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Upgrading of the crude yellowcake to a highly purified form using tris(2-ethylhexyl) phosphate in presence of EDTA or CDTA

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ABSTRACT

Purification of low grade uranium concentrate was carried out using 0.05 mol L^{-1} Tris 2-ethylhexyl Phosphate in kerosene from 5 mol L^{-1} nitrate solution. More than 98% of uranium extracted after 5 stages of contact, shaking time 5 min, volume phase ratio 1/1 and at room temperature. Uranium stripping efficiency reached 99% using double distilled H_2O, 10 min shaking time, (O/A) ratio 4/1 and after three stripping stages. The masking agents used to improve the yellowcake purity compared to the experiment without additives, with Ethylene diaminetetracetic acid (EDTA) ensuring the highest purity. The result obtained can be attributed to complexation of impurity elements with EDTA, preventing their precipitation from the stripping solution.

1. Introduction

The processes of uranium recovery from its containing aqueous systems are of essential scientific and practical importance, not only in the protection of both being health and environmental safety, but also in uranium reutilization resources and potential expansion of nuclear energy [1]. The nuclear fuel cycle may be broadly defined as the set of processes and operations such as (uranium mining and ore processing, uranium refining and conversion and uranium enrichment) needed to manufacture nuclear fuels. Uranium is mined by conventional methods (either open pit or underground). Uranium ores usually contain 0.1–0.2% U_3O_8 (1–2 kg/t) although higher grades have been found in several cases. Several processes, such as acid leaching, alkaline leaching, heap leaching and in situ leaching, are available for this purpose. The uranium concentrate obtained from these ores is known as the yellowcake in which uranium assay more than 65%. This product would be further treated for purification from undesirable elements before its being suitable for manufacturing of nuclear fuel.

Nuclear grade $[(NH_4)_2U_2O_7]$ is obtained by dissolving commercial grade or low grade uranium concentrates in HNO_3 acid, then purified by liquid extraction and precipitated by ammonia solution. It is also transformed to uranium UO_3 by calcination and then reduced to uranium dioxide, which is used to fabricate fuel for heavy water reactors. Uranium (VI) may occur in solution as cations or complex anions and so it is easily separated from other elements by the use of either cationic or anionic exchangers [2,3]. Most metals form stable complexes with EDTA, uranium (VI) is unlike. On passage of an EDTA solution through a column of strongly acid cationic- exchanger, uranium (and also Be and Ti) is retained in the column, the other metals passing to the eluate as anionic complexes [4].

Brintzinger and Hesse [5] studied the formation of a salt having the composition $UO_2^{2+}H_2$ $(C_{10}H_{22}N_2O_8)$. H_2O by dissolving the solid ethylenediaminetetracetic acid in an aqueous uranyl salt solution which, readily decomposes to yield a precipitate of the hydroxide. Cabell [6] stated that the complex formed between uranyl ions and EDTA is unstable, it is rapidly hydrolyses and uranium is precipitated as hydroxide with pH increasing. The instability of U(VI)-EDTA complex has been utilized by Pribil and Vorlicek [7], for uranium precipitation by the addition of ammonium hydroxide in the presence of EDTA, which inhibits other cations precipitation. Hara and West [8], have also observed that, when a solution of uranyl nitrate is mixed with a solution of ethylenediaminetetracetic acid, the pH of the mixture is found to be less than that of either component which emphasis that chelation takes place with a consequent release of hydrogen ions from the organic addendum. By carrying out the high frequency oscillometric-titration of uranium (VI) with EDTA and its salts, they have established that the reacting ratios of metal to addendum are 2:1.

Uranium separation from nitrate solution of monazite mineral leaching by tris(2-ethylhexyl-phosphate) (TEHP) in comparison with tri-butyl-phosphate (TBP) dissolved in *n*-paraffin under different operating conditions such as HNO_3 acid, extractant and metal ion concentrations etc. was done by Biswas, et al. [9]. Uranium distribution ratio (D_U) is increased with increasing acidity up to 5 mol L^{-1} HNO_3 after that a reduction is observed. The separation factors of uranium

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Abbreviations: CDTA, 1, 2-C D T A (1,2-cyclohexanediamine-tetracetic acid) diamino-cyclohexane N, N, N^-, N^-,tetra acetic acid; EDTA, ethylene diaminetetracetic acid

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Table 1
XRF- elemental analysis for crude yellowcake and the final refined Y.C. produced in presence or absence of EDTA or CDTA additions.

Element Oxides (%)	Crude Y.C. (Original)	Final Y.C. without additions	Final Y.C., the strip has EDTA addition	Final Y.C.,the strip has CDTA addition	Final Y.C. extracted in presence of EDTA	Final Y.C. extracted in presence of CDTA
U_3O_8	68.92	97.75	98.87	96.54	97.30	97.17
P_2O_5	–	0.02	–	0.39	0.28	0.16
SO_3	21.26	0.24	–	0.28	0.34	0.57
K_2O	0.29	0.18	–	–	–	0.09
CaO	1.40	0.34	0.44	0.57	0.32	0.53
Fe_2O_3	3.30	0.07	0.03	0.17	0.15	0.09
NiO	0.20	0.01	0.02	–	0.03	–
CuO	–	0.06	0.01	0.01	0.02	0.03
ZnO	0.09	0.02	–	–	–	–
ZrO_2	0.34	0.06	–	0.07	0.04	0.02
La_2O_3	0.23	0.14	–	–	–	–
CeO_2	0.19	0.13	0.13	0.19	–	0.12
Pr_6O_{11}	0.01	0.14	0.05	0.27	0.15	0.02
Gd_2O_3	0.13	0.01	0.03	0.07	0.10	0.08
Dy_2O_3	0.01	0.05	–	–	–	0.06
Ho_2O_3	–	0.16	–	–	–	0.16
Yb_2O_3	–	0.06	0.06	0.11	–	0.02
TiO_2	–	–	0.08	–	0.12	–
MnO	0.50	–	0.06	–	–	–
Tm_2O_3	0.01	–	0.01	0.04	0.05	0.07
MgO	2.88	–	–	0.65	–	–
Y_2O_3	–	–	–	0.06	0.10	0.07
Nd_6O_{11}	–	–	–	0.06	–	–
Sm_2O_3	–	–	–	0.06	0.19	–
Lu_2O3	–	–	–	0.05	–	–
Tb_4O_7	0.21	–	–	–	0.12	0.07
Er_2O_3	–	–	–	–	0.02	0.01
Cr_2O_3	0.22	–	–	–	–	–
SiO_2	0.80	0.54	0.04	0.42	0.41	0.50

upon other metal ions (M) are good for TEHP than TBP at all HNO_3 acid concentrations. The data used in the construction of McCabe-Thiele diagrams for the recovery uranium by TEHP as the extractant was taken from batch solvent extraction experiments. A process flow sheet has been proposed with 0.2 mol L^{-1} TEHP in *n*-paraffin as solvent for the recovery of U(VI) from simulated monazite nitrate leach solution.

Among several methods for uranium separation is solvent extraction [10–20] and ionic exchanger resins [20,21] being considered as the simplest, applicable and the cheapest one depending on uranium ores grade. Several solvents were used for either yellowcake purification or uranium extraction such tri-butyl-phosphate, tri-capryl-methyl- ammonium chloride, di-nonyl phenyl phosphoric acid, Cyanex 272 and tri-ethyl-hexyl-phosphate [9,10,12–15], which varied in its selectivity and costs, among all of these solvents; organophosphrous solvents came being exceedingly used in respect of its low price in comparable to other solvent and more being selective.

TEHP [9,15] is a neutral extractant in regarding with other organophosphrous solvent shows very high selectivity and potentiality to be used in uranium extraction in only one publication and as an ionophore in potentiometric sensor for uranium determination with high accuracy and wide detection limit and life span for uranium potentiometric sensor [9], so it was recommended and demand as simple low price solvent for production of highly purified yellowcake prior to enrichment processing of uranium without any more upgrading processes. In this concern we utilize the high selectivity and potentiality of TEHP, complexes stability between EDTA or 1, 2-Diamino-cyclohexane N, N, N^{-}, N^{-},tetra acetic acid (CDTA) with the impurities present in our product and the instability of uranium-EDTA or CDTA complexes to get highly purified yellowcake or nuclear grade material without further purification processes.

2. Experimental

2.1. Chemicals, reagents and instrumentations

1 The chemicals and reagents used TEHP (Merck, Germany, 97%), Nitric acid (BDH, England, 68%), Sodium salt of EDTA (LOBA Chemie, India, 99%) and CDTA (Merck, Germany, 99%) were of analytical grade and all solutions were prepared in calibrated flasks with distilled water.
2 The hydrogen ion concentration of the different solutions was measured using the pH-meter used was HAANA pH-mV-temp, provided with H11270 combination electrode and thermometer sensor made from stainless steel.
3 The extraction and stripping experiments for uranium were conducted using 50 mL glass beaker and the agitation was performed

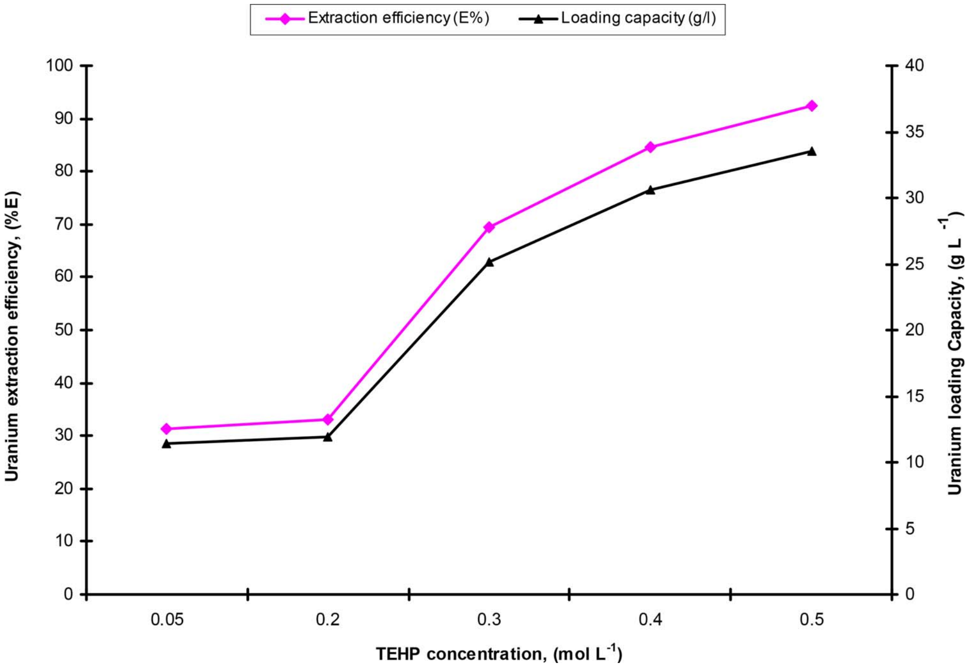

Fig. 1. Effect of TEHP concentration on the uranium extraction efficiency and loading capacity.