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TECHNETIUM-99 IN SRP HIGH-LEVEL WASTE AND SALTSTONE

by

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MEMORANDUM

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TO: G. W. WILDS/ E. L. ALBENESIUS

FROM: J. R. FOWLER, B. A. HAMM, J. R. COOK

J.R. Fowler *B.A. Hamm* *J.R. Cook*

TECHNETIUM-99 IN SRP HIGH-LEVEL WASTE AND SALTSTONE

SUMMARY

Analyses of sludge and soluble waste samples¹⁻³ and the inventory of sludge⁴ and soluble waste^{5,6} have been used to estimate the concentration of technetium-99 (Tc-99) in sludge solids and soluble waste. These data were also used to establish if the source term assumptions for Tc-99 in the Defense Waste Processing Facility (DWPF) flowsheet are accurate and determine the fraction of the Tc-99 inventory in the waste that is soluble. This analysis was needed to establish if the present basis for decontaminated salt feed to the saltstone process is correct.⁷ These results and the projected leach rate for Tc-99 from saltstone can then be used to establish if Tc-99 must be removed from contaminated supernate.

Results show:

- o The inventory of Tc-99 is 31,050 Ci in sludge and soluble waste.

- o "Average" dissolved salt feed to saltstone will contain 0.096 mCi/liter (400 g salt/liter X 240 nCi/g salt) without Tc removal. This level corresponds to 74 nCi/g of solution and is a factor of 2.4X higher than previously assumed.
- o The higher Tc-99 concentration is approximately an order of magnitude lower than the limit imposed by EPA regulations; Tc removal is not required.
- o The source term calculated from experimental data agrees well with the source term calculated from fission yield in the present DWPF flowsheet.
- o Approximately 57% of the Tc-99 is soluble compared to 30% previously assumed.

INTRODUCTION

An in-tank process based on precipitation of cesium tetraphenylborate effectively removes radioactive cesium from soluble waste^{3,8}. The major long-lived radionuclide remaining in the decontaminated filtrate from this process is Tc-99, a weak beta-emitter with a half-life of 2.13×10^5 years.³ Methods to remove Tc-99 from decontaminated salt solution have been developed if removal is required or desired.⁹⁻¹² An estimate of the Tc-99 waste inventory based on experimental data was needed to establish if Tc-99 should be removed from the salt solution before converting it to saltstone.

DISCUSSION

A. Source of Tc-99 in SRP Waste

Tc-99 is a fission product in spent fuel and targets from the SRP and off-site reactors. The source term used in the DWPF flowsheet for Tc-99 is based on fission yield calculations from an assumed mix of depleted uranium targets, enriched uranium fuel tubes from SRP reactors and spent fuel from off-site reactors.

All of the Tc-99 present in these fuels and targets is assumed to be diverted to the waste tanks as a result of processes in the Separations Areas. Because of the diversity of materials that have been processed at SRP and assumptions on splits in the Separation Areas, the source term shown in the DWPF flowsheet for Tc-99 (or any other fission product) may not accurately reflect the actual inventory of fission products in the waste.¹⁴

During processing in the Separation Areas, nitric acid oxidizes Tc to higher oxidation states. None of the isotopes of Tc are stable with respect to nuclear decay. Consequently, Tc does not occur in nature and the chemistry of Tc has not been extensively studied except at nuclear sites.

Table I shows probable reactions for Tc during fuel dissolution with nitric acid. Tc has been found in both soluble and insoluble components of SRP waste. Available data show that hydrated technetium(IV) oxide is the most likely species in the sludge while sodium pertechnetate is the most likely species in the soluble salt.¹²

B. Tc-99 in Soluble Waste

Tc-99 analyses have been done on several SRP soluble waste samples.¹⁻³ Available data for soluble waste were averaged to establish the concentration of Tc-99 in each of the waste types (Table II). Using these averages and the estimated inventory of soluble waste,^{5,6} the total inventory of Tc-99 in the soluble waste was calculated. The concentration of Tc-99 in "average" salt is 240 nCi/g of salt. Results from these calculations are shown in Table III.

C. Tc-99 in Sludge

Calculations for sludge were similar to those used for soluble waste. Available data^{1,2} for sludge samples were averaged to establish the concentration of Tc-99 in each type of sludge presently stored in the tank farm (Table IV). Using these averages and the estimated sludge inventory,⁴ the total inventory of Tc-99 in sludge was calculated. The concentration of Tc-99 in "average" sludge is 4470 nCi/g of dry sludge solids. Results for these calculations are shown in Table V.

D. Tc-99 Source Term for the DWPF Flowsheet

Source terms for fission products in the DWPF flowsheet are based on "as-received, average" waste that is allowed to age either 5 or 15 years without regard to any segregation between soluble and insoluble waste components (see A. above for additional bases). Each gallon of "average" waste is assumed to contain 2.944 lbs of salt (1336 g/gal) and 0.145 lbs of insoluble solids (65.8 g/gal).¹⁴

Using these values for "average" waste and the average Tc-99 concentrations shown in Tables II and III for salt and sludge, the Tc-99 source term and the soluble fraction were calculated for the DWPF flowsheet. Results of these calculations are shown in Table VI. The source term obtained from experimental data is comparable to the value obtained from fission yield calculations, but the fraction soluble is approximately double the value previously assumed for the DWPF flowsheet.⁷ Accordingly, the solubility factor used in the flowsheet should be changed to reflect more of the Tc-99 being diverted to the soluble waste.

E. Tc-99 in Decontaminated Soluble Waste

The flowsheet for the "Saltstone" process assumes that 32 wt% solution of decontaminated salt in water will be combined with cement to produce "Saltstone".¹³ The density of 32 wt% solution of "average" salt is 1.27 kg/liter and would contain approximately 400 g of salt/liter.⁷

Based on an average concentration of Tc-99 equal to 240 nCi/g of dry salt (see Table II), feed to saltstone would contain 0.096 mCi Tc-99/liter of solution (0.36 mCi/gallon). Based on the density of "average" salt solution, 74 nCi of Tc-99 would be present in each gram of decontaminated solution. This level is 2.4 times higher than previously assumed.^{7,13}

F. Tc-99 from Saltstone

The latest mathematical modeling work done by Intera Environmental Consultants indicates that with the current saltstone formulation the concentration of Tc-99 in groundwater should be 45 pCi/liter, using the old source term. Increasing the source term by a factor of 2.4 increases the groundwater concentration to 110 pCi/liter, which is almost an order of magnitude below the EPA National Primary Drinking Water Regulation limit of 900 pCi/liter. Thus the present saltstone formulation will prevent the increased Tc in the feed solution from adversely affecting the environment.

QUALITY ASSURANCE

Data used in these calculations is the best available at the time of writing. Additional sampling and analyses of the waste tanks is planned to broaden the data base for Tc-99 in the waste. When necessary, blind controls will be submitted with these new samples to assure that the quality of data is maintained. These calculations will be updated as required when additional data is available.

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TABLE IPROCESS CHEMISTRY FOR TECHNETIUM IN F AND H AREAS

o Tc present in both sludge and supernate.

TABLE IIDESCRIPTION AND ANALYSES OF SOLUBLE WASTE SAMPLES

<u>SAMPLE TYPE</u>	<u>SOURCE</u>	<u>g SALT/liter</u>	<u>[Tc-99] nCi/g SALT</u>	<u>REF/METHOD (a)</u>
PUREX HAW:	4F	172	680	2/H
PUREX LAW	8F	225	160	2/H
PUREX LAW	8F	185	200	2/H
PUREX LAW	8F	122	180	2/H
PUREX LAW	8F	273	110	2/H
PUREX LAW	8F	273	100	2/H
PUREX LAW	8F	273	110	2/H
PUREX LAW	8F	273	110	2/H
PUREX LAW AVERAGE:			140	
PUREX CONC. SN:	47F	668	430	1/H
PUREX SALT	1F	N.A. (b)	20	1/H
PUREX SALT	1F	N.A.	160	1/H
DISS. PUREX SALT	19F	296	20	1/H
DISS. PUREX SALT	20F	557	60	1/H
PUREX SALT AVERAGE:			60	
HM HAW:	32H	388	620	1/N
HM LAW:	13H	593(c)	670	1/H
HM CONC. SN:	30H	1139	360	1/N
HM SALT	9H	N.A.	4	1/N
HM SALT	10H	N.A.	6	1/N
DISS. HM SALT	24H	444	170	1/H
DISS. HM SALT	24H	593	40	1/H
DISS. HM SALT	24H	575	170	1/H
DISS. HM SALT	24H	420	70	3/H
DISS. HM SALT	24H	470	80	3/H
DISS. HM SALT	24H	388	100	3/H
HM SALT AVERAGE:			80	

(a) H = Hanford Method; N = Neutron Activation Analysis Method.

(b) N.A. = Not applicable.

(c) High salt level indicates this sample is a blend of conc. SN and HM LAW placed in Tank 13H for feeding the waste evaporator.

TABLE III
INVENTORY OF SOLUBLE Tc-99 IN THE WASTE TANKS

<u>WASTE COMPONENT</u>	<u>INVENTORY MET. TONS</u>	<u>[Tc-99] nCi/g</u>	<u>TOTAL CURIES Tc-99</u>
H-AREA:			
HM HAW SN	4900	620	3040
HM LAW SN	4400	670	2950
HM CONC. SN	11000	360	3960
HM SALT	19000	80	1520
Al DISS. ADD'N	1800	---	---
 H-AREA SOLUBLE WASTE	 41100	 290 nCi/g	 11470
F-AREA:			
PUREX HAW SN	800	680	540
PUREX LAW SN	2500	140	350
COATING WASTE	1100	--	--
PUREX CONC. SN	14000	430	6020
PUREX SALT	21000	60	1260
 F-AREA SOLUBLE WASTE	 39400	 280 nCi/g	 8170
 TOTAL SOLUBLE WASTE	 80500	 240 nCi/g	 19640

- o Tc-99 previously estimated to be 100 nCi/g in soluble waste (DPST-82-759).

TABLE IV
DESCRIPTION AND ANALYSES OF SLUDGE SAMPLES

<u>SAMPLE TYPE</u>	<u>SOURCE</u>	<u>[Tc-99] nCi/g SLUDGE</u>	<u>REF/METHOD*</u>
PUREX HAW	4F	2090	2/H
PUREX LAW	8F	280	2/H
PUREX LAW	8F	580	2/H
PUREX LAW	8F	190	2/H
PUREX LAW	8F	410	2/H
PUREX LAW	8F	1100	2/H
PUREX LAW	8F	400	2/H
PUREX LAW	8F	1100	2/H
PUREX LAW	8F	770	2/H
PUREX LAW	8F	210	2/H
PUREX LAW	8F	240	2/H
PUREX LAW	8F	1900	2/H
PUREX LAW	8F	1100	2/H
PUREX LAW	8F	1090	2/H
PUREX LAW SLUDGE AVERAGE:		720	
HM HAW (38 SAMPLES)	15H, 11H	8340	2/H, 1/H
HM LAW	13H	1640	1/H

* H = Hanford Method

TABLE V
INVENTORY OF Tc-99 IN SLUDGE SOLIDS

<u>SLUDGE TYPE</u>	<u>DRY SLUDGE INVENTORY MET. TONS</u>	<u>[Tc-99] nCi/g</u>	<u>TOTAL Ci Tc-99</u>
HM HAW	1060	8340	8840
HM LAW	390	1640	640
H-AREA SLUDGE	1450	6540	9480
PUREX HAW	550	2090	1150
PUREX LAW	1080	720	780
F-AREA SLUDGE	1630	1140	1930
TOTAL SLUDGE INVENTORY	3080	3700	11410
Al-DISSOLVED SLUDGE	2250	4470	11410

o Total inventory of Tc-99 (sludge + salt) = 31050 Ci.

TABLE VITc-99 SOURCE TERM FOR THE DWPF FLOWSHEET

<u>Isotope</u>	<u>Ci/gal</u>		<u>% Soluble</u>	
	<u>Old</u>	<u>New</u>	<u>Old</u>	<u>New</u>
Tc-99	5.5E-4	5.6E-4	30	57

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