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

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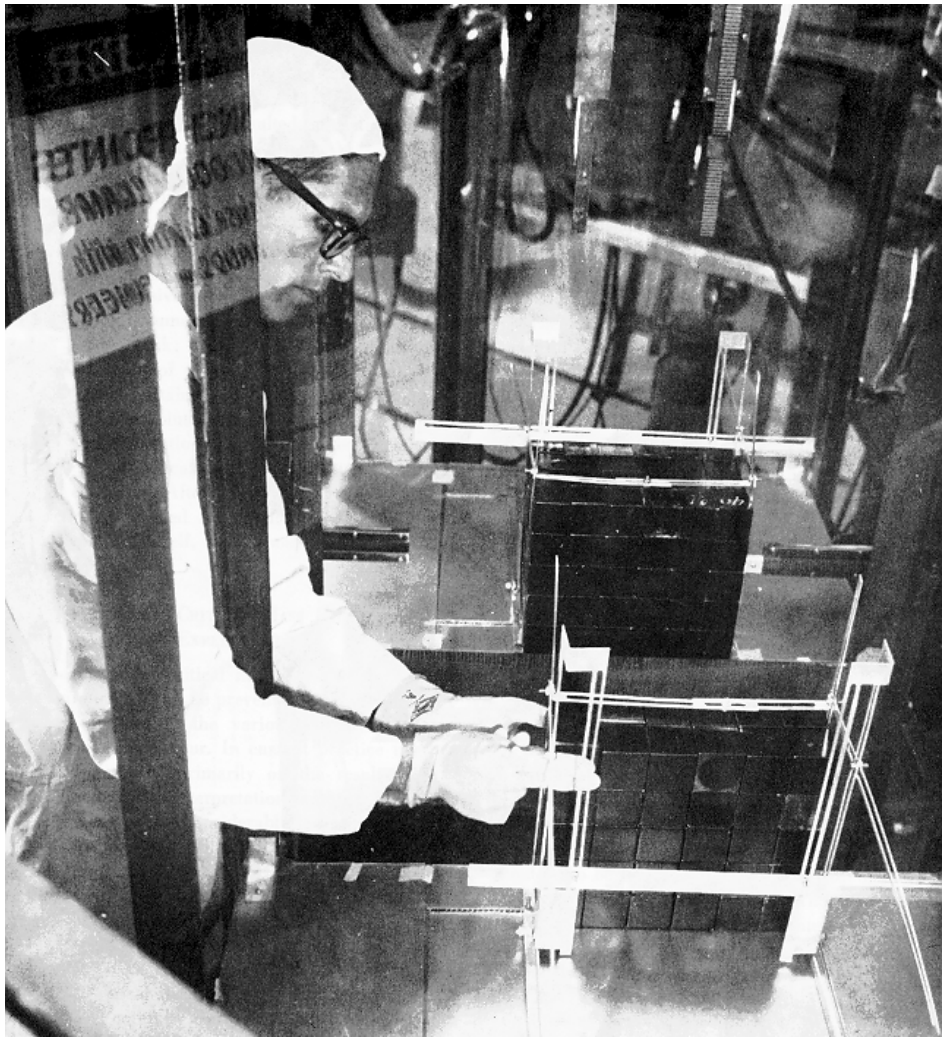
Assessment of Problem



- 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.

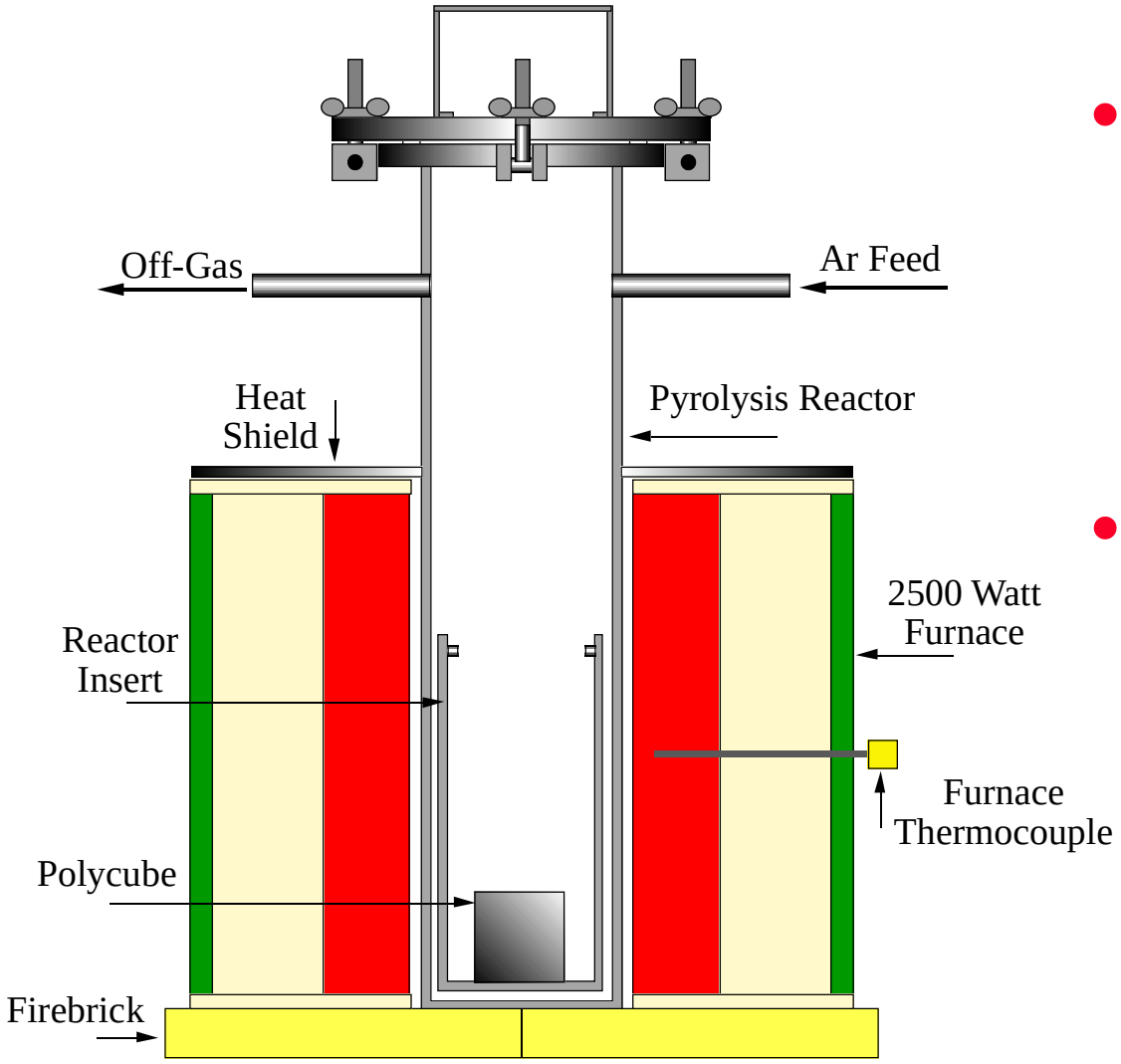
Assessment of Problem

- 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

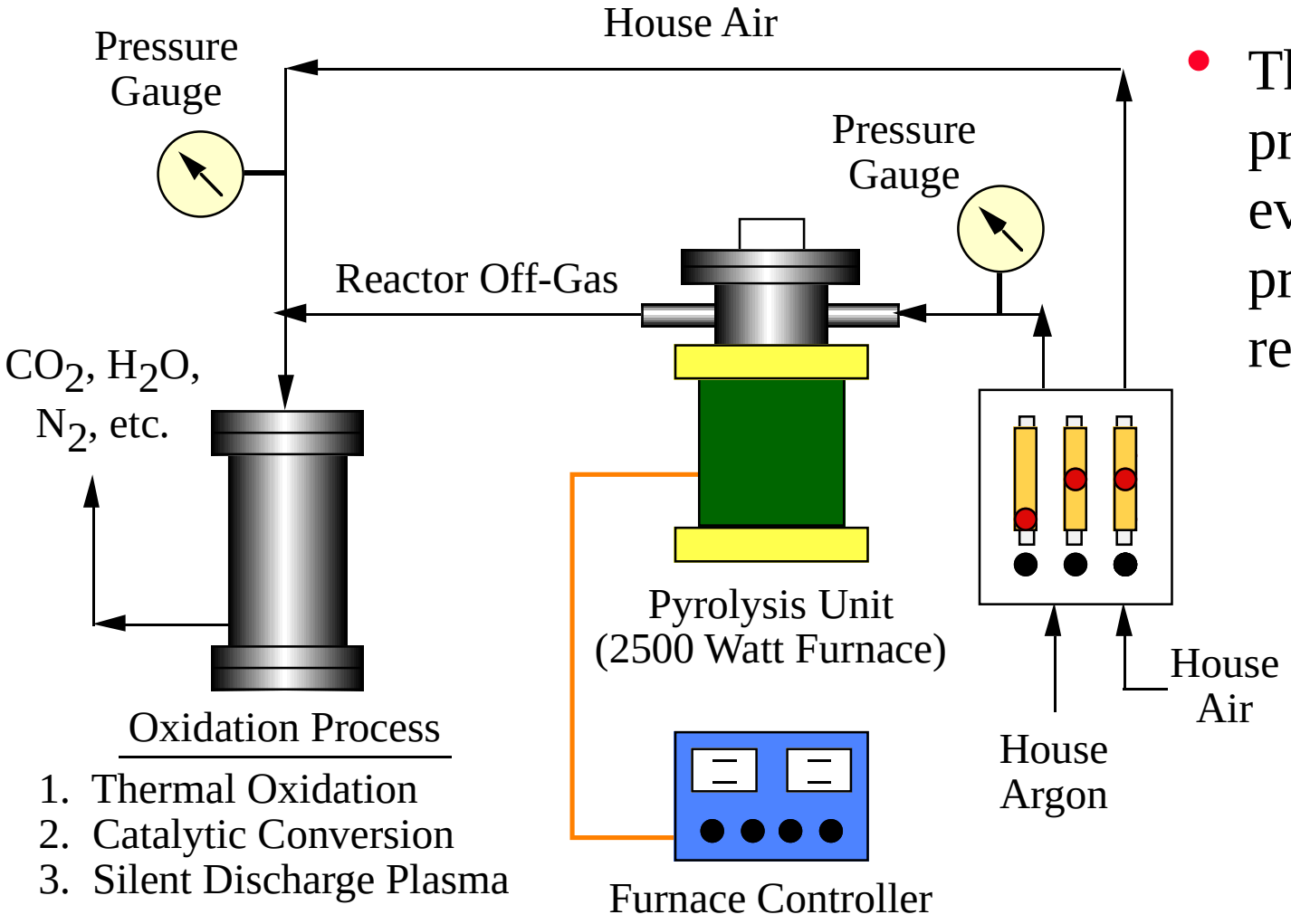
- The goal of this stabilization effort is to design, optimize, and build a pyrolysis process to stabilize the remaining inventory of polycubes at Hanford.
- Requirements for the pyrolysis process:
  - It must effectively destroy the polymer matrix and remove it from the oxides of plutonium and uranium.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

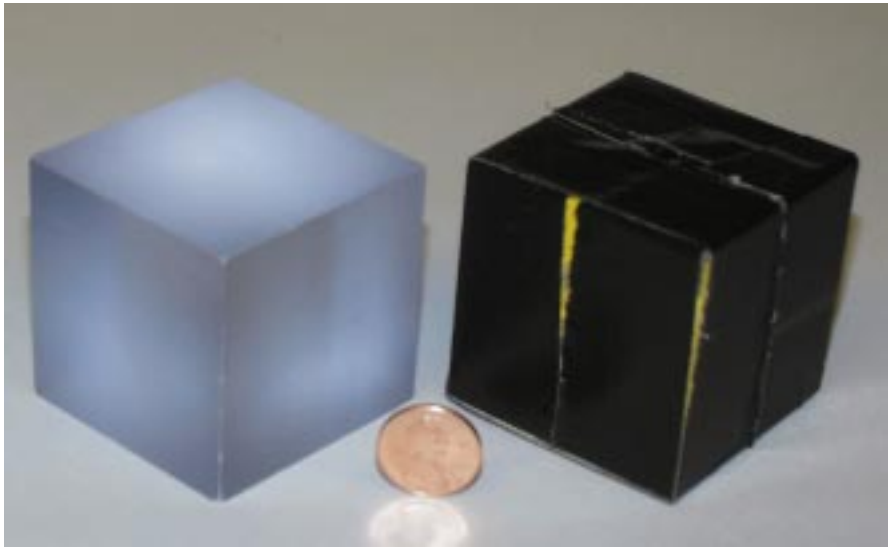
The Oxidation Processes



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

The Performance of the Pyrolysis Reactor

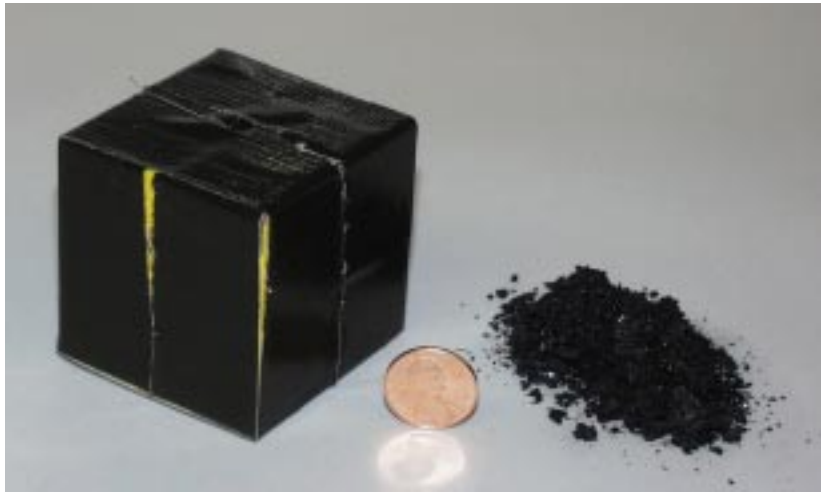
Polycube Before Pyrolysis



- 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

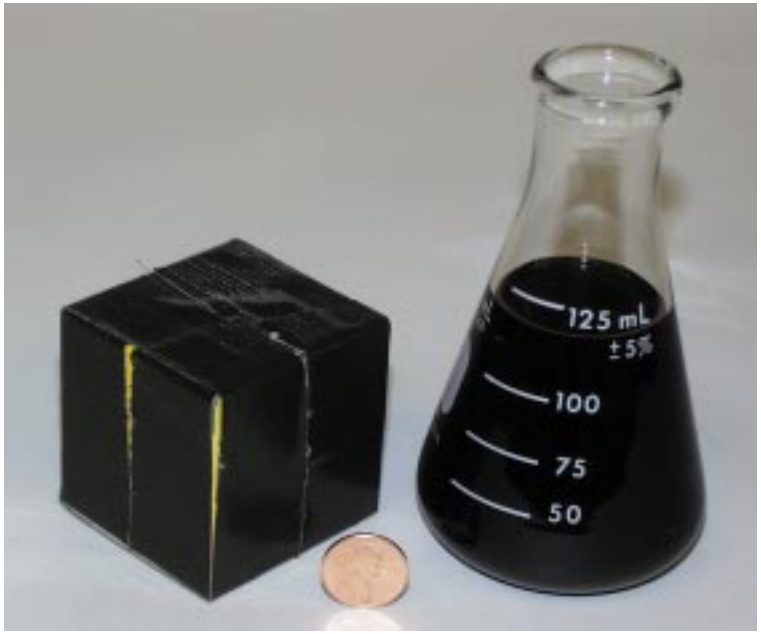
Dry Solids Left in Reactor After Pyrolysis



- 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

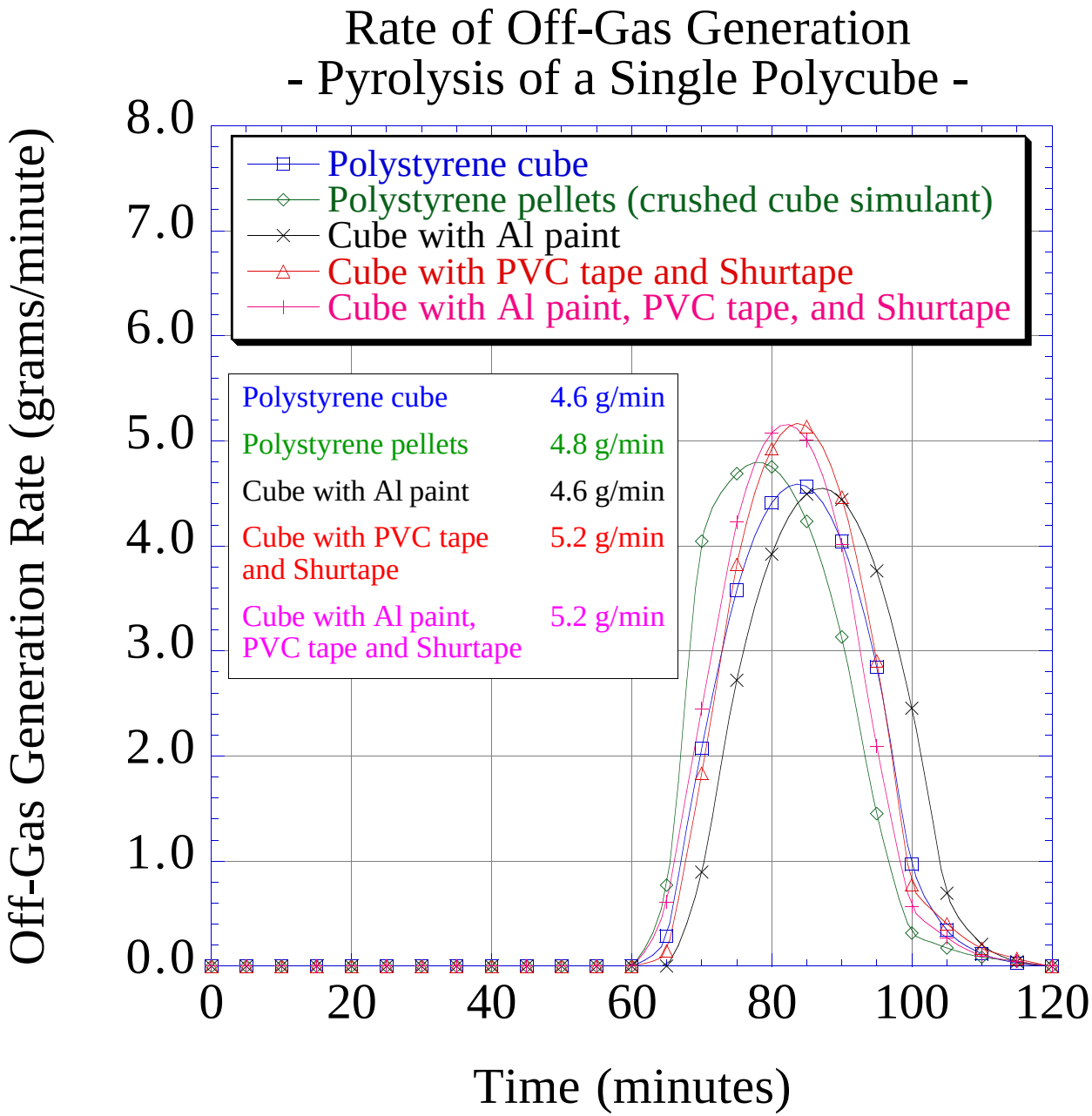
Liquid Phase Fraction of the Reactor Off-Gas



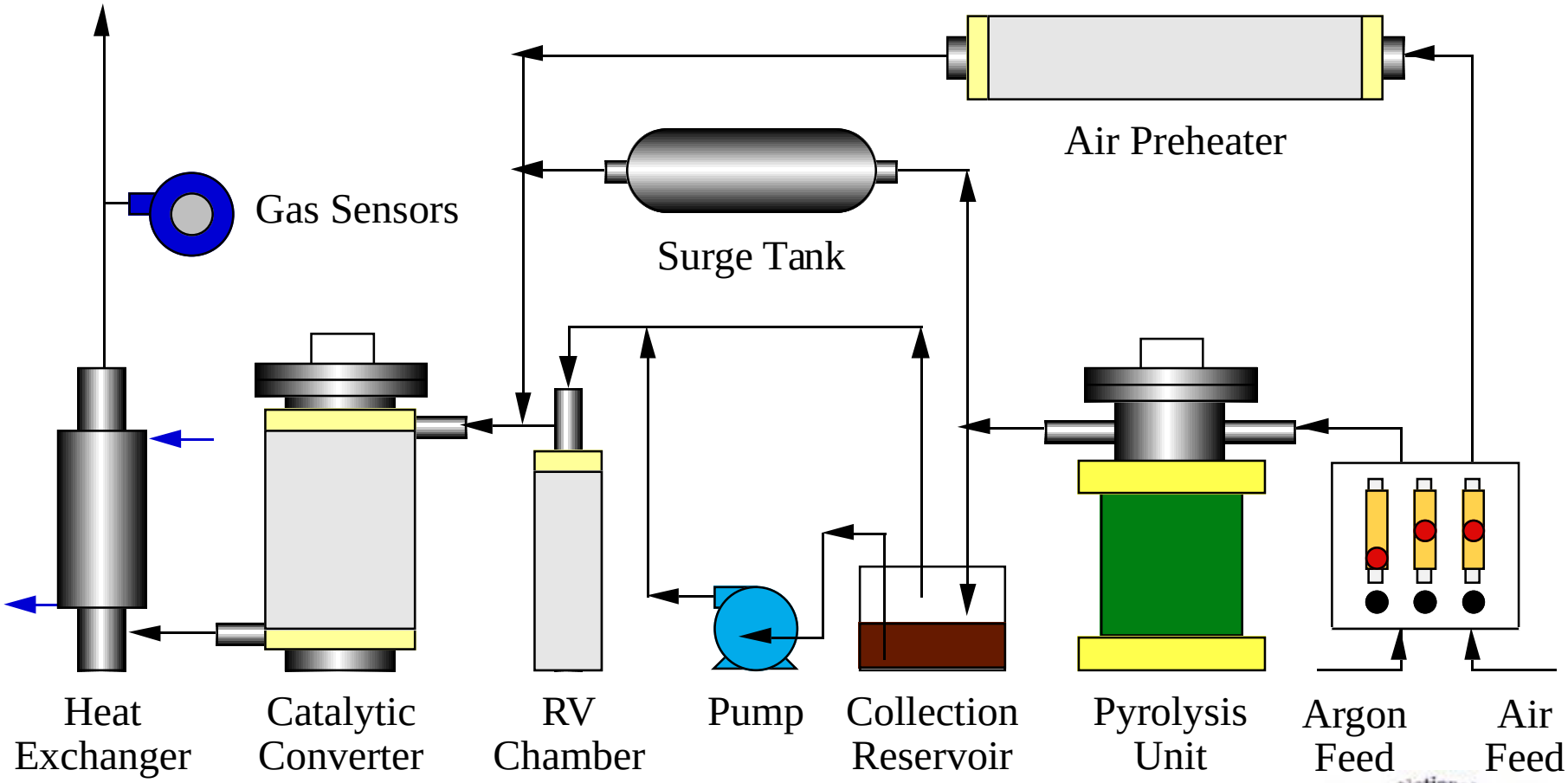
- Composition of the liquid phase:
  - Styrene: 52.4 grams
  - Toluene: 11.6 grams
  - Ethylbenzene: 10.2 grams
  - Other cmpds.: 53.1 grams
  - *Total mass: 127.3 grams*
- Most (86.5%) of the decomposition products of the polymer matrix are liquid phase compounds.

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.

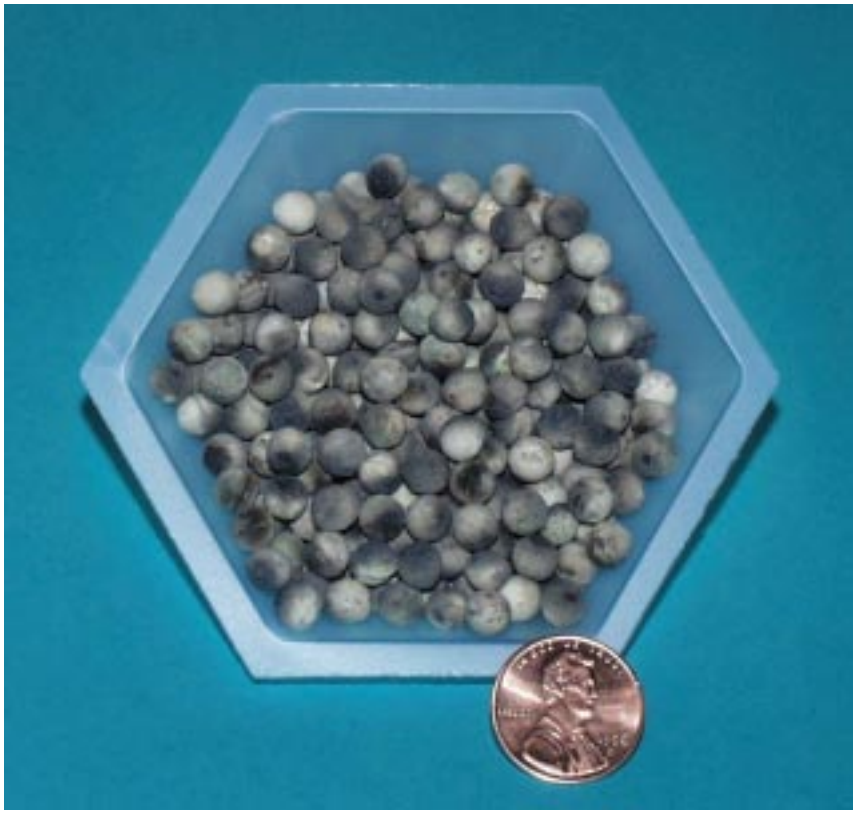

Rate of Off-Gas Generation
- Pyrolysis of a Single Polycube -
Off-Gas Generation Rate (grams/minute)
Time (minutes)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
100
120
Polystyrene cube
Polystyrene pellets (crushed cube simulant)
Cube with Al paint
Cube with PVC tape and Shurtape
Cube with Al paint,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



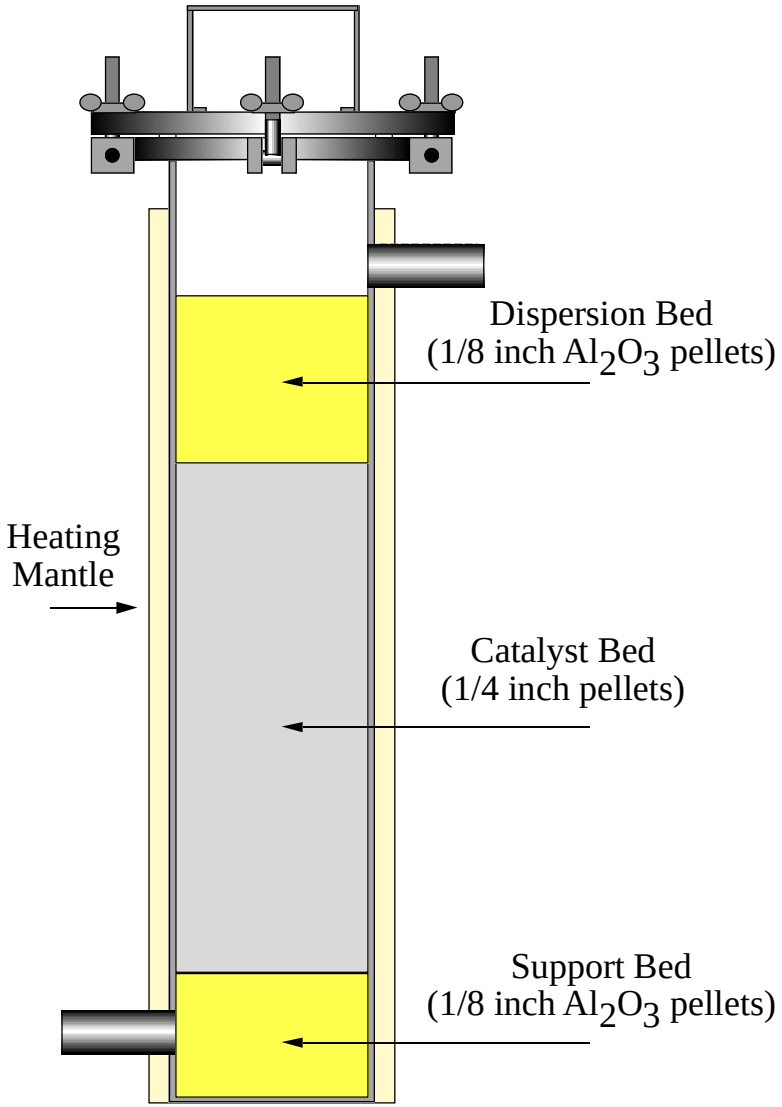
The Catalytic Converter

Catalyst

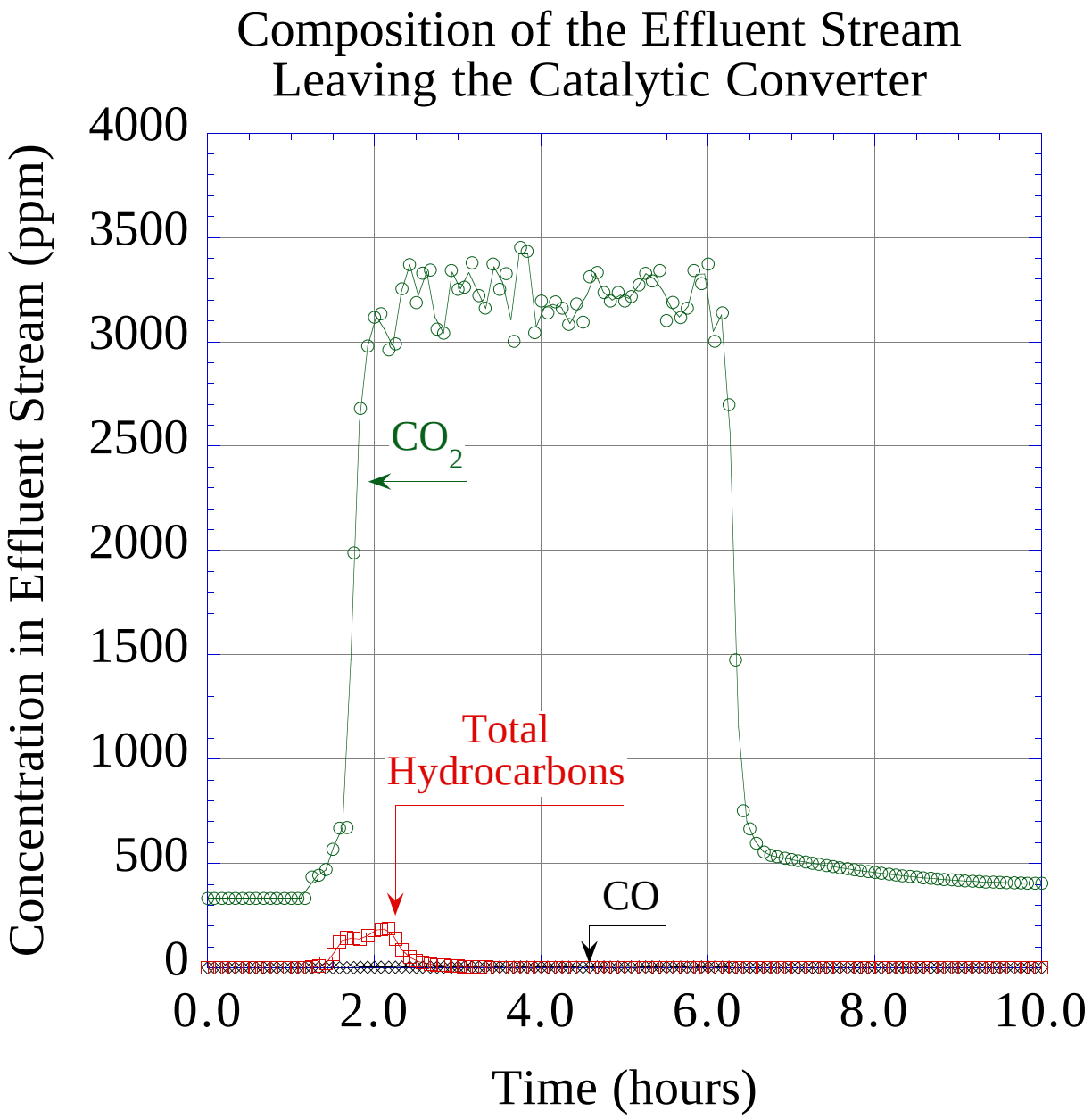


- The catalyst evaluated is the PRO*HHC VOC catalyst from Prototech Company.
  - The catalyst is designed to be resistant to acids formed when oxidizing halogenated hydrocarbons.
  - The catalyst is in the form of 1/4 inch pellets. This facilitates handling in glovebox applications.

The Catalytic Converter



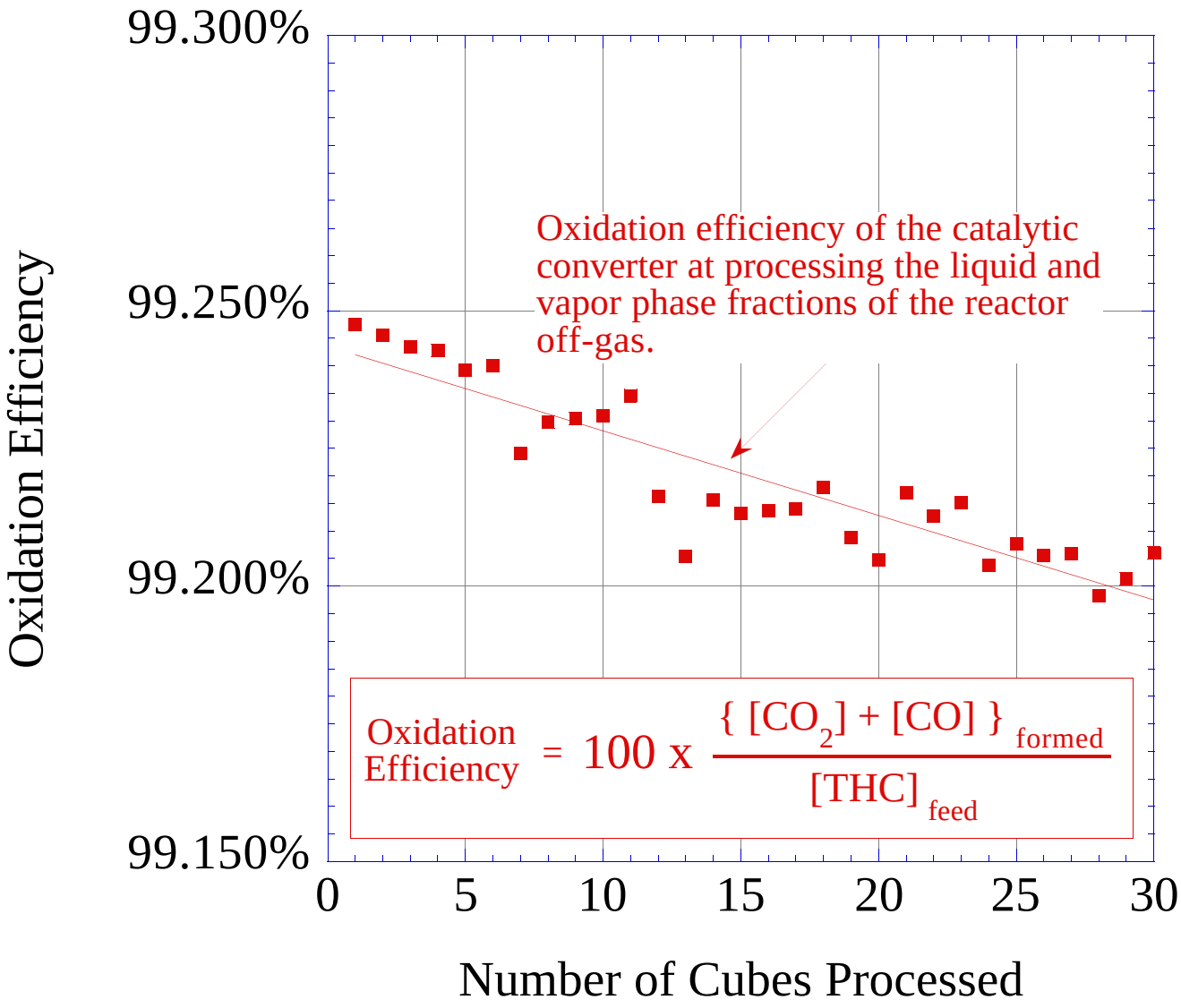
- Three factors are used to evaluate the performance of the catalytic converter.
  - Oxidation efficiency
  - Selectivity
  - Catalyst longevity

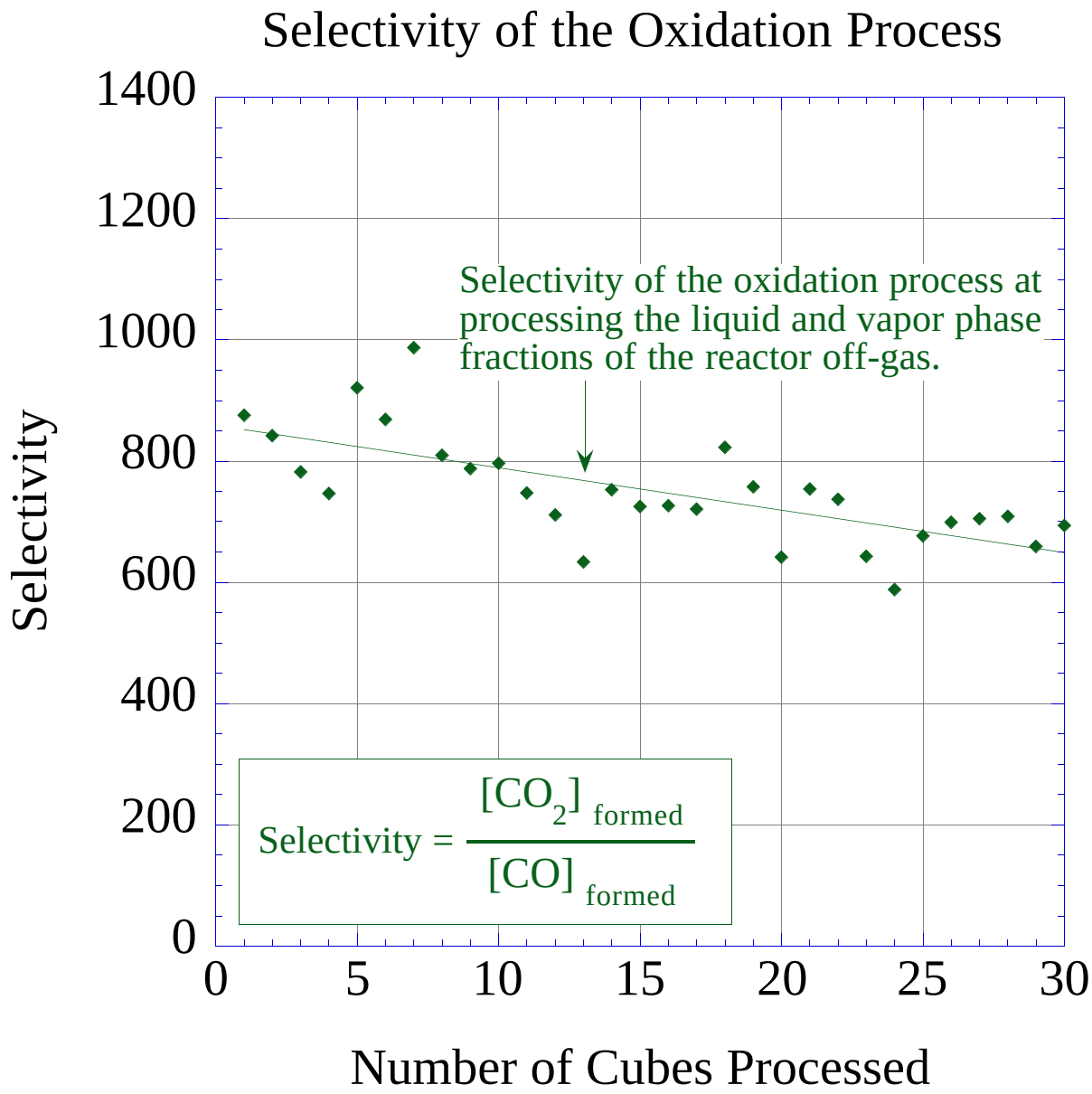

Composition of the Effluent Stream
Leaving the Catalytic Converter
Concentration in Effluent Stream (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
CO2
Total
Hydrocarbons
CO
0.0
2.0
4.0
6.0
8.0
10.0
Time (hours)

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




Selectivity of the Oxidation Process
Selectivity
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
Number of Cubes Processed
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