

Uranium Solubilization from Rock Phosphate in Carbonate Leaching Media

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ABSTRACT

The main objective of present studies was to leach uranium from rock phosphate in sodium carbonate and sodium bicarbonate solutions. The rock phosphate sample was sedimentary-type origin and was found to contain an average uranium content of 0.012% U_3O_8 . Uranium was solubilized from the rock sample in both carbonate and bicarbonate leaching systems. U solubilization was observed higher in leaching system containing Na_2CO_3 solution (leaching solution) as compared with $NaHCO_3$ solution. Uranium solubilization was apparently associated with the concentrations of Na_2CO_3 and $NaHCO_3$ in the leaching solutions. A rise in temperature of the leaching solution increased the rate of uranium solubilization from the rock sample.

Key Words: Rock phosphate; Sodium carbonate; Sodium bicarbonate; Uranium solubilization

INTRODUCTION

Natural abundance of uranium in the earth's crust varies from 2-4 ppm U_3O_8 , which is comparable to that of As, Be, Mo and W, but higher than metals such as Ag, Bi, Cd and Hg (Merritt, 1971). Igneous rocks with a high silica content such as granite have slightly higher U concentration approaching to 6 ppm U_3O_8 , whereas rocks with less silica and more Al, Fe and Mg contents may contain less than 1 ppm U_3O_8 (Taylor, 1979). Apart from uranium ore-deposits, uranium is most abundant in high silica igneous rocks and shales, especially black-shales. For example, Colorado Front Range (USA) and other granites are enriched in alkali content and may contain over 100 ppm U_3O_8 (Merritt, 1971).

Rock phosphate is the raw material for manufacturing phosphate fertilizers and it consists of insoluble calcium phosphate [$Ca_3(PO_4)_2$] generally known as apatite. This material is sometimes called as phosphate of lime. In addition to apatite the rock phosphate also contains other accessory minerals like calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$] clay minerals, quartz (SiO_2), and pyrite (FeS_2) etc. Hydrated apatite is known as hydroxy apatite and its fluorinated type is known as fluorapatite [$Ca_5(PO_4)_3F$] (Souza *et al.*, 1997).

The rock phosphate contains 0.005–0.03% U_3O_8 in isomorphous substitution of Ca (Merritt, 1971; Bunus, 1977; Habashi, 1986). Uranium is commonly present in rock phosphate and about 6.34 million tones uranium exists in rock phosphate deposits throughout the world (Cathord, 1975). The exploitation, processing and persistent use of large amounts of phosphate fertilizers lead the environment to be contaminated by various

radioactive elements like U, Th and other trace elements resulting from the radioactive decay process of uranium (Souza *et al.*, 1997). Therefore, the radioactive wastes resulted from uranium and thorium ore-processing pose a potential environmental and public health problems because of their radioactivity and chemical composition. The radionuclides exist in these wastes are those resulting from the ^{238}U , ^{235}U and ^{232}Th decay series (Bhatti & Malik, 1994; Habashi 1994, 1985; Hussein, 1994; Guzman *et al.*, 1995). Uranium can be recovered more economically as a by-product of wet phosphoric acid process than by the conventional hydrometallurgical process of ores (Hurst 1978; Awadalla & Habashi, 1985, 1986).

The current technology of uranium extraction from its ores and minerals involves leaching with sulfuric acid (H_2SO_4) or sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) solutions. The choice of leaching solution depends on the composition and the effects of several technical, economical and environmental factors such as reagent costs, solubility of contaminants, recovery methods and tailings management. Carbonate leaching process has advantages in the treatment of ores containing high contents of carbonate minerals like calcite and dolomite. Since, these minerals are not attacked by carbonate solutions. The carbonate leaching process is highly selective for uranium extraction from ores containing uranium in the oxidized form (U^{6+}).

The main purpose of the present work was to study the leaching behavior of uranium from rock phosphate in sodium carbonate and sodium bicarbonate ($NaHCO_3$) solutions.

MATERIALS AND METHODS

The rock phosphate sample used in this work was obtained from the Institute of Engineering and Fertilizers

Table I. Chemical analysis of rock phosphate sample

| Constituents | Results (%) |
|---------------------------------------|-------------|
| P ₂ O ₅ (total) | 33.60 |
| CaO | 51.72 |
| K ₂ O | 0.12 |
| MgO | 0.47 |
| SiO ₂ | 1.60 |
| MnO | 0.02 |
| Al ₂ O ₃ | 0.70 |
| CO ₂ | 4.70 |
| Fe ₂ O ₃ | 0.16 |
| Na ₂ O | 1.12 |
| F | 3.92 |
| U ₃ O ₈ | 0.012 |
| Organic matter | 0.21 |

Research (IEFR), Faisalabad. A representative rock sample was ground to 59 µm particle size for chemical and mineralogical analysis and shake-flask leaching studies. Commercial grade sodium carbonate and sodium bicarbonate reagents were used to prepare aqueous solutions of various concentrations (0.1M, 0.2M, 0.5M and 1.0 M).

All the leaching experiments were carried out in 500ml Erlenmeyer flasks containing 100 ml of 1.0 M Na₂CO₃ and 1.0 M NaHCO₃ solutions separately. Each flask was supplemented with 10g finely pulverized rock sample. All the flasks were incubated in the orbital shaker at 30 °C and 100 rev/ min. Periodically, leach suspensions were taken and were centrifuged to remove solid suspension. Supernatants were analyzed for monitoring pH and dissolved uranium content. A highly sensitive and precise spectrophotometric method was used to analyze the dissolve uranium content in the carbonate leach liquors (Bhatti *et al.*, 1991). The effect of various concentrations of Na₂CO₃ and NaHCO₃ solutions and temperature on uranium solubilization from rock sample was observed in shake flask leaching studies.

The concentration of uranium in the rock sample was determined by a spectrophotometric method using dibenzoylmethane (DBM) as chromogenic reagent (Nagi *et al.*, 1974).

RESULTS AND DISCUSSION

The rock sample used in this work was of origin of sedimentary-type rock deposits. Physically, the rock sample was light-brown in color, soft and was alkaline in nature. It was insoluble in water but was soluble to some

extent with solutions of acids and carbonates. The rock sample was being used as a feed-stock for the manufacturing of various types of commercial phosphate fertilizers. The chemical analysis of rock phosphate revealed that a uranium content of 0.012% U₃O₈ (120 ppm U₃O₈) in the rock matrix. This data indicated that a significant amount of uranium was present in the rock sample. Uranium was present in hexavalent state (U⁺⁶) as autonite uranium mineral with general formula of [Ca(PO₄)₂(UO₂)₂] in the rock sample (Bhatti, 2000). The rock sample was of high-grade phosphate rock containing 33.6% P₂O₅. A complete chemical analysis of the representative rock sample is reported in Table I.

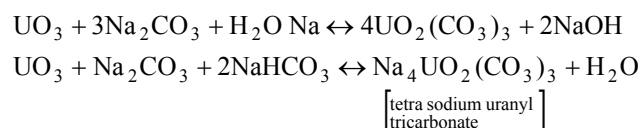
When the rock sample was added into the flasks containing Na₂CO₃ and NaHCO₃ solutions, a chemical reaction was took place in the leaching systems. This chemical reaction was deemed responsible for the slight increase in the pH-values of the leaching solutions (Table II). In NaHCO₃ leaching system, the pH-value of the leach suspension was slightly increased. During such leaching process, U was solubilized from rock phosphate. A maximum uranium solubilization of 75.3%

Table II. Carbonate leaching studies of rock phosphate

| Leaching solution | pH of solution before adding rock sample | pH of leach solution after adding rock sample | U ₃ O ₈ solubilized (%) |
|--|--|---|---|
| Na ₂ CO ₃ solution (1.0 M) | 11.1 | 11.3 | 75.3 |
| NaHCO ₃ solution (1.0 M) | 8.3 | 9.1 | 52.9 |
| Distilled water (Control) | 5.8 | 7.8 | 0.2 |

(Pulp density = 10% pulp density; leaching time = 1hr at 30°C)

U₃O₈ was achieved from rock phosphate when it was treated with Na₂CO₃ solution (Table II). The pH of the carbonate leach liquor was observed a value of pH 11.3. But in case of NaHCO₃ leaching system, a uranium recovery of 52.9% U₃O₈ was obtained under similar leaching conditions. The overall chemical reaction which covers the dissolution of uranium from ores containing uranium minerals in carbonate-bicarbonate leaching system as below:



In carbonate leaching system, uranium is solubilized as tetra sodium uranyl tricarbonat [Na₄UO₂(CO₃)₃], when uranium is present as hexavalent state (UO₃) in the ore matrix (Merritt, 1971). During such leaching system, there is no oxidation-reduction reaction takes place. Bicarbonate {HCO₃²⁻} is added to

the leaching solution to prevent re-precipitation of a part of the dissolved uranium content through chemical reaction with hydroxyl ion (OH^{1-}), which is formed in solution in the absence of bicarbonate as reported in the above chemical reaction. Carbonate leaching process has advantages in the treatment of ores which are high in carbonate minerals like calcite [CaCO_3] and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. These minerals are not attacked by the carbonate leaching solution (s). But a negligible amount of uranium (2.3% U_3O_8) was dissolved in the leaching system containing no carbonate solution (only distilled water). During these leaching studies, some other metal ions might be dissolved from rock sample but they were

solution containing only 1.0 M NaHCO_3 . In both carbonate leaching systems, an appreciable amount of uranium was solubilized from the rock sample within 5-10 minutes of leaching time without shaking. However, with the passage of leaching time, there was a very slight increase in the uranium solubilization in leaching process containing NaHCO_3 solutions; whereas in the Na_2CO_3 leaching system, there was a decrease in the soluble uranium content that might be due to precipitation/immobilization phenomenon. It was reported that at higher alkaline pH (11.0), uranium was precipitated (Merritt, 1971; Zaman *et al.*, 1983). These data suggested that uranium solubilization was pH-dependant.

Table III. Uranium solubilization from rock phosphate at various concentrations of Na_2CO_3 and NaHCO_3 solutions

| Leaching solution | pH of solutions before adding rock sample | pH of leach solutions | | | | U ₃ O ₈ solubilized (ppm) | | | |
|---|---|-----------------------|------|------|------|---|------|------|------|
| | | 10 | 30 | 60 | 120 | 10 | 30 | 60 | 120 |
| Na ₂ CO ₃ solutions | | | | | | | | | |
| 0.1 M | 10.8 | 10.9 | 10.9 | 10.8 | 10.8 | 0.50 | 1.00 | 1.00 | 1.50 |
| 0.2 M | 10.9 | 10.9 | 11.0 | 10.9 | 10.9 | 0.75 | 1.50 | 1.80 | 2.00 |
| 0.5 M | 11.2 | 11.0 | 11.0 | 11.0 | 11.0 | 13.5 | 12.3 | 12.5 | 15.5 |
| 1.0 M | 11.3 | 11.1 | 11.1 | 11.2 | 11.2 | 25.3 | 28.8 | 26.3 | 20.3 |
| NaHCO ₃ solution | | | | | | | | | |
| 0.1 M | 7.7 | 8.6 | 8.5 | 8.6 | 8.8 | 1.50 | 2.00 | 2.25 | 1.25 |
| 0.2 M | 7.9 | 8.0 | 8.4 | 8.5 | 8.7 | | | | |
| 0.5 M | 8.2 | 7.9 | 8.4 | 8.5 | 8.7 | 2.25 | 3.50 | 4.50 | 3.80 |
| 1.0 M | 8.3 | 8.1 | 8.5 | 8.6 | 8.7 | 17.8 | 18.0 | 17.3 | 15.3 |
| Distilled water | 5.8 | 6.7 | 7.0 | 7.3 | 7.3 | 0.25 | 0.25 | 0.50 | 0.50 |

(Pulp density = 10%; Temperature = 30°C; Revolution = 100 rpm)

not analyzed in the leach solutions.

It was observed that uranium solubilization was influenced at various concentrations of carbonate and bicarbonate in the leaching solutions (Table III). It was observed that at higher concentration of 0.5 M and 1.0 M Na_2CO_3 solutions, higher amount of uranium was solubilized from rock phosphate; whereas in bicarbonate leaching system, maximum uranium was solubilized in

Table IV. Effect of temperature on pH of leach suspensions and uranium solubilization in carbonate leaching of rock phosphate

| Temperature (C°) | pH of leach solution | U_3O_8 solubilized (%) |
|--|----------------------|--|
| Na_2CO_3 solution (1.0 M; initial pH 11.1) | | |
| 30 | 11.0 | 15.0 |
| 40 | 10.8 | 20.0 |
| 50 | 10.9 | 19.4 |
| 60 | 11.0 | 22.7 |
| NaHCO_3 solution (1.0 M; initial pH 8.3) | | |
| 30 | 8.50 | 11.8 |
| 40 | 8.95 | 13.2 |
| 50 | 9.00 | 14.1 |
| 60 | 9.10 | 15.0 |

(Pulp density = 50%; leaching time = 1 hr at 100 rpm)

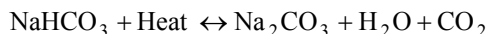
It was observed that U solubilization from rock phosphate was apparently associated with Na_2CO_3 and NaHCO_3 concentrations in the leaching solutions.

The rate of metal extraction from ores and minerals depends upon the surface of substrate to be leached. A set of leaching experiments were carried out to find out the effect of various ore pulp densities (liquid to solid ratio) on uranium solubilization from rock phosphate in Na_2CO_3 and NaHCO_3 leaching process. It was observed that the uranium solubilization from rock sample was influenced with change in the rock pulp density. A maximum recovery of 88% U_3O_8 was obtained from rock pulp density of 5% (5 g rock sample in 100 ml Na_2CO_3 solution) during 1 hr of leaching time at 30 C under shaking conditions (Fig. 1). Similarly, in NaHCO_3 leaching system, a maximum uranium solubilization was 58.7% U_3O_8 in 5% pulp density was achieved under the same leaching conditions. It was observed that rate of uranium solubilization was inversely proportional to the rock pulp density (Fig. I). Several investigations have reported the importance of surface chemistry of minerals in leaching processes (Merritt, 1971; Tuovinen & Bhatti, 1999).

Temperature is an important environmental factor that influences the rate of metal extraction from ores and minerals. The chemistry of leaching process is influenced by temperature of leaching solutions. It was

Fig. 1. Uranium solubilization from rock phosphate at various pulp densities in carbonate and bicarbonate solutions

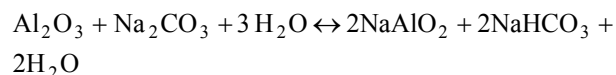
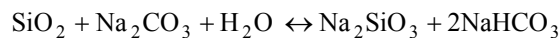
observed that the pH-values of the leach solutions of Na_2CO_3 solution leaching system was decreased from their initial pH-values of the solutions with an increase in the temperature of leaching solutions (Table IV). But in NaHCO_3 leaching system, there was an increase in the pH-values of the leach solutions with the increase of the temperature of the leaching solutions. These data suggested that the chemistry of leaching process was influenced by the temperature of leaching solutions. At higher temperatures of leaching solutions, the accessory minerals present in the rock matrix consumed much HCO_3^{1-} as compared with low temperatures. In fact, the chemical reaction was deemed responsible for the consumption of HCO_3^{1-} ions, thereby resulted in a progressively increase in the pH-values of the leach solutions as the temperature of the leaching solutions was increased. Merritt (1971) reported that at relatively high temperatures, sodium bicarbonate [NaHCO_3] decomposes to sodium carbonate [Na_2CO_3] and CO_2 according to the following reaction:



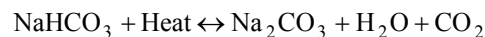
The data indicated that an increase in the pH value of the leaching solution (s) at higher temperature was resulted due to the formation of Na_2CO_3 during the present leaching studies.

Uranium solubilization from rock phosphate was influenced by the change in temperature of leaching solution (Table IV). In general, it was concluded that with an increase of temperature of the leaching solution, there was an increase in the U solubilization of about 2-3% U_3O_8 in the temperature range of 40-60°C. Uranium solubilization was substantially associated with the

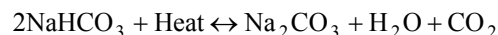
increase of temperature. At higher temperature, Na_2CO_3 may reacts with acidic constituents like silica (SiO_2), and alumina (Al_2O_3) present in the ore-matrix (Merritt, 1971):



Sodium bicarbonate [NaHCO_3] decomposes to sodium carbonate [Na_2CO_3] and CO_2 at relatively high temperatures according to the following reaction:



At higher temperature much HCO_3^{1-} was consumed thereby resulting in higher pH values. It was reported by Merritt (1971) that solution bicarbonate decomposes at temperature to Na_2CO_3 as:



The data obtained suggested that maximum U recovery of 22.7% U_3O_8 was obtained at 60°C. In general it was concluded that with an increase of temperature of the leaching solution, there was an increase of about 2-3% U_3O_8 solubilization from rock phosphate in temperature range of 40-60°C. In case of NaHCO_3 leaching system, the HCO_3^{1-} prevent the precipitation of U solubilized.

CONCLUSIONS

Uranium was solubilized from rock phosphate in both sodium carbonate and sodium bicarbonate solutions. Uranium dissolution was apparently associated with the concentrations of NaHCO_3 and Na_2CO_3 solutions. U solubilization was influenced by rock pulp density and the temperature of the leaching solutions.

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