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ANALYSIS OF TECHNETIUM IN SRP URANIUM PRODUCT STREAMS

by

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To: H. D. Harmon

From: E. G. Orebaugh *eg***ANALYSIS OF TECHNETIUM IN SRP URANIUM PRODUCT STREAMS****INTRODUCTION**

Technetium (Tc) is a major fission product with a fission yield similar to ^{90}Sr and ^{137}Cs . All traces of the natural element have disappeared due to decay over the earth's history. The major isotope present in cooled nuclear fuel is ^{99}Tc with a half life of 2.12×10^5 years. This isotope decays via low energy (0.292 Mev) beta emission which is easily absorbed and contributes little penetrating radiation hazards in fuel reprocessing.

Because it is difficult to detect, the distribution of ^{99}Tc in the F and H area process streams is not generally well known. An early report¹ on Tc distribution was published in 1959. More recent studies have emphasized its presence in SRP waste streams; its long half life makes it significant in the DWPF program².

SUMMARY

Previous studies have shown that a significant fraction of Tc follows uranium through the solvent extraction process. This study was conducted to analyze the ^{99}Tc content of SRP uranium product streams, to assess any hazard due to ^{99}Tc and to evaluate the impact of future higher burnup fuels on ^{99}Tc levels in uranium products. This summary report presents ^{99}Tc assays in uranium streams in F and H areas, relates these concentrations to solvent extraction conditions in the two areas, and compares the incremental radioactivity from ^{99}Tc in the product streams to the uranium itself. Presently the radioactivity contributed by ^{99}Tc is small relative to uranium. The proposed production using Mark 15 assemblies will also result in negligible increase in radioactivity due to ^{99}Tc .

DISCUSSION

Production of Tc

The production rates of Tc cited in this study are based on SRP reactor throughput during fiscal year 1983³. For F area, burnup of MK-31 targets (0.2% ²³⁵U) averaged 208 MWD/MTU. Technetium production can be calculated, given the fission yield is 6.1%:

$$\frac{208 \text{ MWD/MTU} \times 2.68 \times 10^{21} \text{ fissions/MWD} \times 99 \text{ gTc/moleTc} \times 0.061 \text{ moleTc/moleU}}{6.02 \times 10^{23} \text{ fissions/moleU}}$$

$$= 5.6 \text{ gTc/MTU} \quad \text{or} \quad 5.6 \times 10^{-6} \text{ gTc/gU} \quad \text{or} \quad 5.6 \text{ ppmTc/U}$$

For H-area the calculations are similar but require the weighted burnup of MK-16 and MK-22 drivers. When the weighted burnup is expressed in terms of g²³⁵U/gU the result is 31.1%. Therefore the ⁹⁹Tc production is given by:

$$0.311 \times 99/235 \text{ gmoleTc/gmoleU} \times 0.061 = 8 \times 10^{-3} \text{ gTc/gU charged}$$

But since we wish to reference the Tc to the residual total uranium:

$$8 \times 10^{-3} / (1 - 0.311) = 1.2 \times 10^{-2} \text{ gTc/gU residual or 12000 ppmTc/U}$$

These calculations show that H-area processes uranium with over 2000 times as much ⁹⁹Tc/gU as F-area. Because F-area processes about 200 times as much uranium per year, only about 10 times as much Tc is handled in H-area but at much higher concentrations. This result agrees with information from D. A. Sharp, NED.⁴

Distribution of Tc

Upon dissolution, the Tc produced in irradiated fuels and targets is oxidized to the pertechnetate ion (TcO_4^-). This anion might be expected to be rejected to the high activity waste during solvent extraction in F-area or H-area. However, some Tc is known to follow U through the process. Siddall¹ attributed this behavior to a substitution of pertechnetate for nitrate in the extracted uranyl nitrate.

The distribution of Tc throughout the solvent extraction process in both separations areas was investigated by analysis of those product streams in which Tc would be expected from its co-extraction with uranium. Results from analyzing the product streams are presented in Table 1. The 1 ppmTc/U found in the 1EU concentrate and A-line oxide indicates that about 18% of the Tc input to F-area is carried into the uranium oxide product. The 80 ppmTc/U observed in the H-area product amounts to only 0.7% of the calculated input to the enriched uranium process.

Table 1

Process stream sampled	area	assay ppmTc/U
1EU evaporator overheads	F-area	nil
1EU concentrate (420 g/l U in tank 17.7)	F-area	0.99 ppm
UO ₃ product from A-line denitrator	F-area	1.08 ppm
1DF adjusted feed (10 g/l in tank 17.5)	H-area	78 ppm
1EU enriched uranium product (tank 14.5)	H-area	82 ppm

Analysis of the uranium product stream from H-area was made more difficult by the 100 fold increase in ²³⁵U content. The neutron activation method employed for Tc analysis is susceptible to error caused by fission of any residual fissile materials. The anion exchange separation of Tc from the uranium was only marginally sufficient with highly enriched uranium. Therefore the similarity between the 1DF and the 1EU results from H-area should not be used to indicate that the coextraction of Tc in the second uranium cycle was highly efficient. Attempts to assay Tc in the waste streams failed due to contamination by ¹²⁹I. Since our primary purpose was to assay the uranium product, no further effort was expended on the waste stream analysis.

There was an initial concern that Tc might volatilize via its acid anhydride, but the 1EU evaporator overheads in F-area were found to have insignificant Tc content. This observed low volatility is to be expected for a highly ionized dilute acid. Prior studies^{1,5} have shown that volatilization of Tc during denitration in the A-line was no concern even though temperatures far exceed the boiling point of Tc₂O₇.

The Solvent Extraction Behavior of Technetium

The great difference in the solvent extraction behavior of Tc between the F and H-areas can be understood from the original published work of Siddall and the recent studies⁶⁻¹⁰ by other nuclear chemistry groups.

There is general agreement that pertechnetic acid partitions between TBP extractant and aqueous solutions in a manner which is acid dependent as represented by the following equation:

However, the extraction into the organic phase in the presence of uranium is many times that of pertechnetic acid alone. The mechanism for this enhanced extraction of Tc is believed to follow the equation:

Because extraction by this second mechanism is more effective than by the first, and since the second mechanism does not explicitly depend upon the acid concentration, it follows that extraction of the pertechnetate is proportional to the amount of uranyl nitrate TBP adduct⁹⁻¹¹.

Since the relative uranium loadings in both F and H area 1A-banks are approximately equal, then the 7.5%/30% ratio of the TBP should limit the entrained Tc in H-area 1AP to one fourth the amount in F-area 1AP. The assumption is reasonable since the banks are operated with the dual constraints of low uranium losses (excess TBP to assure efficient U extraction) and high fission product decontamination (achieved by high U saturation of the extractant). Again, if the relative loading in the second uranium cycles of both areas are nearly equal one would expect the overall entrainment of Tc to be one sixteenth (one fourth in the first cycle times one fourth in the second cycle) as great in H-area U product as the F-area. The results in Table 1 actually give a ratio of 27. In view of the assumptions made, the agreement between predicted and observed ratios provides reasonable support for Siddall's model.

Radiation Due to ⁹⁹Tc in Uranium Finishing

Radiation considerations due to ⁹⁹Tc in uranium products arise from either increased exposure to personnel involved in U finishing or in subsequent operations if the uranium is assumed to be free of radioactive contaminants.

For the purpose of this analysis the radioactivity contributed by ⁹⁹Tc contamination was compared to the radioactivity of its uranium host. The radioactivity of the F area uranium product under current operations is almost entirely due to ²³⁸U. Since ²³⁵U has a shorter half life than ²³⁸U, enriched uranium has a greater radiological hazard on a weight basis. In addition, enriched fuels accumulate ²³⁶U with each cycle through the reactor. The ²³⁶U adds significantly to the radiological hazard of U but since its abundance depends upon the radiation history of the fuel, the Tc hazard was normalized to the sum of ²³⁸U and ²³⁵U isotopes only.

If doubling of the radiological hazard of the host uranium due to Tc contamination is considered a threshold of significance, then the F-area A-line product must be below 19 ppmTc/U while the H-area product can be as high as 125 ppmTc/U without doubling the specific activity (excluding ²³⁶U) of the end product. This study shows that both F and H areas are within this criteria and can be expected to remain so with the current flowsheets and nuclear materials mixture.

The proposed processing of MK-15 assemblies in F-area (irradiated to 65.5 kWWD/charge) would result in only a 14% increase in activity due to Tc assuming the current flowsheet carry through rates. This result is surprising since the MK-15 assemblies combine the functions of enriched driver and target of the current reactor charges and might be expected to have a higher radiological significance due to Tc. However, the shielding calculations made by P. B. Parks⁴, NED, for the isotopic mixture expected after the programmed irradiation show that the short irradiations necessary to limit the production of ²⁴⁰Pu combined with the only slightly enriched ²³⁵U content limit the relative specific

activity of the Tc fission products. Again this is conservative since the ^{236}U isotopes are not included.

CONCLUSIONS

Technetium fission products are a significant contaminant of uranium recovered from nuclear fuels and targets using solvent extraction processes based upon TBP. However, the radiological significance of this contaminant is small due to its long half-life and its low energy emissions which are highly shielded by the uranium host. Current operations produce a uranium product in both F and H-areas in which the Tc contamination contributes less to the radiological activity than the bulk uranium. Similarly, future processing of MK-15 fuels in F area will present no increase in hazards due to Tc content. This study has determined that uranium product contamination by Tc is not casual but is predictable for a given flowsheet and "burn-up" history of the fuel being processed.

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