ABSTRACT

Studies on solvent extraction and separation possibilities of rare earths from phosphoric acid solutions using phosphorus based extractants and their mixtures.

During the past decades, the separation and purification of rare earths (REs) elements has gained considerable importance with increasing demand for these elements and their compounds individually and collectively. A brief discussion on general chemistry and properties of REs was presented below.

Rare-earths chemistry

REs elements are a collection of 17 chemically similar metallic elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium. Scandium and yttrium are considered rare earth elements since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. The rare earth metals are found in group IIIB of the periodic table, and the 6th period. Solvent extraction and ion-exchange processes are used today to produce cost effective and highly pure rare earth compounds.

Common properties of the rare earths

- The rare earths have a high lustre, but tarnish readily in air and have high electrical conductivity.
- The metals share many common properties. This makes them difficult to separate or even distinguish from each other.
- The rare earths, among themselves show very small differences in solubility and complex formation.
- Rare earths usually exhibit an oxidation state of $3^+$. There is slight tendency to vary the valence.
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**Special Properties of the Rare Earths**

The chemical similarity of all REs can be explained by some properties like

(a) Electronic configuration and

(b) Lanthanide contraction

(a) **Electronic Configuration**

The valence electronic configuration of Sc, Y and La elements can be given as \( ns^2 (n - 1) d^1 \) (\( n = 4, 5 \) or 6). They have no f orbital electrons. The 14 elements following lanthanum (lanthanides), namely, Ce – Lu, have valence electron configurations \( 6s^25d^{1}4f^{n-1} \) or \( 6s^24f^n \). In neutral atoms, the 5d and 4f electrons have similar energies and this is the reason for two typical electronic configurations. Because of the great complexity of the electronic spectra and difficulty in analysis, the electronic configurations of these elements are uncertain.

(b). **Lanthanide Contraction**

The significant and steady decrease in the size of the atoms and ions with the increase in the atomic numbers in the lanthanide series, Ce to Lu is called lanthanide contraction. This steady shrinkage is mainly caused by the incomplete mutual shielding of the 4f electrons (owing to their shape) against the increasing attraction of the nucleus. The peculiarities of the electronic structure of the rare earth elements lead to periodic changes in some physical and chemical properties. However, the importance of the lanthanide contraction arises from its consequences such as occurrence of yttrium with heavy lanthanides and separation of lanthanides.

The lanthanides are commonly divided into: lower atomic weight elements, lanthanum (138.9) to europium (150.9), referred to as the light rare-earth elements (LREs) and higher atomic weight elements, gadolinium (157.2) to lutetium (174.9) and yttrium (88.9), and referred to as heavy rare-earth elements (HREs). Yttrium is usually grouped with the HREs because of
its chemical similarity. The division is somewhat arbitrary and the term middle REs (MREs) is sometimes used to refer to a group of elements namely, samarium, europium and gadolinium.

The main sources of REs are monazite, xenotime and bastnasite. In addition to these; rock phosphates are major source for production of fertilizer grade phosphoric acid also contain minor quantities of rare earth elements. In India, about 10 fertilizer plants uses rock phosphate imported mainly from Jordan, Morocco, Egypt and China. It is reported that about 1.4 million tons of wet phosphoric acid (WPA) is produced in the country by about 10 commercial phosphate fertilizer producing industries. The available rare earth elements in WPA/sludge can be considered as a potential alternate source for the production of individual rare-earths (REs) or mixed REs oxides.

Phosphate rocks generally contain uranium almost 50-300 mg/Kg and other rare earths less than 100 mg/Kg depending on the source of rock phosphate used. Pilot plants trials are in progress to recover uranium from WPA by mixtures di-2-ethylhexyl phosphoric acid (D2EHPA), and tri-n butyl phosphate (TBP) extractants. Using methods such as precipitation, oxidation, crystallization and electrochemical methods, it is difficult to separate metals in a simple and economical way. Solvent extraction is an effective method used widely in extractive metallurgy for metal separation and recovery from ores, secondary resources, recycling of industrial wastes etc.

In analytical chemistry, this method enjoys a favored position among separation techniques because of its simplicity, speed and wide scope. By utilizing simple apparatus like separatory funnel and requiring several minutes to perform. In solvent extraction, aqueous phase containing metal ions are contacted with organic phase containing extractant which can extract metal ion by ion exchange or chelate formation, after phase separation the loaded organic is stripped with a
suitable solution to recover the metal. Selectivity of targeted metal ions, fast kinetics and high capacities are the main advantages.

In the present work, we report detailed studies carried out on the solvent extraction of rare-earths from phosphoric acid solutions using commercially available organophosphorus reagents namely Talcher organo phosphorus solvent (TOPS 99), an equivalent to DEHPA, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272). These extractants were extensively used in the solvent extraction of the metals. Based on the literature survey, these extractants were not explored in detail for the solvent extraction of REs from phosphoric acid. To the best our knowledge, little work done on the separation of REs from phosphoric acid medium. For the first time, we carried out the extraction studies of REs from WPA (3-5 M) using organophosphorus reagents. Screening of extractants was tried for the selection of best extractant for the separation of REs from phosphoric acid. From the distribution data, separation factors are determined and possible separations of one/two/ or group of REs from others are proposed. Among the extractants screened, the technical data obtained for TOPS 99 extraction system showed good separation possibility of REs into 2/3 fractions.

Based on above study results, using TOPS 99, a process flow sheet was developed from 3 M phosphoric acid for the separation of REs into three fractions; light rare earths (LREs) as one fraction, another is Lu+Yb fraction and third fraction is remaining heavy rare earths (HREs). Fundamental extraction studies of individual REs were carried out in order to establish their extraction behavior from phosphoric acid. Extraction studies of individual yttrium (Y) and dysprosium (Dy) were carried out from phosphoric acid solutions to establish the extracted species in the organic phase, extraction of commonly associated REs and determination of
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separation factors for possible separation of REs. Solid-liquid extraction studies were investigated for the extraction of REs using ion exchange resins such as Tulsion CH-90 (amino diacetic acid functional group) and Tulsion CH-93 (amino phosphonic acid functional group).

Objectives of the present work

- The main aim of the present work was to carry out systematic extraction studies to investigate the separation possibilities of rare earths from wet phosphoric acid solutions employing organophosphorus extractants.
- Determination of distribution coefficient and separation factors
- Fundamental systematic studies of yttrium and dysprosium include parameters like, acidity, extraction species, diluents, temperature and other associated rare earths to determine separation of rare earths as individual or group of metals from one another.
- Flowsheet development for the separation and recovery of rare earths from WPA solutions using solvent extraction technique.
- Solid-liquid extraction studies of rare-earths from phosphoric acid solutions were carried out using Tulsion CH-90 and Tulsion CH-93 resins.

This thesis is divided into five chapters.

Chapter I: Introduction

This chapter briefly deals with REs resources and major end uses. It also includes the processing of rock phosphate for the production of phosphoric acid; which contains minor quantities of rare earths. The general techniques used for the separation of rare earths were explained and special attention was given for the solvent extraction, this technique is used for the
present work. The main aim of present work and the literature regarding the rare earths were discussed.

**Chapter II: Materials and methods**

This chapter deals with the experimental part of all systems and theoretical aspects of inductively coupled optical emission spectrometer (ICP-OES). General principles of solvent extraction, chemistry of rare earths and extractants used were discussed. This chapter also deals with chemicals and apparatus used for the present study.

**Chapter III: This chapter is divided into two parts: Part-A and Part-B**

**Part-A: Liquid-Liquid Extraction and separation possibilities of heavy and light rare-earths from phosphoric acid solutions with acidic organophosphorus reagents**

Part-A deals with the solvent extraction behavior of mixture of seven heavy rare-earths (HREs): terbium, dysprosium, holmium, yttrium, erbium, ytterbium, and lutetium and mixture of four light rare-earths (LREs): lanthanum, cerium, praseodymium and neodymium using TOPS 99, PC-88A, and Cyanex 272 extractants. The objective of the present study was to investigate the extraction behavior and separation possibilities among HREs and LREs and also separation of HREs as a group from LREs from phosphoric acid solutions. The parameters studied include time, $\text{H}_3\text{PO}_4$ concentration and extractant concentration. The percent extraction of metal decreases as the acid concentration increases with any given extractant concentration. Mechanism of metal transfer follows ion exchange type. The separation factors were evaluated based on the distribution coefficients in order to estimate the potential of the results for the separation of individual/pair of rare-earths from others and the separation of HREs from LREs. Extraction efficiency of extractants towards lanthanides from $\text{H}_3\text{PO}_4$ solution decreases in the series: TOPS 99> PC 88A> Cyanex 272.
From the present studies, the binary separation of Lu with Tb/Dy and Yb with Tb/Dy and to separate Lu or Yb from phosphoric acid solution containing Tb/Dy or both can be tried using TOPS 99 in the acid range 3-5 M, which is similar to wet phosphoric acid. PC 88A works under low acids, the separation factors obtained with Cyanex 272 were below 2 in the studied acid range.

Mixture of LREs was studied using TOPS 99, PC 88A and Cyanex 272 (0.1M-0.5 M) from $\text{H}_3\text{PO}_4$ (0.5-5 M). Among the studied extractants, PC 88A and Cyanex 272 showed no affinity towards LREs. Only TOPS 99 (0.1-0.5 M) showed extraction efficiency towards LREs. Within 3-5 M acid range there is ~95% extraction was found for Lu and Yb where zero percent of extraction was found for LREs with 0.5 M TOPS 99. From the results it can be concluded that Lu and Yb can be easily separated from other rare earths in a few stages of counter-current extraction using TOPS 99 from WPA.

Among the studied acidic extractants, TOPS 99 is the best extractant in the acid range 0.5-5 M. TOPS 99 (0.1 and 0.3 M) can be applied for the separation of HREs in the acid range 3-5 M, similar to WPA. For the separation of HREs from LREs TOPS 99 is only suitable in the 3-5 M acid range. The separation of HREs from LREs can be tried at high concentration above 0.5 M TOPS 99. Therefore, further studies will be carried out by using TOPS 99 with mixture of LREs and HREs to get possible separation in the acid concentration range 3-5 M.

**Part-B: Solvent extraction and separation of rare-earths from phosphoric acid solutions with TOPS 99**

This part deals with the development of process flowsheet to separate REs into 3 fractions from 3M phosphoric acid solution similar to WPA. Based on the previous studies, TOPS 99 has been employed as extractant for the extraction studies of mixture of rare earths (four light rare-
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earths (LREs) La, Ce, Pr, Nd, and seven heavy rare-earths (HREs) like Tb, Dy, Y, Ho, Er, Yb and Lu) into possible fractions from phosphoric acid solutions. From the acid and extractant effects, 0.1 and 1 M TOPS 99 were suitable for the separation of a mixture of REs into three concentrates. Extraction isotherm predicts the separation of Yb+Lu at an aqueous-to-organic (A/O) phase ratio of 2 in three stages using 0.1 M TOPS 99. Counter-current batch extraction simulation (CCES) of Yb and Lu at an A/O of 2 resulted in a raffinate containing 3.6 mg/L of Yb+Lu, corresponding to an extraction efficiency of 91.9%, whereas other five HREs loss was about 6.7%. Stripping of Yb and Lu as per the predictions of McCabe-Thiele plot from loaded organic (LO) was selected at O/A phase ratio of 3 with 4 M HCl and counter-current stripping simulation studies resulted 100% stripping efficiency. From the Yb+Lu raffinate, remaining five HREs were extracted about 94.4% with 1 M TOPS 99 at an A/O ratio of 3 in three stages. The LREs (Pr and Nd) co extraction is 9.8%. Quantitative stripping of HREs from LO is achieved with 7 M HCl at an O/A ratio of 3 in two stages. Finally, a process flowsheet was presented for the separation of rare-earths into three groups, two HRE fractions (Yb+Lu and Tb, Dy, Ho, Y, Er) and one LREs fraction from 3 M phosphoric acid.

Chapter IV: This chapter is divided into two parts: Part-A and Part-B

Part-A: Liquid-liquid extraction studies of trivalent Yttrium from phosphoric acid solutions using TOPS 99 as an extractant

Part-A: This part deals with the extraction studies of trivalent yttrium (Y) from phosphoric acid solutions using TOPS 99 as an extractant. The parameters studied include equilibration time, acid concentration, extractant concentration, diluent, metal concentration, temperature, stripping and regeneration of extractant. Increase of phosphoric acid concentration in the range from 0.01 to 0.5 M on the extraction of trivalent Y with $6 \times 10^{-3}$ M TOPS 99 decreases the
percentage extraction, indicating the transfer of metal follows ion exchange type reaction. The species extracted appears to be $M(HA_2)_3$ (M: trivalent Y ion). Stripping of metal from the loaded organic with mineral acids indicate sulphuric acid as the best stripping agent. Stripping of metal with HCl from L.O and its recycling for the extraction of Y for six cycles indicated the greater stability of TOPS 99. Extraction of metals such as Tb, Dy, Ho, Er, Yb and Lu which are generally associated with Y showed that there is a possibility for separation of Lu and Yb from Tb and other associated metals. Extraction behavior of associated elements clearly follows their ionic radii with a maximum separation factor ($\beta$) of 414 for Lu-Tb. Results of present study will be applied to rare earths extraction from phosphoric acid solutions for their practical importance.

**Part-B: Studies on solvent extraction of Dy(III) and separation possibilities of rare earths using PC-88A from phosphoric acid solutions**

In this part solvent extraction studies of Dy(III) from phosphoric acid medium has been investigated using PC-88A alone and in combination with acidic, basic and neutral extractants. Systematic studies of Dy(III) using 0.04M PC-88A as a function of equilibrium pH, extractant concentration and metal concentration indicated the extracted organic complex stoichiometry as $\text{Dy} . 3 (HA_2)$. Extraction behavior of other rare earths (REs) with 0.1M PC-88A suggested the possible separation of Lu+Yb from others in the acid range 0.6-1M.

Based on the differences in extraction behaviour of rare earths studied with PC-88A as a function of acidity and extractant concentration, separation possibility of Lu+Yb pair from Dy+Tb pair has been proposed at an A/O ratio of 2.5:1 and 1:1 at 0.6 and 1M acid, respectively.

**Chapter V: Solid-liquid extraction of Gd(III) and separation possibilities of rare-earth from phosphoric acid solutions using Tulsion CH-93 and Tulsion CH-90 resins**
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Commercial resins with Amino phosphonic acid functionality and Amino diacetic acid functionality, supplied by Thermax India Ltd were employed for the solid-liquid extraction studies of gadolinium from phosphoric acid medium. The experimental conditions studied include equilibration time, acid concentration, mass of the resin, metal concentration, loading and elution. The percent extraction of Gd(III) was studied as a function of phosphoric acid (0.05-3M) using Tulsion CH-93 resin. The percent extraction decreased with increasing acid concentration, conforming ion exchange mechanism. Under observed experimental conditions the loading capacity of Tulsion CH-93 for gadolinium was 10.6 mg/g. Among several eluants screened, the quantitative elution of Gd(III) from loaded Tulsion CH-93 was obtained with ammonium oxalate (0.15M). The extraction behavior of commonly associated metals with gadolinium has been studied as a function of phosphoric acid concentration. Tulsion CH-93 resin showed selective extraction towards heavy rare earths (Lu and Yb) which can be separated from other rare earths at 3M H₃PO₄, similar to wet phosphoric acid (3-5M). On the other hand Gd(III) and other rare earths were studied with chelating resin Tulsion CH-90. Light rare earths were highly extracted and these can be separated from heavy rare earths and Gd.

The distinguishing features of the present work are:

- This thesis deals with the separation of rare-earths from H₃PO₄ using organophosphorus reagents and resins by solvent extraction and ion exchange techniques.

- A series of commercially available extractants; TOPS 99, PC88-A and Cyanex 272 were applied for the separation of REs from phosphoric acid solutions. Among the screened extractants, TOPS 99 is the best extractant for the REs separation.
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- A process flowsheet was developed for the separation and recovery of REs into three groups, two HRE fractions (Yb+Lu and Tb, Dy, Ho, Y, Er) and one LREs fraction from wet phosphoric acid solutions using TOPS 99.

- For the first time, we have reported the detailed and systematic fundamental extraction studies and optimized experimental parameters for the separation of Y and Dy from phosphoric acid solutions using TOPS 99 and PC88-A respectively.

- For the first time, we have reported the extraction studies and separation possibilities of Gd from phosphoric acid solutions using Tulsion CH-90 and Tulsion CH-93 resins.

Results of present study can become a source for the separation and recovery of REs with high purity from fertilizer grade phosphoric acid. The flow sheet developed for separation of REs into 3 fractions can be taken up for testing the process on pilot scale. The final outcome of the study is the publication of results in five international journals.