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Separation of Nd from mixed chloride solutions with Pr by extraction with saponified PC 88A and scrubbing

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ABSTRACT

Solvent extraction of Pr and Nd from chloride solution was carried out using PC 88A for the recovery of magnetic grade Nd. The presence of complexing reagents (H_2O_2 and citric acid) affected little the selective extraction of Nd over Pr. The observed maximum separation factor between Pr and Nd was 1.5, indicating that the separation of Nd and Pr by selective extraction was difficult. Co-extraction of two metals with PC 88A followed by selective scrubbing was tried. Batch simulation of counter-current showed that the complete recovery of Nd was possible and a process flow sheet has been presented.

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1. Introduction

Neodymium (Nd) is one of the most abundant elements of rare earths and is used in high energy product, high coercive force magnets for computers and other applications. The separation of Nd from other rare earth fractions, especially its neighbor element praseodymium (Pr), is difficult. The separation of Nd from Pr has been first accomplished by fractional crystallization of the ammonium nitrate double salts, but this process is only of interest in batch mode [1]. However, even in solvent extraction, a large number of stages in a mixer–settler operation are required for the separation of Nd and Pr [2].

Solvent extraction is one of the promising operations to separate the metallic elements due to its technical interest in continuous mode. The mutual separation of Pr and Nd is an important step in producing its pure form, but numerous reports have indicated that the separation factor between Pr and Nd by commercial extractants is very low [3,4]. The literatures show that the research attempts have been made to develop a new concept in solvent extraction for separation of Pr and Nd [5–12]. For instance, Preston described that the separation of magnet grade neodymium with the purity of 95–96% is achieved from nitrate solution containing Pr, Ce and La using continuous counter-current extraction process with amine based extractants [13]. Shaohua et al. [14] reported that a bit of greater separation coefficient between Pr and Nd is achieved with D2EHPA in presence of lactic acid from HCl medium. Lu et al. [15] proposed a process to separate Nd and Pr from mixture of 83% Nd, 15% Pr and 2% other rare earths contained a chelating reagent (DTPA) using Aliquat 336. The achieved results exhibited that 95% recovery of Nd_2O_3 with the purity >99% is attained in 45 stage tube type mixer–settler operation and the authors described that 78.7% purity of Pr could be improved by using box type mixer–settler operation [15]. Furthermore, Minagawa presented an advanced process to separate Pr over Nd from acidic aqueous solutions in presence of DTPA using non-equilibrium extraction with B2EHPA in kerosene [16]. Similarly, Nakayama et al., studied on the separation of La, Pr and Nd using supported liquid membranes in presence of DTPA complexing reagent. In this investigation, the selectivity for Pr with respect to Nd is obtained around 2.5 [17].

Most of the reported methods added some complexing reagents to separate Pr and Nd, whereas few processes have been reported to separate/or recover Pr and Nd from acidic aqueous solutions in absence of complexing reagents. Sherrington et al. [18] reported a complicated process to produce >99% purity of Nd_2O_3. However, in this continuous separation process, the separation factor between Pr and Nd is around 1.5 and 95 to 98% purity of Nd_2O_3 is achieved by employing 60 stages of mixer–settler operation. The maximum

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separation factor between Pr and Nd is about 1.2 to 1.4 in all investigated acid mediums such as chloride, nitrate, perchlorate and mixture of chloride-nitrate systems with D2EHPA [19]. Nevertheless, a higher separation factor value around 5.4 is attained between Pr and Nd with quaternary ammonium salt in presence of amino carboxylic acids [20]. Additionally, Thakur et al. [21] developed an extraction and scrubbing process for the recovery of pure Nd (>96% Nd_2O_3) from mixture of all lighter rare earths using 20% saponified PC 88A and pure Nd solution as a scrub feed. The authors [21] clearly described that the separation factor between Pr and Nd is around 1.64 which is higher than that of D2EHPA reported by Pierce and Peck [22].

Comparing the results obtained up to the present level of investigations, it can be observed that maximum separation factor between Pr and Nd is very low (~1.5) [5–22]. A slight increase in the separation factor values between Pr and Nd was noted in the presence of complexing reagent irrespective of their methodologies such as liquid–liquid extraction and membrane technology [5–17]. Nevertheless, the results reported eventually suggested that the large number of stages is needed to obtain pure metallic species of Pr and Nd [15,18].

In our studies on the recovery of rare earths from monazite sand, it was initially digested with NaOH followed by dilute HCl leaching to dissolve the rare earth elements. The thorium (Th) and impurities (Fe and Al) could be separated from the light rare earth elements by adjusting the pH of leach solution. Subsequently, the resulting leach solution contains metals (composition in g/L): La-7.8, Ce-12.4, Pr-1.19 and Nd-3.3 at pH 5.0. Initially the quantitative recovery of Ce and La is achieved by chemical precipitation and solvent extraction, respectively [23]. In fact, during precipitation of Ce, portion of La, Pr and Nd are co-precipitated along with Ce [23]. Afterwards, the Ce and La free solution contains (composition in g/L): Pr-1.17 and Nd-3.28. In the present study, co-extraction and selective scrubbing of Pr from loaded PC 88A was employed to recover Nd due to many more extraction stages are needed to recover the corresponding metal ions [18,21]. For this purpose, McCabe–Thiele plots for the scrubbing were constructed and batch simulation of counter current experiments was done. The variation in the separation factor between Nd and Pr during extraction is discussed. A process is proposed to obtain pure Nd solution from the monazite sand by hydrometallurgical method with the less number of stages.

2. Experimental

2.1. Reagents

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC 88A) was purchased from Daihachi Chemicals Co. Ltd., Japan, and used as such without any further purification. The sodium salt of PC 88A (30, 40, 50% neutralized) was prepared by adding stoichiometric amount of concentrated NaOH solution and stirring the mixture until a single phase was formed. Escaid 110 was used as a diluent in the present work.

Praseodymium and neodymium chlorides (>99%) were purchased from Alfa Aesar (A Johnson Matthey Company). The stock solution of rare earths were prepared by dissolving the corresponding rare earths chlorides in minimum concentrated hydrochloric acid and the concentration of the metals was controlled by adding doubly distilled water. The desired initial pH values of the rare earth solution were adjusted with HCl/NaOH and all other chemicals used were of analytical grade.

2.2. Apparatus

Spectro arcos model inductive coupled plasma atomic emission spectrophotometer (ICP-OES) and Thermo Scientific (Orion Star A211 model) pH meter were used for the determination of metal concentrations in the aqueous phase and for measuring the pH values, respectively.

2.3. Solvent extraction procedure

Extraction and scrubbing experiments were carried out at room temperature by mixing equal volumes of the aqueous and organic phases (A/O = 1) except for extraction and scrubbing isotherm and their batch simulation of counter-current studies. The shaking time for these extractions and scrubbing experiments was 30 min (initial experiments showed that equilibrium was achieved within 10 min) using wrist action shaker (Burrell model 75 USA). After disengagement of the two phases, the concentration of metals in the aqueous phase, before and after distribution, was measured spectrophotometrically (ICP–OES) and metal contents in the organic phase were determined by mass balance. The distribution ratio (D) was calculated as the ratio of the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From the D values, the percent extraction was obtained by [31],

$$\%E = \frac{D \times 100}{[D + (V_{aq}/V_{org})]} \tag{1}$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively. The separation factor (β) was calculated from the value of distribution coefficients of Nd and Pr and shown as [32],

$$\text{Separation factor} = \frac{D_{Nd}}{D_{Pr}} \tag{2}$$

3. Results and discussions

3.1. Effect of initial pH on the extraction and separation of Pr and Nd by PC 88A

The influence of initial pH on the separation of Nd and Pr was carried out using various concentrations of PC 88A in Escaid 110 diluent. In these experiments, the initial pH values were varied from 3 to 6 at each concentration (0.03 M, 0.05 M, 0.07 M and 0.09 M) of PC 88A. The results obtained are presented in Fig. 1. With increasing PC 88A concentration, the extraction percentage of Pr and Nd showed some increase up to 0.05 M PC 88A from 0.03 M. Afterwards, a slight increase in the percentage extraction of Pr and Nd was observed However, the extraction percentage of Pr and Nd varied in between ~5 to 16% and 9 to 22%, respectively, in entire range of acidity and PC 88A. From these results, the maximum extraction percentage of Pr and Nd was around ~16% and 22%, respectively. In addition, the obtained separation factor values in this investigation were around 1.5. The extraction reaction of REEs (rare earth elements) with this acidic cationic extractants can be represented as follows [26],

$$RE^{3+} + 3(HA)_{2org} = RE(HA_2)_{3org} + 3H^+ \tag{3}$$

where $(HA)_2$ denotes the dimeric form of acidic cationic extractant (PC 88A) and subscript org represents the organic phase.

The equilibrium constant for the extraction of Nd can be represented as follows

$$K_{Nd} = \frac{[RE(HA_2)_3][H^+]^3}{[RE^{3+}][(HA)_2]^3} = D_{Nd}\frac{[H^+]^3}{[(HA)_2]^3} \tag{4}$$

Eq. (4) indicates that the distribution ratio of a metal increases with the increase of extractant concentration and solution pH, which agrees well with our data.

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