Technical Subgroup on Incineration Test Methods for Fluoropolymers

Incineration Testing Proposal

August 19, 2003

Overall Objective

Determine if incineration of fluoropolymers is a potential source of PFOA to the environment

Discussion Objective

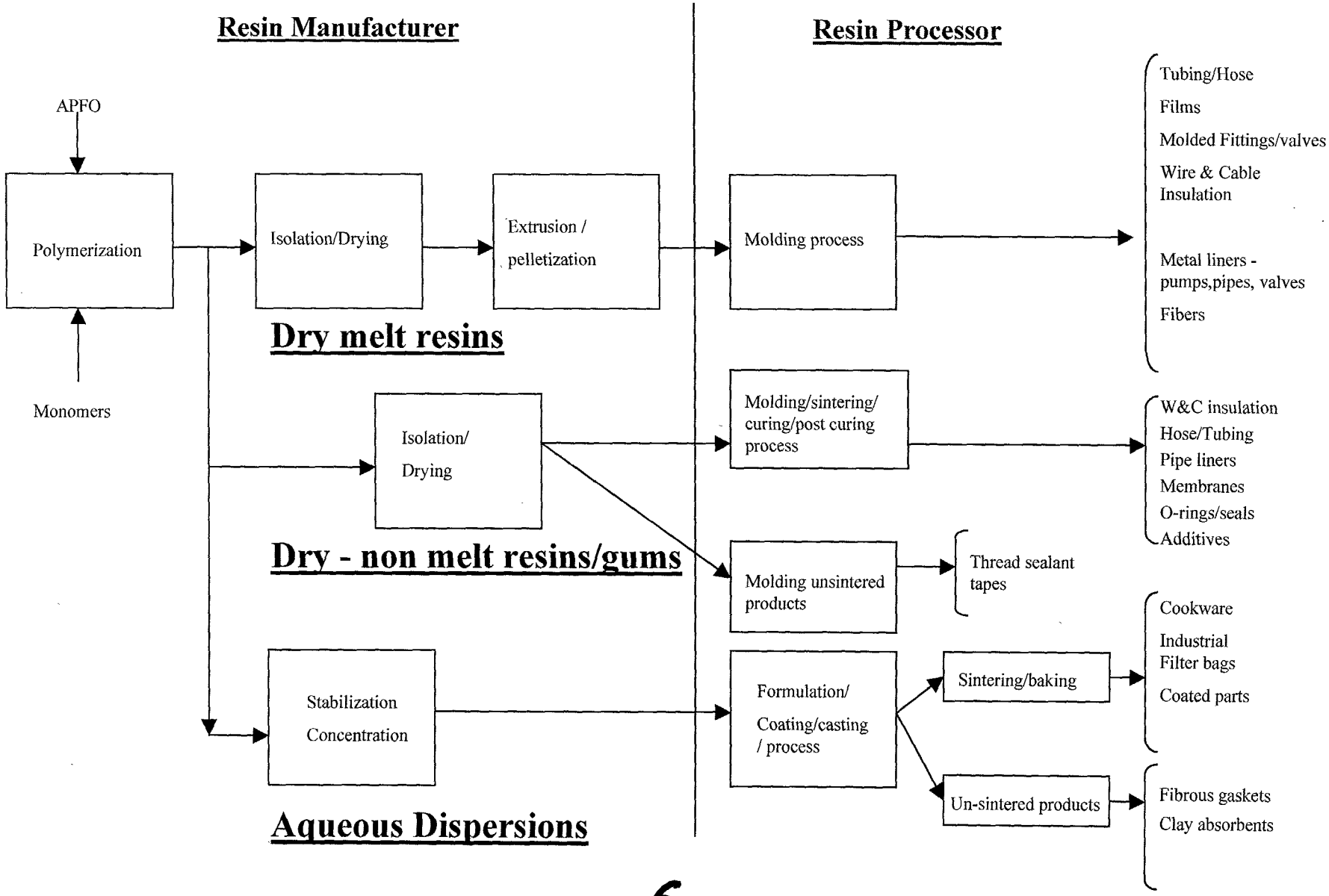
- Work toward agreement on key elements of test program to enable development of test protocol and ECA for incineration testing

Discussion Outline

1. Identify representative materials for incineration testing
2. Review relevant incineration conditions
3. Present key elements of proposed test program
   a. Test objective
   b. Test program phases
   c. Test materials
   d. Experimental apparatus
   e. Experimental conditions
   f. Sampling and analysis
4. Discuss next steps

1. Identify representative materials for incineration testing

Fluoropolymer Industry Overview



Representative Classes

- Dry melt resins
  1. FEP, PFA, THV, ETFE, HTE
- Dry non-melt resins/gums
  2. PTFE (perfluorinated)
  3. Fluoroelastomers (nonperfluorinated)
- Aqueous dispersions
  4. PTFE, FEP, PFA, THV

Proposed Test Materials

- Four composite mixtures (one per class):
  1. Dry melt resins (FEP, PFA, THV, ETFE, HTE)
  2. PTFE
  3. Fluoroelastomers
  4. Aqueous dispersions (PTFE, FEP, PFA, THV)

- Each composite will be mixture of representative fluoropolymers, as solids, in equal proportions across producers for each class

2. Review relevant incineration conditions

Municipal Waste Combustors (MWCs) in U.S. - 2000[1,2,3,4]

Type	No. of Facilities	Annual Capacity (million T/year)
Mass Burn	70	23
Refused Derived Fuel (RDF)	19	6.7
Modular	13	0.4
Total	102	30

Note: 90% of U.S. MWC capacity is at Large MWCs (~60% of facilities)

1 - EPA, "Municipal Solid Waste in The United States : 2000 Facts & Figures", EPA530-R-02-001, June 2002
2 - Integrated Waste Services Association (IWSA), "Fast Facts about Waste-to-Energy" and other information
3 - Eastern Research Group, "2000 National Inventory of Large Municipal Waste Combustion Units", June 12, 2002
4 - EPA, "Emission Guidelines for Existing Small Municipal Waste Combustion Units", 65 FR76380, Dec. 6, 2000

MWC Operating Conditions

- Many incinerators for municipal solid waste are designed to operate in the combustion zone at 1800°F [982°C] to 2000°F [1093°C] [1]
- Combustion gases in traveling grate mass burn units are maintained "at about 1800°F [982°C] to ensure complete combustion of organic compounds" prior to passing to the boiler[2]
- U.S. standards for MWCs include Good Combustion Practices (GCP)
  - "The ability of an MWC to achieve combustion temperatures that are adequate to destroy organics is a fundamental requirement of GCP".[3]
- Refuse derived fuel in a unit in the GCP study (Mid-Connecticut)[3] is combusted at furnace temperature > 1800°F [982°C][4]

1 - U.S. EPA, Decision Maker's Guide to Solid Waste Management, Volume II, 1995

2 - Donnelly, J.R. Waste incineration sources: refuse. In: Buonicore, A.J.; Davis, W.T., eds., Air Pollution Engineering Manual. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold, 1992,. pp. 263-275

3 - U.S. EPA, Municipal Waste Combustion Assessment: Technical Basis for Good Combustion Practice, EPA 600/8-89-063, August 1989

4- http://www.nu.com/energy/stations/south.asp

Modular MWC Temperatures[1,2]

Secondary Chamber Temperature	Oswego Co., NY	Red Wing, MN
Start of campaign	1012	
Mid-range secondary temperature	951	
End of campaign	995	
Low secondary temperature	885	
Mean secondary temperature		954 - 1071

1 - U.S. EPA, Municipal Waste Combustion Assessment: Technical Basis for Good Combustion Practice, EPA 600/8-89-063, August 1989, pp. 4-30 - 4-32; temperatures during which CO emissions met GCP standard

2 - Note modular units are more commonly used at small MWC facilities

Medical Waste Incinerators

- Three types of incinerators are primarily used for medical waste: controlled air incinerators, multiple chamber incinerators, & rotary kiln incinerators[1]
  - All three types of medical waste incinerators (MWIs) use two chambers

	Controlled Air	Multiple Chamber	Rotary Kiln
Primary Chamber	400 to 980°C	540 to 980°C	760°C
Secondary Chamber	980 to 1200°C	980 to 1200°C	980°C

EPA notes that 97% of MWIs are controlled air modular furnaces and 1% are rotary kilns[2]

- "any unit which presently has a residence time less than two seconds at 1000 C (1832 F) does not meet the requirement for good combustion under the new regulations"[3]

1 - Theodore, L. Air Pollution Control and Waste Incineration for Hospitals and Other Medical Facilities, Van Nostrand Reinhold, New York, 1990, pp 313-320..

2 - U.S. EPA, Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin (TCDD) and Related Compounds, Part I: Estimating Exposure to Dioxin-Like Compounds Volume 2: Sources of Dioxin-Like Compounds in the United States, Chapter 3, EPA/600/P-00/001Bb, Draft Final Report, September 2000

3 - Van Remmen, T. Evaluation of the available air pollution control technologies for achievement of the MACT requirements in the newly implemented new source performance standards (NSPS) and emission guidelines (EG) for hospital and medical/infectious waste incinerators, Waste Management, 1998, Vol. 18, p. 394

Proposed Test Conditions

- MWIs typically operate with secondary chamber residence times of 2 seconds at $\geq$1000 °C
- > 90% of municipal solid waste is combusted in MWCs typically operating with secondary stage temperatures ~ 982 °C[1] (res time ~2 seconds)
- Plan testing at MWC conditions
  - Conservatively propose 900 °C at 2 sec residence time

1- Typical secondary stage temperatures for mass burn & RDF units ~ 982 °C based on available information

14

3. Summarize key elements of test program

Test Program Objective

- Investigate incineration of fluoropolymers under laboratory-scale conditions representative of typical municipal waste combustor operations in the U.S. to quantitatively determine emission levels of PFOA

Phases of Test Program

1. Development and approval of Test Protocol/Quality Assurance Project Plan (QAPP)
2. Thermogravimetric analysis of test materials
3. Preliminary gasification & combustion tests for test materials
4. Verification of quantitative transport of PFOA
5. Other method development as needed
6. Combustion tests at specified operating condition(s)
7. Data reduction and report development

Proposed Test Materials

- Four composite mixtures (one per class):
  1. Dry melt resins (FEP, PFA, THV, ETFE, HTE)
  2. PTFE
  3. Fluoroelastomers
  4. Aqueous dispersions (PTFE, FEP, PFA, THV)

- Each composite will be mixture of representative fluoropolymers, as solids, in equal proportions across producers for each class

Experimental Apparatus

- General Description
  - a batch-charged continuous flow reactor system
    - The test sample is gasified and transported to a high temperature reactor
    - In the high temperature reactor, the sample vapors are subjected to controlled conditions of residence time, temperature, and excess air
    - Combustion products are collected for quantitative analysis

Experimental Conditions

- Each test feed will be subjected to laboratory-scale incineration using the experimental apparatus
- Temperature: 900°C for 2 seconds residence time
- Three replicates for each test level (combination of test feed and temperature)
- Also, a blank run for each operating condition
- Amount of test material fed will be large enough to assure ability to detect PFOA in the emissions, but small enough to assure sufficient excess oxygen to be representative of typical MWC conditions

Planned Sampling & Analysis

- Exhaust gas parameters to be monitored:
  - flow rate, oxygen (O_2)[1], carbon dioxide (CO_2), and carbon monoxide (CO)
- Exhaust gas
  - will be collected on suitable sorbent cartridge(s) and / or in aqueous solution trap(s) for off-line analysis to quantify PFOA
- Sampling and analysis methods
  - adapt & validate available PFOA methods for this study
  - investigate total organic fluorine analysis of exhaust gas[2]

1 - O_2 in exhaust gas is planned to be monitored via calculation based on air input flow
2 - Exhaust gas analysis for fluoride ion is planned

Sampling & Analysis Methods

- Sample exhaust gas
  - Sorbent Cartridge
    - OSHA Versatile Sampler (OVS)
    - analyze for PFOA
  - Aqueous Solution
    - use one or more impingers containing aqueous solution
    - analyze for PFOA
- Analyze exhaust gas for PFOA
  - via off-line LC/MS/MS at a qualified commercial laboratory operating under suitable data quality guidelines
- Analyze exhaust for fluoride ion to assist in performing fluoride balance across experimental system

Test Materials Characterization

- elemental analysis to determine carbon, hydrogen, nitrogen, chlorine, fluorine and oxygen by difference
- total organic fluorine

4. Discuss Next Steps