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Measurements of ^3H in soil cores from the Hyrax event (U3bh) subsidence crater

Prepared for the Waste Management Division
U.S. Department of Energy
Nevada Operations Office

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July, 1996

Summary

Core samples were collected from two boreholes drilled in the subsidence crater of the Hyrax event (U3bh). The moisture in the core samples was extracted via freeze drying and tritium was measured in the extracted moisture via ^3He accumulation mass spectrometry or liquid scintillation counting. Elevated tritium concentrations ($1\text{E}4 - 1\text{E}6$ pCi/L extracted moisture as of the time of measurement) were observed in the extracted moisture from virtually all of the core samples with significant increases beginning at about 30 ft depth. No longer-lived fission products (^{144}Ce) or activation products (^{60}Co , ^{152}Eu , ^{154}Eu) were observed by gamma-ray spectroscopy in a subset of the core samples. This likely indicates that a catastrophic failure of containment (if it occurred) did not release significant radioactivities to this shallow depth (30 ft). The presence of ^{137}Cs at much greater depths (≈ 210 ft, 64 m) [D. Smith, private communication, 1996] may indicate that gaseous and/or vapor products were released shortly after the Hyrax event to a depth of about 210 ft. The relatively shallow depth where the elevated tritium is observed makes highly improbable any significant linkage between the elevated tritium concentrations and a Hyrax event containment failure. This may indicate that an additional source of enriched ^3H was introduced at this site.

Introduction:

Soil core samples were submitted to the Isotope Sciences Division (ISD) of the Lawrence Livermore National Laboratory (LLNL) for low-level tritium analysis in support of the Waste Management Division of the Nevada Operations Office of the U.S. Department of Energy. This effort was to assist in the assessment of the U3bh site (Hyrax) at the Nevada Test Site for possible use as a disposal site for low level radioactive waste. The specific intent of this study was to assess the migration of water from the surface by identifying the ^3H atmospheric bomb pulse (tritium concentrations in the range of 10 - 100 pCi/L water were expected) in moisture extracted from core samples taken from the subsidence crater. A detailed review of the Hyrax event is available.¹

Methodology

Freeze drying:

A common technique whereby a sample is encapsulated inside a vacuum vessel which is maintained at moderate to high vacuum for an extended period. The moisture is released from the sample under these conditions and is collected on a cold finger packed with solid CO_2 . With the exception of the initial application of vacuum and a periodic maintenance of vacuum, each freeze drying system remains sealed during the entire process. This method collects only unbound water from the sample and is usually better than 80 to 90% efficient. As this particular study is aimed at measuring the unbound ^3H concentration in the moisture, this method is well suited. These particular samples were expected to contain anywhere between 2% and 10% moisture, by weight² which should be sufficient moisture content to make this separation technique viable, given a few hundred gram of soil sample.

^3He accumulation mass spectrometry:

A detailed review of this technique is available.³ In essence, the extracted moisture from the core sample is transferred to a stainless steel vacuum vessel and repeatedly degassed via freezing of the assembly in liquid nitrogen. The ^3He present in the sample (in the form of dissolved) gas is driven to the vacant headspace above the sample and subsequently removed via application of vacuum. This process is repeated several times and is shown to remove about 95% of the dissolved He with each freezing/vacuum cycle. The last freeze/vacuum cycle establishes the zero time for the sample (t_{zero}) and the sample is set

¹ W. L. Hawkins, Los Alamos National Laboratory Report, unpublished (1995).

² J. Schmeltzer, NTS Bechtel, private communication, 1995.

³ K. A. Surano et al., J. of Radioanal. and Nuc. Chem., 161, p443 (1992).

aside for a known decay interval. After a known decay interval, the ^3He which accumulates in the sample (a result of the decay of ^3H) is measured via noble gas mass spectrometry. The ^3H concentration is calculated from this data, the sample size, instrument efficiency, and decay time relative to tzero.

Liquid scintillation spectrometry:

The 17-keV (max energy) beta emission from the ^3H decay is converted into a light pulse via interaction with an organic fluor. The light pulse is detected via a photomultiplier and the pulse height stored and displayed on a multichannel analyzer. Each sample is counted for 50-100 minutes. The number of counts in the tritium energy region is integrated and corrected for background (as measured with an instrument blank), efficiency (as measured with an instrument standard, and quench, if any). The ^3H concentration is calculated from this information with our SCNTCT code (version 2.0, 02-03-92, or later) based upon the aliquot volume, original sample size and instrument efficiency.

Results:

Sample Receipt:

Samples arrived from NTS in two batches. The first set (U3bh #1) was comprised of 23 samples and the second set (U3bh #2) was comprised of 22 samples. Table 1 is a list of the samples received. The samples were delivered from NTS in an ice chest and each sample was encased in a plastic cylinder which was packaged in an aluminum envelope. Each cylindrical core was 3 inches thick and 3 inches in diameter and weighed between 500 and 800 g.

Gamma-ray measurements:

A subset of the samples (about 10% of the total number of samples distributed over the sampling depth) was measured via gamma-ray spectroscopy to determine whether significant fission product radioactivity was present which might contaminate the ISD-LLNL low-level sample handling laboratory. These samples were previously screened by NTS for gamma emitting radioactivities, but the gamma-ray measurements performed by ISD-LLNL provided additional sensitivity. No man-made radioactivities were observed above background in a subset of these samples in 6-hour counts of the core packaged material. Figure 1 is an example gamma-ray spectrum obtained from a 6-hour count of sample LL201.25-201.5; received in the first set (U3bh #1). Only ^{40}K , ^{226}Ra (likely from non-anthropogenic ^{238}U), ^{228}Ra (likely from non-anthropogenic ^{232}Th) and the Ra

daughters (including ^{228}Th) were detected at levels above the normal instrument background. The presence of these nuclides in soils is common.

Table 1. Samples received from NTS.

Sample Set 1 (U3bh #1), Sample ID (Bechtel)		Sample Set 2 (U3bh #2), Sample ID (Bechtel)	
LL6.5-7.67	LL100.5-100.75	LL 5.25-5.5	LL 92.25-92.5
LL11.50-11.75	LL110.75-111.0	LL 11.0-11.25	LL 101.0-101.25
LL16.25-16.50	LL120.75-121.0	LL 15.5-15.75	LL 110.75-111.0
LL21.0-21.25	LL130.5-130.75	LL 20.5-20.75	LL 121.25-121.5
LL26.5-26.75	LL140.5-140.75	LL 26.0-26.5	LL 132.25-132.5
LL31.0-31.25	LL151.25-151.5	LL 30.75-31.0	LL 141.75-142.0
LL40.25-40.5	LL161.0-161.25	LL 41.25-41.5	LL 151.0-151.25
LL52.0-52.25	LL171.25-171.5	LL 50.75-51.0	LL 161.0-161.25
LL61.0-61.25	LL180.5-180.75	LL 62.0-62.25	LL 171.0-171.25
LL70.5-70.75	LL190.75-191.0	LL 70.75-71.0	LL 181.0-181.25
LL80.5-80.75	LL201.25-201.5	LL 80.75-81.0	LL 191.0-191.25
LL91.5-91.75

Figure 1. Gamma-ray spectrum of sample LL201.25-201.5 as measured in the original packaging for 6 hours via a high-purity Ge detector.

Freeze-drying and ^3He mass spectrometry:

The samples were transferred from the aluminum and plastic wrapping to pre-weighted vacuum flasks in preparation for freeze drying and the flask and sample weighed. Because some of the soil samples appeared very dry ($<$ a few % moisture content by weight) and would likely yield only small amounts of water in the freeze dry process, we elected to freeze dry as much of each sample at one time as practical to increase the measurement sensitivity rather than attempt multiple replicate analysis and not have enough liquid extracted. The samples were freeze dried for 5 days under approximately 30 millitorr vacuum at room temperature and the moisture from each sample collected by condensation on a solid CO_2 cooled cold finger. The weight of the dried soil (and flask) was measured and used to approximate the amount of water which should have been extracted and collected. The volume of water collected was measured and a recovery yield calculated (see Table 2). All handling of the extracted moisture was performed under a dry Ar atmosphere to minimize potential contamination from local air moisture. A copy of the detailed procedure is attached as an appendix to this report. The approximate 30 millitorr pressure was maintained via an automated vacuum manifold.

The liquid extracted from the first set of soil samples (U3bh #1) was transferred under Ar to stainless steel vacuum vessels for the ^3He accumulation measurement. The samples were degassed as described earlier and set aside to permit accumulation of the ^3He . After approximately 2 weeks, the ^3He was measured. Table 2 shows the results for the ^3He accumulation measurements of the samples in set 1 (U3bh #1) as of the measurement time (May, 1996). A blank was analyzed between each sample to check for potential cross-contamination. This became important once it was discovered how much ^3H was really present in these samples as cross-contamination and instrument contamination could have become an issue. The overall water recovery efficiency for the samples in set 1 (U3bh #1) averaged about 84% (see Table 2).

As is indicated by the results shown in Table 2, the measured ^3H values were unexpectedly very high. This resulted in an extreme effort to verify that the ^3He mass spectrometer was not contaminated. Blank samples were analyzed (see Table 3) between each sample and the results indicate that no cross-contamination between samples of this set (U3bh #1) occurred during the degassing and measurement process even though the measured tritium levels were (in some cases) as much as 100000 times higher than had been indicated would be present. Given the high level of tritium in these samples relative to the typical sample

analyzed on this instrument, this is pleasantly surprising. Evidence for contamination of other samples (extremely low level and not related to this study, but present on the instrument manifold system at the same time as these NTS samples) was apparent and required an extensive manifold decontamination effort prior to analysis of additional samples.

Freeze-drying and liquid scintillation counting:

The very high levels of tritium present in the first set of samples was inappropriate for the low-level ^3He accumulation mass spectrometry system. As a result, we elected to analyze the moisture extracted from the second set of samples (U3bh #2) by traditional liquid scintillation.

To 10 mL of Ultima-Gold XR liquid scintillation cocktail was added 5 mL of the extracted moisture. The samples were mixed and set aside in a darkened refrigerator overnight to permit photoluminescence generated by the ambient light to subside. Each sample was placed in the liquid scintillation counter and sequentially counted 2 times for 100 minutes each. The average result of the two measurements for each sample is indicated in Table 4. Instrument standards and blanks were also measured and the results of these measurements are shown in the table. Again, the tritium levels were very high.

Conclusions:

The profile of the tritium distribution as a function of sample depth for sample set 1 (U3bh #1) and set 2 (U3bh #2) is shown in Figure 2 and Figure 3, respectively. The burial depth of the Hyrax event was 216 meters¹ which is much deeper than the maximum in the tritium profile for either borehole (see Figure 2 and Figure 3). The tritium concentration profile in the first borehole (set 1, U3bh #1) peaks at a depth of about 90 ft with a broad distribution of activity between about 30 ft and 150 ft. The tritium concentration distribution in the second set of samples (U3bh #2) appears to be stratified into two regions (see Figure 3), though the statistics preclude a definitive statement in this regard.

The elevated tritium concentrations in the two bore holes is first evident at about 30 ft depth. The absence of additional fission product radioactivities at this depth (as measured by gamma-ray spectroscopy) may indicate that the tritium found at these shallow depths (relative to the 216 m Hyrax emplacement) does not originate from the Hyrax event itself. If these elevated tritium levels were the result of a significant breach in containment, then

additional fission products (^{137}Cs , for instance) would be observed in addition to the tritium at the shallow depths. Based upon this information, it is likely that the elevated tritium concentrations at shallow depth in the U3bh subsidence crater core samples are the result of either a significant migration of tritium from the event center or a secondary source of tritium was introduced at the surface and is not related to the Hyrax event.

The observation of significant ^{137}Cs at depths of approximately 200 ft is significant.⁴ The absence of additional fission products at these depths⁵ appears to correlate with a gas transport mechanism of ^{137}Xe (parent of ^{137}Cs) from the event center up to a depth of about 150 to 200 ft. This does not appear to be sufficient migration to account for the extremely elevated tritium concentrations at much shallower depths (30 ft). This observation and the apparent difference in the ^3H distribution with depth between the two boreholes further substantiates the hypothesis that an additional source of enriched tritium was introduced at this site at some time in the past.

⁴ No previous observations of the migration of fission products with gaseous precursors more than 5 cavity radii from the event center at NTS.

⁵ D. Smith, private communication (1996).

Table 2. ^3H data for NTS U3bh drill core samples, Sample Set 1 (U3bh #1). Tritium concentrations are as of the time of measurement. Measured on Mass Spectrometer VG5400 No. 1.

Sample ID (Bechtel)	% Water Recovery	Measured ^3H pCi/L*	Error (1σ) pCi/L
LL6.5-7.67	89%	591	59
LL11.50-11.75	96%	1700	170
LL16.25-16.50	96%	2220	222
LL21.0-21.25	95%	5410	541
LL26.5-26.75	96%	19800	1980
LL31.0-31.25	97%	65800	6580
LL40.25-40.5	95%	122000	12200
LL52.0-52.25	96%	345000	34500
LL61.0-61.25	95%	161000	16100
LL70.5-70.75	94%	372000	37200
LL80.5-80.75	90%	360000	36000
LL91.5-91.75	95%	149000	14900
LL100.5-100.75	92%	546000	54600
LL110.75-111.0	94%	431000	43100
LL120.75-121.0	56%	346000	34600
LL130.5-130.75	96%	450000	45000
LL140.5-140.75	94%	154000	15400
LL151.25-151.5	90%	112000	11200
LL161.0-161.25	89%	13000	1300
LL171.25-171.5	95%	7250	725
LL180.5-180.75	6% [†]	9970	997
LL190.75-191.0	78%	9960	996
LL201.25-201.5	52%	11100	1110

*pCi/L tritium in the extracted moisture.

Table 3. Results for instrument blank samples as measured between NTS samples by ^3He accumulation mass spectrometry.

Sample	Date	Time	Expected (pCi/L)	Measured (pCi/L)	Error (1σ) pCi/L
Blank	5/2/96	11:21	<30	14.6	1.5
Blank	5/2/96	11:49	<30	26.5	2.7
Blank	5/2/96	13:06	<30	17.5	1.8
Blank	5/2/96	15:20	<30	16.3	1.6
Blank	5/2/96	15:48	<30	8.4	0.8
Blank	5/2/96	16:17	<30	8.4	0.8
Blank	5/3/96	9:55	<30	5.5	0.6
Blank	5/3/96	12:29	<30	6.5	0.7
Blank	5/3/96	14:03	<30	7.3	0.7
Blank	5/6/96	11:28	<30	3.2	0.3
Blank	5/6/96	11:59	<30	6.1	0.6
Blank	5/6/96	12:31	<30	5.4	0.5
Blank	5/6/96	13:04	<30	10.2	1.0
Blank	5/14/96	16:19	<30	1.7	0.2
Blank	5/14/96	16:43	<30	2.6	0.3
Blank	5/15/96	11:40	<30	3	0.3
Blank	5/15/96	12:00	<30	3.2	0.3
Blank	5/15/96	12:21	<30	26.4	2.6
Blank	5/28/96	11:18	<30	5.7	0.6
Blank	5/28/96	12:53	<30	4.5	0.5
Blank	5/28/96	13:11	<30	5.4	0.5
Blank	5/28/96	13:30	<30	2.5	0.3
NTS31604	5/28/96	14:05	<30	14.7	1.5

Table 4. ^3H results for NTS U3bh drill core samples for Sample Set 2 (U3bh #2) as measured on a Packard 2560 liquid scintillation counter (ID 17). Tritium concentrations are as of the time of measurement.

Sample ID (Bechtel)	% Recovery	Measured ^3H pCi/L [†]	Error (1 σ) pCi/L
LL 5.25-5.5	90%	381	381
LL 11.0-11.25	92%	388	388
LL 15.5-15.75	95%	393	393
LL 20.5-20.75	93%	389	389
LL 26.0-26.5	93%	403	403
LL 30.75-31.0	94%	1900	448
LL 41.25-41.5	96%	3060	480
LL 50.75-51.0	91%	68200	1569
LL 62.0-62.25	91%	729000	5103
LL 70.75-71.0	95%	477000	3816
LL 80.75-81.0	82%	31100	1089
LL 92.25-92.5	91%	1760	447
LL 101.0-101.25	97%	1600	451
LL 110.75-111.0	**	5590	783
LL 121.25-121.5	60%	23800	1047
LL 132.25-132.5	73%	8140	716
LL 141.75-142.0	83%	7000	651
LL 151.0-151.25	101%	33600	1142
LL 161.0-161.25	86%	28600	1087
LL 171.0-171.25	82%	2790	497
LL 181.0-181.25	87%	1970	453
LL 191.0-191.25	88%	1930	475
Standard 28805		91400 ^{††}	2200
process blank		417	417
instrument blank		54.1	54

**Changed out trap, glassware. No final weight available

[†]pCi/L tritium in the extracted moisture as measured via liquid scintillation

^{††}Standard with a known concentration of 99100 pCi/L tritium.

Figure 2. Depth profile of tritium concentration in the extracted moisture for Sample Set 1 (U3bh #1) as measured via ^3He accumulation mass spectrometry. Tritium concentrations are as of the time of measurement.

Figure 3. Depth profile of tritium concentration in the extracted moisture for Sample Set 2 (U3bh #2) as measured via liquid scintillation spectrometry. Tritium concentrations are as of the time of measurement.

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