PREDICTIVE MODELING OF RARE EARTH ELEMENT SEPARATION BY SOLVENT EXTRACTION USING METSIM

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ABSTRACT

Simulation of rare earth element solvent extraction processes for plant design and optimization is complex, requires extensive bench scale and pilot scale testing, and is traditionally performed using proprietary algorithms. The complexity of simulation is mainly due to traditional simulation software solvent extraction modules not being designed to simulate rare earth separation processes because of the interaction between each element. This paper presents an alternative method for designing and optimizing rare earth element solvent extraction separation processes using METSIM to converge each stage of the battery individually until the full battery reached ultimate convergence. A feed-forward controller is used to control the organic to aqueous flow ratio feeding the solvent extraction modules. This method minimizes the complexity of simulating such processes by using inexpensive batch solvent extraction data, and allowing for rapid theoretical optimization, by varying the process configuration and parameters from a graphic interface instead of the traditional code-based interface of most proprietary models. Comparison of the model predictions to pilot plant data reveals that the method can be used to accurately model rare earth solvent extraction processes, as illustrated by its application in the development of Rare Element Resources innovative process.

KEYWORDS

Rare earth elements, simulation, solvent extraction, METSIM, pilot plant

INTRODUCTION

The Rare Earth Elements (REEs) consist of 16 metals, specifically the 15 lanthanide elements and yttrium, which is typically found in the same mineral deposits as the lanthanides. Scandium can be associated with the rare earth elements, but is usually only present in trace amounts, and therefore omitted. The term "rare earths" originates from an old term used to designate minerals (earths) and their believed scarcity upon their initial discovery. The rare earths designation is now considered a misnomer because it was demonstrated that the crustal abundance of some rare earth elements, such as cerium, is known to be higher than many common metals, such as copper. However, enriched deposits are fairly uncommon compared to other similarly abundant metals. The REEs are typically divided into groups commonly consisting of light rare earths (LREEs), medium rare earths (MREE), and heavy rare earths (HREEs). Light rare earth elements include lanthanum to neodymium, medium rare earths include samarium to gadolinium and the heavy rare earth elements include terbium to lutetium, and yttrium. The REEs exhibit similar chemical characteristics and are usually extracted from the ore and processed into a mixed rare earth concentrate. The rare earth concentrate requires further processing in order to separate the REEs from each other and produce a series of single element products.

Although many technologies are currently in development for the separation of REE, the only current commercial separation process is solvent extraction. Only a few such facilities are currently in operation, none of which are operating in North America (Gupta & Krishnamurthy , 2005). The two main barriers to entry in the rare earth separation industry are the very low publicly available literature on REE separation process design and the extremely high capital costs associated with such processes. In order to overcome these hurdles, potential new entrants need to first perform extensive and expensive bench scale and pilot scale test work in order to design and scale up their own solvent extraction process as well as raise substantial capital once the process is designed. Simulation of such processes have been addressed previously in the literature (Bazin, Boudrias-Chapleau, & Ourriban, 2013), but most of the proposed models have been programmed using proprietary algorithms, directly related to the solvent extraction modules.

The present paper proposes a method for significantly reducing the schedule and cost associated with the development and design of REE separation processes by solvent extraction using a commercially available simulation software: METSIM. In this method, the solvent extraction modules are directly integrated in the overall process flowsheet. The proposed method was successfully used to assist in the development of Rare Element Resources' patent pending zero-discharge solvent extraction separation process. Although a comprehensive model was built for the various phases of the process development program, only a single battery of solvent extraction cells, from a section of the process will be discussed herein.

METSIM was selected because it is extensively used in the mining and metallurgical industry, and is easily customizable (Qiuyue, Zhang, Lv Guozhi, & Xiaofeng, 2012).

FUNDAMENTALS OF RARE EARTH ELEMENTS SOLVENT EXTRACTION

Solvent extraction (also referred to as liquid-liquid extraction) is a separation method based on the difference of solubility of ions or compounds in different solvents. In the solvent extraction process, ions or compounds contained in an aqueous phase migrate to an organic phase when the two phases are mixed. The organic phase is selected based on three criteria: its capacity to selectively solubilize the targeted ions or compounds, its immiscibility with the aqueous phase, and the absence of a stable emulsion phase between the two solvents. The latter two properties enable a simple gravity separation of the liquids (Aguilar & Cortina, 2008).

Solvent extraction is typically carried out in a group of mixer-settlers, collectively referred to as a battery. Because high loading rates are achieved in the organic phase, the mixer-settlers are usually small in size.

Separation of various elements is achieved by the difference of mass transfer between the phases for each element. The ratio of concentration between the organic and aqueous phases is named "Distribution Ratio", and is often referred to as the equilibrium constant Kd. The second most important parameter is the Separation Factor "SF", defined as the ratio of distribution ratios, illustrating the preferential extraction of one element versus another element. Consecutive REEs tend to have very similar distribution ratios combined with low separation factors, and as such require many stages of solvent extraction for complete separation.

SOLVENT EXTRACTION BASE MODULE

While METSIM currently has preprogrammed solvent extraction modules, they are not directly compatible with the separation of REE because the relative concentration of each REE influences the equilibrium concentration of the module. As such, the REE separation modules were simulated using phase separator modules, which divide the units' discharge flow according to the phase of each of its individual constituents. A typical 4 stage extraction battery flowsheet is presented in Figure 1.
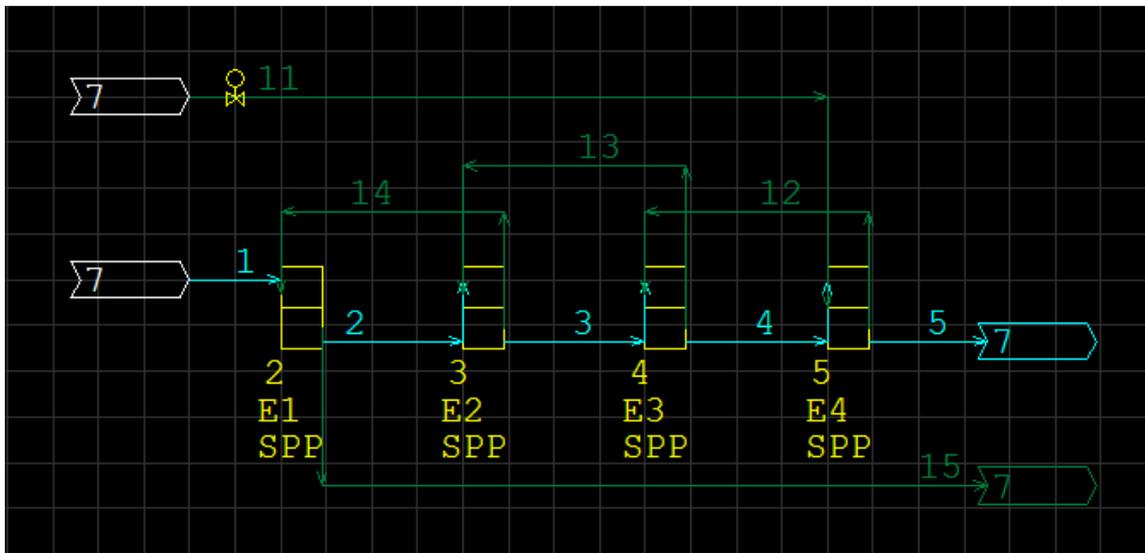

Figure 1 – 4 Stage Extraction Battery

The module chemistry parameter was programmed using equilibrium equations to account for all reactions occurring in the battery. The general equation is presented as Equation (1), where REE represent one of the rare earth elements and "R" represents the proprietary extracting agent. Reactions for all REEs were programmed in each of the modules.

$$REE^{3+} + 3 \text{ R-H} \rightarrow REE\text{-}3R + 3H^+ \tag{1}$$

Each individual reaction extent was then converged to achieve a system equilibrium determined through bench scale experiments. Constraints were established in the model to control each individual reaction based on the solving of a matrix calculation involving each rare earth separation factor related to a single reference element "RfE" and to account for the global distribution ratio of all rare earths. The general equation for the separation factor constraint parameter is presented in Equation (2) and the distribution ratio calculation equation is presented in Equation (3).

$$[REE]_o / [REE]_a / [RfE]_o / [RfE]_a = SF_{(REE/RfE)} \tag{2}$$

$$\sum[REEs]_o / \sum[REEs]_{a = } Kd \tag{3}$$

METSIM is then used to converge each stage of the battery individually until the full battery reaches convergence. A feed-forward controller is used to control the Organic to Aqueous flow ratio feeding the solvent extraction modules.

BENCH SCALE DATA GENERATION, PROCESSING AND MODELING

The first step in bench scale data generation is to perform a series of scoping bench tests using various combinations of extractant, modifier, and diluent, as well as various aqueous feed compositions and acidities/pH. The resulting data can be presented as a matrix, from which selected data can be used for modeling.

In this example, specific bench scale test data was generated using standard methods by SGS Canada Inc. following a period of scoping test work. Once the approximate conditions were identified, a few additional tests were performed to generate data for modeling. For each test, the organic phase was prepared by combining specified ratios of extractant, solvent, and modifier solutions. The aqueous phase was prepared by using the raffinate solution from a previous pilot plant operation, and adjusting its pH using a basic solution (SGS Canada Inc., 2015). The aqueous solution used was initially made using real REE concentrate generated during RER's Bear Lodge Project process piloting. Three (3) co-current contacts were successively made on the aqueous solution using fresh organic each time, at a specified Organic to Aqueous ("OA") ratio. pH, ORP, free acid, and assays were generated for each aqueous solution, along with assays of the loaded organic solution. A mass balance was performed for each contact in order to calculate a theoretical organic assay due to significant imprecision on the organic assay.

The dataset used in the model discussed herein is presented in Table 1, along with calculated Distribution Ratios and Separation Factors relative to neodymium.

Table 1 – Bench Scale Dataset

Element	Unit	Feed	Raffinate	Loaded Organic	Kd	SF[Nd/REE]
La	mg/L	14,200	12,200	1,674	0.14	0.16
Ce	mg/L	2,780	1,870	848	0.45	0.52
Pr	mg/L	1,010	598	394	0.66	0.75
Nd	mg/L	2,630	1,340	1,176	0.88	1.00
Sm	mg/L	97.00	15.70	79.95	5.09	5.80
Eu	mg/L	16.90	1.38	15.05	10.91	12.43
Gd	mg/L	41.70	2.36	37.88	16.05	18.28
Tb	mg/L	3.26	0.07	2.95	42.14	48.01
Dy	mg/L	12.70	0.13	12.21	93.95	107.02
Ho	mg/L	1.77	0.02	1.80	89.77	102.26
Y	mg/L	26.30	0.14	24.89	177.79	202.52
Er	mg/L	3.14	0.04	3.41	85.23	97.08
Tm	mg/L	0.33	0.04	2.13	53.30	60.71
Yb	mg/L	1.45	0.02	1.65	82.50	93.98
Lu	mg/L	0.15	0.03	1.55	51.82	59.03
Total	mg/L	20,825	16,028	4,276	0.267	

The various dataset generated in the follow-up test series were included in the METSIM model, and various scenarios were computed, varying the dataset, the number of stages, and the OA Ratio until an

optimum configuration was established. The optimum configuration was used to design and operate a pilot plant to prove the process, and accessorily test this method. The pilot plant was operated for seventy-two (72) hours, and steady state data was obtained. The exact feed composition from the steady-state portion (12-hours composite) of the pilot plant was input in METSIM to validate the predictability of the model.

Significant differences in concentration were observed between the bench scale feed composition and the actual pilot plant composition. The absolute and REE-relative compositions of both the bench scale and the pilot plant aqueous feed stream, with the relative difference between the two REE-relative compositions are presented in Table 2.

Table 2 – Difference Between the Bench Scale and Pilot Plant Feed Composition

Element	Bench Scale Test Feed Composition [mg/L]	Steady-State Pilot Plant Test Feed Composition [mg/L]	Bench Scale Test REE-Relative Composition	Pilot Plant Test REE-Relative Composition	Difference
La	14,200	5,920	76.1%	79.1%	-4.0%
Ce	2,780	489	11.7%	6.5%	44.0%
Pr	1,010	321	3.7%	4.3%	-15.0%
Nd	2,630	717	8.4%	9.6%	-14.6%
Sm	97.00	21.00	0.10%	0.3%	-186.5%
Eu	16.90	3.00	0.01%	0.0%	-365.7%
Gd	41.70	7.00	0.01%	0.1%	-535.4%
Tb	3.26	< DL	0.00%	N/A	N/A
Dy	12.70	< DL	0.00%	N/A	N/A
Ho	1.77	< DL	0.00%	N/A	N/A
Y	26.30	3.90	0.00%	0.1%	N/A
Er	3.14	< DL	0.00%	N/A	N/A
Tm	0.33	< DL	0.00%	N/A	N/A
Yb	1.45	< DL	0.00%	N/A	N/A
Lu	0.15	< DL	0.00%	N/A	N/A

RESULTS

The METSIM model was updated to include pilot plant data relative to the actual feed of the pilot plant, and was converged using the pilot plant parameters. The predicted composition and extraction rates for each element were compared and are presented in Table 3 and in Table 4. The main objective of the process modelled in the extraction battery was to extract all elements other than lanthanum in order to obtain a raffinate containing >99% lanthanum relative to other rare earths. The difference of lanthanum purity between the METSIM model and the pilot plant is presented in Table 5.

The results confirmed that the simulation method presented herein was applicable for its intended purpose: the design and optimization of solvent extraction processes using limited bench scale data. The pilot plant predicted extractions are similar to the actual extractions (within 1.2%), even if the bench scale test composition was significantly different than the pilot plant feed composition both in total rare earth concentration and in relative rare earth distribution.

It is important to note that the solution assays have their own analytical error and that the pilot plant "steady state" period still included normal variations in the operating parameters. In addition, the accuracy and precision of the analytical measurement was not analyzed. All samples and measurement were taken using SGS standard procedures and all assay data was obtained through ICP-MS analyses.

The objective of this simulation method is to accelerate, de-risk and reduce the expenditures associated with designing and testing rare earth solvent extraction processes, as such, the analytical variance was not considered an important portion of this study.

Table 3 – Feed and Raffinate Streams Composition (METSIM and Pilot Plant)

Element	Unit	Steady-State Pilot Plant Feed Composition	METSIM Predicted Raffinate Composition	Steady-State Pilot Plant Raffinate Composition
La	mg/L	5,920	2,134	2,130
Ce	mg/L	489	12.4	17.9
Pr	mg/L	321	2.4	3.2
Nd	mg/L	717	1.6	4.1
Sm	mg/L	21.00	<0.01	< DL
Eu	mg/L	3.00	<0.01	< DL
Gd	mg/L	7.00	<0.01	< DL
Tb- Ho	mg/L	< DL	<0.01	< DL
Y	mg/L	3.90	<0.01	< DL
Er-Lu	mg/L	< DL	<0.01	< DL

Table 4 – REE Extraction (METSIM and Pilot Plant)

Element	Unit	METSIM Predicted Extraction	Steady-State Pilot Plant Extraction	Relative Difference
La	%	63.8%	64.0%	-0.3%
Ce	%	97.5%	96.3%	1.2%
Pr	%	99.2%	99.0%	0.2%
Nd	%	99.8%	99.4%	0.4%
Sm-Lu	%	100.0%	100.0%	0.0%
Y	%	100.0%	100.0%	0.0%

Table 5 – Lanthanum Purity in Raffinate Stream

Element	Steady-State Pilot Plant Feed La Purity	METSIM Predicted Raffinate La Purity	Steady-State Pilot Plant Raffinate La Purity	Relative Difference
La	79.1%	99.2%	98.8%	0.4%

CONCLUSIONS

The current rare earth element separation process design and operating parameters are kept confidential by the current separation companies, and the capital cost associated with the design and construction of such facilities are extremely high. These two hurdles constitute a formidable barrier to entry in this industry.

This paper presented a novel approach aimed at using the simulation capabilities of METSIM and limited bench scale test work to accelerate, de-risk and reduce the expenditures related to developing rare earth element separation processes by solvent extraction. The method was successfully applied to Rare Element Resources Rare Earth Separation Program. It is important to note that other advantages of the

method such as the development of the integrated process flowsheet, including all equipment related to the solvent extraction mixer-settlers were also included in the full model.

Further application of this method could include the real-time optimization of rare earth separation by solvent extraction processes. A few minor modifications would need to be included in the model to account for this potential application such as the parametrization of the main variables to include the effect of pH on these parameters and the addition of a kinetic component to the equilibrium parameter to account for variations on residence time.

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