Dissolution of Uranium from Rock Phosphate in Citric Acid Solutions

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ABSTRACT

The purpose of this work was to assess the dissolution of uranium from rock phosphate in citric acid solutions. The rock phosphate sample contained a significant amount of uranium content (0.012% U_3O_8). Uranium was present in the hexavalent state (U^{6+}) in the rock sample. An appreciable amount of uranium was solubilized from rock sample in citric acid solutions during shake flasks studies. Uranium solubilization from rock was apparently associated with the concentration of citric acid in the leaching solutions.

Key Words: Rock phosphate; Uranium; Citric acid; Uranium dissolution; Soil contamination

INTRODUCTION

Rock phosphate is the raw material for manufacturing of phosphate fertilizers. The rock phosphate of sedimentary-type contains an appreciable amount of uranium in the range of 0.005-0.03% U_3O_8 in isomorphous substitution for Ca (Merritt, 1971; Awadalla & Habashi, 1985), whereas the rock phosphate of igneous origin contains 10 ppm U_3O_8 associated with an appreciable amount of thorium (^{232}Th) and rare-earth elements (Merritt, 1971). The rock phosphate deposits of USA, North Africa, Israel, Jordon and Morocco etc., contain an average U content of 0.01-0.02% U_3O_8 (Bunus, 1977). But the Brazilian's rock phosphate deposits contain 0.03% U_3O_8 which is higher than the average U content (Habashi, 1986). In India, a calcium phosphate deposit contains 0.04% U_3O_8 present in the uranophane as a main uranium mineral identified (Habashi, 1986). About 6.34 million tones of uranium exists in rock phosphate deposits throughout the world (Cathord, 1975). About 80% of the rock phosphate is being used as raw material for the manufacturing of phosphate fertilizers whereas the remaining 20% rock phosphate is being utilized for the production of detergents, metal surface treatment reagents, chemicals for food industry and phosphorus compounds (Habashi, 1986). During the treatment of rock phosphate with acid, about 80-90% U_3O_8 of the total uranium content present in the rock matrix is solubilized (Habashi, 1994; Hussain, 1994; Guzman *et al.*, 1995).

Citric acid ($C_6H_8O_7$) is a non-toxic tri-carboxylic acid and it forms ternary mixed metal complexes with various metal ions involving the carboxyl and hydroxyl groups. It is commonly used as a chelating/ complexing agent for the extraction of actinides, radionuclides and heavy metals from contaminated soils and geologic rock materials (Glusker, 1980). Citric acid was also used to extract plutonium (Po) from the contaminated soils (Nishita, 1977). Among the several organic acids used in the extraction of metals, citric acid is the most preferred organic acid due to its natural multi-dentate complex formation with metals. Its efficiency towards extraction of metal ions is relatively consistent (Dodge & Francis, 1997). Citric acid was used to dissolve uranium from sedimentary-type sandstone ore deposits (Bhatti *et al.*, 1997). For the present work, the dissolution of uranium was investigated from a rock phosphate sample in citric acid solutions.

MATERIALS AND METHODS

The rock phosphate sample was obtained from the Institute of Engineering and Fertilizers Research, Faisalabad. The rock sample was ground to ≤300 mesh particle size. Chemical analysis of the representative rock sample indicated the following composition (wt/ wt): 0.012% U_3O_8; 33.6% P_2O_5; 51.72% CaO; 0.47% MgO; 1.60% SiO_2; 0.70 Al_2O_3; 0.16% Fe_2O_3; 1.12% Na_2O; 0.12%K_2O; 3.92% F and 0.21% organic matter. X-ray diffraction was used to determine the mineralogical compositions using a Rigaku series diffractometer and PCAPD diffraction software. Ground sample was analyzed as glass mounts using CrKα radiation and a wide range goniometer equipped with a diffracted-beam, curved-graphite monochromator and a compensating slit.

The leaching experiments were carried out in 500-mL Erlenmeyer flasks containing separately 100-mL of citric acid solutions (0.1 M, 0.2 M, 0.5 M and 1.0 M). Each flask was supplemented with 10g finely ground

rock phosphate sample. All these flasks were incubated in the orbital shaker at 30ºC and 100 rev. min^{-1}. In the time course leaching experiments, samples were removed at intervals and centrifuged to remove solid suspension. Supernatants were analyzed for monitoring pH and dissolved U content. The concentration of uranium in the leach solutions was determined by a spectrophotometric method using Arsenazo-III as chromogenic reagent (Bhatti *et al.*, 1991).

RESULTS AND DISCUSSION

The XRD data for the finely ground material are summarized in Table I. The fluorapatite [$Ca_3(PO_4)_2.CaF_2$] was identified as a main phosphorus-containing mineral. In addition to fluorapatite, the rock sample also contained other minerals like albite, illite, gypsum, kaolinite, talc, clinochlore, dolomite, quartz and halite. The diffraction lines for uranium mineral (autonite) was below the level of detection (2% relative intensity). The dolomite was the main acid-consuming gangue mineral present in the rock matrix.

Table I. X-ray powder diffraction data for the rock phosphate sample

Mineral identified	Mineral formula
Fluorapatite	$Ca_3(PO_4)_2•CaF_2$
Albite	$NaAlSi_3O_8$
Gypsum	$CaSO_4.2H_2O$
Illite-1M	$KAl_6Si_4O_{11}$
Kaolinite	$Al_2SiO_7(OH)_2$
Talc-2M	$Mg_3Si_4O_{10}(OH)_2$
Clinochlore-1M	$Mg_5Al_5Si_4O_{10}$
Clinochlore-1M (ferroan)	$(MgAl)_6(SiAl)_4O_{10}$
Dolomite	$CaMg(CO_3)_2$
Quartz	SiO_2
Halite	$NaCl$

In leaching experiments, when the rock sample was treated with citric acid solutions of various concentrations (0.1 M, 0.2 M, 0.5 M and 1.0 M), an acidulation reaction was took place with the effervescence of CO_2. The pH-values of all the treatments were progressively increased due to the chemical reaction, which occurred between citric acid and various acid-consuming accessory minerals like dolomite, clay and silicate minerals present in the rock sample (Fig. 1). At higher acid concentrations, the pH-values of the leach suspensions were found more acidic. This acidulation reaction was deemed responsible for acid consumption that was observed with all treatments. A similar pattern of pH change was observed in the flasks containing only distilled water (control).

Uranium was present in hexavalent state (U^{6+}) as autonite uranium mineral with general formula of [$Ca(PO_4)_2(UO_2)_2.10-12H_2O$] identified in the rock

Fig. 1. pH profiles of the leach suspensions of rock phosphate in citric acid solutions. Control (O); 0.1 M citric acid solution (Δ); 0.2 M citric acid solution (●); 0.5 M citric acid solution (▼) and 1.0 M citric acid solution (▲)
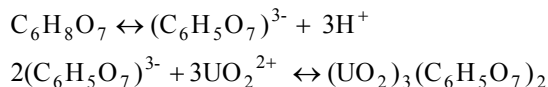
Fig. 2. Uranium dissolution from rock phosphate in various concentrations of citric acid solutions. Control (O); 0.1 M citric acid solution (Δ); 0.2 M citric acid solution (●); 0.5 M citric acid solution (▼) and 1.0 M citric acid solution (▲)

sample (Bhatti, 1999). Uranium was more or less completely dissolved in the citric acid solutions (Fig. 2). It was indicated from the data that an appreciable amount of uranium was solubilized from rock sample in all the acid treatments within 10 minutes of the leaching time without shaking. A maximum uranium solubilization (96% U_3O_8) was obtained at higher concentration of citric acid solution (Fig. 3). In control samples (having no citric acid), uranium dissolution was remained very low regardless to the acid solutions. Uranium solubilization was apparently associated with the citric acid concentration in the leaching solution. Uranium was dissolved as uranyl citrate complex [$UO_2)_3(C_6H_5O_7)_2$]. Under oxidizing conditions, citrate ion primarily forms a binuclear complex with UO_2^{2+} ion. Citric acid contains three carboxylic groups (pKa_1 =

Fig. 3. Uranium recovery (%) at various concentrations of citric acid solutions after 24-hrs of leaching time

Fig.4. A relationship between pH and uranium dissolution from rock phosphate in citric acid solutions. pH profile (O) and uranium dissolution (●)

3.13; $pKa_2 = 4.76$ and $pKa_3 = 6.39$) and one hydroxly group ($pKa_4 = 10.82$) at 25 ^{0}C as possible donators of protons (Skoog, 1992). When citric acid is fully dissociated in aqueous solution and if the uranyl ion (UO_2^{2+}) are present in the system, a complexation/ chelating reaction may takes place. The overall chemical reaction which covers the dissolution of uranium from geological rock materials containing uranium minerals in the leaching system are given accordingly:

$$C_6H_8O_7 \leftrightarrow (C_6H_5O_7)^{3-} + 3H^+$$
$$2(C_6H_5O_7)^{3-} + 3UO_2^{2+} \leftrightarrow (UO_2)_3(C_6H_5O_7)_2$$

Citric acid as complexing/ chelating agent may facilitate the dissolution of U. It was also indicated from the leaching data that U dissolution was pH-dependent (Fig. 4). In addition to U solubilization, some other metal ions might be dissolved from the rock sample due to citric acid attack but they were not analyzed in the leach solutions. U(VI) formed mixed metal complexes with Al (III), Cu (II), Fe (III) and In (III) in the presence of citric acid (Adin *et al.*, 1970).

It is of great advantage that organic acid (s) increases the solubility of metal ions at neutral pH by complexation and thereby, precluding the precipitation of metal (s) as their hydroxides successfully. This phenomenon is suitable in hydrometallurgy where a metal concentration as high as possible is desired. The anions and the protons of an organic acid are able to leach metals by acidolysis and/or complexation phenomenon.

CONCLUSION

Uranium dissolution from rock phosphate was apparently associated with citric acid concentration in the leaching solutions. It was indicated that U solubilization was pH dependent and there was no redox reaction involved during the leaching phenomenon.

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