Selective Leaching for Uranium and Gold from their Bearing Sedimentary Lower Carbonaceous Sandstone Rocks, Southwestern Sinai, Egypt

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Abstract
Uranium as a nuclear element with strategic importance and gold as one of the important economic precious metals made their selective leaching from the sedimentary lower carbonaceous sandstone rocks, Southwestern Sinai, Egypt with economic concentrations (5ppm gold and 160 ppm uranium), an important issue for facilitating either their accurate determination or highest percentage recovery. A sequential leaching of uranium followed by gold was proposed in this work after studying individually their optimized leaching conditions. From the latter; a lixiviant mixture of sample to sodium carbonate ratio 1:1, sample to sodium bicarbonate ratio 1:1 together with sodium thiosulphate, as oxidant, 0.5g was used for the selective leaching of uranium. On the other hand, a leaching reagent mixture of 5% (w/v) from each of potassium cyanide, sodium thiosulphate and 10 ml from 30% hydrogen peroxide was used for the selective leaching of gold where several factors were optimized; concentration of individual component in each lixiviant, agitation time, solid to liquid ratio, temperature and pH. A percentage leaching of 97% and 96% for uranium and gold respectively were reached. Uranium was selectively separated using Amberlite IRA 402 Cl resin ion exchange resin with 99.5% percentage recovery. The recovery of gold needs a large bulk weight from the sample due to its relatively low concentration.

Introduction
The Uranium is recognized to be a critical commodity in the context of satisfying the global energy-demands for the twenty-first century and beyond. Low grade uranium bearing limestone rock, including mining waste, represents now a significant future uranium-resource, provided an economically-viable method of extraction is developed. It is one of the basic elements of the peaceful nuclear power industry, where processing of uranium ores has the important role that would play in solving many energy problems, electrical utilities, and the need for a continuing high level of research activity in this field.

Leaching is a process by which a soluble substance is removed / extracted from gangue (undesirable matter) by the action of a percolating liquid, called lixiviant [1]. Uranium ores are treated by either acid or alkaline reagents with sulphuric acid or sodium carbonate – sodium bicarbonate systems used almost exclusively for commercial uranium recovery. As acidic leaching is a rapid process so the majority of uranium mills employ it but the fundamental advantage of the alkaline leaching is that most of the gangue is not attacked and the carbonate solutions can be regenerated [2]. In carbonate leaching, uranyl tricarbonate \(\text{UO}_2\left(\text{CO}_3\right)_3^{4-}\) ion is formed which is stable and soluble although, the number of \(\text{CO}_3^{2-}\) ions attached to the \(\text{UO}_2^{2+}\) ion is a function of pH and ORP (oxidation-reduction potential) of the solution [3].

Acid leaching is preferred for low-lime ores due to faster leaching kinetics. Sulfuric acid is used almost exclusively in conventional uranium milling because of its low cost and compatibility with ion exchange recovery. Alkaline leaching is used when the ore contains high carbonate content. The advantages of the alkaline leaching process include higher selectivity and a lower corrosively than acid leaching. [2]

A variety of carbonate compounds can be used as complexing agents in the leaching/extraction of uranium from the ore body. The selection of a particular complexing agent depends upon its leaching efficiency, suitability for a particular ore type, easy availability as well as the economical load incurred in its use. However, in case of \((\text{NH}_4)_2\text{CO}_3\), precipitation of solid material started which could be
The Witwatersrand reefs bears gold, uranium, and pyrite in average concentrations of 0.001%, 0.02%, and 1.7% respectively. Reverse leaching followed by a cleaning flotation step for the recovery of the pyrite, was an efficient process. [8]

Several lixiviant systems were proposed for gold dissolution as alkaline lixiviant; cyanide, ammonia-cyanide, ammonia, sulphide, nitriles, neutral lixiviant; thiosulphate, halogens, sulphurous acid, and bacteria where Au(I) or Au(III) complexes were formed and others such as halides, malononitrite, acetonitrile and polysulfides. [9]

Cyanides, still one of the used reagents for recovering gold from its ores, where in refractory ores containing complex minerals, the gold dissolution is not a simple process and its rate becomes depressed after a certain time of cyanidation. Mineralogical identification of the ore and diagnostic leaching are alternative methods for establishing and designing a metallurgical flow sheet for refractory ores [10].

Acid leaching systems for gold may contain thiourea, thiocyanate, chloride and aquaregia and the oxidants include chlorine, ferric chloride, hydrogen peroxide, and nitric acid which produce Au(III) anionic complexes, AuCl. For treating simple auriferous oxide-silicate-carbonate ores, and many other materials, cyanide remains the preferred lixiviant.

Combined leaching techniques were applied to high grade ores, which was processed by grinding, agitated cyanide leaching whereas low grades was heap or dump leached.

Uranium bearing gold ores was treated by cyanidation for gold extraction followed by sulphuric acid leaching of uranium from the cyanidation residue. Cyanide leaching can follow sulphuric acid leaching of uranium in a so called reverse acid leaching process. This can yield much higher gold recoveries by the virtue of the cleaning effect of sulphuric acid on free gold and dissolution of carbonates in the ore, which may contain a portion of gold values. [11,12]

The feasibility of leaching gold and uranium simultaneously from ores were investigated. Samples were leached in aerated solutions containing copper and cyanide made up in carbonate and bicarbonate medium at temperature range from 25°C to 90°C. Results indicated that a temperature of about 50°C to 60°C would obtain uranium extraction between 85% and 90%. [13]

The dissolution rate of uranium dioxide is a temperature dependent while gold is temperature independent in the range 60–80°C. It was found that 85% of the uranium dioxide and 95% of the gold could be dissolved in a simultaneous leaching process. [14]

The extraction of uranium from Randfontein ore has been studied at a temperature of 110°C using sodium carbonate and sodium bicarbonate. The leach was followed by cyanidation of the ore to extract the gold. The results show that 90% of the uranium and 98% of the gold can be extracted by this technique but the
consumption of sodium carbonate, at 65 kg ton⁻¹, is too high for the process to be economically competitive. The use of ammonium carbonate was also investigated and gave similar extraction values with apparently lower reagent consumption. [15]

In the present work, two separate leaching processes using different leaching parameters were studied on two portions of the sample for optimizing the individual leaching conditions for both uranium and gold. On the light of the obtained optimum leaching studied factors, a sequential leaching of uranium using a sodium carbonate / bicarbonate mixture together with sodium thiosulphate followed by gold from the remaining residue in a subsequent separate step using an alkaline medium by the cyanidation process (potassium cyanide, sodium thiosulphate and hydrogen peroxide as oxidizing agent) was performed. The percentage leaching efficiencies for uranium and gold were 99.5% and 98% respectively.

**Materials and Methods**

A technological sedimentary lower carbonaceous sandstone rock sample collected from southwestern Sinai, Egypt was the studied sample. It was crushed, ground to 200 mesh size and quartered for complete analysis for major oxides, trace elements, uranium and gold analysis. Scanning Electron Microscope (SEM) revealed the presence of micro size grains of gold and the radioactive mineral, uranothorite [16]. The total REE, U, Th, As, Cu were analyzed using ICP-MS in Achme Laboratories, Canada, while gold was analyzed and monitored through the whole experiments using a studied developed gold determination procedure using AAS [17], and gold concentration in the rock sample was confirmed using the well known fire assay method in the Egyptian Geological Survey Laboratories and confirmed.

Atomic absorption spectrometer model Unicam 969 supplied with acetylene and nitrous oxide burner heads was used for analysis of gold after extraction with MIBK and stripping from the leach liquor.

The fire assay analysis of gold assured the presence of economic concentrations of 5 ppm gold and 160 ppm uranium analyzed volumetrically by the known Davies and Gray [18]. The chemical analyses of major and trace concentrations in the studied sample were shown in Table (1).

Two representative portions of the studied sample were considered for individual optimization for leaching tests, where different leaching factors were studied namely; effect of solid to liquid S/L ratio, temperature, agitation time, concentrations of individual leaching reagent and pH. On the light of the optimum obtained results a sequential leaching, on a third portion of the sample, for uranium followed by subsequent leaching for gold was performed.

**Results**

**Leaching process of Uranium**

The uranium in rocks and ores is usually present as UO₂ or U₂O₃ and requires oxidation to be converted to UO₃ before its dissolution as UO₃(CO₃)²⁻ ion. Uranium was the leached using alkaline mixture of carbonate-bicarbonate leach solution together with sodium thiosulphate which has the possibility for leaching the hexavalent uranium from carbonate rocks.

In presence of carbonate leaching:

\[ U_3O_8 + \frac{3}{2} O_2 + 9CO_3^{2-} + 3H_2O \rightarrow 3UO_3(CO_3)^{2-} + 6OH^- \]

In presence of bicarbonate leaching:

\[ U_3O_8 + \frac{3}{2} O_2 + 3CO_3^{2-} + 6HCO_3^- \rightarrow 3UO_3(CO_3)^{2-} + 3H_2O \]

For UO₂ the equivalent reaction is:

\[ UO_2 + \frac{1}{2} O_2 + CO_3^{2-} + 2HCO_3^- \rightarrow UO_2(CO_3)^{2-} + H_2O \]

The presence of bicarbonate in the solution is essential to prevent the formation of excess hydroxyl ion, which would lead to the precipitation of sodium uranate. [19] On the contrary insufficient bicarbonate concentration would lead to slow down the reaction rapidly. Several factors were studied for the maximum and selective leaching of uranium namely; concentration of carbonate, concentration of bicarbonate, sodium thiosulphate concentration, pH, temperature, agitation time and solid to liquid ratio (S/L).

**Effect of sample to sodium carbonate ratio**

The effect of sample to sodium carbonate ratio on the efficiency of uranium leaching was studied from 1:0.25 to 1:2 ratio, while the other conditions were kept constant; sample to NaHCO₃ ratio 1:1, e to Na₂S₂O₃ 0.5g, pH 9.5, 2 hours agitation time at 50°C. From the results illustrated in Figure (1), it can be concluded that the percentage leaching efficiency of

| Heading     | Concentration (ppm) |
|-------------|---------------------|
| Al₂O₃       | 5.1                 |
| Fe₂O₃       | 10.0                |
| K₂O         | 160                 |
| MgO         | 513                 |
| Na₂O        | 128                 |
| SiO₂        | 125                 |
| TiO₂        | 0.42                |
| Th          | 0.27                |
| ThO₂        | 0.04                |
| FeO         | 0.92                |
| LOI         | 6.80                |
| Au          | 5.0                 |
| Ag          | 10.0                |
| Cu          | 160                 |
| Cu          | 128                 |
| Cu          | 125                 |

Table (1): Analysis of major, trace, uranium and gold concentrations in the studied sample
uranium increases with the increase of sample to sodium carbonate ratio then becomes constant from a ratio 1:1, which was considered the optimum ratio.

**Figure (1):** Effect of sample to sodium carbonate concentration on leaching uranium leaching

**Effect of sample to sodium bicarbonate ratio**

The effect of sample to sodium bicarbonate ratio on the efficiency of uranium leaching was studied between 1:0.25 – 1:2 ratio, while the other conditions were fixed; sample to Na₂CO₃ ratio 1:1, Na₂S₂O₃ 0.5g, pH 9.5, 2 hours agitation time at 50°C. The results illustrated in Figure (2) concluded that the highest percentage leaching efficiency of uranium reached was at sample to sodium bicarbonate ratio 1:1.

**Figure (2):** Effect of sample to sodium bicarbonate ratio on uranium leaching

**Effect of sodium thiosulphate**

The effect of sodium thiosulphate, as an oxidizing agent, on the maximum leaching efficiency of uranium was studied from 1g till 2g while the other factors were kept constant; sample to Na₂CO₃ ratio 1:1, sample to NaHCO₃ ratio 1:1, pH 9.5, 2 hours agitation time at 50°C. The obtained data presented in Figure (3) clarifies that adding 0.5g of sodium thiosulphate was optimum for maximum leaching efficiency of uranium.

**Figure (3):** Effect of sodium thiosulphate on leaching uranium leaching

**Effect of pH**

The effect of different pH values of the leaching reagent for maximum leaching efficiency of uranium, was studied from 5-11 while the other optimum studied factors were kept constant; sample to Na₂CO₃ ratio 1:1, sample to NaHCO₃ ratio 1:1, Na₂S₂O₃ 0.5g, 2 hours agitation time at 50°C. From the results obtained and illustrated in Figure (4), it was obviously clear that the percentage leaching efficiency increases with the increase in pH till a value of 9.5 after which a plateau was observed where the latter pH was effective in the leaching percentage of uranium as shown.

**Figure (4):** Effect of pH on leaching percentage of uranium leaching

**Effect of agitation time**

The effect of agitation time on percentage leaching efficiency of uranium was studied from 30 minutes till three hours, while the other studied conditions were fixed; sample to Na₂CO₃ ratio 1:1, sample to NaHCO₃ ratio 1:1, 0.5g Na₂S₂O₃, pH 9.5 at 50°C. The data shown in Figure (5) illustrated that the percentage leaching of uranium was increased with time from 30 minutes till 120 minutes (97%), after which there was no increase observed; hence two hours was concluded as the optimum agitation time for maximum leaching percentage of uranium.

**Figure (5):** Effect of agitation time on percentage leaching of uranium.
After studying the optimum conditions for maximum leaching efficiency of uranium from the studied carbonaceous sandstone sample with a percentage leaching efficiency of 98%, hence its recovery as a nuclear strategic element using Amberlite IRA402 Cl [20] was of great importance for further processing, where a percentage recovery of 99.5% for uranium was reached.

Leaching process for gold

After the optimized studied parameters for maximum uranium leaching with percentage leaching efficiency 97% and its separation, leaching experiments on gold were carried out using a second 25g of the sample with 5 ppm gold concentration and a lixiviant mixture of potassium cyanide, sodium thiosulphate and hydrogen peroxide. Experimental leaching parameters studied for gold were 1-5% (w/v) for each of sodium thiosulphate and potassium cyanide (KCN), 1-15 % H₂O₂ (30% v/v) at S/L ratio from 1:3 to 1:6 with leaching time ranging from 0.5 hour to 3 hours, pH from 8-12 at a temperature from 25°C to 60°C.

Effect of potassium cyanide concentration

The effect of potassium cyanide concentration was studied from 0-5% (w/v) while the other leaching conditions were fixed; 5% Na₂S₂O₃, 10 ml from 30% H₂O₂, two hours stirring time, pH 9.5, 25oC and S/L ratio 1:10. From Figure (7) it can be obviously illustrated that 5% KCN was an efficient concentration with 95% percentage leaching efficiency where gold was leached in the form of soluble aurocyanide complex ion, Au(CN)₂- and was presented by the following equation:

\[ 2Au^{3+} + 4CN^{-} + \frac{1}{2} O_2 + H_2O \rightarrow 2Au(CN)_2^{2-} + 2OH^- \]

Effect of sodium thiosulphate concentration

Several leaching experiments were performed to attain the optimum concentration of sodium thiosulphate (from 0 to 5% w/v) for maximum leaching of gold while the other conditions were fixed; 5% KCN, 10 ml from 30% H₂O₂, pH 9.5, 2 hours stirring time, 25oC and 1:10 S/L ratio.

Figure (8) indicated that the highest percentage leaching efficiency for gold (96%) was attained at 5%, (w/v) Na₂S₂O₃.

Effect of hydrogen peroxide concentration

The percentage leaching efficiency of gold without and with different hydrogen peroxide concentrations (30%) affecting gold leaching was studied while the other factors namely; 5% KCN, 5% Na₂S₂O₃, pH 9.5, 2 hours stirring time, 25oC and 1:10 S/L ratio were kept fixed. Figure (9) illustrated that the optimum hydrogen peroxide volume from 30% hydrogen peroxide was 10 ml giving a maximum percentage leaching efficiency value of 95.9% after which a plateau was formed.

Effect of temperature

The effect of temperature, in the range from 25oC till 60oC, on the leaching efficiency of gold was studied, and the other leaching factors were constant; 5% KCN, 5% Na₂S₂O₃, pH 9.5, 2 hours stirring time, 10 ml from 30% H₂O₂, and 1:10 S/L ratio. From the gathered data illustrated in Figure (10) it was obvious that the increase in temperature decreases the leaching efficiency of gold from 96%, at room temperature 25oC, till it reaches 89.2% at 60oC. This may be attributed to the dissociation of hydrogen peroxide, at about 50oC and reaches its maximum at 60oC, to water and oxygen, hence becomes inefficient as an oxidizing agent.
Effect of agitation time

The effect of agitation time on leaching of gold was studied from half to 3 hours, where the other conditions were kept constant; 5% KCN, 5% Na2S2O3, pH 9.5, 10ml from 30% H2O2, 25oC and 1:10 S/L ratio. From the obtained data illustrated in Figure (11), it was obviously clear that the leaching efficiency of gold increases proportionally with time till two hours after which it gives a constant value, thus two hours was selected as the optimum agitation time.

![Figure (11): Effect of agitation time on gold leaching](image1)

Effect of pH

The effect of pH of the leaching solution on gold leaching was studied from pH 8-12 with the other studied factors kept constant; 5% KCN, 5% Na2S2O3, 2 hours stirring time, 25oC, 10ml from 30% H2O2 and 1:10 S/L ratio, the results obtained were illustrated in Figure (12) which indicated that the leaching efficiency of gold increased with the increase of pH till it reached a maximum leaching efficiency of 95.9% at pH 9.5 after which no increase was observed.

![Figure (12): Effect of pH of leaching reagent on gold leaching](image2)

Effect of solid to liquid ratio

The effect of solid to liquid ratio on gold leaching was studied from 1:3 to 1:10, using the previously optimized factors; 5% KCN, 5% Na2S2O3, 2 hours stirring time, 25oC, 10ml from 30% H2O2 and pH 9.5. The obtained gold leaching results illustrated in Figure (13) indicated that as the S/L ratio increases the percentage gold leaching efficiency increase till it reaches 96% at S/L ratio of 1:10.

![Figure (13): Effect of solid to liquid (S/L) on leaching of gold](image3)

From the above studied parameters for gold leaching from its bearing carbonaceous technological sample, it can be concluded that the optimum conditions for the highest leaching percentage for gold (96%) were 1:10 S/L ratio, 2 hours agitation time, 25°C, 5% (w/v) potassium thiocyanate, 5% (w/v) sodium thiosulphate, and 10 ml from 30 % H2O2 at pH 9.5. After optimum leaching conditions were performed on the sample, we reached leach liquor with 4.9 ppm Au concentration, (98% leaching efficiency or recovery).

Table (2) summed up the optimum leaching conditions for both uranium and gold from the studied sample. From the obtained data, it was revealed that selective leaching of uranium followed by gold was most effective for maximum percentage leaching efficiency of both elements in two sequential leaching steps, with two separate leach liquors and percentage leaching efficiencies of 97 % and 98 % for uranium and gold respectively. Uranium was recovered using Amberlite-IRA 402 Cl as it is one of the main important targets of our authority.

![Table (2): Optimum parameters for maximum leaching efficiency for uranium and gold](image4)

On the light of the obtained results for selective leaching of uranium and gold, a technological flow sheet was elucidated also.

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