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ENHANCED SEPARATION OF RARE EARTH ELEMENTS

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ABSTRACT

Industrial rare earth separation processes utilize PC88A, a phosphonic acid ligand, for solvent extraction separations. The separation factors of the individual rare earths, the equipment requirements, and chemical usage for these flowsheets are well characterized. Alternative ligands such as Cyanex® 572 and the associated flowsheets are being investigated at the pilot scale level to determine if significant enhancements to the current separation processes can be realized. These enhancements could be defined as higher separation factors, reduced stage requirements, or reduced chemical consumption. Any of these enhancements can significantly affect the costs associated with these challenging separation proccesses.

A mid/heavy rare earth element (REE) separations flowsheet was developed and tested for each ligand in a 30 stage mixer-settler circuit to compare the separation performance of PC88A and Cyanex® 572. The ligand-metal complex strength of Cyanex® 572 provides efficient extraction of REE while significantly reducing the strip acid requirements. Reductions in chemical consumption have a significant impact on process economics for REE separations. Partitioning results summarized Table 1 indicate that Cyanex® 572 offers the same separation performance as PC88A while reducing acid consumption by 30% in the strip section for the mid/heavy REE separation.

Flowsheet Effluent Compositions		PC88A	Cyanex® 572
Raffinate	Mid REE	99.40%	99.40%
	Heavy REE	0.60%	0.60%
Rich Liquor	Mid REE	2.20%	0.80%
	Heavy REE	97.80%	99.20%
Strip Acid Required		**3.4 M**	**2.3 M**

Table 1 – Flowsheet results comparing separation performance of PC88A and Cyanex® 572 for a mid/heavy REE separation.

KEYWORDS

Rare Earth Element, Solvent Extraction, CMI, Separation, Cyanex® 572, PC88A

INTRODUCTION

Industrial separation of rare earth elements (REE) is typically accomplished using solvent extraction processes. Separation of adjacent REE is particularly difficult due to their chemical similarities. However, small differences in the basicity of each element across the lanthanide series can be exploited for separation using solvent extraction (Gupta, 2005). Currently, the industrial standard for REE separations is PC88A, a phosphonic acid. The separation factors of the individual rare earths, the equipment requirements, and chemical usage for PC88A flowsheets are well characterized within the industry. Alternative ligands such as Cyanex® 572 and the associated flowsheets are being investigated at the pilot scale level to determine if significant improvements to the current separation processes can be realized.

Improvements to REE separation processes include increased separation factors, reduced equipment requirements, or reductions in chemical consumption. Process improvements promote a sustainable, economically viable domestic supply of REE in the United States. Commercially available ligands such as Cyanex® 572 are immediately available for industrial application and have shown significant potential for optimizing and enhancing separation and concentration of individual REE.

RARE EARTH SEPARATIONS

Solvent extraction works on the principle of mass transfer between two immiscible phases. An aqueous solution containing one or more solutes is intimately mixed into an emulsion with an immiscible organic solvent phase. As the two phases mix, the desired solute is selectively transferred to the organic phase from the aqueous phase. The two immiscible phases are then separated by differences in density and the desired component may be recovered by further processing. Several contact stages between aqueous and organic phases are typically required because the desired solute usually is not completely recovered in one stage. A single discrete solvent extraction contact constitutes one theoretical equilibrium stage, and several stages are commonly used in a continuous, counter-current cascade to efficiently achieve high degrees of separation. Counter-current operation maximizes the concentration gradient driving force for mass transfer while still allowing continuous high process throughputs. A counter-current extraction cascade is shown in Figure 1.

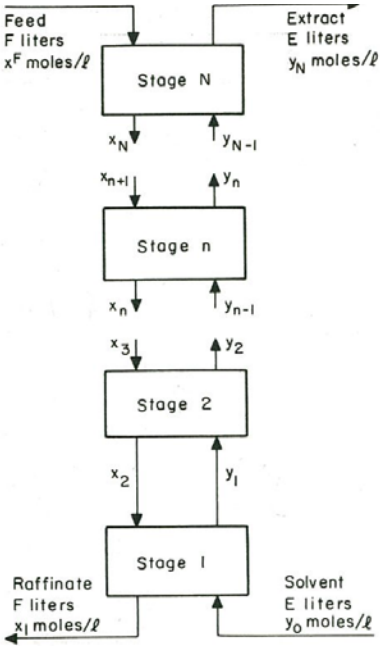

Figure 1 – Principles of the counter-current solvent extraction cascade (Benedict, 1981).

In Figure 1, the aqueous feed or pregnant liquor solution (PLS) enters stage N while the fresh organic solvent enters stage 1. The aqueous feed becomes depleted in solute as it moves down the cascade, and the organic solvent becomes increasingly enriched in the solute as the solvent approaches stage N. During extraction, undesirable solutes are often co-extracted into the organic phase and must be removed to produce high purity products. This is especially true for the separation of individual REE due to the low selectivity among adjacent REE. Several solvent extraction cascades are employed for an overall flowsheet that extracts, purifies, and recovers target species in the process. A typical REE flowsheet is shown in Figure 2:

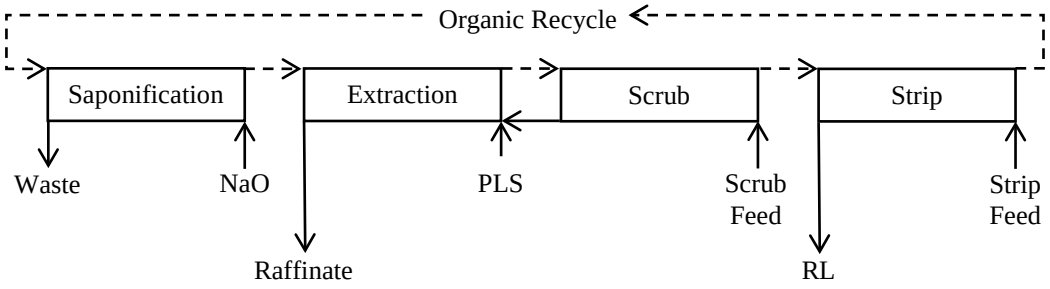

Figure 2 – Simplified design of a single REE solvent extraction circuit.

REE solvent extraction flowsheets usually consist of a saponification section, an extraction section, a scrub section, and a strip section. Saponification is a pre-treatment step for pH control during extraction. The extraction section provides bulk separation of the desired REE from the aqueous phase. The spent aqueous phase exits the extraction section as the raffinate. Loaded organic solvent enters the scrub section, where undesirable REE that were co-extracted in the extraction section are scrubbed from the loaded organic phase. Scrubbing is accomplished by contacting the loaded organic phase with an aqueous solution that alters the acid or REE equilibrium conditions. Undesired REE species are transferred to the aqueous phase, which is typically recombined with the extraction aqueous feed to recover any desired REE that were unintentionally scrubbed out of the loaded organic phase. Finally, the scrubbed loaded organic enters the strip section, where the REE is recovered from the organic phase as a rich liquor (RL) product. The organic phase, now stripped of any solutes, is recycled for reuse.

As previously stated, basicity decreases with increasing atomic weight across the lanthanide series. Consequently, PC88A and Cyanex® 572 have an increasing affinity for extraction with increasing atomic weight. Concentrates produced from the beneficiation of REE ores typically contain all of the REE in varying concentrations, with lanthanum and cerium being the most prevalent in ores such as monazite or bastnaesite (Gupta, 2005). The ligand's affinity for heavier REE is exploited for separations by fractionating the mixed REE concentrate into light, mid, and heavy REE groups, followed by subsequent separations to obtain individual elements (Xie, 2014). Each subsequent step requires a solvent extraction circuit consisting of extraction, scrubbing, and stripping in order to achieve the desired separation. Plants producing multiple single REE products utilize hundreds of stages of solvent extraction equipment and consume large quantities of chemical reagents for recovery, feed adjustment and waste treatment (Soderstrom, 2014). For example, REE separations for ion adsorption clays in China typically consume an average of 10 tonnes of hydrochloric acid, 2-3 tonnes of sodium hydroxide, and 15-20 tonnes of water for every tonne of REE oxide produced (Liao 2013). Solvent extraction of REE using PC88A and Cyanex® 572 behave according to the following ligand-metal equilibrium reaction:

$$[RE^{3+}]_{aq} + 3[(HA)_2]_{org} \leftrightarrow [RE(HA_2)_3]_{org} + 3[H^+]_{aq} \quad (1)$$

According to equation 1, extraction conditions are favored at low acid concentrations and stripping occurs at high acid concentrations. The liquid cation exchange mechanism releases protons into the aqueous phase as extraction occurs, adversely affecting the extraction equilibrium. The ligand is

typically neutralized using sodium hydroxide to control pH during extraction, referred to as saponification. Equilibrium conditions for extraction, scrub, and strip are expressed using the distribution ratio:

$$D = [C]_{org} / [C]_{aq} \quad (2)$$

Here, C_{org} represents the organic phase equilibrium metal concentration and C_{aq} represents the aqueous phase equilibrium metal concentration. The distribution ratio describes the extent of extraction, scrub, or strip in a solvent extraction circuit. The overall degree of separation between two species is expressed using the separation factor, β:

$$\beta_{A,B} = D_A / D_B \quad (3)$$

High separation factors correspond to high selectivity for separation of the two species. PC88A and Cyanex® 572 have similar selectivity for individual REE, but Cyanex® 572 has been formulated to have a lower metal-ligand complex strength (Soderstrom, 2014). Consequently, Cyanex® 572 extracts at a higher pH compared to PC88A. The major benefit is that Cyanex® 572 requires a significantly lower acid concentration to recover REE during stripping than PC88A. The reduction in strip acid requirements is expected to provide significant reagent savings for plant-wide optimization.

METHODS

A mid/heavy REE separation was chosen for flowsheet development to compare the performance of PC88A and Cyanex® 572. The primary purpose of the mid/heavy REE flowsheet was to evaluate the separation performance of both extraction systems and quantify Cyanex® 572's reduction in chemical consumption in the strip section for the mid/heavy REE separation. Flowsheet testing of the two ligand systems under similar operating conditions (number of stages, flow rates, and REE concentrations) provides a means to quantify and compare reagent consumption. A simulated pregnant leach solution (PLS) was prepared in HCl media representing a mid/heavy REE concentrate composed of 60% gadolinium, 30% yttrium, and 10% holmium. Gadolinium was used as a surrogate to represent mid REE, while holmium was a surrogate for heavy REE. Yttrium behaves as a heavy REE in these extraction systems and therefore the RL product recovers both holmium and yttrium. These relative proportions represent an average composition of a REE concentrate produced after separation and removal of the light lanthanides from a bastnaesite ore (Gupta, 2005).

Solvent Extraction Modeling

Modeling software has been developed by Cytec industries Inc. for the design and optimization of rare earth circuits using PC88A or Cyanex® 572 (Soderstrom, 2014). The software uses previously generated equilibrium curves to iteratively solve equilibrium calculations for flowsheet development. The mid/heavy REE separation was first modeled using PC88A to provide a baseline flowsheet to compare against the performance of Cyanex® 572. The PLS feed consisted of 5.52 g/L Gd, 0.92 g/L Ho, and 2.76 g/L Y. This REE feed concentration was chosen to prevent third phase formation and issues due to ligand-metal complex solubility under the chosen operating conditions (Soderstrom, 2014).

As indicated previously, Cyanex® 572 has a separation performance comparable to PC88A but has been formulated to extract at a higher pH than PC88A. The Cyanex® 572 flowsheet was modeled to obtain the same degree of separation as the PC88A flowsheet while reducing the consumption of acid by 30% during stripping and recovery of the heavy REE product. Since the two ligand systems have comparable separation factors and selectivity for REE, the only difference was the pH at which the extraction, scrub, and strip sections were operated. Figure 3 illustrates the proposed 29 stage flowsheet for the mid/heavy REE separation.

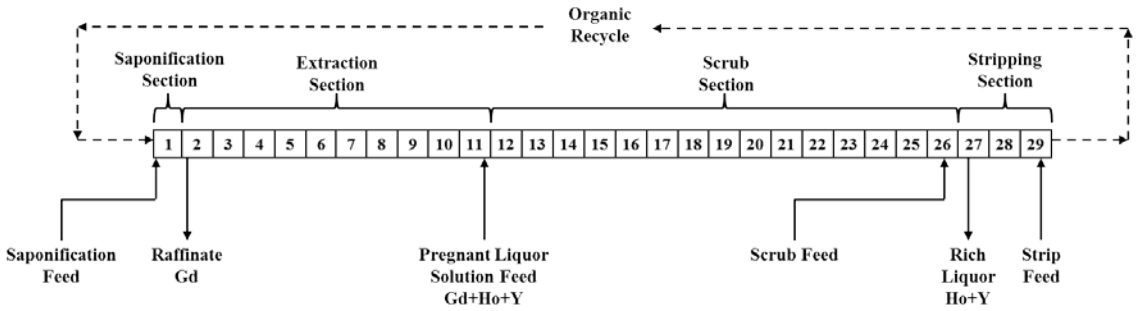

Figure 3- Proposed flowsheet for the separation of Ho and Y from Gd.

Pilot Scale Flowsheet Testing

A thirty stage mixer-settler pilot plant located at the Idaho National Laboratory was used for laboratory validation of the modeling output. The mixer-settlers are constructed of materials that provide versatile chemical compatibility for flowsheet testing and development (i.e. glass, Teflon™, polypropylene). Each stage has an approximate volume of 1200 mL in the settling section and 200 mL in the mixing section. The combined maximum throughput of the system is 0.2 LPM. Each stage has an adjustable jack-leg for interface control and the capability for aqueous phase recycle. The mixer-settlers can be plumbed to accommodate any flowsheet design within the limitation of 30 stages. The mixer-settler system is pictured in Figure 4.

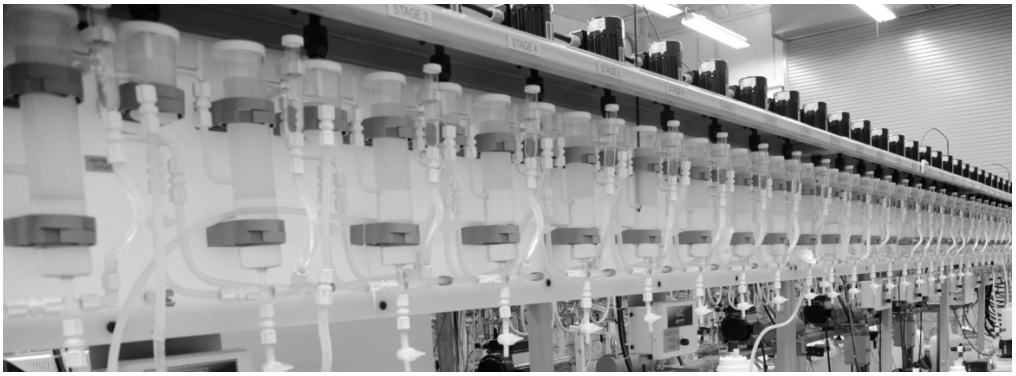

Figure 4 – Thirty stage mixer-settler system at the Idaho National Laboratory.

Two separate flowsheet tests were conducted in the mixer-settler system, one using PC88A and one using Cyanex® 572. Each flowsheet was identical in all aspects with the exception of the corresponding acid concentrations used for the extraction, scrub, and strip feeds required to obtain the desired separation. Operating acid concentration conditions are summarized in Table 1.

Table 1 – Flowsheet free acid concentrations for operation.

Solvent	PC88A	Cyanex® 572
PLS	0.55 M	0.32 M
Scrub Feed	0.70 M	0.35 M
Strip Feed	3.40 M	2.30 M

Start-up and operation of the mixer-settler pilot plant was conducted in two steps. First, stable hydrodynamic equilibrium was obtained in the system with no REE present. Establishing flow in the system was achieved using hydrochloric acid of the same concentration as the aqueous feed solutions and

barren organic solvent. Once system flow was fully established, the PLS containing the mixed surrogate REE feed was introduced and continuously operated for five full turnovers of the organic phase volume present in the system. This correlated to an operating time of approximately 65 hours. Sampling was conducted at various time intervals to monitor the approach to steady state and final samples were obtained to evaluate overall flowsheet performance. Equilibrium aqueous phase acid concentrations were determined via acid-base titration and metal concentrations were determined using ICP-OES or ICP-MS.

RESULTS

Flowsheet Results

Flowsheets were tested for PC88A and Cyanex® 572 to compare performance for the mid/heavy REE separation. The composition of the aqueous raffinate and the rich liquor were determined after 65 hours of operation. The results are shown in Table 2.

Table 2 – Flowsheet results comparing separation performance of PC88A and Cyanex® 572[a].

Flowsheet Effluent Compositions		PC88A	Cyanex® 572
Raffinate	Mid REE (Gd)	99.40%	99.40%
	Heavy REE (Ho+Y)	0.60%	0.60%
Rich Liquor	Mid REE (Gd)	2.20%	0.80%
	Heavy REE (Ho+Y)	97.80%	99.20%
Loaded Organic	Mid REE (Gd)	16.20%	8.70%
	Heavy REE (Ho+Y)	83.80%	91.30%
Strip Acid Required		**3.4 M**	**2.3 M**

[a.] All percentages are on a wt/wt basis.

These results indicate that Cyanex® 572 offers the same separation performance as PC88A, but reduces acid consumption by over 30% during stripping. The raffinate composition was identical for both flowsheets with a very high purity mid REE product being produced. Cyanex® 572 produced a slightly higher purity heavy REE product than the PC88A flowsheet, but both compositions were within reasonable agreement. The loaded organic leaving the extraction section had a higher concentration of Gd for the PC88A flowsheet compared to the Cyanex® 572 flowsheet. The higher Gd concentration was likely the reason the heavy REE product had a lower purity, so a comparison of the equilibrium conditions was used to determine the cause. Distribution ratios and separation factors for each flowsheet are listed in Table 3.

Table 3 – Comparison of averaged flowsheet equilibrium parameters.

Equilibrium Parameter	Extraction		Scrub	
	PC88A	Cyanex® 572	PC88A	Cyanex® 572
D Gd	0.2	0.1	0.2	0.2
D Ho	3.2	1.8	3.8	4.1
D Y	6.1	3.4	6.8	6.9
β Ho/Gd	19.3	22.6	25.3	22.8
β Y/Gd	36.2	42.2	45.3	39.0
β Y+Ho/Gd	55.5	64.8	70.6	61.8

Inspection of the equilibrium data in Table 3 reveals that the Cyanex® 572 distribution ratios were approximately half the value of the PC88A distribution ratios during extraction. This implies that the PC88A flowsheet was operated at a slightly lower acid concentration than required to match the extraction conditions of the Cyanex® 572 flowsheet, and therefore extracted a larger fraction of Gd. Ten extraction stages proved adequate to completely extract Ho and Y in both flowsheets, but the additional Gd extraction in the PC88A flowsheet could not be fully scrubbed out in 15 scrub stages. This accounts for the slight discrepancy for the heavy REE product compositions. The scrub section operated at constant equilibrium

acidity and shows that the distribution ratios and separation factors for each ligand were nearly identical, supporting the claim that the separation performance of each ligand is comparable within their respective acidity range.

Modeling Comparison

Flowsheet results provided valuable validation data for the modeling software. Compositions of the aqueous and organic phase were determined for each stage at the completion of the flowsheet run in order to observe and compare the concentration profile of each species in the circuit. Figure 5 shows the concentration profile for yttrium in the organic phase as an example for model comparison.

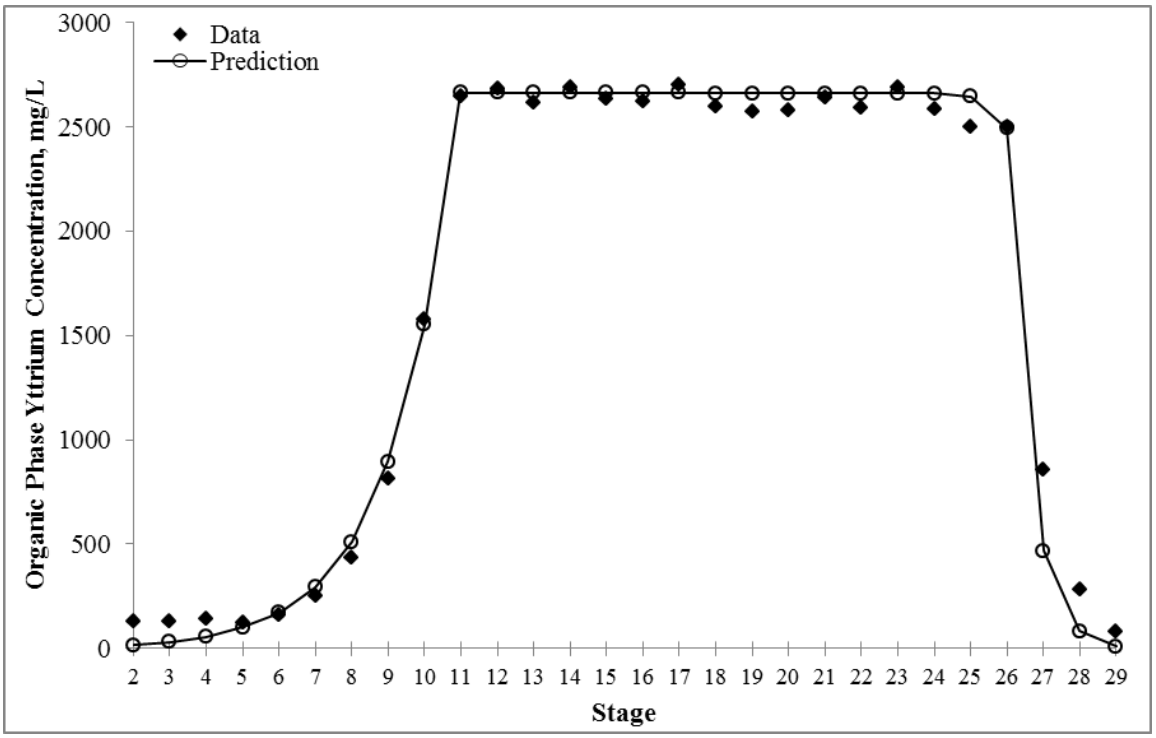

Figure 5 – Organic phase yttrium concentration profile for the Cyanex® 572 flowsheet.

The model output had reasonable agreement with the observed laboratory concentration profile. The slight discrepancy in the concentration during extraction and stripping was attributed to a small recirculating yttrium load during organic recycle due to incomplete stripping. The stripped organic contained 82.7 mg/L yttrium, which was the approximate concentration shown in Figure 4 for stages 2-5. Holmium and the remaining gadolinium were stripped completely with no recirculation during organic recycle. Overall, similar agreement between model output and laboratory data was observed for gadolinium and holmium for all aqueous phase and organic phase profiles. This indicates that the model's equilibrium calculations were suitable for design and prediction of the mid/heavy REE solvent extraction circuit.

CONCLUSIONS

Separation of adjacent REE is a very challenging separation problem due to the chemical similarity among the REE. Plants producing multiple single REE products utilize hundreds of stages of solvent extraction equipment and consume enormous quantities of chemical reagents. Cyanex® 572 has been investigated as an alternative ligand to the industrial standard, PC88A.

Flowsheet modeling and laboratory testing has indicated that Cyanex® 572 achieves the same separation performance as PC88A while reducing the acid requirements by more than 30%. Cyanex® 572 has a potential for commercial application because of its significant reductions in chemical consumption compared to PC88A. However, a complete economic analysis should be completed for specific REE separations considering both capital costs and operating costs. Furthermore, it is expected that the acid savings potential for Cyanex® 572 is much more pronounced for separating heavy REE as opposed to light REE. Either ligand system can reduce strip acid requirements to some extent at the cost of additional strip stages, but there are limitations due to chemical equilibria during stripping. However, for a fixed number of stages, Cyanex® 572 reduces acid consumption by 30% compared to PC88A. It is noteworthy that Cyanex® 572 has similar soluble organic losses as PC88A, which are typically considered a negligible operating cost compared to other reagent costs in a REE separations facility. A comprehensive REE separations plant producing pure individual REE products use a solvent extraction circuit for each step to fractionate mixed REE concentrates into light, mid, and heavy REE groups, followed by subsequent solvent extraction circuits to partition individual elements. The test results suggest the application of Cyanex® 572 has the potential for significant acid savings for plant-wide optimization of solvent extraction circuits and significant reductions in operating costs. Cyanex® 572's enhancements to REE separations provide an opportunity to support an economically viable domestic supply of REE in the United States.

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