



# The behaviour of selected rare-earth elements during the conversion of phosphogypsum to calcium sulphide and residue

Nsaka Ntumba Christophe<sup>1</sup> · Rob McCrindle<sup>2</sup> · Jannie Maree<sup>3</sup> · Veronica Ngole-Jeme<sup>1</sup>

Received: 18 June 2022 / Accepted: 3 March 2023 / Published online: 17 March 2023  
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## Abstract

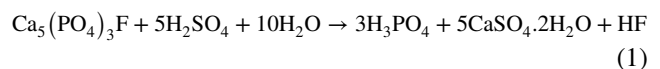
Phosphogypsum (PG) is a large hazardous waste from fertiliser and phosphoric acid industries from which useful products including rare-earth elements (REEs) can be recovered depending on the treatment process. Its conversion to calcium sulphide (CaS) which was achieved at 95% followed by the formation of S, CaCO<sub>3</sub> and residue is one of the plausible treatment processes leading to economic and environmental benefits. This study aimed at monitoring selected REEs behaviour during the conversion of (PG) to (CaS). The concentrations of REEs in the raw PG, the produced CaS and the obtained residue were determined after digestion (microwave and traditional acid leaching) using ICP-OES. The effect of CO<sub>2</sub> and H<sub>2</sub>S used in the process of forming CaCO<sub>3</sub> and S from PG on the concentrations of REEs was also investigated. Microwave digestion proved to be more effective than traditional acid leaching in the recovery of REEs. Microwave digestion using 3 mL HNO<sub>3</sub> + 1 mL HCl was more effective than 1 mL HNO<sub>3</sub> + 3 mL in REEs recovery. CaS contained the highest amount of Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, La and Y with values of 2646, 476, 2255, 320, 60.5, 376, 79.8, 1.24, 476, 1185 and 318 µg/g respectively. Based on these findings, the residue could be further processed to recover REEs despite less than 40% decrease in concentration for the majority of REEs observed due to the use of H<sub>2</sub>S and CO<sub>2</sub>. CO<sub>2</sub> was found to be more suitable as fewer REEs were leached as compared to H<sub>2</sub>S. All things considered, the obtained residue could be a good secondary source of REEs as it is easier to leach, retained good amount of REEs and lesser impurities.

**Keywords** Hazardous waste · Treatment process · Recovery · Rare-earth elements

## Introduction

The demand for phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as one of the basic raw materials for the production of most phosphate fertilisers and other useful products is on the rise to meet the increased needs of an ever-growing population. Phosphogypsum (PG: CaSO<sub>4</sub>·2H<sub>2</sub>O) is a by-product formed during

phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) production by wet process. In this process, phosphate rocks (such as fluoro-apatite, goethite quartz, etc.) are reacted with sulfuric acid in the presence of water as indicated in Eq. 1 [1].



Furthermore, this procedure is known to produce huge amounts of waste by-products. However, it is widely used in the production of H<sub>3</sub>PO<sub>4</sub> due to its affordability. Moreover, for every tonne of phosphoric acid produced, five tonnes of PG are formed. As a result, the global production of PG is estimated to 100–280 Mt, whereas that of H<sub>3</sub>PO<sub>4</sub> is projected to be roughly 50 Mt per annum. Amongst the main PG producers are African countries like South Africa, Tunisia and Senegal [2]. The production of H<sub>3</sub>PO<sub>4</sub> in South Africa by wet process in the Lowveld region has been going on since the 60s [3]. There are large amounts of waste PG in South Africa in various places (Phalaborwa, Potchesfroom,

✉ Nsaka Ntumba Christophe  
Christophensaka@gmail.com

<sup>1</sup> Department of Environmental Sciences, School of Environmental Science, College of Agriculture and Environmental Sciences, Faculty of Sciences, Florida Campus, University of South Africa, Florida, Roodepoort 1710, South Africa

<sup>2</sup> Department of Chemistry, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa

<sup>3</sup> ROC Water Technologies, Die Wilgers, P O Box 70075, Pretoria 0041, South Africa

Modderfontein, Summerset West and Rustenburg) that require processing [4].

Phosphogypsum composition is dominated by gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and sodium fluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) which make up about 90%. The remaining 10% is reported to be made of some inorganic impurities, such as fluorides and metallic elements, together with organic matters [5, 6]. Furthermore, it is necessary to stress that PG composition is strongly influenced by factors, such as the quality of the raw phosphate rock used, the treatment route followed, the handling of the PG, the dumping technique applied, age and at last the dumping site [7]. It is evident that the chemical composition (the concentration of the element of interest e.g. Rare-earth elements and available impurities e.g. Th, U) of PG is by far the determinant of its use and treatment procedure to be followed [8].

In terms of PG treatment, numerous physical and chemical procedures including washing, thermal treatment, wet sieving, alkaline neutralisation, addition of extracting solutions and leaching have been developed and applied with different goals [9]. Nevertheless, most of them are impaired by the presence and the concentration of toxic impurities, mostly radionuclide, in the PG that might either negatively impact living species if dispersed into the environment or interfere during treatment [10]. In addition, the concentrations of metals of interest to be recovered from PG are generally very low making the whole recovery process economically non-viable unless a cost-effective recovery procedure is used. Hence, the development of efficient cost-effective procedures to deal with these challenges is paramount when PG is to be either re-used or recycled.

Cost-effective treatment procedures could also be regarded as those that lead to the recovery of multiples commercial or reusable products to either compensate for the cost of treatment or even generate profit where possible. Products recoverable from PG include S,  $\text{CaCO}_3$  and possibly rare-earth elements (REEs). Sulphur recovery procedures from PG are well investigated by various authors [11, 12]. Amongst the used procedures, there are PIPco, claus and iron three processes which are most popular. PIPco entails the production of elemental S from  $\text{H}_2\text{S}$  gas and includes several complexes and requires elevated temperatures in the sulphur reactor and high pressure in the reaction vessel to prevent the boiling of potassium citrate solution [10, 11]. However, only two-third of the  $\text{H}_2\text{S}$  is converted to S by reacting with the solution of potassium citrate. Additionally, for an effective conversion, high concentration of potassium citrate is required for a good buffering capacity [10], whereas the iron (III) process used in this study seems to rather be simple and cost-effective as it neither requires high pressure nor temperature. The conversion reaction of  $\text{H}_2\text{S}$  to S is effective at room temperature with a solution of iron (III) sulphate [12].

$\text{CaCO}_3$  can be obtained from PG either directly or indirectly in a two-step process that includes: First, the thermal conversion of PG to CaS and second the direct or indirect carbonation of the formed CaS. The choice of a process is generally dictated by the quality of  $\text{CaCO}_3$  to be produced. REEs are obtained after their release from PG through acid leaching followed by a separation process. REEs can be recovered either directly by leaching PG or indirectly by digesting a leftover from a secondary formed product from PG. The second is encouraged as it gives possibility of recovering more than one product. Many researchers have investigated the possibility of converting PG to other useful products [13–15].

$\text{CaCO}_3$ , S and REEs are sought after products that have various applications in different industries.  $\text{CaCO}_3$  is a versatile material with numerous uses. Depending on its purity,  $\text{CaCO}_3$  can be used for acid mine drainage neutralisation and as additive in industries, such as cement, pharmaceuticals and ceramics. S as well is a raw material for many manufacturing companies in the likes of fertilisers, acid, steel and petroleum [13]. REE, which is a group of 17 elements divided into heavy (which are rare and have between 8 and 14 paired electrons) and light (which are abundant and have between 0 and 7 unpaired electron), has exceptional properties that makes it indispensable in the manufacturing of most of the modern technologies, such as renewable energy technologies, electronics, in petroleum, and in magnet industries [16–21]. The demand of REEs between the years 2020 and 2025 is projected to grow exponentially because of their considerably increased use in modern technologies and green energy sources [4, 21]. REEs production is limited to few countries with economically viable reserves whilst the rest of the world is dependent on them [22]. Exportation and pricing of REEs have been under Chinese control for over two decades [23]. For the fear of supply shortage or the abuse of monopoly power by producing countries, the search for new mines and alternative sources of REEs is highly encouraged [24]. REEs constitute 0.4% of phosphate rocks and are often rejected in majority (70 to 80%) together with the PG [7].

Therefore, dumping of PG without proper treatment constitutes both a serious environmental problem and economic loss. Environmental pollution particularly due to the presence of radioactive elements (U and Th) and other toxic substances that can be easily leached out when the material is exposed to different weathering conditions, and is a matter of serious concern because of its toxicity, persistence and potential to bio-accumulate [20, 25–27]. The deterioration of environmental quality caused by metal pollutants results in various lethal and chronic health challenges in living species that get exposed to them [27]. Economically, PG contains a wide range of chemical materials that can be beneficial if economically recovered. Thus, on the one

hand, it is a priority to find effective and economical ways to substantially reduce the amount of PG that is disposed on various land spaces to preserve lives and the environment. On the other hand, PG could constitute a potential secondary source of very important elements such as REEs [28, 29]. This would be environmentally and economically advantageous as there are limited natural resources from where REE could be mined. It also provides a means to mitigate overexploitation of such natural resources that could be at risk of exhaustion.

Irrespective of the various treatment procedures available to deal with PG, it is still up to date in majority dumped either along the coast or on spaces close to the production plants without any treatment and consequently is still an environmental problem [30, 31]. Only a small amount of PG (15%) is reported to be reused in the construction and agriculture industries. This is often attributed to the presence of different toxic and radioactive pollutants present in the PG [32]. This study aimed at tracing the behaviour of REEs throughout the process of converting PG to  $\text{CaCO}_3$  and S, assess the effects of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  used in the process of forming  $\text{CaCO}_3$  and S on the concentrations of REEs and also monitored and identified suitable leaching procedure for the quantification the amount of REEs in the formed residue.

## Materials and methods

### Description of PG source and PG sampling

The PG used in this study was collected from a fertiliser and phosphoric acid producing company in Phalaborwa, Limpopo Province, South Africa. This company uses fluoroapatite rocks as raw material to produce  $\text{H}_3\text{PO}_4$  through wet process. The produced PG is stocked in waste stacks in an open space close to the  $\text{H}_3\text{PO}_4$  factory. Phosphogypsum samples were collected at three different points on the waste stacks (on top, in the middle, and at the bottom of the PG stacks), mixed thoroughly and transported to the laboratory in sealed plastic bags for analyses.

### Conversion of PG to CaS and residue

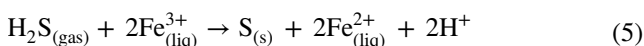
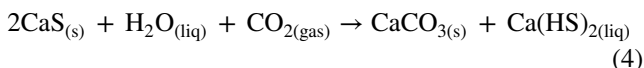
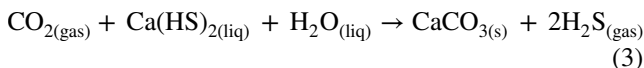
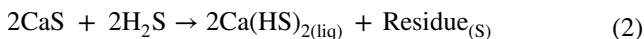
The collected PG was converted to CaS following a thermal reduction reaction. The main purpose of thermal reduction was to produce a suitable starting material for  $\text{CaCO}_3$  and S recovery as well as residue formation. In addition, this process removed both the water of crystallisation and some volatile impurities including the  $\text{CO}_2$  contained in the PG samples [10, 27]. The PG after dewatering was mainly made of  $\text{CaSO}_4$  (97.1 wt%) and  $\text{BaSO}_4$  (1.2 wt%) whilst the rest of impurities were in minimal concentrations not detectable by the instrument. They might be originating from the

contamination of PG with other neutralising agent. No effort was made in identifying their sources as they were in negligible amount and had no effect on the overall composition of the PG. Whilst other minor elements included REEs, Al, Th and others which were in low concentrations. Prior to the commencement of the thermal reduction process, the PG was first oven-dried for 4 h at 105 °C, thereafter it was thoroughly mixed with coal (containing no other elements except carbon (75 wt%),  $\text{SiO}_2$  (7.3 wt%),  $\text{Al}_2\text{O}_3$  (7.5 wt%), water (5.4 wt%) and volatiles (4.8wt%)) in a stainless steel stepped crucible in a ratio of 1-to-2.5 molar mass of PG: coal [33]. Second, the mixture was ground to finest particles possible using a mortar and pestle and sieved with a 0.57  $\mu\text{m}$  sieve to obtain good particle sizes, ensure sufficient surface area for a good reactivity and good enrichment of REEs by decreasing particle size. Finally, after grinding and sieving, the mixture was then placed in a furnace at 1100 °C for 1 h to allow the reduction reaction of PG to CaS to take place. Nitrogen gas ( $\text{N}_2$ ) was pumped into the furnace to remove oxygen before, throughout the reduction until the whole process was completed and the crucible removed from the furnace. Upon completion, the furnace was turned off and left to cool down to room temperature before taking the stainless steel stepped crucible out [33]. The formed CaS was thereafter kept in a desiccator for further analyses and use.

A portion of the formed CaS was processed to produce elemental sulphur,  $\text{CaCO}_3$  and a residue following the process as described: 100 g of CaS was weighed and dissolved in 900 mL of water in a 2.5 L glass container named as reactor A. This reactor A was rubber sealed with two holes on top. The first hole was used to allow the required gas ( $\text{H}_2\text{S}$ ) to flow inside the reactor A, and the second one was to allow a magnetic stirrer in which was used to stir the mixture at 500 rpm at room temperature.  $\text{H}_2\text{S}$  was continuously introduced into the reactor A at a flow rate of 450–1350 mL/min with the intent to solubilise CaS and form liquid calcium bi-sulphide ( $\text{Ca}(\text{HS})_2$  according to Eq. 2 [12]. This reaction was run for a maximum period of 10 min after which the formed  $\text{Ca}(\text{HS})_2$  was separated from the residue through filtration and transferred into the reactor B, which was also a rubber-sealed 2.5 L glass container with two holes on top as well. In this case, the first hole was for the introduction of  $\text{CO}_2$  in excess (at a flow rate of 450–1340 mL/min) via a plastic pipe which was connected to a  $\text{CO}_2$  cylinder in order to form  $\text{CaCO}_3$  following Eq. 3 [33], and the second one was to allow in a plastic pipe connecting the reactor B to reactor C. The  $\text{H}_2\text{S}$  (which is one of the products formed by a reaction between  $\text{Ca}(\text{HS})_2$  and  $\text{CO}_2$ ) released from the reaction taking place in Reactor B travelled through this pipe and was captured in Reactor C where there was a solution of iron (III) Sulphate. The  $\text{H}_2\text{S}$  was allowed to react with the ferric solution to form elemental sulphur as indicated in Eq. 5 [12]. Once enough precipitates were formed in reactors B and C,

the reactions were stopped, and precipitates ( $\text{CaCO}_3$  in reactor B and S in reactor C) were separated from the remaining solutions by filtration.

In another experiment,  $\text{CO}_2$  was used instead of  $\text{H}_2\text{S}$  in reactor A, and the reaction was allowed to take place as shown in the Eq. 4 [10]. In this instance, both  $\text{CaCO}_3$  and  $\text{Ca}(\text{HS})_2$  were formed and separated from the residue:



All the above reactions were successfully achieved at room temperature. The only parameters monitored were the concentration of the reactants and those of the products formed. A schematic presentation of the experimental procedure for the study is shown in Fig. 1

The residue,  $\text{CaCO}_3$  and S were filtered from their respective solutions, washed with deionised water and oven-dried at  $105^\circ\text{C}$  for 72 h. The dried residue and PG as well as the formed CaS were digested using both a microwave digester (CEM Corporation, MARS 240/50 Mathews, NC, USA) and traditional acid leaching for REEs identification and quantification. Digesting solvents were made up of mixing diverse concentrations and combinations of sulfuric and hydrochloric acids. This was conducted with the intent to achieve an effective release of REEs from all solid samples for their consecutive quantification [3, 34]. In an endeavour to recover more  $\text{CaCO}_3$  and S from CaS and facilitate

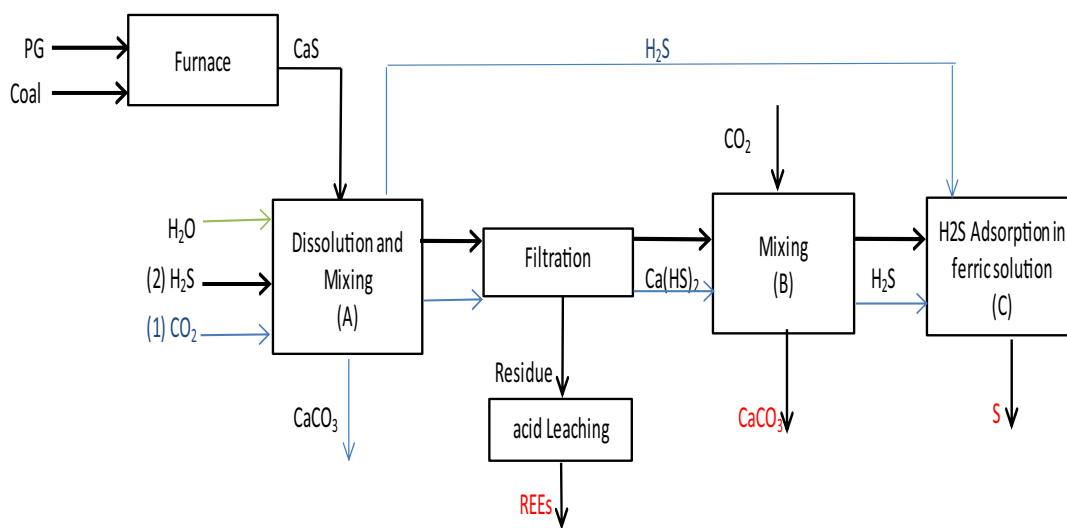
possible REEs recovery from the residue, the amount of some impurities was reduced.

### Characterisation of PG, CaS and residue

The PG, CaS and the residue were characterised prior to the determination of the REEs. A portion of the PG collected from the  $\text{H}_3\text{PO}_4$  factory, was weighed and oven-dried and the determined percentage was found to be 26.67%. All samples were dried and ground to fine particles for characterisation.

Samples excluding  $\text{CaCO}_3$  were analysed using a PANalytical X'Pert Pro powder diffractometer in  $\theta$ – $\theta$  configuration using an X'Celerator detector and variable divergence and fixed receiving slits with Fe-filtered Co– $\text{K}\alpha$  radiation ( $\lambda = 1.789 \text{ \AA}$ ). The sample percentage compositions were estimated using the Rietveld method in percentage form.  $\text{CaCO}_3$  allotropic forms as well as S XRD analyses were reported in studies previously carried out by Ruto et al. [33], De Beer et al. [15] and Masukume et al., who used the same procedure and PG to form them [12]. They were all satisfied with the quality of the  $\text{CaCO}_3$  and S obtained from this very same process. X-Ray diffraction (XRD) analyses were carried out to ascertain the crystal structure of the three sample types. The main reason of characterising the residue, which is not a product but a left over from the reaction (2), was to prove that the reaction between CaS and  $\text{H}_2\text{S}$  was not left to completion but was stopped. This is why it was necessary to determine if there were CaS crystals in it. The samples were prepared according to the standardised Panalytical back-loading system, which provides nearly random distribution of the particles. The phases were identified using X'Pert Highscore plus software.

For the morphology of the PG, CaS and residue, each sample was powdered and separately mounted onto the



**Fig. 1** Process flow chart for the study for the recovery of  $\text{CaCO}_3$ , S and REEs from PG

sample holder of a JEOL JSM – 7500F scanning electron microscopy and energy-dispersive spectroscopy (SEM–EDS) using carbon tape. To obtain cross-sectional images of the particles, the powdered samples were embedded in an epoxy resin and polished after which they were coated with gold to ensure that they were able to conduct electricity. Transmission electron microscopy (TEM) analyses were conducted using JEOL JEM-2100 electron microscope, Hitachi, Tokyo, Japan to examine the nature and structure of all solid samples at a higher resolution to better identify the REE elemental mapping. Sample particles were dispersed onto the holey carbon film supported by the 200-mesh TEM grid and analysed as prescribed by in the user manual.

## Chemical analysis

### Percentage composition of CaS

The percentage composition of CaS was important to be determined in order to confirm the reduction of PG to CaS. This was achieved by analysing both the sulphide and CaS percentage. Sulphide was quantified using the standard iodometry method where 500 mg of CaS was transferred into a 100 mL volumetric flask and filled to the mark with water. An aliquot of 10 mL from the previous prepared mixture was transferred into a conical flask in which 10 mL of standard iodine (0.1N) solution was added as well as 50 mL of deionised water. The solution was acidified with 2 mL of 50% HCl solution. The titration of the prepared solution was conducted with a solution of 0.1 N sodium thiosulphate using starch as an indicator to a colourless end point [35]. The CaS percentage was calculate as described in Eq. 6.

$$\% \text{ CaS} = [(V_{\text{Iodine used}} - \text{Titration volume}) \times 36] / \text{sample mass (mg)} \quad (6)$$

### Determination of REE in PG, CaS and residue

This study focussed on REEs that could be determined with acceptable level of accuracy using an inductively coupled plasma optical emission spectrometer (ICP-OES). Weighed portions of CaS, PG and residue were leached in different concentrations and combinations of H<sub>2</sub>SO<sub>4</sub> and HCl traditionally, and using a microwave digester. Moreover, these acids have been widely used for the release of metallic ions from solid samples in several studies [3, 23]. The concentrations of the acids used were 0.1; 0.5; 1; 5 and 9N. The concentrations of the acids used were varied to study the effect of solvent concentration on the extraction of REEs from the samples. Precisely 5 g of each sample was accurately weighed into a 250 mL beaker and 100 mL of acid were added. The solid–liquid ratio of 1:20 used in this study

was in accordance with recommendations made from optimization studies carried out by Ruto et al. [33] and Masukume et al. [12]. The digestion time was 30 min and mixing was done at 555 rpm to keep suspended solids dispersed. Thereafter digestion, the digest was filtered and the filtrate analysed for REE using an ICP-OES. The ICP-OES conditions were set as recommended by the manufacturer.

Microwave digestion of PG, CaS and residue was also carried out using two sets of acid combination to determine which one was more effective on recovering REEs from the samples. The first combination (A) was made of 6 mL of hydrochloric acid and 2 mL of nitric acid which is aqua regia that has been used in previous studies. The second combination (B) was the opposite of the first one where 6 mL of HNO<sub>3</sub> were mixed with 2 mL HCl. Exactly 1 g of each sample was weighed into microwave vessel, either the combination A or B of solvent was added before sealing the vessel and placing it into the microwave. The microwave was ramped up to 180 °C over a period of 20 min and held at this temperature for a time of 20 min. The microwave power during digestion was set at 50% (400 KW). After digestion, the sample vessels were left to cool down to room temperature and the digests transferred into 25 mL volumetric flasks and made up to volume with de-ionised water. All samples were filtered prior analysis.

### Quality control and quality assurance

All acids used in this study were of analytical grade unless otherwise stated. Reagent preparation was done using deionised water. Spiked recoveries were used to assess the accuracy and precision of the method used for digestion and instrument set-up [36]. The percentage recoveries obtained after spiking with 2.5 mg/L multi-element REEs standards ranged from 92 to 99.9% (Table 1). Lowest recoveries were those of Y and Pr, whereas the highest was that of Ce. The recoveries were considered satisfactory and the method was further used to determine REEs concentrations in different samples. The wavelengths used were in accordance with those applied when determining REEs in geological samples by ICP-OES [37].

## Results and discussion

### Characteristics of PG, CaS and residue

The XRD results of PG, CaS and the residue are shown in Fig. 2. These results indicated that the PG was a mixture of dehydrate (87 wt%), hemihydrate (5 wt%) and anhydrous (8 wt%) calcium sulphate. This revealed that oven drying of PG could not exhaust all crystallisation water molecules it contained. The reduction of PG to CaS was successfully

**Table 1** Spike recoveries for REEs in a 2.5 mg/L geological sample

REEs	Recovery (%)	Wavelength (nm)
Ce	99.9	418.660
Pr	92.8	417.939
Nd	98.5	430.358
Sm	95.7	360.949
Eu	97.8	381.967
Gd	98.3	335.048
Dy	94.4	353.170
Ho	96.8	345.600
Er	93.9	390.631
Tm	95.8	313.126
Yb	97.2	328.937
Lu	98.6	261.541
Y	92.9	371.030
Sc	94.4	361.384
La	95.3	398.812

(95%) achieved as the XRD results indicate CaS as the main component in the formed CaS sample (Fig. 2). Furthermore, this was confirmed as the calculated percentage CaS obtained using Eq. (5). As for the formed residue, results showed that it was mainly made of CaS (Fig. 2). This was as a result of the fact that the reaction in reactor A was not left to completion purposely as the intention was to form a residue which can be further processed in order to recover REEs. No REE mapping was detected in the samples using XRD possibly because of their low concentration.

The PG particles crystal structures were a mixture of large and small particles as indicated in Fig. 3. The morphology or shapes found in PG correlated with those reported in PG from Alberta, Canada, and this could probably be attributed to the similarities in the formation process [3]. The PG used was having a rhombohedral shape. There was an observed difference in the shapes of PG and the formed CaS as shown in the SEM images in Fig. 3. This is surely due to the reduction reaction that took place. The smaller particle size of the formed CaS indicates the thermal reduction process decreased the particle size and distorted the shape of the particles [38]. The residue did not show any precise shape probably because of the reactions it went through in reactor A. The EDS did not register any of the REEs in all samples. Elemental mapping for CaS and residue is shown in Figs. 4 and 5, respectively, and the results presented in these figures indicate the presence of major elemental components including carbon, oxygen, aluminium, sulphur and calcium.

TEM analysis was conducted to investigate the structure and nature of PG, CaS and residue at higher resolution and the results obtained are shown in Fig. 6. PG particles were seen to be a mixture of dispersed small and big rhombohedral structured particles, whilst those of CaS and residue

were agglomerated and predominately very fine particles of a desultory structures. Through SEM and TEM, REEs were hardly detected because of their lower concentration, which made it hard to examine their behaviour. The behaviour of REEs was therefore monitored using the ICP-OES after complete leaching of sample followed by the subsequent analysis of liquid samples.

## Concentration of REEs in samples using manual extraction

### Concentration in PG samples by traditional leaching

The concentrations of Heavy Rare-Earth Elements (HREEs) were either low (Dy, Er and Y) or below the limit of detection (LoD) (Ho, Tm, Yb and Lu) as indicated in Table 2. The highest concentration of HREEs detected when leaching PG with  $H_2SO_4$  was that of Y, followed by Er, whilst Dy had the lowest concentration. Therefore, the PG used could not be considered suitable for HREEs recovery. On the contrary, Light rare-earth elements (LREEs) were found in higher concentrations than the HREEs irrespective of the type of leaching agents used and their different concentrations (Table 2).

The maximum concentration of REEs in the PG was obtained when 5N of  $H_2SO_4$  was used as more PG was possibly dissolved and consequently more REEs released. Using  $H_2SO_4$  at concentrations higher than 5N resulted in fewer amounts of REEs extracted as reflected by the decrease in REEs concentrations in the 5N digests (Table 2). This could be attributed to the increasing concentration of  $SO_4$  ions which could have led to common ion effect resulting in the shift of the chemical equilibrium towards reducing its amount as per Lechatelier's principle.

In the case of HCl, 9N extracted the maximum REEs concentrations in the PG and could be considered the optimal concentration for the leaching of REEs at room temperature with HCl. The concentrations of REE obtained with 9N HCl were higher than those obtained when the same samples were digested with 5N  $H_2SO_4$ . This might be attributed to the absence of common ion effect when HCl is used to leach PG. Therefore, increasing the concentration of HCl up to 9N cannot obstructs the leaching reaction of PG. Thus, a solution of 9N HCl appeared to be a suitable leaching agent for PG at room temperature. Preference is often given to  $H_2SO_4$  as far as extraction of REE from PG is concerned because it is more affordable than HCl, but results from this investigation have indicated that HCl extracted REE much better from PG than  $H_2SO_4$  at room temperature.

The PG used in this study was, irrespective of leaching agent and method used, richer in LREEs (Ce, Pr, Nd and La) than HREEs when compared to what was reported by [7] and [39] in their studies of Tunisian and Canadian PG,

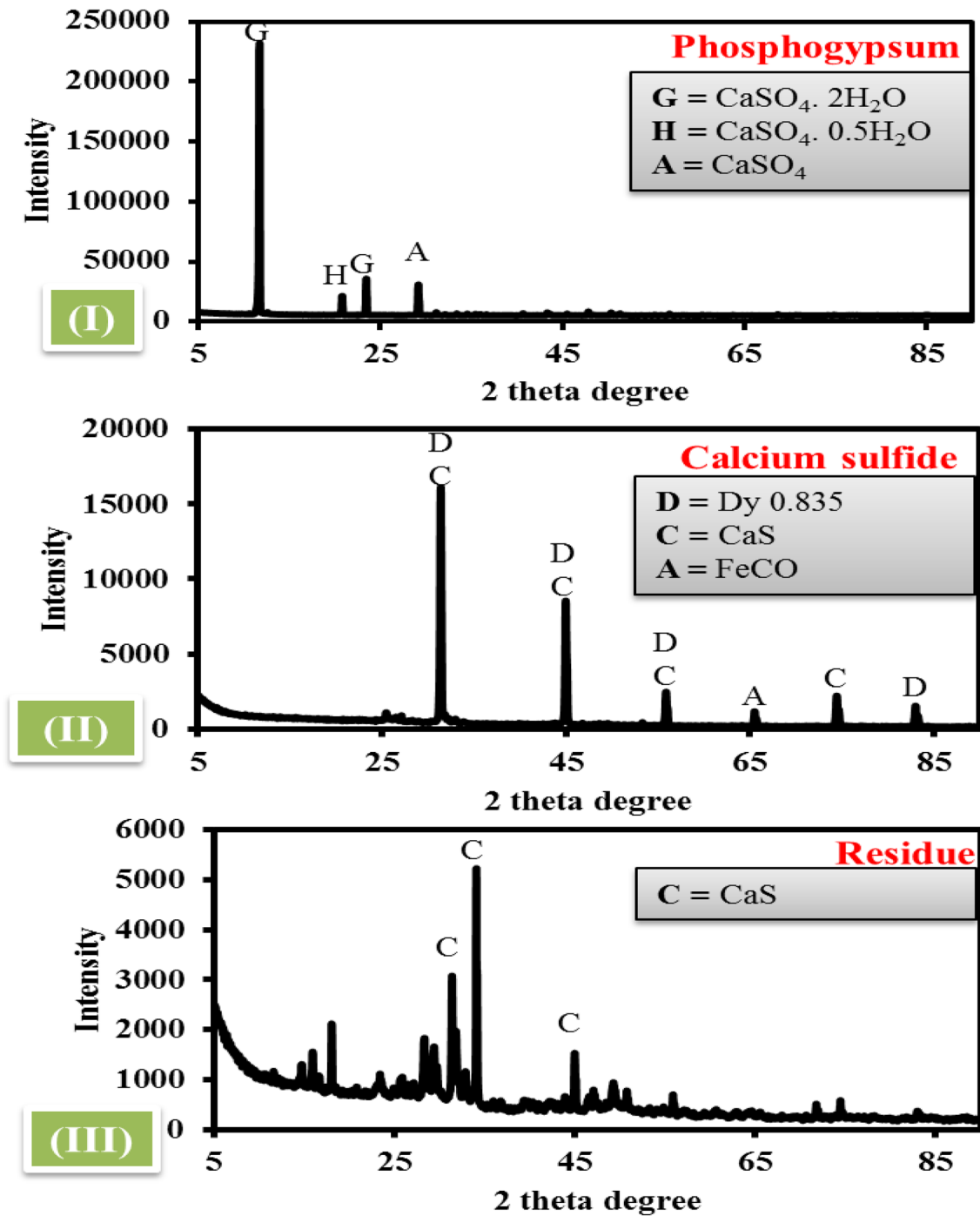
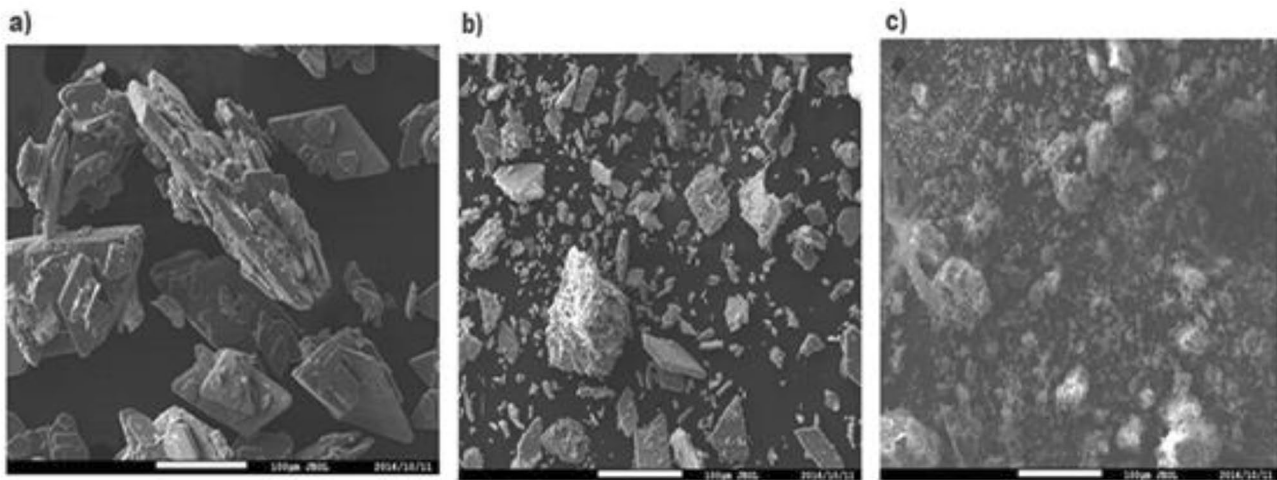


Fig. 2 X-Ray diffraction pattern of PG as received, CaS and residue

respectively (Fig. 7). This could be showing that the South African phosphate ores used to generate PG could contain more REEs than the Tunisian and Canadian PG. Thus, the PG is worth the investigation for a possible recovery of REEs. More studies are however needed to confirm this as the chemical composition of phosphogypsum from these countries has not been reported.

### Concentration of REEs in CaS by traditional leaching

The concentrations of REEs in CaS were slightly higher than those in PG (Table 3). This might be attributed to the elimination of moisture and other volatile impurities as the PG was subjected to a thermal reduction for its conversion to CaS. The capacities of the acids used to extract REEs from



**Fig. 3** SEM images of the **a** as received PG **b** produced CaS and **c** produced residue

CaS were similar to what was observed with PG. The concentrations of LREEs in the CaS samples were also higher than those of the HREEs. Worth noting is the fact that REEs were not leached from CaS by 0.1N  $H_2SO_4$ .

Since REEs seemed to be trapped in the CaS, the detection of REEs is strongly dependent on the dissolution of CaS particles. Optimum concentration of extracting REE from CaS using  $H_2SO_4$  was 1N where the detection of more HREEs was observed compared to what was obtained for PG. Beyond this concentration, there was a decline in REE content as shown in Table 3. This is very different from what was observed with PG. Leaching CaS with different concentrations of HCl revealed a correlation between the concentration of REEs and that of the leaching agents. Rare-earth elements concentrations proportionally increased with the increase in the concentration of HCl solutions. A solution of 9N HCl extracted the highest concentration of REEs and can be considered as the optimal leaching acid concentration when using HCl. This is possibly due to the fact that more CaS were dissolved at this concentration resulting in the extraction of more REEs.

### Concentration of REE in microwave digested samples

#### Microwave digestion of PG, CaS and residue

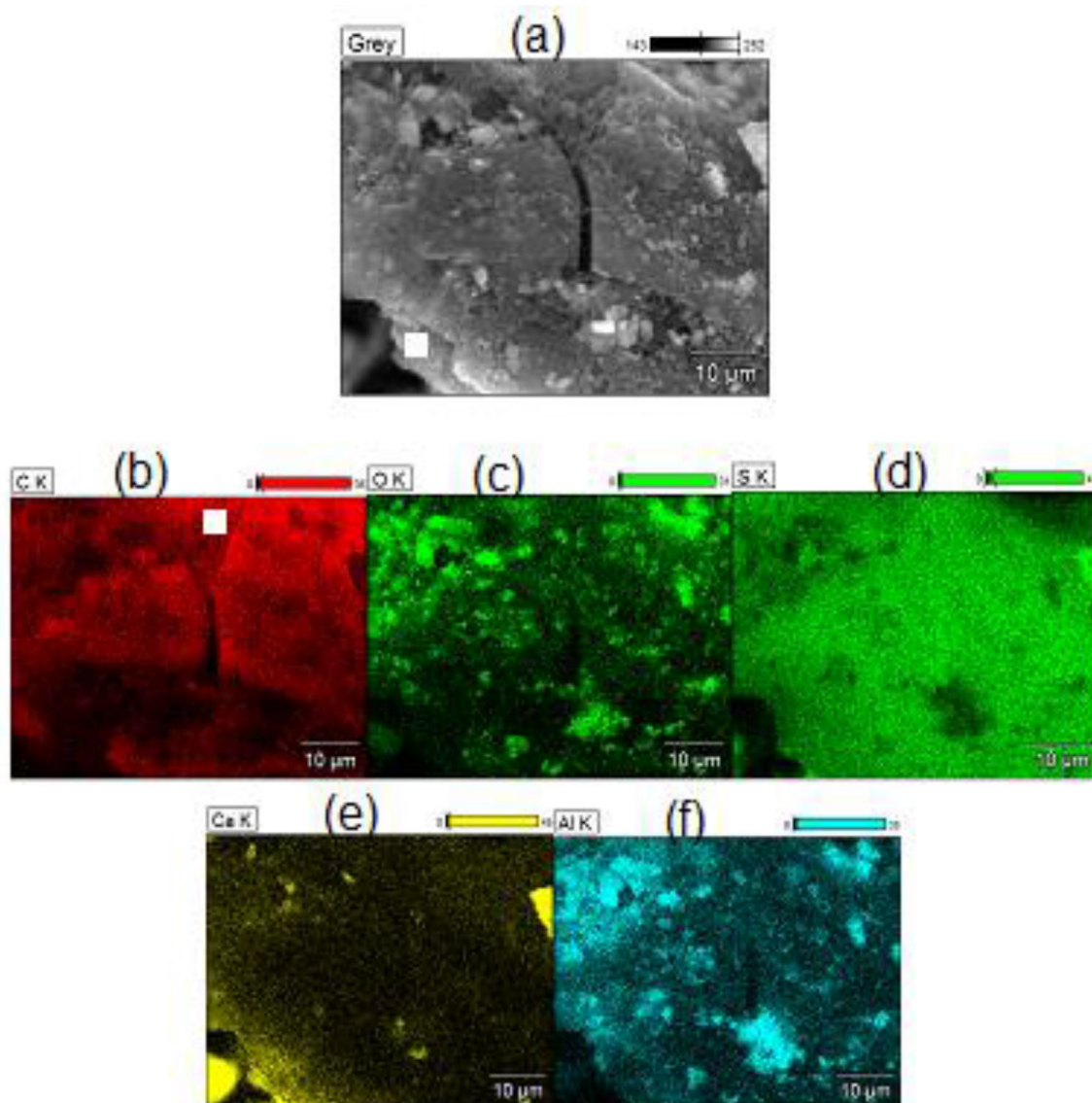
Microwave digestion resulted in higher concentrations of REE in the samples compared to what was obtained with traditional digestion. Table 4 provides the concentrations of REEs ( $\mu\text{g/g}$ ) in PG, CaS and residue after microwave

digestion. It was observed based on the obtained concentrations of REEs that the second acid combination (B) was the most efficient in digesting all the samples. The combination B led to higher amount of REEs probably because it best leached all the samples. In general, the concentration of REEs in the residue was more or less similar to what was obtained in the PG though CaS had higher amounts of REEs. Some amounts of REEs must have been lost during the processing of CaS to  $CaCO_3$  and S when the concentrations of REEs in  $CaCO_3$  and S was compared with what was obtained in CaS and the residue (Fig. 8).

The residue could constitute a potential source of REEs since it retained a good part of the concentration of most of these elements. The processing of PG to CaS and later a residue had little impact on the concentration of REEs when comparing what was previously observed in the PG to what has been left in the residue, except for Pr where a decrease in concentration of 4.6% was observed. However, when looking at REEs concentrations in CaS prior to its processing to  $CaCO_3$  and S and what was left in the residue, there was a decrease in REEs concentration understandably because some might have been lost in the process. Figure 8 reflects the percentage REEs concentration difference between the residue and CaS.

These results revealed that the majority of REEs concentrations decreased by less than 40%. Except for Sc and Ho where a decrease in concentration of above 40% and 100% were respectively observed. Due to their low concentrations in CaS, they were mostly affected by the processing of CaS to  $CaCO_3$  and S. This process could be economically advantageous as more substances can be





**Fig. 4** Morphology of PG particles from which STEM/EDS elemental maps were obtained: (a) SEM result of PG (b–f) elemental maps for Ca, Nd, S, Y and P

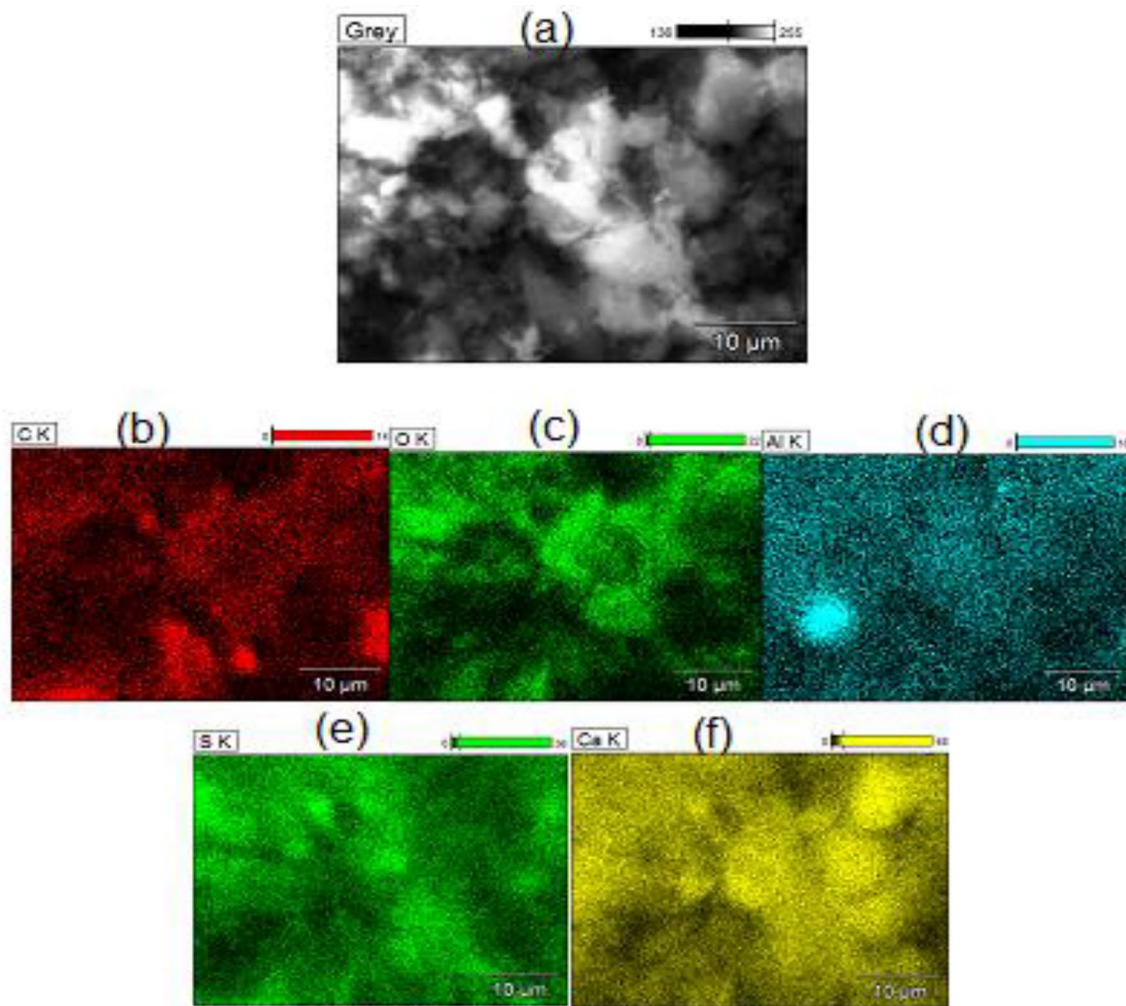
recovered and REEs could still be recovered from a residue that is easily leachable and contains lesser impurities than those in the raw PG.

#### Concentrations of REE leached out from CaS by $H_2S$ and $CO_2$

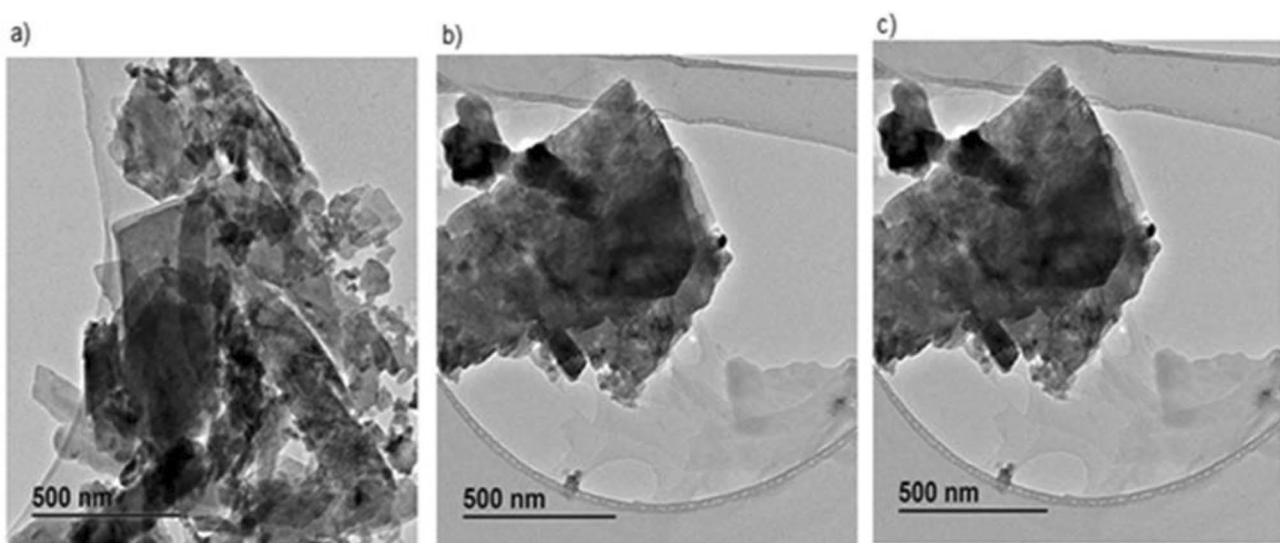
Hydrogen sulphide and  $CO_2$  gases were separately tested by reacting them with CaS in the process of sulphur and  $CaCO_3$  production to see if any REEs contained in the CaS were leached out at this stage of the process. Solutions

were collected after reacting CaS with both  $H_2S$  and  $CO_2$ , filtered and analysed for REEs concentration. The obtained results are shown in Fig. 9. Results indicated that Ce, Pr, Nd, Sm, Gd and La were leached during this process as they were detected in the leachate of CaS. The remaining REEs could not be detected. This could be attributed to either the little effect that both gases had on them or their minimal concentrations that were below the detection limit of the equipment used.

Both gases leached out more or less the same amount for the majority of REEs, except for Ce, Nd and Gd which



**Fig. 5** Morphology of CaS particles from which STEM/EDS elemental maps were obtained: (a) SEM result of CaS (b–f) elemental maps for Ca, Nd, P, S and Y

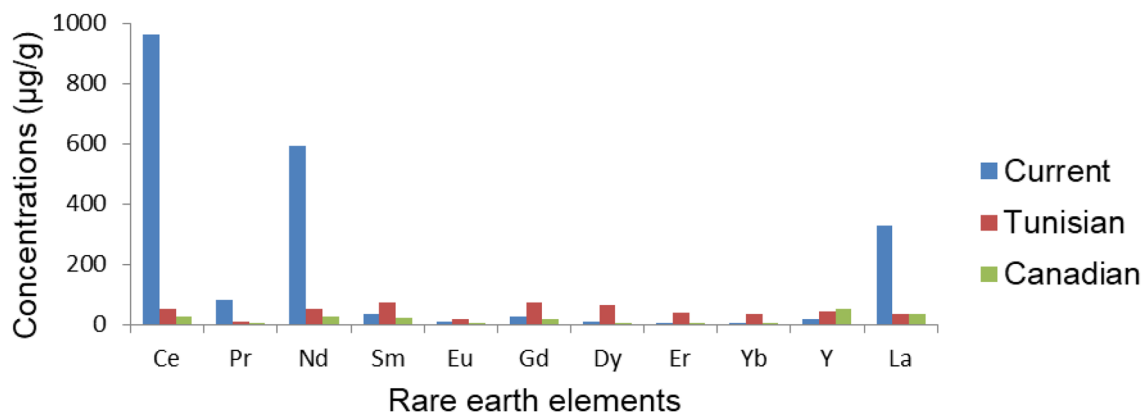


**Fig. 6** TEM images of a) as received PG b) produced CAS and c) produced residue

**Table 2** Concentrations ( $\mu\text{g/g}$ ) of REEs in the PG sample

REEs	$\text{H}_2\text{SO}_4$ (N)					HCl (N)				
	0.1	0.5	1	5	9	0.1	0.5	1	5	9
Ce	32.5	200	209	485	186	75.5	230	197	964	773
Pr	4.49	29.5	30.3	46.9	12.8	14.4	26.5	39.4	79.5	109
Nd	21.1	112	115	271	55.6	53.8	94.6	107	591	414
Sm	3.03	21.8	22.1	34.6	6.67	6.39	16.0	14.4	33.1	69.3
Eu	0.458	3.81	4.04	6.11	1.17	2.23	3.49	5.80	9.06	21.7
Gd	2.46	13.2	13.2	18.0	4.66	7.11	11.5	15.9	24.9	57.9
Dy	0.825	4.32	4.13	5.67	1.67	3.08	4.75	6.07	10.0	22.4
Ho	nd	nd	nd	nd	nd	nd	nd	Nd	0.15	2.45
Er	6.04	14.3	6.80	6.15	6.90	9.70	0.379	4.76	5.27	13.5
La	16.2	71.0	115	115	80.2	37.4	58.2	83.8	327	376
Yb	nd	nd	nd	nd	nd	0.483	0.379	0.37	0.38	0.922
Y	7.17	13.4	12.9	14.6	8.32	16.1	14.1	16.1	15.7	42.3
Sc	nd	0.160	nd	0.205	nd	0.093	0.43	1.10	2.21	6.15

nd not detected

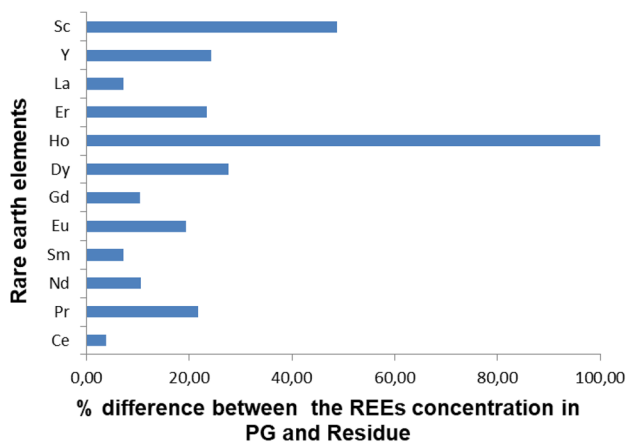
**Fig. 7** Comparison of the concentration of REEs in the PG used in the current study to those from Tunisia and Canada**Table 3** Concentrations ( $\mu\text{g/g}$ ) of REEs in the CaS sample

REEs	$\text{H}_2\text{SO}_4$ (N)					HCl (N)				
	0.1	0.5	1	5	9	0.1	0.5	1	5	9
Ce	nd	8.52	749	435	96.7	4.44	22.3	56.0	1893	2728
Pr	nd	3.58	99.7	48.0	10.2	5.18	14.2	28.8	287	471
Nd	nd	13.7	434	230	38.6	40.4	67.9	119	1216	1665
Sm	nd	3.80	115	37.0	4.04	3.60	10.3	26.6	218	338
Eu	nd	Nd	22.5	8.75	0.919	nd	0.673	2.12	36.8	32.7
Gd	nd	Nd	83.4	29.7	3.56	nd	0.797	7.09	115	89.9
Dy	nd	0.477	30.6	10.9	1.09	nd	1.21	3.81	48.7	33.6
Ho	nd	Nd	4.21	0.727	nd	nd	0.202	1.77	nd	5.54
Er	nd	0.754	37.6	24.3	14.9	1.49	2.98	5.57	36.0	24.7
Tm	nd	Nd	0.242 $\pm$	nd	nd	nd	nd	0.022	nd	0.595
Yb	nd	Nd	1.46	0.142	nd	0.054	0.149	0.315	2.02	1.53
Y	nd	Nd	81.4	31.0	6.51	nd	0.205	2.70	92.2	72.1
Sc	nd	Nd	3.19	0.831	nd	nd	nd	0.179	6.48	9.69
La	nd	Nd	429	200	71.0	3.10	6.46	13.9	669	933

nd not detected

**Table 4** Concentrations ( $\mu\text{g/g}$ ) of REEs in PG, CaS and residue after microwave digestion

REES	PG		CaS		Residue	
	A	B	A	B	A	B
Ce	2385	2580	2599	2746	2213	2641
Pr	363	391	427	476	397	373
Nd	1808	1937	2090	2255	1741	2018
Sm	268	289	299	320	255	297
Eu	41	47.5	53.6	60.5	38.8	48.8
Gd	303	320	343	376	296	337
Dy	43.8	55.4	65.9	79.8	60.2	57.8
Ho	nd	nd	nd	1.24	nd	Nd
Er	79.8	66.3	508	476	417	365
La	889	987	1144	1185	940	1101
Y	200	235	256	318	258	241
Sc	5.42	9.97	19.4	24.6	17.9	12.6

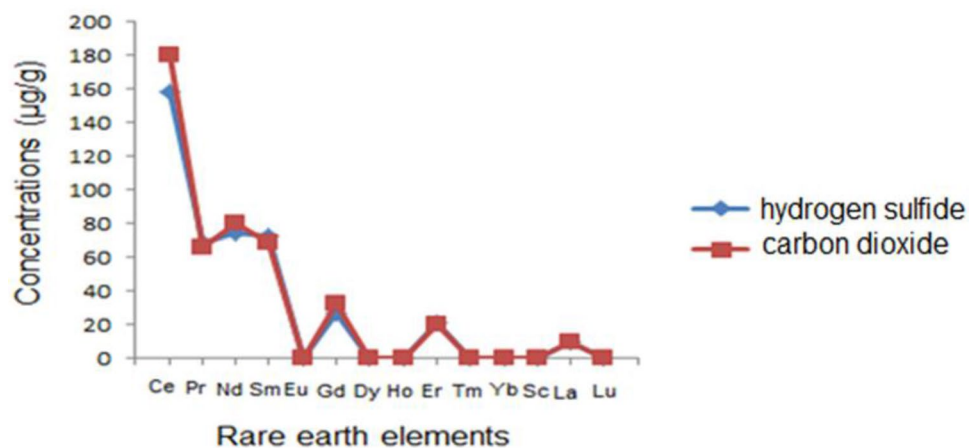


**Fig. 8** %REEs concentration difference between PG and residue

were more affected by  $\text{CO}_2$  than  $\text{H}_2\text{S}$ . Thus, in view of these findings, if the residue is to be used for REEs recovery after CaS processing, it will be preferable to use  $\text{H}_2\text{S}$  in place of  $\text{CO}_2$  gas [40].

The outcomes of this study have provided a scientific evidence to use this process as a possible way of recovering multiple products from readily available PG. In view of the presented results, it can be said with maximum conviction that the residue could constitute a better raw material for the recovery of REE than the raw PG given the amount of REEs, the ease of leaching, and reduction in the amount of impurities [41]. Maximising the recovery of REEs from readily available by-products could assist in mitigating excessive exploitation of little available natural resources and minimise both pollution and cost involved with REEs mining. The amount of PG occupying land space is concerning especially if nothing is done about it. Converting it to useful products

**Fig. 9** Dissolution of REEs during reactions with  $\text{H}_2\text{S}$  and  $\text{CO}_2$  after 30 min



through a viable economic treatment process would substantially assist in reducing the amount of PG waste [39].

## Conclusion

The processing of converting PG to CaS could be beneficial for the recovery of multiple products which is economically advantageous. The conversion process of CaS to CaCO<sub>3</sub>, S and a residue showed that most REEs previously in the PG are left in the residue from where it could be easily leached. Both CO<sub>2</sub> and H<sub>2</sub>S gas had an impact on the concentration of REEs. However, Ce, Nd and Gd were mostly affected by CO<sub>2</sub> than H<sub>2</sub>S as their concentrations were 40% reduced. Thus, the use of CO<sub>2</sub> can be recommended when REEs are to be recovered at a later stage of PG conversion to CaCO<sub>3</sub>. Recovery of REEs from the obtained residue is advantageous as it is easily leachable and contains lesser impurities than the raw PG. The finding of this study has indicated that the residue (with Ce as highest concentration 2641 µg/g and Sc with lowest concentration of 12.6 µg/g) that is left after processing of PG to CaCO<sub>3</sub> can be further processed to recover REEs. The overall process of PG conversion to CaCO<sub>3</sub> had minimal effect on the REE content.

**Acknowledgements** The authors wish to acknowledge the following organisations for financial support and/or technical/scientific input: Tshwane University of Technology, The University of South Africa and ROC water technologies.

**Author contributions** Conceptualization, JM and NNC; Methodology, JM and NNC; formal analysis, NNC, RM and JP; writing—original draft preparation, NNC; writing—review and editing, VNJ, RM and JP; supervision RM, JP and VNJ, Funding acquisition JP and RM. All authors have read and agreed to the published version of the manuscript.

**Funding** Open access funding provided by University of South Africa.

**Data availability** The authors confirm that the data supporting the findings of this study are available withing the article.

## Declarations

**Conflict of interest** The authors declare that they have not known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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