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**GAS ANALYSIS RESULTS FOR PROJECT RULISON
CALIBRATION FLARING SAMPLES**

C. F. Smith

January 7, 1971

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**LAWRENCE
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University of California
LIVERMORE

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Lawrence Radiation Laboratory
UNIVERSITY OF CALIFORNIA
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GAS ANALYSIS RESULTS FOR PROJECT RULISON CALIBRATION FLARING SAMPLES

Abstract

Results are presented and discussed of chemical and radiochemical analyses of seven samples taken from the produced gas from calibration flaring on August 1 and October 4 through 7, 1970, of the Project Rulison nuclear stimulation experiment. The average gas composition observed in these samples is 48.4% CO₂, 32.8% CH₄, 15.7% H₂, 1.73% C₂H₆, 0.28% C₃H₈ and 0.23% C₄₊ hydrocarbons. The most significant radionuclide observed was tritium, present in the gas at 176 picocuries per standard milliliter. Methane contains 82% of the gaseous tritium, while hydrogen (with 11%), ethane (6%) and heavier hydrocarbons contain the balance. Tritium-to-hydrogen ratios (relative to methane) in H₂, CH₄, C₂H₆ and C₃H₈ are 0.5, 1.0, 0.9, and 0.7 respectively. The ⁸⁵Kr concentration is 150 pCi/ml. Other radionuclides measured were present in the following concentrations: ¹⁴C at 0.41 pCi/ml, ³⁹Ar at 1.4 pCi/ml, ³⁷Ar at 10.7 pCi/ml and ²²²Rn at 0.03 pCi/ml.

The total gas volume calculated assuming a total of 960 Ci of ⁸⁵Kr mixed uniformly with the chimney gases, was 6.4×10^9 liters. This volume of gas could be contained in spherical void of radius 23.5 m (77 ft) at a pressure of 200 atm and a temperature of 375°F.

Totals of various radionuclides measured (based on the assumed total amount of ⁸⁵Kr) include: 0.11 g of tritium present as "permanent" gas (corresponding to about 10% of the one-gram expected to reside in the chimney), 2.6 Ci of ¹⁴C (as carbon dioxide), 42 kCi of ³⁷Ar (at detonation time) and 9.2 Ci of ³⁹Ar.

The significantly lower concentration of CO₂ present in the earliest sample taken is explained in terms of a dilution effect resulting from the long-term release of inactive CO₂ in the chimney. This hypothesis predicts the observed radial gradient in CO₂ concentration.

Introduction

The first major release of gas from the Project Rulison nuclear gas stimulation experiment occurred on August 1, 1970. Re-entry drilling was terminated

in late July and the gas release accompanied the unloading of the re-entry well. Unloading (i. e., the cleaning out of drilling mud chips, etc.) was accomplished by

pressurization with nitrogen and was begun at about 14:30 local time on August 1. Short-term flaring operations were initiated about 19:30 after the well was cleaned. Initially nitrogen gas was released. Methane was detected in the produced gas at 20:08 and by 20:12 a continuous undiluted (with N₂) flow of "chimney" gases was attained. This production continued for 29 minutes until the well was shut-in. Peak production rate during this flow was 7.2 million cubic feet per day, and the total gas produced was about 147,000 cubic feet. Samples were obtained at intervals for analysis by the project participants. This report includes the results of analyses performed at LRL for the three samples which we received.

Additional calibration flaring attempts during August did not achieve the desired production rates. Lack of open pathways to the chimney was presumed to be the cause of this reduced production capability. Quite possibly, the gas produced on August 1 was drawn from the chimney, at least partially, through pathways which

subsequently were closed. Because of this inability to produce significant quantities of gas, the decision was made to re-open the re-entry well with additional drilling. Further calibration flaring attempts were deferred until early October. No samples for analyses at LRL were obtained although about 1.2 million cubic feet of gas was released during the interim period.

A series of four calibration flaring tests was conducted between October 4 and October 7, 1970. These tests are characterized in Table 1; for further details consult reports of the field operations. Note that the second test period was punctuated by two shut-in periods of approximately 30 minutes each for equipment changes. Samples were obtained at intervals during these tests, and results from the four samples analyzed at LRL are included in this report.

These tests produced the first samples likely to be representative of the gas in the Rulison chimney. We have gone to some lengths, therefore, to evaluate the concentrations and chemical compositions

Table 1. Project Rulison calibration flaring tests, October, 1970.

Period No.	Start		Finish		Flow rate (10 ⁶ ft ³ /d)		Change	No. shut-ins	Total flow ^a (10 ⁶ ft ³)
	Local time	Date	Local time	Date	Start	Finish			
1	0705	10/4	0833	10/4	2.1	2.75	Nearly constant	0	0.17
2	2100	10/4	1300	10/5	2.2	15.6	Gradually increasing	2	5.25
3	1430	10/5	1700	10/5	15.0	15.5	Nearly constant	0	6.84
4	1405	10/6	1315	10/7	5.8	5.8	Nearly constant	0	12.19

^aFlow from October 4, 1970.

of a number of radionuclides in the produced gas. These results will provide a starting point for evaluation

of changes in gas composition resulting from later high-volume production studies.

Gas Sampling

Two of the three August 1 samples received and analyzed at LRL were taken in the 500 ml stainless steel sample bottles provided for this purpose. Each contained about 10 liters of pressurized gas. The third August 1 sample was provided by Fred Johns of the U. S. Public Health Service (SWRHL), and was a portion of a sample taken for their safety program analyses. Approximately four liters of gas was received in a sample container of five liters capacity. These three samples were collected at the start, middle and end of the August 1 flaring, from the high-pressure tank of the drilling well control unit.

Four samples were collected for analysis by LRL during the early October

calibration flarings. All were taken in the 500 ml stainless steel sample bottles and were pressurized to contain 25 to 30 liters of gas. The first two of these were collected shortly after the start of the second flow period. These were sampled prior to and following the separator unit to see if gas composition was affected by this device. Additional samples were collected prior to the separator during the third flow period and 4 hours prior to the end of the fourth and final test series.

Table 2 summarizes the sampling information and production data associated with each of the samples collected for analysis at LRL.

Table 2. Gas samples for analysis at LRL.

LRL sample No.	Date taken	Local time taken	Flow rate at sampling (10 ⁶ ft ³ /d)	Production since last shut-in (10 ⁶ ft ³)	Cumulative total gas production at sampling time (10 ⁶ ft ³)
8	8/1/70	20:15	3.3	0.017	0.017
9	8/1/70	20:24	5.6	0.044	0.044
10 ^a	8/1/70	20:40	— ^b	0.147	0.147
11	10/5/70	02:18	5.1	0.16	2.0 ^c
12	10/5/70	02:45	5.2	0.28	2.1
13	10/5/70	15:07	15.0	0.39	6.6
14	10/7/70	09:00	5.9	4.5	11.2

^aSample taken for U. S. P. H. S. safety analysis program.

^bTaken at or just following shut-in.

^cIncludes 1.2 × 10⁶ ft³ released during field operations between 8/1/70 and 10/4/70.

Chemical Composition

Table 3. Mass spectrometric analyses.^a Air, based on oxygen, has been removed.

Gas	LRL sample No.							Average ^b of sample Nos. 9-14
	8	9	10	11	12	13	14	
N ₂	1.1	0.82	0.93	1.0	0.75	0.86	0.83	0.87(4.1)
CO ₂	34.0	49.3	49.0	47.8	48.1	48.0	48.1	48.4(1.0)
H ₂	19.8	15.7	15.9	15.6	15.6	16.0	15.4	15.7(1.0)
CH ₄	42.2	31.9	31.9	33.3	33.4	33.0	33.2	32.8(1.0)
C ₂ H ₆	2.22	1.70	1.69	1.74	1.74	1.74	1.75	1.73(1.8)
C ₃ H ₈	0.38	0.25	0.29	0.30	0.25	0.25	0.31	0.28(4.1)
Other	0.28	0.29	0.26	0.14	0.22	0.12	0.36	0.23(16)
Air Removed (% of original sample)	0.144	0.095	0.096	1.53	0.191	0.048	0.096	—

^aResults are given in volume percent. The absolute uncertainty in the mass spectrometric results is one to five units in the last reported figure.

^bNumbers in parentheses are standard deviation of the mean expressed in percent.

Chemical analyses were performed on each of the seven samples by mass spectrometry; results are presented in Table 3. Oxygen is presumed not to be a component of the chimney gas, and therefore its presence in the samples is taken as evidence of air inclusion during snap sampling. The components have been normalized to 100% exclusive of air. This correction was based on the oxygen content of the samples as received and was on the order of 0.1% in each case.

All the samples except for the first one, No. 8, appear to be identical within experimental uncertainty. Therefore, results from these six samples have been averaged. The composition of the first

sample, taken at 20:15, differs noticeably from that of the later two, indicating that several minutes flow were required to attain a stabilized or uniform gas composition.

Since ratios of N₂, H₂, C₂H₆ and C₃H₈ to CH₄ are nearly constant throughout these sampling periods, the only major chemical difference between the first and later samples is in the amount of CO₂ present. If the later samples are assumed to represent chimney gas, we are faced with the problems of explaining both a lack of mixing in the produced gas, and the relatively low levels of CO₂ found initially. This question is addressed in the section titled "Carbon Dioxide."

Radiochemical Analyses

Radiochemical analysis was performed on each of the three samples from the

August 1 flaring, and on two of the four samples taken in early October. The

other two were counted to determine only ^{85}Kr and total tritium. Complete analysis of the five selected samples involved the separation of chemically and radiochemically pure fractions of the gas by elution chromatography. Activity levels of these fractions and of the gross sample were measured, according to the decay energy, either by thin-window proportional counters or by internal beta proportional counters. We compared the results of activity measurements from separated samples with those from gross samples to provide an internal check of the data and of the sample-handling technique

employed. The absolute accuracy of these measurements is unknown, but the uncertainty is most probably less than $\pm 10\%$ of the values reported.

Concentrations of the radioactive constituents of these samples are listed in Table 4. Each result is assigned a precision which is the standard deviation of the mean of the replicate measurements comprising each determination. Results for all but the first sample are considered comparable within experimental uncertainty and have, therefore, been averaged. All results have been decay-corrected to the time of detonation, unless otherwise indicated.

Table 4. Radionuclide concentrations in calibration flaring samples: pCi per milliliter of sample after normal air, based on oxygen, has been removed. (Corrected for decay to the time of detonation, unless otherwise indicated).

Gas	LRL sample No.							Average of sample Nos. 9-14
	8	9	10	11	12	13	14	
^{85}Kr	188 (1.6) ^a	150 (1.7)	155 (1.6)	145 (5) ^b	151 (1.8)	148 (5) ^b	150 (1.8)	150 (0.9)
Tritium								
as HT	20.1 (1.9)	17.4 (1.5)	19.4 (1.6)	—	18.7 (1.7)	—	18.4 (2.0)	18.5 (2.3)
as CH_3T	187 (1.9)	146 (1.9)	147 (1.6)	—	142 (4.3)	—	144 (1.8)	145 (0.7)
as $\text{C}_3\text{H}_5\text{T}$	13.6 (1.6)	9.81 (1.6)	10.8 (1.9)	—	11.0 (1.9)	—	10.3 (5)	10.5 (2.6)
as $\text{C}_3\text{H}_7\text{T}$	1.98 (1.6)	1.73 (1.7)	2.46 (2.0)	—	1.64 (4.8)	—	1.61 (2.3)	1.9 (11)
Total tritium	223 (2)	175 (2)	180 (2)	205 (10) ^b	173 (4)	170 (10) ^b	174 (2)	176 (0.6) ^c
^{14}C as $^{14}\text{CO}_2$	0.50 (3.5)	0.36 (3.2)	0.40 (4.6)	—	0.47 (2.1)	—	0.41 (5)	0.41 (1.0)
$^{39}\text{Ar}^{\text{d}}$	1.84 (1.8)	1.46 (1.6)	1.53 (3.2)	—	1.50 (0.4)	—	1.32 (2.5)	1.45 (5.0)
$^{37}\text{Ar}^{\text{e}}$	8300 (10)	5900 (15)	7200 (6.7)	—	—	—	—	6500 (7.0)
^{37}Ar (at sample time)	13.5 (10)	9.68 (15)	11.8 (6.7)	—	—	—	—	10.7 (7.0)
$^{222}\text{Rn} \times 10^3$ (at sample time)	6.83 (2.1)	30.2 (1.6)	—	—	—	—	—	—

^aNumbers in parentheses are standard deviations of the mean of replicate determinations or of the averaged samples expressed in percent.

^bGross count determinations.

^cTotal of average concentrations of tritiated species.

^d ^{39}Ar measurement assumes a 10% counting efficiency based on ^{85}Kr in our thin-window beta proportional counters.

^eQuoted values for ^{37}Ar are obtained from the difference between total argon activity and the ^{39}Ar measured directly.

Totals of Gaseous Species

If the total quantity of a gaseous material in a nuclear chimney is known, then by assuming uniform mixing it is possible to calculate totals of other species existing in the gas. In the absence of a

known quantity of gaseous tracer for the Rulison event, the fission-product gas ^{85}Kr can be used to infer species totals. Calculations of the total quantity of ^{85}Kr are dependent on the actual fission yield

of the explosive, a quantity which is not well known. In this report a total of 960 Ci of ^{85}Kr is assumed to be present in the Rulison chimney.

An estimate of the total quantity of a gas with which the ^{85}Kr is mixed is obtained by dividing the assumed 960 Ci total by the ^{85}Kr concentration in a given sample. From this total gas volume and the concentrations of the various components, totals of the gaseous materials within the Rulison chimney can be calculated. Implicit to this interpretation of the data are the assumptions of uniform mixing and representative sampling. Table 5 is a compilation of the radiochemical and chemical results expressed in terms of totals based on krypton-85.

The observed total gas volume of 6.41×10^9 liters (STP) could be contained in a void volume of 5.4×10^7 liters* (1.9×10^6 ft³) at 200 atm and 375°F, the approximate pressure and temperature of the chimney gas during the calibration flarings. This void, if assumed to represent the volume of the spherical cavity created by the nuclear explosive, corresponds to a cavity radius of 23.5 m (77 ft).

Total tritium present in the chimney gas is seen to be 1120 Ci (0.112 g), and is approximately 10% of the amount (1 g) of this radionuclide expected to be present in the chimney. Presumably the other 0.9 g is combined with chimney water, a compound not measured in this study.

*At a temperature of ~ 375°F, the pressure of saturated steam is 12 to 13 atm, or about 6.5% of the assumed total chimney pressure. Since the degree of steam saturation is speculative, and the proper temperature of steam in the chimney is not known, the partial pressure of steam has been ignored in these calculations. The calculated chimney volume would increase slightly if these considerations were included.

Table 5 shows that the totals of the various species calculated in this way, both chemical compounds and radionuclides, do not vary significantly throughout these flaring tests, with one exception. The total quantity of CO_2 calculated from sample No. 8 is significantly lower than those calculated from the other samples (thus the total gas volume is also lower for No. 8). Therefore sample No. 8 is excluded from the averages of total CO_2 and total gas volume given in Table 5.

Consistency of these totals through the flaring periods of August 1 and early October is to be expected. Relatively small volumes of gas (compared to the amount of gas in the chimney) were released, so that composition changes resulting from dilution should be negligible. Furthermore after the year of shut-in following the detonation chemical and radiochemical interactions were not likely to be proceeding at a rate which would produce significant changes in gas composition over the two-month observation period. Verification of these expectations is an important result of the Gas Quality Program. Continued examination of the gas from full-scale production testing will help to define the extent, if any, of long-term changes in composition resulting from slow reactions among chimney gas components. Full-scale production testing will also allow experimental evaluation of the total gas volume. This will eliminate the uncertainties associated with our assumption of the total amount of ^{85}Kr present in the chimney, and will contribute to our understanding of the phenomena which determine gas quality.

A detailed examination of these results with regard to their contribution to

Total 5. Total of various species mixed with ^{85}Kr , assuming (1) 960 Ci ^{85}Kr total, (2) uniform mixing, and (3) representative sampling.

Gas	LRL sample No.							Average
	8	9	10	11	12	13	14	
<u>Major components</u>	<u>Gas volumes (10^9 liters STP)</u>							
CO_2	1.74	3.15	3.03	3.16	3.06	3.12	3.08	3.08 (0.7) ^{a,b}
H_2	1.01	1.00	0.985	1.03	0.993	1.04	0.990	1.00 (0.8)
CH_4	2.16	2.04	1.98	2.20	2.12	2.14	2.13	2.11 (1.4)
C_2H_6	0.113	0.109	0.105	0.115	0.111	0.113	0.112	0.111 (1.2)
C_3H_8	0.020	0.016	0.018	0.020	0.016	0.016	0.020	0.018 (4.3)
Total	5.11	6.39	6.19	6.61	6.36	6.49	6.41	6.41 (0.9) ^b
<u>Radionuclides</u>	<u>Curies (at time of detonation)</u>							
Tritium								
as HT	103 (1.9) ^a	111 (15)	120 (1.6)	—	119 (1.7)	—	118 (2.0)	114 (1.2)
as CH_3T	956 (1.9)	936 (1.9)	912 (1.6)	—	904 (4.3)	—	921 (1.8)	926 (0.9)
as $\text{C}_2\text{H}_5\text{T}$	69.4 (1.6)	62.8 (1.6)	66.6 (1.9)	—	69.7 (1.9)	—	66.1 (5)	64.9 (1.8)
as $\text{C}_3\text{H}_7\text{T}$	10.1 (1.6)	11.1 (1.7)	15.2 (2.1)	—	10.4 (4.8)	—	10.3 (5)	11.4 (3.7)
Total tritium	1140 (1.6)	1120 (2.2)	1110 (1.3)	1360 (10)	1100 (3.5)	1100 (10)	1120 (1.5)	1120 (0.7)
^{37}Ar (10^{-4})	4.22 (10)	3.78 (15)	4.46 (6.8)	—	—	—	—	4.15 (2.7)
^{39}Ar	9.42 (1.8)	9.31 (1.6)	9.48 (3.2)	—	9.52 (1.9)	—	8.45 (1.9)	9.24 (1.6)
^{14}C as CO_2	2.55 (3.5)	2.32 (3.2)	2.45 (4.6)	—	2.98 (2.1)	—	2.61 (5)	2.58 (2.5)

^aNumbers in parentheses are percent standard deviation of the mean of replicate determinations or of the averaged samples.

^bAverage excludes samples No. 8.

our understanding of the phenomena which determine gas quality is beyond the scope of this paper. Such interpretation should properly await experimental

evaluation of the total gas volume during production testing, so that the uncertainties associated with the assumption of the total of 960 Ci of ^{85}Kr can be eliminated.

Specific Activity

It is often instructive, when the radiochemistry of tritium and carbon-14 is considered, to examine the ratio of the radioactive isotope to the total amount of the element in each of its various chemical compounds. This ratio, referred to as the specific activity, is conveniently expressed in units of picocuries of tritium or carbon-14 per standard milliliter of the chemical compound of interest. Defined in this way, the specific activity is related to the more conventional definition (based on atom ratios) according to the number of hydrogen or carbon atoms per molecule of the gas. Thus, at a constant tritium-to-hydrogen-atom ratio, the specific activities of hydrogen, methane, ethane, and propane would exhibit a 1:2:3:4 ratio.

Specific activities of some tritium and carbon-14 compounds are listed in

Table 6. Again, the CO_2 fraction of sample No. 8 exhibits the only significant variation from the sample-to-sample norm. Therefore, the CO_2 average given in the table excludes the first ^{14}C data point. Dilution of the $^{14}\text{CO}_2$ observed in sample No. 8 with CO_2 of much lower specific activity is the most probable explanation for this variation; this possibility is examined in the next section. The constancy of the specific activities of the tritiated species through the sampling period indicates a lack of significant exchange or dilution effects, and again, is not unexpected.

Specific activities of methane and ethane exhibit the 2:3 ratio expected if a constant tritium-to-hydrogen ratio is assumed. Other tritiated species are not consistent with this assumption, however. Since tritium exchange equilibria

Table 6. Specific activities of tritium- and carbon-14-containing compounds: PCi per milliliter of isotopic species.

Gas	LRL sample No.							Average
	8	9	10	11	12	13	14	
Tritium								
HT in H_2	102 (2.1) ^a	111 (15)	122 (1.4)	-	120 (1.4)	-	119 (2.0)	115 (3.2)
$\text{C}^3\text{H}_3\text{T}$ in CH_4	423 (2.1)	459 (2.0)	461 (1.4)	-	426 (4.0)	-	433 (1.5)	444 (1.9)
$\text{C}_2\text{H}_5\text{T}$ in C_2H_6	612 (2.4)	577 (2.4)	636 (3.2)	-	629 (2.8)	-	588 (6.0)	608 (1.7)
$\text{C}_3\text{H}_7\text{T}$ in C_3H_8	520 (10)	692 (10)	846 (12)	-	653 (15)	-	518 (12)	646 (9.0)
$^{14}\text{CO}_2$ in CO_2	1.46 (3.1)	0.735 (2.7)	0.810 (4.3)	-	0.976 (2.2)	-	0.845 (5.2)	0.841 (6.0) ^b

^aNumbers in parenthesis are standard deviation of the mean of replicate determinations or of the averaged samples expressed as percent.

^bAverage excludes sample No. 8.

involving HT and either water or methane favor the more complex compounds, the depressed specific activity of the hydrogen fraction relative to methane is an indication that exchange did occur. Pro-

pane might not have participated extensively in tritium exchange, and would not have been a significant component of the early chimney gases. The relatively low specific activity of propane is not unexpected.

Carbon Dioxide

Throughout the preceding discussions the only significant difference observed between samples was related to the CO₂ content of sample No. 8 as compared to the later samples. The observed differences can be explained by assuming a dilution effect resulting from an admixture of more CO₂ into the later samples. To test the dilution postulate, calculations of the expected changes in ¹⁴C concentration, total CO₂, and ¹⁴C specific activity have been made. These calculations are based on the observed fractional CO₂ content of the samples, and the observation that the ratio of ⁸⁵Kr to sample components other than CO₂ is constant (Table 5). For simplicity the additional CO₂ is assumed to contain no ¹⁴C. The observed changes are compared to those calculated in Table 7.

The expressions for the changes expected from dilution of a uniform mixture of gas by inactive carbon dioxide are as follows:

$$\Delta \frac{\text{pCi } ^{14}\text{CO}_2}{\text{ml sample}} = - \frac{(1-\text{CO}_2)_{9-14}}{(1-\text{CO}_2)_8} \quad (1)$$

$$\Delta \text{ total CO}_2 =$$

$$\left[\frac{(\text{CO}_2)_{9-14}}{(\text{CO}_2)_8} \times \frac{(1-\text{CO}_2)_8}{(1-\text{CO}_2)_{9-14}} \right] - 1 \quad (2)$$

$$\Delta \frac{\text{pCi } ^{14}\text{CO}_2}{\text{ml CO}_2} = \left[\frac{(\text{CO}_2)_8}{(\text{CO}_2)_{9-14}} \times \frac{(1-\text{CO}_2)_{9-14}}{(1-\text{CO}_2)_8} \right] - 1 \quad (3)$$

Table 7 shows that the observed changes are consistent with the hypothesis that additional inactive carbon dioxide is the only significant difference between these samples. To explain the apparent lack of mixing and the appearance of additional CO₂ as production proceeded, it is necessary to examine the conditions likely to exist in the nuclear chimney following collapse. We suggest the following model.

At some finite time shortly after chimney collapse the void spaces would be filled to essentially formation pressure with a reasonably uniform mixture of hydrocarbon gases and products of the nuclear detonation including CO₂, H₂, and the radionuclides. The distribution of heat energy through the chimney rubble would be far from uniform, and convective mixing of these gases is postulated. However, as the available heat energy spreads, additional carbon dioxide containing little or no ¹⁴C would be liberated by the decomposition of carbonate minerals. Thus the gases in the

Table 7. Summary of CO₂ and ¹⁴C results.

	Sample No. 8	Sample Nos. 9-14	% change relative to sample No. 8	
			Observed	Calculated ^a
% CO ₂	34.0 (1.7) ^b	48.4 (1.3)	+42	-
pCi ¹⁴ CO ₂ /ml sample	0.50 (3.5)	0.41 (1.0)	- 18	- 22
Total CO ₂ (10 ⁹ liters)	1.74 (2.3)	3.08 (0.7)	+77	+82
Total ¹⁴ C as CO ₂ (Ci)	2.55 (3.5)	2.58 (2.5)	0	0
pCi ¹⁴ CO ₂ /ml CO ₂	1.46 (3.9)	0.841 (6.0)	-42	- 44

^aCalculated changes are based on the observed fractional CO₂ content of the samples and the observation that the ratio of ⁸⁵Kr to sample components other than CO₂ is constant. Inactive CO₂ is assumed to be the diluant.

^bNumbers in parentheses are percent standard deviations of the mean of replicate measurements or of the samples included in the average.

chimney could be driven into the surrounding fracture zone by the increasing CO₂ pressure, and effectively removed from the region where mixing was possible. Liberation of CO₂ would be expected to reach some sort of equilibrium at the temperature and partial pressure existing in the chimney at late times.

It is possible that continued generation of CO₂ causes expansion of chimney gases into the formation at late times. Then one would expect to observe a

gradient in CO₂ concentration (and also in apparent totals, specific activity, etc.) as a function of distance from the chimney. Diffusion could eventually destroy this gradient, but this process is slow at the pressures observed. By drawing gas from the re-entry well, which was connected to the nuclear chimney through the fracture region, we were able to observe a gradient in carbon dioxide content. This is consistent with our hypotheses about conditions in the chimney following collapse.

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