Study Of Optimum Conditions For The Removal Of Ruthenium And Cerium Using Freshly Prepared Manganese Dioxide

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Abstract

The adsorption of Ru and Ce were carried out using manganese dioxide as adsorbent. The Optimization of the adsorption conditions were studied as a function of shaking time, nitric acid, metal ions, concentrations and temperature effects.

A rapid initial adsorption on MnO_2 is followed by a steady and slow increase of metal uptake. The equilibration time is reached after four hours shaking for Ru and Ce and the adsorption is much better from one molar acidic solution and 90°C.

Key words: Adsorption, Uranium, Cerium , Ruthenium

Introduction

Reducing the decontamination load on extraction cycle by partially removing certain of the troublesome fission products is of great importance in reprocessing plants [1]. One of the methods suggested for this reduction is the use of sorbents that is capable of adsorbing the troublesome fission products [2]. Some of the sorbents investigated by other workers are metal oxides, activated charcoal, bentonite, sludge's , silica and other sorbents [3-5]. Sometimes adsorption modifiers are added to these sorbents to improve the adsorption [6,7] . MnO_2 had also been investigated for its adsorption properties by many workers for purification of metals, separation of some fission products [8-11], and in environmental studies for purification and pre concentration of metals from sea water [8-11]. Continuing the research on head end removal of radio nuclides especially Ru^{103}, Ru^{106} and Ce^{144} would appear to be of great importance, Ruthenium removal [12]would be very important because the Ruthenium isotopes cause problems in almost every conceivable way. They contaminate the solvent , the uranium and plutonium product streams; they volatilize into the recovered acid and volatilize environment, and they deposit on all pipes and tanks causing personnel radiation. The Ce^{144} is worth some effort to remove because for relatively short-cooled fuels it is a major contributor (along with Zr^{95}, Nb^{95} and $Ru^{103-106}$ isotopes) to solvent radiation in the first solvent extraction cycle.

Experimental

The following analar grade materials were used in this work;

A- manganese -II- sulphate -1- hydrate ($MnSO_4.H_2O$) Riedel De-Haen production.
B-Potassium permanganate ($KMnO_4$) Riedel De-Haen production.
C- Nitric acid (HNO_3) diluted to the desire molarity .
D-Cerium-144, Ruthenium-103 and plutonium nitrate tracers provided from Amersham England.
E-Cerium-lll-nitrate-6-hydrate and Ruthenium-lll-chloride-3-hydrate Riedel De-Hean Product.

Preparation of Irradiated Uranium Sample: Fifty-milligrams uranium sample were irradiated for 72-hours in the Nuclear-Research Reactor and then dissolved in nitric acid after a cooling time of 1-2 months.

Preparation of manganese dioxide: Many forms of manganese dioxide are known, non-stoichiometric composition and hydrated compounds depending on the methods of preparation and drying temperature.

The manganese dioxide used in this work was prepared by adding drop wise $KMnO_4$ solution (21.3 grams per liter of water) to $MnSO_4$ solution (71.4 grams of $KMnO_4$ per liter of water) heated to about $90^{\circ}C$, the resulting MnO_2 was washed dried at $60^{\circ}C$ and subsequently sieved .The fraction between 100-170 mesh was used.

Kinetics Study: Kinetics study for radioisotopes Ce and Ru were done by shaking in a test tube 7.5 milliliter of 3M nitric acid containing 5 micro liter of the studied isotope with 0.05g of the prepared manganese dioxide. Then shaking for different time intervals ranging from 15 minutes to 7 hours were carried. After the end of the shaking time the test tube was centrifuged for 10 minutes at about 2000 rev/min. using centaur-2 centrifuge. One milliliter of the supernatant solution was taken for counting using NaI detector coupled to a single channel analyzer. For the adsorption kinetics of uranium, a 26 gU/l in 3M HNO_3 was equilibrated with MnO_2 for 15 minutes to 7 hours.

The uranium solution remaining in the aqueous phase was analyzed potentiometrically using Davis and Gray method[13].This method is based on the reduction of uranium (vi) to uranium(iv) in a concentrated phosphoric acid solution containing sulphamic acid.The excess of ferrous is subsequently oxidized by nitric acid in presence of molybdenum (vi) as catalyst after adding sulphuric acid and diluting the mixture with water, the determination is completed by titration with standard potassium dicromate solution using Metrohm Potentiometer by incremental addition .While the kinetics study of plutonium was done in a glove box using trace amounts of plutonium and the plutonium solution remaining not adsorbed being analyzed using α counting system .

Effect of different nitric acid concentration on adsorption capacity of MnO_2: Nitric acid Molarities between 1 and 4 were used. The experimental technique is as that described previously. Shaking time equals to 4 hours was found to be appropriate. The radioisotopes studied were Ce^{144} and Ru^{103}.

The experiments were conducted first on trace level then carriers were added to the system as $Ce(NO_3)_3.6H_2O$, $RuCl_3.3H_2O$. The concentration of the carriers was resembling the concentration of the corresponding fission product in EK-10fuel (14).

Uranium concentration equals to 26 g U/l was used in studying the effect of different concentrations of nitric acid on the absorption ability of MnO_2. While trace amounts were used for the plutonium experiments.

Effect of different temperatures on adsorption: The adsorption behavior of MnO_2 at different temperatures is studied. The temperatures used are 40, 50, 60, 70, 80 and 90°C. A thermostatic water bath was used throughout the work. In a test tube containing 7.5 ml 3M nitric acid , 5 micro liter of the studied tracer and 0.05g MnO_2 were shaken for 4 hours at a fixed thermostatic temperature. Then 1 millilitre of the supernatant solution was taken for counting.

Determination of capacity of adsorbent: This was investigated at 3M nitric acid with $7x10^{-4}$ mole of $MnO_2$and different moles of metal ions. The limiting adsorption capacities for each of the metal ions studied were found.

Irradiated uranium sample adsorption experiments: After choosing the appropriate parameters for the work, the experimental work was devoted towards experiments using irradiated fuel sample. In a test tube 7.5 milliliter of 3M nitric acid containing 25 micro liter of the dissolved fuel and 0.05 grams of manganese dioxide were shaken for 4 hours in a thermostatic water bath at 90°C.

The next step and in order to have a better simulation to the real process, addition of carriers to the fuel solution in concentrations resembling the concentration of the corresponding fission product in EK-10 fuel was done.

Results and Discussion

The results of the kinetics studies experiments are drawn in figure 1 for Ce, Ru and U. Adsorption variation with time was fast in the initial stages but then proceeds slowly and attains equilibrium after 4 hours of shaking for Ce and Ru. While one hour shaking was quite enough to attain equilibrium for U.

Adsorption of the troublesome fission products Ce and Ru on manganese dioxide was studied as a function of nitric acid concentration (1-4M). The results are depicted in figure 2. For the fission products adsorption decrease with an increase in electrolyte concentration. From one molar nitric acid solution being 84% for Ru and 28% for Ce which reduces to 30%

for Ru and 10% for Ce from four molar nitric acid. This acidity changes from (1-4M) affecte both the dissociation degree of adsorbents surface and speciation of metal ions. The adsorbent surface may be suggested as being surrounded by hydroxonium ions (H_3O^+),which prevent the metal ions to approach the binding sites of adsorbent surface .The speciation of metal ion may be explained on a basis of a mechanism involving prior hydrolysis of the metal to give a hydrolysis product which is hydrolytically adsorbed. Thus higher acid concentration would tend to suppress the hydrolysis of the metal ions studied (Ru, Ce) to a higher extent therefore, lower adsorption of the metal would take place from highly acidic solution[11].

Another parameter that influences adsorption is the concentration of the metal ion itself in solution. The adsorption of metal ion on the oxide was measured in both trace and macro amounts which corresponds to many folds of the predicted values (i.e. the fission products concentrations due to fuel burn up) obtained by ORIGIN program for EK-10 spent fuel[14]. The limiting adsorption capacities for Ce and Ru were found from the plots in figure 3, to be equal to 0.005 and 0.039 mole / mole MnO_2.

Temperature influence on the adsorption phenomena for Ce and Ru were studied from $25^{\circ}C$ up to $90^{\circ}C$, the plots in figure 4 shows a remarkable increase in percent adsorption of both fission products studied which indicates an endothermic process. No considerable change in percent adsorption was observed for uranium. For all cases adsorption for uranium was around 4%.

Working on plutonium showed no adsorption for all the acidities between 1 and 4M. The low adsorption percent of uranium and no adsorption for plutonium on MnO_2 surface may be due to large radii of both uranium and plutonium metal compared to smaller size of Ce and Ru[15].

Working on irradiated uranium sample by fixing the parameters that influences adsorption to four hours shaking time at temperature fixed to $90^{\circ}C$ and three molar nitric acid .While uranium and fission products concentrations were made to simulate the concentration of a real spent fuel pin[14] and finally adsorbent of 0.05 and 0.3 grams of MnO_2 were used as adsorbent. Table I gives the results obtained as adsorption percent were by increasing the sorbent dose from 0.05g to 0.3g of MnO_2 and keeping the other experimental parameters constant, a remarkable increase of adsorption percent is observed,67% of Ru and 23% of Ce that are originally present in real spent fuel were removed . This increase can be explained on the basis that the number of active sites in the sorbent surface increases which results in more metal ion can adsorb on the sorbent surface .Table 1 also shows a comparison of adsorption of metal ions with two different concentrations one trace and the other is macro gram quantities simulating the metal ions concentrations as given by Origin program at constant sorbent dose ,which indicate that 0.05g sorbent is not providing enough active sites for adsorption of metal ions.

Conclusions

1-A rapid initial adsorption on MnO_2 is followed by a steady and slow increase of metal uptake .The equilibration time is reached after 4 hours for both Ru and Ce

2-From one molar acidic solution, the adsorption is much better for both Ru and Ce than those at higher acidities .

3-Elavated temperature seems to be favorable for the adsorption phenomena. 4- 0.3g of the adsorbent could remove ,67% of Ru and 23% of Ce having the same composition as that of the real spent fuel given by Origin program.

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Table (1): Percent adsorption of Ru and Ce from a solution representing the real composition of spent fuel pin by 0.05g and 0.3g MnO_2.

Fission Product	Metal ions used is tracer only	Metal ions Conc. Used is according to theoretical value ref.(17)	
	Sorbent used 0.05g MnO_2	Sorbent used 0.05g MnO_2	0.3gMnO_2
Ru	73% Adsorption	4% Adsorption	67%Adsorption
Ce	21% Adsorption	19% Adsorption	23%Asorption

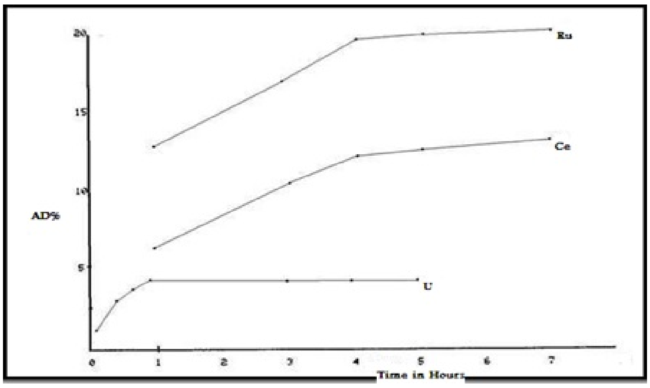

Fig .(1): Variation of adsorption percent (AD%) for U, Ce and Ru with shaking time from 3M HNO_3 solution.

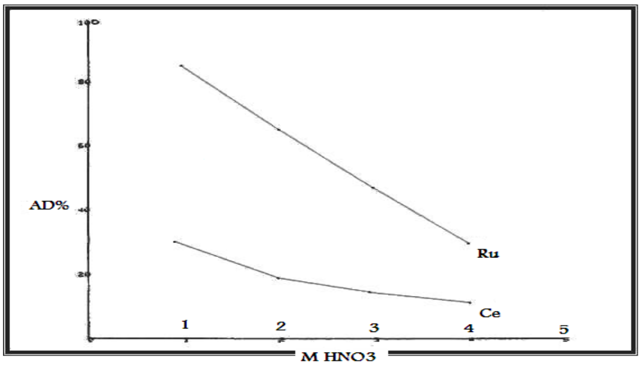

Fig.(2): Adsorption percent (AD%) of Ce and Ru as a function of nitric acid concentration.

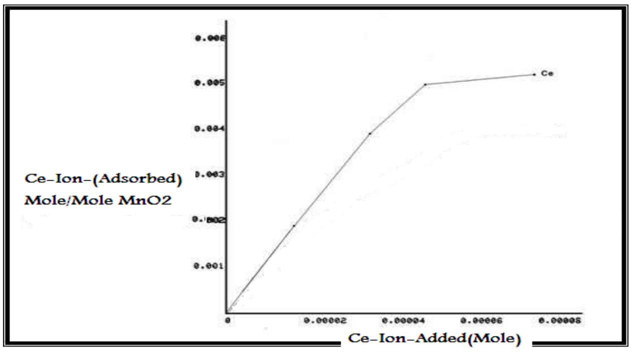

Fig.(3a): The limiting adsorption capacity of Ce metal on 0.05g MnO_2.

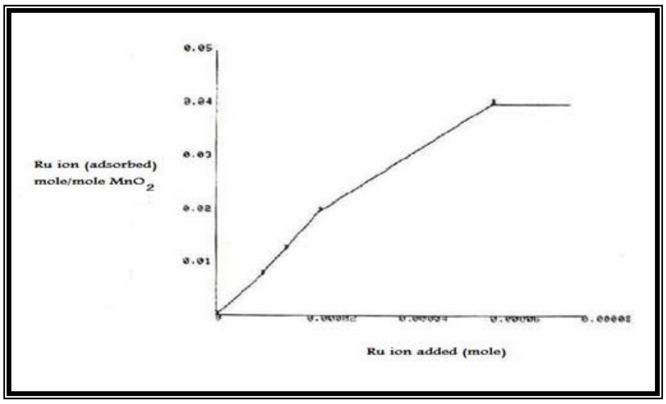

Fig.(3b): The limiting adsorption capacity of Ru metal on 0.05g MnO_2.

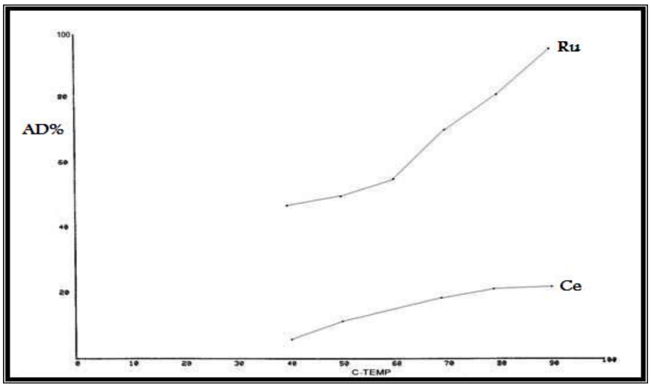

Fig.(4): Temperature influence on adsorption percent (AD%) of Ce and Ru.

دراسة الظروف المثلى لإزالة الروثينيوم و السيريوم باستعمال ثاني أوكسيد المنغنيز المحضر حديثاً

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الخلاصة

درست الظروف المثلى لإزالة الروثينيوم و السيريوم من خلال الامتزاز على ثاني أوكسيد المنغنيز وكذلك دراسة المتغيرات المؤثرة في عملية الامتزاز وهي زمن التماس وتراكيز حامض النتريك والمادة ألمازة وزيادة درجات الحرارة.

لوحظ زيادة سريعة في الامتزاز على MnO_2 يعقبه زيادة بسيطة و استقرا ريه حيث يتم الوصول إلى حالة التوازن بعد أربع ساعات من الرج لكل من الروثينيوم السيريوم ويكون الامتزاز أفضل في 1 مولاري حامض النتريك وبدرجات حرارة مرتفعة.

الكلمات المفتاحية : الامتزاز ، السيريوم ، الروثينيوم ، اليورانيوم .