THERMODYNAMIC MODELLING OF RARE EARTH SOLVENT EXTRACTION

By

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ABSTRACT

Rare Earth Elements (REEs) are becoming increasingly important due to their critical role in the transition to clean energy. In recent times, there has been significant activity and investment in production from mining and recycling. A key area of difficulty for metallurgical production of REEs is their separation, largely due to their similar electron structures which makes them chemically similar.

In this work, a thermodynamic model of solvent extraction (SX) is presented based solely upon experimental data in open literature. This model is embedded in SysCAD connected to PHREEQC⁽¹⁾ via the Thermodynamic Calculation Engines (TCE) interface. In previous work, Heppner⁽²⁾ calculated reaction equilibrium constants for the extraction of Nd and Pr based upon fitting to experimental data of Lyon et al.⁽³⁾. Here, that model is extended using separation factors published by Zhang et al.⁽⁴⁾ and references therein to estimate the equilibrium constants for all 15 REEs. Pitzer parameters and their temperature dependence are calculated for each cation-anion interaction in the REE chloride system from correlations published by Simoes et al.⁽⁵⁾⁽⁶⁾. It is noteworthy that aqueous/organic exchange reactions are written in terms of free acid, not hydrochloric acid, and thus, are suitable for use in any acidic medium (e.g. chloride, sulphate, nitrate).

A test of the model was performed where a solution containing REE chlorides was fed to an extraction, scrubbing, and stripping circuit with conditions typical for initial separation of light, medium, and heavy REE elements. Results of the test model showed trends that are typical of SX separation of REEs in practice, confirming the validity of the approach. This fundamental approach enables a wider range of applicability for the model compared to the use of plant isotherms.

This work focuses on the modelling methodology of the REE SX process, rather than the modelling of a specific processing plant. For this reason, the presented model requires validation against relevant plant data prior to use for plant design or optimisation.

Keywords: Rare earth elements, solvent extraction, SysCAD, PHREEQC, process simulation, process optimisation, process design, digital twin, REE, battery metals

INTRODUCTION

REE Separation Process and Challenges

The solvent extraction separation of rare earth elements involves numerous circuits and hundreds of mixer-settler units. Individual circuits consisting generally of extraction, scrubbing, and stripping are employed to separate different rare earth metals into various cuts, thereby allowing further separation downstream. The resulting process includes significant recycle loads both within individual circuits, as well as between separation areas. The result is a process that is not only complex to simulate, but also to operate. Steady-state conditions can take very long times to achieve. As noted in Turgeon et al.⁽⁷⁾, "it takes 14 days to stabilize a pilot plant for one condition". For this reason, it is important to have a mathematical model of a solvent extraction process.

Conventional approaches to solvent extraction involve the use of plant isotherms and/or distribution coefficients to understand loading behaviour of rare earth elements in different conditions. Plant isotherms, while highly useful, are limited to the chemical solution from which they are obtained. Changes in feed chemistry will affect the loading behaviour due to the competitive nature of the extraction process. Furthermore, isotherms are required for each of the circuits. Distribution coefficients are obtained at a consistent pH and extraction concentration, and thus, are indicative of the separability of adjacent rare earths. These coefficients are also limited in their application to the pH for which they are obtained. Turgeon et al.⁽⁷⁾ presented an equilibrium approach whereby equilibrium constants for individual reactions were calculated by fitting to experimental data. This approach is an improvement in that it is applicable over a wider operating range and adjustable for changing feed conditions. However, it did not consider solution non-ideality. In the work presented herein, the PHREEQC interface is used with SysCAD to model solvent extraction considering non-ideal solution behaviour. Activities of components in the aqueous solution are calculated using Pitzer's model, which accounts for short- and long-range interactions between ions and neutral species.

In earlier work, Heppner⁽²⁾ calculated the equilibrium constants for acid dissociation, neodymium extraction, and praseodymium extraction using experimental data reported by Lyon et al.⁽³⁾. Here, that original work is expanded to include all rare earth elements. Using the calculated equilibrium values from the previous work, separation factors reported by Zhang et al.⁽⁴⁾ are employed as quasi-indicators of equilibrium constant ratios, thereby allowing the calculation of extraction equilibrium constants for the rare earth elements, not including Promethium and Scandium. Together with aqueous speciation and activity calculations, a highly robust model for the calculation of rare earths separation was developed.

MATHEMATICAL MODEL

Background

Aqueous phase chemistry is modelled using the thermodynamic package PHREEQC supplemented with Pitzer's ionic interaction model. PHREEQC is embedded as one of several available thermodynamic engines within SysCAD. Other thermodynamic engine links include OLI, AQSol, ChemApp, and HSC Chemistry. The ChemApp interface allows incorporation of databases generated using FactSage and other data sources. Long-range and short-range interaction terms for Na⁺ and Cl⁻ are obtained from the Pitzer.dat database in PHREEQC. Additional Pitzer parameters for Nd⁺³, Pr⁺³ and Cl⁻ were taken from Roy et al.⁽⁸⁾ and Simoes et al.⁽⁵⁾⁽⁶⁾. Pitzer's parameters are a virial expansion of binary and ternary interactions between cations, anions, and neutral species, incorporating all important permutations and combinations. Debye-Hückel type terms in the equation account for long-range interactions, which scale according to ionic strength. These equations allow calculation of individual activity coefficients for dissolved neutral and ionic species, along with the osmotic coefficient of water.

Information on the electrolyte chemistry models used in PHREEQC are documented by Parkhurst and Appelo⁽¹⁾. In brief, chemical equilibrium and mass balance equations are combined to calculate the reactions which occur to achieve the minimum free energy state of a system. Chemical equilibrium equations are expressed as:

$$K_i = \prod_{j=1}^{N_i} a_{i,j}^{\nu_{i,j}} \tag{1}$$

Where $a_{i,j}$ and $v_{i,j}$ are the activity and stoichiometric coefficient of the jth species involved in the ith reaction. The activity is calculated from the species concentration and the activity coefficient. The activity coefficient is calculated from Pitzer's equations using temperature-dependent terms. With appropriate interaction coefficients, the Pitzer model is typically applicable up to and including the range of 2 – 6 molal concentration, depending on the solute, per Pitzer and Mayorga⁽⁹⁾, and thus is suitable for application to this model.

Cation Extraction

Liquors containing rare earths as dissolved chloride salts are typically processed using suitable cation extractants dissolved in an organic solvent. The relevant equilibria are shown below:

$$PcH = Pc^{-} + H^{+}$$
(2)

$$3 \text{ PcH} + \text{REE}^{+3} = \text{Pc}_3 \text{REE} + 3\text{H}^+$$
(3)

$$3 \operatorname{PcH} + \operatorname{Na}^{+} = \operatorname{PcNa} + \operatorname{H}^{+}$$
(4)

Here, Pc represents the cation exchanger PC88A. The mechanism of extraction involves acid form extractant dissociation, equation (2) and cation exchange, equation (3) as per Lyon et al.⁽³⁾. From previous work⁽²⁾, it was shown that solvation reactions, while reported to occur in certain situations by Sato⁽¹⁰⁾, did not occur in this system at the concentration ranges of interest. In equation (3), the REE species represents all 15 rare earth elements considered in this work. Equation (4) is the saponification of acidified organic, typically using sodium hydroxide solution.

Calculation of the Equilibrium Constants

Equilibrium constants for neodymium and praseodymium extraction were taken from previous work by Heppner⁽²⁾. To extend the database for all rare earth elements, reported separation factors of Zhang et al.⁽⁴⁾ were used. Recall that the separation factor for rare earth *i* from rare earth *j* has the following form:

$$S_{i,j} = \frac{K_{d,i}}{K_{d,j}} \tag{5}$$

Where $K_{d,i}$ is the ratio of rare earth *i* in the organic to that in the aqueous phase at equilibrium, i.e. the distribution coefficient:

$$K_{d,i} = \frac{a_{Pc_3REE_i}}{a_{REE_i^{+3}}}$$
(6)

Separation factors are evaluated at a constant final pH and extraction concentration. Now consider the form of an equilibrium constant for the ith rare earth element:

$$K_{i} = \frac{\left(a_{Pc_{3}REE_{i}}\right)\left(a_{H^{+}}\right)^{3}}{\left(a_{REE_{i}^{+}}\right)\left(a_{PcH}\right)^{3}} = K_{d,i}\left(\frac{a_{H^{+}}}{a_{PcH}}\right)^{3}$$
(7)

As stated previously, the bench scale experiments conducted to evaluate separation factors use the same final pH and same extractant concentration. Since adjacent rare earth elements have similar chemical properties, it is assumed that, in these experiments, acid distributes in a similar manner for both rare earths. By applying this assumption, it is postulated that the separation factor can be related to the ratio of equilibrium constants of adjacent rare earths, i.e.:

$$S_{i,j} = \frac{K_i}{K_j} \tag{8}$$

Using separation factors reported by Zhang et al.⁽⁴⁾, equation (8) was applied to the previously determined equilibrium constants for neodymium and praseodymium to estimate the equilibrium constants of the other 13 rare earth elements considered in this work.

Saponification equilibrium constants were calculated such that 50% saponification of fully acidified organic (0.015 M longuest 801 in kerosene) was achieved when mixed in a 1:1 volumetric ratio with 2 M NaOH solution, as in Zaki et al.⁽¹¹⁾.

Verification of Approach

The approach of using separation factors as a proxy for equilibrium constant ratios was verified through a test of the Nd/Pr system. This system was chosen because both Nd and Pr equilibrium constants were obtained independent of the separation factor approach. As noted earlier, Nd and Pr were obtained by fitting to published experimental data⁽²⁾. The following steps were taken:

- 1. SysCAD models of the shakeout of 1% by mass solutions of both NdCl₃ and PrCl₃ in 2 molar PC088A in kerosene were built.
- 2. Both shakeout test models were used to simulate the experiment where sodium hydroxide was used to achieve a final aqueous solution pH of 1.5.
- 3. Predicted organic and aqueous concentrations from the model were used to compute the distribution coefficients for both Nd and Pr at these conditions.



4. The ratio the equilibrium constants for each of the reactions were also computed.

Figure 1: SysCAD Model of Shakeout Tests for Nd and Pr Extraction

It can be seen from the results shown in Figure 1 that the deviation between the ratio of the distribution coefficient and ratio of the equilibrium constant is less than 0.4%. From equation (7), this close agreement implies that the distribution coefficient for acid is equivalent for adjacent rare earths, thereby verifying the approach.

Solvent Extraction Modelling

Solvent extraction unit operations are modelled as sequential mixer-settler units. Either recovered aqueous or organic may be recycled to control the O/A ratio in the mixer. Incomplete phase separation and crud formation may also be considered. The input parameters for a solvent extraction unit include entrained organic in aqueous, entrained aqueous in organic, and other operational parameters.

In this SysCAD model, each mixer-settler has a PHREEQC thermodynamic calculation embedded, allowing for first principles calculation of the organic-aqueous interfacial reactions. Reactions are not specified in the solvent extraction unit, but rather, are determined by free energy minimisation. Although not done in this work, reaction kinetic effects can also be incorporated through the implementation of constrained free energy methods.

The model incorporates three circuits – extraction, scrubbing, and stripping. Removal of heavy rare earths is modelled using a subsequent black-box model. The organic stream resulting from heavy REE removal is saponified with sodium hydroxide solution to a target saponification extent. Saponification extent is defined as the mole fraction of extractant which is bound to sodium.



Figure 2: SysCAD Model of Extraction Area

Figure 2 shows 36 extraction area mixer-settler cells in series, although only 25 are in service (olivecoloured cells are offline). The cells can be switched on and off in the model to allow easy reconfiguration for process design or operational changes. Similarly, Figure 3 shows 36 scrubbing cells in series, with 15 of them in service.

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Figure 3: SysCAD Model of Scrubbing Area



Figure 4: SysCAD Model of Stripping Area



Figure 5: SysCAD Model of Heavies Processing Area

SIMULATION CASE STUDY

Base Case

Turgeon et al.⁽⁷⁾ provided a typical REE leach solution composition which was used as a basis for the pregnant leach solution feed to the model (Table 1).

Element	Concentration (g/L)
La	57.31
Ce	2.64
Pr	7.06
Nd	22.14
Sm	1.07
Eu	0.19
Gd	0.36
Tb	0.03
Dy	0.05
Но	0.02
Er	0.03
Tm	0.003
Yb	0.01
Lu	0.002
Y	0.09

Table 1: Pregnant Leach Solution Composition

For the base case simulation, the SysCAD model calculated full stream composition data for all intermediate and final process model streams, including the three rare earths exit streams: raffinate, loaded strip, and heavies strip. The distribution of each present rare earth element to each of these three exit streams can be seen in Figure 6 as stacked columns. Notice that in this base case, all

elements distribute to one, or at most two, process area exit streams. The destinations are as expected, with Lanthanum going to raffinate, Ytterbium going to heavies strip, and a smoothly changing distribution for all elements between the two extremes. Note that given their low concentrations, Tm and Yb have been omitted.



Figure 6: Base Case Elemental Distribution to Exit Streams

Sensitivity Analysis

After completing simulation of the base case conditions, the following operational parameters were varied in a sensitivity analysis:

- Organic-to-Aqueous volumetric ratio (O/A Ratio)
- Saponification Extent
- Cell Count (the number of cells in Extraction, Scrubbing, and Stripping)

The base case conditions were:

- Extraction O/A Ratio*: 2.0
- Scrubbing/Stripping Circuit O/A Ratio: 10.0 / 5.0
- Saponification Extent:
- Cell Count (Extraction/Scrub/Strip): 25 / 15 / 4
- *Organic to Pregnant Aqueous Solution Volumetric Ratio

Additional (sensitivity analysis) cases retained all base case conditions except for a single change for each sensitivity analysis case. Sequentially, the single change from the base case for the sensitivity analysis cases were:

25.0%

- Scrubbing/Stripping Circuit O/A Ratio: 11.0 / 5.5
- Scrubbing/Stripping Circuit O/A Ratio: 9.0 / 4.5
- Saponification Extent: 27.5%
- Saponification Extent: 22.5%
- Cell Count (Extraction/Scrub/Strip): 15 / 15 / 4
- Cell Count (Extraction/Scrub/Strip): 25 / 10 / 4
- Cell Count (Extraction/Scrub/Strip): 25 / 15 / 2

These scenarios were selected because they represent typical parameter adjustments used in the design and operation of rare earths separation circuits. Cell count is important for optimising process design. Once in operation, O/A ratios, strip reflux, and saponification extent are some of the parameters adjusted to maintain optimal circuit performance.

Results of the sensitivity analysis are presented in Figures 7 - 15. In all cases, the results are consistent with expected design and operational trends.

Varying O/A Ratios

These scenarios (Figures 7 - 9) predict an increased distribution of elements to the later product streams when the O/A Ratios are increased. At the light elements end, Nd distribution to raffinate decreases, and Nd distribution to loaded strip increases, as the O/A Ratios increase. At the heavy end of the elements, Ho, Y, and Er distribution to loaded strip decreases, and their distribution to heavies strip increases, as the O/A Ratios increase.



Figure 7: Elemental Distribution to Raffinate - Varying O/A Ratio



Figure 8: Elemental Distribution to Loaded Strip – Varying O/A Ratio



Figure 9: Elemental Distribution to Heavies Strip - Varying O/A Ratio

Varying Saponification Extent

The trends for the increasing saponification extent cases (Figures 10 - 12) mirror those for increasing O/A Ratios, with increased distribution of elements to later product streams when the saponification extent is increased. The trends are most noticeable for Nd (light end) and Ho, Y, and Er (heavy end).



Figure 10: Elemental Distribution to Raffinate – Varying Saponification Extent



Figure 11: Elemental Distribution to Loaded Strip – Varying Saponification Extent



Figure 12: Elemental Distribution to Heavies Strip – Varying Saponification Extent

Varying Cell Count

Varying the cell count for this system (Figures 13 – 15) provides results which show little changes except for the case where we decrease the number of strip cells. Decreasing the number of cells by 40% in extraction from 25 to 15 cells, or by 33% for scrubbing from 15 to 10 cells creates minimal changes to the element distributions. Making a larger percentage decrease of 50%, or 4 to 2 cells, in stripping does create a noticeable change for the heavier elements Dy, Ho, Y, and Er, as their distributions decrease for loaded strip and increase for heavies strip. It appears that the extraction and scrubbing areas have more cells than are necessary for the specified conditions.



Figure 13: Elemental Distribution to Raffinate – Varying Cell Count (Extraction/Scrub/Strip)



Figure 14: Elem. Distribution to Loaded Strip – Varying Cell Count (Extraction/Scrub/Strip)



Figure 15: Elem. Distribution to Heavies Strip – Varying Cell Count (Extraction/Scrub/Strip)

Additional Cases

With the process simulation capability, additional cases may be explored in a relatively short amount of time. As one example – a single added case converged to a steady state in 475 seconds on a typical desktop computer using six cores. The TCE (Thermodynamic Calculation Engines) interface in SysCAD supports parallel computing, and in this case, up to 12 PHREEQC calculations could proceed at the same time. In addition to the changes noted above, one could expand or otherwise change the process simulated, change the process layout, feed composition, and change many other process factors, to simulate an existing process or a process being designed.

Further Saponification Sensitivity Analysis

Following the above sensitivity analysis for Scrubbing/Stripping Circuit O/A Ratio, Saponification Extent, and Cell Count, the impact of degree of saponification was further investigated. For these additional cases, the Scrubbing Circuit O/A Ratio and Cell Count were returned to the base case settings. The Saponification Extent was then varied from the base case condition of 25.0% to a maximum of 50.0% in 5.0% increments. This range was chosen because these are typical operating saponification values.

The predicted effect of greater saponification is presented in Figures 16 - 21. The same trends previously seen in Figures 10 - 12 are present at these higher saponification extent values: increased distribution of elements to later product streams when the saponification extent is increased. The trends are most noticeable for Nd (light end) and Ho, Y, and Er (heavy end). Reviewing the results further, in Figures 16 - 18, as saponification increases, the distribution curves shift more in favour of the Heavies Strip than they do against the Raffinate, yielding a narrower distribution curve to the Loaded Strip, Figure 17. Thus, at the highest saponification extents, only Nd distributes more than 50% to the Loaded Strip exit stream.



Figure 16: Elemental Distribution to Raffinate – Increasing Saponification Extent



Figure 17: Elemental Distribution to Loaded Strip – Increasing Saponification Extent



Figure 18: Elemental Distribution to Heavies Strip – Increasing Saponification Extent

Figures 19 – 21 present the data in a different manner – providing a stacked bar distribution for a single element each, across the range of saponification extent values. This visualisation is presented here for three of the elements. Nd (Figure 19) is the only element in this saponification study that ever exhibits a condition with more than 5% distribution to all three exit streams – see the 45% saponification bar, where the distribution is approximately 12 / 81 / 7 % to Raffinate / Loaded Strip / Heavies Strip. For all elements, this type of plot clearly illustrates the shift away from raffinate and towards Heavies Strip exit points. In Figure 20, Eu exhibits a sudden shift from Loaded Strip to Heavies Strip to Heavies Strip as saponification increases. For other elements, not shown graphically, the shift is sometimes sudden and sometimes gradual.



Figure 19: Neodymium Distribution – Increasing Saponification Extent



Figure 20: Europium Distribution – Increasing Saponification Extent



Figure 21: Erbium Distribution – Increasing Saponification Extent

CONCLUSIONS

Through this case study, the capability of a SysCAD model with embedded PHREEQC technology is presented. This technology enables the thermodynamic modelling of rare earths solvent extraction, and the simulation of many different cases in a practical time period. Within the simulation, an industry-typical feed pregnant leach solution was fed to an extraction, scrubbing, and stripping circuit. The demonstrated trends as reported by the simulation are consistent with those expected in industrial applications. Use of the model herein for actual project/operational applications would require model validation. This fundamental approach avoids the need for plant isotherms and provides a wide range of applicability in design and optimisation of rare earths solvent extraction separation processes.

Application of this methodology to a specific plant or project may require expansion of the chemical model in some cases. Such cases could include significantly different operating temperatures, a different extractant than that used in this work, additional elements in the feed, and other changes that could affect applicability of the model. However, this work provides a template for any such needed model expansion.

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