About Biodegradability of Modern Firefighting Foam Concentrates Based on Perfluorinated Surfactants

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ABSTRACT
This article is devoted to the environmental safety of foam concentrates based on perfluorinated surfactants. The article describes the methods of surfactant biodegradability determination. The results of such foam concentrates biodegradability study are presented. The comparative analysis of three generation foam concentrates eco-toxicological parameters is presented. The authors suggest that the environmental risks of updated foam concentrates which are actively sold nowadays are not fully studied yet.

INTRODUCTION

Perfluorinated surfactants (hereinafter referred to as perfluorinated surfactants) are used in many industries, and are also included into special purpose foam concentrates, which have been used since 60th-70th of last century.

The studies by international organizations concerning the environment protection, initiated in the 90th of the XXth century, proven the environmental hazard of perfluorinated surfactants based on PFO carboxylates (hereinafter referred to as PFOC) and perfluorooctane sulfonates (hereinafter referred to as PFOS) with -C₂F₄SO₂So and C₆F₁₃SO₄ fragments [1-2]. These substances are extremely stable in natural environment, they are not hydrolyzed, not biodegradable, but they are bioaccumulative ones [3-5].

To improve the biodegradability and decrease the toxicity of perfluorinated surfactants in foam concentrate compositions the manufacturers offered to modify their molecules: 1) block the sulfonate group of perfluorinated compound with amido-betainic fragments; 2) reduce the amount of perfluorinated carbon atoms in the perfluorinated radical with C₈-C₁₀, to C₄ - C₆; 3) include hydrocarbon fragments of (-CH₂CH₂)ₙ type into perfluorinated surfactants.

Methods:
The biodegradability of foam concentrates was evaluated according to GOST R 50595-93 [6], which was redesigned into GOST 32509-2013 for the Customs Union. The methods of biodegradability determination used in the EU (EN ISO 11733:2004 and 14593:1999), do not allow a clear distinction of surfactants on the ability of their biodegradability for various reasons [7].

In contrast to the specified EU methods the determination of surfactants biodegradability indicators according to GOST R 50595 was carried out using the control and experimental aeration operating in a continuous flow mode. An unadapted active sludge 2.7 ± 0.3 g/dm³ cultivated on a synthetic wastewater (SWW) of a standard composition is loaded into aeration devices. The SWW supplied into an experienced aerotank is administered with surfactant (or surfactant-containing composition) with a constant mass concentration of S_{PAVbh} = const. The test period makes 30 days.

During the tests the residual mass concentration of surfactants is measured and the chemical consumption of oxygen (S_{PAVbh} and HPK_{vyh}) in purified water from the experienced aeration tank and also HPK_{vyh} (cont) of a treated wastewater from control aeration tank. The kinetic dependences of biodegradation [delta] HPK_{vyh} = f (t)
are formed according to the treated wastewater test results. The graphs of kinetic dependences are used for surfactants biodegradability indicators calculation (Fig. 1). The description of indicators is presented below.

![Graph](image)

**Fig. 1:** Kinetic dependence of the total surfactants biodegradability graph.

1. **Induction period** \((T_{ind}, \text{days})\) - the period during which the unadapted activate sludge is adapted to the test surfactant (or surfactant-containing composition). Fig. 1 shows that \(T_{ind}\) is the graph function exit area to the plateau. \(T_{ind}\) duration determines the biodegradability level of surfactants: rapidly degradable - up to 3 days, including; moderately degradable - from 3 to 10 days, including; slowly degrading - from 10 to 25 days and including very slowly degradable: more than 25 days.

2. **The maximum mass concentration of non-functional surfactant in the composition of the synthetic wastewater** \((MNK_0, \text{mg/dm}^3)\) - the concentration of surfactant which does not violate modes of aeration tank operation during the test period.

3. For the authorized surfactant (or surfactant-containing compositions) admission to the market the full degree \((X_{28}^{poln}, \%, \text{mass})\) and primary \((X_{28}^{perv}, \%, \text{mass})\) surfactant biodegradation level is calculated with an unadapted activated sludge for 28 days (shaded areas in Fig. 1). At that \(X_{28}^{poln}\) must be at least 70%.

**Main part:**

I generation foam concentrates, which include PO-6K (alkylbemene sulfonates on kerosene fraction), issued before the end of 70-ies in the XX\(^{th}\) century. The synthetic foam concentrates of the second generation are made on the basis of tri-etanol amine alkyl sulfates, \(C_6-C_{14}\) fraction (TEAS), tri-etanol amine alkyl sulfates, [alpha]-olefin sulfonates and sulfoethoxylate (PO-6TS, PO-6TST). The third generation of foam concentrates includes alkyl sulfates and perfluorinated surfactants or protein hydrolysates and perfluorinated surfactants.

The table shows the main components of foam concentrates biodegradability.

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition % according to mass</th>
<th>(T_{ind}), days</th>
<th>(MNK_0), mg/dm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-etanol amine alkyl sulfates (sodium), (C_6-C_{14}) fraction</td>
<td>1-40</td>
<td>1-3</td>
<td>100-150</td>
</tr>
<tr>
<td>Sodium [alpha]-olefin sulfonates, (C_6-C_{14}) fraction</td>
<td>1-11</td>
<td>2-3</td>
<td>50-100</td>
</tr>
<tr>
<td>Alkyl polyoxy (3) sodium sulfate, (C_6-C_{14}) fraction</td>
<td>1-11</td>
<td>5-6</td>
<td>30-40</td>
</tr>
<tr>
<td>Alkyl dimethyl amine oxides, (C_6-C_{14}) fraction</td>
<td>1-5</td>
<td>3-5</td>
<td>30-40</td>
</tr>
<tr>
<td>Collagen hydrolysates</td>
<td>10-15</td>
<td>1-3</td>
<td>100</td>
</tr>
<tr>
<td>Butanol</td>
<td>1-9</td>
<td>5-6</td>
<td>40-50</td>
</tr>
<tr>
<td>Carbitols</td>
<td>0.5-6</td>
<td>5-6</td>
<td>40-50</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>1-4</td>
<td>1-3</td>
<td>50</td>
</tr>
<tr>
<td>Perfluorine octyl (hetyl) ethylsulfon-amido betaine</td>
<td>0.5-5</td>
<td>(\infty)</td>
<td>(-1)</td>
</tr>
</tbody>
</table>

Fig. 2 demonstrates the comparative data on the biodegradability of different generation foam concentrates, which we evaluated according to the method [6]. The figure shows that the first generation foam concentrates belong to very slowly degradable elements with \(T_{ind} > 30\) days; the second generation foam concentrates refer to quickly and moderately degradable with \(T_{ind} = 3 \div 7\) days, and the third generation foam concentrates refer to an extremely slow degradable ones with \(T_{ind} = \infty\) (i.e. they are not exposed to biodegradability).

Upon the completion of the induction period the foam production among all hydrocarbon foam concentrates stops and the foam concentrates with perfluorinated surfactant continue to produce foam concentrates (even at \([\text{delta}]\) HPK = 0), indicating the presence of the said surfactants or its metabolites in purified water.
Fig. 2: Kinetic dependences on biodegradation processes of foam concentrates.

1 - PO-6K (MNKₐ = 150 mg/l), 2 - TEAS (MNKₐ = 150 mg/l), 3 - PO-6TST (MNKₐ = 60 mg/l), 4 - PO-6TST (MNKₐ = 75 mg/l), 5 - TimeksForafac® 1157N (MNKₐ = 20 mg/l), 6 - Genex (MNKₐ = 10 mg/l), 7 - PO-6FFP (MNKₐ = 14 mg/l)

The Fig. 3 shows the data on the foam column height in the aeration tanks, fixed during the testing of foam concentrates containing a fluorinated surfactant, and the concentrates thereof.

Fig. 3: Kinetic dependences of biodegradation processes of foam concentrates based on fluorinated surfactants.

1 - Forafac® 1157N (Cₗ₉ = 1 mg/l perfluorPAV, HPKₐ = 10 mg / l), 2 - Timeks AFFF (Cₗ₉ = 100 mg/l, HPKₐ = 42 mg/l), 3 - PO-3TF (Cₗ₉ = 15 mg/l, HPKₐ = 10 mg/l), 4 - perfluorPAV concentrate for PO-3TF (Cₗ₉ = 1 mg/l by perfluorine PAV, HPKₐ = 10 mg / l), 5 - PO-3TF (Cₗ₉ = 30 mg / l by perfluorine PAV, HPKₐ = 12 mg/l).

Thus the foam concentrates and concentrates based on perfluorinated surfactants undergo a biological assimilation to “end metabolites” - CₙF₂ₙ₊₁COO and -CₙF₂ₙ₊₁SO₃-, wherein n = 5-8. The presence of these perfluorinated surfactants can be judged by the height of the foam column in an aeration tank. It should be noted that for 98% of surfactants the maximum permissible concentrations in water reservoirs for household purposes are set by a threshold foam concentration.

The toxicity of a number of perfluorinated compounds containing 6-10 carbon atoms in a chain, is well studied [8-10]. However, the ecotoxicological characteristics of modified perfluorinated surfactants in the compositions of modern special-purpose foam concentrates are not considered all together.

Summary:

It was established experimentally that modern synthetic hydrocarbon foam concentrates undergo biological assimilation during the week when they are in contact with the environmental objects. The foam concentrates containing perfluorinated surfactants with hydrocarbon block (modified surfactants) undergo a partial biological assimilation and then they are transformed into dangerous metabolites.

Conclusion:

By blocking the hydrophilic part of the fluorinated surfactants molecules with hydrocarbon fragments the manufacturers mislead consumers of these products with respect to their toxicity and biodegradability. Molecules undergo a partial biological assimilation - only to CₙF₂ₙ₊₁X (where X, as a rule -OH, -COOH, -SO₂ON) whose toxicity considerably exceeds the original materials toxicity.
Environmental and toxicological characteristics of new generation foam concentrates with additives modified by perfluorinated surfactants require careful study.

The comprehensive methods development for wastewater purification contaminated with perfluorinated surfactants is required.

REFERENCES


