

Chemical characterization of phosphogypsum produced from raw phosphate rock from the phosphoric acid manufacturing process

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Abstract:

Phosphogypsum (an industrial by-product) is formed during the production of fertilizers and phosphoric acid from raw phosphate. It consists primarily of CaSO_4 and contains impurities Zn, Pb, Cu, Cd, Ni, Cr, and many rare earth elements such as lanthanum and cerium.

The current article aims to study the chemical elemental content of phosphoric gypsum, and the results showed that the percentage of P_2O_5 in phosphoric gypsum is 2.7%, and the main component is calcium sulphate, with a percentage of 68.5%.

As for the element content, the concentrations of Cr, La, Ni, Ce, Pb, Cd 1 are explained in the research, and the reason for their presence is due to their transfer during the phosphoric acid manufacturing process from raw phosphate to phosphate by the wet method. As for the chemical elemental content of the raw phosphate taken, which was determined using AAS atomic absorption technology, , Cr, Pb, Cd respectively (9.2, 13.5, 10, 4.58, 0.46, 7.02) ppm.

The ETF values showed a high transition rate for both cerium and lanthanum, reaching 72.59% for cerium and 68.47% for lanthanum. In general, it is noted

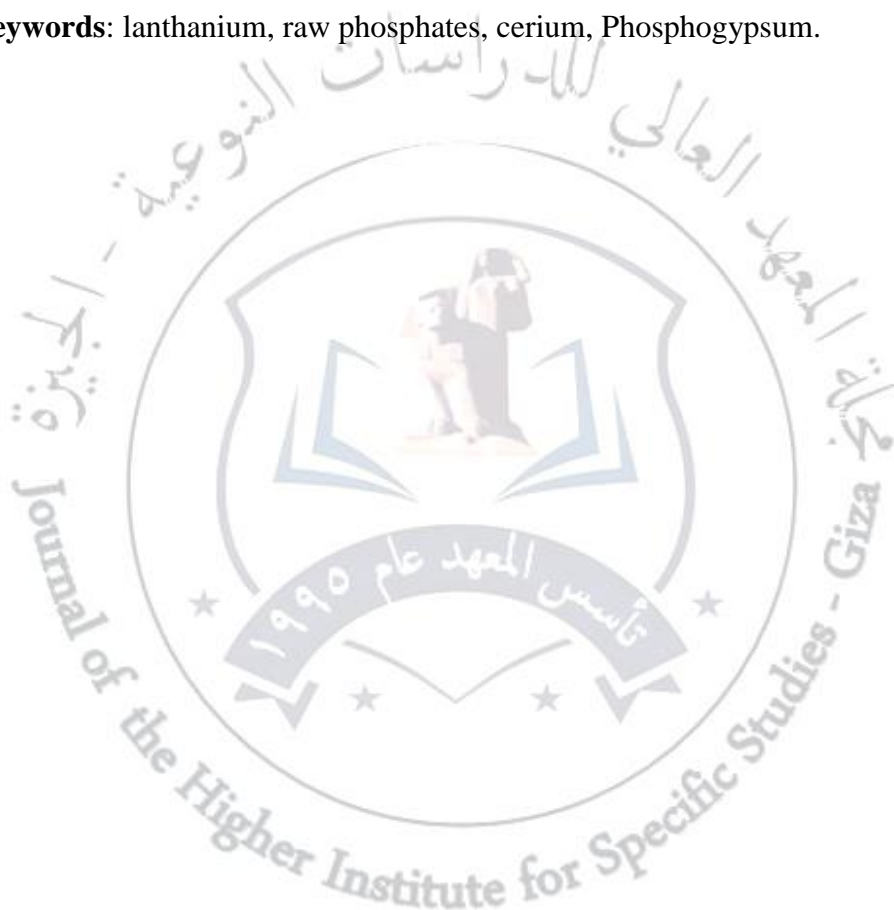
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that the largest percentage of lanthanides (cerium and lanthanum) was transferred to the phosphogypsum resulting from the manufacture of phosphoric acid by the wet method, while the highest percentage of P₂O₅ was transferred to the phosphoric acid formed.

Keywords: lanthanum, raw phosphates, cerium, Phosphogypsum.



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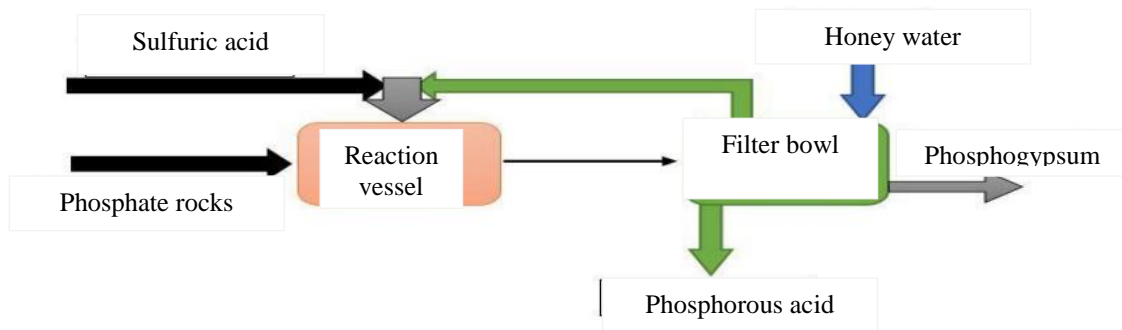
Introduction:

Phosphate is considered the most important natural mineral resource as it is used in many agricultural and food industries, which gives it great importance as an indispensable basic material.

The world's reserve of phosphate, according to figures from the General Companies for Phosphate and Mines in the world, amounts to 180 billion tons of raw material, in addition to the presence of a lower quality reserve of about 5 billion. It consumes annually about 7 million tons of phosphate, which is about 40% of the global production for the production of commercial phosphoric acid and phosphate fertilizers. The rest of the quantity produced is about 32 million tons, or about 80%, is exchanged between countries of the world.[1][2]

Raw phosphate has distinctive properties, such as rapid dissolution in weak acids, which reduces the reaction time in reactors when manufacturing phosphoric acid. It has a great ability to retain heavy metals and nucleolides of natural radioactive chains, and a high adsorption speed.[3]

Phosphate raw materials represent an advanced rank in economic and strategic importance after oil and natural gas raw materials. Because of the widespread use of phosphate in industry, it produces materials that negatively affect public health and the environment. Most of these materials represent phospholipids, which is a secondary product of the wet method of manufacturing phosphoric acid according to the plan: [4]



Gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) represents the main component of phosphogypsum and represents 65-95% of phosphogypsum by weight. There is a small amount of impurities such as phosphate, fluorides, sulfates, heavy elements such as lead, cadmium, etc., some radioactive elements such as U, Ra, Th, and a good percentage of rare earth elements, which is a percentage. These contaminants in phosphogypsum are few and do not pose real and obvious harm to the environment.

The US Environmental Protection Agency (EPA) classified it as a waste with low radioactivity because it contains quantities of Th^{232} and U^{238} , and they are natural radioactive materials that are technically stimulated by TENORM [5-7]. The International Atomic Energy Agency classified them as radioactive materials of natural origin, but as a result of the accumulation of huge quantities of this material. Its storage areas have become a source of pollution, and approximately 50 tons of phosphogypsum are produced when manufacturing every ton of phosphorous acid [8], and global production reaches 280 tons together [9].

In some countries of the Third World in 2004, the quantities of phosphogypsum acid amounted to approximately 350,000 tons [10], and it is stored in earthen cairns lined with PVC. On the other hand, with the aim of

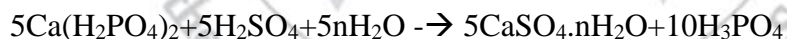
converting phosphogypsum into a by-product of great economic value. There are many scientific studies in the field of industrial ecology that have found the possibility of using it. In many fields, such as construction [11], street paving [12], agriculture, to improve the chemical and physical properties of soil [13], and the recovery of rare earth elements of great importance and wide uses in hybrid cars [14], advanced medical industries [15], and nano-industries [16].

The importance of the research and its objectives:

Within the framework of recovering rare earths from phosphogypsum as waste resulting from the manufacture of Syrian commercial phosphoric acid by the wet process, the aim of part of the research is to study the chemical and elemental distribution in the system: raw phosphorus and phosphogypsum.

Research method and materials:

A sample of raw phosphorus was obtained by reacting part of the sample with sulfuric acid in a manner similar to the manufacture of phosphate by the wet method according to the equation:



Digestion of rock samples for phosphate:

A sample of raw phosphate was ground to a diameter of 1 mm, then dried at room temperature. The weight of 1 gram of the sample was carefully taken, and aqua regia was added in a ratio of $\text{HNO}_3:3\text{HCL}$. We added 6 milliliters of hydrochloric acid, and after 120 seconds, we added 2 milliliters of nitric acid in drops. The sample is heated at 150 degrees for 20 minutes, then we add 2 milliliters of nitric acid to make the ratio 3:2. The sample is left to cool,

then we filter the samples and increase the volume to 50 milliliters, so the sample is ready for analysis.

X-ray spectroscopy:

Phosphate samples were analyzed to determine the percentage of oxides included in its composition. The sample of raw phosphate was ground and sieved to obtain grain sizes of 1 mm for its characterization.

Elemental analysis by absorption spectroscopy:

Its goal is to determine the concentration of many mineral elements in phosphorus and phosphogypsum according to the flame method that is used for elements estimated at parts per million. Standard solutions of the studied elements were prepared and the sample was injected into the device.

Determine the percentage of P₂O₅ in the phosphorus and phosphogypsum sample:

We put a certain volume of the sample +N₁₁H₂SO₄+ on top of the ammonium sulphate, mix well, then add ammonium molybdate, potassium tartrate, and aluminium, then mix well and add ascorbic acid and mix well. After 5 minutes, we measure the absorbance at a wavelength of 650 nm with a UV-VIS device, and using chemical conversion factors, we obtain the concentration P₂O₅. Within the sample by relationship:

$$P = \text{Con PO}_4\% \cdot 0.327$$

$$P_2O_5 = \text{ConP} \cdot 2.2951$$

Determination of sulfate in phosphogypsum:

Sulphate was measured based on the method of forming the turbidity of barium sulphate, where a specific volume of the sample was placed in a 250 ml Erlenmeyer, then an extraction reagent was added, consisting of 30 ml of

chloric acid, 300 ml of distilled water, 100 ml of 95% alcohol, and 75 grams. Of sodium chloride and 50 milliliters of sodium chloride, barium chloride granules were added, a standard curve was prepared with sodium sulfate, and then the absorbance was measured with a spectrophotometer at a wavelength of 420 nm.

Determination of calcium concentration in phosphogypsum:

Calcium was determined by the complex colorimetric method according to the murexide reagent. Calibration is done using EDTA and is calculated from the product of twice the calibration number of 4.008.

Determine the concentration of magnesium in phosphogypsum:

Magnesium was determined by titration using EDTA, and the magnesium concentration was calculated from the relationship:

Magnesium concentration = 2 (hardness titration number - lime titration number). 2.432

Determine the concentration of cerium and lanthanum in phosphate and phosphogypsum:

They were determined according to the colorimetric method by forming a colored complex with oxynol orange at a wavelength of 575 nm for cerium and 576 nm for antanium at a pH of 6, where they worked at room temperature and waited for two hours until the color complex stabilized. **Results and discussion:**

1-Chemical characterization of the studied raw phosphate:

Table 1 shows the results of the chemical analysis of a sample of Syrian raw phosphate taken using XRF technology and the colorimetric method to determine P₂O₅.

Table 1

SiO ₂ Wt%	Al ₂ O ₃ Wt%	Fe ₂ O ₃ Wt%	MgO Wt%	CaO Wt%	SO ₃ Wt%	P ₂ O ₅ Wt%	LOOS%
8.9	0.12	0,39	0.78	48,78	0.51	29.06	8.85

The results of the analysis indicate that the sample has a high content of calcium oxide, greater than 48%, which indicates that the rocks in the studied site follow the composition of limestone rocks, which is close to the results of researchers Shahrour in 2018 in [17] and is close to the results of Abzaly's study in 2015 regarding determining the percentage of P₂O₅. It was 31.96% on site [4]. The concentrations of some heavy elements in the raw phosphate were determined with an atomic absorption device according to Table 2.

Table 2 Element concentration ppm

Cu	Pb	Cd	Mn	Cr	Ni	Zn
18.7	0.46	7.02	7.73	4.58	10	160

From Table 2, we note the presence of appreciable concentrations of the heavy metals lead, chromium, nickel, and cadmium, which are the most toxic elements due to prolonged use of phosphate fertilizers due to their accumulation in the soil and their transfer to plants and organisms. This study shows that the concentration of heavy metals in the sample is relatively low compared to their concentrations in the world, which are very similar [18].

2-Chemical structure of phosphogypsum:

The analyzes showed some indicators of the chemical analysis of phosphogypsum, as shown in Table 3.

Table 3 Percentages

SO_4^{2-}	PO_4^{3-}	Ca^{2+}	Mg^{2+}
68.5%	2.7%	23.20%	0.046%

By comparing our results with the two studies [19][20], it was shown that the concentration of the basic components of phosphogypsum was similar, and that the main component was calcium sulphate at a ratio of 68.5 due to its presence in high concentrations. The reaction of concentrated sulfuric acid with crude phosphate to obtain phosphorous acid produced calcium sulphate as an undissolved precipitate. As for the presence of calcium in concentrations It is high due to its presence in a high percentage in the phosphate rock, which is composed of apatite minerals, the most important minerals of which are fluoroapatite, hydroxyl apatite, and chlor apatite [21]. The concentrations of the heavy elements of phosphogypsum were also determined by AAS absorption spectroscopy, as shown in Table 4.

Cu	Pb	Cd	Mn	Cr	Ni	Zn
3.57	0.33	0.52	2.63	3.63	3.42	43.75

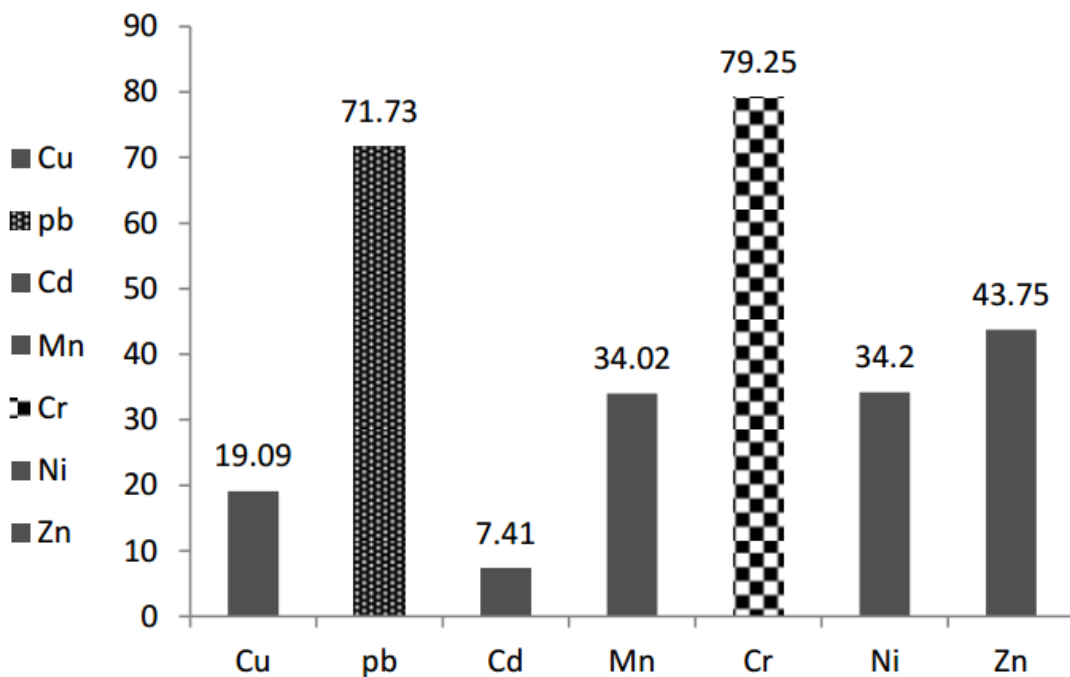
We note from Table 4 the presence of small concentrations of heavy metals, such as lead and cadmium, which are the most toxic and are transferred from phosphate to phosphogypsum. Studies [22] indicate that phosphogypsum is not classified as toxic waste in terms of the heavy elements in it because the concentration of these elements is less than the permissible limit according to [23]. 3- Determine the concentration of the elements cerium and lanthanum in phosphate and phosphogypsum:

The concentration of the elements cerium and lanthanum in phosphate is 13.5 and 9.2, respectively, and in phosphogypsum is 9.8 and 6.3, respectively.

From this we find that the concentrations are good [24] and we can work on recovering and extracting it, especially from phosphogypsum, as it is a waste material resulting from the phosphate industry in large quantities. It is converted from waste into a raw material and used to obtain rare earth elements of great economic value. 4-Study of the elemental distribution between phosphate and phosphogypsum:

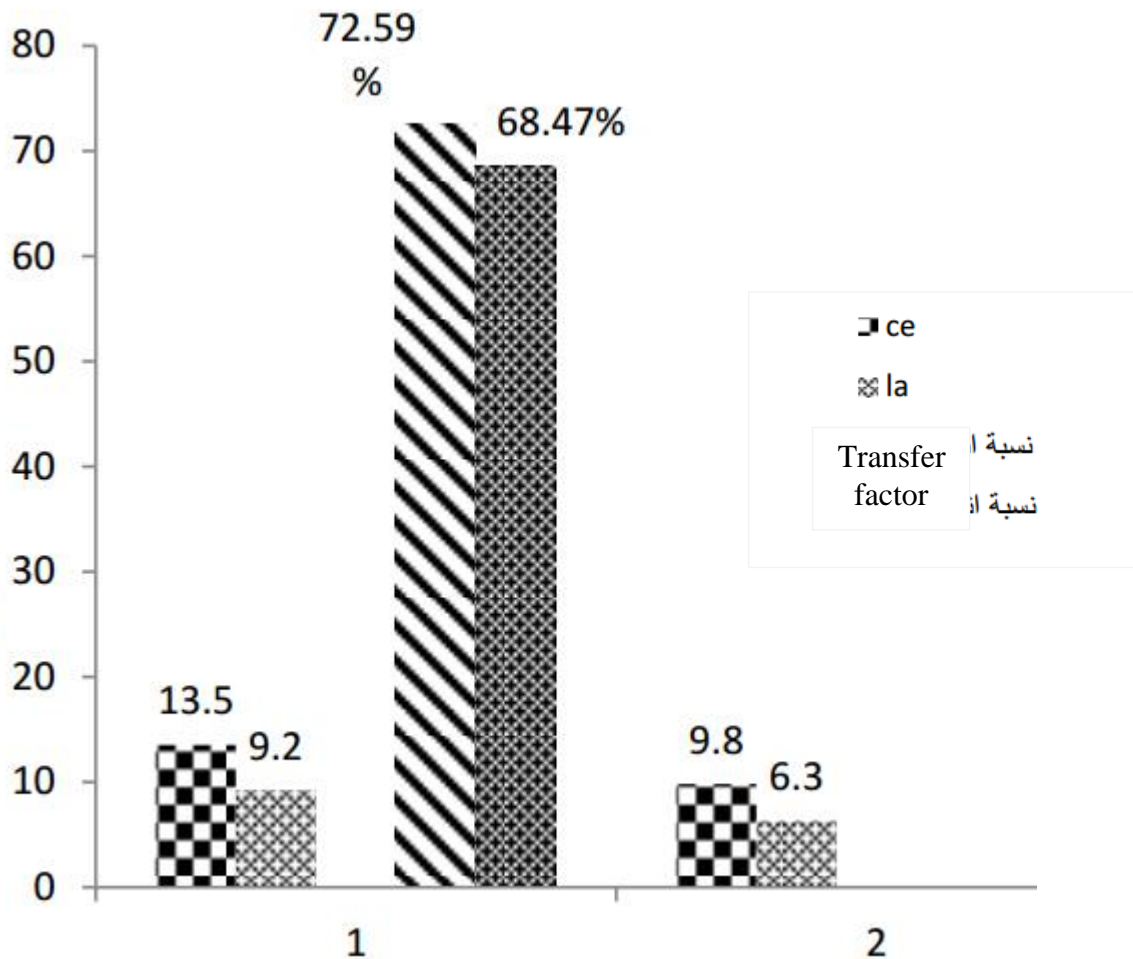
This was done by determining the rate of transfer of heavy metal elements and both cerium and lanthanum from phosphate to phosphogypsum by calculating the ETF coefficient from the relationship:

Transfer factor%=100. (element concentration in phosphogypsum/element concentration in crude phosphate)



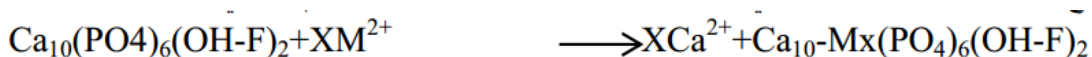
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We note that the ratios are different for the transfer coefficient, but the geochemical behavior is similar for all heavy metal cations and differs in terms of binding sites and surface sites, where ethane dominates for the adsorption of divalent heavy metal elements such as lead, cadmium, and others [25][26] which are:

Adsorption on the metal surface is followed by an ion exchange reaction between the heavy metal ions and calcium ions according to the equation:



Dissolution of apatite metal in an acidic medium, as in the manufacture of phosphoric acid from raw phosphate, which allows the re-precipitation of hydroxypyromorphite or fluoropyromorphite, such as lead:



As for manganese, it is expected that the reason for its presence in low concentrations in phosphate and phosphogypsum is due to manganese replacing calcium in low percentages among the phosphate compounds [27]. As for chromium, cerium, and lanthanum, perhaps the reason for the transfer of a large percentage of them from phosphate to phosphogypsum is due to the possibility of replacing it with iron. And aluminum and its association with the phosphate mineral phases consisting of the association of a positive metal ion with HPO_4^{2-} , H_2PO_4^- and excreted with calcium sulfate in phosphogypsum and it is also possible to replace calcium in phosphogypsum [28].

Conclusions and recommendations:

The results of the chemical analysis of phosphogypsum showed that its main component is calcium sulphate at a rate of 68.5%, while the elemental analysis shows that its highest concentration of zinc is 70 ppm, and the transfer coefficient for both cerium and lanthanum from phosphate to phosphogypsum is large, and it is 72.59% and 68.47%, respectively.

As for the results of the chemical analysis of phosphate, it was found that the basic composition was 48.78% calcium oxide and the percentage of phosphorus pentoxide was 29.06%. The elemental analysis showed the presence of many heavy metals, such as zinc, with a concentration of 160 ppm, and the concentrations of cerium and lanthanum were 13.5 ppm and 9.8 ppm.

From the previous results, we find that phosphate ore is good for investment in the manufacture of phosphate fertilizers and other industries because it contains a good concentration of phosphorus pentoxide, and phosphogypsum can be converted from an accumulated waste raw material with high economic value to recover some rare earth elements such as cerium and lanthanum from it.



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