A Solution Chemistry Approach to the Study of Rare Earth Element Precipitation by Oxalic Acid

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A solution chemistry approach is developed to study oxalic acid efficiency (OAE) in recovering rare earth (RE) elements from the leachates of weathered clays. The optimal pH for precipitation (approximately 2) to obtain the highest RE recovery with the highest purity is identified experimentally and confirmed by solution chemistry calculations. Applying the solution chemistry approach to three case studies, the cause for a larger oxalic acid consumption than that calculated from stoichiometry of RE oxalate precipitation is identified. A typical OAE of approximately 60 pct was determined with 40 pct of excess oxalic acid consumed by precipitating and complexing non-RE elements while maintaining a low residual RE element concentration. Both solution chemistry calculations and experimental results showed that OAE can be improved by processing leachates of high initial RE concentrations.

I. INTRODUCTION

RARE earth elements play a critical role in civilization and human life. In general, they are a critical component in superconductor materials, permanent magnets, catalysts, special steels, and fluorescent powders. Currently, the major source of medium-to-heavy rare earth (RE) elements is from weathered clay minerals formed through complex physical, chemical, and geobiological processes under natural conditions. The rare earth elements, collectively referred to as RE, are often migrated from RE-containing granite and igneous rocks to kaolinite and halloysite, and enriched to a level of economic value. The clay minerals act as an inorganic ion exchange resin onto which the hydrated RE elements adsorb. Therefore, these RE elements can be released into solutions by ion exchange process using certain types of cations, which react with clays stronger than hydrated RE ions. The dissolved RE elements are then recovered by either solvent extraction or precipitation using oxalic acid (H$_2$C$_2$O$_4$). The latter is often used in industrial operation due to process simplicity and effective recovery.

A common observation in RE recovery by precipitation is excess use of oxalic acid with a H$_2$C$_2$O$_4$ to RE$_3$O$_5$ mole ratio greater than 1.5. The exact reason for this excess requirement of oxalic acid is not clear, although other released non-RE metallic species, such as Fe$^{3+}$, Al$^{3+}$, Mg$^{2+}$, and Ca$^{2+}$, are considered to consume a portion of the acid added. In this article, a solution chemistry approach is applied to a phenomenological analysis of the system, which allows quantitative description of various contributions of oxalic acid consumption. With the approach developed here, an operating condition of minimum oxalic acid consumption with a maximized purity of RE oxalates is derived.

II. SOLUTION CHEMISTRY CONSIDERATION

In a typical precipitation process of RE elements by oxalic acid, three main acid consumption mechanisms need to be considered, including stoichiometric requirement, excess acid to achieve complete precipitation, and precipitation and complexation of other coexisting non-RE metallic species. The relative contributions to total acid consumption by each of these mechanisms can be described quantitatively through a solution chemistry analysis as described below.

A. Equilibrium of Diprotic Oxalic Acid

To describe the precipitation reaction quantitatively, it is essential to know the speciation distribution of acid precipitants. For a diprotic oxalic acid, a two-step dissociation equilibrium can be expressed by:

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4 & \rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^- \quad K_1 = 5.90 \times 10^{-2} \quad [1] \\
\text{HC}_2\text{O}_4^- & \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{2-} \quad K_2 = 6.40 \times 10^{-5} \quad [2]
\end{align*}
\]

The total concentration of oxalic acid containing species ([H$_2$C$_2$O$_4$]$_T$) is therefore given by:

\[
[\text{H}_2\text{C}_2\text{O}_4]_T = [\text{H}_2\text{C}_2\text{O}_4] + [\text{C}_2\text{O}_4^{2-}] + [\text{H}_2\text{C}_2\text{O}_4]_{aq}
\]

where subscripts $T$ and $aq$ represent the total and undisassociated oxalic acid concentration in solution, respectively. The fraction of each species with respect to the total acid concentration can then be expressed as:

\[
\begin{align*}
\varphi_0 &= \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4]_T} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_2} \quad [4] \\
\varphi_1 &= \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]_T} = \frac{K_2 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_2} \quad [5] \\
\varphi_2 &= \frac{[\text{H}_2\text{C}_2\text{O}_4]}{[\text{H}_2\text{C}_2\text{O}_4]_T} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_2} \quad [6]
\end{align*}
\]

with $\varphi_0 + \varphi_1 + \varphi_2 = 1$. It is readily seen from the calculated species distributions using Eqs. [4] through [6]...
Fig. 1—Calculated species distribution of oxalic acid in water as a function of solution pH.

(Figure 1) that C$_2$O$_4^{2-}$ is the predominant species at pH greater than 7. At pH = 2, the main species is HC$_2$O$_4$ with a minimal amount of C$_2$O$_4^{2-}$ (approximately 0.45 pct). These balances collectively control the amount of oxalic acid needed to maintain a desired level of C$_2$O$_4^{2-}$, as will be discussed later.

B. RE Oxalate Formation Equilibrium

For the convenience of description, the rare earth elements are collectively described by RE, although they cover a wide range of elements. For a particular element, its precipitation by oxalic acid can be expressed as

$$2\text{RE}^{3+} + 3 \text{H}_2\text{C}_2\text{O}_4 + 10\text{H}_2\text{O} \rightarrow \text{RE}_3(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} \downarrow + 6\text{H}^+$$  \[7\]

where $K_{sp}$ is the solubility product of the resultant RE oxalate. Since the complete solubility product constant for all the RE oxalates encountered in this study is not available in the literature, a typical $K_{sp}$ value of $3 \times 10^{-27}$ for Nd$_3$(C$_2$O$_4)_3$ is used, which gives rise to a $K_3$ value of $1.79 \times 10^{10}$. Such a large $K_3$ value implies a near complete precipitation. Reaction [7] shows that 3 moles of protons are released to precipitate 1 mole of rare earth oxalate, resulting in an excessive acidic solution. Fortunately, the presence of two weak acid equilibria, $\text{HC}_2\text{O}_4 /\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}_2\text{O}_4^{2-} /\text{HC}_2\text{O}_4$, causes the solution to stabilize at pH of approximately 2. At this pH, the concentration of C$_2$O$_4^{2-}$, the active species for RE oxalate precipitation, is minimal.

C. Stoichiometric Dosage of Oxalic Acid

Based on the precipitation reaction (Eq. [7]), the stoichiometric dosage ($H_p$) on a 1 L leachate basis can be readily calculated using

$$H_p = \frac{3}{2} (C_{\text{RE}} - [\text{RE}^{3+}])$$  \[9\]

where $C_{\text{RE}}$ and [RE$^{3+}$] are the initial and final concentrations of RE elements in a leachate (mole/dm$^3$), respectively.

D. Excess Oxalic Acid Needed to Ensure a Complete Precipitation

To effectively recover RE using the oxalic acid precipitation process, an excess acid is needed, as illustrated here. By combining the solubility product ($K_{sp} = [\text{RE}^{3+}][\text{C}_2\text{O}_4^{2-}]^3$) with dissociation equilibrium (Eq. [4]), it is readily shown that the amount of oxalic acid ($H_E$) needed to maintain a desired residual RE concentration ([RE$^{3+}$]) is given by

$$H_E = \frac{[\text{H}^+]^2 + K_i[\text{H}^+] + K_iK_2 \sqrt{K_{sp}}}{K_iK_2} [\text{RE}^{3+}]^3$$  \[10\]

The $H_E$ value can be calculated readily using this equation. The calculated variations of $H_E$ with pH at three different residual RE concentrations are shown in Figure 2. Clearly, a substantial amount of oxalic acid is needed to maintain a relatively low level of residual RE concentration, increasing significantly with decreasing pH below 5. For a typical residual RE concentration of $10^{-5}$ mole/dm$^3$, as much as 60 mM additional oxalic acid is needed, should the precipitation be conducted at pH 1.5, as often encountered in practice.

E. Oxalic Acid Consumed by Non-RE Contaminants

During the ion exchange process of clay minerals with cations to release RE ions, non-RE metallic species, such