

Solution chemistry calculations were performed to provide a fundamental basis for the optimization of the rare earth element (REE) precipitation process using oxalic acid. The method applied in this study followed that of Chi and Xu with key adaptations to accommodate the unique attributes of the feedstock [1]. Initially, the calculations were used to determine the speciation of the oxalate ion in aqueous solution as a function of pH. Next, the various reaction equations and equilibrium constants were used to determine the various oxalic acid consumers, including consumption via REE precipitation, excess dosage needed for complete precipitation, and consumption via non-RE contaminants. The data in this supplemental file shows the calculation steps and intermediate results needed to properly model the system.

#### *Oxalate Speciation*

The reaction equations and equilibrium constants that describe the dissociation of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) in water are provided in Table 3. Recognizing that  $\varphi_0 + \varphi_1 + \varphi_2 = 1$ , one can calculate the fractional distribution of the oxalate ion as a function of pH. **Table S1** shows the results of this calculation.

**Table S1.** Calculated oxalate species fraction with respect to the total acid concentration as a function of pH.

pH	[H <sup>+</sup> ]	$\varphi_0/\% \text{C}_2\text{O}_4^{2-}$	$\varphi_1/\% \text{HC}_2\text{O}_4^-$	$\varphi_2/\% \text{H}_2\text{C}_2\text{O}_4$
0.00	1.0000	0.0000	0.0557	0.9443
0.20	0.6310	0.0000	0.0855	0.9145
0.40	0.3981	0.0000	0.1291	0.8709
0.60	0.2512	0.0000	0.1902	0.8098
0.80	0.1585	0.0001	0.2712	0.7286
1.00	0.1000	0.0002	0.3710	0.6288
1.20	0.0631	0.0005	0.4830	0.5165
1.40	0.0398	0.0010	0.5965	0.4025
1.60	0.0251	0.0018	0.7001	0.2981
1.80	0.0158	0.0032	0.7858	0.2111
2.00	0.0100	0.0054	0.8504	0.1441
2.20	0.0063	0.0091	0.8952	0.0957
2.40	0.0040	0.0148	0.9229	0.0623
2.60	0.0025	0.0239	0.9363	0.0399
2.80	0.0016	0.0378	0.9370	0.0252
3.00	0.0010	0.0592	0.9251	0.0157
3.20	0.0006	0.0912	0.8992	0.0096
3.40	0.0004	0.1377	0.8565	0.0058
3.60	0.0003	0.2024	0.7943	0.0034
3.80	0.0002	0.2871	0.7110	0.0019
4.00	0.0001	0.3898	0.6091	0.0010
4.20	0.0001	0.5033	0.4962	0.0005
4.40	$3.98 \times 10^{-5}$	0.6163	0.3834	$2.59 \times 10^{-4}$
4.60	$2.51 \times 10^{-5}$	0.7181	0.2818	$1.20 \times 10^{-4}$
4.80	$1.58 \times 10^{-5}$	0.8015	0.1985	$5.33 \times 10^{-5}$
5.00	$1.00 \times 10^{-5}$	0.8648	0.1351	$2.29 \times 10^{-5}$

#### *Oxalic Acid Consumption*

Consumption of oxalic acid is governed by three factors, namely the stoichiometric requirement for REE precipitation, the excess consumption needed to ensure complete precipitation, and the consumption via contaminant metals. The equations governing these reactions are given in Table 4., and a summary of the various input variables and

assumed parameters used in this study are given in **Table S2**. The initial concentrations of REEs and  $[\text{Ca}^{2+}]$  represent values determined from the experimental trials, while the final REE concentration was assumed to be  $1.00 \times 10^{-5}$  mol/L, implying a total REE recovery of >99%.

**Table S2.** Input variables and other parameters used in solution chemistry calculations.

Parameter	Unit	Value
$K_1$	--	$5.90 \times 10^{-2}$
$K_2$	--	$6.40 \times 10^{-5}$
$K_{\text{sp}}^{\text{RE}^{3+}}$	--	$3.00 \times 10^{-27}$
$K_{\text{sp}}^{\text{Ca}^{2+}}$	--	$1.96 \times 10^{-8}$
Solution pH	--	1.5
Initial REE Concentration, $C_{\text{RE}}$	mol/L	0.0032
Final REE Concentration, $[\text{RE}^{3+}]$	mol/L	$1.00 \times 10^{-5}$
Initial $\text{Ca}^{2+}$ Concentration, $[\text{Ca}^{2+}]$	mol/L	0.106

The stoichiometric requirement of oxalic acid for REE precipitation can be directly calculated using Equation 8:

$$H_p = \frac{3}{2} (C_R - [\text{RE}^{3+}]) = \frac{3}{2} (0.0032 \text{ mol/L} - 0.00001 \text{ mol/L}) = 0.0048 \text{ mol/L}$$

Next, the excess oxalic acid needed for complete precipitation can be determined using Equation 9. As shown in Table 4, this expression is a function of the various solubility constants, the desired ending REE concentration, and the solution pH. **Table S3** shows this result for various pH values using the fixed final REE concentration of  $1.00 \times 10^{-5}$  mol/L. At a pH of 1.5, which was utilized in experiments,  $H_E$  was determined to be 0.0025 mol/L.

**Table S3.** Calculated excess oxalic acid usage ( $H_E$ ) for REE precipitation at a final REE concentration of  $1.00 \times 10^{-5}$ .

pH	[H <sup>+</sup> ]	H <sub>E</sub>
1.00	0.1000	$1.31 \times 10^{-2}$
1.20	0.0631	$6.34 \times 10^{-3}$
1.40	0.0398	$3.24 \times 10^{-3}$
1.60	0.0251	$1.74 \times 10^{-3}$
1.80	0.0158	$9.79 \times 10^{-4}$
2.00	0.0100	$5.71 \times 10^{-4}$
2.20	0.0063	$3.42 \times 10^{-4}$
2.40	0.0040	$2.09 \times 10^{-4}$
2.60	0.0025	$1.30 \times 10^{-4}$
2.80	0.0016	$8.21 \times 10^{-5}$
3.00	0.0010	$5.25 \times 10^{-5}$
3.20	0.0006	$3.41 \times 10^{-5}$
3.40	0.0004	$2.26 \times 10^{-5}$
3.60	0.0003	$1.54 \times 10^{-5}$
3.80	0.0002	$1.08 \times 10^{-5}$
4.00	0.0001	$7.97 \times 10^{-6}$
4.20	0.0001	$6.17 \times 10^{-6}$
4.40	$3.98 \times 10^{-5}$	$5.04 \times 10^{-6}$
4.60	$2.51 \times 10^{-5}$	$4.33 \times 10^{-6}$
4.80	$1.58 \times 10^{-5}$	$3.88 \times 10^{-6}$
5.00	$1.00 \times 10^{-5}$	$3.59 \times 10^{-6}$

Lastly,  $H_{IP}$  and  $H_{IC}$  can be calculated using Equations 10 and 11, respectively. The  $H_{IP}$  calculation is as follows:

$$H_{IP} = [Ca^{2+}]_T - \frac{K_{sp}^{Ca^{2+}}}{[L]} = 0.106 - \frac{1.96 \times 10^{-8}}{1 \times 10^{-5}} = 0.10 \text{ mol/L}$$

For the conditions given in this study,  $H_{IC}$  was determined to be negligible and is thus not shown.

By summing  $H_P$ ,  $H_E$ ,  $H_{IC}$  and  $H_{IP}$ , the total oxalic acid consumption for the conditions utilized in the study was determined to be 0.11 mol/L or approximately 10 g/L. Using the same approach, this calculation can be repeated at various pH points and solution concentrations to provide a fundamental basis for techno-economic optimization of the rare earth recovery system.

## References

1. Chi, R., Xu, Z. A solution chemistry approach to the study of rare earth element precipitation by oxalic acid. *Metall Mater Trans, B* 1999, 30, 189–195.