

THE PROBLEMS OF PHASEOUT AND REGENERATION OF HALONS IN RUSSIA

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Russia used to be one of the largest manufacturers of Ozone Depleting Substances (ODS) in the world. In 1990 Russia produced 198,000 MT of ODSs representing 15% of global production. Figure 1 represents the ODS consumption at that moment in Russia.

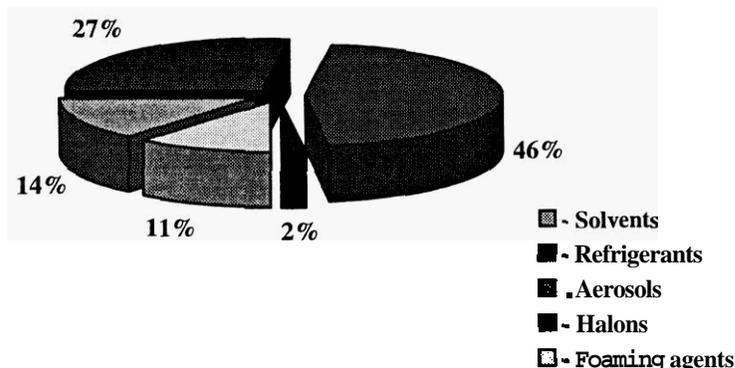


Figure 1. ODS production in Russia in 1990.

Commercial production of Halon 2402 in the USSR was started in 1965. It happened that Halon 2402 was the most widely produced halon because the industrial output of the most available raw material, tetrafluoroethylene, had been mastered in the 1960s. The gaseous-phase method that was first used to obtain Halon 2402 resulted in a lot of byproducts. Thus, in the 1970s a more efficient photochemical process was elaborated and implemented. These processes were developed at the State Institute of Applied Chemistry (GIPH), which was the initial name of the Russian Scientific Centre "Applied Chemistry." In the period (1965-1994) in Russia 34,000 MT of Halon 2402 were produced (Figure 2). All industrial production of Halon 2402 was situated in two chemical factories located in Ural.

Processes for production of Halons 1301, 1211, and 1202 and corresponding pilot plants were also designed in GIPH at the end of 1960s and the beginning of the 1970s. At the end of 1980s Halon 1301 and 1211 production technologies were transferred to an industrial basis. In 1990, the output of these halons reached a peak of 4200 MT.

From 1991 to 1995, to fulfill the demands of Montreal Protocol, Russia significantly reduced by almost 3.5 times the production of ODSs and reduced by 10 times the output of halons (Figure 3). The production of Halons 1301 and 1211 was stopped almost immediately after startup because plants and equipment had not yet been converted to produce them. At the moment the existing extinguishing equipment in Russia uses only Halon 2402 so Russia cannot cancel its commercial output. Russia applied to the Secretary of Montreal Protocol and has gained quotas for Halon 2402 output in 1996-1997. The necessity to make it remains until 2003.

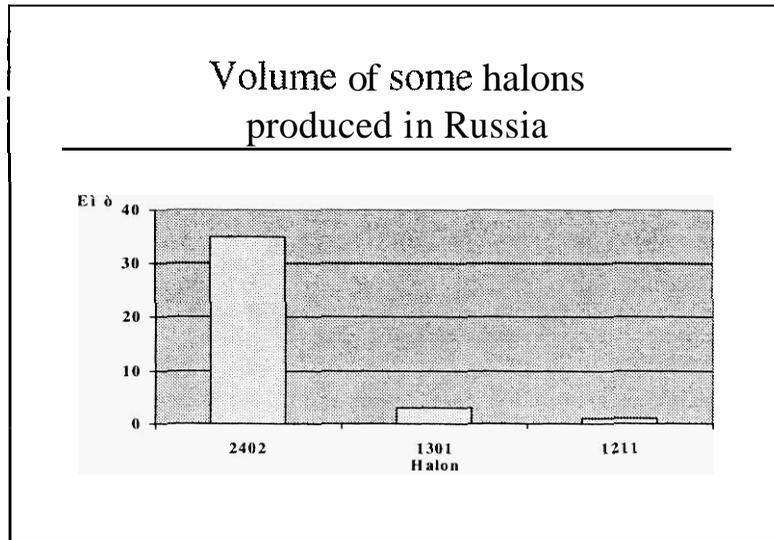


Figure 2. Halon production volumes in Russia.

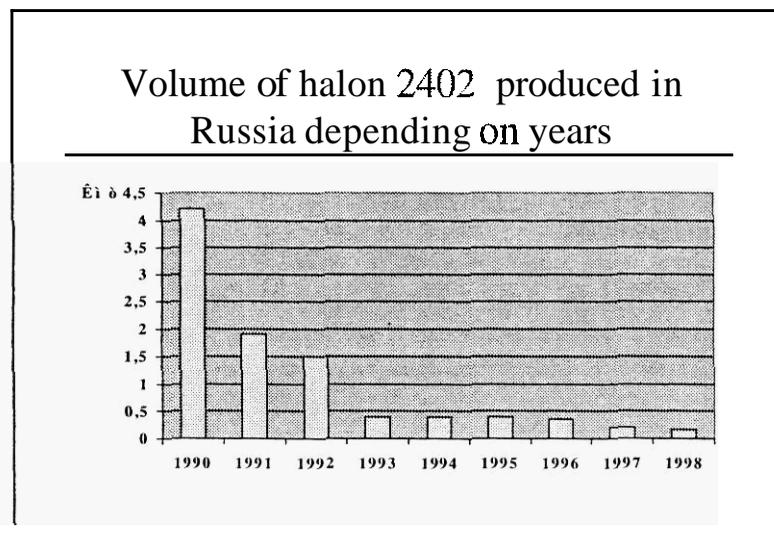


Figure 3. Production reduction of Halon 2402 from 1990 to 1998.

There are a few important reasons why it is impossible to stop Halon 2402 production:

- (1) because Halon 2402 represents 97% of the whole volume of halons being used in Russia,
- (2) Halon 2402 is a liquid with boiling point of 46 °C, and this physical property has influenced to some extent the design of existing extinguishing equipment and systems.

Conditionally four main groups of extinguishing equipment and system can be separated (Figure 4):

- Halon placed-in-tank systems, unit capacity up to 5 tons. Up to 35% of the overall halon output is used in such systems.
- Battery-type systems, total capacity up to 10 tons, which consist of cylinders each with a volume from **40** to 400 L. Up to 45% of the overall halon output is used in such systems.

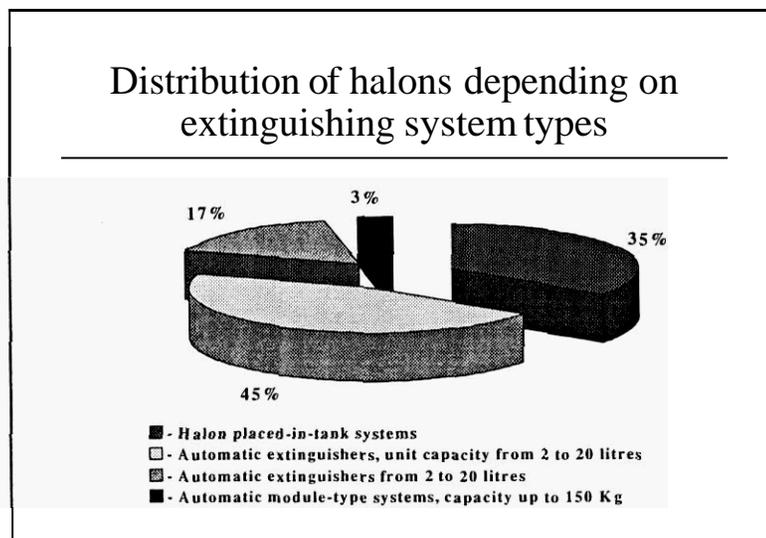


Figure 4. Distribution of halon systems by type in Russia.

- Automatic extinguishers for vehicles with unit capacity from 2 to 20 L. Up to **3 to 5%** of the overall halon output is used in such systems.
- Automatic module-type systems, unit capacity from 40 to 180L, have also been recently developed.

The main reason that it is impossible to stop Halon 2402 production now is that about 75% of all types of existing fire-control machinery cannot use halon substitutes. This is only for equipment placed in Russia because in other countries the machinery can easily be adapted to halon substitutes. Additional expenses and concerns are also due to the poor extinguishing performance of the current halon substitutes. Of course Russia can apply the world's experience in the exploration of extinguishing systems, but the ensuing conversion of existing systems to the modern type requires several years and a lot of investment, which we currently do not have. For instance just the replacement of existing fire-control equipment in civilian aircraft will cost US \$1,500,000,000 and takes 3 to 4 yrs.

The second reason that Halon 2402 production cannot be halted at this time is that Halon 2402 is manufactured only by a limited number of companies in negligible volumes (mostly in Russia). Consequently, Russia is unlikely to be able to replenish it from the halon banks from other parts of the world.

From above mentioned we have come to the conclusion that unfortunately Russia will have to use halons, mostly Halon 2402, for a long time to come.

To maintain the fire-safety of existing objects, regenerated halon can be used as a source of Halon 2402. According to Russian experts' estimates, the total volume of Halon 2402 in Russia reaches to 10,000 to 12,000 MT. Should Russia use these stores it would offer an opportunity to refuse from the quota for production and to keep fire safety of existing objects.

The process of halons regeneration was elaborated in the GIPH in the 1980s and the first pilot plant was implemented in 1989 with an annual yield of 200 MT for Halon 2402. Afterwards

different types of regeneration sets were developed, among them stationary, vehicular, module-type (Figure 5). At the moment there are five regeneration plants in Russia (in Moscow and St. Petersburg) with annual capacities of 500 to 550 MT; however, they currently use only 15 to 20% of their full power. If we take only the total power of them it seems to be enough to cover the needs for regeneration in Russia, but taking into consideration the area of the country, a branched structure of regeneration plants is necessary. A draft proposal for creating such a structure has been presented to the World Bank and we expect a positive decision. After realization of this project Russia will be able to reduce Halon 2402 production and gradually make a transition to ozone-safe halon substitutes.

Halons regeneration plants

Company, Disposition	Type	Annual power, MT	Halon type
RSC "Applied Chemistry" (St. Petersburg)	Stationary	200 20 30	2402 1211 1301
CTO "SPECAVTOMATICA" (St. Petersburg)	Mobile (for cars)	Up to 100	2402
"Ozone" (St. Petersburg)	Module	Up to 80	2402 1211 1301
Gen. NII "GA" (Moscow)	Module	Up to 50	2402 1211
"SPECAVTOMATICA" (Moscow)	Stationary	Up to 100	2402

Figure 5. Types of Halon 2402 regeneration plant in Russia.

The problem of halon replacement in Russia also is in the low economic efficiency of the implementation of substitutes. It is evident from the Figure 6 that on the average the extinguishing performance of substitutes is 2 to 3 times worse when compared with Halon 2402, and the cost of production is significantly higher. Taking into consideration the increased steel required due to the increased size of extinguishing systems an economic efficiency of using the substitutes is from 10 to 12 times lower than for Halon 2402. That is why in Russia conversion now from halons to the substitutes in existing extinguishing systems will require a lot of investment and a long time.

Another significant imperfection of substitutes is their long atmospheric lifetimes; consequently, they have great Global Warming Potentials (GWP).

The third remarkable imperfection is the fact that during thermal decomposition, in a flame zone, the substitutes form significantly more acid products than halons. Now a lot of investigations devoted to decomposition of different substitutes in fire have been performed. Many analysts have come to the dramatic conclusion that substitutes form significantly more acid products (HF) than halons under the same conditions. Further investigations can lead to abandonment of using some substitutes for fire extinguishing in the presence of personnel.

Physical properties halons & new chemical alternatives

Trade name	Formula	BP °C	Pressure (kPag)	Min Design Conc. % V/V	Ratio Agent Mass Req'd to Halon 2402	NOAEL % V/V
Halon 2402	C ₂ F ₄ Br ₂	46.7	37.0	2.5	1.0	300 g/m ³
Halon 1301	CF ₃ Br	-57.8	1430	5.0	1.45	5.0
FE-13	CF ₃ H	-82.2	4193	16.0	2.5	30
FE-25	C ₂ F ₅ H	-48.5	1130	10.9	2.8	7.5
FM-227	C ₃ F ₇ H	-16.4	458	7.0	2.5	9.0
CEA 4.10	C ₄ F ₁₀	-2.0	228	6.0	2.8	40
TRIODE	CF ₃ I	-22.5	480	5.0	1.6	0.2

Figure 6. Physical properties of halons and their substitutes.

Existing capabilities of factories and raw materials will possibly allow the use of HCF-125 and HCF-227 as substitutes, and for aviation, trifluoroiodomethane (CF₃I) (Figure 7). Perfluorobutane and HCF-23 probably will not be widely used in extinguishing systems in our country due to the higher formation of HF in fires.

We have already had certified commercial production of HCF-125 in Russia. In the pilot plant of RSC "Applied Chemistry," the manufacture of HCF-227 and HCF-23 has been implemented. These compounds are mainly used in systems that do not require significant changes in construction. Automatic extinguishers for vehicles need much more alterations, and more time is necessary to provide the complete range of investigations in order to choose an appropriate substitute.

For Russia the following approach can be suggested for a strategy of halons substitution (Figure 8):

- At first a conversion to the substitutes in the module systems and automatic extinguishers that do not require significant changes (protected volumes up to 200 m³, for a period of from 2 to 3 yrs)
- Development of stationary systems equipped with new cylinders for module systems to protect rooms with volumes of up to 10,000m³, for a period of from 3 to 4 yrs
- Design of completely new firefighting systems using substitutes for seacraft
- Provision of the fire protection of long-lived objects (such as control centers, ships, etc.) and machinery from the store of regenerated halons

This program can be carried out only with the strong government support.

The most probable substitutes

- HCF-125
 - commercial production **has** been founded
 - this product has been certified
 - implementation of HCF-125 to the module-type systems is in process
- HCF-227 (FM-200)
 - **pilot production** has been founded
 - certification is in **process**
 - **spheres** of application is developed
- Trifluoriodmethane (CF₃I)
 - **Has** the industrial facilities

Figure 7. The most probable halon substitutes to be used in Russia.

Strategy of replacement of halons in Russia

- Conversion of module type **and** compact automatic extinguishers to the new substitutes (replaceable volume of up to 200 m³, period 2-3 years)
- Application **of** module type systems cylinders for protection of rooms volume up to 5000 m³
- Development of the newest extinguishing systems based on halon substitutes for ships (replaceable volume of up to 10 000 m³, period 3-4 years)
- Utilization of regenerated halon 2402 from reserves for long use machines (ships, etc.)

Figure 8. Strategy for replacing halon in Russia