

# Kinetic studies for Extraction of Rare Earths and Uranium from Rock Phosphate employing Organic Solvents (D2EHPA and TBP)

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## Highlights

- The preferential removal of U over REEs from Egyptian Rock Phosphate.
- Synergistic role of D2EHPA and TBP Increased D up to 10 times as compared to use of D2EHPA alone.
- Process development for selective removal of U, HREEs and LREEs from nitrophosphate route.

## 1. Introduction

Uranium and Rare earth elements are found in notable amounts in many phosphate rocks from around the world. Phosphate rocks generally contain about 50–300 mg of uranium (U) and ≤100 mg of rare earths (REEs) for every kg of rock, depending on the source.[1] These get transferred to the soil by the means of finished phosphate fertilizers applied in fields. Presence of U and REEs not only create a negative impact on soil conditions but can have serious health problems if they end up in the food chain [2]. Thus, removal and recovery of U and REEs should be considered as beneficial in two ways as it mitigates the adverse effects of these metal impurities ending in the soil while these secondary sources can be utilized for fulfilling heightened energy and rare earth supply demands. Attempts to recover uranium and REEs have focused on the intermediate products (wet phosphoric acid and phosphogypsum) produced during the production of phosphatic fertilizers[3], [4]. This work focuses on developing a process to remove U and REEs from Egyptian Rock Phosphate (ERP) and the kinetics involved in the extraction of U and REEs.

## 2. Methodology

*Dissolution of Rock phosphate:* The rock phosphate sample (50 g) was crushed, sieved (0.3mm) and reacted with 67.90 g of 63-67% HNO<sub>3</sub> diluted with 85.2 g of DI water under overhead stirring (650 RPM) maintaining the temperature between 65-70°C and continuing the reaction for 24 h in a 500 ml batch reactor. The reaction mass was allowed to cool to room temperature and then filtered under vacuum. The leachate was weighed and subjected to analyses. The residue was washed with DI water and the washings were recovered and analyzed separately.

*Extraction studies:* 10 g each of leachate and organic extractant were added into a beaker and magnetically stirred at 800 RPM for 30 min at room temperature (28-30 °C). The contents were allowed to stand for 10 min and the aqueous and organic phases were separated, weighed, and the aqueous phase was analyzed using ICP-MS. Percentage extraction (%E) of a constituent was computed from Equation (1), where [A]<sub>initial</sub> and [A]<sub>final</sub> are the concentrations of a given constituent in the leachate before and after extraction, respectively.

$$\%E = \frac{[A]_{initial} - [A]_{final}}{[A]_{initial}} \times 100 \quad (1)$$

## 3. Results and discussion

Based on the extraction data, Distribution coefficient (D) was calculated for (a) D2EHPA, (b) TBP and (c) combination of D2EHPA and TBP and stichometry coefficient and extraction equilibrium was determined.

*Extraction Kinetics:* For combination of D2EHPA and TBP extraction of Metal ion (A<sup>m+</sup>) can be given by



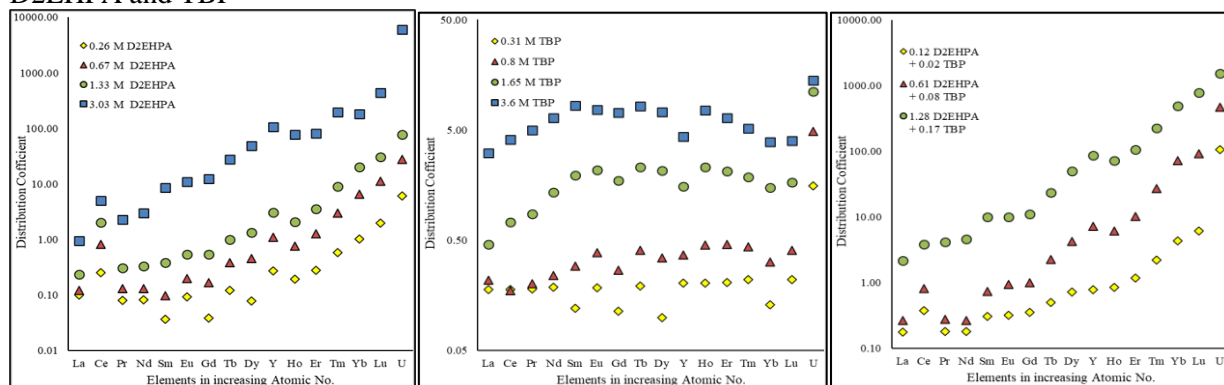
Similarly, the equation to determine K<sub>eq,A</sub> for combination of D2EHPA and TBP can be written as

$$\ln(D_A \cdot [H_{(aq)}^+]^m) = x \ln[(RH)_{2(org)}] + y \ln[(R')_{(org)}] + \ln K_{eq,A} \quad (3)$$

For values of 'x' and 'y' multi-regression analysis was carried out.

To calculate D, the phase ratio (organic to aqueous phase) and density (ρ) for w/w to w/v conversion of concentrations were considered, and the density (ρ) for nitro-phosphate solution and organic solvent at

30°C was experimentally determined with average values of triplicate runs of  $1398 \pm 7$  and  $808.4 \pm 3 \text{ kg.L}^{-1}$ , respectively. Figure 1 presents D for REEs and U for (a) D2EHPA, (b) TBP and (c) combination of D2EHPA and TBP



**Figure 1.** D for REEs and U for (a) D2EHPA, (b) TBP and (c) combination of D2EHPA and TBP

Based on the D and equation 3. Stoichiometric coefficient and  $K_{eq}$  were calculated and is presented in Table 1.

Element	Approximate Eqn.	$K_{eq} \times 10^6$
La	$\ln D.[H^+] = 0.90 \cdot \ln[RH_2] + 1.13 \cdot \ln[R'] + 8.90$	0.0073
Ce	$\ln D.[H^+] = 1.36 \cdot \ln[RH_2] + 1.31 \cdot \ln[R'] + 9.71$	0.0160
Pr	$\ln D.[H^+] = 1.34 \cdot \ln[RH_2] + 1.38 \cdot \ln[R'] + 9.14$	0.0093
Nd	$\ln D.[H^+] = 1.43 \cdot \ln[RH_2] + 1.50 \cdot \ln[R'] + 9.55$	0.0141
Sm	$\ln D.[H^+] = 2.18 \cdot \ln[RH_2] + 1.49 \cdot \ln[R'] + 10.74$	0.0460
Eu	$\ln D.[H^+] = 1.89 \cdot \ln[RH_2] + 1.58 \cdot \ln[R'] + 10.83$	0.0510
Gd	$\ln D.[H^+] = 2.29 \cdot \ln[RH_2] + 1.75 \cdot \ln[R'] + 13.73$	0.9140
Tb	$\ln D.[H^+] = 2.13 \cdot \ln[RH_2] + 1.50 \cdot \ln[R'] + 11.56$	0.1043
Dy	$\ln D.[H^+] = 2.52 \cdot \ln[RH_2] + 1.81 \cdot \ln[R'] + 14.95$	3.1061
Y	$\ln D.[H^+] = 2.34 \cdot \ln[RH_2] + 1.30 \cdot \ln[R'] + 12.53$	0.2757
Ho	$\ln D.[H^+] = 2.34 \cdot \ln[RH_2] + 1.53 \cdot \ln[R'] + 12.44$	0.2535
Er	$\ln D.[H^+] = 2.23 \cdot \ln[RH_2] + 1.45 \cdot \ln[R'] + 12.85$	0.3796
Tm	$\ln D.[H^+] = 2.30 \cdot \ln[RH_2] + 1.34 \cdot \ln[R'] + 13.64$	0.8390
Yb	$\ln D.[H^+] = 2.07 \cdot \ln[RH_2] + 1.45 \cdot \ln[R'] + 14.44$	1.8655
Lu	$\ln D.[H^+] = 2.14 \cdot \ln[RH_2] + 1.24 \cdot \ln[R'] + 14.80$	2.6794
U	$\ln D.[H^+] = 2.39 \cdot \ln[RH_2] + 0.93 \cdot \ln[R'] + 22.58$	4671.1200

The Distribution coefficient and thus the Equilibrium constant ( $K_{eq}$ ) for mixed extractant was found in the following order,  $La < Pr < Nd < Ce < Sm < Eu < Tb < Ho < Y < Er < Tm < Gd < Yb < Lu < Dy < U$ . The studies show preferential removal of U over REEs. This preference can also be observed for HREEs over LREEs.

#### 4. Conclusions

The findings of this investigation indicate that REEs and U can be effectively recovered from Rock phosphate sources employing D2EHPA and TBP as an extractant. The highest extraction was seen in case of mixed extractants. The increase in D for the mixed extractant system found to be ca. 10 times to that of using D2PHA alone. The preferential extraction using above extractant can be used to develop a process for selective separation of U, HREEs and LREEs.

#### 5. References

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