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A review on yttrium solvent extraction chemistry and separation process

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Abstract: This paper reviewed various systems such as neutral phosphorus and acid phosphorus, carboxylic acid and amine extractant for solvent extraction chemistry of yttrium, including thermodynamics, kinetics and yttrium extracting separation process containing the development course and new separation process.

Keywords: yttrium; rare earths; extraction chemistry; separation process

Rare earth element yttrium was the first to be isolated in 1794, which is an important element and in great demand nowadays. There is a wide variety of rare earth, including yttrium minerals known, the mined minerals of xenotime (YPO₄), monazite (Ce, La, Y, Th)PO₄, but the ion adsorption type rare earths notably have been found in the south China in the late 1960s, and Y content was more than sixty percent of them.

Yttrium is widely used in astronavigation, luminescence, ceramics, nuclear energy and metallurgical industries and the purity of Y is strictly required, for example, the fluorescent grade Y_2O_3 requires a content of relevant RE impurities which should be lowered to 1×10^{-4} level or even lower. However, the separation and purification of Y from RE impurities is known to be difficult because of their similar chemical and physical properties. To separate Y from rare-earths, solvent extraction processes for separation of rare earths were reviewed^[6–8]. However, there are few comments about the separation and purification of yttrium^[9]. This article systematically reviewed yttrium extraction chemistry and separation process in different extractant systems.

1 Yttrium extraction chemistry

Sue^[5] thought that using yttrium position changes in lanthanides to separate yttrium, as a result that yttrium in the position of lanthanide was not fixed, with the change of the system and condition with five different positions. Due to the nature of lanthanide shift change, the yttrium in lanthanide occupies several places at the same time. Study of yttrium extraction chemistry in different extraction system is very meaningful, because under the different systems, locations of yttrium in rare earth extraction are different. This is the basis to exploit the new process of yttrium extraction separation.

1.1 Neutral phosphorus extraction systems

In many neutral phosphorus extractants, TBP is the earliest applied in rare earth extraction separation. Warf^[10] demonstrated the value of liquid-liquid extraction in separating cerium (IV) from the trivalent rare earths by TBP from a concentrated aqueous HNO₃. The TBP versus concentrated HNO₃ system appeared promising and was first reported in 1953 by Peppard et al.^[11]. This investigation showed that the distribution ratio Kincreased with increasing atomic number using 15.6 F HNO₃ and undiluted TBP. This initial report suggested, on basis of incomplete tracer studies and an arbitrary assignment of a pseudo-atomic number to yttrium as a pseudo-rare earth, that for this system a plot of lg K versus Z, the atomic number, is a straight line of positive slope approximately 1.9. Extensive study showed that when rare earths with high concentrations were extracted with TBP, positions of yttrium were between Gd and Dy or between Er and Yb. With the decrease of concentrations of rare earths, the positions of yttrium moved to the part of light rare earths, witch was conducive to the separation of yttrium. Based on these features, Thorium Ltd. of Widnes in the United Kingdom with Versatic 911-ShellsolA (yttrium in Gd-Y-DY) firstly extracted rich yttrium heavy rare earths, after that with the TBP-ShellsolA extracting low concentration of rare earth nitrate containing yttrium (1-1.2 mol/L), at the moment yttrium from heavier lanthanide parts removed light lanthanide, use of the two-step total reflux extraction, 99.99% purity Y₂O₃ product from yttrium containing 32% of the raw material^[12] could be obtained. Studies^[2] that showed extraction of rare earths by di-(1-methyl-

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heptyl)methyl phosphonate (P350), salting-out agent not only affected distribution ratios and separation factors, but also influenced positions in a sequence of yttrium in extraction. In 6 mol/L NH₄NO₃, yttrium in samarium or the position of thulium, and no salting-out agent, yttrium was in cerium or the location of the ytterbium. The extraction of RE(III) in HNO₃ solutions by di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP, B)-heptane in the presence of LiNO₃ was studied systematically by Zhao et al.^[13]. Fig. 1 shows the relationship between distribution ratio *D* and atomic number *Z*.

The distribution ratios were found to be a distinct "tetra effect", each extraction sequence element by DEHEHP was as follows: Lu>Tm>Er≈Yb≈Ho>Dy>Y>Tb>Eu>Sm>Gd> Nd>Pr>Ce>La, the arrowhead indicates the position of Y in the extraction list and lies between Tb and Dy. It could be concluded that DEHEHP could be employed for the separation of La from the other rare earths, and Y from light rare earths under certain conditions. Cyanex 923 and Cyanex 925 were the commercially available solvating reagents introduced by American Cyanamid now Cytec Industries. The extractants were, respectively, straight chain and branched chain alkylated phosphine oxide mixtures and the structures were shown as literatures^[14,15]. Chu et al.^[16] reported the extraction of 15 rare earths (III) in nitrate medium with Cyanex 923 in n-heptane, that showed the relationship between distribution ratio D and atomic number Z. To be a distinct "tetrad effect", the position of Y in the extraction list lay between Ce and Pr. The impact results of temperature on extraction equilibrium showed that the temperature from high to low, yttrium part to light rare earth changed gradually. This property can be used to separate yttrium from heavier rare earths (Fig. 2). The composition of extraction complex was RE(NO₃)₃·3 Cyanex 923.

The extraction of yttrium and some trivalent lanthanides from thiocyanate and nitrate solutions using





(1) pH=2.50, LiNO₃=2.61 mol/L; (2) pH=1.89, LiNO₃=2.61 mol/L; (3) pH= 2.50, LiNO₃=1.74 mol/L



Fig. 2 Relationship between atom number Z and $\lg D$

Cyanex 923 (TRPO) in xylene was also investigated by Reddy et al.^[17]. It was found that these trivalent metal ions were extracted from thiocyanate solution as $M(SCN)_3 \cdot n \cdot TRPO$. In genenally, *n* were the values of 4 and 3 for the lighter and the heavier lanthanides, respectively. In both thiocyanate and nitrate systems, it was found that the distribution ratios of trivalent lanthanides increased with decreasing ionic radii and the distribution ratio of yttrium lay along with those of the middle lanthanides. Delloye and Sabbot^[18] reported a process for the preparation of ultrapure Y₂O₃ (99.9999%) with a yield of 98.8% from a feed solution containing a mixture of rare earths (Y₂O₃ 95%, Tm₂O₃ 0.8%, Yb₂O₃ 3.8%, Lu₂O₃ 0.4%) with 75% Cyanex 923 in kerosene.

Mass transfer kinetics of La, Y and Sm extraction with purified Cyanex 923 from nitrate medium was investigated by using a constant interfacial cell with laminar flow at 303 K. The experimental results showed that the mass transfer of La was controlled by both chemical reaction and diffusion, the mass transfer of Y and Sm were controlled by diffusion, chemical reactions occured at the interface^[19,20]. The extraction behavior of lanthanides and yttrium using Cyanex 925 (mixture of branched chain alkylated phosphine oxides) in n-heptane from nitrate medium was studied. The extractability of the lanthanides and yttrium increased with increasing nitrate concentration, as well as with increasing Cyanex 925 concentration. The relationship between the $\lg D$ and lanthanide atomic number Z was also discussed which indicated that extractability of yttrium was between Gd and Tb, and yttrium could be separated from light lanthanides^[21,22], which was different from that reported by Chu et al.^[16] using Cyanex 923. The extractability of yttrium was between Ce and Pr.

Tris(2-ethylhexyl)phosphate(TEHP) was proposed as an extractant for scandium(III) and yttrium(III) from salicylate media. The optimum extraction conditions were evaluated and the method permitted mutual separation of scandium(III) and yttrium(III) and could be used for the separation and determination of scandium(III) and yttrium(III) from binary and multicomponent mixtures^[23]. Download English Version:

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