THERMODYNAMIC AND KINETIC PARAMETERS OF URANIUM RECOVERY FROM SULFURIC ACID SOLUTIONS USING ORGANOPHOSPHORUS EXTRACTION MIXTURES

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Currently, the processing of radioactive waste (RW) is an important and widely discussed topic. The decline of waste volumes will reduce the potential radioactive contamination of environment and allow the return of uranium to the nuclear fuel cycle. One effective method for processing uranium-containing waste is uranium leaching with sulfuric acid, followed by liquid extraction. However, several factors complicate this approach: the heterogeneity and complex composition of the waste and, consequently, of the pregnant leach solutions (PLS), as well as the temperature and duration of the process. The efficiency of the extraction stage directly depends on these factors. Thus, the aim of this work was to study the behavior of uranium under varying temperature and phases contact time during extraction using di-(2-ethylhexyl)phosphoric acid (D2EHPA) diluted in an inert diluent Shellsol D60 from pregnant solutions after sulfuric acid leaching of uranium from RW.

The study was conducted using both model and real pregnant solutions of uranium leaching. The real PLS were characterized by high concentrations of components, g L^{-1}: 0.53 – U; 3.4 – Fe; 2.9 – Mg; 2.8 – Ca; up to 9.2 – F^-; 50 – H_2SO_4. The model solutions (MS) contained, g L^{-1}: 0.5 – U and 50 – H_2SO_4. The extraction process was carried out at an organic and aqueous phases ratio of 1:5.

The effect of temperature on uranium extraction efficiency was investigated in the range of 20 to 80 °C. The experimental results revealed that an increase in process temperature led to a decrease in uranium recovery from both the MS (from 85.77 to 60.02 %) and the real PLS (from 61.93 to 1.91%). The change in Gibbs free energy in the former case increased from -8.3 to -5.9 kJ mol^{-1}, while in the latter this value increased from -5.1 to 6.8 kJ mol^{-1}, indicating a decrease in the reactivity of the system.

Based on the results of the previous experiment, extraction kinetics were studied at 20 °C over a range of 1 to 60 minutes. From the kinetic curves of uranium extraction from the MS, it was established that equilibrium in the "MS – D2EHPA" system was reached within the first 3 minutes and kept constant throughout the remaining time, with uranium recovery reaching 88.66% and ΔG equal to -8.9 kJ mol^{-1}. Subsequent experiments with real PLS yielded, as expected, different results: uranium recovery reached 77.6 % during the first 3 minutes, but decreased to 31.21 % over the remaining time due to the competitive extraction of impurity elements and the displacement of uranium from organic phase. The ΔG value over the considered time interval varied from -6.9 to -2.0 kJ mol^{-1}.

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