# Alkaline leaching of uranium from El-Sibaiya East Phosphorite in the presence of sodium peroxide

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Chemical, mineralogical and radiometric investigation studies were executed on a representative phosphorite sample collected from El-Sibaiya East area to evaluate its suitability for the alkaline leaching of its uranium content. The uranium alkaline leaching was carried out in three phases using $Na_2CO_3$ and a mixture of $Na_2CO_3$/$NaHCO_3$ with/without an oxidant ($Na_2O_2$). Factors include; $Na_2CO_3$, $NaHCO_3$, $Na_2O_2$ concentrations; digestion temperature, reaction time and ore fineness were studied and optimized. The results pointed to that the best leaching efficiency of uranium (83.2%) was conducted using the mixture solution of $Na_2CO_3$/$NaHCO_3$ (0.5M) in the presence of 2.5% $Na_2O_2$ (w/w). The other conditions affected the leaching process were studied and optimized as 80 °C (leaching temperature), 3h (leaching time), 44µm (ore grain size) and a solid/liquid ratio of 2/25. The leached uranium was recovered by precipitation using NaOH solution where the precipitated product was defined by the XRD as sodium diuranate ($Na_2U_2O_7$) of high purity.

## 1. Introduction

The phosphate rocks refer to those ores containing apatite and/or francolite (carbonate-fluorapatite) minerals as the main constituents [1]. Generally, the phosphate rock contains, at least 24% $P_2O_5$, less than 3% $Fe_2O_3$ with CaO: $P_2O_5$ ratio ranges between 3:1 and 3.5:1 [2]. Phosphate rocks of sedimentary origin typically have 30-35% $P_2O_5$ whereas those of igneous origin contain marginally higher $P_2O_5$ (35-40%). Uranium, REEs, gypsum, vanadium, and fluorides are by-products resulted from milling of the phosphate rocks [3, 4].

The Egyptian phosphate deposits are part of the Mediterranean phosphate province that extends from Morocco to Turkey and belong to the late Cretaceous-Palaeogene age [5, 6]. They locate over a band between latitude 24° and 27° N in three main belts which are, from north to south, the northern belt extends from Baharia Oasis to Sinai, the central belt is confined to the area of the Red Sea coast (from Safaga to Quseir), Nile valley (between Kharaga and Dakkla chooses) [5, 7, 8]. The second belt is the one of high economic potentiality to which the area of this study belongs.

The uranium concentration in Egyptian phosphate varies from location to another, but in general, within range of 5 to 200 ppm as U(IV) and U(VI) depends on the mode of the phosphate deposit formation and its age. Hexavalent uranium species are adsorbed on the phosphate grains surface or fixed on phosphate ore to form secondary uranium minerals. Uranium (IV)/(VI) ratio is highly variable but the most abundant form is uranium (IV) [9]. Many researchers attributed that, to the might, the early diagenetic formation of marine phosphate in a reductive environment, uranium (IV) diffuses from the water into sediments.

About 80000 ton of uranium is encountered in the Egyptian phosphate based on the estimated reserves of the phosphate that exceed three billion metric tons, and the calculated average of the uranium content is about 0.001% [10]. About 90%

of phosphate rocks are being used in fertilizers manufacturing while the remaining part is being utilized in the phosphoric acid manufacture, detergents, chemicals, insecticides and in food industries [11, 12]. Trace amounts of the uranium content transfer to the manufactured phosphate fertilizers hence to the agriculture soils that impose a potential risk to the human health in the long run. Accordingly, several researchers interested in the removal of uranium from the phosphate rocks prior to their processing or even from the contaminated soils using the leaching and/or adsorption techniques [13-16].

Chemically, the main methods used for uranium leaching from phosphate samples are the acidic and alkaline processes include hydrometallurgy or pyrometallurgy techniques [17]. The acidic leaching compared to alkaline have advantages include; more effective especially with hard ores, low temperature and time-consuming [18]. Sulfuric acid is the commonly used due to the high solubility of the produced uranyl sulfate complexes [19, 20]. When the gangue materials contain high silica or fluorine minerals, sulfuric acid leaching is preferred, because of its costs less than alkaline leaching beside dissolve uranium minerals more rapidly. During the acidic treatment of phosphate samples using $H_2SO_4$ about 80-90% of the uranium content is leached [21, 22].

In spite of the acidic methods are widely used for uranium leaching, but the alkaline technique is more appropriate especially when the ores have high carbonate content like calcite, dolomite, iron minerals and carbonate hydroxylapatite which made the acidic leaching is more expensive [23, 24]. In addition, the alkali materials are not significantly reacting with silicate and alumino-silicate minerals, which commonly present in the ores [25]. Moreover, the alkaline leaching has other advantages than the acidic are includes the higher selectivity, lower corrosively and low wastes discharge.

The present work delivered two targets. The first is of environmental importance and represented in minimizing the uranium content in the phosphate ores (before their manufacturing to fertilizers and other products) using the alkaline leaching technique by a mixture of $Na_2CO_3$/$NaHCO_3$ (0.5M) in

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the presence of $Na_2O_2$ as an oxidant to enhance the uranium leaching efficiency. The second is of strategic importance through the recovery of the leached uranium by its precipitation from the leach liquor using sodium hydroxide solution. The investigated phosphorite sample was collected as a representative sample from El-Sibaiya East area, East Nile valley, Egypt.

## 2. Experimental

**2.1. Materials and Methods.** El-Sibaiya east phosphorite sample after grinding was subjected to wet chemical analysis. The chemical reagents used either in the chemical analysis of the phosphorite representative sample or in the leaching experiments were of the analar grade. The elemental standard solutions which used for calibration were prepared by dissolving the adequate weigh of the proper chemical reagents in the exact volumes of the de-ionized water. A uranium stock solution containing 1000 mg/L of U(VI) was prepared by dissolving 1.782 g of uranyl acetate in 1% nitric acid solution and diluting to 1000 mL.

The major elemental analysis composition was determined in the oxide forms except for the fluorine content. $P_2O_5$, $SiO_2$, $Al_2O_3$ and $TiO_2$ concentrations were estimated spectrophotometrically [26] using *UNICAM UV2-100* spectrophotometer. Oxides concentration, include CaO, $Fe_2O_3$, and MgO, was defined by the traditional titration method [27] while $Na_2O$ and $K_2O$ concentrations were determined photometrically using *JENWAY PFP7* flame photometer. Moisture content in soil samples was measured by weighing out 2g of the powdered sample and then heating in drying cabinet at 105 °C for 3h until constant weight is obtained. The loss in weight is considered as moisture loss ($H_2O$ content). The above sample, minus its moisture content, is further heated for 3hours at 550-600 °C in a drying cabinet until constant weight is obtained the difference in weight between the sample heated at 105 °C and 550 - 600 °C gives the total organic matter in the sample. Original water presents ($H_2O^+$) is measured by igniting 2g of the powdered sample at 1000 °C in a porcelain crucible. The difference in weight of the sample at the two temperatures (500 °C and 1000 °C) gives the original water present.

The radiometric concentration of U, Th and Ra was measured by the laboratory γ-spectrometry technique using the Multi-Channel Gamma Spectrometer with NaI (Tl) detector which holds in the Nuclear Materials Authority, Egypt. All the samples, after crushing to the relevant size, were carefully quartered and put into covered plastic vessels (212.6 $cm^3$ in volume) then tightly sealed by adhesive tapes. The sealed vessels were covered well by thin aluminum foil to prevent escaping of the accumulating Ra-222 gas then were left for 30 days before the measuring process. Uranium, thorium (in their equivalent forms eU and eTh) and radon were measured and expressed in the ppm unit.

Additionally, uranium was also measured by the wet chemical technique that can identify the concentration of both the old and recent uranium. The exactly weighted one gram of each sample was well ground to less than 0.063 mm (- 200 mesh) in size, then was attacked by a mixture of concentrated acids (HF, $HClO_4$ and HCl) with aggressive heating till the complete dryness. The extra acid attack was applied to assure the full digestion of the solid samples. After cooling and complete dissolution in the distilled water, the concentration of uranium was measured colorimetrically with the chemical reagent "Arsenazo III" using the UV/VIS spectrophotometer [28].

On the other hand, the total REEs concentration and the trace element concentrations were measured using *UNICAM 969 AAS*. The mineralogical investigations were carried out for a whole rock phosphorite sample using Philips X-ray generator model *PW 3710/31* diffractometer with automatic sample changer model *PW1775* and supported by the remarks obtained from the IR analysis. All the employed instruments are in Nuclear Materials Authority, Katameya, Cairo, Egypt.

**2.2. The alkaline leaching of uranium from the El-Sibaiya phosphorite.** The alkaline leaching of uranium from the El-Sibaiya phosphorite was tested using the $Na_2CO_3$ and $NaHCO_3$ in the solution form. It is worth to point that the leaching process was performed in three different phases; the first phase included using $Na_2CO_3$ only as leaching agent; the second tested the leaching efficiency of $Na_2CO_3$ in the presence of $Na_2O_2$ as oxidant; the third phase involved using a mixture of $Na_2CO_3$ and $NaHCO_3$ as leaching solution in the presence of $Na_2O_2$.

The leaching experiments in the three phases were performed in 250 ml glass flask equipped with a water-cooled condenser to minimize the solution loss by heating. The leaching process was carried out using a thermostatic hotplate provided with a magnetic stirrer at 450 rpm stirring speed. The other leaching conditions were fixed during the three phases. After completion of each leaching experiment, the obtained slurry was cooled and filtrated then the uranium concentration was measured in the filtrate and its leaching efficiency was calculated by the ratio of dissolved uranium in the filtrate against its content in the solid phosphorite. The different factors affecting the leaching process include; $Na_2CO_3$ concentration, $Na_2CO_3$/ore phase ratio, $Na_2O_2$ and $NaHCO_3$ addition, reaction time, temperature and ore fineness, were studied and optimized.

The uranium leaching efficiency using 0.5M $Na_2CO_3$ solution was tested under the effect of variable solution/sample ratio (5/1 to 20/1 ml/g), while other conditions were fixed constant (74 µm, 90 °C and 4h).

Under the same conditions of ore grain-size (74 µm) and reaction temperature, a mixture of 0.5M $Na_2CO_3$ and 0.5M $NaHCO_3$ was used for uranium leaching in presence and absence of $Na_2O_2$ under different solution/sample ratios.

The effect of leaching temperature on uranium leaching from the phosphate ore was investigated in the range of 25 to 100 °C. The other leaching condition were ore grain-size (74 µm), $Na_2CO_3$-$NaHCO_3$ solution (0.5M), $Na_2O_2$ (2.5% w/w), solution/solid ratio (25/2) and 4h leaching time.

To study the effect of ore grain size on the uranium leaching efficiency, the phosphate rock was ground then sieved using sieves of gradual size. The alkaline leaching process was performed with various ore grain sizes ranged from 105 to 44 µm. the other applied conditions were $Na_2CO_3$-$NaHCO_3$ solution (0.5M), 80 °C, $Na_2O_2$ (2.5% w/w), solution/solid ratio (25/2) and 3h leaching time. All the experiments were performed in duplicates with experimental error ± 0.5-2 %.

## 3. Results and Discussion

**3.1. General geology.** The Campanian-Maastrichtian phosphate deposits in Egypt nominated as the Duwi Formation (Fig. 1). The Duwi Formation in the Nile Valley region was divided into Mahamid Member (Lower Member), Sibaiya Member and Adayma Member (Upper Member) [29]. This Formation is mainly composed of phosphate beds intercalated with shale, marl, oyster-limestone and chert bands. These phosphate beds are named A, B, and C from base to top. The horizon (A) represents the high economic phosphorite bed in all studied sections where it has the largest thickness and the high phosphorus content. The horizons (B) and (C) didn't consider economic phosphorite beds because they varied in the thickness from 10 to 30 cm and have low phosphorus content.

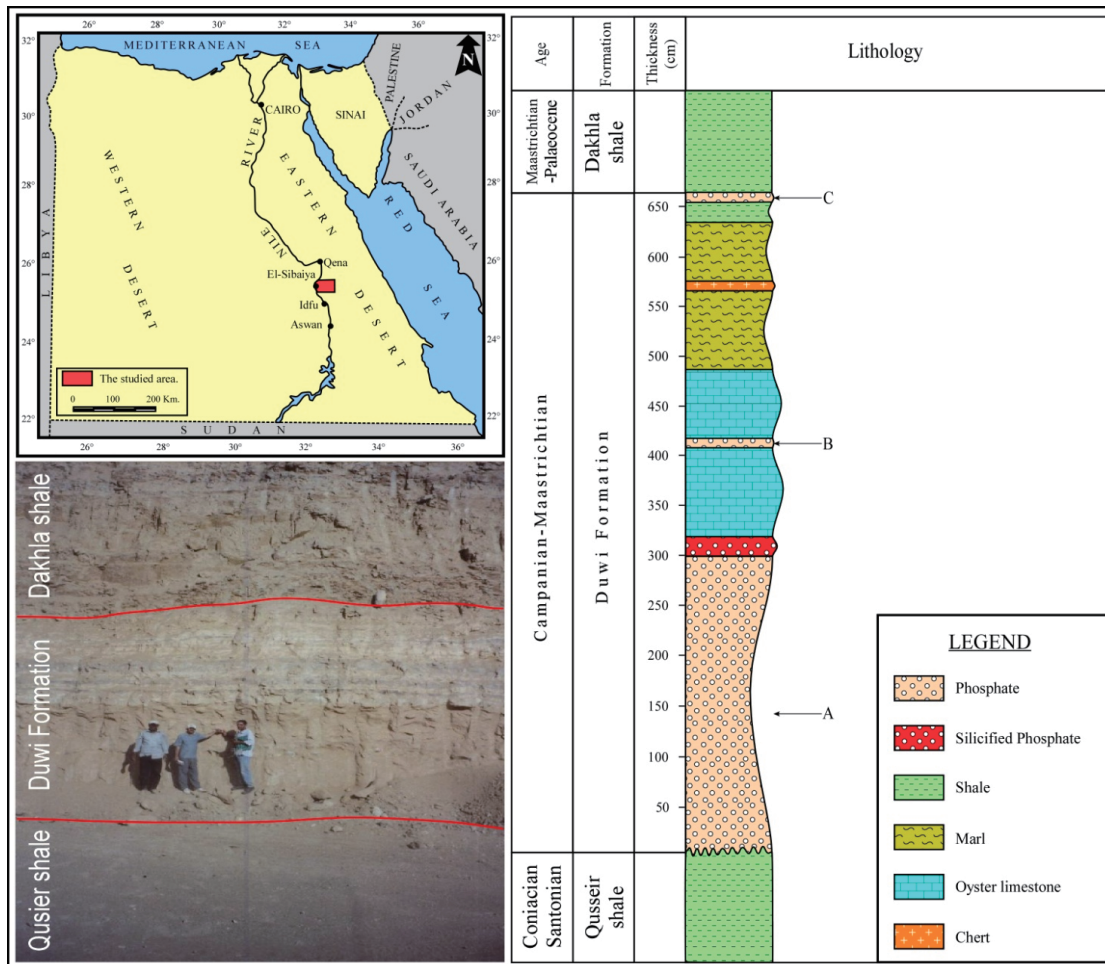**3.2. Mineralogical, chemical and radioactivity charac-**

**Figure 1.** Photograph, Lithostratigraphic composite succession and location of Duwi Formation exposed in El-Sibaiya East area.
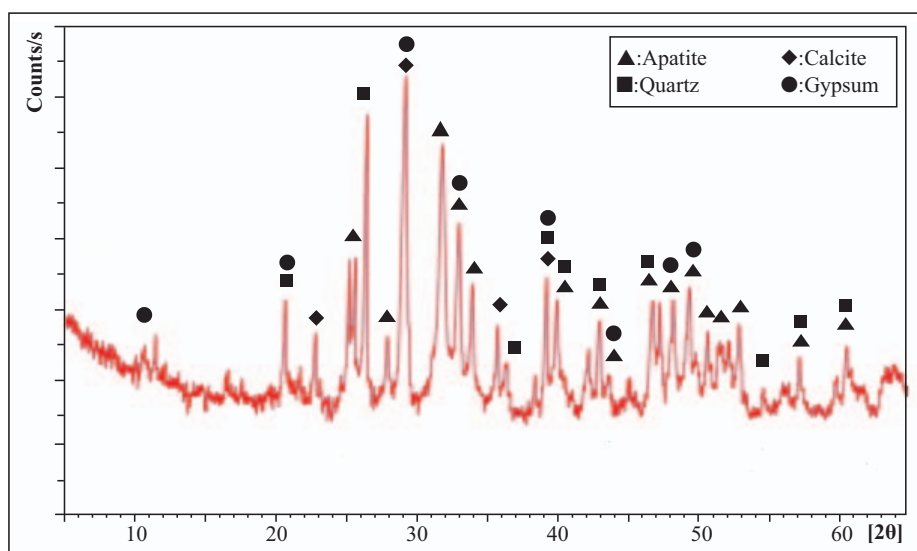


**Figure 2.** X-ray diffraction pattern of El-Sibaiya phosphorite.

**terization.** Before the alkaline leaching process, it was necessary to define the important mineralogical components that encountered the uranium as well as the rock chemical composition to verify the validity of the alkaline leaching to these components. Also, it was an essential issue to determine the radio-element content in the used ore.

　　***3.2.1. The mineralogical composition of El-Sibaiya phosphorite.*** The output of the X-ray diffraction analysis (2.79-2.80 Å, 2.69-2.70Å, and 2.62-2.63 Å) pointed to the presence of francolite (as the major phosphate mineral), calcite, gypsum, and quartz (Fig. 2). Most of the uranium content in the

phosphorite is almost encountered in the francolite because of the open nature of its crystal lattice; the francolite (carbonate fluorapatite) usually exhibits varied chemical composition [30].

　　Moreover, the IR analysis provides several remarks that supported XRD results. The IR spectrum (Fig. 3) indicated that the peak at 1042.7 cm$^{-1}$ reflects the distortion of $CO_3^{2-}$ which resulted from loses an electron due to the effect of uranium and thorium radiation in the used sample. The band of 3426.1 cm$^{-1}$ refers to the substitution of a considerable amount of –OH group for –F in francolite mineral. On the other hand,
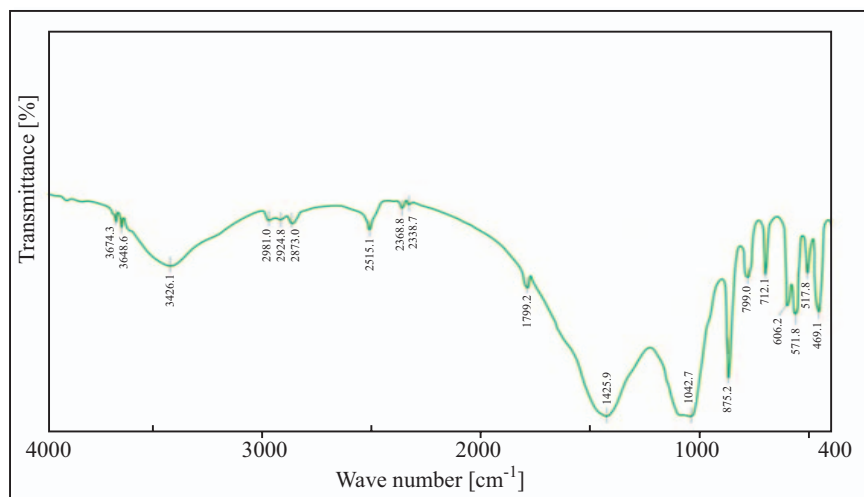
**Figure 3.** IR spectrum of El-Sibaiya phosphorite.

the broadband at 3426.1 cm$^{-1}$ resulted from the molecular water adsorbed by francolite while broad bands at 1425.9 and 712.1 cm$^{-1}$ refer to the calcite mineral appearance [31]. The moderate sharp adsorption bands 517.8, 606.2, 712.1 and 799 cm$^{-1}$ reflect the presence of quartz mineral.

*3.2.2. The chemical analysis of El-Sibaiya phosphorite.* The achievable data from the chemical analysis (Table 1) indicated that there are two essential groups of major elements; the first locate predominantly within the apatite lattice (CaO, P$_2$O$_5$, F and CO$_2$) while the second usually locates outside the phosphate grain, either of detrital origin (SiO$_2$, Al$_2$O$_3$, K$_2$O and TiO$_2$) or by weathering (Fe$_2$O$_3$ and MgO). Trace elements within the apatite lattice generally associated with detrital minerals and organic matter. Generally, the high concentration of alkali metals (Ca and Mg), as well as the presence of high content of the carbonate hydro apatite, encourages the alkaline leaching technique rather than the acidic leaching.

*3.2.3. The radioactivity of El-Sibaiya phosphorite.* The radiometric measured eU, eTh and Ra are listed in Table 2. The recorded uranium concentration either radiometrically (eU, 100.2 ppm) or chemically (145.1 ppm) intimately matches with the values assigned for the worldwide phosphorite. An indicative remark regarding the addition of recent uranium is conducted from the ratio of the chemically measured uranium/ radiometrically measured uranium [32]. The D-factor (U/eU), is equal to the ratio of the chemically determined uranium/ radiometrically measured uranium, indicates the addition or removal of uranium. The value of D-factor of El-Sibaiya East Phosphorite sample is more than unity (1.45), it is clear that chemical uranium is higher than the radiometric uranium in the sample, which reflects disequilibrium due to the addition of uranium. Such recent uranium is more reasonable to be in the hexavalent form (U$^{6+}$) and adsorbed on the phosphorite grains surface rather than its admission into the crystal lattice of the rock-forming minerals [9]. Usually, this kind of the adsorbed uranium is easily leached either by alkaline or acidic solutions. However, the value of the above-mentioned ratio does not indicate a highly significant addition process. The values of the total loss of ignition (L.O.I) at different temperature indicates that the studied sample has high carbonate content.

**3.3. The alkaline leaching by Na$_2$CO$_3$.** Generally the alkaline process relies on formation of highly soluble uranium (VI) tri-carbonate [UO$_2$(CO$_3$)$_3$]$^{4-}$ or uranium (VI) di-carbonate [UO$_2$(CO$_3$)$_2$]$^{2-}$ species as elucidated in the Pourbaix diagram, which visualize the stability of uranium species in the alkaline solution depending on the solution Eh and pH [33, 34]. The

**TABLE 1: Major and trace elements content in El-Sibaiya phosphorite**

| Major elements | | Trace elements | |
|---|---|---|---|
| Element oxide % | % | Element | ppm |
| P$_2$O$_5$ | 24.62 | U | 145.1 |
| CaO | 39.64 | Σ REEs | 244.4 |
| SiO$_2$ | 15.11 | Th | 4.1 |
| Fe$_2$O$_3$ | 2.31 | Sr | 1742 |
| MgO | 3.61 | Ba | 620 |
| Na$_2$O | 1.07 | Zn | 139 |
| Al$_2$O$_3$ | 1.12 | Cr | 135 |
| TiO$_2$ | 0.15 | Mn | 132 |
| K$_2$O | 0.13 | V | 60 |
| F | 2.21 | Y | 51 |
| 110 °C | 0.48 | Rb | 25 |
| 550 °C | 2.45 | Zr | 15 |
| 1050 °C | 5.81 | Cu | 15 |
| Total loss of ignition | 8.74 | Ni | 10 |

**TABLE 2: Equivalent uranium contents of El-Sibaiya phosphorite sample**

| Radioactive metal | Content |
|---|---|
| eU (ppm) | 100.2 |
| eTh (ppm) | 4.1 |
| Ra (ppm) | 129.1 |
| eTh/eU | 0.1 |
| eU/eTh | 25.0 |

different factors affecting the leaching of uranium from El-Sibaiya East Phosphorite using alkaline solutions were investigated to conure the effects these several controlling factors in the leaching process. The results (Fig. 4) pointed to the limited capability of the Na$_2$CO$_3$ solution in leaching the uranium content from the phosphate sample.

The uranium leaching efficiency increased from 4.1 to 13.2% by increasing the solution/ore ratio from 5/1 to 12.5/1. Then decrease with the higher ratio. In the same context, the leaching experiments were performed using 1M Na$_2$CO$_3$ instead of 0.5 M Na$_2$CO$_3$ as a leach solution under the same leaching conditions. The conducted results showed that no noticeable difference results obtained, so the optimum Na$_2$CO$_3$
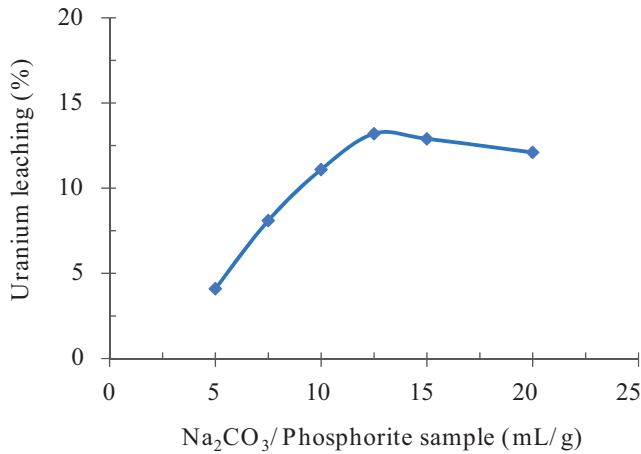
**Figure 4.** Effect of $Na_2CO_3$ solution/sample ratio upon uranium leaching from El-Sibaiya phosphorite.
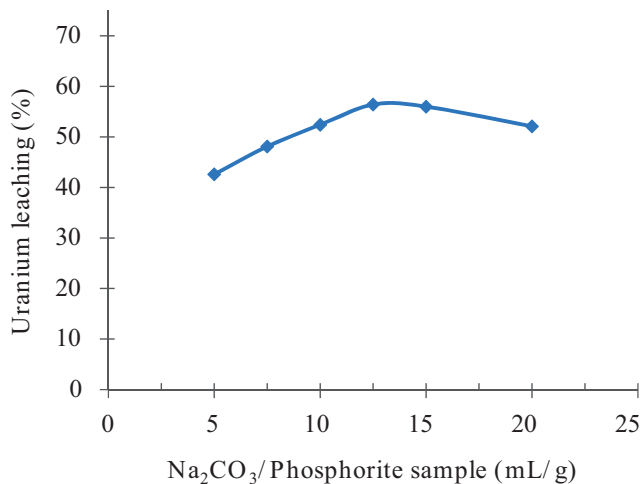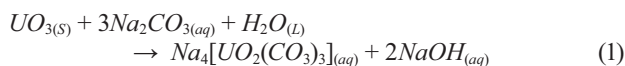


**Figure 5.** Effect of $Na_2CO_3$ solution/sample ratio in presence of $Na_2O_2$ as oxidant on uranium leaching from phosphate rock.

concentration used for uranium leaching was 0.5 M. Generally, the uranium leaching by should behave according to the following equation:

$$UO_{3(S)} + 3Na_2CO_{3(aq)} + H_2O_{(L)} \rightarrow Na_4[UO_2(CO_3)_3]_{(aq)} + 2NaOH_{(aq)} \qquad (1)$$

The low uranium leaching efficiency using $Na_2CO_3$ solution could be described by one or more reasons. The first reason may back to the dominant of $U^{4+}$ in the phosphate sample while the above equation reveals that the $Na_2CO_3$ reacts with $U^{6+}$ species only. The second plausible reason might due to the precipitation of leached uranium as sodium diuranate due to the chemical reaction between the generated sodium hydroxide and the formed uranium carbonate species according to the following equation:

$$2Na_4UO_2(CO_3)_{3(aq)} + 6NaOH_{(aq)} \rightarrow Na_2U_2O_{7(ppt\downarrow)} + 6Na_2CO_{3(aq)} + 3H_2O_{(aq)} \qquad (2)$$
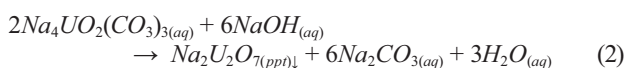
***3.3.1. The alkaline leaching by $Na_2CO_3$ in presence of an oxidant.*** To overcome the effect of $U^{4+}$ content on the leaching process, the previous experiments were carried out but in presence of sodium peroxide ($Na_2O_2$) as an oxidant (2.5% $Na_2O_2$/ ore). Sodium peroxide as oxidant chosen due to two reasons; the first is its high oxidation potential while the second reason is avoiding introducing other metal species than $Na^+$ into the leach liquor.

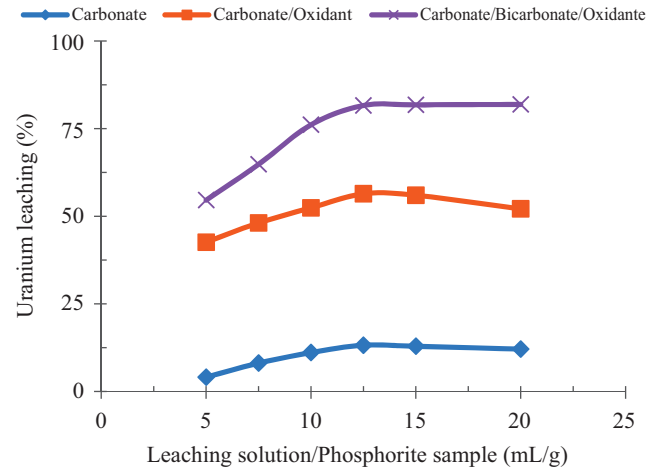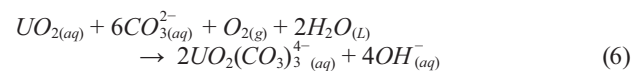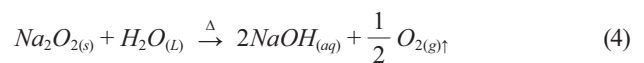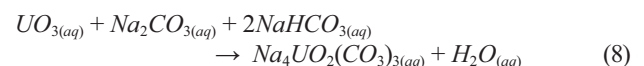The obtained results (Fig. 5) indicated that the uranium
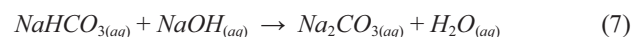


**Figure 6.** Effect of $Na_2CO_3$/phosphate rock on uranium leaching in the presence and absence of $Na_2O_2$ oxidant and $NaHCO_3$ species.

leaching was accelerated from 42.6 to 56.4 % as the solution/ sample increased from 5/1 to 12.5/1. Increasing the alkali solution/sample ratio to 20/1 was accompanied by slight decreasing in the uranium leachability (52.1%). This decreasing is likely ascribed to forming of sodium hydroxide according to the following equations:

$$Na_2O_{2(s)} + 2H_2O_{(L)} \xrightarrow{\Delta} 2NaOH_{(aq)} + H_2O_{2(aq)\uparrow} \qquad (3)$$

$$Na_2O_{2(s)} + H_2O_{(L)} \xrightarrow{\Delta} 2NaOH_{(aq)} + \frac{1}{2}O_{2(g)\uparrow} \qquad (4)$$

$$2UO_{2(aq)} + O_{2(g)} \rightarrow 2UO_{3(aq)} \qquad (5)$$

$$UO_{2(aq)} + 6CO_{3(aq)}^{2-} + O_{2(g)} + 2H_2O_{(L)} \rightarrow 2UO_2(CO_3)_3^{4-}{}_{(aq)} + 4OH^-_{(aq)} \qquad (6)$$

Accordingly, some of the uranium content not leached by the used solutions besides the formed soluble uranium carbonate species might be precipitated as $Na_2U_2O_7$ as a result of eq 2, so the oxidant percent should be adjusted in addition the generated $OH^-$ species should be removed. The role of $Na_2O_2$ oxidant is oxidized $U^{4+}$ (un-leachable form) to $U^{6+}$ (leachable form) using the liberated oxygen or hydrogen peroxide during the vigorous reaction of $Na_2O_2$ with $H_2O$.

***3.3.2. The alkaline leaching by $Na_2CO_3$ / $NaHCO_3$ solution.*** To avoid the negative uranium leaching effect due to the formed NaOH in the two previous phases, the alkaline leaching was examined by a mixture of $Na_2CO_3$ and $NaHCO_3$ in the presence of $Na_2O_2$ as the oxidant. The results (Fig. 6) pointed to increasing the uranium leaching efficiency from 54.6 to 81.4% as increasing the leaching solution/sample ratio from 5/1 to 12.5/1. Above the leaching solution/sample ratio of 12.5/1, there was no significant increase in the uranium leachability. The leaching-enhancing by the added $NaHCO_3$ can be explained by Eq 7, which also shows the reaction of $NaHCO_3$ with the formed NaOH in the leaching medium, hence, prevent the re-precipitation of some soluble uranium carbonate species as sodium diuranate.

$$NaHCO_{3(aq)} + NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(aq)} \qquad (7)$$

$$UO_{3(aq)} + Na_2CO_{3(aq)} + 2NaHCO_{3(aq)} \rightarrow Na_4UO_2(CO_3)_{3(aq)} + H_2O_{(aq)} \qquad (8)$$

***3.3.3. Effect of leaching temperature.*** The achievable data (Fig. 7) revealed a continuous increase in the uranium leachability with the temperature raising and the maximum leaching efficiency was conducted at a temperature of 80 °C. The
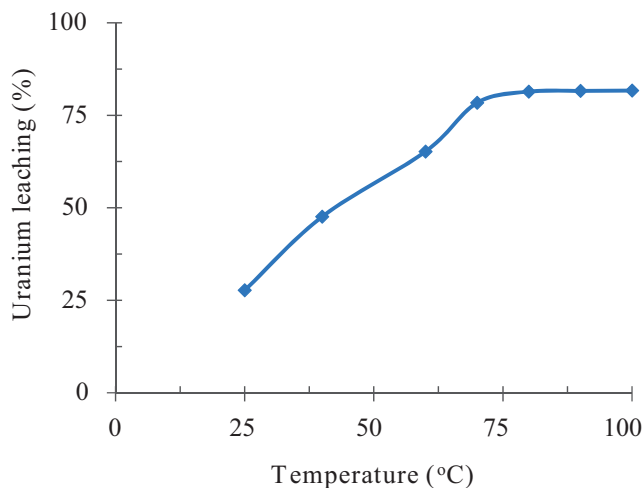
**Figure 7.** Effect of temperature on uranium leaching from phosphate rock using $Na_2CO_3$ and $NaHCO_3$ in presence of $Na_2O_2$ as oxidant.
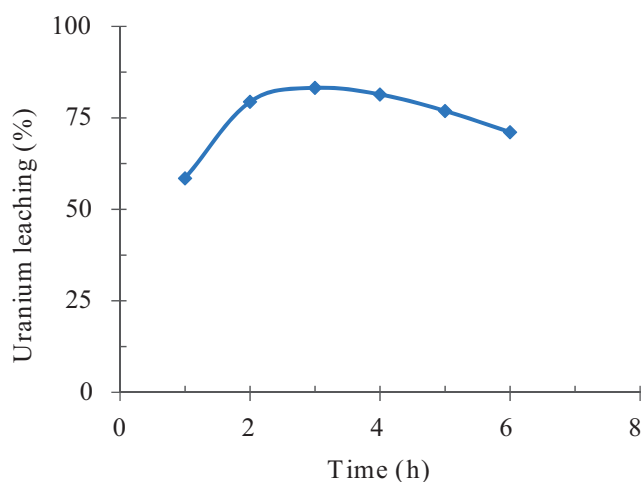


**Figure 9.** Effect of ore fineness on uranium leaching from phosphate rock using $Na_2CO_3$ and $NaHCO_3$ in presence of a $Na_2O_2$ oxidant.



**Figure 8.** Effect of leaching time on uranium leaching from phosphate rock using $Na_2CO_3$ and $NaHCO_3$ in presence of a $Na_2O_2$ oxidant.



**Figure 10.** X-ray diffractogram of the precipitated sodium diuranate ($Na_2U_2O_7$).

uranium leaching increased from 27.7 to 81.3% as the leaching temperature increased from 25 to 80 °C. More temperature elevation (than 80 °C) was not accompanied by any significant increase in the uranium leachability. Improving the uranium leachability with temperature increasing might due to increasing of ions mobility under the effect of given energy. Also, this indicates that the alkaline leaching is an endothermic process.

***3.3.4. Effect of leaching time.*** To evaluate the effect of the leaching time on the uranium leaching from phosphate rock, the leaching experiments were carried out on time ranged from 1 to 6 h at a temperature of 80 °C. The results (Fig. 8) illustrated that as the reaction time increased the uranium leaching increased and the optimum leaching time was found to be 3h (83.2%).

***3.3.5. Effect of ore fineness.*** Generally; the more ore fineness is the faster the digestion attack [35]. The obtained results (Fig. 9) displayed increasing of the uranium leaching efficiency with decreasing the ore grain size, while the maximum uranium leaching efficiency 83.2% was recorded at ore grain sizes of 44 μm and no significant increasing of the uranium leaching with the finer grain sizes. Such behavior is likely interpreted by increasing the surface area in the fine size that leads to increasing of the available reaction-surface between the alkaline agents and phosphate ore hence, facilitates the leaching process. However, another reason should be
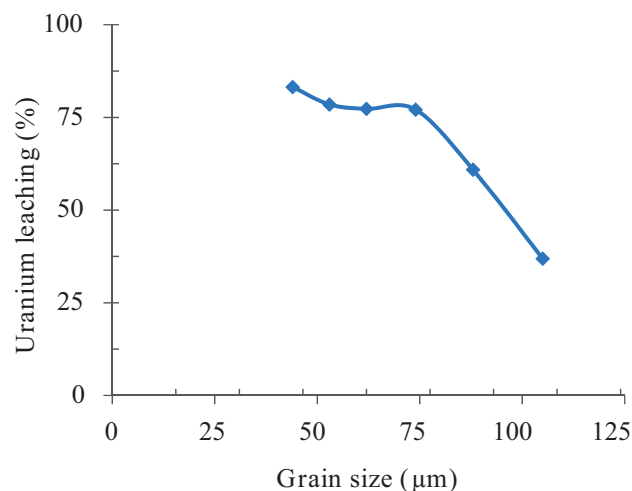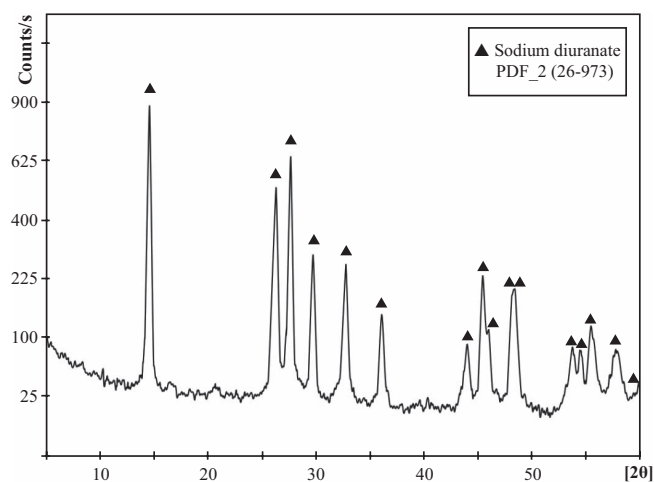
considered where the uranium usually tends to concentrate in the fine-sized grain rather than the coarse ores.

**3.4. Uranium precipitation.** Uranium recovering from the aqueous leach liquors depends on nature and metals content of the liquor solution. In the acidic solutions, solvent extraction or ion exchange techniques are generally applied for metal recovery rather than the precipitation technique due to the various dissolved metal ions in the solution. On the contrary, due to the high selectivity of the alkaline process for uranium leaching, direct precipitation is properly used. In this study, the leach liquor analysis showed that iron, aluminum, titanium species, etc., are nearly insoluble using the use of carbonate solution as found by Lunt et al., [36]. In the obtained leach liquor very low concentrations of phosphates, aluminates as carbonates species were investigated.

In this work, uranium precipitation from the carbonate leach liquor (pH 11.2) was applied using a 25% sodium hydroxide solution at 50 °C for 6h reaction time at pH 11.5-12. The uranium precipitation from El-Sibaiya phosphorite alkali treated solution is presented by eq 9. After concentrating the obtained solution by evaporation, the suspended yellow solution (*fine particles*) was kept for 24h and then separated by centrifugation then gently washed for several times and dried at 100 °C. The obtained sodium diuranate ($Na_2U_2O_7$) product was defined by XRD technique (Fig. 10).

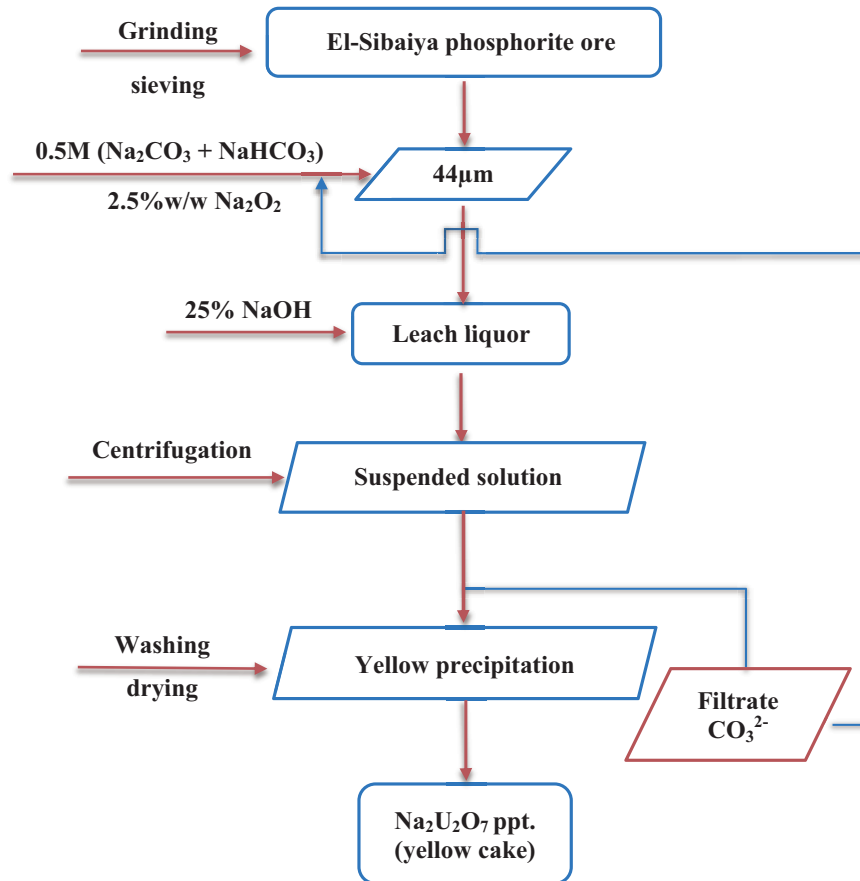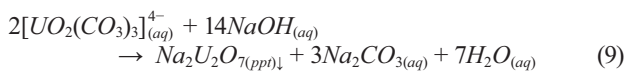**Figure 11.**  The overall uranium leaching and precipitation flow-sheet

$$2[UO_2(CO_3)_3]_{(aq)}^{4-} + 14NaOH_{(aq)}$$
$$\rightarrow Na_2U_2O_{7(ppt\downarrow)} + 3Na_2CO_{3(aq)} + 7H_2O_{(aq)} \qquad (9)$$

The overall treatments that applied on El-Sibaiya phosphorite to leach and precipitate its uranium content were summarized in a flow-sheet (Fig. 11).

## 4. Conclusion

El-Sibaiya east phosphorite representative sample was subjected to alkaline leaching for uranium leaching. Many leaching factors include, leaching solutions concentrations, temperature and reaction time and ore fineness were studied and optimized. Uranium leaching efficiency of 83.2% was obtained. The obtained leach liquor was treated with 25% NaOH to precipitate leached uranium species as $Na_2U_2O_7$ successfully. Referring to this work and the illustrated data, the following points could be concluded:

1. Using the alkaline leaching technique to leach the uranium from its bearing ores should be chosen based on the oxidation state of the present uranium.
2. The successful alkaline leaching should be carried out in presence of an oxidant to guarantee the presence of all uranium ions in the hexavalent state form.
3. A mixture of sodium carbonate and sodium bicarbonate has to be used with the presence of sodium peroxide as an oxidant to conduct the highest U-leaching ratio from El-Sibaiya east phosphorite
4. Under the proper leaching conditions, the alkaline leaching of uranium is more favorable than the acidic leaching for several reasons particularly when the recovered uranium is

needed in highly purified form.

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