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# Optimizing monazite enrichment from zircon for efficient rare earth element recovery using tetraethylammonium bis(2-ethylhexyl)phosphate ([N2222][DEHP]) ionic liquid collector

El-Sayed R. E. Hassan <sup>1,2</sup>, F. Mutelet <sup>3</sup>, N. A. Abdel-Khalek <sup>2</sup>, A. M. Elbendari <sup>2</sup>, Yun Chen <sup>1</sup>

<sup>1</sup> School of Materials and Chemical Engineering, Hunan Institute of Engineering, Xiangtan, China

<sup>2</sup> Minerals Beneficiation and Agglomeration Department, Minerals Technology Institute, Central Metallurgical Research

& Development Institute (CMRDI), P.O. Box 87 Helwan, 11722 Cairo, Egypt <sup>3</sup> Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

\* Oniversite de Lorranie, CNRS, LRGI, 1-54000 Ivancy, France

Corresponding authors: yun.chen2008@hotmail.com (Yun Chen)

**Abstract:** Rare earth elements (REEs) are critical to a wide range of high-tech applications, including electronics, renewable energy technologies, and advanced defense systems. However, the sustainable and efficient extraction of REEs from low-grade ores remains a significant challenge. This study investigates the enrichment of monazite as a REEs-bearing mineral from zircon using mini-column flotation. A pre-treatment process of the zircon sample, containing 57.90% ZrO<sub>2</sub> and 1.22% Rare earth oxides (REOs), was conducted using Carpco magnetic separator in order to recover monazite. Two preconcentrates (A and B) were obtained, with REOs content of 12.50% and 16.54%, and high recoveries of 96.82% and 89.20%, respectively. The flotation process for both pre-concentrates was investigated using tetraethylammonium bis(2-ethylhexyl)-phosphate ([N2222][DEHP]) ionic liquid as a collector for monazite flotation. This approach demonstrated high performance, yielding monazite-rich concentrates with up to 40% REOs content. Box-Behnken design optimized flotation conditions with ([N2222][DEHP]) produced monazite concentrates (A and B) containing 39.88% and 43.37% REOs, with recoveries exceeding 80%. The separation efficiency was evaluated using many analytical techniques which evidenced the potential of ([N2222][DEHP]) as an alternative to conventional collectors and presents a promising pathway for enhancing the sustainable enrichment of REEs.

Keywords: rare earth elements, monazite, zircon, ionic liquids, ([N2222][DEHP])

# 1. Introduction

Rare earth elements (REEs), which include the fifteen lanthanides with yttrium, and scandium, are critical to various high-tech industries such as electronics, renewable energy, and defense systems. Despite their relatively high abundance in the Earth's crust, REEs are typically found in low concentrations, making their extraction and beneficiation challenging. These elements are categorized into light rare earth elements (LREEs) and heavy rare earth elements (HREEs), and they occur in over 250 minerals, mainly bastnasite, monazite, xenotime, and fergusonite. REEs are essential for the production of permanent magnets, catalysts, phosphors, and advanced materials used in cutting-edge technologies (Hassan, 2023; Balaram, 2019; Kołodyńska et al., 2019; Sola et al., 2020). The global demand for REEs has increased due to the growth of renewable energy sectors and markets such as electric vehicles and wind turbines (Abaka-Wood et al., 2016). According to the U.S. Geological Survey (2024), China leads global production, accounting for 68.6% of output and holding 40% of the world's reserves (Chen et al., 2022), with other significant producers including the U.S., Australia, Myanmar, Thailand, and India. Despite its rich mineral resources, Egypt does not have a notable REE production. However, Egyptian deposits, particularly monazite in beach sands along the Mediterranean coast, represent an untapped resource with potential for REE recovery. Heavy mineral sands (HMS), containing ilmenite, rutile, zircon, and monazite, are economically important for their valuable minerals. Monazite (Ce, La, Nd, Th)PO<sub>4</sub>) is a primary source of light REEs such as cerium, lanthanum, neodymium, and thorium.

Egyptian black sand deposits have estimated reserves exceeding 600 million metric tons with monazite concentrations range from 0.01% to 0.6% by weight (El Aref et al., 2020). Previous studies have studied monazite separation using gravity, magnetic, and electrostatic separation techniques, but further research is needed to improve recovery rates and concentrate purity (Moustafa, 2007; Moustafa and Abdelfattah, 2010; Raslan and Fawzy, 2018; Fawzy, 2018; Fawzy et al., 2015). Moustafa, (2007) assessed the sand dunes in the El Burullus-Baltim area, identifying an economic mineral content of 4.66%. Moustafa and Abdelfattah, (2010) developed an efficient flowsheet for recovering monazite from beach sands, while Raslan and Fawzy, (2018) upgraded Wadi Abu Dob pegmatite ore using a shaking table and Carpco magnetic separator to separate fergusonite from zircon. Flotation is a particularly effective technique for separating REEs, with oleic acid and hydroxamic acids commonly used as collectors. For example, flotation of fergusonite has been optimized using a mixed collector of sodium oleate and sorbitan monooleate at pH 5, improving separation and efficiently recovering fergusonite from silicates (Fawzy, 2018). Similarly, flotation of xenotime from ferruginous sandstone in Southwestern Sinai achieved 71.7% recovery and 83.6% enrichment of rare earth oxides (REOs) using sodium oleate at pH 7 (Fawzy et al., 2015). Recent research has explored the use of novel reagents, such as ionic liquids (ILs), which offer unique properties like high polarity, thermal stability, conductivity, a wide electrochemical window, negligible volatility, and nonflammability, making them ideal for separation processes. Azizi et al., (2016) explored tetrabutylammonium bis(2-ethylhexyl)-phosphate as a collector for monazite and bastnäsite, demonstrating its efficacy in REE recovery. Li et al., (2020) investigated the use of ionic liquids for rare earth mineral flotation, further supporting their role in enhancing flotation performance. Qiu et al., (2022) examined the influence of ionic liquids on the flotation of LiAlO<sub>2</sub> and melilite. Hassan et al., (2023) presented the promising use of phosphonium-ammonium based ionic liquids for REE flotation from Egyptian black sands, yielding high grade and recovery rates. Julapong et al., (2023) reviewed the recovery of REEs from primary and secondary resources using flotation, highlighting the increasing importance of ionic liquids in the process. They also studied the floatability of monazite, xenotime, and zircon, noting that pH and temperature significantly affect flotation outcomes when using ionic liquids (Julapong et al., 2024; Marion et al., 2020). Although Egypt possesses vast black sand reserves, commercial rare earth element (REE) production remains underdeveloped due to limited infrastructure, high processing costs, and low-grade deposits. This study presents a method as a trial to overcome these challenges by integrating magnetic pre-concentration with ionic liquid flotation, enabling efficient recovery from low-grade monazite-zircon mixtures without relying on energyintensive hydrometallurgical processes. This approach supports the strategic goal of sustainably of Egypt to utilize its domestic resources. This study investigates the recovery of monazite from zirconrich samples using Carpco magnetic separation mini-column flotation. The flotation process is optimized with ([N2222][DEHP]) using a Box-Behnken design, and advanced analytical techniques are employed to assess the separation efficiency.

#### 2. Materials and methods

### 2.1. Materials

A zircon-rich feed sample, derived from the Egyptian black sand processing at the Rosetta locality, was provided by The Egyptian Mineral Resources Authority (EMRA). The sample had a particle size of - 0.400 +0.100 mm, suitable for magnetic and flotation processing. Tetraethylammonium bis(2-ethylhexyl)-phosphate ([N2222][DEHP]) with over 95% purity was sourced from Io-Liq-Tech, Heilbronn, Germany. Other chemicals, such as sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>), sodium sulfide (Na<sub>2</sub>S), sodium hydroxide (NaOH), and hydrochloric acid (HCl), were obtained from Sigma-Aldrich and were of analytical grade.

## 2.2. Pre-concentration processes

Zircon samples with a size range of  $-400 +100 \mu m$  were pre-concentrated using Carpco dry highintensity magnetic separator (Lift-Type Induced Roll, Model MLH-13-111-5). Carpco separator provides a variable magnetic field intensity ranging from 0.5 ampere (0.13 tesla) to 3.5 ampere (0.95 tesla), and a laminated roll with adjustable speeds. As the feed passes through the magnetic field, monazite particles adhere to the roll, while the non-magnetic zircon fraction is separated. The separation was studied by varying roll speed, field intensity, and feed rate. Both magnetic and non-magnetic fractions were weighed and chemically analyzed (Yassin et al., 2023; Hassan et al., 2020).

## 2.3. Flotation process

([N2222][DEHP]) was used as collector for REEs flotation from the produced paramagnetic preconcentrates. The effects of various flotation parameters were investigated, including pH, collector dosage, depressant type and dosage, and air flow rate. Mini-column flotation experiments were conducted with a 5-minute conditioning period, during which REE pre-concentrates were agitated in an aqueous solution with adjusted pH and added collectors. The conditioned minerals were transferred to a modified mini-column flotation cell, shown in Fig. 1. Air was introduced at a rate of 20-100 mL/min through a sintered porous glass distributor, and a magnetic stirrer was used to maintain particle suspension. Floated minerals were collected as overflow via a slanted launder, skimmed, filtered, dried, and weighed to determine recovery rates. Tailings were removed for subsequent analysis. All experiments were performed in duplicate, and average recovery rates are reported (Hassan et al., 2023; Rostom et al., 2020), (Fig. 2).



Fig. 1. The modified mini-column flotation cell used for REEs separation

## 2.4. Instrumentation

Quantitative chemical analysis of oxide content was performed using a WD Axios Advanced XRF spectrometer (Panalytical, Netherlands) with SuperQ software for standard-based analysis. Samples were prepared by mixing 10 g of material with 2 g of wax binder, pressing it into a disk, and exposing it to X-rays. This method provided a trace element detection limit of 0.01%, with a ±0.004% error margin. Mineralogical phase analysis was conducted using a PANalytical X'Pert PRO XRD system with Cu Ka radiation ( $\lambda = 1.542$  Å), scanning 20 from 5° to 80°. Phase identification was carried out by comparing diffraction patterns with the ICDD database. Photomicrographs were captured using a 1600×8 MP LED digital microscope. REE content was analyzed with a PerkinElmer Optima 2000 DV ICP-OES, equipped with Winlab 32<sup>TM</sup> software. Calibration curves were constructed using five standard solutions, with 0.999 correlation coefficient. Measurements were taken from two wavelengths for each element for precision. Scanning electron microscopy (SEM) imaging and analysis were performed using a Hitachi FlexSEM 1000 II scanning electron microscope. A Quorum 150 RS Plus metallizer with a platinum source was used, operating at a sputtering current of 30 mA for 60 seconds. The tungsten source and is equipped with secondary electron (SE), backscattered electron (BSE), and ultra-variable pressure detectors (UVD). Energy-dispersive X-ray spectroscopy (EDS) was carried out with an Oxford Xplore Compact 30 detector. SEM images were captured at 5 kV with a 30-spot size, spectra were measured at 20 kV with a 60-spot size, and elemental mapping was performed at 20 kV with an 80-spot size (Hassan et al., 2025; Yassin et al., 2023; Hassan et al., 2020; Rostom et al., 2020).



Fig. 2. Flowchart of the proposed methodology for REEs recovery

## 3. Results and discussion

#### 3.1. Characterization of the feed zircon sample

The X-ray diffraction (XRD) pattern of the feed sample displayed the presence of several mineral phases, with zircon (ZrSiO<sub>4</sub>) and rutile (TiO<sub>2</sub>) being the predominant minerals, Fig. 6a. The complete chemical analysis of the sample, presented in Table 1, indicated it is composed of 57.90% ZrO<sub>2</sub>, 20.96% SiO<sub>2</sub>, 13.10% TiO<sub>2</sub>, 0.74% Al<sub>2</sub>O<sub>3</sub>, 1.63% CaO, 1.60% Fe<sub>2</sub>O<sub>3</sub>, and 1.18% HfO<sub>2</sub>. Notably, the sample contains 1.22% of rare earth oxides (REOs) with thorium and uranium oxides (ThO<sub>2</sub> + U<sub>3</sub>O<sub>8</sub>). Scanning electron microscopy (SEM) images and photomicrographs (Fig. 7a) showed that the feed sample primarily consists of zircon and rutile minerals with existence of REEs.

| Product        | ZrO <sub>2</sub> | SiO <sub>2</sub> | TiO <sub>2</sub> | CaO  | Fe <sub>2</sub> O <sub>3</sub> | $Al_2O_3$ | MgO  | $P_2O_5$ | MnO  | HfO <sub>2</sub> | REOs | LOI  |
|----------------|------------------|------------------|------------------|------|--------------------------------|-----------|------|----------|------|------------------|------|------|
| Feed<br>sample | 57.90            | 20.96            | 13.10            | 1.63 | 1.60                           | 0.74      | 0.23 | 0.18     | 0.74 | 1.18             | 1.22 | 0.23 |

Table1. Chemical analysis of feed zircon sample

#### 3.2. Pre-concentration process

REEs are paramagnetic and can exhibit ferromagnetic behavior at low temperatures, enhancing their separability in magnetic fields (Abaka-Wood et al., 2016). In this study, Carpco roll magnetic separation was used to recover monazite from a zircon a zircon-rich sample with a particle size of  $-400 +100 \mu m$ . The magnetic field intensity is a critical factor in separation efficiency. Firstly, the highest field intensity (0.95 tesla, 3.5 ampere) was applied with low roll speed (50 rpm) and feed rate (100 g/min). This led to the enrichment of REOs in the magnetic fraction due to the stronger attraction of paramagnetic monazite (Hassan et al., 2020). High roll speeds can reduce recovery efficiency by decreasing particle adhesion to the magnetic roll, and high feed rates can hinder particle segregation (Yassin et al., 2023). Consequently, applying the highest filed intensity with low roll speed and feed rates, the REOs concentration increased from 1.22% to 12.50%, with a high recovery rate of 96.82%, Table 2. Also, iron oxide was enriched in the

magnetic fraction from 1.60% to 16.31% with recovery reached up to 96.34%. Meanwhile, zircon in the non-magnetic fraction increased from 57.90% to 61.04%, with a recovery rate of 95.46%. The non-magnetic concentrate, nearly free of iron oxides, REEs and radioactive elements, is suitable for high-purity zircon applications in refractories and glass (Okoli et al., 2024). Further electrostatic separation could enhance zircon purity for advanced industrial uses. Secondly, the magnetic fraction (REEs pre-concentrate A) was further processed with successive low and high field intensities of 0.5 and 2.5 ampere respectively in order to get the ferro-, para-, and dia-magnetic fractions. Higher roll speed (80 rpm) and feed rates (200 g/min) were used, improving REOs content in the magnetic fraction but reducing recovery. The ferro-magnetic fraction was enriched with iron oxide (68.49% Fe<sub>2</sub>O<sub>3</sub>), and the dia-magnetic fraction was enriched with zircon (46.28% ZrO<sub>2</sub>). The para-magnetic fraction, REEs Preconcentrate B, contained 16.54% REOs with a recovery of 89.20%, Table 2. Both pre-concentrates (A and B) will be subjected to micro-flotation process using ([N2222][DEHP]) to further enrich REOs.

|                       |                     | ·      |       |           |         |           |                                |           |
|-----------------------|---------------------|--------|-------|-----------|---------|-----------|--------------------------------|-----------|
| Feed samples/Carpco   | Products            | Wt.    | REOs  | REOs      | $ZrO_2$ | $ZrO_2$   | Fe <sub>2</sub> O <sub>3</sub> | $Fe_2O_3$ |
| separation conditions |                     | %      | %     | recovery% | %       | recovery% | %                              | recovery  |
|                       |                     |        |       |           |         |           |                                | %         |
| Feed: zircon sample   |                     | 100.00 | 1.22  | 100.00    | 57.90   | 100.00    | 1.60                           | 100.00    |
| Field intensity 3.5 A | Nonmagnetic         | 90.55  | 0.04  | 3.18      | 61.04   | 95.46     | 0.07                           | 3.96      |
| Feed rate 100 g/min   | zircon concentrate  |        |       |           |         |           |                                |           |
| Roll speed 50 rpm     | Magnetic fraction   | 9.45   | 12.50 | 96.82     | 27.80   | 4.54      | 16.31                          | 96.34     |
|                       | Pre-concentrate (A) |        |       |           |         |           |                                |           |
| Feed: pre-concentrate |                     | 9.45   | 12.50 | 96.82     | 27.80   | 4.54      | 16.31                          | 96.34     |
| (A)                   |                     |        |       |           |         |           |                                |           |
| Field intensity 0.5 A | Ferromagnetic       | 0.77   | 7.60  | 4.80      | 12.76   | 0.17      | 68.49                          | 32.96     |
| Feed rate 200 g/min   | fraction            |        |       |           |         |           |                                |           |
| Roll speed 80 rpm     |                     |        |       |           |         |           |                                |           |
| Field intensity 2.5 A | Paramagnetic        | 6.58   | 16.54 | 89.20     | 23.62   | 2.69      | 14.90                          | 61.28     |
| Feed rate 200 g/min   | fraction            |        |       |           |         |           |                                |           |
| Roll speed 80 rpm     | Pre-concentrate (B) |        |       |           |         |           |                                |           |
|                       | Nonmagnetic         | 2.10   | 1.64  | 2.82      | 46.28   | 1.68      | 1.60                           | 2.10      |
|                       | fraction            |        |       |           |         |           |                                |           |

Table 2. Produced REOs pre-concentrates using Carpco magnetic separation

## 3.3. Flotation of REEs pre-concentrates

([N2222][DEHP]) was used as a collector for REEs flotation, with various parameters such as pH, collector dose, depressant type and dose, and air flow rate being evaluated for their effect on flotation efficiency. The flotation process was applied on the magnetic pre-concentrates A and B in order to further enrich the REOs content.

# 3.3.1. Effect of pH on the flotation process

The pH of the flotation system affects the ionization and hydrolysis of the collector, influencing its adsorption onto the mineral surface, surface charge, and the selectivity of monazite flotation (Xiong et al., 2018; Wei et al., 2010). Flotation experiments were conducted on both pre-concentrates across a pH range of 3 to 11, with a constant collector dose of  $1 \times 10^{-4}$  M, and an air flow rate of 40 mL/min, to assess the performance of ([N2222][DEHP]) for monazite (Fig. 3a). Both pre-concentrates showed similar behavior along the studied range of pH. The results indicated that increasing the pH up to levels of 9.00-10.00 led to a significant increase in REOs content with a decrease in float weight% and REOs recovery%. However, a slight decrease in REOs content along with decline in recovery was observed when the pH exceeded this range. For pre-concentrate A, the highest REOs content of 35.22% was achieved at pH 9.0, with a recovery rate of 73.71% and wt.% of 26.16%. Beyond pH 9, the REOs grade decreased, indicating pH 9 as the optimal value for maximizing REOs content while balancing recovery (Fig. 3a) (Kou et al., 2010). Higher pH values also led to reduced flotation of zircon, enhancing the selectivity for REEs. Pre-

concentrate B followed similar trends and at pH 9, ([N2222][DEHP]) demonstrated selectivity for monazite over zircon, and yielded a REOs content (37.95%) with high recovery (80.81%) and wt.% of 35.22%.

# 3.3.2. Effect of collector dose

The dosage of the collector significantly affects flotation performance, influencing both the efficiency and selectivity of the process. In this study, various concentrations of ([N2222][DEHP]) (ranging from  $1 \times 10^{-5}$  M to  $5 \times 10^{-3}$  M) were tested on both pre-concentrates A and B at pH 9.0, and air flow rate of 40 mL/min. The results (Fig. 3b) displayed the impact of collector dosage on flotation efficiency. At lower doses, flotation efficiency was low due to insufficient collector adsorption onto monazite, while higher doses reduced selectivity by causing the collector to adsorb onto both monazite and zircon, thus diminishing the separation efficiency. The optimal collector dose range was found to be from  $5 \times 10^{-4}$  M to  $1 \times 10^{-3}$ , which resulted in the highest recovery. At a dose of  $5 \times 10^{-4}$  M, ([N2222][DEHP]) achieved final concentrates A and B with 34.58 % and 38.12% REOs and recovery rates of 87.56% and 90.67% respectively (Fig. 3b).

# 3.3.3. Effect of depressant dose

The effect of both sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and sodium sulfide (Na<sub>2</sub>S) as depressants on monazite flotation was studied at various dosage concentrations ranging from  $1 \times 10^{-5}$  M to  $5 \times 10^{-5}$  M, while keeping pH at 9, collector dose at  $5 \times 10^{-4}$  M, and air flow rate at 40 mL/min constant (Fig. 3c). The addition of sodium silicate (depressant A) improved REOs content but caused a reduction in recovery. The optimal balance of REOs grade and recovery was observed at a sodium silicate dosage ranged from  $1 \times 10^{-5}$  M to  $2 \times 10^{-5}$  M, beyond which no further improvements in REOs content was seen but a significant decrease in recovery was observed. Sodium silicate serves as a depressant for silicate minerals, zircon (ZrSiO<sub>4</sub>), which enhances the selective adsorption of ([N2222][DEHP]) onto monazite, improving the separation efficiency (Sis and Chander, 2003). The addition of sodium sulfide (depressant B) led to a slight increase in the REOs content, with a decrease in recovery rate. The sodium sulfide required higher dosage to obtain similar results as this of sodium silicate. The optimal balance of REOs grade and recovery was achieved with a sodium sulfide dosage ranged from of  $3 \times 10^{-5}$  M to  $4 \times 10^{-5}$  M. These results indicate that a sodium silicate dosage of  $2.0 \times 10^{-5}$  M is sufficient to achieve optimal selectivity and efficiency in monazite flotation.

# 3.3.4. Effect of air flowrate

The effect of air flow rate on monazite flotation using ([N2222][DEHP]) was evaluated over a range of 20 to 100 mL/min, with pH maintained at 9.0, ([N2222][DEHP]) dose at  $5 \times 10^{-4}$  M, and sodium silicate dose at  $2.0 \times 10^{-5}$  M constant (Fig. 3d). The results showed that increasing the air flow rate enhanced the total REOs recovery. However, a higher air flow rate than 40.0 mL/min led to a significant decrease in the REOs grade. The optimal balance was achieved at an air flow rate of 40 mL/min, producing final concentrates A and B with 29.00% and 37.08% wt.%, 37.60% and 39.92% REOs and recovery rates of 87.23% and 89.49% respectively (Fig. 3d). This optimal air flow rate was found to be effective in controlling the bubble size distribution, as it improves the capture of hydrophobic monazite particles by micro-bubbles while directing hydrophilic zircon minerals to the sink fraction (Laplante et al., 1983; Sobhy et al., 2022).

# 3.3.5. Application of Box-Behnken design (BBD)

BBD was employed to optimize the enrichment of monazite, a rare earth-bearing mineral, through micro-column flotation using ([N2222][DEHP]) as a collector. This design also helped assess the interactions between different flotation parameters. The best range of each variable was used in the design; pH range from 9.0 to 10.0, ([N2222][DEHP]) collector dose from  $5\times10^{-4}$  M to  $1\times10^{-3}$  M, and Na<sub>2</sub>SiO<sub>3</sub> depressant dose from  $1\times10^{-5}$  to  $2\times10^{-5}$  M. These parameters were applied on the pre-concentrate (B). A second-order polynomial function was used to model the relationship between the independent variables and their response, enabling the estimation of optimal parameters. The general form of the



Fig. 3. Effect of a) pH, b) collector dose, c) depressant dose and type A} Na<sub>2</sub>SiO<sub>3</sub> – B} Na<sub>2</sub>S and d) air flow rate on the use of ([N2222][DEHP]) for the separation of monazite from magnetic pre-concentrates A and B

equation is as follows, Eq. (1) (Hassan et al, 2020; Yassin et al., 2023):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2$$
(1)

where *Y* is REOs oxide grade and recovery %,  $X_1$ ,  $X_2$  and  $X_3$  are studied variables: pH, collector dose and air flowrate;  $\beta_{ij}$  are equation constants and coefficients.

The analysis of variance (ANOVA) results for the REOs enrichment system confirmed the validity of the polynomial model, as the experimental data closely matched the predictions (Table 3). The high model F-values indicate that the model is significant, and the adequate precision ratios of 332 and 289 suggest a strong signal and high reliability of the results. The REOs grade and recovery can be determined using the equations derived from the design, as shown in Eq. (2) and Eq. (3).

$$\mathbf{REO}_{\mathbf{s}}\% = +346.07 - 71.54A + 90965B + 6.09 \times 10^{5}C + 3.79A^{2} - 5.63 \times 10^{7}B^{2} + + 1.09 \times 10^{10}C^{2} - 140AB - 62000AC - 4.24 \times 10^{8}BC$$
(2)

$$\mathbf{REO_s} \operatorname{\mathbf{Recovery}} \% = +575.98 - 88.75A - 1.69 \times 10^5 \text{B} + 63350 \text{C} + 4.41 \text{A}^2 + 8.77 \times 10^7 \text{B}^2 - 4.87 \times 10^{10} \text{C}^2 + 2800 \text{AB} + 67000 \text{AC} + 9.84 \times 10^8 \text{BC}$$
(3)

where: A is pH, B is collector dose (M) and C is depressant dose (M).

| The statistical    | REOs flotation |                  |  |  |  |  |
|--------------------|----------------|------------------|--|--|--|--|
| parameters         | REOs grade, %  | REOs recovery, % |  |  |  |  |
| The standard       | 0.023          | 0.042            |  |  |  |  |
| R-Squared          | 0.9999         | 0.9999           |  |  |  |  |
| Adj R-Squared      | 0.9999         | 0.9998           |  |  |  |  |
| Pred R-Squared     | 0.9997         | 0.9995           |  |  |  |  |
| Adequate precision | 332.89         | 289.41           |  |  |  |  |
| The model F-values | 12426.12       | 10236.46         |  |  |  |  |

Table 3. ANOVA for response surface quadratic model of flotation

Fig. 4(a-f) illustrates the response surfaces for both monazite grade and recovery, demonstrating the variation in performance under different experimental conditions. The pH affects the surface charge of both monazite and zircon, influencing the adsorption of ([N2222][DEHP]) onto the mineral surfaces. At a pH of 9, the ionic liquid exhibits optimal flotation efficiency, resulting in a high REOs concentrate grade and a reasonable recovery rate, (Fig. 4a-d). However, increasing the pH higher than 9, flotation performance decreases, due to changes in the ionic properties of ([N2222][DEHP]), reducing its selectivity for monazite while allowing more zircon to float. Therefore, maintaining the pH at 9.0 is important for achieving high selectivity and efficient flotation. The collector dose also plays a critical role in flotation performance. Low collector doses were insufficient for monazite recovery, while increasing the dose to  $7.5 \times 10^{-4}$  M improved REOs content, (Fig. 4a, c). The optimal ([N2222][DEHP]) dose was assumed to be  $7.5 \times 10^{-4}$  M, providing the best monazite selectivity and REOs grade, though with lower recovery than other doses. Increasing the collector dose further reduced separation efficiency, as excess collector adsorbed onto both monazite and zircon, leading to reduced REOs content and high recovery rates (Figs. 4a, b, e, f). It seems that the collector dose is the most effective factor when addressing the REOs separation efficiency. The depressant dose improves the separation of float (REOs) from the sink (zircon) fractions, enhancing the REOs concentrate grade while slightly reducing recovery, (Fig. 4c-f). The best depressant dose was found to be  $2 \times 10^{-5}$  M. The optimal conditions for monazite separation using ([N2222][DEHP]), based on BBD, are pH 9.0, a collector dose of  $7.50 \times 10^{-4}$ M, and a depressant dose of 2×10-5 M. Applying these optimal conditions on the pre-concentrate (B) yielded a final monazite concentrate (B) with 43.37% REOs and a recovery rate of 85.01%, (Fig. 5a, b, and c) and (Tables 4-5). The optimal conditions were also applied to the pre-concentrate (A) and resulted in a final monazite concentrate (A) with 39.88% REOs and a recovery rate of 83.11%, (Fig. 5) and (Tables 4-5).



Fig. 4. The response surface plots (a, b and c) of REOs % and (d, e, and f) for REOs recovery % resulting from the main effects of flotation variables; pH, ([N2222][DEHP]) collector dose and air flowrate



Fig. 5. Optimization of the monazite beneficiation; a) Desirability, b) REOs grade % and c) REOs recovery % using flotation variables; pH, ([N2222][DEHP]) collector dose and air flowrate

#### 3.4. Characterization of the produced valuable minerals

X-ray diffraction (XRD) patterns of both the feed zircon sample and the non-magnetic zircon concentrate mainly show zircon peaks, with some observation of rutile (Fig. 6a, b). In contrast, the magnetic monazite pre-concentrates A and B display peaks not only for zircon and rutile, but also for monazite and ilmenite (Fig. 6c, e). Fig. 6d shows the ferro-magnetic fraction with distinct peaks of magnetite. The monazite concentrates A and B obtained using ([N2222][DEHP]) collector reveal distinct peaks for monazite, with less pronounced peaks for other associated minerals, (Figs. 6f, g). These XRD results align with those from previous studies which identified similar mineral compositions (Kumari et al., 2015; Okoli et al., 2023; Nuryadin and Triwikantor, 2015). The X-ray fluorescence (XRF) analysis provides a detailed understanding of the distribution of rare earth elements (REEs) and oxides (REOs) in the feed, pre- and final-concentrates (Tables 4 and 5). The results show that the combined processes of magnetic separation and flotation using ([N2222][DEHP]) significantly enriched the REE content in the concentrates. The major enriched rare earth elements include Ce, La, Nd, Y, Pr, and Th. This enrichment confirms the effectiveness of the separation process in concentrating REEs. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) further validate the efficient separation monazite from zircon, in the various concentrates. SEM images (Figs. 7a-g) show the micromorphology of the monazite, revealing subhedral and tabular grains with elongated to subrounded shapes (Hassan, 2023; Dieye et al., 2021). EDS analysis confirmed the presence of LREEs in the produced monazite pre- and final-concentrates A and B (Figs. 7c, e, f, g), including Ce, La, Nd, Y, Gd, Pr, and Th (Anitha et al., 2020). Photomicrographs provide detailed visual evidence of the mineral distribution during the beneficiation process. Fig. 7a shows the feed sample, which contains a mixture of zircon and rutile minerals. The Carpco non-magnetic zircon concentrate (Fig. 7b) is almost pure zircon, with light, white zircon particles indicating its non-magnetic nature. Figs. 7c and 7e highlight the magnetic monazite pre-concentrates A and B respectively, where the paramagnetic monazite is enriched, appearing reddish-brown, and associated with thin, black iron oxide blades. Fig. 7d displays the majority of black ferro-magnetic magnetite. Figs. 7f and 7g show the monazite final concentrates A and B respectively which were obtained using ([N2222][DEHP]), where the rare earth-bearing monazite is clearly visible, with a brown to reddish-brown color.



Fig. 6. XRD of a) feed zircon sample, Carpco products: b) non-magnetic zircon concentrate, c) magnetic preconcentrate A, d) ferro-magnetic fraction and e) para-magnetic pre-concentrate B and ([N2222][DEHP])-Flotation products f) final concentrate A and g) final concentrate B

## 4. Conclusions

This study examined the enrichment of monazite from zircon sample, containing 57.90% ZrO<sub>2</sub> and 1.22% REOs, which was pre-treated with a Carpco magnetic separator to recover monazite. The field intensity played a key role in sample fractionation where, two pre-concentrates (A and B) were obtained, with REOs content of 12.50% and 16.54%, and recoveries of 96.82% and 89.20%, respectively. Flotation experiments, for both pre-concentrates (A, B), were conducted using N2222][DEHP]) as a collector. Many variables, including pH, collector dose, depressant type and dose, and air flow rate, were evaluated and yielded monazite concentrates with up to 40% REOs content. The flotation process was further optimized using Box-Behnken design and the optimum conditions were determined as; pH 9.0, a collector dose of  $7.50 \times 10^{-4}$  M, and a depressant dose of  $2 \times 10^{-5}$  M, with an air flow rate of 40.0 mL/min. Applying these optimal conditions on the Carpco pre-concentrates (A) and (B) yielded final float monazite concentrates (A) and (B) with 39.88% and 43.37% REOs with recovery rates of 83.11% and 85.01% respectively. XRD, XRF, ICP-OES, SEM, EDS, and photomicrographs were used to assess separation efficiency and mineral composition. The proposed method achieved high rare earth oxide (REO) recovery rates (80–85%), but the economic feasibility of ionic liquids such as [N2222][DEHP] requires further evaluation. Preliminary estimates suggest that reagent recycling and lower energy consumption - compared to conventional collectors like hydroxamates - could help offset costs. Scaling up this process will require pilot testing to address challenges such as ionic liquid stability and tailings management. Despite these considerations, this approach presents a promising opportunity to develop the Egyptian monazite resources for industrial REE production. In conclusion, the combined use of magnetic separation and flotation with [N2222][DEHP] offered a promising approach for REEs enrichment. Further refining of the final concentrates by removing of iron and titanium oxides through acid leaching and solvent extraction could enhance the production of high-purity REEs.





Fig. 7. Photomicrographs, SEM images and EDS analysis of a) feed zircon sample, Carpco products: b) nonmagnetic zircon concentrate, c) magnetic pre-concentrate A, d) ferro-magnetic fraction and e) para-magnetic preconcentrate B and ([N2222][DEHP])-Flotation products f) final concentrate A and g) final concentrate B

Table 4. The chemical analysis of produced concentrates of Carpco magnetic separator and micro-column flotation using ([N2222][DEHP]) ionic liquid

| Components                     | Feed   | Non-magnetic | Magnetic        | Ferro-   | Para-magnetic   | Final       | Final       |
|--------------------------------|--------|--------------|-----------------|----------|-----------------|-------------|-------------|
|                                | zircon | zircon       | pre-concentrate | magnetic | pre-concentrate | concentrate | concentrate |
|                                | sample | concentrate  | А               | fraction | В               | А           | В           |
| Wt%                            | 100.00 | 90.55        | 9.45            | 0.77     | 6.58            | 2.462       | 2.133       |
| MgO                            | 0.229  | 0.108        | 1.400           | 0.090    | 1.910           | 0.800       | 0.680       |
| Al <sub>2</sub> O <sub>3</sub> | 0.736  | 0.610        | 1.960           | 0.180    | 2.520           | 1.150       | 0.990       |
| SiO <sub>2</sub>               | 20.962 | 22.105       | 10.200          | 2.680    | 8.750           | 6.450       | 4.900       |
| $P_2O_5$                       | 0.178  | 0.001        | 1.920           | 0.850    | 2.610           | 7.360       | 8.060       |
| SO <sub>2</sub>                | 0.020  | 0.007        | 0.150           | 0.092    | 0.195           | 0.206       | 0.250       |
| Cl                             | 0.012  | 0.012        | 0.019           | 0.015    | 0.022           | 0.014       | 0.015       |
| K <sub>2</sub> O               | 0.110  | 0.093        | 0.270           | 0.002    | 0.314           | 0.300       | 0.240       |
| CaO                            | 1.630  | 1.180        | 5.860           | 0.025    | 7.570           | 4.700       | 4.180       |
| TiO <sub>2</sub>               | 13.100 | 12.400       | 19.540          | 6.770    | 18.580          | 13.800      | 12.230      |
| $Cr_2O_3$                      | 0.131  | 0.085        | 0.570           | 0.070    | 0.790           | 0.450       | 0.800       |
| MnO                            | 0.739  | 0.787        | 0.301           | 0.020    | 0.342           | 0.350       | 0.780       |
| Fe <sub>2</sub> O <sub>3</sub> | 1.600  | 0.070        | 16.312          | 68.490   | 14.900          | 12.220      | 14.010      |
| ZnO                            | 0.009  | 0.000        | 0.101           | 0.001    | 0.144           | 0.380       | 0.450       |
| SrO                            | 0.010  | 0.000        | 0.105           | 0.005    | 0.130           | 0.400       | 0.410       |
| $ZrO_2$                        | 57.900 | 61.040       | 27.800          | 12.760   | 23.620          | 10.500      | 7.850       |
| HfO <sub>2</sub>               | 1.180  | 1.220        | 0.790           | 0.330    | 0.844           | 0.500       | 0.380       |
| PbO                            | 0.003  | 0.000        | 0.032           | 0.001    | 0.038           | 0.120       | 0.120       |
| REOs +                         | 1.220  | 0.042        | 12.500          | 7.600    | 16.540          | 39.880      | 43.370      |
| $ThO_2 + U_3O_8$               |        |              |                 |          |                 |             |             |
| LOI-CO <sub>2</sub>            | 0.230  | 0.240        | 0.170           | 0.020    | 0.180           | 0.420       | 0.285       |

|               | REEs, %                        | Feed             | Non-        | Magnetic    | Ferro-               | Para-magnetic | Final            | Final            |
|---------------|--------------------------------|------------------|-------------|-------------|----------------------|---------------|------------------|------------------|
| Component     | REOs,                          | zircon<br>sample | zircon      | concentrate | magnetic<br>fraction | pre-          | concentrate<br>A | concentrate<br>B |
|               | ,0                             | Sumpto           | concentrate | А           | inaction             |               |                  |                  |
| Scandium      | Sc                             | 0.001            | 0.000       | 0.010       | 0.005                | 0.014         | 0.031            | 0.035            |
|               | Sc <sub>2</sub> O <sub>3</sub> | 0.002            | 0.000       | 0.015       | 0.008                | 0.021         | 0.048            | 0.054            |
| Yttrium       | Y                              | 0.150            | 0.000       | 1.533       | 0.934                | 2.030         | 4.885            | 5.320            |
|               | Y <sub>2</sub> O <sub>3</sub>  | 0.190            | 0.000       | 1.947       | 1.186                | 2.578         | 6.204            | 6.756            |
| Lanthanum     | La                             | 0.183            | 0.000       | 1.875       | 1.137                | 2.500         | 5.985            | 6.550            |
| Lantinantain  | La <sub>2</sub> O <sub>3</sub> | 0.215            | 0.000       | 2.198       | 1.333                | 2.932         | 7.019            | 7.682            |
| Corium        | Ce                             | 0.370            | 0.002       | 3.785       | 2.305                | 5.010         | 12.080           | 13.140           |
|               | CeO <sub>2</sub>               | 0.455            | 0.002       | 4.650       | 2.831                | 6.154         | 14.839           | 16.141           |
| Prasoadumium  | Pr                             | 0.059            | 0.000       | 0.610       | 0.368                | 0.805         | 1.945            | 2.110            |
| Taseouyintuni | $Pr_6O_{11}$                   | 0.071            | 0.000       | 0.737       | 0.445                | 0.973         | 2.350            | 2.549            |
| Noodumium     | Nd                             | 0.145            | 0.001       | 1.490       | 0.902                | 1.960         | 4.750            | 5.145            |
| Neodymnum     | Nd <sub>2</sub> O <sub>3</sub> | 0.169            | 0.001       | 1.738       | 1.052                | 2.286         | 5.541            | 6.001            |
| Dromothium    | Pm                             | 0.000            | 0.000       | 0.000       | 0.000                | 0.000         | 0.000            | 0.000            |
| Fromethium    | Pm <sub>2</sub> O <sub>3</sub> | 0.000            | 0.000       | 0.000       | 0.000                | 0.000         | 0.000            | 0.000            |
| Companium     | Sm                             | 0.008            | 0.000       | 0.081       | 0.050                | 0.105         | 0.260            | 0.275            |
| Samarium      | Sm <sub>2</sub> O <sub>3</sub> | 0.009            | 0.000       | 0.094       | 0.058                | 0.122         | 0.301            | 0.319            |
| Europium      | Eu                             | 0.001            | 0.000       | 0.010       | 0.006                | 0.015         | 0.035            | 0.040            |
| Europium      | Eu <sub>2</sub> O <sub>3</sub> | 0.001            | 0.000       | 0.012       | 0.007                | 0.017         | 0.041            | 0.046            |
|               | Gd                             | 0.007            | 0.000       | 0.072       | 0.045                | 0.095         | 0.230            | 0.250            |
| Gadolinium    | Gd <sub>2</sub> O <sub>3</sub> | 0.008            | 0.000       | 0.079       | 0.050                | 0.105         | 0.253            | 0.275            |
| T 1.          | Tb                             | 0.001            | 0.000       | 0.010       | 0.005                | 0.015         | 0.032            | 0.038            |
| Terbium       | Tb <sub>4</sub> O <sub>7</sub> | 0.001            | 0.000       | 0.012       | 0.006                | 0.018         | 0.038            | 0.045            |
| D .           | Dy                             | 0.004            | 0.000       | 0.041       | 0.025                | 0.050         | 0.130            | 0.130            |
| Dysprosium    | Dy <sub>2</sub> O <sub>3</sub> | 0.005            | 0.000       | 0.047       | 0.029                | 0.057         | 0.149            | 0.149            |
| TT 1 ·        | Но                             | 0.001            | 0.000       | 0.010       | 0.007                | 0.015         | 0.030            | 0.037            |
| Holmium       | Ho <sub>2</sub> O <sub>3</sub> | 0.001            | 0.000       | 0.012       | 0.008                | 0.017         | 0.034            | 0.042            |
| E 1 ·         | Er                             | 0.004            | 0.000       | 0.040       | 0.025                | 0.052         | 0.128            | 0.136            |
| Erbium        | $Er_2O_3$                      | 0.005            | 0.000       | 0.046       | 0.029                | 0.059         | 0.146            | 0.156            |
| 771 1.        | Tm                             | 0.002            | 0.000       | 0.020       | 0.013                | 0.025         | 0.065            | 0.065            |
| Inulium       | Tm <sub>2</sub> O <sub>3</sub> | 0.002            | 0.000       | 0.023       | 0.015                | 0.029         | 0.075            | 0.074            |
| N/// 1 ·      | Yb                             | 0.020            | 0.000       | 0.205       | 0.125                | 0.270         | 0.655            | 0.705            |
| Ytterblum     | Yb <sub>2</sub> O <sub>3</sub> | 0.023            | 0.000       | 0.233       | 0.142                | 0.307         | 0.746            | 0.803            |
| T i i         | Lu                             | 0.010            | 0.000       | 0.103       | 0.065                | 0.135         | 0.328            | 0.355            |
| Lutetium      | $Lu_2O_3$                      | 0.011            | 0.000       | 0.117       | 0.074                | 0.154         | 0.373            | 0.404            |
|               | Th                             | 0.045            | 0.000       | 0.464       | 0.280                | 0.610         | 1.480            | 1.605            |
| Thorium       | ThO <sub>2</sub>               | 0.051            | 0.000       | 0.528       | 0.319                | 0.694         | 1.684            | 1.826            |
|               | U                              | 0.001            | 0.000       | 0.010       | 0.008                | 0.015         | 0.034            | 0.040            |
| Uranium       | U <sub>3</sub> O <sub>7</sub>  | 0.001            | 0.000       | 0.012       | 0.009                | 0.018         | 0.040            | 0.047            |
| Σ Total (%) + | $\Sigma$ REEs                  | 1.012            | 0.0035      | 10.370      | 6.305                | 13.721        | 33.083           | 35.976           |
| Radioactives  | Σ REOs                         | 1.220            | 0.0042      | 12.500      | 7.600                | 16.541        | 39.880           | 43.370           |

Table 5. Σ REEs/REOs of produced concentrates of Carpco magnetic separator and micro-column flotation using ([N2222][DEHP]) ionic liquid

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