

## ANALYSES OF URANIUM IN SOME PHOSPHATE COMMERCIAL PRODUCTS

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### ABSTRACT

The raw materials used in manufacturing of phosphate fertilizer products were derived from rocks. Rocks contain a remarkable of natural radioactivity. Uranium and phosphorous were originally initiated at the same time of the initiated rocks. The purpose of this research is to investigate solubility of uranium phosphate species at the phosphate fertilizer samples. samples including; raw phosphate material, single super phosphates (SSP) granules and powdered, triple super phosphates (TSP) and phosphogypsum samples were obtained from Abu-Zabal factory in Egypt. Solubility of uranium phosphate species was estimated. It was found that, less than half of the uranium phosphate species are soluble in water. The soluble uranium may be enter into the food chains by plant. Therefore, restriction should be done in order to limit contamination of land and the public.

**KEY WORDS:** *Phosphate Fertilizers, Uranium, Solubility.*

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### INTRODUCTION

Every day, humans are exposed to natural gamma and alpha radioactivity that were emitted from building materials, soils, and rocks especially that decay quickly (such as radon). The distribution of naturally – occurring uranium, radon, and other radioactive elements in the environment depending on the distribution of rocks from which they originated and the process which concentrate them. The risks to humans are real , but the level of risk involved is not clearly defined because we do not yet know enough about the distribution and concentration of these. The raw materials of the phosphate fertilizer were derived from rocks. It contains naturally occurring radioactive elements. The mobility of radionuclides in the environment allows to move easily and to contaminate much of land with which humans come in contact. Uranium and its decay product can enter into the food chain through phosphate fertilizer products. Commercial phosphate products are materials commonly containing a remarkable of naturally occurring radionuclides such as uranium-238, The-232 and K-40, have been intensively discussed in a variety of reports and papers <sup>(1- 3)</sup>. The potential radiation risk that can results from the presence of naturally occurring radioactive materials (NORM) in raw materials usually considered as not radioactive and used in the majority of chemical products. Because of the natural radioactive uranium – 238 are presence in phosphate ore, this radionuclide and its daughter products are present in all of the products and phosphate waste products, and because of the public fear of radiation This study aimed to controlling solubility of uranium in the industrial phosphate products. Phosphate ore, single super phosphate (SSP) granules and powdered, triple supper

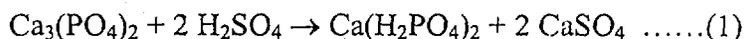
phosphate (TSP) and the waste products of phosphogypsum are the commercial phosphate products were investigated in this study

## EXPERIMENTS

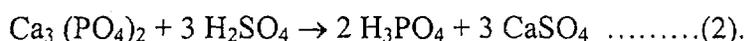
Five of the commercial phosphate fertilizer samples were obtained from Abu-Zabaal fertilizer factory in Egypt including; single super phosphate (SSP), granules and powder, phosphate ore, triple super phosphate (TSP) and phosphogypsum ( $\text{CaSO}_4$ ). The solid samples have the grain size distribution  $\leq 170 \mu\text{m}$  was digested with 5 ml of  $\text{HNO}_3$ , HF, and 0.5 ml of  $\text{HClO}_4$  acid solution on a sand bath in 30 ml of platinum crucible after all the gases were evaporated, the residue was dissolve in 20 ml of 1 : 1 concentrated HCl aqueous solution, then each sample was completed to one liter. Phosphorus concentrations was measured with stannous chloride method<sup>(4, 5)</sup>,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions were measured by using ferron indicator<sup>(6)</sup>, traces of the uranium were measured by using pyridyl-azo-resorcinol (PAR) indicator<sup>(7)</sup>, while concentrations of thorium are in the fertilizer samples were measured by using Arzenazo III indicator<sup>(7)</sup>. Carbonates are in the samples were estimated as calcium carbonates by back titration<sup>(8)</sup>.  $\text{Na}^+$  and  $\text{K}^+$  ions were estimated by the flame photometer. The soluble uranium and phosphate ions were estimated by shaking 50 ml of distilled water with 5 g of the solid samples at 40 rpm for one day, the suspensions were centrifuged at 4000 rpm for 10 minutes, then the aqueous phases were separated. Concentrations of P and U that dissolved in aqueous solutions were determined as before.

## RESULTS AND DISCUSSIONS

The commercial phosphate fertilizer was derived from natural phosphate ore by wet or by thermal process. As results of environmental changes, some impurities such as calcium and magnesium carbonates, iron oxide, alumina fluoride may be present in the commercial phosphate products. Phosphate products including; the raw material, single super phosphate (SSP), triple super phosphate (TSP), and orthophosphoric acid. The phosphate fertilizer by-product is phosphogypsum ( $\text{CaSO}_4$ ). SSP was produced from the reaction of calcium phosphates with sulphuric acid. The production of SSP depending on the relative amounts of sulphuric acid which was added to the phosphate ore, the first step of the reaction was given single super phosphate (SSP) as product was described as follows:



The second step of the reaction was the formation of phosphoric acid  $\text{H}_3\text{PO}_4$ , in which sulphuric acid reacts with the phosphate to yield orthophosphoric acid and gypsum which is filtered:



Triple super phosphate (TSP) was produced from the reaction of calcium phosphates with phosphoric acid as follows:



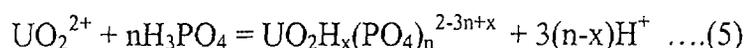
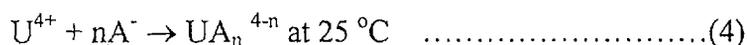
Calcium sulphate is the waste product was used in the manufacture of building materials or in paving road construction. Commercial mineral phosphate merely contain 2 – 4 % of F , most of fluoride ions released and evaporation in the industrial steps. Table 1 shows the chemical analyses of phosphate fertilizers products including; single super phosphate SSP, phosphate ore, triple super phosphate TSP, and by-product of phosphogypsum.

P<sub>2</sub>O<sub>5</sub> content was found between 8 to 15 ppm are within the range 4 and 38 % P<sub>2</sub>O<sub>5</sub> that was reported in other phosphate ores<sup>(9)</sup>. Uranium ions was found in the range 19.6 to 26.8 ppm are within the range of that was found in phosphate ores have the concentrations from 20 to 300 ppm ( 0.26 to 3.7 bq/g) (7 to 100 pCi/g). Thorium was found 0.07 to 0.22 ppm are within the range of the background amounts ~ 1 to 5 ppm (3.7 to 22.2 mBq) (0.1 to 0.6 pCi/g). In nature, phosphorous generally occurs as ortho-, poly- or metaphosphate, all of which constitute dissolved inorganic Phosphorous (DIP). Orthophosphate was released from weathering rocks, whilst the other forms are products of biological metabolism<sup>(10)</sup>. Therefore, small fraction of phosphorous may be present as a soluble organic and inorganic phosphate compounds. The solubility of phosphates depends on the concentrations of the inorganic and organic phosphorous and the pH of the solid sample in water. Since thorium is present in the range of background. Contamination by uranium is very important in our study.

**Table 1.** Chemical analyses of the phosphates industrial products.

Sample	SSP (granules) (%)	SSP (powder) (%)	Ore (%)	TSP (%)	Calcium sulphate (%)
P <sub>2</sub> O <sub>5</sub>	8.04	11.96	15.6	13.7	12.10
Fe <sub>2</sub> O <sub>3</sub>	8.6	9.5	7.1	3.5	3.8
Al <sub>2</sub> O <sub>3</sub>	8.62	6.03	7.8	1.26	2.07
CaO	13.2	11.2	18.0	8.6	21
MgO	4.6	2.0	11.0	16.3	9
Na <sub>2</sub> O	3.7	5.0	6.4	4.2	3.8
K <sub>2</sub> O	0.3	0.7	0.8	1.2	0.3
U <sup>4+</sup> (ppm)	19.6	22.8	28	26.8	2.8
Th <sup>4+</sup> (ppm)	0.07	0.10	0.20	0.10	0.22
Total Carbonates	11	13	15	12	20
Total organics (%)	8.9	5.6	1.5	11.3	1.8
PH	2.33	2.4	7.25	2.34	2.41

The most oxidation state of uranium in nature are U(IV) and U(VI). Uranium ion (U<sup>4+</sup>) and its aqueous complexes predominate in water. The complex –formation reaction between the uranyl ion and orthophosphoric acid is given as follows<sup>(11)</sup>:



Where n = 1, 2,3, 4, 5 and x = 0, 1, 2 with the formation species UO<sub>2</sub>H<sub>2</sub>PO<sub>4</sub><sup>+</sup>, UO<sub>2</sub>H<sub>3</sub>PO<sub>4</sub><sup>2+</sup>, ,,etc. Stability of uranium compounds depending on the pH of the uranium phosphate species in water and the soluble organic and inorganic (PO<sub>4</sub><sup>3-</sup>) ions are in the phosphate products and by- product. The uranyl minerals are least soluble in the pH range 5 –

8.5. phosphate and sulphate complexes are in area of phosphate industry. the presence of impurities such as Fe(III) and Mn oxyhydroxides will form colloidal material with  $UO_2^{2+}$ . our interesting is in the uranyl phosphate species. Table 2 shows the uranium phosphate compounds species and their log equilibrium constant <sup>(12)</sup> ( $t = 25^\circ C$ ), while Table 3 shows the experimental results for the concentrations of the soluble uranium and  $PO_4^{3-}$  ions are in the phosphate products and by-products.

In this analyses, the organic phosphorous was estimated from the different in the total phosphate concentrations before and after ignition of the solid sample at  $500^\circ C$  for two hours. Concentrations of uranium and/or phosphorous ions were calculated as mol/kg (molality). Supersaturation, undersaturation, and the equilibrium conditions are the three states of the possible concentrations of uranium phosphate compounds that may be present in aqueous water.

**Table 2.** The species of dissolution of uranium phosphate compounds and Their Equilibrium constant at  $t=25^\circ C$ .

log [k eq.]	Reaction
-8.41	$UO_2HPO_4 \rightleftharpoons UO_2^{2+} + HPO_4^{2-}$
-18.29	$UO_2(HPO_4)_2^{2-} \rightleftharpoons UO_2^{2+} + 2 HPO_4^{2-}$
-10.23	$UO_2H_2PO_4^+ \rightleftharpoons UO_2^{2+} + HPO_4^{2-} + H^+$
-19.88	$UO_2(H_2PO_4)_2 \rightleftharpoons UO_2^{2+} + 2HPO_4^{2-} + 2H^+$
-28.79	$UO_2(H_2PO_4)_3^{1-} \rightleftharpoons UO_2^{2+} + 3 HPO_4^{2-} + 3H^+$
-12.05	$UHPO_4^{2+} \rightleftharpoons U^{4+} + HPO_4^{2-}$
-21.99	$U(HPO_4)_2 \rightleftharpoons U^{4+} + HPO_4^{2-}$
-30.69	$U(HPO_4)_3^{2-} \rightleftharpoons U^{4+} + 3HPO_4^{2-}$
-38.70	$U(PO_4)_4^{4+} \rightleftharpoons U^{4+} + 3 HPO_4^{2-}$
-1.75	$UO_2(H_2PO_4)_3^{1-} \rightleftharpoons UO_2^{2+} + 3 HPO_4^{2-} + 3 H^+$

**Table 3.** Concentrations (mol/kg) of organic and inorganic phosphates ( $HPO_4^{3-}$ ) with uranium ions are in the phosphate fertilizer samples.

Sample	Total $HPO_4^{3-} \times 10^{-6}$	Inorganic c $HPO_4^{3-} \times 10^{-7}$	Total $UO_2 \times 10^{-7}$	Inorganic $U \times 10^{-7}$
	(mol/kg-Molality)			
SSP (granules)	5.96	4.2	4.76	3.6
Raw material	5.2	6.0	4.76	3.6
SSP (powder)	6.8	32	4.37	3.3
TSP	3.5	1.4	4.53	3.4
Phosphogypsum	5.2	3.0	5.64	4.2

Super saturation conditions were existed when a solution contains more solute than should be present at equilibrium. Undersaturation condition is a dissolution process of a solute, it was occurs when concentration of a solute in solution contain has a solubility less than that was present at the equilibrium state. The equilibrium state was occurred when the concentration of a solute in solution is equal to that was found at the equilibrium state..

The mass action law was applied in order to determine the state of uranium phosphate species in water. The saturation index (SI) was evaluated as<sup>(12)</sup>:

$$SI = \log(IAP) - \log(K_{eq}) \dots\dots\dots(6).$$

Where, IAP is the ion activity product, it was calculated from the experimental results that was given in Table 3. The equilibrium constants of the chemical reactions of the species that was given in Table 2 were used for the estimation of the saturation index. Figs 1-4 show the values of the saturation index (SI) of the different species of the investigated samples.

When  $IAP/K_{eq} = 1$ , uranium phosphate compounds species is in equilibrium state, when

$IAP/K_{eq} > 1$ , uranium phosphate species is supersaturated (precipitate), when  $IAP/K_{eq} < 1$ , uranium phosphate species is undersaturated (dissolved).

- Figure 1 showed the solubility of  $UO_2HPO_4$  species at the equilibrium constant  $-8.41$  for the organic and inorganic part of the investigated samples. it was found that, the SI has a negative values. the results shows, the organic and the inorganic  $UO_2HPO_4$  species are soluble at  $K = -8,4$
- Fig. 2 shows the solubility of  $UO_2H_2PO_4$  species at the equilibrium constant  $K_{eq} = -10.23$ . It was found that SI has a positive values at the organic species. SI has a negative values at the inorganic species except the phosphate ore sample. the results indicated that the organic species for all samples and for the inorganic phosphate ore sample are supersaturated and the inorganic species of the samples SSP granules and powdered, TSP and  $CaSO_4$  samples are under saturated for all the investigated samples at  $K_{eq} = -10.23$ .
- Fig. 3 Shows that, SI of the phosphate fertilizer samples at  $K_{eq} = -12.05$ , it was found that  $SI > 1$  for the organic uranium phosphate species  $UO_2HPO_4^{2+}$ .  $SI < 1$  for all the inorganic species of the investigated samples. the results indicated that the organic species are supersaturated and the inorganic species are under saturated at  $K_{eq} = -12.05$  for all the investigated samples.
- Fig. 4 shows that SI of the phosphate fertilizer samples at  $K_{eq} = -1.75$ . SI is  $> 1$  for the organic SSP granules and for the inorganic phosphate ore samples. the organic species  $UO_2(H_2PO_4)$  are under saturated for the phosphate ore, SSP powder, TSP and  $CaSO_4$  samples. The inorganic phosphate species  $UO_2(H_2PO_4)$  are under saturated for the SSP granule, SSP powder, TSP and  $CaSO_4$  samples.
- All of the other inorganic and organic phosphates species at  $K_{eq} = -18.29, -28.8, -21.99, -30.7$  and  $-38.7$  are supersaturated.

By comparing of the solubility of the organic and the inorganic uranium phosphate species with the initial phosphates that was found at the fertilizer samples. it was found that less than half of the uranium phosphate species at the; SSP granules, SSP powder and TSP are undersaturated and less than of third of the uranium phosphate species at the; uranium phosphate ore and  $CaSO_4$  samples are undersaturated.

It was reported that, the radioactivity in one gram of uranium is due to U-238 was calculated and found to be 12270 Bq/kg. It was reported that the radioactivity of 544.8 Bq/kg, 360.8 Bq/kg and 385 Bq/kg were estimated in phosphate rock, lime stone and super phosphate respectively<sup>(13, 14)</sup>. The maximum initial uranium oxide is 112 mg/kg which is equivalent to 957 Bq/kg, the maximum concentrations of the soluble inorganic uranium oxide in our study is 13 mg /kg is equivalent to 160 Bq/kg. the annual activity of the soluble  $UO_2$  from the application of 300 kg, super phosphates was added is 48000 Bq. By reducing the amount of fertilizer which was added to land to less than 150 kg is equivalent to less than 2400 Bq.

## CONCLUSIONS

Because it was believe that all of the commercial phosphate fertilizer products are soluble in water and feed plant, it was found that uranium and phosphate representing a great part in the phosphate fertilizer products . solubility limit is the major factor that controlling solubility of phosphorous and uranium in the uranium phosphate species of the commercial phosphate fertilizer products. The experimental results showed that it should be use less than half weights of the fertilizer products to reduce the hazardous effect from uranium and to get a good fertility of the land

## REFERENCES

- [1] B. Yaron., R. Cavet., R. Prost. " Soil Pollution" Processes and Dynamics. Springer-Verlag Berlin Heidelberg 1996.
- [2] J. Hofmann., R. Leicht., H. J., Wingender., J. Worner" Natural Radionuclide Concentrations in materials Processed in the Chemical Industry and the Related Radiological Impact". Report EUR 19264. (2000)
- [3] Manyama Makweba, M, et al. The natural radioactivity of the rock phosphate, phosphoric products and their environmental implication the science of the total environment, 133. p , 99-110. (1993). (4)
- [4] Gary. M. Pierzynski" Methods of Phosphorous Analysis for Soils. Sediments, Residual and waters. Southern Cooperative Series Bulletin No. 396. ISBN: 1-58161-396-2 (2000).
- [5] M. C. Rand, Arnold. " Standard Methods for the Examination of water and wastewater." . American Public Health Association. Washington. DC20036. 1 (1979).
- [6] H. L. Golterman." Methods for physical and Chemical Analysis of Fresh Waters." Second edition. Blackwell Scientific Publications. IBP Handbook No. 2 (1978).
- [7] N. Nesmeyanov. " A guide to Practical Radiochemistry." Mir Publishers Moscow. (1980).
- [8] D. L. Rowell. " Soil Science. Methods & Applications". Longman Science & Technical. (1994).
- [9] J. Hofmann., R. Leicht., H. J. Wingender., J. Worner " Natural Radionuclide Concentrations in Materials Processed in the Chemical Industry and the related Radionucliological Impact." European Commission. Report EUR 19264 (2000)
- [10] Sydney J Johnstone. " Minerals for the Chemical and Allied Industries". John Wiley & Sons Inc (1954).
- [11] An. N. Nesmeyanov. " Radiochemistry" Mir Publishers. Moscow. (1974).
- [12] Werner Stumm. " Chemistry of the Solid-water interface. John Willey & Sons, inc. New York (1992).
- [13] M. F. Abdel Sabour and M. A. Rizk. *Isotope & Radiation Res.*, 34, 2, 171-178 (2002).
- [14] R. Niedergesass, C. Schnier and R. Pepelinik, *J. Radioanal. & Nucl. Chem.*, 168 (2), 317-328 (1993).

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