



## Treatment and Purification of Phosphogypsum

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**P**RODUCTION of phosphoric acid and phosphate fertilizers are still generating pollution problem. The (PG) wasted phosphogypsum by product created through the manufacture consists of many valuable materials to be recovered. For each ton phosphoric acid produced, about 4 – 5 tons (PG) waste was generated. The (PG) waste is generally dumped near the production plants causing contamination of ground water, soil and large extensions of land were occupied by (PG) piles. The present work proposed recovery of (PG) waste after purification, while XRF was used to present its main constituents. Valuable materials such as calcium carbonate can be recovered for soil conditioning by sea water treatment. Sodium sulphate was prepared from (PG) purified too and detected by XRD. SEM and EDAX were used to compare between purified and (PG) waste. Solar thermal energy was used to calcine (PG) waste rocks and minimize electrical energy use successfully.

**Keywords:** Phosphogypsum, Sodium sulphate, Calcium carbonate, Purification, Waste powder.

### Introduction

In Egypt there are more than 17 facility producing phosphate fertilizers and phosphoric acid as final bi products. Eight of them are already working and some new industries will be in El Sokhna districted soon. Besides an Egyptian Belgium cooperation industry for phosphate fertilizers and phosphoric acid production will be opened too.

Pollution problems resulting from (PG) which is a synthetic by-product created during the commercial manufacture of phosphoric acid by wet process [1]. For every ton of phosphoric acid produced, about 4-5 tons of phosphogypsum are generated [2]. The (PG) is composed of hydrated calcium sulfate mixed with some impurities such as  $P_2O_5$ , fluorine, organic matter, heavy metals and radioactive elements [3,4]. Generally the (PG) is dumped near the production plants in large stock piles causing pollution and contamination of ground water and soil[5]. On the other hand; large extensions of land are occupied stacks

containing the phosphogypsum, zones that could be available for other uses ( recreation, parking, building, agriculture, roads...etc). Europe, Japan and Australia uses (PG) in cement, wall board, and other building materials [6]. The purification processes of crude (PG) and its different treatments enables plaster production [7].

Morocco produces every year about 15 million tons of (PG) residues of which majority is discharged into the sea [8]. There for, reuse solutions and recovery of such waste has been proposed by several authors [9, 10, 11,12]. The USA and Spain are Pioneers in conversion of PG into building materials. An alternative is to replace natural gypsum by (PG) which has the advantage of resolving partially the environmental problems created by fertilizer industries. (PG) can replace some of the natural components of building materials[13].

Tunisia and Jordan have the same contamination problem of (PG). Spain used non-

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contaminating and free power sources as solar thermal energy for obtaining plaster from the calcination of gypsum rock. Dehydration can be achieved in the shortest time to minimize energy consumption that is a major cost in the thermal process [14]. (PG) waste from phosphate fertilizer production can be converted into sodium sulphate that can be used in paper industries, glass industries and detergents.

Gypsum is one mineral which is widely used in construction and ceramics (mold manufacture, sanitary wares, chalk and artistic sculpture) medicine (to make plaster bandages, dental molds and toothpaste), chemicals and pharmaceutical industry (as a calcium source and drugs component) and in food industry (as water treatment, refined sugar, canned vegetables and animal feed) [15].

## Material and Methods

### Materials

The samples were taken from El Fayom Fertilizer Company in Egypt. Table (1) shows the main composition of (PG) under study. The X-ray fluorescence (XRF) was used to determine chemical composition of the samples before and after purification. The x-ray diffraction was used to determine the mineral species in the prepared chemical products. Fresnel lens framed by aluminum and spacificed by width of 22 cm and thickness of 2mm, length 29.5 cm, focal distance 38 cm.

All chemicals used are pure grade. Sea water was taken from Alexandria sea shore Table (2) shows main constituents.

### Methods

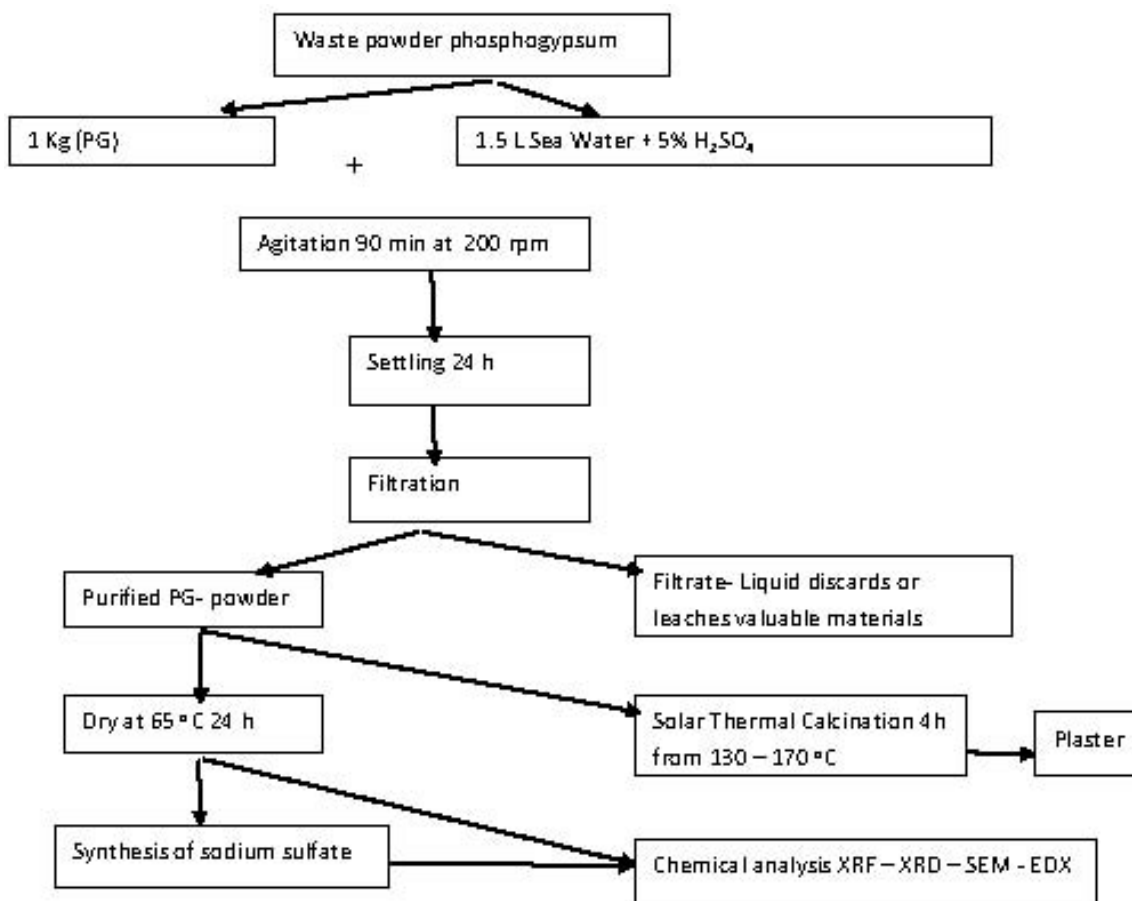
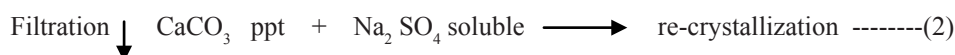
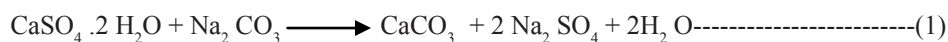


Fig. 1. Scheme For Purification of (PG) powder and precipitation of  $\text{Na}_2\text{SO}_4$  at room temperature.

### Purification of (PG)

The purification was held in two processes. The first by adding 5% citric acid or H<sub>2</sub>SO<sub>4</sub> at 60 °C for each 3 liters of water and one Kg (PG) powder. The pH wash stands at 3.9 and agitation for 30 min at 150 rpm.

The second process was held by using sea water for soaking (PG) powder 24h. 1.5 liter sea water/ one Kg (PG). Then agitation was held at



The recrystallized product was subjected to XRD and SEM to Identify NaSO<sub>4</sub> precipitated.

### The use of Fresnel lens

Figure (2) shows schematic diagram of Fresnel lens used instead of electrical heat to dry or calcine the (PG) purified powder for application as soil conditioner. The area of the Fresnel lens is 1.197 m<sup>2</sup> while the area of the sun image at the focal point is 1.9625 x 10<sup>-3</sup> m<sup>2</sup>. The lenses were positioned perpendicular to solar radiation. Through the experimental tests, when the solar radiation intensity is 1000 W/m<sup>2</sup>, the concentrated solar power at the focal point is estimated 1197 W corresponding to solar radiation intensity 61 W/cm<sup>2</sup>. If the solar radiation intensity is 800 W/m<sup>2</sup>, the concentrated solar power at the focal point is estimated at 958 W corresponding to solar radiation intensity 48.8 W/cm<sup>2</sup> with an average temperature of 300 °C. This means that incident solar radiation Fig. (3) shows the curve of temperature evaluation during exposure time of solar radiation. Solar energy was used for calcination of (PG) purified instead of electric furnace to achieve energy consumption. The acid purification and treatment with seawater was used to remove soluble impurities (phosphate, fluorine, organic matter...) present in (PG) to improve quality and calcium levels in (PG) and can be used in soil improvement Table (3).

TABLE 1. The chemical composition of (PG) waste and purified samples.

Wt%	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	F	LOI
PG	41.84	0.73	28.96	0.86	0.26	0.11	0.43	1.50	0.07	0.14	0.02	---	24.94
PG <sub>1</sub>	5.42	0.03	0.28	0.75	0.06	27.5	0.28	0.04	1.82	41.26	0.16	1.60	20.6
PG <sub>2</sub>	5.71	0.02	0.18	0.52	---	26.78	0.04	0.01	1.0	44.55	0.02	0.61	20.37
PG <sub>3</sub>	5.22	0.01	0.22	0.56	0.03	26.78	0.09	0.03	1.15	43.86	0.03	1.28	20.56

150 rpm for 30 – 45 min. The suspension was then filtrated to eliminate heavy metals and rare earth elements. The cake was dried at 65 °C for 24 h. Both products from first process and second process were subjected to chemical analyses.

### Preparation of Na SO<sub>4</sub> as product from (PG) purified powder:

(PG) purified was dissolved in Sodium carbonate solution at room temperature 1.5 h according to :

## Results and Discussion

Table (1) shows the chemical composition by XRF of (PG) waste powder, (PG<sub>1</sub>) treated with sea water, (PG<sub>2</sub>) treated with sea water and 5% citric acid, (PG<sub>3</sub>) treated with sea water and 5% sulfuric acid :

Table (1) The chemical composition of (PG) waste and purified samples:

From table one the data of treated (PG) shows reduced amounts of SiO<sub>2</sub> and insoluble impurities like (P<sub>2</sub>O<sub>5</sub>). Calcium carbonate shows higher Wt% in treated samples (PG<sub>1</sub>), (PG<sub>2</sub>), and (PG<sub>3</sub>) ranging in 26.8 – 27.5 wt%. This increase in ratio benefits the soil conditioning as it reached values of needed fertilizer. Also purified samples (PG<sub>1</sub>), (PG<sub>2</sub>), and (PG<sub>3</sub>) shows that all methods gave good quality of (PG) treated compared to normal (PG).

Figure (1) shows the scheme of experimental sequence used to treat (PG) and preparation of NaSO<sub>3</sub> by precipitation as in equations (1) and (2)

Both curves shown in Fig. (3) for temperature evaluation and solar energy evaluation during calcinations of PG samples at noon. From Fig. (3), temperature changes detected every five minutes and measured. A plot of Temperature verses solar energy measurement is illustrated too. The solar energy curve shows nearly stable features, but temperature was fluctuated, as few clouds existed on March.

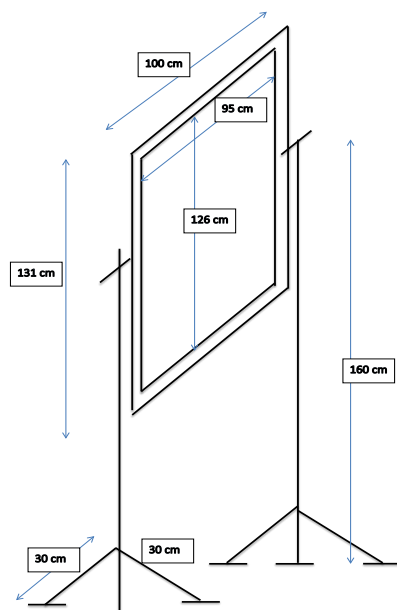


Fig. 2. The scheme of Fresnel Lenses used in calcinations of (PG) powder.

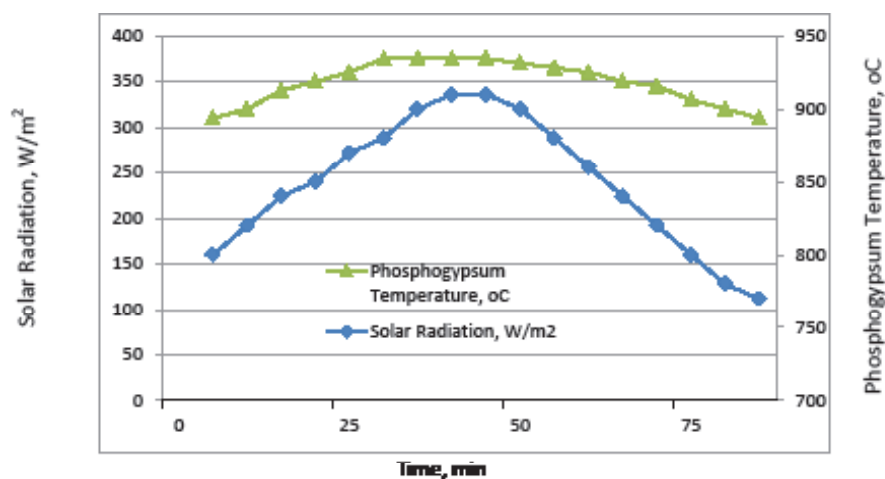


Fig. 3. Evaluation of temperature during exposure time of solar radiation.

TABLE 2. Main constituents in the PG powder before purification:

Element	Weight %	Atomic %	Net Int.	Error %	
C K	3.52	6.27	2.04	27.78	
O K	47.79	63.92	66.43	11.52	
NaK	1.98	1.84	7	20.01	
SiK	0.86	0.66	8.94	16.7	
SrL	0.26	0.06	1.4	65.22	
P K	8.6	5.94	79.53	5.2	
S K	13.49	9.01	123.54	4.54	
		CaK		22.95	12.25

The EDAX in Fig. (4<sub>a</sub>) and Fig. (4<sub>b</sub>) illustrate the contents of PG before and after purification.

From Fig. (4<sub>a</sub>) and Fig. (4<sub>b</sub>) Both tables represents a decrease in the soluble materials in the PG powder and an increase in the calcium content is illustrated which is benefit for soil reclamation. Also a decrease is shown for other residual elements which was present before purification.

The XRD curve indicated the presence of NaSO<sub>4</sub> (Burkeite 94.9%) precipitated from purified PG in normal temperature before recrystallization . One kilo of (PG) purified and dried gives nearly 100 gram of NaSO<sub>4</sub>.

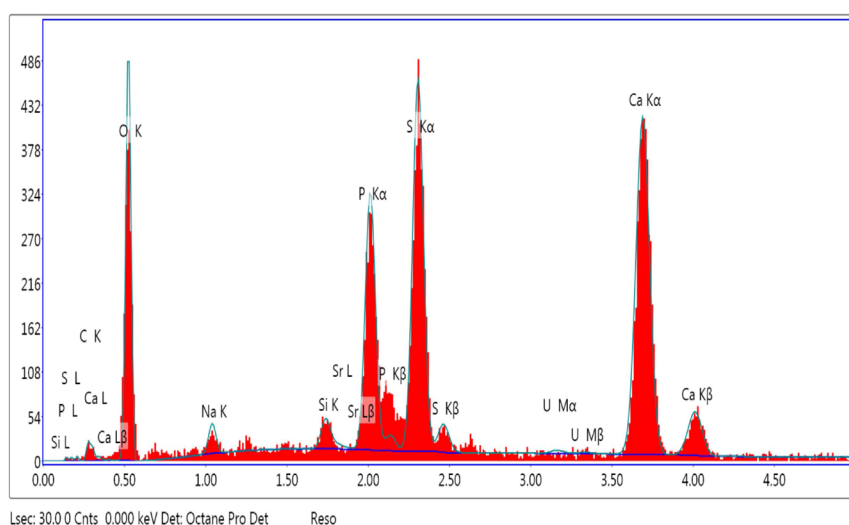
The above tables shows the main constituents of prepared NaSO<sub>4</sub> are Na, 686.53% > S, 387.67 > O, 422.44.

**TABLE 3. Main constituents in the PG powder After purification:**

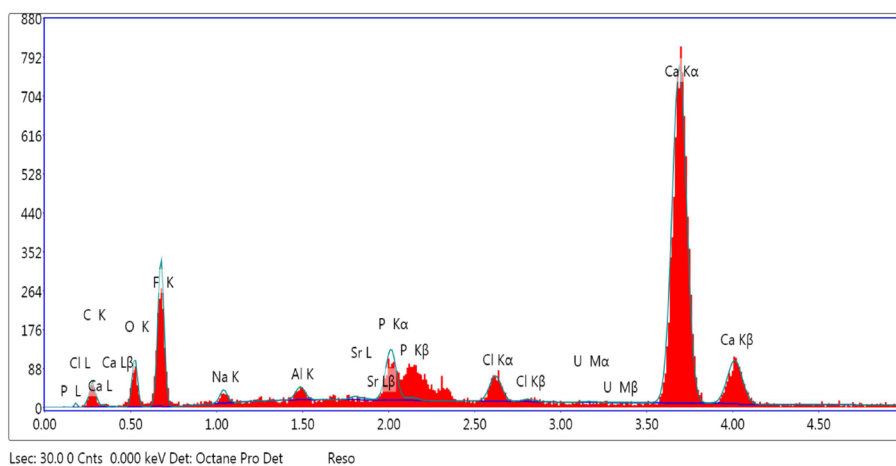
Element	Weight %	Atomic %	Net Int.	Error %
C K	5.51	10.82	5.33	18.65
O K	14.38	21.2	14.12	15.09
NaK	2.05	2.1	5.9	21.03
AlK	0.93	0.81	6.84	22.02
P K	3.42	2.6	28.89	10.21
CaK	41.91	24.66	262.01	2.65

**TABLE 4. shows the main contents of NaSO<sub>4</sub> as product.**

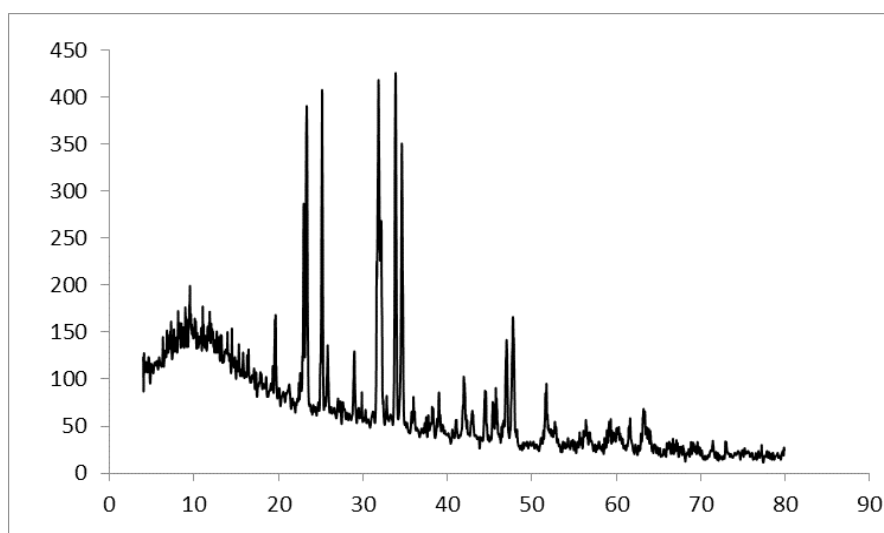
Element	Weight %	Atomic %	Net Int.	Error %
C K	21.64	31.09	70.11	11.77
O K	38.18	41.19	422.44	9.21
NaK	28.83	21.64	686.53	7.32
MgK	0.36	0.26	9.57	23.96
SiK	0.16	0.1	7.07	38.36
P K	0.26	0.15	10.94	21.99
S K	8.47	4.56	387.67	3.57
ClK	2.09	1.02	83.99	6.74



**Fig. 4a. EDAX of PG powder before purification.**

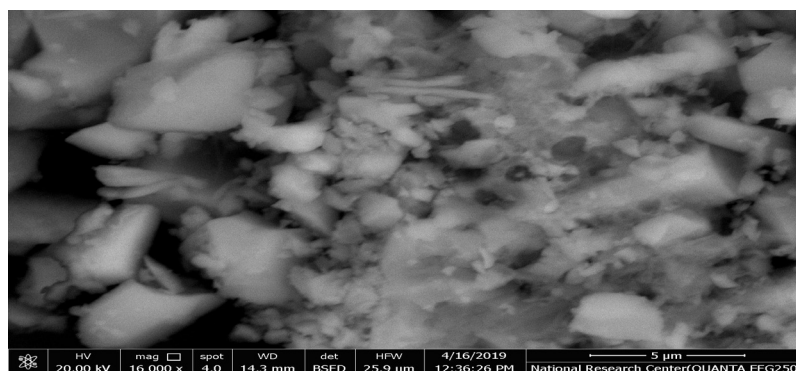


**Fig. 4b.** EDAX of PG after the first purification by sea water and 5% sulphuric acid.



Burkeite 94.4% 1, disodium Carbonate 3.8%, metathenardite 1.3%  
Position [° 2 Theta] (copper(Cu))

**Fig. 5.** XRD of the  $\text{Na}_2\text{SO}_4$  precipitated from PG purified powder.



**Fig. 6.** SEM image of prepared  $\text{Na}_2\text{SO}_4$  representing long hexagonal crystals.

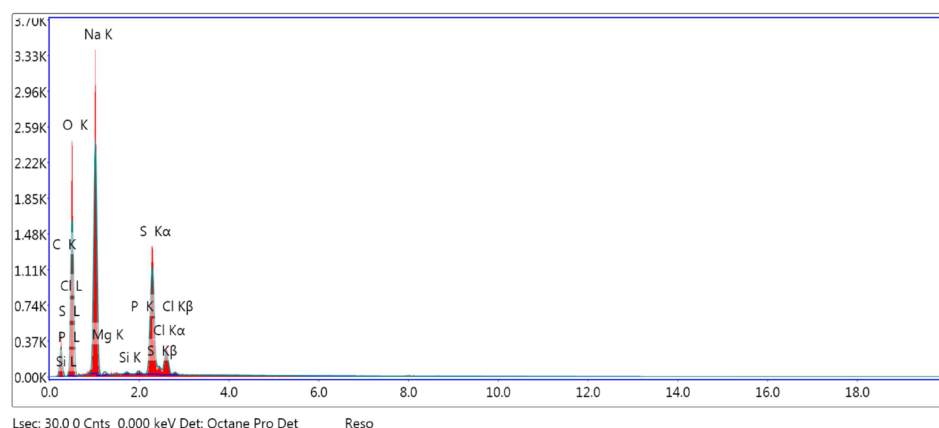


Fig. 7. EDAX of prepared  $\text{Na}_2\text{SO}_4$  as main constituent.

### Conclusion

The treatment of (PG) waste with seawater and acids is a very simple and effective method for recovery of purified (PG) as soil conditioner. The use of solar energy for calcinations of purified (PG) saved electrical energy successfully. The preparation of  $\text{Na}_2\text{SO}_4$  in normal temperature by precipitation from purified PG gave for each one-kilo gram purified PG 100 g of  $\text{Na}_2\text{SO}_4$ . This shows an economic method for recycling benefit materials from (PG) waste powder. The product  $\text{Na}_2\text{SO}_4$  needed more recrystallization.

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