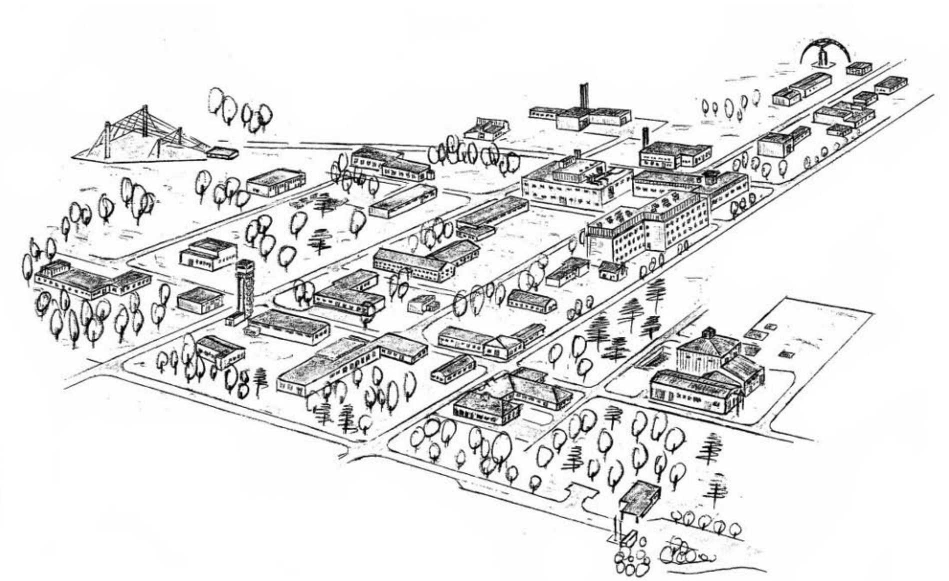
Is there a future for AFFF without fluorine?

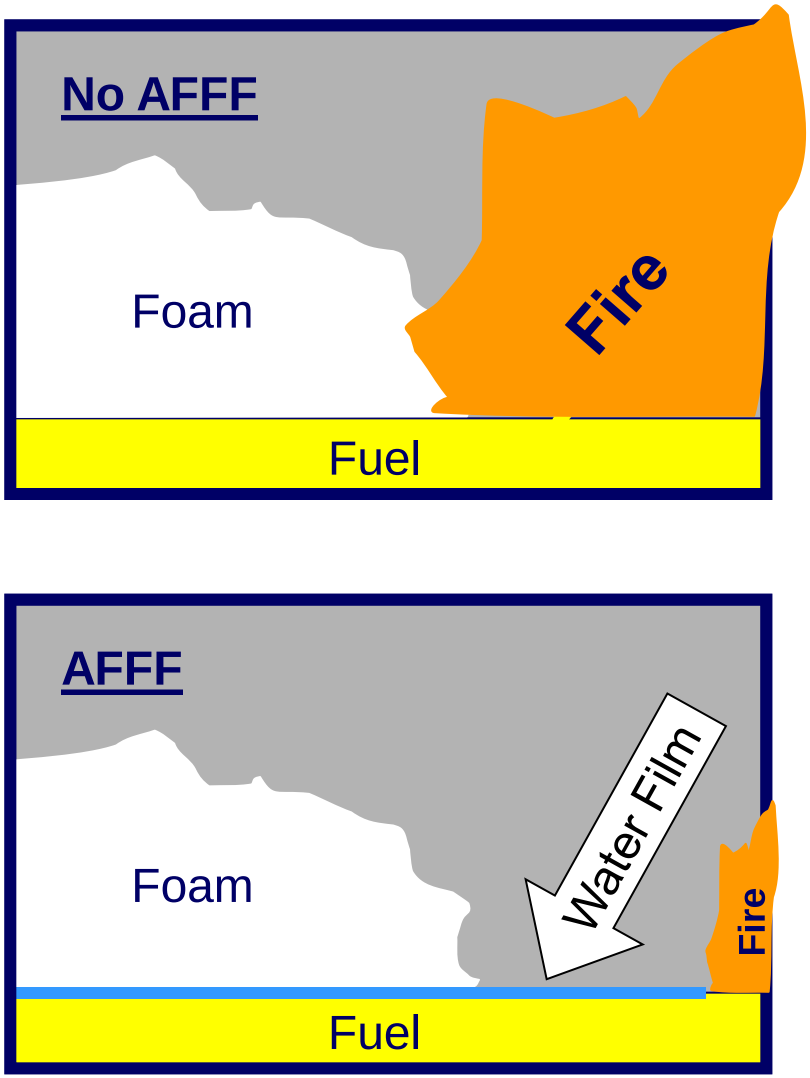
Limitations and Opportunities



Ralf Hetzer

Bundeswehr Research Institute for Protective Technologies and NBC Protection (WIS)

Basics of AFFF



The Aqueous Film…

- … cools the fuel surface.
- … acts as vapor barrier.
- … operates in areas without foam.
- … autonomously closes small perforations of the foam.
- … works as buffer between fire and foam.

The Importance for the Bundeswehr

- High pool **fire risk**.
- Firefighting **help** from **outside** can **not** be **expected**.
- **Fast Firefighting** is **vital** demand the Bundeswehr.

Picture: Luftwaffe/Jan Starcke

Picture: Bundeswehr / PIZ Marine

- Need of the most effective extinguishing agent.

=> To date **AFFF**!

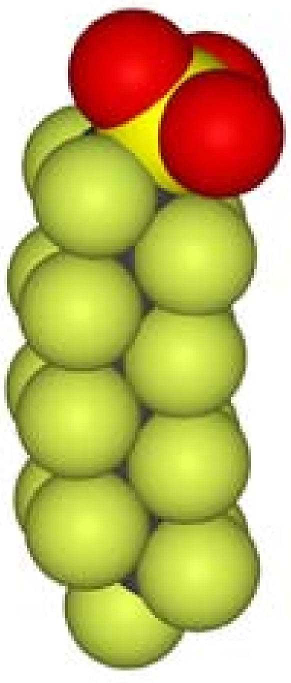
- No possibility for fire water retention.

=> Need of **environmentally-friendly AFFF**!

Actual AFFF use polyfluorinated surfactants for aqueous film formation.

Polyfluorinated surfactants…

- …are **persistent**.
- …can be **bio-accumulative**.
- …can be **toxic**.



Spreading Coefficient (S)

$$S = SFT_{Fuel} - (SFT_{Foam} + IFT)$$

SFT_{Fuel}: surface tension of the fuel
SFT_{Foam}: surface tension of the foam solution
IFT: interfacial tension between the foam solution and the fuel

If S > 0, spreading is possible.
But if S > 0, spreading is not obligatory.

S > 0 is a necessary, but not a sufficient condition.

Surface Tensions of Fuels

	Fuel	SFT_{Fuel} (24 ° C)	Sample Origin
1.	FAME (Biodiesel)	31,5 mN/m	BP Refinery Emsland, Germany
2.	Diesel	28,3 mN/m	BP Refinery Emsland, Germany
3.	Jet fuel	26,7 mN/m	BP Refinery Emsland, Germany
4.	F-34	25,8 mN/m	Bundeswehr (NATO Standard Fuel[i])
5.	Ethanol	22,2 mN/m	BP Refinery Emsland, Germany
6.	Gasoline	20,7 mN/m	BP Refinery Emsland, Germany
7.	Cyclohexan	24,9 mN/m	Reference substance, Sigma-Aldrich

[i] NATO, (1997) Logistics Handbook. NATO, Brussels.

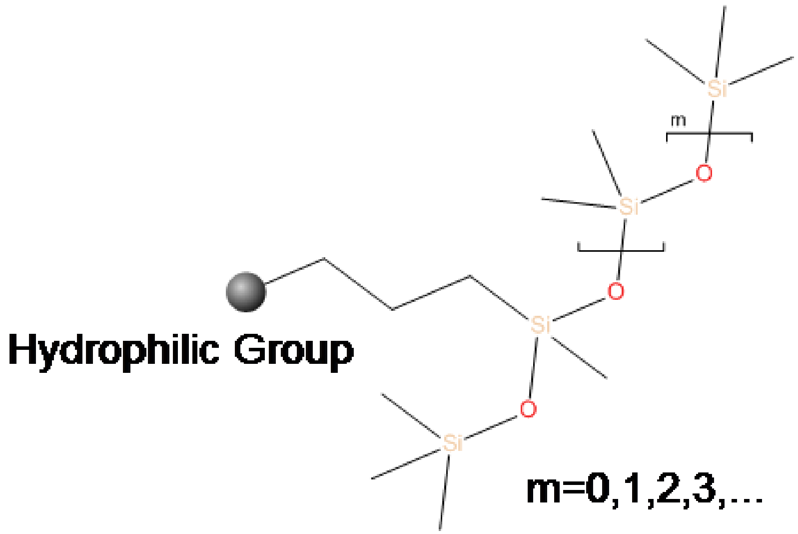
Surface Tension of Aqueous Surfactant Solutions

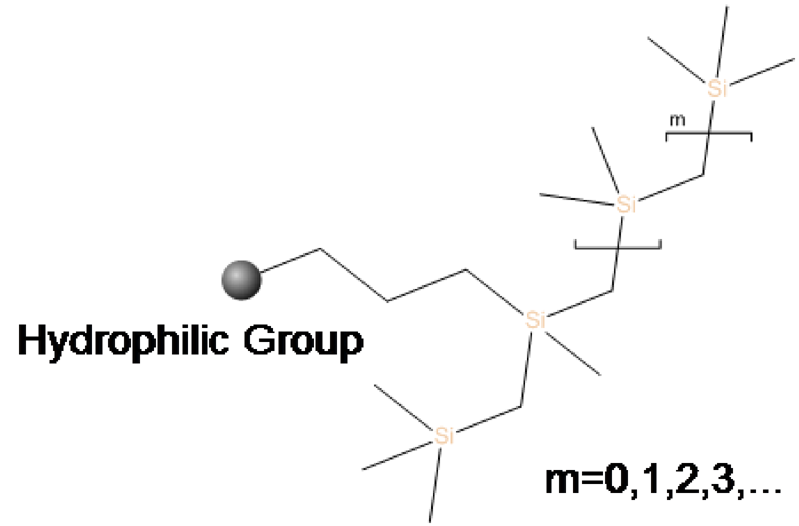
	Surfactant Type	Minimum SFT_{Foam} (aqueous solution; 20 ° C)	Comment
~~1.~~	~~Fluorosurfactants~~	~~15 mN/m~~	
2.	Siloxane surfactants	20 mN/m	
3.	Carbosilane surfactants	23 mN/m	
~~4.~~	~~Alkyl surfactants~~	~~28 mN/m~~	
~~5.~~	~~no surfactant~~	~~73 mN/m~~	~~pure water~~

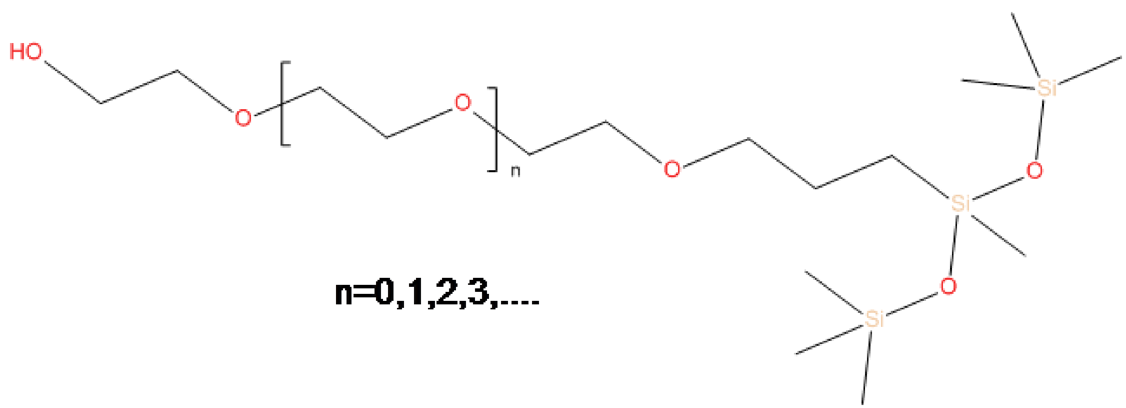
$$S = SFT_{Fuel} - (SFT_{Foam} + IFT)$$

SFT_{Fuel} = 25 mN/m and IFT = ???

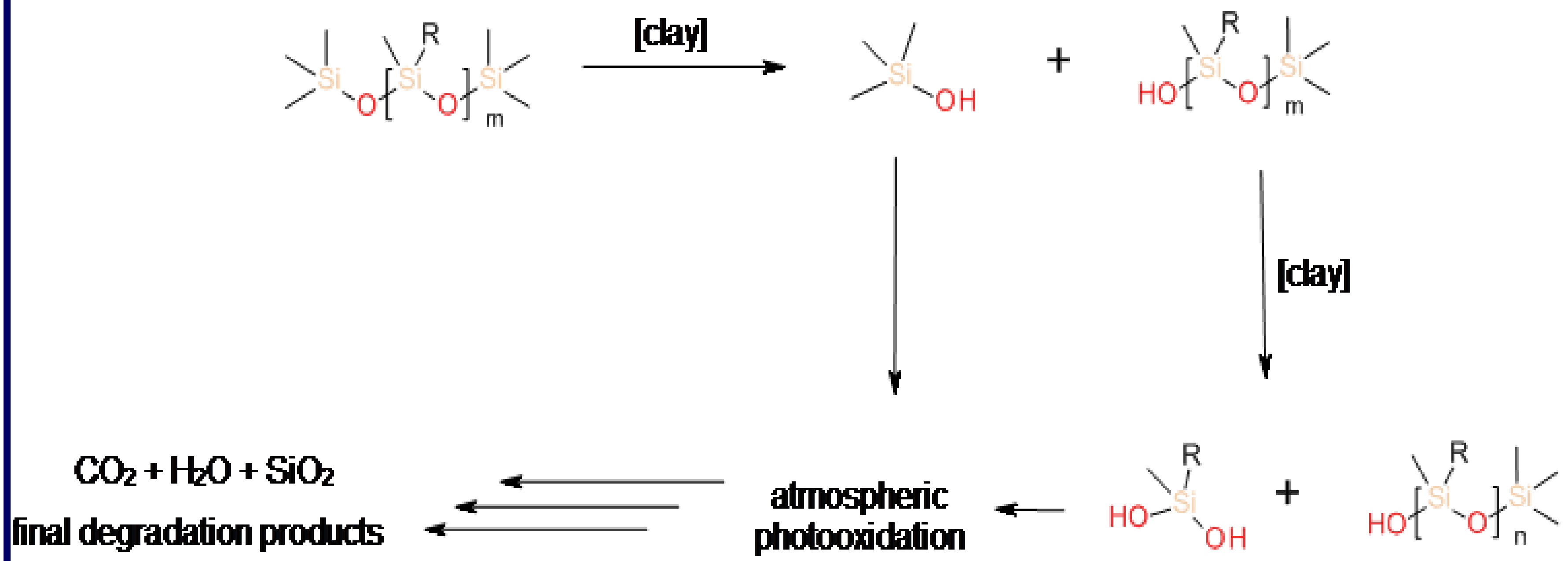
Siloxane and Carbosilane Surfactants







Degradation of Siloxanes



- Primary degradation of the Siloxane group by catalyzed hydrolysis.
- Hydrolysis is catalyzed by clay and other minerals.
- If the fragments of siloxanes are small enough, they are subjected to an atmospheric photooxidation.
- Biodegradation of the No-Siloxane group (R).

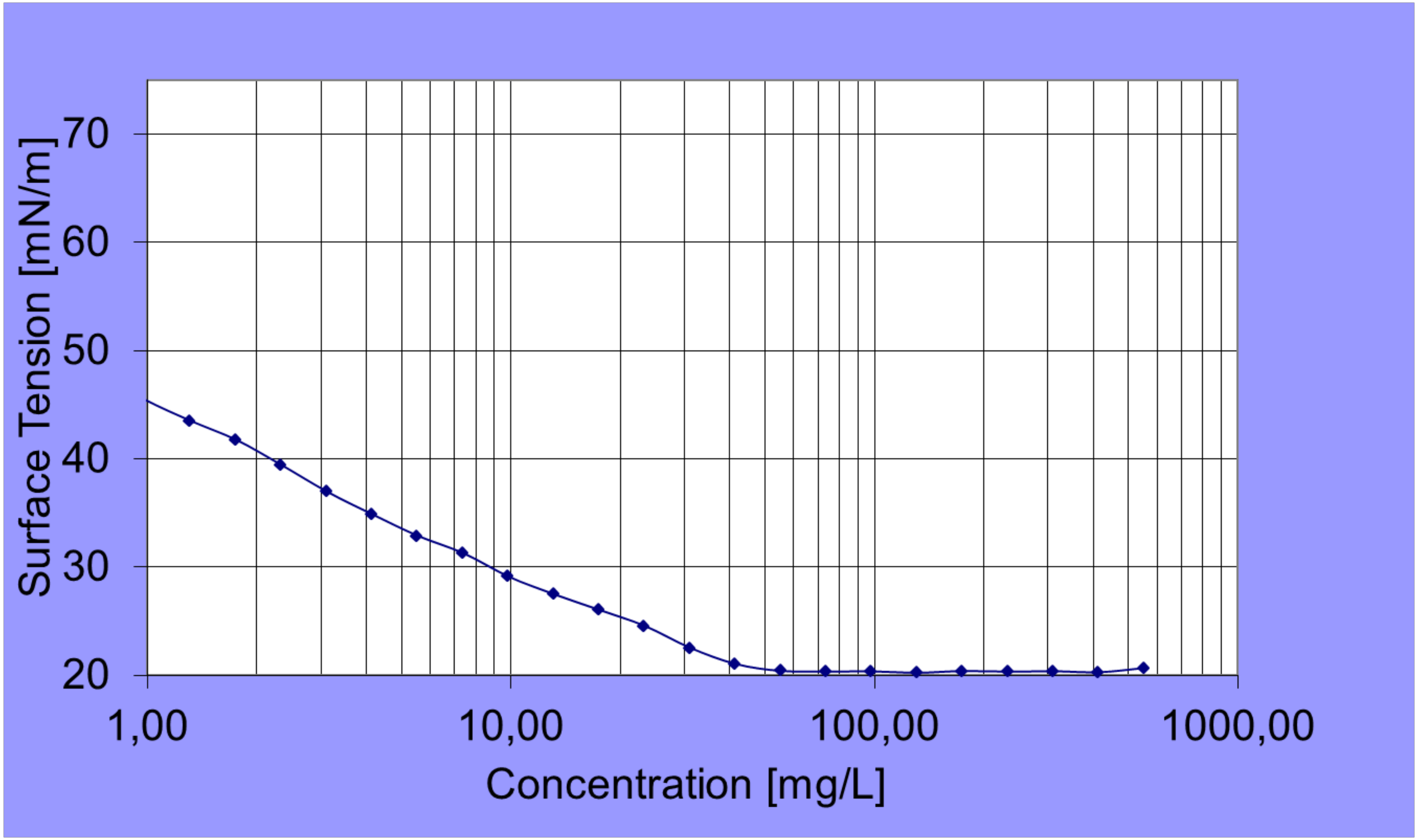
Source: D. Gravier, K.W. Farminer, R. Narayan, Journal of Polymers and the Environment 2003, *11*, S. 129-136.

Synthesized Siloxane Surfactant

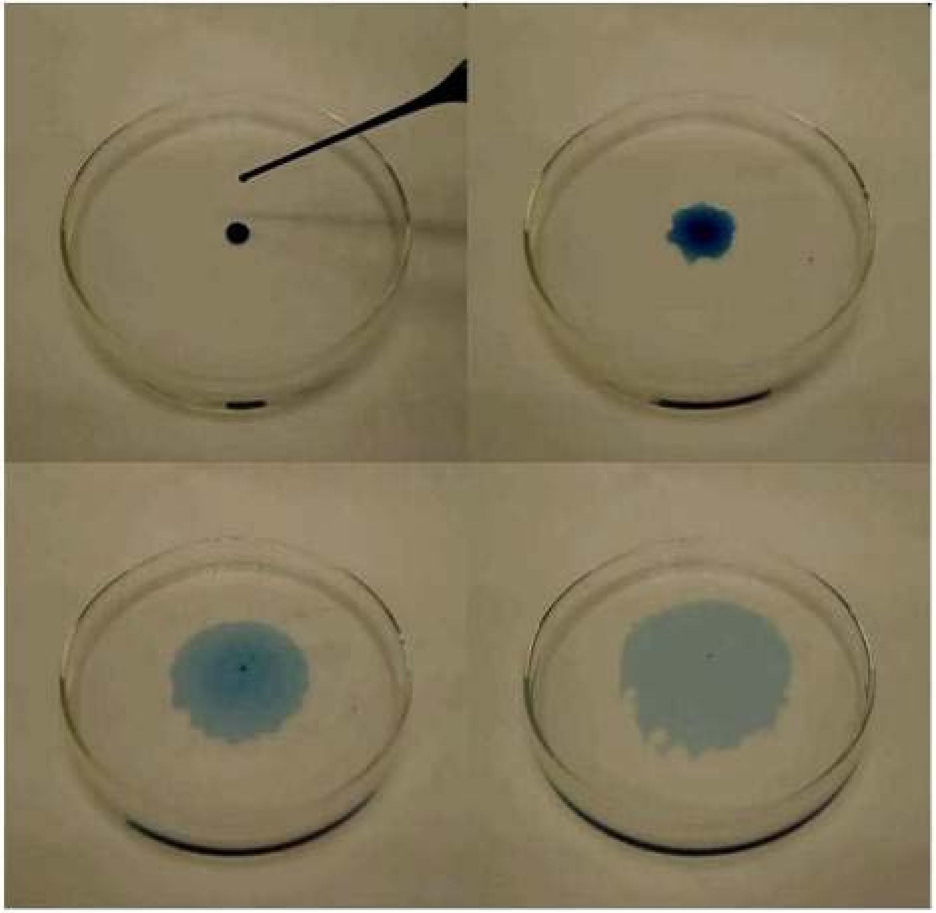
Surfactant	Concentration [mg/L]	SFT [mN/m]	IFT to $c\text{-}C_6H_{12}$ [mN/m]	S# [mN/m]	aqueous film on $c\text{-}C_6H_{12}$
Ethoxy-Siloxane	500	20,6	0,5	3,9	No
BuM14	10188	20,3	2,5	2,2	No
BuM20	10134	20,7	1,2	2,1	No
BuM21	10194	21,2	1,4	2,4	No
KAWI 202	184	20,4	7,9	-3,3	No
KAWI 206	303	21,0	4,1	-0,1	No
KAWI 211	541	20,8	3,8	0,4	No
KAWI 212	126	20,4	9,3	-4,7	No
KASE 017	247	21,3	0,4	3,3	Yes
KASE 018	503	20,2	0,1	4,7	Yes
RH-77	502	20,2	0,1	4,7	Yes

calculated with a SFT of 25 mN/m for $c\text{-}C_6H_{12}$

Critical Micelle Concentration (CMC)

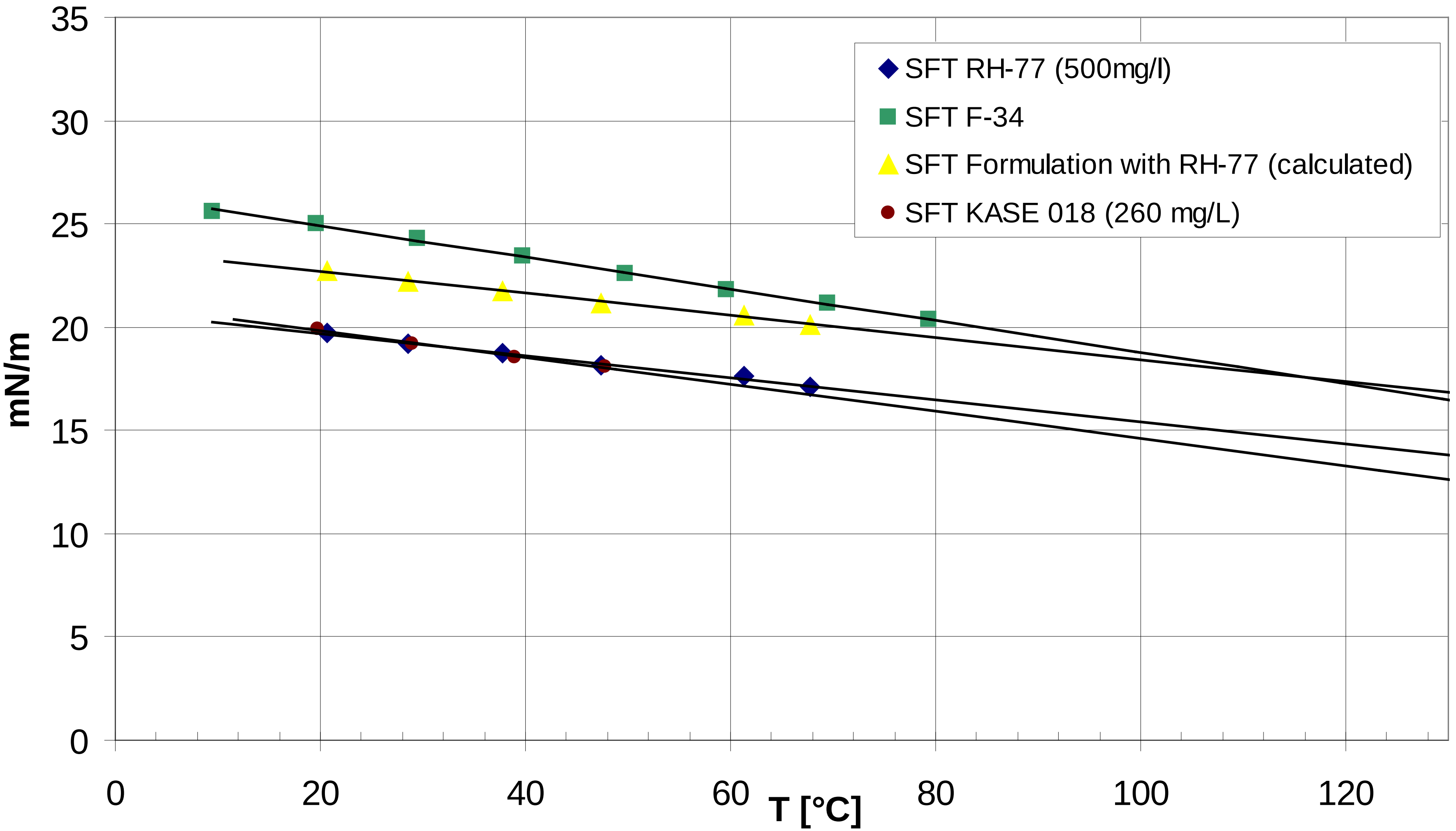


Spreading test of KASE 018 on Cyclohexane.



Pictures: Kai Wirz, Department for Organic Chemistry, University of Cologne.

Temperature Behaviour of Siloxane Surfactant RH-77

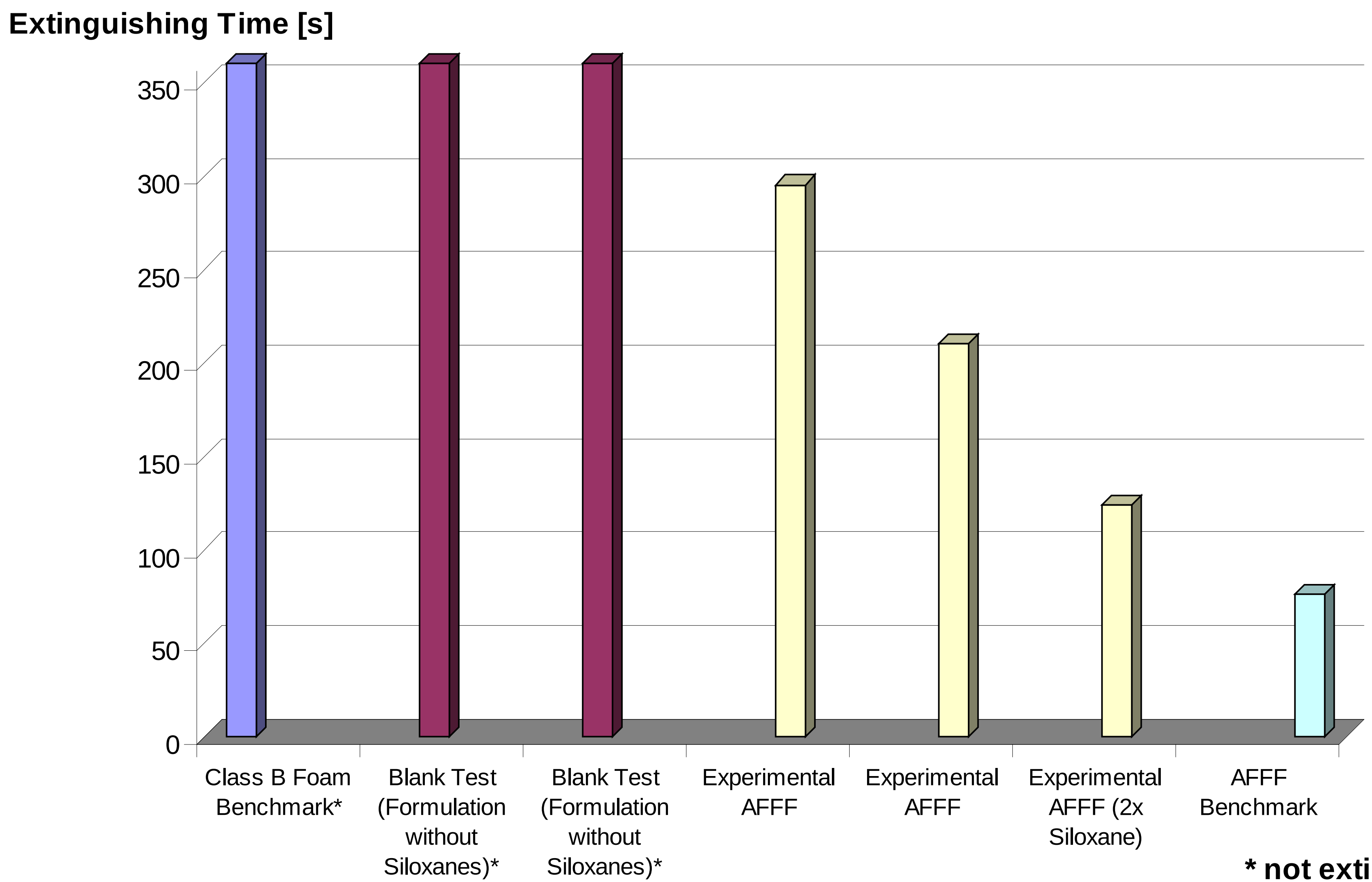


	Tensid	Expansion	Water Time [min]			
			1/8	1/4	3/8	1/2
1.	Benchmark AFFF	8,6	4,38	6,83	8,75	11,15
2.	Siloxane-based foam (RH-77)	6,1	1,67	3,10	4,60	6,20
3.	Siloxane-based foam (KASE 018)	8,3	2,95	5,40	7,60	9,80
4.	Requirements TL 4210-0112*	>5,0	-	>2,50	-	>5,00

*** Technical Specification (TL) 4210-0112,**
Federal Office of Defense Technology and Procurement (BWB).

[1] Das Tensid wurde vorgelegt und mit Leitungswasser auf 5,00 L aufgefüllt.

Small Scale Fire Tests



*** not extinguished**



Small Scale Fire Tests

	Foam Concentrate	Extinguishing Time	Fluorine	Siloxane	Comment
1.	**Siloxane-based AFFF (KASE 018)**	2:04	No	Yes	
2.	**Siloxane-based AFFF (KASE 018)**	3:30	No	Yes	½ quantity siloxane surfactant.
3.	**Formulation of 1. and 2. without Siloxanes.**	> 6:00 min	No	No	Not extinguished!
4.	**Benchmark AFFF**	1:16 min	Yes	n.d.	
5.	**Benchmark Class B Foam**	> 6:00 min	No	n.d.	Not extinguished!

Test Pan: 0,66 m² (round) — **Outside**
Application Rate: 1,1 L/min — **Fuel: 7,0 L F-34**
Buffer: 10,0 L water — **Preburn time: 0 s**

To do:

- Further fire tests and formulation experiments.
- Long time stability and storage tests.
- Simplification of the siloxane surfactant synthesis.
- Large scale fire tests.
- Final determination of the environmental behavior of the identified siloxane surfactants.

Conclusion

- **A fluorine-free AFFF seems to be possible for the military relevant fuels .**
- **Only special siloxane surfactants are suitable for aqueous film forming.**
- **First formulation experiments and fire tests with these siloxanes were successfully conducted.**

WIS - Fire Fighting Technology Center

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Thank you for your kind attention.

Questions?