	0.003	0.001	0.001	0.001	0.534
C1-7	2.77	0.26	0.028	0.102	0.051	0.061	0.203	0.028	0.124	0.031	0.004	0.020	0.003	0.012	0.002	0.003	0.001	0.003	0.001	0.001	0.001	0.547
C1-10	3.20	0.34	0.031	0.111	0.047	0.075	0.235	0.029	0.119	0.026	0.003	0.017	0.002	0.010	0.001	0.003	0.001	0.002	0.001	0.001	0.001	0.571
C1-13	2.65	0.29	0.027	0.080	0.025	0.036	0.097	0.012	0.050	0.010	0.001	0.008	0.001	0.005	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.251
D1	-0.13	0.03	0.023	0.341	0.512	0.398	0.683	0.071	0.296	0.047	0.008	0.077	0.010	0.047	0.007	0.015	0.001	0.005	0.001	0.001	0.001	2.178
C2	0.01	0.00	0.030	0.214	0.007	0.024	0.021	0.002	0.014	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.079
HBA	-0.20																					

Table S9-S4. Solid phase composition (µmol/g) of the Almagrera column after 30 weeks of functioning extracted with the different the sequential steps: C1-x _ where x is the depth from the water-reactive interface in the calcite column; D3= decantation vessel after the calcite column; C5= 2 cm depth in the MgO column; HBA= synthetic basaluminite.

	Al	**Fe**	**Cu**	**Zn**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**	**ΣREY**
STEP I																						
C3-1	5.26	<0.01	0.013	0.478	0.009	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.084
C3-3	2.79	<0.02	0.013	0.050	0.009	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.003	0.003	0.083
C3-5	0.47	<0.03	0.013	0.306	0.009	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.084
C3-7	0.76	<0.04	0.012	0.012	0.009	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.003	0.081
C3-9	1.64	<0.05	0.013	0.388	0.009	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.084
C3-11	0.12	<0.06	0.013	0.347	0.009	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.003	0.003	0.083
C3-13	1.20	<0.07	0.013	0.428	0.009	0.006	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.004	0.085
C3-16	2.75	<0.08	0.013	0.090	0.009	0.008	0.008	0.008	0.008	0.006	0.005	0.007	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.094
C3-19	0.10	<0.09	0.013	0.435	0.009	0.027	0.026	0.026	0.026	0.006	0.005	0.024	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.184
D3	1.21	<0.10	0.231	59.540	0.298	0.132	0.187	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.004	0.003	0.679
C5	0.14	0.01	0.040	0.291	0.010	0.005	0.005	0.005	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.001	0.001	0.080
STEP II																						
C3-1	14.36	318.00	4.688	8.905	0.092	0.063	0.061	0.016	0.086	0.055	0.002	0.009	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.398
C3-3	11.43	132.22	4.939	6.807	0.134	0.089	0.070	0.010	0.113	0.043	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.478
C3-5	23.78	128.45	13.405	7.396	0.150	0.092	0.224	0.042	0.126	0.046	0.002	0.009	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.705
C3-7	46.50	127.55	19.824	8.608	0.172	0.096	0.254	0.047	0.197	0.053	0.002	0.039	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.873
C3-9	137.77	72.04	27.208	8.421	0.180	0.078	0.308	0.050	0.254	0.058	0.002	0.050	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.995
C3-11	214.14	67.68	33.027	11.916	0.192	0.082	0.320	0.052	0.265	0.060	0.002	0.052	0.002	0.009	0.002	0.002	0.002	0.002	0.002	0.001	0.001	1.045
C3-13	419.41	22.46	83.440	11.620	0.336	0.092	0.517	0.061	0.310	0.075	0.002	0.069	0.002	0.050	0.002	0.002	0.002	0.003	0.002	0.001	0.001	1.524
C3-16	337.48	26.52	134.060	9.492	0.356	0.099	0.655	0.071	0.496	0.091	0.003	0.077	0.003	0.057	0.003	0.003	0.003	0.009	0.002	0.001	0.001	1.926
C3-19	374.30	33.80	170.515	11.052	0.391	0.154	0.602	0.078	0.638	0.106	0.010	0.086	0.009	0.070	0.009	0.009	0.009	0.035	0.002	0.001	0.001	2.209
D3	9.36	0.20	4.576	212.697	0.523	0.061	0.070	0.002	0.056	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.734

C5	0.47		2.78	1.155	130.990	0.255	0.048	0.033	0.005	0.016	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.377
STEP III																							
C3-1	20.47		857.01	7.238	7.873	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-3	15.15		407.08	4.365	4.904	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-5	31.72		469.19	7.919	4.429	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-7	39.70		505.43	7.508	3.770	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
C3-9	71.37		434.48	9.781	3.658	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-11	75.47		324.23	9.853	4.322	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-13	454.34		36.42	27.509	6.042	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-16	604.85		33.53	70.456	7.077	0.004	0.003	0.003	0.002	0.003	0.002	0.002	0.003	0.002	0.003	0.002	0.003	0.002	0.002	0.002	0.001	0.001	0.038
C3-19	632.55		41.83	100.698	8.604	0.075	0.011	0.011	0.002	0.010	0.002	0.002	0.009	0.002	0.009	0.002	0.009	0.002	0.002	0.002	0.001	0.001	0.150
D3	0.20	-	0.43	0.109	2.489	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C5	0.31		0.49	0.110	4.899	0.008	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.036
STEP IV																							
C3-1	12.71		928.69	13.149	9.617	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-3	14.88		936.72	13.443	14.392	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-5	11.15		321.60	7.404	5.642	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-7	12.76		240.58	6.134	4.193	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
C3-9	9.10		98.89	3.165	1.791	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-11	7.69		44.51	1.700	1.091	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.033
C3-13	35.32		4.53	2.172	0.584	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-16	34.74		3.08	3.759	0.677	0.004	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C3-19	34.58		3.45	5.093	0.605	0.004	0.003	0.011	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.043
D3	1.43	-	0.11	0.076	7.385	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.034
C5	0.31		0.49	0.050	0.211	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001	0.032
STEP V																							
C3-1	2.26		7.60	0.179	0.339	0.001	0.004	0.006	0.001	0.004	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.026
C3-3	2.25		6.01	0.200	0.537	0.001	0.005	0.007	0.001	0.006	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.030

C3-5	2.10	2.05	0.113	0.240	0.001	0.019	0.008	0.001	0.006	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.045
C3-7	2.55	2.20	0.137	0.223	0.003	0.006	0.009	0.001	0.006	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.035
C3-9	1.60	0.98	0.081	0.138	0.001	0.005	0.007	0.001	0.005	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.029
C3-11	3.98	1.94	0.074	0.174	0.003	0.006	0.009	0.001	0.007	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.036
C3-13	5.11	1.06	0.148	0.091	0.008	0.007	0.014	0.002	0.011	0.003	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.056
C3-16	3.79	0.89	0.074	0.095	0.007	0.007	0.014	0.002	0.012	0.003	0.001	0.003	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.057
C3-19	3.91	0.91	0.131	0.078	0.010	0.008	0.018	0.003	0.017	0.005	0.001	0.003	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.073
D3	0.20	0.05	0.011	0.074	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.015
C5	0.21	0.65	0.050	0.211	0.003	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.019

Table S12-S5.Flow rate, REY and Al concentration of some Acid Mine Drainages from the Iberian Pyrite Belt. Estimated total annual reserves and flow-weighted rates of REY in basaluminite precipitates.

Code	**AMD origin**	**Date**	**X**	**Y**	**pH**	**Q (L/s)**	**Al (mg/L)**	**REY (µg/L)**	**Bas (t/a)**	**REY_2O_3 (t/a)**	**Rate (%)**
TSRA	Mine gallery	06/02/2015	693.859	4.167.461	3.4	4	77	525	41.785	0.086	0.21
POD2	Mine gallery	18/04/2015	705.549	4.180.492	1.8	3	356	11757	144.865	1.446	1.00
SPI	Mine gallery	18/04/2015	704.986	4.182.029	2.5	2	290	4106	78.757	0.337	0.43
MC	Open pit discharge	15/05/2015	704.564	4.183.455	3.1	5	175	1377	118.819	0.282	0.24
BR	Stream	28/05/2015	716.248	4.163.501	2.3	250	13	551	426.072	5.652	1.33
TT2	Acid creek	28/05/2015	715.794	4.177.942	2.6	0.25	139	1838	4.711	0.019	0.40
Perru	Mine gallery	31/05/2015	688.244	4.175.346	2.6	2	439	2841	118.990	0.233	0.20
ME	Mine gallery	27/10/2014	704.101	4.181.645		1	147	863	19.898	0.035	0.18
SM1	Mine shaft	26/06/2015	697.773	4.181.775	2.6	0.75	244	3123	24.832	0.096	0.39
MR	Mine shaft	10/07/2015	694.236	4.183.255	3.1	1	135	7358	18.290	0.302	1.65
Alm1	Roasted pyrite dump	06/09/2015	689.79	4.168.429	3.0	0.5	628	6695	42.548	0.137	0.32
Alm2	Tailings dump	17/09/2015	690.935	4.167.351	3.6	0.15	15	856	0.312	0.005	1.69
ST4	Open pit discharge	04/12/2013	678.792	4.185.643	2.6	5	152	1791	102.717	0.367	0.36
ST5	Mine shaft	14/01/2014	679.293	4.185.762	2.8	0.3	289	3626	11.747	0.045	0.38
ST7	Waste dump	14/01/2014	679.233	4.185.890	2.8	1	28	348	3.745	0.014	0.38
Th13	Waste dump	11/06/2014	668.133	4.162.384	2.8	0.46	655	7605	40.835	0.143	0.35
Th27	Acid creek	08/08/2014	668.888	4.162.935	2.2	0.1	754	10629	10.220	0.044	0.43
Th29	Waste dump	28/10/2014	665.421	4.162.554	2.8	0.7	35	313	3.347	0.009	0.27
Th30	Waste dump	28/10/2014	668.803	4.162.913	2.7	0.5	260	3009	17.626	0.062	0.35
Th31	Waste dump	28/10/2014	668.634	4.162.691	3.0	0.5	179	2792	12.154	0.057	0.47
LAP1	Waste dump	28/10/2014	667.954	4.160.333	2.7	0.5	101	1070	6.881	0.022	0.32
F2	Σ Waste dumps	18/02/2015	706.417	4.177.400	2.8	160	313	1367	6789.217	8.970	0.13
SUM						**438.7**			**8038.367**	**18.362**	**0.23**

UTM coordinates: datum ETRS89. Bas: basaluminite.

Figure S13-S1. Treatment columns of Monte Romero (A and C) and Almagrera (B and D) acid drainage after 18 weeks of percolation. A and B) Calcite-DAS columns showing three zones: a red zone of schwertmannite (1), a white zone of basaluminite (2), and a creamy zone of gypsum and unreacted calcite (3). C and D) MgO-DAS column treating Monte Romero water showing a white zone of gypsum and Zn-hydroxides (4) and unreacted MgO (5). The progression of reactions fronts in Almagrera calcite column (B) is faster than in Monte Romero (A) due to the higher acidity of the Almagrera inflow water.

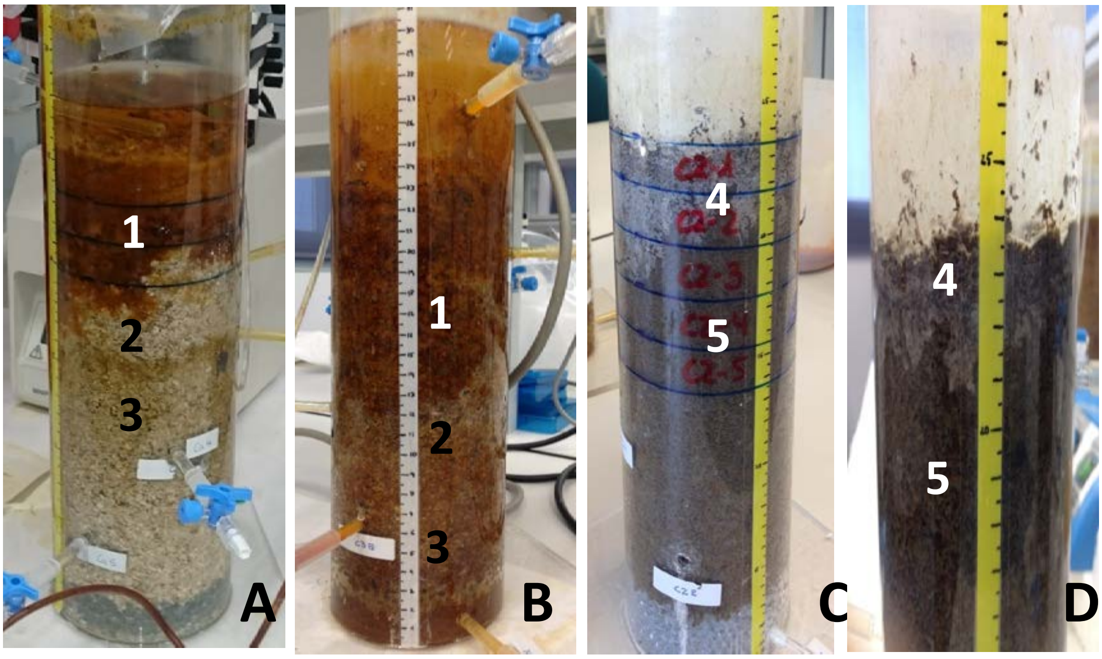
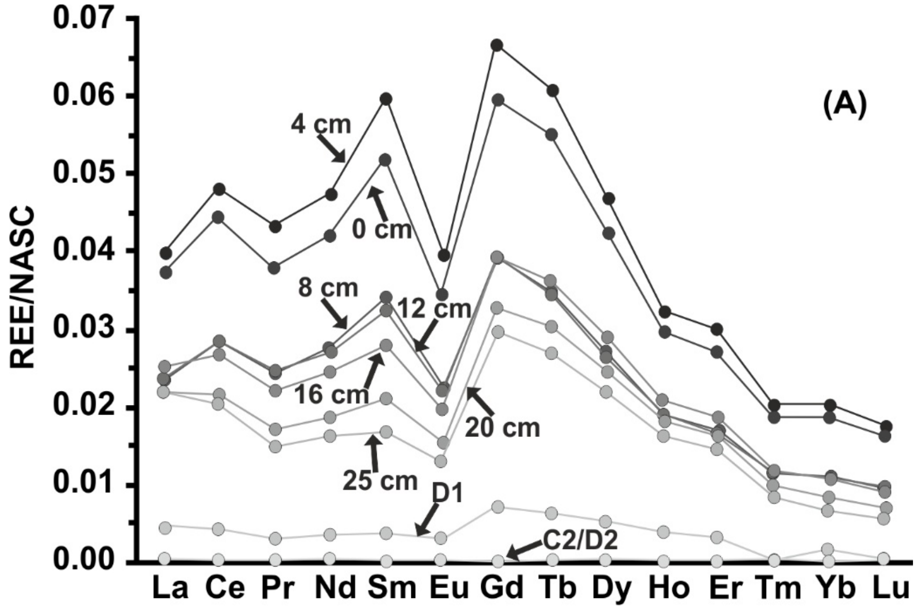


Figure S14-S2. NASC normalized REE pattern of pore water from the Monte Romero (a) and Almagrera (b) treatment lines. The numbers indicate the depth with respect to the calcite column water-solid interface, D1 and D3 are the first decantation vessels and C2 and C5 the first 2 cm of the MgO columns.



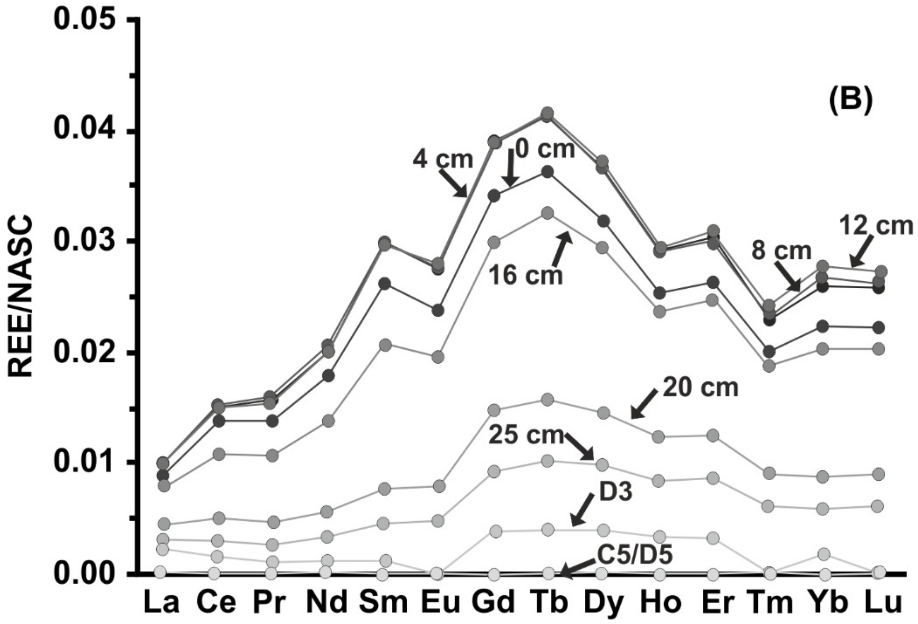
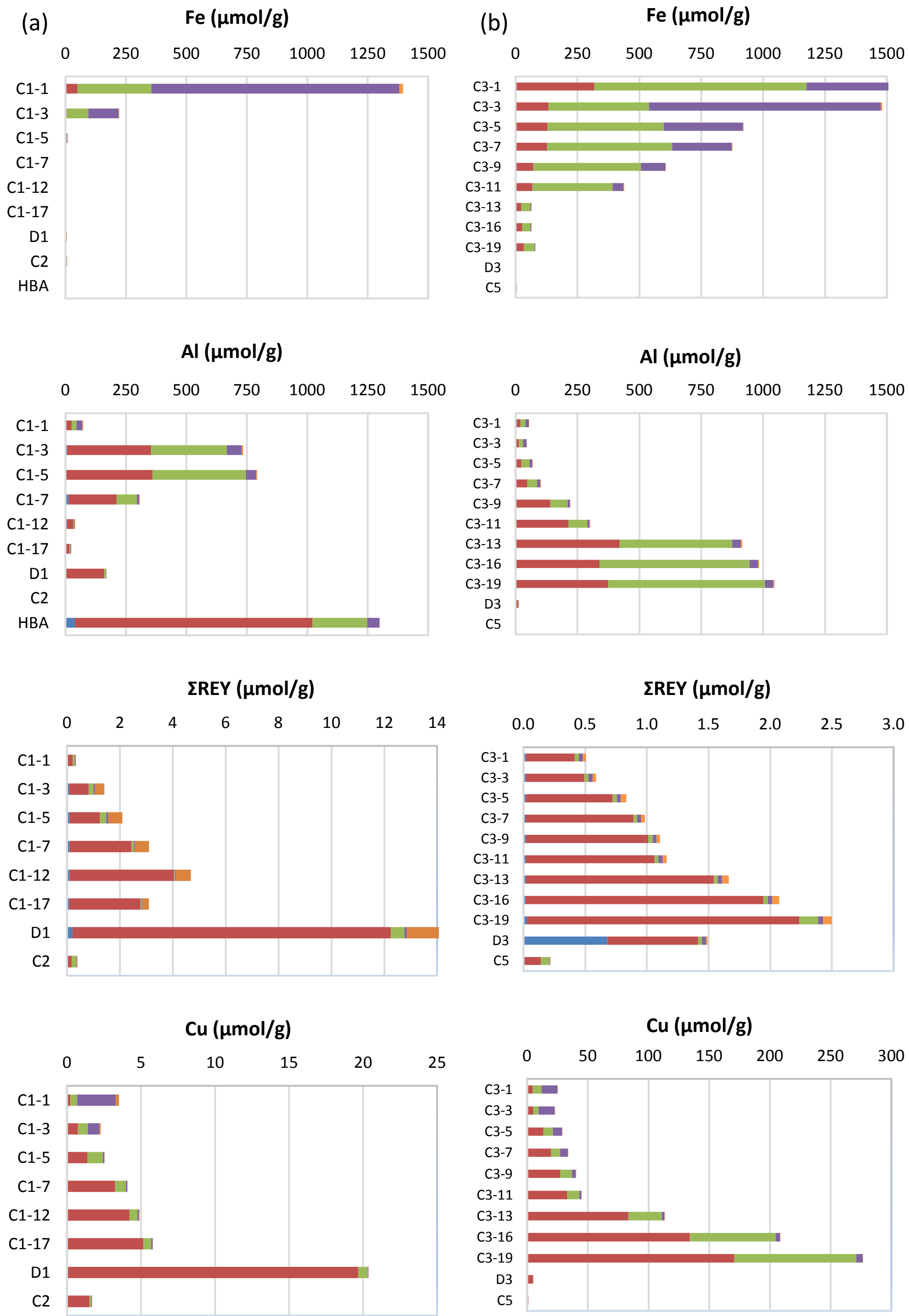
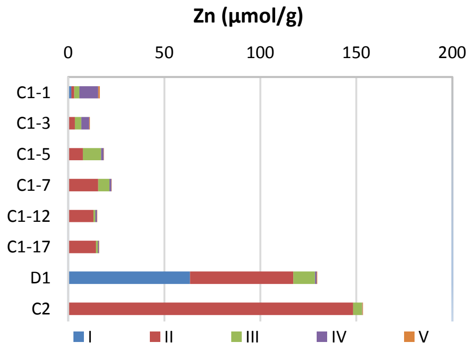


Figure S15-S3. Distribution of element concentration in the solid phase from Monte Romero (a) and Almagrera (b) columns. The numbers of the vertical axes indicate the depth (cm) of the center of each solid slice, D1 and D3 indicate the first decantation vessels and C2-1 and C2-5 correspond to the first 2 cm slice of the MgO column. The different steps of sequential extraction are shown as bars.




Zn (µmol/g)
0
50
100
150
200
C1-1
C1-3
C1-5
C1-7
C1-12
C1-17
D1
C2
I
II
III
IV
V

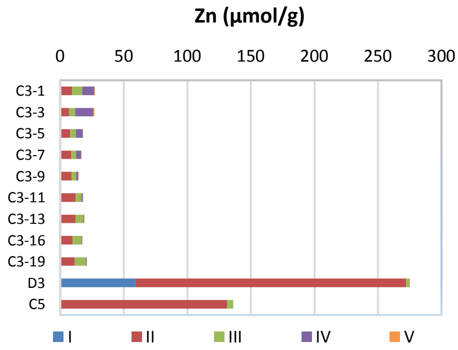

Zn (µmol/g)
0
50
100
150
200
250
300
C3-1
C3-3
C3-5
C3-7
C3-9
C3-11
C3-13
C3-16
C3-19
D3
C5
I
II
III
IV
V

Figure S17-S4. DRX diagram of a D1 sample. Legend: G = gypsum; B = bechererite; F = fluorite.

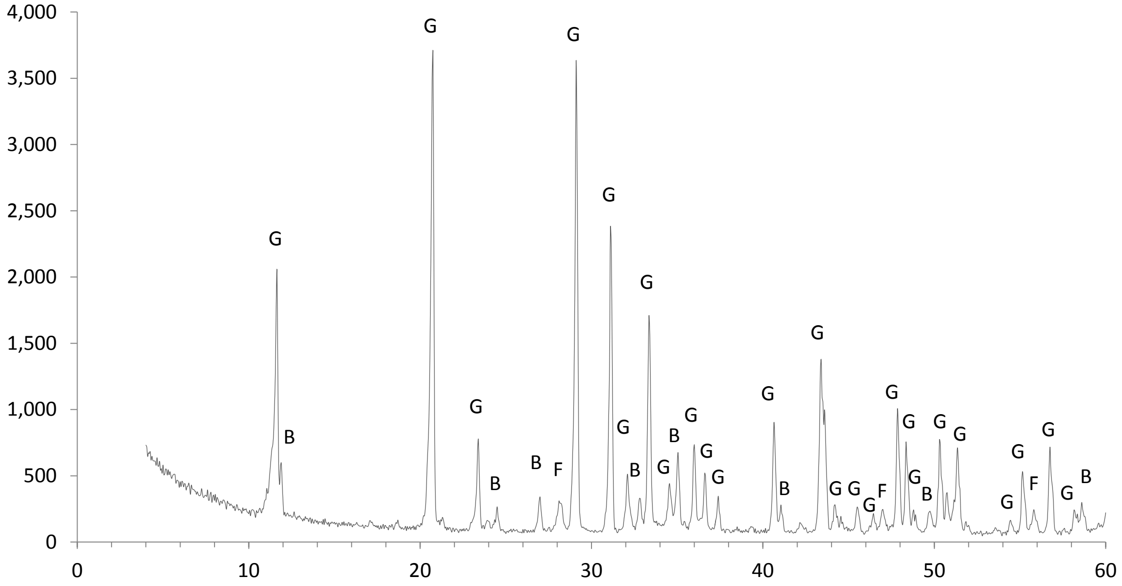


Figure S18-S5. Distribution of fluorine aqueous species with pH along the treatment of Monte Romero (a) and Almagrera (b) AMDs. Vertical scale is the fraction of the total concentration. Calculations made with the code PHREEQC and the LLNL thermodynamic database[S4].

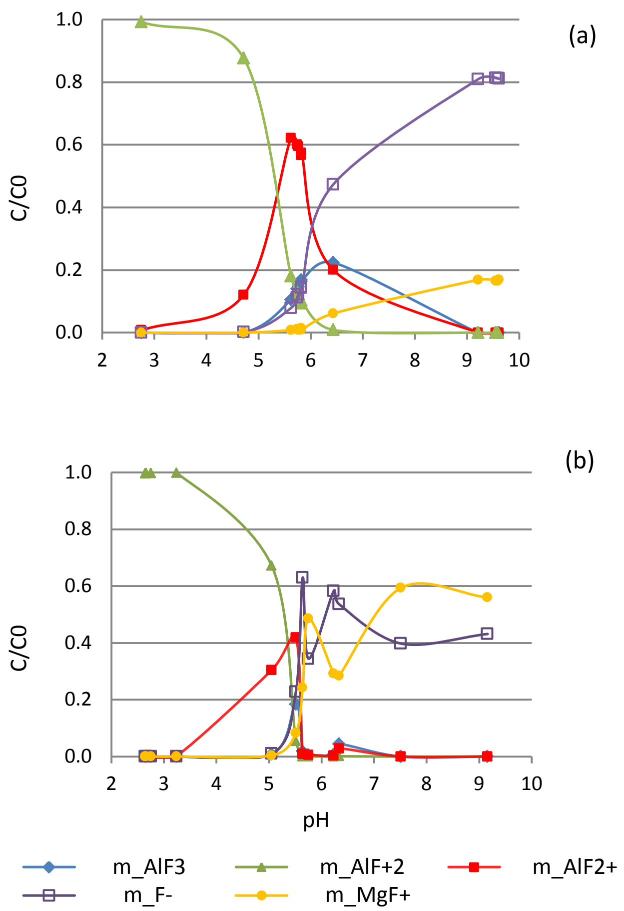


Figure S19-S6. A) View of the Mina Esperanza passive remediation systems after 15 months of functioning. B) Detail of the vertical zonation: calcite-gypsum (1), basaluminite (2) and schwertmannite (3) zones.

References cited

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(S2) Torres, E.; Auleda, M. A sequential extraction procedure for sediments affected by acid mine drainage. *Journal of Geochemical Exploration*, **2013**, 128, 35–41.

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(S4) Parkhurst D. L.; Appelo, C. A. J. User's guide to PHREEQC (Version 2): a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey : Earth Science Information Center, Open-File Reports Section [distributor], Water-Resources Investigations Report 1999; 99,4259, 312 pp.