



High Valuable Materials from Phosphogypsum and Carbon Dioxide

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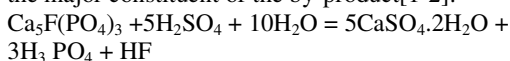
Abstract

Recycling of waste materials resulting from industrial activity, such as phosphogypsum (PG) released during production of phosphoric acid, proved to be economically feasible. Technologies for the management of (PG) Ca-rich waste into useful products became a hot-spot study. Although carbon dioxide and calcium rich waste constitutes a problem but they can be used for the production of calcium carbonate. This paper summarizes a physical and chemical method for the utilization of phosphogypsum to produce five valuable products, such as, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, K_2SO_4 , $\text{Ca}(\text{OH})_2$, $(\text{NH}_4)_2\text{SO}_4$, and CaCO_3 from phosphogypsum (PG). These chemicals are used as catalyst, fertilizers and basic chemicals for food and chemical industries. Results show that Merseburg process is a promising method for the consumption of (PG) as by-product as well as a minimizer for CO_2 emissions. This was done by the capture of carbon dioxide gas during the production of calcium carbonate which reduce CO_2 emissions and impair further CO_2 gas release. The five products obtained were characterized physically and chemically using XRF, XRD, SEM, and EDX analysis. This study supports efficient, safe, environmentally friendly and High-Value materials from two problematic hazard waste phosphogypsum (PG) and Carbon dioxide CO_2 .

Keywords: Phosphogypsum, carbon dioxide, calcium carbonate, Fertilizer, calcium sulphate, Merseburg carbonation;

Introduction

In The near future resources will be more limited according to high demand for both food and energy. Therefore, industrial wastes and by-products has gained increasing importance nowadays. Phosphoric acid is produced from H_2SO_4 reaction with phosphate rocks as slurry which is filtered to give phosphoric acid and phosphogypsum (PG), where $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the major constituent of the by-product [1-2].



Phosphogypsum (PG), may be used in agriculture sector after being treated chemically and physically, it can be also used as raw material in road materials and construction materials [3,4]. Chemical industry mainly using purified (PG) to prepare chemical

substances after purification and replacement. (PG) is mainly converted into other forms of sulphur, ammonium sulphate, potassium sulphate or calcium sulphate. (PG) can generate ammonium sulphate under acidic conditions which is mainly used as fertilizer [5,6]. (PG) can be dispersed in alkaline potassium hydroxide solution and then absorbs carbon dioxide to produce by-products such as alkaline potassium sulphate and calcium carbonate [6]. Phosphogypsum have high calcium content to produce a high yield of CaCO_3 . The homogenous particle size distribution and relatively low particle size of (PG) provide energy consumption by excluding extra mining operation processes including crushing or grinding [7,8].

Acidolysis based on source removal and direct removals based on (PG) post-treatment are two main

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EJCHEM use only; Received date 02 January 2024; revised date 07 May 2024; accepted date 02 June 2024

DOI: 10.21608/EJCHEM.2024.258288.9130

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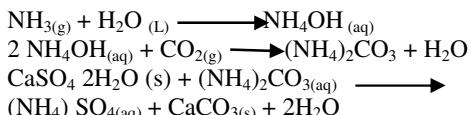
ways to remove impurities from phosphogypsum [9]. The physical treatment method is used to remove soluble impurities and organic matter, this include washing with water, flotation, ball milling, screening and aging processes [10]. Physical method depends on mechanical movement, washing, stirring through the physical interaction to get rid of impurities. No chemical reactions are involved.

Chemical methods for (PG) treatment rely on the addition of some chemicals to transform the impurities to a precipitate or soluble compounds at the end of the reaction. Then (PG) is obtained with stable quality and low organic matter content [11]. The main composition of (PG) is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (more than 90%) so it is economically possible to use (PG) as an alternative raw material in a variety of applications. Researches prove that (PG) is used safely in soil stabilization or as an agricultural fertilizer after purification [12,13].

Ammonium sulphate is widely used as nitrogenous fertilizer and its global consumption growth is estimated to increase by 25% by year 2050. The products of Merseburg process are suitable for many industrial applications in addition to their economic value. Calcium carbonate is also a multipurpose chemical used in various industries such as, paints, rubbers, textile, adhesives, plastics and cement [14]. The ammonia-carbonation reaction of gypsum with ammonium carbonate to produce ammonium sulphate is known as Merseburg process. This process is mainly composed of absorption, conversion, filtration, and evaporation crystallization processes. $(\text{NH}_4)_2\text{CO}_3$ is prepared by the absorption of CO_2 into NH_4OH solution, followed by a conversion reaction between $(\text{NH}_4)_2\text{CO}_3$ and (PG). Filtration of the product is conducted to separate the cake (CaCO_3) and the filtrate $(\text{NH}_4)_2\text{SO}_4$ solution, which is obtained as crystals by further evaporation [14]. Merseburg overall reaction is as follows:



$(\text{NH}_4)_2\text{CO}_3$ is obtained by the reaction between ammonium hydroxide (NH_4OH) and carbon dioxide (CO_2), as follows:



The regular consumption of phosphogypsum helps in increasing the demand for ammonium sulphate and reduce CO_2 emissions. The carbonation process allows the capture of carbon dioxide as stable solid carbonates, hence preventing further carbon dioxide gas release [16]. This work indicates that (PG) has

efficient, safe and environmentally friendly uses, such that, the produced fertilizer would not pollute the soil with rare earth elements.

Experimental

Materials

Phosphogypsum (PG) by-product from Egyptian Fertilizer industrial complex was used as a Ca-rich waste in a solid form. Management of CO_2 gas and Ca-rich (PG) waste to produce calcium carbonate suitable for sale is an interesting idea. All chemicals and reagents used are pure grade.

Methods

The physical and chemical treatments of (PG) aimed to get rid of a serious environmental hazard and to transform this waste to valuable products that can be sold as shown in Fig (1) and Fig(2). Using technology management for recycling (PG) helps to decrease carbon dioxide emissions and reduce pollutants as serious environmental hazards.

The technologies adapted in this work are carried out at normal temperature and pressure (NTP). Compounds produced from this technology such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 , K_2SO_4 , $\text{Ca}(\text{OH})_2$, and $(\text{NH}_4)_2\text{SO}_4$ are economically valuable.

The experimental methods are illustrated in the following sections A, B, C, and D-Merseburg method. The (PG) and products were subjected to XRF, XRD, SEM, and EDX Analysis to study the physical and chemical properties.

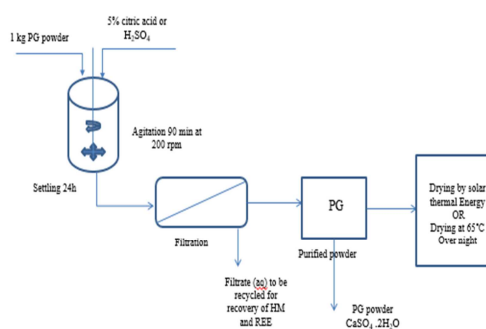


Figure 1: Schematic diagram for physical post-treatment of (PG)

A. Preparation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ from phosphogypsum (PG):-

Purifying the (PG) powder with H_2SO_4 allows its transformation into valuable products such as $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ used as solid catalyst by using acidic leaching [18]. It also limits the impurities of (P_2O_5) and fluorine in gypsum for further use in cement industry.

To decrease the damage in (PG) structure, the pre-treated (PG) with citric acid is preferred Fig (2).

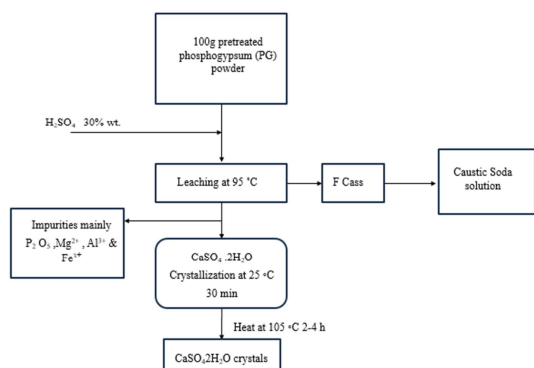
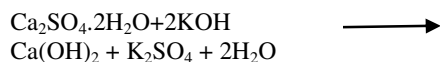


Figure 2: Schematic diagram for crystalline calcium Sulphate

B. Preparation of K_2SO_4 and $Ca(OH)_2$ from phosphogypsum (PG):-

Add 10 g of $[CaSO_4 \cdot 2H_2O]$ to 70 ml distilled water, stir with a magnetic stirrer at room temperature. Then add (KOH) to reach an (OH: Ca ion) molar ratio of (2:1). Continue stirring with magnetic stirrer for 1-3 h, until the formation of two phases. Filter and dry the solid yield at $60^\circ C$ to obtain $Ca(OH)_2$. The liquid will be evaporated at $80^\circ C$ to obtain K_2SO_4 , used as a fertilizer according to the following equation:



The reaction shows the preparation of potassium sulfate and Portlandite (Portland cement).

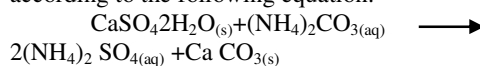
C. Preparation of $CaCO_3$ and $(NH_4)_2SO_4$ using Merseburg Method:-

10 g of $CaSO_4 \cdot 2H_2O$ is added to 400 ml potassium hydroxide according to molar ratio (stoichiometry) of (OH: Ca^{2+}) (2:1). Using a magnetic stirrer dissolve $CaSO_4 \cdot 2H_2O$ in KOH solution until a precipitation of white solid phase of calcium hydroxide, filter and dry the formed solid at $40^\circ C$ to obtain portlandite. Evaporate the supernatant to obtain K_2SO_4 .

Carbonation is the principal process used for the preparation of calcium carbonate on an industrial scale. This process involves the addition of carbon dioxide gas to the reaction mixture being an aqueous solution containing calcium ions. Calcium hydroxide suspension (gas-suspension system) is considered to be the source of Ca^{2+} ions and in this case the alkaline medium facilitates the absorption of CO_2 gas.

NH_4OH solution 24% mixed in the gas bottle by bubbling CO_2 gas 7g/L/m more than 1h to form $(NH_4)_2CO_3$ solution at $44^\circ C$.

Add 192g $CaSO_4 \cdot 2H_2O$ to 400 ml $(NH_4)_2CO_3$ according to the following equation:



Upon filtration the solid $CaCO_3$ is dried at $80^\circ C$ to yield a pure product. The filtrate will be evaporated at $60^\circ C$ giving $(NH_4)_2SO_4$ crystals used as fertilizer.

D. The Merseburg method (Carbonation) is used because it is economically effective for the production of ammonium sulfate.

Results and Discussion

Phosphogypsum (PG) was chemically and mineralogical characterized By the XRF analysis shown in table (1).

Table 1: shows the main constituents of (PG):

Main constituents	Wt%
SiO ₂	10.3
TiO ₂	0.03
Al ₂ O ₃	0.27
Fe ₂ O ₃	0.13
Total	
CaO	29.8
Na ₂ O	0.15
P ₂ O ₅	1.3
SO ₃	45.4
F	0.21
Main constituents	Wt%
LOI	12.1
ZnO	0.01
SrO	0.22
BaO	0.06
Y ₂ O ₃	0.01

From the Table (1) it can be seen that 75% of the of the waste constituent is gypsum [$Ca_2SO_4 \cdot 2H_2O$] calcium sulfate dihydrate. The major oxides are SiO₂ and P₂O₅. Low concentrations of Na₂O, Al₂O₃, Fe₂O₃ are also present. (PG) waste also contains trace elements such as Ba, Sr, Zn, and Y ...etc. These elements cause pollution as they could be absorbed

on the (PG) surface or could be incorporated in its structure [19].

The EDS peaks in Fig. (3) show the content of oxygen, sulfate, and potassium at atomic percent values of 32.77%, 0.44%, and 33% respectively Table 2. Fig. (4) illustrate the SEM image of the K_2SO_4 crystals showing fine scales agglomerate. The XRD pattern in Fig (5) shows the pattern of the prepared K_2SO_4 phase.

The EDS peaks in Fig. (6) Show the content of oxygen, calcium, and carbon at atomic percent values of 38.41 %, 52.33 %, and 9.26 % respectively Table (3). Fig.(7) illustrate the SEM image of commercial calcium carbonate crystal morphology as rhombohedral calcite formed in the presence of spherical vat rite crystals. The XRD pattern in Fig (8) confirmed the calcium carbonate phase.

Table 2: showing the chemical formula of K_2SO_4

Compound Name	Scale Fac.	Chem. Formula
Potassium Sulphate	0.208	K_2SO_4
Potassium Chloride	0.781	KCl

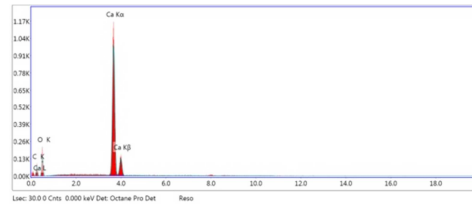


Figure 6: The EDS of $CaCO_3$

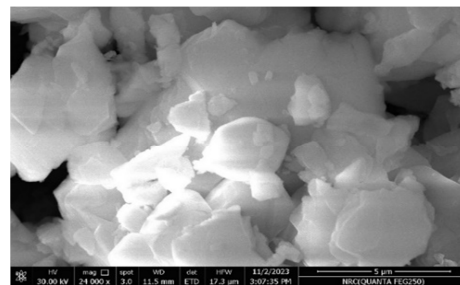


Figure 7: SEM Image (2) of calcium carbonate Rhombohedral crystals

Table 3: showing Chemical formula of calcite

Compound Name	Scale Fac.	Chem. Formula
Calcium Carbonate	0.573	$Ca(CO_3)$

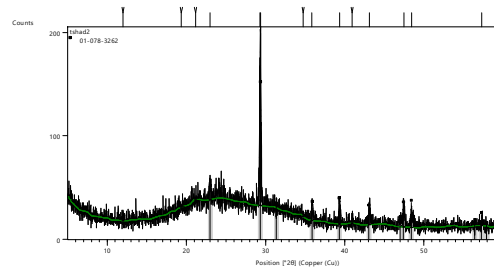


Figure 8: XRD pattern of calcium carbonate

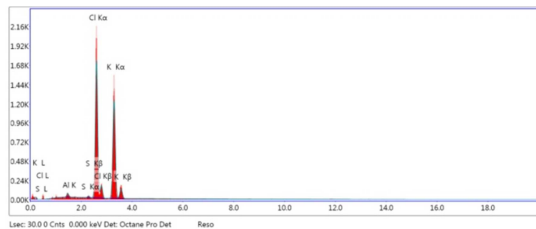


Figure 3: The EDS of K_2SO_4

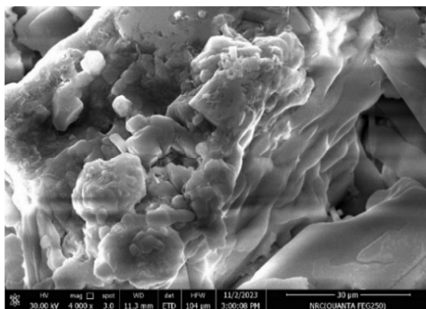


Figure 4: scales agglomerate crystals of K_2SO_4

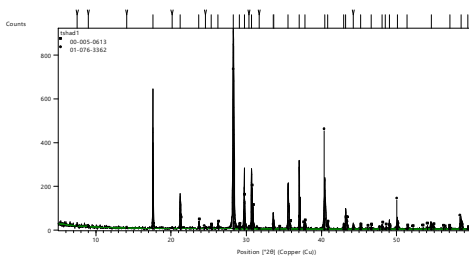


Figure 5: XRD pattern of K_2SO_4

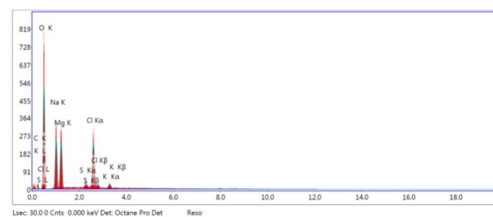


Figure 9: EDS of Sodium Sulfate

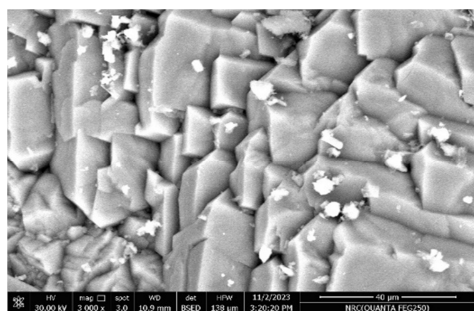


Figure 10: The SEM image (3) of sodium sulphate in squared shapes aggregates

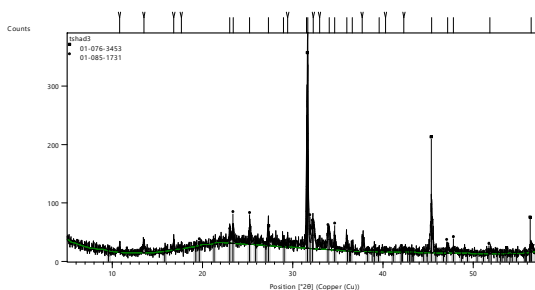


Figure 11: XRD pattern of sodium sulphate

Table 4: Showing Chemical formula of sodium sulphate

Compound Name	Scale Fac.	Chem. Formula
Sodium Chloride	0.845	NaCl
Sodium Sulphate Carbonate	0.137	Na ₄ [(SO ₄) _{1.39} (CO ₃) _{0.61}]

The EDS peaks in Fig (9) show the content of nitrogen, oxygen, and sulfur at atomic percent values of 36.25 %, 50.42 %, and 12.89 % respectively Table (4). Fig. (10) illustrate the SEM image of hexahedral particles. The XRD pattern in Fig (11) confirmed the formation of sodium sulphate phase from phosphogypsum.

The Ammonium sulfate crystals are shown in Fig (12) and SEM image (4) showing morphology of hexahedral particles.

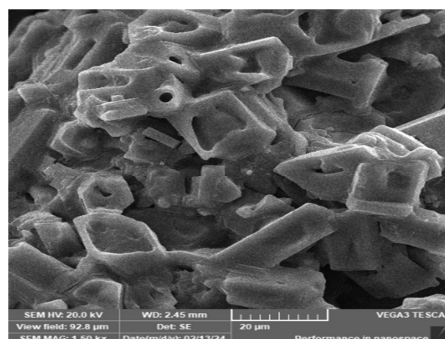


Figure 12: The SEM image (4) of ammonium Sulphate pattern

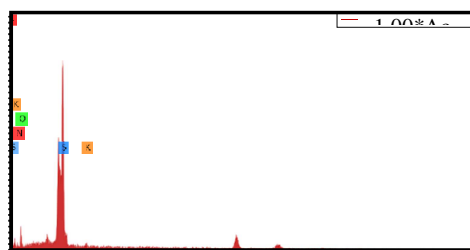


Figure (13): EDS of Ammonium sulphate

Table 5: Showing the elemental content of Ammonium sulphate

Element	Atom %
Oxygen	50.55
Sulfur	23.82
Nitrogen	19.31
Potassium	6.31
	100.00

The EDS peaks in Fig. (13) and Table 5 shows the content of Ammonium sulphate, oxygen, Sulphur, Nitrogen and potassium atomic percent values of 50.55%, 23.82 %, 19.31 % and potassium 6.31%. These atomic ratios confirm the Ammonium sulphate precipitation.

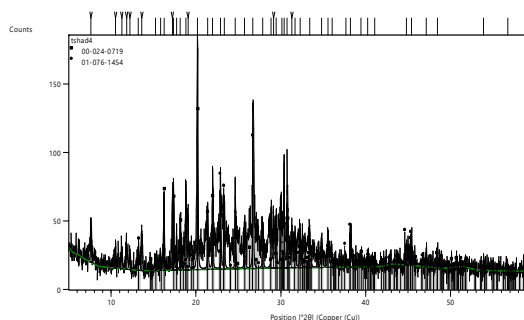


Figure (14): XRD showing presence of calcium carbonate.

The EDS peaks of the product in Fig. (15) and SEM (5a) indicated the content of calcium, carbon, and oxygen at atomic percent ratios 0.66%, 20.56 % and 61.04 % respectively. The calcite prepared by direct precipitation method shown in SEM image (5b) illustrates polymorphs tubule shapes of crystals with shorter length morphology. Fig. (15) shows the SEM image (5c) with an overall morphology of crystal agglomerates. The calcium carbonate product was only calcite and can be used in, rubber, filler for paper, paints and plastics.

Fig. (15) The SEM image (5a) and (5b) illustrating the tubule occlusion of calcium carbonate particles, while SEM image (5c) illustrates an overall image.

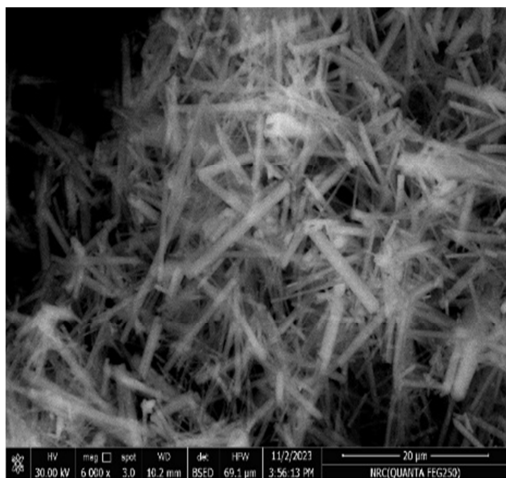


Figure (15): SEM image (5a) of calcium carbonate crystals with polymorphs tubule

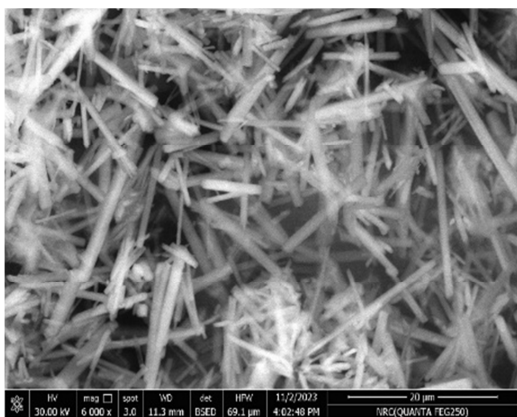


Figure (15): SEM image (5b) of calcium carbonate crystals with polymorphs tubule

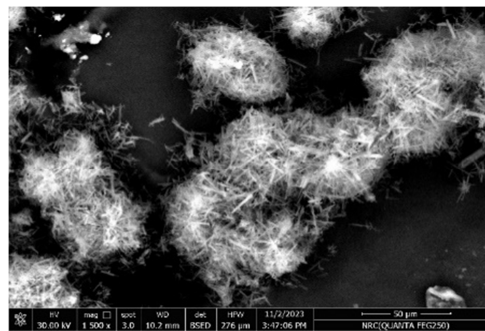


Figure (15): SEM image (5c) shows over all image of calcium carbonate particles

The contents of raw phosphogypsum after physical treatment to get rid of organics and silica and fluorides for work on purified (PG) is shown in Fig (16) and EDS peaks of the PG shows the following contents, oxygen 45.02 %, calcium content 12.03 %, sulphur content 25.1%, C content 0.39 %....etc. Fig. (17) illustrates PG SEM morphology where most types of crystals such as spherical, rhombohedral, hexagonal and squared shapes aggregates and some tubule calcium carbonate is present in low content.

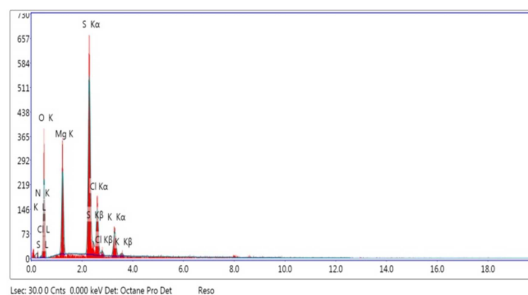


Figure 16: EDS of (PG) contents

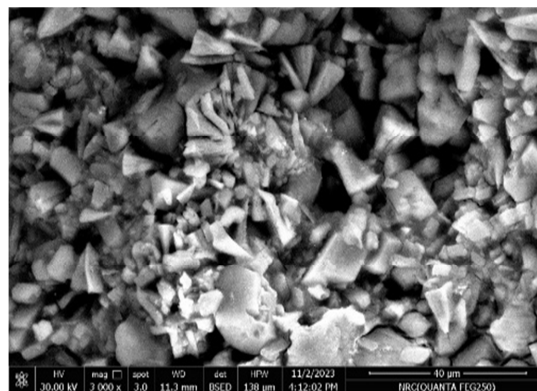


Figure 17: SEM image shows the morphology of raw purified (PG).

From the XRD, SEM and EDS results we can suggest that some rare earth elements (REEs) in raw PG can be roughly removed by washing with H_2SO_4 under normal conditions. This indicates that (REEs) mainly exists into the (PG) structure and crystals as isomorphs minerals [20,21]. In addition, (REEs) precipitates as a separate phase such as oxides and sulphates joined inside the (PG) crystals [23,24].

The above analysis indicates the presence of Fe, Mg, and Al in the EDS suggesting clays. Some elements like Y, Sr, and Mg can react with carbonate ($MgCO_3$, $SrCO_3$, Y, CO_2 ...etc) while the insoluble carbonates complexes remain in the powder. In addition, the presence of chlorides in the precipitate may be due to chlorides existing in the used reagent K_2CO_3 [25].

According to the results exposed in EDS we can assume that the trace elements is transferred from (PG) to the resulting salts. Generally, these elements may be absorbed in the surface of crystals or joined into its structure. Several factors helps in their presence such as: (i) the similar chemical behavior of calcium and these elements; (ii) the presence of these elements in (PG) under insoluble forms ($BaSO_4$), $ZnSO_4 \cdot 2H_2O$ and $CaSO_2 \cdot 2H_2O$ [26,27], The rest are insoluble during the utilization of (PG); (iii) The similarity of the particle size fraction of (PG) and calcite, facilitates the presence of pollutants in the precipitate. From the SEM –EDS K_2SO_4 precipitated is non –toxic and can be used directly as fertilizer [28-31].

From an Environmental and an Economic viewpoint, in this work, we followed a simple and economical process for the preparation of K_2SO_4 from the reaction of (PG) with KOH solution. Potassium sulfate and portlandite are obtained from phosphogypsum. The optimum conditions for the reaction of conversion of (PG) to K_2SO_4 are 80 °C temperature and stoichiometric ratio of (PG) and KOH.

The environmental impact of using this process is decreasing the rejected amounts of (PG) as well as producing $CaCO_3$ as resource. From an economic point of view, about one ton of (PG) could be treated with 0.803 ton of KOH or K_2CO_3 (595 dollars per ton) to produce 0.581 ton $CaCO_3$ (140 dollars per ton) and 1.012 ton of potassium sulfate (700 dollars per ton). Additionally, we can say that this process does not need any challenging procedures for recovering these high value products. So, this economical method allows to gain 312 dollars per ton of phosphogypsum that is converted to other products. This will cover the cost of transportation as well as energy and water consumed during this process.

Conclusion

The preparation of calcium carbonate, potassium sulfate, ammonium sulfate and other products using (PG) as calcium source is considered to be an effective use of the ore. (PG) is characterized by its complex composition due to the presence of various types of impurities, so it is difficult to achieve a complete impurities removal. On the other hand, the preparation of pure and valuable products from (PG) needs high leaching efficiency of (REEs). Since, sulfate ions are counterbalancing ions that occur as metastable amorphous precipitate, this precipitate is adsorbed on the surface of phosphogypsum. So we should focus on this problem by undergoing more pretreatment for (PG) to be suitable for large scale industry applications aiming to increase the value of the products and improve the economic profit correlated with the utilization of phosphogypsum materials.

No Conflicts of interest or Formatting of funding sources.

Acknowledgment

National Research Centre, Cairo, Egypt, supported this work. The Authors would like to thank all colleagues for their continuous support.

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