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Extraction of samarium and gadolinium from aqueous nitrate solution with D2EHPA in a pulsed disc and doughnut column

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ABSTRACT

The extraction of samarium and gadolinium from aqueous nitrate solution with D2EHPA using a pulsed disc and doughnut column was investigated. It was found from batch experiments for separation of Sm(III) from Gd(III) that the initial aqueous pH, concentration of D2EHPA and concentration of nitric acid as a stripping agent were optimized at 1.5, 0.12 M, and 0.1 M, respectively. In continuous experiments, the effects of variables such as pulsation intensity, dispersed and continuous phase velocity on holdup, mean drop sizes, separation factors and stripping efficiencies were studied. Empirical correlations for prediction of the dispersed phase holdup and mean drop sizes in terms of the operating variables and the physical properties were compared with the experimental results. The results of the continuous experiments demonstrated the feasibility of operating extraction process in the pulsed disc and doughnut column, with good efficiency for separation of samarium from gadolinium in the extraction and stripping stages.

1. Introduction

Liquid–liquid extraction is an important separation process that is used in a wide range of industries such as petroleum refining, food industry, nuclear fuel processing, pharmaceuticals, biochemistry, metal extraction, waste management and other areas [1].

The purification and separation of rare earth elements (REEs) by the solvent extraction method have more attention worldwide because of their wide applications in many main technological areas [2].

For example, Gadolinium is used in the medical field as a contrasting agent in images created by magnetic resonance, as well as in the nuclear area, as a thermal neutron absorber. As little as 1% of gadolinium in chromium, iron and related alloys improves the resistance to high oxidation and high temperatures. Samarium; another element of rare earths, has an interesting application in the ceramic industry for coloring glass. The development of the samarium-cobalt permanent magnet, with flux densities extremely higher than those of similar current products has turned samarium into an important industrial material [3].

With the development of rare earth applications, commercial products develop gradually from primary products to single high-purity and high value-added products. The preparation of high-purity rare earth products for the metallurgical industry is of great interest.

Mixer-settlers are virtually the unique extractors used for rare earth purification and separation in the industry. Being stable in operation, easy to startup and less sensitive to changes in feed and environmental conditions can be listed as the main advantages of mixer-settlers. However, large space requirement, long residence time, large solvent inventory and poor sealing of the system are the main problems with the mixer-settlers [1].

Compared with mixer-settlers, columns are found to be highly efficient and economical in respect of stage numbers, settler area, solvent inventory, site area and maintenance. They are suitable for process control, which requires a quick response to changes in operating and environmental conditions [4]. Among the various types of columns, the pulsed extraction columns are recommended for processing the corrosive or radioactive solutions because the pulsing unit can be isolated from the column. Although the rare earth elements are not radioactive, they always coexist with radioactive elements, such as uranium and thorium. Therefore, the pulsed columns are suitable for extraction and separation of rare earth elements.

Benedetto and co-workers investigated the separation of samarium and gadolinium by mixer-settlers with 16 stages. A

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comparative study on batch and continuous scale, has been carried out with three extractants [5]. Abdeltawab and co-workers studied the separation of La and Ce with PC88A from nitrate media by using a multistage counter-current mixer-settler extraction column in seven stages [6].

A process took place for the recovery of lanthanum with mixer-settlers in 22 stages: 8 for extraction, 8 for scrubbing and 6 for stripping by using D2EHPA and HEH(EHP) from chloride medium solution [7]. The recovery of Dy with 98% purity and Y with 93% purity from rare earth chloride solution with mixer-settlers in 20 stages has been reported [8]. Ansari and co-workers employed the mixer–settler unit in 16 stages for extraction of uranium and lanthanides from simulated high-level waste [9].

Takahashi and co-workers investigated the multistage extraction of samarium and gadolinium by means of a mixer–settler extraction column. Then the stage efficiency based on hydrodynamics and mass transfer within the column was studied [10].

Separation factors are typically 1.5–2.5 for neighboring members of rare earth series. The preparation of high-purity products requires 30–60 stages of mixer-settlers. As Megon developed a process for producing high- purity yttrium oxide starting from the xenotime concentrates. The solvent extraction circuit consisted of a selective extraction by D2EHPA followed by four extraction, twelve scrubbing and four stripping unit. Yttrium nitrate solution with other rare earths was fed to the second circuit by using 26, 6, 8 stage for extraction, scrubbing and stripping unit, respectively [11].

Liao and co-workers showed that the reciprocating extraction column is highly promising as an alternative of mixer-settlers in the extraction and separation of rare earth elements (Nd group/Sm group) with D2EHPA extractant [12].

Among the various types of extraction columns, the pulsed disc and doughnut extraction column is one type of extractor whose application has rarely been referred to the literature [13–16]. An installation of the pulsed disc and doughnut columns to treat the uranium solutions from Western Mining Corporations in South Australia has shown that these columns have a clear advantage over the mixer-settlers. The estimated capital expenditure associated with pulsed column is about 20% lower than that of similar size plants using mixer-settlers [13,17]. The success of pulsed columns in the uranium industry is leading to more interest in pulsed columns for other metals- cobalt, zinc, copper and nickel. The use of pulsed columns for the GORO Nickel project in New Caledonia will mark the entrance of pulsed columns into the base metals industry and will lead to applications for other metals, as well [18].

The applications of the pulsed disc and doughnut extraction columns were not observed in the literature for extraction and separation of rare earth elements. Furthermore, the knowledge concerning the design and performance of these columns is still far from satisfactory. The reason relates mainly to the complex behaviors of the hydrodynamics and mass transfer performance. In order to develop the appropriate design procedure, the knowledge of average drop size and dispersed phase holdup in terms of the operating variables, column geometry and liquid physical properties is essential. The empirical correlations have been reported for the dispersed phase holdup and Sauter mean drop diameter in terms of physical properties and operating variables for different operating regimes [19–21].

The purpose of this study was to investigate the feasibility of the pulsed disc and doughnut extraction columns for extraction and separation of samarium and gadolinium from aqueous nitrate solution with D2EHPA extractant and to obtain information on drop size and holdup. The effects of operational variables such as pulsation intensity, dispersed and continuous phase velocities on holdup, drop size and separation factor in extraction and stripping stages were investigated.

2. Experimental

2.1. Reagents

The commercial extractant, 2-ethylhexyl phosphoric acid (D2EHPA) was purchased from Aldrich. This extractant was dissolved in kerosene to achieve the required concentration. The aqueous working solutions were prepared by diluting gadolinium and samarium nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, Middle East Ferro Alloy Company, 99.9% purity) in deionized water. The initial concentrations of two metals were maintained at 500 ppm.

2.2. Batch experiments

The experiments were performed by contacting equal volumes of aqueous phase and organic phase in a shaker for 30 min at room temperature (initial experiments showed that equilibrium was obtained during 10 min). After extraction, the phases were separated by means of a separation funnel. Metal concentrations in the aqueous phase before and after extraction were determined by using a Perkin-Elmer model 5500 inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The distribution coefficient (D), extraction efficiency (E), separation factor (β) and stripping efficiency (S) are defined as follows:

$$D = \frac{[M]_t - [M]_a}{[M]_a} \quad (1)$$

$$\%E = \frac{D}{D + (V_{\text{aq}}/V_{\text{org}})} \times 100 \quad (2)$$

$$\beta = \frac{D_1}{D_2} \quad (3)$$

$$\%S = \frac{[M]_{\text{aq,a}} V_{\text{aq}}}{[M]_{\text{org,o}} V_{\text{org}} + [M]_{\text{aq,a}} V_{\text{aq}}} \times 100 \quad (4)$$

where $[M]_t$ and $[M]_a$ express the initial and final concentrations of metal ions in the aqueous phase, V_{aq} and V_{org} are the volumes of the aqueous and organic phases, $[M]_{\text{aq,a}}$ is the equilibrium concentration of metal ion in the stripping acid and $[M]_{\text{org,o}}$ is the equilibrium concentration of metal ion in the loaded organic phase, respectively.

2.3. Pulsed disc and doughnut column extraction experiments

The extraction experiments were performed at room temperature in a pilot plant using a pulsed disc and doughnut column extraction. The continuous and dispersed phases flowed countercurrently, the aqueous phase in descending direction and the organic phase in ascending direction. The schematic arrangement of column and auxiliary equipment is shown diagrammatically in Fig. 1.

In extraction experiments, the nitrate solution of samarium and gadolinium with 500 ppm concentration was prepared for continuous phase. The dispersed phase organic solution contained 0.12 M D2EHPA extractant diluted with kerosene.

In stripping experiments, the nitrate solution with 0.1 M concentration was prepared for continuous phase. The loaded organic phase of samarium and gadolinium with 500 ppm concentration was used for the dispersed phase organic solution.

The main column section comprised a 76 mm internal diameter glass tube and the effective height of the column was 74 cm. The column divided by 30 pairs of disc and doughnut and was made of stainless steel with a thickness of 2 mm.