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LEACHING OF ^{14}C AND ^{36}Cl
FROM HANFORD REACTOR GRAPHITE

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SUMMARY

The leach rates of ^{14}C and ^{36}Cl were measured on solid cylindrical samples of graphite prepared from a bar retrieved from one of the surplus Hanford production reactors. Static leach tests were conducted in deionized water and Hanford ground water at temperatures of 20°C to 90°C for 8 weeks. The graphite samples were completely submerged in the leachant, and the entire volume of leachant was changed and analyzed weekly.

The leach rates of both ^{14}C and ^{36}Cl decreased with time and appeared to approach steady-state values that were independent of temperature in the case of ^{36}Cl but decreased with temperature in the case of ^{14}C . Both radionuclides leached more slowly in Hanford ground water.

The data are compared with previously measured and estimated leach rates. Implications of the data regarding possible rate-limiting mechanisms are also discussed.

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INTRODUCTION

The Department of Energy (DOE) has published a Notice of Intent in the Federal Register (50FR20489) to prepare an Environmental Impact Statement (EIS) on decommissioning the eight shutdown Hanford production reactors located at the Hanford site near Richland, Washington. As part of the EIS, the DOE must evaluate the potential for release of radionuclides from the decommissioned reactors to the ecosystem. Two of the radionuclides of interest are ^{14}C and ^{36}Cl , which are present in the graphite moderators of the shutdown reactors. Both radioisotopes have long half-lives and are biologically assimilable.

Leaching is one potential mode of release if water should enter the reactor cores. In Appendix D of the draft environment impact statement on decommissioning of the eight surplus reactors at Hanford, ^(a) Morgan reviewed the very limited data on leaching of ^{14}C and estimated the leach rate of ^{36}Cl based on the assumption that its leaching behavior would be similar to that of ^3H . Subsequently, Pacific Northwest Laboratory (PNL) ^(b) was commissioned to obtain actual data on the leach rate of ^{36}Cl , and to obtain an improved understanding of the leaching behavior of ^{14}C . Toward that end, specimens were prepared from graphite bars irradiated in the "Y" test hole at C Reactor. These specimens were leach tested for eight weeks over the temperature range 20°C to 90°C using both deionized water and Hanford ground water. The purpose of this report is to document the results of those leach tests.

(a) U.S. Department of Energy (DOE). September 1988 Draft. Draft Environmental Impact Statement, Decommissioning of Eight Surplus Production Reactors at the Hanford Site, Richland, Washington.

(b) PNL is operated by the Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

EXPERIMENTAL

LEACH SPECIMENS

The graphite specimens used in these leach tests have been described by Morgan (Appendix A). They were right-circular cylinders 3.05 cm long and 3.05 cm diameter with a geometric surface area of 43.8 cm². Specific surface areas of specimens adjacent to the specimens used in the leach tests were measured using the Brunauer, Emmett, and Teller (BET) method; they averaged 5.2 ± 0.2 m²/g. The inventories of ¹⁴C and ³⁶Cl in these specimens averaged 260 ± 37 kBq/g (7.0 ± 1.0 μCi/g) and 2.5 kBq/g respectively.

TEST PROCEDURES

The leach test procedure was based on ANSI/ANS-16.1-1986 "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure" modified as noted below. The major modifications were inclusion of additional leaching temperatures to investigate carbon-oxidation kinetics and restructuring of the leachant-renewal schedule to eliminate unnecessary and expensive radionuclide analyses.

Pretreatment of Graphite Specimens

Prior to starting the leach tests, the specimens were placed in 200 to 300 mL of deionized water and cleaned ultrasonically for 1 to 2 minutes to remove graphite machining dust. Upon removal from the cleaning solutions, the graphite specimens were immediately placed in the leach containers without being allowed to dry, and the cleaning solutions were discarded.

Leachants

Two types of leachants were used, deionized water^(a) and Hanford ground water. The Hanford ground water has been described by Serne et al. (1987); its composition is given in Table 1. Both leachants were sparged with clean air for 10 to 15 minutes prior to use to ensure air saturation.

(a) Per ANSI/ANS-16.1-1986

TABLE 1. Composition of Hanford Ground Water

<u>Element or Ion</u>	<u>Concentration (mg/L)</u>
Al	<0.03
B	0.075
Ba	0.065
Ca	54.9
Cd	<0.004
Cr	<0.02
Cu	<0.004
Fe	<0.005
K	8.4
Mg	14.5
Mn	0.119
Na	26
Pb	<0.06
Si	15.5
Sr	0.251
Zn	<0.02
Cl	23
F	<0.6
HCO ₃	165
NO ₂	<0.3
NO ₃	<0.5
PO ₄	<0.1
SO ₄	69
pH	8.3

Leach Containers

The leach containers consisted of pint-size Kerr fruit jars with specially designed lids to provide a better seal and thereby prevent the escape of CO₂ or other gases during leaching. Specimen holders made of fused silica were used to hold the graphite specimens near the center of the leach containers.

Ratio of Leachant Volume to Specimen Surface Area (V/S)

Leachant volumes were 406 ±4 mL in all the tests; thus V/S = 9.25 cm. The intended ratio of 10.0 cm was based on expected sample dimensions of 2.92 cm, but the leachant volume was not adjusted to correspond to the actual sample dimensions, which were 3.05 cm. This is considered to be an unimportant difference because V/S ratios are important in leach tests only if the leached species approach their solubility limits in the leachate, which is not the case in these tests for either ¹⁴C or ³⁶Cl.

Temperatures

Temperatures were 90°C, 50°C, and ~20°C in the tests with deionized water; they were 90°C and ~20°C in the tests with Hanford ground water. Ovens were used to control the 90°C and 50°C tests to within ±2°C. The leach containers for the ~20°C tests were allowed to stand in a fume hood. Two days after the start of the seventh week-long leach period, a thermocouple was attached to a dummy leach container in the hood, and its output was recorded on a strip-chart recorder. The temperature remained in the range of 17.5°C to 21.0°C for 5 days, including a three-day week end. Then, for an unknown reason, the temperature in the hood dropped to ~14.5°C for 18 hours. When this was discovered, the leach containers were removed from the fume hood and placed on the laboratory bench where they remained for the remainder of the eight-week leach period and where the temperature remained in the range 17.5°C to 21.0°C. It is not known whether other temperature excursions occurred in the approximately six weeks prior to use of the thermocouple.

Leach Periods

The leachates were changed weekly over a period of eight weeks. One of the important features of the ANSI/ANS-16.1-1986 procedure is that the entire quantity of leachate is removed from the leach container at the end of each

leach period and replaced with fresh leachant. However, the ANSI/ANS-16.1-1986 procedure calls for frequent renewal of leachant during the early part of the leaching schedule to avoid saturating the solution with any of the leached constituents. Since the possibility of saturating the leachate with ^{14}C and ^{36}Cl from the graphite was expected to be remote and may even have resulted in ^{14}C and ^{36}Cl concentrations below detection limits, the leachant renewal frequency was reduced.

At the end of each seven-day leach period, the leach containers were removed from the ovens and allowed to cool to room temperature for at least two hours. Approximately 40 mL of leachate were removed from each container and set aside for possible future analyses of pH, cation and anion concentrations, and perhaps other parameters. The remaining quantities of leachates were removed from the containers and replaced with fresh leachant without allowing the graphite specimens to dry. The leachates were treated as follows.

Three to 4 mL of 10 M NaOH were added to each of the deionized water leachates to assure that the ^{14}C was maintained in the carbonate form even though it was expected to already be in the carbonate and bicarbonate forms, as discussed on the following page. NaOH was also added to the Hanford ground water leachates removed after the first leach period, but it was recognized that this could result in precipitation of ^{14}C as calcium or magnesium carbonate (the Hanford ground water had initial calcium and magnesium concentrations of 55 and 15 mg/L, respectively). Therefore, NaOH was not added to subsequent Hanford ground water leachates. In retrospect, the addition of NaOH to the first set of Hanford ground water leachates seems not to have made any difference since there was no obvious effect on the ^{14}C leaching results. Finally, each leachate was passed through a 0.45- μm filter to remove any graphite particles and then placed in a tightly capped sample bottle for transfer to the radioanalytical laboratory.

Procedures used by the radioanalytical laboratory to determine the concentrations of ^{14}C and ^{36}Cl in the leachates are included in Appendix B.

BLANK RUNS

Gray (1982) has shown that the mechanism for "leaching" of ^{14}C from graphite is the water-catalyzed oxidation of carbon by dissolved oxygen to form CO_2 . Because of the potential for CO_2 to escape from solution either during leaching or during preparation of the leachate for analysis, simulated leaching experiments were run with Na_2CO_3 solutions spiked with $\text{Na}_2^{14}\text{CO}_3$ to determine the percentage recovery of the ^{14}C .

Two solutions were prepared; one $\sim 10^{-2} \text{ M}$ Na_2CO_3 and the other $\sim 10^{-4} \text{ M}$ Na_2CO_3 , each spiked with $\text{Na}_2^{14}\text{CO}_3$ ^(a). The two solutions were acidified with HCl to pH values of ~ 4.2 and ~ 5.2 respectively to simulate the effect of adding CO_2 rather than Na_2CO_3 . A portion of each solution was placed in leach containers and allowed to stand at room temperature for seven days and a second portion was placed in leach containers that were placed in a 90°C oven for seven days to simulate leach tests at these temperatures. At the end of seven days, the 90°C samples were allowed to cool to room temperature. Then $\sim 10\text{-mL}$ aliquots were removed from each of the four containers and placed in separate vials containing 0.5 mL of 10 M NaOH to reconvert the CO_2 to the carbonate form prior to submitting the samples to the radioanalytical laboratory.

Recovery percentages for the ^{14}C are given in Table 2. These recovery percentages were judged to be satisfactory for these tests, particularly in view of the fact that the blank runs were conservative in nature. That is, the ^{14}C was essentially all in the form of CO_2 in the blank runs whereas it would have been in the carbonate and bicarbonate forms in the actual leach tests at the prevailing pH values of 6.4 to 9.7 . Thus, it was decided that the equipment and method were adequate to proceed with the graphite leach tests.

-
- (a) CO_2 concentrations as high as 10^{-3} M could have occurred in the actual leach tests if the leach rates of ^{14}C and ^{12}C were the same. However, as discussed later, the leach rate of ^{12}C is expected to be considerably less than the initial leach rate of ^{14}C . If so, CO_2 concentrations in the actual leach tests would have been much less than 10^{-3} M in deionized water. The initial HCO_3^- concentration in the Hanford ground water was $2.7 \times 10^{-3} \text{ M}$, so the leach tests would have had no effect on this.

TABLE 2. Results of Simulated Leach Tests

<u>Na₂CO₃ Concentration, mol/L</u>	<u>Test Temperature, °C</u>	<u>¹⁴C Recovery, percent</u>
10 ⁻²	20	87
10 ⁻²	90	81
10 ⁻⁴	20	89
10 ⁻⁴	90	99

RESULTS

The concentrations of ^{14}C and ^{36}Cl found in the leachates, as well as other experimental parameters, are given in Appendix C. Note that the leachates obtained in the fourth, sixth, and seventh leach intervals were not analyzed due to budget constraints. Data presented in Tables 3 and 4 were derived from the raw data listed in Appendix C according to the following equations:

$$F = \frac{CV}{IM} \quad (1)$$

$$R = \frac{F}{t} \quad (2)$$

$$L = \frac{R}{A} \quad (3)$$

where:

F = total fraction of inventory of radionuclide released in a given leaching interval,

C = concentration of radionuclide in the leachate, disintegrations per minute per milliliter, d/m/mL,

V = volume of leachate, mL,

I = inventory of radionuclide in the graphite specimen, disintegrations per minute per gram of specimen, d/m/g,

M = mass of specimen, g,

R = average fractional leach rate for the seven-day period, day^{-1} ,

t = time, days,

L = average leach rate per unit surface area of specimen, $\text{g/m}^2/\text{day}$,

A = BET surface area of specimen, m^2/g .

The cumulative fraction of inventory leached (Table 4) is given by summing the fraction leached in each leach period. This parameter could not be calculated exactly because leachates from the fourth, sixth, and seventh

TABLE 3. Leach Rates of Five Graphite Specimens

Time ^(a) Days	¹⁴ C Leach Rates									
	DIW-25 ^(b)		DIW-50		DIW-90		HGW-25 ^(c)		HGW-90	
	F ^(d)	L ^(e)	F	L	F	L	F	L	F	L
3.5	2.22E-6	4.27E-7	7.29E-6	1.40E-6	1.80E-5	3.46E-6	2.26E-6	4.34E-7	1.04E-5	2.00E-6
10.5	1.31E-6	2.53E-7	4.46E-6	8.57E-7	1.08E-5	2.08E-6	4.31E-7	8.29E-8	7.96E-6	1.53E-6
17.5	1.31E-6	2.53E-7	3.14E-6	6.04E-7	7.98E-6	1.53E-6	8.52E-7	1.64E-7	4.23E-6	8.14E-7
31.5	1.72E-6	3.30E-7	2.33E-6	4.48E-7	7.07E-6	1.36E-6	2.77E-7	5.33E-8	2.22E-6	4.26E-7
52.5	1.62E-6	3.11E-7	1.62E-6	3.12E-7	6.77E-6	1.30E-6	2.26E-7	4.34E-8	3.32E-6	6.39E-7
³⁶ Cl Leach Rates										
3.5	2.15E-4	4.14E-5	2.48E-4	4.77E-5	2.47E-4	4.76E-5	1.86E-4	3.57E-5	2.25E-4	4.33E-5
10.5	4.41E-5	8.48E-6	1.62E-5	3.11E-6	1.18E-5	2.27E-6	3.17E-5	6.10E-6	9.76E-6	1.88E-6
17.5	1.29E-5	2.48E-6	4.31E-6	8.29E-7	4.30E-6	8.27E-7	6.56E-6	1.26E-6	2.14E-6	4.12E-7
31.5	3.12E-6	6.00E-7	2.70E-6	5.18E-7	2.26E-6	4.34E-7	1.64E-6	3.15E-7	5.36E-7	1.03E-7
52.5	1.29E-6	2.48E-7	1.83E-6	3.53E-7	4.30E-7	8.27E-8	9.84E-7	1.89E-7	6.43E-7	1.24E-7

(a) The times listed are the midpoints of the different weekly leach intervals

(b) DIW = Deionized water. Number is approximate temperature of leach test, °C

(c) HGW = Hanford ground water. Number is approximate temperature of leach test, °C

(d) F = fraction of original inventory leached per day (day⁻¹)

(e) L = mass loss rate (g/m².day)

TABLE 4. Cumulative Fraction of Radionuclides Leached from Five Graphite Specimens

Time, Days	Cumulative Fraction of ^{14}C Leached				
	DIW-25 ^(a)	DIW-50	DIW-90	HGW-25 ^(b)	HGW-90
7	1.55E-5	5.08E-5	1.26E-4	1.58E-5	7.24E-5
14	2.48E-5	8.19E-5	2.01E-4	1.88E-5	1.28E-4
21	3.41E-5	1.04E-4	2.57E-4	2.48E-5	1.58E-4
28	(4.48E-5)	(1.23E-4)	(3.10E-4)	(2.86E-5)	(1.80E-4)
35	5.68E-5	1.39E-4	3.59E-4	3.06E-5	1.96E-4
42	(6.86E-5)	(1.54E-4)	(4.08E-4)	(3.24E-5)	(2.14E-4)
49	(8.03E-5)	(1.66E-4)	(4.56E-4)	(3.41E-5)	(2.35E-4)
56	9.16E-5	1.78E-4	5.04E-4	3.57E-5	2.59E-4

Time, Days	Cumulative Fraction of ^{36}Cl Leached				
	DIW-25	DIW-50	DIW-90	HGW-25	HGW-90
7	1.50E-3	1.72E-3	1.73E-3	1.30E-3	1.57E-3
14	1.81E-3	1.84E-3	1.81E-3	1.52E-3	1.64E-3
21	1.91E-3	1.87E-3	1.84E-3	1.57E-3	1.66E-3
28	(1.96E-3)	(1.89E-3)	(1.86E-3)	(1.60E-3)	(1.66E-3)
35	1.98E-3	1.91E-3	1.88E-3	1.61E-3	1.67E-3
42	(2.00E-3)	(1.93E-3)	(1.89E-3)	(1.62E-3)	(1.67E-3)
49	(2.01E-3)	(1.94E-3)	(1.90E-3)	(1.63E-3)	(1.68E-3)
56	2.02E-3	1.96E-3	1.90E-3	1.63E-3	1.68E-3

Values in parentheses are interpolated.

(a) DIW = Deionized water. Number is approximate temperature of leach test, °C

(b) HGW = Hanford ground water. Number is approximate temperature of leach test, °C

leach periods were not analyzed. Therefore, the fractions of inventory leached during those periods were estimated by linearly interpolating between the radionuclide concentrations of the previous and following leach periods.^(a) That is, for example, the fraction of inventory leached during the fourth period was determined from equation (1) by assuming that the radionuclide concentration in the leachate in the fourth period was midway between the concentrations found in the third and fifth periods.

Figures 1 through 18 display the data listed in Tables 3 and 4. Figures 1 through 10 show fractional leach rates versus time, and in most cases they have been fit to a curve of the form

$$R = A + Be^{-Ct} \quad (4)$$

The form of equation (4) assumes that the leach rate is a composite of two mechanisms consisting of a steady-state term, A, and a term that decreases exponentially with time. The constants A, B, and C were determined by nonlinear regression analyses, and their values are given at the bottoms of Figures 2, 3, and 5 through 10. The constant, A, represents steady-state leach rates that were attained after periods of about 60 days for the present specimens.

Figures 11 through 14 show cumulative fractions of inventories leached versus time and versus square root of time. Note, again, that values for the fourth, sixth, and seventh leach periods are interpolated values as described above.

Figures 15 through 18 plot the ^{14}C data in Arrhenius form. Figure 15 is a plot of the instantaneous ^{14}C fractional leach rates in deionized water for

(a) In principle, interpolations made according to equation (4) would have been superior to linear interpolations wherever the data reasonably fit that equation. However, the data in Figures 1 and 4 were not fit by equation (4), and linear interpolations seemed the best option in those cases. Therefore, for consistency, linear interpolations were made in all cases. Furthermore, inspection of the data in Figures 2, 3, and 5 through 10 shows that linear interpolations provide reasonable approximations to the curves that represent equation (4) in the regions of the fourth, sixth, and seventh leach periods.

each of the periods where the leachates were analyzed. In general, they are not linear, possibly because of uncertainties in the 20°C data, which are discussed below.

Figure 16 shows the cumulative fraction of ^{14}C leached during the entire eight-week test, including the amounts estimated to have been leached during the fourth, sixth, and seventh periods when the leachates were not analyzed. Figure 17 shows the cumulative fraction of ^{14}C leached just during the five periods where the leachates were actually analyzed. This amounts to assuming that the proportion of ^{14}C leached during the fourth, sixth, and seventh periods was the same at each temperature. Figures 16 and 17 show marked improvements in the linearity of the results over those in Figure 15. Using the data shown in Figure 17, activation energies of 5.5 kcal/mol and 5.9 kcal/mol were calculated for deionized water and Hanford ground water, respectively.

Figure 18 shows the steady state leach-rate values for the deionized water leachates normalized on the basis of the BET surface area of the graphite. The steady-state values used at 90°C and 50°C were obtained from the fitted curves whereas the steady-state value used at 20°C was the last value measured. Also shown in Figure 18 for comparison are data obtained by Gray (1982) on non-radioactive powdered graphite at 200°C to 300°C.

It is recognized that water may not have penetrated all of the pores and cracks that are accessible to N_2 gas, which was used in the BET surface-area measurements. However, it is believed that much of the BET surface area is accessible to the water, and because there is no convenient way of measuring the true surface area accessible to the water, the BET surface area was used, as a matter of convenience, in normalizing the leach rates on the basis of surface area.

FIGURE 1. Carbon-14 Leach Rate in Deionized Water, 20°C

FIGURE 2. Carbon-14 Leach Rate in Deionized Water, 50°C

FIGURE 3. Carbon-14 Leach Rate in Deionized Water, 90°C

FIGURE 4. Carbon-14 Leach Rate in Hanford Ground Water, 20°C

FIGURE 5. Carbon-14 Leach Rate in Hanford Ground Water, 90°C

FIGURE 6. Chlorine-36 Leach Rate in Deionized Water, 20°C

FIGURE 7. Chlorine-36 Leach Rate in Deionized Water, 50°C

FIGURE 8. Chlorine-36 Leach Rate in Deionized Water, 90°C

FIGURE 9. Chlorine-36 Leach Rate in Hanford Ground Water, 20°C

FIGURE 10. Chlorine-36 Leach Rate in Hanford Ground Water, 90°C

FIGURE 11. Cumulative Fraction of Carbon-14 Leached Versus Time

FIGURE 12. Cumulative Fraction of Carbon-14 Leached Versus Square Root of Time

FIGURE 13. Cumulative Fraction of Chlorine-36 Leached Versus Time

FIGURE 14. Cumulative Fraction of Chlorine-36 Versus Square Root of Time

FIGURE 15. Instantaneous Fractional Leach Rate of ¹⁴C

FIGURE 16. Cumulative Fraction of ^{14}C Leached During 8-Week Test Period

FIGURE 17. Cumulative Fraction of ^{14}C Leached During Five of the Eight Intervals Where the Leachates were Analyzed

FIGURE 18. Steady-State Leach Rates of ¹⁴C Compared with Previous Results on Non-Radioactive Graphite

DISCUSSION

The following subsection provides an evaluation of the 20°C data, which are the data of primary interest to disposal of the Hanford Production Reactors. This is followed by a subsection that discusses all of the data and its implications regarding leaching mechanisms.

EVALUATION OF 20°C DATA

Most of the ^{14}C and ^{36}Cl leaching data presented in Figures 1 through 10 exhibit a reasonably monotonic variation with time. The major exceptions to this occur with the ^{14}C data at 20°C in both deionized water (Figure 1) and Hanford ground water (Figure 4). It is tempting to suspect that this scatter may be due to temperature variations in the fume hood where the leach containers were kept during most of the eight-week leach testing period. However, if that were the cause, then the deionized water and Hanford ground water data should show similar variations. The fact that they do not suggests some other, as yet unidentified, cause.

Whatever the cause, the scatter in the ^{14}C data at 20°C makes them impossible to reasonably fit with an exponential curve of the sort that fits the other data quite well. Thus, while it is possible to assign steady-state leach-rate values to the ^{36}Cl data and the higher-temperature ^{14}C data with reasonable confidence, it is not possible to do so with the ^{14}C data at 20°C. Data from the fourth, sixth, and seventh leach periods, which are missing because the leachates were not analyzed due to budget constraints, might allow for a better fit.

Despite the lack of well-defined time dependence in the ^{14}C leach data at 20°C, it appears reasonable to assign steady-state fractional leach rates approximately equal to the values observed during the fifth and eighth leach periods ($\sim 1.5 \times 10^{-6}$ per day and $\sim 0.25 \times 10^{-6}$ per day for deionized water and Hanford ground water, respectively). This assessment is based on the fact that the calculated steady-state values for the higher-temperature ^{14}C data are approximately equal to the observed leach rates during the fifth and eighth leach periods and it seems reasonable to expect that the same should hold true for the 20°C data.

For ^{36}Cl , steady-state fractional leach rates of 2.6×10^{-6} per day (Figure 6) and 1.3×10^{-6} per day (Figure 9) were found at 20°C in deionized water and Hanford ground water, respectively.

Differences between the ^{14}C leach rates in deionized water and Hanford ground water may be related to the bicarbonate already contained in the latter. No similarly plausible-sounding explanation for the ^{36}Cl data is apparent; however, the apparent difference between the deionized water and Hanford ground water is less than for the ^{14}C data, and much of the difference may be attributable to experimental uncertainty, which may be on the order of $\pm 1 \times 10^{-6}$ per day for both deionized water and Hanford ground water based on inspection of the 20°C data in Table 3.

It is interesting to note that the steady-state leach rates given above are in reasonable agreement with values previously estimated by Morgan in Appendix D of the draft environmental impact statement on decommissioning of the eight surplus reactors at Hanford^(a). For ^{14}C , Morgan estimated a steady-state leach rate of 6×10^{-7} per day, which is midway between the values observed here for deionized water and Hanford ground water. Since no leaching data were available for ^{36}Cl , Morgan assumed it would have a leach rate similar to that observed for ^3H , 1.0×10^{-6} per day. This is quite close to the value found for ^{36}Cl in the present study with Hanford ground water.

The reader is cautioned that use of the so-called steady-state leach rates quoted here for predicting long term leach rates is subject to considerable uncertainty because not enough is known about the leaching mechanisms. Leach rates after many months or years could be very different, most likely lower, than the apparent steady state values that were determined after eight weeks of testing.

(a) U.S. Department of Energy (DOE). September 1988 Draft. Draft Environmental Impact Statement, Decommissioning of Eight Surplus Production Reactors at the Hanford Site, Richland, Washington.

DISCUSSION PERTAINING TO LEACHING MECHANISMS

Further discussion of the leaching results obtained in this study requires some prior understanding of the nature of the graphite and the origin of the ^{14}C and ^{36}Cl contained within the graphite. The main feature of the graphite itself that must be understood is its large BET surface area, which is due to an extensive interconnected network of small pores and cracks. The extent of this network can be appreciated by comparing the BET surface areas of the graphite specimens (190 m^2) with their geometric surface areas (0.0044 m^2). The major source of ^{14}C within the graphite is from transmutation of nitrogen according to:

Most of the nitrogen in the graphite moderators of the Hanford Reactors was chemisorbed on the graphite surfaces. Therefore, the ^{14}C was formed predominantly on the graphite surfaces. Its rates of assimilation into the graphite crystal lattices by solid-state diffusion into the bulk graphite would be quite low at the temperatures of the graphite moderator, which were generally $\leq 600^\circ\text{C}$. However, as discussed in Appendix D, the atomic displacement processes have probably resulted in a distribution of the ^{14}C atoms which can be described as follows:

- 1) Most of the ^{14}C atoms are randomly mixed with, and practically indistinguishable from, normal ^{12}C atoms; however, there will be some tendency for the relative concentration of ^{14}C atoms to increase with proximity to surfaces accessible by nitrogen.
- 2) Internal surfaces that are accessible to nitrogen probably contain a high concentration of ^{14}C atoms that act as "active sites"; that is, they are situated at the edges of layer planes (or adjacent to vacancy sites) and have unsaturated bonds.
- 3) Some ^{14}C atoms, attached to the internal surfaces, may be chemically complexed with hydrogen, nitrogen, or oxygen atoms.

In terms of relative leach rates, we can expect that the chemically complexed ^{14}C atoms will be the most easily leached; the ^{14}C atoms at active sites will be somewhat more resistant to leaching than the complexed atoms, but less resistant than atoms in normal lattice positions. How these

differences will effect the over-all leach rates cannot be quantified until more is known about the chemical states and physical distribution of the ^{14}C , relative to ^{12}C . We can note, however, that Arnold and Libby (1946) observed that oxidation of irradiated graphite with chromic acid yielded a product that was 50 times enriched in ^{14}C , and that White et al. (1984) reported a 50- to 100-fold reduction in the leach rate of ^{14}C during their 100-day leach test on irradiated graphite.

The source of ^{36}Cl in the graphite is neutron activation of traces of natural chlorine left from purification of the graphite during its manufacture:

Natural ^{37}Cl also activates to ^{38}Cl , but the half life of ^{38}Cl is only a few minutes, so it need not be considered. The chemical and physical form of the chlorine remaining in the graphite after purification is not known, nor is the mechanism for its removal during leaching. Speculation regarding the rate-limiting mechanism during leaching of ^{36}Cl is therefore even more arguable than in the case of ^{14}C .

Having discussed an important feature of the graphite itself as well as the origins of ^{14}C and ^{36}Cl , we now turn to a discussion of the leaching data. Figures 1 through 10 show that the leach rates of ^{14}C and ^{36}Cl decrease with time. There are at least two possible mechanisms for this: 1) depletion of the ^{14}C and ^{36}Cl sources; and 2) diffusion limited rate of transport of either a reactant such as O_2 , or the reaction products, through the static leachant contained within the tortuous pores of the graphite.

Clearly the sources are not being depleted, per se, because the total fractions leached are quite small. But it is possible that a portion of the sources are more reactive or more readily accessible to the leachant than the rest. In the case of ^{14}C , it seems clear that a significant fraction of the atoms at the internal surfaces are both more reactive and more accessible than atoms below the surface layers. If, however, the ^{36}Cl atoms have been injected (by recoil collisions, or other processes) into the graphite lattice, leaching can occur only at the same rate that the overlying

graphite is removed through oxidation. If this hypothesis is correct, once the ^{14}C that is chemically complexed or located at active sites is depleted, the leach rates of both ^{14}C and ^{36}Cl should approach the leach rate of ^{12}C (their rates should differ from that of ^{12}C , only to the extent that their average concentration in the surface layers differs from their average concentration in the remaining graphite). The fact that the steady-state leach rates of ^{14}C and ^{36}Cl approach similar values lends support to this hypothesis.

Alternatively, diffusion of the leached species through the leachant within the pores of the graphite could limit the rate at which ^{14}C and ^{36}Cl enter the bulk solution. Or diffusion of oxygen through the leachant within the graphite pores could limit the rate at which it is available to oxidize the graphite.

The data obtained do not allow a clear determination of which, if either, of the proposed mechanisms is valid. If source depletion, or pseudo depletion, applies and the reaction rate is proportional to the amount of source material, then the leach rates would be expected to follow an exponential decrease with time such as that shown in Figures 1 through 10. In many cases, the fit is quite good, but in others, particularly the ^{14}C data at 20°C , it is not (see discussion on p. 33 regarding scatter in the 20°C data).

If diffusion is the rate-limiting mechanism, then the cumulative release data should be linear with the square root of time. Figure 12 shows that to be true for ^{14}C , but Figure 14 clearly shows that it is not true for ^{36}Cl . Elimination of data from the first leach period in Figure 14 improves the linearity, but the fit is still not good. Also, if diffusion were the rate-limiting mechanism, it would seem that it should apply to ^{36}Cl as well as ^{14}C . The fact that it does not seem to apply to both radionuclides casts doubt on its applicability in either case.

To determine whether oxygen availability could be a limiting factor in the leach tests, it was compared with the amount of carbon oxidized to CO_2 . The solubility of oxygen in water at 25°C and 0.2 atm pressure is about 5.6 mL of O_2 gas at standard temperature and pressure per liter of water. Thus, about 0.1 mmol of O_2 is contained in the ~406 mL of water in each leach

test. In addition, there is about 45 mL of head space in each leach test which would contain about 0.4 mmol of O_2 , or a total of 0.5 mmol of O_2 in each test. This could oxidize 0.5 mmol = 6 mg of carbon.

The maximum fraction of ^{14}C leached was during the first 7-day period at 90°C in deionized water, a total of 1.2×10^{-4} of inventory. Assuming that fraction also applies to the entire 36-g sample, a total of 4.3 mg of carbon would have been oxidized. This is less than the calculated amount based on the amount of oxygen present, but not much less. Therefore, based on the assumption that ^{12}C oxidizes at the same rate as ^{14}C , the limited supply of oxygen could limit the observed leaching of ^{14}C during the first week at 90°C in deionized water. However, the limiting effect would be smaller during subsequent leaching periods because the amount of carbon leached decreases each succeeding week while the initial oxygen concentration is the same each week. Also, the limiting effect would be almost nonexistent at lower temperatures.

As stated, the above calculation was based on the assumption that ^{12}C oxidizes at the same rate as ^{14}C . However, Arnold and Libby (1946) have reported that the initial oxidation rate of ^{14}C is many times that of ^{12}C for irradiated graphite. Thus, a calculation based on a more realistic treatment of the relative oxidation rates of ^{12}C and ^{14}C would show that the limited supply of oxygen in no way limited the observed leach rates of ^{14}C in the present tests.

Not only are the ^{14}C and ^{36}Cl data time dependent, but the ^{14}C data are also temperature dependent. This suggests that oxidation kinetics may constitute a rate-limiting step in the leaching data. To test this idea, four different methods were used in Figures 15 through 18 to display the ^{14}C data in Arrhenius format. Except for Figure 17, the general lack of linearity is obvious, and it is not known to what extent this can be blamed on uncertainty in the 20°C data.

Despite the general lack of linearity in the Arrhenius plots, the data in Figure 17 were used to calculate activation energies of 5.5 kcal/mol and 5.9 kcal/mol for deionized water and Hanford ground water, respectively. These values are less than half that obtained by Gray (1982) at 200°C to 300°C. The change in apparent activation energy may imply a change in

mechanism or, together with the general non-linearity of the present data, may be an indication that the rate-limiting mechanism in the present study is not related to oxidation kinetics.

Interestingly, the ^{14}C data obtained at 90°C in the present study agree well with an extrapolation of the 200°C to 300°C data obtained with non-radioactive graphite by Gray (1982). Although the agreement may be fortuitous, it may indicate that the rate of ^{14}C removal has become limited by the rate of ^{12}C oxidation after less than 60 days at 90°C .

Finally, it is of interest to compare the ^{14}C leaching data from the present study with that obtained by White et al. (1984). Very good agreement exists between the steady-state leach rates obtained by White et al. at 20°C to 25°C in either demineralized water or simulated ground water and the results obtained in this study with deionized water at 20°C . However, White et al. found that the leach rates in demineralized water and simulated ground water at 20°C to 25°C decreased by factors of 50 to 100 after 100 days. This is a far greater decrease with time than observed in the present study. White et al. also reported total fractions of inventories leached after 100 days to be in the range 8.8×10^{-4} to 1.4×10^{-3} under the same conditions of temperature and leachant type whereas the fractions leached at 20°C in the present study were in the range 3.6×10^{-5} to 9.2×10^{-5} . These differences may be a result of differences of neutron fluence, temperature of the graphite, source of the ^{14}C , atmosphere to which the samples were exposed, the pretreatment given the graphite specimens in the present study, or other variables which have not been identified. In particular, the graphite used by White et al. (1984) had been exposed to a lower neutron fluence (thus, reducing the homogenization of ^{14}C with the bulk of the graphite) and it had been irradiated in high-pressure CO_2 , rather than atmospheric-pressure helium or He-CO_2 mixtures, with air impurities (thus, the formation of C-O complexes on the interior surfaces could have been enhanced on the samples used by White et al.).

Our samples were ultrasonically cleaned for one to two minutes in deionized water to remove graphite machining dust. Any ^{14}C removed during the cleaning treatment (whether as mechanically-activated active sites or as loosely-bound agglomerates of chemical complexes) would not have been counted in the total fraction of inventory leached. Thus, if the fraction of

inventory removed during cleaning was significant, the leach rate could have been much higher than was measured during the first seven-day leaching period and might have been in better agreement with the results reported by White et al. (1984).

CONCLUSIONS AND RECOMMENDATIONS

The leach rates of ^{14}C and ^{36}Cl found at 20°C in this study are in good agreement with those estimated earlier by Morgan (see Appendix D of the draft environmental impact statement on decommissioning of the eight surplus reactors at Hanford)^(a). That is, steady-state fractional leach rates of about 1.5×10^{-6} per day and 0.25×10^{-6} per day were obtained for ^{14}C in deionized water and Hanford ground water respectively. For ^{36}Cl , steady-state fractional leach rates of 2.6×10^{-6} per day and 1.3×10^{-6} per day were found in deionized water and Hanford ground water, respectively. Uncertainties of plus or minus a factor of about 2 must be assigned to each of the leach-rate values quoted above due mainly to scatter in the data. Additional, perhaps larger, uncertainties exist because of possible variations that may occur within the moderator stacks and between the different Hanford reactors. It must also be noted that use of the so-called steady-state leach rates quoted here for predicting long-term leach rates is subject to considerable uncertainty because not enough is known about the leaching mechanisms. Leach rates after many months or years could be very different, most likely lower, than the apparent steady-state values that were determined after eight weeks of testing.

To reduce the uncertainties, the following courses of action are recommended:

- Our ability to predict long-term leach rates with confidence can be improved only through enhanced understanding of the leaching mechanisms involved. This would require, at a minimum, additional leaching studies with graphite samples of different size (probably including samples of crushed graphite) and extension of the tests to longer times. A more sophisticated approach (which involves modification of existing techniques to identify surface complexes, reaction sequences, and in-depth concentration profiles of individual isotopes) could reduce uncertainties of projected long-term release rates by one-or-two orders of magnitude.

(a) U.S. Department of Energy (DOE). September 1988 Draft. Draft Environmental Impact Statement, Decommissioning of Eight Surplus Production Reactors at the Hanford Site, Richland, Washington.

- Uncertainties due to variations in graphite grades used in the various reactors (and in the various zones of each of the reactors) could be reduced by more representative sampling within a given graphite moderator stack and by taking samples from different reactors.

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APPENDIX A

PERSONAL COMMUNICATIONS

Memo from W. C. Morgan to J. V. Robinson, "Characterization of Graphite Samples for Leach Test," April 7, 1988, Pacific Northwest Laboratory, Richland, Washington.

Date April 7, 1988
To J. V. Robinson
From W. C. Morgan *WCM*
Subject Characterization of Graphite Samples for Leach Test

DG Doran
MD Freshley
WJ Gray
EB Moore
GL Tingey
File/LB

SUMMARY AND CONCLUSIONS

The inventories of selected radioisotopes have been measured for small samples cut from the inner-most bar retrieved from the "Y" test hole at C Reactor. The measured concentrations of ^{14}C were about 1.5 to 2 times greater than expected, and the measured concentrations of ^{36}Cl were between 5 and 10 times greater than expected. Specific surface area, as measured by adsorption of N_2 , was also about 1 order of magnitude higher than that of unoxidized graphite. The high specific (BET) surface area, and the general appearance of the surfaces of the bar, indicates that the bar was oxidized, probably due to air ingress; however, the average weight loss may have been less than 2%.

Considering the high BET surface area of the samples cut from this bar, the documented history of C Reactor, and the testing program which was used to segregate the various heats of nuclear graphite, it is my considered opinion (although, admittedly, somewhat speculative in nature) that:

1. the peak(a) concentration of ^{14}C in C Reactor may exceed the measured values reported herein, by a factor of 2 to 3;
2. the peak ^{36}Cl concentration in the C Reactor moderator is probably not more than the minimum concentration measured on samples from this bar; and
3. the average BET surface area of the moderator bars may be less than the lowest BET surface area measured on these samples; however,
4. there is no reason to expect that the leach rates of ^{14}C or ^{36}Cl , normalized on the basis of radioisotopic concentrations and BET surface

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- (a) As used herein, "peak" refers to the average value measured on a blended sample taken from several moderator bars exposed to the maximum neutron fluence in the reactor under consideration. Graphite is not homogeneous, thus, a small sample from one bar may not be representative of the average of the material surrounding it. For example, a small sample (A-G-23) from DR Reactor contained $12 \mu\text{Ci/g}$ of ^{14}C ; this concentration was not typical of other samples from DR, nor is it to be considered as a "peak" concentration.

area, are not typical of irradiated, GBF type, graphite (as used in C, KE, KW and parts of H Reactor moderators).

INTRODUCTION

The graphite moderators of the surplus Hanford Production Reactors contain significant quantities of chlorine-36 and carbon-14. Both radioactive isotopes have long half-lives, are biologically assimilable, and decay by emission of low energy beta-rays (which are difficult to monitor); thus, if they are released to the ecosystem, they could constitute a biological hazard.

One potential mode of release is the leaching of either isotope, if water should enter the moderator block.

Morgan(b) reviewed the very limited data on leaching of ^{14}C and estimated the ^{36}Cl inventories in the surplus reactors.(c)(d) However, no data were available on the leaching of ^{36}Cl ; thus, the assumption has been made that the leaching behavior of ^{36}Cl is similar to that of ^3H .(e) In order to determine if this assumption is valid, and to improve our understanding of the leaching behavior of ^{14}C , samples were prepared from graphite bars irradiated in the "Y" test hole at C Reactor. These samples were tested to determine the leaching behavior of the ^{36}Cl and ^{14}C contained in them.

The purpose of this memo is to document the results of work done to characterize the samples.

PEDIGREE OF THE SAMPLES

Three bars (about 3.8 x 3.8 x 24 in.) were retrieved from the rod-room side of the "Y" test hole at C Reactor;(f) these bars had been charged to act as spacers, providing a positive stop for irradiation experiments charged from the "X-level" (experimental access) side. Figure 1 diagrams the location of Bar 3 with respect to the fueled process channels. Oxidation-induced pitting

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- (b) Memo from W. C. Morgan to W. L. Templeton, "Carbon-14 Release Rates," October 11, 1985.
 - (c) Memo from W. C. Morgan to R. A. Winship, "Estimated Chlorine-36 Concentrations in the Graphite of the Old Hanford Reactors," February 24, 1986.
 - (d) Memo from W. C. Morgan to J. A. Adams, "Measured Versus Estimated Chlorine-36 Activities in Irradiated Graphite," October 30, 1986.
 - (e) As measured by White et al. (1984).
 - (f) Informal report by A. E. DeMers. Observations and Recommendations of the Graphite Bar Removal from "C" Reactor. PNL Contract #B-N5095-A-U, Pacific Northwest Laboratory, Richland, Washington. October 21, 1987.

of the bars was evident on all surfaces exposed to the reactor atmosphere; in contrast, the surfaces in contact with the filler bars did not show obvious signs of oxidation.

The grade of graphite from which these bars were machined has not been positively identified; however, it was probably Grade TSGBF, manufactured under either the TSGBF developmental contract (G-3) or the (G-5) contract for production of the moderator graphite used in KW Reactor (Morgan 1982).

SAMPLE PREPARATION AND CHARACTERIZATION

Samples were machined from sections of the inner-most end of the inner-most bar, as shown in Figure 2. Samples 1, 2, 3, 5, and 7 were reduced to about 30 mm diameter by 30 mm long, for use in the isotope leaching tests. Although it would have been preferable to determine BET surface area and isotopic inventories on each sample used in the leach tests, contractual constraints on time precluded exercise of this option. Therefore, Samples 4, 6, and 8 were machined to about the same diameter, then reduced to about 1.25 cm diameter by 2.20 cm long for measurement of BET surface areas; the powder removed during reduction in diameter was then used to determine the inventory of ^{36}Cl and ^{14}C . It is recommended that, in all future investigations, isotopic inventories, BET surface areas, and all other parameters of potential importance for normalization of the experimental results be obtained on each sample used in the leach tests.

The Brunauer, Emmett, and Teller (BET) method for determining the specific surface area is based on the adsorption of a monolayer of nitrogen gas at its normal boiling point on the internal surface of the graphite. The BET surface area is, thus, a measure of the ability of N_2 to reach the internal surface of the graphite; the (larger) H_2O molecules may not have access to the same surface area. Nevertheless, BET surface area may be an index on which to normalize leach rates of the radioactive isotopes in graphite.

BET surface areas were measured(g) on Samples 4, 6, and 8, both after machining and after leaching for 3 weeks in deionized water at $\sim 20^\circ\text{C}$. As can be seen from Table 1, within the limits of precision of the measurements ($\pm 4\%$), the BET surface area was not changed by the leach process.

Table 2 shows the dimensions, weight, and densities of all eight samples; note that the bulk density appears to vary with position in (upper or lower part of) the bar. This is consistent with the observed oxidation pattern on the bar.

(g) Courtesy of M. C. Burt.

Figure 1. Relative Positions of Bar 3 and Fuel Channels.

Figure 2. Relative Location of Samples from Bar 3.

TABLE 1. BET Surface Area Measurement Results

<u>Sample Number</u>	<u>BET Surface Area, m²/g</u>	
	<u>Before Leaching</u>	<u>After Leaching</u>
4	5.4	5.0
6	5.3	5.1
8	5.1	5.3

Average ($\pm 1\sigma$): 5.2 $\pm$ 0.2

TABLE 2. Dimensions and Densities of Samples

<u>Sample Number</u>	<u>Diameter, Inches</u>	<u>Length, Inches</u>	<u>Weight, Grams</u>	<u>Density, g/cm³</u>
1	1.1995	1.205	36.6767	1.644
2	1.2010	1.185	36.0130	1.637
5	1.2000	1.201	36.5030	1.640
6	0.5005	1.255	6.5842	1.627
3	1.1950	1.203	36.5645	1.653
4	0.5015	1.244	6.6575	1.653
7	1.2015	1.203	36.7013	1.642
8	0.5005	1.243	6.5996	1.646

Average density of Samples 1, 2, 5, and 6 = 1.637 $\pm$ 0.007
 Average density of Samples 2, 4, 7, and 8 = 1.648 $\pm$ 0.009

RADIOACTIVE ISOTOPE CONCENTRATIONS

Procedures used to measure the radioactive isotope concentrations will be included in C. W. Thomas' report, and will be forwarded to you separately.

Table 3 lists the measured concentrations for the three samples. There appears to be, generally, an inverse correlation between the oxidation pattern on the bar and the concentration of ^{14}C and ^{36}Cl in the samples; however, concentrations of the other (less-easily-gasifiable) isotopes do not show any such correlation.

TABLE 3. Isotopic Concentrations in Samples

Isotope	Concentration, $\mu\text{Ci/g}$		
	Sample 4	Sample 6	Sample 8
^{14}C	6.92	6.13	8.10
^{36}Cl	0.055	0.052	0.092
^{60}Co	0.136	0.138	0.125
^{133}Ba	0.031	0.029	0.029
^{134}Cs	0.0003	0.0002	0.0003
^{137}Cs	0.026	0.026	0.026
^{154}Eu	0.009	0.007	0.008
^{155}Eu	0.003	0.002	0.002

The average concentration of ^{14}C for these three samples was $7.0 \pm 1.0 \mu\text{Ci/g}$ and that of ^{36}Cl was $0.066 \pm 0.023 \mu\text{Ci/g}$.

COMPARISON WITH PREVIOUS RESULTS

The concentration of ^{36}Cl was measured(d) on various bits-and-pieces of graphite samples "cored" from Tube Channel 1880 at KW Reactor. The results indicated that the (pre-irradiation) chlorine content might have been reduced by a factor of about 11.6, i.e., only about 8.62% of the original chlorine concentration remained in the graphite.

Following the arguments of Morgan,(d) the ^{36}Cl activity in TSGBF graphite can be calculated from the following equation:(h)

$$A_i = A_{\infty}(1 - e^{-\sigma\phi_i})$$

where A_i = the ^{36}Cl activity, $\mu\text{Ci/g}$, at a position where ϕ_i is the thermal neutron fluence,
 σ = the thermal neutron activation cross section for the $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ reaction, 43b, and
 A_{∞} = 0.192 $\mu\text{Ci/g}$ if 100% of the original chlorine remained in the graphite, or
 A_{∞} = 0.0166, if only 8.62% of the original chlorine is retained in the graphite.

At a thermal neutron fluence of $2.21 \times 10^{22}/\text{cm}$ (center of C Reactor, as per Miller and Steffes 1987), the ^{36}Cl concentration in TSGBF graphite should be:

0.118 $\mu\text{Ci/g}$, if 100% of the chlorine was retained
0.0102 $\mu\text{Ci/g}$, if only 8.62% of the chlorine remained.

The measured concentrations would seem to indicate that up to 80% of the original chlorine content was retained; however, as discussed later in this section, other facts lead us to the conclusion that the original chlorine content of this particular bar was much higher than that of a typical C Reactor moderator bar.

Estimates of ^{14}C concentrations (Miller and Steffes 1987) have been based on an average concentration of 2.8 $\mu\text{Ci/g}$ in the active region of DR Reactor: "The carbon-14 inventories for the other older reactors were estimated by using the ratios of the fluences compared to DR Reactor."

Using the ratio of thermal neutron fluences, reported by Miller and Steffes (1987) for C and DR Reactor ($2.21 \times 10^{22}/\text{cm}^2$ versus $1.56 \times 10^{22}/\text{cm}^2$ in DR), we obtain a ^{14}C concentration of 3.97 $\mu\text{Ci/g}$, about one-half the measured concentrations listed in Table 2. However, much higher concentrations (about 18 $\mu\text{Ci/g}$) have been previously measured on broaching dust from a process channel in C Reactor (Barton 1964).

It has been postulated(i) that ingress of air around the process tubes enriched the reactor atmosphere in N_2 , and resulted in fixation of nitrogen on the graphite surfaces, thus, increasing the production rate of ^{14}C . The large increase in BET surface area, and the general pattern of oxidation on the exterior of the sampled bar, seems to indicate that the effects of air in-leakage were not limited to the process channel blocks. Because the bar,

(h) Equation 1 of memo to J. A. Adams(d).

(i) Memo from W. C. Morgan to J. A. Adams, "Migration and Availability of ^{14}C from Irradiated Graphite," July 11, 1984.

from which our samples were cut, was fully exposed to the reactor atmosphere on three sides, it undoubtedly is more heavily oxidized than the average moderator bar in C Reactor. Increased oxidation carries with it the implication that more of the ^{14}C would be gassified (along with other carbon atoms on the graphite surfaces), and that the ^{14}C concentration in this bar may be less than that in an adjacent moderator bar. Moreover, the processed blocks operated at lower temperatures and (see discussion in memo to J. A. Adams, Footnote i) may have peak ^{14}C concentrations of about three times that measured in Sample No. 8.

Oxidation of the graphite, especially oxidation which increased the BET surface area, would also tend to release the chlorine; thus, it is difficult to imagine a mechanism which would allow retention of almost 80% of the original chlorine in Sample No. 8. This dilemma is further highlighted when we note that French researchers have reported(j) that only 15% of the tritium [from the $^6\text{Li}(n,\alpha)^3\text{H}$ reaction] remained in graphite removed from the G-2 Reactor.

It seems most probable that this bar originally contained a much higher concentration of chlorine than was typical of TSGBF graphite. A high concentration of chlorine would have produced a low nuclear (dih) purity,(k) and would have caused a particular heat of graphite to be excluded from use in (at least the central zone of) the Hanford production reactors; bars from the excluded heat would then be considered as "surplus," and made available for other purposes than moderator material. I have not found any indication that low-dih graphite was flagged; it just became part of the overall supply of "surplus material." As such, it could well be used for spacer bars, or any other non-critical application.

If the original concentration in this bar was much higher than the average concentration of typical moderator bars, then (even though the bar was more highly oxidized than normal moderator bars) the peak ^{36}Cl concentration in C Reactor moderator bars may be less than the minimum concentration measured in these samples. It is my considered opinion that the peak ^{36}Cl concentration in C Reactor moderator bars doesn't exceed $0.02 \mu\text{Ci/g}$.

Impact on Leach-Test Results

Test results are normalized on the basis of the fractional concentration leached per unit time; thus, the absolute concentrations will not impact the validity of the results.

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- (j) Letter from A. Cregut to C. Miller, "Answers to Questions Asked by Battelle Institute," January 13, 1986.
 - (k) Memo from W. C. Morgan to J. A. Adams, "Uncertainties in Estimated Chlorine-36 Inventories in the Old Hanford Reactors," December 1, 1986.

The effect of oxidation on the accessibility/leachability of the radioisotopes is not known. I expect that we will be able to normalize the leach rates of ^{14}C and ^{36}Cl on the basis of BET surface area (even though this may be different than the surface area accessed by the H_2O). The leachability of isotopes of other elements (Co, Ba, Cs, Eu, etc.) may well be dependent on the amount of internal oxidation, rather than just BET surface area; however, this has not been investigated.

At the present time, there is no reason to expect that the leach-test results will be adversely impacted by the oxidation or by non-typical concentrations of the radioisotopes.

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- Miller, R. L., and J. M. Steffes (editors). 1987. Radionuclide Inventory and Source Terms for the Surplus Production Reactors at Hanford. UNI-3714, Rev. 1.
- Morgan, W. C. 1982. Graphite Selection for the FMIT Test Cell. PNL-4253.
- White, I. F., G. M. Smith, L. J. Saunders, C. J. Kaye, T. J. Martin, G. H. Clarke, and M. W. Wakerley. 1984. Assessment of Management Modes for Graphite from Reactor Decommissioning. EUR-9232 EN.

APPENDIX B

RADIOANALYSIS METHODS

PNL TEST PROCEDURE

TITLE: GRLT-1, SEPARATION OF CHLORINE-36 BY ION EXCHANGE, DISTILLATION
AND MEASUREMENT BY BETA COUNTING

1.0 APPLICABILITY

This procedure applies to the separation and measurement of chlorine-36 in deionized water-graphite leach solutions or other similar solutions.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURE4.1 Equipment and Materials

- Beaker, glass, 400 mL, 100 mL or other sizes as may be required.
- Stir bar, glass covered, one inch or other suitable size.
- Chloride carrier, 10.0 mg Cl^-/mL -- Prepare by dissolving 1.649 (± 0.001) g of sodium chloride in a 100 (± 0.08) mL volumetric flask with deionized water. Mix thoroughly. Record the weight of sodium chloride and volume in the laboratory record book (LRB) and record the mg/mL chloride, date and initials on the chloride container. Record the balance used in the LRB.
- Nitric acid, concentrated, reagent grade or better.
- Nitric acid, 8 M -- Prepare by diluting 506 (± 1) mL of concentrated nitric acid to 1000 (± 1) mL. Mix thoroughly.
- Ion exchange resin, AG-50W, X-8, 100-200 mesh, H^+ form.
- Ion exchange resin column, as specified by the COGNIZANT SCIENTIST.

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11/2/87			11-4-87
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PNL TEST PROCEDURE

- Silver nitrate, 0.1 M -- Prepare by dissolving 1.70 (± 0.01) g of silver nitrate in 100 (± 1) mL of deionized water; mix thoroughly.
- Filter, 24 mm, Whatman 934-AH glass microfiber or equivalent.
- Filter holder, Swinnex, 25 mm.
- Vial, glass, 35 mL.
- Ammonium hydroxide, concentrated, reagent grade or better.
- Carbonate carrier, 10 mg $\text{CO}_3^{=}$ /mL -- Prepare by dissolving 1.77 (± 0.01) g of sodium carbonate in 100 (± 1) mL of deionized water; mix thoroughly.
- Barium nitrate, 0.1 M -- Prepare by dissolving 2.6 (± 0.1) g of reagent grade barium nitrate in 100 (± 1) mL of deionized water; mix thoroughly.
- Syringe, 10 mL, plastic, Luer-Lok.®
- Dropper, plastic.
- Distillation flask -- Use ^{79}Se still; see HTA-4-18, Figure HTA-4-18.1. Selenium still.
- Nitrogen gas -- Reduce pressure to ~2 psi using a nitrogen gas pressure-reducing valve. A purity of 99.5% nitrogen is acceptable.
- Sulfuric acid, concentrated, reagent grade or better.
- Heating mantle, 50 mL, round bottom.
- Variac, 1.5 ampere output, 0-140 volts.
- Thermometer, to read at least 360°C.
- Mercurous nitrate, 0.1 M -- Prepare by dissolving 2.8 (± 0.1) g of mercurous nitrate monohydrate in 100 (± 1) mL of deionized water plus 3 (± 0.01) mL of concentrated nitric acid. After dissolution is complete add about 1 mL of clean mercury metal to the solution and stir vigorously for at least 2 hours. When making additional mercurous nitrate use the same bottle and leave the mercury metal in the vial. The mercury metal reduces any mercuric ion to mercurous ion.
- Filter, 47 mm Gelman A/E glass.
- Filter holder, millipore, to hold 47 mm filter.

®Luer-Lok is a registered trademark of Becton, Dickenson & Co., Rutherford, New Jersey.

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PNL TEST PROCEDURE

- Methanol, reagent grade.
- Planchet, 2-inch diameter, aluminum.
- LB-1000, low background beta counter.

4.2 Chloride Separation

Chloride-36 is separated from other radioactive species by passing the acidified solution through a cation exchange resin column. The chlorine-36 passes through the column while most cations are retained. The chlorine-36 is further purified by silver chloride precipitation followed by a barium carbonate precipitation from concentrated ammonium hydroxide. The chloride is finally distilled as hydrochloric acid and is precipitated as mercurous chloride for counting.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 400 mL, or other suitable size, beaker or vial the ANALYST shall add a stir bar and a volume ($\pm 1\%$) of test solution specified by the COGNIZANT SCIENTIST. Record the volume taken on the Analytical Report Form.
- Step 2) While stirring add 1.0 (± 0.01) mL of chloride carrier and a volume ($\pm 1\%$) of concentrated nitric acid specified by the COGNIZANT SCIENTIST to make the solution 0.2 (± 0.02) M in acid.
- Step 3) Prepare a cation exchange column containing a volume ($\pm 1\%$) of resin and assembled as specified by the COGNIZANT SCIENTIST.
- Note: The volume of resin must be at least 1/25 the volume of sample taken in Step 1.
- Step 4) Transfer the solution from the beaker or vial in Step 2 to the ion exchange column. Collect the column effluent in a clean beaker or vial of the same size.
- Step 5) After all of the solution has passed through the resin column rinse the beaker from Step 2 with about one column volume of deionized water and transfer the rinse to the ion exchange column. Collect the effluent in the same effluent beaker or vial as Step 4. Discard the empty beaker and ion exchange resin column in the dry radioactive waste.
- Step 6) To the beaker or vial containing the effluent add a stir bar.
- Step 7) While stirring add 4 (± 0.04) mL of 0.1 M silver nitrate. Stir for 15 (± 2) minutes to coagulate the precipitate.

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PNL TEST PROCEDURE

- Step 8) Collect the precipitate by filtering on a 24 mm Whatman 934-AH glass microfiber filter using a Swinnex 25 mm filter holder. Discard the solution (filtrate) in the liquid radioactive waste.
- Step 9) Transfer the filter plus silver chloride precipitate to a 35 mL glass vial.
- Step 10) To the vial add 2 (± 0.1) mL of concentrated ammonium hydroxide. Add a stir bar and stir until the silver chloride dissolves then add 5 (± 0.1) mL of deionized water.
- Step 11) To the vial add 1 (± 0.1) mL of carbonate carrier.
- Step 12) While stirring add 2 (± 0.1) of 0.1 M barium nitrate. Stir for 1-2 minutes.
- Step 13) Assemble a 25 mm Swinnex filter holder with a 24 mm glass filter and attach a 10 mL Luer Lok syringe with the plunger removed.
- Step 14) Position the filter holder on a 35 mL vial in such a manner that will allow the filtrate to flow into the vial.
- Step 15) Using a plastic dropper transfer the barium carbonate slurry from Step 12 into the syringe.
- Step 16) Rinse the vial twice with 2 (± 0.1) mL of water and transfer to the syringe.
- Step 17) After transferring all of the slurry and rinse to the syringe use the plunger to push any remaining solution in the syringe through the filter. Discard the filter assembly and syringe in the radioactive waste.
- Step 18) To the filtrate in the 35 mL vial add a stir bar.
- Step 19) While stirring add 5 (± 0.1) mL of 8 M nitric acid. Silver chloride should form. If not add 1 (± 0.1) mL portions of 8 M nitric acid until the precipitate forms. Add 100 (± 1) μ L of 0.1 M silver nitrate and stir for at least 5 minutes to coagulate the precipitate.
- Step 20) Filter the silver chloride slurry using a 24 mm glass filter placed on a Swinnex 25 mm filter holder base. Transfer the silver chloride to the filter using a plastic dropper.
- Step 21) Wash the vial twice with 2 to 3 mL of deionized water and transfer to the filter. Discard the filtrate (solution) to the liquid radioactive waste.
- Step 22) Transfer the filter plus silver chloride to a 35 mL vial.

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PNL TEST PROCEDURE

- Step 23) To the 35 mL vial add 2 (± 0.1) mL of concentrated ammonium hydroxide and a stir bar. Stir until the silver chloride dissolves.
- Step 24) Using a plastic dropper transfer the solution to a selenium distillation flask (still).
- Step 25) Wash the vial twice with 2 (± 0.1) mL of deionized water and transfer to the still. Leave the filter in the vial and discard in the radioactive waste.
- Step 26) Place the top in the still and bubble nitrogen through the still (10-20 bubbles/second) for at least 10 minutes to remove excess ammonia.
- Step 27) Carefully add 1000 (± 100) μ L of concentrated sulfuric acid to the still. Replace the still top and bubble nitrogen for 5-10 seconds to mix the solution.
- Step 28) Repeat Step 27 until 6 (± 0.6) mL of concentrated sulfuric acid has been added to the still.
- Step 29) Place the still in the heating mantle and place the still outlet beneath the surface of 10 (± 0.1) mL of deionized water in a 35 mL vial in an ice bath.
- Note: Keep the ice bath full of ice. If the water level in the ice bath becomes too high remove some using a vacuum slurp line.
- Step 30) Adjust the nitrogen flow to about five bubbles per second.
- Step 31) Set the variac to 110 and turn on.
- Step 32) Insert a 360°C or a 400°C thermometer into the still thermometer hole and monitor the temperature.
- Step 33) When the temperature reaches 300°C distill for 5 (± 1) additional minutes. Total distillation time is about 45 to 60 minutes.
- Step 34) Turn off the variac and nitrogen. Remove the distillate vial from the still outlet and the ice bath.
- Step 35) Clean the still by pulling the flask contents into a vacuum liquid waste jug through the still inlet. Rinse with deionized water by pulling through the still outlet in the still and through the still inlet into the vacuum radioactive liquid waste jug.
- Step 36) To the vial containing the distillate add a stir bar.

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PNL TEST PROCEDURE

- Step 37) While stirring add 2 (± 0.01) mL of concentrated nitric acid and 4 (± 0.01) mL of 0.1 M mercurous nitrate. Stir for 5 (± 1) minutes.
- Step 38) Dry a 47 mm glass filter at 100°-120°C for at least 20 minutes.
- Step 39) Cool the filter for 5 to 10 minutes and weigh to 0.00001 g or better. Record the weight on the Analytical Report Form.
- Step 40) Assemble the millipore filter holder with the tared glass filter (Step 39).
- Step 41) Using a magnet remove the stir bar from the vial from Step 37.
- Step 42) Swirl the mercurous chloride precipitate and filter with vacuum through the 47 mm glass filter.
- Note: Pour the solution and precipitate rapidly into the filter holder top to provide good mixing and a relatively smooth and equal distribution of the mercurous chloride on the filter.
- Step 43) Rinse the vial twice with 10 (± 1) mL of deionized water and add to the filter.
- Step 44) Rinse the vial with 10 (± 1) mL of methanol and add to the filter. Wash down the inside of the filter holder top with methanol.
- Step 45) Disassemble the filter holder and place the filter in a 2-inch planchet which is fixed with tape to a cardboard beta dish holder. Label the holder with the sample ID and chlorine-36.
- Step 46) Dry the planchet plus filter at 110° to 120° for 20 (± 2) minutes.
- Step 47) Cool for 10 (± 1) minutes and weigh the filter plus precipitate to 0.00001 g or better. Record the weight on the Analytical Report Form and the identification of the balance used. Use the same balance used for Step 39.
- Step 48) Place the filter back in the planchet and count the chlorine-36 activity using the LB-1000 Low Background Alpha and Beta Counter. Record counts, time counted and other pertinent data on the Analytical Report Form.

4.3 Calibrations

4.3.1 Calibration of LB-1000 Counter for Chlorine-36

The LB-1000 is calibrated using NBS SRM-4943 chlorine-36.

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PNL TEST PROCEDURE

An equal volume of chlorine-36 was added to vials containing 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mg of chloride carrier. After thorough mixing the chloride was precipitated with mercurous nitrate and filtered on tared 47 mm glass filters. Each filter was dried, weighed and counted on the LB-1000.

Disintegrations/counts (d/c) were calculated for each weight of mercurous chloride using the known disintegrations/minute (d/m) of chlorine-36 added corrected for recovery and the counts/minute (c/m) obtained on the LB-1000.

From a graphic plot of the d/c versus weight of mercurous chloride a table of sample weight and d/c values was generated. See Table 1, Section 4.4.3, Standard-Disintegrations/Count (d/c).

All data for calibrations may be found in Laboratory Record Book (LRB) BNW 52346, pages 13 through 22.

4.3.2 Daily Performance Check of LB-1000

Daily control checks are made using an alpha source prepared from a plutonium-239 NBS certified solution T-1350.

The beta control source is prepared from a SrY-90 solution T-1204, ICN Lot #705.

NBS traceability is not essential for these sources since they are used only as daily control sources and are not primary standards. Primary calibration of chlorine-36 is described in Section 4.3.1.

4.4 Calculations

4.4.1 Counts/Minute from Sample

$$A \pm \alpha = \left(\frac{B}{D} - \frac{C}{E} \right) \pm \sqrt{\frac{B}{D^2} + \frac{C}{E^2}}$$

Where $A \pm \alpha = c/m \pm 1$ sigma in the sample

B = total counts obtained from sample count

C = total counts obtained from background count

D = time in minutes taken for sample count

E = time in minutes taken for the background count.

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PNL TEST PROCEDURE

4.4.2 Yield Calculation

$$Y = \frac{A-B}{C}$$

where Y = yield (or recovery) expressed as a decimal fraction

A = weight (mg) of filter plus mercurous chloride from Section 4.2, Step 47

B = weight (mg) of filter only from Section 4.2, Step 39

C = 66.586 mg which is the weight of mercurous chloride calculated from 10.0 mg of chloride carrier.

4.4.3 Standard - Disintegration/Count (d/c)

$$W = A-B$$

where: W = weight (mg) of mercurous chloride on filter

A = weight (mg) of filter plus mercurous chloride from Section 4.2, Step 47

B = weight (mg) of filter only from Section 4.2, Step 39.

From Table 1, determine the d/c factor closest to the weight (w) for use in the following sample d/m/mL calculation.

TABLE 1. Disintegration/Count Versus Weight of Mercurous Chloride

<u>wt. mg</u>	<u>d/c</u>	<u>wt. mg</u>	<u>d/c</u>	<u>wt. mg</u>	<u>d/c</u>
20	2.231	38	2.295	56	2.366
22	2.239	40	2.304	58	2.375
24	2.245	42	2.311	60	2.383
26	2.251	44	2.320	62	2.390
28	2.260	46	2.327	64	2.399
30	2.265	48	2.335	66	2.406
32	2.274	50	2.343	68	2.415
34	2.280	52	2.351	70	2.424
36	2.289	54	2.359		

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4.4.4 Sample - Disintegration/Minute/Milliliter (d/m/mL)

$$B \pm \beta = \frac{(A \pm \alpha) \times C}{D \times E}$$

where: $B \pm \beta$ = the sample chlorine-36 d/m/mL ± 1 sigma

$A \pm \alpha$ = the sample c/m ± 1 sigma calculated in Section 4.4.1

C = the d/c factor obtained in Section 4.4.3

D = the volume of sample (in mL) added in Section 4.2, Step 1

E = the yield (recovery) factor calculated in Section 4.4.2.

4.5 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. LRBs and Analytical Report Forms provide a mechanism for control of most records.

4.6 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has received an independent technical review.

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PNL TEST PROCEDURE

TITLE: GRLT-2: CARBON-14 BY DISTILLATION SEPARATION PRIOR TO MEASUREMENT
BY LIQUID SCINTILLATION COUNTING

1.0 APPLICABILITY

This procedure applies to the preparation of graphite-leach or similar solutions for the determination of ^{14}C as measured using liquid scintillation counting (Procedure HTA-4-4).

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- Cognizant Scientist
- Analyst

4.0 PROCEDURES4.1 Equipment and Materials

- Liquid scintillation cocktail, Altex Ready-Solv[®] CP or other tested and adequate cocktail.¹
- Sodium hydroxide, 0.3 M--Dilute 16 (± 0.1) mL of Fisher certified 50 w/w sodium hydroxide solution or equivalent to 1000 (± 1) mL with deionized water; mix thoroughly.
- Sodium carbonate, 2 M--Prepare by dissolving 21.2 (± 0.1) g of reagent grade sodium carbonate (anhydrous) in 100 (± 1) mL of deionized water; mix thoroughly.

1. [®]Altex Ready-Solv is a registered trademark of Beckman Instruments, Fullerton, California.

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PNL TEST PROCEDURE

- Sulfuric acid, concentrated reagent grade or better.
- Sulfuric acid, 1 M--Prepare by diluting 55 (± 5) mL of concentrated reagent grade sulfuric acid to 1000 (± 1) mL with deionized water; mix thoroughly.
- Sodium carbonate, 0.1 M--Prepare by dissolving 1.06 (± 0.01) g of anhydrous reagent grade sodium carbonate in 100 (± 1) mL of deionized water; mix thoroughly.
- Potassium peroxydisulfate, saturated--Prepare by adding reagent grade or better potassium peroxydisulfate to about 100 mL of deionized water in a screw cap bottle. While stirring continue adding the reagent until no more will dissolve. Allow an excess of the reagent to remain in the bottle.
- Silver nitrate, 2 M--Prepare by dissolving 34 (± 0.1) g of reagent grade silver nitrate in 100 (± 1) mL of deionized water; mix thoroughly.
- Zinc metal, 20 mesh, reagent grade.
- Cotton balls.
- Anhydrone[®], anhydrous magnesium perchlorate, reagent grade.²
- Ascarite II[®], 8 to 20 mesh.³
- Carbon distillation apparatus as shown in Figure GRLT-2.1.
- Vials, liquid scintillation, glass, Packard 6001018.
- Vials, 35 mL, glass, screw cap.
- Heating mantle, 100 mL, round bottom.
- Variac, 7.5 amperes, 0 to 140 volts output.

2. [®]Anhydrone is a registered trademark of J. T. Baker Chemical Co., Phillipsburg, New Jersey.

3. [®]Ascarite II is a registered trademark of Arthur H. Thomas Co., Philadelphia, Pennsylvania.

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PNL TEST PROCEDURE

- Thermometer, to 110°C.
- Grease, APIEZON (N) or equivalent.
- Clamps, to fit ball and socket joints in distillation system.

4.2 Carbon Separation

Carbon-14 is separated from other radioactive species by distillation of carbon dioxide from an acidic oxidizing solution. The carrier gas (air) is passed through Ascarite to remove carbon dioxide before entering the distillation system. The distilled carbon-14 dioxide is trapped in a liquid scintillation cocktail made basic with sodium hydroxide.

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To the carbon dioxide trap add 18 (± 0.1) mL of liquid scintillation cocktail plus 2 (± 0.02) mL of 0.3 M sodium hydroxide; swirl until thoroughly mixed.
- Step 2) To the water trap add Anhydron to a depth of about 4 inches. Use cotton plugs to hold the Anhydron in place.
- Step 3) To the scrubber add 70 (± 5) mL of 1 M sulfuric acid.
- Step 4) To the halogen trap add about 5 inches of cotton, about 1 inch of zinc metal (20 mesh), and an additional 1 to 2 inches of cotton.

FIGURE GRLT-2.1

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Step 5) To the CO₂ trap in the carrier gas line add about 6 inches of Ascerite. Hold the Ascerite in place with cotton.

Step 6) Place the heating mantle in position to heat the still.

Step 7) Connect the entire system and regulate the air flow to 40 (± 2) cc/minute as indicated by the flow meter.

Note: Be sure all system joints and connections are well sealed using APIEZON (N) grease. Secure ball and socket joints with suitable clamps.

Step 8) Remove the still inlet and add in the following order.

- 500 (± 5) μ L of 0.1 M sodium carbonate.
- Sample volume ($\pm 1\%$) as specified by the COGNIZANT SCIENTIST.
- Potassium peroxydisulfate solution volume ($\pm 1\%$) as specified by the COGNIZANT SCIENTIST.
- 500 (± 5) μ L of 2 M silver nitrate.

Step 9) Connect the still inlet and allow air flow to mix the solution in the still for 5 (± 1) minutes.

Step 10) Disconnect the still inlet and add 10 (± 0.5) mL of concentrated sulfuric acid to the still.

Step 11) Reconnect the still inlet.

Step 12) Turn on the condenser cooling water; monitor the flow through the flow indicator.

Step 13) Set the variac to 80 and turn on. The temperature in the still should rise to about 102^o-104^oC.

Step 14) Distill for a total of 3 (± 0.1) hours.

Step 15) Turn off the variac.

Step 16) Disconnect the Altex CP CO₂ trap from the Anhydrone trap.

Step 17) Disconnect the Altex CP CO₂ trap from the vacuum line.

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PNL TEST PROCEDURE

- Step 18) Elevate the bubbler in the Altex CP CO₂ trap and allow to drain.
- Step 19) Disconnect the still inlet and the still outlet.
- Step 20) Using a vacuum slurp line to a radioactive liquid waste jug remove the solution in the still through the still inlet.
- Step 21) When all of the solution has been removed, wash the still by introducing deionized water into the still outlet while vacuum is applied to the still inlet, then rinse with methanol and allow to dry with the vacuum still applied.
- Step 22) Wash the trap bubbler by running methanol down the inside of the tube and allowing to flow through the bubbler into the radioactive liquid waste. Repeat with water and methanol again. Use a vacuum line to remove the residual methanol from the bubbler.
- Step 23) Transfer the caustic scintillation cocktail from the CO₂ trap to a 35 mL screw cap vial.
- Step 24) Pipet 15 (± 0.2) mL of the scintillation cocktail into a Packard liquid scintillation vial. Label the vial cap with C-14, sample I.D. and date. Do not write on the glass portion of the vial.
- Step 25) Clean the CO₂ trap using a vacuum radioactive liquid waste jug. Rinse the trap three times with warm tap water and vacuum into the radioactive liquid waste jug. Rinse the trap with tap distilled water and discard down the sink. Dry the trap with methanol.
- Step 26) Measure the ¹⁴C activity in each vial using Procedure HTA-4-4: Liquid Scintillation. Record counting data in the Laboratory Record Book (LRB).
- Step 27) Record volumes, calculations and results on the ¹⁴C analytical report form.

4.3 Blank (Background) Solution Preparation

A blank must be prepared before and after the preparation of each group of samples (four samples/group is recommended).

The ANALYST shall perform the following steps unless otherwise specified.

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PNL TEST PROCEDURE

- Step 1) Prepare ^{14}C blank (background) solution using 50 (0.5) mL or other volume (1%) as specified by the COGNIZANT SCIENTIST. Use deionized water or ground water (depending on sample type) through Section 4.2 Carbon Separation, Steps 1 through 26.
- Step 2) Label the vial caps as "C-14 Blank" and "date". Count the "C-14 Blank" with the samples and standards.

4.4 Calibration Standards Preparation

The ANALYST shall perform the following steps unless otherwise specified.

- Step 1) To a 35 mL screw cap vial add 18 (± 0.1) mL Altex Ready-Solv^R CP liquid scintillation cocktail plus 2 (± 0.02) mL of 0.3 M sodium hydroxide plus 25 (± 1) μL of 2 M sodium carbonate.
- Step 2) To the vial from Step 1) add a measured ($\pm 1\%$) volume ($\leq 100 \mu\text{L}$) of ^{14}C standard solution containing a known amount of ^{14}C ($\sim 3 \times 10^4$ d/m). Standards should be NBS or NBS traceable if possible. Carbon-14 supplier records, all volumes and calculations shall be recorded in the LRB.
- Step 3) Cap the vial from Step 2) and shake vigorously until a clear solution is obtained upon standing.
- Step 4) Pipet 15 (± 0.2) mL of the solution from Step 3) into a Packard liquid scintillation vial.
- Step 5) Cap the vial and label the vial on the cap as "C-14 Std" and "date".
- Step 6) Count the standard with samples and blank solutions as described in Procedure HTA-4-4.

4.5 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory Record Books, controlled according to PAP-1704, and analytical report cards provide a mechanism for control of most records.

4.6 Procedure Qualification

This procedure is qualified by demonstration using an NBS ^{14}C standard to measure recoveries when carried through the separation and counted

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as described in the procedure. Blanks (backgrounds) were also determined when the separation was made with no ^{14}C standard added. Groundwater samples (#6-53-25, 7-8-87) should be corrected for 84% recovery. Deionized water samples should be corrected for 96% recovery.

Data for the qualification are found in LRB 52346, pages 23 to 69.

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TITLE: GRLT-3, LOW BACKGROUND ALPHA AND BETA COUNTING USING THE LB-1000

1.0 APPLICABILITY

This procedure provides instructions for simultaneously measuring the activity of alpha-emitting and beta emitting radionuclides in a low background environment.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

- . Cognizant Scientist
- . Analyst

4.0 PROCEDURES4.1 Equipment and Materials

- . Tennelec Model LB-1000 Low Background Alpha/Beta Counter
- . P-10 gas (90% argon, 10% methane), commercial grade, Union Carbide Corp.
- . Dish, 2-in diameter x 1/8-in deep, flat bottomed, cupped aluminum.

4.2 Calibration Standards

The LB-1000 is initially calibrated by the COGNIZANT SCIENTIST using a series of replicate essentially zero-mass sources prepared by evaporating accurately measured aliquots of NBS ^{239}Pu and ^{90}SrY Standard Reference Materials spread across a 47 mm diameter bottom area of 2-in diameter aluminum dishes. At zero-mass counting efficiency is essentially constant for all alpha energies, but decreases as a function of decreasing beta energy. All beta and non zero-mass alpha counting operations require special calibrations be performed using

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sources simulating the nuclide and chemical composition of the test sample sources. Calibration sources are used only to recalibrate the LB-1000 after instrument repair; to avoid loss of integrity through daily handling, calibration sources are not used to routinely verify counter control.

4.3 Daily Control Standards

Control Standards are sources of high-purity ^{239}Pu and ^{90}SrY used by the ANALYST on a daily basis to insure the LB-1000 is operating within control limits. Each control source is counted ten times when the LB-1000 is initially calibrated for general alpha/beta counting and limits that must be met on a daily basis are defined by statistical analysis of the counting data obtained. Control sources prepared by evaporating radionuclide solution aliquots in 2-in aluminum dishes are rugged enough to retain their integrity with daily handling unless the active deposit is abraded through negligence.

The following daily control standard count procedure shall be used:

Step 1) Carefully pull out the sample transport slide until the stop is encountered. A slight initial resistance due to the position locking mechanism will be felt.

Step 2) Remove the round plastic sample holder from the sample well of the slide. Remove any sample dish currently in the holder, raising it by inserting a finger through the hole in the bottom of the sample holder and grasping the outside of the dish walls.

Insert the ^{239}Pu control source dish into the sample holder and return the holder to the slide sample well. Orientation is not important; the sample holder is automatically repositioned correctly with respect to the counter detector when moved into counting position. Push the slide in until the resistance of the position locking mechanism is felt, then gently push the slide all the way in.

Step 3) Counter operation is controlled from the TIMER module. Adjust the time preset to 10 minutes.

Step 4) Clear existing data from the alpha and beta module registers by pressing RESET on the TIMER module. If the count toggle is in the STOP position, initiate counting by switching the toggle to COUNT. If the toggle is already in COUNT position counting automatically begins when RESET is pressed. Record the time counting was begun in the control log alpha control section in the TIME column of a line labeled with the current date.

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- Step 5) When the preset time interval has elapsed counting will automatically stop. Record the accumulated counts in the alpha and beta channels in the alpha control section of the control log in corresponding columns on the line labeled with the current date.
- Step 6) Calculate the alpha channel count rate, expressed in counts per minute background corrected, and enter the result in the corresponding column. Plot the value on the alpha channel control chart at the current date. If the count does not fall within the limits defined on the control chart, perform a recount. If the initial count or recount is within limits the alpha channel is considered to be operating in control. If both counts are outside limits sample counting must not be performed until control is returned by repair of the instrument.
- Step 7) Repeat steps 3, 4, 5, and 6, using the SrY beta control source, recording and plotting the results of the measurement in the beta control section of the control log.

4.4 Daily Background Count

The ANALYST shall complete the following steps:

- Step 1) When not in use, the LB-1000 is left in indeterminate count mode with a clean 2-in dish in counting position. These background counts will vary in length from approximately 900 minutes during the work week to 3900 minutes over a weekend. When the timer indicates an integral number of minutes have elapsed, switch the count toggle of the timer module to the STOP position.
- Step 2) Label lines in both the alpha and beta sections of the control log with the current date and record the elapsed time of the background count and the observed counts accumulated in the alpha and beta channels in the background columns of their respective sections.
- Step 3) Calculate the alpha and beta backgrounds by dividing the respective accumulated counts by the counting interval and record the results in the corresponding background columns.

4.5 Sample Counting

The ANALYST shall complete the following steps:

- Step 1) Survey the source prepared for sample counting using both alpha and beta survey instruments to insure that alpha and beta activity are both less than 1000 counts per minute.

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Sources exceeding this limit will produce LB-1000 count rates that include significant live time error and may also contaminate the low background counting environment.

- Step 2) Carefully pull out the sample transport slide until the stop is encountered. A slight initial resistance due to the position locking mechanism will be felt.
- Step 3) Remove the round plastic sample holder from the sample well of the slide. Remove any sample dish currently in the holder, raising it by inserting a finger through the hole in the bottom of the sample holder and grasping the outside walls of the dish.
- Insert the sample dish into the sample holder and return the holder to the slide sample well. Orientation is not important; the sample holder is automatically positioned correctly with respect to the counter detector when pushed into counting position.
- Step 4) Counter operation is controlled from the TIMER module. Adjust the time preset to the desired counting interval.
- Step 5) Clear existing data from the alpha and beta module registers by pressing RESET on the TIMER module. If the count toggle is in the STOP position, initiate counting by switching the toggle to COUNT. If the toggle is already in COUNT position counting automatically begins when RESET is pressed.
- Step 6) Record "LB-1000", the date and time the count was begun, the length of the count in minutes, and (as appropriate to the specific sample) the alpha and beta channel accumulated counts and measured background in corresponding parts of the Sample Report Card.

4.6 Sample Calculations

The COGNIZANT SCIENTIST or ANALYST shall complete the sample calculations using the following equations:

The uncertainty 1 sigma of either an alpha or beta count is calculated from the corresponding channel sample and background counts:

$$u = \sqrt{\left(\frac{\sqrt{c}}{t_c}\right)^2 + \left(\frac{\sqrt{b}}{t_b}\right)^2}$$

where u = uncertainty in the observed sample count per minute, background corrected

c = total sample count (Section 4.5)

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t_c = sample count duration (minutes)

b = total background count (Section 4.4)

t_b = background count duration (minutes)

Sample alpha and beta activity are calculated from the corresponding channel sample counts and uncertainties:

$$A \pm a = (B \pm u) \times C \times D$$

where A = activity in disintegrations per minute per milliliter

a = uncertainty in the calculated activity

B = calculated count rate, background corrected, expressed in counts per minute

u = uncertainty in the calculated count rate

C = dilution factor or volume factor to correct the sample aliquot counted to 1 milliliter

D = disintegration to count ratio for the specific nuclide and sample composition

4.7 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

4.8 Procedure Qualification

None required. This procedure is considered self-qualifying due to its dependence on analytical standards. Additionally it is considered qualified because it has received an independent technical review.

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PNL TEST PROCEDURE

TITLE: HTA-4-4, SOLUTIONS ANALYSIS: LIQUID SCINTILLATION

1.0 APPLICABILITY

This procedure provides instructions for the measurement of alpha or beta activity in solution by the liquid scintillation method. This procedure applies to the analysis of samples by the liquid scintillation method prepared using Procedures HTA-4-18 and HTA-4-17.

The form of this procedure may not comply with all the requirements of PAP-501 due to the conversion from Westinghouse Hanford Co. format to PNL format. Exceptions to PAP-501 will be addressed during the next revision of this procedure.

2.0 DEFINITIONS

None.

3.0 EQUIPMENT AND MATERIALS

- Liquid scintillation counting system, Nuclear Chicago Mark I.

3.1 Calibration Standards

Calibration standards of the isotope being counted are prepared in a matrix as nearly identical as possible to that of the sample. See Procedure HTA-4-17, Section 4.2. Standards are NBS or NBS-traceable whenever possible. When no standards are available for an isotope such as ⁷⁹Se an alternate standard isotope of similar maximum and average beta energy may be used. See Procedure HTA-4-18, Section 4.0, Step 23.

3.2 Background Solutions

Background solutions are prepared in a matrix as nearly identical to that of the sample as possible. Such solutions will then give a measure of all sources of background counts when counted before and after the samples and standards. See Procedure HTA-4-17, Section 4.3 and Procedure HTA-4-18, Section 4.2.

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Prepared by <div style="text-align: center; font-size: 1.5em;">ACleaf</div>	Date <div style="text-align: center; font-size: 1.5em;">7/1/87</div>	QAD Concurrence <div style="text-align: center; font-size: 1.5em;">B.O. BARNES</div>	Date <div style="text-align: center; font-size: 1.5em;">6/30/87</div>
Procedure No. <div style="text-align: center;">HTA-4-4</div>	Revision No. <div style="text-align: center;">4</div>	Effective Date <div style="text-align: center;">JUL 01 1987</div>	Page of <div style="text-align: center;">1 3</div>

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Prior to operation, the operator must be adequately trained in Section III, Controls and Readout of the Mark I Liquid Scintillation Counter Manual.

Step 1) Place the standards, background solutions and samples in the automatic sample changer system. The testing order is standard, background solution, samples, standard and background solution. (Note on the data printout the position number for each vial.)

Step 2) Set the counting time to 40 minutes. (All solutions will be counted 40 minutes.)

Step 3) Set the channel width and attenuator to give the maximum efficiency for the isotope being counted. The isotopes counted are ^{129}I , ^{79}Se , and ^{14}C . These isotopes all have essentially the same beta energy, and all are counted with the following settings:

Attenuator Course Setting: D
Attenuator Fine Setting: 5.0
Window Lower Level: 0.5
Window Upper Level: 9.9

Step 4) Set the system to PROGRAM and AUTO RECYCLE. (Solutions will count and change automatically until the system is halted.)

Step 5) Calculate the disintegrations per count (dis/ct) in the standard using the following equation. Counting rates are automatically calculated by the counting system. Use the average of all standard and background counting rates. The average of each standard counting rate must be within 5% of the average of all standard counting rates. If not, two new standards must be prepared.

$$\text{dis/ct} = \frac{A}{S - B}$$

where: A = disintegrations per minute of standard in vial (overall uncertainties of standards used are: ^{129}I = 1% and ^{14}C = 2%, as supplied by Amersham)

S = standard counting rate (ct/min)

B = background counting rate (ct/min).

Step 6) Calculate the disintegration rate in the sample using the following equation. Counting rates are automatically calculated by the counting system. Use the average of all counting rates measured for each individual solution and the average of all background counting rates.

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$$\text{dis/min/mL} = (A - B) \times C \times D$$

where: A = counting rate of sample (ct/min)
 B = background counting rate (ct/min)
 C = dis/ct factor from Step 5
 D = volume factor to convert dis/min/mL of sample

$$D = \frac{1}{V E}$$

where: V = volume of sample taken for separation (mL)
 E = fraction of sample taken that is counted

EXAMPLE: If 0.5 mL of sample is separated and diluted to 20 mL of scintillation cocktail and 15 mL is actually counted, then V = 0.5 mL and E = 15/20.

The estimate of precision is based on the equation:

$$\sigma = \pm \frac{\sqrt{A + B}}{40} \times \frac{1}{V E} \times C$$

where: σ = relative standard deviation ($\pm$ dis/min/mL)
 A = average counts in sample (ct/40 min)
 B = average counts in background (ct/40 min)
 V = volume of sample taken for separation (mL)
 E = fraction of sample taken that is counted
 C = dis/ct factor from Step 5.

Step 7) Retain liquid scintillation data and dis/ct calculations in numbered laboratory notebook. Record dis/min/mL results on the analytical report form.

4.1 Records

Records will be maintained and controlled so as to conform with requirements of PAP-1701. Laboratory notebooks and analytical report cards provide a mechanism for control of most records.

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APPENDIX C

SUMMARY OF RAW DATA

TABLE C.1. Leach Data for Graphite Sample Number 7

Leach Test Identification Number: DIW-25Sample Mass (g): 36.6Leachant: Deionized WaterTest Temperature: Ambient (20°C)

Leach Interval	Start		End		Elapsed Time, h	Leachant Vol., mL	¹⁴ C Conc., d/m/mL	³⁶ Cl Conc., d/m/mL
	Date	Time	Date	Time				
1	11/17/87	1425	11/24/87	1105	164.7	404	22 ±2	20 ±1
2	11/24/87	1110	12/1/87	0845	165.6	410	13 ±1	4.1 ±0.1
3	12/1/87	0915	12/8/87	0930	168.3	408	13 ±1	1.2 ±0.1
4	12/8/87	0948	12/15/87	0900	167.2	410		
5	12/15/87	0925	12/22/87	0915	167.8	405	17 ±2	0.29 ±0.02
6	12/22/87	0930	12/29/87	0900	167.5	407		
7	12/29/87	0920	1/5/87	0900	167.7	406		
8	1/5/88	0920	1/12/87	1400	172.7	406	16 ±2	0.12 ±0.01

TABLE C.2. Leach Data for Graphite Sample Number 5

Leach Test Identification Number: DIW-50Sample Mass (g): 36.5Leachant: Deionized WaterTest Temperature: 50°C

Leach Interval	Start		End		Elapsed Time, h	Leachant Vol., mL	¹⁴ C Conc., d/m/mL	³⁶ Cl Conc., d/m/mL	
	Date	Time	Date	Time					
1	11/17/87	1435	11/24/87	1320	166.8	403	72 ±7	23	±1
2	11/24/87	1325	12/1/87	1230	167.1	404	44 ±4	1.5	±0.1
3	12/1/87	1240	12/8/87	1235	167.9	404	31 ±2	0.4	±0.1
4	12/8/87	1348	12/15/87	1210	166.4	405			
5	12/15/87	1230	12/22/87	1130	167.0	405	23 ±3	0.25	±0.01
6	12/22/87	1145	12/29/87	1240	168.9	406			
7	12/29/87	1255	1/5/88	1130	166.6	406			
8	1/5/88	1340	1/12/88	1400	167.7	405	16 ±2	0.17	±0.02

TABLE C.3. Leach Data for Graphite Sample Number 3

Leach Test Identification Number: DIW-90Sample Mass (g): 36.6Leachant: Deionized WaterTest Temperature: 90°C

Leach Interval	Start		End		Elapsed Time, h	Leachant Vol., mL	¹⁴ C Conc., d/m/mL	³⁸ Cl Conc., d/m/mL	
	Date	Time	Date	Time					
1	11/17/87	1455	11/24/87	1335	166.7	404	178 ±16	23	±1
2	11/24/87	1340	12/1/87	1250	167.2	405	107 ±10	1.1	±0.1
3	12/1/87	1310	12/8/87	1254	167.7	405	79 ± 4	0.4	±0.1
4	12/8/87	1315	12/15/87	1230	167.3	404			
5	12/15/87	1255	12/22/87	1150	167.1	405	70 ± 7	0.21	±0.01
6	12/22/87	1205	12/29/87	1300	168.9	405			
7	12/29/87	1315	1/5/88	1130	166.3	407			
8	1/5/88	1400	1/12/88	1400	168.0	406	67 ± 7	0.04	±0.01

TABLE C.4. Leach Data for Graphite Sample Number 2

Leach Test Identification Number: HGW-25Sample Mass (g): 36.0Leachant: Hanford Ground WaterTest Temperature: Ambient (20°C)

Leach Interval	Start		End		Elapsed Time, h	Leachant Vol., mL	¹⁴ C Conc., d/m/mL	³⁶ Cl Conc., d/m/mL
	Date	Time	Date	Time				
1	11/17/87	1510	11/24/87	1125	164.3	405	22 ±2	17 ±1
2	11/24/87	1130	12/1/87	0920	165.8	403	4.2 ±0.4	2.9 ±0.1
3	12/1/87	0935	12/8/87	1005	168.5	403	8.3 ±0.4	0.6 ±0.1
4	12/8/87	1020	12/15/87	0925	167.1	403		
5	12/15/87	0945	12/22/87	0935	167.8	404	2.7 ±0.3	0.15 ±0.01
6	12/22/87	0950	12/29/87	0925	167.6	406		
7	12/29/87	0935	1/5/88	0925	167.8	406		
8	1/5/88	0940	1/12/88	1400	174.3	405	2.2 ±0.3	0.09 ±0.01

TABLE C.5. Leach Data for Graphite Sample Number 1

Leach Test Identification Number: HGW-90Sample Mass (g): 36.7Leachant: Hanford Ground WaterTest Temperature: 90°C

Leach Interval	Start		End		Elapsed Time, h	Leachant Vol., mL	¹⁴ C Conc., d/m/mL	³⁶ Cl Conc., d/m/mL
	Date	Time	Date	Time				
1	11/17/87	1530	11/24/87	1350	166.3	404	103 ±9.	21 ±1
2	11/24/87	1400	12/1/87	1315	167.3	404	79 ±8	0.91 ±0.03
3	12/1/87	1330	12/8/87	1317	167.8	406	42 ±2	0.2 ±0.1
4	12/8/87	1330	12/15/87	1300	167.5	406		
5	12/15/87	1315	12/22/87	1205	166.8	405	22 ±2	0.05 ±0.01
6	12/22/87	1315	12/29/87	1318	168.0	406		
7	12/29/87	1335	1/5/88	1130	165.9	406		
8	1/5/88	1415	1/12/88	1400	167.8	403	33 ±4	0.06 ±0.01

APPENDIX D

DISTRIBUTION OF CARBON-14 ATOMS

DISTRIBUTION OF CARBON-14 ATOMS

Atomic displacement processes in graphite have been discussed in detail^(a) by deHalas (1962). In graphite moderated reactors, the response function for displaced carbon atoms peaks at a neutron energy of about 1.5 MeV; the resultant displaced ^{14}C atoms would have an average energy of about 200 keV, and would travel several thousand angstroms, $\text{\AA}$, in the graphite lattice before coming to rest. In the process, it would displace many other carbon atoms, which would travel for various shorter distances.

A 1-cm cube of the graphite used for our samples would contain 1.64 g of graphite with a specific (BET) surface area of about $8.5 \times 10^4 \text{ cm}^2$; thus, if the cube was cut from a single graphite crystal, we could envision it as being composed of about 4.25×10^4 thin sheets of graphite (2 sides per sheet), each about $2.35 \times 10^{-5} \text{ cm}$ ($2350 \text{ \AA}$) thick. If, on the other hand, we assume that the cracks are equally oriented in the 3 orthogonal directions, then we could envision the sample as being composed of a stack of cubes, each about $7 \times 10^{-5} \text{ cm}$ ($7000 \text{ \AA}$) on a side. The preferred orientation of the crack system in extruded graphite mirrors the preferred orientation of the coke particles in the bar (parallel to the axis of extrusion); thus, we can expect that the average spacing between cracks should be about $5000 \text{ \AA}$, i.e., about the same distance as the average range of a primary displaced atom in the graphite.

Miller and Steffes (1987) estimated that the graphite bars near the center of C Reactor (where this bar was located) had sustained a thermal neutron fluence of about $2.21 \times 10^{22} \text{ cm}^{-2}$; using a thermal-to-fast ($E > 1.0 \text{ MeV}$) neutron flux ratio of about 6, and about 880 displaced carbon atoms per

(a) The response function is defined as:

$$\int_0^\infty \sigma_d(E) \cdot \Phi(E) \cdot dE \bigg/ \int_E^\infty \Phi(E) \cdot dE$$

where: $\sigma_d(E)$ is the atomic displacement cross section as a function of energy(E), and $\Phi(E)$ is the neutron flux intensity at the energy.

fast neutron per cm^2 (deHalas 1962), we calculate that each carbon atom in this bar has been displaced about 40 times during its residence in C Reactor.

Considering that the average range of a primary displaced atom is about equal to the average spacing between surfaces, and the large number of times each carbon atom was displaced, we can conclude that ^{14}C atoms that were produced early in the life of C Reactor are probably uniformly distributed in the graphite lattice. Those ^{14}C atoms that were produced near the end of operation have a higher probability of remaining on, or near, the surface. Moreover, atoms at the surface have an enhanced probability of being in a chemically active state (due to unsaturated bonds or chemical complexing).

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