Environmental Laboratory 3M

Environmental Fate and Effects of Fluorochemicals

Dr. Robert D. Howell
Senior Environmental Engineer
Environmental Science & Assessment Group

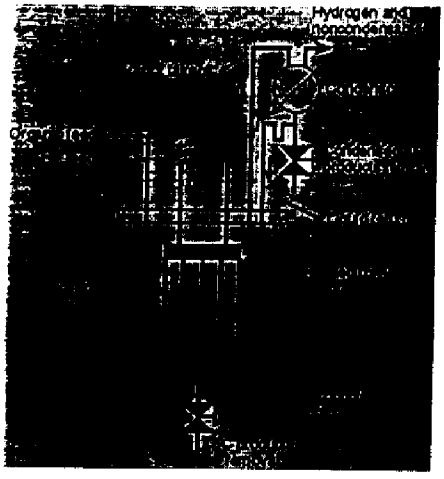
Environmental Laboratory 3M

Environmental Issues of Fluorochemicals

- What are "*fluorochemicals*"?!?!
- How are they made and used?
- What are the environmental issues?
- What has been done to address the issues?
- What are we doing now to address the issues?
- Where are we going from here?

Environmental Laboratory 3M

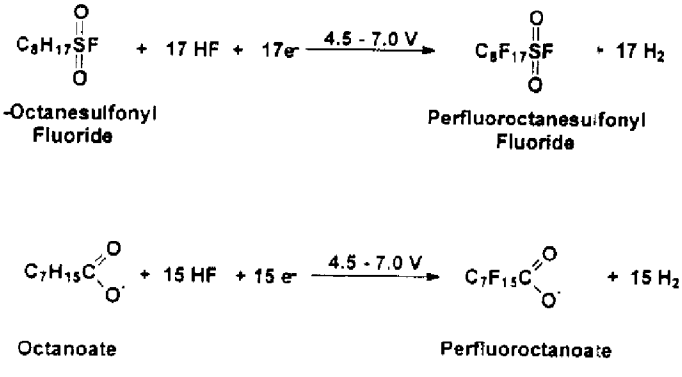
Simons Electrochemical Fluorination (ECF) Process



Hydrocarbon + Anhydrous HF + Electrical Energy ⟶ Fluorocarbon + H_2

Environmental Laboratory 3M

Simons Electrochemical Fluorination (ECF) Process



Environmental Laboratory 3M

Electrochemical Fluorination Cell Products

Desired Product: Perfluorooctanesulfonyl Fluoride (POSF, FX-8)

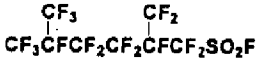
$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2SO_2F$

Also Get-

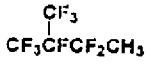
- Other Straight Chain Perfluoroalkyl Products of Various Chain Leng hs

$C_6F_{13}SO_2F$ $C_7F_{15}SO_2F$ $C_8F_{19}SO_2F$ etc. $C_nF_{2n+1}SO_2F$

- Branched Chain Perfluoroalkyl Products of Various Chain Lengths



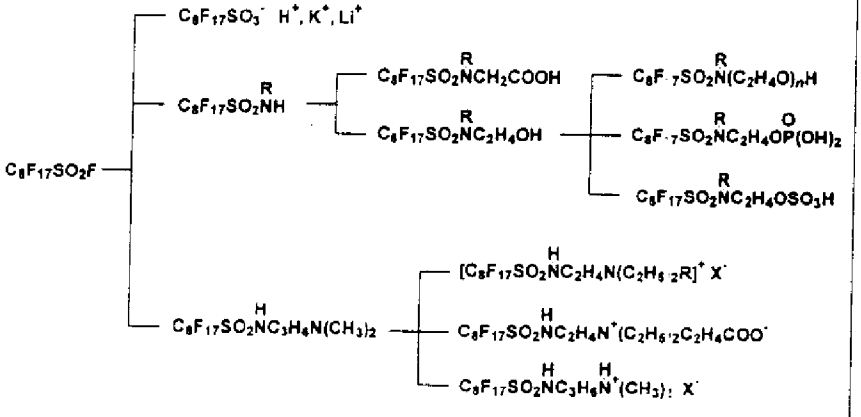
- Other Straight Chain, Branched, and Cyclic Perfluoroalkyl Compounds

CF_4 C_2F_6 C_3F_8 C_4F_{10} C_5F_{12}  

- Tars* and Other By-Products Such As SF_6

Environmental Laboratory 3M

Fluorochemical Products & Intermediates

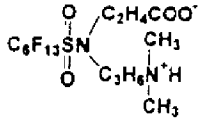


R.A. Guenthner, R.A. and Vietor, M.L. Surface active materials from perfluorocarboxylic and perfluorosulfonic acids. *I&EC Product Research and Development* 1 (1962) 165-169.

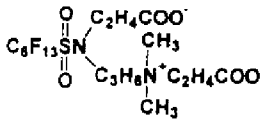
Environmental Laboratory 3M

Example: Surfactant used in AFFF Products

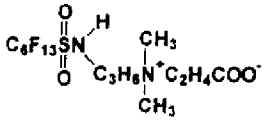
- Three Major Components



"L-4640"



"Diadduct"



- Perfluoro Moiety Primarily Six Carbons Long

Environmental Laboratory 3M

Electrochemical Fluorination Cell Products - *Issues*

- Mixtures of Unknown Composition
  - ~80% straight chain
  - ?% branched of same chain length
  - ?% straight chain of different length
  - ?% branched chain of different chain lengths
- Lot-to-Lot Variability in Composition
  - by cell run
  - by location (Antwerp ≠ Cordova ≠ Cottage Grove ≠ Decatur)
- What Do You Test?
  - Products as they are sold?
  - Specific compounds extracted from the mixture?
  - Do you test the impurities? Which ones?

Environmental Laboratory 3M

Nomenclature An *Enormous* Issue

- Experimental Chemical
  - "L-4640" for AFFF
  - "L-1223" for general surfactant use (e.g. cleaning products)
- MSDS
  - Group Number 04-6084-0; 3M ID 98-0211-5617-3
  - "Amphoteric Fluroalkylamid Derivative Trade Secret"
- Toxicology Services
  - T-2816
- PMNs - "PMN Substance"
- Chemical Abstracts Service Registry Number
- Product Development Lab
  - "Acrylic Foamer" or "The Foamer" or "New Foamer" or "Old Foamer"
- Environmental Laboratory
  - Use "L-Number"
  - May use Environmental Laboratory "Lab Request Number"

Environmental Laboratory 3M

Environmental Issues of Fluorochemicals

- Halogenated
- Persistent
- Widely Dispersed in the Environment
- Potential to Bioaccumulate
- Biologically Active

Environmental Laboratory 3M

Atmospheric Issues

Extensive Program to Evaluate Atmospheric Fate and Effects of 3M Fluorochemicals as CFC and Halon Replacements

- Experimental
  - IR Spectra
  - UV Cross Sections
  - Hydroxyl Radical Reactivity
  - Singlet Oxygen Reactivity
- Data Analysis
  - Radiative Effects
  - Global Warming Potential

Environmental Laboratory 3M

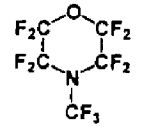
Atmospheric Issues

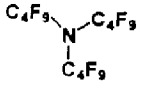
CFC and Halon Replacement Candidates

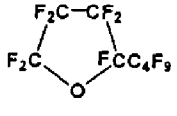
C_4F_{10}

C_5F_{12}

C_6F_{14}





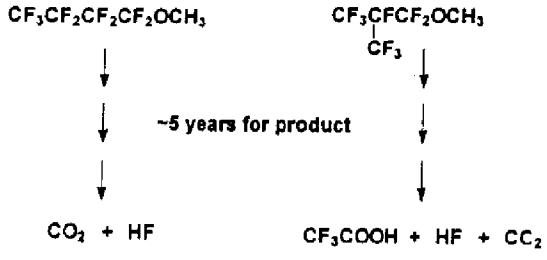


Environmental Laboratory 3M

Atmospheric Issues

CFC and Halon Replacement Candidates

Highly Fluorinated Ethers
HFE 401



Environmental Laboratory 3M

Atmospheric Issues of Perfluorinated Compounds

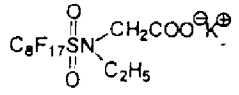
Ozone Depletion Potential
- CFC-11 = 1
- Perfluorochemical = 0
- CFC-113 = 0.8
- 1,1,1-TCE = 0.1

Atmospheric Lifetime
- Perfluorochemicals = 5,000 years
- 1,1,1-TCE = 5.4 years

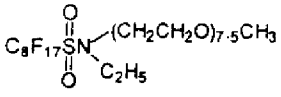
Global Warming Potential
- CO_2 = 1
- n-$C_4F_9OCH_3$ = 300
- C_5F_{12} = 4,100
- C_6H_{14} = 7,400
- CFC-11 = 4,000
- 1,1,1-TCE = 110

Environmental Laboratory 3M

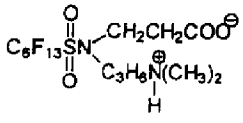
Aerobic Biodegradation Results



37% ThOD in 6.25 hrs. at 30
O_2 uptake



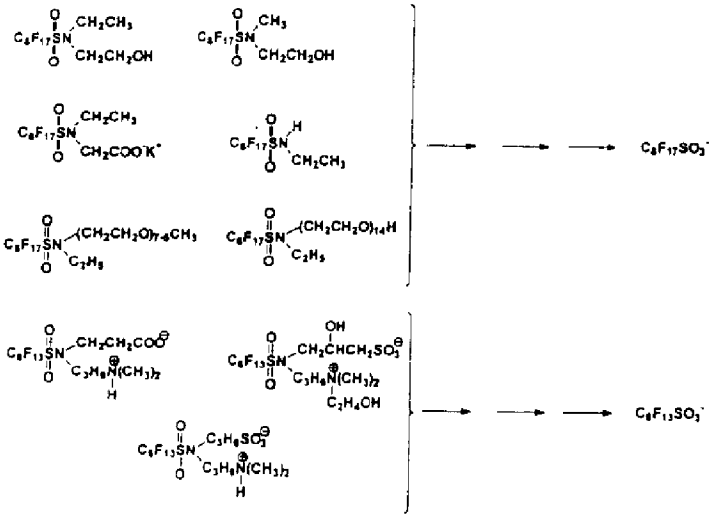
25 to 33% in 2 days
DOC removal



6% in 5 days
CO_2 production

Environmental Laboratory 3M

Aerobic Biodegradation of Fluorochemicals



Environmental Laboratory 3M

Research at Michigan State University

Dr. Craig Criddle
Blake Key

NSF Center for Microbial Ecology and
Department of Civil and Environmental Engineering

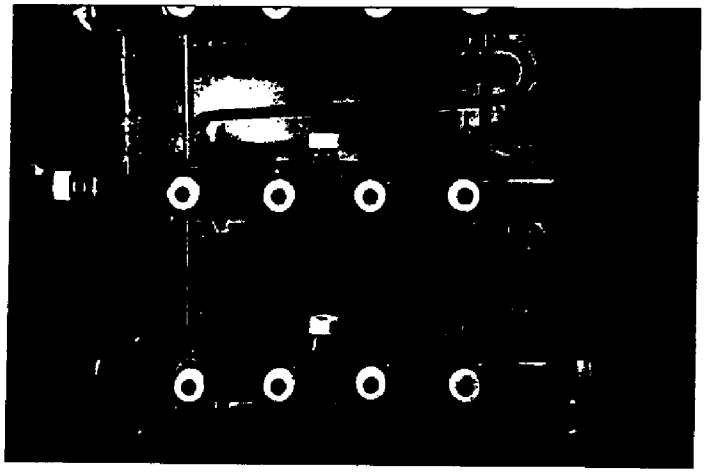
Environmental Laboratory 3M

Research at Michigan State University

Multichamber Microcosms

- Fermenting
- Acetogenic
- Methanogenic
- Sulfidogenic
- Denitrifying
- Aerobic

Environmental Laboratory 3M



Environmental Laboratory 3M

Research at Michigan State University

Fluorinated Sulfonates

$CH_2FSO_3^-$ $CHF_2SO_3^-$ $CF_3SO_3^-$ $C_8F_{17}SO_3^-$

$CF_3CH_2SO_3^-$ $CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2SO_3^-$

Fluorinated Carboxylates

CH_2FCOO^- CHF_2COO^- CF_3COO^-

Fluorinated Sulfonamide

$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2S(=O)(=O)N(CH_2CH_3)CH_2CO_2^-$

CAS 2991-51-7

N-ethyl-N-[(heptadecafluoroocty!)sulfonyl]-glycine potassium salt

Environmental Laboratory 3M

Recent Results

At MSU: Aerobic and Anaerobic Systems

$CH_2FCO_2^-$ and $CHF_2CO_2^-$ $\longrightarrow$ $F^- + CO_2 + H_2O$

$CF_3CH_2SO_3^-$ and $C_8F_{17}CH_2CH_2SO_3^-$ $\longrightarrow$ $nF^- + ? + ? + CO_2 + H_2O$

- several volatile degradation products
- fluoride released concentration dependent

At USGS in Menlo Park, Calif.: Anaerobic Systems

$CF_3CO_2^- \rightarrow CHF_2CO_2^- \rightarrow CH_2FCO_2^- \rightarrow CH_3CO_2^- \rightarrow CH_4$

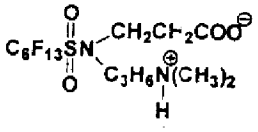
Environmental Laboratory 3M

Light Water™ AFFF Usage Wastes

- Continuing Issue with Customers
  - Fire Fighting Training Sites
  - Fire Protection Equipment Testing
  - Accidental Discharge by Automatic Equipment
  - Simple Operation and Maintenance Required
- Potential Environmental Harm
  - Fish Kills
  - Bird Exposure
  - Disruption of Wastewater Treatment Plants
- Potential Negative Publicity for the Corporation

Environmental Laboratory 3M

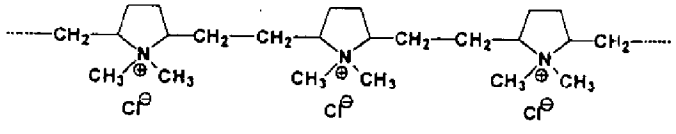
Major Components of 3M AFFF Products

1% "Filmer" FC-95	$C_8F_{17}SO_3^-$
3% "Acrylic Foamer" L-4640	
20% Butyl Carbitol	$C_4H_9OC_2H_4OC_2H_4OH$
8% Octyl Sulfate	$C_8H_{17}OSO_3^-$

Environmental Laboratory 3M

AFFF Waste Treatment

Cationic Polyelectrolytes



MW ~ 200,000 Daltons ~ 160 Daltons

Calgon Merquat 100

Environmental Laboratory 3M

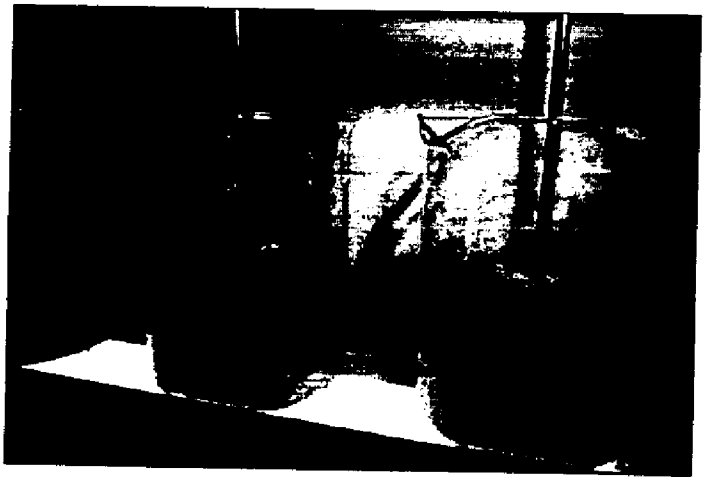
AFFF Waste Treatment

1. Addition of Cationic Polyelectrolyte
2. Flocculation
3. Separation
   - Precipitation
   - Centrifugation
   - Sand Filtration
   - Reverse Osmosis/Ultrafiltration
4. Discharge of Treated Water
5. Disposal of Polymer/Surfactant Precipitate
   - Incineration
   - Landfill

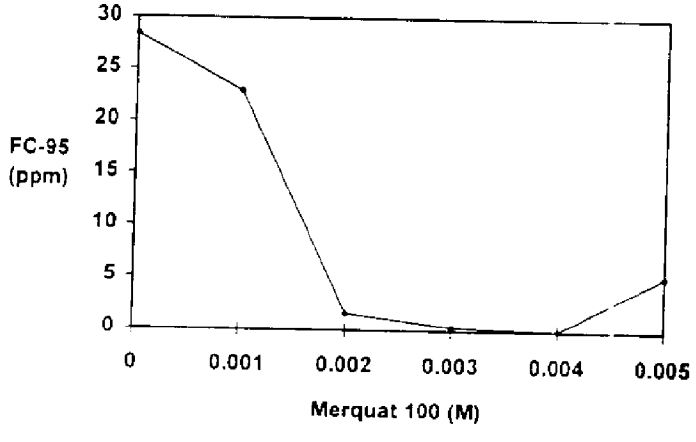
Environmental Laboratory 3M

Environmental Laboratory 3M

Environmental Laboratory 3M

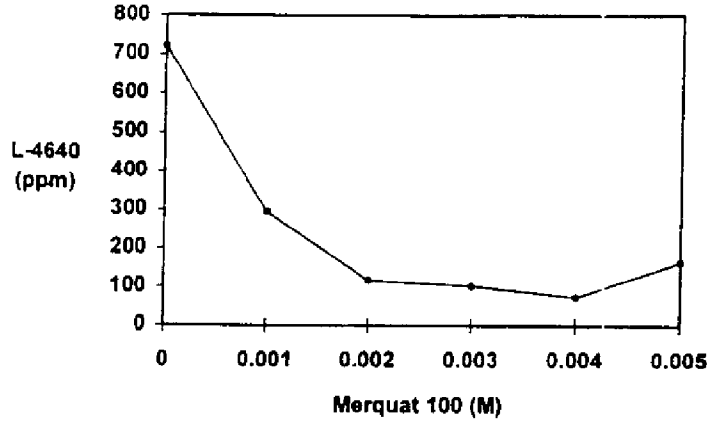


Effect of Cationic Polymer Concentration



Environmental Laboratory 3M

Effect of Cationic Polymer Concentration



Environmental Laboratory 3M

Fluorochemical Surfactant Removal

	Concentration in Supernatant (mg/L)	Removal (%)
L-4640		
Nalco 8157	4.9	99.4
Nalco 7735	3.4	99.6
$FeCl_3$	2.2	99.7
FC-95		
Nalco 8157	0.67	99.8
Nalco 7735	0.02	99.9
$FeCl_3$	0.00	100.0

Environmental Laboratory 3M

Future Work on AFFF Waste Treatment

Separation Method

- Is precipitation sufficient?
- Centrifugation, sand filtration?
- Reverse osmosis/ultrafiltration: too costly, difficult to operate and maintain.

Disposal of Polymer/Surfactant Precipitate

- Incineration of fluorochemicals?
- Landfill possible?

Seeking Wastewater Treatment Firm for Scale-up

Environmental Laboratory 3M

Fluorochemical Bioconcentration in Fish

Uptake Experiment

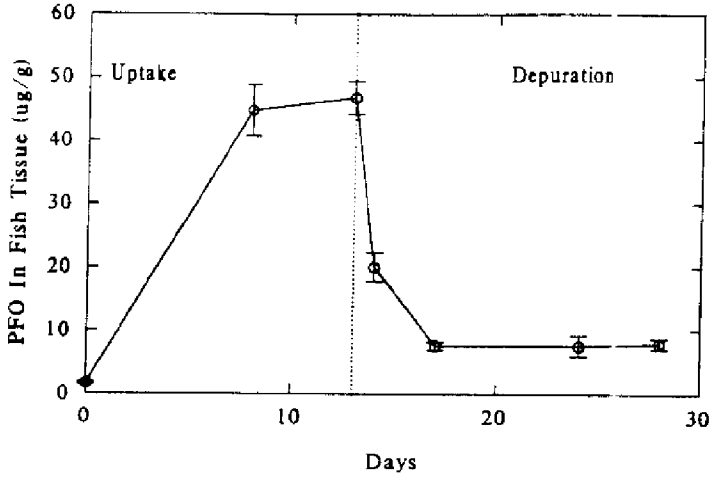
- 25 mg/L ammonium perfluorooctanoate (FC-143)
- 30 fish/tank
- 5 fish removed and sacrificed at day 7 and day 13
- Analysis by combustion and F^- analysis by ISE

Depuration Experiment

- Fish remaining at end of uptake put into fresh water
- 5 fish removed at day 14, day 17, and day 20
- Analysis by combustion and F^- analysis by ISE

Environmental Laboratory 3M

Perfluorooctanoate Bioaccumulation in Fish



Environmental Laboratory 3M

Perfluorooctanoate Bioaccumulation in Fish

[redacted]

Time (days)	PFO in Test Solution (ppm)	PFO in Fish Tissue (ppm)	BCF
8	25.5	44.7	1.75
13	25.9	46.7	1.80

Range of concern: **1,000 < BCF < 1,000,000**

Environmental Laboratory 3M

Fluorochemical Bioconcentration in Fish

Accomplishments

- Developed method for fluorochemical concentration in fish by combustion method
- FC-143 report reviewed by Dr. John Giesey, Environmental Toxicology Dept., Michigan State University
- Incorporated recommendations into protocol
- Presented results to customer and at SETAC 1995

Future Work

- FC-95 (perfluorooctane sulfonate)
- Acrylic foamer (L-4640)
- Ethyl FOSE alcohol
- Others as necessary

Environmental Laboratory 3M

Fluorochemical Products - *Issues*

- Analytical Procedures are Extremely Difficult
  - Hindered by the number of components
  - Techniques/methods valid for one component probably won't work for other components
    - Charged vs. uncharged
    - Positive charge vs. negative charge vs. zwitterionic/amphoteric
  - What matrix?
    - Soil - sand, clay, loam, compost, ...
    - Water - sewage sludge, wastewater, drinking water, sea water, groundwater, ...
    - Animal - rabbit, rat, human, fish, cockroach, ...
    - Tissue - blood, liver, skin, hair, ...
    - Food - pizza, popcorn, food simulating liquid, ...
    - Plant - corn, algae, ...
    - Atmosphere
    - Product

Environmental Laboratory 3M

Fluorochemical Products - *Issues*

- Analysis of Fluorochemicals in Environmental Samples NOT Impossible
- Tremendous Developments Since ~1993
  - Extraction Techniques
  - Separation Techniques
    - GC, HPLC, Supercritical Fluid Extraction, and many others
  - Detection Techniques
    - Mass Spectrometry, FID, PID, FTIR, and many others
  - Automated Sample Handling and Instrument Control to Maximize Throughput
- GLP Methods in Place for Several Fluorochemicals in Several Matrices
  - Including blood, livers, skin, and other animal tissues
- Non-GLP Methods in Place for Several Fluorochemicals in Several Matrices
  - Wastewater sludge, soil, drinking water, air, and others
- Can Detect Any Fluorochemical in Any Matrix

Environmental Laboratory 3M

Fluorochemical Products - *Issues*

- Tremendous Quantities of Fluorochemicals Being Produced
  - Tens or hundreds of millions of pounds/year
  - Don't know production quantities of competitors
  - Don't know their chemistries
- Effects on Biosphere Unknown
  - Human health?
  - Other living creatures?
- Human Health and Environmental Studies are
  - Extremely Difficult
  - Extremely Expensive
- Ultimate Environmental Fate Unknown
- Unknown Liability

Environmental Laboratory 3M

Fluorochemical Products - *Issues*

- Product Composition
  - Unknown
  - Not Critical to Product Use
- Products meet certain QC specifications
  - Boiling Point (Fluorinert Products)
  - Surface Tension (Fluorad Products)
  - Oil & Water Repellancy (Scotchban & Scotchgard Products)
  - Extinguishment (Light Water Products)
  - Other physical/chemical properties as appropriate to meet specifications
- End Use May Be Unknown
  - Don't know who buys them
  - Don't know what kinds of products they are used in

Environmental Laboratory 3M

Fluorochemical Steering Committee

Charles Cowman	*Specialty Chemicals Division*
Thomas Dipasquale	*Legal*
Craig Olson	*Chemical, Film and Allied Group Compliance*
Sik-Toh Ting	*Fluorochemical Technology Center*
Paul Ackerman	*Specialty Materials Division*
Larry Zoebel	*Medical Department*
John Butenhoff	*Toxicology Services*
Dale Bacon	*Environmental Laboratory*
James Sugg	*Industrial Hygiene Services*
Don Theissen	*Corporate Product Responsibility*
Lael Pickett	*Specialty Chemicals Division*
Craig Burton	*Fluorochemical Technology Center*

Environmental Laboratory 3M

Fluorochemical Technical Advisory Committee

Craig Burton	*Fluorochemical Technology Center*
Craig Olson	*Chemical, Film and Allied Group Compliance*
Jim Johnson	*Environmental Laboratory*
Roger Perkins	*Toxicology Services*
Steve Gordon	*Toxicology Services*
Jeff Mandel	*Medical Department*
Robert Howell	*Environmental Laboratory*
John Marhevka	*Corporate Research Laboratory*
Stan Sorenson	*Industrial Hygiene Services*
V. Prothapragada	*Specialty Materials Division*

Environmental Laboratory 3M

Fluorochemical Work in Progress

- New Product Testing (Evaluate 2/week & Test 3/month)
- PMNs (2 - 4/year)
- Water Solubility (e.g. Ethyl FOSE Alcohol)
- FC-129 Degradation Study
- HFE 401 & HFE 402 - Fish, *Daphnia*, Algae
- Michigan State Research Biodegradation
- FC-845 Process Wastewater Ecotox (*Daphnia* & Fish)
- Method Development - Ongoing for different compounds and matrices
- Pesticide Working Group
- Bioconcentration (FC-143, FC-95, Ethyl FOSE, and others)
- GLP Tox Studies Underway (e.g. Dermal Transport)
- Degradable Fluorochemical Building Blocks
- Proposals
  - Soil Sorption
  - Comparison of Extinguishment with AFFF vs. Non-Extinguishment