

ISOLATION OF PHOSPHORIC ACID BY-PRODUCT THROUGH MONAZITE PROCESSING

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ABSTRACT

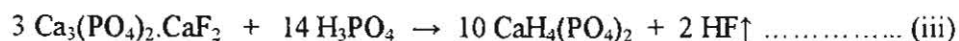
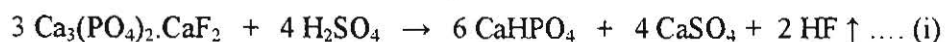
Batches (each is 100 gm) of a crude monazite material are processed with sulphuric acid at different conditions. This is for flowing out phosphoric acid as a by-product whilst producing concentrates of thorium and rare earth elements. The "input" raw, monazite, material was mineralogically investigated with Environmental Scanning Electron Microscope (ESEM) showing Monazite (46% Ln_2O_3), Zircon (ZrSiO_4), Ilmenite (FeTiO_3) and Rutile (TiO_2). The studied conditions are: acid/raw material ratio, breaking down temperature, agataition time, and acid/leaching water ratio. Laser-fluorometry is adapted, in the present work, for rapid analysis of uranium in different lixiviated solutions. Spectrophotometry is, moreover, applied for the rare earth elements, thorium and phosphorous analyses. Results obtained, prove the ability of producing crude, technically phosphoric acid (14% P_2O_5) with the least contaminated elements (0.137% U_3O_8 , 0.03% ThO_2 and 1.6% Ln_2O_3). The relative standard deviations are found to be less than $\pm 4.0\%$ for all analyses works.

Purification and preconcentration of the obtained phosphoric acid will be discussed currently.

INTRODUCTION

Phosphoric acid, the main source of fertilizers, is usually produced when phosphate rocks are leached with H_2SO_4 , HNO_3 or HCl [Fathi Habashi, (1985)].

The following breaking down reaction steps are summarizing the Egyptian treatment of phosphate ores with sulphuric acid in Abu.Zaabal Phosphate Plant [Husseini, (1994)]:

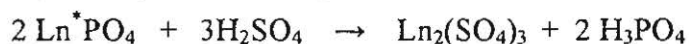


Superphosphate is formed in equation (ii) which contains the hydrated calcium sulphate and triple superphosphate [Smutz, (1958)].

New sources for the acid production is, nowadays, becoming essential due to the great consumption of phosphate rocks (about 130 million tons of the rock/year [Fathi Habashi, (1985)]).

In Egypt; the black sand monazite is considered as a phosphate deposit. It forms about 0.4 - 0.6 % of the highly concentrated surficial black sand and is essentially an orthophosphate of rare earth elements and thorium. Moreover, it is widely distributed along rosetta area on the Mediterranean coast.

Commercial monazite, which is easily obtainable, is processed with sulphuric acid for producing rare earth elements and thorium concentrates [Nesmeyanov, (1980)] as follows;



Phosphoric acid, in this situation, is usually consumed as waste.

Product quantities of thorium, rare earth elements and consequently phosphorous are varied on controlling the acid/raw material ratio, breaking down temperature and sludge leaching temperature [Smutz, (1954); Moneir, et al. (2004) and Moneir, et al. (2004)].

The present work deals with optimizing conditions for isolating phosphoric acid as a by-product leaving behind the main products thorium and rare earth elements undissociated.

EXPERIMENTAL

Chemicals and Reagents

All the used chemicals are highly pure for analysis. Their specifications are as follows :

* Ln is lanthanides and is used, in the present work, as an alternative of rare earth elements in the oxide forms.

Sulphuric acid, 97-99% (Adwic, Egypt), hydrochloric acid HCl, 34-37% (Adwic, Egypt), H_3PO_4 , 85% (Adwic, Egypt), ammonium hydroxide, NH_4OH , 35-37% (Adwic, Egypt), oxalic acid, $(COOH)_2 \cdot H_2O$, 99% (Adwic, Egypt).

Reagents used are; arsenazo III (60%), sodium salt of (2,2-[1,8-dihydroxy-3,6-disulpho-2,7-naphtholene biz(azo)]dibenzene arsonic acid) (Sigma, USA); thorium chloride, $ThCl_4$, 56% (Prolabo-Adwic, Egypt), lanthanum(III) oxide, La_2O_3 , 99% (Merck, Germany), cerium(III) chloride, $CeCl_3 \cdot 7H_2O$, 99% (Winlab., UK); ytterium oxide, Y_2O_3 , 99.9% (Nentegh, UK).

Fluran solution is a synthetic buffer solution (Scintrex, Canada) mixed with uranium solution for laser-fluorometric analysis.

Instrumentation

The conventional binocular stereomicroscope is, firstly used for general identification of mineral composting the raw "in-put" material.

Environmental Scanning Electron Microscope (ESEM), Philips XL30 is, moreover applied for brief qualitative investigation of the in put materials. Operating conditions are : low vacuum, 30 kV, and BSE equals 10.0.

A pH-meter (Schott, Germany) is used for all acidities adjustments. The instrument is calibrated before measurements using two successive standard buffer solutions (4 and 7).

A double beam spectrophotometer (UNICAM, England) is used for all spectrophotometric analyses. The optical system is automatically checked before measurements. The instrument is periodically calibrated using different concentrations of dichromate solutions [Babko, (1971)].

Laser fluorometry (Scintrex, Canada) is applied for uranium analysis in different phosphate matrices. Sensitivity is adjusted between 7 and 10. The instrument is calibrated using fluran starting from 1.4 ppb.

Table (1): conditions for Atomic Absorption measurements of Cr,Cu and Ti.

Element	Lamp Current	Flame type	Wavelength nm	Slit width nm	Working range $\mu g/ml$	D.L
Cr	6 mA	Nitrous oxide/Acetylene	357.9	0.2	2-15	0.05
Cu	3 mA	Air/ Acetylene	324.7	0.5	1-5	0.025
Ti	18 mA	Nitrous oxide/Acetylene	364.3	0.2	50-200	1.1

All measurements are repeated three or five times for calculating the relative standard deviations (RSD).

Processing of the Monazite Raw Materials

1- Series of monazite samples, each is 10 gm., are mixed separately with 20 ml of concentrated H_2SO_4 , covered and heated, with continuous stirring, at different temperature degrees: $50^\circ C$, $75^\circ C$, $100^\circ C$, $150^\circ C$, $200^\circ C$ and $250^\circ C$, for two hours. Each formed sludge is leached with 20-30 ml hot water ($45^\circ C$) and then filtered off. The acid insoluble residue is investigated and P_2O_5 is determined in each filtrate using molybdate procedure [Marcezenko, (1981)].

2- The selected conditions from the previous step, which leach most of phosphorus, is applied in a bench scale through weighing 100 gm and mixing the material with 200-250 ml of concentrated H_2SO_4 . The sludge is then diluted by 200 ml hot water ($45^\circ C$) stirred for 1 hour. The formed lixiviat solution is decanted and completed up to 1 L for analysis. The insoluble residue is then redissociated with sulphuric acid (by the ratio 1:4 w/v) heated at $300^\circ C$, with continuous stirring for 2 hours, leached with iced water as had been illustrated earlier [Smutz, (1954); Moneir, et al. (2004) and Moneir, et al. (2004)].

RESULTS AND DISCUSSION

Mineralogical identification of the raw material helps in expecting elements which will associate phosphorus in the solution and consequently qualifying the acid product. The following figures (1-4) illustrate the existence of monomineralic grains as well as the composite one. The single grains represented by zircon ($ZrSiO_2$), Figures (1, 2), rutile (TiO_2), Figure (3), ilmenite ($FeTiO_3$), Figure (4), chromite ($FeCr_2O_4$), Figure (5), hematite (Fe_2O_3), Figure (6), amphiboles ($Mg Fe Mn Ca Al SiO_4$), Figure (7) and garnet ($Ca Fe Al SiO_4$), Figure (8).

The started raw material had been chemically analyzed earlier [Moneir, et al. (2004)], the major constituents are summarized in table (1).

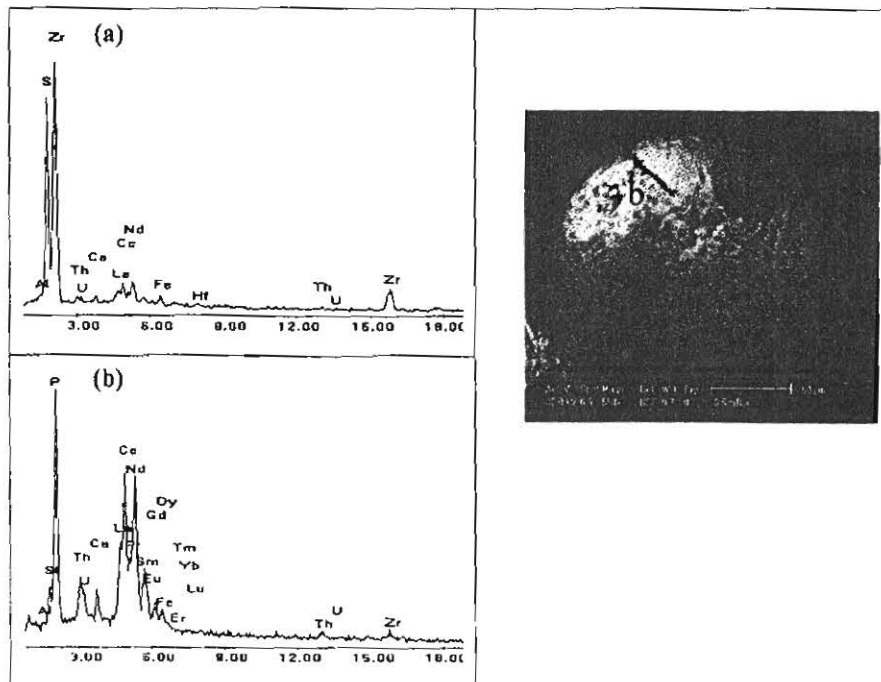


Fig. (1): EDX and BSE investigation of the input raw material showing inclusion of zircon (a) in monazite grain (b).

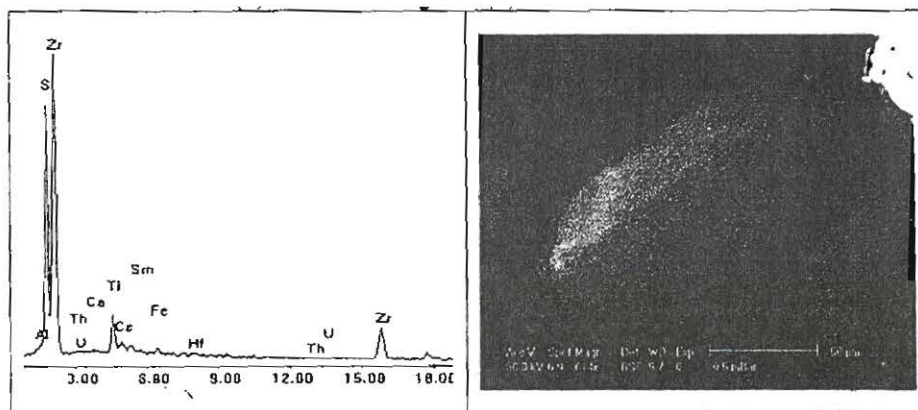


Fig.(2): EDX and BSE image show prismatic bipyramidal zircon grain associated with the input monazite raw material.

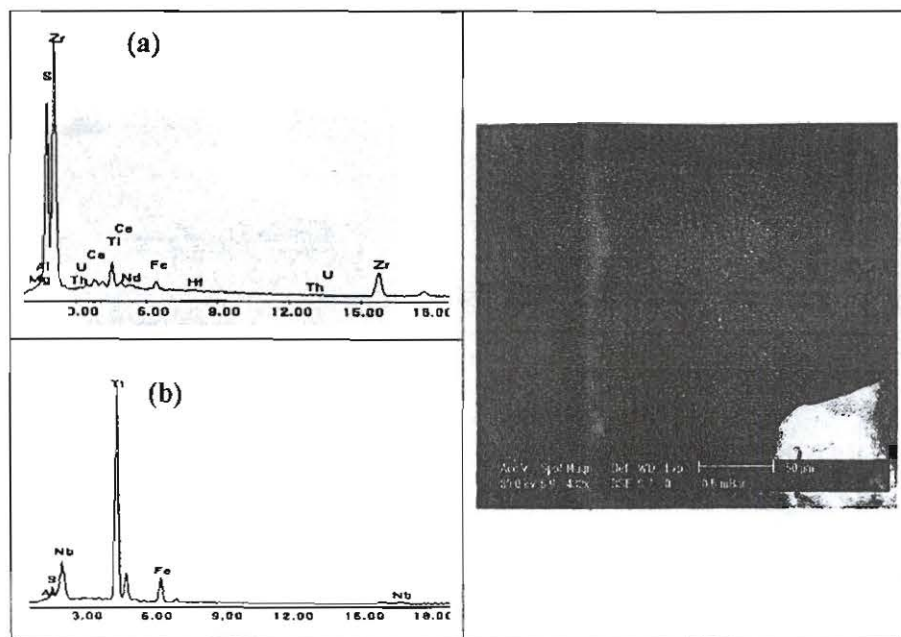


Fig. (3): EDX and BSE image show zircon grain (a) and rutile grain (b) associated with the input monazite raw material.

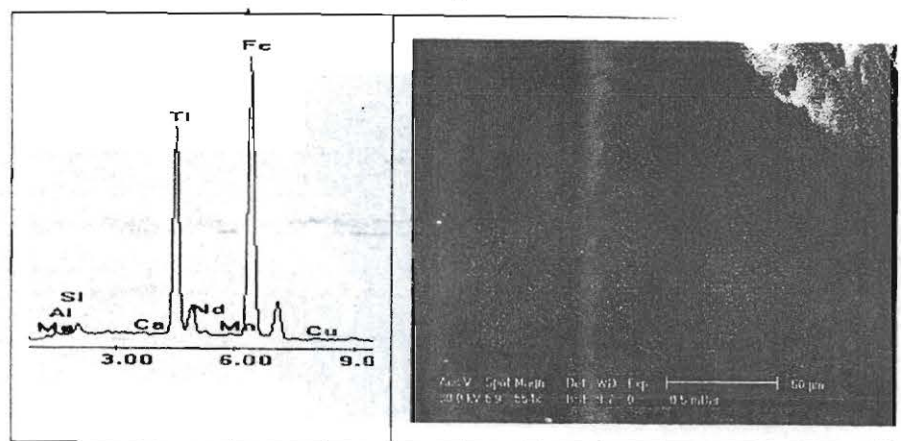


Fig. (4): EDX and BSE image show ilmenite grain associated with the input monazite raw material.

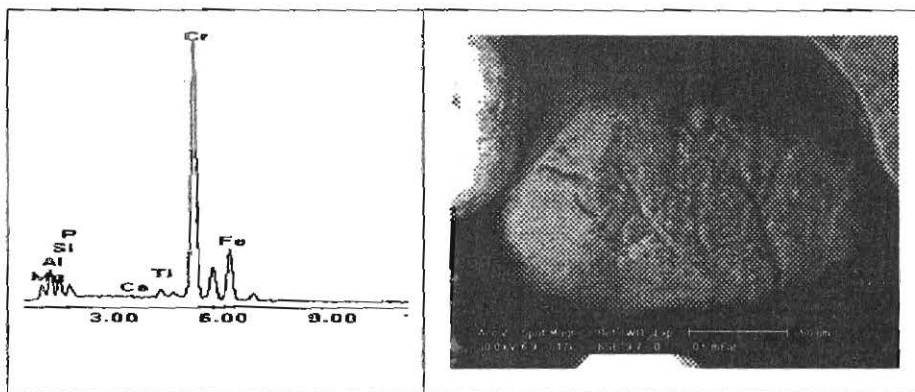


Fig. (5): EDX and BSE image show chromite grain associated with the input monazite raw material.

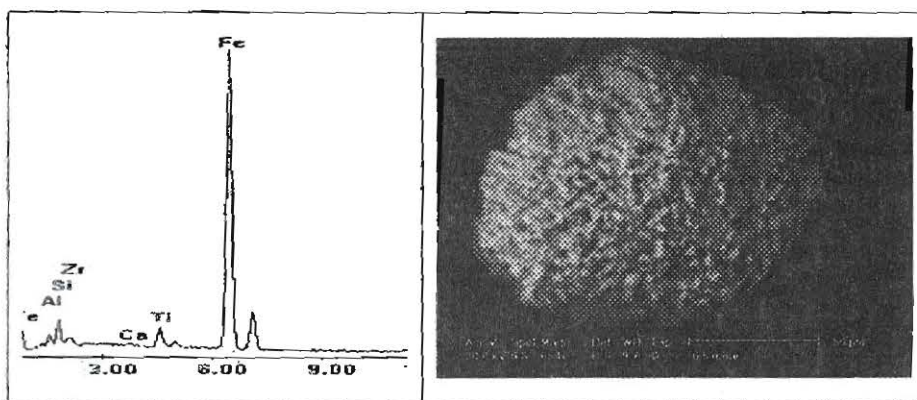


Fig. (6): EDX and BSE image show hematite grain associated with the input monazite raw material.

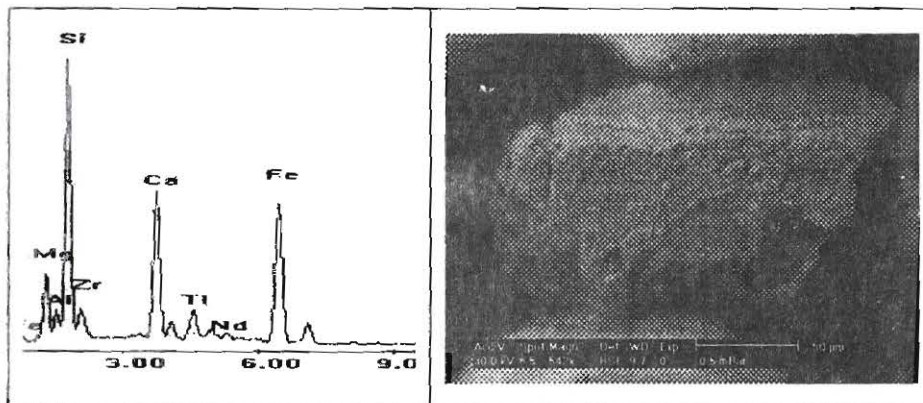


Fig. (7): EDX and BSE image show amphiboles grain associated with the input monazite raw material.

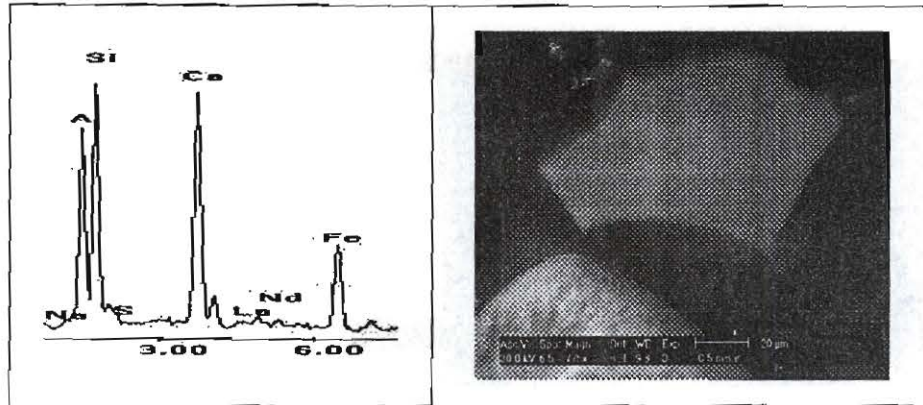


Fig. (8): EDX and BSE image showing garnet grain associated with the input monazite raw material.

Figure (9) shows that the “optimum digestion temperature” is started from 200°C. At which, most of phosphorus are breaking down with keeping most of Ln_2O_3 and ThO_2 in the acid insoluble residue.

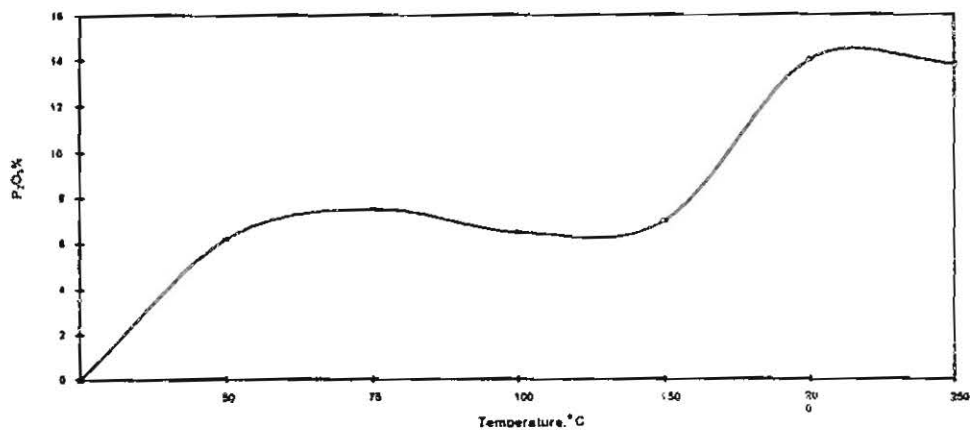


Fig. (9): Effect of Changing the Breaking Down Temperatures on the Dissolution of Phosphorus in the Hot Leach Liquor Solutions (at 45°C). Material/acid ratio is 1:2 (w/v) and acid/water leaching ratio is 1:1 (v/v).

Table (2) : Major constituents of the monazite raw material.

Element	constituent %
P ₂ O ₅	20
Ln ₂ O ₃	46.4
ThO ₂	3.4
U ₃ O ₈	0.39

Although laser-fluorometry shows high sensitivities towards uranium analysis in different matrices, it has some defaults in phosphoric acid media [Wang, et al. (1983); Moneir, (1982) and Aly, et al. (1988)]. Phosphorus causes considerable enhancement in the uranyl fluorescence appearance [Moulin, et al. (1993)]. Figure (10), in this situation, illustrates the ability of determining uranium directly in 0.04 and 0.06 M phosphoric acid with out prior addition of fluoran. It can be applied, in the present work for rapid monitoring of phosphoric acid products via uranium analysis.

The total rare earth elements (REEs) and thorium are determined separately with arsenazo III after separation with oxalate at pH<3 [Marcezenko, (1981)].

The following flow diagram summaries processing steps for crude phosphoric acid production.

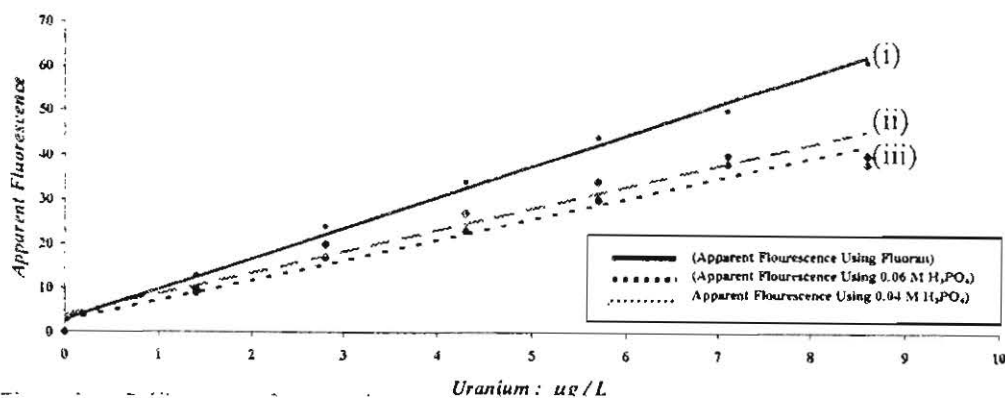


Fig. (10): Calibration of Laser Fluorometry Using Fluoran Buffer Solution (i), 0.06 M H₃PO₄ (ii) and 0.04 M H₃PO₄ (iii) respectively.

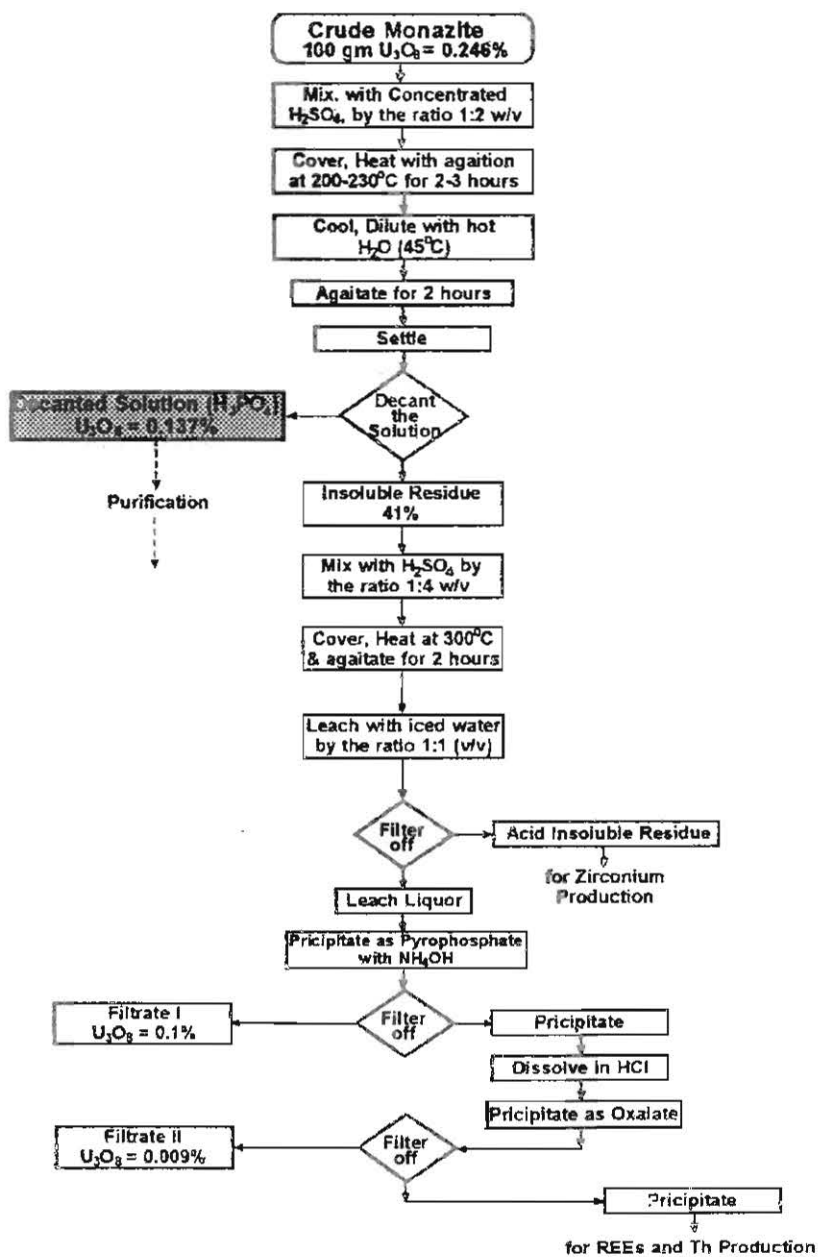


Fig. (11): Flow diagram for the Production of Phosphoric Acid (Decanted Solution) as a By-Product Through out Processing of Commercial Monazite with Sulphuric Acid.

The three solutions, decanted, filtrate I and filtrate II are then treated for chemical analyses. An aliquot portion, 10 ml, is therefore withdrawn from each solution, evaporated (using few drops of H_2SO_4 when necessary), redissolved in diluted HCl (1:1) and then completed up to suitable volume for analysis. Effect of interfering elements on the analysis of P_2O_5 , REEs and Th are examined spectrophotometrically. This has been done through constructing calibration graphs (for the analyzed elements) using different volumes from each sample solution. Figures (12) and (13) show Beer's linearity, in case of determining P_2O_5 , which indicate the absence of interfering elements. Table (2), in the other hand outlines the data obtained. The most serious elements associate the acid, Cu, Cr and Ti are, moreover, determined in the raffinate after extracting phosphoric acid with a suitable organic solvent [Smutz, (1958) and Smutz, (1954)] (as shows table (3)).

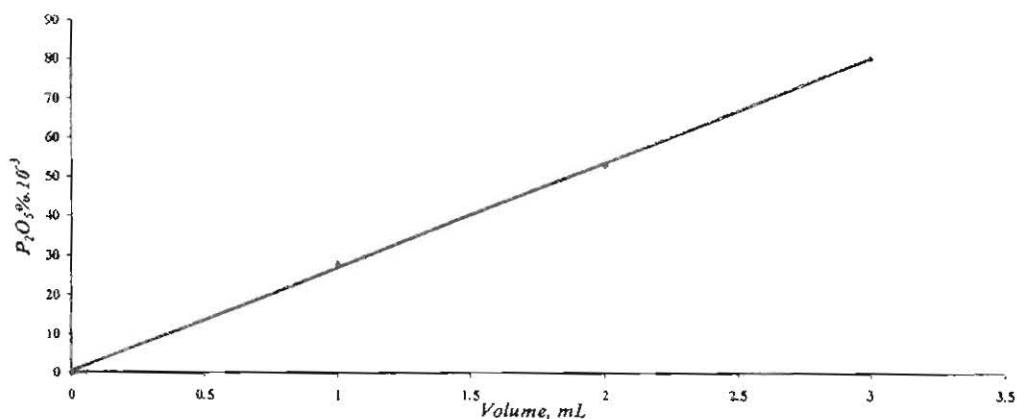


Fig. (12): Effect of Changing Aliquot Volume, mL, on the Determination of P_2O_5 in the Decanted Solution.

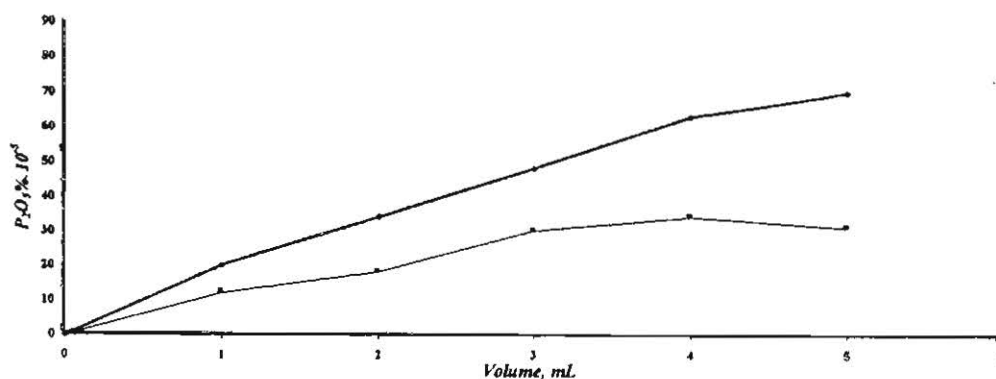


Fig. (13): Effect of Changing Aliquot Volume, mL, on the Spectrophotometric Determination of P_2O_5 in Filtrate I and Filtrate II.

Table (3): Major constituents in the decanted solution, filtrates I and II.

Element (as oxide)	Concentration (%)		
	Decanted Solution	Filtrate I	Filtrate II
P_2O_5	14	0.4114	0.26
Ln_2O_3	1.6	15	0.0009
ThO_2	0.032	0.23	0
U_3O_8	0.137	0.1	0.009

Table (4): The minor constituents in the decanted phosphoric acid product (using Atomic Absorption Spectrometry).

Element	constituent (ppm)
Cr	2400
Cu	1.7
Ti	1480

SUMMARY :

Crude phosphoric acid can be isolated through processing of commercial monazite with sulphuric acid.

Analysis of the isolated acid shows low contaminated elements a factor helps to purify phosphoric acid for fertilization use as well be discussed currently.

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فصل حامض الفوسفوريك كنتاج ثانوى من خلال عمليات معالجة معدن المونازيت

منير عبدالفتاح عبدالحميد ، رجاء الشيخ شهاب ، محسن محمد على ، حامد إبراهيم ميره ،
صلاح البلاقى وأحمد حسين عرابى

تم تشغيل مجموعات من خام المونازيت منخفض النقاوة باستخدام حامض الكبريتيك وعند ظروف متفاوتة بهدف الحصول على حامض الفوسفوريك كمنتج ثانوى أثناء إنتاج ركازات الثوريوم والعناصر الأرضية النادرة. وقبل البدء فى التشغيل تم التعرف على المكونات المعدنية للخام باستخدام تقنية الميكروسكوب الألكترونى وتبين وجود معادن المونازيت ، الزركون ، الألمينيت والروتيل كمعادن أساسية فى الخام.

تم فى أثناء تجارب ضبط ظروف التشغيل المناسبة استخدام جهاز التحليل الطيفى الوميضى (الليزر) للتحليل المتتابع لليورانيوم بجانب تقنية التحليل الطيفى اللونى وذلك لتقدير تركيزات العناصر الأرضية النادرة ، الثوريوم والفوسفور. تم الحصول على حامض الفوسفوريك (الغير النقى) والذى وجد أن به أكسيد الفوسفور الخماسى بنسبة ١٤ %.

سوف يتبع هذا البحث بمشينته تعالى عمليات التركيز والتنقية للمنتج للحصول على حامض الفوسفوريك عالى النقاوه.

