Studies on the Extraction of Uranium and Rare Earth Elements from El-Erediya Ore Material, Central Eastern Desert - Egypt

By

El Sayed Aly El Sayed Aly Haggag

M. Sc. Chemistry 2014

For the Degree of Doctor of Philosophy (Ph. D.) in Chemistry

A Thesis Presented

To Chemistry Dept., Faculty of science

Ain Shams University

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Dedication

To

My father and my mother

To

My sisters

To

My wife

To

My sons

Mohammed, Aly and Yassin

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"First and foremost, thanks are due to **ALLAH**, the Beneficent and Merciful."

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ABSTRACT

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The present work deals with a low-grade Egyptian ore obtained from El-Erediya mineralized rocks area, lies at about 30 km, south Qena-Safaga road at a sign 85 km midway between Safaga, on the red Sea coast and Qena in the Nile Valley to prepare crude yellow cake and rare earth elements concentrate.

El-Erediya mineralized ore was subjected to several hydrometallurgical processes included the leaching step followed by the uranium separation through the extraction by using anion exchange resin Ambersep 400 SO_4 then the elution step and finally precipitation of the crude yellow cake. Additional procedure was applied upon the raffinate solution after the uranium extraction step to prepare rare earth elements concentrate as a by-product by precipitation of REEs by sodium hydroxide**.** The optimum adsorption parameters affecting the extraction of rare earths by using cation exchange resin Dowex 50X8 from chloride medium was studied then the elution step of Dowex 50X8 and finally the eluate solution subjected to selective precipitation of the rare earths constituents by using oxalic acid.

The leaching process of uranium-REEs ore from El-Erediya in a sulfuric acid solution using hydrogen peroxide as an oxidant was investigated. The leaching conditions of temperature, acid type, hydrogen peroxide concentration, sulfuric acid concentration, contact time, particle size, solid-liquid ratio and agitation rate were studied. The optimum process operating parameters were: ore particle size 100-63 µm; acid type sulfuric acid; sulfuric acid concentration 1.5 M; contact time 120 min; solid-liquid ratio 1:3; H_2O_2 concentration 1.0 M and agitation rate 600 rpm at temperature 25°C. The uranium leaching efficiency was about 95.2% while the leaching efficiency of REEs and the iron oxide (III) were about 83.6% and 14.52% respectively. The experimental data were well interpreted with a shrinking core model with diffusion control through a porous product layer. The leaching process follows the kinetic model: $1\text{-}3\ (1\text{-}X)^{2/3} + 2\ (1\text{-}X) = k_1 t$

The apparent activation energies of the leaching reaction of uranium and REEs from El-Erediya ore by diluted sulfuric acid was obtained from

Arrhenius equation to equal 25.0 and 15.3 kJ mol^{-1} respectively. In addition, the reaction order of the uranium leaching was determined to equal 0.8 while the reaction order of REEs was about 1.12. Hence, the leaching rate of uranium and REEs strongly depends on the acid concentration. The linear relationship between the rate constant, k, and the inverse of the initial particle diameter indicates that the rate of uranium and REEs leaching is diffusion controlled.

The equilibrium and kinetic characteristics of the strong base macro reticular resin Ambersep 400 SO_4 from a sulphate liquor of El-Erediya was determined. Different parameters affecting the extraction of uranium from sulfate leach liquor using anion exchange resin (Ambersep 400 SO_4) were studied. The studied parameters affecting extraction were pH, agitating time, temperature as well as liquid to solid ratio (L/S ratio). It was found that the extraction efficiency of uranium reached maximum at pH ~ 1.75. Agitation time of 60 minutes was found to be sufficient to reach equilibrium. As the dose concentration (R/A) increased by increase the volume of solution the extraction efficiency increase and initial uranium concentration.

The obtained data showed that the uranium adsorption efficiency decreased with increasing the temperature; therefore it was preferred to conduct the extraction at room temperature. The thermodynamic parameters were calculated ΔG value was negative, indicating that the adsorption process of uranium ions on to Ambersep 400 SO_4 resins spontaneous. ΔH value is negative indicating that the process is exothermic in nature and the negative ΔS parameter suggests decreasing the system randomness at the solid-liquid interface during the adsorption process. Uranium elution was later performed using 1.5 M NaCl in diluted H_2SO_4 (pH 1.0) solution by an aqueous/resin (A/R) of 6/1 at contact time of 60 minutes from the loaded resin with minimum amount of eluate. The elution efficiency reached 96wt% for Ambersep 400 SO_4 resin after contact between the loaded resin and fresh eluate solution. The properly collected eluates fractions were then subjected to selective precipitation of uranium using hydrogen peroxide to precipitate as $UO_4.2H_2O$.

The effluent solution, containing rare earth elements, was then subjected to study the precipitation of rare earth elements by adjusting the pH using 10% sodium hydroxide to be in the range 3.5 to 9.5 with 1.0 increments and using 10% NaOH to be in the range 3.5 to 9.5. This step aimed to upgrade rare earth elements concentration from the effluent solution, where complete rare earth elements precipitation was achieved at pH 9.5 for sodium hydroxide. The precipitated of the hydroxide cake was analyzed by inductive coupled plasma optical emission spectroscopy (ICP-OES) to identify its constituents from rare earth elements; it was found that it contained about 1.8% rare earth elements by using sodium hydroxide. Thus sodium hydroxide was used to upgrade rare earth elements concentration from the effluent solution.

The suitable conditions for extracting rare earths from hydrochloric acid medium using the cation exchange resin Dowex 50X8 were studied. The studied parameters affecting extraction were pH, contact time, temperature, REEs initial concentration, as well as resin to liquid ratio (R/S ratio). It was found that the extraction efficiency of rare earths reached maximum at pH ~ 1.25. Agitation time of 75 minutes was found to be sufficient to reach equilibrium. However, the dose concentration (R/A) increased by increase the volume of solution the extraction efficiency decrease and initial REEs concentration. Also, the equilibrium and kinetic characteristics of the strong acid macro reticular resin Dowex 50X8 from a hydrochloric acid medium of El-Erediya was determined. The thermodynamic parameters were calculated negative value of ΔG indicating that the adsorption process of REEs ions on to Dowex 50X8 resin is spontaneous. ΔH value was negative indicating that the process is exothermic in nature and the negative ΔS parameter suggests decreasing the system randomness at the solid-liquid interface during the adsorption process. Rare earth elements elution was done using 4.0 M HCl by an aqueous/resin (A/R) of 6/1 at contact time of 120 minutes from the loaded resin with minimum amount of eluate. The elution efficiency reached 93wt% for Dowex 50X8 resin after contact between the loaded resin and fresh eluate solution. The properly collected eluates fractions were then subjected to selective precipitation of the rare earths constituents by using oxalic acid.