

## ANALYSIS OF THE ECOLOGICAL CHARACTERISTICS OF ENVIRONMENT FRIENDLY FIRE FIGHTING CHEMICALS USED IN EXTINGUISHING OIL PRODUCTS

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### ABSTRACT

The ecological properties of fire extinguishing agents used in extinguishing fires of classes A and B are analyzed. A significant negative effect of fire-extinguishing foams (fluorine containing and fluorine-free) on the environment has been observed. Gel-forming systems, containing inorganic substances as components for extinguishing fires of oil products, are proposed. A number of gel-forming systems were obtained and they have been analyzed by ecological and ecotoxicological parameters. Gel-forming system based on magnesium chloride was suggested as the most environmentally safe. Ecologically safe granular foam glass was proposed as a carrier of gel-forming systems.

**KEY WORDS :** Firefighting chemicals, Fire fighting foam, Aqueous film-forming foams, Environment, Gel-forming system

### INTRODUCTION

To prevent and extinguish fires in natural ecosystems and fires of technogenic objects, various systems and agents are used. Depending on the type and class of fire, they can be water, sand or fire fighting systems of various compositions. Of the above, foams for firefighting have the greatest use for today (FSM,1998, Sharovarnikov and Sharvoarnikov, 2005). Special substances – retardants are used to protect wood and polymer structures from fires.

Given the obvious negative impact of the fire itself on the environment, much attention has recently been paid to the environmental friendliness of retardants and directly to fire fighting systems (Tureková and Balog, 2011; Tychino, 2012; Kalabokidis, 2000).

For example, in the European Union, the REACH

Regulation on the regulation, production, placement on the market and the use of various chemicals has been proposed at the legislative level. The purpose of this Regulation is to improve the protection of human health and the environment (Regulation (EC) No 1907/2006). Modern fire fighting systems containing a specific set of chemical components must also have certain environmental properties to comply the REACH requirements.

The effect of retardants on human health and the environment, in particular, their predominant influence on aquatic ecosystems is discussed in (Kalabokidis, 2000). The need to assess environmental risks in each case was noted. Recommendations are proposed to mitigate potential consequences for human health and the environment from the use of chemical fire extinguishing agents.

Authors (Tychino, 2012) discuss a number of

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impregnating fluids for the protection of wooden structures, taking into account, among other things, the environmental properties of the material.

Foams can be used to extinguish both Class A fires (for example, burning carbon compounds) and Class B (for example, burning liquid oil products). Although the composition and physico-chemical properties of these compositions may be very different, an additional single criterion for firefighting chemicals is their environmental impact today.

Some authors consider directly the chemical composition of foams and their physicochemical properties, biodegradability, toxicity as factors of negative impact on the environment. Other researchers focus on the accumulation of foam decomposition products in environmental objects.

Alkaline surfactants are used as fire-fighting foams for class A fires. These agents have little impact on the flora and fauna as compared to aquatic ecosystems (Adams *et al.*, 2004).

In research (Adams and Simmons, 1999) is spoken about the impact of fire fighting foams on aquatic ecosystems and about the necessity to comply fully with the existing guidelines for handling foam in the field. In (Hideobu Mizuki *et al.*, 2007), the authors study a new soap-based reagent (sodium oleate, potassium laurate and potassium palmitate), noting, in addition to physico-chemical characteristics, its low toxicity and high biodegradability. In (Takayoshi Kawahara *et al.*, 2016) it is proposed to use a foam, also consisting of soap (potassium laurate potassium oleate and sodium oleate), a chelating agent and diluents to extinguish forest fires (class A). Their optimal ratio is recommended. Chelating reagents are investigated. Methyl Glycine Diacetic Acid was taken as . High biodegradability and environmental friendliness of this foaming agent are noted.

If fires of flammable or combustible liquids (class B) are considered, then aqueous film-forming foams (AFFFs), in particular, fluorine-containing foams (Guidelines, 1999), are the most effective today and they are often used for fire extinction.

Fire extinction of oil products has a number of features that affect the choice of foaming agent, in particular, it is necessary to ensure both the cessation of combustion and create the conditions for prolonged prevention of re-ignition. The authors of (Voevoda *et al.*, 2012) discuss the joint application of foaming agents of various compositions in extinguishing fires of oil and oil products in tanks.

The main emphasis is on compatibility of foaming agents without taking into account their ecological properties. The difficulties of extinguishing fires of oil products are discussed in (Kokorin *et al.*, 2012). The authors note fluorine-containing foams as the most effective. It is proposed to extinguish by supplying low expansion film-forming foam in the bottom of the tank directly into layer of fuel. The ecological compatibility of the use of such a foam is not discussed.

One of the AFFFs ingredients is perfluorooctane sulfonate (PFOS) - toxic to aquatic life and a persistent chemical that accumulates in the blood of humans and other animals. Further perspectives for the use of PFOS, the possibility of replacing them with consideration of the environmental impact are presented in (Sontake *et al.*, 2014). The paper (Klein, 2009) discusses options for minimizing environmental risk when using fluorine-containing foams, the decomposition products of which are very stable and pollute the environment.

The toxic effect of the decay products of film-forming foaming agents for special purposes, which are used for the extinguishing of flammable liquids, is described in (Bocharov and Raevskaja, 2014). The persistence of PFOS and PFOA (Perfluorooctanoic acid) to biodegradation and oxidation with Fenton Fe (II)/H<sub>2</sub>O<sub>2</sub> and Raffa Fe (III)/H<sub>2</sub>O<sub>2</sub> reagents and their high subchronic toxicity are noted.

In recent works (CRC CARE 2017, Part 1; CRC CARE 2017, Part 3), the accumulation, impact, transport of PFOA and PFOS in soil, groundwater, surface water, fish consumption, and sediments are considered, their toxic effect on the environment is noted. These compounds are studied due to their frequent occurrence in the environment, known persistence, and bioaccumulative properties. Fluorine-containing foams for fire extinguishing (aqueous film forming foams) (CRC CARE 2017, Part 1) is called as one of the sources of formation of these compounds.

A detailed review of the application of Fire Fighting Foam with perfluorochemical and their effects on the environment and humans is presented in (Seow, 2013). There is a worldwide trend towards a departure from the use of fluorine-containing fire extinguishing agents due to their negative impact on the environment. Fluorine-containing substances (perfluorochemicals) have anthropogenic origin, accumulate in organisms, and they are not easily biodegradable, affect humans, aquatic and terrestrial ecosystems. Part of the countries (Norway, Canada,

Germany, EU countries) have taken steps to phasing out fluorinated substances contained in fire fighting foam, but some (USA) continue to use. A number of Australian agencies are also avoiding the use of fluorine-containing fire extinguishing agents (Seow, 2013).

At the same time, it can not be said about the exceptional harm to the environment of AFFF only. Thus, the author (Bezrodnyj, 2013) states that the use of both AFFF and Fluorine-free fire forming foams is unsafe for the environment, because of direct ingress of pollutants into the environment in high concentrations (Fluorine-free fire forming foams), or their bioaccumulation (AFFF).

And now, for air-foam fire extinguishing agents, a contradiction has arisen between environmental and fire-fighting characteristics.

An additional negative factor is the contamination of oil products by fire-extinguishing agents and the complexity, or even impossibility, of their further application.

The above points out the relevance of the further search for firefighting chemicals that are safe for the environment, and allow effectively to perform fire extinguishing of oil products belonging to class B.

Extinguishing flammable liquids involves the cessation of combustion and the creation of a condition for prolonged prevention of re-ignition. The most rational way to create such conditions is to form an insulating layer between the surface of the combustible liquid and the gas phase.

From works in this direction it can be noted (Melkozerov *et al.*, 2012), where it is said about the perspectives of oleophobic fast-hardening compositions of thermal protective foam for extinguishing the flame of oil and oil products. Ecological safety of the ecosystem is ensured by the protection of the spillage of oil products from ignition and the development of degassing

Bogdanova and co-authors consider a sprayed polyurethane foam with inorganic additives as a flame retardant in the spread of fires over cable cages of civil buildings, and also as a fire extinguishing agent for extinguishing fires of various classes A and B (Bogdanava *et al.*, 2016). However, the environmental friendliness of the material obtained is not investigated

A series of works with the use of fast-curing foam based on silica as a fire-fighting agent is known. The authors of (Gusev *et al.*, 2016) propose to organize fire-prevention foam strips in extinguishing forest massifs. Abduragimov and co-authors also discuss

the use of fast-hardening foams to prevent the spread of fire in forests (Abduragimov and Kuprin *et al.*, 2016). The authors of (Vinogradov *et al.*, 2015) also offer fast-hardening silica-based foams with exceptional thermal stability, mechanical durability, and full biocompatibility for fire fighting and fire prevention. In the authors' opinion (Abduragimov and Vinogradov *et al.*, 2016), this material can be used, among other things, for extinguishing fires of oil products.

It is known that high insulating properties provide gel-like layers that are formed by the use of gel-forming systems (GFS) for fire fighting (Borisov *et al.*, 2005; Savchenko and Ostroverh, 2016). GFS are used for extinguishing solid combustible materials and are a binary system consisting of two separately stored and separately supplied compositions. Both compositions are aqueous solutions, which facilitates storage and supply to the combustion zone. Compositions are chosen so that when they are mixed at the boundary of the phases between the components, a reaction occurs, leading to the formation of a non-flowing layer (Abramov and Kireev, 2015).

The purpose of this work is to obtain an environmentally friendly fire extinguishing agent for extinguishing flammable liquids (by the example of oil products) and to study its ecological characteristics.

In this paper, the possibility of using GFSs for extinguishing of oil products in reservoirs has been examined. Analysis of the ecological and ecotoxicological characteristics of the initial substances and products of GFS formation has been made, and the most ecologically friendly system of the investigated ones has been proposed.

## MATERIALS AND METHODS

In the work, substances of purity of qualification "Pure" were used. The liquid glass of  $\text{Na}_2\text{O} \cdot n\text{SiO}_2$  was taken as gelling agent. The formation of GFS occurs under normal conditions, directly by mixing the gelling agent with aqueous solutions of calcium, sodium, aluminum, magnesium, potassium or ammonium salts (so-called gelling catalysts) during the fire-fighting process.

Concentrations of gelling catalysts are 3-12% w/w,  $\text{K}_2\text{CO}_3$  – 40 % w/w. The character of the medium of gelling catalysts is weakly acidic (pH ~ 5).

To extinguish oil products on a granular foamed glass with a grain size of 2 - 3 cm, a layer of GFS was

applied. Later we studied this system.

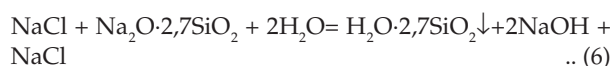
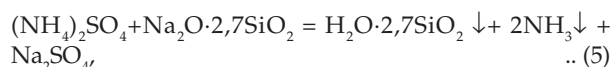
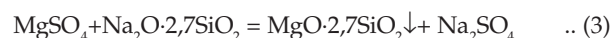
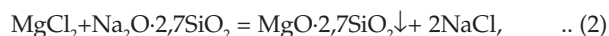
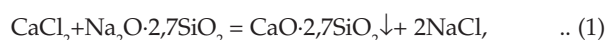
## RESULTS AND DISCUSSION

GOS was formed with a gellant-liquid glass ( $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ ). A number of metal salts was used as catalysts for gelling in such systems. Based on studies of insulating properties of GFSs obtained using various gelling catalysts (Abramov and Kireev, 2015), it was established that the coefficient of evaporation slowing down for thin layers of gel ( $\sim 1.5$  mm) for all studied systems varied within the range 26-37. This means that all gel-like layers exhibit insulating properties that are sufficient for the fire-fighting process. In the work, GFS ( $\text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{NaCl}$ ) was obtained and studied, its ecological properties were analyzed and compared with the environmental properties of a number of other previously obtained GFSs.

Gelation processes occurring during the interaction of soluble sodium polysilicates with solutions of ammonium salts and divalent and trivalent metals are discussed in the monograph of Idler (Idler, 1979). On the basis of an analysis of a large number of experimental factors, it was concluded that the main substances forming the "skeleton" of the gel are silica gel (in the case of ammonium salts) and silicates of two- and three-charged cations (Idler, 1979).

From the point of safety assurance of the environment, it is advisable to use the components of GFS in equivalent quantities, since after the fire-fighting process, the used extinguishing agents must be utilized.

Typical gelling reactions proceed as follows:



As can be seen from the above data, in the case of using stoichiometric concentrations of the components of the GFS, in addition to water-insoluble metal silicates or silicic acid gel, sodium chloride, sodium sulfate and ammonia are formed (in the case of ammonium salts).  $\text{K}_2\text{CO}_3$  and  $\text{NaCl}$

cause gelling of sodium polysilicate leading to the formation of silicic acid and sodium hydroxide. Table 1 shows the interaction products between the gelling agent and the gelling catalyst for some of the studied systems, including  $\text{NaCl}$ . The table also shows the values of the minimum concentrations of components of GFS that were determined earlier (Abramov and Kireev, 2015). Based on these data the minimum stoichiometric concentrations of the gelling agent and the gelling catalyst were calculated. In the case of using the minimum concentrations of components in excess, gelling catalysts are found and the corresponding salt is formed.

The masses of the corresponding soluble substances, calculated on the basis of the stoichiometry of the reaction for obtaining the investigated GFS, are presented in Table 2.

These components, when released into the environment, affect not only human health (Fawell, 1993), but also other living organisms.

The work carried out a comparative analysis of the environmental characteristics of substances that can enter the environment when using the data listed in Table 1 components of gelling. Depending on the stoichiometry of the reaction, they may be the mother substances and reaction products.

Part of these substances can have a hydrated and dehydrated form. Since less stringent restrictions are given for solution of compounds than for pure substances or hydrates, data on individual substances were used for a comparative evaluation. The characteristics taken into account the most dangerous indicators of substances when considering.

Data from the European Commission on Pesticides - EU Pesticides database (ECBD), Material Safety Data Sheet Listing data (MSD), database PubChem (the system is maintained by the National Center for Biotechnology Information, a component of the National Library of Medicine, which is part of the United States National Institutes of Health) (PCD), information on the chemicals of the European Chemicals Agency (the official body of the EU responsible for the implementation of REACH) (DECA). The results are shown in Table 3.

As can be seen from the presented data, such substances as  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaBr}$  represent the greatest danger for the environment.  $\text{FeSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$  are dangerous for long-term exposure.

Further, we carried out a more detailed

comparative analysis of the ecological and ecotoxicological properties of possible products of the gel formation reaction, which can enter the environment, taking into account the stoichiometry of the reaction (Table 2). The data presented in Brief Profiles of the relevant substances were used according to European Chemicals Agency (ECHA) data (DECA). According to the world trends in the harmonization of chemical classifications (GHSCLC, 2011), a mandatory characteristic for labeling of chemical substance must be a description of its environmental hazard. As characteristics were used, acute aquatic toxicity, chronic aquatic toxicity, bioaccumulation potential and rapid degradability. Also, the predicted no effect concentration (PNEC) value was used as a characteristic, i.e. value is the concentration of a substance.

Although, depending on the methodology of the definition and the initial data set, PNEC values can vary over a fairly wide range and even differ by several orders of magnitude for one substance (Hahn *et al.*, 2014). Comparative characteristics of environmental parameters used in firefighting components of GFS is presented in Table 4 - 6. It should be noted that the comparison of data is complicated by the way they are presented. So, for the ecological characteristics of substances, Lethal Concentration (LC), No observed effect concentration (NOEC), Lowest observed effect concentration (LOEC), Concentration associated with x% response (ECx) are used. However, since the information is a summation of automatically processed data entering the ECHA, the quality and correctness of the information remains with the data

**Table 1.** The values of the minimum concentrations of the components of the gelling system - sodium polysilicate ( $\omega_1$ ) and gelling catalysts ( $\omega_2$ ), causing rapid gel formation, minimum stoichiometric concentrations of sodium polysilicate (st.  $\omega_1$ ) and gelling catalysts (st.  $\omega_2$ ) and the composition of the main product of their interaction.

No.	Gelling catalyst	The main products of the reaction	$\omega_1, \%$	$\omega_2, \%$	st. $\omega_1, \%$	st. $\omega_2, \%$
1.	CaCl <sub>2</sub>	CaO·2,7SiO <sub>2</sub> + NaCl	3	3	6	3
2.	MgCl <sub>2</sub>	MgO·2,7SiO <sub>2</sub> + NaCl	5	4	9.5	4
3.	MgSO <sub>4</sub>	MgO·2,7SiO <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub>	5	4	7.5	4
4.	FeSO <sub>4</sub>	FeO·2,7SiO <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub>	4	4	6	4
5.	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O·2,7SiO <sub>2</sub> + K <sub>2</sub> CO <sub>3</sub> + NaOH	25	40	-	-
6.	AlCl <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> ·8,1SiO <sub>2</sub> + NaCl	3.5	3	7.5	3
7.	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> ·2,7SiO <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub>	4	3	6	3
8.	NH <sub>4</sub> Cl	H <sub>2</sub> O·2,7SiO <sub>2</sub> + NaCl + NH <sub>3</sub>	8	8	17	8
9.	NH <sub>4</sub> Br	H <sub>2</sub> O·2,7SiO <sub>2</sub> + NaBr + NH <sub>3</sub>	8	10	11.5	10
10.	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O·2,7SiO <sub>2</sub> + Na <sub>2</sub> SO <sub>4</sub> + NH <sub>3</sub>	8	12	20	12
11.	AlBr <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> ·2,7SiO <sub>2</sub> + NaBr	3	4	5	4
12.	NaCl	H <sub>2</sub> O·2,7SiO <sub>2</sub> + NaCl + NaOH	20	20	-	-

**Table 2.** The values of the masses of soluble substances formed during the interaction of the components of the GFS with the calculation of 100 kg of the system for minimum and stoichiometric concentrations of the components.

No.	Minimum concentrations		Stoichiometric concentrations	
	soluble substances	mass, kg	soluble substance	mass, kg
1.	CaCl <sub>2</sub> ; NaCl	0.8; 1.3	NaCl	1.6
2.	MgCl <sub>2</sub> ; NaCl	1.0; 1.3	NaCl	2.4
3.	MgSO <sub>4</sub> ; Na <sub>2</sub> SO <sub>4</sub>	0.7; 1.6	Na <sub>2</sub> SO <sub>4</sub>	2.0
4.	FeSO <sub>4</sub> ; Na <sub>2</sub> SO <sub>4</sub>	0.7; 1.3	Na <sub>2</sub> SO <sub>4</sub>	1.8
5.	K <sub>2</sub> CO <sub>3</sub> ; NaOH	20; 4.5	-	-
6.	AlCl <sub>3</sub> ; NaCl	0.8; 0.9	NaCl	2.0
7.	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ; Na <sub>2</sub> SO <sub>4</sub>	0.5; 1.3	Na <sub>2</sub> SO <sub>4</sub>	1.9
8.	NH <sub>4</sub> Cl; NaCl	2.1; 2.1	NaCl	4.4
9.	NH <sub>4</sub> Br; NaBr	1.5; 3.7	NaBr	5.3
10.	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; Na <sub>2</sub> SO <sub>4</sub>	3.6; 2.5	Na <sub>2</sub> SO <sub>4</sub>	6.5
11.	AlBr <sub>3</sub> ; NaBr	0.8; 1.4	NaBr	2.4
12.	NaCl; NaOH	10.0; 3.6	-	-

**Table 3.** Ecological characteristics of investigated substances.

Basic substance	Maximum Residue Levels (MRL) (for plants), mg/kg (ECBD)	Toxicological and Ecological Information (MSD)		Information about substance (PCD)	Environmental Hazards (DECA)
		Toxicity to Animals	Products of biodegradation and toxicity of the Products of Biodegradation		
NaCl	Default MRL of 0.01 mg/kg Herbicide	Acute oral toxicity (LD <sub>50</sub> ): 3000 mg/kg [Rat.]. Acute dermal toxicity (LD <sub>50</sub> ): >10000 mg/kg [Rabbit].	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The product itself and its products of degradation are not toxic.	Food Additive, Herbicide, Drug products. Cases are known in which the deaths in pigs were followed suddenly after feeding with large amounts of sodium chloride in food. Excess salt intake in some animals results to diarrhea, muscle tremors, seizures, and coma.	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking.
NaOH	Default MRL of 0.01 mg/kg Herbicide	LD <sub>50</sub> : Not available	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The product itself and its products of degradation are not toxic.	Food Additives, Herbicide. Agricultural chemicals (non-pesticidal). Esophageal burns were induced in male rats by the administration of 10% sodium hydroxide. Solution NaOH showed severe necrosis of all epidermal cell layers and dermis for pigs. At times this lesion extended deep into the subcutaneous layers.	Data about hazardous to the atmospheric environment is lacking. Harmful to aquatic life with long lasting effects. Harmful to aquatic life.
CaCl <sub>2</sub>	Default MRL of 0.01 mg/kg Fungicide, Plant growth regulator	LD <sub>50</sub> not available	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The product itself and its products of degradation are not toxic.	Fungicide, Plant growth regulator, Food Additive, Drug	Data about chronic hazardous to aquatic and atmospheric environment is lacking. Harmful to aquatic life with long lasting effects.

Table 3. Continued

Basic substance	Maximum Residue Levels (MRL) (for plants), mg/kg (ECBD)	Toxicological and Ecological Information (MSD)		Information about substance (PCD)	Environmental Hazards (DECA)
		Toxicity to Animals	Products of biodegradation and toxicity of the Products of Biodegradation		
MgCl <sub>2</sub>		Acute oral toxicity (LD <sub>50</sub> ): 8100 mg/kg [Rat.].	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The products of degradation are more toxic.	Drug	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking
MgSO <sub>4</sub>	_____	LD <sub>50</sub> : Not available.	Possibly hazardous short term degradation products are not likely. However, long-term degradation products may arise. The products of degradation are more toxic	Safe when used in accordance with good manufacturing or feeding practice.	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking
Na <sub>2</sub> SO <sub>4</sub>	_____	Acute oral toxicity (LD <sub>50</sub> ): 5989 mg/kg [Mouse]	Possibly hazardous short-term degradation products are not likely. However, long term degradation products may arise. The product itself and its products of degradation are not toxic	Surface active agents, Drug In excess causes weight reduction of plants and animals	Data about acute hazardous to aquatic and atmospheric environment is lacking. Harmful to aquatic life with long lasting effects
FeSO <sub>4</sub>	_____	Acute oral toxicity (LD <sub>50</sub> ): 1520 mg/kg [Mouse]	Possibly hazardous short-term degradation products are not likely. However, long term degradation products may	Drug, Used for water or sewage treatment, as a fertilizer ingredient. Hydrates occur in nature as minerals:	Data about acute hazardous to the aquatic and atmospheric environment is lacking. Harmful to aquatic life with long lasting effects.

Table 3. Continued

Basic substance	Maximum Residue Levels (MRL) (for plants), mg/kg (ECBD)	Toxicological and Ecological Information (MSD)		Information about substance (PCD)	Environmental Hazards (DECA)
		Toxicity to Animals	Products of biodegradation and toxicity of the Products of Biodegradation		
$K_2CO_3$	—————	Acute oral toxicity (LD <sub>50</sub> ): 1870 mg/kg [Rat].	<p>arise. The product itself and its products of degradation are not toxic. May affect genetic material (human) (mutagenic). It is excreted in maternal milk in animal</p> <p>Possibly hazardous short-term degradation products are not likely. However, long term degradation products may arise. The products of degradation are less toxic than the product itself</p>	Drug, Agricultural chemicals (non-pesticidal)	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking
$AlCl_3$	—————	Acute oral toxicity (LD <sub>50</sub> ): 1990 mg/kg [Mouse].	<p>Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The product itself and its products of degradation are not</p>	Astringents in medicine. Very toxic to aquatic life Very toxic to aquatic life with long lasting effects	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking
$Al_2(SO_4)_3$	—————	Acute oral toxicity (LD <sub>50</sub> ): 6307 mg/kg [Rat]. (hydrated)	<p>May affect genetic material of human (mutagenic). May cause adverse reproductive effects based on animal test data Possibly hazardous short-term degradation products are not</p>	Bactericide, Firming agent. Noncombustible and nontoxic. It is used in papermaking, in firefighting foams, and in sewage treatment and water purification. The substance is toxic to aquatic organisms.	Data about hazardous to the atmospheric environment is lacking. Very toxic to aquatic life. Very toxic to aquatic life with long lasting effects, Toxic to aquatic life with long lasting effects.



Table 3. Continued

Basic substance	Maximum Residue Levels (MRL) (for plants), mg/kg (ECBD)	Toxicological and Ecological Information (MSD)		Information about substance (PCD)	Environmental Hazards (DECA)
		Toxicity to Animals	Products of biodegradation and toxicity of the Products of Biodegradation		
			likely. However, long-term degradation products may arise. The product itself and its products of degradation are not toxic.	It is strongly advised not to let the chemical enter into the environment.	Harmful to aquatic life with long lasting effects.
NH <sub>4</sub> Cl	_____	Acute oral toxicity (LD <sub>50</sub> ): 1300 mg/kg [Mouse]	Possibly hazardous short-term degradation products are not likely. However, long term degradation products may arise. The product itself and its products of degradation are not toxic	Acidifying agent, Drug, Microbiocide, Agricultural chemicals (non-pesticidal) The substance is toxic to aquatic organisms.	Toxic to aquatic life with long lasting effects. Very toxic to aquatic life
NaBr	_____	Acute oral toxicity (LD <sub>50</sub> ): 3500 mg/kg [Rat].	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The product itself and its products of degradation are not toxic	Drugs. Not irritating. Not sensitizing.	Data about hazardous to the atmospheric environment is lacking. Very toxic to aquatic life. Very toxic to aquatic life with long lasting effects
NH <sub>4</sub> Br	_____	LD <sub>50</sub> : Not available.	Possibly hazardous short-term degradation products are not likely. However, long term degradation products may arise. The products of degradation are more toxic	Microbiocide, Drug	Data about acute and chronic hazardous to aquatic and atmospheric environment is lacking

Table 3. Continued

Basic substance	Maximum Residue Levels (MRL) (for plants), mg/kg (ECBD)	Toxicological and Ecological Information (MSD)		Information about substance (PCD)	Environmental Hazards (DECA)
		Toxicity to Animals	Products of biodegradation and toxicity of the Products of Biodegradation		
$(\text{NH}_4)_2\text{SO}_4$	—————	Acute oral toxicity ( $\text{LD}_{50}$ ): 640 mg/kg [Mouse].	Possibly hazardous short-term degradation products are not likely. However, long term degradation products may arise. The product itself and its products of degradation are not toxic	Von-CNS depressant anesthetic agent, Herbicide Data about acute hazardous to the atmospheric environment is lacking. Very toxic to aquatic life. Toxic to aquatic life with long lasting effects	
$\text{AlBr}_3$	—————	Acute oral toxicity ( $\text{LD}_{50}$ ): 1598 mg/kg [Rat].	Possibly hazardous short-term degradation products are not likely. However, long-term degradation products may arise. The products of degradation are less toxic than the product itself	Anhydrous aluminum bromide is hazardous because of its affinity for water. It may cause tissue burns, and both it and the hydrate may be toxic upon ingestion.	No data

authors. This explains the scatter in the presented values and also complicates the generalization of information. Conditions of the research vary for each substance. This also makes it difficult to compare the data. For some substances and for a number of parameters, data are not available.

As can be seen from the data presented, according to PNEC, the most dangerous are  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Br}$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaBr}$ ,  $\text{NaCl}$ ,  $\text{AlCl}_3$ . However, as already mentioned, PNEC can not be the only reliable characteristic of the environmental hazard of substances.

According to the data in Tables 5-6, such substances as  $\text{AlCl}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  are the most dangerous in the short and / or long-term effects on aquatic and surface organisms.

The lack of data on  $\text{FeSO}_4$  and  $\text{K}_2\text{CO}_3$  makes it

difficult to assess their environmental impact. Although short-term toxicity to fish is noted for  $\text{K}_2\text{CO}_3$  ( $\text{LC}_{50}$  (4 days) 68 mg/L) (Table 5). However, considering that  $\text{K}_2\text{CO}_3$  needs a significant amount for the formation of GFS (Table 1), the need for its use is limited by the economic factor.  $\text{NaOH}$  data are practically absent. However, short-term toxicity to aquatic invertebrates ( $\text{EC}_{50}$  (48h) 40.4 mg/L) is noted (Table 5).

Provided that the interpretation of PNEC can be ambiguous, from an environmental point of view  $\text{MgCl}_2$  is most convenient in the firefighting of oil products using GFSs. When  $\text{NaCl}$ -based GOS is used, the limiting factor is the formation of  $\text{NaOH}$  (Table 2), which, as mentioned above, exhibits short-term toxicity to aquatic invertebrates.

Thus, taking into account the above-mentioned,

**Table 4.** Predicted No-Effect Concentration (PNEC) of investigated substances

Parameters	Magnesium chloride	Sodium bromide	Sodium chloride	Aluminum bromide	Aluminum chloride	Magnesium sulphate	Ammonium chloride	Ammonium bromide	Ammonium sulphate	Aluminium sulphate	Potassium carbonate	Sodium sulphate	Iron sulphate	Calcium chloride	Sodium hydroxide
Hazard for Aquatic Organisms:				No Brief Profile							No data			No data	No data
• Freshwater	3.21 mg/L	150 µg/L	5 mg/L		300 ng/L	680 µg/L	250 - 1 200 µg/L	520 µg/L	312 µg/L	4.5 mg/L		11.09 - 22 mg/L	No hazard identified		
• Marine water	320 µg/L	75 µg/L	No data: aquatic toxicity unlikely		30 ng/L	68 µg/L	25 - 11 200 µg/L	41 mg/L	31.2 µg/L	64 mg/L		1.109 - 2.2 mg/L	No hazard identified		
Hazard for Terrestrial Organism (soil)	662.77 mg/kg soil dw	3.2 mg/kg soil dw	4.86 mg/kg soil dw		No hazard identified	No data	163 - 50 700 µg/kg soil dw	3.2 mg/kg soil dw	62.6 mg/kg soil dw	58 mg/kg soil dw		1.54 - 2.61 mg/kg soil dw	No hazard identified		
Hazard for Predators	No potential for bioaccumulation	3.333 mg/kg food	No potential for bioaccumulation		No data	No potential for bioaccumulation	No potential for bioaccumulation	No potential for bioaccumulation	—	150 mg/kg food		No potential for bioaccumulation	No potential for bioaccumulation		

**Table 5.** Toxicity of investigated substances to Aquatic Organisms

Parameters	Magnesium chloride	Sodium bromide	Sodium chloride	Aluminum bromide	Aluminum chloride	Magnesium sulphate	Ammonium chloride	Ammonium bromide	Ammonium sulphate	Aluminium sulphate	Potassium carbonate	Sodium sulphate	Iron sulphate	Calcium chloride	Sodium hydroxide
Short-term toxicity to fish	LC50 (4 days) 541 - 2 119.3 mg/L	LC50 (4 days) 440 - 24 000 mg/L	LC50 (4 days) 5.84 g/L	-	LC50 (4 days) 420 - 186 000 µg/L	LC50 (4 days) 680 mg/L	LC50 (4 days) 42.91 - 209 mg/L	LC50 (4 days) 440 - 1 000 mg/L	LC50 (4 days) 53 - 57.2 mg/L	LC50 (8 days) 122.17 - 161.4 mg/L	LC50 (4 days) 68 mg/L	LC50 (4 days) 7.96 - 13.5 g/L	No data	LC50 (4 days) 4.63 g/L	No data
					LC50 (4 days) 156 - 1 000 µg/L		LC50 (48 h) 240 mg/L	NOEC (4 days) 320 - 1 000 mg/L		LC50 (6 days) 560 - 6 650 µg/L					
							LC50 (24 h) 275 mg/L			LC50 (5 days) 1.05 - 20.8 mg/L					

Table 5. Continued

Parameters	Magnesium chloride	Sodium bromide	Sodium chloride	Aluminum bromide	Aluminum chloride	Magnesium sulphate	Ammonium chloride	Ammonium bromide	Ammonium sulphate	Aluminium sulphate	Potassium carbonate	Sodium sulphate	Iron sulphate	Calcium chloride	Sodium hydroxide
Long-term toxicity to fish	No data	NOEC (4.133 months) 7.8 - 78 mg/L NOEC (3 months) 32 mg/L NOEC (34 days) 250 - 7 800 mg/L NOEC (30 days) 10 mg/L	NOEC (33 days) 252 - 533 mg/L	-	NOEC (60 days) 13 - 26 µg/L NOEC (33 days) 71.5 - 558.1 µg/L	No data	NOEC (28 days) 11.8 mg/L EC10 (30 days) 4.28 mg/L	NOEC (4.133 months) 10 mg/L	EC10 (30 days) 5.29 mg/L	NOEC (60 days) 180 - 1670 µg/L NOEC (30 days) 250 - 1670 µg/L NOEC (28 days) 29.8 - 44.9 mg/L	No data	No data	No data	No data	No data
Short-term toxicity to aquatic invertebrates	LC50 (48 h) 140 - 548.4 mg/L	EC50 (48 h) 5.8 g/L LC50 (48 h) 6.7 - 11 g/L NOEC (48 h) 1 - 4.3 g/L	LC50 (48 h) 4.136 g/L	-	EC50 (48 h) 214 - 200 µg/L	LC50 (48 h) 720 mg/L	EC50 (48 h) 98.5 - 136.6 mg/L	EC50 (48 h) 1 g/L NOEC (48 h) 1 g/L	EC50 (48 h) 121.7 - 169 mg/L	EC50 (48 h) 1.4 - 100 mg/L LC50 (72 h) 1.52 - 19.5 mg/L	EC50 (48 h) 200 mg/L NOEC (48 h) 120 mg/L	EC50 (48 h) 3.15 g/L LC50 (48 h) 1.766 - 6.499 g/L	No data	EC50 (48 h) 2.4 g/L LC50 (48 h) 2.4 g/L NOEC (48 h) 2 g/L	EC50 (48 h) 40.4 mg/L
Long-term toxicity to aquatic invertebrates	EC10 (21 days) ) 82 - 321 mg/L	NOEC (21 days) 7.5 - 91 mg/L LOEC (21 days) 19 mg/L	NOEC (21 days) 314 mg/L LOEC (21 days) 441 mg/L	-	NOEC (28 days) 53.1 - 4281.8 µg/L	No data	NOEC (21 days) 14.6 mg/L LOEC (21 days) 30.2 mg/L	NOEC (21 days) 7.5 mg/L LOEC (21 days) 19 mg/L	EC10 (70 days) 3.12 mg/L LOEC (21 days) 19 mg/L EC10 (16 days) 43 mg/L	NOEC (28 days) 12 mg/L LOEC (28 days) 27 mg/L	No data	LOEC (7 days) 1.329 - 4.436 g/L EC50 (7 days) 1.698 - 2.156 g/L LC50 (7 days) 3.03 - 3.611 g/L	No data	EC50 (21 days) 610 mg/L LC50 (21 days) 920 mg/L	No data
Toxicity to aquatic algae and cyanobacteri	EC50 (72 h) 100 mg/L NOEC (72 h) 100 mg/L	EC50 (4 days) 10 g/L EC50 (72 h) 8 - 20 mg/L NOEC (4 days) 2.5 g/L NOEC (72 h) 440 - 2500 mg/L	EC50 (5 days) 2.43 g/L	-	EC50 (4 days) 460 - 570 µg/L EC50 (72 h) 40 - 14000 µg/L NOEC (72 h) 20 - 1000 µg/L	EC50 (18 days) 2.7 g/L	EC50 (18 days) 440 mg/L EC50 (72 h) 1.3 g/L	EC50 (72 h) 440 mg/L	EC50 (18 days) 2.7 g/L EC50 (72 h) 1.605 g/L	EC50 (5 days) 3.011 - 19,091 g/L EC50 (72 h) 100 mg/L	No data	EC50 (5 days) 1.9 g/L	No data	EC50 (72 h) 2.9 - 27 g/L	No data



from the considered GFSs it is optimal to use the systems formed by magnesium chloride.

Another attractive factor for using GFS in extinguishing fires of oil products is the fact that the components of GFS are insoluble in hydrocarbon combustible liquids. Consequently, the components of the proposed fire fighting system do not contaminate these liquids, which facilitates their further processing and use.

Since the gel in the investigated systems is drowning in most flammable liquids, it is impossible to directly use it for extinguishing flammable liquids. The use of a light carrier for the gel layer on which it will be formed - granulated foam glass (Dadashov *et al.*, 2016) has led to the study of the environmental characteristics of this material. Foamglass is a non-combustible, non-volatile, environmentally friendly material used in housing construction. According to the European Chemicals Agency data (DECA), the main component of foam glass - Silicon oxide - is not classified as a hazardous substance. After the suppression of fire, the layer of foam glass, collected from the surface of the liquid oil, after drying of the GFS can be used again, which makes it attractive from the economic point of view. At the same time, the storage of foamed glass is not limited in time and it does not require special storage conditions.

### CONCLUSION

Gelling fire fighting systems, containing inorganic substances as components, were proposed to use for extinction of flammable liquids.

Significant fluctuations in the parameters of environmental characteristics or their absence make it difficult for the environmental assessment of the considered GFSs. Proceeding from the examined data as the most ecologically safe it is offered to use the system formed by magnesium chloride. For sodium chloride-based GFS, the limiting factor is the formation of NaOH, which exhibits short-term toxicity to aquatic invertebrates.

Granular foam glass that is not hazardous to the environment was proposed to use as a light carrier providing the flotation of the fire fighting layer of the gel on the surface of the flammable liquid. It can be reused and it has a long shelf life without special conditions.

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