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Pulsed electric discharge treatment of uranium leaching solutions: A method for accelerated extraction

I. Kornev [a,*], G. Osokin [a], N. Yavorovsky [a], A. Morozov [b], V. Litvinenko [b]

[a] Tomsk Polytechnic University, Institute of High Technology Physics, Tomsk, Russia
[b] Priargunsky Industrial Mining and Chemical Union JSC, Krasnokamensk, Russia

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ABSTRACT

Depletion of uranium ore deposits is leading to a need for more efficient uranium extraction techniques. In this study, gas-phase electric discharge is applied to an aqueous leaching solution dispersed between electrodes as a technique for enhancing acidic extraction of uranium. Application of the electric discharge treatment resulted in a 1.5 to 2.0 times increase in the leaching rate and an improvement in uranium recovery of 4%. The enhanced extraction method was found to involve oxidation of ferrous ions in the acidic aqueous solution by nitrogen-containing ions generated in the spark discharge channels.

1. Introduction

Increase in demand for nuclear fuel and depletion of global uranium ore deposits require implementation of more efficient uranium extraction technologies. Furthermore, the number of nuclear power plants in industrial nations is increasing: China, India and Russia are planning to commission forty-six new nuclear power plants in the coming years (IAEA online database). Yet, uranium extraction from natural sources is expected to decline, starting from the 2030s, due to depletion of uranium reserves (Dittmar, 2013). Extraction of uranium from low-grade ores, however, requires greater efficiency in the leaching processes used. Improvement in the uranium extraction rate at minimal additional energy cost is critical for Russian deposits, which are characterized by relatively low uranium content ranging from 0.1 to 0.3% U (IAEA-TECDOC-1629, 2009).

Uranium is extracted from ores using acidic or carbonate leaching processes (Mamilov et al., 1980; Edwards and Oliver, 2000). Acidic leaching is normally utilized for ores with low carbonates content. Aqueous solutions of sulfuric acid, however, dissolve uranium (IV) poorly, extracting only better soluble uranium (VI). Therefore, acidic leaching requires preliminary oxidation of uranium (IV) using strong oxidants such as ferric ions Fe^{3+}:

$$U^{4+} + 2Fe^{3+} \rightarrow U^{6+} + 2Fe^{2+} \quad (1)$$

As a result of the reaction (1), ferrous ions accumulate in the leaching solution. To maintain the rate of uranium oxidation, the ferrous ions have to be oxidized back to the ferric state. Conventional oxidants used for this purpose include manganese dioxide (Edwards and Oliver, 2000), oxygen (Mamilov et al., 1980), nitric acid (Litvinenko et al., 2013), hydrogen peroxide (Eligwe and Torma, 1986) and sulfur dioxide (Ho and Quan, 2007). Oxidation of uranium can be accelerated by ultrasonic irradiation (Avvaru et al., 2008) and mechanical agitation of the uranium-containing pulp (Kovacheva et al., 2004).

Disadvantages of chemical oxidation methods include the necessity of chemicals delivery to often remote locations and a need for safe chemicals storage, making the *in-situ* production of strong oxidants beneficial. *In-situ* methods include oxidation with oxygen at elevated temperature and pressure (Mamilov et al., 1980; Edwards and Oliver, 2000), electron beam irradiation (Smirnov et al., 2009) and treatment with ozone (Filipov and Nesterov, 2009). These methods, however, have not been widely applied because they suffer from a number of disadvantages. Pressure oxidation with oxygen incurs high operational costs and imposes stringent safety requirements. The use of electron accelerators involves expensive sophisticated equipment, has low energy efficiency, and creates a need for additional radiation safety measures. Ozonation is a costly process due to high energy consumption and the necessity to maintain high concentrations of dissolved ozone to ensure a sufficiently high reaction rate (Filipov and Nesterov, 2009).

A method for iron oxidation in acidic solutions using pulsed electric discharges in air has been presented in which the treated solution is dispersed into droplets of a few millimeters in size (Osokin et al., 2012). Electric discharge treatment has also proved to be a viable method for

* Corresponding author.

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oxidation of aqueous dissolved organic substances (Panorel et al., 2011; Kornev et al., 2014). The process efficiency is higher than that of conventional ozonation due to the generation of active short-lived oxidant species, such as hydroxyl radicals and atomic oxygen, in close proximity to the surface of the droplets. The energy of these species is utilized in the oxidation process, supported also with ozone formed in the discharge and absorbed by the treated solution in the reaction chamber (Kornev et al., 2014).

Previous work has demonstrated the ability of a pulsed dielectric barrier and spark discharges to oxidize dissolved ferrous iron in acidic solutions (Osokin et al., 2012). Thus far, however, no experimental research has been undertaken to determine the effect of electric discharge treatment on the process of uranium extraction. In the present study, electric discharge treatment was applied to a uranium leaching solution from Priargunsky Industrial Mining and Chemical Union JSC (Eastern Siberia, Russia). The company uses underground mining to excavate uranium ore. Extraction of uranium from thin ores is carried out by heap leaching. Acidic solutions percolate the ore at ambient temperature and pressure over several months until 70–80% of the uranium is extracted. Oxidation of uranium (IV) occurs due to the reaction of the uranium with the air oxygen penetrating the bulk of the heap. The concentration of sulfuric acid in the leaching solutions ranges from 5 to 10 g/L and the dosage of sulfuric acid varies from 71 to 74 kg per 1 kg of extracted uranium (Litvinenko et al., 2008). To achieve best performance, leaching solutions are reused after separation of uranium and replenishment of sulfuric acid.

2. Materials and methods

2.1. Electric discharge setup

Acidic leaching solutions were treated by electric discharge using the experimental setup shown in Fig. 1. The setup consisted of a rectangular stainless steel reactor column with a system of electrodes, a high-voltage pulse generator and a storage tank. The reactor column had dimensions of 0.1 × 0.1 × 1.0 m. The spark discharge occurred between two rectangular stainless steel electrodes with an inter-electrode gap of 10 mm. The cross sections of the electrodes were 30 × 10 mm and 80 × 10 mm for the high voltage and the grounded electrodes, respectively. The distance between the electrodes was selected to provide stable ignition of the discharge at the maximum available length of a channel. At longer interelectrode distances, the discharge becomes unstable, whereas shorter distances result in a decreased yield of active species (Rahman et al., 2011).

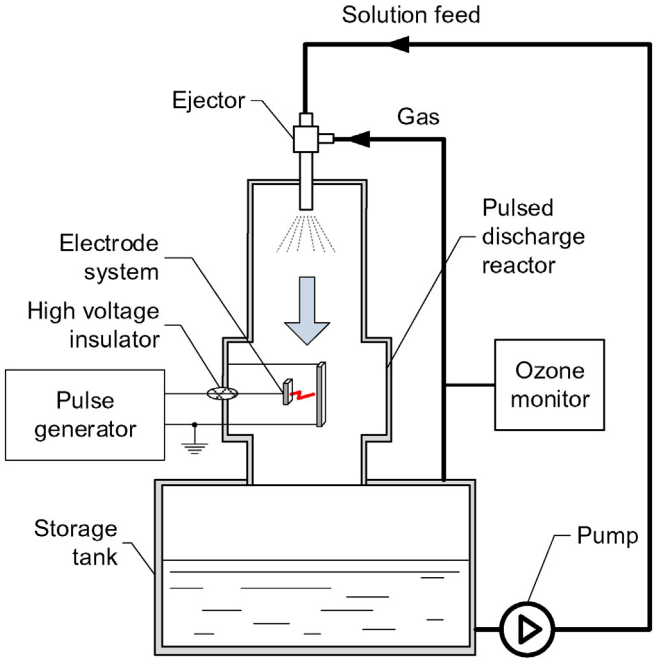

Fig. 1. Experimental setup.

The electrode system was energized by a thyristor pulse generator with magnetic pulse compression stages (Polyakov, 2004). The 0.9 nF storage capacitor was charged to a high voltage and then discharged to the electrode system using a saturating magnetic inductor. The energy of a single pulse was 0.32 J at a peak pulse voltage of 20 kV and pulse repetition rate of 800 pulses per second (pps).

The storage tank was filled with four liters of leaching solution, which was circulated through the electric discharge reactor. The duration of the electric discharge treatment varied from 40 to 60 min. The solution was fed to the upper part of the discharge chamber and dispersed with an ejector into droplets of diameter ranging from 1 to 2 mm. The solution passed through the electric discharge reactor with a volumetric flow rate of 0.06 m^3/h and collected in the storage tank.

2.2. Leaching setup and materials

The outline of the experimental leaching setup is shown in Fig. 2. The system included leaching solution storage tanks (1–2), leaching columns (3–6), leachate storage tanks (7–10), ion-exchange columns (11–14) and the spark discharge setup (15). Each leaching column was filled with 10 kg of aluminosilicate uranium-containing ore with a grain size of less than 5 mm and grain size distribution as shown in Table 1. The grain size distribution was sufficient to prevent clogging of the leachate flow. The ore contained 7.5% carbonate substances, calculated as $CaCO_3$; the major constituents of the ore were trahydacite and basaltic andesite. The major uranium minerals present in the ore were uraninite and coffinite, providing an average uranium content of 28 ppm and 50 ppm for U(VI) and U(IV), respectively.

The leaching procedure used in the experiments comprised the following steps. Aqueous solutions of sulfuric acid from tanks (1) and (2) were fed into leaching columns (3–6) of a height of 1 m and inner diameter of 0.11 m. The flow rate of the solution passing through each column was 0.083 L/h or approximately 2 L/day. The solution was fed to the top of the columns in the trickling flow mode and collected from the bottom outlet of the columns, simulating the conditions of the heap leaching process. The top of the columns remained open throughout the experiment, making it possible for air oxygen to reach the bulk of the ore in the column. After the treatment, the leaching solutions collected in the tanks (7–10) were then transferred to the stage of selective uranium sorption using an ion-exchange resin (columns 11–14). An AMP anionic exchange resin (Russia) based on vinylbenzene and divynylbenzene copolymers with benzyl pyridine

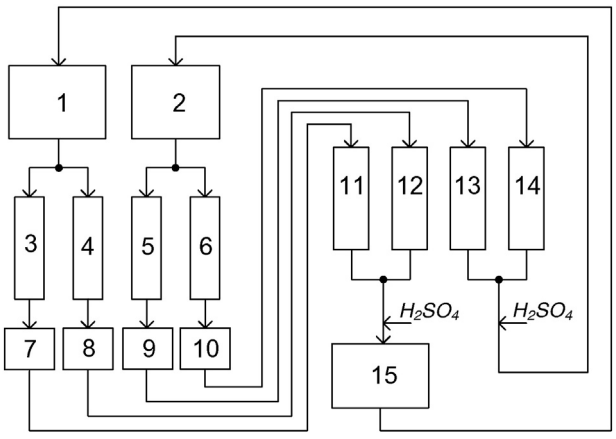

Fig. 2. Experimental leaching setup. 1–2 tanks, 3–6 leaching columns, 7–10 leachate storage tanks, 11–14 ion-exchange columns, 15 spark discharge treatment.