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## Treatment of discarded fire fighting foam premixes Project 704-011

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## Conclusions and summary

Discarded premixes of various fire extinguishing foam products are considered as hazardous waste and are treated as such by the means of evaporation and incineration. The premixes contain a considerable share of water, between 94 and 97 per cent and the destruction is expensive (6000 to 7000 SEK per m<sup>3</sup> or roughly 600 to 700 euro).

The RO treatment of is an effective method for minimising the volumes to at least 14 per cent of the original volume.

However, some components of the premixes pass the RO membrane and the concentrate is therefore unsuitable for reuse as fire extinguishing foam material.

The chemical and treatability properties of the permeates from the RO treatment of various foam extinguishing products exhibit that the permeates are amenable to discharge and treatment in municipal treatment plants.

Fluorinated surfactants and compounds in certain foam extinguishing products are retarded to a great extent by the RO treatment, but trace concentrations are present in the permeates. As some of the fluoro compounds belong to a group of highly persistent bioaccumulating chemicals, the discharge of RO permeates from these products is not recommended also the concentrations are extremely low.

The capital cost of the investment for RO equipment with a capacity of 10 m<sup>3</sup> per week amounts to about 200 000 SEK. The operating costs, including energy requirement, replacement of membrane and disposal of concentrate, depend on the treated volume. The operational costs are dominated by the cost of the waste disposal.

Similar pollution circumstances are apparent at fire fighting training centres where foam products are used and at real fire fighting situations with or without the use of foam products.

Run-off waters from these situations contain beside the foam products also contaminants from the fire itself. None of these run-off waters were investigated in the present work, but the similarity of contamination suggests that RO-treatment is a suitable method to reduce contamination from fires.

A mobile RO-equipment mounted on a truck would be a suitable solution for solving the pollution problems even from these areas.

## 1. Introduction

Fire extinguishing foam products are used in diluted solutions of concentrated products. The water-diluted solutions contain between 3 and 6 per cent of the concentrated product. These solutions are also called premixes.

The compositions of fire extinguishing foam products vary depending on the character of the fire. The products contain one or more foam forming surface active compound (surfactant), some of them fluorinated, foam stabiliser, solvent, anti freeze component and sometimes a biocide.

The shelf life of premixes of various fire extinguishing foam products is limited due to readily biodegradable components in the mixtures. When the shelf life of a product is exceeded, the product must be discarded because of changes of fire fighting properties. Discharge to municipal sewage treatment is not permitted since high concentrations of organic components may have adverse effects on biological treatment plants. Beside that, the film forming products contain fluorinated surface-active surfactant that is biologically not degradable (persistent) and the discharge of it is not permitted.

Discarded premixes are considered as hazardous waste and must be destructed as such by evaporation and incineration. The premixes have high water content, and therefore the volumes of discarded products are considerable and the destruction is costly (6000 to 7000 SEK per m<sup>3</sup>, roughly 600 to 700 euro per m<sup>3</sup>).

The purpose of the present investigation is to produce a water phase amenable for biological treatment by separating the water from the discarded products. Separation of water from a mixture like the discarded products can in principle be performed by evaporation, which in this case is almost impossible due to foaming, but also by reversed osmosis filtration (RO) which separate salts and organic substances from water.

Three typical types of fire extinguishing foam products were investigated. One of them in form of a discarded premix, the other 2 with newly prepared premixes, as no discarded products was available.

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## 2. Material and method

The following premixes were involved in the investigation:

A. Discarded AFFF premix containing 6% of the concentrated product. The discarded premix was obtained from AB Svenska Tempus. The product is produced by 3M and contains:

- 2-(2-butoxyethoxy)ethanol
- amphoteric derivative of fluorinated alkyl amide
- salt of alkyl sulphate
- salt of perfluoro alkyl sulphonate
- residual monomer of fluorinated substance (perfluoro octane sulphonate, PFOS, which is extremely persistent and generally distributed in the environment. The production has been stopped in May 2000 by 3M Perfluoro alkyl sulphonate contains 0,001 percent or less PFOS).

The COD<sub>Cr</sub> content of premix A is 25.2 g/l.

B. - An FFFP-AR premix, 6%, prepared from new product. The product was obtained from AB Svenska Tempus. The product is produced by Angus Fire Ltd. and contains:

- 1,2-hexane diol
- water soluble polymer
- hydrolysed protein
- fluorinated surfactant
- biocide.

The fluorinated surfactant in the product is produced according to an other technique (telomerisation) than the electrochemical method of 3M and no residual monomer, PFOS, is formed in the process, according to the producer.

The COD<sub>Cr</sub> content of premix B is 17.4 g/l.

C. - A synthetic detergent based premix, 3 %, prepared from new product. The product was obtained from DAFO Brand AB. The product was produced by TOTAL WALTER Feuerschutz Lösmittel GMBH and contains:

- 2-butoxyethanol
- synthetic detergents (3 compounds)
- fatty alcohols, C10-C14.

The COD<sub>Cr</sub> content of the premix is 11.3 g/l.

The water phase from the premixes were separated by reversed osmosis, RO. Tube membranes, AFC-99 from PCI were used for the RO filtration. The pressure was 50 bars and the temperature was kept at 30°C. The treatment time for each premix was 9 to 10 hours. The membranes were cleaned between treatment of the various premixes by washing with Ultrasil (detergents and alkali) and deionized water.

The water phases separated from the RO treatment of various premixes were investigated concerning chemical and ecotoxicological properties according to the following:

BOD<sub>7</sub>, Swedish Standard SS 028143-2  
COD<sub>Cr</sub>-NL, according to LCK 114/814, Dr. Lange  
TOC, SS 028199, Astro 2001  
pH, SS 028122-2  
Conductivity, SS-EN 27 888  
Kj-N, Technicon Industrial Method 376-75/B and Technicon Industrial Method 695-82W  
EGOM, Extractable Organic Matter, Extraction with cyclohexane, gas chromatography, FID, quantification with n-alkan, ITM 921029  
Fluorinated surface active compounds (A and B) performed by Fraunhofer Institute, Germany by LC/MS

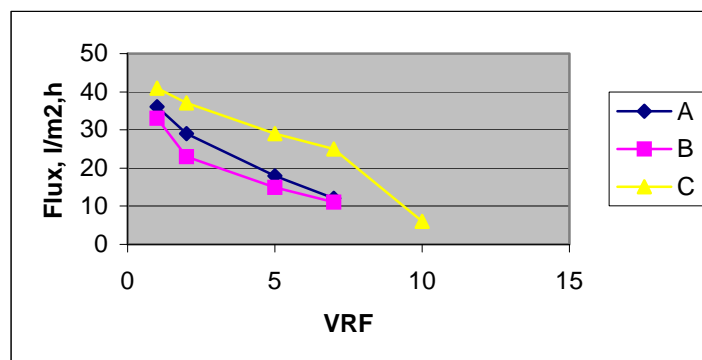
And

Acute toxicity, bioluminescent bacteria (Microtox), IVL B 1100  
Growth inhibition of green algae  
Inhibition of respiration of activated sludge, ISO 8192, Method A  
Inhibition of nitrification.

## **3. Results and comments**

### **3.1 RO treatment**

The premix is separated by RO into a concentrate and a permeate, which is the water phase passing through the membrane. The permeates obtained were crystal clear and not foaming. Measurements of the flow through the membrane (flux) at different volume reduction factors (volume of premix at start/volume of concentrated premix), VRF, was used to follow the RO treatment of the premixes. The flux, which is a measure of filtration capacity of the membrane, is expressed in liter/m<sup>2</sup>membrane, hour. Low flux through the membrane is limiting the feasibility of the RO treatment. The flux changed in the following manner:



As seen from the figure, the flux is decreasing through the membrane when VRF is increasing. Control of the permeate by analysis of  $\text{COD}_{\text{Cr}}$  show also an increase. The increase shows that certain organic constituents of the premixes are passing the membrane and end up in the permeate. When the VRF decreased to about 10 to 12  $\text{l/m}^2$ , hour, the RO treatment was stopped. This is the limit of feasibility for the treatment.

The obtained VRF values for the 3 discarded premixes mean that the volume of A and B can be reduced 7 times (from  $1 \text{ m}^3$  to  $0.14 \text{ m}^3$ ) and premix C 10 times or from  $1 \text{ m}^3$  to  $0.1 \text{ m}^3$ . This means further an equivalent reduction of the disposal costs for the hazardous waste.

The increase of  $\text{COD}_{\text{Cr}}$  in the permeate implicates that certain components in the premix are passing the RO membrane and the original aim of the investigation, e.g. to concentrate the premix to the original product concentration was not possible. The component, which passes the membrane from premix A and B, is the solvent, butoxyethanol and hexane diol, respectively. Previous work with glycols at IVL gave similar results.

The surfactants in the premixes are in the form of micelles, which are conglomerates of single surfactant molecules of relatively big size. The RO membrane separates them to a high degree from the mixture.

### 3.2 Chemical properties of the RO permeates

The permeate from the RO treatment of various premixes exhibit the following chemical properties:

Table 1. The chemical composition of RO treated permeates

Premix	BOD <sub>7</sub> mg/l	COD <sub>Cr</sub> mg/l	TOC mg/l	Kj-N mg/l	pH	Conductivity mS/m	EGOM* mg/l	VRF
A	290	410	110	2.0	6.0	1.71	0.8	7
B	280	390	120	16	6.7	5.60	0.10	7
C	510	750	250	<0.2	6.7	<1	0.52	10

\*Gas chromatograms in Attachment 1

The COD<sub>Cr</sub> content of the discarded premixes was given in the description of the products. The values for the actual product content in the premixes were 69 600, 16 000 and 11 300 mg/l for A, B and C. The removal of COD<sub>Cr</sub> by the RO treatment is effective. For premix A 99.5 per cent, for B 98 per cent and for C 94 per cent of COD<sub>Cr</sub> is removed.

The biodegradability of the organic content of the permeates can be valued from the relation between BOD<sub>7</sub> and COD<sub>Cr</sub>, which are 0.71, 0.72 and 0.68. These values implicate that the organic content in the permeate is readily biodegradable or biologically treatable.

The nitrogen content is low except for product B that is based on natural protein. The low values for conductivity show that the permeate contains no inorganic salts.

The EGOM content, which is a measure for the maximum content of potentially bioaccumulative organic matter is low for permeate B (protein based) and somewhat higher for the other permeates. The gas chromatograms exhibit relatively few peaks (components). According to the composition of the products, the solvents in product A and B are not fat soluble, with a log P<sub>ow</sub> of 0.15 for 2-(2-butoxyethoxy)ethanol and -0.14 for hexane diol. None of these are extractable by the method used in the determination of EGOM. The components in the permeate are most probably impurities in the other chemicals in the products. As the organic matter is readily biodegradable, also the extractable portion should be biodegradable. As the EGOM content is quantified with an n-C20 alkan, it can be calculated as a TOC content. Calculated in this manner the EGOM content of the permeate represent about 0.6 per cent of the total organic content of A, 0.06 per cent in B and 0.18 per cent in C.

The content of fluorochemicals in the permeate of product A and B is shown in the next table:



Table 2. Fluorochemicals in RO treated permeates, µg/l

Compound	A	B
Perfluorooctanesulfonate, PFOS	> 1 (app. 4.4 µg/l)*	>1 (Apr. 1.1 µg/L)*
Perfluorooctane sulfonylamide, PFOSA	<0.010	0.0145
Perfluorohexanesulfonate, PFHS	>1 (app. 3.4 µg/l)*	0.344
Perfluorononanoic acid, PHAA	0.102	0.0422
Pentadecafluorooctanoic acid, POAA	0.703	<0.010

\*Concentration is above the calibration range 0.010 - 1.000 µg/l

Fluorinated compounds are components in both products according to the MSDS (Material Safety Data Sheet).

The results concerning Product B are surprising because the fluorinated component should not contain PFOS according to the producer. The producer of product B informs that the fluoro surfactant used in the product is produced by another process, so-called telomerisation by Atofina and Ciba Speciality Chemicals. "This process does not have PerFluoroOctanyl sulphonate (PFOS) as breakdown product of its FS (fluorosurfactant) products".

The low concentrations in both permeate raised suspicions of cross-contamination in the RO-treatment. The treatment of Product A was performed prior to the RO-treatment of product B. The RO unit used in the treatment was thoroughly washed and rinsed between the treatments, but it seems that a contamination occurred. In order to prove the possibility of contamination, untreated samples of product A and B were analysed concerning fluorochemicals. The results are as follows:

Table 3. Fluorochemicals in untreated A and B, mg/l

Compound	A	B
Perfluorooctanesulfonate, PFOS	179	ND (non-detectable, <10µg/l)
Perfluorooctane sulfonylamide, PFOSA	ND	ND
Perfluorohexanesulfonate, PFHS	29	ND
Perfluorononanoic acid, PHAA	7.5	ND
Pentadecafluorooctanoic acid, POAA	4.9	ND

The results of the analysis show that none of the analysed fluorinated components are detected in the untreated product B. This implicates that the occurrence of the fluorinated compounds in the RO-treated sample B is a contamination from the equipment.

Product A contains 2 groups of fluorinated surfactants (1 of them is an amide) and residual monomer of an organic fluorochemical. The residual monomer is PFOS.

The removal efficiency of the fluorochemicals from product A based on the values given in table 3 is >99.999 per cent.

Product B cannot be valuated in the same manner, due to the absence of the components in the untreated sample.

The RO-treatment is extremely effective in removing fluorinated surfactants, but the occurrence of these at the presented concentrations is an obstacle for the discharge to municipal sewage treatment.

The results of the chemical properties of the permeates show that parts of the foam extinguishing products are passing the RO-membranes. The concentrates are therefore not suitable for reuse as fire fighting products. This part of the investigation was omitted after discussions with SP Swedish National Testing and Research Institute, Department of Fire Technology.

### 3.3 Biochemical properties

The properties, which influence biological treatability, are the inhibition of respiration of activated sludge and the inhibition of nitrification.

The investigation of the inhibition of respiration of activated sludge by the permeates gave the following values:

Table 4. Inhibition of respiration by permeates of RO treated premixes, % vol./vol.

Permeate	EC <sub>20</sub>	EC <sub>50</sub>	Inhibition at 90 vol-% permeate
A	>90	>90	4
B	40	>90	39
C	>90	>90	-0.5

The interpretation of the values in the table above is that permeate A has a very low inhibitory effect on the respiration (oxygen consumption rate) of activated sludge which is a mixture of micro-organisms responsible for biological treatment of organic substances in a biological treatment plant. Permeate B is the most toxic toward degrading microorganisms but at a dilution of >3 times, the inhibitory effect is below 20 per cent (EC<sub>20</sub>), which is the limit of disturbance in a biological treatment plant. Permeate C is practically non-toxic and the indicated value at a dilution of 1.1 (90 vol-%) exhibits an increase in respiration.

The investigation of inhibition of nitrification by the permeates showed the following results:

Table 5. Inhibition of nitrification of permeates of RO treated premixes

Permeate	Per cent inhibition	
	at dilution 1/5 (20 vol-%)	at dilution 1/1 (50 vol-%)
A	<20	20
B	<20	54
C	<20	<20

The inhibition of nitrification is low for the various permeate. The inhibition at a dilution of 1 to 5 is less than 20 percent for all permeates. Permeate B, which originates from a protein-based product, exhibits the highest inhibition.

### 3.4 Ecotoxicological properties of permeates

The acute toxicity toward bioluminescent bacteria, *Vibrio fischerii*, (Microtox) of the tested permeates was the following:

Table 6. Acute toxicity (Microtox) of RO permeates, vol./vol.-%

Permeate	EC <sub>20</sub>		EC <sub>50</sub>	
	5 min	15 min	5 min	15 min
A	69	42	>100	>100
B	6.6	5.2	32	22
C	57	37	>100	>100

The acute toxicity of A and B are low even if 20% inhibition of bioluminescence (Effect Concentration, EC<sub>20</sub>) can be measured. The effects are eliminated at dilutions of 5 to 10 times. Permeate B is more toxic according to the method applied. A dilution of at least 30 to 50 times is needed for eliminating the toxicity.

The acute toxicity values towards bioluminescent bacteria are in the same order of magnitude as acute toxicity toward fish and invertebrates.

The organic content in the 3 permeates exhibit a considerable biodegradability judged from the BOD/COD ratio. According to the values in table 1, the ratios were 0.71, 0.72 and 0.68. The high degree of biodegradation contributes also to the elimination of acute toxicity.

The other ecotoxicological property that was investigated concerned growth inhibition of green algae, *Pseudokirchneriella subcapitata*. The results are compiled in table 6:

Table 7. Growth inhibition of green algae by RO permeates, vol./vol.-%

Permeate	EC <sub>50</sub>	EC <sub>20</sub>	EC <sub>10</sub>	NOEC
A	>90	>90	52(39-74)	3.2
B	9.8(9.1-10.4)	4.6(4.1-5.0)	3.6(3.2-3.9)	1.0
C	>90	>90	>90	>90

As before, the permeate from product B has the highest growth inhibition effect. Permeate A has lower inhibitory effect, while permeate C has no effect at all. Product C contains no fluorinated surfactant, but 3 different surfactants, fatty acids and a butoxyethanol. None of them are specifically inhibiting growth of algae.

Biodegradation of the organic content in all permeates lowers or eliminates the inhibitory effect.