Fluorine-free Aqueous Film-Forming Foam

Project Number WP-2738

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PI's Organization National Foam Inc.

Project Outbrief
DATE 9/13/2019

SERDP
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Project Team

- **National Foam**
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    - Formulation chemistry
  - **Ms. Anne Regina –PI**
    - Fire-fighting foams
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    - Fire-fighting foams
  - **Dr. Kate Schofield**
    - Environmental science
  - **Dr. Katie Shelbourne**
    - Surface / colloid chemistry
  - **Ms. Lucy Richardson**
    - Surface / colloid chemistry
- **Oregon State University**
  - **Prof. Jennifer Field**
    - Analytical chemistry
  - **Prof. Bill Stubblefield**
    - Environmental toxicology

Background

- SON Number: WPSON-17-01, project started 2017
- AFFF foams are used by the military and civil aviation to extinguish liquid fuel fires
- AFFF contain fluorocarbons
  - Long chain >C6 are persistent, bioaccumulative, toxic
  - Short chain C6 are persistent, toxicity under investigation
- Fire fighting foams that meet MIL-F fire performance but without fluorine would maintain safety but reduce environmental impact
- Current commercialized fluorine-free foams can meet some standards (ICAO B, C) but not MIL-F

Technical Objectives

Develop a fluorine-free fire-fighting foam that meets the performance standards in MIL-F 24385F

Increased understanding of the physical chemistry involved in fire-fighting foams

Complete a life cycle assessment of foam manufacture and use, and compare environmental impacts of fluorine and fluorine-free foams

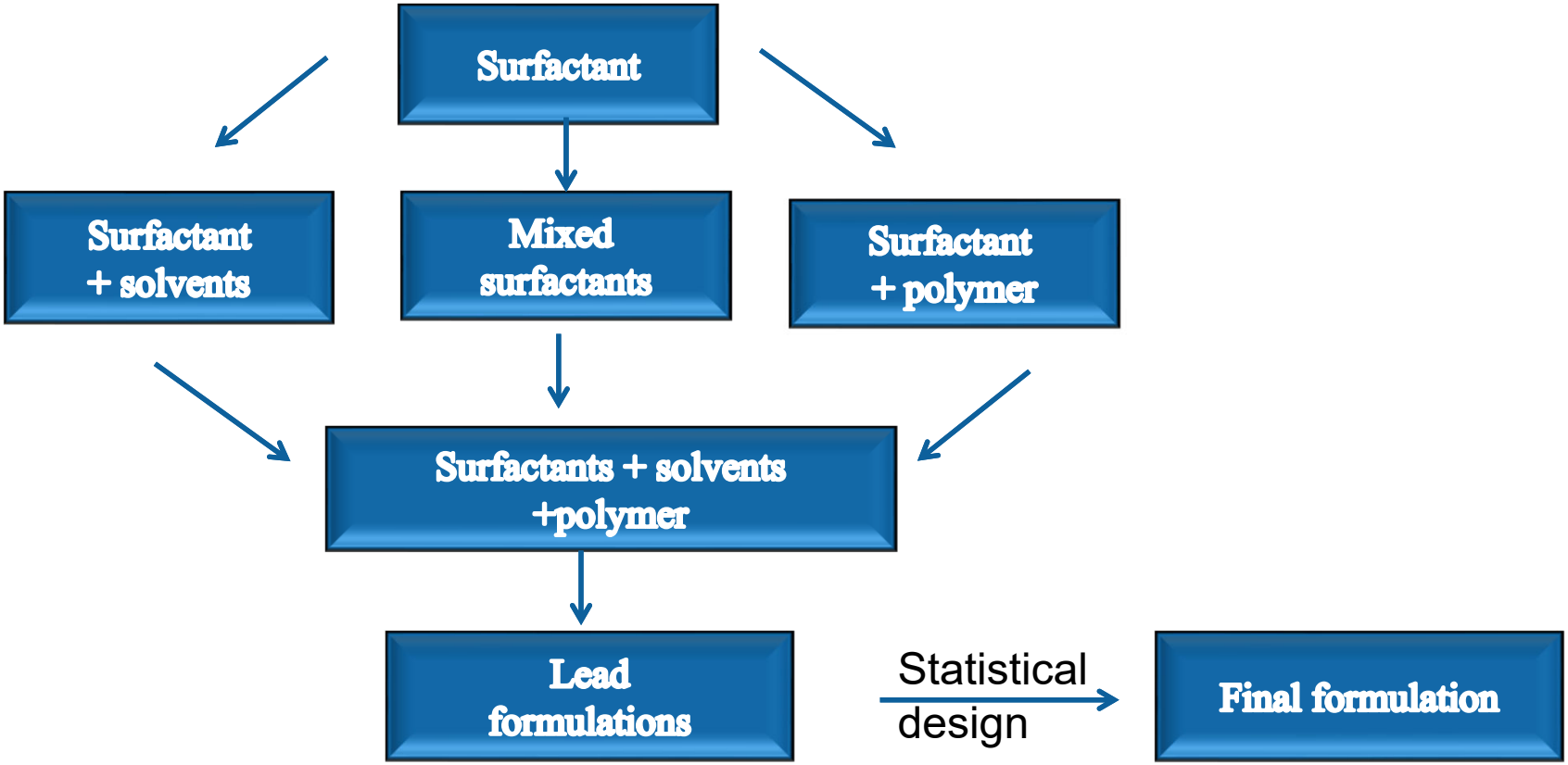
Technical Approach – Understand the science

- **Development of new F-free foam**
  - Physical chemistry of foam components
  - Foam properties
  - Fire performance

- Lab tests → small scale fire tests → large fire tests

- **Life cycle assessment**
  - Life cycle inventory analysis
    - What happens when AFFF foam is applied to a fire?
  - Impact Assessment

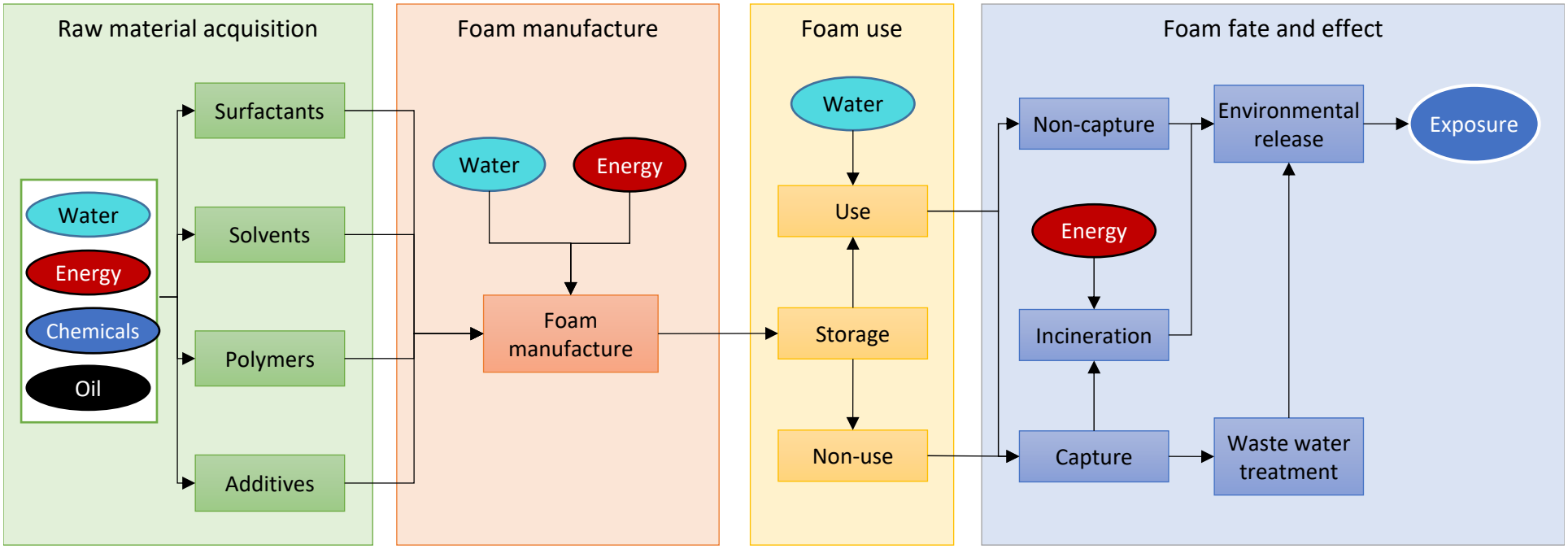
Technical Approach – Foam development



Start with simple systems to correlate formulation with physical chemistry and foam properties

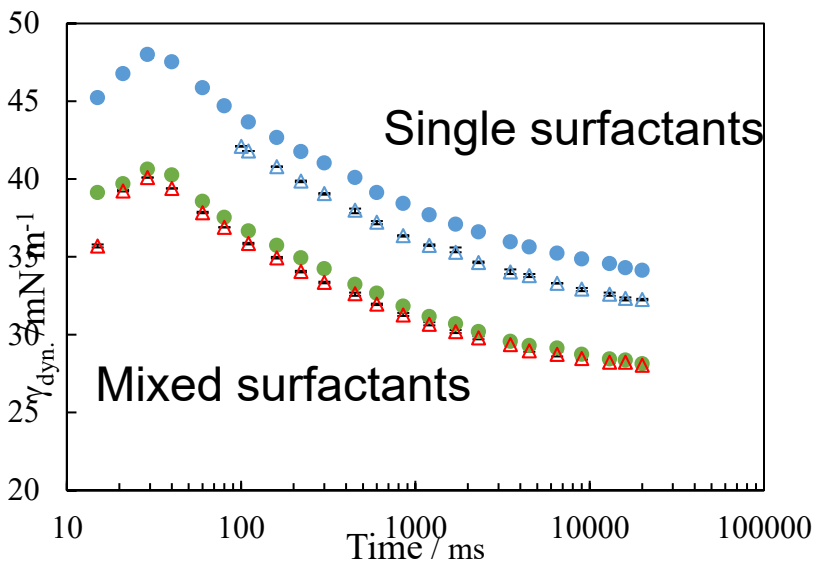
Systematically increase the complexity

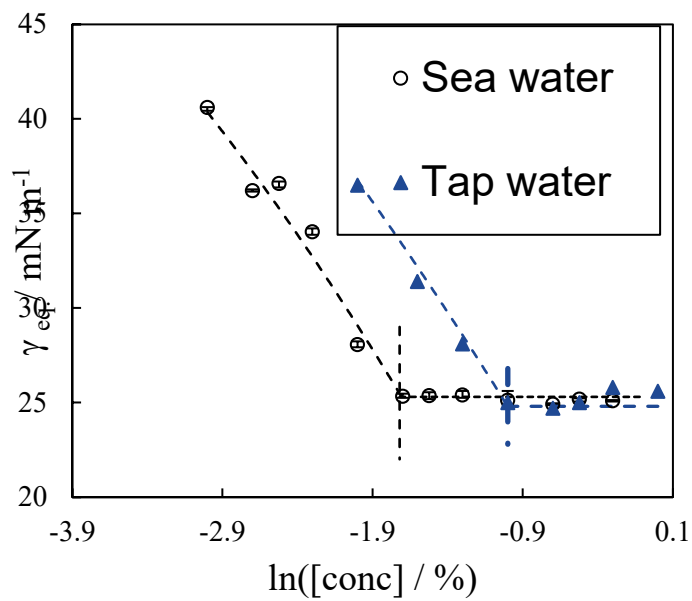
Technical approach LCA –product flow



Primary surfactants

- Must rapidly lower surface tension
  - Requires high critical micelle concentration
  - Dynamic and equilibrium surface tension measurements

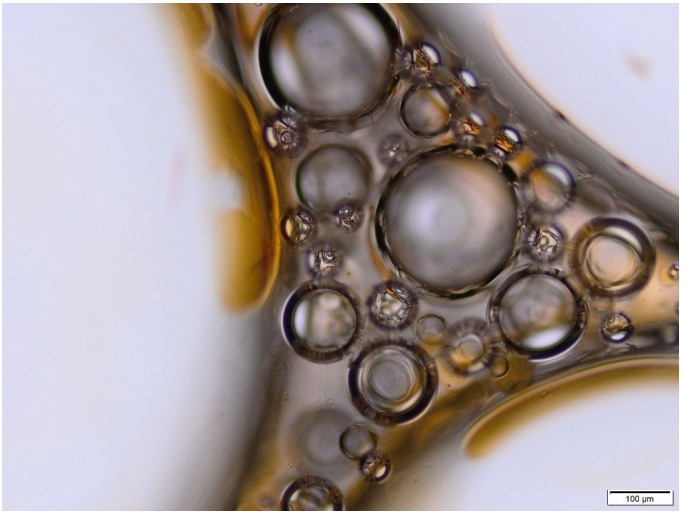


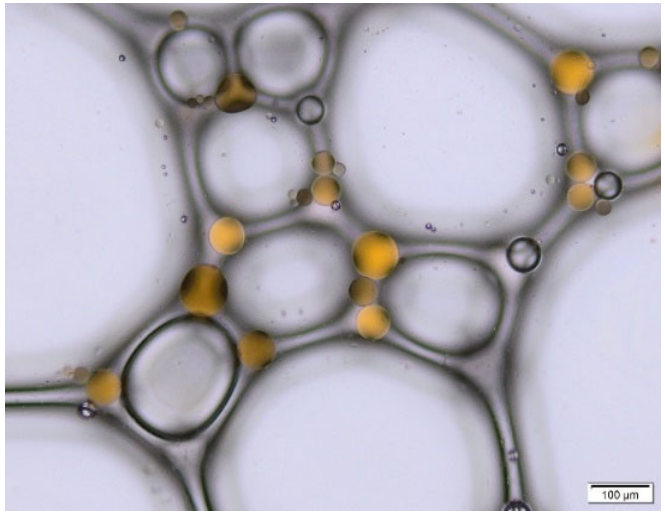


  - Mixture of anionic + amphoteric gives best results

Primary surfactants

- Stable to fuel destruction
  - Close packing of surfactant molecules at interface
  - Similar chain lengths give an ordered surface layer
  - Microscopy demonstrates bubble stability





  - Two candidate surfactant packages identified

Effect of solvent

- Fire-fighting foams usually contain glycol ether type solvents, known as foam boosters
  - Purpose is to increase solubility of the fluorocarbons

- Do fluorine-free foams need solvent?
  - In fresh water, hydrocarbon surfactants have good solubility, high cmc
  - Solvent increases fuel emulsification on application
  - Solvent does more harm than good

  - But in sea water surfactants get “salted out”
  - Solvent helps with solubilising and increases cmc

Secondary surfactant

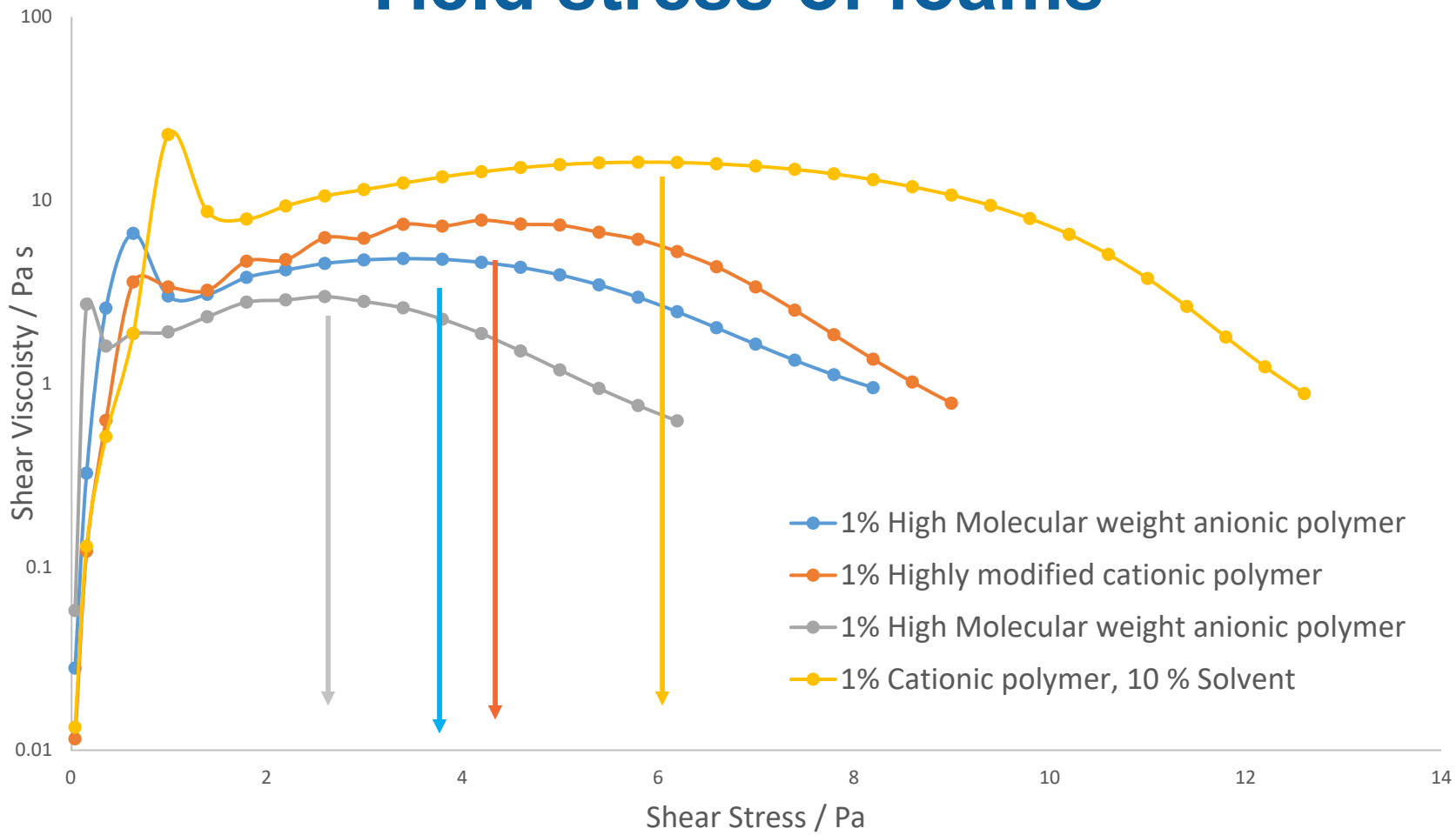
- Adsorbs more slowly than primary surfactant
  - Not greatly involved in initial foam generation
- Makes foam stiffer/ more fuel resistant
  - Fatty acids / alcohols
    - Low solubility
  - Polypeptide
    - High MW
    - Denature on adsorption
- Measure foam stability on hot fuel

Polymer

- Polymers in the foam structure can:
  - Affect rheology, giving a stiffer foam with a greater yield stress
  - Increase foam drainage time
    - Foam is longer lasting
- Improve fuel stability

- BUT polymers can also
  - Make the foam concentrate too viscous to proportion
  - Increase foam viscosity and slow down spreading

Yield stress of foams



The yield stress is where the foam properties change from elastic to viscous and the foam starts to flow

Summary of foam components

Component	Function	Mechanism	Chemistry	Timescale
Primary surfactant(s)	Generate foam, resist fuel	Adsorbs rapidly at new air/water interface	Hydrocarbon surfactants with high water solubility	<1 second
Secondary surfactant	Stiffen and stabilise foam	Slower adsorption	Hydrocarbon surfactants with high water solubility Polymeric surfactants	1-10 seconds
Solvent	Foam booster	Solubilises surfactants	Glycol ether	<10 seconds
Polymer	Solidifies foam	Increased viscosity Cross-link bubbles	Polysaccharide Poly(ethylene)imine	>10 seconds

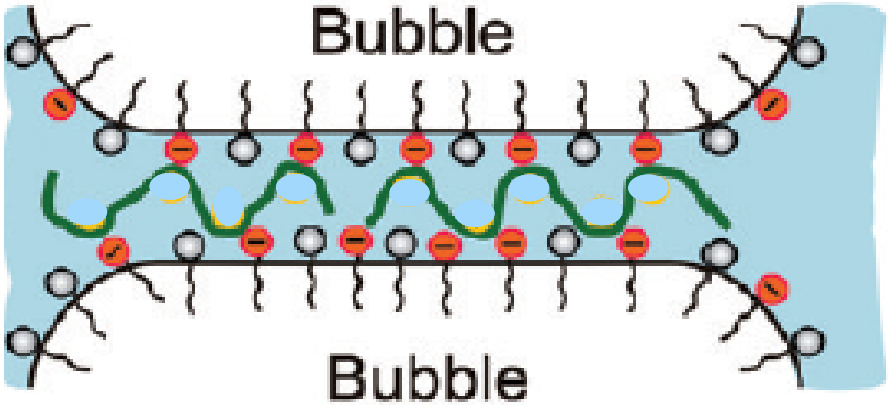
Components act over different timescales to change foam properties
Ideal foam is initially very fluid, then thickens

Lead formulations

- Two lead formulations have been developed
- Formulation pathway 1
  - Aimed at rapid control and extinguishment in fresh water
  - Anionic / amphoteric surfactant blend
  - Fatty acid
  - Polymer
- Formulation pathway 2
  - Aimed at good performance in sea water
  - Amphoteric surfactant blend – no anionics
  - Polypeptide
  - Cationic polymer

Formulation pathway 1 – fresh water

- Amphoteric / anionic surfactant blend
  - Generates foam
- Long chain fatty acid
  - Increases foam yield stress
- Polysaccharide
  - Thickens foam solution



Fire performance – heptane / fresh water

90% control 23”

99% control 36”

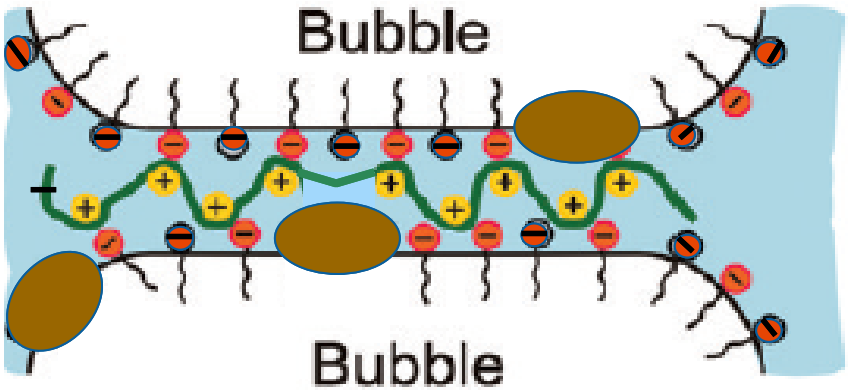
Extinguishment 43”

Burnback > 360”

28ft2 fire test on heptane in fresh water, formulation 1.
MIL-F 24385G proposal requires 35” extinguishment and >360” burnback

Formulation pathway 2 – sea water

- Amphoteric surfactant
  - Generates foam
- Polypeptide
  - Stabilises interface
- Cationic polymer
  - Cross-links and gives structure



Fire performance – gasoline / sea water

90% control 29”

99% control 43”

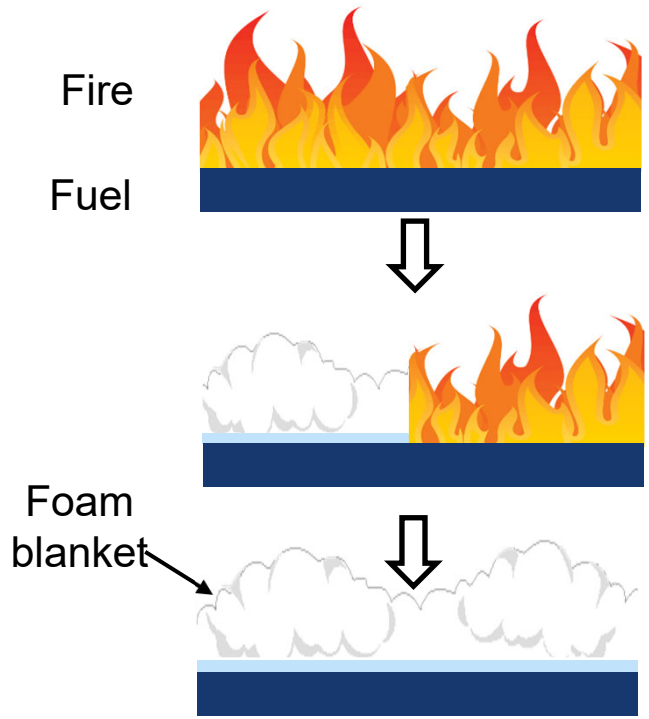
Extinguishment 75”

Burnback 286”

28ft2 fire test on gasoline in sea water, formulation 2.

Requirements of a MIL-F fire fighting foam

- Rapid control and extinguishment (0 – 30”)
  - Spreading over fuel
    - Dynamic and equilibrium surface tensions
    - Expansion ratio
    - Rheology
  - Stability to fuel
    - Resistance to fuel destruction
    - Bubble size distribution



- Long burnback (60 – 420”)
  - Resistance to vapour permeation
    - Drainage time
    - Microscopy
    - Rheology

Fire performance

- In fresh water
- Rapid control of fire on both heptane and gasoline fuels
  - 90 and 99% control within 30 seconds
- Extinguishment around 43 – 50”
- Very good burnback
  - For protection of life and assets, this is equivalent to the current MIL-F specification

- In sea water
- Foam is poorer quality
  - 90% control is rapid
  - 99% control and extinguishment are slower
- Burnback not yet at 360”

Final Formulation

- Design of Experiments (DoE) will used to optimise the two formulations
- Previous experience suggests this will give an improvement in extinguishment and burnback times

Life Cycle Analysis

- Chemical fate of fluorocarbons applied to a fire
- Life cycle inventory analysis
- Life cycle analysis

Fate of foam components

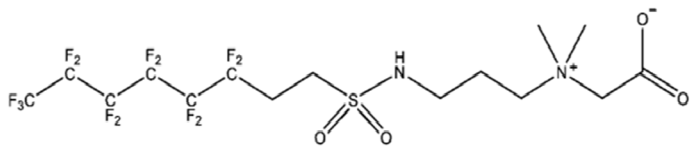
- What happens to fluorocarbons in a foam that is applied to a fire
  - No published data

- Does degradation occur?
- Can C6 fluorocarbons form higher chain PFAS?

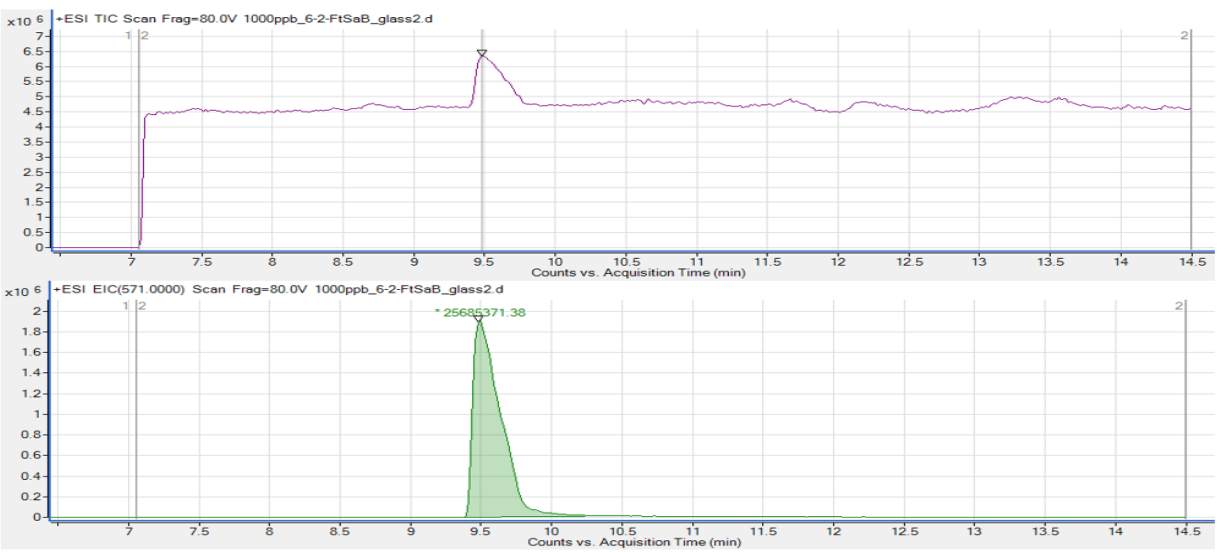
2.7 ft^2 fire pan

Foam fate: Results

Analysis conducted using HPLC-QToF-MS



Fluorotelomer sulfonamido betaine (6:2 FTSaB)

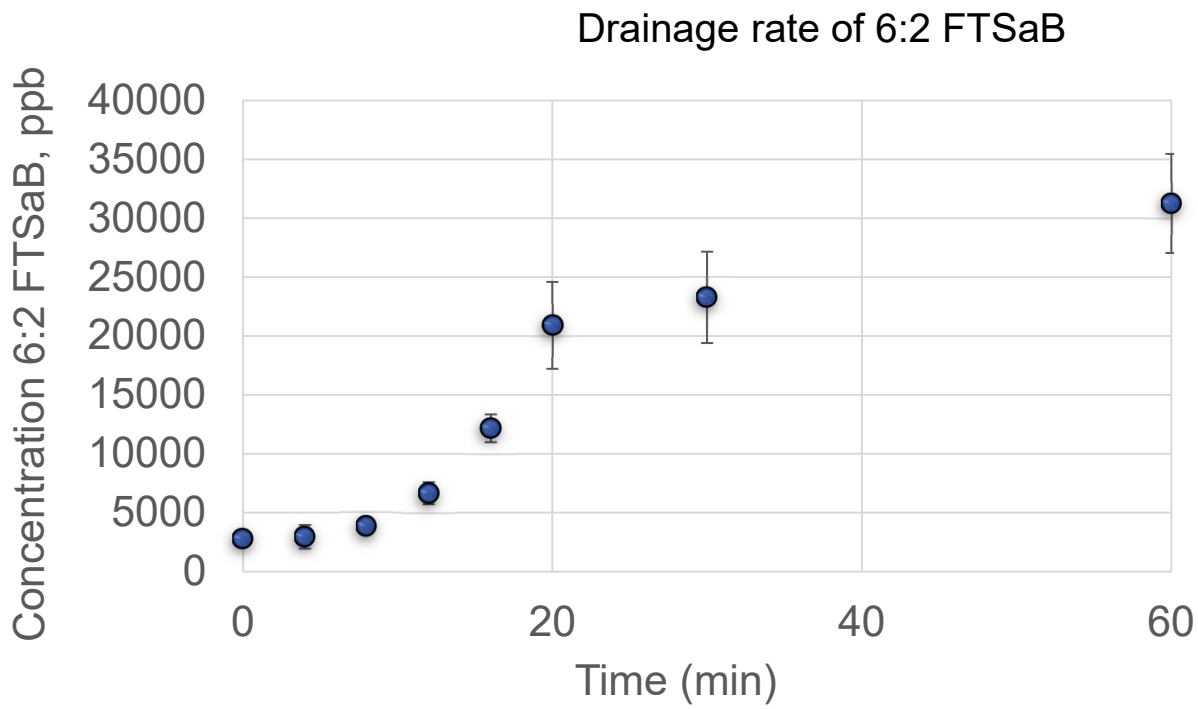


No significant differences in PFAS composition of the control and the fire exposed samples.

Foam fate: Drainage

Concentration of fluorosurfactant (6:2 FTSaB) in the foam solution was much lower in the early drainage samples.

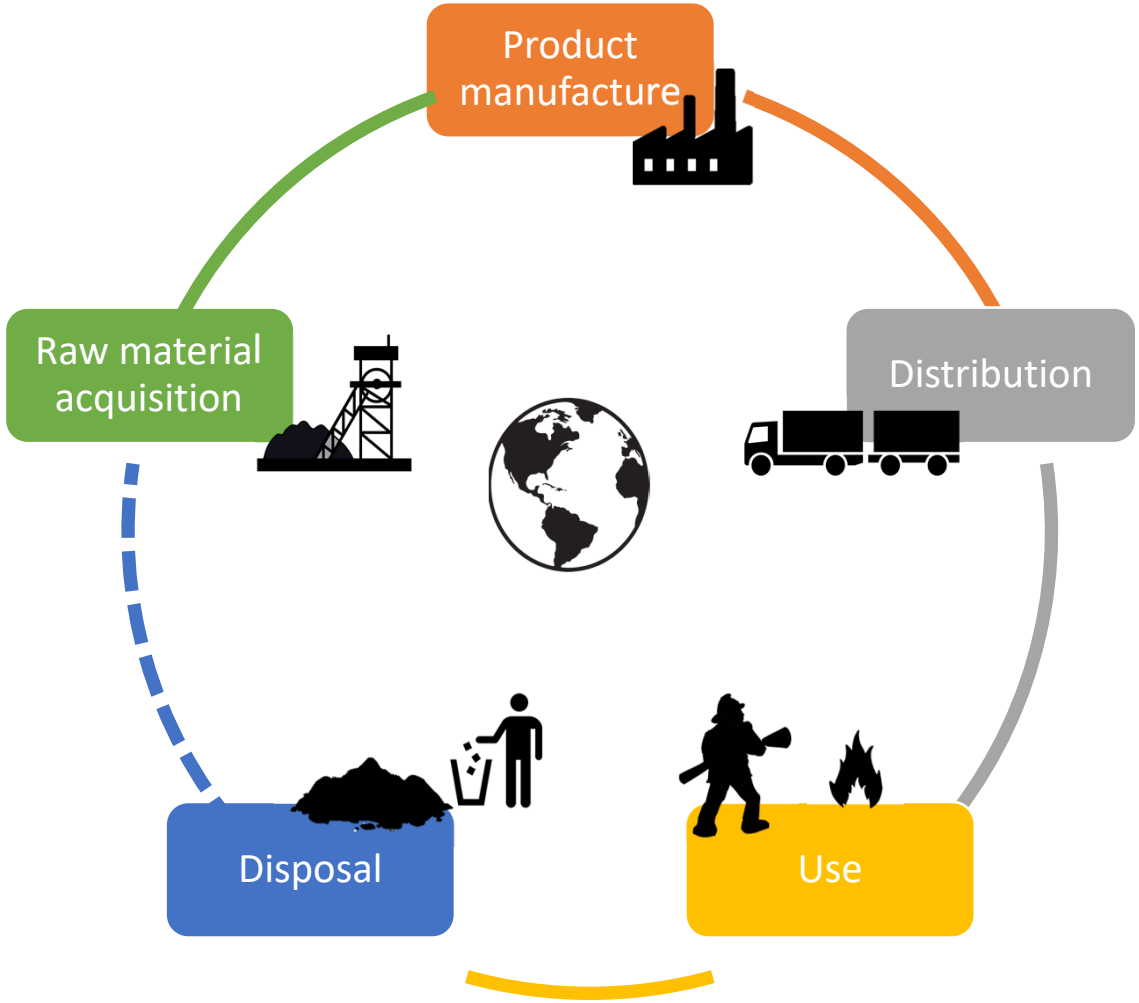
This has potentially significant implications for both foam clean-up and understanding for foam-system behaviours.



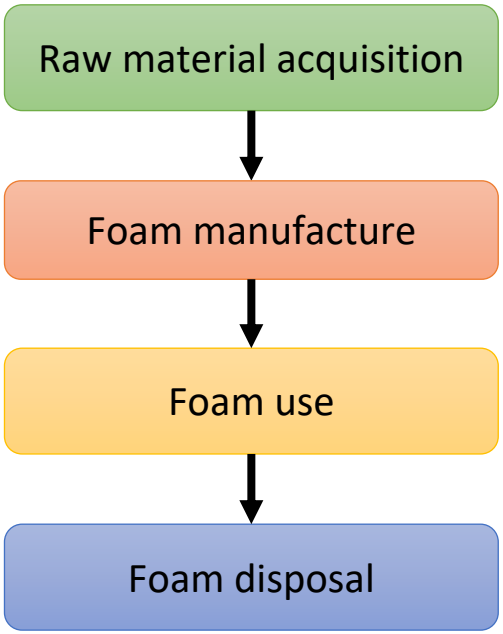
Life cycle analysis (LCA) - Outline

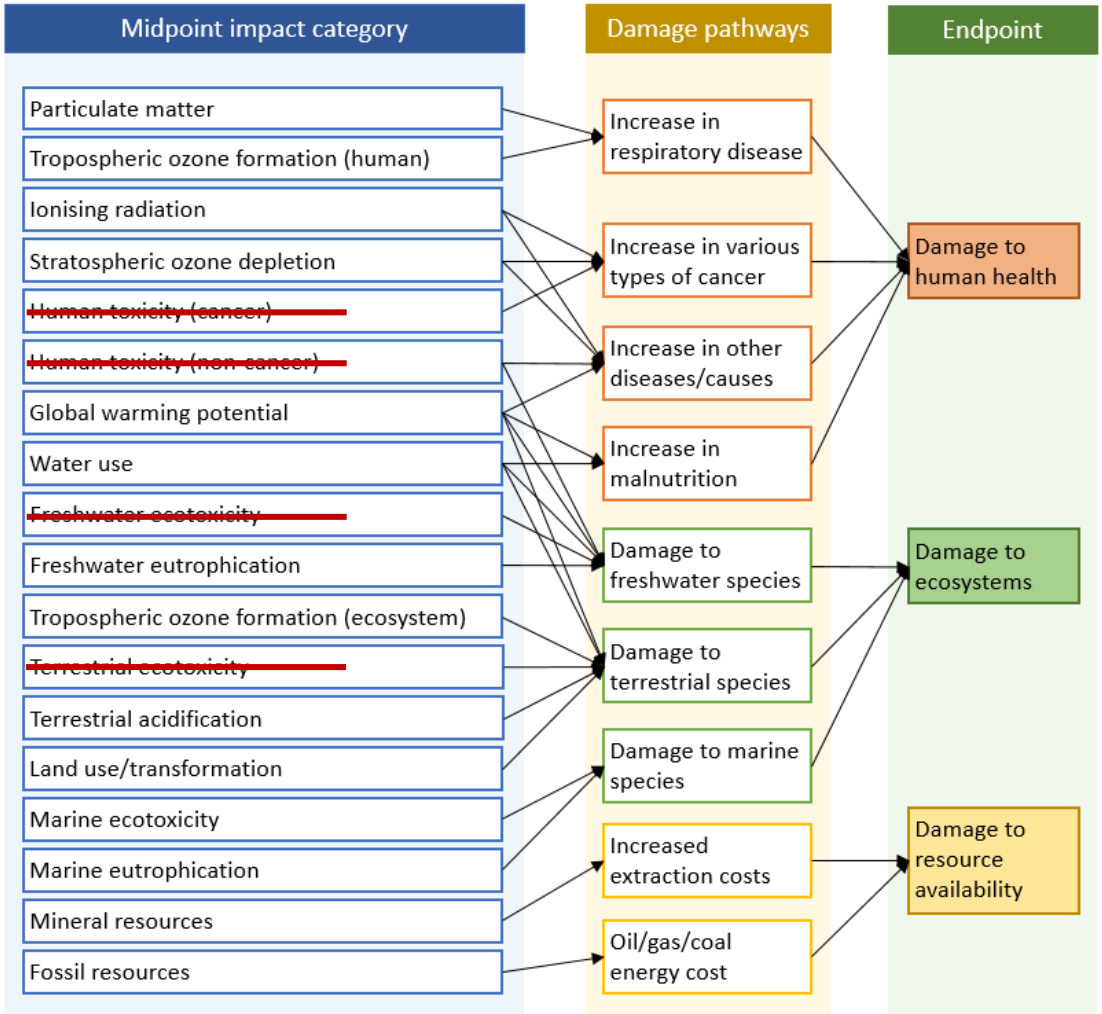
Life cycle assessment considers the environmental impacts across all life stages of a product.

The ReCiPe method was used to compare 2 MIL-F fluorosurfactant foam products with 2 fluorine-free foam products.



Midpoint and endpoints calculated for each life cycle stage on a hierarchist (100 year) basis



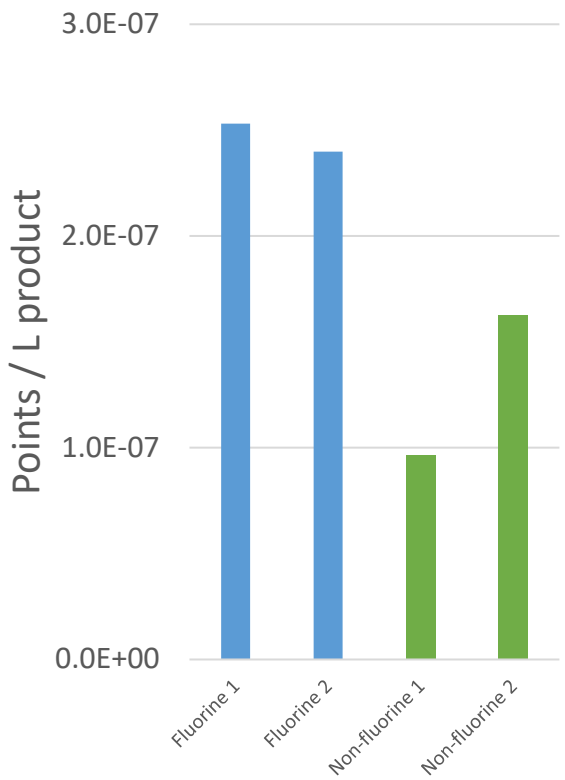


Data sources:

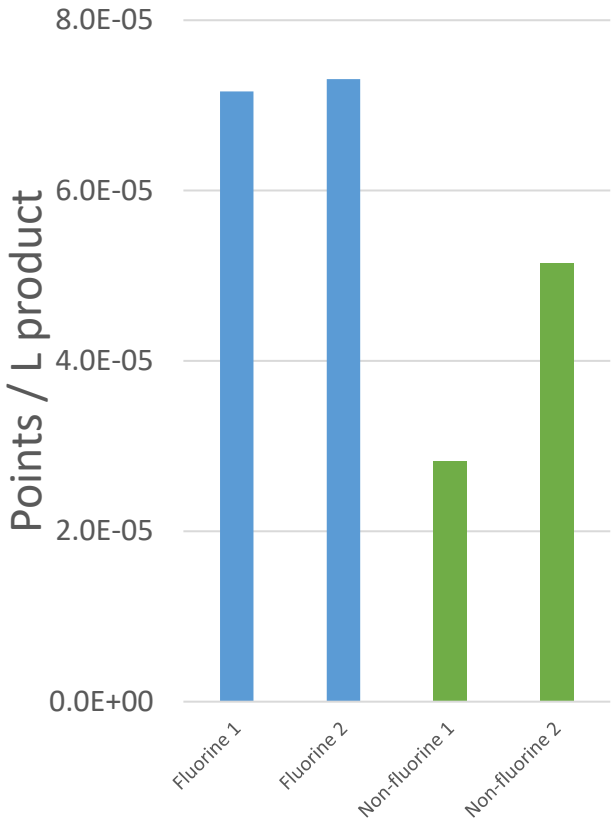
- ReCiPe methodology
- Ecoinvent database
- Peer-reviewed publications

Comparison of C6 AFFF with F3

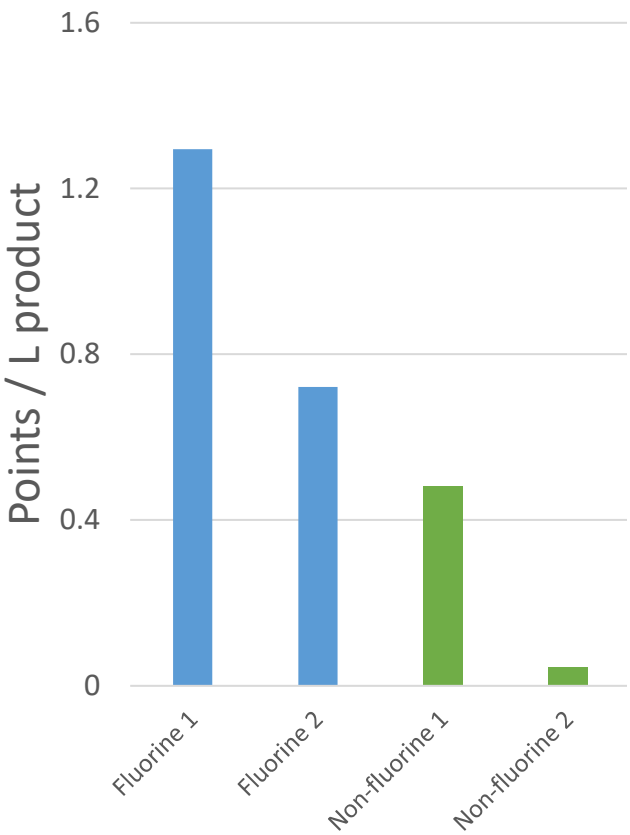
Ecosystem quality



Health quality



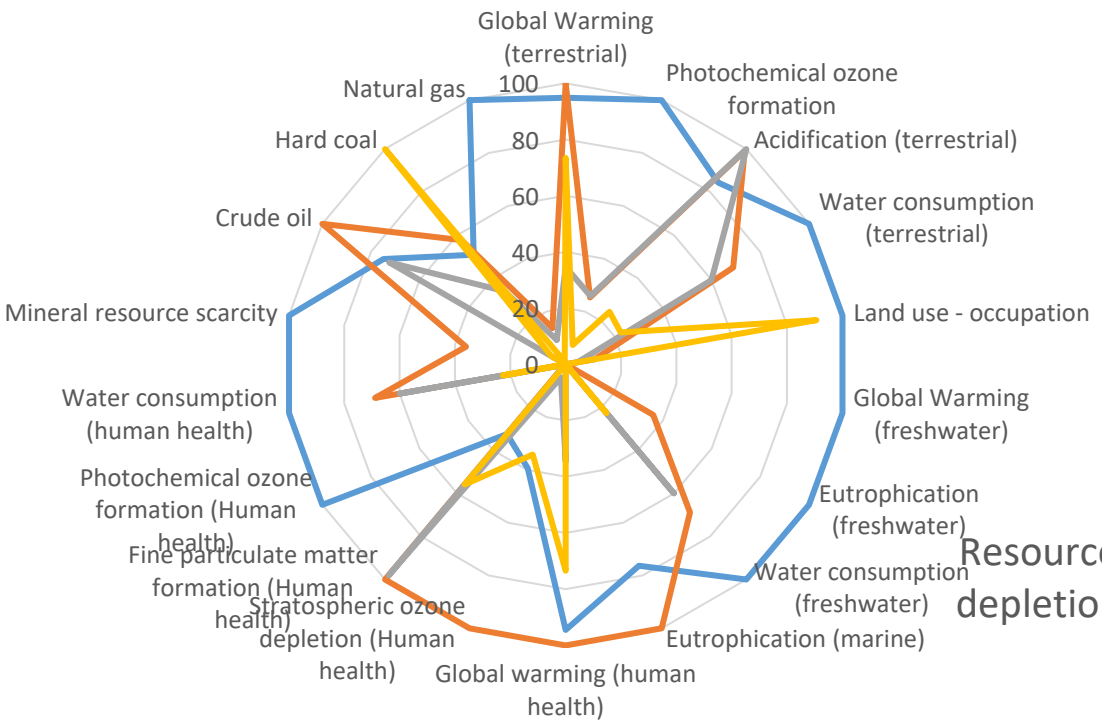
Resource depletion



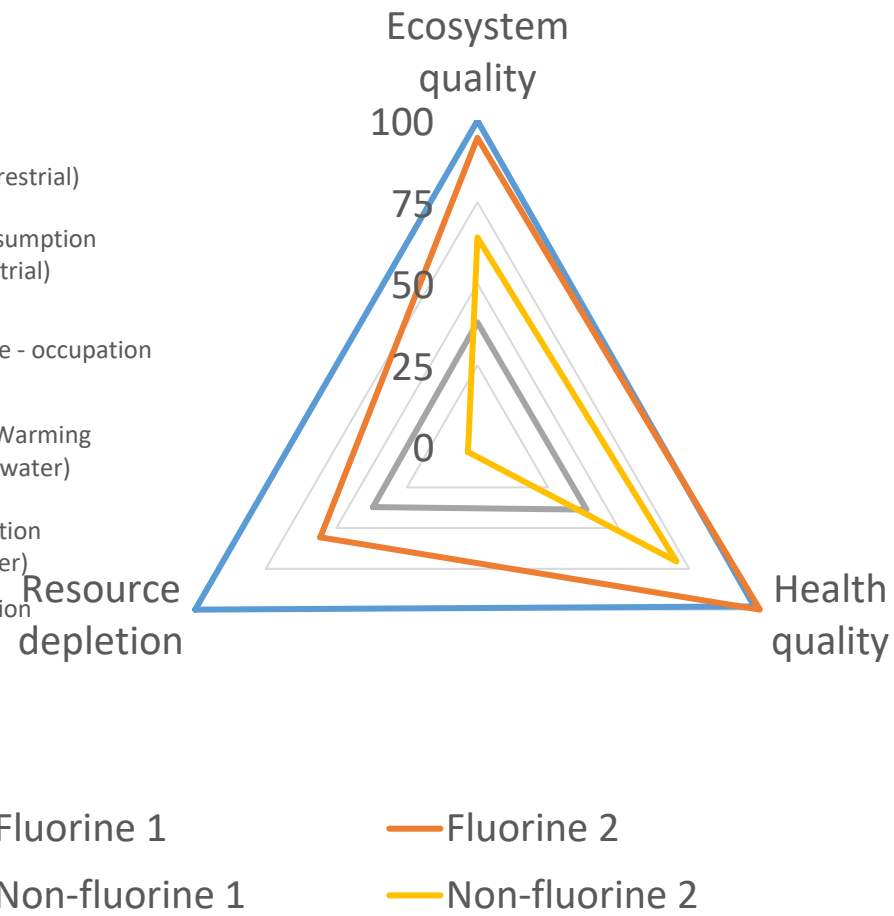
Fluorine 1: C6 MIL-F 24385F approved, Fluorine 2: C6 ICAO B approved
Non-fluorine 1: ICAO B approved, Non-fluorine 2: UL and EN approved

Comparison of AFFF with F3

Fluorine-free foams generated a lower impact in most mid-points.



Fluorine-free foams were lower in all endpoint categories.



Summary of results to date

- Increased understanding of how foam components affect foam properties and fire performance
- Two formulation pathways investigated
  - Fire tests in fresh water show rapid control, extinguishment does not yet meet MIL-F target, very good burnback
  - In sea water, reasonable control, extinguishment and burnback not good enough
  - Statistical optimisation to be carried out
- Fate of fluorocarbon in foam investigated
- Life Cycle Analysis shows fluorine free foams have lower impact over all endpoints

Next steps

- Develop new MIL-F 24385 specification for fluorine-free foams
- Improve formulations to deliver MIL-F performance in fresh and sea water:
  - Extinguishment on heptane <35”, burnback >360”
- Address user concerns
- Qualify foams and make available commercially
- Publish life cycle analysis method and results
  - Apply LCA methodology to foams

Transition plan - Revision of MIL-PRF-24385-F

- Current specification is designed around fluorocarbons

- Modify specification to be appropriate for fluorine-free foam
  - Requirement to contain fluorocarbons
  - Positive spreading coefficient

- National Foam has provided a MIL-PRF-Fluorine Free draft specification in fresh water
  - Various suggestions
  - Seek end user feedback

First Article Test (FAT)

- Complete formulation work, select optimised product and manufacture small pilot batch
- Conduct specification testing for proof of results & grade compliance to proposed new MIL-PRF-24385F standard
  - Fire tests in fresh & sea water
  - Corrosion
  - Aquatic toxicity
- Manufacture small pilot batches of foam for field testing
  - Structure usage and performance plan review for user community
  - Field test new foam, using current application equipment at user training facilities
  - Solicit user feedback

Transition plan – Commercialisation of Foam

- National Foam to conduct full MIL-PRF-New Fluorine Free Foam site acceptance testing based on production batches
- Elevate foam to “Qualified Products List”
- Finalize supporting documentation
  - MSDS
  - Use and Handling
  - Training Guidance
  - Other

Transition plan - Life Cycle Analysis

- Publish findings
- Highlight sustainability and environmental safety differences between F and F-free foams
- Inform future foam development
- Inform best practices for use of foam in training, equipment commissioning and deployment

Key points

- Improved understanding of fluorine-free fire-fighting foams
- Foam formulations developed for fresh and sea water show promising results
- Method developed for life cycle analysis of foams
- Fluorine-free foams show a significant reduction in environmental impact compared with AFFF

Publications

- Posters presented at SERDP Symposium, Washington 2017, 2018 and planned December 2019
- Poster at SCI Formulation Conference London Jan 2018

- 3 publications currently planned
  - Comparative life cycle analysis of two fluorinated vs two fluorine-free fire fighting foams
  - Short communication on dynamics of surfactant concentration in drained foam
  - Chemical fate of PFAS exposed to fires

WP-2738: Fluorine-free aqueous film-forming foam

Performers: John Payne, Kate Schofield, Katie Shelbourne, Nigel Joslin, Anne Regina

Technology Focus

- *Study physical chemistry processes to guide development of a new F-free foam*
- *Identify and generate data needed for life cycle analysis*

Research Objectives

- *Develop F-free foam that meets MIL-F fire performance in fresh and sea water*
- *Complete life cycle analysis of F and F-free foams*

Project Progress and Results

- *Foam properties needed to pass test defined*
- *Candidate formulations give good 90% and 99% control, excellent burnback in fresh water MIL-F fire test but flickers give long extinguishment time*
- *Fate of fluorocarbons in fire investigated*
- *Life cycle analysis completed*

Technology Transition

- *Redefine MIL-F specification for F-free foams*
- *Approve F-free foam onto QPL*
- *Manufacture and market new foam to users*
- *Publish life cycle analysis to inform industry*