Gamma Radiation stability Studies of Mercury Fulminate

by

F. F. Fondeur

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

W. R. Wilmarth

S. D. Fink

DOE Contract No. **DE-AC09-96SR18500**

DISCLAIMER

WSRC-RP-99-01090, Rev. 0

keywords: explosive, infrared, thermal analysis
retention: Permanent

Gamma Radiation Stability Studies of Mercury Fulminate

F. F. Fondeur
W. R. Wilmarth
S. D. Fink

December 06, 1999

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

SUMMARY

Mercury fulminate completely decomposed in a gamma source (0.86 Mrad/h) after a dose of 208 Mrad. This exposure equates to approximately 2.4 years in Tank 15H and 4 years in Tank 12H, one of the vessels of concern. Since the tanks lost the supernatant cover layer more than a decade ago,[2] this study suggests that any mercury fulminate or closely related energetic species decomposed long ago if ever formed.

1 Introduction

Chemical processing of nuclear materials at the Savannah River Site (SRS) produced a waste sludge containing transition metal and rare earth metal oxides. Radiolytic heating within the sludge removes liquid, drying the sludge. Tanks 12H and 15H store dry sludge containing measurable amounts of mercury (Hg) resulting from transfers from the separation facilities and silver from cleaning Berl saddles.[1] Recent analysis of an archived sample from Tank 12H reported 0.14 wt % silver (Ag) based on total dried solids.[2] Also, the potential exists that sludge tanks contain various organic species. Current understanding of the chemistry during drying can not preclude the existence of energetic compounds formed from these metals and carbon.[3]

Previously, Savannah River Technology Center (SRTC) personnel investigated the behavior (sensitivity) of two mercury compounds – mercury oxalate and mercury fulminate – to determine their behavior with simulated sludge.[5] While that study provided a basis for sampling of the tanks, the experiments did not conclusively show complete mercury fulminate destruction. Experimental results examined only a short residence time in a 0.02 Mrad/h Gamma source. Recently, a panel of explosive experts evaluated this program and recommended additional testing in a high radiation field to ensure that more than 90% of the original mercury fulminate could be destroyed.[6] This work seeks to demonstrate mercury fulminate decomposition using a 0.86 Mrad/h Gamma source. The time to achieve 90% decomposition provides an estimate of the lifetime in the tanks.

2 Experimental Conditions

These experiments investigated the stability (lifetime) of mercury fulminate under gamma radiation exposure. Personnel added 195 mg of mercury fulminate to a quartz tube and placed it in the center of a Shepperd Gamma source (0.96 Mrad).[7] Periodically, we removed about 2 mg of mercury fulminate from the source and characterized by thermal means. Thermal characterization used a DSC (Differential Scanning Calorimeter) 6 from Perkin Elmer. We also analyzed portions of the sample with infrared spectroscopy. The testing used the safety protocols extensively detailed in the earlier work.[9-12]

3 Results and Discussion
Radiation Effects

Radiation deriving from nuclear decomposition consists of alpha, beta and gamma radiation. Available sources at SRTC include Co-60 gamma irradiators of two different field strengths, 10^4 and 10^6 rad/h. Previous studies[5] utilized the lower dose rate source. To determine more realistically the radiation lifetime of the mercury fulminate, we used the higher dose rate source . Therefore, we exposed mercury fulminate to a gamma source for approximately nine days.

Figure 1 shows the results of thermal analysis (DSC) of samples of mercury fulminate exposed to gamma radiation exposures of 5.2 to ~210 Mrad. One observes a decrease in the exothermic peak height associated with the decomposition of mercury fulminate with increased absorbed dose. Additionally, the onset temperature for decomposition decreases with total dose, going from a value of approximately 160 °C – i.e., the literature value[13] – to temperatures of 150 °C or less after exposure to radiation. The material completely decomposed after 209 Mrad of gamma dose, as indicated by the lack of exothermic decomposition. The shift in onset temperature most probably indicates decomposition of mercury fulminate to other unstable species.

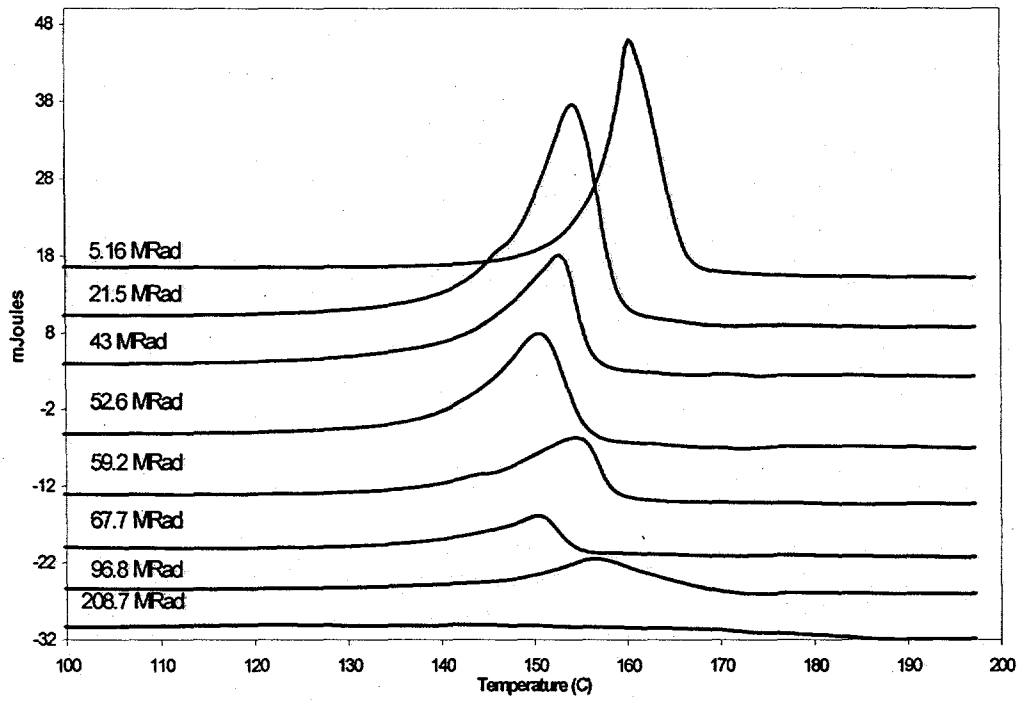

Figure 1. The effect of gamma irradiation on mercury fulminate

Figure 2 shows a plot of the measured enthalpy of mercury fulminate decomposition calculated from the peak areas in Figure 1. The starting measured enthalpy does not match the literature value of 1824 J/g[13] and likely reflects either slight impurities in composition or the influence of the 5.2 Mrad exposure. A fit of the data to a logarithmic expression reveals the equation:

$$\text{Enthalpy} = -190 \ln(\text{Radiation Exposure}) + 1110 \qquad R^2 = 0.94$$

Calculating the enthalpy at zero absorbed dose gives an enthalpy of 1900 J/g. We desire to know the dose at which the mercury fulminate completely decomposes. This dose of 209 Mrad equates to about two years and five months in Tank 15H and four years in Tank 12. Therefore, even if the fulminate formed in the tank, over 10 half lives passed since the tanks went dry.

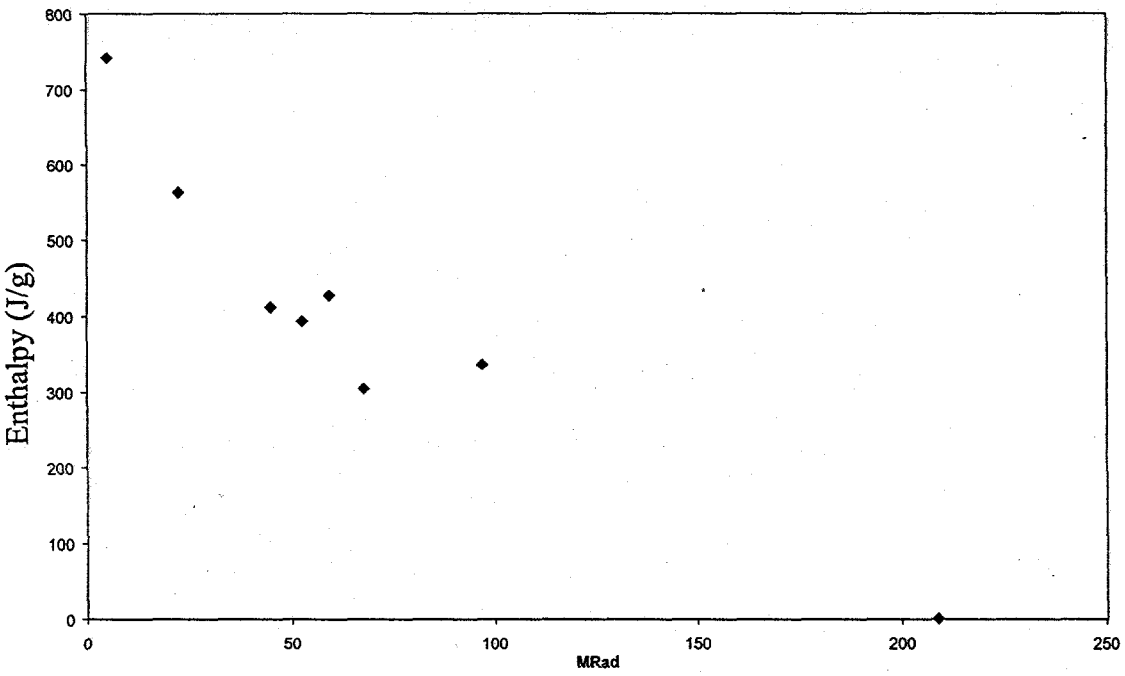

Figure 2. The effect of gamma irradiation on the energetics of mercury fulminate

Additionally, the researchers experienced difficulty in synthesizing pure mercury fulminate. This synthesis proves sensitive to process parameters such as rate of alcohol addition, the extent of the addition, the length of reaction time and purity of the starting materials. Every synthesis attempt under strict controlled conditions led to the formation of impurities in the mercury fulminate and occasionally a complete failed synthesis. The mixtures always had less decomposition energy than mercury fulminate. Given the difficulty in preparing the compound under ideal laboratory condition and its rapid decomposition under non-optimal conditions, it seems rather unlikely the compound could form or

survive long in the highly caustic radiation field of the waste tanks. We found evidence of metallic mercury as one decomposition byproduct (see Figure 3). Looking at Figure 3, some mercury fulminate grains have metallic mercury islands.

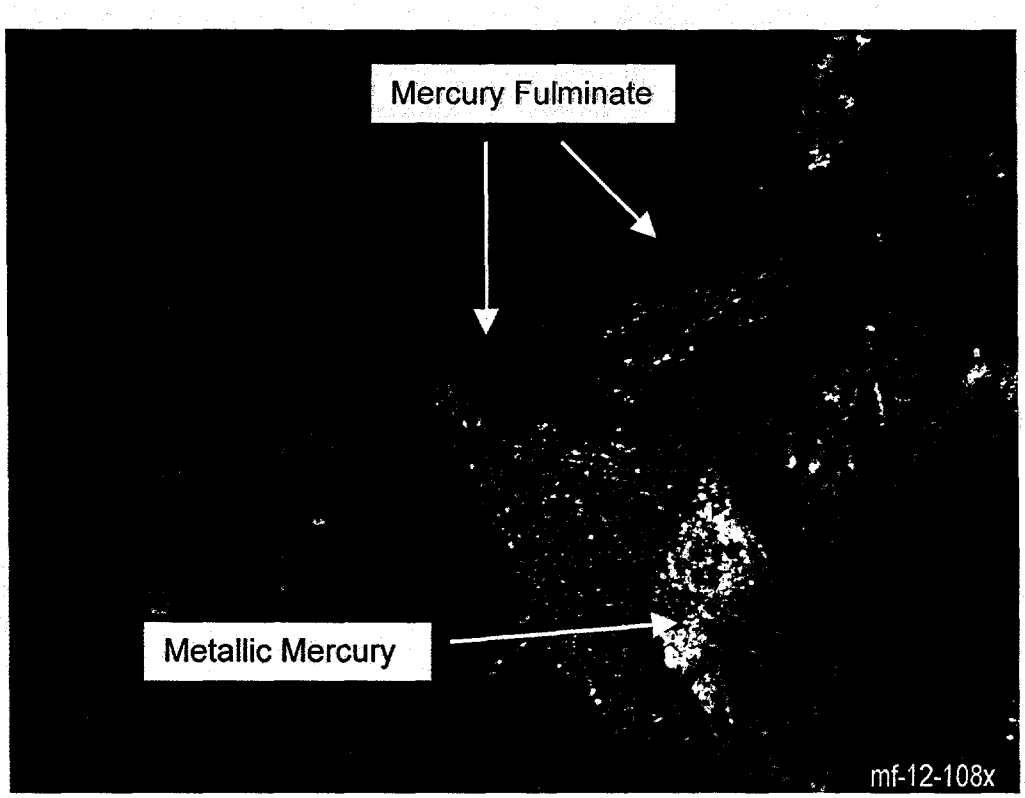

Figure 3. The effect of 62 Mrad dose on mercury fulminate

Molecular vibrational spectroscopy of irradiated mercury fulminate also allowed us to follow the decomposition of mercury fulminate. figure 4 shows the infrared spectra of irradiated mercury fulminate from absorbed doses of 5.2 Mrad to 209 mRad. Previously, Nakamoto and McCarthy[14] examined mercury fulminate by IR and noted its spectrum exhibits two characteristic vibrations centered at 2190 and 1220 cm^{-1}.

With increased absorbed dose, the spectrum of the mercury fulminate changes. These changes appear very noticeable in the spectra obtained from the sample after 96.8 and 208.7 Mrad absorbed dose. New infrared bands (3320, 1595, 1390, 960, and 780 cm^{-1}) appeared. These bands represent nitrites and amine groups.[14] This data suggests nitrogen hydroxylation and salt formation occurs during decomposition.

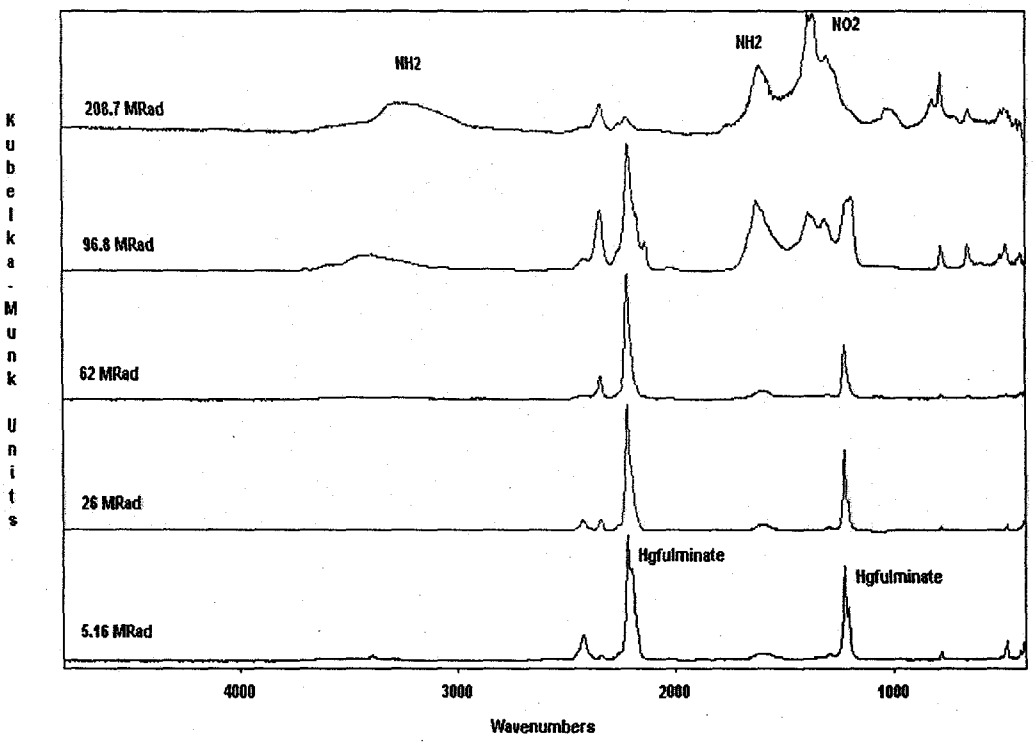

Figure 4. Infrared spectrum of mercury fulminate after irradiation

One can also examine the decomposition kinetics by examining the peak height of the vibrational band in the IR spectra. Figure 5 plots the peak heights of the IR band located at 2190 cm^{-1} as a function of absorbed dose. Although this technique proves less sensitive than thermal analysis, we can obtain information regarding the individual chemical species. Figure 5 shows the peak height decreasing with increasing absorbed dose. The shape of the peak appear less classical than that observed in the thermal analysis and this distortion may reflect instrumental limitations. However, analysis of the curve from 62 Mrad to 209 Mrad provides an estimate of the exposure that leads to 50% decomposition for mercury fulminate as 30 to 60 Mrad. This equals about two-thirds of the value obtained from thermal analysis. One must remember that thermal analysis includes exothermic reactions from the by-products of the mercury fulminate decomposition. The approximate agreement between the independent

measurements provides confidence in estimated exposure that causes 50% destruction.

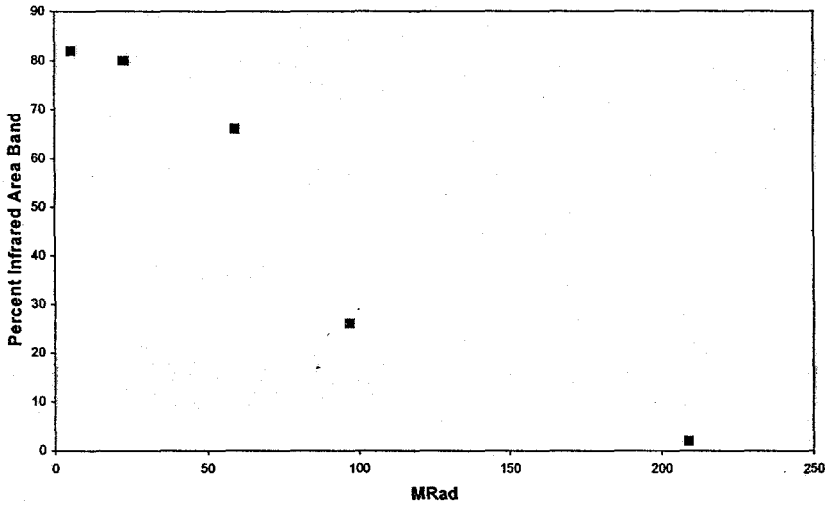

Figure 5. The effect of gamma dose on the infrared bands of mercury fulminate.

4 Conclusion

Mercury fulminate completely decomposed in a gamma source (0.86 Mrad/h) after a dose of 208 Mrad. This exposure equates to approximately 2.4 years in Tank 15H and 4 years in Tank 12H, one of the vessels of concern. Since the tanks lost the supernatant cover layer more than a decade ago,[2] this study suggests that any mercury fulminate or closely related energetic species decomposed long ago if ever formed.

5 References*

[1] R. E. Peterson and C. L. Crawford, "Task Technical Plan for Hydrogen Production from Radiolysis of Sludge," WSRC-RP-98-01073, September 18, 1998.

[2] S. Hall, "Evaluation of Waste Tanks Containing Dry Sludge," NI-HLW-96-018, Rev. 4, March 30, 1999.

[3] D. T. Hobbs, "Possible Explosive Compounds in the Savannah River Site Waste Tank Farm Facilities," WSRC-TR-91-444, Rev. 1, April 30, 1995.

[4] M. J. Barnes, L. O. Dworjanyn, S. D. Fink, F. F. Fondeur, M. W. Geeting, M. S. Hay, R. F. Swingle, and W. R. Wilmarth, "Examination of the Potential for Formation of Energetic Compounds in Dry Sludge," WSRC-TR-98-00407, November 2, 1998.
[5] F. F. Fondeur and W. R. Wilmarth, "Synergystic and Alkaline Stability Studies of Mixtures of Simulated High Waste Sludge with Selected Energetic Compounds," WSRC-TR-99-00592, Rev. 0, July 12, 1999.
[6] F. F. Fondeur and W. R. Wilmarth, "Independent Panel Evaluation of Dry Sludge PISA Program," WSRC-RP-99-00727, August 30, 1999.
D. T. Hobbs, "Recommended Standard Materials for Evaluation of Dry Solid Energetic Reactions," WSRC-TR-98-00262, August 19, 1998.
[7] H. M. Rizvi, "Cobalt Source Calibration," WSRC-TR-99-00303, Rev. 1, October 5, 1999.
[8] R. M. Wallace, "Explosion Hazard of Mercury and Silver Oxalates During Cleaning of Tank 16H," DPST-78-258, February 24, 1978.
[9] W. R. Wilmarth, "Mercury Fulminate and Mercury Oxalate Synthesis and Associated Sludge Testing," I-WPT-001, January 21, 1999.
[10] W. R. Wilmarth, "Contingency Plan for Shock-Sensitive Compound Handling," SRT-LWP-98-0123, Rev. 1, July 31, 1998.
[11] "Mercury Oxalate," SRS Material Safety Data Sheet Equivalent #26988.00.
[12] "Mercury Fulminate," SRS Material Safety Data Sheet Equivalent # 26970.00.
[13] R. Meyre, "EXPLOSIVES," 2nd ed., Verlag Chemie, 1981, Deerfield Beach, FL.
[14] K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," John Wiley & Sons, 1968.

6 Approval

Fernando Fondeur 1-10-2000

F. Fondeur, Task Leader — Date
Waste Processing Technology

1-10-2000

W. R. Wilmarth, — Date
Waste Processing Technology

D.T. Hobbs 1-10-2000

D. T. Hobbs, Design Checker — Date
Waste Processing Technology

Samuel D. Fink 1-10-2000

S. D. Fink, Level 4 Manager, — Date
Waste Processing Technology

1-18-2000

B. L. Lewis — Date
CST Engineering Support

F. F.Fondeur

DISTRIBUTION

T. E. Britt, 703-H
B. L. Lewis, 703-H
W. L. Tamosaitis, 773-A
S. D. Fink, 773-A
W. B. Van-Pelt, 773-43A
M. J. Barnes, 773-A
R. F. Swingle, 773-A
W. R. Wilmarth, 773-42A
M. S. Hay, 773-42A
P. E. Lowe, 773-41A
F. F. Fondeur, 773-A
D. T. Hobbs, 773-A
L. O. Dworjanyn, 735-11A
R. H. Ross, 703-H
G. J. Hutchens, 703-H
T. A. Nance, 723-A
E. J. Freed, 742-5G
S. R. Wilson, 704-28S
TIM
LWP Files c/o C. Canada, 773-A