Influence of microwaves on the leaching kinetics of uraninite from a low grade ore in dilute sulfuric acid

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HIGHLIGHTS

- U leaching from a low-grade Si-rich ore studied in H_2SO_4 medium with (MW) irradiation.
- MW heating is more efficient in terms of U recovery, kinetics and purity of liquor.
- U leachability of 84% obtained in 90 min at 95 °C with 0.38 M H_2SO_4 at 450 mV with MW heating
- Conventional conductive heating gave about 74% leachability with less purity liquor.
- U leaching was found follow product layer diffusion as controlling mechanism.

ARTICLE INFO

ABSTRACT

This paper describes a study on microwave assisted leaching of uranium from a low-grade ore of Indian origin. The host rock for uranium mineralization is chlorite-biotite-muscovite-quartzo-feldspathic schist. The dominant presence of siliceous minerals determined leaching of uranium values in sulfuric acid medium under oxidizing conditions. Process parametric studies like the effect of sulfuric acid concentration (0.12–0.50 M), redox potential (400–500 mV), particle size (600–300 μm) and temperature (35°–95 °C) indicated that microwave assisted leaching is more efficient in terms of overall uranium dissolution, kinetics and provide relatively less impurities (Si, Al, Mg and Fe) in the leach liquor compared to conventional conductive leaching. The kinetics of leaching followed shrinking core model with product layer diffusion as controlling mechanism.

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1. Introduction

Uranium is an important strategic metal where large supply demand gap is predicted in coming decades [1]. The interest in uranium metal stems from its widespread use in commercial nuclear power reactors (Light Water or Pressurized Heavy Water variety) as main fuel source [2]. Nuclear energy is attracting renewed worldwide attention, particularly in developing nations like China and India, as a large-scale energy generating source, mainly because it is bestowed with the advantage of very-low or negligible green house gas emissions (GHG) during the process [3]. The main source of uranium is conventional ore deposits. Uranium is recovered from any land based resource like ores or tailing dumps etc. by hydrometallurgical process, consisting of size reduction, leaching, solid-liquid separation, purification and precipitation of dissolved uranium as yellow cake [4–6]. Leaching is a critical unit operation in the process flowsheet and temperature of reaction is an important controlling parameter for this unit operation. The complexity in processing lean tenor ores or resources arises predominantly due to the chemical reactivity of gangue or unwanted minerals along with minerals of interest or valuable minerals. During chemical leaching, which is the stage where the release of various ionic species from solid mineral phase/s to aqueous medium occurs, presence of unwanted ionic species in solution phase increases the rigorousness of purification operations like ion exchange or solvent extraction, besides aggravating the effluents treatment protocol [5]. Therefore, research is pursued in various laboratories on methods of achieving selectivity during the leaching stage itself to the extent possible. The chief methods pursued in this endeavor include manipulation of chemical conditions [6] or/and application of microwaves which is having the attribute of selective heating of minerals [7].

The application of microwave technology in minerals processing is pursued by isolated groups world-wide for last two decades [7–20]. Considering its potential, several reviews on principles and application of microwaves in different ore processing unit operations like size reduction, roasting, flotation, leaching etc. was reported [7,8]. However, its relevance for low-grade or other complex resources processing is better felt now than ever before due to concomitant developments in scaling-up of the microwave processing technology [21]. With regard to leaching operation microwave has distinct advantage over conventional conductive heating method. Microwave heating is rapid and selective in nature, distributes uniformly in the cavity, high efficiency, fast switch on and off as well as flexible and available in modular design. Microwave heating is a kind of electro-heat process such as induction, radio frequency, direct resistance, and infrared heating that utilize specific parts of electromagnetic energy [17,18]. Microwave energy is non-ionized electromagnetic radiation which has frequencies changing in the range of between 300 MHz to 300 GHz. Materials that couple to microwave energy are called dielectric and contain dipoles. The dipoles align themselves in an electric field and flip around in an alternating electric field. Stored internal energy is lost through friction thus heating the minerals. Based on rate of heating (with microwaves) the minerals are classified into hyperactive, active, difficult-to-heat and inactive. From the large number of minerals and inorganic compounds tested by several laboratories it was noted that most silicates, carbonates and sulfates, and some oxides and sulfides are transparent to microwave energy, while most sulfides, arsenides, sulfosalts and sulfarsenides, and some oxides, heat well when subjected to microwave irradiation [7]. For instance it was reported that pure UO_2 attained a temperature of $1100\,^\circ C$ in 0.1 min of irradiation with MW of 2450 MHz and heating rate noticed was $200\,^\circ C/s$ [7]. In comparison to this the SiO_2 and $CaCO_3$ which are the common host rocks for uranium minerals heats at the rate of 2–5 and $5\,^\circ C/s$ [7].

In view of such positive factors like improved extraction efficiency and attractive leaching kinetics, investigations on application of microwaves for leaching of uranium values from a low-grade ore under oxidizing conditions using sulfuric acid as lixiviant was carried out and results discussed. MW assisted dissolution of spent nuclear fuel and thorium was reported earlier [22,23] however, it is for the first time that an attempt is being made on evaluating its role on leaching of uranium from an ore. Though the application of MW for treating the ores is highly energy intensive, the enormous energy packed in uranium nucleus would definitely give net positive energy balance and this factor is the driving force behind the investigations [24].

2. Leaching chemistry

Leaching of oxides of uranium in sulfuric acid medium takes place by two steps, (i) oxidation of insoluble U (IV) to U (VI) and (ii) complexation of oxidized U (VI) by sulphate anions to form uranyl sulphates. The uranyl sulfates remain as stable aqueous complexes under specified redox and pH conditions [4–6]. The leaching process is reported to follow electrochemical mechanism depicted in the Eqs. (1)–(3) [25]. Sulfuric acid leaching of uranium minerals requires the presence of Fe (III) regardless of the reagent used as an oxidant [26,27]. Fe (III) oxidizes U (IV) as given in Eq. (1), while the oxidant reagent oxidizes the Fe (II) to Fe (III) as given in Eq. (2); thus, the Fe (II)–Fe (III) couple serves as an electron transfer catalyst between the oxidant and UO_2.

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+} \tag{1}$$

$$2Fe^{2+} + MnO_2 + 4H^+ \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \tag{2}$$
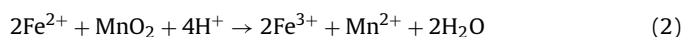
The chemical interaction of soluble UO_2^{2+} species with sulphate anions yields uranyl sulphate complexes like $UO_2\,(SO_4)_n^{2-2n}$ as illustrated in Eq. (3).

$$UO_2^{2+} + nSO_4^{2-} \rightarrow UO_2(SO_4)_n^{2-2n} \tag{3}$$

Satisfactory leaching of uranium values occurs by maintaining a redox potential (Eh) of 400–500 mV vs saturated calomel electrode (SCE) [26,27].

3. Experimental

3.1. Characterization studies

The uranium ore sample used in the present studies was collected from Narwapahar mine, Singhbhum district, Jharkhand, India. The ore was crushed and ground to $600\,\mu m$, $425\,\mu m$ and $300\,\mu m$ size using laboratory jaw crusher and rod mill. All the chemicals used in the test work were of AR grade from standard chemical suppliers like BDH, Loba and Merck.

Identification of various phases in the ore sample was made using Siemens D500 X-ray diffractometer (XRD) with CuKα radiation $(1.5418\,\text{Å})$ as source. The accelerating voltage and amperage was 35 kV and 22 mA. A 1° divergence slit was used to analyze between the 2θ range of $5–90^\circ$ with a step size of 0.02° and 2 s/step on a 30 s delay. Phase identification was made with the aid of International Centre for Diffraction database (ICDD). Quantitative mineralogical composition of the Narwapahar uranium ore was estimated using optical microscopy. Micro-morphological study on the leach residue was performed using Philips XL-20 Scanning Electron Microscope attached with Energy Dispersive analyzer (SEM-EDS).

Uranium content in the ore and various product streams was determined using pellet fluorimetry on Model FL6224 fluorimeter (M/s Electronic Corporation of India Limited, India). Powdered rock sample weighing 1 g accurately was mixed with 3 ml HF and 5 ml HNO_3 and the contents were evaporated to dryness on hot-water bath. This was carried out for two more times. 5 ml of HNO_3 was further added to the contents and re-evaporated to dryness. This was also repeated for two times. Finally, 10 ml of HNO_3 was added to the residue in the container and after about 30 min of digestion the mixture was filtered. The filtrate was collected in 100 ml volumetric flask and the balance volume adjusted with 10% HNO_3. Uranium was extracted with ethyl acetate using aluminum nitrate as the salting-out agent. The aliquot from the organic layer was dried under an infrared lamp, combined with a flux (Na_2CO_3:NaF = 4:1) in a platinum planchet, and fused at $850\,^\circ C$. After cooling, the fused pellet was irradiated using Hg-vapor lamp at 365 nm wavelength. The characteristic uranium fluorescence emanating from the sample pellet at 555 nm was measured by PMT detector.

Silica content in the ore was determined by UV–vis spectrophotometer (Unicam) by molybdenum-blue method. The procedure involves decomposing the ore samples (0.20 g) with NaOH in nickel crucibles, followed by water leaching and acidification with HCl. The clear solution was used for estimations in UV–vis spectrophotometer.

Na and K were determined by Flame photometer (Flame photometer-128, M/s Systronics, India). 0.04 g of sample was weighed in a platinum crucible; 2 ml of hydrofluoric-sulphuric acid mixture was added followed by heating the crucible gently on a hot plat until white fumes of sulphuric acid evolved. The contents were cooled and 5–10 ml of warm de-ionized water added to bring the solid residue into solution. The contents were transferred to a 50 ml volumetric flask and diluted to desired volume with de-ionized water followed by aspiration.