TOXIC *HAZARD* ASSOCIATED WITH FIRE EXTINGUISHING AEROSOLS: THE CURRENT STATE OF THE ART AND A METHOD FOR ASSESSMENT

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Total-flooding aerosol systems, widely applicable now, were engineered in the last decade of the 20[th] century. For an actuator they offer an extinguishing aerosol generator that houses an aerosol generating composition charge. The composition constitutes a formed heterogeneous mixture of an oxidizer (nitrate potassium, perchlorate potassium), a binding fuel (phenol formaldehyde resin, epoxy resins, rubbers, etc.) and various purpose additives (stabilizers, catalytic agents, etc.).

Compositions are chemically stable under normal conditions. However, when heated by an electric helix, a pyrotechnic cartridge or a fire source, they start burning intensively and emitting a solid-phase extinguishing aerosol. A high extinguishing efficacy of the aerosol is observed, in case its mass proportion of a solid phase to a gaseous phase ranges from **50/50** to **40/60 [1]**. The solid phase aerosol includes mostly fine particles of alkaline salts and hydroxides (K_2CO_3 $2H_2O$, $KHCO_3$, KOH, KCI, KNO_3). The mass fraction of a particle size from 0.1 **up** to **5** micrometers is equal to 85-90%. Due to small particle sizes, the buoyant aerosol is able to occupy a whole volume of the protected premises for a long time **[1, 2]**.

Gaseous combustion products contain chiefly nitrogen (N_2) and carbon dioxide (CO_2). Also registered are nitrogen oxides (NO_x), carbon oxide (CO), and water vapors. Ammonia (NH_3), hydrogen chloride (HCl), hydrogen cyanide (HCN), hydrogen carbons, and some other compounds are also present.

The toxic hazard of pyrogenic aerosol extinguishants is explained by multi-component combustion products of solid fuel extinguishing compositions and the presence of substances detrimental to human health. This was demonstrated by comparison tests with burning extinguishant samples, investigations into hazardous substances given off therewith, and their toxicity parameters and biological effects [3-6].

Chemical and toxicological examination methods have identified the components (nitrogen oxides, carbon oxide, and solid aerosol particles) that are, for the most part, responsible for a harmful agent released into the enclosure on combustion of aerosol generating compositions. The toxic agent exposure is most pronounced where CO and NO_x concentrations exceed permissible levels. At the same time, skin and eye irritating effects and interference with pulmonary functions due to penetration of large quantities of fine solid particles of potassium salts [7, 8] are reported at low concentrations of CO and NO_x.

It is also established that those compositions appropriate for generator charges may considerably differ in combustion products toxicity parameters. For example, a relatively short 6 to 15-min exposure to some compositions, having an extinguishing concentration of gaseous products, has turned out **to** be lethal for test animals. In other cases, only a 60-min exposure has been registered to be lethal and even sublethal at a two-fourfold increase of combustion products concentration **[2, 4]**.

Aerosol extinguishant toxicity depends upon a chemical composition of the charge, oxidizer-fuel mixture as well as agents catalyzing low-temperature oxidation of carbon oxide and reduction of nitrogen oxides. In addition, the list of the factors, affecting this characteristic includes source component particle sizes, charge technology, and cooling elements or heat absorbers embedded in the generator. The toxicity is considered to be more manifest where extinguishing aerosols involve the following: coarse-grained source components (greater than 100 micrometers); fuel enriched nonstoichiometric compositions; and generators with cooling agents [1, 9, 10].

Table 1 contains concentrations of toxic gases and carbon dioxide measured in tests with a charge sample and cooled and uncooled types of generators [11]. It is obvious from the table that the last two factors cited above are able to affect considerably the CO content of volatile combustion products.

TABLE 1. GAS CONCENTRATIONS IN TESTING AEROSOL EXTINGUISHANT CHARGE AND GENERATOR SPECIMENS.

Test Specimen	Charge Mass, g	Chamber Vol, m^3	Gas Concentration, $mg\ m^{-3}$				
			CO	CO_2	HCN	NO_x	NH_3
Charge formulation 1	13	0.145	343	19800	N/F	10	N/F
Uncooled generator, charge formulation 1	92	1.00	572	23400	10	N/F	50
Cooled generator (marble crumb, 91 g) and charge formulation 1	91	1.00	4800	18000	10	N/F	350
Cooled generators (marble crumb, 1300 g) and charges:							
Formulation 1 (α=0,68)	1070	11.85	4000	18360	13	30	N/F
Formulation 4 (α=0,82)	1070	11.85	3435	14400	15	40	50
Formulation 5 (α=0,89)	1050	11.85	920	14400	N/F	50	N/F
Formulation 6 (α=0,99)	1110	11.85	460	15840	N/F	106	N/F
Formulation 3 (α=1,02)	1110	11.85	1360	15840	15	100	N/F

a - oxidizer utilization factor
N/F – not found

The data presented can be considered as a prerequisite to the statement of a practical problem to assess the toxic hazard of fire extinguishing aerosols. This is an important performance characteristic of generators, a primary one for those designed for fire protection of occupied premises. At the same time, the statement of the problem is becoming a requirement because of (1) a wide choice of types and modifications of generators on the market [1, 12], and (2) licensing the use of generators in premises where 50 people are simultaneously present [13].

To meet the challenge, the All-Russian Research Institute for Fire Protection has carried ont special research and proposed for official acceptance an assessment method of the toxic aerosol extinguishant hazard. The method consists of generator environmental testing and determining the qualitative and quantitative indices characteristic of the threat of a gaseous aerosol medium to the test volume.

The test facility schematically shown in Figure 1 comprises:

- a test compartment of an alterable volume (up to 50 m^3) where several generators are placed
- a forced gas aerosol product circulation unit including two exhaust outlet tubes of large diameter, periodic flow converters, and a low pressure ventilator
- an operator room equipped with a ***0.2*** m^3 chamber for animal exposition, a sampler, a gas analyzer, and an instrumented power supply unit

Tests are conducted under the following conditions:

- a test volume should correspond to the rated volume of the Compartment to be protected by the generator
- an opening factor should not exceed a permissible value (0.001 m-1)
- a generator should be actuated by an electric signal, unless otherwise specified

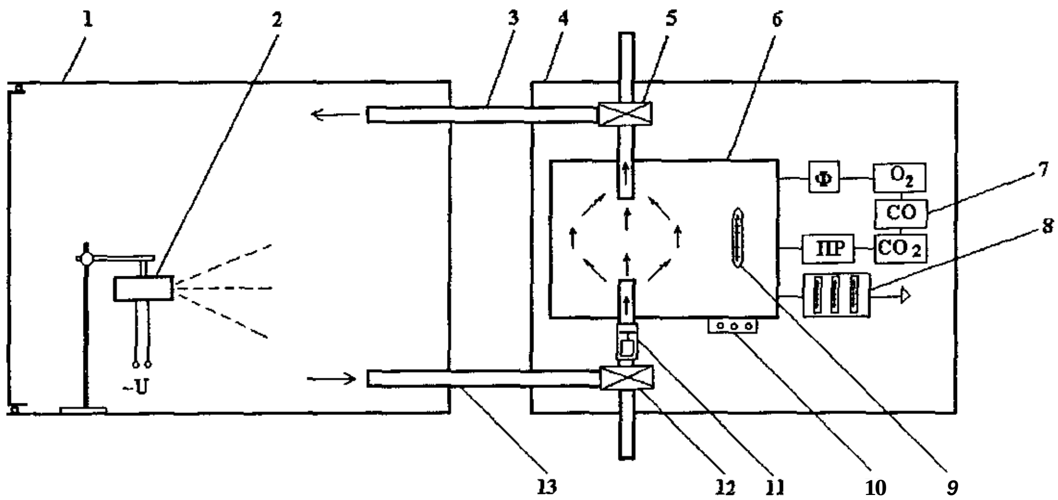

Figure 1. Aerosol toxic test facility (1 – atest compartment, 2 – agenerator with a fixture (–U – connecting to an actuating circuit), 3,13 - exhaust outlet tubes, 4 – an operator's room, 5,12 – a periodic gas aerosol products flow converter, 6 – an animal exposure chamber, 7 – automatic CO, CO,, O, analyzers (ПР – gas flow rate booster, Φ - gas purification filter), 8 – a gas sampler, 9 – thermometer, 10 – a cable electrocardiograph connector, 11 – ventilator).

The tests are performed to measure hazardous characteristics and biological effects of the gas aerosol agent generated in a quasi-tight test compartment. The first group of indices is not limited to include CO, CO,, NO,, NH,, and HCN concentrations. If necessary, it extends further due the presence of hydrogen halides and other toxic compounds. The other group are biological factors defined during and after a 15-min gas aerosol exposure of test animals (white rats and white mice). These are animal survival, physical fitness, blood content of carboxihemoglobin and methemoglobin (specific indices for assessing CO and NO effects on a living organism), respiration and heart rates, bronchopathomorphology, and pulmonary tissues (indices characterizing an irritating effect of the gas aerosol agent).

Assessing the toxic extinguishing aerosol requires the consideration of (1) toxic and permissible concentrations of analyzed hazardous substances at a short exposure time (Table 2); (2) a cumulative hazardous factor, calculated from the additivity formula

$$Iad = \sum_{i=1}^{n} \frac{C\exp_i}{Ctox_i}$$

where *Iad* – an additive (cumulative) hazardous factor of toxic effects of analyzed gaseous components; **i** - a hazardous substance; $Cexp_i$ - a hazardous substance concentration determined in tests; $Ctox_i$ - a lethal hazardous substance concentration on a 15 minute exposure of people (CO – **3500** mg m^{-3}, CO, – **13 0000** mg m^{-3}, NO, – **300** mg m^{-3}, NH, – 700 mg m"); and **(3)** the nature and extent oftest animal disorders.

Aerosol generators installed in occupied premises should meet the following requirements:

(1) On generator actuation, the hazardous concentrations of produced aerosol extinguishants in protected rooms should not exceed **3500** mg m^{-3} for carbon oxide; **300** mg m^{-3} for nitrogen oxides; 100 mg m^{-3} for hydrogen cyanide; 700 mg m^{-3} for ammonia
(2) Cumulative toxic exposure index of gaseous aerosol components should be equal to 1.5 or less
(3) A 15-min aerosol exposure should not be lethal to test animals during the next 14 control days

TABLE 2. TOXIC AND PERMISSIBLE GAS CONCENTRATIONS.

Gases	Concentrations at a 5-15-min Exposure, mg m^{-3}		
	Lethal for animals	Dangerous and lethal for humans	Permissible
Carbon oxide	6000-9000*	3500-5700	400-700
Carbon dioxide	1000000* (54.9% by vol.)	130000-200000 (7-11% by vol.)	27000 (1.5% by vol.)
Nitrogen oxides (on conversion to NO,)	400-1500**	300-700	35-60
Hydrogen cyanide	200-380*	100-300	10-20
Ammonia	10000-18000**	700-3000	30-40

Note: * - for white mice; ** - for white rats

(4) Biological aerosol effects are not compatible with changes that are critical to a living organism and its separate systems including immobility, disability, emphysema, and a more than 40% total increase of carboxyhemogloblin and methomoglobin.

Based on these requirements, the permissible level is defined as the safety level, ensuring survivability and possibility to leave a dangerous area on a short aerosol exposure (up to 5 min) during a sporadic extinguishing system actuation, The compliance of generator test results with the specified level confirms its feasible use for rooms constantly or periodically attended during working hours.

Data on toxic aerosol hazards [14] are essential for the sanitary assessment of generators and their fire safety certification. Implementing the generator regulation approach based on these data will allow for better safety measures, which are stipulated by design codes of total-flooding aerosol systems (escape guarantee, early warning of the oncoming generator actuation, etc.) [13]. This approach is considered to be most important for poisoning prevention with a view to possible unauthorized generator actuation.

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