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RECOVERY OF SOME TRACE ELEMENTS FROM IRAQI PHOSPHATE PRODUCTS

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ABSTRACT

Trials have been attempted to evaluate the recovery of some trace elements in the Iraqi phosphate rocks and phosphate fertilizers products since the nineties of the twentieth century. Leaching solid-liquid extraction was conducted for the recovery of Cd and Zn from the basic slime wastes produced in the Iraqi Al-Qaim fertilizer complex using various inorganic acids, basis and ammonium salts. Almost quantitative recovery was obtained for Cd and Zn by ammonium chloride and ammonium nitrate solutions.

A method has been developed for the recovery of U, Th and other heavy elements from the acidic phosphogypsum produced as waste at Al-Qaim fertilizer complex using the concept of preferential solubility of phosphogypsum over other trace elements sulfates and phosphates in potable water. The undissolved or partially dissolved metal salts remain hanged as colloids then accumulated after 30 – 60 minutes. Most of the trace elements are expected to exist in water as sparingly or insoluble sulfates, phosphates, silicates and fluorides. Chemical analysis of the isolated phosphogypsum, after water evaporation, showed reasonable purity suitable for various industrial applications. The method has been further developed recently using pH, conductimetric and turbidometric techniques to follow the solubility of phosphogypsum as function of various parameters.

Uranium, on the other hand, was recovered on industrial scale, from green phosphoric acid by liquid-liquid extraction technique and di-2-ethyl-hexyl-phosphoric acid (DEPA)-trioctylphosphene oxide (TOPO)-kerosene/ phosphoric acid solutions. The plant installed at Al-Qaim depends on mixer settlers as contactors. More than 150 tons of uranium was recovered as yellow cake, but the plant was destroyed during the 1991 war. High purity phosphoric acid was produced from green phosphoric acid on a pilot plant scale using liquid-liquid extraction technique and mixer-settler contactors. The extraction system "40% tributyl phosphate (TBP)-kerosene" was applied as the organic phase. The process revealed group removal of U, Th and other heavy metals as by-products in 20% green phosphoric acid.

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استخلاص بعض العناصر النزرة من منتجات الصناعة الفوسفاتية في العراق

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المستخلص

تتناول هذه الورقه دراسة وتقييم إمكانية استخلاص بعض العناصر النزره المتوفره في صخور الفوسفات العراقيه ونواتج صناعة الأسمده الفوسفاتيه والتي بدأت في العراق منذ عقد التسعينات من القرن الماضي. أمكن ومن خلال تجارب مختبريه استخلاص واسترجاع الكادميوم والخارصين من مخلفات السلايم القاعديه الناتجه عن عمليات تركيز الفوسفات في مجمع القائم لإنتاج الأسمده الفوسفاتيه باستعمال حوامض غير عضويه وقواعد وأملاح الأمونيوم وتم تحقيق استرجاع شبه متكامل لهذين العنصرين باستعمال كلوريد الأمونيوم ونترات الأمونيوم. كما تم تطوير طريقه لاسترجاع اليورانيوم والثوريوم وعناصر ثقيله أخرى من مخلفات الفوسفوجبسم الحامضيه الناتجه عن إنتاج حامض الفوسفوريك بالطريقه الرطبه في المجمع أعلاه باعتماد قابلية الذوبان الانتقائي للفوسفوجبسم بالمياه العذبه بالمقارنه مع كبريتات وفوسفات العناصر الثقيله حيث تبقى المركبات غير الذائبه عالقه كمحلول غروي وتترسب بعد ٣٠ – ٦٠ دقيقه. بينت التحليلات الكيميائيه للرواسب المسترجعه المجففه نقاوه مناسبه للعديد من الاستعمالات الصناعيه وقد تم تطوير الطريقه باعتماد أساليب جديده. بدأ استخلاص اليورانيوم من حامض الفوسفوريك الأخضر صناعيا في مجمع القائم للأسمده الفوسفاتيه باعتماد التقنيات المتاحه عالميا (DEPA-TOPO) وأمكن خلال سنوات تشغيل وحدة التنقيه استرجاع ما يقرب من ١٥٠ طن من أوكسيد اليورانيوم (الكعكه الصفراء) غير أن هذا النشاط توقف بعد تدمير وحدة الاستخلاص خلال حرب الخليج عام ١٩٩١. أمكن إنتاج حامض الفوسفوريك عالي النقاوه من حامض الفوسفوريك الأخضر من خلال تجارب رياديه باستعمال تقنية الاستخلاص (TBP-kerosene) لإزالة العناصر الثقيله والمواد العضويه.

INTRODUCTION

Marine sedimentary phosphorites are geochemical sinks for many minor and trace elements; some of which are of economic importance and/ or of environmental hazard. In calcareous phosphorites these elements tend to fractionate between the three main products of the phosphate fertilizer production process which includes phosphate concentration by calcination and disliming followed by sulfuric acid attack of the concentrate. These products are phosphoric acid, lime sludge (slime) and phosphogypsum.

Phosphoric acid is considered an important alternative source of uranium in the world (IAEA, 1989). The world's phosphorite resources are estimated by about 300 billion tons (USGS, 2012; in Al-Bassam *et al*., 2012), about 18 billion tons of which are classified as economic reserves with 50 – 200 ppm uranium content (IAEA, 1989). About 85% of all phosphate rocks produced worldwide is used in the fertilizers industry and more than half of the world's production of phosphatic fertilizers is via the production of phosphoric acid (Derry, 1981). About two decades ago there were about 400 wet process phosphoric acid plants in operation worldwide; from which some 13000 tons of U_3O_8 could, in principle, have been recovered each year, considering 50 – 200 ppm U content (IAEA, 1989).

Intensive fertilization brings problems as the process of wet phosphoric acid production from phosphate rocks, following the attack with sulfuric acid, accompanied by the solubilization of the major part of the heavy metals and radionuclides contained in the rock, including Cd, U, Ni, Pb, Zn, Cr, and Cu (Ortiz *et al*., 2002). The extraction of uranium and other metals from phosphoric acid is considered an example of conservation of natural resources; if not recovered they will be lost forever from the economy (Zhang, 2014). Moreover, uranium and some other toxic metals like cadmium, if not removed; they will remain in the final products (fertilizers, detergents, etc.) and can produce health problems and environmental hazards.

Phosphate rocks (PR) are non-renewable resource essential for plant growth and crop production. There is an increasing worldwide interest for the many valuable trace elements

(TE) that exist in phosphate rocks, which may play significant role in the development of various key technologies. These elements include some transitional heavy metals, rare earths, uranium and thorium (Tolsidas, 2012). A thorough study has been published recently assured the industrial and commercial trend for TE recovery from phosphate industry due to decreasing natural resources of U and REE (Zhang, 2014).

Environmental, energy and economic incentives have urged many worldwide academic and industrial institutions to visualize the potential recovery of trace elements (TE) abundant in the phosphate rocks (PR), slime, phosphogypsum and phosphate fertilizers products (Chen and Greadel, 2015). These demands are more essential in Iraq for both environmental requisites and ore scarcity of metals needed by the industry. Iraqi phosphate industry depends on phosphate rocks located in the Western Desert of Iraq. Since the commencement of production in 1983, Al-Qaim fertilizer complex has produced millions of tones of technical grade green phosphoric acid (GPA) and various phosphate fertilizer products. Slime (SL) and phosphogypsum (PG) are produced in large volumes as waste materials. Trace elements such as uranium (U), thorium (Th), rare earth elements (REE), heavy metals (HM) such as zinc (Zn), cadmium (Cd) and many others are of natural abundance in the phosphate raw material. Partitioning and redistribution of the TE occur when the ore is processed starting from mining, comminution, beneficiation and productions of GPA, fertilizers and the accompanying wastes of SL and PG. Some HM and the decay schemes radionuclides of uranium (^{238}U, ^{235}U, ^{234}U) and thorium(^{232}Th) series (e.g. ^{226}Ra, ^{220}Po, ^{210}Pb) in addition to ^{40}K, became important sources of environmental pollution (Santos *et al*., 2006; Tayibi, *et al*., 2011; Burnett and Elzeman, 2001). On the other hand, some of the TE may be of high commercial value.

Beneficiation of the phosphate raw material is accomplished via two stages; first, is calcination at around 1000 °C where CO_2 and water vapor are liberated producing mainly calcium oxide and trace of magnesium oxide; second, is converting the Ca-oxides to hydroxides by water treatment producing the basic lime sludge named slime (SL). After water washings, the sludge is disposed as SL wastes. Beneficiation of one million ton of the phosphate ore produces around 220000 tone of SL solid waste as by-product. The beneficiated PR are then directed for the sulfuric acid treatment which leads to the production of GPA accompanied by PG formation as waste and each ton of GPA produced leads to the formation of 4 – 5 tons of PG as waste. Trace elements in the phosphate rocks are fractionated and partitioned over various products of the industrial stages of fertilizers (FR) production including beneficiation, production of technical or green phosphoric acid (GPA), FR and the wastes of PG and SL (Kremer and Chohshi, 1989; Santos *et al*., 2006). Chemical analysis of representative SL samples has shown the accumulation of some heavy metals such as Zn and Cd. Phosphogypsum is polluted, during chemical processing, by radioactivity produced from the decay schemes (TE-NORM) of uranium ^{238}U and thorium ^{232}Th. Rare earths, barium, strontium, copper, zinc, cadmium, nickel and iron are also enriched in the produced PG matrix (El-Didamony *et al*., 2012).

Several scientific and technical articles have been published on the extraction and leaching of trace elements using aqueous and organic solutions (Zhang, 2014). Uranium extraction from phosphoric acid has become a routine practice in the phosphate fertilizers industry in the world. Since the seventies of the past century, plants for the commercial extraction of uranium from phosphoric acid have been built in the USA and other countries including Iraq. The potential extraction of REE from phosphorites has been outlined in the sixties (Altschuler *et al*., 1967).

Phosphate fertilizers industry in Iraq depends mainly on the phosphate rocks of Akashat Formation (Traifawi and Hirri members) located in the Western Desert. The industrial phosphorite is composed of 60% carbonate fluorapatite and 30 – 35 % of calcite with minor or trace amounts of dolomite, quartz, palygorskite and smectite (Al-Bassam, 1976). Giant phosphate deposits have been discovered and assessed in the period 1986 – 1990 which include Swab, Marbat, Dwaima and Hirri (Al-Bassam *et al*., 1990).

This work is based on industrial applications practiced at Al-Qaim fertilizers complex and on results of scientific research concerned with the potential recovery of some trace elements naturally occurring in the Iraqi phosphate rocks and their fractionation in various products of the chemical processes involved in the fertilizer production at Al-Qaim fertilizer complex, hoping to be considered in the future development of Iraqi phosphate and fertilizers industry.

TRACE ELEMENTS CONTENT IN THE IRAQI PHOSPHATES AND PRODUCTS

▪ Trace elements in the raw phosphate rocks

The Iraqi phosphorites are found in various geological units ranging in age from Upper Cretaceous to Eocene. They have been shown to contain significant concentrations of trace elements including U, Y, V, Cr and Zn (Table 1).

The industrial (mineable) phosphate rocks of Akashat and Swab deposits contain many valuable trace elements including U, Zn, Cd, V, Cr and Y (Table 2). Total REE content in the purified (uncalcined) apatite components (peloids, coprolites and phosphate bioclasts) of the Akashat phosphorites ranges from 66 to 160 ppm (Aba Hussain *et al*., 2010). Uranium, REE and most of Sr and Zn are hosted by the apatite phase, whereas most of Cd, Sr and Ni are incorporated in the carbonate phase.

Table 1: Trace elements in the Iraqi phosphorite-bearing units (Al-Bassam *et al*., 1990)

Element (ppm)	Digma Formation	Traifawi Member	Hirri Member	Dwaima Member	Damluk Member
U	**39**	**37**	**34**	**44**	**37**
Y	**37**	**88**	**75**	**n.a**	**179**
V	**150**	**95**	**183**	**n.a**	**176**
Cd	**8**	**29**	**62**	**22**	**37**
Cr	**112**	**39**	**240**	**n.a**	**96**
Ni	**40**	**5**	**43**	**n.a**	**38**
Cu	**6**	**7**	**13**	**n.a**	**34**
Zn	**n.a**	**124**	**611**	**n.a**	**110**

Table 2: Average concentration (ppm) of trace elements in the phosphorite deposits of Akashat and Swab (after Al-Bassam, 2017; this issue)

Element	Akashat	Swab	Element	Akashat	Swab
U	42	37	**Cu**	16	25
Cd	67	55	**Cr**	212	269
V	117	172	**Ni**	42	72
Y	45	89	**Zn**	444	5

- **Trace Elements in the Products of Phosphate Industry**

The industrial process at Al-Qaim fertilizers complex requires beneficiation of the raw phosphate rocks by calcination, washing and disliming which results in a slime waste [$Ca(OH_2)$] and phosphate concentrate. The wet process is used to produce phosphoric acid, which results in a phosphogypsum waste and green phosphoric acid. The trace elements are fractionated between the phosphoric acid and the waste material. Those in the phosphoric acid will end up in the fertilizers produced. The heavy metals in all products of the fertilizers industry are harmful to the environment if not extracted. Cadmium and zinc have been analysed in the raw phosphates of Akashat deposit and some products at Al-Qaim fertilizers complex (Table 3).

The slime waste was found rich in several trace elements especially Zn, Ni, Cd, Cr, and Sr (Table 4). Uranium and thorium were found to concentrate in the phosphoric acid (Table 5).

Table 3: Distribution of zinc and cadmium in the raw phosphate of Akashat and products of the Al-Qaim fertilizers complex (Al-Qaragouli, 1983)

	Cd (ppm)	**Zn (ppm)**
Phosphate rocks	51.7	310
Calcined phosphates	42.0	370
Phosphate concentrate	34.3	340
Slime (waste)	119.7	520
Phosphogypsum (waste)	4.7	12
Triple Super Phosphate	25.7	560

Table 4: Heavy metals in the slime waste at Al-Qaim fertilizer fertilizers complex (ppm) (Humaidi, 2002)

Zn	620
Cu	18
Ni	130
Cd	112
Co	58
Pb	12
Cr	259
Sr	2000

Table 5: Uranium and thorium concentrations in the products at Al-Qaim fertilizers Complex (Humaidi, 2002)

Element (ppm)	**Phosphogypsum**	**Phosphoric Acid**	**Phosphate Concentrate**
U	22	125	40
Th	13	70	20

EXTRACTION OF TRACE ELEMENTS FROM PHOSPHORIC ACID AND WASTE MATERIALS

▪ Extraction of Uranium from Phosphoric Acid

The first plant to recover uranium from phosphoric acid was built in 1952 in Illinois, USA where U was precipitated as phosphate. Two other plants were built in 1955 and 1957 in Florida using solvent extraction process. Following the dramatic increase in uranium prices in the world market in the 1970's, new plants were built in the USA, Canada, Spain, Belgium, Iran, Iraq, Taiwan and some other countries.

The best operational processes for U extraction from phosphoric acid are (Hurst, 1989; Botella and Gasos, 1989):

1. Solvent extraction, which is the only important process applied on a commercial scale using organic solvents. Three main processes have been developed; OPAP (octyl phenyl acid phosphate), DEPA-TOPO (di-ethylhexyl phosphoric acid and trioctyl phosphine oxide) and OPPA (octyl pyro phosphoric acid).
2. Ion exchange, which includes the use of solid ion exchanges for the recovery of U from phosphoric acid. This method becames more attractive by the development of more selective resins capable of extracting low U concentrations that do not contaminate the acid with organic solvents and the recovery of U is less affected by the concentration of the phosphoric acid and temperature.
3. Precipitation, where uranium is reduced and precipitated with Na-hydrosulfate ($Na_2S_2O_4$), then the filter cake is washed and redissolved in H_2SO_4 under oxidizing conditions. Uranium is then reprecipitated with Na_2CO_3 as U_3O_8.

Commercialization of the three main solvent extraction processes has shown that the DEPA-TOPO process offers the best technology available for the recovery of U from wet process phosphoric acid (Hurst, 1989; Botella and Gasos, 1989). The DEPA-TOPO process includes the following:

1. Acid pretreatment (P_2O_5 concentration of acid 25 – 30 %), cooling, decolorization, clarifying and solid removal.
2. Primary solvent extraction; the acid is contacted with DEPA-TOPO solvent dissolved in kerosene in a counter-current mixer/settler system, where U is transferred to the solvent phase and the lean phosphoric acid is returned to the plant.
3. Primary solvent stripping; the pregnant organic containg U as U^{6+} state is treated with reducing agent to convert it to U^{4+} and the contacted with more concentrated phosphoric acid in another mixer/settler system.
4. Secondary solvent extraction; the loaded primary strip acid is oxidized to convert U^{4+} to U^{6+} back. The strip acid is then contacted with DEPA-TOPO solvent in a mixer-settler system where concentrated U is transformed to the solvent phase and further concentration takes place.
5. Secondary solvent stripping; the secondary pregnant organic is contacted with an alkaline solution in a mixer/ settler system where U is stripped from the organic solvent and transferred to the alkaline solution in a more concentrated form.
6. Refining; the acidic uranium solution is reacted with H_2O_2 to precipitate UO_2, then thickened, dried and calcined to produce U_3O_8.

Uranium balance after H_2SO_4 attack of phosphate rock shows that 90% of U content are found in phosphoric acid and a small amount is lost in the phosphogypsum (Ortiz *et al.*, 2002). However, it was reported that provision of oxidizing conditions during acidulation of the phosphate rock can lead to significantly higher concentration of U in the phosphoric acid, whereas reducing conditions can lead to significant losses of U to the phosphogypsum waste (Hurst, 1989). Uranium, if not removed from phosphoric acid, will end up in the phosphate fertilizers, causing environmental problems, due to its radioactive properties. In the mean time, uranium is a strategic and valuable element of inherent value, useful to recover as a byproduct.

Iraq built a plant for uranium extraction from phosphoric acid at Al-Qaim fertilizer complex in 1984 using DEPA-TOPO process. The designed capacity of the plant was 72000 Ib/year (equivalent to about 35000 Kg/year) (Walters *et al*., 2008). The plant was destroyed in the 1991 Gulf War and never has been rebuilt.

- **Leaching of Cd and Zn from the Slime Waste**

– **Sulfuric acid and ammonia solutions route:** The following procedure was adapted for leaching purposes (Al-Bassam and Jalhoom, 1999):

Treatment with sulfuric acid solutions to ensure the conversion of cadmium and zinc to metal sulfate species according to the following reaction:

$$CdCO_3 + CaCO_3 + 2H_2SO_4 \rightarrow CdSO_4 + CaSO_4 + 2CO_2 + 2H_2O \text{ …… } 1$$

Treatment with ammonia solution as shown in equation 2 and 3:

$$CdSO_4 + 2\,NH_3 + 2H_2O \rightarrow Cd(OH)_2 + (NH_4)_2SO_4 \text{ …… } 2$$

$$Cd(OH)_2 + (NH_4)_2SO_4 + 2NH_3 \rightarrow [Cd(NH_3)_4]SO_4 + 2H_2O \text{ …… } 3$$

Treatment with sulfuric acid and ammonia resulted in a 66% extraction of cadmium from the solid slime wastes.

– **Ammonium chloride and ammonium nitrate solutions route:** Extending ammonia solutions extraction to other ammonium salts highlighted more promising results (Humaidi, 2002). Direct solid-liquid ammonium salts solutions extraction leaching is considered more economic and more acceptable environmentally compared with the mineral acid treatment. Laboratory solid liquid extraction experiments were performed (Humaidi, 2002) in a refluxed controlled temperature round bottom flask of 250 ml volume supplied with stirrer. 2 – 10 gm. of the SL solid wastes (usually have light gray color contain also silica and clays), dried and sieved for – 45 micron mesh size then mixed with 25 – 100 ml of ammonia or ammonium salts. The mixture refluxed at 70 °C for a certain period of time. After cooling and filtration, the samples were washed and dissolved in concentrated hydrochloric acid for chemical analysis. For comparison, chemical analysis of samples roasted at 900 °C in a muffle furnace has also been made.

Tables 6, 7 and 8 show the results obtained for the direct leaching experiments with ammonia and ammonium salts solutions for both calcined and uncalcined samples (Al-Bassam and Jalhoom, 1999; Humaidi, 2002). Ammonium salts as chloride, nitrate and sulfate gave almost quantitative recovery for Cd and Zn from the slime wastes. Displacement reaction with one molar ammonium sulfate at 100 °C for 15 minutes resulted in the recovery of Zn, Cd, Cr and Ni (Table 8).

Displacement reactions can be represented as follows:

$$nNH_4X + M^n(OH)_n \rightarrow NH_4OH + M^n(X)_n \text{ ……………… } 4$$

at 100 °C ammonia solution may be formed consequently reacts as follows:

$$nNH_4X + sNH_3 + M^n(OH)_n \rightarrow M^n(NH_3)_sX_n + M^nX_n + n\,NH_4OH \quad \ldots\ldots\ldots\ 5$$

where M represents the heavy metal.

Table 6: Extraction of Zn and Cd from slime using 25% ammonia solution

	Unroasted Samples (ppm)		**Roasted Samples (ppm)**	
	Zn	**Cd**	**Zn**	**Cd**
Solution	100	21	250	35
Residue	320	126	710	88
E%	11%	14.3%	26%	28%

E% = percent metal recovery

Table 7: Leaching of Zn and Cd from slime by ammonium salts

	Unroasted Samples (ppm)				**Roasted Samples (ppm)**			
	Zn		**Cd**		**Zn**		**Cd**	
	NH_4Cl	**NH_4NO_3**	**NH_4Cl**	**NH_4NO_3**	**NH_4Cl**	**NH_4NO_3**	**NH_4Cl**	**NH_4NO_3**
Solution	760	783	140	143	890	860	145	150
Residue	180	192	10	19	63	23	10	8
E%	81%	80.3%	93.3%	88.3%	96.1%	97.4%	93.65	94.9%

E% = percent metal extracted

Table 8: Leaching of Cd, Zn, Ni and Cr from slime using one molar aqueous ammonium sulfate at 100 °C and 15 minutes contact time

Element	**[M] ppm**	**E%**
Cd	80	47%
Zn	460	34.3%
Ni	38	71%
Cr	17	95%

E% = percent metal extracted

Examining the data mentioned above, the following general remarks can be formulated:

A. Treatment with ammonia solutions revealed the recovery of only 11% zinc and 14% cadmium at one batch contact.
B. Increasing contact time for leaching with ammonia solutions has no effect on the power of extraction.
C. Roasting at 900 °C enhance the extraction of zinc up to 26% and cadmium to 28% when ammonia solutions are used.
D. Ammonium salts increased zinc extraction up to 80 – 81 % and cadmium up to 88 – 91 %.
E. Roasting of samples enhanced the extraction up to 96 – 97 % for zinc and 93 – 95 % for cadmium.
F. Ammonium salts give almost quantitative extraction leaching efficiency from the basic slime solutions, irrespective of the anion used at least for Cl^- and NO_3^- ions.

- **Recovery of Uranium and Thorium from Phosphogypsum Waste**

A method has been developed for the recovery of the trace elements partitioned with the PG depending on the concept of preferential solubility of phosphogypsum in potable water (PW) over other existing insoluble or sparingly soluble trace metal sulfates, phosphates, silicates and other species (Humaidi, 2002; Alwan, 2017). The concept is environmentally green and depends on using water for partial or complete removal of toxic heavy and radioactive trace elements to produce PG suitable for industry. The solubility of PG is 0.64 gm in potable water at room temperature 25 ± 3 °C (Alwan, 2017). Insoluble clays and silica settle down which can be easily isolated from the matrix, while the insoluble and sparingly soluble metal sulfates and phosphates form colloids in the aqueous solution. The colloid flocculates within 30 – 40 minutes, which can either be filtered out or separated by floatation technique. The filtrate contains mainly the PG which can be further recovered by either open pond evaporation or ion exchange technique. The method has been further developed for other heavy metals using demineralized water where the PG solubility increased, membrane technique is suggested for water and PG recovery (Alwan, 2017).

The method developed depends on using potable water for complete dissolution of the dehydrate calcium sulfate leaving most of metal phosphates and or sulfates, silica and clays as insoluble residue (Humaidi, 2002). Most of the metal species are flooded in the colloidal layer formed over the aqueous layer leaving the solid un-dissolved silica and clays which have higher density at the bottom of the reactor. The ratio applied was 0.64 gram of dried PG to one liter of water. PG was dried at 115 °C for 2 hrs. Complete elemental chemical analysis for the separated three layers was performed using induced plasma emission and atomic absorption spectrometry (Humaidi, 2002). The PG dissolves by the proportion 0.64 gm/liter of water depending on total dissolved salts of the potable water. Meanwhile, U and Th remain as un-dissolved phosphates in fine colloidal particles ascending upwards the reactor by upward water flow to fall out of the reactor on a filter which separate U and Th phosphates and or sulfates as solid precipitates. The dilute solution of the dissolved calcium sulfate could be drained to an open basin to precipitate pure calcium sulfate (~ 99%) by evaporation. The black precipitate of the recovered precious metal sulfates and phosphates are dissolved in hot aqua regia for accurate analysis (Table 9).

Table 9: Analytical data of U and Th in phosphogypsum and isolated solids and precipitate after water treatment (ppm) (Humaidi, 2002)

Element	phosphogypsum	Separated Samples
Uranium	**41**	**58**
Thorium	**16**	**43**

FUTURE PROSPECTS

- **Production of High Purity Phosphoric Acid (HPPA): A mean of trace elements recovery as by-products**

High Purity Phosphoric Acid (HPPA) is an essential material for the production of phosphate salts required by the food and pharmaceutical applications (SYBETRA, 1981; Austen, 1984; Kaladah, 1989). Environmental Protection Agency (EPA) obligations are directed for the sustainable phosphate and fertilizers industry; the recovery of radioactive and toxic heavy metals has become almost mandatory for the phosphate fertilizers industry (Dissanyaka and Chandrajith, 2009). Production of high purity phosphoric acid (HPPA) means at the same time the recovery of the group trace elements companion GPA. The dry and wet processes have been implemented for the production of HPPA, but the wet process became more favorable in the last decades.

– **The dry process:** The dry method to produce phosphoric acid depends on burning the phosphate rocks in the presence of silica and cock inside arc furnace to produce phosphorous pentoxide, the later is then reacted with water to produce HPPA (Curtis, 1935). The global trend is in favor of the wet process mainly for energy and environmental considerations. Many phosphate producing companies are in favor of the wet process because of many environmental hazards connected with the dry process, such as the liberation of silicon halides gases to the atmosphere and formation of bulk solid wastes in addition to the presence of some trace toxic elements like arsenic and lead which need further treatment via electrochemical precipitation (Zhang, 2014).

– **The wet Process:** Various inorganic acids have been used for the treatment of the phosphate ore and production of phosphoric acid including sulfuric, nitric and hydrochloric acids (Davistor and Brock, 1982; Raymond and Kent, 2003). However, sulfuric acid treatment override other acids for the last few decades, hydrochloric acid, on the other hand, had also showed increasing interest by several international firms in Canada, Japan, Belgium and others., Sulfuric acid has been used at Al-Qaim phosphate fertilizer complex in the wet process which can be illustrated by the following reaction:

$$CaF_2 3Ca_3(PO_4)_2 + 10H_2SO_4 + H_2O \rightarrow 6H_3PO_4 + 2HF + 10CaSO_4.H_2O \quad \ldots\ldots\ldots 6$$

Technical grade or green phosphoric acid (GPA) produced has companions or partitioned trace elements as shown in Table 10. The purification process of green phosphoric acid means the removal of organic and inorganic impurities including some valuable trace metals. It includes two main steps:

A. Removal of the trace organic impurities (around 150 ppm) by washing with petroleum ether using one stage mixer settler as shown in Fig.1 (Shroeder, *et al*., 1985).
B. Removal of colloids. It is expected that particles of various impurities, include organic species, having size range of 0.05 – 1 micron will not settle down and remain as suspended colloids. Gross estimation using absorption spectroscopy indicated the presence of around 150 ppm of colloids**.** Settling for one hour was found to be effective to isolate the precipitate in the settling tank.

The final pure PA of 85% concentration is obtained via the following steps leading to specifications compatible with the Iraqi health standard as shown in Table 11 (Humaidi, 2010):

- Removal of the trace organic impurities (20 – 30 ppm) by petroleum ether extraction which is recycled by distillation at 60 – 80 °C as shown in Fig.2. This procedure reflected better energy and environmental aspects in comparison with the thermal-pressure treatment used by other companies.
- Passing the PA product over a column of activated carbon with 1.5 meter height and 10 cm diameter to separate any trace organic species remained from the extraction cycle.
- Vacuum distillation of the acid to the required concentration using evaporator made from stainless steel SS-316 reaching the 85% concentration of P_2O_5 as the final product.

Table 10: TE in green PA, purified PA 1st cycle and purified PA 40% TBP

Elements ppm	GPA ppm	PPA First cycle ppm	PPA 40% TBP ppm
U*	158	< 0.005	< 0.005
Fe	3900	0.76	0.66
Si	1136	21	31.9
Co	430	< 0.05	< 0.05
Ni	114	0.5	0.5
Cr	72	< 0.1	< 0.1
Mg	6800	< 0.05	< 0.05
Al	5000	< 0.5	< 0.5
Zn	867	< 0.01	< 0.01
Cu	60	0.05	< 0.05
Sb	70	3.9	3.9
K	157	< 0.05	< 0.05
Sn	183	2.9	3.1
Pb	10.9	1.3	1.2
As	6.9	< 0.2	< 0.2
Cl^-	891	7.7	16
F^-	0.2	260	390
SO_4^{2-}	11620	< 1	< 1
Ti	635	-	-

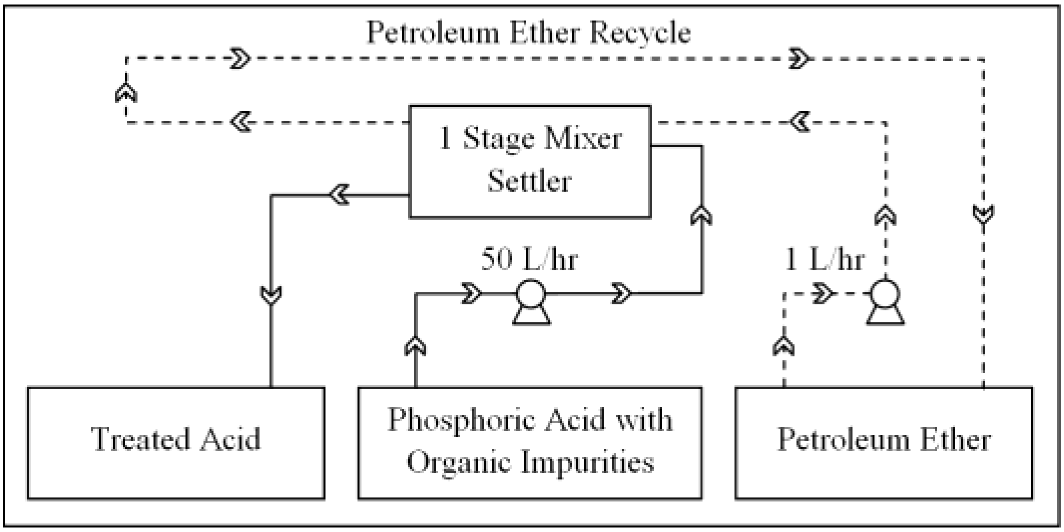

Fig.1: Removal of organic trace impurities in the GPA (Humaidi, 2010)

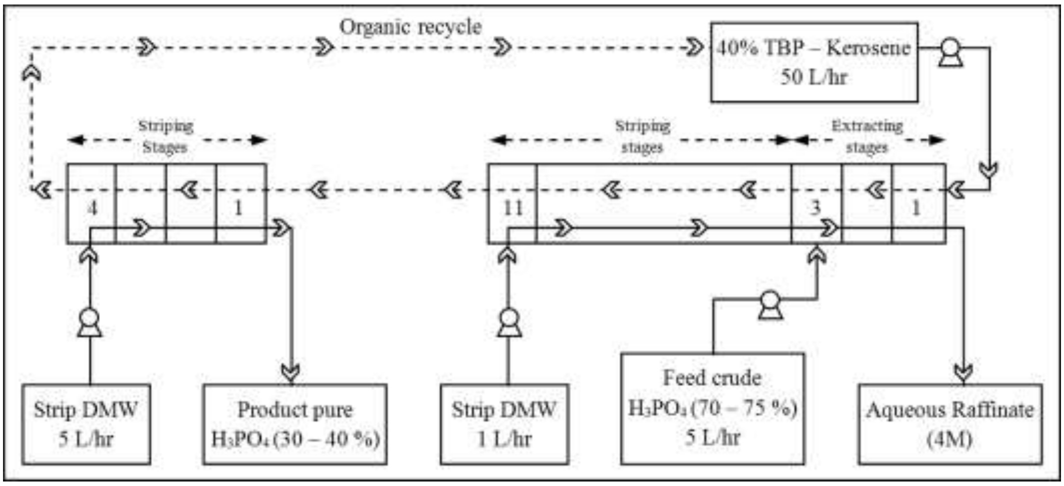

Fig.2: Purification of GPA by 40% TBP – Kerosene (Humaidi, 2010)

Table 11: Final specification of produced high purity phosphoric acid (Humaidi, 2010)

Element	Imported acid	Purified acid	Iraqi standard
P_2O_5 %	85%	> 75%	> 75%
Pb	10 ppm	7 ppm	5 ppm
K	50 ppm	1.1 ppm	---
Zn	20 ppm	1.8 ppm	---
Cu	20 ppm	2.9 ppm	---
Fe	50 ppm	3.7 ppm	---
As	2 ppm	0.7 ppm	< 3 ppm
SO_4	50 ppm	250 ppm	1500
F	10 ppm	0.22 ppm	< 100 ppm
Cl	50 ppm	< 0.5 ppm	< 10 ppm
Acid			< 10
Heavy Elements			< 10
NO_3			< 5

CONCLUSIONS

The industrial phosphorite deposits of Iraq contain appreciable amounts of some valuable trace elements, including U, Th, Cd, V, Y, Cr, Zn and Sr.

These trace elements are fractionated during the fertilizers production scheme between phosphoric acid (finally in the fertilizers) and waste material (slime and phosphogypsum). Most of U, Th, Y, and V are concentrated in the phosphoric acid and to a lesser extent in the phosphogypsum, whereas most of Sr, Cd and Zn are concentrated in the slime.

The global and local experience (industrial- and/ or laboratory-scale) proved the possibility of extracting some of these elements, as by-products from phosphoric acid or by simple chemical routs from the slime and the phosphogypsum waste materials.

Production of high purity phosphoric acid (HPPA) should be considered in the future fertilizers plants which means at the same time the recovery of a group of trace elements including those toxic and/ or radioactive . The dry and wet processes have been implemented for the production of HPPA, but the wet process became more favorable in the last decades.

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