

**TOWARDS THE RECOVERY OF RARE EARTH ELEMENTS AS
A BY-PRODUCT THROUGH PROCESSING OF ABU TARTUR
PHOSPHATE ROCKS**

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ABSTRACT

Two concentrated samples representing the weathered and unweathered phosphate ores of Abu Tartur area, Western Desert, Egypt, have been mineralogically qualified as the input raw materials for the present work. In the two samples respectively, the rare earth elements (REEs) assay 0.13% and 0.14% as oxides, the phosphorus assay 31.2% and 32.2% as P_2O_5 and uranium* assays 35 ppm and 36 ppm as U_3O_8 . The raw materials are processed with sulphuric acid in a mini-pilot plant for introducing phosphoric acid and phosphogypsum products. The latter are the source of REEs, which are leached with diluted nitric acid. The REEs leachabilities are examined through spectrophotometric scanning for neodymium (Nd) spectrum in perchlorate media. Analysis of the output crude REEs concentrates of weathered and unweathered phosphorites, respectively show 0.91% and 0.76% of rare earth oxides, 0.016% and 0.014% of U_3O_8 , 5.42% and 6.90% of P_2O_5 , 0.07% and 0.18% Fe_2O_3 , 8.11% and 8.40% CaO besides traces of MgO (<200 ppm). The relative standard deviation, RSD%, does not exceed $\pm 5.0\%$ for all analyses. Results obtained encouraged to go through purifying both products as will be discussed later on.

INTRODUCTION

Abu Tartur Plateau is located in the South Western Desert of Egypt, about 50 km to the west of El-Kharga town. It contains a huge

* The tetravalent uranium is mostly remained undetected.

phosphorites reserve, which reaches up to billion tons. Phosphorites which are the main source of fertilizers worldwide, represent a terminal annual production of about 500,000 ton of rare earth elements [Habashi (1985)].

Although monazite, bastnaesite and xenotime are the most common REEs ores (~ 30-65%), their recovery from phosphate rocks as a by-product is a step towards the conservation of natural resources [Habashi (1985)]. Moreover, their recovery along side with phosphoric acid production is considered more economic.

The relative abundance of lanthanide oxides Ln_2O_3 ($\text{Ln} = \text{REEs}$), in some Egyptian phosphorites is represented in Table (1). Figure (1) shows the abundance of Ln_2O_3 in phosphorites worldwide. Abu Tartur phosphorites show a promising resource of REEs.

Table (1): The average Ln_2O_3 content (%) in some Egyptian phosphorite localities*

Locality	Safaga	Hamrawin	E. El-Sebaiya	W. El-Sebaiya	El-Mahameed	Abu Tartur
Ln_2O_3	0.006	0.007	0.018	0.022	0.028**	0.130-0.203***

** After Habashi (1985).

*** After El-Kammar (1974).

The average REEs content in Abu Tartur phosphorites (~ 0.2%) is relatively high especially with respect to the huge amount of phosphorite reserve [Basta et al. (1974); Dardir and Kobtan (1980); El-Bassiony (1995)]. This high content of REEs is an advantage that could increase the economic potentiality of the ore when extracted as a by-product.

Spatial distribution of Abu Tartur phosphorites is outlined in Figure (2). The Phosphate Formation bearing thick high-grade phosphorite beds cropping out along the rims of the plateau. These beds are restricted to the lower member of the formation and showing their maximum thickness at the southeastern corner of the plateau where they are of potential economic importance [Wassef (1977); Issawi et al. (1978)].

* Analyzed by the second author using ICP-MS technique in the XRA Lab, Div. of SGS, Canada.

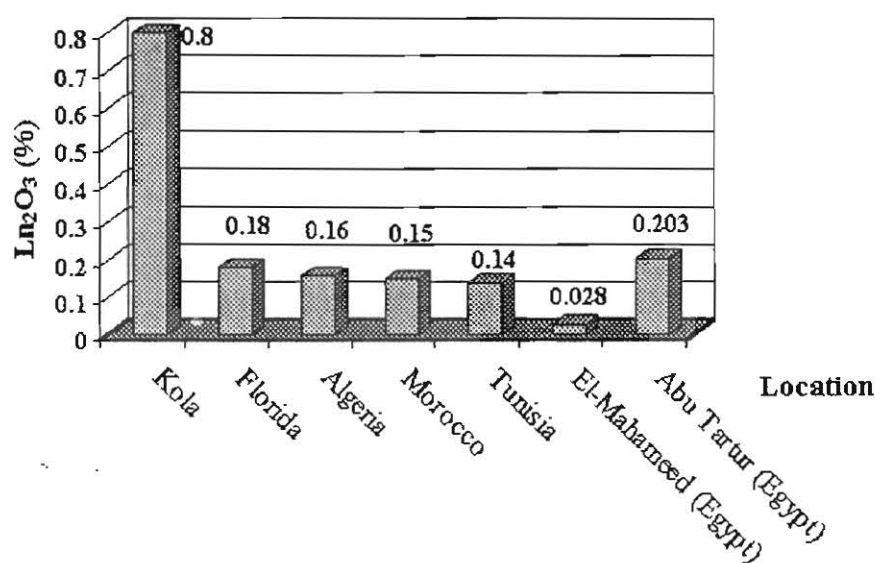


Fig. (1): The average Ln₂O₃ content (%) in some phosphorites worldwide [After Altschuler et al. (1967); Bliskowskii et al. (1969); El-Kammar (1974) and Habashi (1985)].

The total thickness of these beds varies from 3 to 7 m at the mining area of the phosphate project, which is currently under commercial high-grade phosphatic ore production. Preliminary exploration of this mining area (~108 km²) led to an estimation of 987 million tons as economic reserve with an average P₂O₅ content not less than 25% [Wassef (1977)].

Mining processes comprise two main types of phosphorites. The first type is the fresh unweathered phosphorites that produced by longwall-face underground mining. This type is dark grey to black in colour because of pigmentation by sulphides (pyrite and marcasite) and organic matter [Schröter (1989)]. The second type is the weathered phosphorites that produced through opencast mining. This type is of brownish yellow colour where the sulphides have been totally oxidized forming limonite and gypsum by reaction with carbonates. The zone of weathering follows the outcrops at the plateau rims with several tens of meters thick inward [El-Kammar and Basta (1983)].

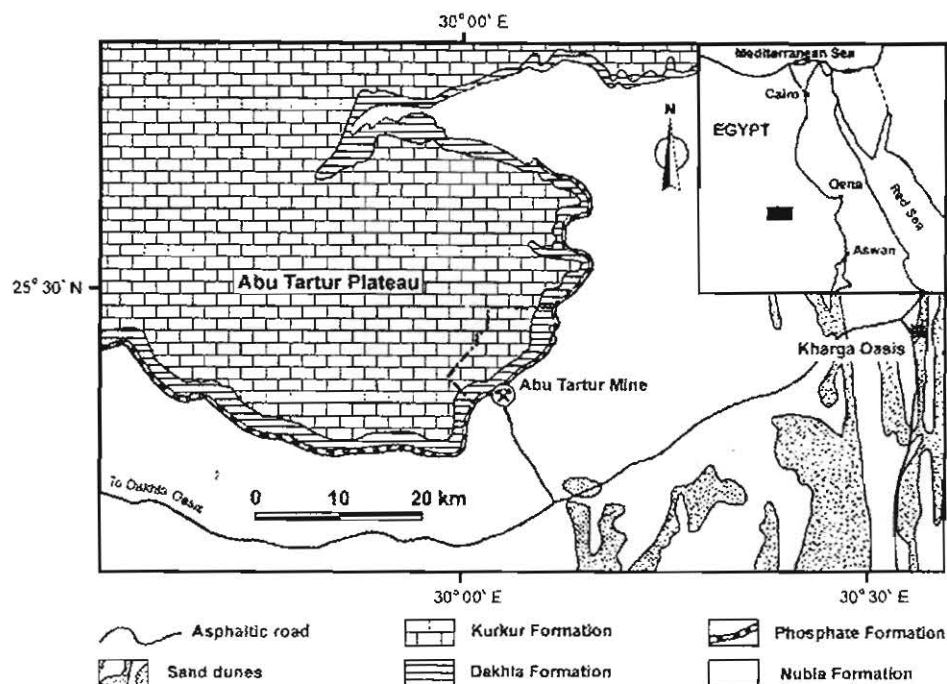


Fig. (2): Geological map of Abu Tartur area.

In the Egyptian Abu Zaabal Fertilizers and Chemicals Company, the wet process phosphoric acid (WPPA) plant was constructed for phosphorite processing with sulphuric acid [El-Hazek et al. (2001)]. The present work is, therefore, dealing with concentrating REE from Abu Tartur phosphorites so as to be applicable as a terminal unit in Abu Zaabal plant.

EXPERIMENTAL

Materials

Two batches of high-grade phosphate ores, weathered and unweathered, are collected after their in situ ore dressing processes. Their phosphate contents, as indication of REEs are determined spectrophotometrically after attacking 1g of each sample with concentrated hydrochloric acid [Habashi (1985)]. Both samples are moreover mineralogically identified as the input raw materials.

All the chemical reagents are highly pure for analysis. These are; sulphuric acid, 97-99%; hydrochloric acid, 34-37%; perchloric acid, 6%; oxalic acid, 99%; ammonium hydroxide, 35-37%; arsenazo III, sodium salt of (2,2-[1,8- dihydroxy-3,6-disulpho-2,7-naphthalene bis(azo)]) dibenzene arsonic acid (60%); neodymium oxide, 99.9%; ammonium molybdate; ammonium metavanadate; uranyl nitrate, >99.99% and Fluran buffer solution.

Instrumentation

Binocular polarizing microscope and X-ray diffractometer (Philips-PW 3710), are utilized for mineralogical identification of the raw materials. A double beam spectrophotometer (UNICAM-UK) is used for instrumental analyses of phosphorous using metavanadate procedure, REEs with arsenazo III [Marcezenko (1990)], and also applied for the qualitative analysis of Nd. Atomic absorption spectrometry (UNICAM 969-UK) supplied with acetylene and nitrous oxide are used in the present work for minor and trace element analyses. On the other hand, laser fluorometer (Scintrex, Canada), is applied for uranium analysis in the in/output products.

Acid processing of the phosphorites

A batch (100g) of each phosphate raw material (weathered and unweathered) is mixed with 95ml of H_2SO_4/H_2O (1:1.2) at constant temperature, 65°C [Belg (1980)]. The two slurries are agitated for two hours, left to cool and then filtered off and washed with water and ethanol. The formed lixivate is mainly phosphoric acid and the residue formed is the phosphogypsum which is treated with 1M nitric acid for REEs leaching. The solid/acid ratio is 1:1(w/v) and agitation is carried out for 48 hours [Perston et al. (1996)]. The leach liquor is then filtered off and washed with water. An aliquot, 10ml, is withdrawn and evaporated then redissolved in 10ml of 1N $HClO_4$ for Nd-spectrophotometric examination.

In pilot plants, the leach liquor is directly introduced to the mixer settler [Perston et al. (1996)]. In the present work, precipitation from the leach liquor is firstly performed with saturated oxalic acid solution where the pH is slightly raised with ammonia to 2.5. The formed precipitate is washed and dried then converted to the oxide at 650°C for 1 hour. Four grams of each oxide concentrate is dissolved in the least amount of hot

HCl, evaporated and redissolved in 100ml of 1N HClO₄ for Nd-spectrophotometric examination [Perston et al. (1996); Abdelhamied et al. (2004)].

RESULTS AND DISSCUSION

Mineralogical studies of the two samples representing the weathered and unweathered phosphorites are carried out petrographically and supported by X-ray diffraction analysis (XRD). Petrographical studies of thin sections prepared from the natural rock samples and grain-mounted slides prepared from the physically concentrated samples reveal that they are composed of fine to medium sand-size phosphatic grains (pellets, bones and lithoclasts) cemented by gypsum and carbonate (mainly dolomitic) cement. Other clastic components comprise minor amounts of quartz, glauconite and clay minerals.

XRD identifications reveal that the main phosphate minerals in the studied two samples are fluorapatite and carbonate-apatite (Fig. 3). These two minerals are characterized by the strong diffraction lines 2.80, 2.70, 2.77 and 3.44 Å (ASTM Card 15-876); and 2.78, 2.68 and 3.46 Å (ASTM Card 19-272), respectively. The main gangue minerals include minor amounts of quartz, gypsum, dolomite and traces of pyrite detected only in the unweathered sample.

Moreover, detailed mineral chemistry studies reveal that carbonate-fluorapatite (francolite) is the essential mineral detected in the phosphatic grains [Kamel et al. (1977); El-Kammar and Basta (1983)].

Chemical analyses of both raw materials before and after in situ physical concentration to enrich their economic constituents are illustrated in Table (2). Minor and trace element contents are not determined. The acid insoluble residue is mainly quartz and has no considerable content of lanthanides (Ln₂O₃) [Bliskowskii et al. (1969)].

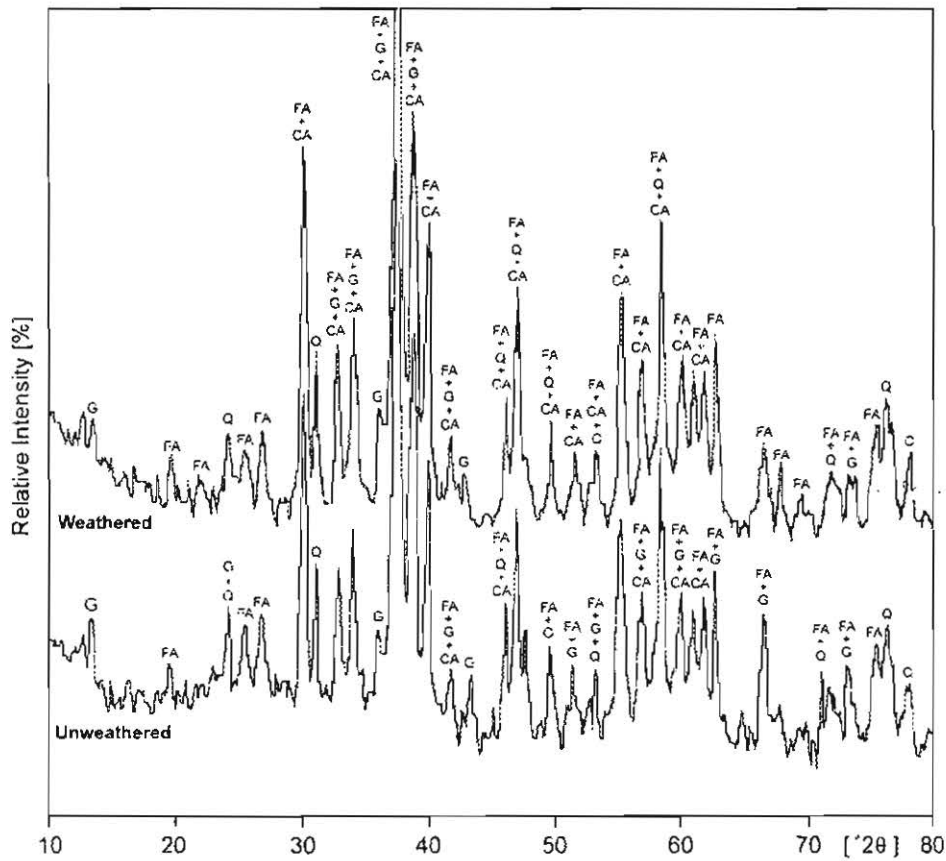


Fig. (3): X-ray diffraction patterns of the weathered and unweathered phosphorite samples (FA = Fluorapatite, CA = Carbonate-apatite, Q = Quartz and G = Gypsum).

Table (2): The main constituents (%) of Abu Tartur phosphorites before and after in situ physical concentration.

Element (Oxides)	Weathered phosphorite (%)		Unweathered phosphorite (%)	
	Before conc.	After conc.	Before conc.	After conc.
P ₂ O ₅	23.90	31.22	24.64	32.20
CaO	40.03	47.50	41.64	51.10
Ln ₂ O ₃	0.11	0.13	0.11	0.14
U ₃ O ₈	0.0025	0.0035	0.0028	0.0036

Figures (4-8) show qualitative identification of the product solutions. Direct scanning of the solutions is not suitable for accurate identification (e.g. Figure 5), whilst the third derivative gives good results (Figures 6, 7, 8).

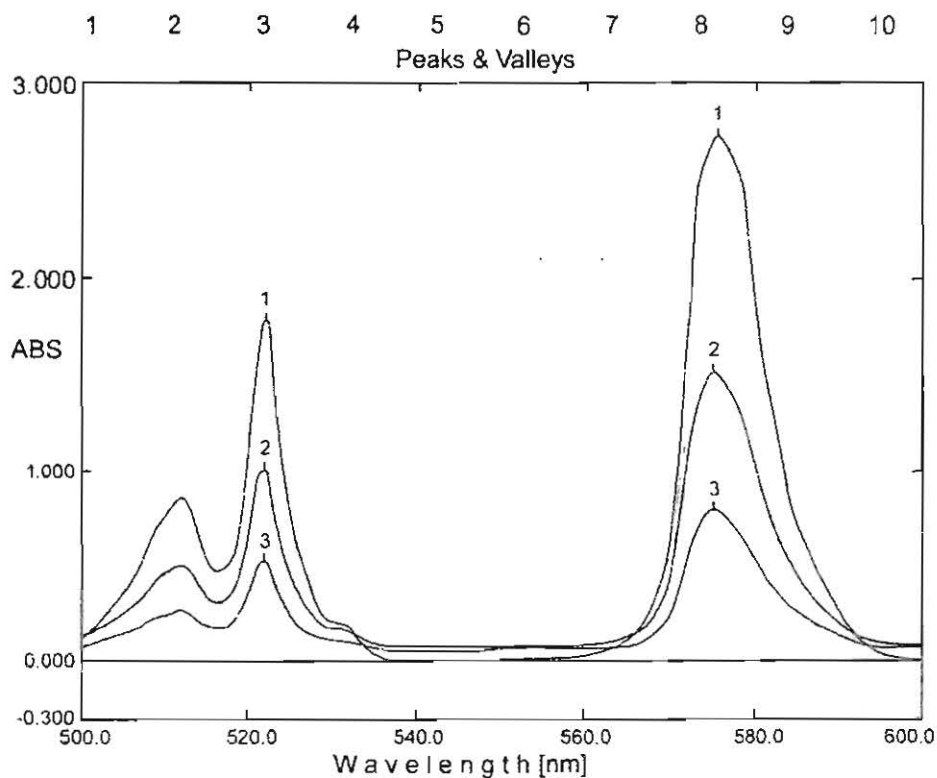


Fig. (4): Spectrophotometric scanning of synthetic neodymium standard solutions; (1) 2.05%, (2) 1.025% and (3) 0.513% in 1N HClO₄. The absorbance values are: 2.749, 1.496 and 0.804 for the solutions 1, 2 and 3, respectively at the maximum absorption wavelength $\lambda_{\text{max.}} = 575 \text{ nm}$.

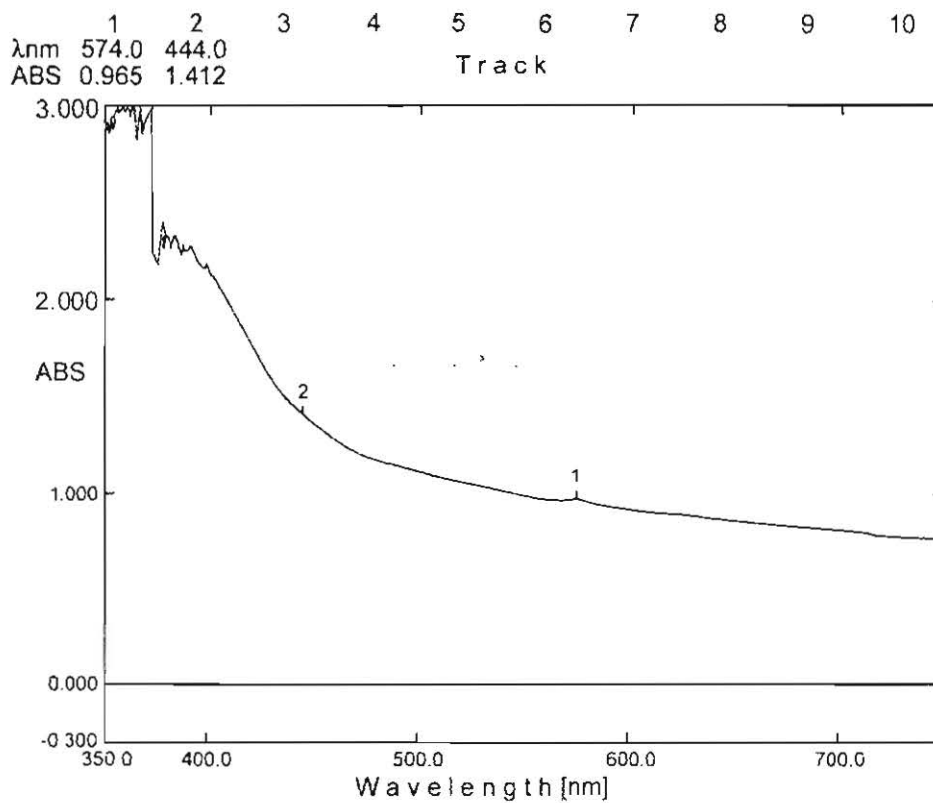


Fig. (5): Qualitative investigation of Nd through scanning of REEs concentrate solution (4gm in 100ml 1 N HClO_4) produced from the unweathered sample. Absorbance value $A_1 = 0.965$ at 575 nm (for Nd). A_2 represents absorbance value 1.412 at 444 nm (the maximum absorbance value of Pr).

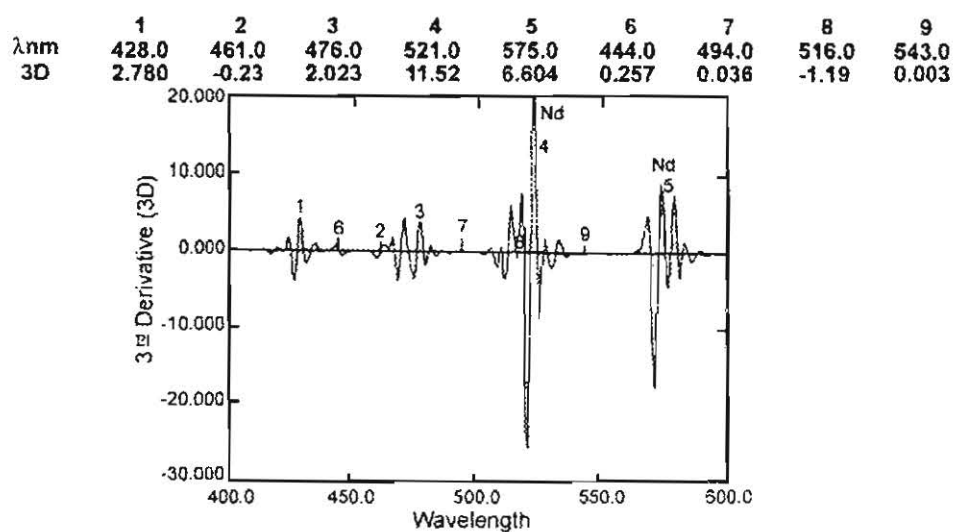


Fig. (6): The third derivative (3D) of Nd absorption bands, 3D = 6.604 at λ 575 nm for 2.05gm Nd_2O_3 /100ml of 1N HClO_4 .

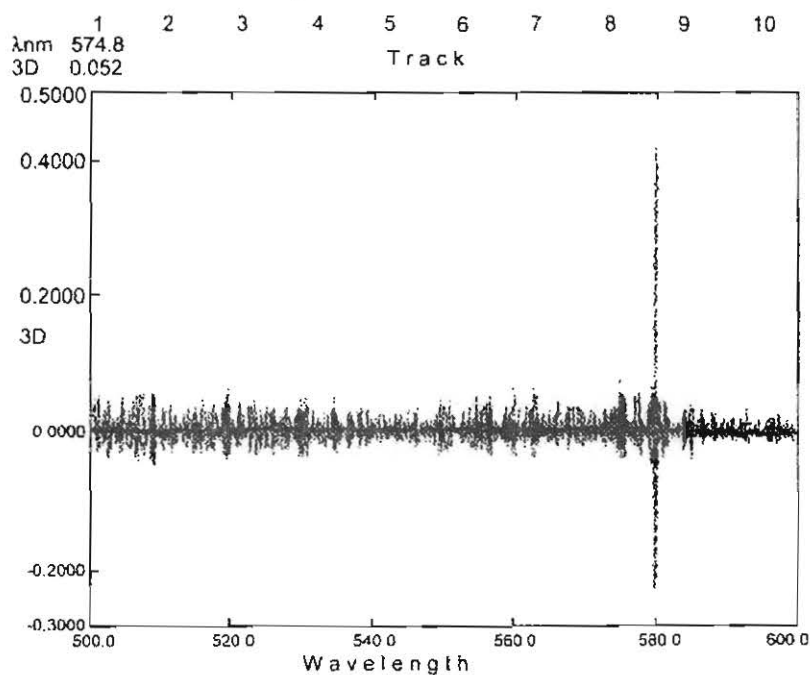


Fig. (7): The third derivative 3D of the output REEs concentrate solution, showing Nd spectrum at λ 575 nm ($A = 0.290$), produced from the weathered phosphorite sample (0.622gm/100ml of 1N HClO_4).

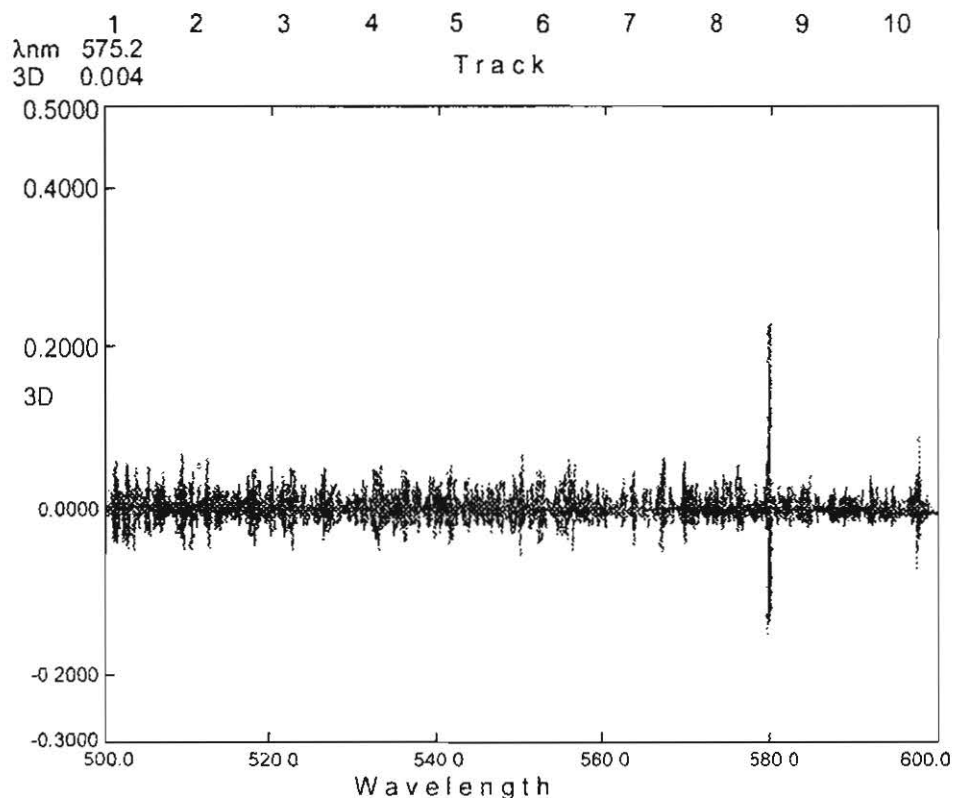
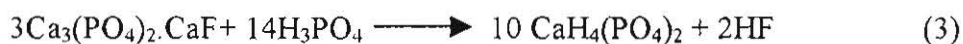
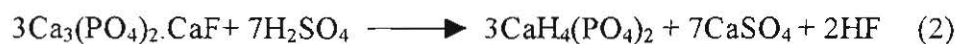


Fig. (8): The third derivative 3D of the output REEs concentrate solution, showing Nd spectrum at λ 575 nm ($A = 0.210$), produced from the unweathered phosphorite sample (0.27gm/100ml of 1N HClO_4).

In contrast to igneous rocks, the lanthanides in phosphorites do not form their own minerals but enter to the crystal lattice of calcium phosphate in isomorphous substitution for calcium [Habashi (1985)]. Breaking down of phosphorous is therefore proportional to the occurrence for lanthanides according to the following equations:



Superphosphate is formed in equation (2), which contains the hydrated calcium sulphate and triple superphosphate (Fao et al., 1958). Analysis of phosphoric acid shows that the P_2O_5 contents are 24.5% and 28.7% for the weathered and unweathered phosphorites, respectively.

It is expected that more than 97% of REEs as well as uranium are co-precipitated with phosphogypsum [Belg (1980)]. The resulted phosphate residue (phosphogypsum) undergoes nitric acid leaching and filtration. No considerable Nd-absorption peaks is observed at λ_{max} 575nm [Abdelhamied et al. (2004)]. This may refer to the interfering elements such as Ca, P and Fe, besides other REEs.

Four grams from each of the produced concentrates (after oxidation at $650^\circ C$) are dissolved in the least amount of hot hydrochloric acid, evaporated then redissolved in 100ml of 1N $HClO_4$.

The dried precipitate product is identified through applying laser fluorometry and spectrophotometry. Problems of elemental interference, which may encounter the determination of uranium, phosphorous and REEs can be eliminated through applying internal standard addition and dilution methods. Linearity in both figures (9) and (10) proving the absence of interference effect. Table (3) summarizes the results obtained.

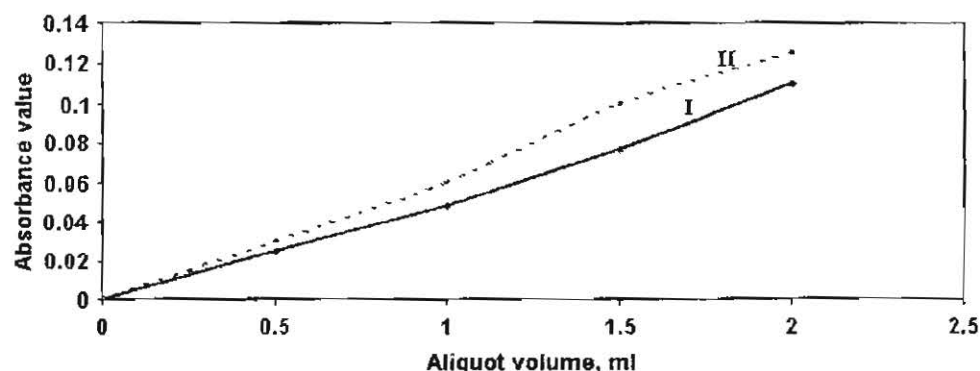


Fig. (9): Effect of changing the aliquot volume of phosphorus-molybdate on the corresponding absorbance values of the product I (produced from weathered phosphorite), and the Product II (produced from the unweathered phosphorite).

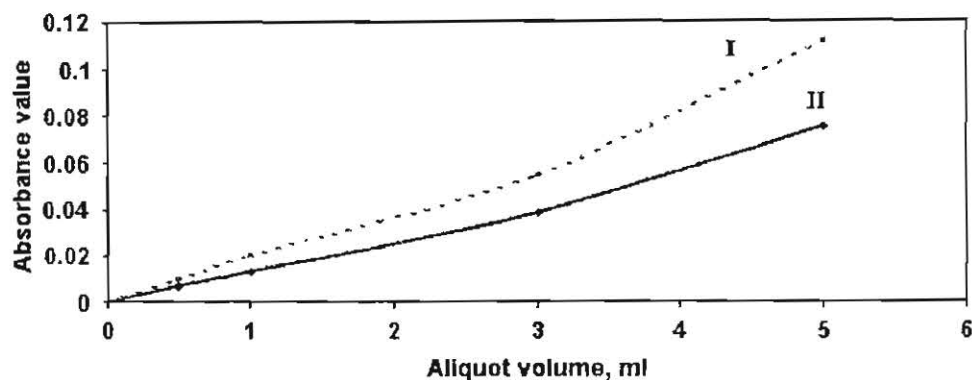


Fig. (10): Effect of changing the aliquot volume of REEs-Arsenazo III on the corresponding absorbance values of the product I (produced from weathered phosphorite), and the product II (produced from the unweathered phosphorite).

Table (3): Constituents of the two final products (I) and (II) resulting from the processing of weathered and unweathered samples, respectively.

Element (Oxides)	Product (I) (%)	RSD (%)	Product (II) (%)	RSD (%)
P ₂ O ₅	5.42	± 4.80	6.90	± 4.90
CaO	8.11	± 4.00	8.40	± 3.90
Fe ₂ O ₃	0.071	± 1.95	0.18	± 3.00
Ln ₂ O ₃	0.91	± 4.00	0.76	± 4.00
U ₃ O ₈	0.016	± 2.00	0.014	± 1.30
LOI*	84.00	----	83.60	----

* Loss on Ignition

SUMMARY

Experimental work is applied on the leaching of REEs from Abu Tartur phosphorites. They are then coagulated as RE-hydroxides/oxalates concentrates. Analytical procedures of assaying the product contents are adjusted for accurate determinations of phosphorous, calcium, iron and REEs. The end products are more concentrated in REEs by 5-7 times than the ore phosphorites. Accordingly, extraction of REEs for purification purposes can be successfully applied in other work as will be discussed later on.

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نحو إستخلاص العناصر الأرضية النادرة كمنتج ثانوي أثناء تشغيل

خامات فوسفات أبوظرطور

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هيئة المواد النووية، ص ب ٥٣٠ المعادى، القاهرة.

في هذا العمل تم اختيار ركازين من خامات فوسفات أبو طرطور، الصحراء الغربية، كخامتين أوليتين لعمليات التشغيل. مثلت إحدى هاتين الخامتين راسب الفوسفات السطحية المكشوفة بينما الأخرى تمثل الخامات المستخرجة من المناجم تحت سطحه. و قد تم تقويم مدى صلاحية هاتان العينتان من الناحية المعدنية للاستخدام كخامات أولية. و من الناحية الكيميائية تبين أن المحتوى الأساسى لكل من الخام السطحي و تحت السطحي هو على التوالي ٠,١٣ ، ٠,١٤ % لأكاسيد العناصر الأرضية النادرة و ٣١,٢ و ٣٢,٢ % لخامس أكسيد الفوسفور بينما وجد أن تركيزات ثمانى أكسيد اليورانيوم هي ٣٥ ، ٣٦ جزء فى المليون.

وقد استخدم حمض الكبريتيك المركز فى عمليات تشغيل الخامات على المستوى المعلى الذى أنتج حمض الفوسفوريك و مركب فوسفات الجبس والذى بدوره يحتوى على العناصر الارضية النادرة التى تصفى باستخدام حمض النيتريك عالى التخفيف. وقد أمكن إختبار مدى إستخلاص العناصر الأرضية النادرة من الناحية الكمية بالمسح الطيفى بواسطة جهاز التحليل الطيفى اللوني. كما تم بعد ذلك فصل العناصر الارضية النادرة بالترسيب من المحلول الأزوتى.

وجد أن تركيزات العناصر الأرضية النادرة فى منتجات المعالجات السابقة هي ٠,٩١ ، ٠,٧٦ %، على التوالي و كذلك تركيزات ثمانى أكسيد اليورانيوم هي ٠,٠١٦ ، ٠,٠١٤ % بينما تركيزات خامس أكسيد الفوسفور هي ٥,٤٢ ، ٦,٩٠ % و تركيزات أكاسيد الحديد هي ٠,٠٧ ، ٠,١٨ % و تركيزات أكسيد الكالسيوم هي ٨,١١ ، ٨,٤٠ % بالإضافة إلى مقادير ضئيلة من أكسيد الماغنسيوم لا تتعدى ٢٠٠ جزء فى المليون. ووجد أن قيم الانحراف المعيارى النسبية للتحاليل الكيميائية لا تتعدى $\pm ٥\%$.

وهذه النتائج تعتبر مشجعة للاتجاه نحو تنقية هذه المنتجات كما سيتم مناقشته فيما بعد.