ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Silica Foams for Fire Prevention and Firefighting

Alexander V. Vinogradov,*[†] D.S. Kuprin,[‡] I.M. Abduragimov,[§] G.N. Kuprin,[‡] Evgeniy Serebriyakov,[||] and Vladimir V. Vinogradov[†]

[†]ITMO University, St. Petersburg, Russia

[‡]JSC NPO "SOPOT", St. Petersburg, Russia

[§]Bauman MSTU, Moscow, Russia

[||]JSC ≪IVHIMPROM≫, Ivanovo, Russia

Ⓢ *Supporting Information*

ABSTRACT: We report the new development of fire-extinguishing agents employing the latest technology of fighting and preventing fires. The in situ technology of fighting fires and explosions involves using large-scale ultrafast-gelated foams, which possess new properties and unique characteristics, in particular, exceptional thermal stability, mechanical durability, and full biocompatibility. We provide a detailed description of the physicochemical processes of silica foam formation at the molecular level and functional comparison with current fire-extinguishing and fire-fighting agents. The new method allows to produce controllable gelation silica hybrid foams in the range from 2 to 30 s up to 100 Pa·s viscosity. Chemical structure and hierarchical morphology obtained by scanning electron microscopy and transmission electron microscopy images develop thermal insulation capabilities of the foams, reaching a specific heat value of more than 2.5 kJ/(kg·°C). The produced foam consists of organized silica nanoparticles as determined by X-ray photoelectron spectroscopy and X-ray diffraction analysis with a narrow particle size distribution of ∼10−20 nm. As a result of fire-extinguishing tests, it is shown that the extinguishing efficiency exhibited by silica-based sol−gel foams is almost 50 times higher than that for ordinary water and 15 times better than that for state-of-the-art firefighting agent aqueous film forming foam. The biodegradation index determined by the time of the induction period was only 3 d, while even for conventional foaming agents this index is several times higher.

KEYWORDS: *fire, sol−gel, foam, silica, AFFF*

■ INTRODUCTION

Thanks to a number of unique properties, perfluorinated surfactants (hereinafter perfluorosurfactants) have been widely used in Europe and United States since the 1960s and 1970s. Because of their high extinguishing efficiency, including that for solid combustibles and polar (water-soluble) liquids, these foaming agents are still leading in terms of production and use in many developing countries. However, during extinguishing fires these agents are almost completely absorbed by the soil and surface water. In this regard, while using foaming agents, along with their specifications, one must take into account the ecological and hygienic characteristics, such as biodegradability, phytoxicity, and zootoxicity.

Environmental protection investigations initiated in the 1990s proved extreme environmental hazard of perfluorosurfactants based on perfluorooctane carboxylates and perfluorooctanesulfonates including "branched" or "linear fragments" $-C_7F_{15}COO^-$ and $-C_8F_{17}SO_3^-$ produced "electrochemically" or by "telomerization of tetrafluoroethylene", respectively.[1,2] These substances are extremely stable in the environment, unhydrolyzable, and non-biodegradable, but they are actively bioaccumulated and migrate in the food chains.[3,4] Major manufacturers of long-chain fluorocarbons (such as 3M, DuPont, Daikin, etc.) have ceased or cease the production and sale of fluorocarbons, replacing them with alternative short-chain substances. At the moment the target technology is $-(CF_2)_6F$ (or C6), using fluorocarbons based on $-CF_3$ (C1) and $-CF_2CF_3$ (C2).

To improve the biodegradability and toxicity of perfluorosurfactants in foaming agents, during the past decade manufacturers have performed the following modifications of their molecules:[2] (1) blocking the sulfonate group by amidobetaine fragments; (2) reducing the number of carbon atoms in a perfluorinated radical from C_8-C_{10} to C_4-C_6; (3) incorporating hydrocarbon fragments $(-CH_2-)_n$ into perfluorosurfactants. However, these measures do not provide adequate biocompatibility of derived foaming agents and do not allow to classify them as safe even in the near future.

In this regard, the goal of the present work is developing and investigating new extinguishing materials possessing improved

Received: September 16, 2015
Accepted: October 22, 2015
Published: October 22, 2015

DOI: 10.1021/acsami.5b08653

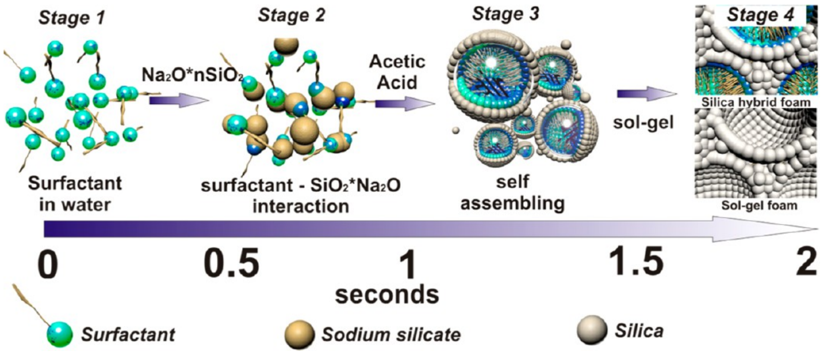

Figure 1. Chemical mechanism for the formation of silica hybrid foams.

(compared to perfluorosurfactants) extinguishing efficiency for solid and flammable liquids, combustibles, completely eco-friendly, and providing the same economic attractiveness.

Taking into account these characteristics, we focused on a class of hybrid sol−gel materials that possess unique extinguishing properties but have been poorly studied for use in the field because of the difficulties in obtaining large-scale sol−gel foams. The persisting key challenges are (1) a need for fast hardening, (2) blockage of foam generators and short duration of their action, (3) an inhomogeneous distribution of hardening phases and, as a consequence, of gas inclusions over time, (4) high price, and (5) nonscalability. However, apart from these drawbacks, organic−inorganic hybrid materials prepared by sol−gel approach represent a growing and attractive area of nanoengineered materials because of their promise to provide specific peculiarity and multifunctional alternatives to pure organic foams for preventing fires and explosions.[5−8] Formation of sol−gel materials in the process of foaming a flow of a liquid with low surface tension leads to a three-phase state comprising all active components, accelerating the extinguishing process. Formation of the solid phase in the foam significantly decreases most of the functional indices: multiplicity, heat capacity, dispersion, etc., but promotes the fire-extinguishing efficiency due to increasing its adhesion, thermal stability, durability, and other physical properties. In this paper we show for the first time a unique approach for the formation of dispersed phase and subsequent sol−gel transition in the course of producing the surfactant foam, which allows one to maintain the classic behavior of air foams while providing new properties like thermal and mechanical stability and high explosion efficiency in contrast to the well-known studies on the formation of foamed silica gel by multistage methods.[9−11]

■ EXPERIMENTAL SECTION

Materials, Syntheses, and Methods. All the materials used in this study were obtained directly from the manufacturer and subjected to a preliminary verification of the initial composition.

These were as follows:

1. Sodium dodecyl sulfate (SDS; ChimMed, ≥ 99.0%);
2. Perfluorooctanesulfonate (PFOS; ChimMed, ≥ 95.0%);
3. Sodium silicate solution, $Na_2O(SiO_2)x{\cdot}xH_2O$ (ChimMed, Na_2O, ∼10.6%, SiO_2, ∼26.5%);
4. Glacial acetic acid (ReagentPlus, ≥ 99%);
5. Commercially available fluorinate surfactant aqueous film forming foam (AFFF) (≪MMM≫ , USA)
6. Distilled water.

Producing Large-Scale Self-Hardening Silica-Based Foams. To produce large-scale self-hardening silica-based foams, two solutions were prepared. The first one consisted of an aqueous surfactant (one of the type forms SDS, PFOS, or AFFF) solution (vol 6%) and sodium silicate (vol 10−50%), and the second was an aqueous solution of acetic acid with a vol 20−50% concentration. Mixing was performed by ejecting the acetic acid solution, as shown in Figure 2, on the commercially available fire extinguisher FHF-30. The pH adjustment was performed by changing the ratio between the first and second solution while determining the rate of hardening for silica-based foams, Figure 5. Dispersing the air in the liquid flow was performed using a two-component action-modified air-foaming agent.

Characterization Techniques. Investigating the time of hardening was performed autokinetically using a Brookfield HA/HB viscometer. Selection of a spindle and frequency of its rotation provided controlling an increase in viscosity to 100 Pa·s. Evaluation of thermomechanical properties of produced silica hybrid foams was performed using a TMA 402 F1 Hyperion analyzer. X-ray diffraction analysis was performed using a D8 Advance (Bruker) multifunction X-ray diffractometer operated with copper anode. Measurements of specific surface area by the Brunauer−Emmett−Teller method and pore size distribution were made using low-temperature nitrogen adsorption−desorption on a Quantachrome Nova 1200 equipment. All samples were previously degassed at 90 °C for 7 h.

To study the samples using scanning electron microscopy (SEM), a silicon wafer was coated with the composite and, after complete drying in a vacuum desiccator, was investigated without additional sputtering using an ultrahigh resolution electron microscope Magellan 400L (Field Emission Inc.). The samples for high-resolution transmission electron microscopy (HRTEM) were prepared by dispersing small amounts of samples in ethanol to form a homogeneous suspension. A drop of the suspension was deposited on a carbon-coated copper grid for HRTEM observation (FEI TECNAI G2 F20 operating at 200 kV). X-ray photoelectron spectroscopy (XPS) studies were performed using a PerkinElmer 1257 model at 300 K with a nonmonochromatic Al Kα line at 1486.6 eV.

■ RESULTS AND DISCUSSION

Hybrid sol−gel materials have long been known and involve multicomponent entrapment or adsorption of unstable organic materials, such as polymers, dyes, biomolecules, etc., promoting synergistic effects.[12−14] Among the best-known is the ability to increase thermal stability of compounds while maintaining their functional properties.[15] Mesoporous silica is most frequently used for these purposes, as it retains its structure after annealing and removal of the template.[16−18] Either micellar surfactant structures altering their conformation with a change in pH or supramolecular structures of coordinatively active polymers[5,19] are commonly used as pore templates. The surfactants give commercially important advantages compared with the coordinative polymers.[20] They are easily removable, nontoxic, biodegradable, and relatively inexpensive. Thermal decomposition of the organic phase promotes the formation of highly organized ceramic structure with exceptional porosity and thermal stability. In our case we deal with the formation of ceramic foam via air bubbles injection.

The stage of inorganic polycondensation in conjunction with dispersing gas inclusions in aqueous surfactant solutions is the major focus of our work, since it allows to increase mechanical durability and heat resistance to conventional foams used for preventing fires and explosions. The formation of silica hybrid foams is a complex of multicomponent chemical interactions with dispersing the air phase proceeding in the flow of the liquid phase (water), Figure 1. We used anionic SDS surfactant for preparation of silica hybrid foam for increasing air content inside the liquid flow. It is well-known that SDS reduces the surface tension of a liquid flow[21] because of amphiphilic nature, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads), Figure 1, stage 1. When water-soluble metal silicates (sodium silicate in our case) are added at pH ≥ 11, SDS easily coassembles with the inorganic silicate species during the course of the reaction,[22] Figure 1 (stages 1, 2). Generally, the silica hybrid foam formation can be separated into two different steps: (1) SDS interaction with sodium silicate in aqueous media (stages 1 and 2, Figure 1), which is clearly described before,[22,23] and (2) sol−gel transition of sodium silicate into silica after the acetic acid injection (stages 3 and 4). The full mechanism of phase transition and foam formation is presented in Figure 1.

Injection of hydrolysis catalyst (acetic acid in our case) in the hydrodynamic flow of the liquid phase promotes effective dispersion of the "hardener" in aqueous media and the beginning of the sol formation stage (stage 3, Figure 1). The concentration of acetic acid was selected so that, upon adding sodium silicate to the solution, viscosity does not reach 20 mPa·s within 2 s, ensuring the stable operation of the foam generator. Ejecting and dispersing the air in the liquid flow occurred at the final stage, as shown in Figure 2.

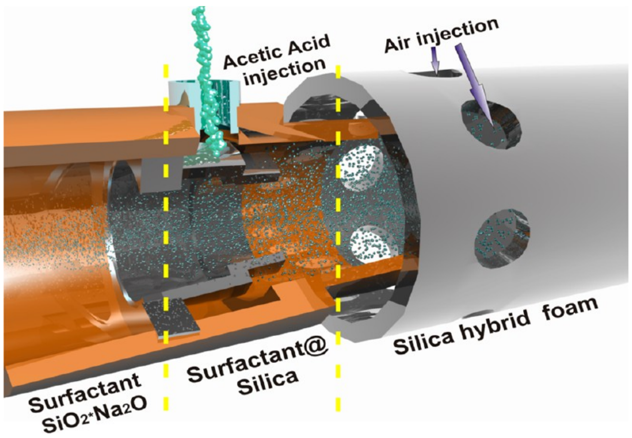

Figure 2. Physical process of the formation of silica hybrid foams under the conditions of hydrodynamic stirring.

Depending on the surfactant concentration, the multiplicity (the ratio between foam volume and volume of initial solution) of the produced foams varies in the range from 5 to 50, Figure 3A. This is because an increase in the surfactant content results in a decrease in the surface tension of the liquid phase and an increase in the capacity for gas dispersion. Using these foams without addition of acetic acid already promotes an increase in extinguishing capability due to high-temperature crystallization of sodium silicate and its increased adhesion and insulating capabilities.[24]

However, gelation of foams to yield silica results in a multiple-fold improvement of heat resistance. Thus, attaching new mechanical properties, Figure 7, and increased specific heat capacity capability to a foam is achieved by ejecting a hydrolysis catalyst in the flow of a liquid, Figures 2 and 3A,B, due to the formation of silica solid phase. The scanning transmission electron microscopy (STEM) and HRTEM data clearly show that such properties are due to not only the chemical nature of silica but also its structure. Figure 3B unambiguously demonstrates the highly porous nature of the silica formed due to emerging cavities between the nanoparticles, as confirmed by the HRTEM data, Figure 3D, illustrating the SiO_2 network formed of monodisperse nanoparticles. Since sol−gel silica is amorphous, Figure 3B, the analysis of the material composition was performed using XPS, Figure 4, in the range from 0 to 1200 eV.

During photoemission studies, survey spectra after sputtering show sharp peaks of C 1s (285 eV) and O 1s (537 eV). An inset in Figure 4 shows the Si(2p) core level spectra. The value of elemental Si(2p) is 99.15 eV, so the appearance of Si(2p) at 104 eV confirms that Si is in the SiO_2 state. The presence of C is due to the air atmosphere and the surfactants used for the preparation of silica sol−gel foam.

The phase transition process for self-hardening large-scale silica-based foams occurs in flight. After the phase transition, the particles are easily fixed on any surface effects producing a thermally stable fire resistance layer. Such sol−gel shells are characterized by a complete spontaneous recovery after mechanical destruction.

The key factor determining an increase in mechanical durability is the initial concentration of the precursor (sodium silicate) and catalyst (acetic acid). Thus, these foams may be generated directly in a single stage at the disaster site and at the stage of its emergence and development due to scalability and adjustability of the transition to the solid state (100 Pa·s) in the range from 2 to 30 s, depending on pH of a hydrolysis catalyst, Figure 5. The dynamics of the phase transition is shown in Figure 5.

Determination of dynamic viscosity in the range up to 100 Pa·s (solid state) was performed depending on the concentration of acetic acid while keeping the sodium silicate content constant. The minimum detectable value of the sol−gel transition is 2 s, and the maximum is unlimited. However, given the peculiarities in fire-extinguishing properties of water foams, in the experiments we limited ourselves to a range of no more than 30 s, allowing the foamed silica hybrid gel to solidify after filling remote areas engulfed in flames. The structure of the foamed mass after removal of the solvent (water) reproduces the structure of the formed framework, Figure 6, as confirmed by the SEM data, Figure 6C. Moreover, the removal of the liquid phase while drying up to 200 °C results in the compression and structurization of the surface topography, Figure 6D. This morphology promotes fire resistance properties and a high adhesion to the substrate.

According to thermal analysis, in the course of applying external heat the foamed silica can withstand short-term exposure to temperatures up to 1000 °C with minimal changes in its mechanical state. These experimental data correlated with the thermomechanical study results are shown in Figure 7. Previously it was found that certain organic polymeric materials are unable to withstand prolonged heat exposure and

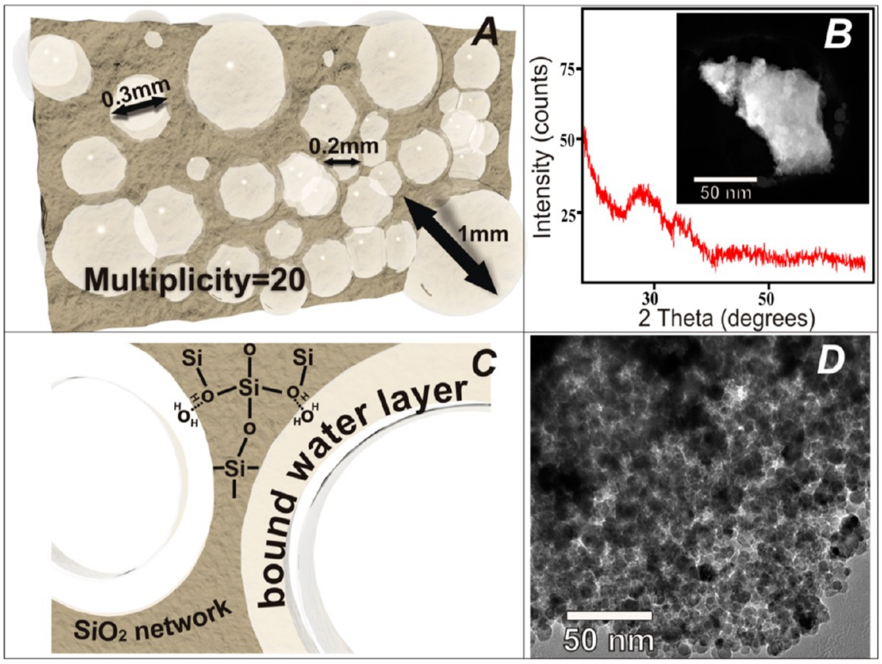

Figure 3. Visualization of the formation of solid sol−gel foam (A) with a SiO_2 network (C), X-ray diffraction with STEM image (as insert) of silica foam (B) and HRTEM of as-synthesized SiO_2 nanoparticles (D).

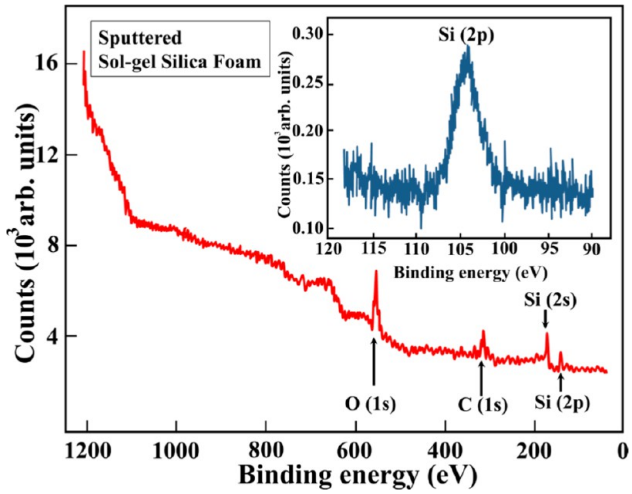

Figure 4. XPS survey scanning spectra of sputtered sol−gel silica foam with Si(2p) as insert.

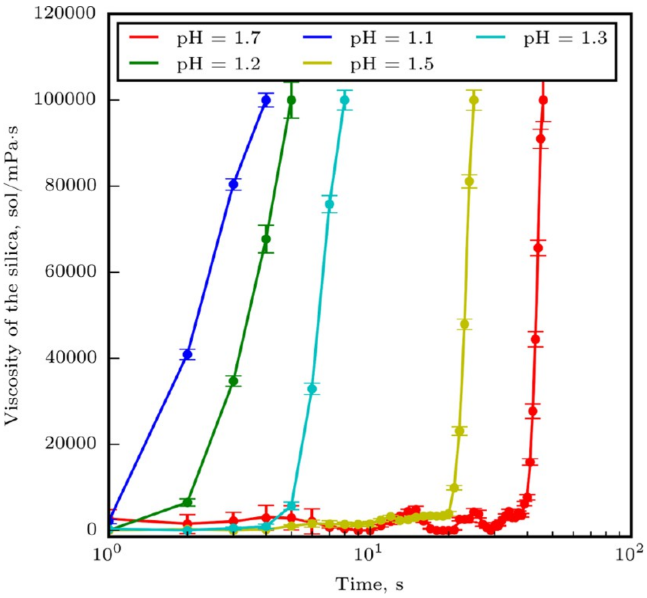

Figure 5. Viscosity behavior of the silica sol at various catalyst pH values.

experience severe plastic deformation as temperature increases, which eventually results in a complete destruction. Our case is the opposite.

Regardless of the silica content, the change in thermomechanical properties during heating maintains its character. In the temperature range from 25 to 300 °C, one observes a significant mass compression due to the removal of the solvent, decomposition of surfactants, etc.

Thus, it is impossible to achieve 100% decomposition below 800 °C, since hybrid silica foam does not experience full compression during heating but, despite the partial deformation, only gains durability, demonstrating the reverse characteristics as compared to conventional organic materials. No less surprising, but quite expected, is an increase in the fire-extinguishing and fire-fighting efficiency. We used a model fire seat described in Supporting Information and composed of ~4.7 m^2 of highly developed surface with an alternate shape. Given the same liquid consumption, extinguishing time for silica-gel-based foam did not exceed 5 s.

While using conventional water, the flame was extinguished only after 35 s, and conventional foam generated with the same surfactant concentration as that used in producing the foamed silica gel eliminated the fire after 25 s. In case of the most expensive and most efficient fluorinated foaming agent with unique film-forming abilities, the fire was eliminated after 20 s. A test on resetting the charred wood on fire revealed the impossibility of reignition in the presence of silica hybrid foam, which renders the treated materials inflammable. So, there are obvious advantages of using gelated silica hybrid foams, Table

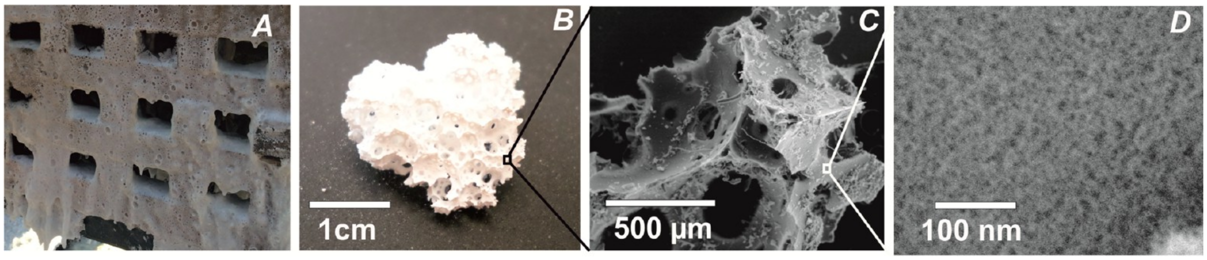

Figure 6. (A, B) Photographs and (C, D) SEM images of hybrid silica foam.

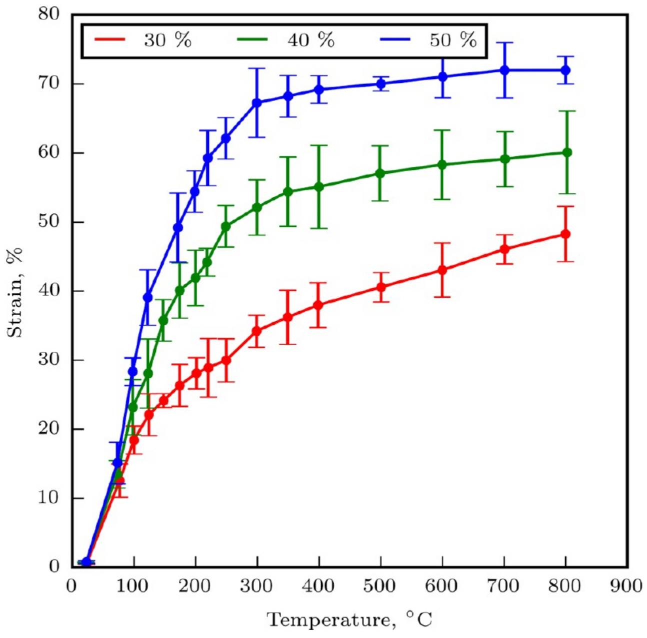

Figure 7. Silica hybrid foam strain vs temperature with different solid-phase contents.

1. However, given the different foam consumption per unit of time, we introduced a new term, index of fire-fighting efficiency (IFFE), determined by the following equation: IFFE = $S/(Q{\cdot}t)$, where S is the square of extinguishing in m^2; Q is the consumption of extinguishing solution in liters; t is the time of extinguishing in seconds.

This indicator has a definite physical meaning: the larger area can be extinguished with 1 L of extinguishing agent for some time, or the faster one can extinguish a larger fire area with 1 L of extinguishing agent, the higher the extinguishing efficiency. According to the data obtained, extinguishing efficiency for silica sol−gel foams is almost 50 times higher than that for ordinary water and 15 times better than that for the state-of-the-art fire-extinguishing agent AFFF, Figure 8.

A characteristic feature of extinguishing using gelated foams is the complete absence of reignition of the treated surface during prolonged exposure to open flame, in contrast to using

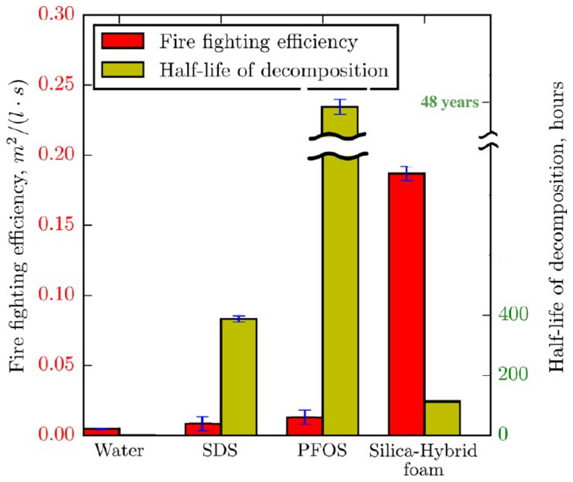

Figure 8. Comparison of fire-fighting efficiency and biodecomposition properties for agents used in extinguishing solid combustibles.

conventional extinguishing agents. This effect is achieved by combining high efficiency of fire suppression by proposed foamed silica gel-based gelated foams. It is known that the greatest contribution to extinguishing the burning material is provided by the ability to quickly withdraw heat from its surface.

This is why air foam is widely used nowadays, which, apart from its high wetting properties, blocks the direct contact between the burning material and oxygen, substantially increasing the fire-fighting efficiency. However, the high temperature of the heated areas and gaseous flows results in almost instantaneous thermal degradation of classic foams, which requires a special fire-fighting control to avoid prolonged effects of high temperatures on the foam and previously extinguished fire seats. In this regard, there is every reason to believe that the high adhesion of gelated foam to the surface of a solid combustible and a substantial increase in its thermal resistance (and even fire resistance) would result in a multiple increase in its efficiency while extinguishing solid flammable materials. It is also known that the sol−gel phase transition is accompanied by a very high adhesion of the gel to the substrate upon the transition to the solid state. This feature allows the

Table 1. Parameters of Fire Extinguishing for the Tested Means

extinguishing agent	extinguishing time[a], s	IFE, $m^2/L{\cdot}s$	reignition time after exposure to direct flame, after	specific heat capacity, kJ/(kg·°C)
water	35 ± 4	0.004 ± 0.0005	10 ± 4 s	4.2 ± 0.1
6% SDS solution	25 ± 2	0.008 ± 0.001	20 ± 6 s	0.6 ± 0.3
6% AFFF solution	20 ± 4	0.012 ± 0.002	35 ± 8 s	0.8 ± 0.4
≪silica hybrid foam≫[a]	5 ± 2	0.187 ± 0.002	absence of reignition for >30 min	2.5 ± 0.4

[a] Self-hardering silica-based foam contains 6% SDS, 30% pure SiO_2, and 64%H_2O.

Figure 9. Complete cessation of fire spread upon the contact with a silica-based foam fire retardant belt after 2 d. Self-hardening silica-based foam was generated via FHF-30 extinguisher and contains 6% SDS, 30% pure SiO_2, and 64% H_2O. The estimated foam multiplicity is 20. The square 500 m^2 were treated with consumption index 1.06 L/m^2. The full demonstration available here https://www.youtube.com/watch?v=kwKB0r4i2Hk.

formed material to be fixed on vertical (and particularly on horizontal, "ceiling") surfaces. An important feature of large-scale fast-hardening sol−gel foams to improve efficiency is turning the foamed silica gel into a ceramic foam material while simultaneously releasing chemically bound water in the course of a polycondensation reaction, Figure 3C. The presence of high temperatures accelerates this process, which, in fact, is the limiting stage of firefighting.

Given the enormous heat capacity of water, this process significantly accelerates withdrawal of heat by adjusting in time. The presence of foamed silica on the solid surface makes its reignition impossible due to the heat resistance up to 1000 °C at a layer thickness of ~1 cm or more.

A set of these properties makes the use of hardening foams in some cases of spreading forest fires indispensable. A fire situation when it is rational is not to extinguish the fire seat, but to allow it to burn out by the natural laws of diffusion combustion for solids of forest origin, is very likely. All available forces and means of fire protection, including helicopter aircraft, could be mobilized to build fire-resistant, flame-retardant belts to ensure the localization of the forest fire seat in its origin and prevent the spread of combustion beyond flame-retardant belt, Figure 9.

In this case, air foams with adjusted hardening time from 2 to 3 to 30−40 s or more become absolutely indispensable and rivalless. Using the described formulation, one can employ medium multiplicity foams to produce a reliable fire protection belt with virtually any desired width and thickness of fire-resistant foam coating, with the time of its effective existence for practically the entire fire season, Figure 9.

Given the fact that all of the synthetic fire-fighting foaming agents harm living microorganisms and the ecosystem of the planet, we performed comparative tests to determine the time of the induction period (T_{ind}) using surfactant-unadapted activated sludge (see Supporting Information for details). Biochemical testing of the induction period show the half-life time of decomposition and can be classified Like isomeric value with T_{ind}. Since the synthesized large-scale fast-hardening sol−gel foams are based on silica known for its bioinertness,[25] the results in Figure 8 are very clear. The data obtained suggest that the perfluorosurfactant-based foaming agents decompose very slowly ($T_{ind} = \infty$), that, they are "completely non-biodegradable," while T_{ind} for DDS was 7 ± 1 d and for as-synthesized silica foam 3 ± 1 d, Table S1. Thus, large-scale fast-hardening sol−gel foams are the world's first completely safe fire-extinguishing agents.

It should be emphasized that when foaming agents are absorbed by water and soil, the limiting factor in their bioassimilation under natural conditions is though a small (0.1−0.5%) content of perfluorinated components. Given that surfactant-bioassimilating microorganisms are active for 3−5-month cycles of the warm period, during the cold period the accumulation of surfactants in water and soil persists. So, thousands of tons of highly toxic and completely non-biodegradable components have been accumulated by biological systems around the world for over 20 years. In this regard, the use of alternative firefighting technologies is extremely important, and we hope that this work will significantly affect the current situation of polluting our planet with biohazardous fluorinated foaming agents by replacing them with silica-based self-hardening sol−gel foams.

■ CONCLUSIONS

In this study, we demonstrated for the first time the possibility of an in situ production of large-scale ultrafast gelation foams with extremely high fire prevention efficiency and complete biodegradation. Reaching a specific consumption value of 1.06 l/m^2 was possible owing to a fundamentally new extinguishing mechanism and exceptional thermal stability, which does not allow the materials to reignite. The presented description shows a firm solution to the problem and achievement of the desired technical result, namely, the ability to implement and industrially use the technically and technologically simple sol−gel method for the production of silica gel foam at atmospheric pressure, without heating at an ambient temperature from −2 to 50 °C, with a controllable rate of formation and solidification from 2 to 30 s, with the possibility of its preferential use as an extinguishing agent in fighting fires and for other purposes.

The fire-extinguishing tests have revealed that the silica-based sol−gel foams exhibit an almost 50 times higher extinguishing efficiency than that for ordinary water, and 15 times better than the state-of-the-art fire-extinguishing agent AFFF, and its use for the localization of forest fires allows for mobile and highly efficient management of this process by firefighters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08653.

> Discussion of testing biodegradability; biodegradability and phytotoxicity indicators for foaming agents; discussion of testing extinguishing efficiency; experimental parameters; description of experiment. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: avv@scamt.ru.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Russian Government, Ministry of Education (Research was made possible due to financing provided to the Customer from the federal budget aimed at maximizing Customer's competitive advantage among world's leading educational centers).

■ REFERENCES

(1) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C.; Mabury, S. A. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ. Sci. Technol.* **2004**, *38* (2), 373−380.

(2) Giesy, J. P.; Kannan, K. Peer reviewed: perfluorochemical surfactants in the environment. *Environ. Sci. Technol.* **2002**, *36* (7), 146A−152A.

(3) Kannan, K. S.; Corsolini, S. J.; Falandysz, J. G.; Fillmann, G. K. S.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Wouwe, N. V.; Yang, J. H.; Aldous, K. M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ. Sci. Technol.* **2004**, *38*, 4489−4495.

(4) McLachlan, M. S.; Holmström, K. E.; Reth, M.; Berger, U. Riverine discharge of perfluorinated carboxylates from the European continent. *Environ. Sci. Technol.* **2007**, *41* (21), 7260−7265.

(5) Zhang, X.; Blanchard, G. J. Polymer Sol−Gel Composite Inverse Opal Structures. *ACS Appl. Mater. Interfaces* **2015**, *7* (11), 6054−6061.

(6) Wang, X.; Jana, S. C. Synergistic Hybrid Organic−Inorganic Aerogels. *ACS Appl. Mater. Interfaces* **2013**, *5* (13), 6423−6429.

(7) Yang, F.; Yngard, R.; Hernberg, A.; Nelson G. L. Thermal Stability and Flammability of Polymer-Silica Nanocomposites Prepared via Extrusion. In *Fire and Polymers IV;* ACS Symposium Series 922; American Chemical Society: Washington, DC, 2005; Chapter 12, pp 144−154.10.1021/bk-2006-0922.ch012

(8) Avnir, D.; Coradin, T.; Lev, O.; Livage, J. Recent bio-applications of sol−gel materials. *J. Mater. Chem.* **2006**, *16* (11), 1013−1030.

(9) Delaney, P.; Hanrahan, J. P.; Copley, M. P.; O'Byrne, J.; Holmes, J. D.; Morris, M. A. Synthesis of Porous Silica Foams via a Novel Vacuum-Induced Sol−Gel Method. *J. Am. Ceram. Soc.* **2009**, *92* (11), 2798−2800.

(10) Tomita, T.; Kawasaki, S.; Okada, K. A Novel Preparation Method for Foamed Silica Ceramics by Sol-Gel Reaction and Mechanical Foaming. *J. Porous Mater.* **2004**, *11*, 107−115.

(11) He, J.; Fujikawa, S.; Kunitake, T.; Nakao, A. Preparation of Porous and Nonporous Silica Nanofilms from Aqueous Sodium Silicate. *Chem. Mater.* **2003**, *15* (17), 3308−3313.

(12) Avnir, D. Organic chemistry within ceramic matrixes: Doped sol-gel materials. *Acc. Chem. Res.* **1995**, *28* (8), 328−334.

(13) Sanchez, C.; Julian, B.; Belleville, P.; Popall, M. Applications of hybrid organic−inorganic nanocomposites. *J. Mater. Chem.* **2005**, *15*, 3559−3592.

(14) Vinogradov, V. V.; Avnir, D. Exceptional thermal stability of therapeutical enzymes entrapped in alumina sol-gel matrices. *J. Mater. Chem. B* **2014**, *2* (19), 2868−2873.

(15) Crepaldi, E. L.; Soler-Illia, G. J. A. A.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C. Controlled formation of highly organized mesoporous titania thin films: from mesostructured hybrids to mesoporous nanoanatase TiO_2. *J. Am. Chem. Soc.* **2003**, *125* (32), 9770−9786.

(16) Zhou, Y.; Schattka, J. H.; Antonietti, M. Room-temperature ionic liquids as template to monolithic mesoporous silica with wormlike pores via a sol-gel nanocasting technique. *Nano Lett.* **2004**, *4* (3), 477−481.

(17) Trewyn, B. G.; Slowing, I. I.; Giri, S.; Chen, H. T.; Lin, V. S. Y. Synthesis and functionalization of a mesoporous silica nanoparticle based on the sol−gel process and applications in controlled release. *Acc. Chem. Res.* **2007**, *40* (9), 846−853.

(18) Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Whilton, N. T.; Walsh, D. Sol-gel synthesis of organized matter. *Chem. Mater.* **1997**, *9* (11), 2300−2310.

(19) Verdolotti, L.; Lavorgna, M.; Lamanna, R.; Di Maio, E.; Iannace, S. Polyurethane-silica hybrid foam by sol-gel approach: Chemical and functional properties. *Polymer* **2015**, *56*, 20−28.

(20) Ryoo, R.; Kim, J. M. Structural order in MCM-41 controlled by shifting silicate polymerization equilibrium. *J. Chem. Soc., Chem. Commun.* **1995**, *7*, 711−712.

(21) Mysels, K. J. Surface tension of solutions of pure sodium dodecyl sulfate. *Langmuir* **1986**, *2*, 423−428.

(22) Huang, M. H.; Dunn, B. S.; Zink, J. I. In situ luminescence probing of the chemical and structural changes during formation of dip-coated lamellar phase sodium dodecyl sulfate sol-gel thin films. *J. Am. Chem. Soc.* **2000**, *122*, 3739−3745.

(23) Mehrali, M.; Shirazi, S. F. S.; Baradaran, S.; Mehrali, M.; Metselaar, H. S. C.; Kadri, N. A. B.; Osman, N. A. A. Facile synthesis of calcium silicate hydrate using sodium dodecyl sulfate as a surfactant assisted by ultrasonic irradiation. *Ultrason. Sonochem.* **2014**, *21*, 735−742.

(24) Porai-Koshits, E. A.; Averjanov, V. I. Primary and secondary phase separation of sodium silicate glasses. *J. Non-Cryst. Solids* **1968**, *1* (1), 29−38.

(25) Wang, X.; Schröder, H. C.; Wiens, M.; Ushijima, H.; Müller, W. E. Bio-silica and bio-polyphosphate: applications in biomedicine (bone formation). *Curr. Opin. Biotechnol.* **2012**, *23* (4), 570−578.