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A method for adsorbing fission products from uranium solutions has been studied on the laboratory scale. More than 90 % of the ^{95}Zr- ^{95}Nb pair can be retained on colloidal silica from liquids simulating the dissolver solution of reprocessing plants.

INTRODUCTION

Although the number of nuclides produced during fission is very large, the number of fission products of real importance in reprocessing or the handling of irradiated nuclear fuel is limited to about a dozen. Most of these can be separated from uranium and plutonium in solution because they follow clean cut chemical reactions. In wet reprocessing it is mostly zirconium, niobium and ruthenium that depress the decontamination factors[1].

Ruthenium is known to form strong nitrosylruthenium complexes[2] some of which have high extraction coefficients in organic solvents. Zirconium and niobium are genetically related

as fission products and these elements have many physico-chemical properties in common such as their ability to form complexes, hydrolyzation products and colloids. In problems with interfaces, they are generally the main contaminants. Furthermore in typical thermal reactor fuel reprocessing the zirconium-niobium fraction of the fission products constitutes more than half of the total γ activity and is the strongest in the 600 - 800 keV energy group. Its elimination between the steps of dissolution of the fuel and extraction of the fissile products to be recovered is therefore highly desirable. This paper describes a possible procedure.

EXPERIMENTAL

Reagents

Stock solutions of zirconium were made up imitating conditions in the dissolver of a reprocessing plant, one with 2M nitric acid only and one with 0.4M nitric acid and 1.9M in aluminium nitrate /p.a. Mallinkrodt/. The zirconium used was nitrate /p.a. Merck/ irradiated in the RA-3 Reactor. Hafnium is a major contaminant in these cases. A stock of active solution of 100 mg/liter in nitric acid was made up from which aliquots were taken and boiled for five hours in the two acid solutions to imitate dissolver conditions.

Activation analysis was used for the zirconium determination using zirconium oxychloride /$ZrOCl_2.8H_2O$ p.a. Merck/ as standard.

Uranium solutions were made up from purified $UO_2/NO_3/_2.6H_2O$ and diluted to 200 and 2 g/l in both acid solutions.

To study the behaviour of neptunium, plutonium and fission products, a small amount of ^{237}Np was irradiated for one hour in the RA-3 Reactor with a flux of 10^{13}n cm^{-2} sec^{-1}. The amounts of ^{238}Pu and fission products produced in this way were sufficient to act as tracers.

Scavenging agents used were sodium metasilicate /$Na_2SiO_3.9H_2O$/ p.a.Baker/ and silica /"aerosil" Degussa/ with a specific area by B.E.T. of 330 $\pm$ 3 m^2/g [3].

The floculant used for the clarification of the solution was commercial gelatine.

Apparatus

Measurements were carried out with an Intertechnique BM-96 B multi-channel analyzer with Ge-Li crystal, which could resolve the Y-lines belonging to ^{95}Zr and ^{95}Nb or with a well-type NaI/Tl/ crystal.

Uranium determinations were made with a coulombimeter model XV-101 CNEA[4,5].

Clarification of solutions resulting from silica elimination was followed using spectrophotometry with a Beckman D.B.

Method used

Different solutions were boiled for five hours under reflux in glass vessels, after which a sample was taken. A known amount of scavenging agent was added and the solution stirred with a magnetic stirrer. The experiment was done at room temperature or otherwise boiled for a prefixed time. The solids were separated by adding 100 ppm floculant followed

by centrifugation, as described in a previous report[6]. The aqueous phase was then separated and analyzed. The amount of adsorbed ions was calculated by difference.

The uranium content in these solutions was varied from 0 to 200 g/l in 0.4M or 2M nitric acid. The time of stirring and separation of the phases ranged from 30 minutes to five hours. The amount of scavenging agent was progressively increased.

RESULTS

By using the individual lines from ^{95}Zr and ^{95}Nb as measured with the multi-channel analyzer, in all experiments it was found that niobium has, within the experimental error, the same behaviour as zirconium and hafnium during its adsorption. For this reason measurements by well counter showed the same adsorption values as those given by integrating individual gamma peaks.

Fig.1 shows the adsorption of the ^{95}Zr-^{95}Nb pair as a function of the concentration of the scavenger, expressed as SiO_2 g/l of solution. In the case of sodium metasilicate a

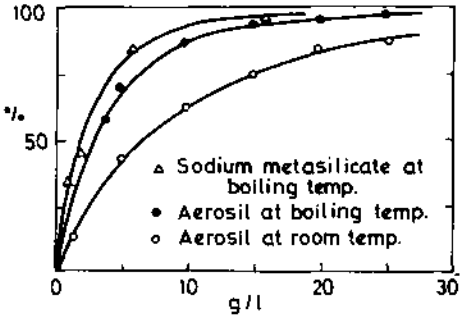

Fig.1. Percentage of absorption of the Zr-Nb pair as a function of the scavenger concentration at 2M HNO_3

gelation process takes place at concentrations higher than about 20 g/l, so that this procedure was discarded. It can be seen from this figure that aerosil is a better scavenging agent at boiling temperature than at room temperature.

Fig.2 shows the adsorption percentage of the Zr-Nb pair in 2M nitric acid on 10 g/l of SiO_2 /aerosil/ as function of stirring time at room temperature and at the boiling temperature. It follows that adsorption equilibrium is reached fairly

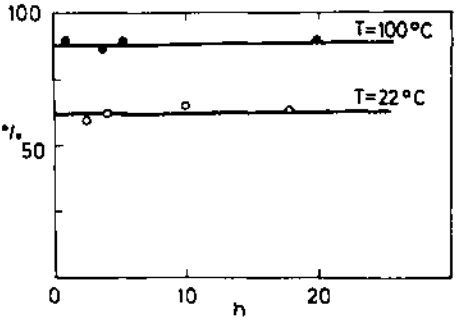

Fig.2. Percentage of absorption of the Zr-Nb pair as function of stirring time at 2M HNO_3 with 10 g/l SiO_2

quickly. An agitation time of five hours and a scavenger concentration of 10 g SiO_2/l solution was selected for further trials with Zr-Nb.

The same type of experiments were made on uranium solutions containing between 2 and 200 g U/l with 0.4 or 2M in nitric acid. In the case of the solution with 0.4M acid, 1.9M aluminium nitrate was added. Small amounts of irradiated ^{237}Np were also added in some cases.

Trials showed that uranium, neptunium and plutonium adsorption are not detectable in any case. The only detectable adsorption, apart from the Zr-Nb pair, was due to ^{233}Pa /53 %/

and ^{141}Ce /22 %/ in a solution with 2 g U/l 0.4M nitric acid and 1.9M aluminium nitrate.

Separate experiments indicated that the adsorption of the Zr-Nb pair does not change appreciably within the range of acidity studied. By repeating the adsorption process on the clarification solution it was found that a new Zr-Nb fraction could be extracted. In this way by using 10 g/l SiO_2 in the first step and 15 g/l SiO_2 in the second, it was found that more than 99 % of the pair could be eliminated.

A further advantage of the method is that the silica can be regenerated and the Zr-Nb pair recovered by washing with oxalic acid.

A possible explanation of the adsorption increase with the temperature of treatment could be an increase of superficial OH groups on the particles. Such behaviour is supported by previous studies on silica[7,8]. In this case the adsorption would mainly be due to ion exchange or the formation of superficial complexes.

REFERENCES

1. F.R.Bruce, Progress in Nuclear Energy, Series III, Vol.1 Pergamon Press, London /1956/ p.130.
2. J.M.Fletcher, Progress in Nuclear Energy, Series III, Vol. 1 Pergamon Press, /1956/ p.105.
3. A.J.G.Maroto, O.Griot, Anales Asoc.Quím.Arg., 58 /1970/ 175.
4. "Metodos Analiticos Planta de Reprocesamiento de elementos combustibles irradiados". Departamento de Reprocesamiento CNEA /1965/.
5. W.J.Krausse, G.A.Dupetit, CNEA/EN 192 /1967/.
6. C.A.Peluffo, A.J.G.Maroto, CNEA/EN, 22/69 /1972/.
7. O.Okkerse, J.H.Boer, Silicates Ind., 27 /1962/ 195.
8. A.J.G.Maroto, O.Griot, Com.Cientif. /Argentina/16 /1972/ 1.