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

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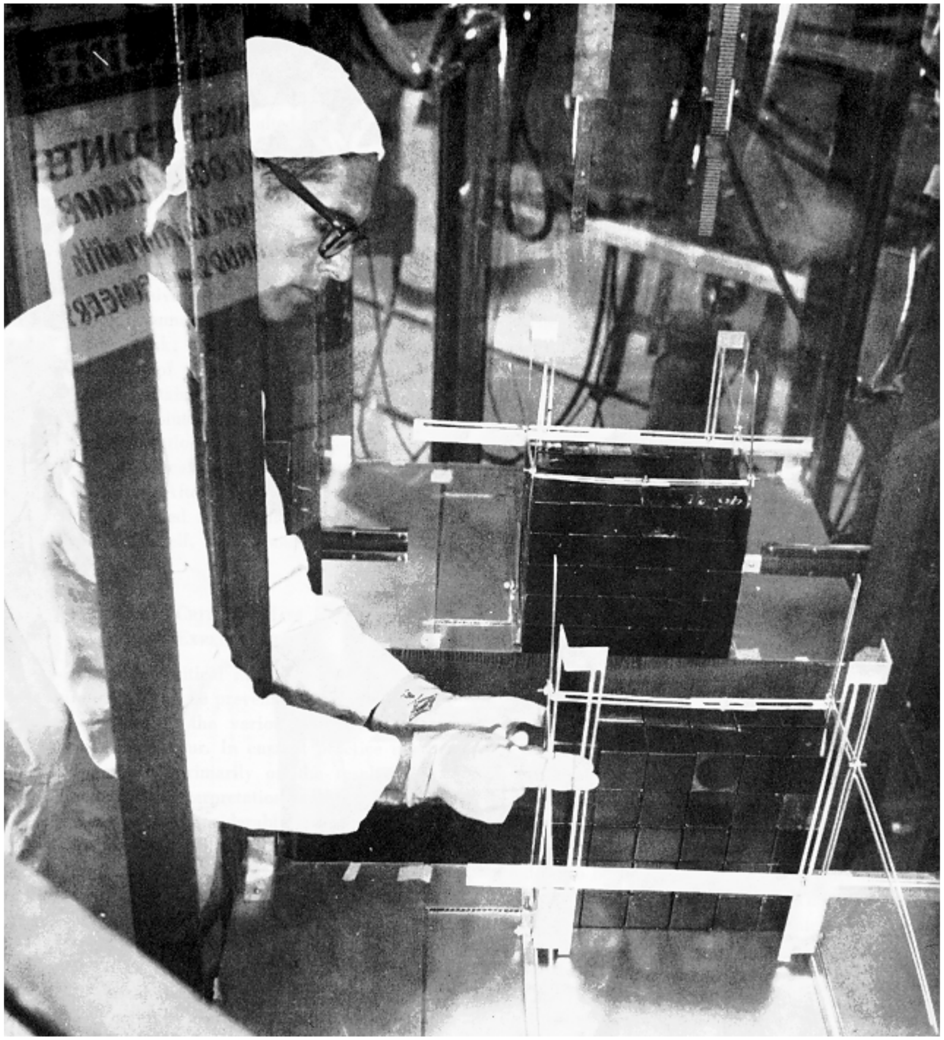
Assessment of Problem



- 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.

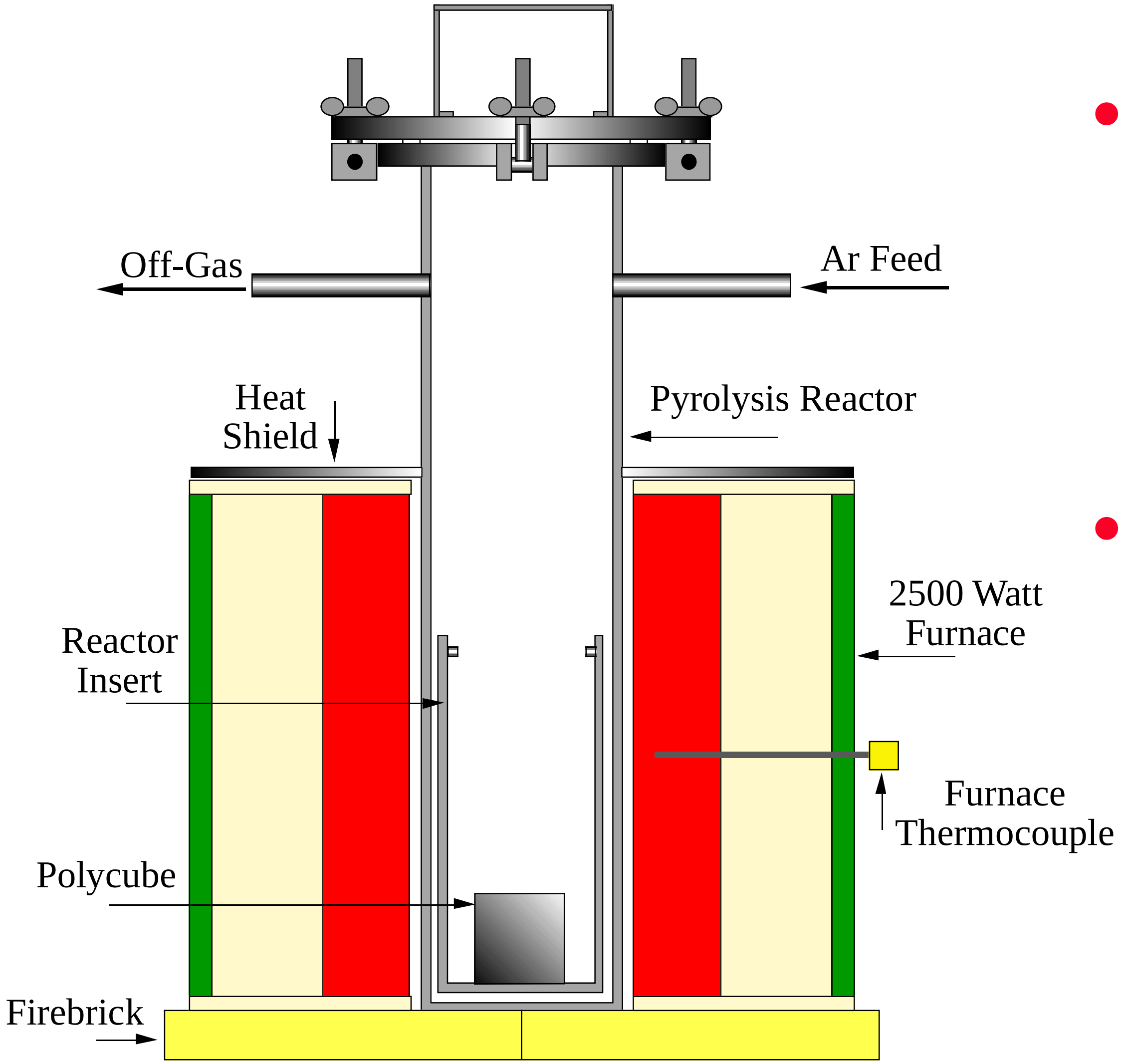
Assessment of Problem

- 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

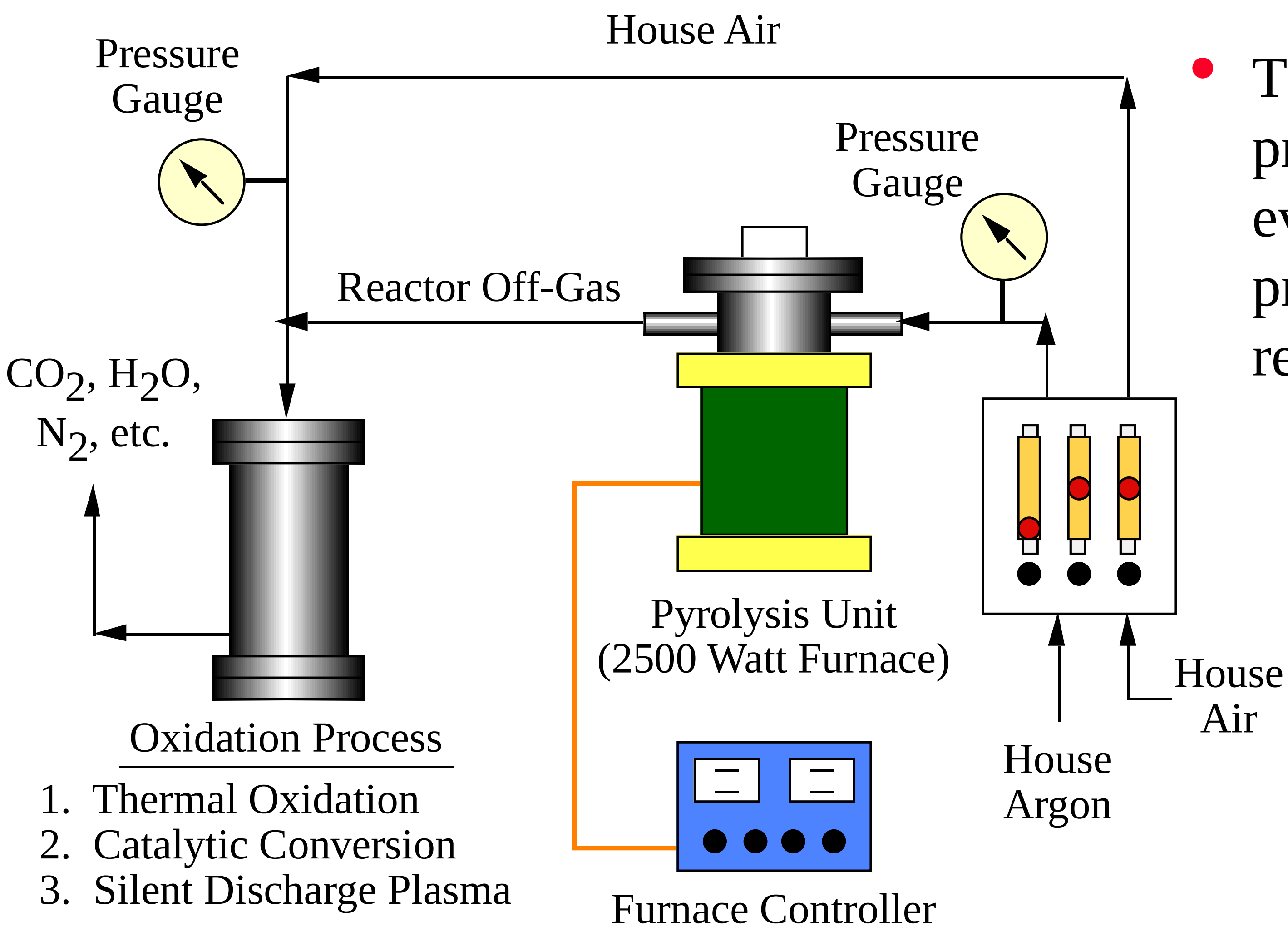
- The goal of this stabilization effort is to design, optimize, and build a pyrolysis process to stabilize the remaining inventory of polycubes at Hanford.
- Requirements for the pyrolysis process:
  - It must effectively destroy the polymer matrix and remove it from the oxides of plutonium and uranium.
  - 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.

The Pyrolysis Reactor



- 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.

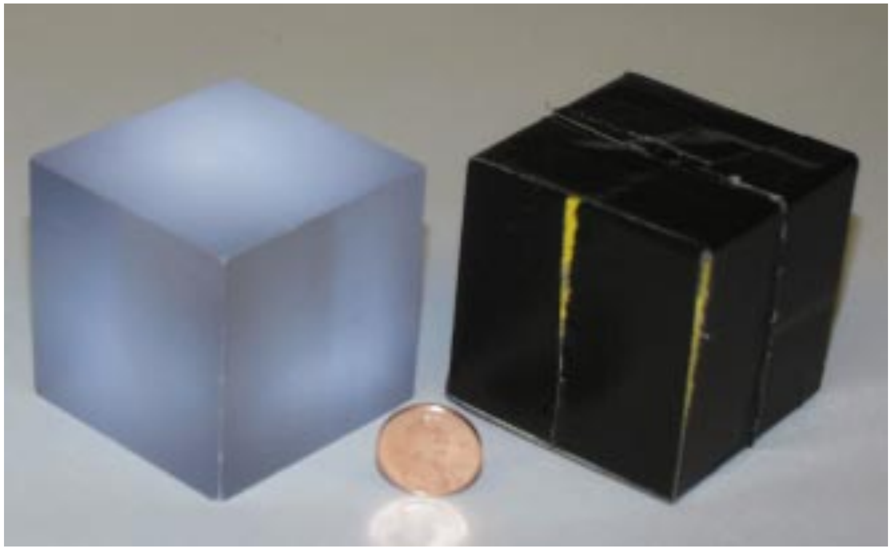
The Oxidation Processes



- Three oxidation processes were evaluated to process the reactor off-gas.

The Performance of the Pyrolysis Reactor

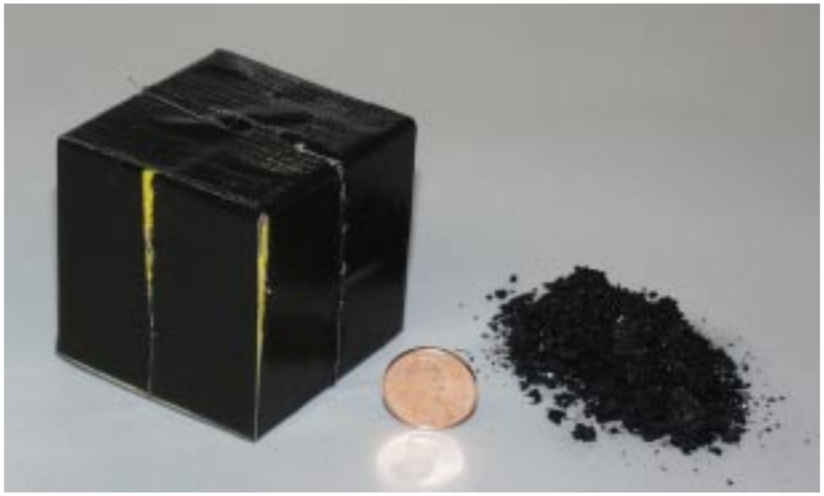
Polycube Before Pyrolysis



- 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

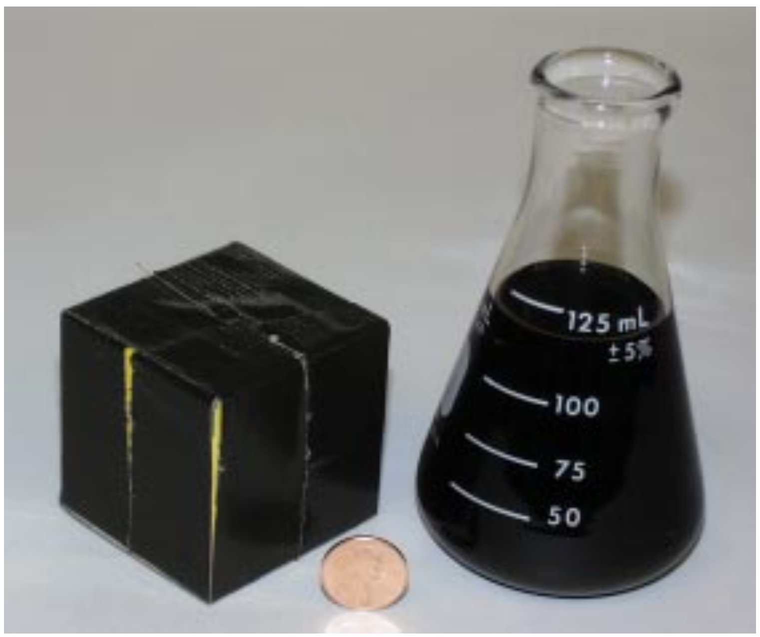
Dry Solids Left in Reactor After Pyrolysis



- 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

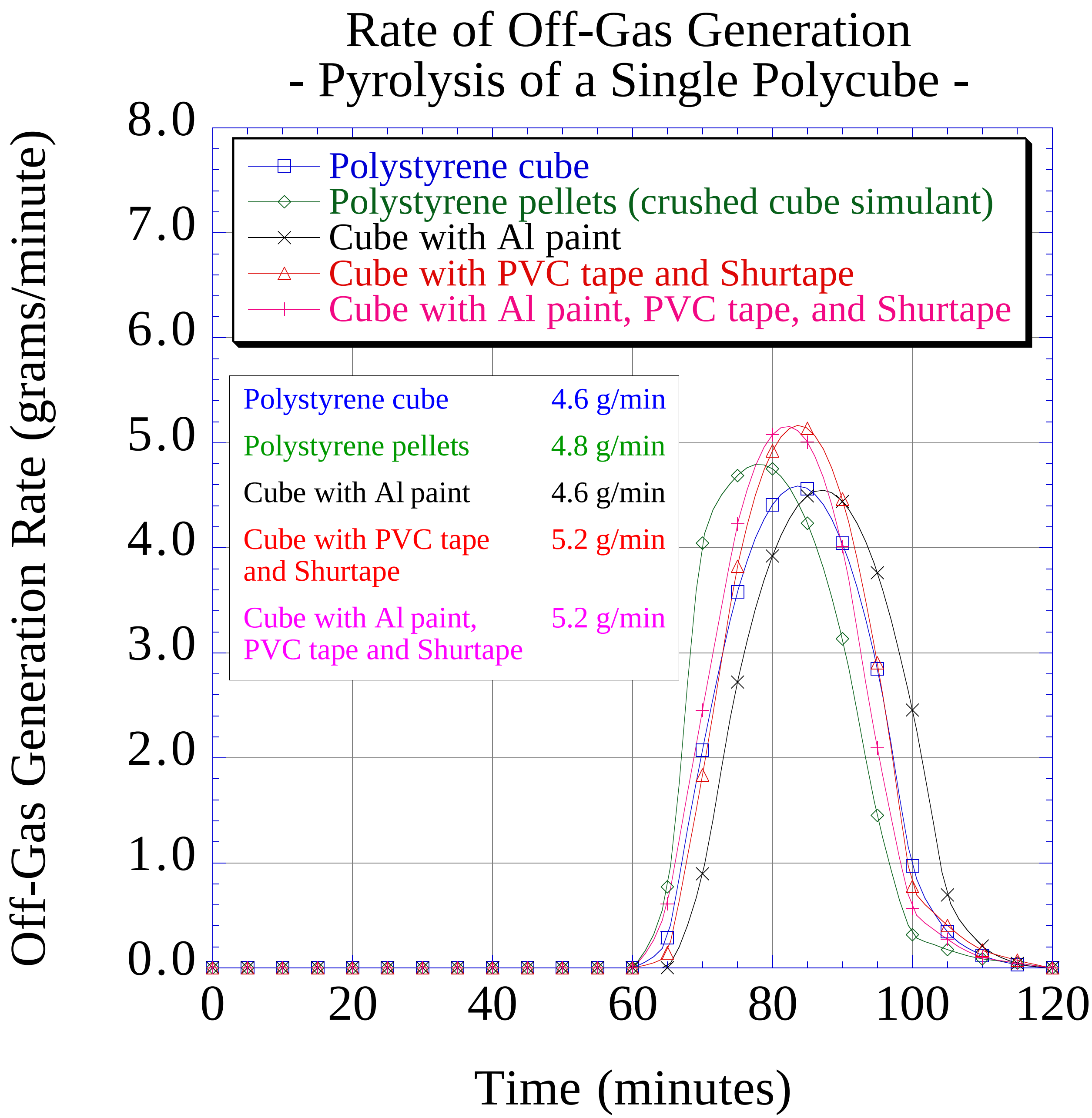
Liquid Phase Fraction of the Reactor Off-Gas



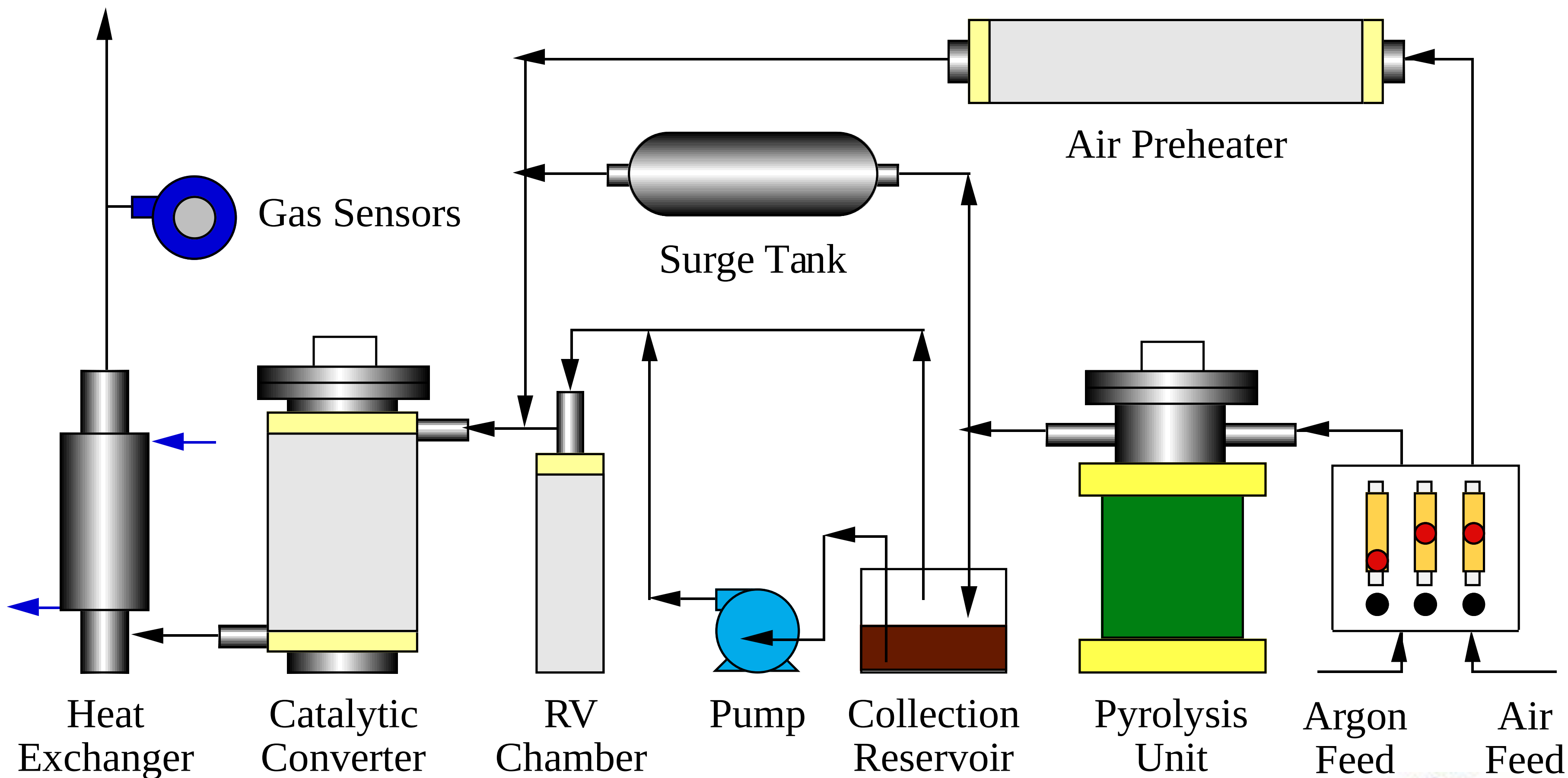
- Composition of the liquid phase:
  - > Styrene: 52.4 grams
  - > Toluene: 11.6 grams
  - > Ethylbenzene: 10.2 grams
  - > Other cmpds.: 53.1 grams
  - > *Total mass: 127.3 grams*
- Most (86.5%) of the decomposition products of the polymer matrix are liquid phase compounds.

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.

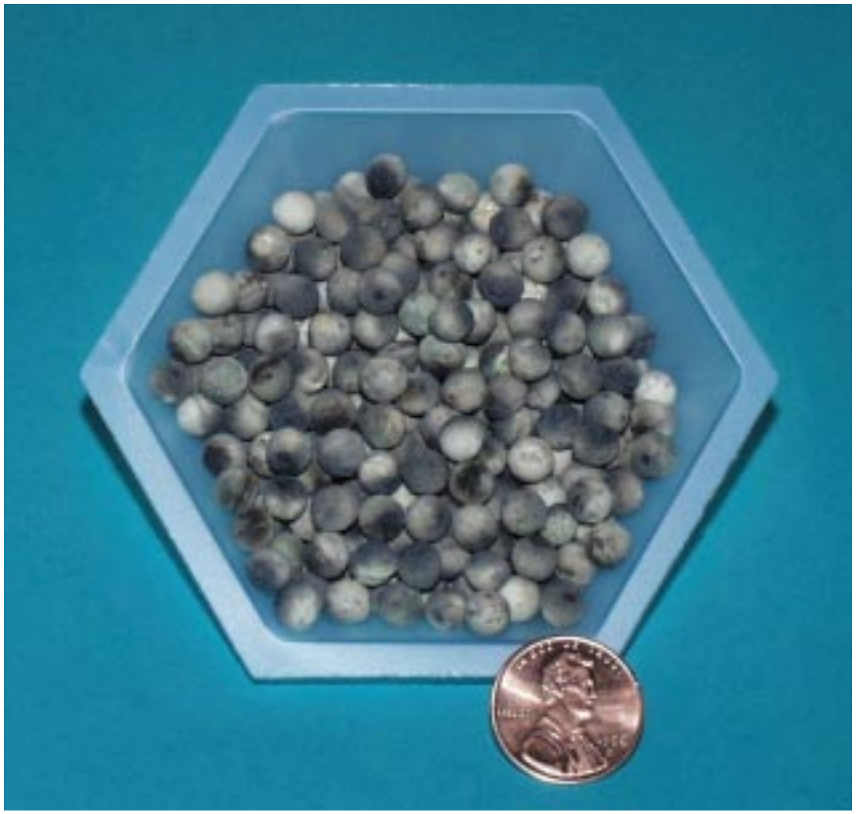

Rate of Off-Gas Generation
- Pyrolysis of a Single Polycube -
Off-Gas Generation Rate (grams/minute)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
100
120
Time (minutes)
Polystyrene cube
Polystyrene pellets (crushed cube simulant)
Cube with Al paint
Cube with PVC tape and Shurtape
Cube with Al paint, 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 -



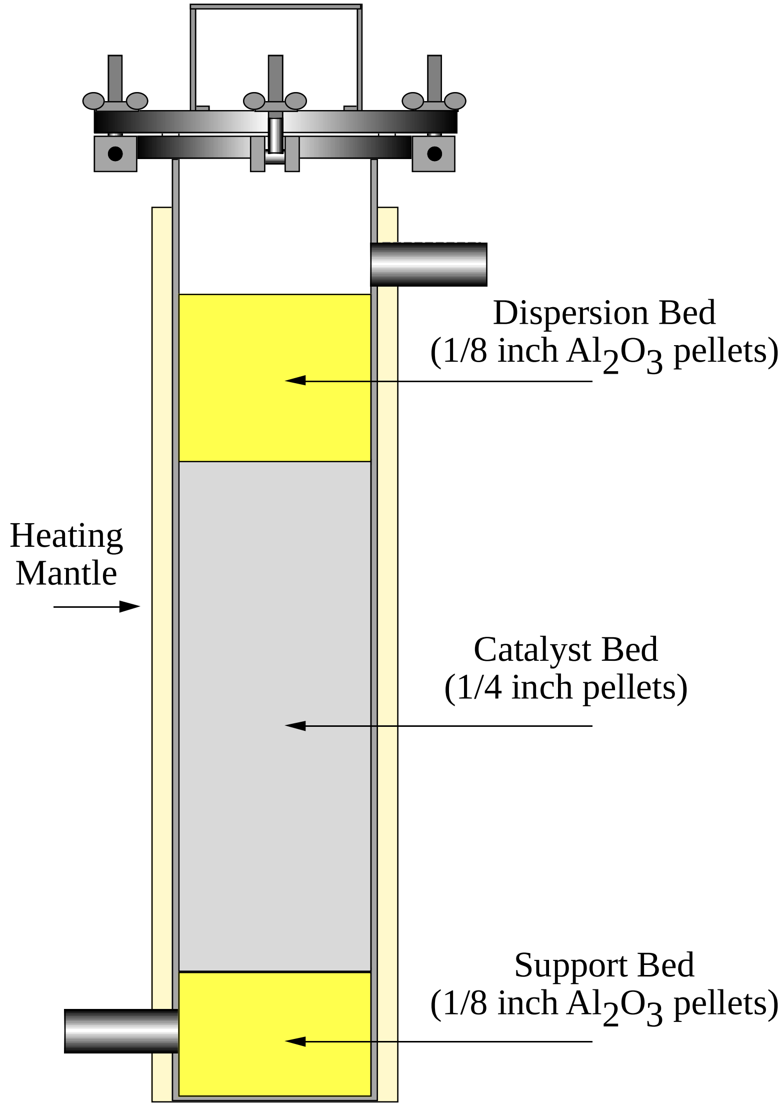
The Catalytic Converter

Catalyst

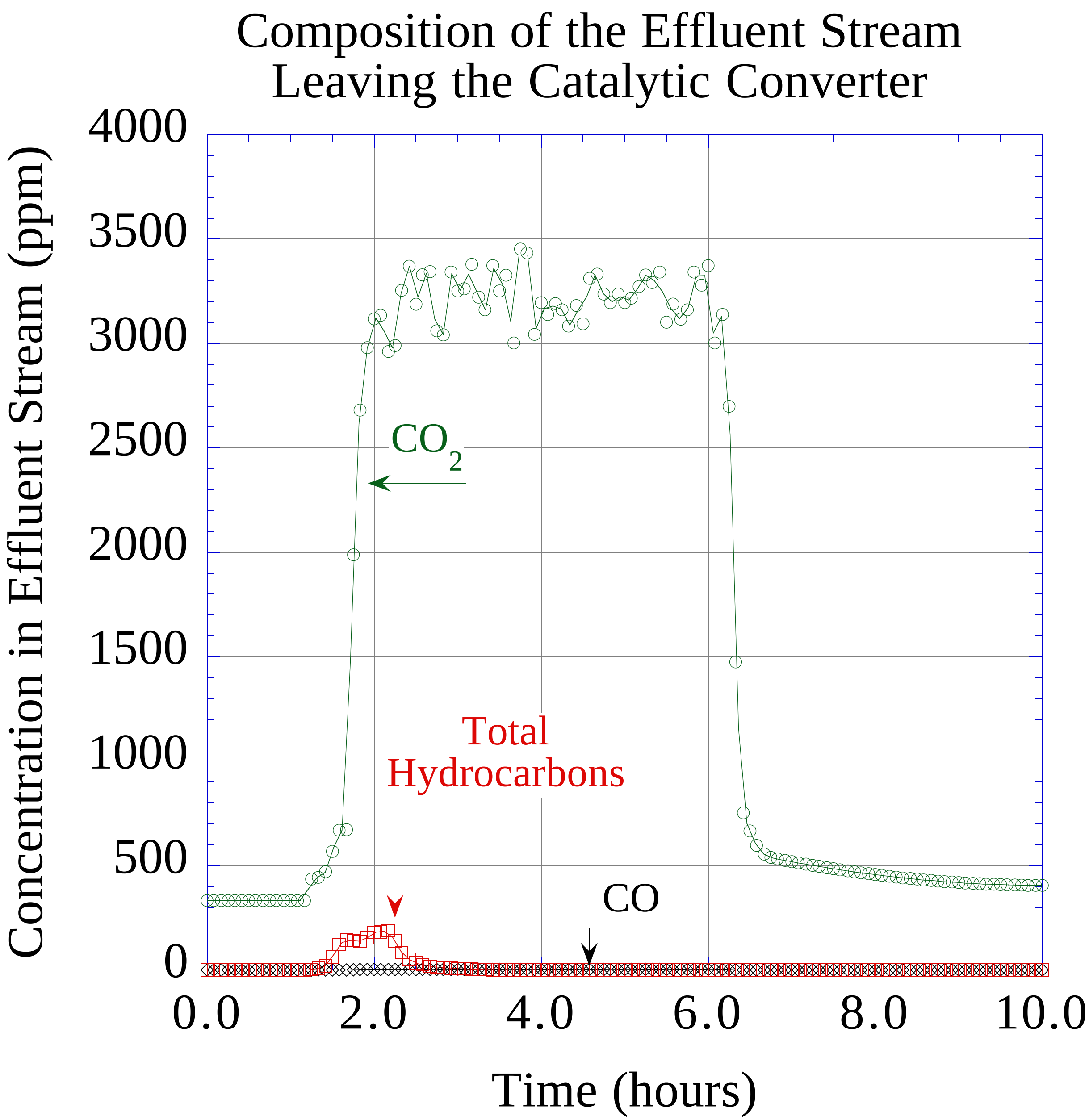


- The catalyst evaluated is the PRO*HHC VOC catalyst from Prototech Company.
  - > The catalyst is designed to be resistant to acids formed when oxidizing halogenated hydrocarbons.
  - > The catalyst is in the form of 1/4 inch pellets. This facilitates handling in glovebox applications.

The Catalytic Converter



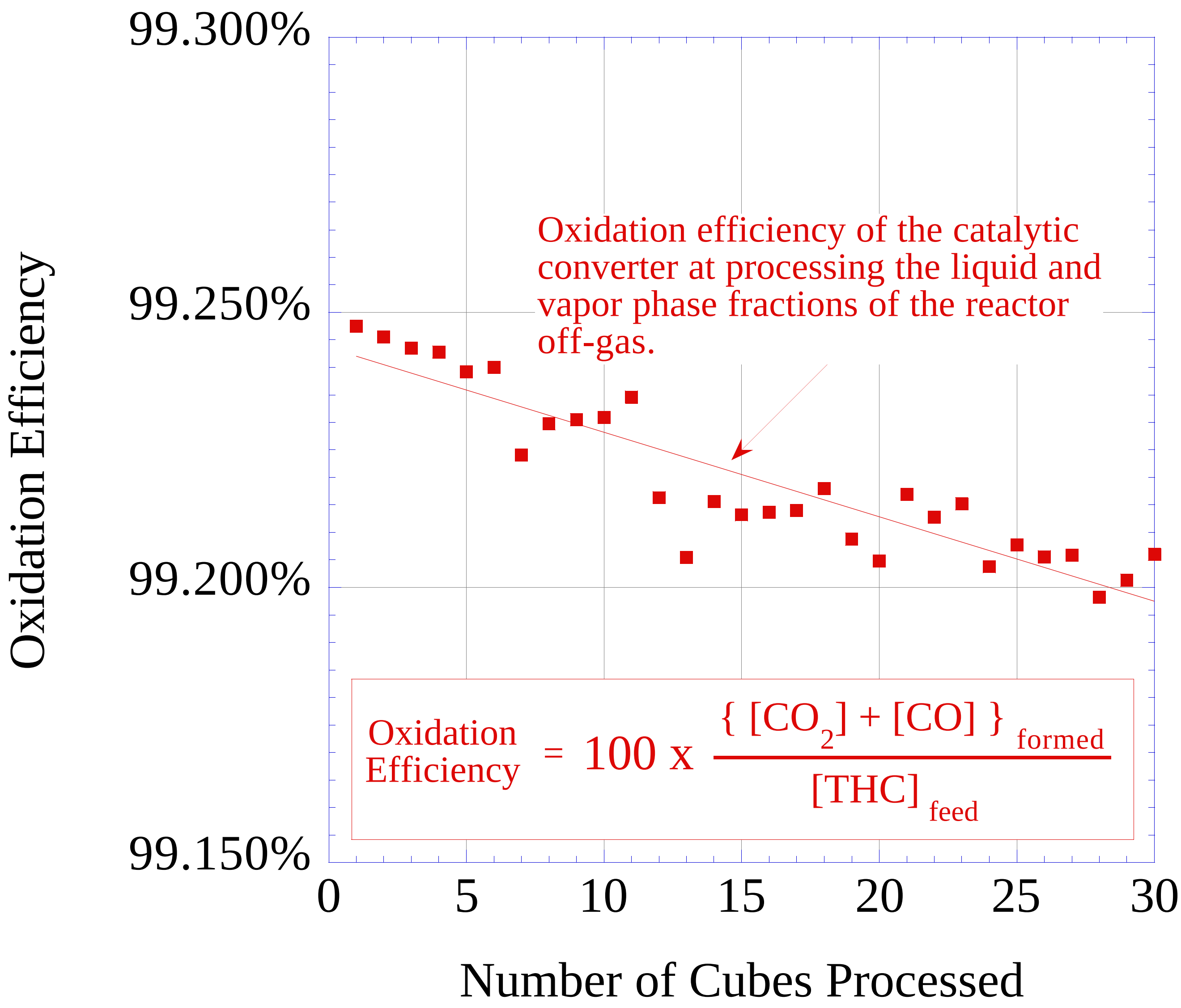
- Three factors are used to evaluate the performance of the catalytic converter.
  - Oxidation efficiency
  - Selectivity
  - Catalyst longevity


Composition of the Effluent Stream
Leaving the Catalytic Converter
4000
3500
3000
2500
2000
1500
1000
500
0
Concentration in Effluent Stream (ppm)
CO_2
Total
Hydrocarbons
CO
0.0
2.0
4.0
6.0
8.0
10.0
Time (hours)

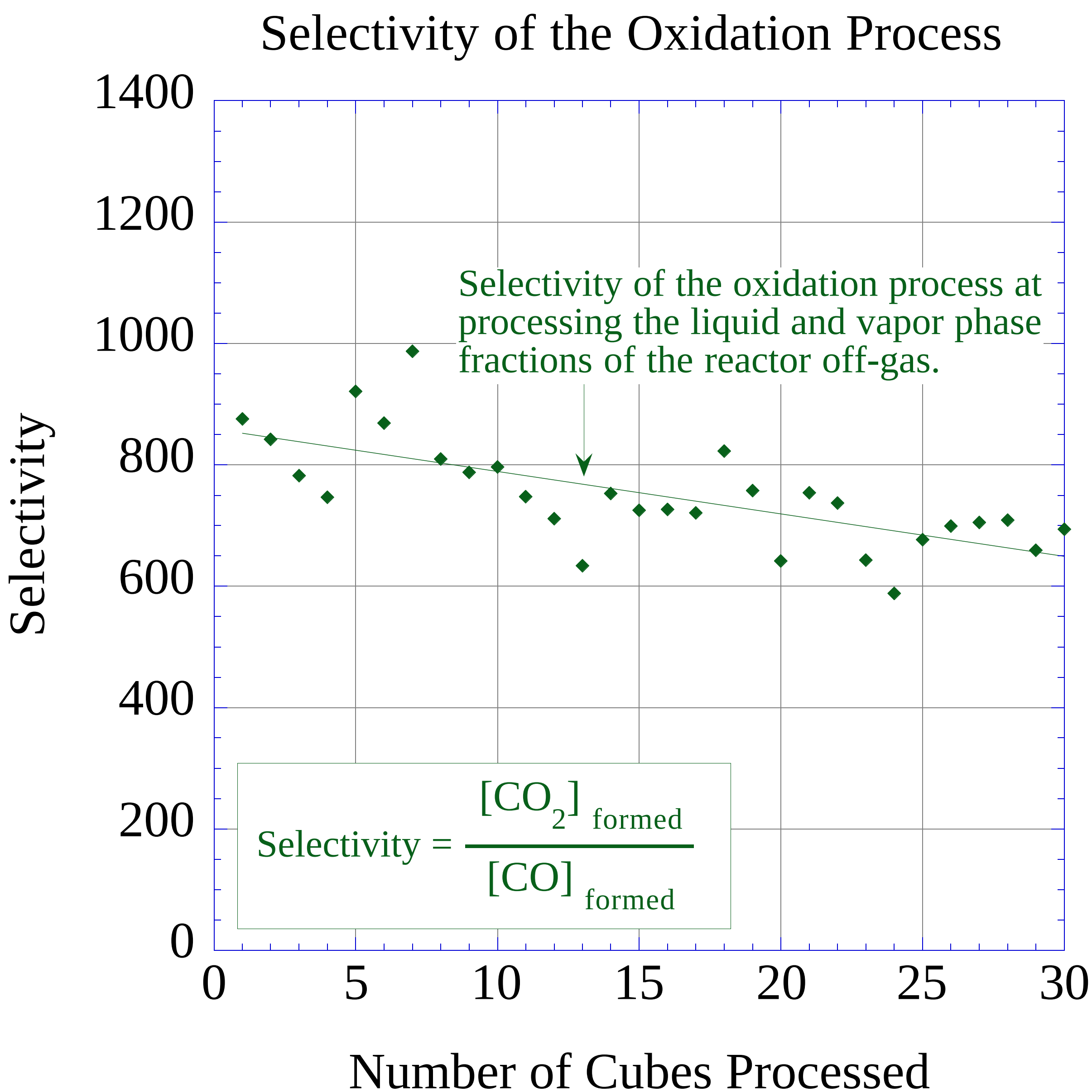
The Performance of the Catalytic Converter

- 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 $[CO_2]/[CO]$ selectivity is greater than 800.
  - The catalytic converter not only oxidizes the hydrocarbons, it oxidizes them completely to CO_2.

Oxidation Efficiency of the Catalytic Converter



$$\text{Oxidation Efficiency} = 100 \times \frac{\{[CO_2] + [CO]\}_{formed}}{[THC]_{feed}}$$



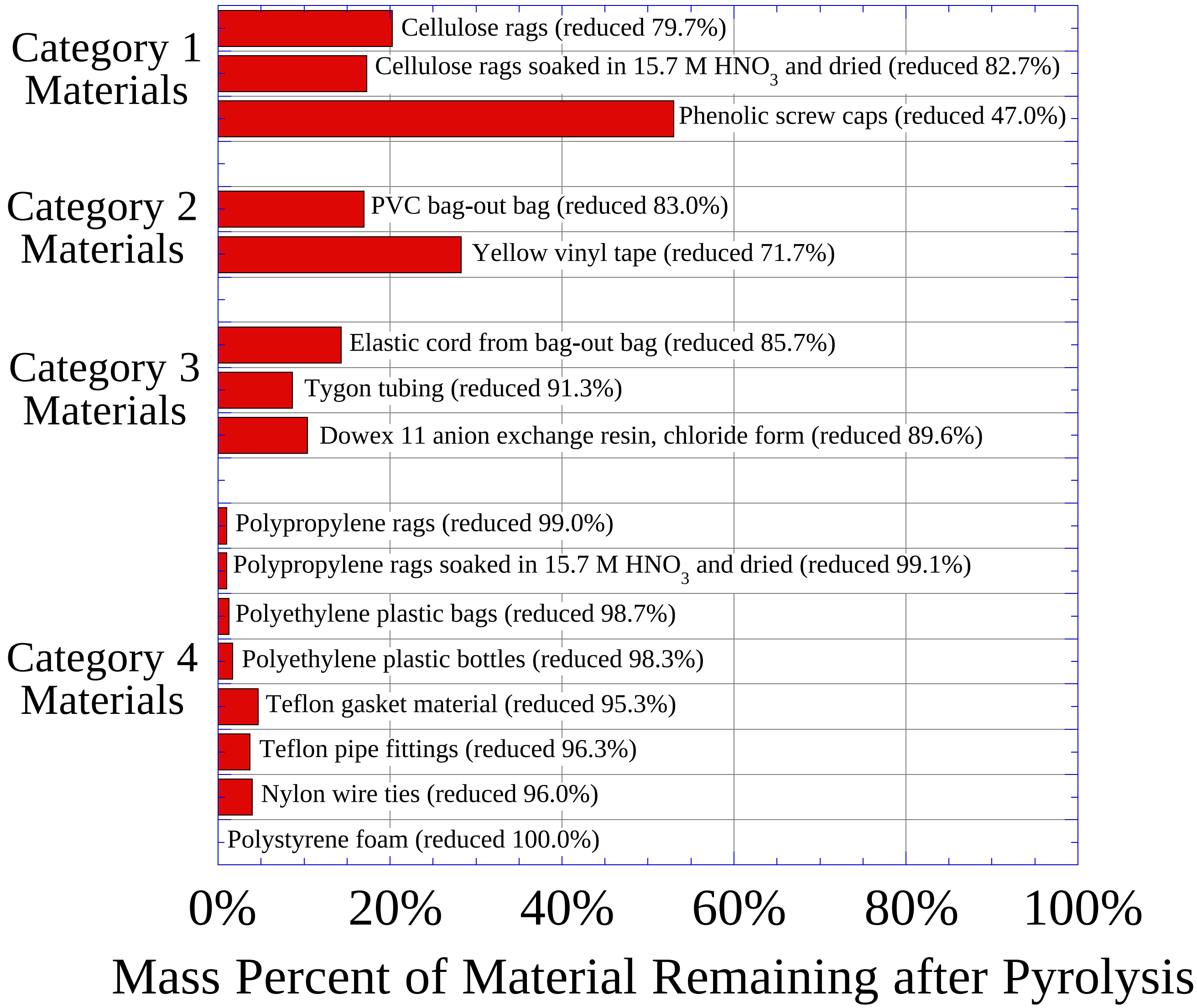
Selectivity of the Oxidation Process
Selectivity
Number of Cubes Processed
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
Selectivity of the oxidation process at processing the liquid and vapor phase fractions of the reactor off-gas.
Selectivity = [CO2] formed / [CO] formed

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



Plutonium Stabilization - Research & Development