The Stabilization of Polymeric Materials Generated in Nuclear Materials Applications Using Pyrolysis with Catalytic Oxidation

Daniel J. Kathios
Los Alamos National Laboratory
Nuclear Materials Technology Group, NMT-2
Mail Stop E511, Los Alamos, New Mexico 87545

American Institute of Chemical Engineers
1998 Annual Meeting
General Topics in Environmental Reaction Engineering Session

Miami, Florida
November 18, 1998

LA-UR-98-4697
Assessment of Problem

- Polycubes are mixtures of plutonium and uranium oxides that are cast in a polystyrene matrix.
- The polycubes were fabricated during the Cold War for the purpose of conducting criticality studies.
Assessment of Problem

• Approximately 1600 polycubes are in storage at Hanford.
  > The polycubes are in a variety of sizes, the largest of which is 2 inches x 2 inches x 2 inches.
  > Some of the polycubes are coated with aluminum paint, PVC tape, or Shurtape.
  > The polycubes are now packaged in vented food pack cans with 5 to 8 cubes per can.
  > The presence of Pu$^{240}$ and Am in the polycubes causes them to represent a significant exposure hazard.

• *The polycubes are not suitable for long-term storage.*
Goal of Stabilization Effort

• The goal of this stabilization effort is to design, optimize, and build a pyrolysis process to stabilize the remaining inventory of polycubes at Hanford.

• Requirements for the pyrolysis process:
  > It must effectively destroy the polymer matrix and remove it from the oxides of plutonium and uranium.
  > It must be suitable for glovebox operations.
  > It must allow for minimal handling of the polycubes.
  > It must be complete with off-gas treatment to oxidize the hydrocarbons resulting from the decomposition of the polymer matrix.
A pyrolysis reactor was designed and built at Los Alamos specifically for this application.

The reactor is built to be “user-friendly” for glovebox operations.
Three oxidation processes were evaluated to process the reactor off-gas.

1. Thermal Oxidation
2. Catalytic Conversion
3. Silent Discharge Plasma

The Oxidation Processes

- Pressure Gauge
- House Air
- Reactor Off-Gas
- CO₂, H₂O, N₂, etc.
- Pyrolysis Unit (2500 Watt Furnace)
- Furnace Controller
- House Argon
- House Air

Oxidation Process
1. Thermal Oxidation
2. Catalytic Conversion
3. Silent Discharge Plasma
The Performance of the Pyrolysis Reactor

Polycube Before Pyrolysis

Composition of a polycube:

- Polystyrene: 134.7 grams
- Al paint: 1.4 grams
- PVC tape: 4.2 grams
- Shurtape: 6.9 grams
- Total mass: 147.2 grams
The Performance of the Pyrolysis Reactor

Dry Solids Left in Reactor After Pyrolysis

- Composition of the dry solids:
  - The dry solids are presumed to be a form of carbon.
  - *Total mass:* 6.9 grams

- Only 4.7% of the original mass of the polymer matrix remains in the reactor.

- The dry solids are to be calcined to remove any residual carbon, and then packaged in a 3013 storage container.
The Performance of the Pyrolysis Reactor

Liquid Phase Fraction of the Reactor Off-Gas

• Composition of the liquid phase:
  - Styrene: 52.4 grams
  - Toluene: 11.6 grams
  - Ethylbenzene: 10.2 grams
  - Other cmpds.: 53.1 grams
  - Total mass: 127.3 grams

• Most (86.5%) of the decomposition products of the polymer matrix are liquid phase compounds.
The Performance of the Pyrolysis Reactor

• Composition of the Vapor Phase:
  > The vapor phase contained volatilized versions of the compounds found in the liquid phase (i.e., styrene, toluene, etc.).
  > The vapor phase also had appreciable amounts of vinyl chloride, chloroethane, and 1,2-dichloroethane resulting from the decomposition of the PVC tape.
  > Total mass: 13.0 grams

• Approximately 8.8% of the decomposition products of the polymer matrix are vapor phase compounds.
Rate of Off-Gas Generation  
- Pyrolysis of a Single Polycube -

Off-Gas Generation Rate (grams/minute)

Time (minutes)

- Polystyrene cube
- Polystyrene pellets (crushed cube simulant)
- Cube with Al paint
- Cube with PVC tape and Shurtape
- Cube with Al paint, PVC tape, and Shurtape

Polystyrene cube 4.6 g/min
Polystyrene pellets 4.8 g/min
Cube with Al paint 4.6 g/min
Cube with PVC tape and Shurtape 5.2 g/min
Cube with Al paint, PVC tape, and Shurtape 5.2 g/min
Pyrolysis Process with Catalytic Conversion
- Configured with Condense and Treat Option -

- Heat Exchanger - Catalytic Converter - RV Chamber - Pump - Collection Reservoir - Pyrolysis Unit - Argon Feed - Air Feed
The catalyst evaluated is the PRO*HHC VOC catalyst from Prototech Company.

- The catalyst is designed to be resistant to acids formed when oxidizing halogenated hydrocarbons.
- The catalyst is in the form of 1/4 inch pellets. This facilitates handling in glovebox applications.
Three factors are used to evaluate the performance of the catalytic converter.

> Oxidation efficiency
> Selectivity
> Catalyst longevity
Composition of the Effluent Stream Leaving the Catalytic Converter

Time (hours)

Concentration in Effluent Stream (ppm)

0.0 2.0 4.0 6.0 8.0 10.0

CO₂

Total Hydrocarbons

CO
The Performance of the Catalytic Converter

• **Oxidation Efficiency:**
  > The oxidation efficiency of the catalytic converter is greater than 99.0%.
  > The oxidation efficiency surpasses the 99.0% design specification required by Hanford.

• **Selectivity:**
  > The \([\text{CO}_2]/[\text{CO}]\) selectivity is greater than 800.
  > The catalytic converter not only oxidizes the hydrocarbons, it oxidizes them completely to \(\text{CO}_2\).
Oxidation Efficiency of the Catalytic Converter

Oxidation efficiency of the catalytic converter at processing the liquid and vapor phase fractions of the reactor off-gas.

\[
\text{Oxidation Efficiency} = 100 \times \frac{[\text{CO}_2] + [\text{CO}]}{[\text{THC}]_{\text{feed}}} \text{ formed}
\]
Selectivity of the Oxidation Process

Selectivity = \frac{[\text{CO}_2]_{\text{formed}}}{[\text{CO}]_{\text{formed}}}

Selectivity of the oxidation process at processing the liquid and vapor phase fractions of the reactor off-gas.
The Overall Performance of the Process

• **Catalytic Converter:**
  > The performance of the catalyst decreased only slightly during the duration of the pilot-scale test. The oxidation efficiency decreased approximately 0.05% per 30 polycubes processed.

• **Other Units:**
  > There was no noticeable deterioration in the performance of the pyrolysis unit, the air preheater, the pump, etc.
Reduction in Mass of Characteristic Glovebox Materials Subject to Pyrolysis

<table>
<thead>
<tr>
<th>Category 1 Materials</th>
<th>Mass Percent of Material Remaining after Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose rags</td>
<td>(reduced 79.7%)</td>
</tr>
<tr>
<td>Cellulose rags soaked in 15.7 M HNO₃ and dried</td>
<td>(reduced 82.7%)</td>
</tr>
<tr>
<td>Phenolic screw caps</td>
<td>(reduced 47.0%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Category 2 Materials</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC bag-out bag</td>
<td>(reduced 83.0%)</td>
</tr>
<tr>
<td>Yellow vinyl tape</td>
<td>(reduced 71.7%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Category 3 Materials</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic cord from bag-out bag</td>
<td>(reduced 85.7%)</td>
</tr>
<tr>
<td>Tygon tubing</td>
<td>(reduced 91.3%)</td>
</tr>
<tr>
<td>Dowex 11 anion exchange resin, chloride form</td>
<td>(reduced 89.6%)</td>
</tr>
<tr>
<td>Polypropylene rags</td>
<td>(reduced 99.0%)</td>
</tr>
<tr>
<td>Polypropylene rags soaked in 15.7 M HNO₃ and dried</td>
<td>(reduced 99.1%)</td>
</tr>
<tr>
<td>Polyethylene plastic bags</td>
<td>(reduced 98.7%)</td>
</tr>
<tr>
<td>Polyethylene plastic bottles</td>
<td>(reduced 98.3%)</td>
</tr>
<tr>
<td>Teflon gasket material</td>
<td>(reduced 95.3%)</td>
</tr>
<tr>
<td>Teflon pipe fittings</td>
<td>(reduced 96.3%)</td>
</tr>
<tr>
<td>Nylon wire ties</td>
<td>(reduced 96.0%)</td>
</tr>
<tr>
<td>Polystyrene foam</td>
<td>(reduced 100.0%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Category 4 Materials</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene plastic bottles</td>
<td>(reduced 98.3%)</td>
</tr>
<tr>
<td>Teflon gasket material</td>
<td>(reduced 95.3%)</td>
</tr>
<tr>
<td>Teflon pipe fittings</td>
<td>(reduced 96.3%)</td>
</tr>
<tr>
<td>Nylon wire ties</td>
<td>(reduced 96.0%)</td>
</tr>
<tr>
<td>Polystyrene foam</td>
<td>(reduced 100.0%)</td>
</tr>
</tbody>
</table>