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UCRL-51153

**GAS ANALYSIS RESULTS
FOR PROJECT RULISON PRODUCTION TESTING SAMPLES**

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MS. date: November 29, 1971

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GAS ANALYSIS RESULTS FOR PROJECT RULISON PRODUCTION TESTING SAMPLES

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Abstract

Results obtained by chemical and radiochemical gas analysis of samples taken from the flowing gas stream during the Project Rulison nuclear gas stimulation experiment are presented and discussed. These results cover the production testing period from October 26, 1970 through April 23, 1971, when nearly 420 million ft³ of gas were flared in three testing periods. The combined effects of production and dilution of the initial chimney gases resulted in a reduction in the radionuclide concentrations present in the produced gas by about a factor of 50. The most significant radionuclide, tritium, decreased from 176 to 3.7 pCi/ml of produced gas, while ⁸⁵Kr changed from 150 to 2.9 pCi/ml. Throughout the testing period the distribution of tritium among the gases was approximately 81% in CH₄, 11% in H₂, 6% in C₂H₆ and 1% in C₃H₈. The chemical composition of the produced gas also changed significantly during production. Carbon dioxide concentration dropped from 48% to 22%, and that of H₂ from 15.7% to 1.0%. Concentrations of the components of formation gas increased through the test period by about a factor of 2. The methane concentration went from 32.8% to 71.6%, that of ethane from 1.7% to 3.6%, and that of propane from 0.3% to 1%. The anomalous behavior of

CO₂ is due to late-time introduction of this material from at least two sources. One of these, containing ¹⁴C and accounting for a 15% increase in the total CO₂ available, may be evidence for the release of gas dissolved in chimney water. The second source released CO₂ which was free of ¹⁴C, and accounted for an 8% increase in total CO₂ in the chimney. This material could be the result of continued decomposition of carbonate minerals. A similar ebullition effect, though to a considerably lesser extent, is seen in the behavior of H₂. The specific activity of hydrogen gas is constant throughout the test, and is consistent with the maintenance of tritium exchange equilibrium between water and hydrogen gas. We have not observed any other tritiated species in tritium exchange reactions. Based upon an assumed total quantity (1100 Ci) of ⁸⁵Kr in the preproduction chimney gas and the reasonably constant total gaseous tritium-to-⁸⁵Kr ratio, we infer that a total of 1300 Ci of tritium was present in the chimney gas before production. This is 13% of the total of 1g of this material which was predicted to be present following the detonation. The remaining 87% is presumed to be bound in nonvolatile compounds, water and solidified melt.

Introduction

Project Rulison was the second joint Industry-Government experiment to establish the technology for stimulation of gas production in a low-permeability, gas-bearing rock matrix using nuclear explosives. A nominal 40-kt explosive device was detonated 2573 m below the ground surface near Rifle, Colorado, on September 10, 1969. The first gas release from the nuclear chimney followed completion of the reentry well and occurred on August 1, 1970. A limited quantity of gas was produced during August and October of 1970 to calibrate release monitoring equipment and to characterize the chimney gas composition as a part of the safety program. During these calibration flaring

periods, a total of 11.3 million ft^3 (M^2CF) of gas was released.

Actual production testing of the nuclear chimney well began on October 26, 1970. There were three distinct test periods, separated by temporary shut-in periods, and terminated on April 23, 1971 by an extended shut-in for long-term pressure buildup measurements. During these tests, a total of nearly 420 million ft^3 of dry gas was flared. Twelve samples, obtained during production, were analyzed at LLL as a part of our continuing Flow-share gas quality program. The results of these analyses are presented and discussed in this report.

Production Testing Operations

Before presenting the gas analytical results we will briefly describe the gas production tests which were conducted at Rulison. Although the following discussion is adequate to provide the basic information necessary to interpret the gas quality results, considerably more detail is available in the open literature, if such is desired.¹⁻⁴ The data summarized here are taken from the latest available open file information, and have been corrected to a dry gas basis.

Figure 1 shows the quantity of dry gas withdrawn from the Rulison chimney as a function of time. The solid lines represent the three production test periods, and are connected with horizontal dotted lines during shut-in periods. The circles represent conditions at the time samples

were obtained for LLL analysis. Sampling information is summarized in the next section.

The first, or high-rate, production test was performed between October 26 and November 3, 1970. It was designed to investigate gas flow in the areas of highest permeability near the nuclear chimney, and to obtain a measure of chimney size. Gas flow rates were initially about 20 million ft^3 per day (M^2CFD) and were allowed to decline through the test to about 12 M^2CFD just before shut-in. The total quantity, 104 M^2CF , of dry gas produced caused a chimney pressure reduction from 3150 psig to 2120 psig.

The Rulison reentry well remained shut-in between November 3 and December 1,

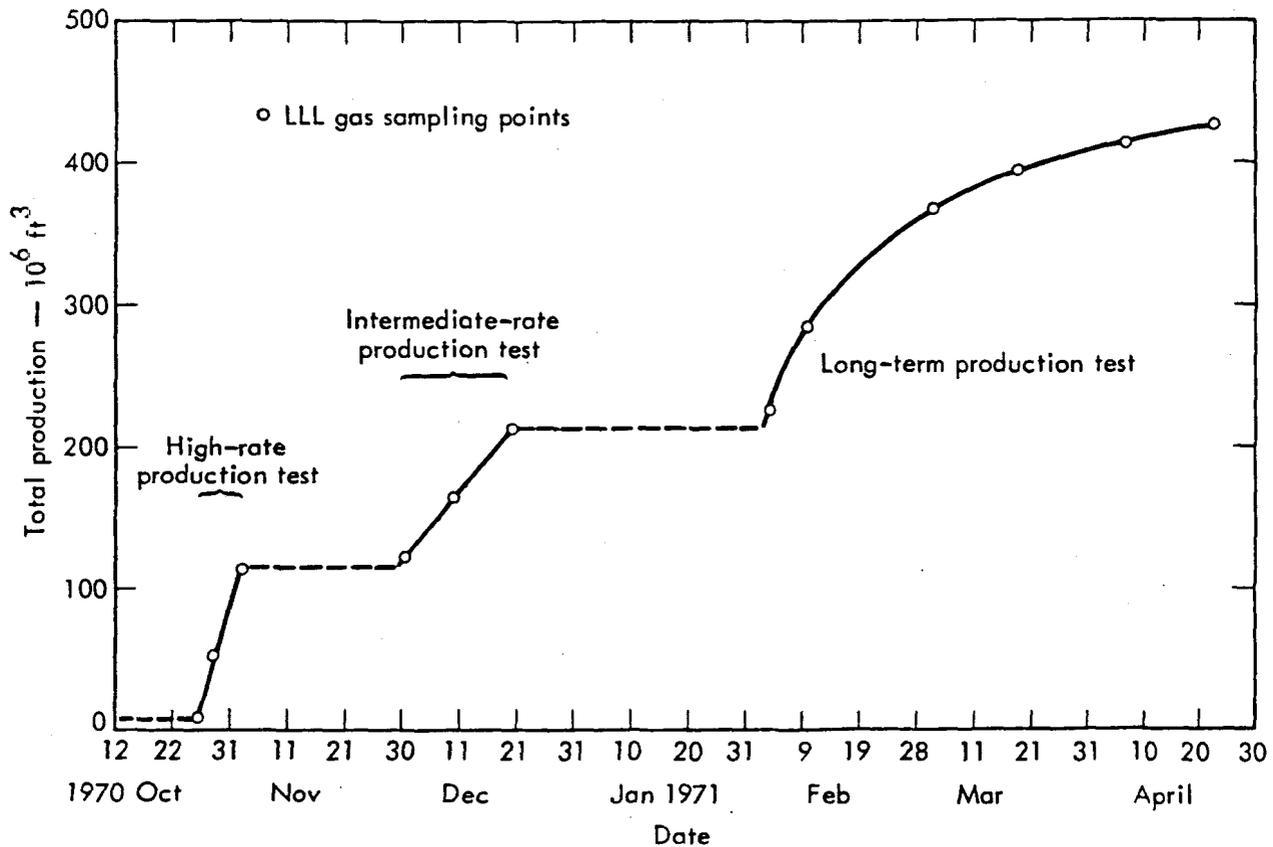


Fig. 1. Project Rulison production testing. Dry gas produced is plotted as a function of time.

1970, when the second (intermediate-rate) production test was begun. This test continued at a reasonably constant production rate of $5 \text{ M}^2\text{CFD}$ until December 20, 1970 when the well was again shut-in to observe pressure buildup. About $98 \text{ M}^2\text{CF}$ of dry gas was flared during this period. Chimney pressure, which had increased to 2330 psig before this test, was 1485 psig when the test was completed. The intermediate-rate production test program was intended to measure the gas flow characteristics in the formation beyond the fracture region.

During the shut-in period following the second production test, the down-hole pressure increased to about 1710 psig. Flaring again began on February 3, 1971 when the reentry well was opened to start the third

(long-term) production test. It was intended to reduce the chimney pressure so that gas influx could be monitored. Accordingly, we established an initial flow rate of $10 \text{ M}^2\text{CFD}$. Gas flows decreased rapidly at first, reaching $2 \text{ M}^2\text{CFD}$ by early March and about $1 \text{ M}^2\text{CFD}$ by mid-April. The well was flowing $< 0.9 \text{ M}^2\text{CFD}$ dry gas when it was shut-in on April 23, 1971 to begin an extended pressure buildup monitoring period. The down-hole pressure at shut-in was about 250 psig. Total gas produced in this test was $212 \text{ M}^2\text{CF}$.

The total flow during the last test has been corrected by Montan⁴ for noncritical flow through the flow prover. The correction is significant only for the last two samples, and is $4.5 \text{ M}^2\text{CF}$ when applied to the total gas production from Rulison.

Gas Sampling

The goal of the LLL Technical Gas Analysis program for Rulison was to investigate gas quality as a function of time and production. Most information regarding the radionuclide concentration in the produced gas was gathered for the Rulison safety program by on-site continuous monitors.^{2, 3} Our intent was to supplement these measurements with a limited number of detailed analyses, and to examine the results from a technical viewpoint. For this purpose, 12 gas samples were collected and analyzed at LLL. During each of the first two test periods, these collections occurred shortly

after the start of production, about at the test mid-point, and just before shut-in. Because of the extended and uncertain time period associated with the long-term production test, sample collection was planned at 1- to 2-week intervals. As a result, six samples were obtained and analyzed during the long-term flow test. The relationship of each of these twelve samples to the total gas production is indicated in Fig. 1. Table 1 summarizes pertinent sampling information and production data associated with each of the production test samples analyzed at LLL.

Table 1. Gas samples for analysis at LLL.^a

LLL sample No.	Date taken	Local time taken	Flow rate at sampling (M ² CFD)	Production since last shut-in (M ² CF)	Cumulative total gas production at sampling time (M ² CF)
<u>High-rate test</u>					
15	10/26/70	2035	17	1.4	13
16	10/29/70	0900	14	40	51
17	11/3/70	1117	11	103	114
<u>Intermediate-rate test</u>					
18	12/2/70	1244	5.2	5	121
19	12/10/70	1500	5.2	47	163
20	12/20/70	0950	5.1	98	213
<u>Long-term test</u>					
21	2/3/71	0947	10	11	225
22	2/10/71	1530	6	69	283
23	3/4/71	0900	2.2	152	365
24	3/19/71	1600	1.4	178	393
25	4/7/71	1215	1.0	200	414
30	4/23/71	1146	0.9	212	426

^aGas flow rates and total production figures are referenced to normal temperature and pressure (60°F, 14.7 psig).

The samples were collected downstream from the separator in 500-ml evacuated stainless steel sample bottles which were opened to the flowing gas stream. Gas volumes varied as a result of the pressure decrease accompanying gas production. When testing began, samples were of the order of 30 liters, corresponding to nearly 1000 psig. Sample volumes during the long-term test were limited by

the available well-head pressure, and ranged from 15 liters (600 psig) to about 2 liters (40 psig). In most cases, 1 liter of sample was enough for the analyses reported here. Note that, as indicated in Table 1, enough gas was produced before each sample collection to assure that gas samples were representative of existing down-hole conditions and composition.

Analytical Results

CHEMICAL COMPOSITION

Mass spectrometry was used to chemically analyze each sample received. The results are presented in Table 2 and in Fig. 2. The average composition of six calibration flaring samples is included as a reference point. These analyses have been described in some detail in a previous report.⁵ Oxygen is assumed not to be a component of chimney gas, and therefore its presence in a sample is taken as evidence of air inclusion during snap sampling. Where this occurred the quantity of normal air, based on the observed oxygen, has been subtracted from the analysis. The remaining components (exclusive of air) were then renormalized to 100% to obtain the results presented here. The percentage of each original sample which was assumed to be air is given in Table 2. In most cases, the air correction is seen to be small.

Figure 2 shows concentrations of the main components of the produced gas plotted as a function of gas production. The gradually increasing fraction of the gas produced, which is hydrocarbons, is

due to the influx of formation gases into the chimney as production proceeds. Note that the C_2H_6 concentration is about 5% of the CH_4 and that C_3H_8 is about 1% of the CH_4 . These ratios are reasonably

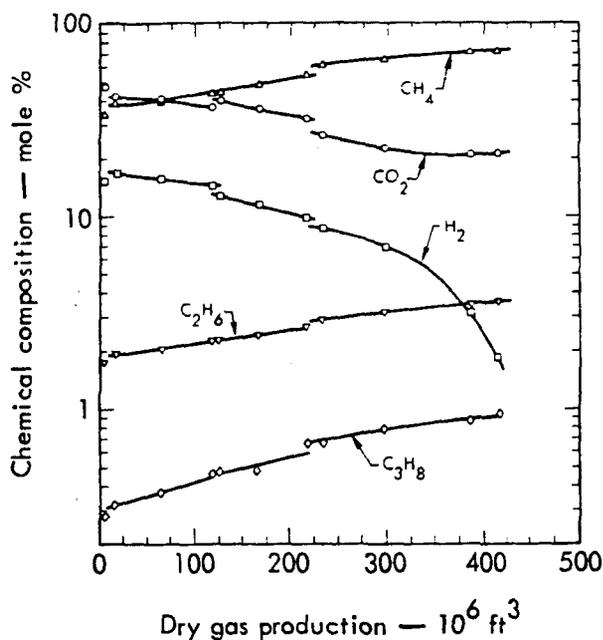


Fig. 2. Chemical composition of gas produced at Project Rulison plotted as a function of dry gas production. Data points at $5 \times 10^6 \text{ ft}^3$ are the average of five samples collected during calibration flaring. Solid-line segments define the three production test periods.

constant throughout the production test period, and are in good agreement with similar ratios obtained from preshot gas analyses.*

*Average of preshot analyses from Austral well 25-95-A (the Rulison emplacement well) indicate the following ratios: $C_2H_6/CH_4 = 4.3\%$ and $C_3H_8/CH_4 = 1.0\%$ (see Table 2).

The concentrations of H_2 and CO_2 , the major nonformation gas components of the produced gas, are also plotted in Fig. 2. If dilution of chimney gas by formation gas influx was the only important factor affecting the H_2 and CO_2 concentrations, we would expect these curves to be parallel and to drop off at an increasing rate, as determined by the amount of formation gas

Table 2. Chemical composition – air based on oxygen has been removed.^a

Pot	N_2	CO_2	H_2	CH_4	C_2H_6	C_3H_8	Other	Air removed (% of original sample)
<u>Formation gas composition^b</u>								
	1.42	Trace	–	92.3	4.0	0.93	0.96	–
<u>Calibration flaring^c</u>								
Av	0.87	48.4	15.7	32.8	1.73	0.28	0.23	–
<u>High-rate test</u>								
15	0.92	41.3	16.9	38.5	1.95	0.32	0.11	0.239
16	0.83	42.1	15.7	38.9	2.02	0.37	0.13	0.096
17	0.69	37.1	14.4	44.9	2.27	0.46	0.19	0.143
<u>Intermediate-rate test</u>								
18	0.59	39.4	12.7	44.4	2.23	0.48	0.24	0.143
19	0.46	36.1	11.6	48.7	2.38	0.48	0.23	–
20	0.30	32.2	9.8	54.0	2.67	0.66	0.36	–
<u>Long-term test</u>								
21	0.29	25.8	8.3	58.8	2.80	0.64	3.39	–
22	0.40	22.5	7.0	65.8	3.16	0.79	0.39	–
23	0.08	21.1	3.2	70.7	3.46	0.86	0.65	0.29
24	0.11	21.5	1.9	71.6	3.53	0.93	0.50	0.24
25	–	23.2	1.2	70.6	3.50	0.95	0.71	0.14
30	0.02	22.2	0.98	71.6	3.60	0.98	0.68	0.29

^aResults are given in vol%. The absolute uncertainty in the mass spectrometric results is 5 units in the last reported figure.

^bAverage of five analyses of samples taken during March and April, 1969, from Austral well 25-95-A (Rulison emplacement hole).

^cRef. 5.

influx and the total amount of these materials removed from the chimney. As will be seen, neither of these species behaves in this manner, although the disparity is most obvious in the CO_2 concentration. Apparently, a source of CO_2 was contributing this material to the chimney gas at late times to maintain its concentration at about 20%. The behavior of CO_2 at early times in the production testing is also anomalous.⁵ Note that an apparent depression in the CO_2 content of the produced gas occurred in the high-rate test period. The decreased CO_2 concentration is reflected by proportionate increases in other chimney gas components, as seen in Fig. 2. These observations will be expanded and discussed in more detail following presentation of the radionuclide concentration results.

RADIOCHEMICAL ANALYSIS

Radiochemical analysis was performed on each of the 12 samples obtained during production testing. These analyses involved the separation of chemically and radiochemically pure fractions of the gas by elution chromatography. Activity levels of these fractions were measured either by thin-window proportional counters or by internal beta proportional counters, depending upon the decay energy. Each sample was also counted by both techniques before separation to provide gross activity level measurements for later comparison with the sum of the individual fractions. This comparison provided an internal check of the results 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.

Table 3 lists concentrations of the radioactive constituents of these samples, and Fig. 3 plots the concentrations as a function of gas production. Each result is assigned a precision which is the standard deviation of the mean of the replicate measurements which constitute each determination. All results have been decay-corrected to the time of detonation.

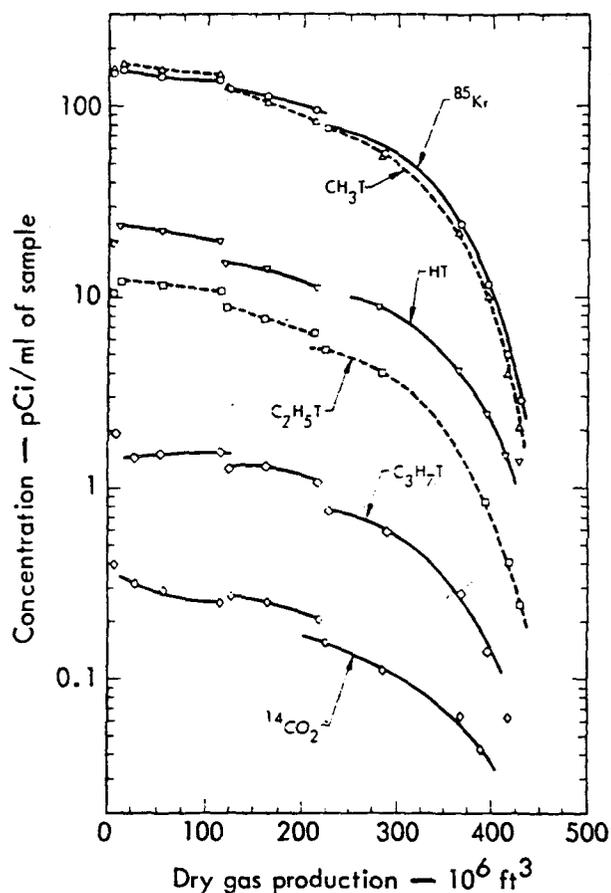


Fig. 3. Concentration of principal radionuclides during Project Rulison production testing plotted as a function of dry gas produced. Data points at $5 \times 10^6 \text{ ft}^3$ are the average of five samples collected during calibration flaring. Solid-line segments define the three production test periods.

Table 3. Radionuclide concentrations: pCi/nl STP sample^a after removal of normal air based on oxygen. Corrected for decay to the time of detonation (9/10/69).

Pot	Kr	HT	CH ₃ T	C ₂ H ₅ T	C ₃ H ₇ T	Total T	¹⁴ C ₂
<u>Calibration flaring</u>							
Av	150 (0.9)	18.5 (2.3)	145 (0.7)	10.5 (2.6)	1.9 (1)	176 (0.6)	0.41 (1.0)
<u>High-rate test</u>							
15	158 (1.6)	23.9 (3.4)	167 (1.7)	12.1 (1.5)	1.48 (1.7)	204 (3.8)	0.319 (4.4)
16	144 (3.1)	22.3 (3.3)	157 (2.7)	11.5 (5.6)	1.52 (4.7)	192 (6.0)	0.290 (6.4)
17	138 (1.6)	19.8 (1.6)	145 (3.2)	10.5 (1.7)	1.56 (3.0)	176 (3.5)	0.260 (3.1)
<u>Intermediate-rate test</u>							
18	122 (4.7)	14.9 (3.7)	121 (5.7)	8.86 (3.7)	1.28 (3.7)	146 (6.1)	0.275 (14)
19	111 (2.5)	14.3 (3.0)	101 (3.6)	7.62 (2.4)	1.30 (6.2)	124 (5.8)	0.260 (20)
20	94.7 (3.6)	11.5 (2.8)	81.0 (2.8)	6.42 (3.3)	1.09 (9.4)	101 (7.6)	0.207 (18)
<u>Long-term test</u>							
21	76.5 (2.2)	13.5 (5.2)	73.1 (2.6)	5.35 (2.2)	0.765 (1.9)	~90	0.153 (2.4)
22	57.7 (3.4)	8.86 (6.2)	56.7 (2.7)	4.15 (2.6)	0.596 (4.8)	70.3 (6.1)	0.114 (6.4)
23	24.1 (2.3)	4.02 (2.4)	22.2 (7.0)	—	0.277 (2.3)	~28	0.061 (~30)
24	12.0 (1.9)	2.47 (2.6)	9.81 (1.7)	0.861(2.0)	0.134 (2.2)	13.3 (3.0)	0.145 (~30)
25	4.98 (1.7)	1.46 (3.5)	4.00 (2.9)	0.440(2.8)	0.025 (4.9)	5.9 (5.1)	0.058 (~30)
30	2.86 (1.7)	1.38 (1.6)	2.03 (2.7)	0.248(2.0)	0.065 (4.7)	3.7 (4.2)	—

^aNumbers in parenthesis are standard deviations of the mean of replicate determinations. The absolute accuracy of these measurements is unknown, but the uncertainty is most probably < ±10% of the values reported.

Examination of Fig. 3 reveals a striking similarity in shape of the radionuclide concentration curves. In particular, with regard to the tritiated species, this similarity is evidence that no compositional changes due to exchange interactions are occurring. This topic will be discussed in greater detail in the next section. The shape of the curves in Fig. 3 is determined by the amount of diluent gas influx from the formation and the fraction of these species which remain in the chimney as production proceeds. These data are, therefore, useful in the interpretation of the results of production testing, and have been used in this manner by Montan in his analysis of the Rulison experiment.⁴ Based on the rapid decline of these curves

near the end of the long-term production test and the declining down-hole pressure and the chemical composition of the produced gas, it is reasonable to assume that essentially all the original chimney gas components have been produced.

SPECIFIC ACTIVITY

It is often instructive when the radiochemistry of tritium or ¹⁴C 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 ¹⁴C per standard milliliter of the chemical compound of interest. Defined in this way the

specific activities of hydrogen, methane, ethane and propane would exhibit a 1:2:3:4 ratio at a constant tritium-to-hydrogen ratio. Table 4 lists specific activities of the compounds of interest, and Fig. 4 plots selected curves.

Three distinctly different classes of behavior are evident from the curves in Fig. 4. The specific activity of methane is decreasing markedly, as would be the expected effect of dilution of chimney gas by influx of formation gas. Ethane and propane, though not shown in Fig. 4, exhibit the same behavior. Taking the ratio of specific activities of either ethane or propane to that of methane, one obtains the relative tritium-to-hydrogen ratios indicated in Table 5. Note from Table 5 that the ethane-to-methane ratio is slightly less than the 3:2 ratio which would be expected for an equal tritium-to-hydrogen ratio in the two compounds. Propane contains only about half as much tritium as would be expected on the same basis. The constancy of the ratios listed in Table 5 indicates that no significant tritium exchange involving the light hydrocarbons has occurred.

Since hydrogen is not a component of formation gas, dilution is not important in effecting changes in its specific activity. The most likely such influence would be exchange with water in the chimney. Fig. 4 demonstrates that this effect is unimportant or that exchange equilibrium has been established. This is also demonstrated by the constancy of the data in Table 4.

Carbon dioxide might also be expected to demonstrate only exchange effects in

the shape of its specific activity curve. However, as will be seen later, the amount of ^{14}C which is mixed with the chimney gas is essentially constant, implying the absence of exchange effects. Therefore, the pronounced deviation from a constant CO_2 specific activity, illustrated in Fig. 4, must be due to dilution effects. Since carbon dioxide is not a major component of formation gas, we must postulate a late-time generation of CO_2 which is available to mix with and dilute the chimney gases during the production testing. This subject will be considered in the next section of this report.

Although we made few analyses of tritiated water as a part of the LLL study, daily determinations were made as a part of the documentation of radionuclides

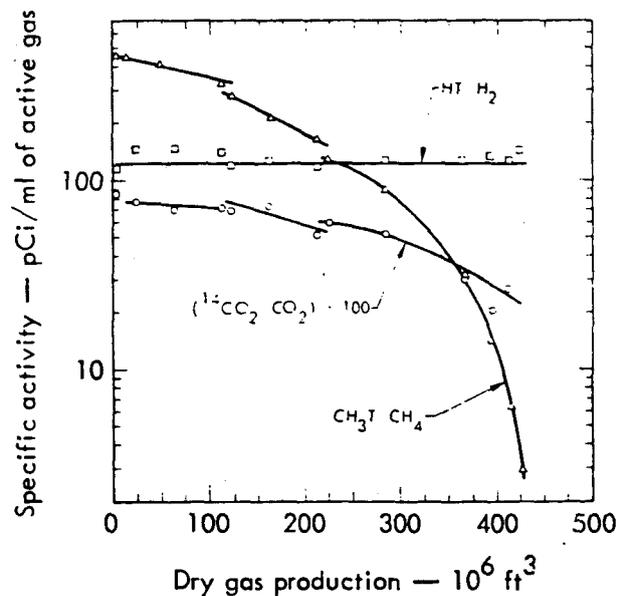


Fig. 4. Specific activity of selected chimney gas components during production testing at Project Rulison plotted as a function of dry gas production. Data points at $5 \times 10^6 \text{ ft}^3$ are the average of five samples collected during calibration flaring. Solid-line segments define the three production test periods.

Table 4. Specific activities of compounds containing tritium and ^{14}C : pCi/ml of isotopic species.

Pot	HT in H_2	CH_3T in CH_4	C_2H_5 in C_2H_6	C_3H_7 in C_3H_8	$^{14}\text{CO}_2$ in CO_2
<u>Calibration flaring</u>					
Av	115 (3.2) ^a	444 (1.9)	608 (1.7)	646 (9.0)	0.841 (6.0)
<u>High-rate test</u>					
15	141 (3.0)	433 (0.8)	621 (0.2)	462 (0.7)	0.775 (4.2)
16	142 (2.2)	404 (1.0)	570 (5.0)	410 (4.0)	0.689 (5.9)
17	137 (0.5)	322 (2.8)	460 (0.6)	339 (2.6)	0.703 (2.7)
<u>Intermediate-rate test</u>					
18	117 (1.2)	273 (4.5)	397 (1.2)	266 (1.1)	0.698 (13.5)
19	124 (2.1)	207 (3.0)	320 (1.1)	271 (5.9)	0.721 (20)
20	117 (0.4)	152 (0.4)	240 (1.8)	165 (8.9)	0.507 (18.0)
<u>Long-term test</u>					
21	162 (6.2)	124 (1.8)	191 (1.0)	120 (0.1)	0.591 (1.4)
22	127 (5.6)	86.1 (0.6)	132 (0.1)	75.5 (4.1)	0.509 (5.9)
23	127 (1.4)	31.4 (0.4)	—	32.2 (2.3)	0.291 (30)
24	131 (1.9)	13.7 (0.4)	24.4 (1.2)	14.3 (1.4)	0.201 (30)
25	126 (3.1)	5.66 (2.4)	12.6 (2.3)	2.61 (4.6)	0.267 (29)
30	140 (0.4)	2.83 (2.2)	6.88 (1.2)	6.62 (4.4)	—
Av	125 (2.1)	—	—	—	—

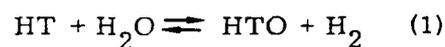
^aNumbers in parenthesis are % standard deviation of the mean of replicate determinations.

released during production.¹⁻³ Although some variation in the measured concentrations of tritium in the produced water vapor was observed, it was remarkably constant as compared to Gasbuggy experience. The average specific activity reported during the production test periods was $0.4 \pm 0.1 \mu\text{Ci}/\text{cm}^3$ of liquid water.* Converting to units comparable to those listed in Table 4, this average corresponds

*This average includes 257 determinations involving both water recovered from the separator and water trapped from the gas stream.

to 320 ± 80 pCi/ml vapor. Table 6 compares the specific activities of the tritiated species.

If isotopic exchange equilibrium was established, the ratio of selected specific activities should approximate the equilibrium constant for the reaction. For example, the equilibrium constant for the reaction



is

$$K_{\text{eq}} = \frac{\text{HTO}/\text{H}_2\text{O}}{\text{HT}/\text{H}_2} \quad (2)$$

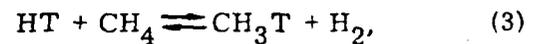
Table 5. Specific activity ratios of ethane and propane to methane.

Pot	C_2H_5T/C_2H_6	C_3H_7T/C_3H_8
	CH_3T/CH_4	CH_3T/CH_4
<u>Calibration flaring</u>		
Av	1.37	1.45
<u>High-rate test</u>		
15	1.43	1.07
16	1.41	1.01
17	1.43	1.05
<u>Intermediate-rate test</u>		
18	1.45	0.974
19	1.55	1.31
20	1.59	1.09
<u>Long-term test</u>		
21	1.54	0.961
22	1.53	0.877
23	-	-
24	1.78 ^a	1.04
25	2.23 ^a	0.46 ^a
30	2.43 ^a	2.34 ^a
Av	1.44 (1.6)	1.19 (5.0)

^aExcluded from average.

Using the specific activities measured in Rulison samples, the observed equilibrium constant is 2.6. This value for the equilibrium constant is that expected for an equilibrium established at 210°C (410°F).⁶ Since the measured down-hole temperatures have, for the most part, been between 400° and 430°F, we conclude that tritiated hydrogen is in exchange equilibrium with water in the chimney. Because of this evident maintenance of exchange equilibrium at existing chimney temperatures and the constancy of the hydrogen specific activity throughout the production testing, there cannot have been significant incursion of water into the Rulison chimney during this period (such as that which occurred at Gasbuggy).

A similar calculation for the tritium exchange between methane and hydrogen,



reveals an apparent equilibrium constant of 3.5, corresponding to an equilibrium temperature of 315°C (600°F).⁷ No evidence exists for maintenance of this

Table 6. Comparison of tritiated compounds – specific activities.

Compound	Specific activity (pCi/ml)	Normalized to $CH_3T/CH_4=2$	Expected ratio, assuming equal T/H (high-temperature)
HT/H ₂	125 ± 3 ^a	0.56 ± 0.2	1
HTO/H ₂ O	320 ± 80	1.45 ± 0.4	1
CH ₃ T/CH ₄	442 ± 8 ^b	2.00	2
C ₂ H ₅ T/C ₂ H ₆	610 ± 10 ^b	2.76 ± 0.05	3
C ₃ H ₇ T/C ₃ H ₈	620 ± 50 ^b	2.80 ± 0.2	4

^aAverage of all samples.

^bAverage calibration flaring plus first High-Rate test sample.

equilibrium during production testing. If significant tritiation of methane by exchange with hydrogen occurred, it was evidently limited to times when chimney temperatures were above those observed following reentry. Note that the apparent temperature of 315°C is a lower limit to the "quenching" temperature for this reaction since continued exchange of HT with water at temperatures lower than the actual quenching temperature reduces the specific activity of the hydrogen below that which would have existed at the time of quenching.

The position of the exchange equilibrium between water and methane is not a strongly varying function of temperature. The initially observed ratio of specific activities of these species, 0.72, is not unreasonable. However, as will be seen in the last section, no evidence exists for an increase in the amount of tritiated methane mixed with the krypton, in spite of the observed decrease in methane specific activity of nearly two orders of magnitude. Evidently, the observed specific activity change is due only to dilution, and the rate of tritium exchange reactions involving methane must be slow under conditions existing in the chimney.

Formation of ethane and propane during the gas condensation phase in the cavity created by the nuclear explosion is not favored by high-temperature thermodynamics. Any of these species which were present were certainly diluted greatly by the influx of formation gases as the cavity cooled. Tritiation of these species probably occurred through various high-temperature exchange mechanisms. If the concept of an effective quench

temperature for exchange reactions is extended to these species, the observed specific activities are indicative of temperatures in excess of that which was obtained by inference from the methane-hydrogen exchange reaction.

Interpretation of the heavier hydrocarbon specific activities is further complicated by the effects of pyrolysis and/or radiolysis of the chimney gases. Laboratory investigations indicate that either of these effects can lead to the formation of ethane, propane and other polymerization products. The extent to which such effects are important in influencing gas composition and tritium distribution in a gas stimulation environment is a subject of continuing study.

STABLE GAS CONCENTRATION CHANGES

Just as the specific activity is used to observe relative changes taking place in concentrations of radioactive species, the ratio of the concentration of a stable gas to some unchanging component of the chimney gas can be used to identify dilution effects. Of the chimney gases, ^{85}Kr is perhaps the most useful since it appears to reside 100% in the gas, and is essentially all present within 10 min after detonation. In Fig. 5 these concentration ratios to ^{85}Kr are plotted for CH_4 , a typical component of formation gas, and CO_2 and H_2 , typical cavity gas components.

As expected, influx of formation gases coupled with withdrawal of ^{85}Kr causes a continuous, gradual increase in the $\text{CH}_4/^{85}\text{Kr}$ ratio. The observed increasing ratios for CO_2 and H_2 deserve further consideration. In the absence of dilution

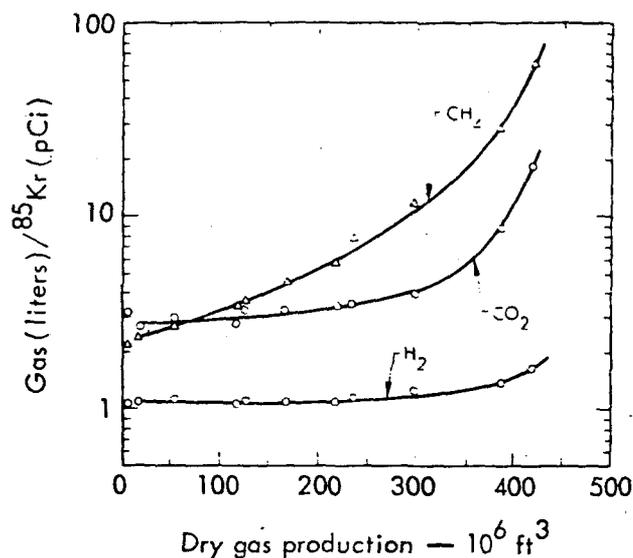


Fig. 5. Ratio of selected chimney gas components to ^{85}Kr during production testing at Project Rulison plotted as a function of dry gas produced. Data points at $5 \times 10^6 \text{ ft}^3$ are the average of five samples collected during calibration flarings.

effects involving additional H_2 or CO_2 which was not initially mixed with the ^{85}Kr , the curves should remain flat. The fact that they apparently do not is indicative of late-time generation of these gases. One possible source is ebullition of dissolved CO_2 or H_2 from water in the chimney as gas pressures fell due to production. Continued generation of CO_2 by reactions between carbonate and silicate minerals has also been suggested as a possible late-time source of this material.³

It is instructive to examine the absolute quantities of these gases which are required to produce the observed changes in the gas-to- ^{85}Kr ratios. This can be done by performing a regression analysis between the total ^{85}Kr and the total of the species in question which remain in the chimney at any given time. Such an analysis requires an assumed knowledge of the initial total of a gaseous species

which is expected to mix uniformly with the chimney gases, and which is not subject to chemical, radiochemical or anomalous dilution effects. The fission product gas ^{85}Kr is such a material. Assuming uniform mixing, the total of a species, X, remaining in the chimney at any time is given by

$$\text{total X remaining} = \frac{[X]}{[^{85}\text{Kr}]}$$

$$\times \text{total } ^{85}\text{Kr remaining, (4)}$$

where $[X]$ and $[^{85}\text{Kr}]$ are measured concentrations of these species in a sample. The problem is then reduced to one of estimating the total ^{85}Kr initially present, and applying appropriate corrections for the quantity removed as a result of production testing.

The total amount of ^{85}Kr produced by a nuclear explosive can be calculated if the actual fission yield of the device is known. Such is not the case for the Rulison explosive, and it is necessary to infer the total from production testing information. Two different methods can be used: Estimation of the total amount of gas containing a known concentration of ^{85}Kr , and integration of the ^{85}Kr released during production testing.

Montan⁴ has estimated a total gas volume of $250 \text{ M}^2\text{CF(NTP)}^*$ of dry gas in the chimney before the start of production testing. Montan bases his calculation on observed flow, pressure and temperature data obtained at Rulison. During calibration

* Most volume measurements in engineering units are referenced to normal temperature and pressure, NTP (60°F, 14.7 psia).

testing, we obtained an average ^{85}Kr concentration of 150 pCi/ml. The implied total ^{85}Kr at zero time is 954 Ci. However, at the start of the high-rate production test, a ^{85}Kr concentration of 158 pCi/ml was observed, implying a total ^{85}Kr of 1005 Ci at zero time. Because of possible dilution effects, the higher number is preferred.

Based on release estimates obtained from production monitors, ²⁻⁴ and using dry gas flow, Aamodt⁸ has calculated that 1112 Ci of ^{85}Kr were released at zero time. Since essentially all the original chimney gas has been released from Rulison, this total can be compared directly with others. Although the daily integration reported by Aamodt is considered to be the most reliable such result, we can obtain a comparable value by integrating the ^{85}Kr versus production curve shown in Fig. 4. This integral is 1080 Ci at zero time.

These estimates of total zero-time ^{85}Kr are summarized in Table 7. It is somewhat remarkable that the agreement between these estimates is as good as it is. However, the integrated release estimates are considered somewhat more reliable since they eliminate assumptions as to the extent and uniformity of mixing.

Table 7. Total curies of krypton-85 at zero time.

85 Kr monitor – daily flow integration (Aamodt)	1112
85 Kr concentration – smoothed flow integration (LLL)	1080
85 Kr maximum concentration – total gas volume (Montan)	1005
Av	1066 ± 20

We shall therefore adopt an assumed total of 1100 zero-time curies.

The amount of ^{85}Kr remaining in the chimney at any time is, of course, the 1100-Ci initial total less that removed by previous production. For the sake of consistency with our measured ^{85}Kr concentrations, we have chosen to obtain these produced quantities through integration, by section, of the ^{85}Kr concentration curve versus gas production curve shown in Fig. 4. However, this curve was first normalized to correspond to a total production of 1100 Ci, and to agree with the fraction of the total release which occurred during each production period according to the daily flow integration reports.⁸ Thus, the obtained release estimates as a function of gas production should be both internally consistent and representative of the larger mass of information available in the open files.²⁻⁴

To get an estimate of the errors associated with the differencing technique used to obtain ^{85}Kr totals remaining in the chimney, we have assumed somewhat arbitrarily that the error associated with the numerical integration and normalization of the Kr production curve is ±5%. This is compounded with the ±2% "uncertainty" in the total initially present and with the precision of the ^{85}Kr concentration measurements as indicated in Table 3. These errors and the calculated totals are presented in Table 8.

We have calculated the total CO_2 and H_2 remaining in the chimney by combining these values for ^{85}Kr remaining and the data of Tables 2 and 3, and using Eq. (1). The data are displayed in Fig. 6, where total residual H_2 is plotted as a function of ^{85}Kr remaining, and in Fig. 7, which

Table 8. Total ^{85}Kr remaining in the Rulison chimney during production.

LLL sample No.	Test period	Total previous production (M^2CF)	^{85}Kr remaining (Ci)
—	Shut-in	0	1100 ± 20
9-14	Calibration flaring	11.3	1049 ± 20
15	High-rate production	12.7	1042 ± 20
16	High-rate production	51.3	880 ± 22
17	High-rate production	114.4	627 ± 26
	Shut-in	115.7	623 ± 25
18	Intermediate-rate production	121.2	605 ± 26
19	Intermediate-rate production	162.6	452 ± 27
20	Intermediate-rate production	213.2	288 ± 28
	Shut-in	214.1	285 ± 28
21	Long-term production	225.0	256 ± 28
22	Long-term production	283.4	132 ± 29
23	Long-term production	365.6	34 ± 29
24	Long-term production	392.6	10 ± 29
25	Long-term production	414.0	5 ± 30
30	Long-term production	425.6	$< 1 \pm 30$
	Shut-in	425.8	$< 1 \pm 30$

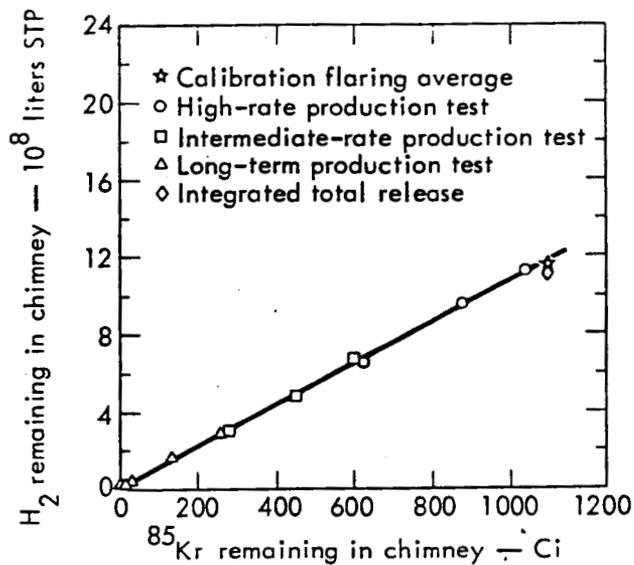


Fig. 6. Remaining H_2 in the Rulison chimney as a function of remaining ^{85}Kr .

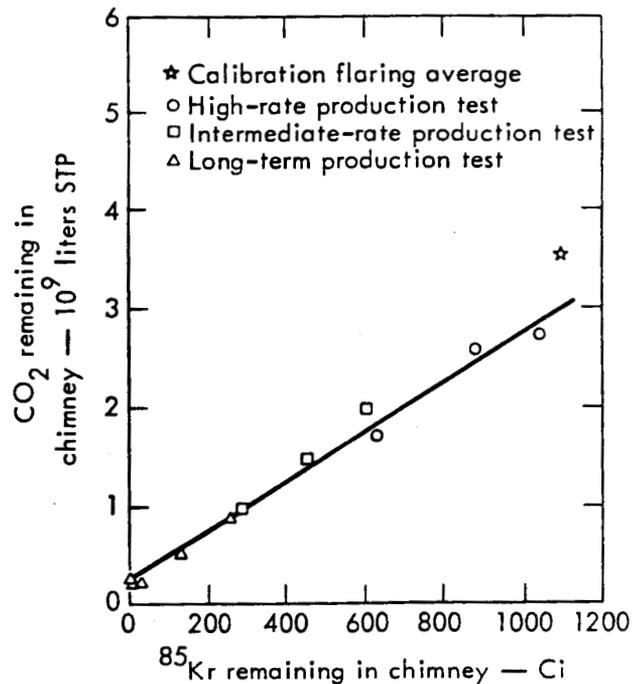


Fig. 7. Remaining CO_2 in the Rulison chimney as a function of remaining ^{85}Kr .

is a similar correlation involving CO₂. The lines through the data are the result of a weighted regression analysis (linear, least-squares) involving only production testing results. Data points were weighted according to

$$w_i = \frac{1}{1/\sigma_{xi}^2 + 1/\sigma_{yi}^2}, \quad (5)$$

where

- w_i = weighting factor for ith data point,
- σ_{xi} = standard deviation of the ith ⁸⁵Kr data point as shown in Table 8, and
- σ_{yi} = standard deviation of the ith data point for the gas to be correlated, obtained by combining errors in the gas measurement with those of Table 8.

The data are fit to the general equation,

$$\text{Gas} = m(^{85}\text{Kr}) + b \quad (6)$$

where m is the slope of the line and b is the intercept when ⁸⁵Kr is zero. Note that b is the quantity of the gas being correlated which is not initially mixed with ⁸⁵Kr. The intercept is thus a direct measure of the total volume of gas introduced to the chimney by whatever late-time generation or ebullition mechanism is assumed. Similarly, the value obtained for the gas "remaining" in the chimney when ⁸⁵Kr is taken as 1100 Ci is equal to the quantity initially present.

Results of the least-squares fit to the data can be expressed as:

$$\begin{aligned} \text{H}_2(10^9 \text{ liters STP}) &= (1.07 \pm 0.01) \\ &\times 10^{-3} (^{85}\text{Kr Ci}) - (3.3 \pm 4.5) \times 10^{-3}, \quad (7) \end{aligned}$$

$$\begin{aligned} \text{CO}_2(10^9 \text{ liters STP}) &= (2.49 \pm 0.12) \\ &\times 10^{-3} (^{85}\text{Kr Ci}) + (0.245 \pm 0.082). \quad (8) \end{aligned}$$

It is seen that $(3.3 \pm 4.5) \times 10^6$ liters STP of H₂ and $(2.45 \pm 0.82) \times 10^8$ liters STP of CO₂ are present in excess of that initially mixed with ⁸⁵Kr. This amount of H₂ is $(0.3 \pm 0.4)\%$ of the 1.18×10^9 liters of H₂ present before production, and is not statistically different from zero. The small upturn in the H₂/⁸⁵Kr ratio plotted in Fig. 5 does lend credence to the idea that a slight increase in total H₂, probably the result of ebullition of dissolved gases from chimney water, did occur. The observed quantity of excess CO₂, $(2.45 \pm 0.82) \times 10^8$ liters STP, is statistically different from zero, and amounts to $(8.2 \pm 0.4)\%$ of that volume of CO₂ (3.0×10^7 liters) obtained by extrapolation to the initial ⁸⁵Kr total. The significance of this and other observations relative to the observed behavior of CO₂ is discussed in detail in the next section of this report.

THE CARBON DIOXIDE ANOMALY

Throughout previous discussions, we have called attention to observations pertaining to what might be termed anomalous behavior of CO₂ and ¹⁴CO₂. In this section we shall attempt to examine this, and also some additional observations regarding these species.

Even before beginning the high-rate test, it was noted that CO₂ was not following the general dilution patterns exhibited by other gases. The first samples taken during calibration flaring were low in CO₂ relative to those obtained later. However, the ¹⁴CO₂/⁸⁵Kr ratio in these early

samples agreed with those measured later in the calibration period. These observations, as well as other composition changes between the first and later samples, were shown to be consistent with a volume dilution of gas of the initially observed composition with CO₂ containing little or no ¹⁴C.⁵ Based upon the observed ¹⁴CO₂-to-⁸⁵Kr ratio and an assumed 1100-Ci ⁸⁵Kr total, the indicated total ¹⁴CO₂ for calibration flaring samples was 2.96 Ci. A similar calculation for CO₂ produces a total of 3.52 × 10⁹ liters STP of this material. The CO₂ present in later samples exhibited a specific activity of 0.84 pCi ¹⁴CO₂/ml STP CO₂, slightly more than half that of the first sample.

The relationship between ⁸⁵Kr and CO₂ for the production testing period has been discussed briefly in the preceding section. Using Eq. (4) and data from Table 3 and 8, we can construct a correlation between ⁸⁵Kr and ¹⁴CO₂. The resulting relationship is presented in Fig. 8. The following relationship is obtained by performing a weighted least-squares fit, as previously described, to the production data only:

$$\begin{aligned}
 {}^{14}\text{CO}_2 \text{ (Ci)} &= (2.02 \pm 0.09) \\
 &\times 10^{-3}({}^{85}\text{Kr Ci}) - (7.3 \pm 47) \times 10^{-3}.
 \end{aligned}
 \tag{9}$$

The implied total number of curies of ¹⁴CO₂ present initially (when ⁸⁵Kr is 1100 Ci) is 2.2. No statistically significant excess ¹⁴CO₂ is observed at the ⁸⁵Kr = 0 intercept.

Recalling from Fig. 7 that (2.45 ± 0.82) × 10⁸ liters STP CO₂ were apparently introduced to the chimney gas during

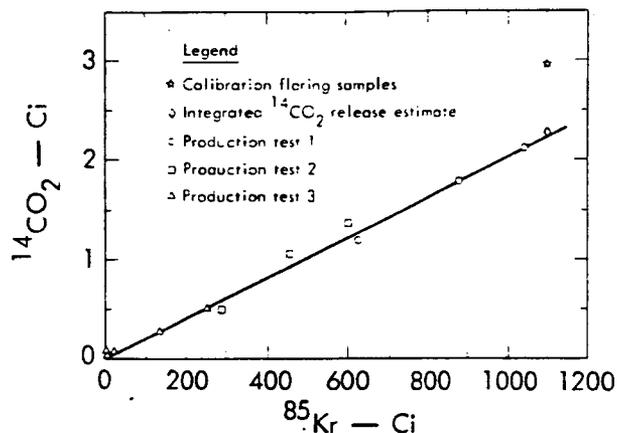


Fig. 8. Remaining ¹⁴CO₂ in the Rulison chimney plotted as a function of the remaining ⁸⁵Kr.

production testing, we see that the absence of a significant ¹⁴CO₂ excess implies that the diluent CO₂ was relatively free of ¹⁴C. The decreasing specific activity of the CO₂ throughout production testing (Fig. 4) is consistent with this conclusion. Furthermore, if the 2.45 × 10⁸ liters of additional CO₂ introduced was of the specific activity observed early in the production period, the excess ¹⁴CO₂ obtained would have been about 0.2 Ci, a quantity clearly inconsistent with the observed (-7.3 ± 47) × 10⁻³ Ci. We conclude that the CO₂ introduced during Rulison production testing was of significantly lower (perhaps zero) specific activity than that in the chimney gas.

Let us now consider the cross correlation of ¹⁴CO₂ with CO₂ as shown in Fig. 9 which includes the production testing data points, the average of the later five calibration flaring samples, and the ⁸⁵Kr = 0 and 1100-Ci intercepts from Figs. 7 and 8. Data points for the several sampling periods are differentiated. Because of the nature of this plot, the specific activity at any point is given by the slope of the line connecting that point and zero. The

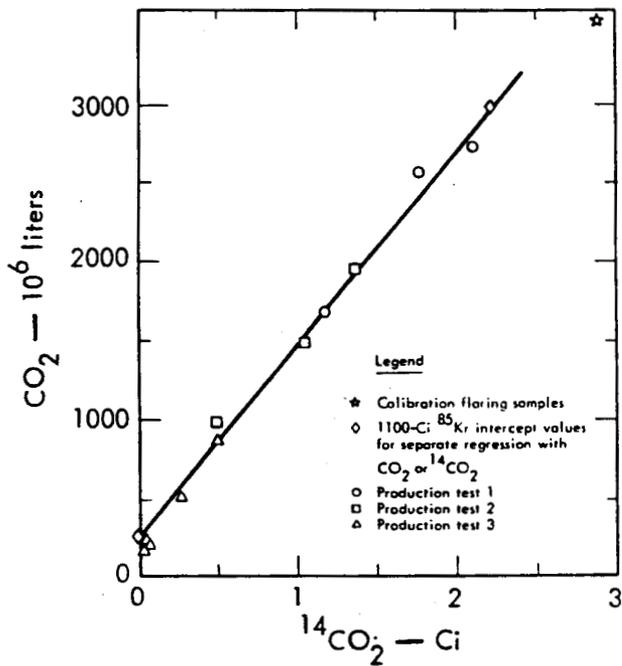


Fig. 9. Remaining CO_2 in the Rulison chimney plotted as a function of the remaining $^{14}\text{CO}_2$.

intercept of the weighted least-squares fit of the data is clearly nonzero, and correlation of the data with a straight line is quite good. The amount of excess CO_2 thus appears to be given by the difference between the regression line shown in Fig. 9 and the line passing through zero and the initial specific activity. The excess CO_2 released at anytime is, therefore, a linear function of the $^{14}\text{CO}_2$ remaining at that time. Since $^{14}\text{CO}_2$ appears to be a "good" cavity gas, a linear correlation similar to that for $^{14}\text{CO}_2$ must exist between excess CO_2 and the pressure of CO_2 in the chimney. To emphasize this point, in Fig. 10 we have plotted the remaining $^{14}\text{CO}_2$ versus the partial pressure of CO_2 in the chimney. The latter data were calculated from reported bottom-hole pressure measurements and the CO_2 concentrations given in Table 2. The equation of the least-squares fit to these data is

$$^{14}\text{CO}_2 \text{ (curies remaining)} \\ = (1.75 \times 10^{-3}) P_{\text{CO}_2} \text{ (psia)}. \quad (10)$$

Combining equations, we obtain

$$\text{excess } \text{CO}_2 \text{ released (} 10^9 \text{ liters)} \\ = -0.219 \times 10^{-3} P_{\text{CO}_2} + 0.25. \quad (11)$$

Thus, whatever the source of CO_2 contributing this excess to the chimney gas, it is inhibited by CO_2 pressure in the chimney. This behavior is expected for sources such as equilibrium thermal decomposition, chemical reaction, and ebullition from water. Note, however, that if chimney water is the source, then it is difficult to understand the quite low specific activity of the excess CO_2 . Solution equilibrium

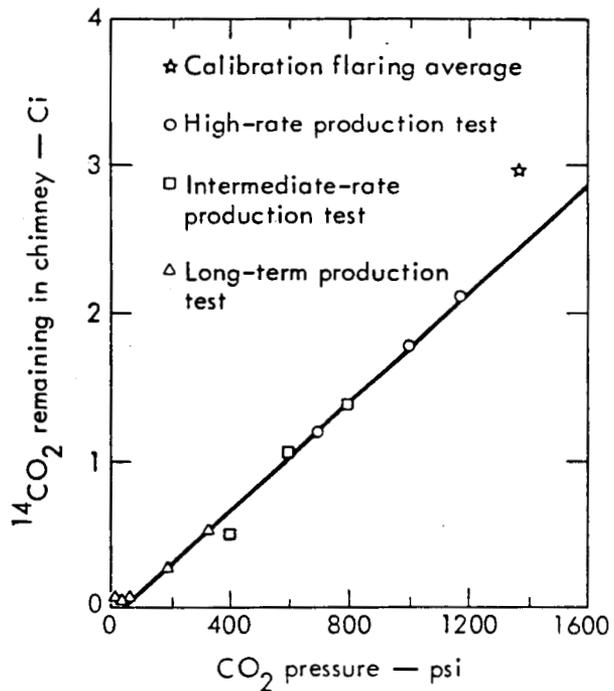


Fig. 10. Remaining $^{14}\text{CO}_2$ in the Rulison chimney as a function of the partial pressure of CO_2 .

with the gas would be expected to distribute $^{14}\text{CO}_2$ in very nearly the same manner as CO_2 . Therefore, of those mechanisms which have been suggested, we tend to favor equilibrium decomposition of carbonate minerals through reactions with silicates as the most probable source of excess CO_2 .

Returning to Fig. 9, note that the data from high-rate and intermediate-rate tests overlap. As has been mentioned previously, additional CO_2 appears to have been mixed with the chimney gas during the shut-in period between these tests. Since these overlapping points are on the same $^{14}\text{CO}_2$ versus CO_2 line, the additional CO_2 which mixed into the chimney gas at that time was of essentially the same specific activity as that previously present. Significant pressurization of the chimney by any influx of formation gas also occurred during this shut-in, and quite possibly swept CO_2 from the surrounding matrix into the chimney where it could mix with chimney gases. However, if at some time before reentry the chimney was pressurized to greater than formation pressure by continued generation of CO_2 , one might expect the gas injected into the formation to have a significantly higher specific activity than that remaining behind to be diluted. The more probable source of this material is ebullition from chimney water. CO_2 swept into the formation would be mixed with ^{85}Kr , while that coming from water would not. The irregularities in the data shown in Fig. 8 ($^{14}\text{CO}_2$ versus ^{85}Kr) would appear to support the latter concept, although the uncertainties with the data preclude a definitive answer to this question.

TOTALS OF GASEOUS SPECIES

Knowledge of the presence of a unique total of some gaseous material in the chimney gas permits its use to obtain totals of other species with which it is mixed. The fission product gas, ^{85}Kr , is such a material. It is not only unique to the chimney, but is also present at early times and can be expected to mix with the chimney gases in a reasonably uniform manner. If uniform mixing is assumed, then the total of a species, X, is given by

$$\text{Total X} = \frac{[\text{X}]}{[^{85}\text{Kr}]} \times \text{total } ^{85}\text{Kr}, \quad (12)$$

where $[\text{X}]$ and $[^{85}\text{Kr}]$ are measured concentrations of these species in a sample (sample in units of ml or pCi/ml).

Table 9 lists the results obtained for the production testing samples.

Note that the total is, in fact, a concentration ratio, and would be expected to remain constant throughout production only in the absence of physical and chemical phenomena which affect one or the other concentrations. Thus, constancy in the ratio implies the absence of exchange reactions, late-time gas generation, and mixing anomalies. For species which do change relative to ^{85}Kr , a meaningful total can be obtained by regression analysis with the actual total amount of ^{85}Kr remaining in the chimney. In the special case of Rulison, essentially all the initial chimney gases were produced. It is, therefore, possible to obtain an estimate of the initial quantity of a chimney gas component by integration of the concentration versus gas production data. Totals

Table 9. Totals of chimney gases mixed with ^{85}Kr .^a

Pot	(Curies at detonation time)						10 ⁹ liters STP	
	HT	CH ₃ T	C ₂ H ₅ T	C ₃ H ₇ T	Total T	¹⁴ CO ₂	H ₂	CO ₂
<u>High-rate production</u>								
15	166 (6)	1160 (5)	85 (5)	10 (5)	1420	2.2 (6)	1.18	2.88
16	170 (6)	1200 (6)	88 (7)	12 (7)	1470	2.2 (8)	1.20	3.22
17	157 (5)	1150 (6)	83 (5)	12 (6)	1400	2.1 (6)	1.15	2.95
<u>Intermediate-rate production</u>								
18	134 (6)	1090 (7)	80 (6)	12 (6)	1320	2.5 (15)	1.15	3.56
19	142 (6)	995 (6)	75 (5)	13 (8)	1220	2.6 (6)	1.15	3.57
20	134 (6)	952 (6)	75 (6)	13 (10)	1170	1.9 (7)	1.14	3.74
<u>Long-term production</u>								
21	194 (5)	1050 (5)	77 (5)	11 (5)	1330	2.2 (5)	1.20	3.71
22	169 (8)	1080 (6)	79 (5)	11 (7)	1340	2.2 (8)	1.34	4.29
23	184 (5)	1010 (8)	—	13 (6)	(1290)	2.8 (7)	1.45	9.62
24	227 (5)	902 (5)	79 (5)	12 (5)	1220	4.0 (8)	1.73	19.7
25	323 (6)	883 (6)	97 (6)	5.5 (7)	1310	13.6 (7)	2.66	51.1
30	532 (5)	780 (6)	95 (5)	25.0 (7)	1430	—	3.78	85.3

^aAssumes 1100 Ci ^{85}Kr total, uniform mixing, and representative sampling. As described in the text, these totals are constant only in the absence of exchange effects or late-time gas generation. The absolute uncertainty of these measurements is most probably $<\pm 15\%$.

^bNumbers in parenthesis are % standard deviation of the mean of replicate determinations.

of various species obtained by some or all of these procedures are listed in Table 10 for calibration flaring and for production testing. The estimate considered most reliable is also indicated. In most instances this will be the average values obtained using Eq. (12) and based on total ^{85}Kr , since these are the most direct interpretation of the experimental data. Regression analysis results and integrated release totals based on only 12 samples are considered less reliable, but have been used for those species which do not exhibit relatively constant ratios to ^{85}Kr because of nonuniform mixing.

Inspection of Table 10 reveals general good agreement between calibration flaring and production testing results based on total ^{85}Kr , and between the three methods used to calculate the total initial quantities. There are, however, obvious disagreements in the totals obtained for CO₂, ¹⁴CO₂, HT, and the hydrocarbon gases. These somewhat disparate results most likely are real, and not a result of the calculational and experimental processes. Because of continued evolution of CO₂ in the Rulison chimney and environs, mixing phenomena are expected to affect CO₂ totals based on the total ^{85}Kr assumed

Table 10. Totals of gaseous species -- Project Rulison.^a

Major components (gas vol $\times 10^9$ liters STP)	Calibration flaring average ^b	Product testing				Preferred values	
		High-rate test ^b	Samples 15 - 21 ^{b, c}	Regression analysis ^d	Integrated release ^e	Totals initially present	Based on average of columns
CO ₂	3.53 ± 0.02	3.0 ± 0.1	3.4 ± 0.3	3.0 ± 0.1	3.7 ± 0.4	3.0 ± 0.1	2, 4
H ₂	1.14 ± 0.01	1.18 ± 0.02	1.16 ± 0.02	1.17 ± 0.01	1.1 ± 0.1	1.15 ± 0.01	1, 3
CH ₄	2.42 ± 0.03	2.7 ± 0.1 ^f	—	—	—	2.7 ± 0.1	2
C ₂ H ₆	0.127 ± 0.001	0.14 ± 0.01 ^f	—	—	—	0.14 ± 0.01	2
C ₃ H ₈	0.021 ± 0.001	0.022 ± 0.001 ^f	—	—	—	0.022 ± 0.001	2
Total	7.34 ± 0.07	7.0 ± 0.1	—	—	—	7.0 ± 0.1	2
Radionuclide totals (Curies at detonation time)							
Tritium as HT	130 ± 2	163 ± 8	150 ± 20	162 ± 2	170 ± 20	150 ± 20	3
as CH ₃ T	1060 ± 10	1170 ± 40	1070 ± 90	1140 ± 50	1020 ± 100	1065 ± 5	1, 3
as C ₂ H ₅ T	74 ± 1	85 ± 3	80 ± 5	84 ± 5	75 ± 8	77 ± 3	1, 3
as C ₃ H ₇ T	13 ± 1	11 ± 1	11 ± 1	11.9 ± 0.8	11 ± 1	12 ± 1	1, 3
Total tritium	1280 ± 10	1430 ± 30	1340 ± 100	1400 ± 50	1280 ± 120	1310 ± 20	
³⁷ Ar $\times 10^{-4}$	4.8 ± 0.1	—	—	—	—	4.8 ± 0.1	1
³⁹ Ar	10.6 ± 0.1	11.1 ± 0.6 ^f	—	—	—	10.7 ± 0.1	1, 2
¹⁴ C as ¹⁴ CO ₂	2.96 ± 0.07	2.2 ± 0.1	2.2 ± 0.2	2.2 ± 0.1	2.3 ± 0.2	2.2 ± 0.2	3, 4, 5

^aIndicated uncertainties are one standard deviation of the mean.

^bBased on 1100 Ci ⁸⁵Kr and uniform mixing assumed. Calibration samples reported previously have been renormalized. (Ref. 5)

^cAverage includes high- and intermediate-rate production test samples and the first long-term production test sample.

^dValues are the 1100 Ci ⁸⁵Kr intercept of the weighted least-squares fit to the total gas remaining in the chimney as a function of the total ⁸⁵Kr remaining. Uncertainties are derived from the uncertainty in the slope representing the best fit to the data (see text).

^eIntegrated volume released during all production. Assumes no residual in the chimney and is based on I.L.L. experimental results. A somewhat arbitrary ±10% uncertainty has been applied.

^fInitial high-rate production test sample only.

present, and dilution of the gas with CO_2 will change the experimental totals obtained for components of formation gas. It is believed that the disparity between calibration and production samples for both total CO_2 and total $^{14}\text{CO}_2$ can be ascribed to mixing problems. Truly representative chimney gas obtained until high-flow-rate production was sustained in the first testing period. Note that the extrapolation of the chimney CO_2 specific activity line (Fig. 9) is in reasonable agreement with the calibration flaring average. It would appear that the calibration flaring gas was enriched in CO_2 relative to ^{85}Kr as compared to the production test gas. Thus for both of these species the preferred initial total, as indicated in Table 10, is that obtained during the high-rate testing. Since it is likely that the calibration flaring samples will be diluted with CO_2 , the preferred totals of formation gases are also the first measurements made during high-rate testing. Since H_2 is not a component of formation gas, its concentration relative to ^{85}Kr is unaffected by dilution, and the totals obtained by all methods agree well.

The disparity between the integrated release total of CO_2 and that observed during high-rate testing very likely represents the total incremental CO_2 introduced to the chimney during production testing. We have estimated that 0.245×10^9 liters STP CO_2 which was free of $^{14}\text{CO}_2$ were so introduced, and have mentioned the evident ebullition of CO_2 from water into the chimney gas. About 0.2×10^9 liters of CO_2 containing ^{14}C were added to the chimney between the high- and intermediate-rate produc-

tion tests. This incursion was probably not the only such influx of CO_2 . Taking the integrated release value of $(3.7 \pm 0.4) \times 10^9$ liters at face value, it is tempting to estimate an overall total CO_2 contribution from the surroundings of $(0.7 \pm 0.4) \times 10^9$ liters STP of which 35% was free of $^{14}\text{CO}_2$. It was not possible to observe the few tenths of a curie of $^{14}\text{CO}_2$ which could have been introduced if the maximum observed specific activity characterized the remaining $(0.45 \pm 0.4) \times 10^9$ liters of CO_2 . This is not surprising, in view of the uncertainties involved in the measurements of totals and the decreasing specific activity observed in the produced CO_2 .

The increased apparent total HT during production testing as compared to calibration test samples is probably due to exchange effects. Recall that the specific activity of the H_2 gas was also significantly lower in the calibration samples. The higher values observed throughout production testing were characteristic of the equilibrium exchange between HT and H_2O . We are thus led to conclude that the tritium content of the hydrogen sampled during calibration flaring was less than would be expected, while the hydrogen gas itself was "typical." The most probable mechanism for removing tritium from hydrogen is by exchange, possibly with water at a lower temperature than existed in the chimney. The early production testing totals are therefore preferred. Note that the integrated release of HT appears slightly higher than the total initially present. Because of the uncertainties involved, it is not possible to identify an incremental introduction of HT to the chimney.

Recall also that the regression analysis result for incremental H_2 was $(3.3 \pm 4.5) \times 10^6$ liters STP. Assuming the incremental H_2 is nonzero, the incremental HT would be of the order of 1 Ci, and would not have been observable. It is therefore not possible to quantize the late-time generation of hydrogen gas because of experimental uncertainties, even though an increase in the HT/ ^{85}Kr and the $H_2/^{85}\text{Kr}$ ratios was observed. The incremental H_2 is certainly no more than 1% of the 1.15×10^9 liters initially present.

Table 10 summarizes the available information for the total amount of gaseous tritium which was present in the Rulison chimney gas just before production. At zero time, a total of 1300 Ci of gaseous tritium is obtained, corresponding to 13% of the 1 g of this radionuclide expected to be present in the chimney. We assume the remainder of the tritium is bound in

chimney water or nonvolatile compounds not measured in this study, and tied up in solidified melt. We cannot verify this assumption without knowledge of the total amount of available water in the chimney and analyses of representative samples of the solidified melt.

The total of the preferred values in Table 10 for major constituents is 7×10^9 liters STP dry gas (270 $M^2\text{CF}$ at NTP). The agreement with the 250 $M^2\text{CF}$ at NTP obtained by fitting the production test data is satisfactory, especially since chimney gases could have been driven into the formation by pressurization of the chimney above formation pressure as a result of continued CO_2 generation or by simple diffusion. The gases could then occupy a somewhat larger volume than the high permeability void (the "chimney") measured by production testing.

Acknowledgments

The work presented here is the result of the combined effort of many individuals in the gas quality analysis and evaluation program. Radiochemical gas analyses and data reduction were performed by K. Burchette, J. Fontanilla and J. Rego of the LLL Gas Analysis Group. Chemical gas analyses were performed by R. Crawford and C. Otto of the General Chemical Analytical Group. Sampling information and collection services were provided by the Eberline Instrument

Corporation through the cooperation of the Austral Oil Company. Field coordination was handled by members of the O.P.N.E. staff, Nevada Operations Office of the Atomic Energy Commission.

I wish to particularly express my appreciation for the information, consultation, and suggestions provided by F. Momyer, R. Taylor, D. Emerson and D. Montan which were incorporated in this work.

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