



Beneficiation of rare earth elements contained in phosphogypsum using sequenced treatment process

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ABSTRACT

Concerns regarding the availability of rare earth elements (REEs) and the depletion of natural resource reserves have made it necessary to look for a significant breakthrough that may pave the way for the mining of several low-grade deposits and secondary resources. Phosphogypsum (PG) is one of the promising alternatives to preserve a steady flow of REEs and mitigate the loss of natural reserves. Nonetheless, the low concentration of REEs in PG implies the necessity of an enrichment step prior to any extraction attempt. To tackle the difficult challenges of REEs concentration from diluted phosphate-derived by-products, this study concentrated on determining the likely speciation of REEs and their beneficiation, as well as conducting an economic assessment of the potential industrial value of REEs present in PG. It was found that the alkaline solubilization of the gypsum phase of PG using Na₄EDTA favored the beneficiation of different qualities of PG. Moreover, it was found that the abatement of residual undesirable phases by mineral acid (HF) for quartz (SiO₂) elimination, or pyrometallurgical process, improved the enrichment of REEs in the residual concentrate. A REEs concentration of 4390.23 ppm and 4317.55 ppm were achieved after sequenced alkaline, neutral, and acidic treatment of low-grade PG (238.22 ppm); and sequenced alkaline, neutral, and pyrometallurgical treatment of high-grade PG (389.75 ppm), respectively. Furthermore, an elementary assessment of REEs speciation revealed that REEs could potentially be present as insoluble rare earth fluorides (REF₃) and/or rare earth phosphates (REPO₄).

1. Introduction

Rare earth elements (REEs) are special strategic resources [1–3]. They have unique physico-chemical properties that allow them to greatly enhance the performance and functionality of other products [4, 5]. REEs are indispensable and ubiquitous in advanced electronics, lighting, power generation, etc. Consequently, rare earth production and consumption have increased rapidly, rising from 75,500 tons of REO in 2000 to 210,000 tons of REO in 2019 [6,7]. As well, the forecasted studies unveiled a persistent growth in REEs demand in the future [6,8, 9]. Over the past years, China has faced scrutiny and criticism over its monopoly of the rare earth supply and for gradually reducing export quotas of these resources [10]. Hence, because of the worrisome supply risk effects on modern technologies, REEs have been considered as critical metals by the European Commission Criticality of assessment for Raw Materials; especially the high critical elements, i.e., dysprosium, terbium, europium, neodymium, and yttrium [11].

In 2006, China started to protect its rare earth resources, limit exports, and set a maximum target for rare earth production [12,13]. Consequently, other nations began to investigate the possibility of reopening decommissioned plants or investing in new alternative deposits in order to create a rare earth supply chain that extends beyond China [8]. Recently, copious research projects have focused on the recovery of REEs from secondary resources such as phosphogypsum (PG), red mud mine tailings, metallurgical slags, etc. [14–23]. The main advantage of these REEs resources is the absence of the costs associated with mining and disintegrating natural raw materials [24].

Over the last decade, resurgent interests about REEs recovery from phosphate rocks (PRs) and its derived products, i.e., phosphoric acid (PA), phosphogypsum (PG), and phosphoric sludge (PS), have gathered selective attention [25–29] because of the huge reserve of natural phosphate rock, which is estimated at about 60–100 billion tons [30, 31]. The United States Geological Survey (USGS) estimates an annual mining of about 250 million tons of PRs [32]. The concentration of REEs

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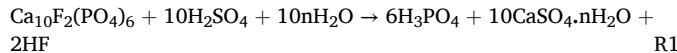
Table 1

Permutations protocol for residual gangue removal from WBS.

		Config 1	Config 2	Config 3	Config 4	Config 5	Config 6
Mass of WBS	(g)	4	4	4	4	4	4
HF volume	(mL)	40	40	10	20	20	20
HF concentration	(mol/L)	10	10	20	20	20	20
Agitation speed	(rpm)	300	300	300	200	300	300
Contact time	(h)	6	4	4	4	4	3

in PRs depends on the ore's sources, e.g., igneous or sedimentary. The concentration of REEs in the PRs of Kola, Palfos, Florida Pebble, Morocco (Khoribga), Algeria (Djebel Onk), Kovdor, Jordan, and Israel is 0.84–0.88 %, 0.48 %, 0.29 %, 0.14–0.16 %, 0.13–0.18 %, 0.14 %, 0.01 %, and 0.01 %, respectively [31].

PRs treatment using concentrated sulfuric acid is the prevalent process in the phosphoric acid plant, i.e., the wet process that culminates in the production of phosphoric acid [33–36]. Approximately 3.5 tons of PRs are needed for the production of one ton of crude phosphoric acid (28 % P₂O₅) and the five tons of phosphogypsum (PG) byproduct that go along with it [37]. The reaction which occurs during the PRs decomposition is as follows (R1). Typically, the significant percentage of REEs present in PRs (70–85 %) co-precipitates within PG [19,38,39]. Worldwide, around 7 billion tons of PG have been produced up to date with a current production rate of 200–280 million tons per year [40]. Thus far, just 15 % of the PG produced worldwide has been upcycled. The remaining (85 %) is disposed untreated in huge heap banks (gypsum stacks) in the plants' vicinity or released into the marine environment [41–47]. Given the huge amount of accessible PG, a large amount of REEs can be recovered from PG, which will diminish the depletion of natural REEs ores reserve while preserving a persistent influx of REEs. Thus, implement the necessity of developing research in order to valorize encapsulated REEs.



Several research investigations have examined the use of mineral acids to extract REEs from PG. Most of them were devoted to leach REEs with sulfuric acid due to their cheapness and availability in the phosphoric acid plant [19,48,49]. In addition, strong acids (e.g., nitric acid and hydrochloric acid), weak acids (e.g., boric acid, malic acid, and citric acid), and solvents (e.g., tri-butyl phosphate (TBP) and tri-octyl phosphine oxide (TOPO)) have been studied as well [14,19,50–52]. To enhance the recovery of REEs, researchers have developed a hydro-thermal pre-treatment for PG. The technique was found to result in re-crystallization of gypsum with the release of REEs phase encapsulated in the lattice, as it proved that dehydration of the PG resulted in the release of REEs locked in the PG structure. This technique heightens the effectiveness of the leaching process [53]. However, since rare earths are found in small quantities in PG, Hammas-Nasri et al. [54] by analogy with extraction processes from ores, put forth a process to concentrate REEs in PG through minimizing impurities in order to concentrate rare earths prior to the extraction step. The process involves the use of saline water (25 g/L NaCl) to dissolve water-soluble components of PG. This method has allowed a total REEs enrichment of 81 %. Moreover, it was stated that the alkaline treatment of PG by mineral bases favored the beneficiation of REEs in the solid phases. The carbonization of PG with Na₂CO₃ or NH₃+CO₂ allowed the transformation of PG to calcium carbonate within which REEs are co-precipitated [17,55]. In the same vein, the transformation of phosphogypsum using NaOH generated an end product of calcium hydroxide wherein REEs are enriched [56,57]. Genkin et al. [58] used an upstream treatment to concentrate REEs in PG during the wet digestion of PRs through the addition of sodium or potassium salts. The procedure depended upon the poor solubility of double sulfates NaREE(SO₄)₂ and NaREE(SO₄)₂ compared to sulfate rare earth elements REE₃(SO₄)₂, which promoted the precipitation of REEs

within PG particles during the digestion stage.

However, due to the limited number of research on REEs enrichment from PG prior to acidic leaching that is extensively studied in the literature and in view of the subdued beneficiation factor of REEs by mineral bases, i.e., inferior to 2, the development of new technologies for effective enrichment of REEs is of paramount interest. Thus, the main aim of this work is to develop a novel processing approach to benefit REEs present in PG. The central aspects explored in this study encompassed (i) the evaluation of the economic potential value of REEs present in PG; (ii) investigating REEs enrichment by a chelating agent (Na₄EDTA) capable of solubilizing the substantial component of PG (gypsum phase) and concentrating REEs; (iii) assessing the abatement of residual undesirable phases contained in beneficiated concentrate by distilled water (DW), mineral acid (HF), or thermal approach; and (iv) deciphering the probable speciation of REEs enclosed in beneficiated REEs concentrate.

2. Materials and methods

2.1. Phosphogypsum sampling

The PG samples studied in this work were collected from phosphoric acid plant located at Jorf Lasfar, El Jadida, Morocco. A total of two PG samples were freshly recovered from the rotary table vacuum filter at different time intervals. Each collected sample was oven-dried overnight, homogenized, ground, and sieved through a 250 µm mesh to scatter the grains.

2.2. Chemical reagents

Anhydrous EDTA tetrasodium salt (VWR Chemicals), hydrofluoric acid (Fisher Chemical), yttrium (III) trifluoromethanesulfonate and yttrium (III) sulfate octahydrate (Strem Chemicals), samarium (III) phosphate hydrate (Sigma-Aldrich), praseodymium (III) carbonate octahydrate (Alfa Aesar), calcium sulfate dihydrate (Scharlau), anhydrous calcium fluoride purchased (Acros Organics), distilled water (3.3 µS/cm) and deionized water (obtained by Adrona E30) were used as reagents.

2.3. Beneficiation approach

REEs beneficiation was carried out by solubilizing the gypsum phase (calcium sulfate dihydrate, CaSO₄·2 H₂O) of PG using Na₄EDTA at the optimum conditions disclosed in the study of Chanouri et al. [40]. To that, 230 g of PG was added to 4 L Na₄EDTA (0.4 mol/L) solution. The PG and EDTA mixtures were agitated by mechanical marine propeller stirrer for 15 min at 200 rpm. Subsequently, the liquid phase and residual insoluble solid phase (BS) were separated by centrifugation for 15 min at a steering speed of 3000 rpm. In succession, the BS was washed using distilled water before that obtained washed solid (WBS) was oven-dried overnight, homogenized, ground, and sieved through a 250 µm mesh.

Following the above steps, the WBS was treated through two approaches. The first method (i), analogous to REEs ores enrichment using pyrometallurgical approach [59], features the calcination of WBS at 700 °C for 3 h, while the second technique (ii) consists of solubilizing the

Table 2
Concentration of REEs and main metal elements of PG.

Elements		PG1		PG2	
		Avg	Sd	Avg	Sd
Sc	ppm	0.24	0.02	4.55	0.12
Y	ppm	107.50	5.29	120.76	5.87
La	ppm	44.55	2.32	77.88	3.23
Ce	ppm	22.99	1.06	52.75	1.69
Pr	ppm	5.48	0.29	16.13	0.89
Nd	ppm	25.59	0.90	54.82	0.46
Sm	Ppm	5.69	0.29	8.25	0.35
Eu	Ppm	1.12	0.06	3.82	0.27
Gd	ppm	7.13	0.28	14.12	0.76
Tb	ppm	3.79	0.13	3.10	0.14
Dy	ppm	6.89	0.17	10.67	0.56
Ho	ppm	1.47	0.05	4.20	0.16
Er	ppm	5.97	0.36	9.14	0.39
Tm	ppm	0.41	0.02	1.89	0.10
Yb	ppm	4.34	0.23	5.96	0.34
Lu	ppm	0.51	0.02	1.73	0.10
Σ REEs	ppm	238.22	9.46	389.75	21.12
Al ₂ O ₃	ppm	1219.37	52.63	1312.60	82.13
Fe ₂ O ₃	ppm	89.10	6.07	102.60	6.96
MgO	ppm	180.49	10.49	235.40	15.56
Na ₂ O	ppm	2358.36	116.05	2372.60	148.63

Avg: the average concentration in ppm; Sd: the standard deviation in ppm.

substantial component of WBS, i.e., quartz (SiO₂), using hydrofluoric acid (HF). Thereof, the mixed HF and WBS were agitated by a stirrer magnet in a teflon beaker at diverse configurations (Table 1) to assess and optimize the hydrometallurgical parameters that control the solubilization of SiO₂, i.e., concentration, magnetic agitation speed, and contact time. Thereafter, the slurry was vacuum filtered to separate the solid phase (TWBS) from the filtrate solution, and the solid was oven-dried overnight, homogenized, ground, sieved through a 250 µm mesh, and stored for further characterization and chemical analysis.

2.4. Physico-chemical characterization

All pre-oven-dried, ground, sieved, and homogenized samples (PG and its post-treatment solids) were characterized in a systematic manner. The mineralogical composition of the samples was determined following the analytical methodology described by Danouche et al. [60] and Brahim et al. [61]. REEs were analyzed by Inductively Coupled Plasma Mass Spectrometry ICP-MS (PerkinElmer NexION 300X, Waltham, MA, USA), with a detection limit for elemental REEs of >0.51 ppb (µg/kg); while Al₂O₃, Fe₂O₃, MgO, and Na₂O concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometry ICP-OES (Thermo Jarrell Ash IRIS/AP). PG and its post-treatment solids were prepared by digestion of 1 g of the sample in

perchloric acid at 250 °C, followed by dilution using deionized water and filtration prior to analysis. The elementary analyses were reiterated a minimum of three times to determine the average content of REEs, Al₂O₃, Fe₂O₃, MgO, and Na₂O, and reproducibility tests verified that the data's accuracy fell within a range of ±5 %. As well, sulfates were analyzed by gravimetric technique using barium sulfate (BaSO₄) according to the Indian standard IS 255; calcium was determined by volumetric method using ethylene glycol-bis(2-aminoethyl ether)-N, N, N', N'-tetraacetic acid (EGTA); silicon analysis was carried out by Atomic Absorption Spectroscopy AAS (PerkinElmer PinAAcle 900 T); phosphorus concentration was determined by an automated wet chemistry analyzer (SKALAR 5000) using vanadomolybdate method; fluorine content was measured by a fluorine ion selective electrode (METTLER TOLEDO); and the mass spectra (ESI-MS) of the solutions were recorded on a Bruker Daltonics Esquire 3000+, subsequent to solids dissolution in deionized water and filtration.

The X-ray powder diffraction (XRD) patterns of samples were recorded on a BRUKER D8 ADVANCE diffractometer using Cu K α radiation ($\lambda = 0.154060$ nm), at 20 angular range of 5° to 70°. Following data collection, the crystalline phases were identified using HighScore software equipped with Crystallography Open Database (COD). Additionally, the samples morphology and REEs mapping were carried out by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX) using a ZEISS EVO 10.

3. Results and discussion

3.1. Content and distribution of REEs in the raw PG samples

The results of ICP-MS and ICP-OES (Table 2) for REEs and other minerals assessment in PG samples showed that the concentration of total REEs in Moroccan PG varies between 238.22 ppm and 389.75 ppm. Likewise, the concentration of Al₂O₃, Fe₂O₃, MgO, and Na₂O were found to range between 1219.37–1312.60 ppm, 89.10–102.60 ppm, 180.49–235.40 ppm, and 2358.36–2372.60 ppm, respectively. The variation in the concentration of REEs, Al₂O₃, Fe₂O₃, MgO, and Na₂O between the first sample (PG1) and the second sample (PG2) is a consequence of the strong dependence of PG nature and characteristics to the PRs ores and the geological stratum being treated to generate PG [40,60–62].

The distribution of REEs in PG, as shown in Fig. 1, indicates that Y, La, Nd, and Ce are the prevailed elements. Those four elements, which compose beyond 80 % of total REEs existed in PG are typically the most industrially usable elements (above 90 %) compared to the remaining REEs [6]. This constitutes a significant advantage because the substantial REEs components of PG match global demand.

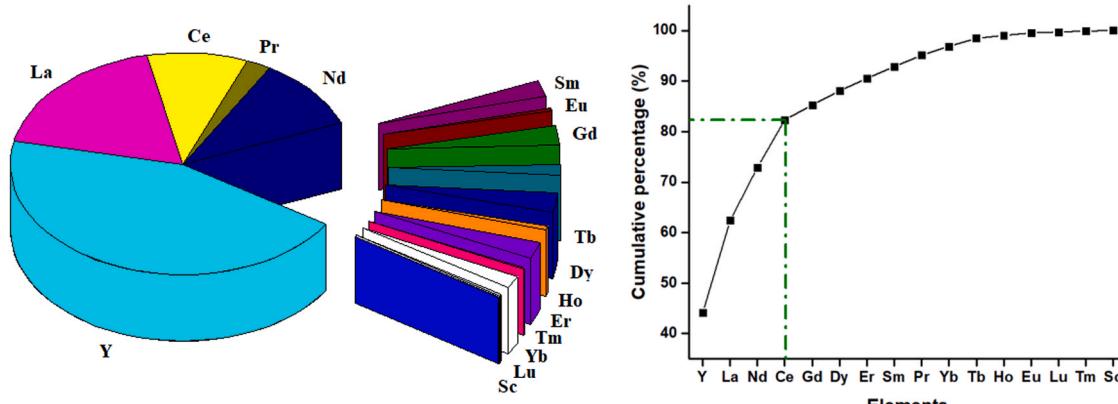


Fig. 1. Distribution of REEs in Moroccan PG.

Table 3

$C_{outlook}$ (outlook coefficient) of REEs primary and secondary resources.

Geographic location	REEs source	$C_{outlook}$	
California, USA	Mountain Pass*	Bastnaesite	0.23
China	Bayan Obo*	Bastnaesite	0.38
Florida, U.S.A.	Green Cove Spring	Monazite	0.49
*			
Malaysia	Lehat*	Xenotime	5.13
China	Longnan*	Xenotime	13.73
Pennsylvania, USA	Site A*	Acid mine	2.65
	Site B*	drainage	1.89
	Site C*		1.83
	Site A*	Sludge	2.76
	Site B*		1.79
	Site C*		1.94
Phosphogypsum, Morocco (Our sample)	Jorf Lasfar	PRs by-products	3.04 – 5.07

* Data obtained from Hassas et al. [64] and Vaziri Hassas et al. [68].

3.2. Economic evaluation of the potential value of REEs present in PG

Prior to the recovery of REEs from resources, the evaluation of the economic potential of REEs contained in the matrix is of paramount importance. The ideal composition of deemed valid ores should comprise a high concentration of critical REEs and a minimal presence of excessive REEs. Hence, Seredin [63] devised a novel categorization that delineates REEs into three groups, i.e., critical (Nd, Eu, Tb, Dy, Er, and Y), non-critical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu). This classification considered market dynamics and anticipated supply and demand in the next years. Based on the aforementioned categorization, researchers developed an outlook coefficient (Eq. (1)) for resource evaluation by calculating the ratio of the relative amount of critical REEs in the ores to the relative amount of excessive REEs [64, 65].

$$C_{outlook} = \frac{\text{Critical REEs}}{\text{Excessive REEs}} = \frac{(Nd + Eu + Tb + Dy + Er + Y) / \sum \text{REEs}}{(Ce + Ho + Tm + Yb + Lu) / \sum \text{REEs}} \quad (1)$$

The resources of high $C_{outlook}$ are the most prominent auspicious ores in terms of their potential industrial value. Herein, the comparison of calculated PG $C_{outlook}$ and known REEs resources $C_{outlook}$ (Table 3) showed that PG has a higher potential value than that of Pennsylvanian Acid mine drainage/sludge stemmed from pyrite treatment process and common-known REEs ores, e.g., bastnaesite ($\text{REEs}(\text{CO}_3)\text{F}$) and monazite ($(\text{REEs}, \text{Th})\text{PO}_4$). Regarding the high potential value of the REEs present in PG and the positive correlation of the REEs distribution with worldwide demand (previously disclosed in Section 3.1), the recovery of REEs from PG is contemplated as an attractive economic resource. Moreover, the recovery of REEs from PG has not only been hailed as a new resource for REEs but also conceivably has complementary environmental benefits since it allows the purification of PG [66, 67]. In light of the above, REEs recovery from PG is of paramount economic and environmental interest.

3.3. X-ray diffraction analysis of PG and beneficiated concentrates

Despite the considerable economic potential of REEs contained in PG, the hindrance posed by its low REEs content has constrained their direct acidic leaching [69, 70]. Therefore, to address the challenges associated with processing low-concentration resources, a beneficiation approach focused on removing substantial components of PG and concentrating REEs becomes imperative. Herein, the abatement of the major components of PG was assessed using X-ray diffraction (XRD) as it is a widely prevalent technique that allows the exploration of the alteration of the mineralogical composition of different matrices [71].

The XRD analysis of PG and beneficiated solid (BS) (Fig. 2a) showed that the alkaline treatment of PG using Na_4EDTA allowed the solubilization of the predominant compound of PG, i.e., calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), which is crystallized in a monoclinic system with the space group C2/C. The major components of residual BS are the

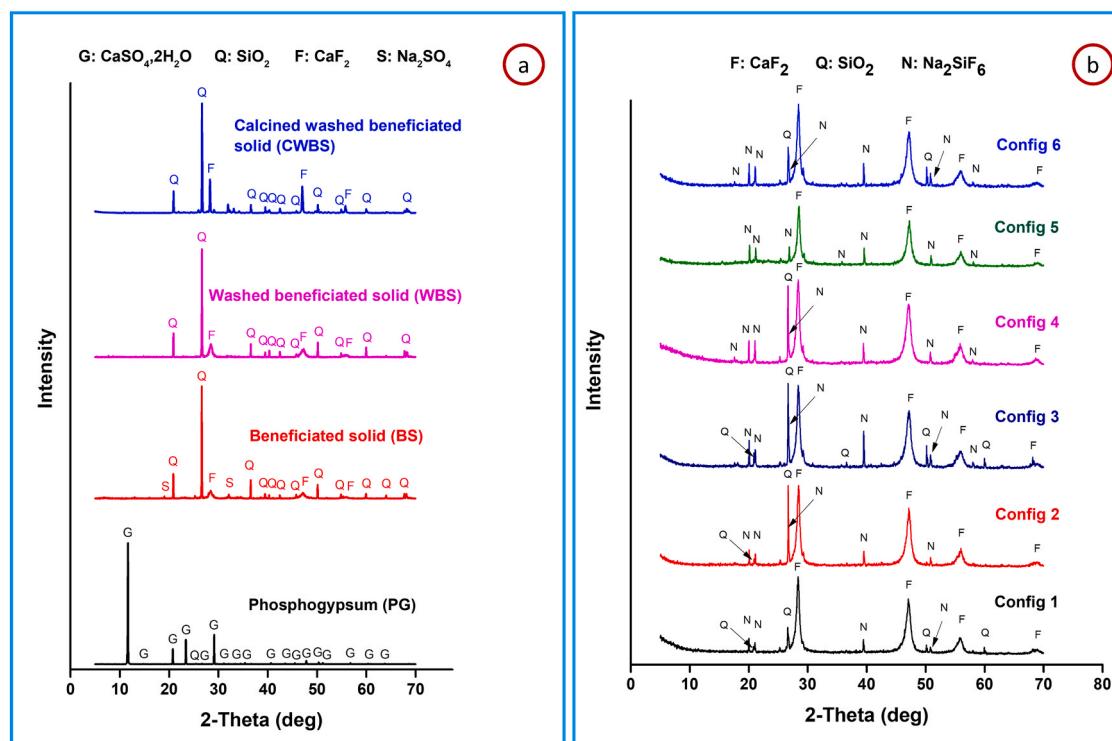


Fig. 2. X-ray diffraction pattern of (a): PG, BS, WBS, CWBS, and (b): TWBS obtained from different configurations.

Table 4

Concentration of REEs and main metal elements in BS, WBS, and CWBS obtained from PG2.

Elements	BS (ppm)		Enrichment (%)	WBS (ppm)		Enrichment (%)	CWBS (ppm)		Enrichment (%)
	Avg	Sd		Avg	Sd		Avg	Sd	
Sc	11.16	1.06	59.23	13.45	1.14	66.17	13.35	1.07	65.92
Y	641.83	27.27	81.19	1555.01	79.40	92.23	1746.38	41.48	93.09
La	191.69	13.53	59.37	471.34	14.73	83.48	557.94	24.06	86.04
Ce	308.01	2.83	82.87	706.41	20.08	92.53	905.02	52.92	94.17
Pr	46.72	1.17	65.48	90.57	4.70	82.19	109.83	6.00	85.31
Nd	239.61	13.40	77.12	352.85	17.59	84.46	356.45	21.42	84.62
Sm	24.10	0.51	65.77	57.44	1.16	85.64	70.28	1.62	88.26
Eu	12.85	0.23	70.27	24.68	1.01	84.52	26.87	0.43	85.78
Gd	88.85	2.65	84.11	153.79	8.00	90.82	173.10	7.90	91.84
Tb	10.25	0.75	69.76	20.85	0.97	85.13	22.79	0.89	86.40
Dy	35.47	2.45	69.92	84.38	4.34	87.35	102.32	2.78	89.57
Ho	16.76	0.60	74.94	34.01	0.89	87.65	36.54	0.94	88.51
Er	45.96	1.54	80.11	82.07	3.63	88.86	82.62	2.48	88.94
Tm	8.69	0.47	78.25	17.08	0.48	88.93	18.03	0.42	89.52
Yb	29.77	1.71	79.98	69.71	3.68	91.45	82.12	2.58	92.74
Lu	9.70	0.40	82.16	18.99	0.87	90.89	19.60	0.80	91.17
Σ REEs	1721.42	53.15	77.36	3752.63	162.74	89.61	4317.55	124.56	90.97
Al ₂ O ₃	3501.03	151.72	62.51	7770.67	485.78	83.11	7857.00	448.51	83.29
Fe ₂ O ₃	602.32	30.96	82.97	1248.33	38.89	91.78	1494.50	24.50	93.13
MgO	804.07	31.45	70.72	1742.00	80.33	86.49	1671.50	111.49	85.92
Na ₂ O	79007.01	3970.00	97.00	34980.00	939.33	93.22	32400.00	1917.78	92.68

Avg: the average concentration in ppm; Sd: the standard deviation in ppm.

unattacked quartz (SiO_2), sodium sulfates (Na_2SO_4), and calcium fluoride (CaF_2), which crystallized in a hexagonal, orthorhombic, and cubic system under the space group P3121, Fddd, and Fm-3 m, respectively. In addition, it was disclosed that the washing technique allowed the elimination of soluble Na_2SO_4 from the WBS.

The decrease in broadening peaks in calcined washed beneficiated solid (CWBS) as compared to WBS revealed that the thermal treatment promoted the crystallization state of the calcium fluoride (CaF_2) but did not favor the elimination of any phase. Dash et al. [72] demonstrated that CaF_2 crystallization occurs at 900 °C; however, doping CaF_2 with Yb and Er favored the decrease of CaF_2 crystallization to 600 °C, which explained the crystallization of CaF_2 present in CWBS at the used temperature (700 °C). Thus allowed a better comprehension of the crystallization changes of the minor compound contained in PG, i.e., CaF_2 , as the interference between the major components of PG and coexisting

compounds hindered the deep understanding of the thermal behaviors of this matrix.

Moreover, the assessment of the quartz (SiO_2) removal from WBS (Fig. 2b) demonstrated the high impact of all the hydrometallurgical parameters, i.e., concentration, magnetic agitation speed, and contact time. Unlike other configurations, the fifth configuration allowed a total elimination of the quartz phase. However, other peaks corresponded to sodium fluorosilicates (crystallized in a hexagonal system with the space group P321) were identified in the treated WBS (TWBS) indicating the transformation of a segment of solubilized quartz phase to sodium fluorosilicates.

The above disclosed elimination of the major phase contained in PG, i.e., calcium sulfate dihydrate (CSD) was due to the high solubility of CSD in alkaline solutions of EDTA. The solubility of CSD is drastically influenced by changes in pH and concentration [40,73,74]. However, Chanouri et al. [40] reported that alkaline conditions exhibited the highest solubilization of PG, i.e., 50.49, 66.89, 83.53, 99.36, 110.54, and 118.2 g/L at a concentration of Na_4EDTA of 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mol/L, respectively. Thus, explaining the absence of CSD in BS. On the other hand, the solubilization of the SiO_2 present in WBS was controlled by different mechanisms. Park et al. [75] reported that it is necessary to break the siloxane covalent bonds in order to liberate silicon and break down the network for effective quartz (SiO_2) removal. The dissolution of SiO_2 by HF is a heterogeneous reaction that occurs in two major steps: (1) SiO_2 reacts with hydrofluoric acid to give silicon tetra-fluoride (SiF_4) and water; and (2) SiF_4 reacts with HF to produce alkali hexa-fluorosilicate or hexa-fluorosilicic acid [76]. However, the first substitution of the oxygen by fluorine (step 1) is the rate-determining reaction step [76] as this reaction occurs in four steps, i.e., (a) binds of HF to oxygen, (b) formation of $\text{Si}-\text{O}-\text{H}-\text{F}$, (c) dissociation of the $\text{Si}-\text{O}$ bond, and (d) formation of SiF_4 [77]. Hence, the solubilization of SiO_2 by hydrofluoric acid is a time-dependent reaction, which is confirmed by the high elimination of SiO_2 from WBS within 6 h (config 1) compared to 4 h (config 2) at the same other parameters. Furthermore, it was stated that SiO_2 reacts with the HF_2 and HF, but not with H^+ and F^- [77,78]. Consequently, the high concentration of hydrofluoric acid is more preferable to solubilize SiO_2 because increase in the concentration of hydrofluoric acid favors a drastic increase in the concentration of HF with a low increase in the concentration of H^+ , H_2F_3 , HF_2 , and F^- [79]. This explains the total elimination of SiO_2 from the WBS at a high concentration of 20 mol/L (config 5) compared to 10 mol/L (config

Table 5

Concentration of REEs and main metal elements in WBS and TWBS obtained from PG1.

Elements	WBS (ppm)		TWBS (ppm)		Enrichment (%)
	Avg	Sd	Avg	Sd	
Sc	3.93	0.62	7.24	1.47	96.69
Y	769.37	36.97	1470.70	45.89	92.69
La	318.54	17.42	542.51	24.23	91.79
Ce	770.32	9.62	1303.11	64.59	98.24
Pr	37.12	1.59	92.18	5.91	94.06
Nd	190.87	6.59	410.84	18.77	93.77
Sm	30.66	1.15	65.63	3.14	91.33
Eu	6.19	0.33	13.04	0.92	91.41
Gd	123.74	1.78	268.15	16.28	97.34
Tb	4.47	0.25	9.29	0.55	59.20
Dy	32.20	1.31	67.58	3.28	89.80
Ho	6.90	0.32	14.19	0.83	89.64
Er	24.58	1.29	49.46	2.62	87.93
Tm	3.74	0.21	7.51	0.44	94.54
Yb	27.89	1.43	55.84	3.05	92.23
Lu	4.20	0.21	8.48	0.37	93.99
Σ REEs	2354.71	101.52	4390.23	106.54	94.57
Al ₂ O ₃	4536.63	236.63	10057.04	572.73	87.88
Fe ₂ O ₃	990.65	60.65	1940.18	117.13	95.41
MgO	834.86	43.49	1450.02	20.42	87.55
Na ₂ O	29313.21	913.21	60500.00	2960.15	96.10

Avg: the average concentration in ppm; Sd: the standard deviation in ppm.

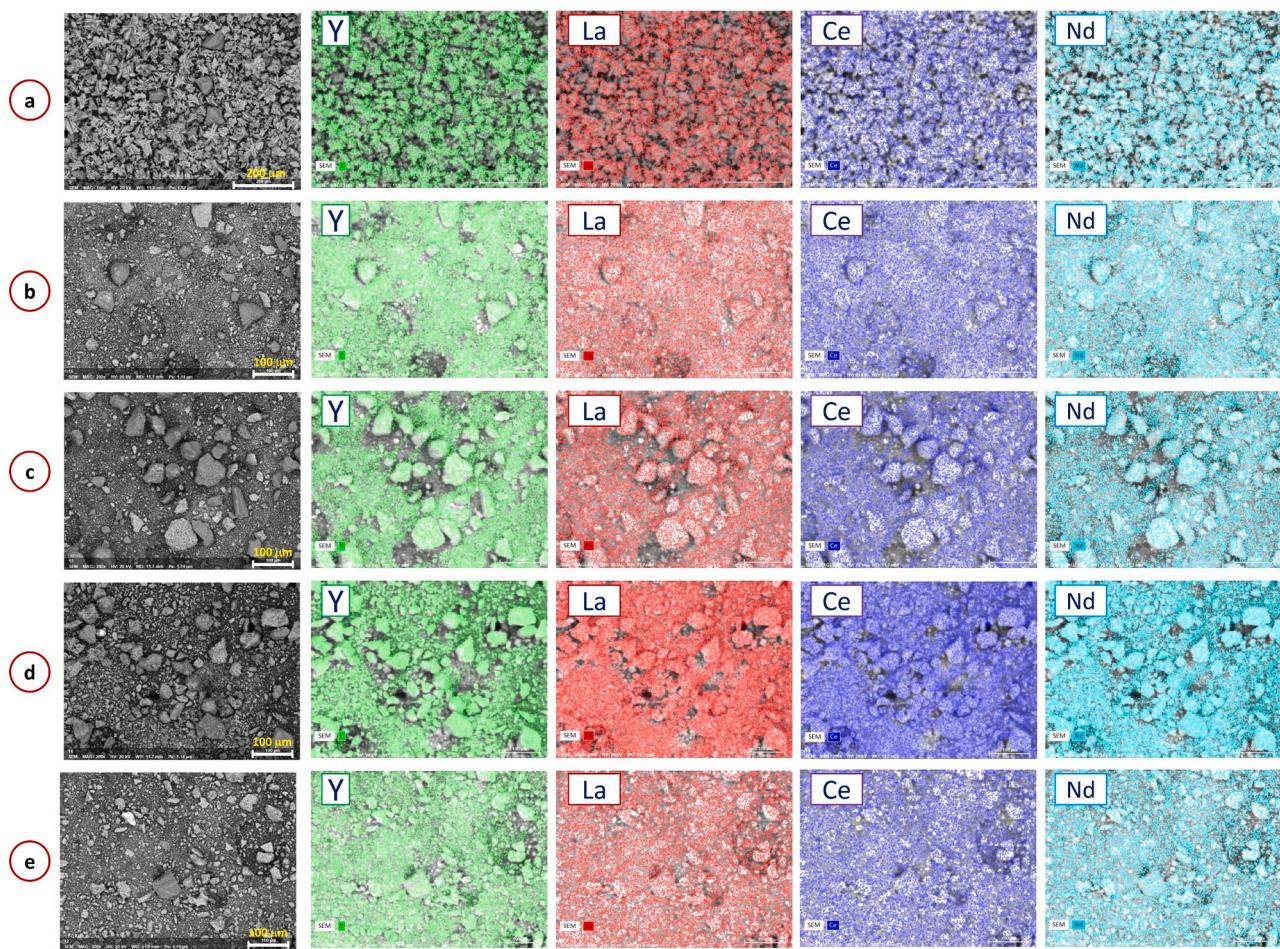


Fig. 3. Spatial distribution of Y, La, Ce, and Nd in PG (a), BS (b), WBS (c), CWBS (d), and TWBS (e).

2), at the same contact time and agitation speed. Moreover, the agitation speed is of great importance as it promotes the consistent collision between the reactant molecules. Herein, it was disclosed that in comparison to 200 rpm (config 4), an agitation speed of 300 rpm (config 5) favors the removal of SiO₂.

3.4. Content of REEs in beneficiated concentrates

Following the abatement of major components contained in PG, REEs and metallic elements were analyzed in different beneficiated concentrates (Table 4). The results showed that PG prominent compound dissolution (CSD phase) allowed the enrichment of REEs in the beneficiated concentrate; and the concentration of REEs in BS reached 1721.42 ppm starting from a PG of 389.75 ppm. Subsequent washing of BS followed by thermal treatment favored further increases in the concentration of REEs to 3752.63 ppm and 4317.55 ppm in WBS and CWBS, respectively. In the same vein, the concentration of Al₂O₃, Fe₂O₃, and MgO increased, while the concentration of Na₂O decreased in the WBS. The significant decrease in the concentration of Na₂O (from 79007.01 ppm to 34980.00 ppm) is due to the elimination of Na₂SO₄ during the washing process, which is in line with the XRD analysis.

Moreover, the analysis of the concentration of REEs after SiO₂ removal from WBS (Table 5) elucidated the enrichment of the TWBS concentrate in REEs. The concentration of REEs was increased from 2354.71 ppm to 4390.23 ppm, which corresponds to a total concentration factor of 18.42 starting from a feed PG of 238.22 ppm. Likewise, the Al₂O₃, Fe₂O₃, and Na₂O increased in the TWBS with the same pattern as REEs.

The assessment of the variation of REEs, Al₂O₃, Fe₂O₃, and MgO

enrichment (Tables 4 and 5) showed an enrichment of total elements. Herein, total REEs enrichment in BS, WBS, CWBS, and TWBS is in the order of 77.36 %, 89.61 %, 90.97 %, and 94.57 %, respectively. However, elemental REEs enrichment assessment showed that the beneficiation process is an elemental-independent technique as the observed enrichment does not adhere to a particular pattern. The elemental REE enrichment was calculated as follows (Eq. 2):

$$\text{REE enrichment}(\%) = \frac{(\text{REE}_{(\text{concentrates})} - \text{REE}_{(\text{PG})})}{\text{REE}_{(\text{concentrates})}} \times 100 \quad (2)$$

Further processing of the highly enriched concentrates requires an elucidation of the distinct particles' morphology and the spatial distribution of REEs across the surface of PG and the different obtained beneficiated concentrates. In light of the foregoing purposes, the Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray (EDX) mapping of PG (Fig. 3a) demonstrates the presence of an agglomerate arrangement of crystals and other irregular simultaneously existed clusters, which is different from the particles' morphology observed in the other concentrates, i.e., BS, WBS, CWS, and TWBS (Fig. 3b, c, d, and e). Indeed, these agglomerate crystal arrangements are made up of acicular and tabular particles of about 150 μm diameter size. However, the size of the irregular clusters of PG and other concentrates is under 88 μm. Furthermore, it was disclosed that major REEs, i.e., yttrium (Y), Lanthanum (La), Cerium (Ce), and Neodymium (Nd) are homogeneously dispersed on the surface of PG, BS, WBS, CWS, and TWBS, providing insight for better efficiency of subsequent recovery of REEs.

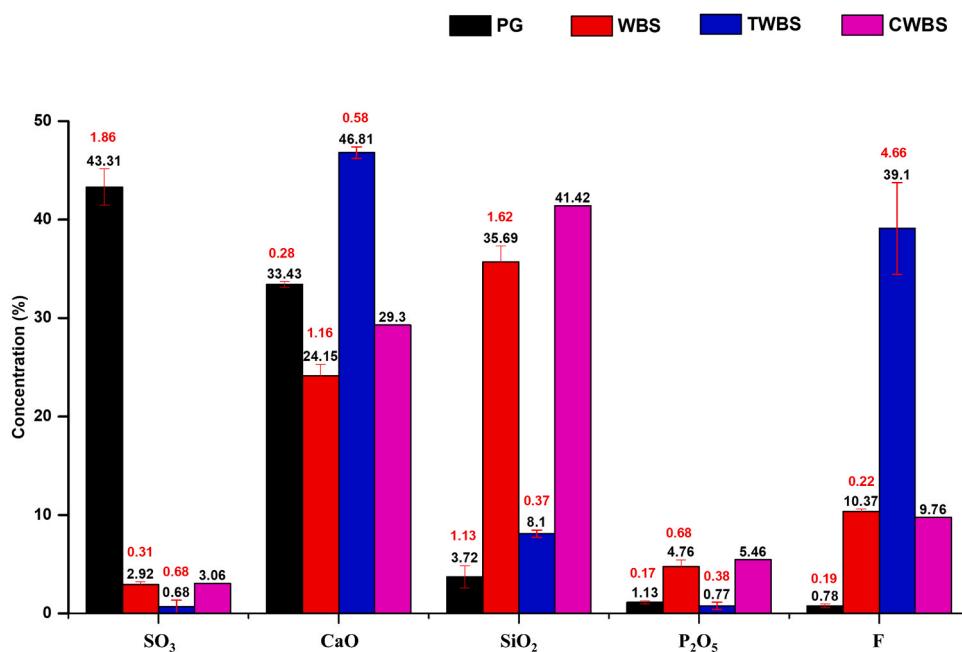


Fig. 4. The evolution of major components of PG and beneficiated concentrates.

3.5. Chemical characterization of PG and beneficiated concentrates

The chemical analysis of PG and beneficiated concentrates (Fig. 4) revealed the consistency of the composition of each matrix with the obtained XRD spectrum (Fig. 2). PG was found to contain majorly CaO (33.43 %), SO_3 (43.31 %), and SiO_2 (3.72 %), which were identified as calcium sulfate dihydrate and quartz. After solubilization of 96.09 % of total PG mass using Na₄EDTA, the analysis of residual solid (WBS) showed that it contains majorly CaO (24.15 %), F (10.37 %), and SiO_2 (35.69 %), which were identified as calcium fluoride and quartz. Similarly, the analysis revealed that CWBS contains the same major and minor components as WBS with a slight increase in the concentration of elements in favor of CWBS. However, the TWBS obtained after solubilization of 48.50 % of total WBS mass by HF was found to contain majorly CaO (46.81 %), F (39.1 %), and SiO_2 (8.1 %) identified as calcium fluoride and sodium fluorosilicates. Noteworthy to mention that the increase in the concentration of REEs in each beneficiated concentrate was due to the reduction in the mass of solids due to the solubilization of specific phase at each step.

The monitoring of the evolution of CaO , SO_3 , SiO_2 , and potential REEs bearing compounds, i.e., P_2O_5 and F, showed that the increase in REEs concentration in WBS and CWBS is positively correlated with the increase in phosphorus pentoxide and fluorine, while a negative correlation was perceived for calcium oxide and sulfur trioxide. The decrease in the concentration of CaO and SO_3 in the WBS was attributed to the high solubility of the gypsum in EDTA at alkaline conditions [40]. However, the increase in the concentration of silicon dioxide is ascribed to the quartz's resistance to dissolution, while the increase in the concentration of fluorine and phosphorus pentoxide is due to the formation of stable metal fluoride and metal phosphate during the PG dissolution process [80–83]. Likewise, the removal of the major WBS phase, i.e., SiO_2 , by hydrofluoric acid showed a sharp decrease in the concentration of silicon dioxide, phosphorus pentoxide, and sulfur trioxide in TWBS along with a significant increase in the concentration of fluorine and calcium oxide. This elucidated the efficient solubilization of SiO_2 and other undesirable gangue, and may exhibit the transformation of the metal phosphate -previously formed during the first enrichment process using EDTA- to metal fluorides; however, there is a reticent about rare earth phosphate transformation to rare earth fluoride [84]. Moreover, the chemical analysis of CWBS revealed an identical chemical

composition to WBS with a slight increase in favor of CWBS, confirming the sole variation of the crystallization of WBS observed by previously disclosed XRD results. Hence, the increase in REEs concentration in CWBS was resulted from the evaporation of free and interstitial water (bounded and structural water) at a temperature of about 380 °C, other than the decomposition of organic matter at a temperature of about 600 °C [40,85].

3.6. Speciation of REEs in beneficiated concentrates

In addition to the determination of the chemical composition of different matrices, i.e., PG and beneficiated concentrates, and the spatial distribution of REEs (previously disclosed in Section 3.4), the deciphering of the speciation of REEs is crucial for better comprehension of the physico-chemical properties of REEs bearing mineral. It is noteworthy to mention that REEs occur in nature as: (i) independent rare earth minerals; (ii) weathered crust elution deposits; and (iii) isomorphism substitution [86]. The distribution of REEs in PG is strongly depended on their ionic radii, ions interactions, REEs ion hydration energy, and PG crystalline structure [87]. Studies assemble three possible modes of REEs occurrence: (i) lattice bound REEs in gypsum; (ii) surface adsorption on gypsum; and (iii) auxiliary REEs-bearing phases on PG surface or in-between gypsum crystals [88]. It was found that REEs can be incorporated into the calcium sulfate lattice due to heterovalent isomorphic replacement in the presence of alkaline ions as charge compensators [24]. Generally the most possible carriers of REEs are sulfates, phosphates, fluorides, and carbonates [89], which implies that REEs could bind differently and exist as a mixture of compounds in the gypsum lattice. Hence, the determination of REEs exact speciation is of paramount importance, as it represents the pedestal factor for the development of effective processes for REEs recovery [88].

The assessment of the metal complexes with EDTA (0.001 mol/L) using mass analysis in negative mode (Fig. 5) at EDTA/Metal stoichiometry of 1 elucidates that calcium sulfates, yttrium sulfates, and praseodymium carbonate are highly soluble in EDTA. However, calcium fluoride, samarium phosphate, and yttrium trifluoromethanesulfonate are moderately complexed with EDTA, as other peaks of EDTA, e.g., $[\text{EDTA}-\text{H}_3^-]$ at 291.3, $[\text{EDTA}-\text{Na}-\text{H}_2^-]$ at 313.3, and $[\text{EDTA}-\text{Na}_2-\text{H}^-]$ at 335.4, are still available indicating the non-total complexation of Sm and Y with EDTA molecules. These results are in line with the literature.

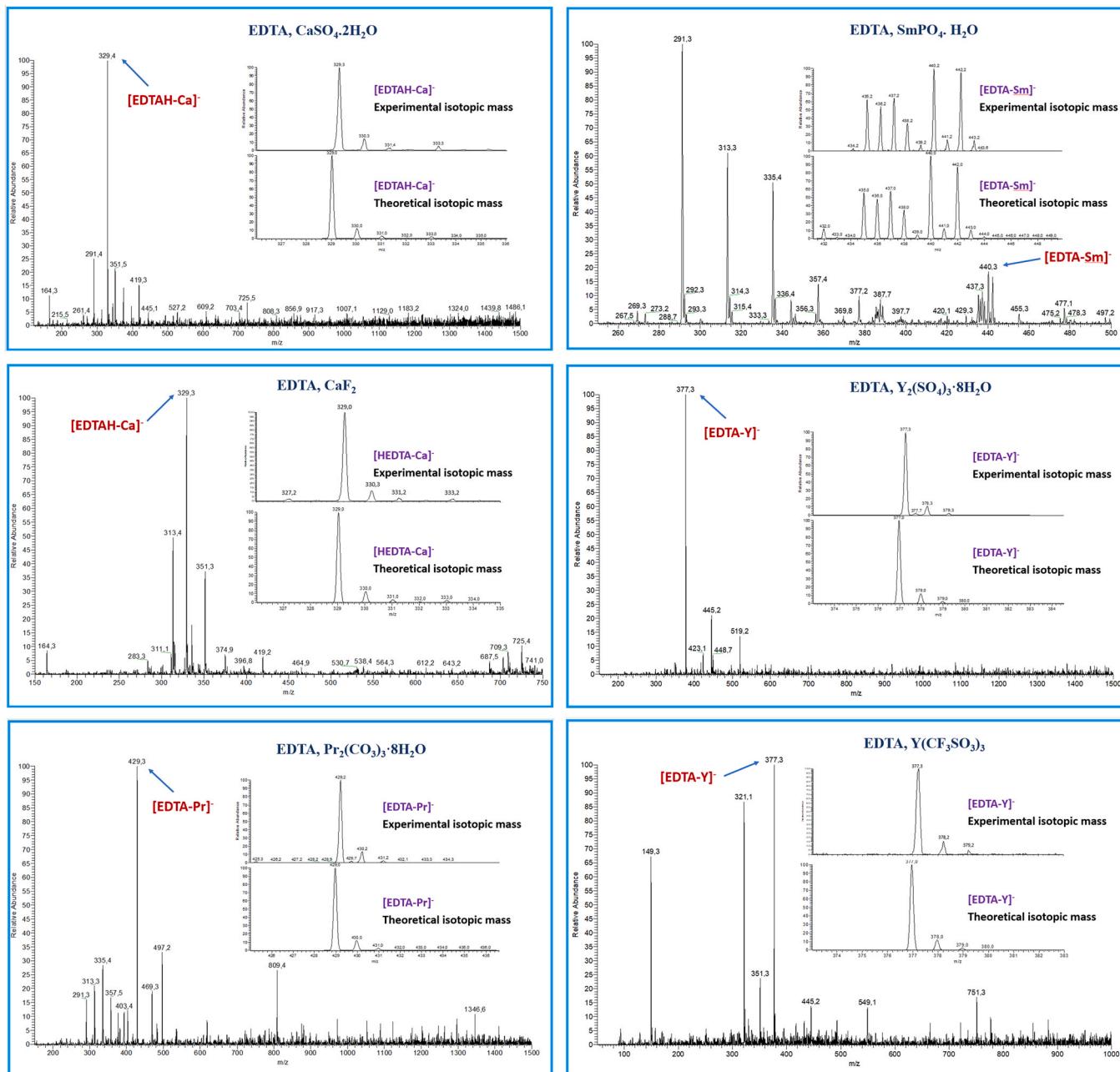


Fig. 5. Integrated negative mode ESI-MS spectra of EDTA-metal compounds.

Hou et al. [90] and Dinic et al. [80] disclosed that calcium and REEs coprecipitate during hydro- and solvo-thermal synthesis of nanostructure with EDTA in the presence of fluorine. The crystallization of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ phase is sensitive to the reaction time and precursors concentration, while the crystallization of $\text{YF}_3\text{:Yb}^{3+}/\text{Er}^{3+}$ phase is attained through lowering the dopant concentration or by altering the duration of hydrothermal treatment [80]. Moreover, EDTA was found to play a crucial role in the morphological development of REEs phosphate (REEPO_4) crystals [82,83]. The monodispersed crystalline particle was found to be controlled by the stability of the REE-EDTA chelate precursor defined by $[\text{EDTA}]/[\text{PO}_4]$ and pH [91]. In addition, it was shown by Song et al. [82] that the composition of the synthesized $\text{YPO}_4\text{:Eu}^{3+}$ was modified to hydrated $\text{YPO}_4\cdot 0.8 \text{ H}_2\text{O}\text{:Eu}^{3+}$ by increase in the quantity of EDTA.

With respect to all of the above, REEs are beneficiated in WBS due to the coprecipitation of REEs with phosphate and fluorine (preexisted in

PG) during the elimination of prominent gypsum compounds by solubilization with EDTA. Similarly, other metallic elements, e.g., Al, Fe, etc., coprecipitate with phosphorus, thereby increasing their concentration in WBS [92]. These findings are in line with demonstrated alteration of the chemical composition of PG, as the dissolution of PG by EDTA was found to favor the increase of phosphorus and fluorine concentration in WBS due to the formation of metal-fluoride and/or metal phosphate; however, the revealed potential REEs bearing minerals were not identified by XRD (see Fig. 2) since the concentration of REEs in beneficiated concentrates is below the XRD detection limit, i.e., 10,000 ppm [93,94]. Considering all the aforementioned, REEs extraction from obtained concentrates is advantageous compared to PG owing to the higher concentration of REEs and the limit REEs possible bearing minerals in the beneficiated concentrates.

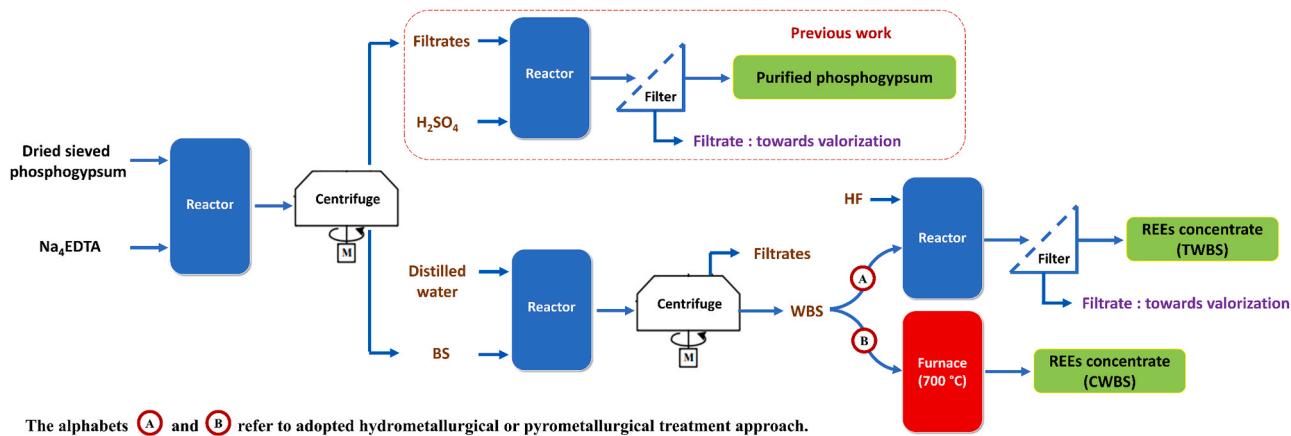


Fig. 6. Proposed flowsheet for combined PG purification and beneficiation of REEs.

3.7. Broad framework and process flowsheet

Due to the low REEs content in PG and the volatility of REEs price, the sole targeting of REEs was judged as a high-risk approach, which limited the upscale of previously developed technologies [70]. Therefore, the essence of this study is to overcome the aforementioned drawbacks; in particular, the development of an efficient process for sustainable REEs recovery using an approach that consists of valorizing the used reagents and PG components with the objective of integrated valorization of total components. To address these challenges, alkaline EDTA and HF were used as prior treatments to concentrate REEs and valorize the gypsum and quartz. Noteworthy to mention that the recovery of REEs from PG by acidic EDTA was reported by Guan et al. [39]; however, this technique only focused on REEs leaching, as EDTA is a pH-dependent chelating agent, which limited the efficient purification of the gypsum phase rather than the separation of insoluble PG components. Likewise, the PG conversion to calcium fluoride using HF was studied by Ennaciri et al. [95,96]; however, the generation of CaF₂ as a high-value product is the only focus of these studies. In this context, the sequenced treatment of PG for the valorization of total PG components is the major pedestal of the developed-combined treatment by alkaline EDTA and HF process.

Based on the disclosed data, a suggested conceptual flowsheet is illustrated in Fig. 6. This flowsheet primarily consists of three sequential stages, namely alkaline, neutral, and acidic or pyrometallurgical enrichment. During the alkaline processing, PG is treated with Na₄EDTA to solubilize major PG components (gypsum phase) in order to increase the concentration of REEs in the obtained BS. The resultant BS is washed with distilled water for water-soluble compounds removal, i.e., the nardite, then subjected to pyrometallurgical treatment or acidic removal of quartz phase by hydrofluoric acid. In addition to the beneficiation of REEs, the quartz removal is of paramount interest as it raises technical challenges in upcoming treatment of enriched REEs concentrate, such as reactor damage caused by erosion-corrosion [97,98]. The major allied advantage of the use of HF is the compatibility of the developed process with pre-existing necessary equipment in the phosphate plants, i.e., HF gaseous treatment scrubber, storage and handling equipment, etc. [99–101]. In contemplation of total component valorization, the post PG solubilization filtrate, i.e., Ca-EDTA, was explored in a previous work for the precipitation of purified calcium sulfate dihydrate [40]. However, further treatment of co-generated filtrates to recover sodium sulfates, recycle EDTA [102,103], and explore the obtained fluorosilicic acid for upcoming valorization or channeled to the fluorosilicic acid storage being generated as co-products during phosphate rock treatment [104] represent a core pedestal for integrated processing of PG with a by-product to high added value products strategy.

4. Conclusions

With a view to overcome the challenges posed by processing prominent auspicious low-grade PG resources for REEs recovery, this research studied the beneficiation of phosphate-derived byproducts to enrich REEs using sequential treatment by EDTA, distilled water, and HF or calcination. The results showed that the sequenced removal of prominent PG compounds enabled the enrichment of REEs in the obtained concentrates. Moreover, it was disclosed that the enriched concentrates of REEs demonstrate the presence of a dispersed compound consisting of rare earth phosphate and/or rare earth fluoride. Hence, due to the known REEs probable speciation in the enriched phases and the high concentration of REEs that reached 4390.23 ppm after the alkaline, neutral, and acidic treatment, which corresponds to a concentration factor of 18.42, the recovery of REEs from the beneficiated concentrates is advantageous compared to raw PG. The high approved REEs concentration and total REEs enrichment in TWBS (94.57 %) combined with purified PG and other potential high added value products production makes the sequenced valorization of PG as a starting material of utmost interest, as it promotes an integrated processing of PG for an effective byproduct to high added value products strategy.

CRediT authorship contribution statement

Rachid Benhida: Writing – review & editing, Supervision, Project administration, Funding acquisition. **El Mahdi Mounir:** Resources, Project administration, Funding acquisition, Formal analysis. **Said Amal:** Validation, Investigation, Formal analysis. **Hamza Chanouri:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Khaoula Khaless:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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