Treatment of Irradiated Graphite from French Bugey Reactor – 13424

Thomas Brown*, Bernard Poncet**
* Studsvik, Inc., 5605 Glenridge Drive NE, Suite 705, Atlanta, GA, thomas.brown@studsvik.com
** Électricité de France, 154 Avenue Thiers, CS 60018, 69458 Lyon Cedex 06, bernard-r.poncet@edf.fr

ABSTRACT

Beginning in 2009, in order to determine an alternative to direct disposal for decommissioned irradiated graphite from EDF's Bugey NPP, Studsvik and EDF began a test program to determine if graphite decontamination and destruction were practicable using Studsvik's thermal organic reduction (THOR) technology. The testing program focused primarily on the release of C-14, H-3, and Cl-36 and also monitored graphite mass loss.

For said testing, a bench-scale steam reformer (BSSR) was constructed with the capability of flowing various compositions of gases at temperatures up to 1300 °C over uniformly sized particles of graphite for fixed amounts of time. The BSSR was followed by a condenser, thermal oxidizer, and NaOH bubbler system designed to capture H-3 and C-14. Also, in a separate series of testing, high concentration acid and peroxide solutions were used to soak the graphite and leach out and measure Cl-36.

A series of gasification tests were performed to scope gas compositions and temperatures for graphite gasification using steam and oxygen. Results suggested higher temperature steam (1100 °C vs. 900 °C) yielded a practicable gasification rate but that lower temperature (900 °C) gasification was also a practicable treatment alternative if oxygen is fed into the process.

A series of decontamination tests were performed to determine the release behavior of and extent to which C-14 and H-3 were released from graphite in a high temperature (900-1300 °C), low flow roasting gas environment. In general, testing determined that higher temperatures and longer roasting times were efficacious for releasing H-3 completely and the majority (80%) of C-14. Manipulating oxidizing and reducing gas environments was also found to limit graphite mass loss.

A series of soaking tests was performed to measure the amount of Cl-36 in the samples of graphite before and after roasting in the BSSR. Similar to C-14 release, these soaking tests revealed that 70-80% Cl-36 is released during roasting tests.

INTRODUCTION

In 2008, following the general French plan for nuclear waste management, Électricité de France (EDF) tried to find for irradiated graphite an alternative solution to direct storage at the low-activity long-life storage center in France managed by the national agency for wastes (ANDRA). EDF management requested that its engineering arm EDF CIDEN study the graphite treatment alternatives to direct storage.

In mid-2008, this study revealed the potential advantage for EDF to use a steam reforming process known as thermal organic reduction, "THOR" (owned by Studsvik, Inc., USA), to destroy the graphite matrix and limit the quantity of secondary waste to be stored. However, there were concerns about the radiological releases that would be generated with respect to their effect on the environment.

In late 2009, EDF began a test program with Studsvik to determine if the THOR steam reforming process could be used to destroy the graphite. Once confirmed, the program also sought to determine if the graphite could be treated to release the bulk of activity while minimizing the gasification of the bulk mass of the graphite. Subsequently, the decontaminated graphite could be either gasified or disposed at reduced activity concentrations. This test program continued until September 2011, focusing on the release behavior of C-14, H-3, and Cl-36 from irradiated graphite as a function of variable purge gas compositions.

DESCRIPTION

Bench-Scale Steam Reformer (BSSR)

A bench-scale steam reformer was developed and constructed for laboratory tests to treat the graphite. The BSSR consisted of a high-temperature vertical furnace capable of temperatures up to 1300 °C. Quartz sample tubes (ID = 25 mm) containing sized graphite particle samples (up to 30 g) were inserted into the BSSR for each test. The inlet of the quartz sample tube was fitted with gas lines to meter in steam, oxygen, nitrogen, and other gases which could be used to gasify (high flow) or roast (low flow) graphite samples at different rates and for extended amounts of time up to 18 hours.

Next, the off-gases from the quartz tubes were directed into a condenser to capture H-3 and steam as condensed water. The remaining off-gases were sent through bubblers designed to capture C-14 as Na_2CO_3, Cl-36 as NaCl, and any remaining H-3 as water. The off-gases continued from the bubblers to the thermal oxidizer (TO) to ensure that the remaining gases were oxidized to water and CO_2. The TO prevented any C-14 in the form of CO or CH_4 from bypassing the bubblers. The TO was followed by another set of bubblers designed to capture any remaining oxidized C-14, H-3, and Cl-36. The BSSR apparatus is shown in Fig. 1 below.

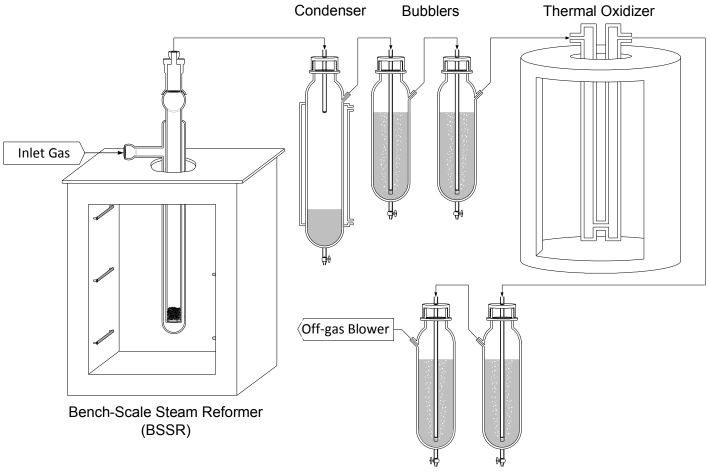

Fig. 1. Bench-Scale Steam Reformer Apparatus

Liquid samples were collected at specified time intervals from these bubblers. All collected bubbler and condenser liquid samples and any remaining graphite samples at the end of the test were analyzed to determine the time release behavior of the radionuclides and the graphite mass loss.

Sample Preparation and Homogeneity

The graphite sleeve received from EDF came as one solid, contiguous piece and required crushing and homogenization prior to performing the planned bench scale tests. This was necessary to ensure the radionuclides of interest were uniformly distributed throughout each sample prior to testing. Representative samples for each test were generated by crushing the sleeve into small particles and sieving those particles to obtain a uniform size fraction of 2380 – 4000 microns. Once a substantial amount of the size fraction was obtained, the particles were further homogenized in a 1 L container placed on a tumbler from which sub-samples were taken for testing. The figure below demonstrates the process of homogenizing the graphite.

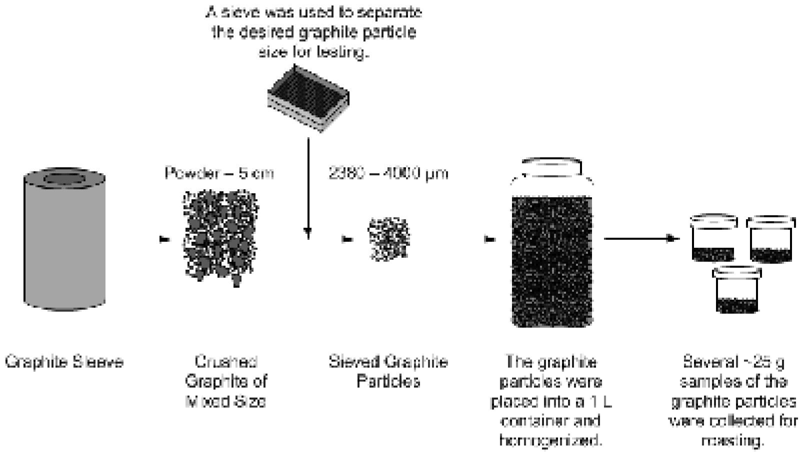

Fig. 2. Graphite Sample Preparation [1, p.20]

Sample Analysis

Before and after samples from each test were measured for two major results, mass loss and activity remaining. Mass loss revealed the extent of oxidation resulting from each test, and activity remaining revealed the efficacy of a given set of conditions to remove activity from a sample. While mass loss data were simple to collect, determining the activity of C-14 and H-3 remaining required the use of a Harvey biological oxidizer and subsequent liquid scintillation counting (LSC). Sub-samples were collected and measured for C-14 and H-3 for each sample before and after testing as shown in the figure below. Samples containing less activity after various treatments helped to suggest treatment protocols most effective for removing activity.

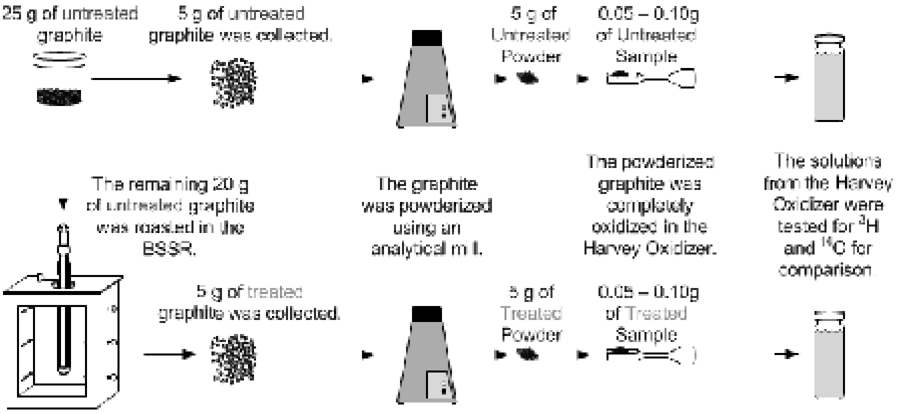

Fig. 3. Graphite Sample Preparation [1, p.22]

DISCUSSION

Gasification Tests

The goal of the gasification tests was to determine if graphite could be gasified at acceptable rates such that after decontamination the graphite may be gasified as an alternative to direct disposal. Steam and steam with oxygen were flowed into the BSSR over samples of excess irradiated graphite (20 g each) at a flow rate of 300 cc/min for 6 hours. Table I shows the gasification rates by temperature and gas composition.

Table I. Graphite Gasification Rates [2]

Test Run	Temperature	% Steam	% Oxygen	Rate
1	900 °C	100	0	0.16 g/hr
2	1100 °C	100	0	1.13 g/hr
3	900 °C	60	40	0.83 g/hr
4	1100 °C	60	40	1.35 g/hr

These tests proved that test run 4 at higher temperature and higher oxygen content processed graphite over 8x faster than for test run 1 at a temperature 200 °C lower using just steam. Still, test runs 2 & 3 demonstrate that appreciable gasification rates can be obtained at higher temperatures using steam only or at lower temperatures with increased oxygen content.

Decontamination Tests

After gasification tests, focus shifted to decontamination of graphite. Samples of irradiated graphite (20 g each) were roasted at 900-1300 °C in a low flow inert carrier gas for 6 – 18 hours with low concentrations of oxidizing gases at a flow rate of 60 cc/min (1/5th of the gasification flow rate) to preferentially remove volatile radionuclides with the goal of minimizing the graphite mass loss to 5%. To determine ultimate decontamination, as mentioned previously, sub-samples of graphite before and after treatment were measured for C-14 and H-3 via Harvey biological oxidizer.

Effect of Temperature and Time

Completed in April 2010, 'Phase I' testing revealed that >90% of H-3 and up to 46% of C-14 were released with 6% mass loss when processed at temperatures above 1100 °C [3]. For this reason, future testing focused on higher temperature processing up to 1300 °C in order to maximize activity release. Equipment upgrades and refined process conditions were implemented and additional testing performed. Completed in September 2011, 'Phase II' testing revealed that >99% of H-3 was removed during 8 of 11 runs using various concentrations of nitrogen, steam, and oxygen at low flows of 60 cc/min at 1300 °C [1, p.26]. In fact, roasting the samples in nitrogen alone for 6 hours (the shortest duration test) achieved >99% removal of H-3.

While H-3 proved to be readily removed, C-14 was removed to a lesser extent. During 'Phase I,' 46% of C-14 was removed from a 20 g sample after roasting for 6 hours using a low concentration of steam at 1200 °C [3]. In the following year, 'Phase II' tests were designed to enhance the C-14 removal by testing the effect of higher temperature and extended processing time. 18 tests were completed to determine the optimal composition of gases to remove C-14. Information from these tests was used in a set of optimized tests where the BSSR temperature was increased to 1300 °C in a lowly oxidizing environment, and the roasting time was increased from 6 hours to 8 hours. Optimized test conditions achieved up to 69% C-14 removal with a sample mass loss of 3.3% [1, p.44].

A final round of tests was performed using low oxidation or reducing gas concentrations to process samples at 1300 °C while testing the effect of further extending process times up to 18 hours. Complications occurred during longer duration testing due to devitrification and cracking of the quartz sample holders suggesting more robust materials may be beneficial to determine the effect of extended processing time to release C-14. The longest test completed lasted 14 hours and achieved 80% decontamination of C-14 accompanied by 12% mass loss in a reducing atmosphere [4, p.7]. While the C-14 removal was higher for this extended test than for the previous 8 hour test, the mass loss of the sample, which is primarily released as C-12, was also higher.

While specific testing conditions and corresponding results are currently proprietary, the following conclusions were drawn from the above described tests and corresponding data:

- Higher temperature environments (up to 1300 °C) more rapidly remove C-14 and H-3.
- H-3 can be nearly completely removed at higher temperatures using a variety of low concentrations of steam and oxygen in nitrogen.
- Longer process times release more activity but also may cause additional C-12 mass loss.
- Mass loss can be limited by a reducing environment.

Soaking Tests

The release behavior of Cl-36 depends on different processes such as water saturation or water access into graphite pore spaces [5]. This release can be exploited if the pores can be more easily accessed. Since Cl-36 could not be measured using the Harvey oxidizer, soaking methods were developed and performed using successive concentrated acid and peroxide solutions. These soaking methods were used to expand the graphite and its pores to increase the removal of Cl-36 and facilitate measurement of Cl-36 in sub-samples of graphite before and after roasting in the BSSR. Similar to the 80% release of C-14 previously measured, these tests revealed that roasted graphite contained 70-80% less Cl-36 than graphite that had not been roasted [4, p.14].

CONCLUSION

Future work seeks to explore the effect of reducing gases to limit the bulk oxidation of graphite. If the graphite can be decontaminated of long-lived radionuclides while limiting gasification of C-12, this would minimize any volume of secondary waste streams, and potentially lower the waste class of the larger bulk of graphite. Alternatively, if a high decontamination of C-14 is achieved, the graphite may be completely destructed (i.e. gasified) in accordance with an agreement with the French regulatory authority.

Future work will also explore alternative measurement methods to confirm Cl-36 measurement data. Ultimately, it may be possible to pre-treat or post-treat the graphite to remove as much Cl-36 as possible and minimize its likelihood of leaching after disposal. It is also possible that the reducing conditions of the bed can be refined such that Cl-36 is removed as HCl during roasting and will not require a soaking treatment.

REFERENCES

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