OVERVIEW OF TOXICITY / EFFECTIVENESS ISSUES

by

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Introduction

The Inert gases are known to have fire extinguishing propemes for many years. Before the early 19th century, the only fire extinguishant widely known and used was water. As today it was commonly available, cheap, and the inventors and other industrious people were working hard to improve supply techniques such as pumps, and means of transportation by vehicles.
The 17th and 18th centuries were challenging years where scientists struggled to discover the laws of physics and chemistry, and to investigate the surrounding world. The swedish chemist Carl Wilhelm Scheele discovered in 1772 that air was a mix containing two principal substances: Oxygen and Nitrogen. (Also the french scientist A. Lavoisier, 1743-1794, was making similar observasions, as he found that a combustion consumes Oxygen and leaves behind "the thing that has no life" Azote).
Some years later the danish physicist H. C. Øhrsted (1777-1851) was studying the elements later to be classified in the periodical system. On the basis of the work done by Scheele he discovered that the components of air, Oxygen and Nitrogen, behaved very differently. He saw that oxygen was taking actively part in a chemical proces such as combustion and Nitrogen was not. On the countrary Nitrogen would actually suffocate a fire, and after this discovery he gave the element Nitrogen the danish name "Kvælstof" which means the element that suffocates fire.
Still later the periodical system was completed (Niels Bohr) arid the real inert gases Helium, Neon, Argon, Krypton and Xenon were identified.
Nitrogen and Carbon Dioxide are not classified as true inert gases, since they can participate to some degree in chemical processes, but in a fire this ability is insignificant, and later on they are included whenever the term inert gases is mentioned in this paper.

One of the characteristics of the Inert gases is that they do not take place in chemical processes, not even at high temperatures produces by combustion *(Note: Krypton and Xenon are known to react with Fluorine at hich temperature and pressure, but this is not relevant to fire extinguishing), so* by introducing them into an enclosure at high concentrations, they dilute the Oxygen and extinguishes fire. The normal atmospeheric Oxygen content is 20.95%, and by reducing that to about 13%, most commonly present combustibles are extinguished.

The inert gas rediscovery

One day in the spring of 1982 a client was asking for a real demonstration to show that Halon 1301 could actually extinguish a fire and the atmosphere of the enclosure at the same time remains habitable. The first demonstration was made with kerosene lamps, and a 10cm x 10cm (4"x4") gasoline fire pan in a 50 cubic meter enclosure (1670 cubic feet). The fire was extinguished as expected, and there was no serious discomfort observed. However the client wished to see "a real fire" so a 1 square meter (11.1 sq. feet) gasoline tire pan was arranged in the same room. The system was controlled by flame detectors and a 7% design concentration was used, but even though the total time from ignition to extinguishing was less than 10 seconds, the atmosphere turned out to be extremely uncomfortable due to the decomposition products. It was very clear that in certain applications it would be preferable to use a gas that would not decompose: inert gas. Using inert gases alone would lead to other safety problems. but a few days after that incident the idea was born to use a small amount of Carbon Dioxide to compensate for the low Oxygen required for fire extinguishing. Later on (1987) the idea was filed as a patent application and in 1991 commercialized based on a cooperation between Dansk Fire Eater A/S, Denmark, and Air Products & Chemicals, Pennsylvania.
The name of the process to compensate for Oxygen deficiency by Carbon Dioxide, in fire fighting, is INERGEN. Today more than 100 systems are installed in Denmark and more than 100 in other European countries. The majority is new installations, but there are several Halon retrofits included.

Today there are a number of licensees using INERGEN as a Halon alternative and replacement, and as INERGEN enjoyes a lot of succes, there are a few installers supplying inert gas mixtures almost identical to INERGEN, but without Carbon Dioxide.

Safety/toxic effect

Since the days of H. C. Øhrsted it was commonly known that the reduction of Oxygen had some side effects: The suffocating effect of Nitrogen did certainly also apply for human beings, not only for the fire. This is true, but only in more severe cases of Oxygen deficiency.
Outside the fire extinguishing industry a need appeared, to know more about oxygen deficiency, the medical term being Hypoxia. Aviators were exposed to hypoxia during high unpressurized flights, and from the 1930´es physiologists were researching this field intensively. Also astronauts and mountain climbers are exposed to hypoxia, and that has provided a broad platform of scientific literature

and data, to support the theoretical background of INERGEN, and to some degree other inert gases or gas blends.

It is important to understand, that the Inert gases (He, Ne, Ar, etc.) and Nitrogen do not have any toxic effects at normal atmospheric pressures. And it is even more important to understand, that Carbon Dioxide **do not** have any toxic'effects, but it has physiologic effects as a very important part of the human metabolism, and regulatory mechanisms in Oxygen supply.

When a Carbon Dioxide system is known to involve high personnel **risks,** it is due to the high concentrations used: More than 30% exceeds the human short term tolerance, and will result in unconsciousness in a matter of minuttes.

Hypoxia

Hypoxia is the medical term for the lack of Oxygen in man. The symptoms varies by the Oxygen concentrration, and the exposure time. There are. different reasons for hypoxia, but of course the most interesting one at this occassion, is the hypoxia caused by the use of fire extinguishing gases. Acute hypoxia occurs, when the Oxygen concentration is reduced in the matter of hours or less, as this does not allow for the natural compensation, having effect in a matter of days in prolonged gradual hypoxia.
When the inspired oxygen is reduced, it leads to a reduction in the blood oxygen partial pressure. Initially this is detected by chemoreceptors in the major arteries, and automatically induces an increase in lung ventilation. Due to this, the equilibrium Carbon Dioxide partial pressure slightly decreases, and the initial respiration increase is outweighed. At 12% inspired Oxygen there is only little, or no change in ventilation. If the Oxygen concentration is further decreased, the lowered arterial Oxygen pressure will take effect, and ventilation will gradually increase, untill about the 8-9% limit at which unconsciousness is often observed in young healthy males within a few minutes (2-4). There is a significant individual sensitivity to both the lowering of the arterial Oxygen, and Carbon Dioxide partial pressure.
Hypoxia is especially essential to the brain tissue, since the brain metabolism depends critically on the partial cerebral (brain cells) Oxygen pressure and the acidity. If the partial pressure drops below a certain limit, it results in immediate unconsciousness.
An unpublished paper by the Institute of aeronautical medicine, Copenhagen, suggests the folllowing limits of consciousness, for well trained male fighter pilots:

10.6%	30 minuttes
8%	3-5 **minuttes**
6.3%	1.5-2.5 minuttes
5.2%	1 minutte
3.8%	0.5 minutte
2.4%	0.25 minutte

The paper indicates that there are great individual differences, and that age, overweight, smoking, and a physical condition other than well trained. will decrease the tolerance to low Oxygen considerably.

In a broad population of "normal subjects" the first light symptoms of hypoxia can be observed at about 15.5% Oxygen. The symptoms such as impaired judgement. clumsiness, diminished visual acuity and slowered reaction times are becoming more signifcant as the Oxygen concentration drops to 1I-12%.
As the Arterial Oxygen level drops within 5 seconds, the symtoms *starts* with practically no delay. One of the very serious effects of severe acute hypoxia is, that is not identified by a large number of individuals. On the countrary they are experiencing a light intoxicating or lightheadedness, and will be likely to respond irrationally to warnings, or signs of danger.

Down to about 12% Oxygen, most physioigists agree, that short exposures do not cause any permanent injuries by exposures up to 30 minuttes, and only in very few cases it leads to unconsciousness.

At a design concentration chosen for the inert gas system of 50% (0.5 m3 gas per m3 room), the average high (average of the upper 5% of measured discharges) Oxygen concentration is 12.6%, Average 12%, and average low (average of the lower 5% of measured discharges) 11.4%, the statistical basis being 139 full scale discharge tests under real life conditions. The enclosures ranged from 18 m3 to 690 m3, and were measured to an accuracy of +/- 3 cm. Cylinder pressure was gauged to a temperature compensated accuracy of +/- 2%, and room temperatures were within the range 19-24 C. these tolerances do not explain the otherwise satisfactory tolerance ***of*** +/- 0.6% Oxygen concentration achieved, but enclosure hghmess and atmospheric pressure and humidity, have possibly the major influence.

In fire situations Oxygen concentrations have been experienced to drop to 8-10% after discharge of extinguishing gas, due to the Oxygen consumption ***of*** fire and the increased enclosure temperature.

In applications like ships engine rooms the average for a 50% design concentration has been 11.1% (but the statistical material only covered 4 installation tests), which is mainly explained by the loss of enclosure volume because of engines and other equipment, and possibly also a less accurate volume measurement, and slightly higher room temperature.

The system design required to extinguish fires, and the safety limits are very close to each other for Inert gas systems. They can be used safely if all the design conditions are strictly held, and by very short exposures (less than 2 minuttes) it is obvious that they do not represent an acute risk within reasonable tolerance limits and influences of the surroundings. However there is a simple, reliable and natural way to expand the exposure tolerance to low Oxygen: adding a small amount of Carbon Dioxide to the Inert gas mixture.

Acute adaption to acute hypoxia

As earlier mentioned, Carbon Dioxide is a very important part of the human physiology. It is a product of metabolism, and the primary regulator of the acidity of blood and tissues, through its conversion to Carbonic acid and the hydrogen ion. During exercise the amount of Carbon Dioxide is increased in blood, and in the expired air, and it represents the major drive to ventilation increase. Increasing the inspired Carbon Dioxide (hypercapnia), will like excersise, raise the acidity (lower Ph) and increase the ventilation, depending on the inspired Carbon dioxide concentration.

As Carbon Dioxide above 8% concentration is clearly beginning to cause some problems at prolonged exposures, one could be temptated to make the following conclusions: Hypoxia is bad, Carbon dioxide is bad. Combined hypoxia and hypercapnia is twice as bad as the problems are adding up. 1 + 1 = 2. This is good arithmetics, but absolutely not the case: on the countrary. It should rather be viewed as 1 + -1 = status quo! this statement, not being scientifically correct, anyhow reflects the real effect.

In case of a lowered Carbon dioxide concentration the Ph rises. This causes a vasoconstriction in the brain. In case of hypercapnia the result is a vasodilation. In plain and simple words: The brain have a shunting valve mechanism that allows for an increased blood flow through the brain at high Carbon dioxide concentrations and decreases when concentration falls. This is easily demonstrated: After hyperventilating for a minutte or two dizzyness is felt strongly, and if continued it will lead to fainting. This is simply a result of the decreased Carbon Dioxide, and this little experiment clearly demonstrate the statement in ref. 1: "Carbon Dioxide is no less vital to life than Oxygen".

Some interesting effects of Carbon Dioxide are:
During tests carried out by Gibbs and others, ref. 2, subjects were in four experiments breathing 6% Oxygen + 5% Carbon Dioxide for three minuttes, then 4% Oxygen + 5% Carbon Dioxide for another three minuttes. EEC remained normal and consciousness was fully maintained. Two subjects went even further: 2% Oxygen + 5% Carbon Dioxide for two minuttes. EEC remained normal and they were able to add and subtrac, and obey demands.
Of course this experiment is way out in the extremes, but clearly indicate what it is about.
Another interesting experiment, ref. 1. shows that a test individual unconscious due to a 5%/95% Nitrogen atmosphere. recovered consciousness immediately after addition of 5% Carbon Dioxide (inspired gas 90% Nitrogen, 5% Oxygen, 5% Carbon Dioxide). Again a very clear indication that the Carbon Dioxide is the life insurance needed in the use or' Inert gases and gas blends.

Carbon Dioxide is giving acute adaption to acute hypoxia!

Hypoxia, hwercaunia and Carbon Monoxide

Bringing a new product, or rather a new way of thinking, to the market will always make others try to find ways to kill it. And so it must be, since it puts the pressure on, to make us do our best, and increase our depth of knowledge.
During a fire a lot of awful smoke and decomposition products will be produced. The most significant one being Carbon Monoxide. Statistical information collecred out of post mortems on human fire fatalities indicate that 70% had more than 30% Carboxyhaemoglobin (Blood cells bound to Carbon Monoxide) which will have incapacitated the victim.
The mechanism of Carbon Monoxide is to bind to the blood cells with an affinity 200-250 times that of Oxygen and thereby reducing the blood Oxygen carrying capacity. This situation is physiologically similar to hypoxia.
One can, especially being a competitor to a certain product, suspect that the use of an inert gas , especially one containing Carbon Dioxide, will show combined detrimental effects: The fire produces Carbon Dioxide, and thereby hypoxia, the fire extinguishant is then even adding to hypoxia, and if at the same time Carbon

Dioxide is added, ventilation is increased, and even more Carbon Monoxide enters the body.

There is some good common sence in the above assumptions, and there has also been marketed some ideas in Europe, especially in Denmark where the INERGEN copy Argonite **is** originating **from.**

But if we leave the phrases like "it may be expected", "It is very likely", and the similar, and instead turn to the real world situation the picture changes.

What are the limits tolerable of Carboxyhaemoglobin? Basically Carboxyhaemoglobin is not at all desirable, but to some people a part of their life: very heavy smokers and citizens of a large city. Heavy smokers may have a preload of Carboxyhaemoglobin of 10-15% as an extreme. And this is actually very close to "an acceptable level" .

As the inert gas blend containing Carbon Dioxide puposely increases the ventilation this will naturally lead to an additional Carbon Monoxide exposure:

There are **5** very important factors:

1- The Carboxyhaemoglobin preload.
2- The exposure time.
3- The Carbon Monoxide concentration.
4- The Oxyhaemoglobin saturation.
5- The rate of ventilation.

The rate of ventilation is increased by *2.5* times at *5%* Carbon Dioxide in 12.2% Oxygen, and the heart rate is increased by 10/min. (ref. 3)

CO PPM	6 l/min.	18 l/min.	30 l/min.	40 l/min.
500	6.14	8.42	110.71	12.68
1000	7.28	11.84	116.42	20.26

CO **peaks** at about **400** PPM (after full discharge 320 PPM)
Oxygen low 8%
Carbon Dioxide high 5%
Temperature **peak** 163 Celcius (325 F).

The conclusion is very clear: By using INERGEN it is not at all recommendable to stay in **room** during the fire and extinguishing (Temperature 163 C!), but the gas situation in the enclosure will support consciousness for quite a while. It is more than doubtful1 that consciousness will be maintained for more than 1-2 minuttes if Carbon Dioxide level was not increased above 3%.

It is also very clear that the flushing effect of the high extinguishing gas concentration, is reducing the amount of smoke compounds in the enclosure. In applications where large amount sof smoke and rapid fire development is foreseeable, and there is **a** considerable **risk** that personnel may be trapped, or cannot escape for other reasons, this effect *can* be used to even further increase the survivability of the atmosphere. After the initial fire extinguishing a back-up supply containing **4%** Carbon Dioxide, 10% Oxygen 20% Argon and 66% Nitrogen, can be used for flushing the enclosure with a clean survivable modified air atmosphere, with inerting properties.

Enclosure escape precautions

Even though that the inert gas systems containing Carbon Dioxide offers a very high degree of safety to man, it is under no circumstances recommended to stay in the enclosure during fire extinguishing, or during fire extinguishing system discharge. The suppliers of any such equipment should never refer to it by terms susch as "Product xxx will present absolutely no health hazards to people in the **room**" since **this** may lead people to have an over-trust in the product. Fire is a dangerous thing, and we should never forget to emphasize this.

When inert **gases** and inert gas blends are used there are certain additional advantages (and disadvantages): The gases are stored under high or low pressure, but always in the gaseous form. During discharge of the gas there is no significant condensation of air moisture, and therefore escape route visibility, is not decreased by the *iire* extinguishant.
During **Hypoxia** the physical **performance** will slightly decrease, but **at a 12%** concentration, there is only **little** change in **a** *graded* exercise **performance**

measurement. This degree of hypoxia, will not be the reason for anybody to unsuccesfull escape.

Possibly the most important factor in succesfull escape out of the enclosure is: The preservation of consciousness and a normal response behaviour. At this point the INERGEN inert gas blend has an absolutely unique performance. Down to extreme degrees of hypoxia, the Carbon Dioxide provides extended consciousness, and improved psychomotor abilities.

It has been said by the suppliers of INERGEN-like products without Carbon Dioxide, that the atmosphere produced by INERGEN is practically unbearable, and that the stress induced on the heart is quite significant. A lot of reports, scientific work and tests have described the degree of discomfort. Of course there are individual perception of how uncomfortable it is, but by the hundreds of people, who have experienced it during full scale system discharges in Denmark, the comments are typically: "it feels like normal walking". This is not far from the truth: the stress on people in an INERGEN extinguishing atmosphere is very much like the walking or taking the staircase one level up.

If the Carbon Dioxide concentration increases to a level at which it is uncomfortable it is on the other hand giving a very fine warning against staying in the enclosure. By 5-6% Carbon Dioxide this becomes significant, and should not be referred to as something negative, but rather an additional safety feature.

Extinguishing efficiency

The Inert gases require higher concentrations, and therefore they have often been looked upon, as less efficient than the Halon type extinguishants.

From a mere cost/weight/space point of view it is correct. This is the week spot of the inert gas systems. High concentration requirement and gaseous storage, require very large storage volume and/or high pressure.

From a fire extinguishing point of view, the inert gases are no less efficient than the Halon type extinguishants. Maybe except for the speed of extinguishment. The Halon type compounds are ususally discharged 10 seconds or less, and this is not very practical to do with a large volume of inert gas. But on the other hand, there is really not the same need for the very fast Halon type discharge. The inert gases do not produce any decomposition products, and therefore it becomes more an engineering question, to optimize the inert gas system. Enclosures with a relatively low fire load, such as electrical rooms and similar, can do with a quite long discharge time, whereas a combustible liquids storage room, may require fast discharge in order to stop fire and reduce damages. In the latter case, a complete discharge in 60 seconds, will extinguish most fires in about 10 seconds, and this is practically achievable, even in large enclosures.

Another aspect of the system efficiency, is the extinguishing concentration *soak* time. At this point the inert gas blends (slightly heavier than air), are much more efficient than the Halon types, and are less sensitive to enclosure leaks.

Efficiency also concerns the ability to extinguish class A fires, and materials heated to very high temperatures, without contaminating the enclosure with toxic decomposition products. At this point the inert gases are also offering an improvement, compared to Halon and Halon like substances.

To answer the unavoidable question to be raised: "Is INERGEN a viable alternative to Halon?"

–Yes it is, not only in theory, but practical experience has confirmed it fully.

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