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## Selective heavy rare earth element extraction from dilute solutions using ultrasonically synthesized Cyanex 572 oil droplets and Cyanex 572-impregnated resin

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### ABSTRACT

The extraction of heavy rare earth elements (HREE) from a dilute leach solution using current routes poses crucial challenges including solvent loss, high solvent consumption, and phase disengagement difficulties for rare earth industry. This study proposes the selective extraction of HREE from dilute solutions using the ultrasonically-generated Cyanex 572 oil droplets (UGCOD) and Cyanex 572-impregnated resin (CIR). Oil/water (O/W) emulsion (EM) is a colloidal suspension, which is composed of micron and sub-micron sized oil droplets introducing a very high interfacial surface area in the aqueous solution. Sodium dodecyl sulfate (SDS) and hexadecyl trimethyl ammonium bromide (HTAB)-coated Cyanex 572 oil droplets were synthesized to investigate the impact of surfactant dosage on the zeta potential of EM, droplet size distribution, and extent of selective HREE extraction. Fourier transform infrared (FTIR) results clearly showed that the cation-exchange mechanism is involved in rare earth elements (REE) ions extraction by Cyanex 572 oil droplets. However, the addition of cationic and anionic surfactants markedly changed the REE extraction trend, which was due to the electrostatic interaction between REE ions and the outer charged layer formed at the surface of droplets. EM showed very fast HREE extraction compared to that of CIR and solvent extraction (SX).

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### Introduction

Many mining companies have turned their attention towards the processing and separation of rare earth elements (REE) due to their critical role in the development of high-tech products. REE are separated into the light REE (LREE) group, from lanthanum (La) to gadolinium (Gd), and the heavy REE (HREE) group, from terbium (Tb) to lutetium (Lu) as well as yttrium (Y). Canada possesses a significant rare earth resource potential, which accounts for approximately 40–50% of the world's known REE reserves [1]. If developed, Canada would not only be able to provide the rest of the world with REE, but also improve its own rare earth-based advanced technologies and industry. Therefore, efforts have been conducted to develop fast, efficient and low-cost approaches to selectively extract and separate REE from solutions [2–4]. Hydrometallurgical processes employed to extract REE are grouped into three steps: (i) baking or cracking the REE

concentrate; (ii) leaching, neutralization, and precipitation processes; (iii) separation and purification techniques including solvent extraction (SX) and ion exchange (IX). The first step, selected based on the type of REE-bearing minerals, aims to disintegrate the mineral's structure and render REE soluble in a weak acid solution. As initial quantities of REE in these solutions are very low, a series of stepwise leaching, neutralization, oxidation ( $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$ ), and precipitation processes (Fig. 1) is implemented to remove impurities (Fe, Al, and Th), and consequently increase the REE concentration prior to solvent extraction (SX).

SX is a key technique in the industrial hydrometallurgical operations to separate REE from concentrated solutions, where the concentration of metal ions is relatively high [5]. However, solvent loss, high capital outlay, high solvent consumption (organic/aqueous ratio (O/A)  $\sim 1$ ), and phase disengagement difficulties are obstacles once SX is applied to treat solutions containing a low concentration of metal ions ( $< 1000$  mg/L) [6]. Several methods were developed on the basis of increasing surface area between extractant and the dilute solution such as, air-filled emulsion (AFE) [7], air-assisted solvent extraction [8,9], colloidal liquid aphrons

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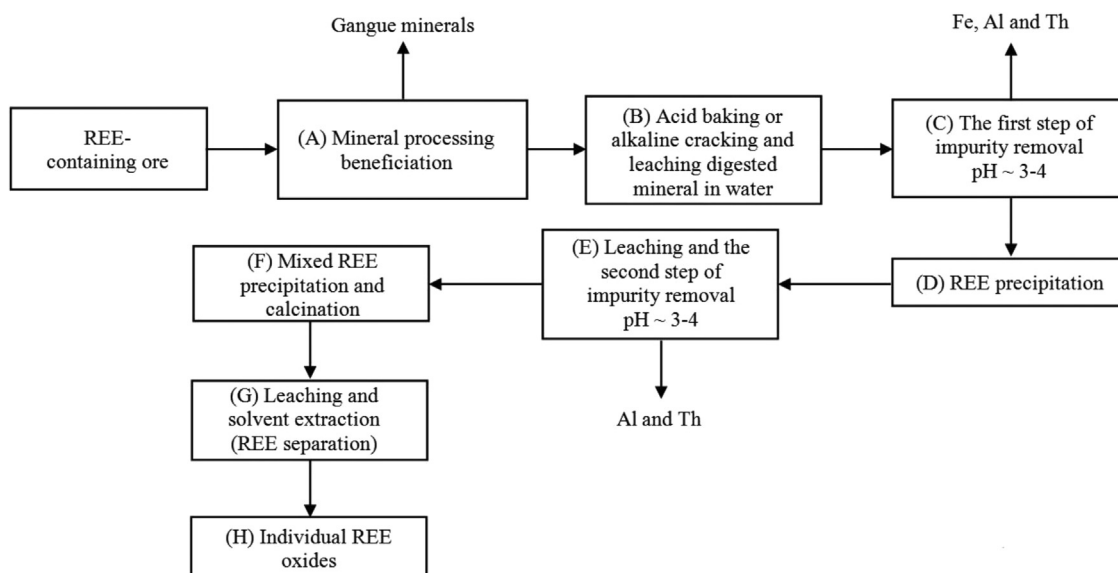


Fig 1. A typical flow diagram of individual REE extraction.

[10], emulsion liquid membrane (ELM) [11,12], supported liquid membrane (SLM) [13–15], and colloidal gas aphyrons (CGA) [16,17] in order to overcome the challenges associated with SX for treating dilute metal-bearing streams.

The ambition to overcome the impediments associated with SX leads to experimentation with ultrasonically synthesized oil in water (O/W) emulsion (EM) to treat dilute REE solutions. The technique is potentially efficient for extraction of metal ions even at low metal ion concentrations, <500 mg/L, due to the introduction of a very high interfacial surface area between extractant and REE ions. This not only leads to a markedly reduced amount of organic, extraction time, and diffusion length required; but also renders an increase to both contact time and extraction kinetics.

An O/W EM is naturally unstable, since the contact between dispersed oil droplets and the aqueous medium is thermodynamically unfavorable [18,19]. Therefore, in order to construct micron-sized oil droplets, an energy input greater than the Laplace pressure acting across the O/W interfaces is required. This energy is furnished through various means, including rotor-stator devices, an ultrasonic probe, a high-pressure homogenizer, and a porous membrane. In addition, the energy is directly proportional to the interfacial tension. The energy required to form a droplet increases as the interfacial tension elevates, and the nature of the forces capable of droplet formation are based on the type of apparatus used. In general the ultrasound emulsification process is more efficient compared to mechanical agitation in terms of droplet size and reduced surfactant amount as well as energy consumption [20–22]. The mechanism behind formation of an O/W EM is combination of two steps: (i) interfacial waves generated by an acoustic field cause the oil phase to be erupted in the form of oil droplets in the aqueous medium [21,23]; (ii) acoustic cavitation, which is responsible for the generation of extreme turbulent micro-implosions. This leads to the breakup of the distributed oil droplets into the sub-micron sized droplets [24].

A novel extractant known as Cyanex 572 has been recently released by CYTEC (now called Solvay) which is a mixture of phosphinic and phosphonic acids. Cyanex 572 is specifically designed to extract HREE over LREE with a lower acid requirement for the stripping stage [25]. According to the authors' knowledge, this work is the first to use ultrasonically generated Cyanex 572 oil droplets (UGCOD) to selectively extract HREE from dilute solutions.

In this study, Cyanex 572-impregnated resin (CIR) was also synthesized to compare the functionality of solvent-impregnated resins (SIR) to EM for HREE separation from the dilute REE solutions. The concept of SIR is similar to the extraction chromatography (EXC) on the basis of impregnation of a macroporous solid support as a stationary phase with a chelating extractant through the physical linkage [26,27]. The advantages of the SIR process over conventional SX process are: (i) reduced organic solvent entrainment into the aqueous solution through immobilization of the extractant on the resin surface; (ii) higher metal separation efficiency owing to the very high interfacial surface area between extractant impregnated resins and the aqueous solution.

The effect of operational conditions such as type and dosage of surfactant, solution pH, and O:A ratio on REE extraction was probed qualitatively and quantitatively. Furthermore, the functionality of SX, CIR, and EM at similar dosages of Cyanex 572 with respect to the extent of HREE separation and contact time was compared.

## Materials and methods

### Materials

Diaion HP-2MG resins were purchased from Sigma Aldrich (USA). REE sulfate octahydrate salts (Alfa Aesar, USA) were used to produce aqueous solutions of yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), terbium (Tb), erbium (Er), and ytterbium (Yb). Reverse osmosis purified water (pH of 5.5 at 25 °C) was used to produce all solutions. Nitric acid and acetone (Fisher Scientific, Canada) were purchased in order to wash resins before the impregnation process. Ethanol (96%) (Fisher Scientific, Canada) was used to dilute Cyanex 572 in the production of CIR. Solution pH was regulated using  $10^{-1}$  M sodium hydroxide and  $10^{-1}$  M hydrochloric acid (Fisher Scientific, Canada). Cytec (now Solvay) kindly supplied the organic extractant, Cyanex 572. Kerosene (Fisher Scientific, Canada) was used to dilute Cyanex 572 in the SX experiments. Sigma Aldrich (USA) provided sodium dodecyl sulfate (SDS) and hexadecyl trimethyl ammonium bromide (HTAB), anionic and cationic surfactants.  $10^{-3}$  M KCl (Fisher Scientific, Canada) was utilized as a supporting electrolyte to quantify the zeta potential of the EM. Sulfuric acid was sourced

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