TRITIUM ANALYSES OF COBRA-1A2 BERYLLIUM PEBBLES - D. L. Baldwin (Pacific Northwest National Laboratory)*

OBJECTIVE

The purpose of this work was to provide quantitative tritium analyses for prototypic irradiated beryllium pebbles. Such pebbles are under consideration as the neutron multiplier medium in the European Fusion Technology Program Helium Cooled Pebble Bed (HCPB) Blanket.

SUMMARY

Selected tritium measurements have been completed for the COBRA-1A2 experiment C03 and D03 beryllium pebbles. The completed results, shown in Tables 1, 2, and 3, include the tritium assay results for the 1-mm and 3-mm C03 pebbles, and the 1-mm D03 pebbles, stepped anneal test results for both types of 1-mm pebbles, and the residual analyses for the stepped-anneal specimens. All results have been reported with date-of-count and are not corrected for decay. Stepped-anneal tritium release response is provided in addenda.

PROGRESS AND STATUS

Introduction

Beryllium pebbles are being considered for the neutron multiplier medium in the European Fusion Technology Program Helium Cooled Pebble Bed (HCPB) Blanket. That design is also being considered for testing in ITER. The pebbles to be used are an inexpensive form of beryllium produced in an intermediate step of the production of higher purity beryllium. The opportunity to determine tritium inventories for prototypic fast neutron irradiated pebbles became possible after pebbles were irradiated in the US/DOE COBRA 1A2 experiment in EBR-II. Experimental details are provided in a companion paper. [1] The tritium release measurements were funded by Forschungszentrum Karlsruhe.

Experimental Procedure

The tritium assay and residuals results are been determined by the method of high-temperature sweep gas extraction. The basic method has been described previously [2], but has been modified using sweep gas instead of vacuum. The sweep gas method is used instead of the vacuum method due to much lower method detection limits due to vacuum manifold contamination. The method has an estimated precision and accuracy of 5%. Briefly, the weighed sample is melted, at 1700°C, in a sweep gas of He+0.1% H_2 at 100 SCCM, with the released hydrogen isotopes oxidized on copper oxide, collected in a pair of water bubblers, and measured by liquid scintillation counting, traceable to NIST. Since the extraction takes place in helium, no residual helium measurement in the stepped-anneal Be specimens is possible. See Figure 1 for the schematic.

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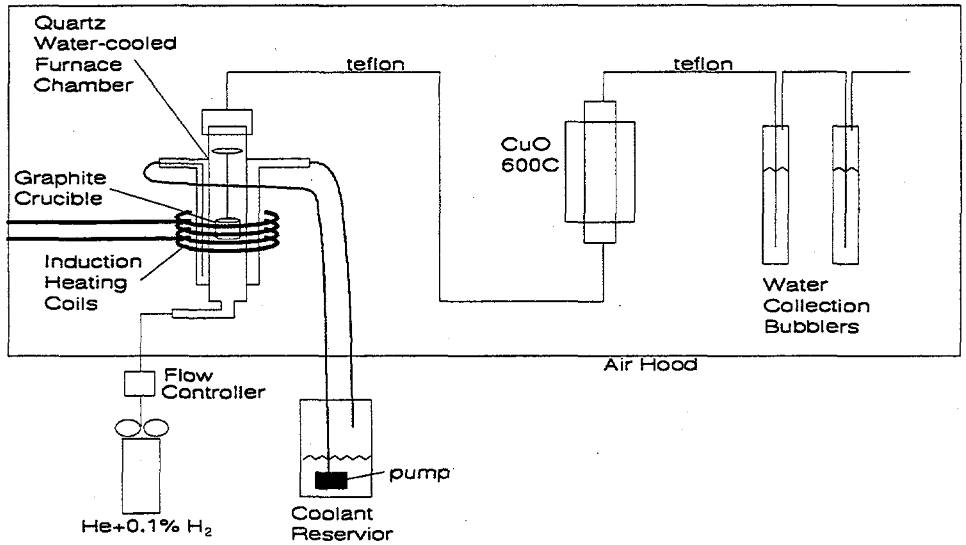
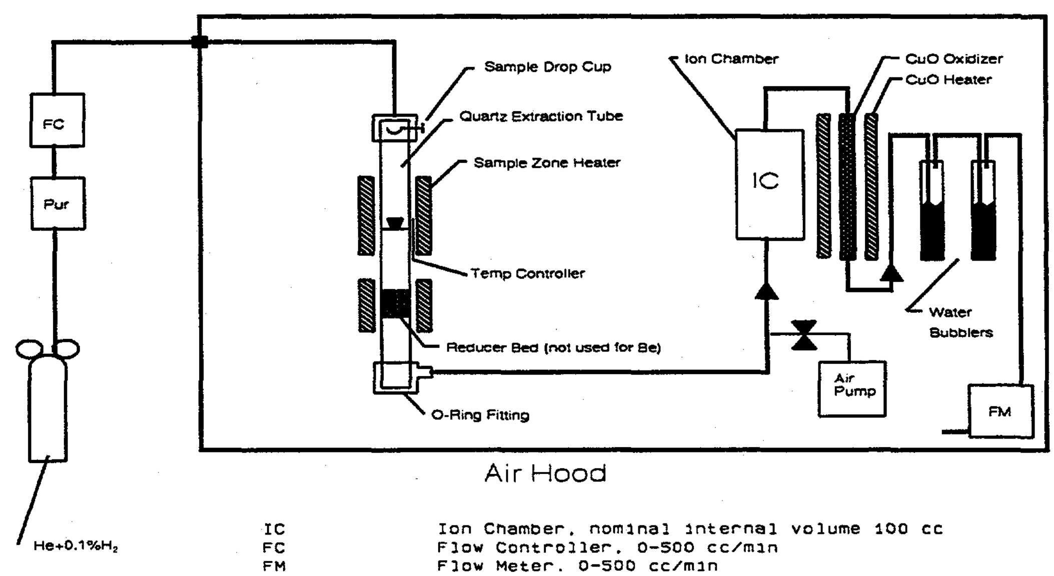


Figure 1. Schematic of method for tritium assay

The stepped-anneal tritium release test method has been described previously [3,4]. The test temperature range is 350-850°C. Briefly, the sample is heated in sweep gas of He+0.1%H_2 at 100 SCCM, the released tritium measured in real-time by ion chamber, oxidized on copper oxide and collected in a pair of water bubblers, and measured by liquid scintillation counting. See Figure 2 for the schematic.



IC	Ion Chamber, nominal internal volume 100 cc
FC	Flow Controller, 0-500 cc/min
FM	Flow Meter, 0-500 cc/min
Pur	Gas Purifier for oxygen and moisture, <50 ppb O_2 + H_2O
Zn	Reducer Bed of Zn
Furnace Tube	Tube with or without reducing bed can be used
Air Pump	Small ambient air pump

Figure 2. Schematic of method for stepped-anneal tritium release

<u>Discussion of Results</u>

The assay results, shown in Table 1, appear to be very self-consistent. Note the 1-mm pebble measured/produced ratios are low, at a consistent 0.73 and 0.71. The 3-mm meas/prod ratio is much higher at 0.93. This apparently indicates the diffusive loss of tritium in-reactor is dependent on pebble diameter. The precision for the C03 pebble duplicate results is 9.8% RPD (Relative Percent Difference) which is surprisingly large, probably due to the use of too-small sample size, 3 pebbles compared to 10 pebbles. The duplicates precision for the 1-mm D03 is much better at 2.6% RPD, and for the 3-mm C03, the precision is 1% RPD. The low RPD for the latter two indicates adequate sample size.

Table 1. Tritium assay results

sample	#of Pebbles	sample weight (g)	Measured (Bq/g)	Meas. (appm)	date of count	Produced (appm)	Avg Meas/ Prod
1-mm C03	3	0.0035	1.187E+09	9.96	21-May-97	13.1	0.73
	10	0.0121	1.076E+09	9.03	21-May-97		
3-mm C03	2	0.0700	1.474E+09	12.38	30-May-97	13.2	0.93
	2	0.0699	1.461E+09	12.26	30-May-97		
1-mm D03	5	0.0043	1.107E+09	9.29	29-May-97	12.9	0.71
	5	0.0055	1.078E+09	9.05	29-May-97		

The stepped anneal tests results are shown in Tables 2 and 3. In the original interest of saving time and funds, some time intervals for selected temperature steps were cut short. In retrospect, this is a limitation in the data set, and longer time intervals for all steps would be useful. For the C03 test, which used 5 pebbles, the 850 step was originally at 7.5 hours. When the cumulative tritium was calculated and determined to be quite low, it was decided to test additional time at 850°C. Therefore, the sample was reheated (it had not been removed from the test apparatus) to 850°C for an additional duration of 25 hours, followed by additional cooldown and purge. This additional step released more tritium, though it was still releasing at 850°C after the total of 33 hours. The total cumulative released at 350-850°C was 75% of the total inventory. The residual remaining tritium, measured by melting the sample at 1700°C, was about 25% of the total inventory, with the totaled cumulative quantities agreeing relatively well with assay result.

For the D03 stepped-anneal test, and learning from the experience of the C03 test, 10 pebbles were used, and generally longer step durations, with the final 850°C step held for 72 hours. This test resulted in much higher cumulative quantities released. From 350-750°C 20% was released and by the end of the 850°C step 94% was released. The residual remaining tritium, of about 6% of the total inventory, brought the total cumulative into excellent agreement with the assay results.

Table 2. 1-mm C03 stepped-anneal tritium release results

Sample	Temp, C	Time (hr)	Bubbler Result (Bq/g)	date of count	Cumulative (Bq/g)	Cumulative (appm)	% of Total
1-mm C03 5 pebbles wt = 0.0066 g He+0.1% H_2 100 SCCM	ambient purge	17.97	2.69E+06	5-May-97	2.69E+06	0.023	0.2
	350	5.88	2.29E+06	5-May-97	4.98E+06	0.042	0.4
	450	18.06	3.85E+06	5-May-97	8.83E+06	0.074	0.7
	550	6.00	7.90E+06	5-May-97	1.67E+07	0.14	1.4
	650	18.38	8.93E+07	5-May-97	1.06E+08	0.89	8.6
	750	23.11	2.40E+08	5-May-97	3.46E+08	2.91	28.0
	850	4.09	2.24E+08	5-May-97	5.70E+08	4.79	46.1
		3.42	1.19E+08	5-May-97	6.89E+08	5.78	55.7
	cool-down	65.4	2.58E+07	5-May-97	7.15E+08	6.00	57.8
	additional 850	24.68	2.10E+08	17-May-97	9.25E+08	7.76	74.8
	cool down	25.00	5.78E+06	17-May-97	9.31E+08	7.81	75.3
	Total Released	—	9.31E+08	17-May-97	9.31E+08	7.81	75.3
Residual Analysis	melted	—	3.06E+08	6-Jun-97	1.24E+09	10.38	100.0
Total released plus residual	—	—	1.24E+09	6-Jun-97	1.24E+09	10.38	100.0

Note for both stepped anneal tests, less than 2% of inventory was released at 350-550°C. A very consistent cumulative about 8.7% was released after 650°C. After 750°C, the cumulative released was 20-28% for both tests. The major difference between the two tests is seen at the 850°C step, though time duration at temperature is definitely a factor.

All tritium data is reported with date-of-count and is not decay-corrected.

Table 3. 1-mm D03 stepped-anneal tritium release results

Sample	Temp, C	Time (hr)	Bubbler Result (Bq/g)	day of count	Cum. (Bq/g)	Cum. (appm)	% of Total
1-mm D03 10 pebbles wt = 0.0098 g He+0.1% H_2 100 SCCM	ambient purge	0.33	1.39E+05	12-May-97	1.39E+05	0.0012	0.01
	350	17.42	3.41E+05	12-May-97	4.80E+05	0.0040	0.04
	450	7.87	1.87E+05	12-May-97	6.67E+05	0.0056	0.06
	550	17.03	6.71E+05	12-May-97	1.34E+06	0.011	0.12
	650	23.75	9.71E+07	12-May-97	9.84E+07	0.826	8.81
	750	22.83	1.27E+08	12-May-97	2.26E+08	1.89	20.2
	850	72.49	8.28E+08	12-May-97	1.05E+09	8.84	94.3
	Total Released	---	1.05E+09	12-May-97	1.05E+09	8.84	94.3
Residual Analysis	melted	---	6.35E+07	6-Jun-97	1.12E+09	9.38	100.0
Total released plus residual	---	---	1.12E+09	6-Jun-97	1.12E+09	9.38	100.0

There were some experimental problems with the ion chamber (IC) resulting in a noisy signal. The IC signal data will be acceptable, but is still being worked on and cleaned up, and prepared for plotting. This data, in plot and digital form, will be sent to you when completed.

FUTURE WORK

This work is completed.

ACKNOWLEDGEMENTS

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REFERENCES

1. D. S. Gelles, "US/DOE OFES Neutron Irradiation Experiments containing Beryllium," in this DOE/ER-0313/23 report.

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3. D. L. Baldwin and M. C. Billone, J. Nucl. Mater. 212-215 (1994) 948-953.

4. D. L. Baldwin, O. D. Slagle, and D. S. Gelles, J. Nucl. Mater. 179-181 (1991) 329-334.

Addendum A:

STEPPED-ANNEAL TRITIUM RELEASE IN COBRA-1A2 C03 BERYLLIUM

SUMMARY

This addendum includes the plot, and data in spreadsheet format, of the tritium stepped-anneal test on the C03 1-mm pebble specimens.

Experimental

The stepped-anneal test for tritium release kinetics was performed on the C03 1-mm pebbles using 5 pebbles with total sample weight of 0.0066g. The test temperature range was 350-850C, in 100C steps. Briefly, the sample was heated in sweep gas of He+0.1%H_2 at 100 SCCM, the released tritium measured in real-time by ion chamber, oxidized on copper oxide and collected in a pair of water bubblers, and then measured by liquid scintillation counting.

Discussion of Results

The plot of the stepped-anneal test data is shown in Figure 1. In the original interest of saving time and funds, some time intervals for selected temperature steps were shortened. In retrospect, this is a limitation in the current data set, and longer time intervals for some steps would have been useful. For this C03 test, using 5 pebbles, the 850C step was originally set at 7.5 hours. When the cumulative tritium was calculated and determined to be quite low, it was decided to test additional time at 850C. Therefore, the sample was reheated (it had not been removed from the test apparatus) to 850C for an additional period of 25 hours, followed by additional cooldown and purge. This additional step released more tritium, and it was still releasing at 850C after the total of 33 hours. The total cumulative released at 350-850C was 75% of the total inventory. The residual tritium, measured by melting the sample at 1700C, was about 25% of the total inventory, with the totaled cumulative quantities agreeing relatively well with assay result.

There were some experimental problems with the ion chamber (IC) resulting in a noisy signal and narrow spikes. The major cause of the noise and spikes is simply the very low range of release rate, at less than 150 Bq/s, with portions of the curve at less than 15 Bq/s.

Numerous single point spikes were manually removed from the data set. As has been done previously, the IC cumulative release curve in MBq/g, calculated from the release rate curve in Bq/s, was normalized to the collection bubbler results in MBq/g, by adjusting the IC baseline and/or IC calibration factor. This method assumes the collection bubbler results are always correct and reliable, therefore, the IC curve must be adjusted to obtain agreement.

Figure 3 below shows the release rate, as measured by the IC in Bq/s on the left axis, with cumulative tritium (both integrated IC signal and collection bubbler results) in MBq/g on the right axis, and temperature in degrees C, also on the right axis.

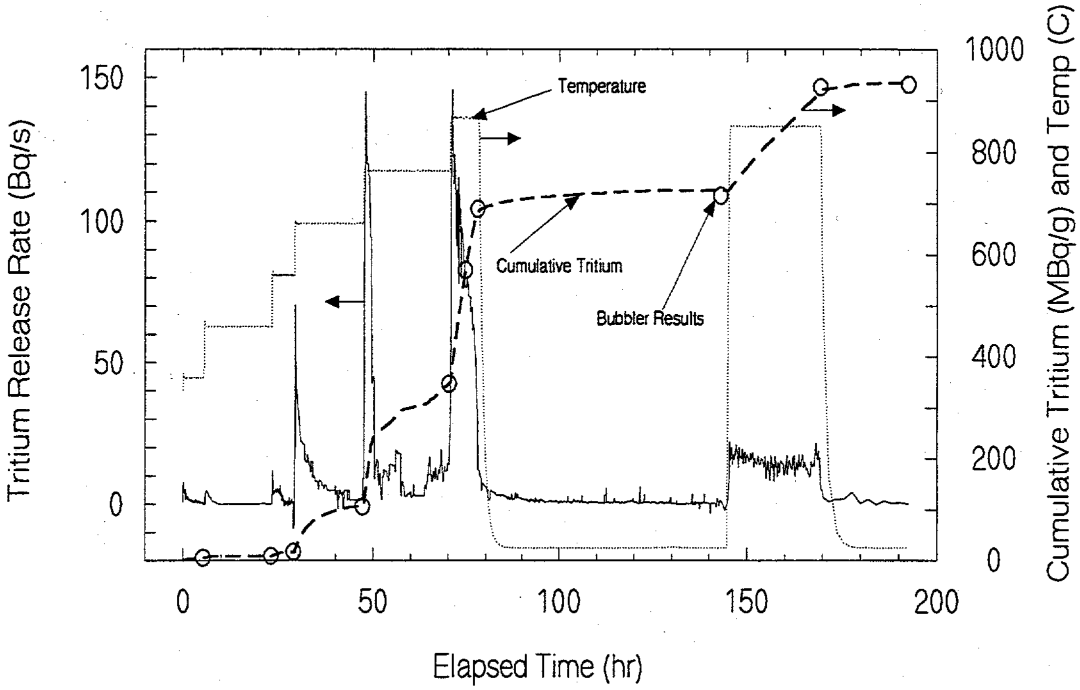

Figure 3. Stepped-anneal tritium release test of C03 (1-mm) beryllium

Addendum B:

STEPPED-ANNEAL TRITIUM RELEASE IN COBRA-1A2 D03 BERYLLIUM

SUMMARY

This addendum B includes a brief discussion of the test, the data shown plotted on both linear and log axes, and the test data in spreadsheet format in an attached file, of the tritium stepped-anneal test on the D03 1-mm pebble beryllium specimens. The tabulated temperatures, time, bubbler results, and assay results, were shown in the first report of June 19, 1997.

Experimental

The stepped-anneal test for tritium release kinetics was performed on the D03 1-mm pebbles using 10 pebbles with total sample weight of 0.0098g. The test temperature range was 350-850°C, in 100°C steps. Briefly, the sample was heated in a sweep gas of He+0.1%H_2 at 100 SCCM, the released tritium measured in real-time by an ion chamber, then oxidized on copper oxide and collected in a pair of water bubblers, and finally measured by liquid scintillation counting.

Discussion of Results

The plots of the stepped-anneal test data are shown in Figures 4 and 5, with Figure 4 showing the release rate on a linear axis and Figure 2 showing the same release rate data on a log axis. This test, compared to the earlier C03 test, used generally longer time intervals as well as a slightly larger sample size (10 pebbles versus 5 pebbles). The total cumulative released tritium at 350-850°C was 1050 MBq/g or 94% of the total inventory of 1120 MBq/g. The final temperature step of 850°C was held for 72 hours, resulting in greater cumulative levels. These compare with 75% of the inventory released for the C03 test. The residual tritium, measured by melting the sample at 1700C, was about 6% of the total inventory, with the totaled cumulative quantities agreeing relatively well with assay result.

A major difference between the C03 and D03 stepped-anneal tests is the release rates at the lower temperatures of 350-550°C. The D03 material showed much lower release rates at these lower temperatures. At the higher temperatures of 650-850°C, the release rates were more comparable between the two sample materials.

Due to the very low release rates (<1 Bq/s) at the lower temperatures of 350-550°C, the IC signal contained a great deal of noise with large narrow spikes, similar to what was seen in the earlier C03 test. The noise and spikes were removed in the data cleanup process. Release rates for the 650 and 750°C steps were larger, but still low at <100 Bq/s. The bulk of the released tritium, 74%, did not come off until 850°C. Due to the still relatively small sample size, the bubbler liquid scintillation results should always be considered the more reliable data, when compared to the IC results.

As has been done previously, the IC cumulative release curve in MBq/g, calculated from the release rate curve in Bq/s, was normalized to the collection bubbler liquid scintillation results in MBq/g. This was done by adjusting the IC baseline and/or IC calibration factor once for each bubbler data point. This method assumes the collection bubbler liquid scintillation results are always reliable and accurate, therefore, the IC curve must be adjusted to obtain agreement.

Figures 4 and 5 below show the release rate, as measured by the IC in Bq/s on the left axis, with cumulative tritium (both integrated IC signal and collection bubbler results) in MBq/g on the right axis, and temperature in degrees C also on the right axis.

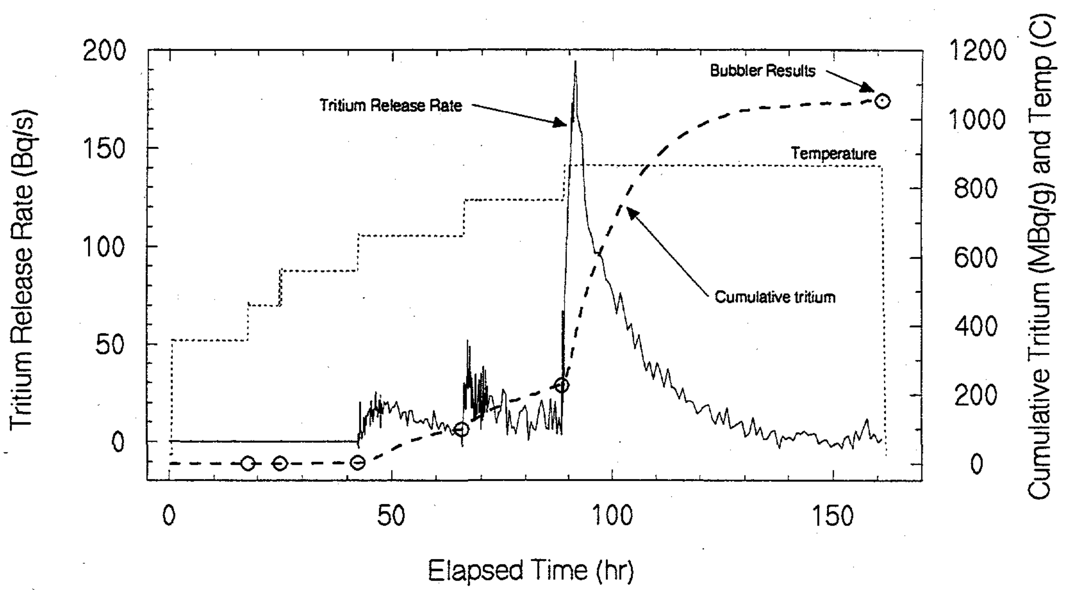

Figure 4. Stepped-anneal tritium release test data, 350-850°C in 100°C steps, for D03 (1-mm) beryllium, 10 pebble sample size.

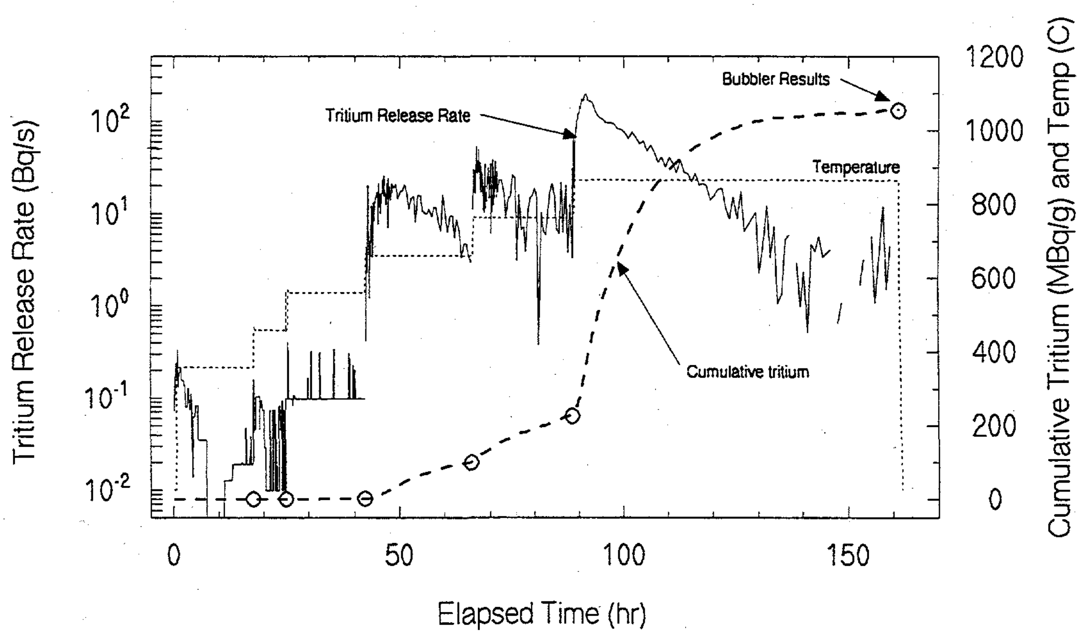

Figure 5. Stepped-anneal tritium release test data for D03 (1-mm) beryllium pebbles. Release rate data are plotted on log-axis to show release rates at lower temperatures.