

CONTROLLED ALKALI TREATMENT OF ROSETTA MONAZITE FOR THE PREPARATION OF URANIUM -FREE TRISODIUM PHOSPHATE

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ABSTRACT

The present work deals with a controlled alkali treatment of Rosetta monazite through caustic soda breakdown followed by proper dilution and washing of the obtained hydrous oxide cake. The various relevant factors of these operations have been studied. These include the grain size, the reaction time, the reaction temperature and the soda to sand weight ratio beside the dilution ratio and the number of water washings. From the obtained results, it has been found that about 98% monazite breakdown was obtained together with only 10% co-dissolved uranium. The latter was however kept in the excess caustic soda for recycle during salting out of the resultant trisodium phosphate through proper methylation.

Key words: Rosetta, monazite, uranium, trisodium phosphate.

INTRODUCTION

Monazite is a phosphate of lanthanons in which portions of the latter have been replaced by thorium and to a much less degree by uranium. Monazite occurs essentially as an accessory mineral in granites, gneisses and pegmatites in which it occurs in concentrations up to 0.1%. By weathering of such rocks, monazite would be liberated to be later concentrated into beach and dunes deposit by the action of wind and water. Large commercial occurrences of such detrital deposits are found in Australia, USA, India, Brazil and Egypt.

Monazite occurs actually as large reserves in the black sands that are distributed along the beaches of the northern parts of the Nile Delta from Rosetta to Damietta where the monazite content of the black sands can attain about 1%.

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However, important monazite sand deposits occur mainly at Rosetta and Damietta where they constitute one of Egypt main sources of a thorium and uranium. The monazite of Rosetta has a thorium content of about 6% and also contains over 0.4% of uranium which, in view of the size of the deposit, makes it an important source of uranium, (Saleh, 1966). In Rosetta deposit, monazite is associated with other heavy minerals such as ilmenite, magnetite, zircon, and rutile (Rittman and Nakhla, 1958; Higazy and Naguib; 1958, Anwar and Abdel-Rehim, 1970; and Moller et al., 1989). By proper ore dressing methods, almost pure monazite concentrates from such sands can be prepared for chemical processing.

There are indeed several techniques that are used for the chemical breakdown of monazite to extract thorium, uranium and the lanthanides (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 and flux (sodium fluoride) at 800-825°C, sintering with sodium hydroxide at 400-500°C besides chlorination of its mixture with coal at 700-800°C. However, both the acid and the alkaline leaching methods are commonly used for commercial processing, but the latter is most preferable and widely used as it has many advantages. The most important of these advantages are the simultaneous removal of phosphorous during leaching, and the production of the useful sodium phosphate as a by-product (fertilizer and/or detergent) as well as the possible regeneration of alkali (Abdel-Rehim, 2002).

The present work is actually concerned with the breakdown of Rosetta monazite by the sodium hydroxide method under controlled conditions followed by proper dilution and washing in a manner to keep behind most of the uranium content in the hydrous oxide cake. As will be later shown by the author and co-workers in a subsequent work (under publication), it has been possible through salting out of the trisodium phosphate by methylation to keep the small co-dissolved uranium amount in the excess alkali solution. Accordingly, the salted out trisodium phosphate would be exempt of any radioactivity.

EXPERIMENTAL

For the analytical work, all chemicals and reagents used to perform this work were of the analytical (A.R.) while caustic soda used for breakdown was of pure quality.

1. Monazite Breakdown Procedure

A representative sample of Rosetta monazite sand concentrate was used in this work (96% purity). The latter has been kindly provided by the NMA mini pilot plant unit of the Physical Dressing Department at Inshass. For studying the breakdown procedure, several experiments were performed using 5 grams of the ground monazite concentrate. Sodium hydroxide was added to the ground monazite at different concentrations and the reaction pulp was stirred for the required time at the destined temperature. The experiments were performed in a half-liter glass flask fitted with one opening to allow inserting a thermometer. At the end of each breakdown experiment, the slurry was diluted with water (6 times the weight of monazite sand), heated for 1 hr at 110 °C and the slurry was then filtered and washed till become free from soda and phosphate. The obtained hydrous cake was dried to about 25% moisture content and was then properly analyzed for the unreacted monazite.

Un-reacted monazite weight X100 Under these operating conditions, the resultant weight of the obtained hydrous oxide cake would be almost equal to that of the input monazite (Saleh, 1966). Therefore, the control analysis was performed by directly sampling the former and its dissolution in a proper amount of concentrated HCl at 80-90°C for 1 hr. The un-dissolved residue left behind was then filtered, washed, dried and weighed to calculate the un-reacted monazite according the following equation:

$$\text{Monazite reacted\%} = \frac{\text{Un-reacted monazite weight} \times 100}{\text{Input monazite weight}}$$

2. Analytical Procedures:

2.2.1. Monazite Analysis

For the complete analysis of the working monazite concentrate, a representative sample has been dissolved in concentrated sulfuric acid in a 120 ml TFM container with continuous heating on a hot plate for 2.5 hr. The slurry was cooled and poured into crushed ice to avoid the formation of any sulfate precipitate that would be difficult to re-dissolve. The slurry was then transferred into a glass beaker with the aid of 1:1 sulfuric acid. The mixture was stirred to dissolve the precipitated soluble salts and was then filtered. The sample residue with the filter paper was ashed, and the residue was boiled for 10 min with 5.0 ml concentrated sulfuric acid, and was then treated with the same procedure (as

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described for the original sample). The process was repeated, if necessary, until the sample was almost completely dissolved. The solution was then transferred into 100ml measuring flask and made to volume with double distilled water. From the latter, different aliquot samples were taken for the required analyses.

For U, Th, REEs and P₂O₅ the respective spectrophotometric method were used (Marczenko, 1967). Thus for U, the arsenazo III method was used and the absorbance was measured at 655nm. For thorium, it was also determined spectrophotometrically using arsenazo III method at 655nm but under different conditions while for RE, the same reagent was used however; the absorbance was measured at 650 nm. On the other hand for P₂O₅, it was also spectrophotometrically determined using the ammonium molybdate method at 425 nm.

For the other minor and trace elements analyses namely TiO₂, Fe₂O₃, PbO and SiO₂, the flame atomic absorption was used at the following wavelengths:

Element	Wavelengths, nm
Ti	364.3
Si	251.6
Pb	217.0
Fe	248.3

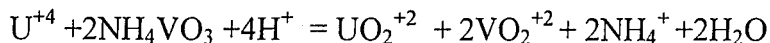
However, for CaO, a photometric method was applied using a Jenway Flame Photometer PFP7. The obtained results of the complete analysis of the working monazite are shown in Table (1).

Table (1): Chemical Analysis of the Working Rosetta Monazite Concentrate (about 96% purity)

Constituent	Wt.%
ThO ₂	5.94
RE ₂ O ₃	60.32
U ₃ O ₈	0.44
TiO ₂	0.23
Fe ₂ O ₃	0.44
CaO	0.52
PbO	0.12
P ₂ O ₅	26.32
SiO ₂	2.40
Insol.	2.08
Total	98.81

2.2.2. Uranium Analysis

For the follow up of possible uranium dissolution in the obtained breakdown filtrate ($\text{Na}_3\text{PO}_4/\text{NaOH}$), the latter together with the washings were collected in 200 ml measuring flask and made up to volume. From the latter, aliquot sample solution were drawn for uranium analysis using spectrophotometric analysis method of arsenazoIII at 655nm and which was sometimes checked by the oxidimetric titration vs NH_4VO_3 method. This procedure is based on the titration of U^{+4} with ammonium vanadate NH_4VO_3 ; namely



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

RESULTS AND DISCUSSION

1. Controlled Alkali Breakdown of Monazite

According to Calkins (1950), complete digestion of monazite requires a relatively great excess of sodium hydroxide; a matter which entails the disadvantage of partial dissolution of uranium with the trisodium phosphate. Saleh, (1966) has been able on a pilot scale (25kg monazite/batch) to realize more than 98% breakdown after 3hr at 130-140°C when working with 90% of sand -350 mesh size (100% less than 325 mesh size) mixed with 1.5 weight ratio of caustic soda as 45% solution. In the light of the above, several series of experiments have been planned in the present work to optimize the monazite breakdown conditions such as (particle size, time, temperature and soda to monazite sand ratio). The purpose is to choose the least values matching with the maximum decomposition percent of monazite that doesn't allow any accompanying uranium dissolution.

1.1. Effect of Particle Size

A representative monazite sample portion has been finely ground and subjected to screening to different mesh sizes ranging from 120 down to 325. The differently ground sized fraction (100% of a certain size range) were then subjected to similar digestion conditions; namely a weight ratio of 1.5:1 caustic soda to sand as 45% solution 140°C for 4 hr. at the end of each experiment, the unreacted part was filtered, washed dried and analyzed for unreacted monazite by

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dissolving in concentrated HCl solution. The obtained results are tabulated in Table (2) and plotted in Fig (1).

**Table (2) Effect of Grain Size upon Monazite Breakdown Efficiency
(1.5:1 caustic soda/sand as 45% conc., 140C, 4hr)**

Grain size, (mesh)	Monazite reacted, (%)
-115+120	50.9
-120+135	52.2
-135+170	58.7
-170+230	75.0
-230+325	89.3
-325	99.0

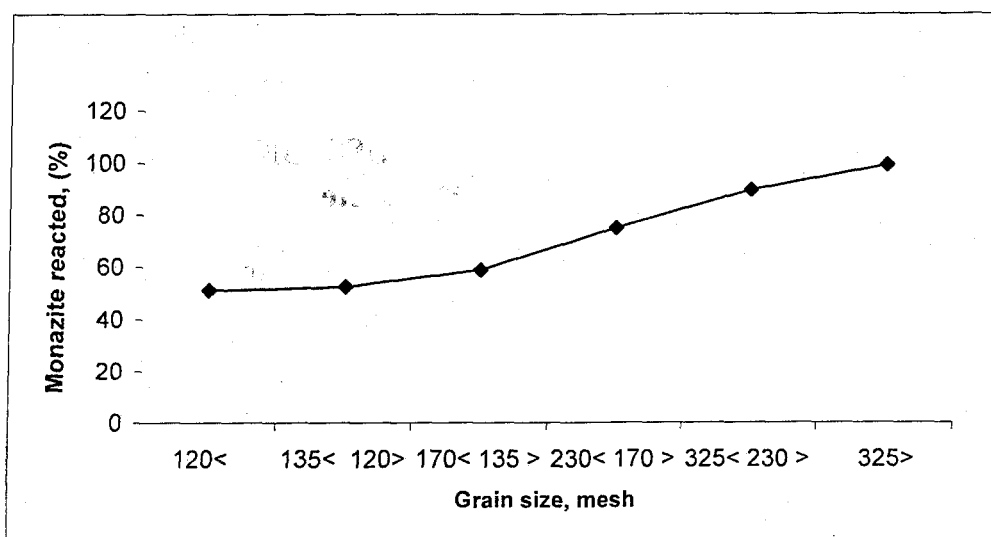


Fig.(1): Effect of Grain Size upon Monazite Breakdown Efficiency

From the obtained results, it is clearly evident that, the particle size is quite important for monazite breakdown where at the sample size range of -115+135 mesh, only about 51 to 52% has been reacted while at -170 +230 mesh size, the monazite reacted percent increased to 75%. At -325 mesh size sample, almost complete breakdown of monazite (99%) has been obtained.

The working temperature of 140°C represents indeed the minimum temperature required for almost complete monazite breakdown under the working conditions. Fixing the latter and decreasing the reaction temperature to 100, 120 and 130°C resulted in a breakdown efficiency of 72.4, 80.3 and 90.3% respectively. Therefore, in studying the effect of the other breakdown conditions

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upon both monazite reaction and uranium dissolution, the reaction temperature was fixed around 140°C beside fixing the working grain size at 100% -325 mesh.

1.2. Effect of Time

It was also found necessary to evaluate the effect of time upon the former. For this purpose, another series of monazite breakdown experiments was performed for reaction time varying from 1 up to 5 hr. The other breakdown conditions were fixed at 1.5:1 caustic soda to monazite sand weight ratio as 50% solution at a temperature of 135-140°C and using sand sample ground to 100% - 325 mesh. The obtained results shown in Table (3) and plotted in Fig (2) indicate that monazite breakdown efficiency at 1 hr reaction time was only 72.5% and rapidly increase to about 90% by increasing the reaction time to 1.5 hr. Therefore, the monazite breakdown efficiency steadily increased to 92.4 and 95.6% at 2 and 2.5 hr. respectively. Increasing the latter to 3 to 4 hr increased the monazite breakdown efficiency up to about 97 to 99% respectively.

Table (3) Effect of reaction Time upon Monazite Breakdown Efficiency (1.5:1 caustic soda/sand as 50% conc., 135-140C, 100% -325 mesh)

Time, hr	Monazite reacted, %
1	72.5
1.5	90.1
2	92.4
2.5	95.6
3	96.9
3.5	97.7
4	98.7
4.5	99.0
5	99.0

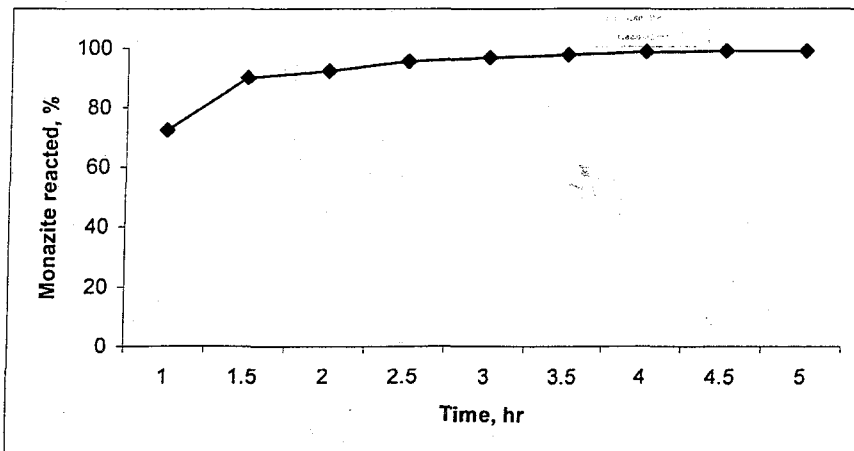


Fig.(2) : Effect of Reaction Time upon Monazite Breakdown Efficiency

1.3. Effect of Temperature

A series of experiments was then performed to investigate the effect of temperature upon the efficiency of monazite reaction and possible uranium dissolution in the range of 130 to 150°C. In this series, the other breakdown conditions were fixed at a caustic soda/sand ratio of 1.5:1 as 50% concentration for 4 hr and using monazite samples completely ground to -325 mesh. At the end of each experiment, the obtained slurry was filtered and washed and the hydrous oxide cake was treated as previously mentioned while the original filtrate (Na₃PO₄/NaOH) was made to a volume of 200 ml before uranium analysis. The obtained results are summarized in Table (4) and plotted in Fig (3).

Table (4): Effect of Temperature upon Monazite Breakdown Efficiency and Co-dissolved Uranium (1.5: caustic soda/sand as 50% conc., 4hr, 100% -325 mesh)

Temperature, °C	Monazite reacted, %	Co-dissolved uranium	
		Conc, (mg/l)	% dissolved
130	90.30	4	4.32
135	94.80	18	19.45
140	98.70	25	27.02
150	99.0	35	37.84

From these results, it is clearly evident that at 130C, the reacted monazite amounts to 90.3% while the co-dissolved uranium is only 4.3%. Increasing the temperature to only 5°C increased the reacted monazite to about 95% while the co-dissolved uranium increased to 19.4%. Working at 140°C and 150°C has resulted in almost complete monazite reaction and the co-dissolved uranium increased to about 27 and 38% respectively. These results thus indicate that higher reaction temperatures are accompanied by higher uranium dissolution.

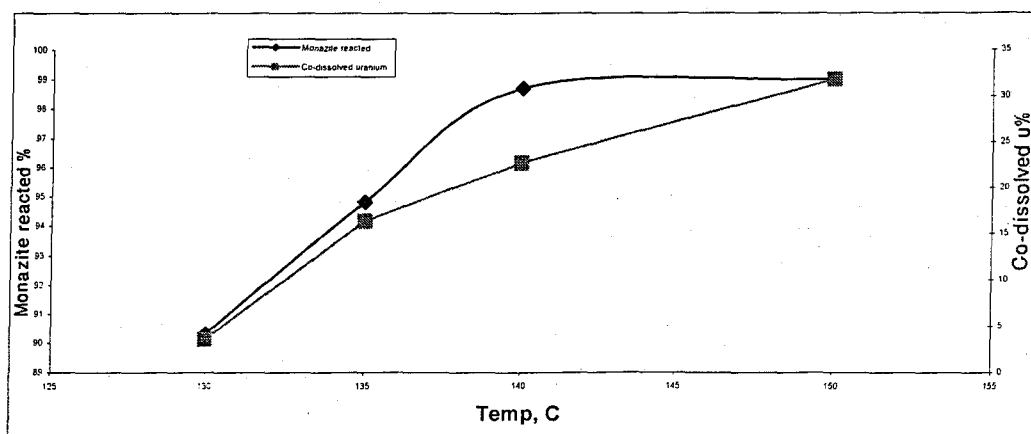


Fig. (3) Effect of Reaction Temperature upon Monazite Breakdown Efficiency and Co-dissolved Uranium.

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1.4. Effect of Soda to Monazite Sand Ratio

The effect of soda to monazite sand ratio upon the efficiency of monazite breakdown and uranium co-dissolution was then studied in the range of 1:1 up to 3:1 as 50% concentration. In this series, the other breakdown conditions were fixed at the most optimum values; namely, a reaction temperature of 135-140°C for 4 hr and using monazite sample portions completely ground to - 325 mesh size. The obtained data are shown in Table (5) and plotted in Fig (4).

Table (5): Effect of Soda/Monazite Sand weight Ratio upon Monazite Breakdown Efficiency and Co-dissolved Uranium (50% caustic soda conc., 4 hr, 135-140°C, 100% -325 mesh)

Soda/Sand wt. ratio	Monazite reacted, %	Co-dissolved uranium	
		Conc, (mg/l)	% dissolved
1	88.6	8	8.6
1.5	97.7	17	18.4
2	98.9	22	23.8
3	99.0	36	39.0

In a trial to decrease the co-dissolution of uranium in the alkali trisodium phosphate liquor, the effect of concentration of the caustic soda during the breakdown was investigated between 40 and 60% while keeping its weight ratio to the monazite sand fixed at 1.5:1. The other breakdown conditions were fixed at temperature of 135-140°C and using sand samples ground 100% to -325 mesh. The obtained results showed that at 40 and 45% NaOH concentration, uranium co-dissolution attained 7.5 and 12% respectively while at 60%, it attained to 43%.

It can be concluded that the optimum conditions for obtaining about 98% monazite reaction would involve working at 1.5:1 soda/sand wt. ratio and at 50% caustic soda concentration at 130-140°C for 4 hr. under these conditions and which involve water dilution of the reacted slurry with 6 parts water and heating for 1 hr at 110°C before dilution, the co-dissolved uranium attained 18.4%. However, by proper subsequent treatment it has been possible to decrease this value.

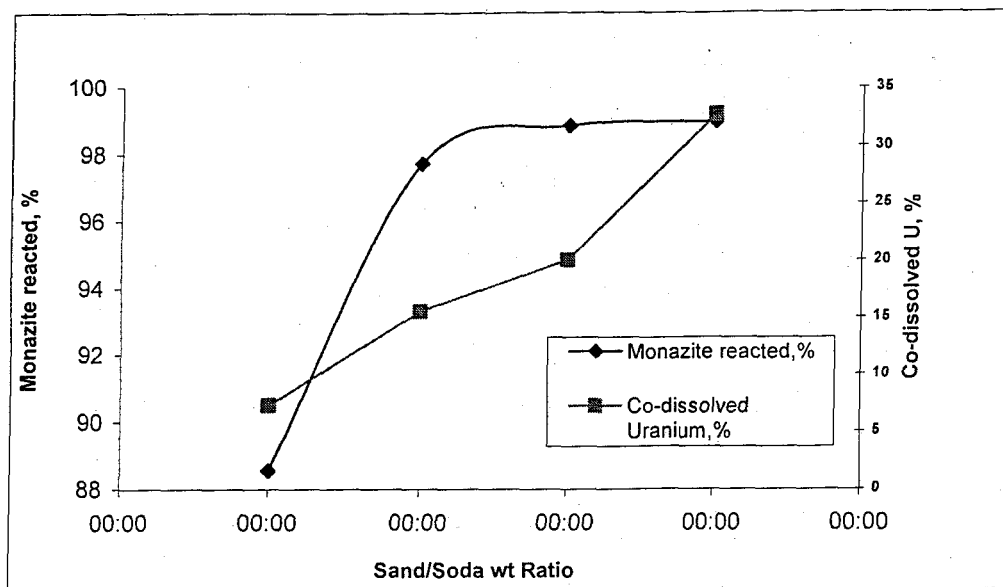


Fig. (4): Effect of Soda /Monazite Sand weight Ratio upon Monazite Breakdown Efficiency and Co-Dissolved Uranium

2. Controlled Treatment of Monazite Rosetta Slurry

As previously mentioned, monazite breakdown by caustic soda results in the dissolution of its phosphate component as trisodium phosphate. The latter would actually be contaminated with caustic soda remaining from the input quantity which in the present work was found to amount to 150% the working monazite weight. In other words, the produced trisodium phosphate should be properly separated from the remaining caustic soda as well as from the co dissolved uranium (18.4% of the original amount). The reaction mass or the so called process slurry produced after completion of monazite reaction should thus be properly treated.

This involves indeed a prior water dilution and according to Calkins (1957), water is added to the slurry so that about one liter of the total slurry would be obtained per 100g input monazite. This amount represents an optimum value for minimum uranium solubility which would increase with increasing the concentration of NaOH. In the meantime, it would be advantageous to heat the diluted slurry to ensure a maximum solubility of the produced Na_3PO_4 . From this discussion, it was found necessary to study the two relevant factors of the extent of water dilution and that of washing the obtained hydrous oxide cake.

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2.1. Effect of Water Dilution

To study the optimum quantity of water dilution compatible with maximum solubility of Na_3PO_4 and NaOH together with minimum uranium solubility, a series of experiments was carried out using 5 gm monazite sample portion. After breakdown of the latter using the previously determined optimum conditions (1.5:1 caustic sod/ sand as 50% conc., 135-140°C, 100% -325 mesh, 4hr), the reaction slurry was diluted with different water weight ratios to the input monazite weight followed by heating at 100-105°C for about 1hr. The diluted slurry was then filtered and the insoluble hydrous cake was washed with fixed amount of water (20ml) before made to volume (100ml) for analysis of both P_2O_5 and uranium. The obtained results are shown in Table (6) and plotted in Fig (5) after referring the analytical results to the P_2O_5 and uranium content in the input 5g monazite portion (1.3g P_2O_5 and 18.5 mg U).

Table (6): Effect of Water Dilution on P_2O_5 and U Dissolution in the Alkali Filtrate after Breakdown of Rosetta Monazite Sand

Dilution Factor (water/monazite wt.ratio)	P_2O_5		U	
	Conc., g/l	Recovery%	Conc., ppm	Dissolution %
4	9.00	69.20	3.00	1.60
5	9.23	71.20	3.20	1.70
6	9.40	72.50	4.00	2.20
7	10.20	78.40	4.25	2.30
8	10.38	79.80	6.70	3.60
9	10.44	80.30	8.00	4.30
10	10.66	82.00	9.65	5.20

From the obtained results, it can be found that a water/monazite weight ratio of 7 can be considered as optimum with respect to both high P_2O_5 recovery and low uranium dissolution. Thereafter, improvement in the former is slight while it brings a perceptible increase in uranium dissolution. It is interesting in this regard to mention that the fixed wash of 20 ml following dilution and filtration has a significant effect upon decreasing U dissolution from the hydrous oxide cake.

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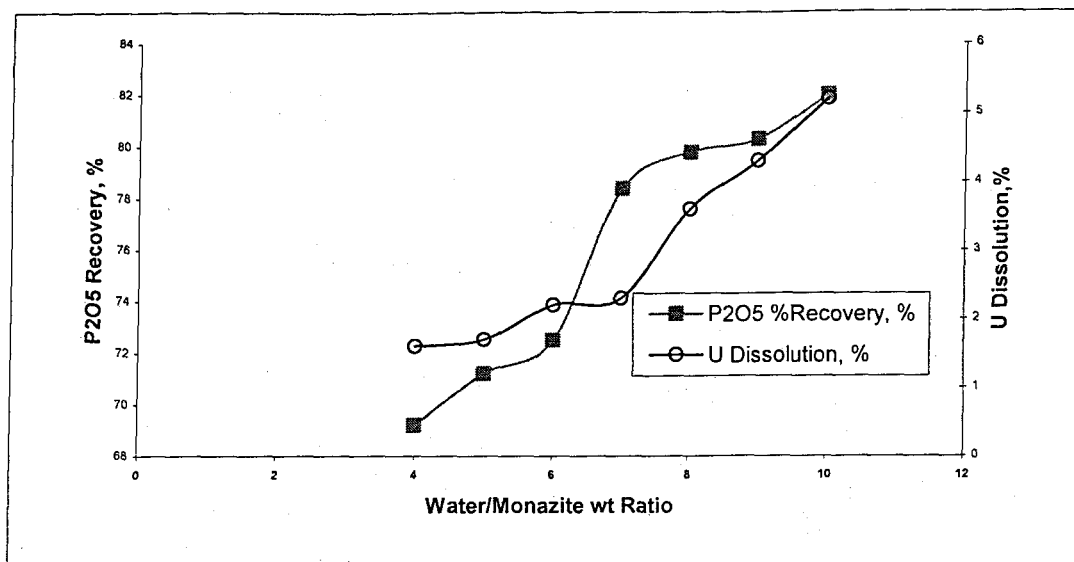


Fig.(5): Effect of water Dilution on P_2O_5 and U Dissolution in the Alkali Filtrate after Breakdown of Rosetta Monazite Sand

2.2. Effect of Water Washing

The 7 fold water/monazite dilution ratio in the above mentioned series of experiments followed by one water wash of the cake (4 times the input monazite weight) was not adequate for acceptable phosphate recovery (78.4%). This decreased recovery would represent an economic loss of P_2O_5 besides consuming more acid in the subsequent acid dissolution of the hydrous cake. Therefore, another experiment was performed in which several water washes of the cake have been carried out. The obtained results for further 6 hot water washes (20 ml water in each wash) after dilution to 100 ml are shown in Table (7). From the latter, it is clearly evident that 6 extra water washes are required for almost complete recovery of the input P_2O_5 content. However, to avoid excessive dilution and in turn increased costs for phosphate recovery, 3 extra washes would be adequate. In this case, the P_2O_5 recovery in the filtrate would amount to about 96.4%. In the meantime, a U dissolution percent of 10% has been found (i.e about 2 mg of the working 5 gm monazite sample input).

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Table (7): Effect of Water washes of the Hydrous Cake upon P₂O₅ Recovery Efficiency

Water wash No. (X=20ml)	P ₂ O ₅	
	Conc., g/l	Recovery, %
7 fold dilution + 1 wash	10.20	78.40
2	1.10	8.46
3	0.80	6.15
4	0.44	3.38
5	0.28	2.15
6	0.12	0.92
7	Nil	Total=99.46

CONCLUSION

Laboratory scale processing of Rosetta monazite was carried out using the alkali breakdown procedure. Several relevant factors have thus been studied. For 98% monazite breakdown, the latter involved working at 1.5:1 soda/sand ratio and at 50% caustic soda concentration at 130-140°C for 4hr. and grinding the input monazite to -325 mesh size. Under these conditions and using 6 times water dilution and heating at 110°C for 1hr before dilution and washing till P₂O₅ and soda free, the co-dissolved U amounted to 18.4%. However, by 7 times dilution and 4 washes (20ml each), it has been possible to attain 96.4% P₂O₅ recovery associated with only 10% uranium dissolution.

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التحكم فى المعالجة القلوية للمونازيت بمنطقة رشيد لتحضير ثلاثى فوسفات الصوديوم خالى من اليورانيوم

خالد فؤاد محمود

هيئة المواد النووية المصرية

يتناول هذا العمل طريقة التحكم فى المعالجة القلوية لتركاز معدن المونازيت من منطقة رشيد وذلك باستخدام هيدروكسيد الصوديوم والذى يتبعه تخفيف وغسيل كعكة الاكاسيد المتحصل عليها. ولقد تم دراسة بعض العوامل المؤثرة على عملية الفتح وتشمل حجم حبيبات المعدن، زمن التفاعل، درجة حرارة التفاعل بالاضافة الى نسبة وزن الصودا الكاوية الى وزن المونازيت وكذا نسبة التخفيف وعدد مرات الغسيل. وقد اتضح انه تحت الظروف المثلى يتم الحصول على كفاءة فتح للمونازيت تبلغ حوالي ٩٨% مع اذابة ١٠% فقط من اليورانيوم والذى يمكن الاحتفاظ به فى محلول هيدروكسيد الصوديوم الذى يتخلف من ترسيب فوسفات ثلاثى الصوديوم والذى يتم تدويره.