Commentaries
on
Oxygen and Other Oxidant
Fire and Explosion Safety

Barry L. Werley

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01 October 2019

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Barry L. Werley[1]

Introduction

REFERENCE: Werley, B. L., **“Introduction”**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety*, Self-published opinion, 2019, p. 5-8.

ABSTRACT: Several topics of interest to the historical oxygen safety community are examined.

KEY WORDS: oxygen, compatibility. fire, flammability, safety .

The writer has over thirty years of industrial experience between 1962 and 1999 working with industrial fire and explosion hazards and testing most commonly with oxygen but often with other oxidants and fuels, as well. He is a charter member (1975) of ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres, having served in numerous offices including full Committee chair. He has offered several papers at their symposia, seminars and published some in their Special Technical Publication series, chairing and technically editing their first one in 1982 (yielding their first Special Technical Publication STP 812). He has served as principal author for numerous first generation ASTM standards. He was the second chair of their Education subcommittee and drafted the first edition of the course text.

Since retirement in 1999, he has retained an interest in the subject area and has continued to comment formally (via the internet) perspectives/opinions on numerous topics on an as is and use at your own risk basis. Typically these are subjects that were of interest that never rose to the level of urgency to compel their being addressed. Often they are intended to fill gaps and supplement materials in the general subject area, occasionally they suggest new directions and needs. Most of these post-retirement efforts were posted to a personal website beginning in 2001 to allow open access and comment.

Although it is said the Internet retains everything, forever, things on the web are not nearly as accessible and permanent as legend has it, at least for common folk. The personal website was scrapped after nearly ten years. Hence, he has begun to convert his analyses and opinions into public domain print and electronic file format. Some volumes deal with a single topic, however this collection brings together disparate topics.

Many of these topics have been proposed as starting points for new ASTM oxygen safety standards or for revision to existing standards. However, few have been accepted. In the early 2000s, G-4 was under pressure to become efficient and was narrowing its priorities and efforts to core needs (stated as existing standards maintenance, symposium survival, and

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[1] No mailing address. Long–term archive copy.

its ongoing education course. and then in the next decade pressures due to the 9/11 attack and then economic meltdown both made things worse. Whether or when new efforts will be possible is unknown, so these suggestions can only be the opinion of a single commentator.

This volume uses the format of individual papers. A few papers were revised cosmetically for format but were largely unchanged, some were editorially adjusted, but a few are new and from more recent perspective as of 2019.

"Bizarro Ignition: Cosmic-Ray and Atom-Decay Induced Fires in Oxygen? and *"Bizarro Ignition: Real Oxygen Safety Science or Just Science Fiction?"* both speculate on causes of unexplained fires in oxygen (UFOs). Numerous fires and explosions have occurred going back to the beginnings of the oxidant industry that have never been adequately explained. Some defied simulation. These first two papers were prepared in 2010 and 2013,

The first analysis takes a coarse look at ionizing radiation (like x-rays, γ-rays, random atomic decay and cosmic rays) that could be a factor in un-reconciled incidents and would be near-perfectly random in their behavior. Indeed, the writer (with training in physics and math) found them energetic and of sufficient temperatures that they could be unidentified factors in otherwise seemingly fickle fires and explosions. In the second paper, subject of a verbal remote presentation before a Committee G-4 regular meeting seminar session in 2013, the thesis was expanded and further supported. Its plausibility was asserted to be sufficient to recommend that two ASTM Standards, the G 88 Design Guide and the G 145 Incident Investigation Standards, need to include statements either ruling the putative ignition/aggravation mechanism in, ruling it out, or flagging its possibility if neither position could be established.

Last word the writer has heard was that G-4 intended to seek a second opinion from a NASA physicist and in 2013 revised G88 with no comment included. It comes up for review again in 2018. G145 was re-approved with no changes in 2016 and comes up again in 2021.

"Technical and Human Factors Affecting Special Cleaning of Oxidant-Rich Systems" was prepared in 2007. The writer had prepared a literature search in 1982 for ASTM G-4's first symposium on flammability of oil films in oxygen systems to support the establishment of cleanness specifications in Standard G 93. In the 1990's concerns grew over the practices for use of lubricants in an emerging recreational diving industry, and the writer chaired the initial efforts of a CGA Committee to develop a position on these practices. In support of that effort the earlier work was updated and supplemented with interviews with many industry and government experts, The position statement (CGA PS13), published in the early 2000s but CGA decided not to publish the data behind it.

As a result, a portion of the supporting data based on literature data was reconstructed and revised. However, the interviews and other material could not be redone.

As of 2019, neither of the two unclear issues cited (role of humidity on fire limits and liquid-phase fire limits) appear to be reconciled.

"Ideal Adiabatic Compression-Traps" was prepared in 2002 as a logical extension of several earlier efforts to codify distance/volume pieces for the protection of polymer-lined flexible oxygen pigtails. In other words, if the end of a pigtail could be configured to prevent near adiabatic compression ignition of polymer-lined hoses, then similar volumes could be introduced and positioned strategically so as to similarly contain hot compressed oxygen and prevent or at least lessen the severity of its contact with other end-point polymers in an oxy-

gen system.

"Supplemental Suggestions for Oxygen-Fire-Incident Prevention and Investigation" is a revised condensation of a draft paper: *"Proposed Additions to ASTM G 145 on Incident Study"* that was prepared and posted on the Web in 2007. The writer drafted the first version of G 145 on incident study in the 1990s and it was structured to address accident investigation techniques that are unusual or easily misapplied to the examination of oxygen fires. The structure was modular so that additional techniques could be simply inserted (appended) into various sections. However, through the 1990s the oxygen production industry from which much of the energy to develop standards derives, was intensely focused on quality and efficiency improvements the previously cited refocusing of G4's priorities and perhaps other factors thwarted a revision even to the current date. Hence the original paper in ASTM format has been revised to document the issues and items that were proposed.

"Is Carbon Steel Both Over- and Under-Exploited in Oxygen Systems?" Industry experts have avoided addressing the role that carbon plays in the flammability of carbon steel. Carbon steel has always been treated as being "generic". Since the 1990s, the writer has speculated that some carbon steels (of low carbon content) may be much more flammable than believed, while other carbon steels of high carbon content may be much less flammable than believed. This paper recapitulates the bases for this hypothesis and attempts to restate the hypothesis in an alternative, perhaps more friendly, perspective.

"The Case for FLLAME in ASTM G-4" was posted in 2001 when the writer was proposing adoption of a standard and PC algorithm for estimating the fire limits of gas mixtures from published (largely Bureau of Mines) experimental data using binary, ternary and quaternary diagrams. Arguments against G4 taking on such a task included that gas mixtures are not structural materials and so not relevant to oxygen system design. This paper sought to consider fire limits of solid mixtures and liquids. A Task Force was appointed to examine the situation. Apparently, no meeting was held nor report has been issued.

"A Coarse Comparison of the Fire Hazards of Oxygen with Other Important Oxidants" is extracted from draft text the writer assembled in the early 2000s in a draft proposal for a standard addressing oxidants other than oxygen that was submitted in 2007, Although interest was significant for a number of years, effort on any such standard ended in the later 2000s. However, some of the overview materials may be of use and so were extracted into this comparative overview.

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Bizarro Ignition: Cosmic-Ray and Atom-Decay Induced Fires in Oxygen?

REFERENCE: Werley, B. L., **"Bizarro Ignition: Cosmic-Ray and Atom-Decay Induced Fires in Oxygen?"**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety***,** Self-published opinion*,* original publication 2010, public domain 2019, p. 9-16

ABSTRACT: Desperate, even fantastic, theories are often used to explain intractable technical problems. Extreme notions as to potential causes of apparently random oxygen systems fires are suggested and analyzed.

KEY WORDS: cosmic ray, radioactive isotope, atomic decay, oxygen.

Oxidant Safety Practitioners (OSPs) have been long interested in the causes of ignition and fire in oxidant systems. Much progress has been made in identifying them. However, in some cases, there have been incidents that have not been adequately explained. In some cases even massive simulation programs have failed to reproduce some of the most nagging accidents. And in some cases, straws have been grasped to explain some of the most recalcitrant events.

Incident investigations always seek the cause, the operation, the upset, the pressure swing, that caused an ignition, but some events do not seem to be connected to specific "causes". This leads one to wonder if some ignitions are bizarre random events? If they are fickle?

The writer was an attendee of one the early offerings (about 1973, maybe even the first offering) of Chester Grelecki's now famous AIChE seminars on *Fundamentals of Fire and Explosion Hazards* (shamefully and regrettably no longer offered). In that session, Grelecki mused, and the writer does not know if he mused similarly in the hundreds of following classes, that static electricity is often cited as the cause of an accident ….*until the real cause is found*. Static electricity is something that can be sold. People know what it is. They will believe you. But he added that static electricity is not nearly as dangerous as myth would have it[2].

Today in some accidents and even series of accidents, we might as well be blaming them all on static electricity as what we currently fault. This has led to further grasping at straws. For several years, "flow friction" has been cited to explain a number of events [*1*][3]

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[1] No mailing address, archive copy.

[2] Hydrogen gas releases are similarly mythic, often thought of as igniting nearly every time they occur, although the writers experience is that they are not nearly so reliable.

[3] Italic numbers in brackets refer to the reference list at the end of the paper.

and is discussed in the ASTM Standard *G 88-03 Designing Systems for Oxygen Service*. Flow friction, like static electricity, is also plausible. Everyone knows what friction is. And "flow" friction [*1*] posits that under the exposure to moving oxidant that "surface waves" in polymers or shards or strings of fuzzies will shake rattle and rub, will pulsate and throb and wiggle, flexing internally and heating to a frenzied point of ignition. This mechanism would be a boon, because a plausible flow friction effect could well have been present in many incidents that can not be otherwise explained. It is the best we got just now.

Unfortunately, as of this writing, despite very creative efforts to make material ignite under flow friction in the laboratory [*1*], there has been significant progress made, but there has been as yet no final joy. So flow friction is presently a "tentative" explanation, credible in theory, and the first one to demonstrate its practical efficacy in vitro will be a hero. That day may come. Or not.

The fictitious detective Sherlock Holmes's fame includes famously saying: "When you have eliminated the impossible, whatever remains, however improbable, must be the truth." And Holmes was the best. And today, this thinking underpins many an incident investigation.

So maybe when old-fashioned science fails, one can turn to fiction-driven science and bizarro theories. This seems to be especially in vogue with those currently in government of both political parties. It is more important to them that science give them the desired results than that it conform to any set of constricting rules. In frustration, but also in keeping with this spirit, the writer once upon a time, long long ago (more than two decades ago), also attempted an exercise along these same lines with a bizarro draft unpublished but feel-good manuscript: "**Virus Induced Fires in Oxygen**" (not under his control and likely to remain unpublished).

But bizarro is a deep well one can return to often that can refresh the thirsty in so many ways. And so this effort will chase down some "remaining yet perhaps improbable explanations" and focus on the similar bizarro prospect of *Cosmic-Ray and Atom-Decay Induced Fires* in keeping with the subtitle to this paper.

Cosmic Rays

Cosmic rays (CRs) are not cutting-edge physics. They were well known of and were used to study and formulate atomic physics nearly a hundred years ago. A quick review of the cosmic-ray data in the Encyclopedia Britannica [*2*], Weidner and Sells [*3*], and Wikipedia.com[4] revealed the following background.

A CR is a particle moving at great speed with great kinetic energy (up to 10^{20} electron volts, eV, and most over 10^{9} eV). Some come from the sun but most come from far beyond. Often it is an atomic nucleus or an electron. The majority (85%, it is said) are protons (hydrogen nuclei), but a bunch (12%) are helium nuclei.

Because they are electrically charged, cosmic magnetic fields make CRs fly along huge corkscrew paths and so their origins cannot be predicted and they may come from any direction regardless of their origin.

When they get to us, many smack into the atmosphere, and "smack" is a euphemism as used here. The impact produces some number of secondary particles which may all be

[4] Wikipedia entries change so often that a regular reference is not attempted.

moving fast enough to still qualify as cosmic rays. These particles themselves soon collide and produce tertiary particles, all potentially still cosmic ray in intensity. Next come quaternary impacts and on and on in what the atomic physics types call a cascade. Wikipedia suggests that lightning is caused by these cascades, an interesting and reasonable prospect. Indeed, early identification of CRs involved the way in which charged electroscopes discharge over time under their influence [*3*].

"Flow friction" in the presence of particles (dust or ice crystals or the like) rubs electrons off some portions of the atmosphere setting up an intense electrical field just waiting until its field-strength exceeds the insulating capacity of the atmosphere, or until some trigger (some ignition) event starts a current and an avalanche of electrons. Indeed, the Geiger Counter is a tool that charges a chamber and waits for ionizing radiation to impinge into the chamber to set off similar cascades that manifest themselves with a "click" of sound.

The writer once flew west over the great planes states over what seemed like a thousand-mile-long thunderstorm (thousand-mile-long Geiger Counter?) and could look down to see the random flashes of lightning far below. Random in frequency and random in location. Were these all ignited by cosmic rays that had flown past the plane? If so, the rate was great enough to give pause. These strikes may have occurred only when there was *both* a cosmic ray passing and a simultaneous charge separation. The actual population of cosmic rays must be greater than the observed rate of lightning. Some of those rays must have been hitting people and oxygen systems on that airplane and on the ground.

And indeed, there have been speculations that in the course of one's life, perhaps more so in the latter years of greater vulnerability, a cosmic ray might strike for the umpteenth time and smack one's DNA setting off an evolutionary process, possibly including a cancer (whether that process is a draw of the evolutionary cards or whether the cosmic ray was aimed at one specifically with perfection by a cruel Intelligent-Creator/God).

Potential Ignition Scale

Among the necessary criteria that must be exceeded before an ignition can occur are the minimum ignition temperature and minimum ignition energy. What are these numbers for a single cosmic particle in the range of 10^9 eV to 10^{20} eV?

Temperature relates to velocity. Statistical thermodynamics teaches the temperature of a gas is related to its average velocity/kinetic-energy (Boltzman's Law: $E=3KT/2$). On this basis, the average kinetic-energy of a single particle is its actual kinetic energy. For a 10^9 eV to 10^{20} eV particle, the temperature would be about 10^{13} to 10^{24} K, fairly high enough to meet any common minimum ignition-temperature requirements. Minimum ignition energy requirements data are less well obvious and more likely to be the limiting threshold.

Physicists express such energies in the electron-volt units. Electron volts are energy units uncommon to Oxygen Safety Practitioners. One eV is the energy that would be achieved by a particle with a one electron charge passing through a one volt differential potential. This is $1.6x10^{-19}$ Joules. Therefore a 10^9 eV to 10^{20} eV cosmic particle would provide from 1.6×10^{-10} to 16 Joules of energy. Keep in mind that gaseous fuel/oxidant mixtures typically have minimum ignition energies ranging from fractions of a milliJoule to several tens of milliJoules. Automobile spark ignition systems, which ignite gasoline/air mixtures with high reliability, provide sparks up to several hundred milliJoules. The upper end of this

(1.6×10^{-10} to 16 Joules) range is equivalent to a 4 gram-calorie energy.

This suggests that cosmic rays have energies over a range that should easily ignite gases and perhaps precarious liquids like dry-boiled hydrocarbons in LOX sumps and fuel/GOX mixtures (which using Holmes's approach in the past have often been attributed to fickle [unstable] acetylides of copper). They might be in the lower end of the range necessary to ignite perhaps some fines and polymers. But they should be marginal or unlikely for direct ignition of metals, if current igniters are any reflection of the minimum energy parameter for metals (ASTM G 124 employs about 1400 calories of combusting aluminum as "strong" ignition).

The writer is unaware of any work done by high energy physicists to explore the ignition potential of high-energy particles. The Encyclopedia Britannica [*2*] indicates that the following extreme particle generators are in service:

Stanford Linear Accelerator: electrons of 50 billon eV
Los Alamos labs: protons of 800 MeV.
Protons in classical cyclotrons: <25 MeV
Synchrocyclotron particles: ~1 GeV

And the Large Hadron collider (proton collisions at up to 7 teraelectron volts, 10^{12} eV) is still bigger and is expected to shed "temporary" black holes.

These energies might allow for meaningful experiments to be accomplished—but perhaps not cheaply. Still within the writer's knowledge no one has ever set a Geiger counter or other ionization detector into an oxygen system to crudely estimate the frequency of potential events over time.

Related Events: Atomic Decay

Besides cosmic rays, other phenomena that may operate similarly include electromagnetic radiation (X-rays and gamma rays) from ionizing radiation sources and induced fission or natural decay (the latter of which does not require stimulation).

Induced fission and natural decay are interesting prospects. Tramp neutrons with appreciable velocity have great penetration ability. However slow neutrons are inevitably captured. When captured, something that is greatly increased in probability when neutrons are moderated (slowed down in certain media), neutrons create isotopes, many of which are stable but some of these isotopes of which are unstable and decay (some quickly in cases like the atom bomb). The mechanics of decay are a favorite study of high-energy physicists. A decaying isotope may spew numerous secondary sources of energy (for example, beta-ray or alpha particles or electromagnetic radiation in the form of X– or Gamma-rays) and many can trigger avalanches in Geiger Counters. A few prospects of interest to designers of materials for oxygen systems are shown in Table 1 [*4*], since these atoms are often found in polymers or alloys of common metals that are used in oxygen.

The scale of this energy for a single atomic decay is up to a few MeV. Table 1 lists them but does not split them into specific radiation types. These particles, even for the decays that yield the atom bomb, are of much smaller energies than those of cosmic rays, but then these particles may be generated within an oxygen system and do not have to slam through an atmosphere or system to impinge upon the vulnerable targets.

In other words, if a rare neutron, bumps around sufficiently in passing through the

TABLE 1—*Radioactive Isotopes of selected common oxygen system materials* [*4*].

When an isotope, such as $_8O^{18}$ (which is stable and represents 0.204% of natural oxygen abundance, captures a neutron, its atomic number increases by one, in this case to $_8O^{19}$ which has a 29.4 second half-life and yields a 4.8 MeV decay energy in the form of Beta ray and Gamma ray radiation.

Target	**Abundance**	**Product**	**Half Life**	**Decay Energy**
$_8O_{18}$	0.204%	$_8O^{19}$	29.4 Seconds	4.8 MeV
$_1H^2$	0.015%	$_1H^3$	12.26 Years	0.0181 MeV
$_2He^4$	99.99987%	$_2He^5$	$2x10^{-21}$ Seconds	Not specified
$_6C^{13}$	1.11%	$_6C^{14}$	5750 Years	0.156 MeV
$_7N^{15}$	0.37%	$_7N^{16}$	7.35 Seconds	8.7 MeV
$_9F^{19}$	100%	$_9F^{20}$	11 Seconds	7.03 MeV
$_{12}Mg^{26}$	11.17%	$_{12}Mg^{27}$	9.5 Minutes	2.62 MeV
$_{13}Al^{27}$	100%	$_{13}Al^{28}$	2.3 Hours	4.65 MeV
$_{14}Si^{30}$	3.09%	$_{14}Si^{31}$	2.62 Hours	1.48 MeV
$_{18}Ar^{36}$	0.337%	$_{18}Ar^{37}$	34.3 Days	0.82 MeV
$_{18}Ar^{38}$	0.063%	$_{18}Ar^{39}$	260 Days	0.57 MeV
$_{18}Ar^{40}$	99.60%	$_{18}Ar^{41}$	1.83 Hours	2.49 MeV
$_{22}Ti^{50}$	5.34%	$_{22}Ti^{51}$	5.80 Minutes	2.46 MeV
$_{24}Cr^{50}$	4.31%	$_{24}Cr^{51}$	27.8 Days	0.75 MeV
$_{24}Cr^{54}$	2.38%	$_{24}Cr^{55}$	3.5 Minutes	2.8 MeV
$_{25}Mn^{55}$	100%	$_{26}Mn^{56}$	2.58 Hours	3.71 MeV
$_{26}Fe^{54}$	5.82%	$_{26}Fe^{55}$	2.7 Years	0.231 MeV
$_{26}Fe^{58}$	0.33%	$_{26}Fe^{59}$	45 Days	1.56 MeV
$_{27}Co^{59}$	100%	$_{27}Co^{60}$	5.27 Years	2.82 MeV
$_{28}Ni^{58}$	67.88%	$_{28}Ni^{59}$	$8x10^4$ Years	1.07 MeV
$_{28}Ni^{64}$	1.08%	$_{28}Ni^{65}$	2.56 Hours	2.10 MeV
$_{29}Cu^{63}$	69.09%	$_{29}Cu^{64}$	12,8 Hours	1.68 MeV
$_{29}Cu^{65}$	30.91	$_{29}Cu^{66}$	5.1 Minutes	2.63 MeV
$_{30}Zn^{64}$	48.89%	$_{30}Zn^{64}$	245 Days	1.35 MeV
$_{30}Zn^{68}$	18.57%	$_{30}Zn^{69}$	14 Hours	0.44 MeV
$_{30}Zn^{70}$	0.62%	$_{30}Zn^{71}$	3.9 Hours	3.9 MeV
$_{42}Mo^{92}$	15.84%	$_{42}Mo^{93}$	6.9 Hours	2.43 MeV
$_{42}Mo^{98}$	23.78%	$_{42}Mo^{99}$	66 Hours	1.38 MeV
$_{42}Mo^{100}$	9.13%	$_{42}Mo^{101}$	14.6 Minutes	2.82 MeV

earth and slows down to where it might be easily captured as it passes into the sump of an air separation plant and happens to be captured by an atom there (or by a tramp uranium or a copper acetylide particle, or a hydrocarbon in a dry boiled slurry or even the oxygen itself) it conceivably might release only up to 10^{-10} mJ of energy, not nearly enough to provide the minimum ignition energy for what might appear to be a random direct-ignition event of even combustible gas mixtures, but nonetheless, enough to trigger a cascade current if there is a charge separation (“static electricity”) present.

Might this (like the cosmic ray prospect) provide the random or otherwise fickle igniter that produces seemingly un-triggered events in oxygen systems? For example, the unexpected past LOX-sump explosions occurring when acetylene levels rose to provide a required concurrent condition.

Carbon Effect

There are a few scant data that might support the thesis of this manuscript, one involves the behavior of carbon. Carbon is a very interesting material that the writer has speculated may be important in several ways in controlling or enabling oxygen fires [*5-7*].

In the past, carbon was considered for possible use as a “safe” explosive. The writer is aware of only one or two papers that relate this experience and does not have access to any at present, but one may be reference [*8*]. The idea was to place containers of safe fine-carbon particles in mines and the like with blasting-cap detonators or even just simple igniters. Then when the explosion is required, to fill the containers with LOX as one evacuates the mine, rendering the carbon fines into a potent high explosive. If anything were to go awry, then the LOX could be allowed to evaporate and the mine could be re-entered safely.

However, in laboratory tests of the explosive carbon/LOX mixtures, it exhibited a tendency to ignite early at inopportune times. It was fickle and apparently was therefore never commercialized.

Perhaps the carbon mixtures were being ignited by cosmic rays or atom decays. Carbon is a well known moderator for neutrons. It is one of the more effective materials used to slow neutrons down to facilitate fission in atomic reactors. Perhaps cosmic rays were impinging. Perhaps carbon/LOX mixtures were slowing passing neutrons capturing them or allowing them to be captured by other materials leading to atomic decay and ignition. In a LOX/carbon slurry, charge separation might also be a quite plausible concurrent condition.

Potential Work

Literature searching for instances in which flammable gas mixtures may have been exposed to naturally radioactive isotopes might lend credence to this notion. If none are found, then at significant but not inordinate expense radio-isotopes might be placed in standard gas phase flammability test apparatuses, possibly as one plate that is charged like a Geiger counter cell. Any positive results would be a red flag for the need for additional work. Detectors for ionizing radiation could also be placed in oxygen systems for long-term measurement of whether there is any measurable rate of cosmic-ray or atom-decay events.

Conclusions

- Cosmic rays and atomic decays are ubiquitous. They occur at universal rates that are beyond our powers to count. And if ignition obeys a normal statistical distribution then infrequent incidents that have no obvious cause may just result from a statistical event, even if one far out on the tails of one of these processes’ distributions.
- Although efforts to simulate a cosmic-ray- or atom-decay-induced ignition in

oxygen hardware would be very costly (possibly prohibitively expensive), it would be quite practical to put Geiger or other radiation detectors into oxygen hardware to identify if non-ignition events are occurring and at what frequency. And it might be possible to study fickle carbon/LOX ignition relative to CR, neutron capture or natural decay probabilities.

- If rays and decays are present in oxidant equipment, then the industry should seek to identify patterns that may be important. Are there "seasons" of CRs (like during sun-spot activity or when the earth passes through certain regions of space in which random events are more likely. If there are patterns, they may be relatable to past random incident timings. And plants could someday be equipped with monitors to alarm if any high-rate events are possible.
- Similarly, if atom decay is observed during a survey, it may be possible to identify what the decadent material is and factor such information into future designs. For example materials likely to contain radioactive isotopes or to produce them upon neutron capture, or to have more significant decay products can be avoided.

Summary

There are random "bullets" in the form of high-energy atomic particles and ionizing radiation that permeate us and our equipment or are spontaneous events therein. On occasion they apparently starts fires, big ones, with a mammoth kindling chain when they trigger lightning that ignites forests. The prospects for the same thing to happen in much smaller scale in oxygen equipment has been considered. While this theory is grasping at straws in some ways, to explain apparently random oxygen system fires, and while it contains only a very improbable germ of possibility "however implausible" for some kinds of apparently random incidents in oxidants, like flow friction, they may be the best explanation we got.

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[*2*] *Encyclopaedia Britannica 2001*, Cdrom, keywords: "cosmic ray", particle accelerator history, 2001.

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[*4*] *CRC Handbook of Chemistry and Physics*, 52nd Edition, R. C. Weast, Ed., CRC Press, Cleveland, Ohio, 1967, pp. B-4 to B-92.

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Bizarro Ignition: Real Oxygen Safety Science or Just Science Fiction?

REFERENCE: Werley, B. L., **"Bizarro Ignition: Real Oxygen Safety Science or Just Science Fiction?"**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety*, Self-published opinion, original publication 2013, public domain 2019, p. 17-28.

ABSTRACT: Some fires in oxygen defy explanation and force the consideration of bizarre causal theories. Lacking anything better, fantastical hypothesis can not be ruled out and arguments for several are reviewed. The current state of bizarre hypothesis is examined, including that of "flow friction". Ionizing radiation alternatives are upgraded that may be even more farfetched, but may be more realistic, possibly more valid, and hopefully more easily reduced to practice.

KEY WORDS: cosmic ray, radioactive isotope, atomic decay, oxygen.

Fires in oxygen are great motivators and educators. Often, they capture the imagination of management and convince management to the point that it funds oxygen fire science. Fires also tell us when remediation has succeeded, when they stop happening. Oxygen safety science has made significant progress against these fires. We know this because the types and numbers of fires of numerous kinds have decreased significantly. However, to this day, oxygen safety science is incomplete. We know this, too, because a body of fires that defies explanation persists.

Many of these defiant fires have not been commonly discussed in the literature. They are not a dirty little secret, but it has simply been more productive to focus on things where one can do the most good. However, as the body of oxygen safety science has matured, these exceptions have been brought into focus. And there have been efforts to attribute at least some of these unexplained fires to the best explanation we can find, the most likely if not ideal suspect, and so a "provisional" cause of "flow friction" has been used to explain some of these events.

These embarrassments have never been named generically, and it is said: "when you give it a name, you know what it is". Very recently, Davis [*1*][2] has boldly given them a name: "Ignition Happens But Nobody Knows Why (formerly known as flow friction) (IHBNKWFNFF)". And this effort will mimic that advance. After initially considering less voluminous alternative names such as Fires of Unexplained Causation (FUCs), or Fires that Resist Explanation (FREs), this paper will unashamedly settle on calling them Unexplained Fire in Oxygen (UFO). UFOs have been documented back to the early days of the industry, and several from the 1950s/60s are a basis for this paper.

The writer first learned of the dangers of oxygen back in those 1960s. At that time and for decades before, the oxygen safety collegium had begun to form. The publication: *Safety in Air and Ammonia Plants* (1960-1968) would chronicle several reviews of explo-

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[1] No mailing address, archive copy.

[2] Italic numbers in brackets refer to the reference list at the end of the paper.

sions in air separation units (ASUs) [***2-8***] and are abstracted in the Appendix. These events were studied by some of the giants in the oxygen safety field, past and present ASTM Committee G-4 members who would ultimately conceive and birth ASTM G-4 (The Clyde McKinleys, Jack Gilbertsons, Frank Kerrys and others). They often attributed these ASU explosions to assorted hydrocarbon contaminants, but most often and most diligently to acetylene.

Acetylene is an endothermic molecule (it releases energy when it splits apart). It is easy to ignite and was not completely removed or was inadvertently released by the plant front-end cleanup systems (typically silica gel). Acetylene does not require oxygen to explosively decompose, and has gaseous explosive limits ranging from zero percent oxygen to mixtures with very high oxygen concentrations[3]. Although oxygen is not necessary for an acetylene fire or explosion to occur, the presence of oxygen can make them much more severe and destructive.

This writer can not rule out if small scale fires were happening and were not being noticed. Such things have happened in the industry even with some fairly important fires that went undetected. However, when an accumulation of acetylene formed in the distillation column or a similar sump that exceeded a limit (perhaps either a fire limit or the saturation limit at which condensation would occur, or perhaps even just a minimum volume that would be destructive) a destructive explosion (one that would not go undetected) was possible, and on several occasions such destructive fires occurred [see Appendix]. These events were eliminated not by the common remedy of preventing ignition, but by scrupulously, perhaps even to this day, testing the LOX inventory to keep acetylene presence below a limit (typically one ppm). However, speculation for the direct cause, the actual ignition source, for at least some of these explosions was sometimes attributed to copper acetylides [***2***] that were taken to be erratic and "unstable" (fickle), but yet the presence of acetylides was apparently never actually proven. Are copper acetylides purely statistical creatures or is there a precursor direct cause, albeit a statistical cause for its "instability"? Or is there some other explanation for these events?

In intervening years, UFOs have often been similarly dealt with. When one can not prevent a given material from ignition, one can eliminate the material itself (even if just to replace it with a material that does not burn). This is a common and valid practice, however, in each such case the more elementary ignition cause becomes unimportant and may go unexplained.

In addition, Oxygen Safety Practitioners (OSPs) often face the prospect of low probability events. When a chain of events occurs and one deduces or even just surmises a cause and alters their hardware and finds that the events appear to stop, the stoppage is fairly convincing proof that the solution was effective whether the deduction/surmise was correct or not. But when low probability events occur no similar confidence is possible. A remedy applied after a single event that occurs after a decade or so of blissful operation may take one or more decades before its empirical risk can be validly confirmed. Hence any apparent stoppage may not always be significant.

As a result, the most robust of accident investigation scenarios, involves the assign-

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[3] Apologies to the members of ASTM Committee G-4 which has expressed a disdain for the writer's past efforts to introduce fire-limit definition and interpretation standards into its body of work and has even labeled them nearly irrelevant to their oxygen safety mission. Fire limit discussion herein will be held to a minimum.

ment of a cause and deliberate demonstrations (simulations) of that candidate cause producing a faithful repetition of the accident,….providing the incident is small enough to simulate or can be validly scaled down to manageable size.

As a result, erroneous accident investigation solutions can sometimes be implemented that may not find the real direct cause and yet the error may go unnoticed for a long time. Notwithstanding those unknown numbers of rare cases, there are numerous other cases where investigations, even very thorough investigations, have simply not succeeded. We know that we do *not* know the direct causes of some fires in oxygen.

The Best We Got

Oxygen Safety Practitioners (OSPs) are forced to analyze such incidents with the best tools they have. Often variations on existing fire mechanisms are formulated and sometimes even flights of fancy are considered. This is how, in recent years "flow friction" has been included in this latter category. Flow friction is easy to understand qualitatively. Flow has viscosity and causes deformations of, or motions, of components which rub internally or externally and heat up. Low level heating like this has been demonstrated, but so far actual ignition has been illusive in lab tests by Gallus and Stoltzfus [***9***]. Flow friction was, nonetheless, added to the ASTM G 88 Design Guide in 2005 in a very gingerly treatment of this possibility. It was listed for speculative consideration in those cases where there is no better explanation but any who used it were warned about the fragility of its invocation.

In 2012, a bold new speculation [***10***] was proposed by Stoltzfus, Gallus and Sparks that marries the demonstrated low level heating of flow friction with an extrapolation of the thermal theory of ignition to suggest perhaps flow-friction-facilitated spontaneous thermal ignition is possible. This is apparently only at the hypothesis stage and will need to undergo experimentation. If this can now be validated, the bold effort may catalog another demonstrated direct cause, and reduce the number of UFOs, but it will *not* solve *all* outstanding UFOs.

For that reason, in 2010 this writer speculated on a pet flight of fancy of his own. That predecessor to this paper "**Bizarro Ignition: Cosmic Ray and Atom Decay Induced Fires in Oxygen**" suggested that maybe, just maybe, cosmic rays and/or atom decay (CRADs) might be ignition sources [***11***]. That previous effort examined the theoretical temperatures of these particles and rays (often moving at a significant fraction of the speed of light) and it found they are orders of magnitudes (indeed orders of magnitude of orders of magnitude) greater than minimum ignition temperatures required to ignite any common unoxidized materials in oxygen systems [4]. However, for ignition, one needs to provide not only temperature above a minimum but an energy transfer above a minimum ignition energy, as well.

The known kinetic energies of some cosmic rays clearly exceed the known minimum ignition energy of numerous flammable gas mixtures and some high surface-area-to-volume oxygen system materials, but they are less than robust with regard to apparent ignition energies of some bulk polymers and possibly most if not all bulk metals. Atom decay is much lower in energy and does not approach the known minimum ignition energies of even

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[4] When Boltzman's Law, E=3KT/2 was used to calculate the average temperature for a cosmic ray of given energy from 10^9 to 10^{20} eV, cosmic ray temperatures of 10^{13} to 10^{24} K were estimated.

TABLE 1—*Radioactive Isotopes of selected common oxygen system materials* [***11***].

When an isotope, such as ^{18}O (which is stable and represents 0.204% of natural oxygen abundance, captures a neutron, its atomic number increases by one, in this case to ^{19}O which has a 29.4 second half-life and yields a 4.8 MeV decay energy in the form of Beta ray, (β^-) (4.6 MeV) and Gamma ray radiation.

Target	Product	Half Life	β^- Energy	β^- Velocity[a]	β^- Velocity[a]	T - °K[b]
^{13}C	^{14}C	5750 Years	0.156 MeV	0.64c	119k mi/s	1.21×10^{9}
^{15}N	^{16}N	7.35 Seconds	10.4 MeV	0.999c	184k+ mi/s	8.04×10^{10}
^{19}F	^{20}F	11 Seconds	5.42 MeV	0.996c	185k+ mi/s	4.19×10^{10}
$_{18}$O	^{19}O	29.4 Seconds	4.6 MeV	0.995c	185k+ mi/s	3.56×10^{10}
^{27}Al	^{28}Al	2.3 Hours	2.87 MeV	0.988c	~184k mi/s	2.22×10^{10}
^{26}Mg	^{27}Mg	9.5 Minutes	1.75 MeV	0.974c	181k+ mi/s	1.35×10^{10}

[a] These are relativistic velocities calculated with the formula:

$$v/c = [\,1 - (E_o/E)^2\,]^{1/2}$$

Where v is the relativistic velocity in mi/s, c is the speed of light in mi/s (186,000 mi/s), E_o is the rest energy of an electron (0.51 MeV), and E is the total energy of the beta ray (the rest energy of the electron plus the decay energy in MeV).

[b] Temperature is calculated using Boltzmann's Law;

$$E = 3KT/2\,, \quad T = 2E/3K$$

Where the kinetic energy, E, was taken as the β^- energy above , and K is Boltzman's constant.

sensitive flammable gas mixtures as determined with spark ignition tests. Table 1 repeats and expands upon some examples from the first paper.

Keep in mind that the reported minimum spark ignition energy of a very easily ignited material like acetylene (in mixture with air) is 0.017 mJ [***12***] which is about 10^8 MeV. Hence all of the common atom decay particles of Table 1 would seem, despite their incredible temperatures, to come up more than a million times too short on energy.

However, if they were somehow viable, the assorted possibilities that this speculation suggests would allow for randomness (a relatively calm liquid-oxygen sump may suddenly ignite because a cosmic ray or atom decay just happens to happen). It would also allow for epidemics (a series of fires that may begin and end in sync with sun spots or galactic storms or plant-ingestion of certain radio-atoms in batches).

Therefore, instead of basing this paper only on the highest energy cosmic rays as viable ignition sources, for those cases where cosmic rays or atom decays are too low in energy to directly initiate any given incident, this will take the same approach as the proponents of flow friction used. It will examine new ways to accentuate or interpret the effect of that energy, therefore will seek ways to identify and amplify the effects of all CRAD kinetic energy. Specifically, effects due to multiple events (simultaneous impacts or decays) and the specific secondary mechanics of these events will be explored.

However, it is important to note that even if some fires in oxygen occur because of this crapshoot, it does not mean that no control over them is possible. Thankfully, this theory does not mean oxygen safety is a lost cause. Therefore coping tools for the oxygen system designer will also be considered.

Multiple Events

Since cosmic rays and atom decays are statistical on a macro scale, there is a probability of any event, P(e), occurring in a given volume, V. Given that probability per unit volume, P(e)/V, one can calculate the probability of two or more simultaneous local events

Clearly if two cosmic rays or atom decays occur at the same time in the same place, the energy transferred is doubled. Greater numbers of simultaneous events produce proportionally greater energy transfers.

In this category, one must consider sequential decays that may be infrequent but which tend to occur by definition in a common local volume that would act to therefore increase effectiveness. For example, a case where a neutron might be captured by an atom that becomes unstable and later, if only microseconds later, decays to release a decay energy and produces a daughter atom that is also unstable with a short half life and that will therefore quickly decay to produce a second decay energy and multiply the local energy transfer.

In this case, one can speculate on ways to double or triple the energy transfer. But, alas, even ten simultaneous decays would only increase the yield by one order of magnitude, and that would still seem negligible. The gap between published MIE and decay energy would have to be much smaller than this.

Secondary Mechanics of CRADs

Multiple events (rays or decays or both) imply multiplied energy transfer but also multiplied power inputs and in general, past testing of minimum ignition energies for gaseous mixtures (using spark ignition primarily), has shown that increased ignition power results in decreased minimum ignition energies [***13***].

When ignition is successful, an amount of energy equal or greater than a minimum threshold has been introduced. If the energy is gradual and pervasive (if the whole system is slowly heated) the minimum energy needed can be enormous. If the energy is local and concentrated, it may be much more efficient. And as demonstrated in other fields, generally, the greater the power level of the energy (the shorter the period of time over which the energy is introduced and/or the smaller the volume into which it is introduced), the more efficient it will be. A flammable gas mixture that is slowly heated should require more energy to ignite than if the ignition energy derives from a small spark that has a high local temperature and a very intense local power level. Spark minimum ignition energy can be many orders of magnitude smaller than those for general, bulk, heating.

Indeed, that begs the question whether CRADs may be even more efficient, perhaps much more efficient, than sparks. CRADs are typically at much higher temperature (higher than plasma discharge) and their energy can be circumstantially transferred in much smaller local volumes. A typical spark ignition energy might be delivered into an arc length of 0.1 inches to perhaps 0.2 inches. Yes, sometimes a high energy particle may pass completely through a system, transferring only a portion of its energy and disrupting only assorted electrons in the medium, but sometimes it will smack directly into a nucleus and transfer all of its energy in a volume as small as an nucleus, to wit, an Angstrom unit. The power level can be astronomical.

(Perhaps too) Extreme Extrapolation Example:

Min Ignition Energy of acetylene in air [*12*] = 0.017 mJ = 10^{14} eV , (@1.60 x10^{-19} eV/J)

Dimension of typical nucleus = about 1 Angstrom units ~ 10^{-10} Meters

Dimension of typical spark gap = 0.1 in. ~ 2.5 x 10^{7} Angstrom units

Number, n, of power doublings ~ 2.5 x 10^{7} Å / 1 Å = 2^n

Therefore n ~ 25 power doublings, hence 25 min ignition energy halvings would be:

$$10^{14}\text{ eV}/2^n \sim 4\text{ MeV}$$

This (extremely extrapolated) MIE for acetylene is within the range of kinetic energies of the particles in Table 1.

Fig. 1—*Extreme extrapolation of minimum ignition energy for acetylene.*

One spark ignition test program found that minimum ignition energy decreased by about a factor of two when the power delivery rate was doubled [*13*]. It is doubtless very risky to extrapolate this result over many orders of magnitude, but if such an extrapolation proved valid, then Figure 1 would suggest the minimum ignition energy of acetylene might extrapolate down to roughly 4 MeV for power-dense, temperature dense beta-ray ignition. This is now, in fact, within spitting distance of the kinetic energy of any of the decay beta rays listed in Table 1. Furthermore, the minimum ignition energy of acetylene in oxygen should be much less than in air. And there is the prospect of multiple decays occurring at the same time. So are these beta rays far too low in energy to cause ignition or are they way high enough? The truth is somewhere in between. Clearly this crude surmise could be in extreme error in either direction, but it does not rule out atom decay as a potential ignition source.

Unfortunately at present there do not appear to be data for the efficacy of high energy particles as ignition sources. Fortunately there may be a number of clever experiments that might allow such data to be inferred without too great a complexity and cost or overly elaborate apparatus. Only an empirical test is likely to resolve this uncertainty.

Living in a Random World

On the atomic scale, nuclei and particles within the nuclei, are in constant vibration and motion, similarly to gas molecules in a vessel. Just as there is a chance the air molecules in the vessel we call a room may abruptly all move to one corner producing vacuum where you sit, there is also the chance that the nuclear or particle motions may all combine to split the atom or particle into parts (a uranium atom may suddenly split into a krypton and a barium atom or many other possible complimentary pairs, e.g. xenon and strontium), and similarly a much smaller neutron may suddenly emit an electron and turn into a proton.

If it were possible to see into the nucleus of an atom and to measure the positions and velocities of each particle then it might be possible to predict when such fission decay will occur. Even more difficult would be to see into the internals of an even smaller particle within the nucleus to measure and to predict when any particle might decay. However, we can *not* retrieve these data, and so, the decay of radioisotopes this way is a purely statistical process when viewed from our macro perspective.

But that does *not* mean that we and our equipment are helpless and hopeless and that we must just sit here with targets on our backs. Nor, indeed, does that mean that if CRADs are able to induce oxygen fires, that therefore the only way to cope with oxygen fires is to use materials incapable of burning with all the attendant issues that brings. This paper cited acetylene and copper acetylide issues as earlier examples, and considers the atomic and nuclear properties of carbon to be of particular interest, partly because its radioactivity has been studied to a great degree, but also there is very useful data available from the technology of radio-carbon dating of fossils[5].

For example, in radio-carbon dating of fossils [***14***], the atmosphere is viewed as a sink of roughly constant but very dilute radio-carbon. The atmosphere is constantly bombarded with radiation specifically neutron radiation and rays that can generate carbon 14 (^{14}C) at the same rate that the resident radioactive ^{14}C is decaying.

Naturally-occurring carbon, principally contains two stable isotopes Carbon, ^{12}C (about 98.9%) and ^{13}C (about 1.1%). In the atmosphere, carbon dioxide in which a ^{13}C atom absorbs a neutron (n), will then contain radioactive ^{14}C and will at some time over the next 80,000 years or so, decay to release a beta ray (β^-) to become nitrogen, ^{14}N, according to:

$$^{13}\mathrm{C} + n \rightarrow {}^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^-$$

However this is not cited in the literature as the most likely source of ^{14}C production. Since there are far greater amounts of ^{14}N in the atmosphere (99.62% of the 79% nitrogen in air), it is far more likely that nitrogen will absorb any neutrons. It can potentially become ^{15}N. However, ^{15}N is cited as a stable isotope, and yet for unexplained reasons reaction into ^{14}C and hydrogen, ^{1}H, is cited according to the following equation which apparently takes place during the actual neutron impact:

$$^{14}\mathrm{N} + n \rightarrow {}^{14}\mathrm{C} + {}^{1}\mathrm{H}$$

This resulting carbon atom is expected to chemically react quickly with oxygen in the atmosphere to yield carbon dioxide. The upshot is that about one in a trillion carbon atoms in the atmosphere are thought to be radioactive ^{14}C.

When plants and animals and the like that ingest or absorb carbon dioxide that contains ^{14}C die, or that eat them, the rate at which they absorb new ^{14}C stops and the radioactivity of the existing material in them decays by half every 5750 years.[6] At time zero, "fresh"

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[5] The writer has argued that carbon presence is a crucial factor in the flammability and compatibility of steel for several decades, a concept that has been somewhat censored, marginalized and excluded. While there are numerous data that defend the behavior of carbon this way, they may or may not be related to any of these atomic and nuclear issues.

[6] Some argue the universe is only about 5000 years old, and if this were the case, it would not alter the conclusion here. It would merely mean that the half-life of carbon is in error and that the number of half lives that are calculated would be the same, and we would still calculate the same amount of ^{14}C activity.

carbon containing trace ^{14}C, is estimated to produce about 14 disintegrations per minute per gram of carbon.

Hence when copper acetylides or even just endothermic acetylene are present in a ASU column in a concentration exceeding a fire limit (more humble apologies to G-4), it may have some measurable quantity of ^{14}C in it. At that point, an ignition caused by ^{14}C decay (if possible) would be a pull of the slot machine handle, and would obtain whenever the required decay events or multiple events occurs.

This presumes that ^{14}C is capable of causing ignition, but even if Carbon 14 decay-induced ignition can be ruled out, there remains the myriad of other, perhaps less well studied, less probable, spontaneous and more powerful decays or rays that would be harder to quantify but may be equally or more viable.

Carbon is Carbon is Carbon, Not

The previous hypothesis, nay speculation, offers a potential direct statistical explanation for those random historical explosions of acetylene in quiescent ASU sumps and vaporizers. Clearly the more acetylene accumulated the more decay that would occur, the greater the chance of spontaneous ignition. However, not all acetylene is the same, and some acetylene accumulations would be significantly (indeed perhaps massively) more radioactive than others.

First consider two common sources of acetylene. Within the limited knowledge of the writer, acetylene was historically produced typically by mixing water with calcium carbide (CaC_2) according to:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

The calcium carbide is produced by high-temperature mixing of lime (CaO) and coke (C) according to:

$$CaO + 3C \rightarrow CaC_2 + CO$$

A second method of production is the partial combustion of methane (CH_4).

For all of these methods, the sources of the carbon in the acetylene, namely CaC_2 (which has been mined) or coke (which has been mined) or methane (CH_4 which has probably been extracted from deep under ground) could be eons old and virtually nil in ^{14}C [7].

Next consider acetylene byproducts from other types of combustion. When organic materials, including gasoline, alcohol, methane and wood are burned in engines or stoves or forest fires, any ultimately produced equilibrium products may include acetylene. If the fuel in the combustion was petroleum derived (gasoline, or extracted natural gas), the carbon in it might again be eons old and any ^{14}C may have decayed away long ago. However, if the fuel is alcohol (produced from recently grown corn) or recently harvested wood, or biological emissions, the amount of ^{14}C in it might be very near the level of ^{14}C in the atmosphere.

Indeed, acetylene in an ASU sump might be exposed to ^{14}C decays resulting from other carbon-bearing materials, carbon dioxide, organic atmospheric contaminants, even smoke, that are not removed in the front-end clean-up. Then too, there are other carbon at-

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[7] Even though under ground for millions of years or more, carbon may still be struck occasionally by cosmic rays to produce small amounts of fresh background ^{14}C.

oms in polymers that may be present. And then there are all the other tramp radioactive materials that might obtain. As a result, the sump of an ASU or a vaporizer may be very calm radioactively or it may be subject to relative storms of radioactivity.

Un-Natural Events

Atmospheric atomic and nuclear weapons testing, nuclear plant incidents (Three-Mile Island, Chernoble, Fukashima) and modern technology (radiation cancer treatments, smoke detectors) all have altered the nature and mix of radioactive materials in the environment. In many cases introducing isotopes that heretofore had long ago decayed away.

Where to Next: Baby Steps

This paper continues to extend the speculation on this mechanism, in hopes of someday, designing a modest experiment that might begin to develop hard data. Although much ionizing radiation work is onerous in its demands on the experimentalist, many baby steps are possible and the writer hopes to undertake a few. The rate of natural radiation and perhaps much more significantly the variations among seemingly identical items, can be easily measured in numerous materials of interest to oxygen systems that contain carbon: PTFE, CTFE, Viton, Nylon, SBR, And perhaps even some hydrocarbon gases. Geiger counters are modest in cost, and radiation hygiene considerations are nil since only natural radiation levels are being measured. Batch-to-batch variations and vendor-to-vendor variations can thereby be revealed. The identification of products which use stale carbon, or which use fresh carbon, or which are erratic in use, should all be pretty easy baby steps to take.

Indeed, knowing the range of radioactivity of assorted carbon-bearing contaminants, might allow a relatively simple real-time continuous quantitative analysis of the acetylene levels in an ASU sump. Installation of GM counters in ASU sumps has been proposed in the first of these papers, and is again encouraged to those who have access to such sumps.

In addition, a number of experimental designs can be detailed to answer the main question of whether radioactivity can play or has already played a role in past incidents[8]. Perhaps some designs are amenable to the solitary worker, but, alas, at least some of the more convincing tests that might actually result in fires, explosions and shock waves (like for example comparative observations of fresh and stale acetylides for relative stability), would require the assets of a fire-test laboratory. So to a fair degree, this effort must attempt to attract interest among those who are ensconced in a suitable lab setting.

To the latter point, it is worth noting that since the advocates of flow friction have evolved to seek additional energy in the form of thermal self-heating, that there is the prospect of radio warming and atomic decay that might also be viable as a incremental energy source, if not a direct energy source, especially if one considers that the latest flow-friction speculation [***10***] relies on a thermal self-heating of cellulose fines. To wit, (1) fines are easier to ignite than most materials, and (2) the fines being contemplated are cellulose from filters (very highly likely recently harvested cellulose rich in fresh ^{14}C). And such cellulose fines are likely insulating and may also allow for electrostatic charge separation, and therefore

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[8] Although oxygen systems are of greatest concern to ASTM Committee G-4, one can wonder how many other fire-related accidents may have been similarly ignited.

cosmic ray- or atom-decay-induced avalanche discharging (as occurs in lightning strikes, and Geiger-Mueller tubes) becomes an additional prospect. Hence those pursuing flow friction as a bizarre ignition prospect may benefit from a consideration of this theory, and they are hereby encouraged to take on that exercise.

Summary

The random bullets (CRADs) that continuously rain down upon and assault us and our oxygen hardware, have been examined for a second time, and the reasonable mechanisms by which they may initiate fires, such as simultaneous events, and intense impacts have been examined. The credibility of their hazard has been shown to be realistic. The variability of these mechanisms in carbonaceous settings based on the age of bulk carbon, as an example, has shown how radioactivity from carbon or other radio-atoms might be a potential factor in the randomness of some historic UFOs. Although seeming like science fiction, this conjecture has been bought much closer if not yet to the very verge of valid oxygen safety science.

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Appendix

Several pertinent historical UFOs involving fires in Air Separation Units and/or apparent acetylene involvement have been reported in the Series *Safety in Air and Ammonia Plants* (*SAAP*) [***2-8***] and are abstracted as follows:

1. Karwat, Ernst, **"Safety Measures in Low Temperature Separation of Acetylene-Containing Gas Mixtures"**, *SAAP*, Vol. 3, AICHE, NY, NY, August, 1960, page A-18.

   Karwat cites coke oven gas as containing 600-2000 ppm acetylene, and that in many gas mixtures, it experiences self-decomposition, and/or forms explosive carbides. Room temperature acetylene can explode above roughly 20-30 psia. Karwat disputes opinion and patents at the time that felt dissolution into higher hydrocarbons prevents explosion. He warns that separation plants made of copper pose a special risk. "A most brisant species of copper acetylide can be obtained in the laboratory by reacting at low temperature (-40 degrees C) an ammoniacal solution of cuprous salt with acetylene. The precipitated copper acetylide after filtering can be exploded even by the smoothest touch."

2. Matthews, L. G., **"Oxygen Plant Explosion"**, *SAAP*, Vol. 3, AICHE, NY, NY, August, 1960, page 12-13.

   Matthews described an explosion attributed to hydrocarbons in an ASU main condenser (reboiler) and a portion of the fractionating column. Neither the exact hydrocarbon nor the mechanism of ignition were ascertained.

3. Wright, G. T., **"Oxygen Plant Vaporizer Explosion"**, *SAAP*, Vol. 3, AICHE, NY, NY, August, 1960, page 9-12.

   Wright describes one of three vaporizers whose inlets were filtered with silica gel exploded. An earlier small explosion had led to warming of the hydrocarbon filters and may have desorbed some contaminants, including acetylene. Also, there were coke ovens in the vicinity (a source of acetylene). Hours after restart, a larger explosion occurred, that was attributed to hydrocarbons, probably acetylene.

4 Karwat, Ernst, **"Hydrocarbon Control in Air Separators"**, *SAAP*, Vol. 3, AICHE, NY, NY, August, 1960, page 5-9.

   An explosion occurred as liquid was being drained from a liquid oxygen separator. Although acetylene was largely ruled out as a cause, propane was a strong candidate.

5. Panel Discussion, **"Reboilers and Vaporizers"**, *SAAP*, Vol. 2, AICHE, NY, NY, May, 1960, page 5-9.

   Panel discussion is subtitled "Acetylene is the most critical hydrocarbon constituent of low temperature oxygen plants. Its concentration should be kept below 1 ppm".

6. Rotzler, R. W., Glass, J. A. , Gordon, W. E., and Heslop, W. R., **"Oxygen Plant Reboiler Explosion"**, *SAAP*, Vol. 2, AICHE, NY, NY, May, 1960, page 31-35.

   A reboiler explosion occurred in the midst of normal operation that was attributed to either co-crystals of acetylene and nitrous oxide or of acetylene and carbon dioxide. Damage equivalent to two pounds of TNT (one pound of acetylene) was estimated. The location of the damage suggested a very thin layer of explosive material laying quiescently on the bottom tube sheet concentrated near its perimeter. "Only a very sensitive explosive would be expected to detonate in this manner." Acetylene was immediately suspected as "an ever-present contaminant in air plants even without an acetylene unit next door." Nitrous oxide was an unanticipated contaminant. Carbon dioxide was ruled out as a factor because crystals dense enough to sink did not detonate in tests. Similarly, silica gel dust was ruled out. The acetylene and nitrous oxide were concluded to have entered the reboiler *six months* before the explosion during a partial regeneration of one of two silica gel filters. Liquid sampling was taken from a point that did not sample the very bottom of the reboiler and so may have given faulty results. It was found that the acetylene/nitrous-oxide crystals may have remained un-dissolved for the full six months or that its composition may have gradually changed to become explosive when the explosion occurred. Possible sources of initiation in either case were not cited.

7. Boyne, W. J., **“Liquid Oxygen Disposal Vessel Explosion”**, *SAAP*, Vol. 8, AICHE, NY, NY, May, 1966, page 7-11.

   Boyne describes an explosion in a bulk waste liquid vaporizer reminiscent of the many cases of similar explosions that have occurred due to boiling crude liquid oxygen to dryness in a vessel that may approximate calm and even stagnant conditions. A cryogenic waste stream from an ASU containing one to two percent oxygen is purged to a disposal vessel, and hydrocarbons especially acetylene and ethylene were present. The vaporizer had been in use for some time, and the paper seeks to identify if some unique circumstance may have produced a liquid over a fire limit in this case, but as for most reviews does not consider if the ignition may have merely been random at that time during normal circumstances.

Barry L. Werley[1]

Ideal Adiabatic Compression Traps[2]

REFERENCE: Werley, B. L., **"Ideal Adiabatic Compression-Traps"**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety***,** Self-published opinion*,* original publication 2002, public domain 2019, p. 29-36.

ABSTRACT: One way to configure distance/volume pieces in oxygen systems is as compression traps that "breathe" to reduce the quantity of hot oxygen produced near vulnerable system end points. Methods for understanding, designing and optimizing these devices are presented.

KEY WORDS: oxygen, oxygen compatibility, flammability, compression trap, adiabatic compression, distance piece, distance/volume piece, pressure wave.

Approximately-adiabatic compression is an often-cited cause of oxygen system fires. Among methods used to cope with it, oxygen compatibility practitioners seek to pressurize systems slowly, to choose materials with high ignition temperatures, to carefully heat-sink components against metallic materials, and to use distance/volume pieces (DVPs) [*1-3*][3]. One area that has been a focus has been polymer-lined flexible hoses, and the use of distance pieces has become common with them.

The purpose of the distance piece is to contain within a metallic section the hot slug of end-gas that forms during compression. Fig 1, Part A, exhibits a polymer flex-hose containing oxygen. In part B the oxygen initially in the hose has been compressed "as if by piston" into a 3500 psig (24.2 MPa) hot slug of oxygen at the flex-hose end point. This hot oxygen can cause ignition of the polymer. A distance piece adds a metal section at the end point to contain the slug, so that it is not exposed to nor soaks in contact with the vulnerable polymer hose lining. Part C exhibits a "single-ended" DVP on a flex hose that is pressurized in one direction only. Part D exhibits the final slug that is fully contained within the added metal distance-piece section. The final slug that forms is slightly larger than the slug formed in the hose alone in Part B, because it also contains the compressed oxygen that was initially in the added distance piece. Part E exhibits a flex hose that might be pressurized in either direction. Part F exhibits the final slug that forms for pressurization in one of those directions and it is contained within the distance piece on the respective end. The final slug is slightly larger than the slug that forms in Part D, because it contains the compressed oxygen that was initially in both added distance pieces, and for this reason, each of the double-ended distance pieces must be slightly larger than those for single ended use. These two DVP design strate-

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[1] No mailing address, archive copy.

[2] This paper was prepared for the Fall 2002 meetings of ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres on 10-12 September 2002 in Huntsville AL.

[3] Italic numbers in brackets refer to the reference list at the end of the paper.

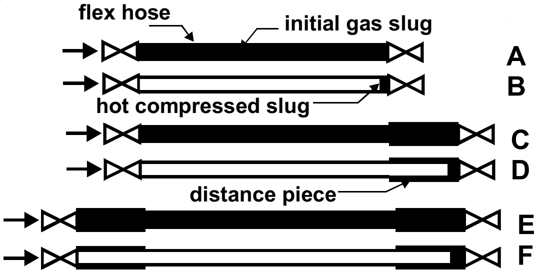

FIG. 1—*Distance/Volume pieces.*

gies (single ended and double ended) have been described [*3*].

The basic distance piece is ideally configured to protect the lining of an attached hose which is upstream of the distance piece. However, with the basic distance piece, a valve or other component may still be connected downstream of the distance piece and may contain portions of polymer seats or packings which are still exposed to the hot gas slug. To cope with this remaining hazard, one can reduce the effect of that hot slug by using "breathing" distance/volume pieces. Fig 2 exhibits a breathing DVP analogous to that of Parts C and D of Fig. 1. These devices have no flow through them, instead, they fill and empty, "breathing" as it were. These variations were first described in an earlier paper [*3*], and their design is to "trap" the majority of a compressed gas slug at a location removed from the end-point valve inlet, creating a region that is "temporarily downstream" of the polymers during pressurization. By minimizing the amount of the slug in proximity to the end-point polymer (assuming the valve inlet is of relatively small volume), they can be fairly effective and the available temperature, the duration of its exposure, and its heat transfer to the polymers can be reduced.

The concept of a compression trap is reasonable and plausible, and the writer would feel better about the compatibility of a system that incorporated them than for one that did not. However, there is no systematic study of the efficacy or optimum configuration for compression traps. Nonetheless, it is not unusual to apply theoretical principles to the design of oxygen systems where there is a dearth of hard data. Doubtless some component geometries have been used that could exhibit the compression trap effect, but there does not appear to be a published experience base that would be of use. So these breathing DVPs or "compression traps" will be explored in more detail than before. And an effort will be made to systematize and optimize their potential design. Hopefully, the collection of some practical test data can be inspired.

The temperature and distance piece or compression trap size estimates cited in this section and throughout the paper were made using the G-4 algorithm, G4Math, Version 1.1/1.2.

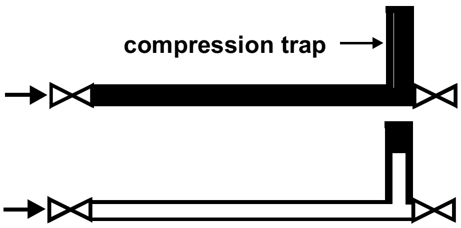

FIG. 2—*Basic compression trap.*

Distance/Volume Pieces Reviewed

The ideal gas model for adiabatic compression in a flexible hose equipped with a distance piece is reviewed in references [*1-3*]. Fig 3 exhibits temperatures produced by ideal adiabatic compression within a polymer-lined hose as a function of initial gas slug size. A simulated hose is shown above the graph which assumes there is no mixing of oxygen initially in the hose with the expanding incoming oxygen. The key points along the hose at which the initial slug achieves various temperatures (ignoring heat loses) are flagged. Note that these data indicate that for lower final pressures, the final slug size is larger but the final temperature is lower.

The hose shown in Fig 3 flags two key slug sizes. One is the point at 18.7% of initial size at which the slug achieves a temperature of 572°F (300°C). The other is the point at a final pressure of 3500 psig (24.3 Mpa) for which the slug is at 1.99% of its initial volume. These represent temperature-controlling (or TC) and final slug containment (or FSC) points [*3*]. Distance pieces used to contain these slugs would be arbitrarily slightly larger (20% has been used in examples to date) than needed to contain the hot slug. Note that a temperature-controlling (TC) distance piece would contain the final slug regardless of the final pressure, unless the final pressure is so low (less than 139 psig [1.05 MPa] in this case) that it would produce a temperature that does not pose a risk and would render a DVP unnecessary.

Compression-Trap Operations in Detail

In the preceding analysis, there may be an exposed polymer valve seat or packing at the very end of the flex hose and distance piece. The slug of hot gas is pressed against that area. Indeed, if a volume piece (a larger diameter vessel containing the same volume as the distance piece but typically less surface area) is used instead of the distance piece of Fig 1, then the hot slug is even more likely to concentrate and sustain heating of the seat region due to a reduced surface-area-to-volume. While the distance/volume piece is downstream from the hose polymer, the valve seat is still downstream from the distance/volume piece and is immersed in the hot slug. A compression trap, as shown in Fig. 2, adds additional volume that effectively parcels a portion of the hot gas slug into another, hopefully remote location.

Fig 4 exhibits the ideal dynamics of compression traps added to the basic flex hose of Fig. 3. This analysis is again based on the same ideal-gas, piston-like model typically used

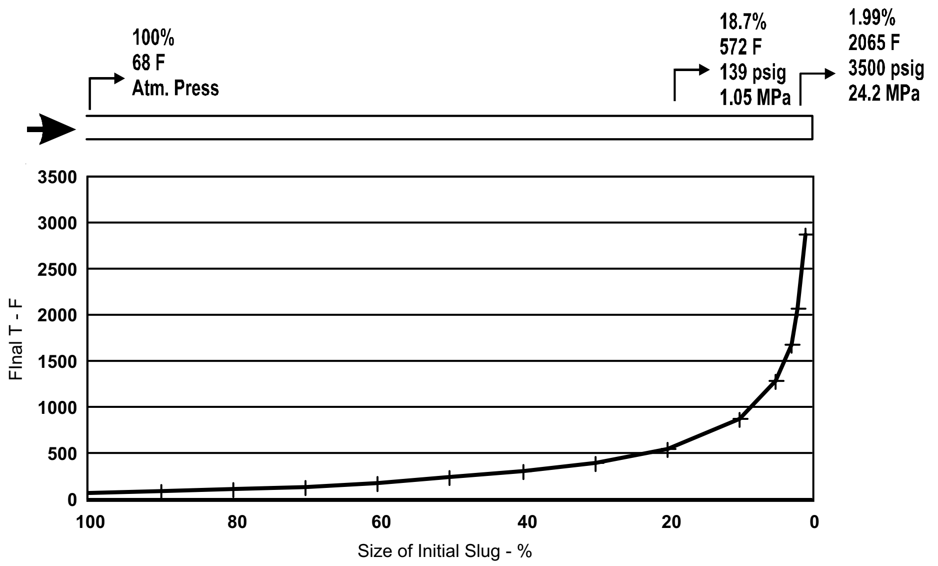

FIG. 3—*Slug temperatures during compression..*

for these analyses. Temperature-controlling compression traps should be more effective than final-slug-containment types, and they are analyzed first. Various theoretical temperatures produced during compression are indicated. In case A, a single-ended distance piece is shown upstream of the valve, which is taken to have negligible inlet volume. In the remaining cases, a "tee" is added to the end of the flexible hose and the end-point valve is installed on one branch and the compression trap on the other branch. Note that when the initial slug boundary has been compressed to the point of the Tee inlet, it is approaching (depending on the safety factor used) the control temperature of 572°F (300°C), which is the proposed [*3*] maximum transient temperature you wish a PTFE polymer hose to experience, and then it splits and simultaneously fills the two branches. In actual practice this split may be complex but in the ideal case, we will take it to be precise and proportional. The continuing flow compresses the two split fractions into the respective branches.

Figure 4 is intended to illustrate the effect of inlet volume in the endpoint valve. Any volume in the inlet may be counted as volume that helps protect the upstream hose and therefore as part of a distance piece, but it does not necessarily help protect the valve polymers. Fig 4 shows how the final ideal scenarios would exist if the compression trap volume were divided variously between the two regions: valve inlet and added compression trap. Note that the size of the high temperature slug that forms in the end-point valve would increase linearly with its inlet volume. However, in the preferred case, where very little volume is associated with the end-point valve (Case B), a trivial amount of the final high-temperature gas slug is present near the potential polymer seat. The ignition stress should be greatly reduced in that case.

Figure 4 qualitatively illustrates flow-splitting in single-ended compression traps and requires no elaborate math to select the most preferred implementation. It is the one that minimizes the size of the hot slug near the vulnerable polymer. In the case of a 30-in. (76-cm)

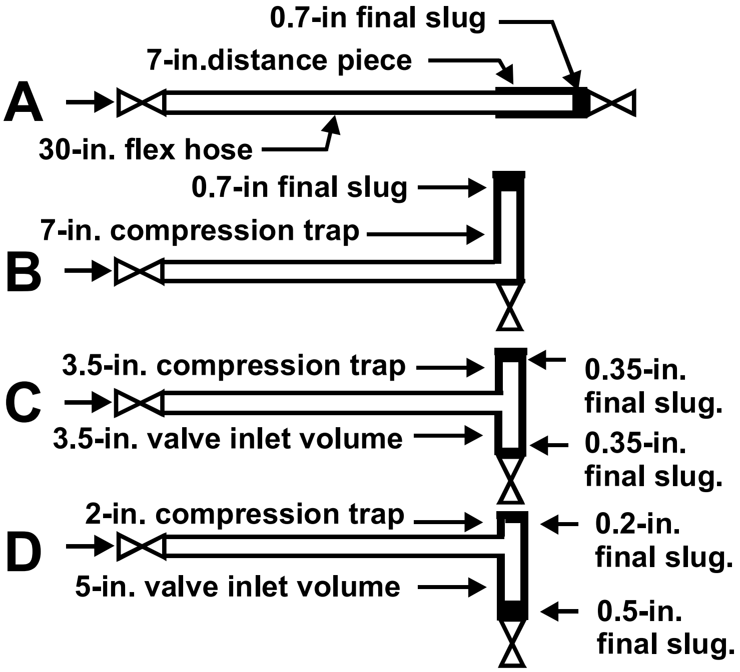

FIG. 4—*Compression traps including varying valve inlet volumes..*

flex-hose with a 6.9-inch (17.5-cm) compression trap (ignoring any safety factor), shown as 7-in., compressed to 3500 psig, the 0.685-inch-long (1.7-cm-long) high-temperature slug (Case B), shown as 0.7-in., that finally forms is buffered from the potential polymer site by a 6.3-inch (16-cm) slug of lower temperature gas, and this is the preferred case.

Secondary Benefits

In Fig. 4, Case B, additional mechanisms are operating to favorable effect. As drawn, the compression trap is above the flex line. Note that buoyancy of the hot slug would act to retain it at the top of the compression trap. This is desirable. Any smaller amount of hot gas formed near the end-point valve would attempt to “buoy” upward and away from the polymer seat. This is also desirable. In addition, because the compression trap is positioned above the flexible hose, it would not tend to accumulate particles that are prone to ignition. This is yet another desirable feature with regard to the compression trap (however, as shown, it would collect particles near the valve inlet, which is an undesirable feature).

If the positions of the compression trap and valve were reversed, all three of these effects would reverse and reduce the effectiveness of the device.

Normally, the empty volume which a compression trap represents would be discouraged in oxygen systems as an unnecessary sump or dead-end, however, if properly designed, these empty spaces can perform a sophisticated safety function.

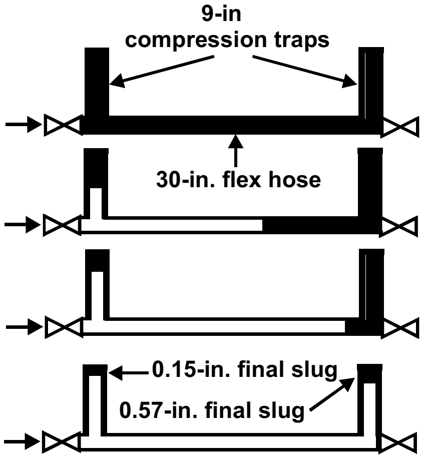

FIG. 5—*Double-ended compression traps.*

An Interesting Consequence

Fig. 1 exhibits distance pieces applied to a flex hose. Parts C and D are single ended and rapid pressurization occurs only from left to right. A 30-inch (76-cm) hose would require a distance piece nearly 7-in. (18-cm) long (nearly 9-in [23-cm] with a 20% safety factor) to protect the hose. Parts E and F are double ended and might be pressurized in either direction, mandating distances pieces on both ends. This results in DVPs nearly 9-in (23-cm) long (about 12-in [30-cm] with a 20% safety factor) on each end. The increase in length is because the presence of the distance piece on the opposite end results in a larger initial slug of oxygen. That is, a 9-in. (23-cm) distance piece upstream of the hose increases the total length by about 23%, and this demands an increase in the length of the downstream distance piece by about 23%. Therefore, the distance piece on the upstream end must also be the same larger size (if the final pressure in that direction is greater than 139 psig (1.05 MPa) as in the example). Remember that the size of the distance piece does not depend on the final pressure except to the extent that no distance piece is needed if the final pressure is below that which will produce the controlling temperature.

Now if double-ended compression traps were to be used with this 30-inch (76-cm) hose, it yields an interesting consequence. This is depicted in Fig 5. Note that in this case, as a pressure wave enters the line, there is an immediate division of the flow that occurs already at the first trap. The initial volume that is contained in the upstream compression trap is compressed into that very same trap. Then the pressure wave proceeds onward to the downstream compression trap forming a slug with the same amount of oxygen as for a single ended DVP. So in this case, the oxygen in the upstream compression trap does *not* add required volume to the downstream compression trap. Therefore, there is no need to use the double-ended distance-piece calculation to design the volumes needed for double-ended compression traps——they can be designed to the volume for single-ended distance pieces. In the case of 30-in. (76-cm) flex hoses this reduces the minimum volume (no safety factor) of the double-ended protective device from about 9-inches (23-cm) to about 7 inches (18 cm), a

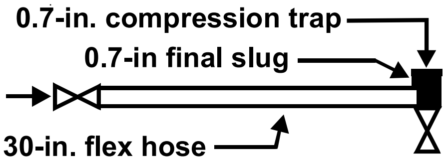

FIG. 6—*Final-slug-containment compression trap.*

23% reduction.

What about Final-Slug-Containment Compression Traps?

Recall that final slug containment distance pieces are sized only to contain the final slug volume plus a safety factor (and so far 20% has been used in example calculations—a value that has not been experimentally validated).

Fig 6 shows an analogous FSC compression trap (ignoring a safety factor). Clearly for this class of devices, the compression trap design offers much less benefit, as the slug does not form as substantial a distance away from the vulnerable polymer seat.

Indeed, if the pressure source is not at the design limit or if the pressurization is interrupted before the final pressure is achieved, then the final slug is larger and will not be contained fully in a distance piece or compression trap. This is why temperature controlling distance pieces are more conservative.

Alternative Designs

As drawn in earlier figures, compression traps appear as straight lengths of tubing that project upward from a flex-hose termination. Figure 7 exhibits additional configurations that might be incorporated into compressions traps to make them more practical.

In Fig. 7 Part A, the tubing is shown spiral-wrapped around the flex-hose termination. This geometry does not employ buoyancy as effectively as the other, but would be more compact and practical.

In Fig 7, Part B, a cylinder inlet fitting is modified to produce a flow-split very near the valve seat, minimizing valve inlet volume, and trapping the hot slug in an annular space in the inlet fitting. The farther the internal tubing projects into the inlet fitting, the smaller will be the effective valve inlet volume, but care would be needed to avoid impinging the flow directly onto the valve polymer that needs protection. The maximum practical available volume for this design might be limited.

Summary

The most basic principles and practices of using distance/volume pieces were reviewed. Breathing variants of these devices, herein called adiabatic compression traps, were exam-

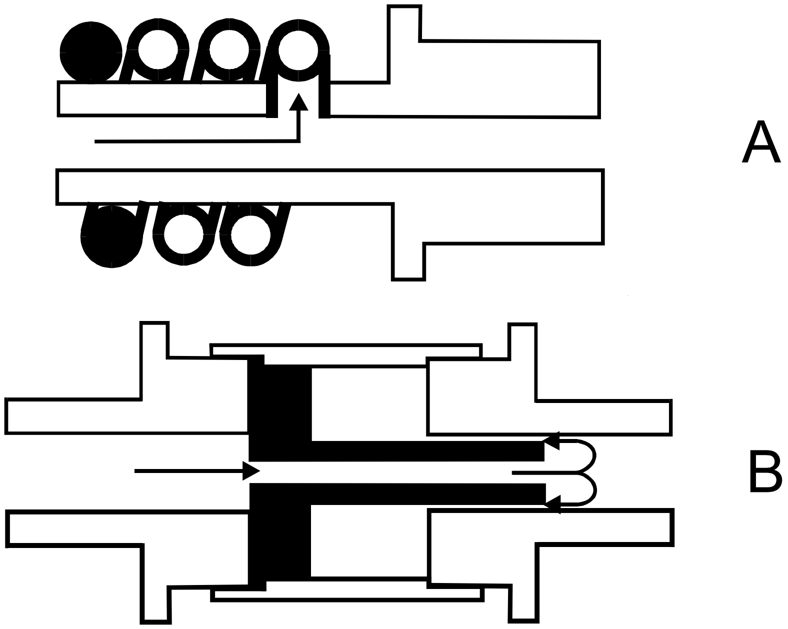

FIG. 7—*Alternative compression-trap designs.*

ined in greater detail than heretofore. Compression traps appear to offer comparable protection to upstream polymers and potentially good protection to certain downstream polymers as well. They do this by producing a transient downstream region into which a hot compressed oxygen slug can flow that is remote from the location of polymers.

In addition, double–ended compression traps have been found to be more economical in terms of size and contained oxygen than would be double-ended distance/volume pieces. Finally, the marginal benefits of final-slug-containment compression traps have been seen to be much less than those of temperature-controlling compression traps, which are therefore preferred protection.

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Barry L. Werley[1]

The Case for FLLAME[2] in ASTM G-4[3]

REFERENCE: Werley, B. L., **"The Case for FLLAME in ASTM G-4"**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety***,** Self-published opinion*,* original publication 2001, public domain 2019, p. 37-48.

ABSTRACT: As ASTM Committee G-4 contemplates the adoption of a standard on fire-limit specification and estimation, the key issues appear to be whether there is sufficient need and use for such a product within G-4, or whether it would be better situated in another committee. A proposed approach, FLLAME (Fire Limits for Linearly Afflicted Minds, Everywhere) is related to the specific G-4 needs, especially in other-than-gas-phase combustion.

KEY WORDS: Fire Limits, Flammability Limits

A proposal [*1,2,3*][4] to adopt a standard on fire-limit specification and estimation is before ASTM Committee G-4. The approach proffered, FLLAME[2], seeks to pattern fire limits after those used historically with gas-phase flammability limits, including but not exclusively, employing obscure ternary diagrams. However, whereas five fire limits tend to be published in the literature (upper and lower flammability limits in air or oxygen and minimum oxygen for combustion in air), the proffer seeks to designate all fire limits as minima or maxima of a wide range of possible threshold conditions. The proffer further cites applicability to fire limits in liquids, solids, or mixture of phases but does not cite examples of applicability in all these scenarios. Indeed, at present, FLLAME is in flux, seeking optimal notation, and may itself change significantly.

Committee G-4 and oxygen compatibility (OC) practitioners are familiar with the importance of gas-phase fire limits. The autogenous ignition temperature test (as with G-4's standard G 74) requires the achievement of a fire-limit concentration before a positive result can be obtained. Further, when easily dispersed contaminants (gases, liquids or dusts) appear in oxygen systems, they can lead to a gas- or mixed-phase incident if a fire limit is exceeded. The Committee's version of the oxygen index test (G 125) is also a form of fire limit.

Further, there have begun to appear in the Committee's symposium series, papers that include ternary diagrams that are best understood if one is practiced in their analysis. In 1997, a paper [*4*] related fire limits in mixtures of oxygen, nitrous oxide, and intestinal gases, and in 2000, a paper [*5*] offered a technique to compare the oxidizing nature of gases and

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[1] No mailing address, archive copy.

[2] Fire Limits for Linearly Afflicted Minds, Everywhere.

[3] This paper was published at the Spring 2001 seminar session of ASTM Committee G-4 on Compatibility and Sensitivity of Materials in Oxygen-Enriched Atmospheres on 28 March 2001 in Phoenix AZ.

[4] Italic numbers in brackets refer to the reference list at the end of the paper. .

gas-mixtures to air by employing gas-phase fire limits.

However, apparently few OC practitioner's have spent time estimating or applying fire limits, and especially interpreting them with the use of ternary, much less more advanced, diagrams. And few can visualize the need for such technology that has been principally used with gas-phase fires when the primary focus for OC practitioners is on solid or liquid materials that are used in oxygen hardware. Would such a standard be better housed in another committee (such as ASTM E-27 on Hazard Potential of Chemicals)? Is there a legitimate role for it within G-4? How does this approach apply to solids and liquids in oxygen systems?

Bases for Adoption Within G-4

A bottom line of sorts is that a fire limits standard is *not* crucial to ASTM G-4 at present. In the past, G-4 has managed without such technology and even without some technology much more nearly in its primary scope of activity. Furthermore, today, G-4 is quite comfortable using heat of combustion standards and LOX mechanical impact standards that are under the jurisdiction of other Committees. In two cases where outside standards (D 2512 on LOX mechanical impact testing and D 2863 on oxygen index) were in need of features for G-4's use, it either wrote related standards or actually imported other standards into its own versions. These were reasonable prerogatives to exercise.

There are a number of practical and technical bases for the adoption of a fire limits standard within G-4.

- Familiarity with fire limits and their use even for gas phases is an important ancillary skill to the oxygen compatibility practitioner, and there does not appear to be a good way to develop this skill. Transferring such a standard to another organization will not produce a needed learning step within G-4's ranks and is likely to result in a significantly protracted development cycle for the standard.

- Now and more so in the future, the basic tactics of fire-limit analysis may have significance to the thought processes applied within G-4, and when it becomes more commonplace, cross pollination may result from the deployment of this skill.

- The concept of fire limits (which are important in at least two of G-4's standards) is important to the safety of oxygen systems. The most conservative system is one that operates outside of it fire limits.

- Most importantly, as will be reviewed in more detail, below, ternary analysis does have a significant role in understanding fire limits in solids and liquids (and elsewhere) and whether these materials are acceptable in oxygen systems, and there is no adequate method at present of specifying these limits.

Liquid- and Solid-Phase Fire-Limit Data

In attempting to describe cases where the concepts of uniform-mixture fire limits are important to OC practitioners, it is first important to note that even for gas-phase analysis, the volume of data is not vast. The U.S. Bureau of Mines has published an appreciable amount of data for air-systems [*6,7*]. Recently, there appears to be some research into fire limits [*8,9*] being published. But many more data, specialized data in particular, would be welcome.

The concept of studying uniform mixtures of liquids, solids or mixtures of the phases enjoys very few data at all. It is understandable that the value of these analyses would be hard to envision when there has been negligible analysis like this done in the past. Presumably this is at least in part due to the few who use ternary diagrams for actual analysis. Therefore, one can only speculate on systems for which such analysis would be worthwhile *were the data to be available*, and hopefully, thereby, to help encourage it collection.

Liquid Mixtures

A scenario that the writer considers especially important to the oxygen producing and using groups, and that will be examined in some detail, is that of oil contamination in oxygen systems and the solubilities of oxygen and water in them. An important recent controversy focuses on the oxygen concentration of enriched air that requires hardware to be scrupulously cleaned. Some groups have argued special cleaning is not needed up to at least 40% oxygen concentrations and apparently have good safety records—much to the surprise and skepticism of many traditional OC practitioners.

In comparison, the oxygen-producing industry has experienced serious incidents at concentrations significantly more dilute than air. The new systems are not likely to be nearly as dry as traditional cryogenic oxygen circuits. Might this humidity thwart electrostatic ignition events? Might it prevent the absorption of oxygen? Might it dilute combustion in the fashion of Davy's Principle [*2,3,10*]?

ASTM G-4 has recently (1998, 1999) considered whether data are needed to appraise this hazard and in particular whether water is an important factor. This was inspired by a Compressed Gas Association Task Force (*11*) effort to understand the factors important to cleaning thresholds. Many incidents are attributed to hydrocarbon oil contamination in oxygen systems, but such events have not all been adequately simulated in lab tests and are not all understood. The oil contamination hazard appears to be fickle.

There are few fire-limit data available to lend clear insight into this issue, so only speculation can be offered as to how such data might appear and how they might allow important conclusions to be made about oxygen system cleanness and compatibility. This speculation will be focused on the prospect for a liquid-phase fire within the contamination of an oxidant system (and for which some incidents lend credence). Specifically, might oil become sensitized at some pressure after some period of soaking to produce some level of dissolved (incorporated) oxygen? If so might it then combust without need for oxidant in an adjacent gas phase or in a way that aggravates a fire with gaseous oxidant through evapora-

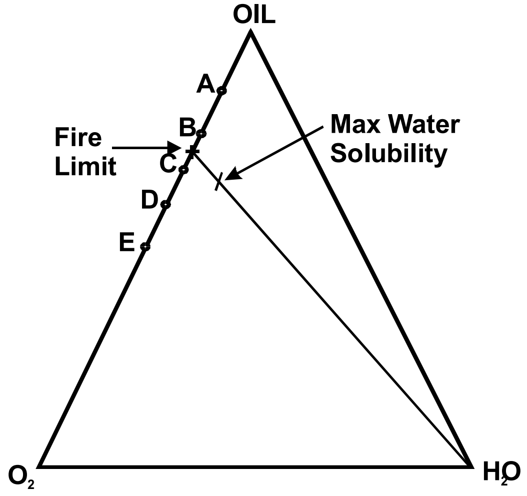

FIG. 1—*First ignition or fire point.*

tion or dispersal?

Lacking actual data, let's fabricate some hypothetical fire-limit data. Consider Figure 1 which is a ternary diagram with each respective apex representing pure oil, pure oxygen and pure water (fuel, oxidant and diluent, if you please). Oil that is introduced into an oxidant system would be expected to be pure and perhaps dry (top apex). If it is in contact with bone-dry oxygen for a period of time, some oxygen will dissolve into the oil, say to point A. The oxygen and oil will occupy the same volume as a mixture. If the system pressure is raised, the solubility would be expected to increase to, say, point B. Higher pressures might place the solubility at points C, D, E, etc. Perhaps at some point indicated on Figure 1 by a "+" sign, a liquid-phase ignition or combustion might be possible. Liquid-phase events are expected to be sensitive, very explosive (fast) and destructive.

From this plot, we would observe that at pressures less than those corresponding to the fire point, there is one less hazard present in a contaminated system. That is, below this pressure, liquid-phase reactions or explosions of the contamination would not be possible.

Fig. 1 also exhibits a line drawn from the fire point to the water apex. All mixtures of water with the fire-point mixture of oil and dissolved oxygen lie along this line. Since water is both a good heat sink and diluent and is noncombustible in this system, it is expected to interfere with and prevent combustion. Since the fire-limit point is considered to be an onset threshold, the increasing presence of water along the line to the water apex should prevent any respective ignition or combustion. In general, however, there is only a certain solubility of water in the oil/oxygen mixture and an arbitrary saturation point might be as indicated.

If the system pressure is raised, the solubilities of water and oxygen should both increase. Say the pressure is increased to the point corresponding to D. Since pressure tends to increase flammability, this point should again be above the fire limit (indeed, the onset point might be at a lower level also). In this case, Figure 2 shows a positive sign at point D, and a line drawn from there to the water apex indicates all mixtures of the oil/oxygen mixture at D with water. Since pressure tends to enhance combustion, in this case, D would be above a

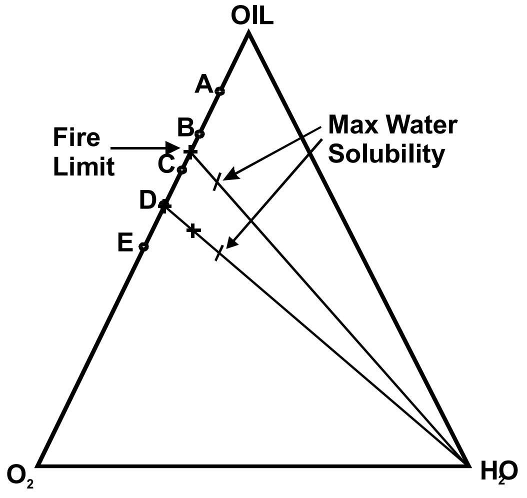

FIG. 2—*Fire limits at higher increased pressure.*

threshold condition. So as one adds water along the line from D, one would expect to find some flammable conditions at least at the lower water concentrations. If one moves far enough along the line to greater water concentrations, then sufficient water might ultimately prevent combustion. Let's assume that combustion is possible as indicated with the positive sign up to a point short of the indicated maximum water solubility. If this flammability threshold were to exist and to be *above* the maximum water solubility (that is, closer to the water apex), then clearly water could not be counted upon to thwart combustion in the system at this pressure.

Figure 3 exhibits the previous analysis for yet a higher pressure that represents point E. Here again the fire limit as indicated on the line from E to the water apex is taken to be less than the solubility of water in the oil-oxygen mixture, again since the reverse case would

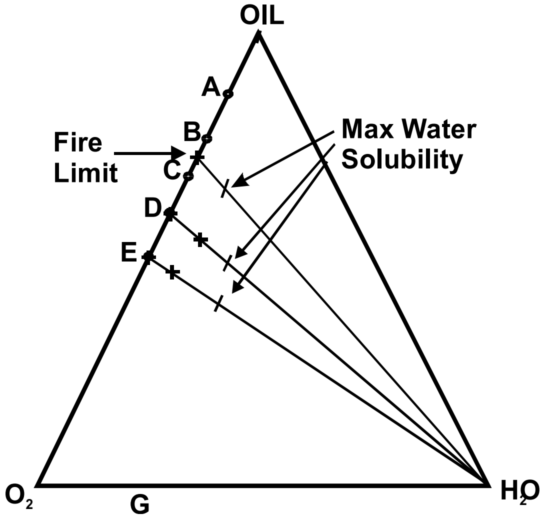

FIG. 3—*Fire limits at still higher increased pressure.*

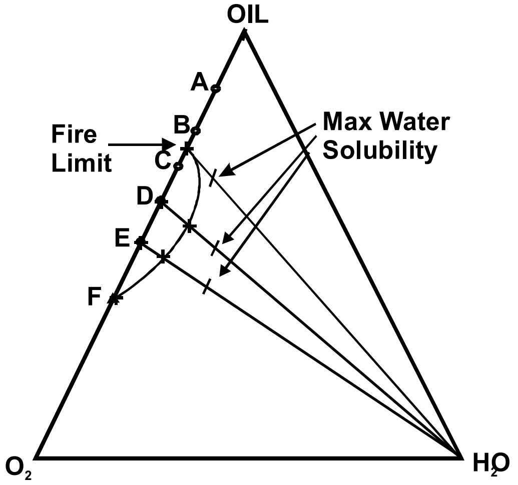

FIG. 4—*Fire limits at still higher increased pressure.*

mean that water is not protective (contrary to the starting hypothesis).

Remember that there is a limit to the amount of water that can be present, and it depends not only on pressure but temperature as well. Even if water is unable to thwart combustion, it might prevent electrostatic charge separation and ignition-producing sparks, or it may make adiabatic compression ignition less likely and so may be beneficial at reducing sensitivity (increasing compatibility).

If we repeat this analysis at many pressures, we might find (and admittedly this is speculation) that there is a fire-limit curve such as is shown on Figure 4. It is perhaps likely that this curve swings around ultimately and returns to the perimeter at (let's speculate) point F. If this fire-limit curve lies within the water solubility curve, then sufficient water vapor in the gaseous oxygen stream might prevent or reduce the number of some kinds of ignition or fire. Figure 5 shows a diluent metric, G, which indicates the maximum amount of water for combustion, which is the same as the minimum amount of water *to prevent* combustion. A related point, H, on the oxygen-water (bottom) side, represents a dissolved binary water/ oxygen mixture. A line drawn from this point to the oil apex is a metric that shows the maximum amount of water in the binary-mixture that allows combustion to occur, which is the minimum binary amount to prevent combustion in the oil film. If this equilibrates against or is less than equilibrium levels of water that are present in the oxygen product from membrane or PSA or water-doped cryogenic plants, then it may support the argument that some oxidant systems do not require extreme cleanness. But it all depends on the solubilities of oxidants and diluents in the specific oils in question.

Actual data are not available to conduct this analysis but hopefully will be measured some day. Note, however, that there is no parameter defined to specify the fire limits we have just speculated on if they should happen to exist. Indeed, one might also be interested in other fire limits indicted in Figure 6 by the #1 metric lines, the #2 metric lines, the #3 metric lines, or the dashed metric lines at the oil and O_2 apexes. These are all at different concentrations and their significance is left to the reader to contemplate. But the FLLAME approach

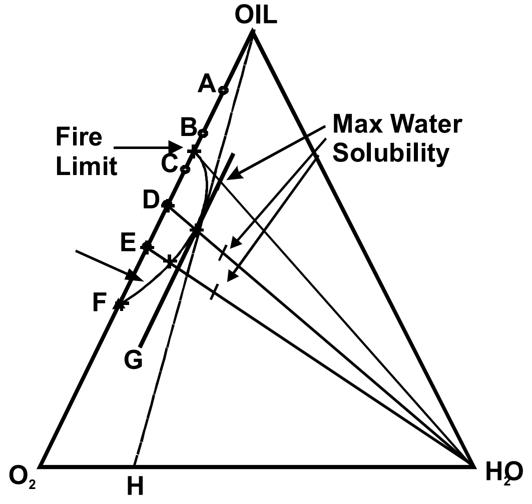

FIG. 5—*Pertinent O_2/H_2O binary fire-limit metric.*

provides a tidy way to define these numerous parameters that one might wish to reference relative to a system like this, including: Min oil/water (oil, water, oxygen), min oxygen (oil, water, oxygen), etc.

Very noteworthy is that "solubilities" in porous solid or cellular media would also be analyzed in the same way. Indeed, when standard fire tests (autogenous ignition temperature, oxygen index, etc.) are conducted on some of these materials, the achievement of conservative results may dictate that they be soaked in dry oxygen for protracted periods at use conditions or at elevated pressures to saturate them with oxygen or deplete them of other materials. At present we do not know the most flammable internal conditions of most liquid and solid materials.

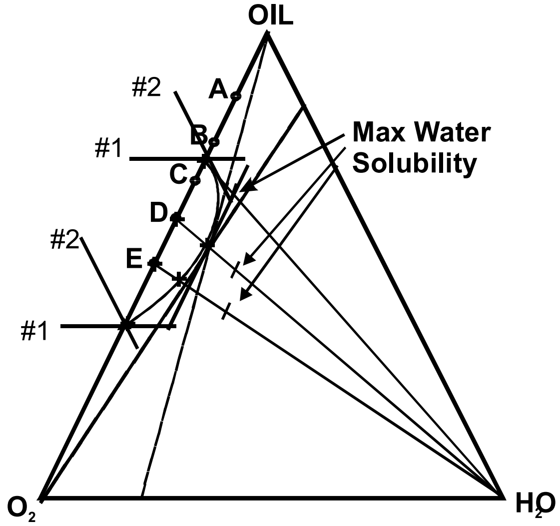

FIG. 6—*Assorted pertinent fire-limits metrics.*

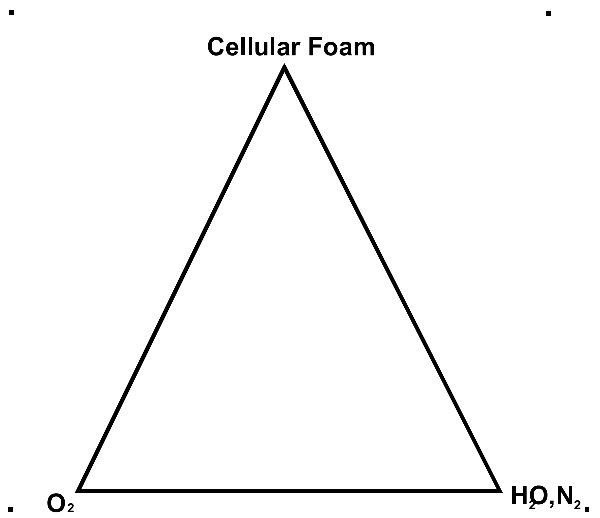

FIG. 7—*Potential ternary field for cellular foams.*

And let us not forget that if water is a protective constituent, one can not rule out the prospect that newly prepared oils or polymers may contain fractions of water or other active materials. Delayed reactions that are sometimes observed in oxidant systems after days or months or even years may be a consequence of these materials diffusing out of a material (drying is an aging mechanism!) as much as due to deterioration mechanisms.

Cellular Materials

The OC community has long been concerned with porous materials in oxidant service. In particular, cellular foam insulation, especially in cryogenic service has been an issue for decades. Cellular foams in LOX are justifiably feared. Is an open cell foam in liquid air service also a risk? What about in intermediate concentration mixtures?

A cellular foam that contains a gas or liquid oxidant is a reasonably uniform binary mixture. When in combination with perhaps an oil coating in the cells or when a diluent is in the cells or added to the gas or liquid oxidant, this becomes a ternary or even quaternary system which exhibits fire limits that are analyzed and exhibited with systems similar to FLLAME and its planned successors. In each of these cases, the materials may be viewed as occupying the entire volume of the material. Fig 7 exhibits a field on which data like those in Figs 1-6 might be plotted for cases with cellular foam.

Based on the works of Hokkanen [*12*] and others, one can only speculate what a fire map for a cellular foam might look like. However, the writer is aware of incidents involving oxidants and foams that have circumstantially produced combustion ranging from negligible propagation, to fires, to highly destructive detonation. Ternary or higher analysis promises understanding of these events, if data are pursued.

Indeed, a 1998 article [*13*] describes curing polymers into which oxygen gas has been sparged at 21 to 210 atmospheres to produce a foam upon cooling. This resulting "solid" is then used as a solid fuel for amateur rocket enthusiasts with a specific impulse approaching

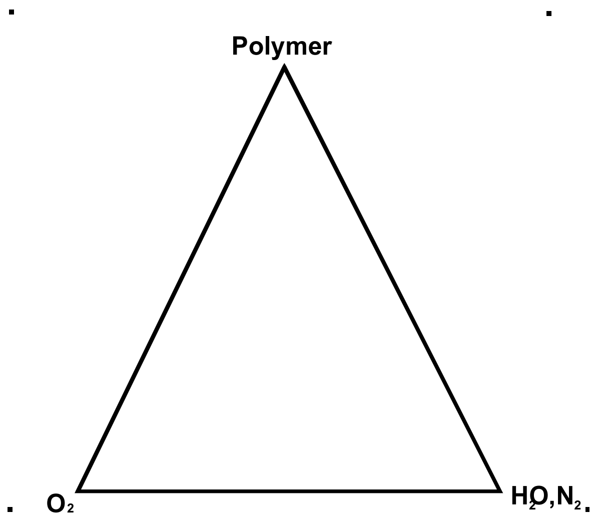

FIG. 8—*Potential ternary field for a polymer.*

that of the Space Shuttle boosters. A ternary plot would be the appropriate approach to determine the tolerable fractions of diluents that would be present in the oxygen gas used to prepare this material, therefore the required amounts to prevent the combustion prospect. OC practitioners should contemplate that if oxygen bubbled in large amounts into a material can produce a monopropellant, that it may produce varying degrees of altered compatibility in lesser amounts. This lesser effect would be best assessed with a FLLAME-type approach. Remember that as with many gas phase mixtures, small amounts of oxidant can facilitate combustion in combination with other influences. As oxidant content crosses a fire-limit, self-sustained combustion becomes viable, and as content approaches stoichiometric levels, increasingly fast or explosive fires are typically possible.

Solid Mixtures

Papers [*14, 15*] have discussed the "swelling" nature of FKM polymers. These polymers have been likened to a sponge, soaking up gas either in pores and/or solubility. Indeed, internal "capacity" can be assessed in part by soaking them at pressure which allows them to incorporate oxygen and perhaps approach equilibrium with the external pressure, then suddenly depressurizing them and measuring the apparent transient volume gains as they "blow up" like a balloon. In some cases, very rapid depressurization (called explosive decompression) of very porous or soluble polymers can cause rupture which at one time was speculated (and does not appear yet to be proved) to be an ignition cause.

The polymers, after processing, initially contain gases unlikely to be oxidants in their structure, and internal pores may be coated with variable amounts of polymer-processing liquids (such as plasticizers) or contaminants such as oils. These pores can not be cleaned in any practical way. There are no data as to how quickly oxygen diffusing into the polymer allows the concentration in pores to approach pure oxygen or even any applicable fire limit concentration. Such combinations of polymer, contaminants, oxidants and diluents can represent uniform mixtures, and each of the materials may be viewed as occupying the entire

TABLE 1—*Potential elements of a nongaseous ternary or quaternary analysis.*

F Fuels	O Oxidants	D Diluents
1. Cellular matrix (foam insulations) 2. Oil contamination	1. LO 2. GO	1. LD 2. GD 3. Foaming gas 4. Moisture
1. Polymers 2. Processing Chemicals	1. LO 2. GO	1. LD 2. GD 3. Processing Chemicals 4. Moisture
1. Oil 2. Contaminants	1. LO 2. GO	1. LD 2. GD 3. Moisture 4. Inert powder
Fines accumulations (Dusts) (Powders) (Particle layers) Contaminations	1. LO 2. GO	1. LD 2. GD 3. Moisture 4. Inert powder

LO-liquid oxidant (e.g. O_2), GO—gaseous oxidant.
LD—liquid diluent (e.g. N_2), GD—gaseous diluent

volume of the polymer. A ternary one might use to plot these data is shown in Fig 8

The writer has knowledge of hardware that contained FKM polymers as the only nonmetallics, and that apparently experienced surprisingly brisant fires, rupturing and bulging components. Such reactions are usually consistent with a fast combustion typical of uniform mixtures. These incidents were not adequately reproduced in laboratory tests at the time, perhaps because the test polymer was not saturated with oxygen (or other quantities in the right amount) or did not contain the appropriate pores or solubility for attainment of a fire-limit condition. These incidents were not consistent with what one would expect of polymer fires based on existing property test data, deliberate ignition simulation, and OC evaluation techniques. Could certain polymers cross a fire limit at some pressure, pore size, soak period, temperature, etc., to become a rather explosive, perhaps sensitive, mixture?

Oxygen, contaminants and diluents distributed throughout the structure of a polymer *can* be treated as a uniform mixture (because it is one) suitable for analysis as a ternary or even quaternary fire system. In fact, even if the dissolved amount does not approach stoichiometric or even a fire-limit condition, it is known that threshold conditions for polymers burning in gas oxidants are altered substantially by temperature. If a low level of incorporated oxidant reacts and helps to warm a polymer during an ignition and approaching fire, then it may lower the threshold condition and alter the oxygen compatibility.

Accumulations of Fines

A tenet of OC practice is to avoid high surface-area-to-volume materials. This includes sharp edges, small particles and especially accumulations of particles, powders and dusts. Carbon granules [*16*] have been tested and found to be intense, unstable (meaning unpredictable) high explosives in combination with liquid oxygen. Nonetheless, their hazard in an oxidant system, depends upon other powder and or diluents that may also occupy their entire superficial volume along with the other considerations of particle size distribution and the like. Again FLLAME-like analysis is the appropriate hazard-evaluation technique.

Summary and Conclusions

Which came first: the chicken or the egg? ASTM G-4 faces a similar dilemma. Should it develop fire-limit specification and analysis technology and wait for data to become available? Or should it collect data to be later evaluated when fire-limit technology becomes available? Or neither?

ASTM Committee G-4 may have little practical experience with the use of ternary analysis, but it is unlikely there is any other organization that has labored with it to the point that their experience would greatly facilitate the development of a fire-limits standard pertinent to G-4. OC practitioners may encounter a number of fire-limit scenarios, several as detailed here and summarized in Table 1, that are unique to the oxidant safety field and would be unlikely to be addressed early in the development of such a system by any other committee. And finally, ASTM G-4 has shown a remarkable ability to implement the standards process efficiently.

The use of ternary analysis is applicable to G-4's interests (including for solid and liquid materials) although a shortage of data limits such analysis at present. This is not new to G-4, which developed numerous standards in the past before there were data to analyze.

However, it must be admitted that a fire limits standards is largely a forward looking initiative. Since the raw data to perform the analyses needed are not in existence, one can only hope that perhaps increased sensitivity to the data need would surface when the facility (technology) for the analysis is present and the consciousness of the OC community is raised.

A fire-limits standard would be a substantial effort for ASTM Committee G-4. Beyond that, G-4 may be entering a period of diminishing returns on its efforts. Many of the historically practiced compatibility tactics have been documented and studied. Doubtless these were the highest priority, but they were most likely also the easiest cases. However, some hazards and incidents are still unresolved. Solving these may require more difficult analytical techniques that require greater efforts than in the past. The approaches of FLLAME or derivatives of it may or may not enable understanding of some of the erratic, currently unexplained incidents, but it is a reputable effort that appears to address problems not presently being addressed.

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Barry L. Werley[1]

Technical and Human Factors Affecting Special Cleaning of Oxidant-Rich Systems[2]

REFERENCE: Werley, B. L., **"Technical and Human Factors Affecting Special Cleaning of Oxidant-Rich Systems "**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety*, Self-published opinion*,* original publication 2007, public domain 2019, p. 49-64.

ABSTRACT: Data pertinent to contamination fire hazards thresholds for ignition, propagation, and consequence are considered as a function of oxygen concentration. Most current criteria for threshold concentrations of special cleaning appear to be based on jurisdiction and caution more than on precise hazard thresholds. Research into the effects of moisture and liquid phase flammability is encouraged and might yield better understanding and increased latitude in the cleaning of oxygen systems. Improved fire-limit interpretation techniques are also needed.

KEY WORDS: Special cleaning, oxygen rich, oxygen enriched, oxygen compatibility

Special cleaning has long been associated with oxidant-rich hardware. For many years and for many systems, special cleaning was the only specified safety precaution. And indeed, even in today's much more advanced technology, whenever any precautions are taken at all, scrupulous cleaning is *always* one of them, and is always one of the most important.

As a result, virtually any group that has confronted the issue of oxidant safety has of necessity confronted the issue of when cleaning becomes a requirement. At what oxidant concentration? At what pressure? To what degree? Fortunately, as would be expected and hoped, almost every group that asserts an opinion, has adopted similar (but not identical) criteria.

However, in the 1990s, an emergent group, the recreational diving industry, adopted considerably different and novel practices for oxygen-enriched breathing-gas systems than were commonly observed. These differing practices were doubtless driven in part by the economy achieved by less scrupulous cleaning, such economy of which can be substantial. This led many in industry, government and others to re-examine there own opinions about special-cleaning thresholds and to defend their practices. Various correspondence contemplated the differing practices, and the Compressed Gas Association launched a Docket 96-86 to explore it. The Docket, in turn, launched a Task Force to study the basis for establishing

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[1] No mailing address, archive copy.

[2] This paper was prepared for the author's former and now defunct web site.

such criteria and make a recommendation to the CGA.

The 96-86 Task Force was initially chaired by the writer until his retirement in 1999 and contained members from a spectrum of companies. Its charter was to consider the experiential, theoretical, and experimental bases for adopting threshold criteria. The majority opinion among old-guard practitioners of oxidant safety was that the emergent practices were too liberal. However, if the emergent practices could somehow be validated, that perhaps then the economies could be exploited in other systems as well.

The Task Force surveyed and interviewed numerous old-guard practitioners (in industry, government, military and academia) as to what their internal criteria were and why. It also conducted a literature search for incidents, standards, and experimental data, and it speculated on open issues. It kept ASTM Committee G-4 apprised of its efforts and solicited its input.

Ultimately, the CGA published a position statement (PS-13) in the early 2000s (revised in 2007). The writer has not seen the final product but late drafts of it were largely consistent with traditional practices, which are deemed conservative. Most criteria like this do not elaborate on the bases for the position taken.

And that leads to a subplot for this paper dealing with the human factors involved in adopting technical practices such as the full body of CGA and ASTM G-4 work. In the mid 1970s, the writer bought into the practice of justifying safety (among other) technology practices, which prescribes the documenting and publicizing of bases for all positions and practices. The writer has been a harsh critic [*1*][3] of standards and especially codes that do not defend their bases and are not open to examination. In that spirit, this paper recapitulates, revises, and updates the technical data and some of the human speculations that were a part of the CGA Task Force early effort and attempts to elaborate upon them and give them an improved context.

A part of this subplot is a proposal to ASTM G-4 in 2000 that went wrong. The writer sought back then to pursue a standard on defining and estimating fire limits in homogeneous mixtures to be supported with a computer utility for making such estimates from empirical or theoretical data. ASTM G-4 (among others) declined such effort citing as bases the complexity (and it is a complex subject that is poorly documented), lack of energy, and lack of pertinence to the oxygen compatibility subject (the latter disputed by the writer [*2*]). The subject of defining and assessing the hazards of cleaning threshold concentrations is a powerful example of why ASTM G-4 and oxygen safety practitioners need both this knowledge and capability.

Justifying Safety Technology

Even if there are many settled oxidant safety practices, oxidant compatibility is by no means settled science. The foundations for many oxidant safety practices are surmised, based on "what has always been done", "what has worked", and 'what is probably going on." Today, ASTM G-4 does far better at justifying safety than most. It includes numerous technical notes in its standards and cites extensive references, and many of its standards are based upon and buttressed by a significant public body of technical analysis and discussion in its own series of oxygen safety publications: *Flammability and Sensitivity of Materials in Oxy-*

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[3] Italic numbers in brackets refer to the reference list at the end of the paper.

gen-Enriched Atmospheres, Volumes 1-11.

The ASTM body of work is impressive but there is no concerted effort to provide a basis for each and every criterion or design principle that the Committee advocates—an effort that would be well undertaken.

The argument to justifying safety is that those who manufacture, design, use and operate oxygen systems will better fulfill their duty if they know the significance of each task, each rule. There are many historical incidents that could be cited to exemplify the philosophy. In the writer's case, his first exposure involved an incident in which a small chemical plant was lost when the operator failed to realize the relative critical nature of certain of his duties. While diligently performing some required functions, other functions went haywire and were not monitored nearly as closely as needed. There is a big difference between controlling a valve *because failure to do so will cause an explosion or fire*, and failure to maintain a clean workspace *because failure to do so may cause slips and falls*. The writer could try to make a case (on the basis of reports in the perhaps too-often unreliable news media) for the NASA Challenger incident being in this same category. While the hazard was known to some, and while some were diligently doing their duties, some didn't perceive or didn't know the critical nature of other events. And finally, the writer would certainly cite the National Highway Traffic Safety Administration (NHTSA) and its abominable stewardship of car safety in the United States as a grievous offender but has already elaborated on them elsewhere.

And so for a time, the writer worked in an environment and contributed to a philosophy that no safety rule should be prescribed without giving a basis for it. And in cases where guesses are being made in a data vacuum, even knowledge of that can be valuable.

This paper will attempt to overview some of the issues of oxygen concentration thresholds above which special cleaning is needed against the perspective of the literature review assembled for the CGA Docket 96-86 Task Force. It will examine traditional practices and the controversial differing practices and try to defend and support both. It will seek to provide the writer's opinion (his speculation) of the bases for cleaning recommendations such as the CGA PS-13, ASTM G 94 and others documents, although only the originating sources could correctly and properly do that, and perhaps they will choose to offer their own commentary on portions.

Oxygen Concentration Cleaning Thresholds

ASTM Standards itemize numerous bases by which one might adopt specific oxidant safety practices, including:

- Whether a fire can occur at all
- The probability of ignition being acceptably low.
- The consequence of a fire being tolerable

The most conservative approach is to operate under conditions where fire is not possible, that is outside of the fire limits, and this is used whenever realistic. But often it is not. Indeed, the largest amount of engineering material on a mass basis in oxygen applications is that of pipelines which are almost exclusively made of carbon steel which is usually capable

TABLE 1—*Examples of Cleaning-Threshold Criteria Circa 1998*

CGA G-4.1	Clean for oxygen	Clean for oxygen as specified in G-4.3
CGA G-4.3	Oxygen specification	Oxygen is in the high 90% range.
CGA G-4.4	Piping for oxygen	Oxygen is >23%
CGA G-4.6	Oxygen compressors	Oxygen is >90%
CGA G-4.7	Electric LOX pumps	LOX is >95%. Care needed at 25% to 99.5%.
CGA G-4.8	Structured packing.	Incidents are all at >99.5%
CGA G-4.9	Heat exchangers	Applies to 80% to 99.9%.
CGA P-8	Working atmospheres.	Safe at 19%-23% oxygen.
CGA P-14	Accident prevention.	O_2 enriched is >23% or >175 torr partial pressure.
CGA P-25	Flat bottom tanks	O_2 enriched is >23% or >175 torr partial pressure
ASTM G-4	All standards	O_2 enriched is >25%.
NFPA 53	O_2 enriched atmospheres	O_2 enriched is >21% or >160 torr partial pressure.
NFPA 99	Healthcare facilities	O_2 enriched >23.5%
NFPA 99B	Hypobaric facilities	O_2 enriched >23.5%
US DOT	Oxidizing NOS mixtures	O_2 >23.5%
US OSHA	Confined spaces	O_2 >23.5% is hazardous.
US OSHA	Commercial diving	Oxygen service is >40%, clean of flammables.
EIGA 33/86	Cleaning Guideline	Clean for oxygen and mixtures with O_2>25%

of combustion if ignited. However, practices have been developed to limit the probability of steel ignition to acceptably low levels in many cases and to a low consequence in others.

Historically, most oxygen safety practitioners have applied special cleaning to most oxygen-enriched systems. Some elected to specify cleaning of simply oxygen-enriched air, while most specified cleaning at enrichment levels beginning at from 23% to 25% oxygen. These were apparently all single-sided criteria. That is, cleaning was required above the threshold, but it was not intended to exonerate systems below the level from any cleaning. Indeed, many systems can experience fires, and indeed, numerous incidents have resulted in systems exposed to actual air and sub-air oxygen concentrations.

What Are the Pertinent Data?

CGA Task Force 96-86 searched the literature in the late 1990s and found numerous valuable information. Numerous documents cited thresholds of their own applicability that defined and distinguished "oxygen" from other gases in terms of purities near 100%. Some defined thresholds of applicability for oxygen without being specific to cleaning thresholds. And some were explicit as to when special cleaning was needed. Table 1 lists clear thresholds that were identified, some of which affect cleaning.

However, these thresholds are not typically predicated upon the exact boundary at which fire or ignition is possible, nor separated from it by either a safety margin or safety factor. In the writer's experience and view, these are largely based on jurisdiction. These may all be based on the existence of the fire hazard at the lowest level of some jurisdictions. In the case of the ASTM Committee G-4 criteria, a major factor was the desire to concentrate on oxygen enrichment and to avoid addressing air systems. However, some are based on incidents that might happen in some equipment without exemption for other similar equipment at similar conditions that might not experience the same hazard. That is to say, a more conservative approach was taken with cleaning than was taken for other thresholds that define fire hazards resulting from polymers or metals.

Test Data

The following literature is a subset of the literature reviewed by the CGA 96-86 Task Force, as prepared originally by the writer, thinly revised and in some cases expanded.

Burgoyne and Craven [***3***] treat a primary hazard of air systems as when an oil film is removed from a surface and either dispersed or vaporized with the air. Mechanical effects (flow and shock wave) may remove the film. Adiabatic compression or other heating may vaporize the film.

They appear to apply the traditional approach used with lower fire limits for hydrocarbon fuels which finds that the limits for a wide range of hydrocarbons is at a constant heat loading and temperature, and because most hydrocarbons are basically chains of two hydrogen atoms for each carbon atom, the limit is at a near-constant density of the fuel in the oxidant gas.

This is equivalent to saying the oil achieves a fire limit when:

$$t = CDP/4d \qquad (1)$$

where: t = film thickness; P = absolute pressure in atm; C = min. weight of oil per pipe volume at the oil's lower flammability limit at one atmosphere pressure in g/m^3; D = pipe diameter in m; and d = oil density in g/m^3 .

Since thorough mixing of a dispersed or evaporated oil film would be more likely to occur in smaller tubing than in larger pipes, this formula appears to be more appropriate to smaller inside diameters (providing they are not smaller than the quench dimension). If evaporated oil were to be concentrated near the wall of a large pipe, it might yield an envelope of flammable mixture in the affected sub-volume at lower than apparent bulk or average fire limits that might be predicted with this equation for a uniform mixture.

Presti and DiSimone [***4***] rapidly compressed oxygen into oil-coated dead-end pipes. Their work suggests that an incoming pressure wave might strip oil from piping and transport it to the dead end, yielding a greater concentration locally than would be calculated based on average bulk conditions. Even though their work suggests fires are possible locally at conditions below those predicted by the equation in Burgoyne and Craven, their work also appears to support the notion that the oil may burn only when it has been removed from the surface by mechanical gas actions or evaporation rather than through liquid-phase reactions.

Ignition temperature can decrease with increasing oxygen concentration. Hence enriching a system may enable a fire and explosion due to oils or contamination that was not possible before, but this effect is not addressed and may be small.

Werley [***5***] ignited oil films applied to thin vertical brass substrates at atmospheric pressure in oxygen/nitrogen concentrations near that of air and at oxygen-enriched levels. The combustion observed was local and candle-like and slowly moved along the surface.

Loison [***6***] studied two air compressor incidents and conducted related experimentation. He passed heated atmospheric-pressure oxygen or 100-psig air over oil. The hot oxygen led to spontaneous heating of the oil at approximately 150 °C to 160 °C (300 °F to 320 °F). Spontaneous heating occurred as low as 137 °C, and flaming combustion occurred as low as

151 °C. Flow rate was significant in limiting the self-heating.

Loison also studied air in contact with oil at room temperature and 100 psi. These test cases employed hot-wire ignition with a localized gaseous fuel/air or fuel/oxygen-enriched air mixture. Fuel air ignition led to extensive combustion and fuel/oxygen-enriched air ignition led to massive damage.

Perlee and Zabetakis [*7*] studied causes of ignition. They concentrated on the work by Loison and many others and review it, and they conclude that ignition and explosion in compressed air systems at pressures at least as low as 100 psi were most typically caused by combustible vapors resulting from the presence of oils. The cause of the vapor production and the vapor/oil ignition was less certain and almost certainly the result of several mechanisms.

These authors cite and examine:

- Oil vapor or mist abruptly introduced into a system as a result of seal or other failures.
- Exothermic decomposition of oil to produce spontaneous heating of oils.
- Oil decomposition to yield volatile constituents.
- Iron oxides that can catalyze oil reactions.
- Removal and dispersal of oil into a flammable state by shock waves.
- Prevention of air compressor fires and explosions by periodic cleaning and re-cleaning.

Coward and Jones [***8***] and Zabetakis [***9***] are time-honored references on "flammability limits" which this writer prefers to call “fire limits”. Traditionally experimentation and publication has focused on the lower flammability limit (LFL), the upper flammability limit (UFL) and the minimum oxygen for combustion (MinO_2). However, fire limits can be arbitrarily defined in many ways. The lower and upper limits vary the amount of fuel in an oxidant and seek to identify the lowest and greatest amounts, respectively that just allow a fire. The MinO_2 is defined much more subtly. To measure MinO_2, they vary the amount of oxygen in a two component mixture with a nonreactive gas, then test various mixtures of that two-component mixture with a fuel, and the MinO_2 is the minimum amount of the oxygen *in the two-component mixtures* that will just allow a fire for *any* mixture with the fuel. The MinO_2 is **not** the amount that is present in the three component flammable mixture including fuel and is numerically larger.

This definition is consistent with the parameter of interest regarding special cleaning needs. In the case of enriched air, one is interested in how much oxygen can be present in the (basically) two-component oxygen/nitrogen mixture that may pose a fire risk regardless of the oil or contamination that may be present in a system.

Fire limits will generally widen if the temperature or pressure of a system is raised. However, at room temperature and atmospheric pressure, simple hydrocarbons (namely the paraffin's, all tend to have lower flammability limits near 45-50 ml/l (but there are important exceptions, see Zabetakis [***9***], p. 20).

Early theories on fire-limit behavior are reviewed in Zabetakis, Lambiris, and Scott [***10***] and among the earliest is that the lower limit is fixed by heat liberated by a mole of lean-limit mixture (which is nearly constant for many mixtures), to the later perspective that the adiabatic flame temperature of lean-limit mixtures is approximately constant.

TABLE 2—*Oxygen Concentration Threshold Versus Pressure* (Benning [*14*]) and Ikeda [*12*]).

Material	Oxygen Index
Polyacetyl	14.7
Polypropylene	17.6
Poly(methyl Methacrylate)	17.7
Silicone Rubber	21-32
Buna N	22
Nylon 6	24
Polycarbonate	27.4
Poly (vinyl chloride)	38.1
Vespel	53
Viton	56-100
Polytetrafluoroethylene	100

The correlation between the pressure of an oxidant gas and the spontaneous ignition temperature of two oils is reviewed by Zabetakis, Scott and Kennedy [*11*]. This suggests oils not only have wider limits at higher pressures, but pressure may also make them easier to ignite.

Solid materials also exhibit a minimum required oxidant concentration in the gases they can burn in, defined as the oxygen index. Ikeda [*12*] reviews some of the experimental data, and Werley [*13*] reviews the correlation between the MinO_2 measurements for mixtures and blended gas streams. The lowest polymer oxygen index among those Ikeda reports is 14% for polyacetyl. Many polymers will burn in air and most will burn in less than 30%. Only a few require concentrations approaching pure oxygen or resist burning even there.

Table 2 exhibits the data presented in the CGA 96-86 Task Force report. When pressure and temperature are increased, polymers, like gases, become easier to burn (Benning [*14*] and Ikeda [*12*]).

Benning [*14*] reports that polytetrafluoroethylene (PTFE) experiences a decrease in index from nearly 100% to about 50% as pressure approaches 300 psig.

Metals also exhibit oxygen concentration limits, and among those that have been studied, the limits decrease with increasing temperature and pressure much as for polymers. In the case of carbon steel, Benning and Werley [*15*] report that that the oxygen concentration threshold in mixture with nitrogen fell from about 80% at about 1 MPa (132 psig) to about 50% at 8-20 MPa (1000-3000 psig).

A First Speculation

The CGA 96-86 Task Force confronted two speculations dealing with dissolved oxygen in oils and the role of moisture (the latter to be covered later).

Flammable liquid mixtures are always a concern. Often owing to their densities, they can exhibit exceedingly fast reaction and often fall into the category of “high” explosives. Among the materials in this category are granulated frozen or fine structured solid material in liquid oxygen, which can be awesome, sometimes erratic, explosives. The more uniform the mixture, the more explosive these materials tend to be.

What if oxygen gas were sufficiently soluble in oils at elevated pressure to pass through a fire limit condition? And if such a condition were possible, how long would it take to come to saturation? In some cases, incidents in oxygen cylinders have happened after long periods of time. Could a long dissolution time explain the delay?

However, most literature seems to suggest (perhaps unintentionally) that an oil contamination must become dispersed before a fire is possible. These analyses take the tack that the oil must filter into the oxygen and raise its fuel concentration above the lower flammability limit. In comparison, oxygen diffusing into a liquid oil would have to raise its oxygen concentration through the limit for a "fuel-rich" fire (that is, through the upper flammability limit from above).

At first blush, this is curious. For many hydrocarbon gases, it requires only a few percent of fuel in air or oxygen to achieve the lower fire limit, whereas it requires much greater addition of oxygen into gaseous hydrocarbons to achieve the upper limit. However, as pressure and temperature rise, both limits widen. Also keep in mind that in the condensed state the density of most materials is hundreds to a thousand times greater than for the gas. This increased density will render an oil film fire to be much more adiabatic (much less likely to have radiation escape for example) than would be the case for a gas-phase fire. This is to a large extent why condensed explosives can be so "angry".

When oxygen is the limiting reactant, the heat produced (and therefore explosive energy) in an oil film fire would be related to the amount of oxygen present rather than the amount of fuel present. Hence the "upper" limit for an oil film may be at a much lower oxygen concentration than is required for fire in a corresponding gas-phase mixture.

There is a possibility, perhaps supported by anecdotal observation over the years, that even in the absence of an explosive fire between oil and oxygen dissolved into it, there might also be a lower-order exothermic release that might react the oxygen and evaporate some of the leftover oil to produce a gas-phase flammable condition.

Grumer [***16,17***] reports that dust layers require less oxygen for reaction than do the same dust layers when dispersed in air. Superior adiabaticity in the layer may be the cause. However, this may also argue that the level of dissolved oxygen in an oil film may be less than needed for a gas-phase limit.

Unfortunately, there do not appear to be any data today that would allow for meaningful assessment of liquid-phase fire limits. Much work has been put into predicting gas-phase fire limits, yet most limits that are employed are based on experimental data. Just what are the lower and upper limits for powder in LOX and for oxygen dissolved into oils? These data would be valuable to have.

The 96-86 Task Force examined data from an Air Products' database that predicts solubility of oxygen and nitrogen in hydrocarbons. These data are fairly well established. Indeed the writer has heard of patents for the separation of air that employ preferential dissolution of oxygen and nitrogen in hydrocarbons (possibly unused today due to an explosive risk). At elevated pressures, the concentrations of oxygen possible were in the several percent range. This is high enough to lend credence to the fire possibility. A paper exploring the solubility patterns of oxidants among various hydrocarbons at various pressures would be worthwhile and is encouraged.

A second worthwhile paper would be an analysis of the fire-limit behavior of fuel-rich hydrocarbon-oxygen mixtures at elevated pressures approaching the density of liquids.

Today various Gibbs free energy minimization methods are used to make such estimates and if the required “lower flammability” limit for oxygen in hydrocarbon gas (which is the upper flammability limit for hydrocarbon gas in oxygen) tends towards the low percentage range (even ignoring any latent heats of evaporation), then this is a hazard that Oxygen Safety Practitioners need to address.

Incident Experience

Contamination may be the most frequently cited factor in oxygen-enriched system fires. Sufficient oil that burns will rupture many a system. In lesser amounts it can burn and wreak widespread heat damage. In still lesser amounts it may ignite other components or metals which may then provide a major heat source. And in still lesser amounts, it might just possibly sensitize other materials and render them more vulnerable to direct ignition by traditional ignition processes.

Only a very small fraction of the incidents that occur are ever reported in the literature. However, among the few are several of great interest here [**6,7**].

There is no doubt whatsoever that compressed air in combination with a fuel material and ignition can be destructive and has on occasion ruptured pipes and blown the sides off of buildings. Cars compress actual air, mix it with gasoline and with high reliability produce power.

Ball [***18***] elaborates on the data of Zabetakis, Lambiris, and Scott [***10***] and Zabetakis, Scott and Kennedy [***11***] and describes actual incidents involving impure nitrogen compressors which experienced fires and explosions at oxygen concentrations as low as 3.5-5%. One of these incidents was in the second stage of a high-pressure compressor and occurred at 180 psig. These events are attributed to wide flammability limits that result at elevated pressures and/or elevated temperatures.

And yet these incidents are most significant, because they are the seeming exceptions that test the rule. Events like this are rare despite the massive numbers of both large and small compressed actual-air systems and blended air systems. Such events *can* happen but seldom do.

Setting Thresholds

The review above presents the cold hard data. Now what about the human factors that go into selecting a threshold concentration for cleaning?

How does one go about setting a threshold concentration for the cleaning of oxygen or other oxidant systems? At first blush, a conservative approach would say to clean every system exposed to any oxygen or oxidant concentration above the lowest at which an incident or experiment has shown the possibility of a fire developing. And this would be the conservative initial approach. However, as life became complicated, this approach would suffer.

This approach is comparable to encouraging use of nonflammable polymers and metals in every system at any concentration, pressure or temperature above which any incident or experiment has indicated a fire limit could be exceeded or was exceeded in the past. Needless to say, this is not how polymers and metals are always selected (though *sometimes* they are selected this way). They are perhaps more often selected on the basis of whether a fire limit is crossed, but also on whether a probability of ignition is too high, or whether there is an unacceptable fire-consequence possible. This is a much more sophisticated and flexible approach. However to date there has been no known effort to adopt “limits” of approval for situational cleaning requirements that are dependent functions of not only percent concentration but pressure, temperature, phase, and contacting materials, etc.

As the writer among others has noted [***5***], oils also tend to migrate throughout a system in very complex ways. They collect into puddles. And so very quickly one would come up against the issue of "How clean is clean?" "Completely clean" is not a realistic goal and so there would soon arrive (as there has) a whole spectrum of cleaning levels that are acceptable. And all of them are considered to be "clean". But clearly they are not equal.

So specifiers must then specify both an oxidant concentration threshold and a threshold contamination-level. On the basis of the above data, fire is possible in oxygen concentrations at least as low as 3.5 percent. However, 3.5 percent does not qualify as "oxygen enriched" which clearly starts at concentrations above that of air, and so such a specification would quickly lead to demands for more sophisticated criteria. This is a strong incentive for those interested in oxygen to forego the adoption of criteria for systems at and below the composition of air.

Is it really a problem for the oxygen safety community to specify cleaning for systems above 3.5 percent when it knows of incidents that have occurred at 3.5 percent? What is the impact of requiring cleaning of systems at 25 percent but not at 21 percent? Today, the 21 percent case is outside the oxygen-enriched region. Don't we need to avoid fires at 21 percent? And even at 3.5 percent? Should those who demand cleaning of 23 percent oxygen systems also similarly clean their own compressed actual-air systems (many may not)?

Although there have been severe incidents in air systems and even at lower concentrations, there is also a compelling body of experience that would argue that many air systems even ones not specially cleaned are indeed safe (at least up to a 100 psig or so). Why is that? Are the air incidents being ignored? Are the air users more careful?

The 96-86 Task Force contemplated an issue that the data do not resolve. Although, speculation, there is a vast assortment of generic compressed actual air in use and it may be significantly different from industrial gas-blended air and selected compressed actual air. The vast majority of compressed air systems in use are indeed actual-atmospheric-air that has been compressed. As a result, it contains small, but perhaps not insignificant, amounts of assorted gasses besides oxygen and nitrogen, except for selected, typically larger, systems that employ driers. Its largest tertiary constituent is water. And if one performs fire limit study on the effect of water on the flammability of other materials, for example gases, water (the most widely employed of extinguishers as a liquid) often (but not always) has a fire inhibiting effect even as a gas.

Water vapor also has the effect of preventing static electricity (unless it freezes to form crystals in which case it can aggravate static electricity). It narrows fire limits and can even swamp a fire. There is appreciable water vapor present in a massive majority of those air compressors in auto service facilities. In all those home air compressors. In all those compressors used to power tools and spray paint. In all those compressors that are seldom maintained, many of which are likely to suck organic materials and dust and solvents and paints into their intakes. To the designer of oxygen-enriched systems, this scenario would be a nightmare. And yet it appears there is seldom if ever a fire. And this experience is vast.

The CGA Task force recognized this prospect, and the ASTM Committee G-4 in 1998 posted a potential proposal [***19***][4] to suggest studying the effect of water on oils in contact with oxygen. However the experiments were not conducted (or at least not made public). Nonethe-

[4] ASTM G-4 posted a draft ISP (Industry Sponsored program) proposal for potential study of water on ignitability and of dissolution of oxygen in oils on its web site.

less, it begs the question whether the humid oxygen in some air compressors is less hazardous (even to dissolved oxygen in oils) than the dry oxygen in oxygen/nitrogen mixtures, or possibly even to dried compressed actual air, that are both similar to air in concentration but have produced fires in industrial systems and even in crude (albeit warm) nitrogen that still contained only 3.5 percent oxygen from its original air.

Enter The Recreational Diving Dilemma

As reviewed by Gabel and Janoff **[*20*],** in the 1990s, oxygen-enriched air came into common use by recreational SCUBA divers. Previously enrichment had only been used by small groups such as the Navy. Concentrations used were divided (perhaps arbitrarily) into two classes, up to 40 percent and above 40 percent. The historical base of experience was therefore small and there may have been incidents, but this commentator is not aware of any. However, spreading this practice widely to potentially less thoroughly trained divers raised the specter of a new hazard. In addition, as a new industry, its promoters were entrepreneurial to a high degree and were enthusiasts, as well as vendors. However, they were also largely outsiders to the subject of oxygen safety as it was being promoted by the CGA and ASTM G4.

The equipment and practices observed in these systems at up to 40 percent oxygen were little different from those used with commercial compressed actual air, however, the pressures used for diving were well above the pressures in most compressed actual-air systems. There was little or no special cleaning. Gabel and Janoff [***20***] lament the industry's arguments that it had had no incidents to date (which was relatively weak because the statistics were so small). But there was another factor operating that was subtle. The Occupational Safety and Health Administration (OSHA) had published a "presumably single-sided" criterion (CFR §1910 Subpart T Commercial Diving Operations, §1910 430i Oxygen Safety) which dictated that

> "(1) Equipment used with oxygen or mixtures containing over forty percent (40%) by volume oxygen shall be designed for oxygen service" and (2) Components (except umbilicals) exposed to oxygen or mixtures containing over forty percent (40%) by volume oxygen shall be cleaned of flammable materials before use."

Clearly cleaning was mandated above 40 percent but that was *probably* not intended to imply that it was totally unnecessary below 40 percent. But that is how it was apparently interpreted. The groups that were used as a model for the legislation apparently reverted to high pressure air standards below 40% for which they still employed some degree of contamination control. This is the same issue as for the single-sided threshold for enriched air. Cleaning that is required above 21-25 percent does not mean to imply that incidents can not happen below 21 percent (and they have happened down to at least 3.5 percent). But this single-sided subtlety is easy to misinterpret.

So there were two dilemmas. Industry cleaned above 21-25 percent because it was oxygen-enriched and capable of fire or explosion but was much less cautious with cleaning below this threshold (at least at lower pressures) even though there were few if any technical data defending that boundary as a fire limit. And now here was an industry, using a similar single-sided criteria to justify the omission of cleaning at higher levels than 21-25 percent, which also apparently had no compelling relation to any local boundary as a fire limit.

If at least some generic actual-air compressors can be safe (and statistically they apparently are) without special cleaning, then why can't recreational diving systems (albeit based on much flimsier statistics and for higher pressure systems)?

These dilemmas become much more problematic when one considers that in many cases (perhaps not all of the time) the recreational diving industry was employing breathing gases with much higher levels of moisture than were present in industry systems or in the previously blended mixtures used for diving. In some cases, they were using the reject stream from membrane nitrogen generators which contain the atmospheric humidity (nitrogen apparently filters through the membrane leaving the oxygen, water and all the other gases behind in enriched quantities). This was (and maybe still is) a very economical way to obtain oxygen-rich respirable gas. In some cases, oxygen from pressure swing adsorption plants (another lower cost source of oxygen enrichment that also apparently has much higher levels of moisture present) may have been used. In comparison, all of the mixtures used by the previous generation of divers may have employed bone-dry cryogenically produced blended-gas mixtures of nitrogen and oxygen alone.

Suddenly the two dilemmas are joined. The recreational divers may have had good but small statistics to defend their practice, and they may have also had moisture (and in most cases other gases) present that is also one of the potentially most significant differences that might explain a difference between industrially blended "air" and compressed actual air.

If the moisture effect (or other gas effect) is real and significant, it may not only be of great importance but of great value to understand ….and to exploit.

Fire Limits and FLLAME

Contamination in oxygen service is one of the first hazards identified and one of the most important. Special cleaning is one of the first and most widely practiced safety measures. In some systems in which no other precautions may be needed, cleaning can still be crucially important.

Throughout the preparation of this paper, as is the case in many instances in the oxygen safety literature, one encounters citation of the "fire triangle" concept to simplify (the writer likes to think over-simplify) and explain traditional fire-limit hazard analysis. The fire triangle cites three factors necessary but not sufficient for a fire to obtain. The fire triangle is a useful tool for introducing a few of the key factors in the occurrence of a fire, but it is much less useful for the actual evaluation of a fire risk for the sake of prevention. Nonetheless, the fire triangle is very popular.

The fire-triangle level of sophistication is best characterized as a blunt tool, a bludgeon, when applied to oxidant systems. The writer apologies for previous writing (2000) [***21***] which discussed (with perhaps a tad too much sarcasm and mocking) the fire square, fire pentagon, fire hexagon, fire heptagon and fire octagon[5]. One can design systems based on the absence of one or more of the three triangle legs (fuel, oxygen and ignition) or other "legs" (up to at least eight in number) that can be assigned to a more complex, but more powerful, symbolic figure,

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[5] In the 1970s or before, a slightly more sophisticated artifice was created, the Fire Tetrahedron—a pyramid in which each of the four triangular sides were the key factors, three representing the usual fire-triangle legs, and adding a forth in the form of "chemical reaction" or "chain reaction". Apparently for some time there has also been another formulation of a "fire square" that used "extreme weather" as its fourth factor. All of these however appear to derive from the firefighting industry and seek to itemize factors which allow for the extinguishment of a fire. The fourth side was added because of Halon fire extinguishers which do not employ any of the first three factors (legs or sides) in their operation.

but in an oxygen system there is always a fuel (the system), and oxygen (the stuff being contained) and preventing ignition actually demands a pretty steep knowledge of fire theory. To a large extent, practical prevention of fire often demands more detail from the discipline within the body of fire practice known as fire limits.

In evaluating fire limits, the fire triangle is an extremely and excessively simplified model[6]. But there are few oxygen safety practitioners who are steeped in fire-limit analysis. Indeed, in many cases, fire-limit practice is such a complex and empirical subject that theoretical analysis of systems proves flawed. Few today would calculate a fire limit and trust it solely. As a result, today much and perhaps most fire-limit analysis is based on empirical data that is interpreted and interpolated and the larger theoretical context is used to validate and buttress empirical data. Often fire limits are not even referred to as fire limits but instead employ less intimidating terms like "threshold" or "boundary" or "index". Prediction of fire limits is still not attempted for many materials, and fire limits that are calculated are seldom taken as certain. And once fire limits are estimated or actually measured, the interpretation of the importance of those data is still a challenging task, still a real mountain to climb.

The writer has climbed on that mountain for decades, with only limited success and a lot more frustration. The fire triangle, useful as it is for step one in a training process, has not held him in good stead thereafter. In retirement for nearly a decade, he still struggles to convince ASTM G-4 to build a body of standards and tools to deal with the practices for fire limits. G-4 has demurred so far based on the complexity of even the basic material that would be initially tackled, but they have also cited low levels of available energy and interest.

However it is the commentator's conviction that the subject of oxygen compatibility can not be complete nor adequately addressed without practical (if somewhat complex) tools to address basic fire limit issues and much more. It can be surprising how little use it can be for one to know that a lower fire limit of a fuel in oxygen is "x" per cent, or that an oil film of "y" thickness could produce a fire-limit concentration, or that a polymer will burn in "z" percent oxygen in nitrogen.

In reviewing the data in this paper, one should be impressed at how dependent the physical hazards for threshold concentrations for cleaning are on fire-limit perspectives. These are some of the most crucial safety measures Oxidant Safety Practitioners face. The oxygen safety community needs to deal in some detail with fire limits, needs to take on standards in the area, and most of all needs to simplify the material but to a level far more sophisticated than the basic fire triangle.

Reconciliation

It is meaningful to recommend cleaning of oxygen systems starting at 21-25 percent as has been done. This may have been done, probably was done, more for human than for technical reasons but nonetheless it will provide safety. For the same reason, it is meaningful to recommend "complete cleaning". And it is also meaningful to recommend making all oxygen sys-

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[6] The writer is loathe to condemn any efforts at simplification, having recently used simplification as justification for a massive effort of his own to make adiabatic compression processes in oxidant gases more comprehensible to the ordinary Oxygen Safety Practitioner. But incongruity arises when one scans the body of ASTMG-4 work and some of its extreme esoteric analysis then confronts diametrically extreme efforts to simplify fire limits. Perhaps a fair and balanced approach might be to allow some additional complexity regarding fire limits and strive to simplify more of these other topics.

tems of copper and using only minimal amounts of PTFE polymers at strategic regions. This too will usually provide safety. However today the oxygen safety community provides rather complex situational and circumstantial strategies for employing metals other than copper and polymers other than PTFE, and it even provides so-called weasel room on certain dimensions of cleaning, too.

Similarly, it is meaningful to recommend cleaning of systems starting at 3.5% oxygen and yet this is not done, and the writer believes for good reason. This paper has elaborated on what the writer sees as dilemmas in the practice of oxidant safety. If indeed (as can be argued), many compressed actual-air systems up to some pressure that can not be precisely identified are safe without special cleaning, then recommending cleaning at 3.5 percent would be an overly conservative and wasteful limit, because not every 3.5 percent system is at risk.

If moisture or any of the other constituents of actual air provides any degree of protection to actual-air compression systems (as statistics may suggest) or to some range of actual-air based oxygen-enriched gases, then it would provide a valid basis for the practice of using these systems with reduced or no special cleaning.

Indeed in the distant past, there was a time in the air separation industry when high pressure compressed oxygen was compressed using soap/water lubricated compressors. The oxygen was much more humid and there were corrosion issues in the steel cylinders. But there may have been (and the writer surmises there was) a reduced risk of fire, but here again documented experience is smaller and less reliable to assess.

In the medical industry, there is concern for the use of halogenated polymers in oxygen systems. They resist burning but when they do burn they can produce highly toxic chemicals (like phosgene, the WWI WMD gas) and can poison patients downstream. Less fire-resistant materials that produce less toxic gases offer a way to balance the risk, by reducing a fire's toxic consequence at the cost of increasing its potential frequency. If water is protective, then perhaps medical oxygen should contain a water constituent as a safety measure. Although this would not appeal to the users of steel cylinders because of potential corrosion, the medical industry also likes aluminum cylinders (despite their own fire risks) and much of its hardware may be more able to tolerate moisture. Indeed, since aluminum itself is capable of spectacular fire, the water might also serve to mute the hazard therein (but this is speculation and one must also consider that at some high pressures moisture may freeze into crystals during gas expansion that promote static electricity and an increased potential for ignition). Humidity, even in small amounts might even change the fire limit of aluminum cylinders (as do some other diluent gases even in very small amounts), or might change the fire limit of lubricants and contaminants. And since bone-dry oxygen is often not desirable for the patient, moist oxygen might have multiple benefits. But the writer is unaware of any analysis of how much humidity might be possible or how much might be needed in various applications, or data that would allow for real insight into these apparent dilemmas. These data would be worthwhile to have.

What the writer thinks he knows is that the reported incidents at 3.5 and 5 percent are sufficient to prove that the fire limit is that low in at least some systems. He also thinks he knows that the body of home and industry compressed actual-air use at common pressures is so huge and public (and therefore so challenging to careful use principles) that it is unlikely to prove that actual compressed air is a hazard in those systems even with some degree of lubricants and contaminants present, and this effect is likely to extend at some higher-than-air oxygen concentrations, as well.

Human factors may ultimately dictate whether any benefit of moisture or other minor constituents is too small or complex to warrant modification of current practices. Any inconsistency or dilemmas in the oxygen concentration threshold recommendation may therefore be sustained for human-factors reasons unrelated to safety, fire limits, or other fundamental and technical safety issues, and it is important for the OSP to be aware of these bases.

Summary

Data that relate to the oxygen concentrations at which fire or other hazard limits are crossed were reviewed. The data do not appear to establish a fire limit, or ignition boundary, nor consequence threshold in the vicinity of the composition of air. Some fire limits may be crossed at much lower concentrations, and for some systems, the risk of fire due to fire limits or ease of ignition or even consequence may be low at significantly higher oxygen concentrations than that of air.

As a result, the cleaning of systems at or above the approximate concentration of oxygen in air is a conservative approach well taken because the knowledge of fire limits and ignition behaviors above this level is scant. However, numerous air systems provide a solid statistical basis to claim cleanliness is much less an issue in many compressed actual-air systems at common pressures, and it may be due to moisture or other low level gases present in these systems. When systems are drier or purer or warmer or at high pressures, the fire hazard may extend down to very low oxygen concentrations of even just a few percent.

The importance of knowing this background and the bases for choosing practical thresholds of special cleaning has been asserted both to aid those who may someday wish to establish the safety of higher thresholds, and to avoid misleading those who operate at the conditions of air or less-than-air.

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Supplemental Suggestions for Oxygen-Fire Incident Prevention and Investigation[2]

REFERENCE: Werley, B. L., **“Supplemental Suggestions for Oxygen-Fire-Incident Prevention and Investigation”**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety*, Self-published opinion, original publication 2007, public domain 2019, p. 65-76.

ABSTRACT: ASTM G 145 was adopted in 1996 and has not been significantly altered since. Potential new material, elaboration and modifications were proposed in 2007 and are revised and expanded upon here for evaluation and possible inclusion in a future-generation document. New proposed items are additional factors, scenarios and analytical methods that do not alter existing standard content but rather append to it in its original spirit.

KEY WORDS: oxygen safety, oxygen incident, accident investigation.

Oxygen fire-incident prevention and investigation are often two sides of the same coin. ASTM Committee G4 addresses incident prevention with the publication of its standard G 88 *Oxygen System Design Guide* supported by several test methods, a cleaning standard and other related support standards. It describes consensus methods believed to prevent or mitigate ignition and/or fire propagation in oxygen systems. Hence an investigation for the direct cause of a fire in oxygen should consider if and how well the recommendations in G 88 were applied and if any of the underlying factors or discrepancies in application could be the direct cause. However deploying G 88’s advice is one thing and determining whether any of the underlying mechanisms may have contributed to an incident can be another.

ASTM G 145-96 Standard Guide for Studying Fire Incidents in Oxygen Systems was approved in October 1996. It was re-approved largely unchanged several times since then on the basis that its content was still correct and applicable and that Committee G 4 was not able at the time to launch an expansion of it. The writer proposed revision materials in 2007 and flagged them when its mandatory review was approaching. Indeed, those suggested revision materials were more in the form of additional material rather than corrections to existing materials. Earlier, in 2002, the Committee had just launched a major effort to revise the much more dated standard G 88 Design Guide (in addition to a challenging agenda of business already underway) which had not been changed greatly since its much earlier original

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[1] No mailing address, archive copy.

[2] This paper was self-published for the writers oxygen safety-opinion web site.

publication (1984). It had just wrapped up in 2005 and the writer, who prepared the original first drafts of both, and the G 88 revision, considered the updated G 88 would have provided desirable resource material for several items to include in a revision of G 145. G 88 has again been revised to a lesser extent in 2013.

To a significant extent, every design ethic cited in G 88 represents a factor that might have been missed, or misapplied or an inadequately understood factor in the causation of an incident. However, unlike G 88 which cites the ethics, G 145 is intended to help appraise the subtleties of any ethic in an incident study, focusing on those cases where the interpretation or common knowledge might be counter-intuitive. It also highlights factors found to be significant in past incident investigations and pitfalls that were encountered in assessing incident factors.

The writer's 2007 proposed revisions were posted for several years on a personal web site, However, from the early 2000s (and somewhat before) G4 was under great energy pressures and was refocusing its efforts on core needs (maintaining existing standards, training efforts and its symposium series). The G 88 revision was one of the few expansion efforts launched in the period and to this day. And these pressures were magnified by the 9/11 attack and economic crises of the decade. In the early 2010s, the writer made a formal request and volunteered to prepare drafts. At that time the standards leadership wanted to hold off while also developing some additional materials. To date that has not happened. And apparently no efforts focus on new needs. Unfortunately documentation of G-4s efforts have been scant.

Since the writer's web site is no longer in service, those earlier proposals, and more similar new ethics for G 88, are being rephrased and documented here for what ever unvetted use they may be in the future whether efforts ever allow for incorporation into G 145 and G 88 or not.

G 145 was not launched nor professed to be comprehensive for either forensic or informal investigations. Many of those methods are well-documented elsewhere. Instead, G 145 was an effort to portray a series of unique and uncommon insights and techniques that had been useful in the effort of seeking to identify the direct causes of oxygen system fire incidents. This included listing the mechanisms that had most frequently or most uniquely seemed to be involved in incidents as well as mechanisms and observations that have often been overlooked or proven misleading in past investigations. It did not seek to elaborate all of the failure mechanisms that might apply, nor claim to even know all of them, just several which were known or referenced where others had already published. G 145 was structured as hints and suggestions so that additional techniques and insights could simply be appended. At the same time (1996), G-4 launched a reinvigoration of its seminar series with a specific effort to in large part seek out papers applicable to gaps in incident study tactics that existed, and several have been published in the intervening years, for example [***1-6***][3]. Ultimate incorporation into G 145 was anticipated.

As of this writing, G4 has completed a major revision and expansion of its design Guide G 88 in 2005 and included ethics for speculative issues (specifically flow friction) even though not yet validated. Not every incident in oxygen has been adequately explained and hence even speculation on previously unidentified prospects that have not been consid-

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[3] Italic numbers in brackets refer to the reference list at the end of the paper.

ered can be useful. The suggestions herein also speculate on previously unrecognized prospects.

So as to not divert energies from other efforts underway, the writer is publishing the suggestions herein for future Committee consideration in a format that may facilitate editing and conversion into a ballot form. Use of or modification of any text is welcome. The reader wishes to remind that these are proposals only that have *not* been validated in every case *nor* agreed upon by the Committee's consensus mechanism. It may require years before that process can be launched and possibly even further years before it can be completed. Therefore this material should only be viewed as opinion, speculation and sources of ideas. Indeed, some of this material may prove to be in error or may ultimately be adopted in a different fashion.

Nonetheless, having been in situations where all known incident causes had been evaluated and many tested without establishing the cause of an incident, the value of having even speculative suggestions to examine can not be underestimated.

The items listed here are potentially new "Factors Affecting an Incident Study" related to G 145's Section 9, "Common Incident Scenarios" related to Section 10, or new "Analytical Techniques" related to Section 11. In addition, the writer has extensively examined adiabatic compression in real and ideal gases [*7*], which has previously been examined in the G-4 collegieum [***8,9***] some features of which bear mention in the G 145 and G 88 standards.

All of these items are listed below even though some of the data and analysis are not elaborated in other references and could not be confirmed or cited.

Finally, this proposal was and still is presented in this fashion because waiting for its incorporation into the formal full consensus standard can delay the time when these data become available by years. Indeed, since submitting the original material, the G 145 standard has undergone yet another approval in 2016 and will not be due for review again until 2021. Of course, revision may begin at any time but G 145 does not appear to have sufficient priority for that to happen. And those performing incident study may benefit from access to the techniques reviewed even if the validity must be viewed as tenuous or suspect. G 88 was due for review in 2018 but may again be offered for re-approval.

Factors Affecting an Incident Study:

Heat of compression versus temperature of compression (G 145 and G 88)

From its earliest standards, G-4 references the hazard of "Heat of Compression" and then proceeds to appraise the risk by virtue of the near-adiabatic temperatures that might be produced compared to the autogenous ignition temperatures of candidate materials. More accurately, however, the mechanical work energy done in compressing oxygen is a hazard in its own right and the temperature it produces, the "Temperature of Compression" is a different, if derivative, independent hazard.

For an oxygen fire to launch, both a minimum temperature of compression and a minimum heat energy of compression must obtain. This is why a system that is compressed slowly limiting the peak temperature achievable will not ignite. It is also why a system that experiences a static spark that is small will not ignite despite its plasma temperatures far beyond any measured autogenous minimum.

As a result, G 88 and G 145 should cite both *Heat and Temperature of Compression* and their synergistic interactions as hazards to design against and to consider as causes of incidents.

Temperature of compression contributes to ignition by exposing materials to temperatures above their *in-situ* autoignition temperature. Peak compression temperatures for a given final pressure are greatest when the initial pressure is smallest [**7**]. Oxygen mixed with gases of lower specific heat will produce higher final temperatures than oxygen alone during compression. Oxygen mixed with gases of higher specific heat will produce final temperatures [**7**] that are not as high as for oxygen alone.

Heat of compression contributes to ignition by exposing a material to a heat transfer greater then its minimum *in-situ* ignition energy. Maximum possible heat transfer during compression is greatest when the initial pressure is at an optimum level [**7**] and may be more severe for a lower AIT materials at one pressure yet more severe for a higher AIT material at a different pressure. Oxygen mixed with gases of lower specific heat will shift the worst case initial pressure and will increase the heat transfer possible in comparison to oxygen [**7**] and may increase the risk of ignition. Oxygen mixed with gases of higher specific heat will result in heat transfer less than for oxygen at all starting pressures.

Since *both* minimums must be exceeded to launch a fire, preventing either one or verifying either one was not exceeded should be both a design ethic and investigation goal. Maximum possible heat of compression is most severe at an optimum pressure, one should always assess the range of potential starting pressures possible in any potential adiabatic compression-induced incident. Often it is easy to produce and overlook uncharacteristically elevated pressures that may have been present in hardware. For example, reference [**7**] describes how much more severe conditions may obtain if an oxygen gas regulator is pressureized that was *incompletely* vented when last shut down.

Crevice hazards (G 145)

In the 2005 revision of G 88 an ethic was added to address seal-weld hazards. Seal welds inherently produce crevices[4]. If a seal weld fails or becomes porous, oxygen may migrate into the crevice and potentially lead to ignition, or contamination from the crevice may migrate into the oxygen. Crevice incidents are reported. In 2009, Schmidt et al [***10***] reported that some incidents have been observed in instances where the crevice might fill with liquid cryogen and pressurize to the point of hydraulic mechanical damage upon warming, a mechanism first proposed in the early 1980s by Jacob N. Geist. A fire occurred in four of nine incidents they cited.

Crevices are suspected to have led to fires in other LOX cases where mechanical failure led to failure of the crevice structure, and in cases where a differential temperature could present and could expand or contract a nozzle and abruptly warm or cool it.

An incident investigation should always survey whether crevices might have been

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[4] G 88 refers to crevices (narrow openings resulting from a split or crack: fissure), to refer to these trapped spaces while Schmidt et al [***10***] refer to some as "cavities" (unfilled spaces within a mass), and in some cases "clearances" (the clear space between objects)], "annuluses" (a ring) or "voids" (empty space, opening, gap) might better describe the geometries that can present in oxygen hardware.

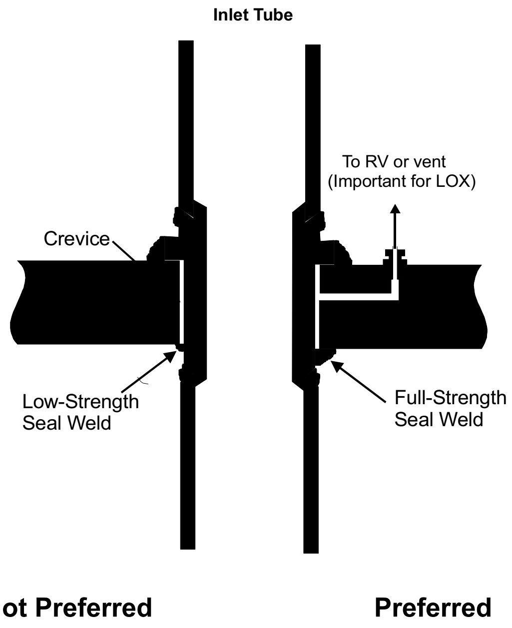


FIG. 1—*Seal welded crevices.*

present in the damaged areas, especially if there was exposure to liquid crogen or if there could have been mechanical failure that could affect a crevice. A weld failure for example might expose a crevice to sudden oxygen during a friction situation.

Fig 1 exhibits two approaches to a seal-welded nozzle through a heavy vessel wall forming an annular crevice. Because the nozzle is lighter and more temperature responsive than the heavier wall, cold or warm liquid oxygen that passes through the nozzle can produce greater contraction/expansion in the nozzle than in the adjacent wall leading to stress, fatigue, and failure at the weakest point, which in this case is the lower-strength seal weld. Furthermore, any open crevices that are situated so as to serve as a sump (see G 88, 9.4), whether seal welds were adequately designed for the maximum likely stresses, and whether the contained crevice was vented to a safe area to prevent crevice pressurization in the event of weld failure.

Mechaincal or igntion failure that exposes crevices/voids can also lead to "dry boiling" episodes like Schmidt et al [*10*] describe in one of their examples.

Explosive/Mechanical Energy (G 145):

When an oxygen fire occurs, it can produce pressure releases and shock waves that damage the area, and when damage is inspected after an oxygen incident, it can often be related back to the size of the event that produced it. These two "faces' of an analysis can allow important inference on causation. If area damage is consistent with a given TNT equivalency, and yet the vessel itself has not been consumed to yield at least that amount of damage, then one's attention should focus on contamination. In one case, components were buckled and bent in a way for which the minimum energy needed to mechanically damage them could be calculated. This was related directly to the amount of metal that would have to burn to yield the energy and since that amount did not burn, a metal fire could be ruled out and the approximate amount of various contaminants that must have been present could be estimated. TNT-equivalency estimation techniques are reviewed variously [***7, 11-13***]. Caution: the TNT equivalency of liquefied gas systems is difficult to assess, and while there are many who would assume the TNT equivalency of "expanding" liquid cryogens is small due to the low compressibility of liquids, this assumption can be seriously flawed. Liquid cryogens near saturation temperatures can release significant amounts of energy during a burst or rupture of a oxygen vessel [7].

Fluid Dynamic Effects (G 145)

Fluid dynamic effects can be very difficult to assess in adequate detail. What paths will particles take? Where will they impact? When will they be fluidized or elutriated? Do their velocities differ from the gas velocity? All of these calculations can be daunting to perform. However, software use is emerging that can help answer many of these questions in an incident study. To date, such software has been used to perform analysis is several papers at G-4 symposia papers [***6,8,9,14***].

Statistical Analysis (G 145)

One of the most preferred bases on which to defend a materials oxidant system practice is a log history of safe use. Oftentimes incidents fit a pattern and a study involves sorting out common failure modes. Sometimes an incident can be extraordinary. When incidents appear so rare as to be unique, it can be worthwhile to examine the similar body of equipment that has *not* experienced fires. Because one of the most time-honored bases for proving the acceptability of hardware is a statistically significant history of safe use of similar equipment in similar service. When hardware previously considered safe experiences a fire, the statistical bases warrant consideration. Such a statistical analysis should seek to identify whether the hardware in the incident had changed in such a fashion as to render it of a characteristically different risk pattern, whether the statistical record was not adequate after all, or whether the incident was a true low-probability event that reflects the risk pattern of all similar equipment in the future. In these cases, a single fire is much less informative than multiple or even just two, fires. When one event occurs it is difficult to calculate a meaningful failure rate probability. However when there have been two or more incidents, the reliability of the failure rate calculation is markedly improved and allows for much stronger conclusions and inference.

Unexpected Fire Limits (G 88, G 145)

Often oxygen-fire incidents have occurred in circumstances that might seem to be outside the necessary conditions for a fire to proceed even when ignition has occurred. However, Ball describes two fire events [***15,16***] in which oxygen concentrations were only 3.5 and five percent (far below published values of the minimum oxygen for combustion) but for which elevated temperatures must have widened the in-situ fire limits. In other cases, normal variations in material composition that are within specifications my yield some materials that are inside their fire limits and others that are outside. Even today, much testing is being done and much more is needed to determine the threshold at which fires can and do occur in oxygen. Fire-limit estimation is still a field in which theory is to a large extent inadequate and empirical measurements are the main basis for predicting thresholds. When an incident occurs, it is proof that a fire *was* possible, and the possibility that conditions normally thought to be outside the fire limits may have actually allowed for fire must be carefully assessed. Examples follow:

Oxygen Variability (G 145)

Benning et al. [***17***] revealed how an aluminum alloy would not burn in oxygen containing just a few tenths of a percent of argon but which burned intensely at lower argon concentrations, all of which were within commercial specification. Wells [***18***] found that increasing the purity of commercial-grade oxygen increased the rate at which steel would burn several fold. Hence, whether a component is or is not capable of burning and whether it will burn fast or slow may depend on what the precise commercial purity of the oxygen is that day, as well as, what the temperature and pressure of the exposure is.

Steel Variability (G 88, G 145)

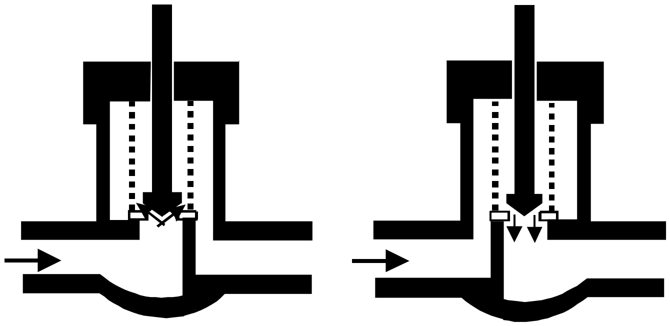
Benz et al., [***19***] found that decarburizing 440C Steel (from 0.9-1.2% to 0.2% carbon) reduced the pressure of oxygen in which it would burn from 17.2 MPa (2500 psig) to about 6.9 MPa (1000 psig). Zabrenski et al., [***20***] found that annealing cold-worked Alloy 304 steel reduced the pressure in which it would burn from >10.34 MPa (>1500 psig) to ≤6.03 MPa (≤875 psig). Lanyi [***21***] reviewed how carbon is protective of iron combustion through the formation of carbon monoxide that reduces iron oxides at high temperature. Hence, whether a steel component is or is not capable of burning may depend on what its exact composition is, especially its carbon constituent, even though it may be within specification, as well as, what the temperature and pressure of its exposure is.

Paradoxical Diluent Behavior (G 145)

In some cases, diluents, even inert gases, can act contrary to expectations. Adding argon to a system in certain ways can *produce* a fire hazard. Some diluents (like argon and helium) can increase peak adiabatic compression temperature and heat transfer, can act (like helium) to increase the rates of material combustion, can act (like argon and helium) to widen fire limits. As a result the addition or presence of any gas, even inert gas, prior to any oxygen incident must be evaluated for any paradoxical tendency to facilitate or aggravate combustion.

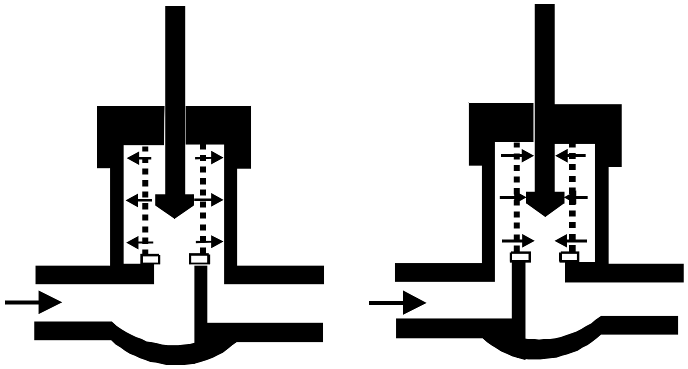
Flow Directionality (G 145)

A component specifically designed for oxygen service can have its compatibility nullified if improperly installed. Fig 2 from ASTM G 88-05 exhibits how particle impact risk can change when oxygen flow through a valve is reversed. Valves are usually marked with



Normal Flow
Pressure Drop at Seat

Reverse Flow
Pressure drop at seat



Normal Flow
Pressure Drop at Cage

Reverse Flow
Pressure Drop at Cage

Fig. 2—Reversing flow through a common cage-type valve.
(From ASTM G 88-05)

an arrow to indicate the forward flow direction. However often flow may be bi-directional and sometime the preferred flow direction is against the arrow to achieve quieter operation or other benefits. Flowing through a component in the opposite direction to that for which it is designed can produce mechanical impacts, adiabatic compression and particle impact among other mechanisms at locations that are vulnerable and unanticipated. Every component involved in an incident should be examined not only as to its basic design, materials of construction, and cleanness but also as to whether its specifics of installation and operation were correct.

Nonroutine Operation or Behavior (G 145)

A common observation during incident study is that they most often seem to have been triggered. The fire occurs after a valve is operated, after a flow has been adjusted, after a system has been pressurized or upset, after a component has failed. Although not unheard of, it is far rarer for an incident to occur in a system that has been operating smoothly for a long period of time. For this reason it can be crucial to identify every deviation from "normal" operation. Was a valve opened more quickly than usual? Were there any uncommon delays? Had the system been shutdown normally and completely in its last use? Had there been any maintenance or repairs? Any of these events may provide a clue to a "triggering" event.

Common Incident Scenarios

Check Valve Hazards (G 145):

Potential check valve behavior in oxygen incidents bears particular scrutiny. Check valves are often used for safety functions but can also be used for flow logic. However check valves can suffer from a series of common and frequent failure mechanisms that must all be considered and can in some cases be so frequent as to be considered probable. Check valve seats can corrode or be damaged by particle or mechanical impact or can accumulate material that prevents seating. Some flappers can be operate so rapidly as to produce mechanical impact, damaging or breaking components and creating loose debris in a system putting the downstream regions at risk. If the reverse pressure is not sufficiently high many check valve will not form a complete seal and will not isolate oxygen from entering forbidden regions of a system. For these reasons some system designers forego the use of check valves in safety roles and substitute PC-controlled isolation valves instead. But as a result, in any incident, the condition and potential operation of all check valves involved in the fire or upstream of it should be studied carefully.

Spontaneous Palladium Oxide Reactions (G 145):

In a number of incidents, palladium oxide getter used in vacuum-jacketed insulation had gettered trace hydrogen, which spontaneously ignited (under palladiums catalytic effect) when mechanical failure introduced oxygen into the jacketing. In other cases, the palladium oxide migrated into the oxygen system through mechanical failure where it similarly was involved in ignition (through hydrogen reaction or other catalytic or alloying reaction-promoting effects of palladium) (See G 88-05, 7.15.3, 7.15.4). This mechanism must be considered in any incident in which palladium or its oxides may have been present.

Speculative Fire Causation:

Several mechanisms have been proposed to explain numerous fires that could not otherwise be explained.

Flow friction—In the 1990s workers began speculating that gas flow over surfaces causing waves in the surface might (through internal friction) cause heating to the point of ignition. Low level heating has been observed in experimentation [***22,23***] but to date ignition has not resulted. Nonetheless this prospect may warrant consideration where no other explanation can be proven (G 145). Whereas flow friction is undemonstrated as an ignition source in oxygen systems, it viability may be (and probably is) much more plausible in gases like fluorine [***24***] (G 145).

Ionizing radiation—Cosmic rays and radioactive-atom disintegration have been evaluated [***25,26***] as sources of ultra small size but ultra-high-velocity, ultra-high temperature, particles and alpha–, beta–, and gamma-rays that have massively high temperature but low energy-transfer ability compared to minimum ignition energies of common materials. Ignition has not yet been tested in the lab nor has the oxygen safety community taken a position in favor of or opposed to this possibility. Nonetheless this prospect may warrant consideration where no other explanation can be proven (G 88, G 145).

Analytical Techniques

Computational Fluid Dynamics (CFD) Analysis. (G 145)

Computer-based programs for performing finite element fluid dynamic analysis are being cited in the ASTM G-4 collegium [***6,8,14***]. These have included the commercial programs: CFX-5 [***6***], Fluent [***14***], and the proprietary program TOPAZ [***8***]. This software can help surmise flow, mixing, heating, particle impact and other dynamic patterns in an incident.

Fluid Properties Analysis (G 145)

PC based thermodynamic properties are cited in several papers [***7,27***] being cited in the ASTM G-4 collegium, including databases from NIST [***28,29***], Outokumpu [***30***], NASA [***31***] and there are others available also. These databases can be used to calculate burn ratios [***27***], mechanical TNT equivalencies [*7*], maximum real-gas velocities [*7*], maximum total real-gas pressure [*7*], peak adiabatic compression temperatures and heat transfers [*7*] and much more including theoretical thermodynamic, thermo-chemical behaviors..

Summary

A few investigation techniques useful in both design and accident investigations of oxygen incidents or even unique to oxygen incident study were proposed for a revision of ASTM Standards G 145 on incident study . However at the time and since, G-4 has been unable to devote the energy and time to expansion of this standard. So as to inject them into the community conscience, they have been extracted and presented here and further supplemented. Most have been used at one time or another. Though not yet adopted by consensus, all have been presented for consideration for inclusion in ASTM Standards G 145 or in a few cases, G 88. Since, none has been balloted and validated by ASTM G-4, all must be considered “as is” speculation, but may nonetheless suggest avenues of study and design until time and energies allow a consensus position to be established.

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Barry L. Werley[1]

Is Carbon Steel Both Over– and Under– Exploited in Oxygen Systems?

REFERENCE: Werley, B. L., **“Is Carbon Steel Both Over– and Under– Exploited in Oxygen Systems**?”, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety,* Self-published opinion, 2019, public domain 2019, p. 77-82.

ABSTRACT: Carbon in steel effects flammability inversely, the more carbon, the less flammability. Industry and ASTM Committee G-4 have been ignoring the possibility that carbon content may allow greater steel use in some applications, but may also curtail usage in other applications

KEY WORDS: .carbon, steel, oxygen compatibility, flammability.

“Carbon steel” is far and away the most commonly used material in oxygen system hardware. It is used in miles and miles of pipeline and in selected other components as well. There is no practical alternative to it, and yet it is among the more flammable of common engineering metals in oxygen systems. It ignites and burns relatively easily. As a result, methods have been established to use it safely, nearly all of them focused on preventing and coping with ignition rather than resisting combustion although there are a few instances in which it is treated as being fire-resistant (when pressures, temperatures, and/or oxygen concentrations are not too high). Gas velocities are limited to prevent particle impacts from igniting fires. Critical sections are changed to more fire-resistant metals. Internal and external shields and fire-breaks and “distance-pieces” are installed. Cleanness is a high priority.

Stainless steels are somewhat more fire resistant than carbon steels. As a result they are treated as nonflammable in somewhat more severe services. But in some cases the differences can be small.

Steel strength is designed. Its corrosion protections are designed. It toughness is designed. But when it comes to native flammability, steels have been treated as a generic metal. And yet, individual steels (not just families of steels but individual batches within a family) may not be created equal in this important regard. Even more so, there are data that suggest there may indeed be significant variations in steel flammability specifically resulting from the amount of carbon in the alloy, and in some cases those allowed variations might just allow steel to be “designed” to allow for an increase in the safety margins enjoyed or might support the use of steel in hardware for which it is presently avoided. It might also flag where current steel risks are greater than currently believed.

This aspect does not appear to be codified by industry experts and indeed, seems to be disdained from consideration. In the 1990s, the writer sought to include carbon as a study

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[1] No mailing address, archive copy.

TABLE 1—*Categories of Carbon Steel by Weight %*
(Wikipedia entries circa 2019)

Mild (low carbon)	0.05-0.24% C
AISI Low carbon	0.05-0.3% C
Higher Carbon	0.3-1.7% C
AISI Medium Carbon	0.3-0.6% C
AISI High carbon	0.6-1.0% C
AISI Ultra-High carbon	1.25-2.0% C
Cast irons	2-4% C

variable in cooperative industry-sponsored test programs, but the role of carbon was so controversial that there was strong opposition that prevented it. In fact, due to the possible variability of carbon in assorted carbon steel and related alloys, carbon or its lack should not be ignored as a risk factor and as a explanation, even a causal factor, when carbon-steel incidents obtain.

The role of carbon on flammability is long known in some quarters, more so outside of ASTM Committee G-4 than within, but has apparently even to this date not been studied to support steel designs for oxygen fire-resistance.

Generic Steel

Carbon steel basically has two constituents: iron and a little bit of carbon, cited as up to 2.1% by weight. Some carbon steel specifications are listed in Table 1. Many steels merely seek to guarantee that carbon is at or below these levels.

Literally, in some cases, in making carbon steel today one takes iron or recycled scrap and adds excess carbon to it, heats it externally, and blows oxygen into it to extract some of the heat of combustion from the carbon to help heat the iron. Then when molten, one continues the oxygen "blow" to preferentially consume the carbon down to the concentration that passes specification muster. Throughout the process the carbon and its gaseous products prevent combustion of the iron and in fact convert any iron oxides back into pure iron (reverse combustion or de-combustion).

There can be great variability in the amount of carbon in assorted specifications and within a single specification. Significantly, cast iron is typically iron with carbon in the range of 2-4%. Stainless steels are more complicated but also contain carbon and it is significant to the mechanical performance of the metal. One may then add materials to fine tune "to design" the alloy desired but other than that, carbon limit conformance may be within rather wide ranges relative to the fire risk.

What is the Flammability of Steel?

More steel is actually burned than any other metal. Not only does the basic oxygen process "burn" the molten metal to final specs, but an entire industry is based upon the ability to heat product steel to where it glows red or preferably melts then spraying oxygen onto it to burn it away and cut or shape the parent.

As Lanyi [1][2] and much earlier Wells [2] report, the rate at which cutting occurs and

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[2] Italic numbers in brackets refer to the reference list at the end of the paper.

the ability to cut steel is related specifically to the amount of carbon in the steel and/or the amount of certain diluent gases in the oxygen, even where diluent gases may only be in small amounts.

The flammability of some steels has been tested [*3*] but in general it is to evaluate "carbon steel" for a specific application and rank it and then any results tend to be applied to the entire family of steels as if they are all alike. In most if not all cases the precise carbon content is simply not known. But there are data that suggest all steels, even just all carbon steels are *not nearly* alike.

Important Benchmarks

NASA WSTF Early 1980s

The NASA WSTF was beginning promoted combustion testing that would evolve into ASTM Standard G 124 in the early 1980s and reported at an ASTM G-4 meeting (believed to have been at Jacksonville Florida in 1983) that in testing a high carbon steel (440C, 0.9-1.2%C), they found it resisted propagation even at pressures up to 2500 psig. This result was far higher than for many other tested steels and stainless steels. The specimens were then decarburized (a process in which the specimens are heated to a high temperature in a gas that will react the carbon out of the metal). The process is slow because it takes time for the carbon to diffuse to the surface.

After decarburization to a reported 0.2%C, the specimen burned in 1000 psig, much lower but still a very high threshold. These 0.2%C data were shared with ASTM Committee G4 but have never been included in the standard G 94 yet were listed in the Addenda of data used with the G4 Standards Technology Training Course [*4*] (now called TPT: Technical and Performance Training).

Air Products and Chemicals, Inc. Early 1980s

John Zabrenski also began testing a range of alloys in the early 1980s and measured the threshold pressures with a test that predated but was similar to G 124, and found alloy 304 rods 0.25-in. in diameter burned at a threshold pressure of about 725 psig [*5*]. Wanting to do some further study, he ordered some more "generic" 304 rods and found they resisted burning at the 1500 psig test vessel limit. Micrographic analysis of both batches found the first batch to be annealed but slip lines on the second batch showed >25% work hardening. So the second batch was annealed (a process that like decarburization warms the metal for a long time in a specific atmosphere) and the few available remaining rods burned in at least as low as 875 psig. A third annealed batch replicated the 725 psig threshold. He reported this effect of "hardness" in the 1989 G4 Symposium (STP 1040). Conceivably, annealing might have altered the carbon or its distribution akin to the NASA WSTF work.

Air Products and Chemicals, Inc. 1996

The writer and Joseph Slusser set out to find recently reported [*6*] massive excess oxygen in the slags of steel combustion and plunged some slag droplets from burning welding rods into tall columns of liquid nitrogen, gaseous argon, or water. These brief results were reported at the first G-4 seminar session in Norfolk, and were self-published by Air

Products and Chemicals Inc. in 1998 [*7*]. Although evidence of massive excess oxygen was not found, it appeared that slag droplets on burning steel rods were inflating, and that the only oxide formed while the slag was on the rod was wustite.

The paper was met with such extreme skepticism that it could not be included in STP 1319. However, two engineers at Air Products with specialized expertise not only confirmed the possibility of slag inflation but noted that the likely gas to fill the bubbles was doubtless carbon monoxide.

Air Products and Chemicals, Inc., 1999

In 1999 Michael Lanyi presented a paper at the G4 Spring seminar in Seattle which published in STP 1395 [***1***] to interpret and elaborate upon the results in the preceding section. Lanyi explained that in the making of steel, carbon is protective of the steel combustion. Literally carbon and carbon monoxide that forms will reduce iron oxide back to iron at elevated temperatures. Indeed, if one places rusty steel into a carbon/carbon monoxide atmosphere and warms it, the rust will revert back to iron. Lanyi reviews how some modern steel is made in a way in which molten steel plus carbon are heated and then high velocity oxygen is injected into the hot iron bath. Although some iron oxide (wustite) forms, the oxygen does not bulk combust with the iron while there is appreciable carbon present. Instead an oxygen blow is continued until the steel carbon content is brought down to specification. If the carbon is allowed to be near-fully consumed, iron combustion does occur and large amounts of oxide slag and particle plumes are produced.

Lanyi opines that control of carbon content in steel should allow the flammability to be tailored and that steel with the maximum amount of carbon should be the least flammable.

Flawed Perspectives

In the mid-to-late 1990s, industry-sponsored testing of the effect of oxygen velocity and temperature on threshold pressures was being launched. This was intended to give perspective on how to design valves including those that experience high gas velocities. Does the ranking preserve when metals are tested in a gas velocity? Based on the previously cited data, the writer suggested studying, monitoring and varying the carbon content of studied steels, but this was before Lanyi's clarification when the writer's paper [*7*] was subject to much skepticism and derision and such heated opposition that its publication in the G-4 forum could not be negotiated. Unfortunately that skepticism had overlap into other issues and may have remnants to this day that may still be dissuading work on and resolution of this issue.

Minimum Ignition Energy.

Minimum ignition energy is a topic covered to only scant degree in G-4 standards and should be elaborated upon greatly [***8***]. To a large extent the most important potential steel ignition mechanism recognized in today's technology is particle impact in which a particle of, for example, an unoxidized metal as opposed to a metal-oxide particle is accelerated in the flowing oxygen stream, acquiring kinetic energy and impacts a carbon steel surface.

In the impact the kinetic energy is converted into thermal energy and a local high temperature develops during which NASA testing [*9,10*] suggests ignition of the particle may promote ignition of the steel-pipe impact site. Indeed to control this risk, industry standards such as the historical CGA pamphlet G-4.4 [*11*] (which has been harmonized with EIGA standards today) has been the principle way to design steel piping and its principle strategy was to limit oxygen velocity so as to prevent particle impact ignition.

Since carbon concentration in steel has been seen to be directly related to propagation threshold, one could surmise the amount of carbon present in the local impact site of a high velocity particle would also affect the site's minimum ignition energy. If higher carbon is protective of the iron-oxygen reaction, then more carbon should present a need for more particle velocity, or particle size, or particle number to burn off the local carbon and launch a fire. Yes, this is speculation, but it could be important enough to warrant testing to rule it in or out.

Indeed, to the extent that velocity criteria for designing carbon steel pipelines is predicated upon experimental test data (it might be more nearly empirical statistics for existing piping), it is important to recognize that those test data are probably from steel with uncertain carbon concentration below the specification threshold.

Conclusions

1 Carbon interferes with combustion of steel piping.
2. Common steel piping is limited in maximum carbon content but little is known about what the actual concentrations are in the massive amount of steel in service, and they could vary significantly.
3. Systematic knowledge of the carbon effect might significantly alter the mix of desirable and acceptable metals for use in oxygen system hardware. Carbon steel might in some cases become more practical for use (increased exploitation) and yet might in some other cases also become more restricted (reduced exploitation).

Summary

A strong case has been made based on experimentation and steel industry knowledge that carbon affects steel flammability significantly, but knowledge is lacking on the precise effect of carbon content on practical steel-metal flammability. This may be limiting the practical use of steel hardware but may also mean some steel systems may have smaller safety margins than suspected. Remnants of early unpleasant skepticism for the writer's work may have polluted the community's consciousness within ASTM Committee G4 and its ability to objectively see this need in a way that is a disservice to its charter and mission.

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Barry L. Werley[1]

A Coarse Comparison of the Fire Hazards of Oxygen with Other Important Oxidants

REFERENCE: Werley, B. L., **"A Coarse Comparison of the Fire Hazards of Oxygen with Other Important Oxidants"**, *Commentaries on Oxygen and Other Oxidant Fire and Explosion Safety***,** Self-published opinion*,* original publication 2019, public domain 2019, p. 83-90.

ABSTRACT: ASTM Committee G-4's mission since 1975 has included oxidants other than oxygen, and occasionally papers have been published in its symposia dealing with other oxidants. In the 2000s an effort was made to launch standards efforts but did not succeed. A coarse effort by the writer to begin an abstract standard comparable to G 128 for oxygen was a part of that effort. This paper extracts selected descriptive material from that draft.

KEY WORDS: oxygen, nitrous oxide, fluorine, nitrogen trifluoride, ozone.

Oxygen is by far the largest volume commercial oxidant. However there are other oxidants that also pose a fire/explosion risk, including fluorine, nitrogen trifluoride, nitrous oxide, and ozone. Each of these oxidants poses a risk but a risk that is different in scale, nature and severity. Each has a history of materials that have been used with them in the past, and each has its own track record and reputation for scale of risk and incident history. Nonetheless, the same principles often used to evaluate oxygen systems for safety are adapted for these other oxidants when the need arises. Indeed each oxidant is used in ways often similar to those for oxygen but also significantly different in some ways from oxygen-system practices.

There are industry documents that serve as guidance in some cases. However, none approaches the compelling series of standards for risk avoidance developed by ASTM Committee G-4 for oxygen.

This shortfall is not because ASTM G-4 does not intend to address other oxidants. Indeed, G4 has often forecast effort in these areas. In many cases test efforts and published papers have been undertaken and published in anticipation of G-4 taking up standardization efforts. In the 2000s, G-4 had an operating task force assigned to "Oxidants Other than Oxygen" and focused in particular on Nitrogen trifluoride at the time. However, the economic crisis of the late 2000s severely restricted available energies for all of G-4's activities. That crisis is less severe today, but its legacy remains. When, or even if, G-4 is to ever return to this remains to be seen.

Prior to that crisis, one issue regarded how to integrate and relate other oxidants into the G4 body of work. The writer has had hands-on experience with all four of these oxidants,

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[1] No mailing address, archive copy.

and had proposed an approach and potential drafts for consideration but the thread of effort appears to have been lost.

The writer's proposal back then was for launching a series of individual or unified standards akin to ASTM G 128 *Control of Hazards and Risk in Oxygen Enriched Systems*. G 128 is the G-4 abstract standard for oxygen intended to introduce the oxygen hazard and to overview what is known and how G-4's specialized standards are used. The writer's proposal would have created an abstract standard (or collected series of abstract standards) with wide-overview intent that replicated the structure of G 128 and compared and contrasted properties and risks of these four oxidants to oxygen, and suggested how they may be adopted or extrapolated theoretically to support these other oxidant systems. However, ASTM G-4 appears to have been fully consumed addressing oxygen for the present.

A rough and incomplete draft in ASTM format was begun and posted to the writer's personnel website for several years. The website was dropped in the late 2000s.

Inasmuch as standards in this area now appear a distant future effort if at all, this comparison is intended to help tyros to these other oxidants gain a relative perspective should issues regarding them arise. It extracts some of the materials from that earlier draft to compare/contrast these four oxidants.

Oxygen

Oxygen is a diatomic molecule, O_2, with a low boiling point (-297.37°F, -182.9°C), and molecular weight 32.00 [*1*][2]. It is commonly handled as both a gas at typical pressures to nearly 3000 psig (20.6 MPa) and a liquid at low pressures to perhaps several hundred psig and is stable in both states. Isentropically (adiabatically) compressed from room temperature it heats much as an ideal gas with a ratio of room temperature specific heats of 1.397 [*2*] compared to ideal diatomic gas with a ratio of 1.4. Figure 1 compares real and ideal gas temperature estimates for theoretical adiabatic compression of oxygen [*3*].

Fire incidents have involved destruction of property, loss of production and most importantly injury and loss of life. One of the largest property loss incidents in history in economic terms not loss of life, was an oxygen plant fire.

Fire incidents have occurred in both gas and liquid states due to such things as rapid compression, particle impact, localized heating, friction, spontaneous reactions and several more mechanisms. Not every incident is fully understood. Fires are avoided with the aid of industry standards such as the ASTM Standards for oxygen hardware, the Standard G 88 Design Guide, G 63 for nonmetals selection, G 94 for metals selection and G 93 for cleaning.

Every oxygen system warrants scrupulous cleaning, and as the severity of the exposure increases, fire-resistant non-metals are needed and then as severity continues to increase fire-resistant metals are needed. Design ethics are covered by G 88 and are employed circumstantially.

Fluorine

Fluorine is a diatomic molecule, F_2, with a low boiling point (-306.86°F, -188.26°C), and molecular weight 38.00 and as such has similar thermodynamic properties to oxygen [*1*]. It is a heavier atom and appears to be sold only as a gas and to cope with its greater hazard, cylinder pressure is limited to 400 psig (2.7 MPa) though mixtures with nonreactive gases

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[2] Italic numbers in brackets refer to the reference list at the end of the paper.

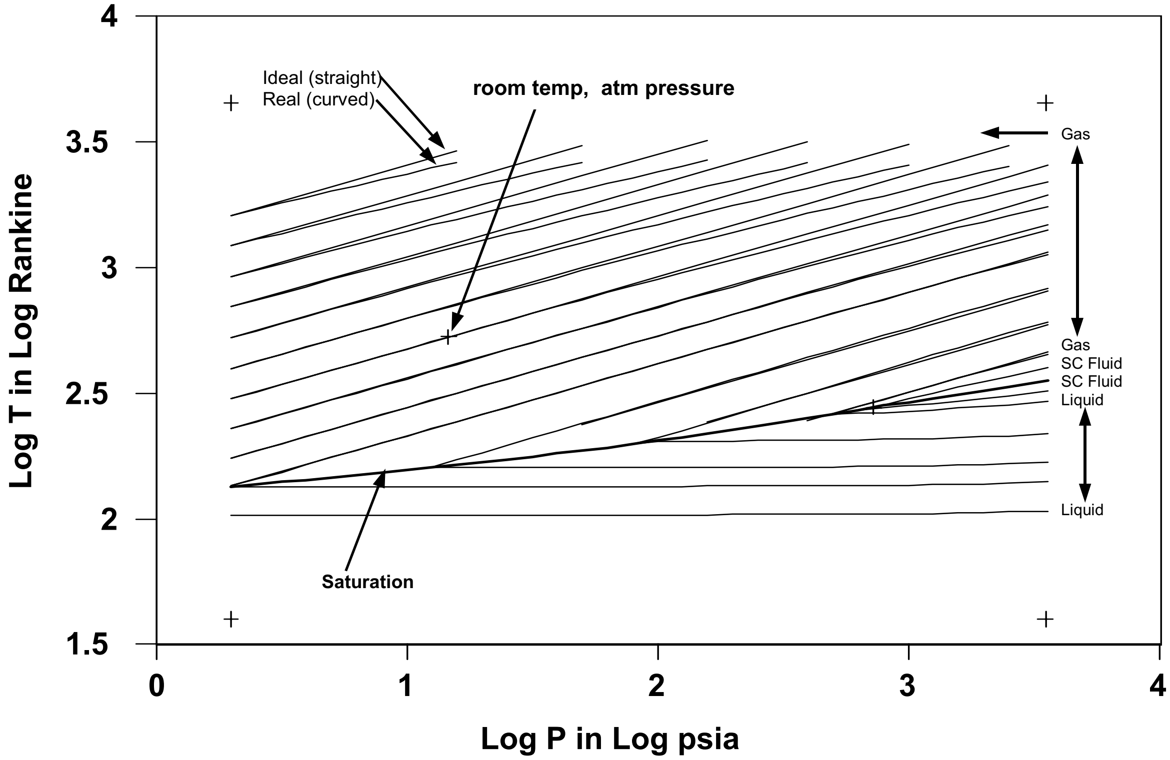

Fig. 1—*Real- and Ideal-Oxygen Adiabatic Temperature Vs. Pressure from NIST 12 DB* [*2*].

like nitrogen are also marketed at higher pressures. It is also handled as a liquid during production to distill for purification and is stable but very reactive in both states. Isentropically compressed from room temperature it heats much as an ideal gas with a ratio of room-temperature specific heats of 1.364 [*2*] compared to a ratio for an ideal diatomic molecule of 1.4. Figure 2 exhibits real-gas temperature estimates for theoretical adiabatic compression of fluorine [*3*].

Fire incidents have been attributed to rapid compression, particle impact, localized heating, friction, spontaneous reactions and several more mechanisms. Unlike oxygen gas for which “flow friction” is an unproven ignition cause, fluorine has a reputation for igniting because of high velocity through vulnerable materials that may well be “flow friction induced”, such as leakage though flange gaskets incidents which have occurred even with PTFE gasket materials. Fire incidents have involved destruction of property, loss of production and most importantly injury but loss of life statistics are not certain. It poses a toxic hazard as well. However, unlike oxygen, and perhaps as a result of the lower use-pressure, and smaller quantities that are used at a time, large scale incidents are not known to the writer. Cylinders have had holes burned into their walls, valves have had holes burned into their bodies, but these have not tended to be highly explosive events. To some extent this may also be due to the tendency of fluorine to react with some metals to produce products that at room temperature are liquid or solid rather than gaseous combustion products [*4*].

Fire prevention is based upon the guidance of industry lore such as using only the most fire-resistant of materials for comparable oxygen service (Monel, Nickel, PTFE, and PFPE oils). CTFE greases and plastics are avoided because the high reactivity of fluorine can

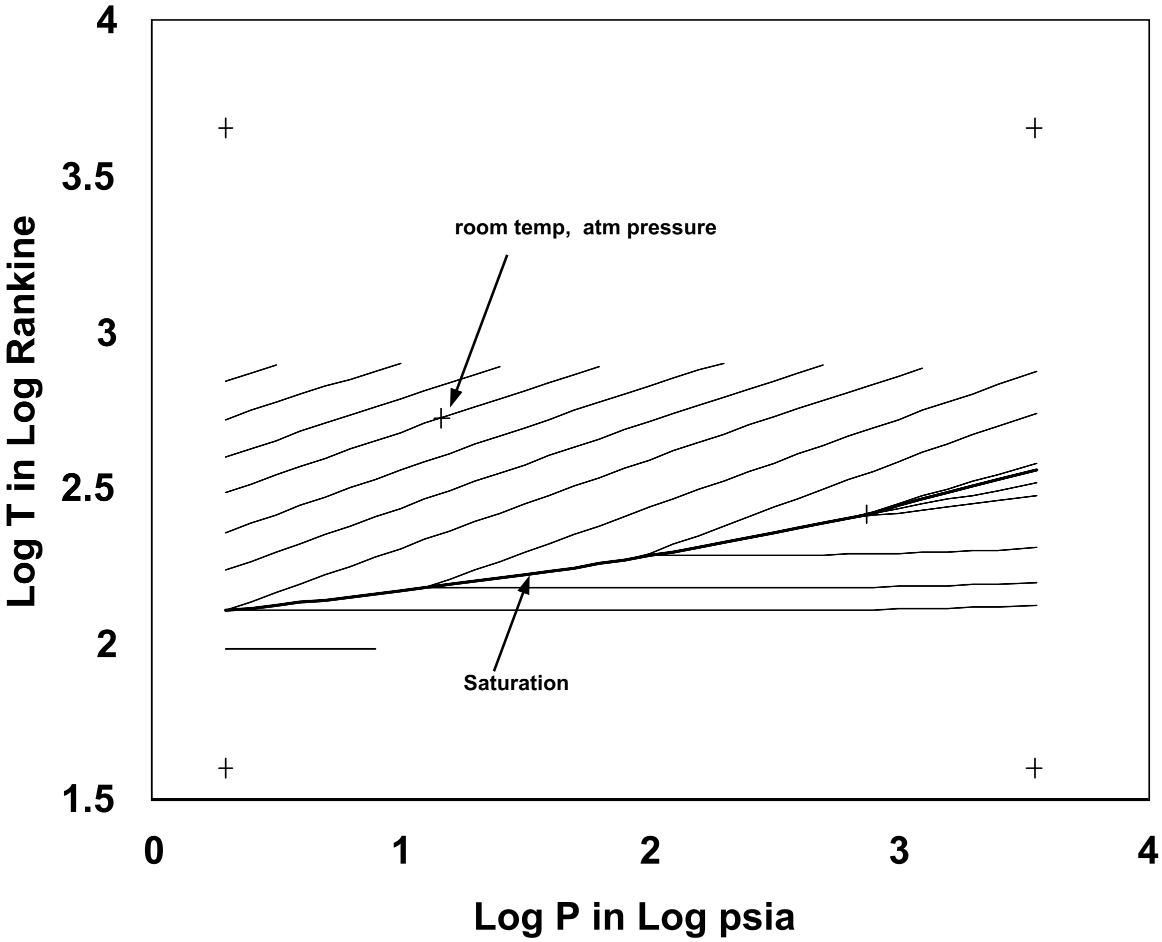

Fig. 2—*Real Fluorine Adiabatic Temperature Versus Pressure from 2007 NIST 12 DB* [*2*].

liquefy them upon replacement of the chlorine atom by the fluorine. ASTM Oxygen Standards for the design of oxygen hardware such as Standard G 88 Design Guide, G 63 for nonmetals selection, G 94 for metals selection and G 93 for Cleaning are useful but not perfectly applicable to F_2 system design. Design ethics covered by G 88 are employed circumstantially. Many fluorine systems are shielded and remotely operated to cope with both fire and toxicity concerns.

Every fluorine system warrants scrupulous cleaning at least as scrupulous as would be used for oxygen service, but following that F_2 systems are then passivated by exposures to a dilute, low-pressure fluorine low-reactive gas mixture and the fluorine concentration and mixture pressure are increased to react away any residual traces of contaminants and to in theory produce a several-atom thick layer of metal fluoride on all surfaces, all of which are believed helpful in avoiding ignition and fires.

Nitrogen Trifluoride

Nitrogen trifluoride is a tetra-atomic molecule, NF_3, and it has a boiling point that is low (-200.2°F, -129°C), and molecular weight 71.01 [*1*]. It is a heavier molecule than fluo-

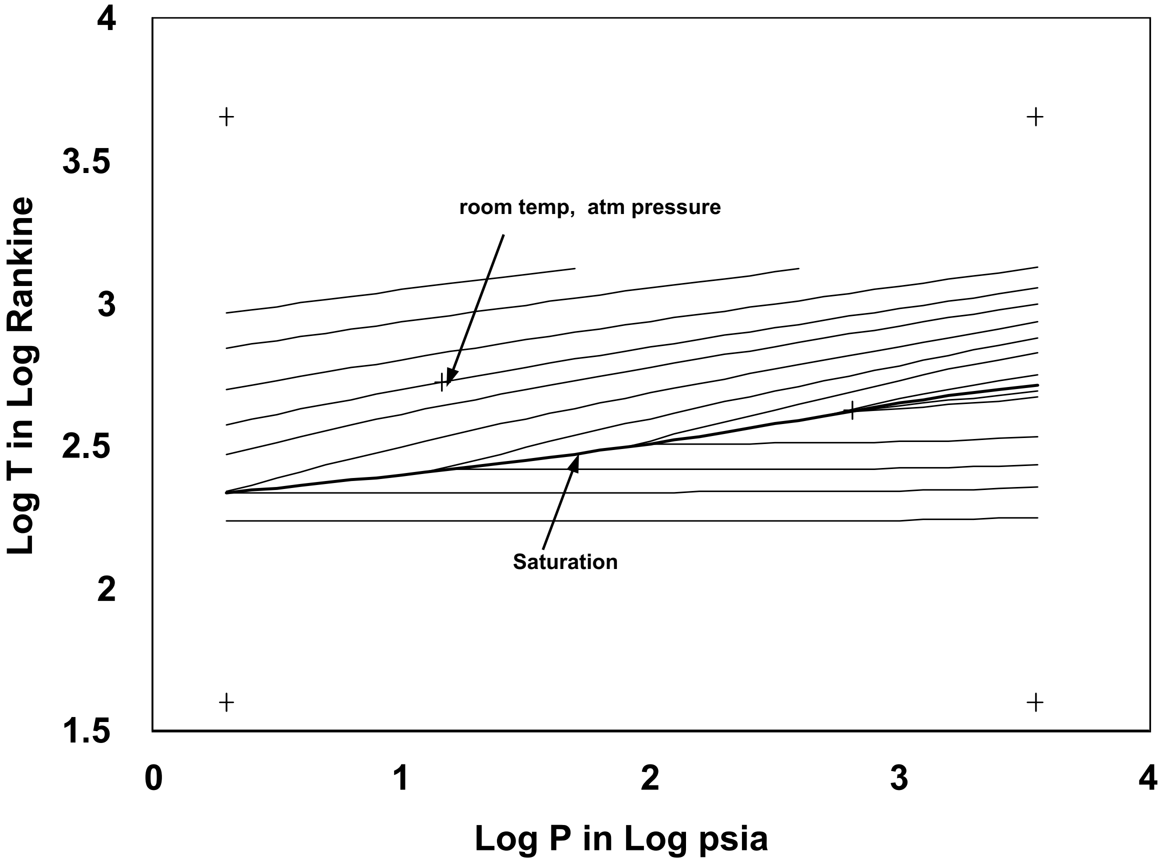

Fig. 3—*Real Nitrogen Trifluoride Adiabatic Temperature Versus Pressure from 2007 NIST 12 DB* [*2*].

rine or oxygen (71 vs. 38 vs. 32). Its heavier molecule produces significantly different thermodynamic properties than oxygen or fluorine. Like fluorine it is sold only as a gas but is purified as a liquid. It is generally recognized as being less aggressively reactive than fluorine but perhaps more reactive than oxygen, and as such is sold at pressures up to at least 1570 psig (10.8 MPa). Isentropically (adiabatically) compressed from room temperature it heats much as an ideal gas with a ratio of room temperature specific heats of 1.189 [*2*]. Figure 3 exhibits real-gas estimates for theoretical adiabatic compression of nitrogen fluoride [*3*].

Fire incidents have occurred in both states due to rapid compression, particle impact, localized heating, friction, spontaneous reactions and several more mechanisms. Whether "flow friction" is an ignition cause is uncertain. Fire incidents have occurred but are few in number and not well publicized. Like fluorine it is expected to react with some metals to produce liquid or solid rather than gaseous combustion products.

Fires are avoided with the guidance of industry lore for fluorine experience and also by using only the most fire resistant of materials for oxygen service (Monel, Nickel, PTFE, and PFPE oils). ASTM Standards for the design of oxygen hardware such as Standard G 88 Design Guide, G 63 for nonmetal selection, G 94 for metals selection and G 93 for Cleaning are useful but not perfectly applicable to NF_3 system design. Design ethics covered by G 88

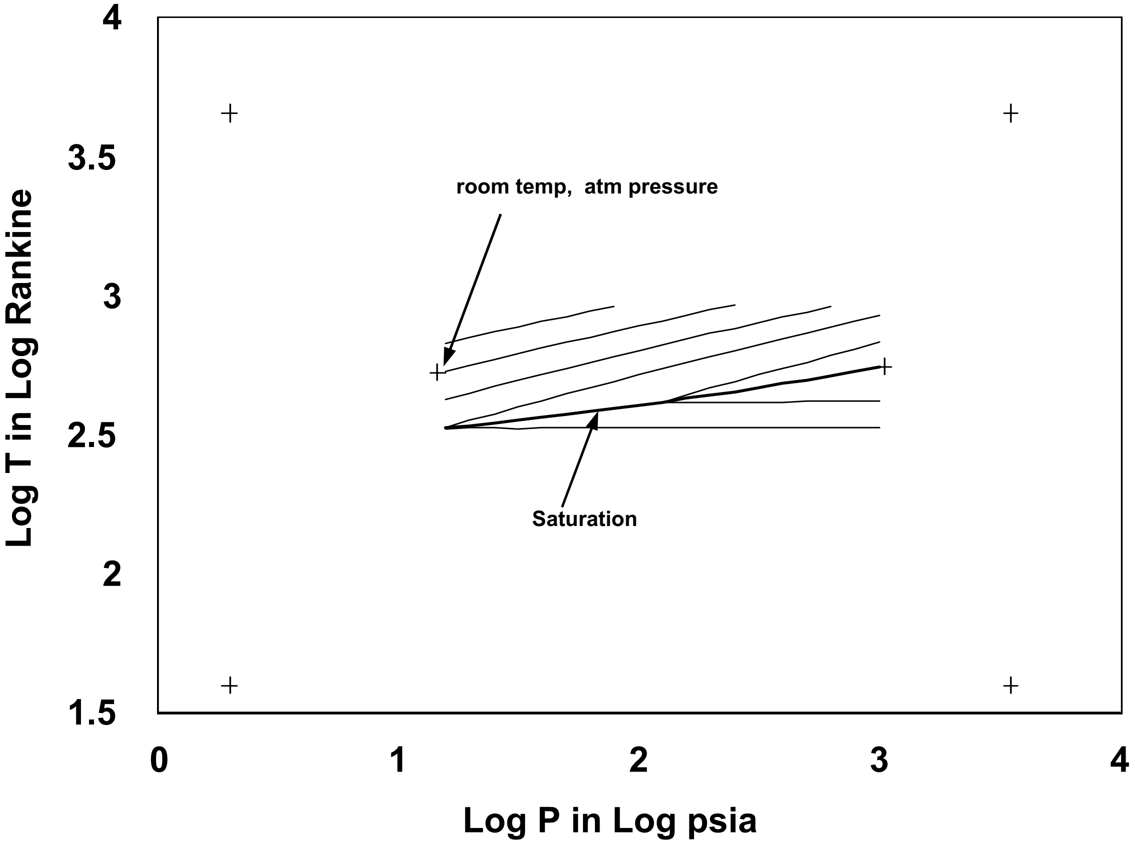

Fig. 4—*Real-Dinitrogen Oxide (Nitrous Oxide, N_2O) Adiabatic Temperature Versus Pressure From 2007 NIST WebBook*

are, again, employed circumstantially. Often, if not commonly, NF_3 systems are shielded and treated as is the case for F_2 and ventilated to address toxicity concerns.

Every NF_3 system warrants scrupulous cleaning at least as scrupulous as would be used for oxygen service, but then NF_3 systems are often passivated by exposures to an increasing low pressure NF_3 or fluorine in a non-reactive gas mixture and the concentration and pressure are increased to react away any residual traces of contaminants and to in theory produce a several-atom thick layer of metal fluoride on all surfaces, all of which are believed helpful in avoiding ignition and fires.

Nitrous Oxide

Nitrous oxide is a triatomic molecule, N_2O, with a low boiling point (-127.2°F, -88.4 °C), and molecular weight 44.01 [*1*]. Although the boiling point is low, it is not nearly as low as for oxygen, fluorine, or nitrogen fluoride. It is most commonly sold in cylinders as a compressed liquefied gas at a saturation pressure of ~745 psig (5.1 MPa) at room temperature, but high volume use applications can be supplied from a large tank that is filled with liquid. Isentropically (adiabatically) compressed from room temperature it heats much as an ideal gas with a ratio of room-temperature specific heats of 1.27 [*5*]. Compression heating is limited by both the large molecule and the tendency to condense at its saturation pressure. Figure 4 exhibits real-gas estimates for theoretical adiabatic compression of nitrous oxide [***3***]. When nitrous oxide is throttled from a high pressure its refrigeration during expansion can condense liquid in the downstream system and introduce the liquid hazard and overpressurization upon dead-ending.

Nitrous oxide is an endothermic molecule, meaning if broken into its constituent atoms there will be a release of "decomposition energy". Hence N_2O at elevated pressures or as a liquid can be ignited in many instances even in the absence of a fuel material and it has a TNT equivalency of about 0.4 [***6***]. When combustion of materials in N_2O occurs there is both a release of the decomposition energy and of the heat of combustion of any fuel. Decomposed N_2O yields a mixture of 33% O_2 in N_2. Materials burn in nitrous oxide less aggressively than they burn in oxygen but owing to the heat of decomposition, can burn more aggressively than they would in a 33% O_2/N_2 mixture.

Fire incidents have involved destruction of property, loss of production and most importantly injury and loss of life. In the distant past, numerous N_2O fires occurred in dentists office installations, that apparently are now rare, but there was an instance in which welding on a liquid N_2O vessel resulted in an explosion and fatality.

Fire incidents should be anticipated in both gas and liquid states due to such things as rapid compression, particle impact, localized heating, friction, spontaneous reactions and several more mechanisms. Fires are avoided with the aid of industry standards such as the ASTM Standard for the design of oxygen hardware, the Standard G 88 Design Guide, G 63 for nonmetal selection, G 94 for metals selection and G 93 for cleaning.

N_2O systems are commonly cleaned similarly to the way oxygen systems are cleaned. However, a greater latitude is taken with nonmetals than for oxygen because many nonmetals that burn in oxygen do not appear to burn in N_2O. Still wider latitude is taken with metals because few if any common piping metals appear to burn in N_2O. Design ethics as covered by G 88 are employed circumstantially.

Ozone

Ozone is a triatomic molecule, O_3, with a low boiling point (-168.3°F, -111.3°C), and molecular weight 48.00 [***1***]. Like nitrous oxide, O_3 is an endothermic molecule, and if broken into its constituent atoms there will be a release of "decomposition energy". Hence O_3 can be ignited in many instances in the absence of a fuel material and its TNT equivalency was not located. When combustion of materials in O_3 occurs there is both a release of the decomposition energy and of the heat of combustion of any fuel. Decomposed O_3 yields O_2. Materials should burn in ozone more aggressively than they burn in oxygen but ozone does not appear to be prepared nor sold for use as a pure chemical. Nor does ozone appear to be liquefied commercially and unverified lore has it that liquid ozone is both explosive and prone to spontaneous ignition.

Isentropically (adiabatically) compressed from room temperature, O_3 should heat much as an ideal gas with a ratio of room-temperature specific heats of about 1.26.

Ozone is widely used for sterilization of water and is produced on-site as low pressure mixtures in oxygen using ultraviolet light or in the corona of an electrical discharge. Ozone is so reactive that it tends to attack many nonmetals and to aggressively corrode metals, so once a system is clean, as is the case for fluorine, low rates of contamination introduction will tend to be continuously reacted away by the ozone.

Summary

A suggestion and proposed draft material [7] was offered to ASTM Committee G-4 in the 2000s regarding a possible approach to standardizing hardware design and operating practices for oxidants other than oxygen. G-4 has been unable to devote the time and effort to such an undertaking.

Until such time as G-4 undertakes such standardization a comparative overview was felt desirable to give context to those currently using or facing use of these other oxidants.

Some of the known risks of four important oxidants (F_2, NF_3, N_2O, and O_3) have been compared to the risks of oxygen which is used in far greater amounts and has much more mature and extensive safety practices developed. Such information can only be provided as tentative, as is, use at your own risk basis and should be verified for currency. Practices for hardware design are scattered, and importantly, whereas each chemical has commonality with oxygen and can employ some of the oxygen practices, one can not conclude that any system suitable for oxygen is therefore suitable for these other four oxidants, or vice versa, because each also has the unique properties and independent risks reviewed that must be appraised separately as is suggested here.

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