ELSEVIER Journal of Hazardous Materials B68 (1999) 193–203

Journal of Hazardous Materials

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Results from the low level mercury sorbent test at the Oak Ridge Y-12 Plant in Tennessee

W. Hollerman [a,*,1], L. Holland [b], D. Ila [b], J. Hensley [c], G. Southworth [c], T. Klasson [d], P. Taylor [d], J. Johnston [e], R. Turner [f]

[a] *Acadiana Research Laboratory, University of Southwestern Louisiana, P.O. Box 44210, Lafayette, LA 70504, USA*
[b] *Center for Irradiation of Materials, Alabama A&M University, Normal, AL 35762, USA*
[c] *Y-12 Plant Environmental Restoration Program, Oak Ridge, TN 37831, USA*
[d] *Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
[e] *TN & Associates, Oak Ridge, TN 37830, USA*
[f] *Frontier Geosciences, Seattle, WA 98109, USA*

Received 1 November 1998; received in revised form 9 February 1999; accepted 10 February 1999

Abstract

A mercury sorbent test was performed near the headwaters of the Upper East Fork Poplar Creek at the Oak Ridge Y-12 Plant in Tennessee. The sorbents SIR-200 (ResinTech), Keyle:X (SolmeteX), and GT-73 (Rohm and Haas) were the best materials tested for low level mercury removal. Each of these sorbents has a thiol-based active site. None of the tested sorbents reduced the mercury concentration to less than the existing 12 ng/l NPDES limit. For this small scale test, SIR-200, Keyle:X, and GT-73 reduced the mercury concentration to less than 51 ng/l, which is a regulatory treatment goal. The other sorbents tested, including granular activated carbon (Filtrasorb 300), did not reduce the mercury concentration below 51 ng/l at any tested flow up to 5 bed volumes per minute. Because of the cost and large volume of sorbent, a wastewater treatment plant for this stream would be prohibitively expensive to construct and maintain. Published by Elsevier Science B.V.

Keywords: Sorbent; Mercury; Mercury contamination; Mercury pollution; Method 1631

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[*] Corresponding author. Tel.: +1-318-482-6184; Fax: +1-318-482-6190; E-mail: wah0320@us.edu or wahollerman@mindspring.com

[1] Home address: 309 Timothy Drive, Lafayette, LA 70503, USA. Home phone: +1-318-406-0464. Websites: http://www.usl.edu/Research/ARL; http://www.mindspring.com/ ~ wahollerman

0304-3894/00/$ - see front matter Published by Elsevier Science B.V.
PII: S0304-3894(99)00027-8

1. Background

Beginning in 1951, mercury was used at the Oak Ridge Y-12 Plant as part of a lithium isotope separation and purification process. During its use, more than 330 metric tons of mercury were lost to the surrounding environment [1]. Much of the lost mercury is now sequestered in and near the Y-12 Plant. Physical, chemical, and biological processes in the environment have altered some of this mercury into a variety of other organic and inorganic forms.

Over the last 15 years, the Department of Energy (DOE) has been identifying and remediating sources of mercury in and near the Upper East Fork Poplar Creek at the Y-12 Plant. The driver for this work has been the National Pollution Discharge Elimination System (NPDES) permit for the Oak Ridge Y-12 Plant. The existing permit mandates the creek will have a net mercury concentration of no more than 12 ng/l by April 27, 2000 [2]. Modification of state water quality standards proposed by the Tennessee Department of Environment and Conservation (TDEC) could raise the NPDES mercury limit from 12 ng/l to 51 ng/l. It is not known when this new limit may take effect.

The headwaters of the creek, as defined by TDEC, arise at the North–South drainage pipe at the Y-12 Plant, where water from the pipe discharges into an open channel. Water pumped from building sumps, groundwater, storm drains, and natural springs composes flow in the North–South drainage pipe. Approximately 6 m downstream from this discharge source, water from the Clinch River is added to Upper East Fork Poplar Creek to maintain a NPDES required base flow. The creek exits the Y-12 Plant at Station 17, about 2565 m downstream. The average flow rate measured at the outflow from the North–South pipe was 5300 l/min in water year 1997 (October 1996 to September 1997) [1]. The corresponding average water flow rate measured at Station 17 was about 17,730 l/min [1] in 1997.

This study evaluated the capacity of various sorbents to reduce the mercury concentration of the creek near the outflow of the North–South pipe. The sorbents were tested as received, and the only pretreatment of the wastewater was filtration at 1 μm nominal pore size. These short-term tests determined the maximum flow rate that can be treated by each sorbent to achieve a target discharge concentration. An additional long-term test will be required to determine the volume of creek water that can be treated using the selected sorbents.

2. Analytical methods

The total mercury concentration in water samples was determined using the proposed EPA Method 1631 [3,4]. Method 1631 uses atomic fluorescence to measure the mercury concentration for selected water samples.

- Water samples are chemically oxidized using bromine chloride, which frees mercury that is bound to solids, chemically-complexed, or sorbed to the inside of the sample bottle. The mercury is then reduced to the elemental form using stannous chloride.

- The sample is purged with nitrogen to release any mercury into the vapor state. All mercury from the water sample is captured in a gold-coated sand trap. The trap is then heated and argon is passed through the sample trap, sending the mercury into a second gold analysis trap. Mercury from this second trap is released by heating and then carried to the fluorescence cell for measurement.
- An ultraviolet lamp in the cell excites the mercury atoms carried by the flow of argon. The amount of mercury in the sample is proportional to the magnitude of fluorescence light generated in the cell. The mercury detection limit for this method is 0.2 ng/l.

Strict procedures must be used to handle each sample to minimize the potential for contamination or loss of mercury. For example, breathing near the mouth of an open sample bottle may affect the measured mercury concentration of the sample, as the mercury amalgam in tooth fillings provides a source of contamination. Final approval for EPA Method 1631 is currently pending. Other EPA approved chemical methods for determination of mercury levels have a limit of about 200 ng/l [5].

3. Selected sorbent materials

A selection of important physical and chemical properties for each sorbent is shown in Table 1 [6–11]. Product information and recommended operating conditions for each sorbent were obtained from individual manufacturers.

The 'flow rate' column on the right side of Table 1 is the range of values recommended by the manufacturer for use with a given sorbent column. It is often expressed in bed volumes per minute (BV/min) to allow the results to be independent of the column size. The 'total capacity' column in Table 1 is the maximum amount of mercury that the material can absorb per unit volume. This theoretical limit is usually expressed in mass equivalents per liter (eq/l). The total capacity is quoted as a measure of the ability of the sorbent to collect mercury. However, the actual mercury capacity of sorbent materials is a function of concentration and cannot be easily expressed by a single number. Specific information on each sorbent is shown in the subsections that follow.

Table 1
Selected physical and chemical properties of mercury sorbents

Sorbent type	Matrix type	Active site	Nominal particle size (mm)	Useable pH range	Recommended flow rate (BV/min)	Total capacity (eq/l)
Filtrasorb 300	Carbon	Activated Carbon	0.8–1.0	1–14		3.9
Keyle:X	Polyacrylate	Thiol	0.6–0.8	1–14	0.54–1.07	3.4
GT-73	Polystyrene	Thiol	0.3–1.2	1–13	0.27–1.07	1.4
SR-4	Polystyrene	Thiol	0.3–1.0	1–14	0.08–0.33	2.0
S-920	Polystyrene	Isothiouronium	0.9–1.5	1–13	0.27–0.80	1.5
SIR-200	Polystyrene	Thiol	0.3–1.0	2–10	0.13–0.40	1.2
Forager Sponge	Polymer	Amine	12.7	1–14	0.10–0.50	0.1
Mersorb 1.5 mm	Carbon	Sulfur	1.5–4.0	6–8	0.13	3.7

3.1. Filtrasorb 300

The standard sorbent against which others were compared is Filtrasorb 300. It is manufactured by Calgon Carbon and is a granular activated carbon product. It is not selective and has a total capacity of 3.9 eq/l. Filtrasorb 300 was used as the test standard because its particle size is comparable to the majority of sorbent candidates used in this study and is already being used at several locations in the Y-12 Plant.

3.2. Keyle:X

Keyle:X is manufactured by SolmeteX and is a thiol-based proprietary sorbent that selectively binds mercury. This resin can be used over a pH range of 1 to 14. According to SolmeteX, it has the highest total capacity (3.4 eq/l) for any of the noncarbon materials and cannot be regenerated. The total removal efficiency assumes a linear flow velocity of 2.5 m/h. The removal efficiency drops to 0.2 eq/l when the linear flow velocity is increased to 15 m/h. Keyle:X, along with GT-73, has the highest practical recommended flow rate of 1.07 BV/min.

3.3. Duolite GT-73

Duolite GT-73 is a thiol-based mercury sorbent manufactured by Rohm and Haas. It has a recommended flow rate range of 0.27 to 1.07 BV/min, total capacity of 1.4 eq/l, and a useful pH range of 1 to 13.

3.4. Ionac SR-4

Ionac SR-4 is manufactured by Sybron Chemicals and has a thiol active site that preferentially binds mercury and other heavy metals. This resin can be used over a pH range from 1 to 14 and has good chemical stability. This material binds ionic forms of mercury and can be regenerated with acid. This resin is similar in form to GT-73.

3.5. Purolite S-920

The Purolite manufactures Purolite S-920. It is an isothiouronium active resin, similar to Ionac SR-3. Purolite S-920 has a recommended pH range of 1 to 13.

3.6. SIR-200

SIR-200, manufactured by ResinTech, is an ion exchange resin containing thiol functional groups. It has chelating properties for mercury and other divalent metals. The total capacities for divalent mercury and nickel are 1.2 eq/l and 0.2 eq/l, respectively. This resin is stable over a pH range of 2 to 10 and ResinTech recommends that it not be regenerated. ResinTech also recommends the removal of free chlorine from the test water before use.

3.7. Forager sponge

The Forager Sponge is manufactured by Dynaphore and is an open celled cellulose sponge. It incorporates an amine-containing polymer having selective affinity for heavy metals in aqueous ionic solutions. At saturation, the sponge will contain between 4% to 15% (dry) mass of absorbed ions with an approximate total capacity of about 0.1 eq/l.

3.8. Mersorb 1.5 mm

Mersorb 1.5 mm is manufactured by Nucon International and is an activated carbon product impregnated with sulfur. The sorbent is selective for mercury. This material binds ionic mercury, but it also adsorbs other forms on the activated carbon substrate. This sorbent has a total capacity of 3.7 eq/l, greater than any of the resin based materials. The sorbent is unstable in acid solutions and cannot be regenerated. The tested sorbent is similar to the commercially available Mersorb LW, but has a smaller particle size.

3.9. New ADA sorbent

ADA Technologies is developing a proprietary sorbent that has the potential to reduce the mercury content of water to the Y-12 NPDES permit level of 12 ng/l. Currently, ADA can produce only 10 kg of this material per batch. Since the ADA sorbent is in development, information concerning its physical and chemical properties is not available, and thus specific information concerning this sorbent is not displayed in Table 1.

4. Test apparatus

Fig. 1 is a schematic diagram of the sorbent test equipment. Flow from the North–South pipe was pumped through six parallel test columns, each 25.4 mm in

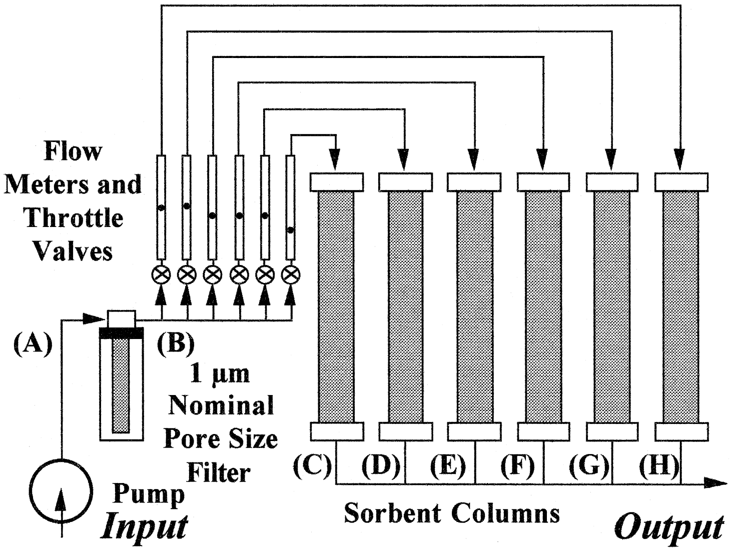

Fig. 1. Sorbent test system schematic diagram.

diameter and 203 mm long. One column contained Filtrasorb 300 to serve as a baseline treatment. Four of the test columns each contained a candidate sorbent material. A sixth empty column acted as a control to determine the amount of mercury lost in the test apparatus.

Flow in each column was from top to bottom to prevent levitation of the sorbent. Each column was coupled to a separate meter and control valve to ensure equal flow rates. Water samples were taken at points (A) through (H) as shown in Fig. 1. Comparisons of samples taken at (A) and (B) determined the fraction of particulate adsorbed on filterable materials.

Sorbents were tested near the outflow of the North–South pipe over a 3-week period in early 1998. Samples were collected at approximate flow rates of 0.1, 0.3, 1.0, 3.0, and 5.0 BV/min. A second 0.1 BV/min measurement was repeated after the 5.0 BV/min test to determine whether flow rate effects affected the passthrough fraction. Limitations in test equipment set the maximum measurable water flow rate at 5.0 BV/min.

At least two samples were collected after approximately 20 and 24 h of operation at each flow rate. After the 24-h samples were collected, the flow was adjusted to the next desired rate. The program schedule allowed for two complete sets of measurements (four sorbents per set) to test all of the selected sorbent materials. Filtrasorb 300 was used to standardize the results between the two sets of measurements. Filtrasorb 300, SR-4, Mersorb, GT-73, and the ADA sorbent were tested in the first sample group. Filtrasorb 300, Keyle:X, S-920, SIR-200, and the Forager Sponge were tested in the second sample group. The height to diameter aspect ratio was no less than 4.25 for any of the tested sorbents.

5. Mercury passthrough fraction

Effectiveness can best be determined by measuring the fraction of mercury that passes through a sorbent as a function of flow rate. The passthrough fraction (f_s) is defined as the mercury that passes through a selected sorbent material. It is more commonly known as the initial breakthrough of mercury and is equal to

$$f_s = \frac{c_0}{c_{00}},$$

where, c_0 = output concentration of mercury for a given column (ng/l), and c_{00} = concentration of mercury in the empty column (ng/l).

The fraction f_s was used as a figure of merit to compare the effectiveness of individual sorbents to remove mercury from water in the creek.

6. Results and discussion

Fig. 2 shows the raw mercury passthrough fractions for each sorbent. Over the range of tested flow rates, it is apparent that the mercury passthrough fraction can be written as a power function. Fig. 3 shows a plot of the best fit power function for the resulting

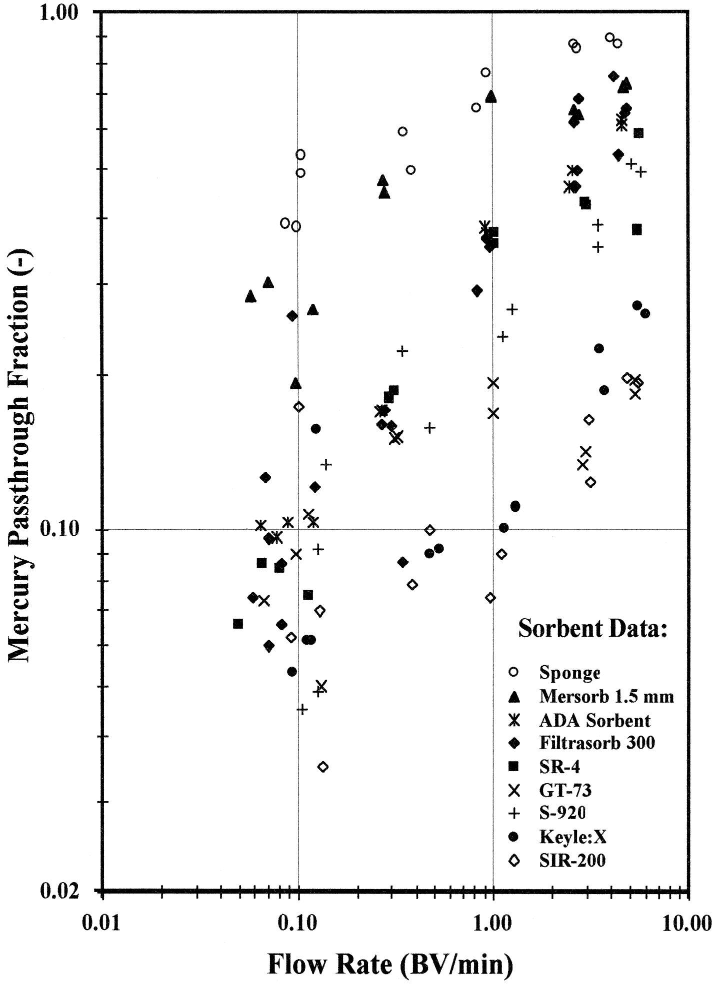

Fig. 2. Raw mercury passthrough fraction plot.

mercury passthrough fraction for each sorbent vs. flow rate. The best-fit curves shown in Fig. 3 are valid only over the range of tested flow rates of 0.1 BV/min to 5.0 BV/min. These curve fits are empirical and do not represent an analytical model of the mercury passthrough fraction.

The thiol-based SIR-200, Keyle:X, and GT-73 sorbents have the smallest mercury passthrough fractions over the range of tested flow rates (Fig. 3). SIR-200 was found to have the lowest overall mercury passthrough fraction as a function of flow rate for water from the North–South pipe.

Fig. 4 shows the average mercury concentrations as a function of flow rate for SIR-200, Keyle:X, GT-73, and Filtrasorb 300. None of the tested sorbents reduced the mercury concentration to the existing NPDES limit of 12 ng/l. For this small scale test,

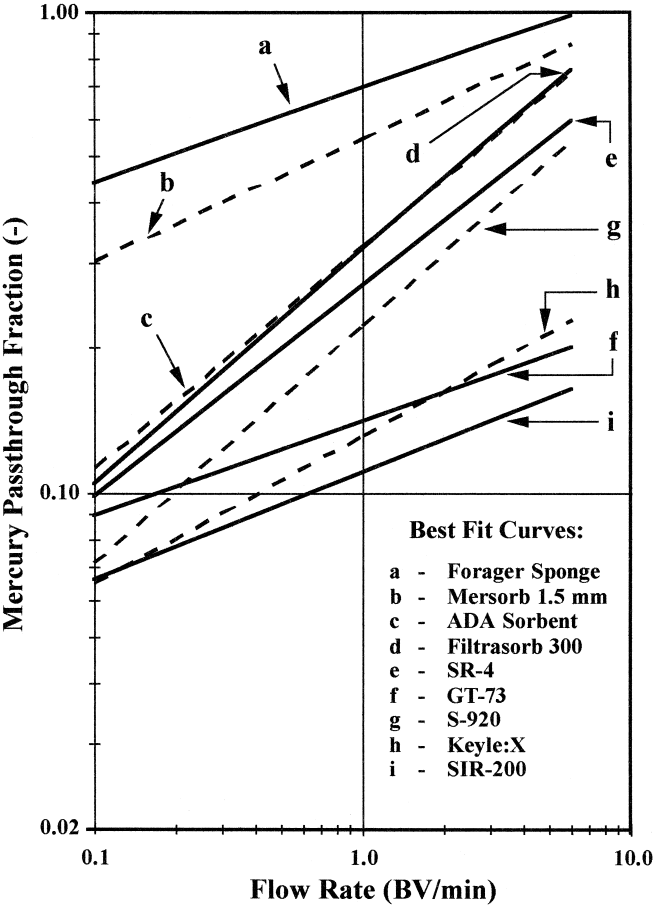

Fig. 3. Best fit mercury passthrough fraction plot.

SIR-200, Keyle:X, and GT-73 reduced the mercury concentration to less then the revised limit of 51 ng/l at a flow rate of 0.1 BV/min. Additionally, SIR-200 and Keyle:X reduced the mercury concentration to less than the proposed limit at a flow rate of 0.3 BV/min. Only the SIR-200 sorbent reduced the mercury concentration to less than 51 ng/l at a flow rate of 1 BV/min. Filtrasorb 300 and the remaining sorbents did not reduce the mercury concentration below the proposed or existing limits at any tested flow rate. We note that GT-73 was used in the first group of tests and that Keyle:X and SIR-200 were used during the second group of tests. Variations in water composition (such as pH, temperature, particulates, etc.) may have contributed the apparent difference in performance.

The raw data indicate no significant difference in passthrough fractions between the two 0.1 BV/min measurements. This suggests that the sorbent did not show signs of breakthrough due to mercury loading. Additional inspection of the Filtrasorb 300 data

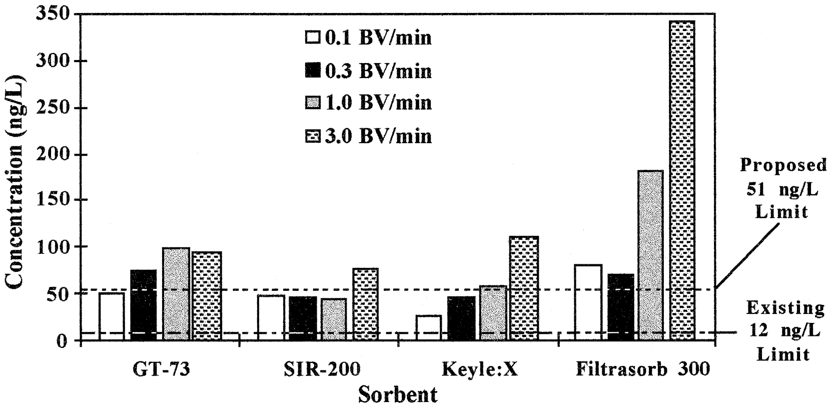

Fig. 4. Average mercury concentrations achieved by four sorbents.

indicates that the mercury passthrough fractions calculated at the measured flow rates were similar for both sample groups. No standardization of concentration or passthrough fraction was required for data analysis.

The average inlet mercury concentration collected from 23 measurements during the sorbent test was 1276 ± 940 ng/l. However, a value of 5286 ng/l was measured for one of the measured water samples. It was later determined that a large quantity of suspended matter was observed in this sample during the analysis procedure. Since this high value is not representative, the average mercury concentration is 1093 ± 354 ng/l, which is consistent with earlier measurements completed during 1997 [1]. The relatively large standard deviations shown in this data indicate a high degree of variability in mercury concentration at the site.

The average mercury concentration downstream of the nominal 1 μm filter was 767 ± 571 ng/l. The corresponding average mercury passthrough fraction for the 1 μm filter was 0.60 ± 0.31. This indicates that no more than 40% of the mercury in the water was in a particulate form or was absorbed by the filter. The mercury passthrough fraction for Filtrasorb 300, used extensively around the Y-12 Plant, was near the median of tested sorbents.

7. Conclusions

A mercury sorbent test was performed near the headwaters of the Upper East Fork Poplar Creek at the Oak Ridge Y-12 Plant in Tennessee. Data obtained from the study makes it easier to negotiate concentration levels specified in future NPDES permits. Results from the test indicated the following.

- SIR-200, Keyle:X, and GT-73 removed the largest concentrations of mercury from the creek. Each of these sorbents is thiol-based.
- The large deviation in the measured mercury concentrations at the outflow of the North–South pipe indicates a wide variability in mercury levels.

- During these tests, less than 40% of the mercury measured at the outflow of the North–South pipe was adsorbed to particulates larger then 1 μm.
- For this small scale test, SIR-200, Keyle:X, and GT-73 reduced the mercury concentration to less then the proposed 51 ng/l limit at a flow rate of 0.1 BV/min. SIR-200 and Keyle:X reduced the mercury concentration to less than the proposed limit at a water flow rate of 0.3 BV/min. Only SIR-200 reduced the mercury concentration to less than 51 ng/l at a water flow rate of 1 BV/min. The large volume of required sorbent and its cost makes treatment plant at these flow rates. The other sorbents did not reduce the mercury concentration below the proposed or existing NPDES limits at any tested flow rate.
- The standard, Filtrasorb 300, was near the median of tested sorbents for mercury removal. Filtrasorb 300 did not reduce the mercury concentration in the creek to less than the proposed or existing NPDES limits at any of the tested flow rates.

Acknowledgements

The mercury sorbent test was performed from December 1997 to April 1998 at the Oak Ridge Y-12 Plant in Tennessee. TN & Associates completed this research under subcontract 18K-GWU11C for Bechtel Jacobs, LLC, contract DE-AC05-98OR22700 (formerly Lockheed Martin Energy Systems, contract DE-AAC05-84OR21400), for the United States Department of Energy. The Howard J. Foster Center for the Irradiation of Materials at Alabama A&M University participated in this research using subcontract 395064-14-AMU with TN & Associates. Partial funding for this research was also provided by the United States Department of Energy Mixed Waste Focus Area. The authors wrote this paper for the United States Government under contract DE-AC05-98OR22700.

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