
RECOVERY OF NON-RADIOACTIVE TRI-SODIUM PHOSPHATE BY-PRODUCT THROUGH CONTROLLED ALKALI BREAKDOWN OF ROSETTA MONAZITE

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Abstract

The present paper deals with proper separation of trisodium phosphate as a valuable by-product from the associated excess caustic soda of the reaction filtrate of controlled alkali breakdown of Rosetta monazite. Two procedures are applied for this purpose; namely a direct crystallization procedure of the phosphate product or else its salting out by using methanol.

XRD and IR analysis of the separated by-product indicated a structural formula of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Analysis of the latter was revealed about 100 ppm uranium in the product separated by crystallization while that separated by methylation was completely exempt of uranium.

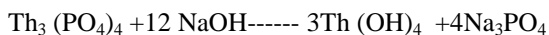
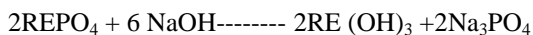
Introduction

Monazite is one of the most important commercial sources of lanthanides beside a relatively minor amount of thorium and a much smaller amount of uranium that could be extracted as important by-product. Monazite is actually a wide spread mineral that generally occurs as a common accessory mineral in rocks as pegmatites, granites and gneisses. However it frequently occurs as a detrital mineral in placer deposits principally in river and beach sands. Large commercial detrital deposits are mainly found in Australia, USA, India, Brazil and Egypt. In such deposits, monazite is generally associated with other heavy minerals such as ilmenite, magnetite, zircon, and rutile (Anwar and Abdel-Rehim, 1970; Cuthbert, 1958; Rittman and Nakhla, 1958; Higazy and Naguib, 1958, Moller et al., 1989). Several Egyptian workers (Anwar and Abdel-Rehim, 1970; Rittman and Nakhla, 1958; higazy and Naguib, 1958) have shown that monazite occurs as large reserves in black sands that are found along the beaches of the northern parts of the Nile Delta from Rosetta to Damietta where it assay about 1%.

Indeed, several techniques could be used for industrial monazite processing to extract thorium, uranium and lanthanide (Habashi, 1999; Doyle and Duyvesteyn, 1992). These techniques include sulfuric acid leaching at 155-230°C, alkaline leaching with sodium hydroxide solution at 140°C, sintering with sodium carbonate

at 900°C or with sodium carbonate together with a flux (sodium fluoride) at 800-825°C, or else with sodium hydroxide at 400-500°C as well as chlorination of a mixture with coal at 700-800°C. However from the commercial point of view, both acid and alkaline leaching are commonly used with the latter being the most preferable and widely used as it has many advantages. The most important of these advantages are simultaneous removal of phosphorous during leaching, and the production of useful by-product (sodium phosphate) and the recovery of the excess of alkali in put (Abdel-Rehim, 2002).

The present work is mainly concerned separation of non-radioactive tri-sodium phosphate as significant by product from the filtrate of Rosetta monazite alkali breakdown. This has been possible via two techniques namely; direct crystallization of the latter or its salting out through proper methylation. The chemical reaction of alkaline processing of monazite may be represented as follows:



Where the phosphate value reports in solution as sodium salt while the REEs, Th and U would remain insoluble in what is called hydrous oxide cake. As a matter of fact some U might be co-dissolved and which might partially contaminate the by-product trisodium phosphate during its crystallization. On the other hand, it is interesting to indicate that the alkali breakdown of monazite consumes only about one third of the input caustic soda required for its high breakdown efficiency. In other words, the remaining un reacted two thirds of the caustic soda are mixed with the tri-sodium phosphate product. Separation of the latter as an industrial useful by-product would also be beneficial in recycling the remaining caustic soda for the breakdown of the next monazite batch treatment. To realize the main objective of preparing a non-radioactive phosphate by-product, the authors studied the alkali breakdown of Rosetta monazite under controlled conditions to minimize co-dissolution of uranium (under publication). The working optimum monazite breakdown conditions by caustic soda involved 100% -325 mesh grain size, 135-140 °C reaction temperature, 4 hr reaction time, 1.5:1 soda to sand weigh ratio and using 50% caustic soda concentration. Applying the above optimum conditions it was found that about 98% monazite breakdowns was obtained with only 18.4% co-dissolved uranium. However, proper treatment of the monazite slurry after breakdown (controlled dilution and washing) has decreased U solubility. Accordingly, the obtained solution that was subjected to trisodium phosphate recovery was assayed 5 g NaOH, 1.3 g P₂O₅ and 2 mg Uranium.

Experimental Technique

Chemical and Reagents

All chemicals and reagents used to perform this work were of the analytical (A.R.) while those used for breakdown and recovery procedure were pure qualities, without further purification and treatment.

Tri-sodium Phosphate Recovery Procedure

In the present paper two techniques have been studied for the recovery of tri-sodium phosphate from the associated excess caustic soda, these included the crystallization technique of trisodium phosphate by proper evaporation and the salting out (methylation) techniques.

Crystallization of Tri-sodium Phosphate

In this technique, the prepared solution was allowed to evaporate at 130-135°C to increase NaOH concentration and to crystallize the dissolved phosphate as $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$ (as mentioned by Calkins, 1957). The crystals obtained were then separated from the concentrated sodium hydroxide solution by filtration and the filtrate left behind was subjected to both P_2O_5 and possible co-precipitated U.

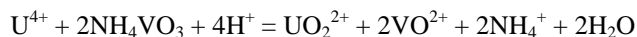
Methylation Technique

In this technique, methyl alcohol was added to the prepared solution obtained from the monazite breakdown in varying volumes ranging from 1:1 to 4:1. The purpose was to salt out the trisodium phosphate leaving behind the excess NaOH. The salted out precipitate was then filtered and washed with methyl alcohol and the filtrate was analyzed for P_2O_5 and possible co-precipitated U.

Control analysis

Uranium Analysis

Uranium was spectrophotometrically determined using Arzenazo III at 655 nm (Marczenko, 1967). In the meantime, this analysis was confirmed by the oxidimetric volumetric determination of uranium using ammonium metavanadate. This procedure is based on the titration of U^{4+} with ammonium vanadate NH_4VO_3 ; namely



Thus, uranium in solution should first be transformed into U^{+4} and for this purpose ferrous sulfate is used.

phosphate analysis

Phosphate was spectrophotometrically determined as P_2O_5 using ammonium molybdate method at 425 nm (Marczenko, 1976)

Infrared and X-ray Diffraction Analysis

A representative sample of the prepared trisodium phosphate was subjected to infrared analysis using FT-IR spectrometer (Nicolet, Model 670, MA, USA) and X-ray diffraction analysis using Philips Pw 3710/31 diffractometer equipped with a scintillation counter. Measurement was made using Cu-target and Ni filter at 40 kV and 30 mA.

Results and Discussion*Crystallization of Tri-sodium Phosphate*

According to Calkins (1957), tri-sodium phosphate solubility in aqueous solution is reduced by the presence of sodium hydroxide and become quite low by increasing the concentration of NaOH by what is known by the common ion effect.

Saleh (1966) has been achieving nearly complete separation of the phosphate (99%) by concentrating the reaction filtrate through evaporation of the excess water until the boiling temperature reached 132-135°C. At the latter, the NaOH concentration attained about 50% by weight and the formed phosphate crystals were filtered hot. Table (1) shows the present composition of the reaction filtrate and the recovered soda solution (Saleh, 1966).

Table (1) Percent Composition of the Reaction Filtrate and Recovered Caustic Soda Solution.

Constituent	Reaction filtrate,%	Recovered caustic liquor%
NaOH conc.,	20.10	52.30
SiO ₂	0.18	0.25
P ₂ O ₅	3.60	0.20
U ₃ O ₈	Nil	Nil

Absence of U has been attained through repeated filtration to keep the co-dissolved U, which was present in the filtrate in a colloidal form (about 15%) in the hydrous cake.

Table (2) show the typical composition in wt % for the obtained tri-sodium phosphate cake from the monazite typical run, after being air compressed for about 15 min.

Table (2) Composition of tri-sodium phosphate obtained from typical run.

Constituent	Wt.,%
Water-insol.	0.50
SiO ₂	0.35
NaOH	12.51
U ₃ O ₈	Nil
P ₂ O ₅	32.62

According to the above results, it is obvious that uranium in Inchass pilot plant didn't show up either in the recovered caustic soda or in the obtained phosphate cake. Calkins (1957) mentioned that there are two factors that affect the recovery of tri-sodium phosphate crystals with minimum quantity of uranium. These include the sodium hydroxide concentration and the storage time between the crystallization process and the separation of the crystals from the NaOH solution.

In the present paper, two series of experiments were performed to study the effect of caustic soda concentration and storage time to achieve maximum P₂O₅ recovery with minimum uranium association.

Effect of Caustic soda concentration

To perform this effect, 6 reaction filtrates each measuring 100 ml have been prepared from water dilution and washings of the breakdown step. These solutions contain 5gm sodium hydroxide, 1.3 gm P₂O₅ and 2 mg uranium. These solutions subjected to evaporation to achieve different NaOH concentration varying from 10% to 60%. However, by evaporation to have 10 and 20% NaOH concentration, the obtained crystallization was very weak. On the contrary, evaporation to more than 60% NaOH concentration has resulted in some NaOH crystallization. The obtained data are given in table (3) and its corresponding plot as in Fig. (1).

Table (3): Effect of NaOH Concentration upon P₂O₅ Recovery and Uranium Association

NaOH Conc., %	P ₂ O ₅ Crystallization, % of Input	U loss*, % of Input
30	72.55	78.0
40	83.72	72.0
50	90.55	52.7
60	95.74	47.5

*Associated with the crystallized P₂O₅

From the obtained data, it is obvious that evaporation to have 50 to 60 % NaOH concentration (12.5 to 15N) would bring more than about 92% P_2O_5 recovery associated with only about 1mg uranium. In this regard, Calkins in his patent (1957) mentioned that, the concentration of NaOH during tri-sodium phosphate crystallization has a noticeable effect on the loss of uranium with the phosphate crystals. It has thus been found that from the more concentrated solutions, a denser phosphate, namely $Na_3PO_4 \cdot 10H_2O$ crystallizes out which-without re-crystallization contains uranium in quantities amounting to a loss of 2% (with respect to input value). From less concentrated NaOH solutions, a less dense trisodium phosphate precipitate which has a higher affinity for the uranium and causes losses up to about 10%. In two trials achieved by this author, he found that from an 8 N NaOH solution, 47% of the uranium present in solution was found in the Na phosphate crystals while from 23 N NaOH solution, only 11% of the uranium was present in the crystal mass. Accordingly, the NaOH concentration, prior to crystallization should be at least 10N. Thus, from a 50% NaOH, 95% of the trisodium phosphate was removed by crystallization at its boiling point and the resultant trisodium phosphate crystals contained 2.5% of NaOH present in the solution together with 1% of the uranium present in the sand.

Effect of Storage Time

According to Calkins (1957), the trisodium phosphate crystals should immediately be removed after their crystallization by filtration from the NaOH solution. This is because the uranium loss would increase by increasing the storage time where NaOH which in contact with phosphate crystals for 24 hr before filtration has yielded a uranium loss of 6%. While by filtration immediately uranium loss was only 1%.

In this work a series of experiments was carried out in which the storage time increased up to 48 hr. The obtained results are shown in Table (4) and plotted as in Fig. (2).

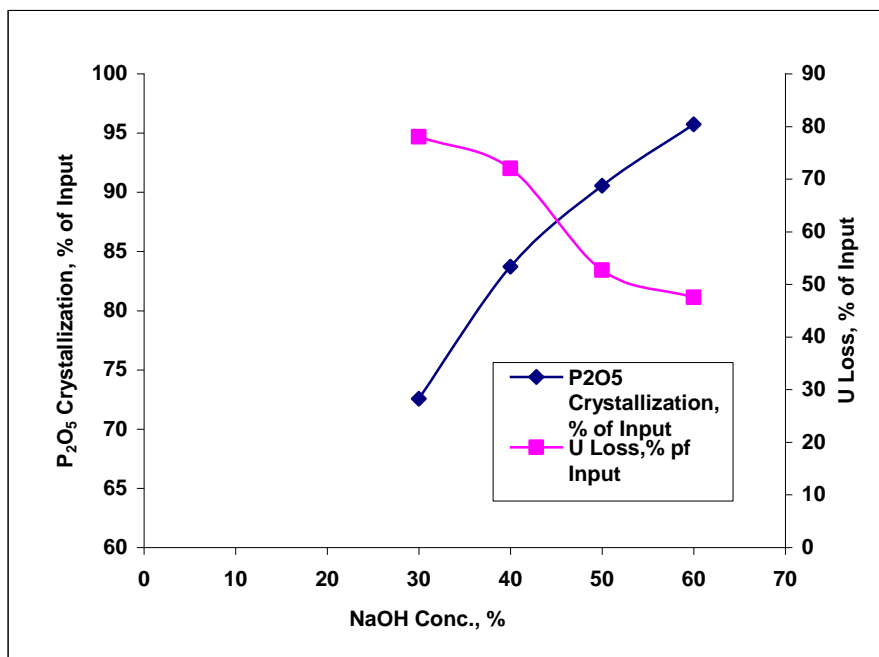


Fig.(1): Effect of NaOH Concentration upon P₂O₅ Recovery and U Association.

Table (4) Uranium Distribution during Phosphate Crystallization and Assay of the Product (Na₃PO₄.10H₂O)

Storage Time, hr.	Uranium Distribution, %		Uranium Assay in Na ₃ PO ₄ .10H ₂ O, ppm
	Dissolved in Caustic	Precipitated with Na ₃ PO ₄	
0	64.7	35.3	112
1	63.9	36.1	114
2	61.5	38.5	122
3	53.5	46.5	148
5	53.5	46.2	147
10	47.6	52.4	166
13	47.0	53.0	168
20	47.0	53.0	168
24	47.2	52.8	168
48	47.2	52.8	168

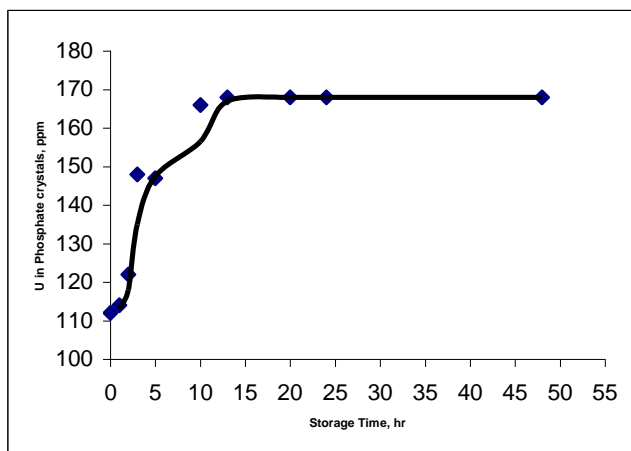


Fig. (2): Effect of Storage Time upon U Assay in the Phosphate Product

From the obtained data, it is clearly evident the storage time has a serious effect upon uranium incorporation with the crystallized phosphate. Consequently, while 35.3% of the input uranium is associated with the precipitated phosphate crystals, this percent increased to 46.2 and 52.4 at a storage time of 5 and 10 hours respectively. After 10 hours, almost no further uranium has been precipitated. With respect to the $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$ product, the associated uranium amount assay only 112ppm.

Salting out of Tri-sodium phosphate

Based on the fact that methyl alcohol would insolubilize dissolved salts, methylation of the caustic solution of trisodium phosphate as an alternative of crystallization technique was applied. For this purpose, the working caustic/phosphate filtrate was subjected to a series of methylation experiments in which the MeOH volume ratio to the filtrate was varied between unity and 4. The precipitated phosphate was filtered and after its washing with methanol was analyzed for its P_2O_5 content and the obtained results are shown in Table (5).

Table (5): Effect of MeOH/Filtrate Volume ratio upon Phosphate Precipitation.

MeOH/Filtrate Vol.Ratio	Salted-Out P_2O_5 , % of input
1:1	Small ppt.,
2:1	72.7
3:1	92.8
4:1	98.2

From the obtained data, it is obvious that almost complete phosphate has been crystallized (98.21%) as compared to that obtained by crystallization through increasing the caustic concentration (95.74%). On the other hand, the phosphate product salted out by 4 volume of MeOH was proven to contain no uranium. This result justifies actually the methylation of the phosphate instead of crystallization by evaporation.

To confirm the structure of the prepared tri-sodium phosphate, a representative sample was subjected to infrared analysis using FT-IR spectrometer. The obtained spectrogram is almost identical to that obtained from a commercial tri-sodium phosphate product

On the other hand, to reveal the structure of the obtained trisodium phosphate, it was subjected to x-ray diffraction analysis using Philips Pw 3710/31 diffractometer. From the obtained results comparison with the commercial product, it was found that the prepared sample matches with the structure $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (ASTM card No. 1-0957). Possible mixing with small amounts of other compounds have however been noticed.

It has revealed from XRD analysis that the structure of the tri-sodium phosphate product is $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. So, in this regard the uranium assay in the crystallized trisodium phosphate would be 100.6 ppm instead of 112 ppm.

Conclusion

The study of the laboratory processing of Egyptian monazite by alkali leaching followed by preparation of non-radioactive tri-sodium phosphate from the monazite breakdown was performed. The following conclusion may be drawn:

Two techniques have been applied; namely crystallization of tri-sodium phosphate and salting out of tri sodium phosphate. The crystallization is applied by evaporation, this have been acquired the studying of caustic soda concentration and the storage time upon P_2O_5 crystallization. From the obtained results, it can be recover 95.74% of the P_2O_5 present in monazite as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ associated with only 100 ppm uranium under 50-60% concentration of NaOH during crystallization and zero storage time.

The second technique used is the salting out (methylation). By applying this technique, 98.21% of the P_2O_5 can be recovered as $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ that is free from uranium by using MeOH/filtrate volume ratio of 4:1.

Acknowledgments

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