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REPORT ON CARBON-14 GENERATION AND RELEASE AT SOME OF THE HANFORD REACTORS

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REPORT ON CARBON-14 GENERATION AND RELEASE AT SOME OF THE HANFORD REACTORS

By

G. B. Barton

Fission Product Chemistry
Chemical Research
Chemical Laboratory
HANFORD LABORATORIES

December 14, 1964

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REPORT ON CARBON-14 GENERATION AND RELEASE
AT SOME OF THE HANFORD REACTORS

G. B. Barton

INTRODUCTION

The Hanford graphite-moderated reactors have an enclosed gas circulation system to maintain control of the composition of gas atmosphere in the graphite stack. This investigation was undertaken to answer several questions concerning the generation and release of Carbon-14 in the operation of these graphite moderated reactors. The principle question was: Will an increase in the nitrogen content of the reactor atmosphere increase the release of Carbon-14 sufficiently to create a health hazard? Other questions were: 1) What are the main sources and the main release routes? 2) How much does carbon-14 build up in the graphite in the reactor stack? and 3) Is the total release of carbon-14 to the atmosphere sufficient to enhance the C^{14} levels in the vegetation surrounding the reactors?

The major precursors of carbon-14 are carbon-13 and nitrogen-14. The respective reactions are: carbon-13 (n, γ) to carbon-14, and nitrogen-14 (n, p) to carbon-14. The cross-section for the reaction with nitrogen is about 2,000 times larger than for the reaction with carbon. This difference is more than enough to offset the larger quantity of carbon in the reactor moderator (about 1500 times more carbon). The first part of the investigation dealt with the increase in carbon-14 generation upon substitution of nitrogen for carbon dioxide as part of the pile atmosphere.

For a number of years the Regional Monitoring group made routine measurements of the carbon-14 release in the reactor building stack gas. These were reported as quarterly averages from 1951 to 1956. During this time there were four quarters in which one or more of the reactors indicated an average release exceeding the reported detection limit of 6 millicuries per day. Starting in 1957 the analytical method and data handling were improved and the results reported as a monthly average release rate. Since 1957 samples are measured on each the results for a

given reactor showed wide variation. For example, in 1960 the results for the KE reactor were reported as 51×10^{-5} curies/day for June and 2400×10^{-5} curies/day for February. After introduction of nitrogen to the atmosphere of KE in July 1961 the range of monthly averages was 790 to 4000×10^{-5} c/d and for KW operating on the standard helium-carbon dioxide mixture the range was 200 to 4300×10^{-5} c/d. The average for KE for the remainder of the year (after introduction of nitrogen) was 2820×10^{-5} c/day and for KW 1565×10^{-5} c/day. This probably would be considered a significant increase if the results for the first half of the year had not been KE 2070×10^{-5} c/d and KW 944×10^{-5} c/d. Since the sampling method collected only a few four-hour samples monthly, it was deemed desirable to sample on a near continuous basis.

To cover the various parts of the problem, samples were collected from the reactor atmosphere, the building exhaust gas, the reactor atmosphere drier condensate, and the reactor graphite. The twin reactors KE and KW were most extensively sampled but a few additional samples were obtained from other reactors. The total amount of carbon-14 was measured on all samples and the chemical form in which it occurred was measured in the reactor atmosphere samples. In addition, a few samples of vegetation were analyzed to measure the amount of carbon-14 enrichment near the release point.

SUMMARY

This investigation provided the answers to the questions posed in the Introduction. By measuring the carbon-14 released in the reactor building stack gas and in the condensate from the silica gel dryers it was determined that the release was insufficient to be a major health hazard. The maximum measured release was 0.25 curies per day for the KE reactor. Use of a mixture of helium and nitrogen for the reactor atmosphere in place of a mixture of helium and carbon dioxide increases the average release by about two and one half times (from 0.039 to 0.10 curies per day). Greater than 95 percent of the carbon-14 released is released in the stack gas with the balance going in the condensate from the silica gel dryers.

It was determined that a substantial fraction of the carbon-14 in the condensate was present as simple or complex cyanides.

By separating the reactor gas constituents with a gas chromatograph it was found that less than one percent of the carbon-14 was in a chemical form other than carbon dioxide or carbon monoxide.

Measurements made on a few graphite samples indicated the buildup of carbon-14 to be ten to twenty-five times the daily release. This buildup is at a faster rate than one would calculate for the usual nitrogen content of the reactor atmosphere. The maximum level of carbon-14 measured was $13 \mu\text{c/g}$

Development of a large volume cell (250 ml) for liquid scintillation counting of the carbon-14 in the carbon dioxide produced by oxidation of vegetable matter permitted simplified measurement of the enhancement of the carbon-14 level in vegetation surrounding the reactor areas. This enhancement varied widely with location from unmeasurable increase to approximately three times natural level

EXPERIMENTAL

A. Counting

The method used for measurement of C-14 was an adaptation of a liquid scintillation counting method, described by Jaffey and Alvarez (1). The liquid scintillator solution consisted of a 1:10 mixture of ethanalamine, methoxyethanol, and toluene with 6 g/l PPO (2,5 diphenyl oxazole) and 0.1 g/l POPOP (1, 4-di[2-(5-phenyl-oxazolyl)] benzene) in the toluene. The sample in the form of carbon dioxide was absorbed in a solution of ethanalamine with approximately 1.4 times its volume of methoxyethanol added to dissolve the carbonate salt. This solution was then diluted with the remainder of the methoxyethanol-toluene mixture. This solution would dissolve a certain amount of aqueous sample so it was useful

also for measuring condensate samples by direct introduction of them without the necessity of separating the carbon dioxide or other carbon-14 containing compounds from the solution. The modifications of this general method that were made for vegetation samples will be described separately under the general topic of vegetation.

B. Gas Chromatography

A Perkin-Elmer Vapor Fractometer was used to analyze the condensate and pile gas sample for Carbon-14 in chemical species other than carbon dioxide and carbon monoxide. The presence of Carbon-14 in the outlet gas stream from the Vapor Fractometer was detected by flowing the gas through an ion chamber connected to a vibrating reed electrometer. The volume of the ion chamber was 275 ml. The sensitivity of the ion chamber was such that had approximately 1 to 3% of the total Carbon-14 activity been in a chemical form other than carbon dioxide or carbon monoxide it should have been detected. Columns were employed with packings of silica gel, Linde molecular sieve, and Carbowax on Teflon. These substances were chosen as the most likely ones to reveal the presence of such substances as methane, methanol, HCN, or other volatile Carbon-14 containing species. Silica gel provides a separation between carbon dioxide and carbon monoxide, or other highly volatile species similar to it. A molecular sieve column provides separation between carbon monoxide and other highly volatile species, but retains carbon dioxide completely. The Teflon-Carbowax column will separate such things as methanol, formaldehyde, cyanide, etc., from carbon dioxide, but the carbon dioxide and carbon monoxide will go through together.

Response of the ion chamber to a known amount of Carbon-14 was determined by using one of the analyzed condensate samples as a source. The gas sample for this calibration was prepared by taking an aliquot of sodium hydroxide-carbonate solution containing the desired amount of carbon dioxide, transferring it into a bulb, and then adding acid to liberate the carbon dioxide. The solution and evacuated space were allowed to come to equilibrium; the bulb was filled to slightly greater

than atmospheric pressure with helium and allowed to stand for some time for mixing to occur. Aliquots of gas from this bulb were then transferred with a transfer bulb to the gas sampling system of the chromatograph. These aliquots were then run through the chromatograph, using different carrier gas flow rates, and the response of the ion chamber to this known amount of carbon-14 dioxide was determined. The response was measured as 2.8 nanocuries per square unit under the curve on the chart paper of the recorder. Subsequent measurement of a few of the very small peaks indicated that approximately .02 to .05 of a square unit could be measured. The total activity in the samples used would generate a peak with an area of 2 to 9 square units. Therefore, it should have been possible to detect 1% of the activity in other chemical forms.

C. Sample Collection

1. Stack Gas

Sampling of the Reactor building ventilation exhaust air was carried out in a sampling train consisting of (a) three 250-ml gas washing bottles, each containing approximately 200 ml of 2.4 M sodium hydroxide to trap the carbon dioxide, (b) a tube containing cupric oxide, heated to approximately 325 C to oxidize the carbon monoxide to dioxide, and (c) a second set of 3 gas wash bottles to trap the additional carbon dioxide formed. The volume of gas drawn through the system was measured by a wet test meter. The flow rates ranged from 0.7 to 6.0 cubic feet per hour. Gas was drawn through the system continuously, except for the time required to change the absorber solutions, which was done three times weekly (Monday, Wednesday, and Friday). The samples were drawn from the stack air sampler loop that was installed when the reactors were originally built. To determine whether there were oxidizable carbon compounds in addition to the carbon monoxide, a parallel train was set up in which the gas stream was heated to 625 C in contact with the cupric oxide bed before being passed through the gas wash bottles. This parallel sampling was carried on from June 27 to July 16 at the KE reactor.

Sampling at the KE and KW reactors was started April 13, 1962 and carried on until July 18. Each sample listed in Table I represents the sample collected from the starting date or the immediately preceding date. During most of this period the KW reactor was operating with the standard helium-carbon dioxide atmosphere that contained 2 - 15% CO₂. On July 8 the atmosphere was changed to helium-nitrogen mixture. The KE reactor was operating with an atmosphere of helium-nitrogen. The nitrogen content was varied over the range of 6 to 30% as operating conditions dictated.

For comparison purposes, samples were collected from the B and C reactor building exhaust systems starting on September 5, 1962 at C and September 6 at B. During this period these reactors were operating with the normal helium-carbon dioxide mixture that was contaminated with about 0.2% nitrogen from air in the C reactor and about 0.6% in the B reactor.

2. Reactor Atmosphere

Samples of the gas being circulated through the reactor were collected from the outlet sampling manifold of the KE and KW reactors. The samples were collected in evacuated two-liter flasks and allowed to stand until the short-lived nuclides decayed before the samples were removed to the laboratory. These samples (listed in Table VI) were grab samples representing the gas flowing through the sampling manifold at that particular time.

3. Condensate

Regeneration of the silica gel driers is accomplished by circulating hot gas through them and a condenser. The water from the condenser contains ammonium carbonate and usually an excess of ammonia together with smaller quantities of other volatile materials that had been adsorbed in the silica gel. The K reactors were tight so there was little water collected from them. The individual operating periods were not recorded but in general the K reactor samples represent periods of 2 to 3 weeks while the others were 10 to 24 hours. The nitrogen content of the

circulating gases was not estimated since for the short periods there were no coincident samples available and the long period required extensive integration. Typical volumes of condensate for the K reactors are 3 to 10 gal. per week while for the others it is of the order of 100 gal. per week.

The analyzed samples were aliquots of the routine sample collected by the operating department.

4. Graphite

The analyses discussed below were obtained from four samples. Three of these (C, KW-1 and KW-2) represent powder collected from a broaching tool run through the tube channels prior to new tubes being inserted. The other (D) was a 0.25 inch diameter core drilling taken from tube 3773 of D reactor in March 1958. This was broken into 3 pieces. The first was 3-4 mm thick from the outer end; the second, the middle (approx. 2 mm), and the third, the inner or tube end (4 mm) of the piece.

5. Vegetation

Of the twenty-four vegetation samples listed in Table VIII the first sixteen were collected personally on November 21, 1962 so they represented an integrated sample over their growing season. Samples 17 through 21 were collected by members of the Biology Laboratory Operation in the vicinity (southwest) of F reactor area in the summer of 1962. Samples 23 and 24 were collected in the vicinity of 200 E by the Environmental Survey people. Sample 23 was 1 mile SE of the 200 E stack and 24 was 2 miles SE. Sample 22 was a background sample collected approximately 20 miles NW of the reservation.

The location and approximate distance from the reactor stacks are indicated in Table VIII.

D. Sample Processing

1. Absorption - Train Samples

The contents of each wash bottle were treated individually so a correction

could be applied for incomplete absorption of the carbon dioxide. The carbonate content of each solution was determined by an acidimetric method based on the Winkler method (2) for assay of caustic. This depends on the removal of carbonate as an acidimetrically titratable species by precipitation with barium chloride. From the calculated carbonate concentration, a suitable aliquot was measured to yield approximately 5.5 millimoles of carbon dioxide when the solution was acidified. The measured aliquot was placed in a 500 ml suction flask equipped with a dropping funnel for the addition of sulfuric acid and a "T" tube to which was attached a vial containing approximately a gram of potassium hydroxide in 3 to 5 ml of water. To avoid pressurization of the system when the carbon dioxide was released, the system was evacuated before addition of the acid. This evacuation also increased the transfer rate somewhat. After acidification, the system was allowed to stand overnight to complete the transfer of the carbon dioxide to the potassium hydroxide solution. In a similar fashion, the carbon dioxide was again transferred from the potassium hydroxide solution to one of ethanolamine in methoxyethanol, the absorber solution previously described. For the stack gas samples, 2 ml of absorber solution were used and these were later diluted with 13 ml of toluene-methoxyethanol-scintillator. The solution was placed in a half-ounce polyethylene bottle and the radioactivity was measured in a Packard "Tri-Carb" liquid scintillation counter. The capacity of this solution was approximately 6.6 millimoles of carbon dioxide, giving a margin of about 20% for impurities or safety in case the yield of the aliquot was greater than calculated. The method was calibrated, using a standard solution of sodium carbonate, supplied by the Bureau of Standards which contained 1250 d/s/g of solution. Weighed quantities of the standard were added to weighed quantities of sodium carbonate, and the mixture carried through the procedure. The average efficiency of recovery and counting was 56%. This figure was used in the calculation of the concentration of C-14 in the gas stream. An occasional sample gave low results because of incomplete transfer or loss of some of the organic carbonate in the equipment.

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From the ratio of activities in the successive absorbers as compared to the chemical determination of carbon dioxide, it was possible to spot the gross losses and calculate a correction based on the specific activity of the carbon dioxide. Most errors tend to be in the direction of loss of the activity before measurement, but there were also random fluctuations in counting, pipetting, etc., that may be in the order of 5%. The results on the standard sodium carbonate indicated that a value is nearly always low if it is in error.

In addition to the diffusion transfer method described above, another method employing a carrier gas stream bubbled through the sample solution was used. For this, air was drawn through an Ascarite tube to remove carbon dioxide, then through the sample solution, carrying the liberated carbon dioxide into the absorber solution contained in a small gas bubbler tube. Two tubes in series were used to insure complete collection of the carbon dioxide. A study of the variables involved in this method finally resulted in an adjustment of conditions such that 68% efficiency in liberation, collection and counting of the carbon dioxide was achieved, as measured on the National Bureau of Standards solution.

2. Drier Condensate Samples

Most of the condensate samples were of a deep blue color which appeared to be the copper ammonia complex color. The copper is dissolved from the brass valves and fittings by the ammonia which is formed by irradiation of the nitrogen and water vapor in the reactor gas mixture. The samples from the K reactors were particularly rich in ammonia, since they represent an extended period of operation. These reactors are quite dry and tight so the silica gel dryers require only infrequent regeneration. When an aliquot from sample KE 3-28-62 was diluted and acidified a precipitate formed which appeared to be cupric ferrocyanide (Spectrographic analysis of the precipitate detected copper, iron, and silicon). The ferrocyanides are resistant to oxidation by alkaline permanganate so that little, if any, C^{14} present in this form would be included in the " $C^{14}O_2$ plus oxidizable" measurement. The C^{14}

present as cyanide, ferrocyanide, and ferricyanide ions was determined by precipitation of silver-cyanide, ferrocyanide, and ferricyanide from an aliquot of the condensate after addition of carrier sodium cyanide. For counting, the precipitate was suspended in the liquid scintillator solution gelled with Cab-O-Sil.

In addition to the C^{14} measurements, chemical measurements were made of the carbonate and ammonium ion contents and the pH of the solutions. The carbonate was determined by liberating CO_2 with sulfuric acid, absorbing the CO_2 in Ascarite, and weighing. The ammonia was liberated with sodium hydroxide, distilled into standard HCl, and determined by back titration with sodium hydroxide solution.

3. Vegetation Samples

The carbon content of these samples was determined by burning a small aliquot in oxygen and determining the resulting carbon dioxide by the differential titration method referred to above. From these results, a weight was calculated to yield 3.66 grams of carbon dioxide (1 g carbon). This size sample was weighed out and slowly oxidized with 60 ml of a chromic-phosphoric-sulphuric acid mixture recommended for wet ashing of vegetation. (340 g CrO_3 in 400 ml H_2O diluted to 1 L with 85% phosphoric acid. 60 ml of this mixture was slowly added to the sample in 200 ml of 1:1 H_2SO_4 - H_3PO_4 mixture.) The carbon dioxide was swept from the oxidation flask into the absorbent (33 ml of the ethenolamine absorbent mixture described above). Considerable heat was generated as the carbon dioxide was absorbed, and the first sample developed a yellow color, so the absorption bulbs were immersed in an ice bath for subsequent samples. This eliminated the formation of the yellow color. The mixture became very viscous as the carbon dioxide was absorbed, but did not precipitate or solidify, even though at this stage it was about 2.5 molar in carbonate. The final counting solution was 0.33 molar in carbonate.

It was found that the analytical method applied to the stack gas samples could be used to detect $C-14$ in vegetation at or near contemporary levels. A cell was designed to contain 250 ml of a liquid scintillation sample solution. This was sufficient to dissolve 3.66 grams of carbon dioxide (1 g carbon). Whether or

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not such a cell would have sufficient efficiency to give usable net counting rates was a major question. As the separation of the two photo tubes used in the liquid scintillation counter increases, the efficiency falls off, particularly if there is a light absorbing substance between them.

A report of investigation of large cells⁽³⁾ contained a graph from which it was estimated that an efficiency of 30% might be achieved. This would be usable if a low background could also be achieved. With these considerations in mind, a cell was designed in which the photo tubes served as the windows of a spherical chamber. The design is shown in Figure 1. The overall inside diameter was 8 centimeters, and the distance between windows approximately 7 centimeters. Initially, the seal between the tubes and the cell was made with Viton O-rings. These swelled so much in the solvent they finally popped out of place. The seal was then made with room temperature setting silicone rubber. This was still satisfactory after a period of 5 months. The background of this cell, measured with a Packard Tri-Carb counting system in its standard manual shield was about 135 counts per minute. It was found that repeated counts on the same background solution, when alternated with samples, increased by approximately 2 1/2 counts per change. This would not appear to be contamination from the samples, since this is about 10% of the highest samples measured. The cell was rinsed twice with toluene between sample and background solutions. This increase in background count is one of the unexplained phenomena which was observed.

The efficiency of the large cell was determined by adding measured volumes of the NBS sodium carbonate solution described above. The counting efficiency was 48% at the conditions selected. Two samples of the NBS oxalic acid carbon dating standard were measured and gave 105 and 102 counts per minute per gram of contained carbon.

It has been observed that the CO_2 containing solutions turn brown on standing in the laboratory, but only slowly acquired a yellow tinge when kept in the refrigerator at 2°C. Whether this was a light-induced phenomenon or an oxidation process

was not investigated.

RESULTS AND DISCUSSION

A. Results for Stack Gas Samples

The results of these measurements are summarized in Tables I, II and III. The concentration of C^{14} was calculated from the measurements as follows:

$$C^{14} \text{ } \mu\text{c/cc of air} = \frac{\Sigma[(c/m - \text{Bkg}) \times 250/\text{sample volume}] \text{ all absorbers}}{2.22 \times 10^6 \times \text{Efficiency} \times \text{Vol. of Air}}$$

where: c/m is the gross counting rate of the sample

Bkg is the background counting rate

Sample volume is the aliquot taken for liberation of CO_2

2.22×10^6 is the disintegrations per minute per microcurie

Efficiency is the combined recovery and counting efficiency. It was obtained from measurements on an NBS sample of sodium carbonate and averaged 56%

Volume of air is the sample size, obtained from the wet test meter readings and corrected to standard temperature and pressure.

The percentage of CO was calculated from the counting results on the individual absorbers from the equation:

$$\% \text{ CO} = \frac{TC_4 - \frac{(R^3/2 + R^5/4)}{2} TC_3}{TC_{1-6}}$$

where: TC_3, TC_4 is the total count in absorbers 3 and 4, respectively

$R^3/2, R^5/4$ is the ratio of the total counts in the absorbers indicated

TC_{1-6} is the total count in all absorbers.

The average concentration of C^{14} (Table I) in the gases from KE was about 2.6 times that in KW when the former was operating with a helium-nitrogen mixture while the latter was operating with a carbon dioxide-helium atmosphere. If the flows used for calculations of daily release are correct, the daily C^{14} release from KE was 2.8

times that from KW.

Examination of some of the operating data indicate the greatest correlation is to be found with the daily gas loss. This seems to be true whether the reactor is operating or not. Shutdown of the reactor seems to bring some reduction in C^{14} release but the correlation is not strong. This would be expected where only a fraction of a reservoir that was recharged sporadically was being lost continually. Variations in the nitrogen content about the average operating level, do not appear to result directly in variation in C^{14} release. Of course, change of gas composition ultimately changes release rates or there would be no difference between KE and KW. However, the short term variation is lost in the fluctuating gas losses. Power level variation is so small as to be completely swamped by the other variables.

A few measurements on the B and C reactors are presented in Table II for comparison. It was expected the lower power level of these reactors and smaller nitrogen content of the gas, would result in considerably lower release rates than from KE. However, the higher total gas losses seem to compensate so the release rates are nearly comparable.

When the results in Table III are compared with the mass spectrographic analyses of gas samples taken during the same period it is observed that the percentage of CO is much higher in the reactor gas than is the percentage of activity present as CO. Thus, the C^{14} , as it is formed, must be oxidized up to CO_2 rather than stopping at CO or reaching exchange equilibrium with the chemical species in the gas mixture.

When the above release figures are compared with those previously reported by Regional Monitoring for 1961⁽⁴⁾ it appears that the present results are about a factor of three or four higher. Examination of the sampling methods indicates this to be the likely source of the difference. In the 1961 work, a single scrubber with a gas flow some ten to thirty times greater than in this study was used. The measurements on the individual absorbers used in this study show the first absorber traps about 70% of the CO_2 at a flow rate of 2.2 cft/hr. There is an inconsistency

between the results obtained on KE and KW. A scatter plot of the results show a trend towards decreasing absorption with increasing flow rate for the measurements from KW. Over a range of approximately 1-4 cubic feet per hour the absorption in the first absorber decreased from 94% to 50%. On the other hand, the results from KE do not show a trend over the flow range 2-6 cubic feet per hour even though there is considerable scatter of points ranging from a low of 38% to a high of 70% in the first absorber. The absorption efficiency of the particular apparatus used was apparently variable.

Specific activity was calculated for each absorber to see if the isotopic enrichment effect reported by Jones⁽⁵⁾ was operating. (He found higher specific activity in the end absorbers.) It appears that the solubility of Na_2CO_3 in 50% NaOH (the starting material used in this work) was sufficient to dilute the active CO_2 in the bubblers toward the end of the train so there was not an observable enrichment.

From the highest observed specific activity and the gas loss reported for that sample period it was calculated that the reactor atmosphere in KE contained 145 atoms of inactive CO_2 per atom of C^{14}O_2 . For KW with its He- CO_2 atmosphere a similar calculation gives 1500.

The specific activity was observed to increase in a somewhat irregular manner with time from mid-April to mid-July. This is possibly related to the meteorological conditions that would control the amount of carbon dioxide from the power plant that was introduced into the building air supply.

The concentration of C^{14} in the stack gas was compared with that in the atmosphere and was found to be higher by a factor of from 1.37×10^4 in KW (lowest sample in KW) to 2.8×10^5 in KE (highest sample in KE).

TABLE I

Measured C¹⁴ in Stack Gas from K Reactors **

Date	KE		KW	
	Concentration CO ₂ +CO μc/cc	Daily Release at 141,000 cfm curies/day	Concentration CO ₂ +CO μc/cc	Daily Release at 135,000 cfm curies/day
4/17	22.2 x 10 ⁻⁹	.128	5.4 x 10 ⁻⁹	.030
4/18	24.3	.140	5.4	.030
4/20	22.9	.132	2.1	.011
4/23	19.0	.109	9.3	.051
*4/25	5.7	.033	18.6	.102
4/27	23.7	.136	8.1	.045
4/30	12.0	.069	1.9	.010
5/2	16.7	.096	5.1	.028
5/4	16.5	.095	3.2	.018
5/7	13.3	.076	3.9	.021
5/9	12.7	.073	5.3	.029
5/11	15.3	.088	3.1	.017
5/14	15.3	.088	4.8	.026
5/16	13.6	.078	3.4	.019
5/18	9.6	.055	5.0	.027
5/21	13.5	.078	5.5	.030
5/23	13.7	.079	13.3	.073
5/25	28.5	.164	6.5	.036
5/28	26.3	.151		
6/1	16.6	.095	6.1	.033
6/4	16.2	.093	3.6	.020
6/6	18.9	.104	9.2	.051
6/8	21.0	.121	5.9	.032
6/11	11.7	.067	8.5	.047
6/13	20.7	.119	10.5	.058
6/25	~ 11 Total C ¹⁴	~ .063 Total C ¹⁴	7.7	.042
6/27	21.3 μc/cc	.122	9.2	.050
6/29	21.2 24.3 x 10 ⁻⁹	.122 .140	9.0	.050
7/3	20.9 27.1	.120 .156	7.4	.041
7/6	35.5 43.1	.204 .248	9.2	.050
7/9	31.1 25.4	.179 .146	10.9	.060
7/11	15.2 15.1	.087 .087	8.8	.049
7/13	16.4 25.2	.094 .145	10.5	.058
7/16	17.9 16.2	.103 .093	13.4	.074
7/18	8.5	.049	10.7	.059
Average	17.97	.103 .145	7.16	.0394

* Partial sample was analyzed from this date.

** Nominally KE operated with 12% N₂-88% He but N₂ ranged from 7.5% to 22%.
KW operated with approx. 3% CO₂ - 97% He but CO₂ ranged from 1.6 to 15%.

TABLE II

Measured C^{14} in Stack Gas from B and C Reactors*

Date	C		Date	B	
	Concentration $\mu\text{c}/\text{cc}$	Daily Release at 135,000 cfm curied/day		Concentration $\mu\text{c}/\text{cc}$	Daily Release at 100,000 cfm curies/day
9/7	2.1×10^{-9}	.012	9/7	4.1×10^{-9}	.017
9/10	6.0	.033	9/10	10.9	.044
9/12	4.7	.026	9/12	16.0	.065
			9/14	12.0	.049

* Nominal gas compositions 32% CO_2 - 68% He
 N_2 B 0.5
 C 0.2

TABLE III
 DISTRIBUTION OF CO AND CO_2 IN REACTOR ATMOSPHERE

Date	Percentage of Activity Present as CO		Mass Spectrometer Analyses			
	KE % CO	KW % CO	KE		KW	
			CO	CO_2	CO	CO_2
4/17	- *	1.1				
4/18	-	.48	< .01	1.04		
4/23	1.85	.30	< .01	1.26	0.83	8.79
4/27	-	.33				
4/30	.76	1.6	< .01	.88	0.38	8.94
5/2	2.2	.20				
5/4	5.3	.07				
5/7	2.1	.06	2.87	0.59	0.30	3.40
5/9	1.7	.10	< .01	0.97	< .01	2.35
5/11	.69	-				
5/14	-	.3				
5/16	2.3	1.9				
5/18	.9	.3				
5/21	2.0	.0				
5/23	1.9	.4	0.53	0.78	0.24	3.23
5/25	2.1	-				
5/28	2.9	-				
6/1	2.2	-	0.50	0.85		
6/4	1.5	.2	< .01	0.90	< .01	2.47
6/11	1.3	-				
6/13	-	.05				
6/25	-	.4			0.34	4.66
6/27	.3	-				
6/29	.17	.19				
7/3	-	.25				
7/9	-	.02				
7/11	-	.37				
7/13	1.1	-				
7/16	.39	.13				
7/18	2.4	.10				

*Dash (-) indicates no calculable CO .

B. Condensate Samples

The results from the C^{14} analyses on the condensate samples are tabulated in Table IV. The "Total" C^{14} column values are the sums of the " $C^{14}O_2$ plus oxidizable" and the $C^{14}N^-$ values. This probably includes all of the C^{14} compounds in the condensate, but the values could be high if some of the cyanide compounds are oxidizable, or could be low if there are C^{14} -containing compounds present which are not oxidizable by alkaline permanganate. Since the presence of unoxidizable compounds other than the ferrocyanides seems unlikely and since the purpose of these studies was met with the present measurements, no true C^{14} measurement was made.

Individual sample results vary widely, with an especially marked difference between the K reactors and D, DR and F reactors. This is due in part to the much lower moisture content of the K reactors. Also, because of the low moisture content of the K reactor cooling gas the dryers are used for long times before regeneration. This allows the ammonium ion content of the silica gel to build up. The direct adsorption of ammonia by silica gel is much greater than for CO_2 and the adsorption of ammonia increases the retention of the CO_2 by formation of ammonium carbonate or bicarbonate.

Typical volumes of condensate produced during this period are 3-10 gal/wk (1500-5000 ml/day) for the K reactors and 100 gal/wk (~50,000 ml/day) for D reactor. Thus, at the average level of 1.29 $\mu\text{c}/\text{ml}$, the K reactor dryers retain from .002 to 0.006 curies of C^{14} per day. The D reactor dryers retain approximately 800 $\mu\text{c}/\text{day}$. The C^{14} released via stack gases as reported in Table I were 0.15 c/day for the K reactors and 0.035 c/day for B and C reactors. Thus for the K reactors, from 1.4 to 4.2% of the C^{14} from the reactor coolant gas is removed via the condensate. For the D reactor the value is about 2%. Thus the release via the condensate is a significant but minor route of loss of C^{14} from the reactor coolant gas.

The results of the chemical analyses of the condensate samples are presented in Table V. In most of the samples there is an excess of ammonia over that required to combine with the measured amount of carbon dioxide for the formation of ammonium carbonate. The measured pH generally reflects the excess ammonia rather than the total ammonia. The samples from D and F reactors show the effect of more rapid water collection with consequent shorter time to accumulate ammonia.

C. Analysis of Reactor Gas Samples

Samples of pile gas from the two "K" reactors were collected and analyzed primarily for two reasons: the first, to compare the amount of carbon-14 present in the pile gas with the amount in the reactor stack gas. This comparison should allow us to estimate whether or not there was any appreciable fraction of the carbon-14 being lost by routes other than the ventilation air. The second, to determine whether or not there are appreciable amounts of chemical species containing carbon-14 other than carbon dioxide and carbon monoxide. This was determined largely by gas chromatography. Two of the pile gas samples were analyzed for total carbon-14 content. By treating the gas with alkaline permanganate for a 16 hour period, it should be possible to convert nearly all the carbon compounds to carbonate. The carbonate solution was then analyzed for C¹⁴ in the same way as the stack gas absorber samples. The remaining samples were analyzed by gas chromatography. The gas chromatograph was used to separate the carbon monoxide, from carbon dioxide, and to look for other chemical species containing carbon-14. The results for the measurements on the gas chromatograph are summarized in Table VI.

TABLE IV
CONDENSATE C¹⁴ ANALYSES

Sample	C ¹⁴ O ₂ plux Oxidizable	C ¹⁴ O ₂	C ¹⁴ N ⁻		"Total"* C ¹⁴
	μc/ml	μc/ml	μc/ml	% of total	μc/ml
KE 3-28-62	3.95	3.24	0.78	16.5	4.73
KE 9-28-62	1.15	1.10	0.32	21.8	1.47
KE 10-24-62	0.59	0.57	0.36	42.3	0.85
KE 11-30-62	0.58	0.27	0.089	13.3	0.67
KE 12-3-62	0.49	0.30	0.15	27.8	0.54
KW 6-23-61	0.025	0.0077	0.16	84.2	0.19
KW 12-3-62	0.38	0.35	0.20	34.5	0.58
Average K Reactors	1.02	0.83	0.29		1.29
D 10-31-62	0.0003	1.9 x 10 ⁻⁵	0.0064		0.0067
DR 6-5-59	0.00034	0.09 x 10 ⁻⁵			
DR 6-9-59	0.00017	< 9 x 10 ⁻⁶			
F 11-30-62	0.00063	14 x 10 ⁻⁵	0.025		0.025
Avg. D, DR, F Reactors	0.00036	5.3 x 10 ⁻⁵	0.015		0.016

*"Total" C¹⁴ column values are the sums of the C¹⁴O₂ plux oxidizable and the C¹⁴N⁻ columns. (See text).

TABLE V
CONDENSATE CHEMICAL ANALYSES

Sample	CO ₂ M	NH ₃ M	pH
KE 3-28-62	1.73	3.19	9.32
KE 9-28-62	0.87	1.72	9.47
KE 10-24-62	0.41	1.59	9.90
KE 11-30-62	0.28	1.11	9.80
KE 12-3-62	0.28	1.03	9.77
KW 6-23-61	0.16	1.28	9.00
KW 12-3-62	0.40	0.91	9.60
D 10-31-62	0.002	< 0.001	6.58
F 11-30-62	0.0039	0.015	7.72

TABLE VI
GAS CHROMATOGRAPHIC ANALYSIS OF REACTOR GAS SAMPLES

Sample	Gas Chromatograph		Activity measured by Ion Chamber			
	Molecular Sieve % CO	Silica Gel % CO ₂	Silica Gel Column CO μc/l	Column W CO ₂ μc/l	Molecular Sieve CO μc/l	Column W Total μc/l
KW-5-23	0.18	3.32	0.032	0.24	0.018	0.26
	0.17	3.24	0.034	0.25	0.015	0.25
KW-5-25	0.12	2.94	0.032	0.26	0.024	0.25
	0.12	2.54	0.027	0.25	0.012	0.25
KW-5-28	0.08 (.25)*	2.59 (2.20)	0.029	0.32	0.015	0.29
		2.61	0.039	0.29	0.007	0.31
KW-6-4	0.074 (<.01)	2.64 (2.47)	0.044	0.25	0.003	0.28
	0.082	2.82	0.034	0.27	0.004	0.28
KW-6-6	0.071	2.51	0.020	0.30	0.023	0.30
	0.072	2.61	0.024	0.30	0.022	0.29 0.30
KE-5-23	0.39 (.53)	0.75 (.78)	0.41	0.67	0.35	0.91
	0.40		0.39		0.37	0.93 0.90
KE-5-28	0.52 (.15)	1.33 (1.20)	0.39	0.81	0.43	1.14
	0.51	1.32	0.39	0.94	0.36	1.15
KE-6-4	0.26 (<.01)	0.62 (.90)	0.29	0.74	0.30	1.05
	0.28	0.62	0.30	0.73	0.29	1.08

*Numbers in parenthesis are mass spectrographic results for an independent sample taken the same day.



The gas chromatographic and mass spectrometric results are in reasonable agreement for the days when both analyses were made. They were not on the same samples or on samples taken at the same time so complete agreement should not be expected.

The measured activity of CO when using a silica gel column for the separation is generally higher than for the Molecular Sieve column. This may arise from tritium accompanying the CO through the silica gel column since this column does not separate CO and H₂. There was resolution of an earlier activity peak from CO on the Molecular Sieve column thus bolstering the above agreement. When the results are converted to specific activity for CO and CO₂ they are found to be the same within the limits of the measurements. There were no other chemical species detectable (detection limit 1% of the total activity.)

The sum of activities reported as CO and CO₂ are generally in good agreement with the total measured on column W. Since there were no other activities detected this is what one would expect.

If we combine the figure of 1.14 $\mu\text{c}/\text{l}$ (Total KE-5-28 Table VI) with the reported gas loss of 4545 cubic feet for KE-5-28 we calculate 0.146 curies/day as the loss. This can be compared with the measured stack loss of 0.151 curies/day given in Table I for sample KE-5-28. One of the reactor gas samples (KW-6-1) was analyzed by absorbing the CO₂ in alkaline permanganate (which also oxidized the other carbon containing compounds to CO₂) and then carrying an aliquot of this solution through as if it were one of the absorber samples of the stack gas train. This analysis indicated the gas contained 5.4 $\mu\text{c}/\text{ft}^3$. On this day the gas loss was reported as 6389 ft^3 making a calculated loss of 0.034 curies/day. Table I gives 0.033 c/d for the stack gas content that day. Thus, the stack loss accounts for the major part of the gas activity. This is in agreement with the measurements on the dryer condensate indicating 1 to 4% loss by this path.

D. Graphite Samples

A weighed amount of the graphite was oxidized in a stream of oxygen after being mixed with cupric oxide. The resulting carbon dioxide was trapped in sodium hydroxide and the solution subsequently analyzed as the previous samples had been. The results of these analyses are summarized in Table VII. As can be seen, the replicated results show some variation, and the averages chosen to represent the sample are not strictly arithmetic averages, but are weighted somewhat according to sample size and other factors that were taken into account. It is seen that the solid sample, (D 1, 2, 3) when broken into smaller pieces, shows a definite variation in carbon-14 content along its length. At first this was interpreted as being a definite indication of flux gradient. However, in the light of more careful examination of the influence of nitrogen content on carbon-14 generation, there is considerable uncertainty as to whether the gradation represents a gradation in nitrogen content and availability to the graphite, or whether it represents a flux gradation. The difference between the K and C reactors may be largely the result of lower average nitrogen content of the atmosphere in K. The shorter operating period and somewhat higher flux for the K reactor would not account for the whole difference.

An attempt was made to reconcile these graphite analyses with the measured stack gas losses, and condensate losses reported above.

The steady state formation of C^{14} in a K reactor was estimated using the following assumptions:

1. The in-reactor gas volume is about 10,000 ft³
2. The average gas temperature in the reactor is 450°
3. The perfect gas laws hold accurately enough
4. The average flux in the reactor volume is 7.2×10^{13} n/cm²sec
5. The nitrogen content of the gas is 10%
6. The n,p cross section of N^{14} is 1.75×10^{-24} cm².

7. The graphite volume in the active flux 36,000 ft³
8. The cross section of $C^{13}(n,\gamma)C^{14}$ is 9×10^{-28} cm².

The basis of the assumptions:

1. In-reactor gas volume was estimated by J. P. Cook⁽⁶⁾ to be about 10,000 ft³ or less. Leo Lessor⁽⁷⁾ and P. J. Zimmerman calculated volume at 10,000 ft³ from argon dilution and activation measurements. Calculations of the open space in the active part of the graphite stack were made for such things as gap around tube (overbore)⁽⁸⁾, gap around tube block, corner chamfer, vertical safety rod holes, and test holes. These total approximately 1300 ft³. The graphite stack inside the reflector has an over-all volume of approximately 36,500 ft³ with about 3000 ft³ removed for holes of various types. The initial density of graphite has been given as 1.64. This corresponds to a void volume of 27.8 per cent or about 10,000 ft³. How much of this void volume is open to the circulating gas is a very difficult question to answer. One can calculate that approximately 2,000 ft³ of 10% nitrogen-90% helium mixture would suffice to give an average gas generation rate of 0.145 curies/day of C^{14} (which was the measured average loss over a period of approximately three weeks.)

2. The maximum temperature has been indicated to be 750-800°. With the tube walls near 100 the upper of these temperatures leads to an arithmetic average of 450°.

4. This figure was obtained from R. A. Chitwood.

5. The nitrogen content varies, but 10% is well within the operating range.

6. Chart of the Nuclides. Istitut fur Radiochemie

7. The graphite volume in the active flux may be larger than this because this figure includes none of the reflector.

8. This figure is used and the nitrogen contribution calculated in the void volume

TABLE VII

CARBON-14 CONTENT OF REACTOR GRAPHITE

<u>Sample</u>	<u>Weight mg</u>	<u>μc</u>	<u>μc/g</u>
C-1	22.4	.40	18.0
		.393	17.5
		.404	18.0
		.386	17.2
C-2	61.6	1.09	17.7
		1.05	17.0
		1.07	17.4
D-1 (outer)	301.6	.756	2.51
		.650	2.15
		.682	2.26
D-2 (middle)	187.5	.501	2.67
		.451	2.40
		.464	2.47
D-3 (Inner)	321.3	1.16	3.60
		1.09	3.39
		1.01	3.15
KW-1A	44.0	.0219	.498
		.0176	.400
KW-1B	41.7	.0224	.538
		.0122	.291
KW-1B		.0285	.683
		.0292	.70
KW-2A	58.2	.0825	1.42
		.0769	1.32
KW-2B	91.7	.177	1.93
		.169	1.84
KWL-A1	44.0	.0330	.751
		.0277	.630

Samples C, KW-1 and KW-2 were powder from broaching tool. D sample was taken from a core mined from tube 3773 at D reactor.

Carbon¹⁴ from nitrogen 14

Atoms of nitrogen in one cc of gas at 450°.

$$N = \frac{0.10 \times 273 \times 2 \times 6.023 \times 10^{23}}{22,400 \times 723} = 2.03 \times 10^{18} \text{ atcm/cc}$$

Neutron capture cross section

$$\Sigma = 2.03 \times 10^{18} \times 1.75 \times 10^{-24} = 3.55 \times 10^{-6} \text{ cm}^{-1}$$

Formation rate

$$\phi\Sigma = 7.2 \times 10^{13} \times 3.55 \times 10^{-6} = 2.56 \times 10^8 \text{ atoms C}^{14}/\text{cc.sec}$$

Daily formation in whole reactor

$$2.56 \times 10^8 \times 10,000 \times 2.83 \times 10^4 \times 8.64 \times 10^4 = 6.26 \times 10^{21} \text{ atoms C}^{14}/\text{day}$$

$$\frac{6.26 \times 10^{21}}{9.703 \times 10^{21}} = .645 \text{ c/day}$$

Carbon-14 from Carbon-13

1.55 x 10⁹ g of graphite in 9.5 x 10⁸ cc

Concentration of C¹³ = 1.1%

Total C Atoms/cc

$$\frac{1.64}{12.01} \times 6.023 \times 10^{23} = 8.22 \times 10^{22}$$

C¹³ atoms/cc

$$N = 8.22 \times 10^{22} \times 0.011 = 9.10 \times 10^{20} \text{ atoms C}^{13}/\text{cc}$$

Carbon¹³ capture cross section

$$\Sigma = 9.10 \times 10^{20} \times 9 \times 10^{-22} = 8.19 \times 10^{-7} \text{ cm}^{-1}$$

Formation rate

$$\phi\Sigma = 7.2 \times 10^{13} \times 8.19 \times 10^{-7} = 5.9 \times 10^7 \text{ atoms/sec.cc.}$$

Daily formation rate

$$5.9 \times 10^7 \times 26,400 \times 9.5 \times 10^8 = 4.84 \times 10^{21} \text{ atoms C}^{14}/\text{day}$$

$$\frac{4.84 \times 10^{21}}{9.703 \times 10^{21}} = .499 \text{ c/day}$$

These calculations give somewhat lower formation rates than those reported

previously⁽⁹⁾⁽¹⁰⁾ but are higher than the measured stack loss.

From the measurements made on a few graphite samples as reported in Table VII one should be able to make some estimate of the retention (net increase) of the carbon-14 generated. From the two samples of KW graphite one estimates average retention rates of 0.43 and 1.17 curies/day for the whole reactor. These bracket the retention one would estimate from the generation and loss figures given above. For the D sample an integrated flux figure was estimated⁽¹¹⁾ of 6.5×10^{21} Nvt. This would result in the formation of 0.55 $\mu\text{c}/\text{cc}$ from C^{13} compared with 3.6 to 5.4 $\mu\text{c}/\text{cc}$ measured. To have generated 5.4 $\mu\text{c}/\text{cc}$ there would have to have been 0.083 cc (STP) of nitrogen per cc of graphite. Since this is much beyond what would be expected from physical adsorption and more than has been desorbed from graphite in high temperature degassing measurements⁽¹²⁾ it appears that there is still an area to be explored before we understand the generation of carbon-14 in a graphite reactor. The results on the sample for C reactor further emphasizes this last statement since the 29 $\mu\text{c}/\text{cc}$ measured would have required 1.28 cc N_2 (STP)/cc of graphite or a C^{13} enrichment of 15 fold (or some combination between these two effects).

E. Results on Vegetation Samples

There was some evolution of the counting method as these samples were measured. At first, daytime background count was combined with over night sample count. Since the background count was of the order of 135 counts per minute and the sample count only about 10 counts more than this, any uncertainty in either sample or background count would represent a large uncertainty in the net sample count. Therefore, the back-round counts were extended to over night counts as well, and the samples were counted alternately with the background.

Since it was observed that a nearly constant background count was obtained each time a fresh background solution was used and that a coal sample gave a slightly lower counting rate than the background (the counts for the coal and background sample were: new background solution 134.82 c/m (990 min.) coal sample 134.29 c/m (2420 min.), recount on background 136.19 c/m (3860 min.))

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the net counting rate listed in Table VIII is based on use of a constant background figure of 135.9 c/m. This was the average of six fresh background solutions counted over night. One background solution was counted for ten days and gave an average rate of 136.45 c/m with a maximum spread of 3.4 c/m (± 1.7 c/m).

The over-all reproducibility of the method may be indicated by comparing results for the leaves and twigs of the bitterbrush samples listed in Table VIII. It is seen that they check within the limits of counting statistics (standard deviation) given.

The locations from which the samples were collected are listed in Table IX. It can be seen that there is a relation of activity to proximity to a high source of C^{14} . The prevailing air movement also influences the uptake. Most of the samples were to the east of the sources and showed enhancement. Samples 17 through 22 were to the west of the major nearby source and were at background level. Samples 1 and 2 were directly east of the B-C stacks and about $3/4$ mile away. They could be either below the stack plume touchdown point or south of the prevailing plume direction. The variability among the four samples (13-16) collected northeast of the D reactor is unexplained. Differences in the growth pattern of the species of plants involved might play a part since there appears a similar pattern in the group (8-12) i.e., the trees leaves are lowest and the Russian thistle is highest.

TABLE VIII

COUNTING RATE FOR VEGETATION SAMPLES FROM THE
HANFORD RESERVATION AND ENVIRONS

<u>Sample No.</u>	<u>Kind</u>	<u>Activity</u>
1	Grass (Fall growth)	11.0 ± 0.8 c/m g. carbon
2	Russian thistle	9.9 ± 0.8
3	" "	12.3 ± 0.8
4	" "	27.4 ± 1.1
5	" "	23.0 ± 1.1
6	" "	19.0 ± 1.1
7	" "	23.1 ± 0.9
8	Chinese Elm (?) leaves	16.1 ± 0.8
9	Sweet clover	18.8 ± 0.9
10	Russian thistle	24.6 ± 0.9
11	Sage brush	22.7 ± 0.8
12	Grass (Fall growth)	25.5 ± 0.6
13	Apricot leaves	12.3 ± 0.8
14	Russian thistle	25.4 ± 0.6
15	Grass (Summer growth)	11.3 ± 0.9
16	Sweet clover	17.7 ± 0.6
17	Rabbit brush twigs	8.9 ± 0.8
18	Bitter brush #1 twigs	9.2 ± 0.8
19	" " #1 leaves	8.8 ± 0.8
20	" " #2 twigs	8.9 ± 0.8
21	" " #2 leaves	9.2 ± 0.8
22	Sage brush leaves	9.1 ± 0.6
23	" " "	29.7 ± 0.8
24	" " "	19.1 ± 0.8
	NBS Dating Standard Oxalic Acid	10.3 ± 0.6
	" " " " "	8.3 ± 0.8

TABLE IX

LOCATION OF VEGETATION SAMPLE COLLECTION

<u>Sample No.</u>	<u>Location</u>
1 & 2	Approx. 3/4 mile 90° from B-C reactor stacks
3	Approx. 1.4 mile at 80° from B-C reactor stacks
4	Approx. 0.5 miles at 60° from KE stack
5	Approx. 0.7 miles at 70° from KE stack
6	Approx. 1.0 miles at 115° from KE stack
7	Approx. 0.3 miles at 90° from D stack
8-12	Approx. 1.0 miles at 80° from D stack
13-16	Approx. 1.7 miles at 30° from D stack
17-21	Approx. 1 mile at approx. 220-270° from F stack
23	Approx. 20 miles northwest of reservation
22	Approx. 1 mile southeast of 200 East
23	Approx. 2 miles southeast of 200 East

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