

# Uranium Solubilization from Rock Phosphate in Carbonate Leaching Media

IRAM BAJWA, HAQ NAWAZ AND TARIQ MAHMOOD BHATTI†

National Institute of Biotechnology and Genetic Engineering (NIBGE), Faisalabad-577 †Department of Chemistry, University of Agriculture, Faisalabad-38040, Pakistan

## 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 [ $Ca_3(PO_4)CaF_2$ ] (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 <sub>2</sub> O <sub>5</sub> (total)	33.60
CaO	51.72
K <sub>2</sub> O	0.12
MgO	0.47
SiO <sub>2</sub>	1.60
MnO	0.02
Al <sub>2</sub> O <sub>3</sub>	0.70
CO <sub>2</sub>	4.70
Fe <sub>2</sub> O <sub>3</sub>	0.16
Na <sub>2</sub> O	1.12
F	3.92
U <sub>3</sub> O <sub>8</sub>	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 Na<sub>2</sub>CO<sub>3</sub> and 1.0 M NaHCO<sub>3</sub> 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 Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> 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% U<sub>3</sub>O<sub>8</sub> (120 ppm U<sub>3</sub>O<sub>8</sub>) 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<sup>+6</sup>) as autonite uranium mineral with general formula of [Ca(PO<sub>4</sub>)<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>] in the rock sample (Bhatti, 2000). The rock sample was of high-grade phosphate rock containing 33.6% P<sub>2</sub>O<sub>5</sub>. A complete chemical analysis of the representative rock sample is reported in Table I.

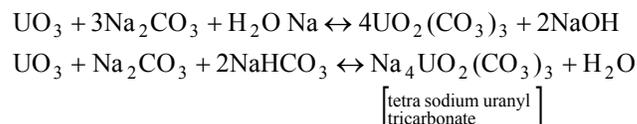
When the rock sample was added into the flasks containing Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> solutions, a chemical reaction was took place in the leaching systems. This chemical reaction was deemed responsible for the slight increase in the pH-values of the leaching solutions (Table II). In NaHCO<sub>3</sub> 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 <sub>3</sub> O <sub>8</sub> solubilized (%)
Na <sub>2</sub> CO <sub>3</sub> solution (1.0 M)	11.1	11.3	75.3
NaHCO <sub>3</sub> 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)

U<sub>3</sub>O<sub>8</sub> was achieved from rock phosphate when it was treated with Na<sub>2</sub>CO<sub>3</sub> solution (Table II). The pH of the carbonate leach liquor was observed a value of pH 11.3. But in case of NaHCO<sub>3</sub> leaching system, a uranium recovery of 52.9% U<sub>3</sub>O<sub>8</sub> 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 tricarboxylate [Na<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>], when uranium is present as hexavalent state (UO<sub>3</sub>) in the ore matrix (Merritt, 1971). During such leaching system, there is no oxidation-reduction reaction takes place. Bicarbonate {HCO<sub>3</sub><sup>2-</sup>} is added to

the leaching solution to prevent re-precipitation of a part of the dissolved uranium content through chemical reaction with hydroxyl ion ( $\text{OH}^-$ ), 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 [ $\text{CaCO}_3$ ] 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%  $\text{U}_3\text{O}_8$ ) 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  $\text{NaHCO}_3$ . 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  $\text{NaHCO}_3$  solutions; whereas in the  $\text{Na}_2\text{CO}_3$  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  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions**

Leaching solution	pH of solutions before adding rock sample	pH of leach solutions				$\text{U}_3\text{O}_8$ solubilized (ppm)			
		10	30	60	120	10	30	60	120
<b><math>\text{Na}_2\text{CO}_3</math> solutions</b>									
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
<b><math>\text{NaHCO}_3</math> solution</b>									
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
<b>Distilled water</b>	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  $\text{Na}_2\text{CO}_3$  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	$\text{U}_3\text{O}_8$ solubilized (%)
<b><math>\text{Na}_2\text{CO}_3</math> solution (1.0 M; initial pH 11.1)</b>		
30	11.0	15.0
40	10.8	20.0
50	10.9	19.4
60	11.0	22.7
<b><math>\text{NaHCO}_3</math> solution (1.0 M; initial pH 8.3)</b>		
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  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  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  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  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%  $\text{U}_3\text{O}_8$  was obtained from rock pulp density of 5% (5 g rock sample in 100 ml  $\text{Na}_2\text{CO}_3$  solution) during 1 hr of leaching time at 30 C under shaking conditions (Fig. 1). Similarly, in  $\text{NaHCO}_3$  leaching system, a maximum uranium solubilization was 58.7%  $\text{U}_3\text{O}_8$  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**

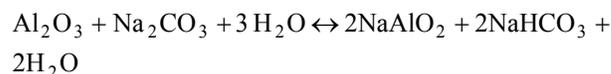
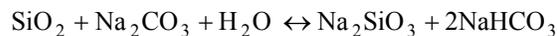
observed that the pH-values of the leach solutions of Na<sub>2</sub>CO<sub>3</sub> solution leaching system was decreased from their initial pH-values of the solutions with an increase in the temperature of leaching solutions (Table IV). But in NaHCO<sub>3</sub> leaching system, there was an increase 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<sub>3</sub><sup>1-</sup> as compared with low temperatures. In fact, the chemical reaction was deemed responsible for the consumption of HCO<sub>3</sub><sup>1-</sup> 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<sub>3</sub>] decomposes to sodium carbonate [Na<sub>2</sub>CO<sub>3</sub>] and CO<sub>2</sub> according to the following reaction:



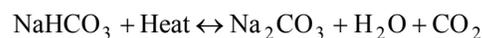
The data indicated that an increase in the pH value of the leaching solution (s) at higher temperature was resulted due to the formation of Na<sub>2</sub>CO<sub>3</sub> during the present leaching studies.

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<sub>3</sub>O<sub>8</sub> in the temperature range of 40-60°C. Uranium solubilization was substantially associated with the

increase of temperature. At higher temperature, Na<sub>2</sub>CO<sub>3</sub> may reacts with acidic constituents like silica (SiO<sub>2</sub>), and alumina (Al<sub>2</sub>O<sub>3</sub>) present in the ore-matrix (Merritt, 1971):



Sodium bicarbonate [NaHCO<sub>3</sub>] decomposes to sodium carbonate [Na<sub>2</sub>CO<sub>3</sub>] and CO<sub>2</sub> at relatively high temperatures according to the following reaction:



At higher temperature much HCO<sub>3</sub><sup>1-</sup> was consumed thereby resulting in higher pH values. It was reported by Merritt (1971) that solution bicarbonate decomposes at temperature to Na<sub>2</sub>CO<sub>3</sub> as:



The data obtained suggested that maximum U recovery of 22.7% U<sub>3</sub>O<sub>8</sub> 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<sub>3</sub>O<sub>8</sub> solubilization from rock phosphate in temperature range of 40-60°C. In case of NaHCO<sub>3</sub> leaching system, the HCO<sub>3</sub><sup>1-</sup> 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<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions. U solubilization was influenced by rock pulp density and the temperature of the leaching solutions.

## ACKNOWLEDGMENTS

We are grateful to Dr. Anwar-ul-Haque, Director, Institute of Engineering and Fertilizers Research, Faisalabad, for providing the rock phosphate sample for these studies.

## REFERENCES

- Awadalla, F.T. and F. Habashi, 1985. The removal of radium during the production of nitrophosphate fertilizer. *Radiochimica Acta* 38: 207-10.
- Awadalla, F.T. and F. Habashi, 1986. The recovery of uranium during the purification of phosphoric acid by organic solvents. *Separation Sci. Tech.*, 21: 327-37.

- Bhatti, T.M., A. Mateen, M., Amin, K.A. Malik and A.M. Khalid, 1991. Spectrophotometric determination of uranium (VI) in bacterial leach liquors using Arsenazo-III. *J. Chem. Tech. and Biotech.*, 52: 331–41.
- Bhatti, T.M., T. Yasmin, M. Amin and A. Mateen, 1999. Leaching of uranium from rock phosphate by *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. In: *Proc. Int. Sym. Hydrometallurgy (IBS'99)*, June 22-25, Madrid, Spain.
- Bunus, F.T., 1977. Determination of low levels of uranium in solutions obtained by acid attack on phosphate rock. *Talanta* 24: 117–20.
- Cathord, I.B., 1975. Uranium in phosphate rock. U.S. Geological Survey Open File Report.
- Habashi, F., 1985. The recovery of lanthanides from phosphate rock. *J. Chem. Tech. and Biotech.*, 35A: 5–14.
- Habashi, F., 1986. Fluoridation of water supplies and the phosphate industry. *Arab Mining J.*, 6: 62–4.
- Hurst, F.J., 1978. Recovery of uranium from phosphoric acid. *Chemical Abst.*, 91: 165151S.
- Hussein, A., 1994. Determination of uranium and thorium concentration in rock sample. *J. Radio Analytical and Nuclear Chem.*, 188: 255–65.
- Merritt, R.C., 1971. *The Extractive Metallurgy of Uranium*. Colorado School of Mines Research Institute, Golden, USA.
- Nagi, F.I., J. Anwar, M. Naeem, Z. Umar and A. Ali, 1974. Spectrophotometric determination of uranium in rock samples by dibenzoylmethane. *J. Nat. Sci. and Math.*, XIV: 165–77.
- Zaman, N., T. Mahmood, B.A. Khan, and M. Ilyas, 1983. Carbonate heap leaching of Baghalchur ore (Column Tests). Technical Report No. OPG/3, BC-1 Project, PAEC, D.G. Khan, Pakistan.

(Received 05 January 2000; Accepted 19 March 2000 )