ULTRA-SENSITIVE MASS SPECTROMETRIC AND OTHER METHODS APPLIED TO ENVIRONMENTAL PROBLEMS

Distribution of ^{99}Tc and ^{129}I in the vicinity of underground nuclear tests at the Nevada Test Site

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^{99}Tc and ^{129}I are important contributors to risk assessment due to their long half-lives and high mobility as aqueous anionic species. We analyzed ^{99}Tc and ^{129}I in groundwater samples in and near 11 underground nuclear tests and in melt glass and rock samples retrieved from the Chancellor test cavity, Nevada Test Site. The ^{129}I/^{127}I ratio ranges from 10^{-3} to 10^{-6} in cavity water and 10^{-4} to 10^{-9} in satellite wells. The ^{99}Tc concentration ranges from 3 to 10^{-4} Bq/l in cavity waters and from 0.3 to 10^{-4} Bq/l in satellite wells. Downstream migration is apparent for both radionuclides. However, it is affected by both retardation and initial distribution. In-situ ^{99}Tc and ^{129}I K_ds calculated using rubble and water concentrations are 3 to 22 ml/g and 0 to 0.12 ml/g, respectively, and are suggestive of mildly reducing conditions. ^{129}I distribution in the melt glass, rubble and groundwater of the Chancellor test cavity is 28%, 24% and 48%, respectively, for ^{99}Tc, it is 65%, 35% and 0.3%, respectively. Our partitioning estimates differ from those of underground tests in French Polynesia, implying that fission product distribution may vary from test to test. Factors that may influence this distribution include geologic conditions (e.g., lithology, water and CO_2 content) and the cooling history of the test cavity.

Introduction

^{99}Tc and ^{129}I are actinide fission products with long half-lives ($2.15 \cdot 10^5$ years and $1.57 \cdot 10^7$ years, respectively), both of which occur as high-solubility anionic species in groundwater. Due to their weak sorption characteristics, both ^{99}Tc and ^{129}I have a high potential for migration in the subsurface environment.

At underground nuclear testing sites, the migration of ^{99}Tc and ^{129}I in groundwater is influenced by the initial distribution of these radionuclides in nuclear test debris. Unfortunately, very little information is available on this initial distribution. Our current understanding of ^{99}Tc and ^{129}I distribution within the test cavity-chimney is based primarily on IAEA experience from French underground tests in French Polynesia.[1] Based on both physical and chemical characteristics, the fraction of ^{99}Tc and ^{129}I incorporated into melt glass from an underground nuclear test was estimated to be 80% and 50%, respectively.

The main objectives of this investigation were to: (1) measure the ^{99}Tc and ^{129}I concentrations in melt glass and rubble samples from an underground test cavity, and use the results to empirically assess the IAEA partitioning estimates; (2) measure ^{99}Tc and ^{129}I in groundwater samples from a number of NTS near-field wells; and (3) compare groundwater and test debris data to determine water-rock partitioning (K_d).

Experimental

Sample preparation

Technetium analyses: For groundwater samples, we used TEVA resin columns to enrich and separate ^{99}Tc from interfering elements.[2] Depending on the ^{99}Tc concentration, sample volumes of 10 ml to 2 liters were used. For melt glass and rock samples, a fusion method[3,4] was used wherein a powdered sample was reacted sodium peroxide and low carbonate sodium hydroxide at 700 °C for 30 minutes. This method is effective in fusing all rock-forming minerals while minimizing Tc volatilization (and hence, potential loss) during the digestion process. The fusion cake was then dissolved in nitric acid and a TEVA column was used to separate and purify the ^{99}Tc. A modified isotope dilution ICP-MS method was used for ^{99}Tc analyses. We used NIST SRM-4288A and an aqueous solution of 32.61 ± 0.37 kBq/g ^{99}Tc(VII) in $1 \cdot 10^{-3}$M KOH as ^{99}Tc reference standards. Stable rhenium was spiked in each sample (both groundwater and solid) as a tracer to monitor rhenium and, by analogy, ^{99}Tc recovery.

Iodine analyses: NTS groundwater samples are normally in the neutral to slightly alkaline pH range and were directly analyzed for stable iodine after spiking with 5 µg/l of internal standard (rhodium, Rh) in 1% CFA-C. The CFA-C is a surfactant that coats the glassware and reduces the memory effect of iodine in the ICP-MS introduction system.[5] Groundwater samples were prepared for ^{129}I analysis on the Accelerator Mass Spectrometer (AMS) using standard methods reported in the literature.[6]

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A microwave sample preparation system was used to digest and extract iodine from melt glass and rock samples. 4 ml of 5% tetra-methyl ammonium hydroxide (TMAH) solution was added to 0.5–1 g of powdered sample in a Teflon vessel for the microwave digestion.[7–9] The power level and time for each digestion stage were programmed to reach a maximum value of 800 W over 15 minutes, and held there for an additional 10 minutes. To minimize potential iodine loss, the maximum temperature and pressure was not allowed to exceed 90 °C and 1241 kPa, respectively. After digestion, 6 ml of 1% CFA-C was added to the sample vessel. The total iodine in the supernatant was analyzed directly by ICP-MS. The ^{129}I targets were made using a stable ^{127}I carrier containing low ^{129}I to form AgI solid,[10] the ^{129}I/^{127}I ratio was measured by AMS.

Results and discussion

Results of groundwater samples

A total of 24 groundwater samples from 13 sampling sites were analyzed for ^{99}Tc and ^{129}I. Table 1 presents the measured ^{99}Tc concentrations in NTS groundwater samples using the ICP-MS method. For comparison, data from independent AMS[11] and liquid scintillation counting (LSC; this study) measurements of the same samples are also included. Measurement uncertainties reported in Table 1 are calculated from replicate analyses. The instrumental uncertainties for ^{99}Tc and ^{129}I analyses are <2% by ICP-MS measurements and 2–4% for ^{129}I/^{127}I ratio measurements by AMS. However, the error propagation in overall procedures for groundwater samples is between 5–10%. Table 1 also includes an Irish Sea Water sample as a reference standard.[11] Our measured ^{99}Tc value for the reference standard is in good agreement with the accepted value (0.22±0.01 Bq/l).

In general, cavity water samples contained higher concentrations of ^{99}Tc compared to near-field satellite wells. The highest values were observed in well U-3cn PS2a (the Bilby test), with 3.1 Bq/l in 2001 and 2.3 Bq/l in 2004. Only three NTS near-field wells have produced water with ^{99}Tc activities above 1 Bq/l. Concentrations lower than 0.3 mBq/l ^{99}Tc were found in near-field satellite monitoring wells. Downstream migration of ^{99}Tc is apparent. However, local geochemical conditions, such as reducing conditions (sometimes encountered in test cavities) may be limiting ^{99}Tc migration from the test cavity.

Using Re to trace extraction efficiency, the ^{99}Tc concentration in U-19ad PS1A groundwater (Chancellor test) was measured to be 1.70±0.01 Bq/l. This value was confirmed by an independent set of standard addition measurements. Using a TEVA column for pre-concentration and purification of 1-liter water samples,

ICP-MS can provide a ^{99}Tc method detection limit (MDL) of 0.13 mBq/l. This is about one order of magnitude higher than that achieved by AMS, which has a reported MDL of 0.01 mBq or 1·10^8 atoms with 15–25% error for a 1-liter sample volume.[11] The LSC detection limit is ~37 mBq/l.

The total stable ^{127}I concentrations, ^{129}I/^{127}I ratios, and corresponding ^{129}I activities in NTS groundwaters are also reported in Table 1. The ratio of ^{129}I/^{127}I in cavity and satellite well samples range from 10^{-3} to 10^{-6} and 10^{-4} to 10^{-9}, respectively. The ^{129}I/^{127}I ratio of uncontaminated environmental samples is $\leq 10^{-13}$. The results suggest that ^{129}I is migrating at a rate similar to ^{99}Tc.

Results of solid samples

Melt glass and rubble samples were recovered from the Chancellor (U-19ad) underground test cavity during a drilling operation in 2004. Figure 1 shows the spatial distribution of samples collected from the test cavity. Samples were chosen over a wide depth interval (~130 meters). Table 2 lists the measured ^{99}Tc, total iodine, and ^{129}I/^{127}I ratios in the test debris samples. The uncertainties in measurements of ^{99}Tc and ^{129}I/^{127}I ratios for the solid samples are similar to if not smaller than those for the water samples. We obtained >95% chemical recovery of total iodine from three IAEA/SRM soil samples using the microwave digestion/TMAH extraction method. However, iodine recovery in melt glass samples may be lower due to the difference in sample matrix (soil vs. melt glass). We are currently assessing the quartz tube combustion method reported by MURAMATSU and WEDEPOHL[12] for total iodine measurement in rock samples.

^{99}Tc concentrations correlate with sample type. ^{99}Tc in the dark melt glass exhibits a fairly uniform distribution, with a narrow range of 600–750 ng/kg. The non-melted volcanic rock contains <100 ng/kg ^{99}Tc. The ^{129}I activities in the solid samples range from 0.006 to 83 mBq/kg with highest concentrations found in the dark melt glass samples. The two samples (CH01a and b) that have very low ^{129}I activities also have the lowest ^{99}Tc concentrations of all samples.

Radionuclide distribution in a test cavity

Based on the announced yield of the Chancellor test (143 kt of TNT equivalent),[13] the depth of burial, and the bulk density of the overlying rock, we estimate the test cavity radius[14] and generated mass of melt glass[15] to be 61 m and ~1.43·10^8 kg, respectively. Assuming a density of 2.5 g/cm^3 and porosity of 30% for the melt glass and test debris, we can estimate the volume of melt glass and rubble in the cavity.

Table 1. Technetium and iodine in NTS groundwater samples

Test name	Sampling well/location	Sampling date	^{99}Tc (ICP-MS), Bq/l	^{99}Tc (other methods), Bq/l	Total iodine, µg/l	^{129}I/^{127}I	^{129}I, mBq/l
Aleman	UE-3e #4; 58 m from working point	09/23/1998	0.32 ± 0.01	0.48 ± 0.01 [a]	11.3	n.a.	n.a.
Almendro	U-19v PS1ds; Cavity/chimney	08/18/1999	2.8E-03	n.a.	7.4	1.06E-03	53
		07/23/2003	4.1E-04	n.a.	10.1	1.41E-03	95
Bilby	U-3cn PS2; Chimney	12/18/2001	3.06 ± 0.03	2.96 [b]	9.1	9.74E-05	5.9
		12/09/2004	2.32 ± 0.23	2.50 ± 0.07 [b]	9.5	1.48E-04	9.4
Bourbon	UE-7nS; 137 m from working point	08/21/2001	<0.04	n.a.	23.1	1.47E-07	0.023
	RNM-1; Cavity	06/03/2004	<1.3E-4	<0.037 [b]	16.2	2.06E-07	0.022
Cambric	RNM-2S; 91 m from working point	10/11/1999	<1.3E-5	(4.8 ± 2.6)×1E-5 [a]	11	2.12E-07	0.016
		07/10/2003	<1.3E-6	n.a.	12.2	6.16E-07	0.050
	UE-5n; 510 m from RNM-2S	09/09/1999	1.7E-04	(8.5 ± 7.0)×1E-5 [a]	30	3.51E-09	0.0007
		02/12/2004	2.7E-04	n.a.	19	5.02E-07	0.064
Camembert	U-19q PS1d; Chimney	10/21/1998	n.a.	(3.1 ± 0.7)×1E-3 [a]	4.1	5.54E-06	0.15
		07/16/2003	4.8E-04	n.a.	4	2.77E-06	0.074
Cheshire		07/25/1998	n.a.	1.15 ± 0.25 [a]	5.9	n.a.	n.a.
	U-20n PS1ddh; Cavity	09/21/1998	0.80 ± 0.04	0.74 ± 0.02 [a], 0.422 [b]	5.8	n.a.	n.a.
		10/12/1999	0.57 ± 0.04	0.83 ± 0.16 [a]	13	4.91E-05	4.3
Chancellor	U-19ad PS1A; Cavity	09/27/2004	1.70 ± 0.01	n.a.	19.4	5.59E-04	73
Dalhart	U-4u PS2a; Chimney	08/16/1999	0.49 ± 0.02	0.59 ± 0.02 [a], 0.55 [b]	5.8	2.80E-05	1.1
		10/09/2003	1.30 ± 0.13	1.29 ± 0.07 [b]	7.1	1.04E-04	4.9
Nash	UE-2ce; 183 m from working point	08/22/2001	<1.3E-4	n.a.	9.4	1.88E-05	1.2
Tybo/Benham	ER-20-5 #1 (701-784 m)[d]; 280/1300 m from Tybo /Benham working points	07/09/1998	0.022	0.010 ± 0.002 [a]	7	2.14E-04	10.0
		11/30/2004	0.017	<0.04 [b]	5.4	1.99E-04	7.2
	ER-20-5 #3 (1046-1183 m)[d]; 280/1300 m from Tybo /Benham working points	04/30/1998	<0.04	<0.001 [a]	8.2	n.a.	n.a.
		11/29/2004	7.0E-04	n.a.	4.7	1.66E-06	0.052
Irish Sea Water	IAEA-381		0.2	0.22 ± 0.01 [c]			

n.a.: Not analyzed.
[a] ^{99}Tc analyses performed by LSC.
[b] ^{99}Tc analyses performed by AMS.
[c] Literature reported value.
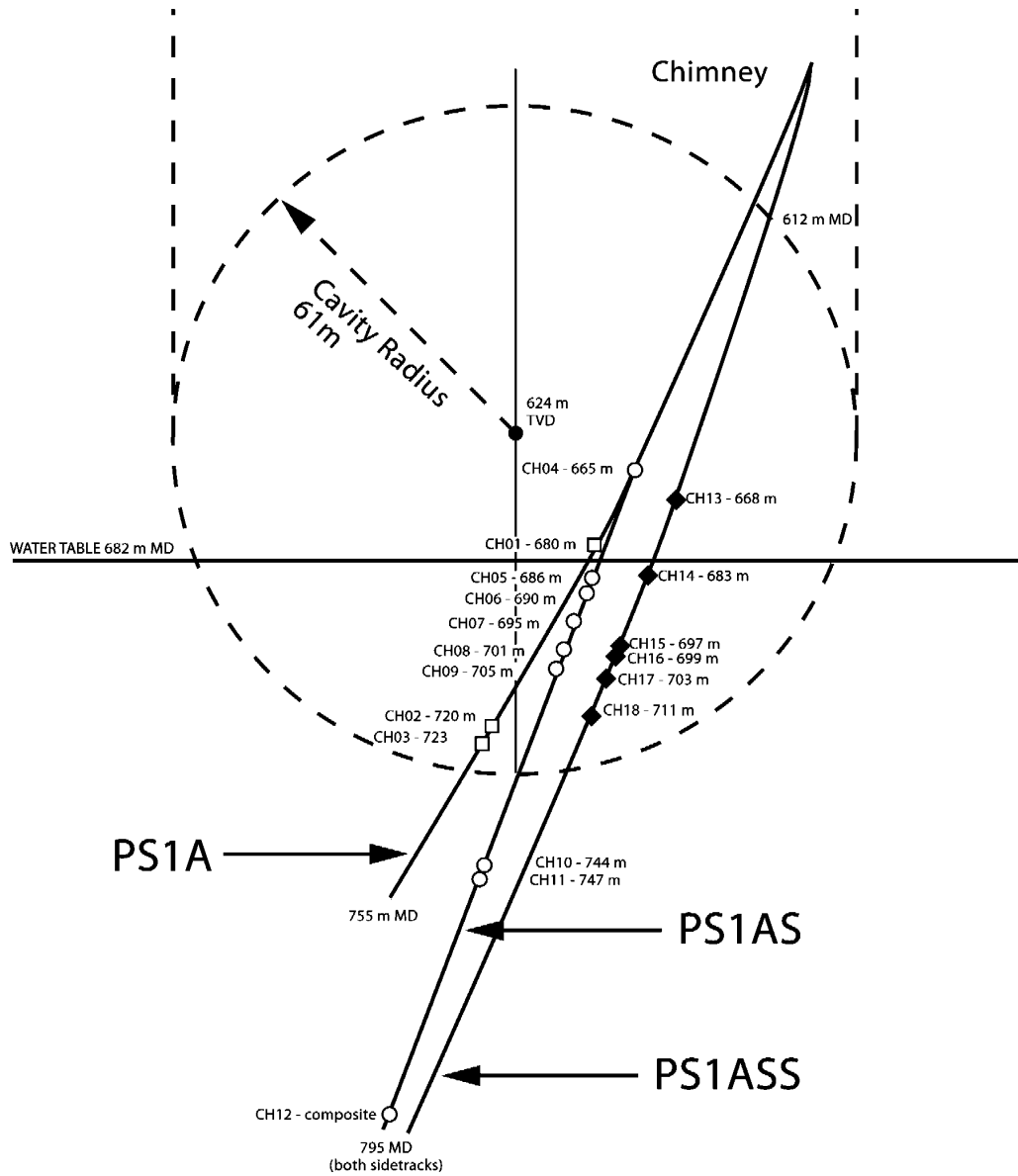[d] Open interval where sampling occurred.

Fig. 1. Cross section of the Chancellor cavity, chimney, and post-shot boreholes showing the locations of sidewall core samples that were used in this investigation. Main hole (PS1A); first sidetrack (PS1AS) and second sidetrack (PS1ASS). MD: measured depth, TVD: total vertical depth

The volume of groundwater in the cavity can be calculated assuming the saturated zone porosity is fully saturated and unsaturated zone is only 50% saturated. The results are reported in Table 3.

Using the measured ^{99}Tc and ^{129}I concentrations in the melt glass, rubble, and groundwater, the partitioning of ^{99}Tc and ^{129}I can be estimated (Table 3) and compared with IAEA estimates.[1] Approximately 65% of the ^{99}Tc is associated with the melt glass, and 35% is associated with the rubble. Our estimate agrees with IAEA values to within ±15%. Only a very small proportion of ^{99}Tc (0.3%) was dissolved in the cavity water, which is expected given its strong sorption and under moderately reducing conditions.[16] Based on

rubble and water concentrations, we estimate the ^{99}Tc K_d to be between 3 and 22 ml/g. Both Eh and iodine speciation measurements support the conclusion that the groundwater was reducing.

Using the same approach for ^{129}I, we estimate 28%, 24% and 48% of ^{129}I is in the melt glass, rubble and groundwater phases, respectively. Compared with IAEA estimates,[1] our results show that a larger fraction of the ^{129}I is present in groundwater, and a lower fraction is contained in the glass and rubble. Given the high volatility of iodine and its mass 129 fission product precursors, together with the solubility of iodine in groundwater, the high fraction of ^{129}I in the cavity fluid would appear to be reasonable.

Table 2. Technetium and iodine data of solid samples from the Chancellor Test Cavity

Sample ID	Sample description	^{99}Tc, ng/kg	^{99}Tc, Bq/kg	Total iodine, µg/kg	^{129}I/^{127}I	^{129}I, mBq/kg
Blank		<1	<1		3.0E-13	
CH01a	Gray volcanic rocks	9	5	23.6	3.1E-07	0.049
CH01b	Gray volcanic rocks with some black melt glass on surface	1.9	12	26	3.7E-08	0.0064
CH03a	Reddish-brown melt glass, non-vesicular	729 ± 31	458 ± 20	14.3	8.8E-04	83
CH03b	Pale-gray volcanic rock mix with small portion of melt glass	39 ± 4	24 ± 3			
CH04a	Vesicular brown melt glass	669	420	40.3	1.7E-04	45
CH04b	Volcanic rock, some partially melted to form light-colored vesicular glass	61 ± 3	38 ± 2	12.6	1.1E-04	9.1
CH06a	Black melt glass	597	375	5	1.3E-03	44
CH06b	Black melt glass mixed with volcanic rock	632	397	3.4	7.2E-04	16
CH09a	Dark brown/black melt glass	742	466	0.9	3.9E-03	23
CH09b	Dark brown/black melt glass	695	436			
CH12	Black melt glass	645 ± 17	405 ± 11	14.1		
CH14	Volcanic rock, some partially melted to form light-colored non-vesicular glass	49 ± 3	31 ± 2	16.7	4.4E-05	4.9
CH16	Dark brown/black melt glass	747	469	3	2.4E-03	49

Table 3. Distribution of radionuclides in the Chancellor Test Cavity

	Total mass, g	Total ^{99}Tc, MBq	^{99}Tc, %	^{99}Tc, % IAEA	Total ^{129}I, MBq	^{129}I, %	^{129}I, % IAEA
Melt glass	1.43E11	6.14E4	65	80	7.0	28	50
Rubble	1.52E12	3.35E4	35	20	5.3	24	40
Groundwater	1.80E11	3.07E2	0.3	0	13.0	48	10

Based on rubble and water concentrations, we estimate the ^{129}I K_d to be between 0 and 0.12 ml/g. However, ^{129}I was measured in only a few rubble samples, and our procedure lacked an iodine tracer to monitor recovery. Incomplete recovery of ^{129}I from solid samples would lead to an overestimation of ^{129}I partitioning into the groundwater phase and an underestimation of K_d. Quartz-tube combustion experiments for measuring low-level total iodine in rock samples are underway and will be used to compare with TMAH microwave digestion results described here.

While the partitioning estimates developed during this study are approximate, it is notable that the values differ from those reported by the IAEA for French underground tests.[1] To some extent, these differences may reflect variations in the underground test conditions. For example, the type of geologic media and the water or CO_2 content of the rock can influence the amount of time that the cavity stands prior to collapse of the overlying rock. Cavity collapse results in the rapid cooling of the system, and disrupts communication between the vapor phase and melt. The timing of this 'quenching' event has a significant effect on the fission product distribution because the partitioning of these fission products is largely determined by the chemical behavior of fission chain precursor elements.[17]

For example, most of the mass 99 and 129 fission chains are 'born' as short-lived precursors that decay to ^{99}Tc and ^{129}I on relatively short-time scales (half-lives of seconds to days). The chemical properties of these precursor elements will determine how the mass 99 and 129 species are distributed between the melt and vapor phases at the time of cavity collapse. Since each precursor species decays on a different time-scale, test cavities that are 'quenched' soon after the detonation will have a different fission product distribution than those that stand for a longer period of time. The future evaluation of radionuclide partitioning in underground test cavities that represent diverse cooling histories would provide additional constraints on the range in partitioning behavior.

Conclusions

^{99}Tc and ^{129}I in groundwater samples from 13 wells and in test debris from the Chancellor underground nuclear test cavity were analyzed using ICP-MS, LSC and AMS. In general, concentrations in the satellite wells are lower than in the test cavities for both ^{99}Tc and ^{129}I. Interestingly, ^{99}Tc and ^{129}I K_ds calculated using rubble and water concentrations are 3 to 22 ml/g and 0 to 0.12 ml/g, respectively, and are suggestive of mildly reducing conditions. Though both radionuclides appear to be relatively mobile, ^{99}Tc is likely to be retarded as a results of its reduction from the TcO_4^- anion to the more sorbing and insoluble TcO_2 species. Using the analytical results of the water and test debris samples, we have estimated the distribution of ^{99}Tc and ^{129}I between the melt glass, rubble and groundwater phases in the Chancellor test cavity and compared them to reported values from underground tests in French Polynesia. Differences in the two sets of partitioning values may be affected by analytical uncertainties, but variations in geologic conditions and the cooling history of a test cavity are expected to play an important role in determining the observed partitioning of fission products.

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