Development of Peduoroalkanes As Clean Extinguishing Agents

TOXICITY TEST PROTOCOLS

by

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Toxicology Protocols

Introduction:

As the deadline for the cessation of production of halon clean fire extinguishing agents (CEAs) draws closer, the development programs for acceptable replacement agents are also accelerating. Halon production will stop as of December 31, 1993 per the latest Montreal Protocol revision and new CEA's will begin to replace halons in existing and new installations. These development programs have taken years and millions of dollars in investment to complete.

The process of developing a new CEA includes chemical synthesis and production, environmental evaluations, fire extinguishing testing, code writing, development of standards for testing new agents and systems, and extensive toxicological testing. The list of characteristics to be maximized in selection a new CEA are shown in the following table:

Table I CEA Desirable Characteristics

- Clean - leaves no residue
- Electrically non-conductive
- Effective Fire Extinguishment
- Non-flammable
- Chemically stable
- Zero ozone depletion potential
- Low global warming effect
- Low toxicity
- Acceptable overall environmental impact
- Acceptable thermal decomposition products
- Materials compatibility
- Ease of handling
- Available and cost effective

As can be seen from this formidable list, the development of acceptable candidates is not simple or quick. Often the process includes a compromise in the desirable characteristics as some are mutually exclusive in the practical world.

In the fire protection systems arena, one of, if not the most important characteristic of a new CEA is low toxicity. The design of a fire protection system is based on life safety and property protection. The life safety aspects are paramount in the engineer's mind and agents that lead to significant toxicological risks cannot be tolerated. In order to better understand this aspect of CEA development, this paper will outline the typical toxicological tests done and their relationship to life safety in the fire protection world. Also, it will give some highlights of the toxicity test protocols and typical results of these tests on the perfluorocarbon CEA candidates, PFC-410 (total flooding applications) and **PFC-614** (streaming applications).

General:

The types of toxicological test usually associated with fire protection applications are the lethal concentration test (LC_{50}), the cardiac sensitization test, the 14-day inhalation test and the 90-day inhalation test. These test protocols are conducted with non-human subjects (rats and dogs) and are loosely related to the human toxicity scenarios described on the table below.

Table II Relationship *to* Human Exposures

Toxicology Test Description	Related Human Toxicity Scenario
Lethal concentration (LC_{50}) - Concentration at which death results in 50% of the subjects	High concentration from an inadvertent discharge of the agent into the breathing area of the hazard occupants, fire fighters or oroduction workers
Cardiac sensitization concentration - Concentration at which significant cardiovascular effects are seen in a challenged subject.	Inadvertent or purposeful (fire emergency) discharge of the design concentration of the CEA into the breathing area of a hazard occupant
14-day inhalation testing - Range finding tests for 90-day inhalation testing - Indication of long term effects - Multiple dose levels	Repeated exposure of production or system filling personnel (indication only)
90-day inhalation testing - Long term exposure - Multiple dose levels as per range finding test	Long term repeated exposure to production or system filling personnel

The above testing protocols are used *to* indicate the toxic potentials of the new CEAs in the real life scenarios described.

In these tests it is important to identify the concentration of CEA at which no adverse health effects are seen. This concentration is the highest level at which **a** CEA is recommended to be used in normally occupied spaces. Several toxicological criteria could be used to delineate the No Observed Adverse Effect Level (NOAEL). Criteria such as lethal concentration, the concentration that reduces the oxygen concentration to a specified level or the cardiac sensitization level could be used. The NFPA 2001 Committe for Clean Agent Fire Extinguishing System, in the technical committee recommendation, however, has recommended that the cardiac sensitization level be used to determine the NOAEL concentration and that the agent "use" concentration must be below this NOAEL if it is to be used in normally occupied spaces.

Test Protocol Highlights

The following table gives the highlights for each of the previously described tests. This table is by no means totally inclusive and is not intended to give the reader more than a cursory knowledge of these tests.

Table II Protocol Highlights

Test	Highlights
Lethal concentration (LC_{50})	- Protocol current with OECD, EEC, and U.S. EPA - Subjects, Sprague-Dawley rats (60) - Whole body exposure, 4 hrs. + equilibrium time - Hourly observations & data recorded - 14-day observation 8 holding time - Macroscopic exam after holding time - Data, calculations, reports kept in archives for 10 yrs.
Cardiac sensitization	- Protocol based on Reinhard et al (methods 8 principles) - Subjects, beagle dogs (4) - Conditioning to restraints, masks & adrenaline - CFC-11 used as a test control - Criteria for significant cardiac effect is "5 or more multifocal ventricular ectopic beats or ventricular fibrillation" - Data, calculations, reports kept in archives for 10 yrs.
2-Week inhalation [Range Finder Tests)	- Protocol current with U.S. EPA (TOSCA) & OECD - Subjects, Sprague-Dawley rats (50) - Whole body exposure, 5 days/week @ 6 hrs./day - Variable dose levels - All clinical signs 8 data recorded daily . Data, calculations, reports kept in archives for 10 yrs.
13-Week inhalation	- [illegible] U.S EPA (T [illegible] and C Subjects, Sprague-Dawley rats (130) Whole body exposure, 5 day/week @ 6 hrs./day Three dose levels (low/med/high) around range finder results . All clinical signs 8 data recorded daily . Subjects sacrificed one week after test period for tissue studies . Data, calculations, reports kept in archives for 10 yrs.

OECD = Organization for Economic Cooperation and Development

Perfluorocarbons

In addition to their other superior CEA characteristics, one of the primary reasons to use perfluoroalkanes as CEA's is their inherent chemical stability that leads to their low toxicity characteristics. The PFC-410 (perfluorobutane) and the PFC-614 (perfluorohexane), which are intended to be replacements for Halon 1301 and Halon 1211 respectively, are members of the perfluoroalkane family of chemicals and as such exhibit exceptional low toxicity. The test results demonstrating these properties for these perfluoroalkanes are summarized on Table IV.

Table **IV** Typical **Perfluoroalkane** Toxicological Results

Test	**PFC-410** (Perfluorobutane)	**PFC-614** (Perfluorohexane)
LC_{50}	in air > 100,000 ppm In oxygen > 800,000 ppm (4 hr.)	> 300,000 (1 hr.)
Cardiac sensitization	NOAEL > 40% in air	NOAEL > 18% in air
2-Week inhalation	No adverse effects at 100,000 ppm	No adverse effects at 50,000 ppm
90-Day inhalation	No toxic signs observed at 25,000, 50,000, or 100,000 ppm	No toxic signs observed at 5,000, 15,000, or 50,000 ppm

Note: The above data does not indicate that PFC-614 is more toxic than PFC-410. Rather, the data reflects the upper practical exposure limits at which the products were tested.

Summary

The toxicity evaluation/testing described above is of the utmost importance in developing candidate CEA's to replace halon fire extinguishing agents. The life safety aspects of any fire protection system design should be of primary concern for the agent manufacturer, equipment manufacturer, design engineer, installer, and inspection contractor. The testing described above should be conduced, interpreted, and fully documented by only professional toxicological testing institutions. Full reports are to be the basis of determining the applicability *of* any candidate **CEA** for normally occupied areas, where contact between the agent and the hazard occupants can occur.

The perfluorocarbon CEA candidates, PFC-410 and PFC-614, offer some exceptional characteristics in the areas of low toxicity. They are among the top CEA candidates when viewed from the overall desirable characteristic discussed earlier in this paper and as such should be strongly considered as replacements for halon agents in systems both new and existing.

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