

FULL SUPPRESSION OF HYDROGEN EXPLOSION USING PHLEGMATIZATION ADDITIVES. EXPERIMENTAL RESULTS

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ABSTRACT

The paper presents results of experimental investigations of different phlegmatizator substances and its binary compounds used for full hydrogen combustion suppression. The work was performed in experimental facilities of three different scales (small, medium and large) at normal initial pressure and temperature range 20 — 120 °C. Ten individual substances and six binary compounds were tested in a small scale experiments. Three individual halogen containing substances capable of full suppression of hydrogen combustion were found in a series of small scale experiments (tube length – 1 m, ID – 66 mm). The minimum concentration of the most effective substance was 11% at 20°C and 14% at 120°C in a small scale experiments. Medium scale confined and large scale unconfined experiments confirmed the possibility of full combustion suppression. The minimum concentration of the most effective binary mixture was found to be 12 % at 20°C in a large scale experiments.

1.0 INTRODUCTION

The problem of hydrogen safety is very important for everyday use of the hydrogen technologies and nuclear power plant safety. There are different ways to suppress hydrogen combustion in a volume: usage of different types of recombiners, creation of inert atmosphere, injection of phlegmatizator substances.

Problem of Nuclear Power Plant hydrogen safety is very important for many years and still is highly actual because of last events in Japan. The actuality of the hydrogen safety increases with the growth of importance of hydrogen energy as an energy carrier. There are many ways to suppress hydrogen explosion in a closed volume: creation of inert atmosphere, usage of different types of recombiners, injection of phlegmatizator additives etc. Phlegmatization effectiveness of different compounds and mixtures are not widely tested at different scales and initial conditions.

Available systems that remove hydrogen from enclosure have limited performance. Formation of explosive hydrogen air mixtures with steam is possible in emergency situation for some rooms inside NPP containment. Taking into account that maximum operational pressure could be up to 4.8 atm even the slowest combustion mode – laminar burning can be extremely dangerous. Thus in our work the attempt of full hydrogen-air mixture combustion suppression with special flegmatizing additives was done.

The main requirements that apply to phlegmatizator substances are the following:

- minimum phlegmatizator concentration providing complete suppression of combustion processes in the whole range of hydrogen concentrations must be low and practically implemented;
- aggregate state of phlegmatizator substances under normal conditions - gas or liquid with a sufficiently high vapor pressure needed to create phlegmatizing concentration in the room;
- phlegmatizator substance should not have high chemical aggressiveness and toxicity under normal conditions.

Accident with the release of hydrogen may occur at various industrial sites with a wide range of possible initial conditions. For example, it is known that during the development of nuclear power plant accident pressure inside the containment can varied from 1 to 4.8 atm., temperature from 20°C to 200°C, water vapor concentration from 0 to 74%, and the hydrogen concentration can reach 40 percent or even more . Therefore, an important characteristic is the dependence of minimum phlegmatizing concentration that provides complete suppression of the combustion on temperature. One way to reduce the temperature dependence is the use of multicomponent phlegmatizator mixtures.

Ability to completely suppress the combustion of a stoichiometric hydrogen mixture with phlegmatizator content in the mixture up to 20% is adopted as a criterion for selection of primary material suitability as a key component of the multicomponent phlegmatizator mixture. Substance that significantly reduces the rate of combustion of the mixture when added in a small amounts (few percent), but not completely suppress the combustion process, can be considered as additional components of the multicomponent phlegmatizator mixtures.

Effect of scale for the process of mixture inflammation is associated with geometric size of the ignition source if sufficiently high ignition energy is applied. Decay of the combustion process at an early stage because of the high losses associated with the small radius of curvature of the flame front is possible at small sizes of the heated surface, which is a source of ignition. Therefore, the final test examined the phlegmatizing ability of additives should be set at a sufficiently large scale, equipped with the ignition system, which simulates the size of the possible sources of ignition in an accident at the plant. This fact is taken into account when creating a large-scale installation ignition device and determining the geometry of the planned experiments on desensitization mixtures.

It should be noted that when testing the phlegmatizing ability of the investigated additives the only requirement for the geometry of the setup is that the size of the test volume should be significantly larger than the ignition device. Other geometric properties of the test volume (shape, conjection, etc.) do not affect the minimum phlegmatizing concentration.

Preliminary experiments on hydrogen air mixture phlegmatization were performed in a small scale facility to minimize expenses and to test wider range of phlegmatizator substances. Binary mixtures of perspective individual substances were combined to find effective compounds that have minimal temperature dependence on minimum phlegmatizing concentration. Best individual substances and binary mixtures were selected for following medium and large scale test.

All experiments were performed for hydrogen-air stoichiometric mixture as the most volatile.

2.0 EXPERIMENTAL

Small scale experiments were conducted in a heated tube of 1 m length, 66 mm internal diameter, total volume 3.5 l. Initial temperature in experiments varied from 20 to 120°C, initial pressure was 1 atm. Four pressure gauges and 10 light sensors were installed in facility. Ignition was performed with heated platinum wire of 15 mm length and 0.8 mm diameter, estimated temperature of the wire $T \sim 1500^\circ\text{C}$.

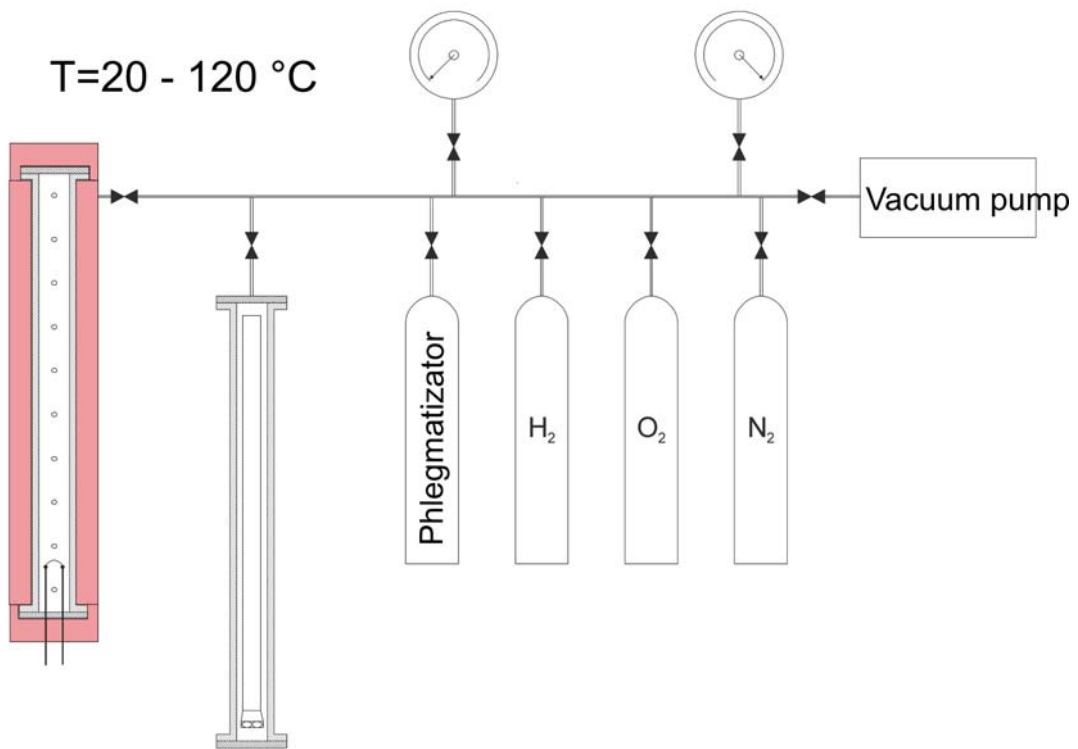


Figure 1. Small scale experimental facility.

Medium scale facility is a heated tube of 8 m length, internal diameter 121 mm, total volume 92 l. Initial temperature in experiments varied from 20 to 120°C, initial pressure was 1 atm. Ignition was performed with heated nichrome surface 30 cm², estimated temperature T~1500°C. Registration system of medium scale facility consists of 16 collimated photodiodes and 1 tensoresistive pressure gauge.

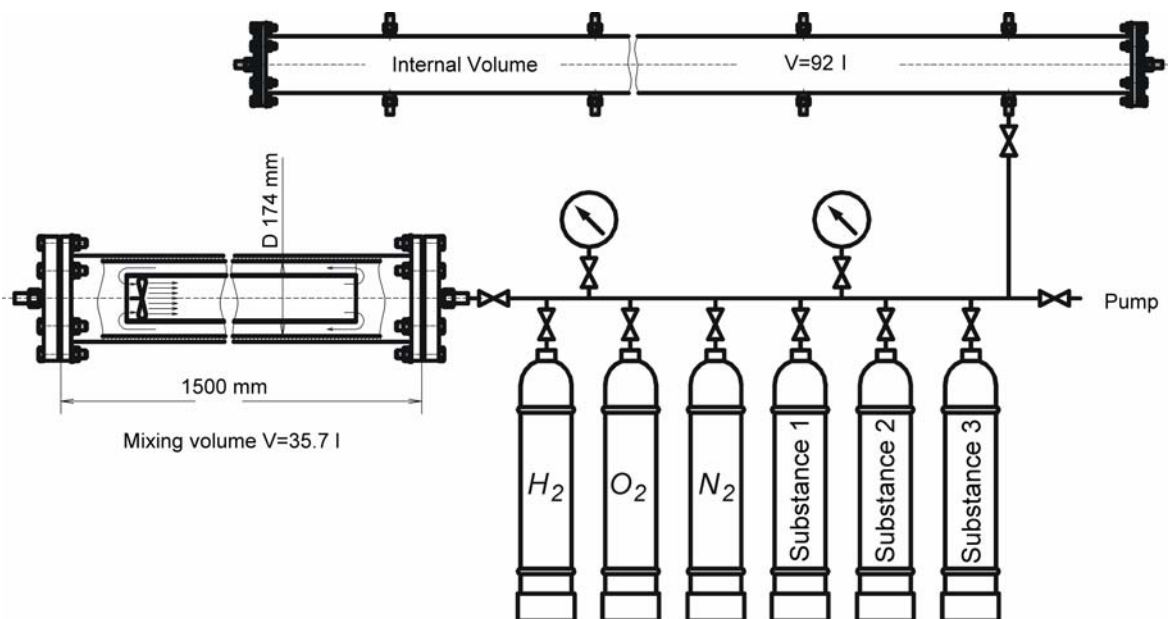


Figure 2. Scheme of medium scale experimental facility.

Volume of large scale experimental facility is 10.6 m^3 . Experimental volume of facility is semicylinder 1.5 m internal diameter made of 120 μm polyethylene film. Maintenance of a given operating temperature of the mixture at $T = 20^\circ\text{C}$ provided with the use of temperature control system consisting of a second external plastic shell (see Fig. 4). Ignition system consists of nichrome plates (total surface 200 cm^2) temperature rise time, $<30 \text{ ms}$, temperature decay time $>1 \text{ s}$, estimated temperature $T \sim 1200^\circ\text{C}$. Initial temperature in experiments was 20°C , initial pressure - 1 atm. Data acquisition system recorded the following data in the experiments: high-speed video recording of combustion processes and combustion and explosion parameters (pressure and light data).



Figure 3. Ignition system of large scale facility.

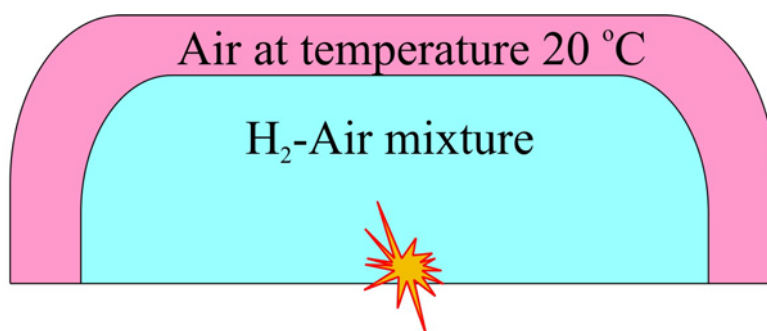


Figure 4. Schematic view of large scale facility.

3.0 RESULTS AND DISCUSSION

3.1. Individual phlegmatizator substance.

Ten individual substances belong to halogenide class were selected as perspective phlegmatizators for small scale tests. Stoichiometric hydrogen-air mixture was used as a combustible mixture in all experiments. Below is an example experimental data for the two substances with a significant phlegmatizing ability, one of which completely suppresses combustion ($\text{C}_2\text{F}_4\text{Br}_2$), and another - not (CF_3I).

3.1.1. Individual substance $\text{C}_2\text{F}_4\text{Br}_2$

Results of hydrogen-air mixture phlegmatization by individual substance $\text{C}_2\text{F}_4\text{Br}_2$ in a small scale tests are presented in Table 1.

Table 1. Experimental results with addition of $C_2F_4Br_2$ in a small scale tests.

$C_2F_4Br_2$, %	Initial temperature, °C	Maximum overpressure, bar	Flame velocity, m/s	combustion
3	23	5.5	31	burn
10	23	2.3	1.5	burn
11	23	0.4	0	decay
12	22	0.4	0	decay
13	22	0.2	0	decay
14	22	0	0	decay
15	27	0	0	decay

Flame velocity – average flame front velocity near the tube end. Maximum concentration dependence on phlegmatizator $C_2F_4Br_2$ concentration in a small scale tests is presented on Fig. 5.

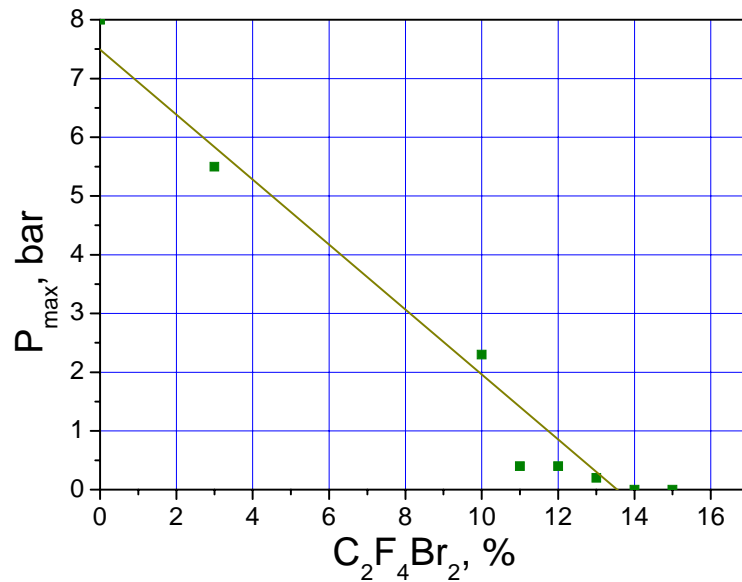


Figure 5. Maximum overpressure vs. $C_2F_4Br_2$ concentration

Average flame front velocity dependence on $C_2F_4Br_2$ concentration is presented on Fig. 6.

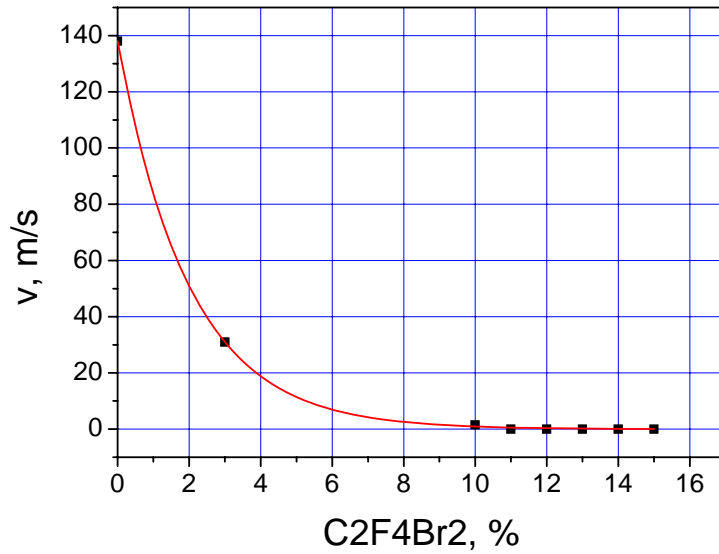


Figure 6. Average flame front velocity vs. C₂F₄Br₂ concentration.

Full stoichiometric hydrogen-air mixture combustion suppression achieved at 11% of phlegmatizator C₂F₄Br₂ for T=23°C in a small scale tests (see Fig. 7a).

Full stoichiometric hydrogen-air mixture combustion suppression achieved at 14% of phlegmatizator C₂F₄Br₂ for T=120°C (see Fig. 7b).

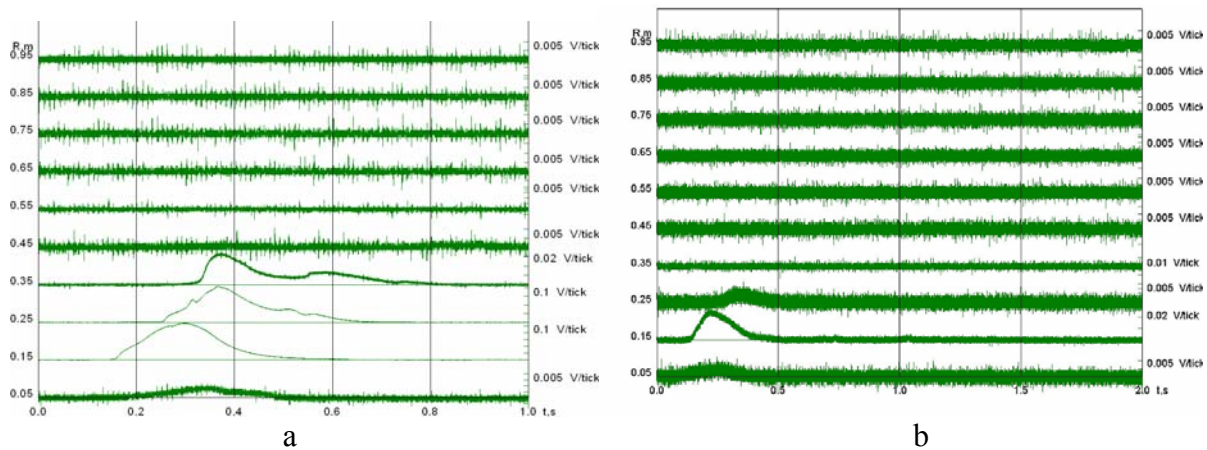


Figure 7. X-t diagram of combustion decay for 11% C₂F₄Br₂ and T=23°C (left) and for 14% C₂F₄Br₂ and T=120°C (right) in a small scale tests.

3.1.2 Individual substance CF₃I

Results of hydrogen-air mixture phlegmatization by individual substance CF₃I in a small scale tests are presented in Table 2.

Table 2. Experimental results with addition of substance CF₃I in a small scale tests.

CF ₃ I, %	Initial temperature, °C	Maximum overpressure, bar	Flame velocity, m/s	combustion
3	25	5	50	burn
10	25	2	1	burn
15	25	2.2	0.9	burn
20	25	1.2	0.8	burn

Flame velocity – average flame front velocity near the tube end. Maximum concentration dependence on phlegmatizator CF₃I concentration in a small scale tests is presented on Fig. 8.

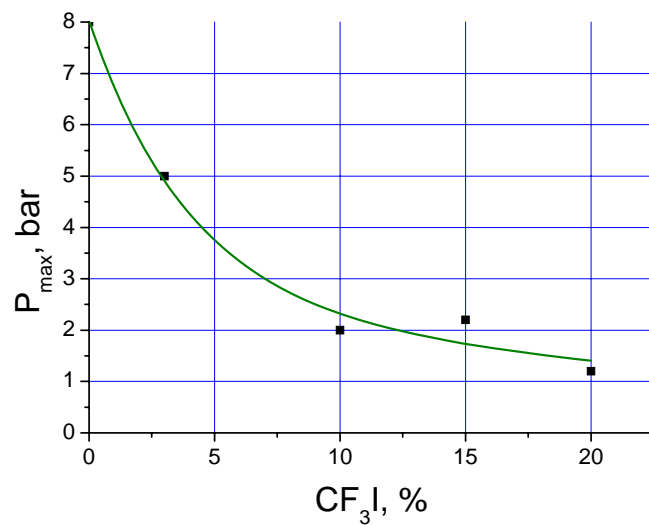


Figure 8. Maximum overpressure vs. phlegmatizator CF₃I concentration.

Average flame front velocity dependence on CF₃I concentration is presented on Fig. 9.

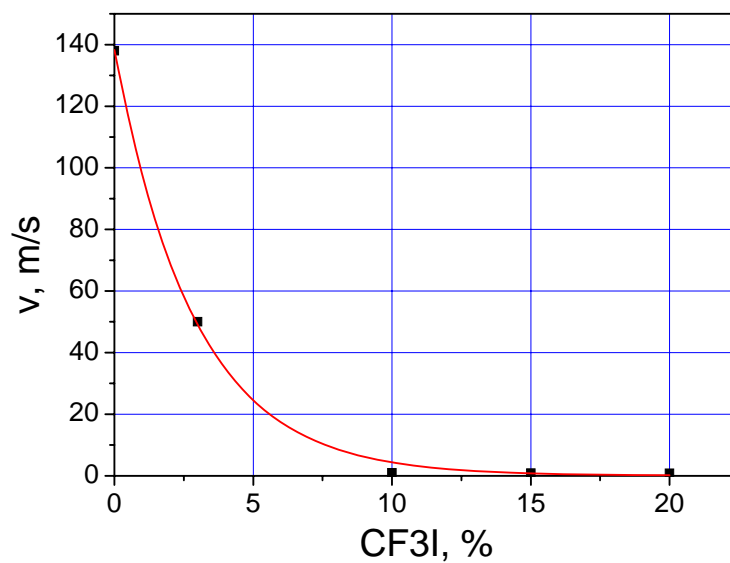


Figure 9. Average flame front velocity vs. CF₃I concentration.

Full stoichiometric hydrogen-air mixture combustion suppression did not achieved in a small scale tests with addition of phlegmatizator CF_3I for $T=25^\circ\text{C}$. Experimental data show that the decrease in burning velocity with increasing CF_3I concentration in the mixture has fairly sharp dependence, and already 10% of CF_3I reduces burning velocity to the order of 1 m/s. At the same time further increase of CF_3I concentration in the mixture up to 20% has no significant effect on the parameters of combustion.

3.1.3. Results of small-scale experiments.

Experimental results of testing 10 halogenated compounds in a small scale by the method described above are shown in Table 3. It identifies the flame front velocity at a content of each of the tested phlegmatizators in the mixture in an amount of 3%, 10%, 15% and 20%.

Table 3. Flame front velocity at a content of each substance in the mixture in an amount of 3%, 10%, 15% and 20%.

#	Substance	v_ϕ (m/s), 3% phlegmatizator	v_ϕ (m/s), 10% phlegmatizator	v_ϕ (m/s), 15% phlegmatizator	v_ϕ (m/s), 20% phlegmatizator	Minimum phlegmatizing concentration, %
1	$\text{C}_2\text{F}_4\text{Br}_2$	31	1,5	decay	decay	11
2	CF_3Br	53	2,6	1	decay	19
3	$\text{C}_2\text{F}_3\text{Cl}_3$	70	7,6	0,7	decay	20
4	CF_3I	50	1	0,9	0,8	-
5	CF_2Br_2	31	1,7	0,8	0,5	-
6	$\text{C}_2\text{F}_3\text{ClBr}_2$	16	-	-	-	-
7	$\text{C}_2\text{F}_2\text{Cl}_2$	140	27	9,3	-	-
8	CF_2ClBr	-	8	2,5	0,8	-
9	CH_2Br_2	50	-	-	-	-
10	SiF_4	50	28	13	6	-

v_ϕ – average flame front velocity before the stage of inhibition at the end of the tube

Based on the results of small-scale experiments one can distinguish three types of substances according to their phlegmatizing impact on hydrogen-air mixtures combustion.

The first type is a substance that can completely suppress the combustion of a stoichiometric hydrogen-air mixture of. Among the tested substances first type mixtures were $\text{C}_2\text{F}_4\text{Br}_2$, CF_3Br and $\text{C}_2\text{F}_3\text{Cl}_3$. Minimum phlegmatizing concentration in a small-scale tests at the initial temperature $T = 25^\circ\text{C}$ are 11% for $\text{C}_2\text{F}_4\text{Br}_2$, 19% and 20% CF_3Br for $\text{C}_2\text{F}_3\text{Cl}_3$.

The second type are substances which are not able to completely suppress the combustion even for the normal temperature, but significantly reduced combustion rate of the mixture, even when added in a small quantities (few percent). Such substances can be considered as an additional component of composite phlegmatizators used to reduce the total amount of phlegmatizator necessary to ensure non-

combustibility mixture and reduce the temperature dependence of the minimum phlegmatizing concentration of composite phlegmatizator. Among the tested substances to the second type can be referred CF_2Br_2 and CF_3I . $\text{C}_2\text{F}_3\text{ClBr}_2$ substance may also be included to the second type: because of the low saturated vapor pressure it could not be tested at content in a mixture of more than 3.4%, but even with such content in a mixture flame front velocity was ~ 2 times smaller than the same content in a mixture of tests leader - $\text{C}_2\text{F}_4\text{Br}_2$. However, the small saturated vapor pressure makes it difficult to use this substance as a phlegmatizator because of evaporation problems.

The third type are substances that are not strongly influence the combustion process to treat them as components of effective phlegmatizator compositions. These are SiF_4 , CH_2Br_2 , CF_2ClBr and $\text{C}_2\text{F}_3\text{Cl}$.

In a Table 3 substances are down according to their suitability for use in the binary phlegmatizators. Substance $\text{C}_2\text{F}_3\text{ClBr}_2$, located in the sixth line, is not suitable as a component of the binary phlegmatizator because of the low saturated vapor pressure. Thus, $\text{C}_2\text{F}_4\text{Br}_2$ substance should be taken as the basis for binary phlegmatizator capable completely suppress the combustion of a stoichiometric hydrogen-air mixture at the lowest concentration, and as additional component material from lines 2-5 are appropriate for usage. Substance of the last four rows of Table 3 has been shown to be ineffective as a phlegmatizator.

3.3. Experiments with binary phlegmatizators.

An experimental search for binary phlegmatizators that are effective in the temperature range 20-120°C, and also would have a weak (less than the best individual phlegmatizator $\text{C}_2\text{F}_4\text{Br}_2$) dependence of the minimum phlegmatizing concentration on temperature was carried out. Results for the best of the found phlegmatizators are shown in Table 4.

Table 4. Minimum phlegmatizing concentration for different individual and binary phlegmatizators in a small scale experiments

#	Phlegmatizator	Concentration for T=20 °C, %	Concentration for T=120 °C, %
1	$\text{C}_2\text{F}_4\text{Br}_2$	11	14
2	$\text{C}_2\text{F}_4\text{Br}_2 + \text{C}_2\text{F}_3\text{Cl}_3$	13 (9+4)	14 (10+4)
3	$\text{C}_2\text{F}_4\text{Br}_2 + \text{CF}_3\text{I}$	11 (9+2)	13 (10+3)
4	$\text{C}_2\text{F}_4\text{Br}_2 + \text{C}_2\text{F}_3\text{ClBr}_2$	11 (9+2)	14 (12+2)

Experiments with phlegmatizator binary mixtures showed that binary mixture has the same phlegmatizing concentration for individual substance $\text{C}_2\text{F}_4\text{Br}_2$ and lower (for phlegmatizator #3) phlegmatizing concentration than individual substance $\text{C}_2\text{F}_4\text{Br}_2$ for 120°C.

3.4. Medium scale experiments

Medium-scale experiments generally confirmed the results obtained in a small scale experiments. The minimum phlegmatizing concentrations were slightly adjusted upward. Results of experiments for binary mixtures that have shown the best results are presented in Table 5.

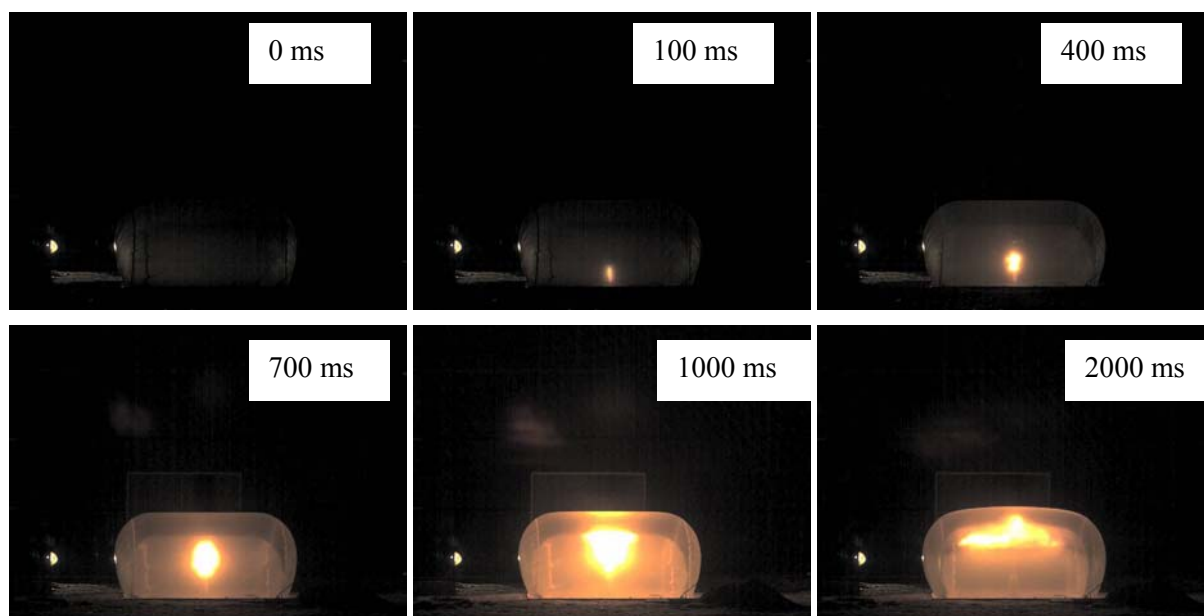
Table 5. Minimum phlegmatizing concentration for different individual and binary phlegmatizers in a medium scale experiments

#	Phlegmatizer	Concentration for T=20 °C, %	Concentration for T=120 °C, %
1	$C_2F_4Br_2$	12	14
2	$C_2F_4Br_2 + C_2F_3Cl_3$	12 (8+4)	13 (9+4)
3	$C_2F_4Br_2 + CF_3I$	12 (10+2)	15 (12+3)

3.5. Large scale experiments.

Large scale experiments confirmed possibility of stoichiometric hydrogen-air mixture full combustion suppression for individual $C_2F_4Br_2$ and for binary mixture $C_2F_4Br_2 + CF_3I$.

An example of an experiment in which the phlegmatizer concentration was insufficient and the development of the combustion process was observed is shown in Fig. 10.



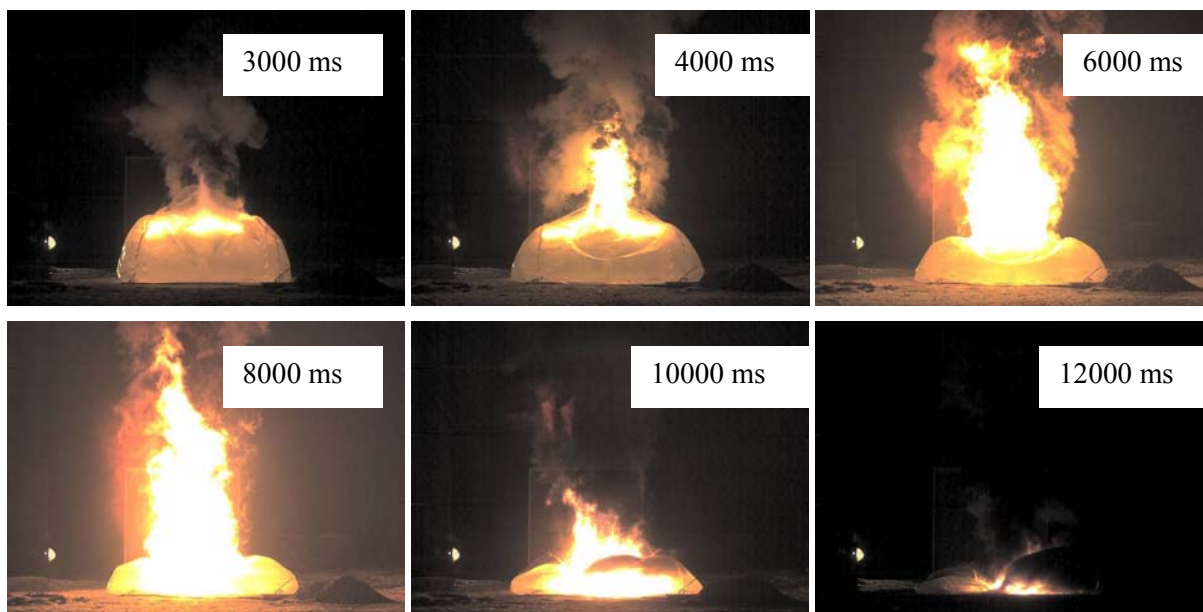


Figure 10. Combustion of stoichiometric hydrogen-air mixture with addition of 8.5% C₂F₄Br₂ phlegmatizer. High-speed video record frames.

Example of experiment with full combustion suppression is shown in Fig. 11.

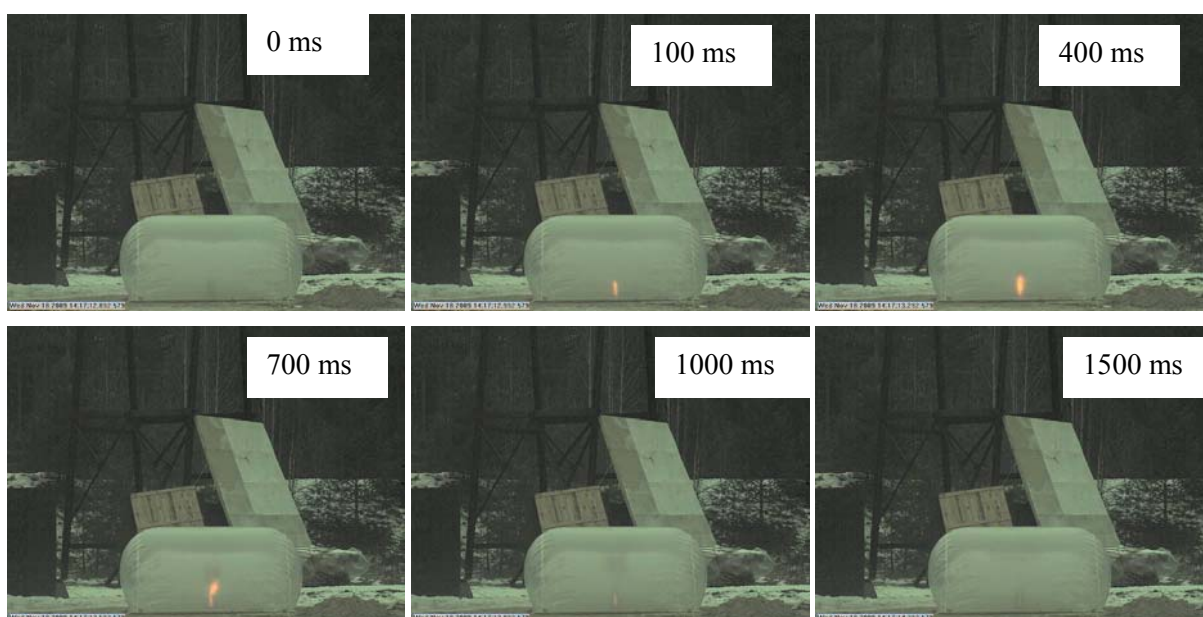


Figure 11. Full combustion suppression of stoichiometric hydrogen-air mixture with addition of 10.4% C₂F₄Br₂ + 1.7% CF₃I phlegmatizer mixture. High-speed video record frames.

Results of large-scale experiments showed that all compounds that suppress combustion in experiments of small and medium-scale also suppresses combustion in large-scale experiments. This evidence of effectiveness of tested phlegmatizer compounds for a large scale is proof of the possibility of using these compositions as nuclear power plant safety systems and in industrial and household hydrogen safety.

4.0 CONCLUSIONS

Hydrogen mixture phlegmatization experiments of different scale showed that:

- Ten individual compounds and six binary mixtures were tested as phlegmatization additives;
- The most effective individual compound that fully suppresses hydrogen-air mixture combustion is $C_2F_4Br_2$. Its minimal concentration was 12% at $T=20^\circ C$ and 14% at $T=120^\circ C$;
- The use of binary mixtures does not lead to a substantial decrease in the minimum phlegmatizing concentration, but allows varying the molecular weight and phasing composition of the input components to optimize the technical realization of phlegmatizer injection in volume of the room. It is also possible to vary the temperature dependence of the minimum phlegmatizing concentration by changing the ratio of the components of a binary mixture.
- Based on experiments performed in three different scales, one could argue that addition of the experimentally found phlegmatizer in an amount corresponding to the bulk concentration of 1 / 7 (14% vol.) and more can always completely suppress the combustion of hydrogen-air mixture of any composition at $T \leq 120^\circ C$ and pressure 1 atm.

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