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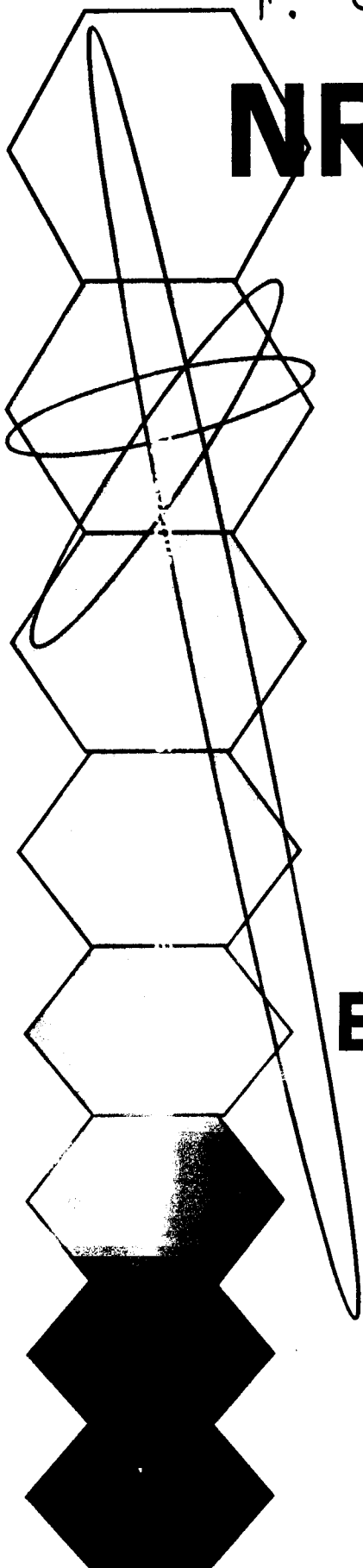
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RECOVERY CONTROL AND ANALYSIS OF TECHNETIUM-99 IN THE REPROCESSING OF SPENT FUEL

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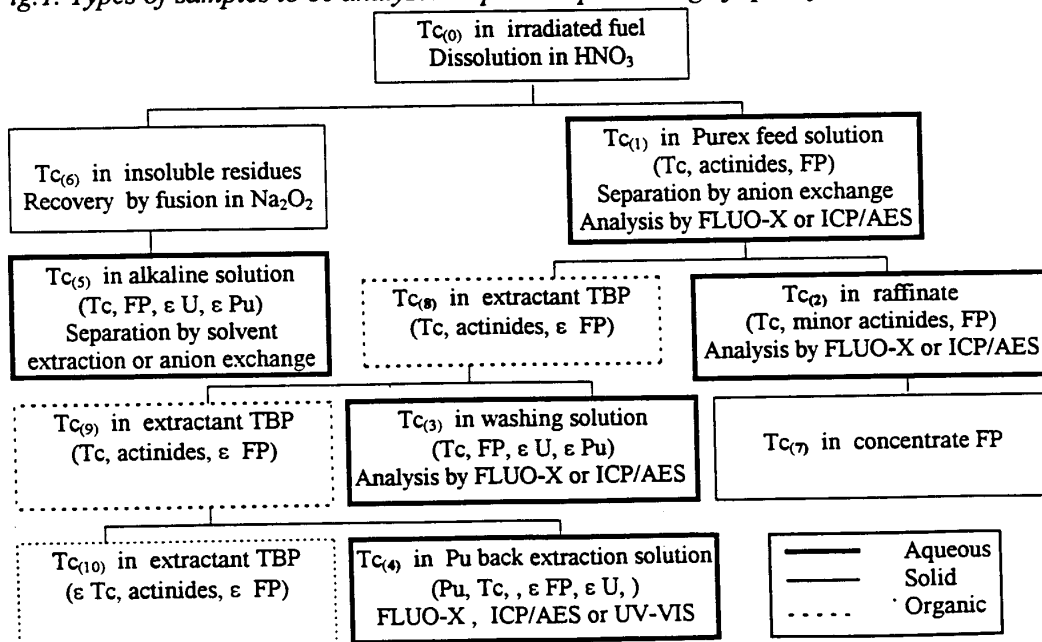
ABSTRACT

The work has been focused on the R&D of the methods of technetium analytical control in the spent fuel reprocessing solutions, insoluble residues and solid products. ⁹⁹Tc anion exchange and liquid extraction separation methods as well as preparation of technetium γ -tracers (⁹⁶Tc and ^{95m}Tc) and its application to recovery factor control were analyzed and developed. ICP/AES, FLUO-X and UV-VIS spectrophotometry were used for technetium detection. With respect to technetium conversion to carbide or metal, some structural, thermic and solubility properties of several intermediate pertechnetates with organic cations were studied.

1. INTRODUCTION.

The recent decades of the spent fuel reprocessing are marked with a special conclusion concerning technetium-99: due to possible effect on 1) the efficiency of U/Pu separation, 2) the radiochemical purity of retreated fuel, 3) the period of long-term storage of glassified wastes - it should be managed specially [1,2]. According to the distribution of technetium in purex reprocessing, more complicated when fuel burn-up is getting higher, this management concerns the great part of purex solutions and residues (see Fig. 1) and needs the adequate methods of analytical control, which are not evident as technetium-99,

Fig. 1. Types of samples to be analyzed in purex reprocessing of spent fuel.



on the contrary to the major part of the fission products, is not a γ -emitter.

For the analytical mass balance of technetium in this scheme it is normally enough to control the technetium presented in the aqueous phases. (Analysis in organic or solid phases is also possible, for example by ^{99}Tc -NMR [3], but neither this, nor the problems of debit control in the continuous and reflux processes were the subject of this presentation). Here we would like to discuss :

- the preparation of γ -tracers, $^{96}\text{Tc} / ^{95\text{m}}\text{Tc}$, and its application to recovery factor control,
- the preparation of samples for Tc control in the aqueous solutions and insoluble residues,
- the structural, thermal and solubility properties of several intermediate pertechnetates with organic cations perspective for technetium conversion to carbide or metal.

2. EXPERIMENTAL

All reagents were analytical grade. ICP/AES measurements were carried out at «Plasma 40» and «Plasma 400» Perkin Elmer spectrometers. Analyses FLUO-X were made at SIEMENS SRS 200 spectrometer. «Specord UV-VIS» and «Shimadzu UV-3101 PC» were used for the registration of electron spectra while «Specord M 40» and «Hitachi» - for vibrational ones. «Derivatograph Q 1500» and original thermobalances were used for the thermogravimetical study of thermal decomposition and volatility, «Mettler» balance - for gravimetry. Liquid scintillation counting was carried out at SL 20 Intertechnique and «Tri Carb 1000» Packard counters. Macroquantities of U and Pu were measured by FLUO-X, up to 10^{-5} mol/l of U we determined polarographically, smaller quantities by luminescent method.

3. PREPARATION OF $^{96}\text{Tc} / ^{95\text{m}}\text{Tc}$

Of the two types of possible γ -tracers ($^{96}\text{Tc} / ^{95\text{m}}\text{Tc}$ and $^{99}\text{Mo} / ^{99\text{m}}\text{Tc}$) we have chosen the one with the higher half-life time considering it more convenient for some long analytical procedures. Disc 10 g targets of natural molybdenum were irradiated with 25 MeV deuterons or 30 MeV protons at cyclotron of CERI (Orleans), producing $^{95\text{m}}\text{Tc}$ with the yield of 25 and 10,3 $\mu\text{Ci}/\mu\text{Ah}$ correspondingly, mainly according to the reactions of ^{96}Mo and ^{95}Mo presented (15,7 and 16,5%). This yield corresponded to 20 - 25% efficiency relative to this predicted for the thin target. After cooling of the targets for 1 week, two types of dissolution (in 15% $\text{H}_2\text{O}_2 + 1.5\text{M NH}_4\text{OH}$ or 7M HNO_3) were shown to be quite efficient, application of smaller or higher concentrations led to the formation of undesirable precipitates. After partial evaporation, the residue was dissolved in 3M NH_4OH . Liquid extraction with acetone or tetraheptylammonium chloride in CCl_4 , anion exchange and precipitation of Mo in form of BaMoO_4 were tested. In the last case 60 % of $^{95\text{m}}\text{Tc}$ is being lost as co-precipitate with molybdate. In case of anion exchange the lost of $^{95\text{m}}\text{Tc}$ was 20%. The best decontamination and recovery factors were obtained when the separation of $^{95\text{m}}\text{Tc}$ was carried out by liquid extraction with acetone from alkaline molybdate solution ($D_{\text{Tc/Mo}}=10^4$, $R=95\%$). On the application of this method the precautions should be taken to avoid the acetone polycondensation which could be achieved by rapid evaporation of acetone after the extraction stage. When higher activity was desirable, the decrease of cooling time permeated to obtain ^{96}Tc by analogous treatment of the same targets.

4. ANALYSIS OF Tc IN PUREX FEED SOLUTION

One of the problem of Tc analysis in purex process is the positive excess mass balance. The possible explanation could be the incomplete recovery of $\text{Tc}_{(1)}$ before analysis which is difficult to control in case of real solutions. There could be two reasons for this: incomplete sorption of TcO_4^- itself and co-existence of Tc in different chemical forms, some of which could be difficult to separate by anion exchange. Recovery factors for the anion exchange chromatographic separation of TcO_4^- from the simulated initial feeding

anion exchange chromatographic separation of TcO_4^- from the simulated initial feeding solution (1M $\text{UO}_2(\text{NO}_3)_2$ in 1M HNO_3) were determined with the help of $^{99\text{m}}\text{Tc}$ tracer prepared as mentioned above. To check the influence of ^{99}Tc concentration, three feeding solutions (with 1g-Tc/l, 0.1g-Tc/l and 0.01g-Tc/l) were tested. In all the cases the recovery factors were 99,9% and decontamination factors $D_{\text{Tc/U}}$ varied from 10^6 to 10^5 . As Tc in the tracer solution is present in TcO_4^- form only, it could not be used directly to verify the possibility of Tc co-existence in different chemical forms in dissolution process. On the contrary, the freshly irradiated Mo target at cyclotron if added to the dissolved fuel in real hot test could help to clarify the situation. To our mind the formation of non dissociated $\text{ZrO}(\text{TcO}_4)_x(\text{NO}_3)_{2-x}$ complexes or polymers could be also responsible for this phenomenon. The recovery factors for the liquid extraction separations from the simulated initial feeding solution (1M $\text{UO}_2(\text{NO}_3)_2$ in 1M HNO_3) were determined using the tetraheptylammonium chloride in the CCl_4 as extragent. The value of $R=96\%$ was obtained.

5. ANALYSIS OF Tc IN RAFFINATE, WASHING AND Pu BACK EXTRACTION SOLUTION

FLUO-X is traditionally used for Tc determination in nuclear fuel processing wastes [4]. Within this method the angles 2Θ of LiF 110 crystal analyzer were selected to ameliorate the selectivity of Tc direct determination in presence of either U or Pu. As low as 10 mg/l of Tc could be determined with the precision 1-3% in the solution of $80 \text{ g}\cdot\text{U}^{-1}$ ($2\Theta_{\text{TcK}\alpha} = 27^\circ 48$, $\text{KTcU} = 3,5 \cdot 10^{-4}$) or $8 \text{ g}\cdot\text{Pu}^{-1}$ ($2\Theta_{\text{TcK}\beta} = 24^\circ 38$, $\text{KTcPu} = 3 \cdot 10^{-3}$, precision 2-5%). $\text{Tc}_{(2)}$ in raffinate could be analyzed by ICP/AES.

6. ANALYSIS OF Tc IN INSOLUBLE RESIDUE

As technetium heptaoxide has an acidic character, application of alkali peroxides permitted to stabilize technetium as less volatile pertechnetates. Evaporation rates from 0.37 to 3.2 $\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}$ were reported for NaTcO_4 [5]. Kuranov and others have obtained by high temperature Knudsen effusion mass-spectrometry $\Delta H_{\text{evap}}(\text{KTcO}_4) = 213 \text{ kJ/mol}$ and $\Delta H_{\text{evap}}((\text{KTcO}_4)_2) = 282 \text{ kJ/mol}$ [6]. Gibson has confirmed evident evaporation of KTcO_4 and $(\text{KTcO}_4)_2$ into vacuum at 500 - 550 °C [7]. This value is too close to the temperature limit of standard fusion procedure. As evaporation rates under atmospheric pressure often differs from those in vacuum, we have carried out a thermogravimetric study of pertechnetate volatility. No sublimation of KTcO_4 and CsTcO_4 was noticed. Its vapor pressures were evident only after fusion. Sublimation of NaTcO_4 under atmospheric pressure starts at 620 - 640 °C. Evaporation rate decreased in the row $\text{NaTcO}_4 > \text{KTcO}_4 > \text{CsTcO}_4$ at 620 - 820 °C, but the situation is inverse at 850 - 1000 °C, indicating the lower ΔH_{evap} for NaTcO_4 . These observations permeated to utilize the standard fusion in $\text{Na}_2\text{O}_2 + \text{NaOH}$ at 450 - 550 °C for the leaching of technetium from insoluble residues together with other noble metals. After dissolution of resulting melt in water, technetium was removed from alkaline solution by anion exchange at macroporous anionite. Extraction with MEK was also used in some cases. $\text{Tc}_{(5)}$ in the resulting samples could be analyzed analogously to the determination of $\text{Tc}_{(1)}$ and $\text{Tc}_{(3)}$.

7. ANALYSIS OF STRUCTURAL, THERMAL AND SOLUBILITY PROPERTIES OF PERTECHNETATES PERSPECTIVE FOR Tc CONVERSION

In precipitation used to prepare the solid compound of technetium we have tested some different cations both traditionally used for Tc precipitation (for example - tetraphenylarsonium) and some new compounds containing only C,H,O,N - atoms, providing the waste which could be easily transformed into gases. Some properties being

valuable from technological point of view (solubility, densities, association constants) have been determined. In cold tests the corresponding rhenium compounds were synthesized and the characterized by their X-ray patterns, as earlier some of them were shown to be isostructural [8]

The solubility of new R_4NTcO_4 salts does not depend practically on the ionic forth of the solution but increases in the same manner as it was shown earlier for Bu_4TcO_4 [8] with the acidity of the solution, the later effect being higher as the size of cation increases.

Table 1. Properties of some Tc-99 compounds perspective for the precipitation and further conversion to technetium carbide (cubic, $a=3,98 \text{ \AA}$) or metal (hexagonal)

Pertechnetates of the following organic cations	Density, g/cm^3	Solubility in water at 25°C, mol/l	Preferable Tc conversion product
Tetramethylammonium	1,67	0.135 ± 0.005	Metal
Tetraethylammonium	1,34	$(2.5 \pm 0.7) \times 10^{-2}$	Metal
Tetrapropylammonium	1,26	$(8.7 \pm 0.2) \times 10^{-3}$	Metal/ Carbide
Tetrabutylammonium	1,17	$(4.3 \pm 0.20) \times 10^{-3}$	Metal/Carbide
Tetrapentylammonium	1,12	$(7.9 \pm 0.2) \times 10^{-4}$	Carbide
Tetrahexylammonium	1,07	$(7.1 \pm 0.5) \times 10^{-5}$	Carbide
Tetraheptylammonium	1,03	$(8.8 \pm 0.8) \times 10^{-6}$	Carbide
Triphenylguanidinium	1,15	$(3.9 \pm 0.3) \times 10^{-3}$	Carbide
Cetyltrimethylammonium	1,1	$(6,8 \pm 0.5) \times 10^{-3}$	Carbide
Tetraphenylarsonium	1,5	$(4.0 \pm 0.2) \times 10^{-4}$	Metal

After partial denitrification of simulated washing solution with formic acid, $Tc_{(3)}$ was precipitated in form of tetraalkylammonium pertechnetates. The thermal properties of the resulting compounds were tested at thermobalance and they were shown to be easily converted into technetium carbide or metal by thermal decomposition in argon or argon + 6% hydrogen correspondingly. The gaseous products were eliminated with gas carrier and burned in a special burner.

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REFERENCES

1. Phillips C. In : Waste Management'92. Vol.1. Eds.: R. Post & M.Wacks. p.1041 - 1045.
2. Kudryavtsev E.G., Egorov N.N., Lazarev L.N., Lubtsev R.I., et all., *ibid.* p.791 - 795.
3. Tarasov V.P., Kirakosyan G.A., Guerman K.E. *Z. Naturforsch.* 1992, v. 47a, p.325- 329.
4. Metcalf S.G. *Analytica Chimica acta.* 1977, v.93, p.297-299.
5. Guerman K.,Peretroukhine V.12 *Radiochem.conf. Marian.Lazne, May 1990, CSSR, Abs.* p. 24.
6. Kuranov K.,Semenov G. et all., 4-th USSR conf. on mass-spectr., Sumy,1986, Abst. N 3, p.89.
7. Gibson J.K. *Radiochimica acta,* 1993, v.62, p. 127 - 132.
8. Guerman K.E., Kryuchkov S.V., et all. *J.Radioanal.Nucl.Chem.,A.,* 1988, v. 121, No 2, p. 515.