

Measurement of ^{222}Rn Flux, ^{222}Rn Emanation, and
 ^{226}Ra Concentration from Injection Well Pipe Scale

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Abstract

Radon 222 flux (Bq s^{-1}) was measured from the ends of twenty sections of produced water injection tubing (pipe) containing barite scale contaminated with naturally occurring radioactive material (NORM). Exposure measurements near the pipes were as high as $300 \mu\text{R h}^{-1}$. Flux measurements were accomplished by first purging the pipes with dry nitrogen and then collecting the outflow (nitrogen and radon) on charcoal columns affixed to the end of the pipe for 66 hours. Analysis was performed using a 3×3-in NaI detector coupled with a multichannel analyzer. Following the radon release measurements, pipe scale was removed and a representative sample was taken for ^{226}Ra and ^{232}Th concentration measurements and determination of ^{222}Rn emanation fractions. The samples were also analyzed for gross mineral content. Radon 222 flux from the ends of the pipe ranged from 0.017 Bq s^{-1} to 0.11 Bq s^{-1} and emanation fraction measurements ranged from 0.02 to 0.06. Radium 226 concentrations ranged from 15 Bq g^{-1} (400 pCi g^{-1}) to 39 Bq g^{-1} (1042 pCi g^{-1}).

Introduction

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The presence of Naturally Occurring Radioactive Material (NORM) has been recognized since the early 1930s in petroleum reservoirs and in oil and gas production and processing facilities. NORM was typically observed in barite scale that accumulated on the interior of oil production tubing and in storage tank and heater-treater separation sludge. Recent concern has been expressed over the health impacts from the uncontrolled release of NORM to the public. There are several potential exposure pathways to humans from oil-field NORM. Among these is inhalation of radon gas and its daughter products. For this exposure pathway to be of any significance, radon must first be released from the NORM matrix and diffuse in free air. The radon emanation fraction refers to the fraction of radon atoms produced by the decay of radium, that migrate from the bulk material as free gaseous atoms.

The purpose of this investigation was to characterize the radon release rates from NORM-scale contaminated production tubing being stored above ground, characterize the radon emanation fraction of the bulk scale material when removed from the tubing, and characterize the radium concentrations of the scale. Accurate characterization of ^{222}Rn emanation fractions from pipe scale may dictate the type of disposal options available for this waste. Characterization of radon release from stored pipes will assist in determining if controls are needed for workers or members of the public downwind from the source. Due to the sensitive nature of this data, the location of this facility is not disclosed.

DISCLAIMER

Methods

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Twenty sections of 2 3/8-inch production tubing (pipe) from a produced water injection well having the highest surface gamma exposure rate readings, were selected for evaluation. These sections ranged in length from 8.92 m (29.25 ft.) to 10.00 m (32.80 ft.). The general approach adopted for the radon flux (Bq s^{-1}) measurement was to purge the pipe volume with a carrier gas (dry nitrogen) thereby entraining any radon emanating from the scale. The purge gas stream was passed through an activated carbon bed to collect the radon. Following the collection interval, the activated carbon was returned to the laboratory for gamma analysis to determine the radon activity collected.

Commercially available bottles of dry nitrogen were used as the source of the carrier gas. The pipe sections were purged of any accumulated radon prior to the start of the sample collection interval so that the measurement would reflect the true radon release rate from the pipe. Carrier gas flow rates of approximately $2.5 \text{ liter min}^{-1}$ were employed. A sample collection interval of approximately 66 hours was used to ensure that sufficient radon was collected for an accurate gamma measurement. Sample decay times (Δt from end of sample collection to start of counting) ranged from approximately 26 to 37 hours. The activated carbon bed was fabricated from a length of 1-inch, schedule-40, PVC pipe, packed with approximately 180 g of coconut-husk-type activated carbon. Gamma analysis of the radon laden activated carbon samples was carried out using a 3×3 -inch sodium iodide scintillation detector and support electronics.

Equation 1, after Hartley and Freeman (1986,) was used to reduce the raw count data to a radon flux in Bq s^{-1} .

$$J = \frac{C \lambda^2}{K (1 - e^{-\lambda T_1}) (e^{-\lambda (T_2 - T_1)} - e^{-\lambda (T_3 - T_1)})} \quad (1)$$

Where: J = measured radon flux ($Bq s^{-1}$)
 C = net counts for the region of interest (counts)
 λ = decay constant for radon-222 (s^{-1})
 K = calibration factor for the region of interest (counts $s^{-1} Bq^{-1}$)
 T_1 = sample collection time (s)
 $T_2 = \Delta t$, start of sample collection to start of counting (s)
 $T_3 = \Delta t$, start of sample collection to end of counting (s)

The calibration factor K was determined from repeated analysis of two different 226-Radium-on-activated-carbon standards of the same counting geometry as the samples.

After measurement of the radon flux was complete, a sample of the pipe scale was obtained for ^{226}Ra analysis and ^{222}Rn emanation fraction measurements. Pipe scale samples were obtained in a somewhat crude manner. Each pipe section was hoisted about two meters off the ground and tipped to one side. Several oil field workers then beat the pipe with sledge hammers to dislodge the scale and “rattle” it down the pipe to a five-gallon collection bucket on the end. This procedure was repeated by tipping the opposite end of the pipe down and collecting sample from the other end of the pipe. About 0.006 m^3 (1.6 gallons) of *dislodged* scale was collected from each pipe. The broken-up scale was then mixed with a trowel and a one liter sample was extracted and placed in a polyethylene container. The sample collection bucket and trowel were rinsed with water and wiped clean with a paper towel between samples to avoid cross contamination. Gamma exposure measurements were made of the each sample and ^{226}Ra concentrations were estimated based on calculations using the Microshied© code and assuming 16 percent equilibrium (1 day ingrowth) between ^{226}Ra and daughter products. This was done to

ensure DOT activity limits for shipping limited quantity radioactive material were not exceeded. An aliquot of approximately 130 g was forwarded to the University of Texas at Austin for gross mineralogical identification.

The radon emanation fraction was measured using an aliquot of the 1 liter scale sample recovered from each tubing section. The general approach to this measurement was to flush the free gaseous radon from the sample matrix and then transfer the sample to a hermetically sealed container, thereby establishing a zero time for radon ingrowth of the emanating fraction. A gamma spectrum was obtained within a few hours of sealing the sample container, and again several weeks later. An analysis of the measured activity from the 352 keV peak of ^{214}Pb and the 609 and 1764 keV peaks from ^{214}Bi at the two different times allow calculation of the radon emanating fraction based on the theoretical ingrowth curve.

Fig. 1 shows the theoretical radon ingrowth curve. The sample activities at times t_1 and t_2 (I_1 and I_2) are described by equations 2 and 3 below.

$$I_1 = I_0 + N (1 - e^{-\lambda t_1}) \quad (2)$$

$$I_2 = I_0 + N (1 - e^{-\lambda t_2}) \quad (3)$$

Where:
 I_1 = Activity at time t_1
 I_2 = Activity at time t_2
 I_0 = Bound Radon Activity at time t_0
 N = Free, or Emanating Radon Activity at Radioactive Equilibrium
 λ = Radon Decay Constant

These two equations can be solved simultaneously for the unknown quantities I_0 and N .

Substituting A for $(1-e^{-\lambda_1 t_1})$ and B for $(1-e^{-\lambda_1 t_2})$ simplifies the equations. The solutions are given in equations 4 and the emanation fraction F is computed from equation 5.

$$N = \frac{(I_1 - I_2)}{(A - B)}, \quad I_0 = \frac{I_2 A - I_1 B}{A - B} \quad (4)$$

$$F = \frac{N}{(N + I_0)} \quad (5)$$

It should be noted that it is not necessary to determine the actual sample activities (I_1 and I_2) at times t_1 and t_2 . The net count rates (C_1 and C_2) observed at t_1 and t_2 are proportional to the activities (I_1 and I_2) through a calibration constant, which cancels out when the final ratio is taken in equation 6. Thus C_1 and C_2 may be substituted for I_1 and I_2 .

The radon emanating fraction of most granular materials is dependent upon the grain size (surface to volume ratio) as well as the moisture content of the sample (Cole` et al., 1981).

Because of this concern, the samples prepared for radon emanation fraction measurement were not crushed or otherwise further reduced in size beyond that which occurred during the field sampling until the emanation fraction measurements were completed. It was felt by the authors that the method of obtaining the scale samples used in this investigation would produce a grain size distribution representative of scale materials removed from tubing and pipe by the "rattling" process, commonly used in the past. The emanation fractions reported here are not intended to be representative of those belonging to scale materials removed by the underreaming process, which is currently employed.

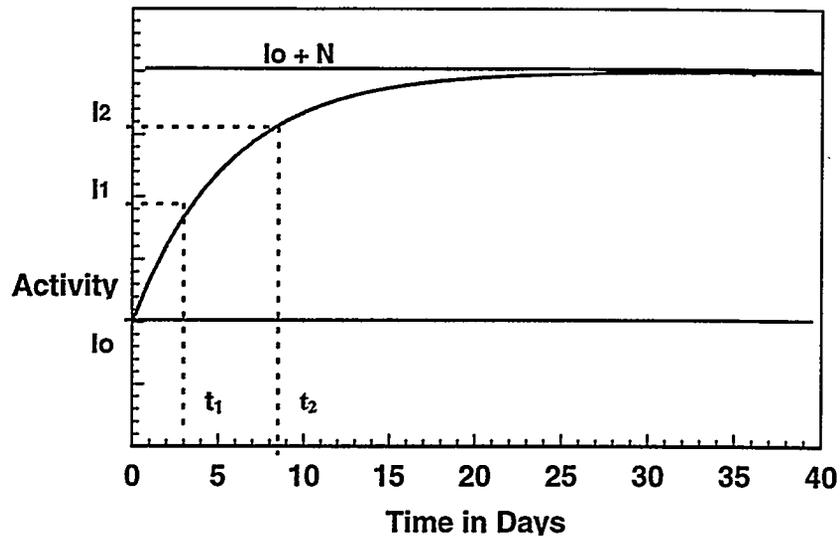


Figure 1. Radon ingrowth curve defining I_0 , I_1 , and I_2 .

Representative 0.4 liter aliquots of the 1 liter scale samples were obtained by the cone-and-quarter method. Each aliquot was placed, as a thin layer, in a flushing chamber constructed from a 70 cm length of 4-inch PVC pipe. A small laboratory air pump was used to draw conditioned air through the flushing chambers at a flow rate of approximately 1 liter min^{-1} . Previous experience with uranium mill tailings materials, using room air for flushing, resulted in significant drying of the sample. In order to avoid this problem, a humidifying system was employed to condition the air stream drawn into the flushing chamber to 98% relative humidity, and maintain it at the same temperature as the flushing chamber. By maintaining the air stream close to the saturation moisture content, intergranular moisture would neither be added nor removed from the sample. Weight gains were, however, observed in all of the samples following removal from the flushing chambers. The weight gains were probably the result of the iron oxide minerals taking up hydration waters from the saturated atmosphere. There is no question that the measurement process affected the moisture content of the samples, relative to the "as-collected"

condition. It can be argued, however, that the saturated air of the measurement condition closely approximates the moisture conditions that exist in most soils.

The spectral gamma measurements were obtained with a high purity, planer germanium detector used with a personal computer based multichannel analyzer. Two spectra were collected for each sample at two different times t_1 and t_2 during the ingrowth period. Count durations were 1500 s for each count. The net peak areas were obtained for three different regions of interest comprised of the 352, 609, and 1764 keV lines for each count. The net peak areas from these three regions of interest were pooled for each count time and used as C_1 and C_2 in equations (5) and (6) above to determine the emanation fractions, as listed in Table 1.

The same 0.4 liter aliquot used in the emanation fraction measurements was used as the starting sample material for the ^{226}Ra and ^{232}Th analyses. The 0.4 liter aliquots were first dried at 110°C and then crushed to a sieve size of 80 mesh and thoroughly blended. A 100 gram aliquot was then extracted and placed in a metal container, sealed and allowed to sit 21 days for daughter ingrowth. Each sample was counted on a high purity germanium detector (HPGE) using the 0.609 MeV photopeak. Samples were corrected for density differences between the sample matrix and the calibration standards.

Results and Discussion

Radon flux from the tubing ends (Table 1) ranged from $1.7 \times 10^{-2} \text{ Bq s}^{-1}$ (0.47 pCi s^{-1}) to

Table 1. Measurement Results

| Pipe No. | Scale Volume (liters) | Average Scale Thickness (cm) | Radon Flux (Bq s^{-1}) | Radon Emanation Fraction | Weight Gain Ratio | ^{226}Ra (Bq g^{-1}) | ^{232}Th (Bq g^{-1}) | Loss on Drying (%) |
|----------|-----------------------|------------------------------|-----------------------------------|--------------------------|-------------------|--|--|--------------------|
| 1 | 3.44 | 0.25 | 0.030 | 0.06 | 1.04 | 33.1 | 55.8 | 6.7 |
| 2 | 6.72 | 0.49 | 0.061 | 0.04 | 1.03 | 79.6 | 109.4 | 10.7 |
| 3 | 3.24 | 0.21 | 0.017 | 0.03 | 1.03 | 73.2 | 110.7 | 5.5 |
| 4 | 3.12 | 0.23 | 0.030 | 0.03 | 1.03 | 71.8 | 103.2 | 5.3 |
| 5 | 12.22 | 1.08 | 0.104 | 0.03 | 1.00 | 79.8 | 111.0 | 20.7 |
| 6 | 7.63 | 0.54 | 0.038 | 0.05 | 1.03 | 14.7 | 19.0 | 9.0 |
| 7 | 6.84 | 0.53 | 0.033 | 0.05 | 1.04 | 15.7 | 19.8 | 9.4 |
| 8 | 2.96 | 0.20 | 0.040 | 0.03 | 1.03 | 101.7 | 150.4 | 4.9 |
| 9 | 3.85 | 0.26 | 0.019 | 0.03 | 1.03 | 38.6 | 60.0 | 6.2 |
| 10 | 3.65 | 0.24 | 0.039 | 0.02 | 1.03 | 85.9 | 133.9 | 5.0 |
| 11 | 4.00 | 0.28 | 0.089 | 0.04 | 1.04 | 82.3 | 138.8 | 5.8 |
| 12 | 3.27 | 0.23 | 0.034 | 0.03 | 1.03 | 97.3 | 149.4 | 4.1 |
| 13 | 4.23 | 0.28 | 0.024 | 0.04 | 1.04 | 26.5 | 48.6 | 7.3 |
| 14 | 4.21 | 0.28 | 0.034 | 0.03 | 1.04 | 86.5 | 133.4 | 5.5 |
| 15 | 4.85 | 0.33 | 0.073 | 0.04 | 1.04 | 102.2 | 149.9 | 5.2 |
| 16 | 4.91 | 0.33 | 0.025 | 0.035 | 1.04 | 26.2 | 47.9 | 8.8 |
| 17 | 3.56 | 0.25 | 0.038 | 0.030 | 1.03 | 93.6 | 149.8 | 4.2 |
| 18 | 4.77 | 0.32 | 0.020 | 0.034 | 1.04 | 24.3 | 50.5 | 6.5 |
| 19 | 3.98 | 0.26 | 0.033 | 0.033 | 1.03 | 83.5 | 124.3 | 4.6 |
| 20 | 3.64 | 0.25 | 0.024 | 0.057 | 1.04 | 21.9 | 55.6 | 6.5 |

0.10 Bq s^{-1} (2.8 pCi s^{-1}) with a mean of $4.0 \times 10^{-2} \text{Bq s}^{-1}$ (1.1 pCi s^{-1}) and a standard deviation of $2.3 \times 10^{-2} \text{Bq s}^{-1}$ (0.62 pCi s^{-1}). It is, perhaps, most meaningful to compare the radon flux values measured from the tubing segments with the range of radon-flux density values observed in a variety of soils. Wilkening, et al., 1972, give a worldwide average of $1.6 \times 10^{-2} \text{Bq m}^{-2} \text{s}^{-1}$ (0.43 $\text{pCi m}^{-2} \text{s}^{-1}$) for radon-flux density from natural soils, with a range from $2.2 \times 10^{-4} \text{Bq m}^{-2} \text{s}^{-1}$ (0.006 $\text{pCi m}^{-1} \text{s}^{-1}$) to $5.2 \text{Bq m}^{-2} \text{s}^{-1}$ (1.4 $\text{pCi m}^{-1} \text{s}^{-1}$). Thus the average section of NORM contaminated pipe from this site is comparable to approximately 2.5m^2 of average ground surface, in terms of radon production potential.

Radon emanation fractions ranged from 0.02 to 0.06 with a mean of 0.04 and standard deviation of 0.01. These values are significantly lower than emanation fractions measured for natural soils

and uranium mill tailings which typically range from 0.1 to 0.3. Radium-226 concentrations in the pipe scale ranged from 15 Bq g^{-1} (400 pCi g^{-1}) to 102 Bq g^{-1} (2760 pCi g^{-1}) with a mean of 62 Bq g^{-1} (1670 pCi g^{-1}) and standard deviation of 32 Bq g^{-1} (870 pCi g^{-1}). Natural soils typically have ^{226}Ra concentrations in the 0.019 Bq g^{-1} (0.5 pCi g^{-1}) to 0.074 Bq g^{-1} (2 pCi g^{-1}).

Mineralogical analysis indicated barite as the predominate mineral in the scale followed by Lepidocrocite and Goethite, both iron minerals.

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