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Flow Friction or Spontaneous Ignition?

ABSTRACT: "Flow friction," a proposed ignition mechanism in oxygen systems, has proved elusive in attempts at experimental verification. In this paper, the literature regarding flow friction is reviewed and the experimental verification attempts are briefly discussed. Another ignition mechanism, a form of spontaneous combustion, is proposed as an explanation for at least some of the fire events that have been attributed to flow friction in the literature. In addition, the results of a failure analysis performed at NASA Johnson Space Center White Sands Test Facility are presented, and the observations indicate that spontaneous combustion was the most likely cause of the fire in this 2000 psig (14 MPa) oxygen-enriched system.

KEYWORDS: Flow friction, spontaneous combustion, ignition mechanism, pressurized oxygen-enriched systems

Introduction

The concept of "flow friction" as an ignition mechanism in pressurized oxygen-enriched systems has been discussed in the literature [1,2]. Several fires in oxygen systems ranging in pressure up to 9000 psi (62 MPa) have been reported which have been attributed to the unintentional flow of oxygen past polymer valve seats or system seals [3-6]. In many of these cases other ignition mechanisms such as particle impact, heat of pressurization, electrical arc, mechanical impact, and mechanical friction were eliminated as possible causes of the fire events. Because leaks

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had been observed in the location of the fire events, it was concluded that the cause of the fires was associated with the oxygen gas leaking past a polymer seat or seal.

Experimental evidence related to "flow friction" has been difficult to come by. Attempts to simulate leaks involving polymer seats and seals at pressures up to 10,000 psi (69 MPa), and thereby cause ignition, have failed. This inability to reproduce fire events in a controlled laboratory environment has led to justifiable skepticism regarding the reality of "flow friction" as an ignition source in real oxygen systems. This paper presents another mysterious fire event that lacks the more verifiable ignition mechanisms mentioned above and, yet again, points to a known oxygen-enriched, 2000 psi (14 MPa) gas leak as a contributor to the cause, but with a twist. In the event described herein, a potential heat-generating causal factor exists that has been heretofore undiscussed in this context: spontaneous heating and ignition.

Spontaneous Heating and Ignition in Air

The U.S. Department of Energy defines spontaneous combustion as the ignition of a combustible material caused by the accumulation of heat from oxidation reactions and indicates that fires caused by spontaneous combustion are due to spontaneous heating, pyrophoricity, and hypergolic reactions [7]. Spontaneous heating is the slow oxidation of an element or compound which causes its bulk temperature to rise without the addition of an external heat source. It may occur because of the oxidation of hydrocarbons (e.g., oils, coal, and solvents) or because of the action of microorganisms in organic materials. Pyrophoricity relates to the ignition of a substance upon exposure to the atmospheric oxygen in air. Although there are some pyrophoric liquids and gases, most pyrophoric materials are very finely divided metals. A hypergolic reaction describes a material's ability to spontaneously ignite or explode upon contact with any oxidizing agent.

The spontaneous combustion of coal is a well-known phenomenon, especially with coal that is extremely friable and breaks down into smaller particles. Hossfeld and Hatt [8] report that moist,

volatile subbituminous coal will not only smolder and catch fire while in storage piles at power plants and coal terminals, but has been known to be delivered to a power plant with the rail car or barge partially on fire.

Tsuchiya and Sumi [9] indicate that spontaneous ignition is a complex phenomenon of combustible material ignited by its own heat of reaction without external heat or other source of ignition. The factors contributing to spontaneous heating and ignition are heat generation and heat dissipation. If heat generates faster than it dissipates, it accumulates (i.e., the temperature increases). The authors state:

> One of the best known examples of spontaneous ignition is that of a drying oil such as linseed oil absorbed in cotton waste. Linseed oil slowly takes oxygen from the air to form a skin of solid material, a process caused by an oxidation reaction that produces heat. If the oil is absorbed in cotton waste, the heat cannot escape rapidly and the temperature of the waste increases. This accelerates the rate of oxygen absorption and results in further temperature increase. If this process continues, the temperature of the oil-soaked waste may gradually rise until ignition occurs spontaneously [9].

Tsuchiya and Sumi further state that, in general, fibrous and finely divided materials are more susceptible to spontaneous ignition due to their lower thermal conductivity than solid materials and their increased surface area [9]. Powdered metals are much more easily ignited than solid metals, for example. When finely divided materials form a large pile, self-heating is a common problem. The larger the pile, the easier it is for self-heating and ignition to occur. This is because heat generation is proportional to the volume of the pile by the 3rd power of the radius; the heat loss, however, is proportional to the surface area of the pile by the 2nd power of the radius. The critical size, above which spontaneous ignition can occur and below which spontaneous ignition does not occur, is called the "critical diameter" or "critical radius."

Tsuchiay and Sumi also discuss the effect of ambient temperature [9]. High surrounding temperature increases self-heating and restricts heat loss. The critical temperature, above which

spontaneous ignition can occur and below which it does not occur, is called the "critical surface temperature." A theoretical relation between the critical ambient temperature and critical radius of various materials is shown in Fig. 1. The higher the ambient temperature, the smaller the critical radius. If the ambient temperature is below the critical temperature, the material self-heats but does not ignite. When it is slightly higher, spontaneous ignition can occur after a long period. The time to ignition is called the "induction period"; the higher the ambient temperature above the critical temperature, the shorter the induction period.

Spontaneous Ignition in Oxygen-Enriched Atmospheres

As the preceding paragraphs indicate, good data exist in support of spontaneous heating and ignition in ambient air conditions which is, in some measure, related to the critical radius of the accumulation of high-surface-to-volume-ratio fuel particles. The authors propose here that those processes leading to fire events in oxygen-enriched, pressurized, flowing (such as would occur in a leak) environments will occur in dramatically smaller accumulations of fuel particles, especially if the particles are very small. It is proposed that three factors will reduce the critical radius at which spontaneous heating and ignition will occur: 1) oxygen purity and pressure, 2) forced convection, and 3) particle size. If it can be shown that the additive effects of these three factors can reduce the critical radius of white pine sawdust, for example, from 15 in. (38 cm) at 177 °F (81 °C) to 0.063 in. (0.16 cm) at 177 °F (81 °C), then spontaneous heating and ignition would be a possible ignition mechanism in small, leaking, oxygen-enriched components such as those used in laboratory-scale oxygen systems.

A Possible Real-Life Spontaneous Ignition Fire Event

The NASA White Sands Test Facility (WSTF) Oxygen Group was requested to perform a failure analysis on an oxygen-enriched system which had undergone a fire event. The following is a

description of the fire event hardware, the salient features of the failure analysis findings, and a possible ignition scenario involving spontaneous heating and ignition.

Description of Fire Event Hardware

The system in which the fire event occurred was a portable pressure-swing-absorption oxygen concentration system which supplied approximately 95 % oxygen for medical purposes. The maximum system operating pressure was 2250 psi (15.5 MPa). The fire event started in a three-way valve that directed the flow of pressurized product gas either to storage tanks or to vent (Fig. 2).

Fig. 2 shows the product gas inlet on the left, the burned outlet fitting on the bottom of the valve which connected to the storage tanks and product output lines, and the burned fitting and vent line on the right.

Fig. 3 shows the damaged 3-way valve with the valve stem/Teflon[®4] seat assembly removed and located on top of the valve body in the same orientation it had inside the valve when the fire occurred.

Fig. 4 is a schematic representation of the valve indicating the product gas inlet line from the compressor on the left, the outlet on the bottom (this flow path supplied product gas to the storage tanks and provided a reverse flow option to vent the storage tanks), and the vent line on the right. The cross-sectional view A-A, indicated in Fig. 4, is shown in Fig. 5.

Failure Analysis Findings

*Improper Valve Configuration—*Upon disassembly of the damaged valve, it was determined that the valve had been improperly configured. Fig. 5 and 6 show the internal parts of the damaged 3-way vent valve. Fig. 6a illustrates the proper configuration of the seat of the ball valve as indicated in the vendor's catalog. The seat was a Teflon capsule which was molded over the stainless steel ball of the valve and was therefore unable to be removed without damage. Since the

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[4] Teflon[®] is a registered trademark of E. I. du Pont de Nemours and Company, Wilmington, Delaware.

valve could not be fully disassembled, it was not possible to clean the individual valve parts to a cleanliness level appropriate for use in oxygen-enriched environments. The factory-installed lubricant between the stainless steel ball and the Teflon seat was silicone, a material not recommended for use in oxygen-enriched environments.

At the inlet or OPEN port position, through which the inlet product gas would flow, a side ring was supposed to be positioned (Fig. 6a). At the CLOSE position, a side disc was intended to be positioned; and at the VENT port position, a second side ring was to be positioned. These rings, fabricated from metal alloy, were intended to provide support the to the Teflon seat material to keep it in the position and configuration necessary to maintain a proper seal between the seat and the stainless steel ball and between the seat and the stainless steel valve body.

Post-fire analysis of the partially consumed valve revealed that there was, in fact, no seal ring at the OPEN position port; and instead of a side disc, there was a side ring at the CLOSE position, as shown in Fig. 6b.

Known Valve Leakage—Two additional illustrations of the improperly configured valve are shown in Fig. 5. The valve was known to have a leak which flowed from the OPEN position port to the CLOSE position. In this configuration, the valve is closed, but the gas leaking from the inlet side of the valve, pressurized to approximately 2200 psi (15 MPa) maximum, would flow between the unsupported Teflon seat and the stainless steel ball.

Cellulose Particulate Contamination—A third important observation from the failure investigation was that cellulose particles were present in the high-pressure oxygen-enriched portion of the system. Paper (cellulose) filters were used upstream of the compressors in the product gas system and in the high-pressure portion of the system, and fiber/particle remnants of a paper (cellulose) towel were found (Fig. 7). The fiber and particle diameters ranged from 30 to 60 µm.

It is postulated that cellulose particulate and fibers migrated from these sources in the high-pressure system to the damaged 3-way vent valve and became trapped in the lubricated space between the ball and the seat, as indicated in Fig. 5.

Possible Ignition Scenario

With most unintended oxygen-enriched fires it is extremely difficult, if not impossible, to determine the actual root cause of the fire. The main reason is that most, if not all, of the evidence at the point of ignition is typically consumed in the fire, leaving very little physical evidence from which to investigate or reconstruct the scenario before the fire started. As a result, it is necessary to identify the known possible ignition mechanisms in oxygen-enriched environments and eliminate as many as possible based upon the system operational parameters and procedures, witness accounts, and physical evidence. Those remaining sources of ignition, or some unknown source of heat, must then be investigated as the probable source of ignition for the fire event. ASTM Manual 36 [1] lists several ignition mechanisms known to have caused fires in oxygen-enriched environments. That list is shown in Table 1.

Ignition Mechanisms Ruled Out—Using the evidence provided to the WSTF failure investigation team, a number of different hypothetical ignition sources were considered and ruled out as possible causes of the fire, because the characteristic elements or necessary conditions for those ignition mechanisms to be active were not present in this scenario.

Particle Impact. If the 3-way valve had been opened while pressurized, sonic velocity oxygen-enriched product gas would have impinged the opposite side of the stainless-steel ball at up to a 90 degree impact angle at a high velocity. However, this valve was not opened during or just prior to the fire event, and as such, product gas was not flowing through the valve at the time of the fire event. Therefore, particle impact was not considered a possible cause of this event.

Heat of Compression. Based upon witness statements and knowledge of the system configuration prior to the fire event, it was determined that the maximum temperature that could have possibly occurred at the valve inlet due to rapid pressurization was 81 °C (177 °F). The autoignition temperature of the silicone grease in the ball/seat assembly is 216 °C (421 °F). Clearly, the fire event was not caused by the heat from rapid pressurization alone.

Flow Friction. This ignition mechanism will be discussed in conjunction with the possible spontaneous heating and ignition of the cellulose particles entrapped in the valve ball/seat assembly.

Mechanical impact was not present for obvious reasons. *Mechanical friction* was eliminated because no motion of the 3-way valve had occurred immediately prior to the fire event. *Fresh metal exposure* was deemed not possible because there was no evidence of such exposure in the ball or valve body at the location of the initiation of the fire at the upstream side of the burned Teflon valve seat. *Static discharge* was considered not possible because the metal body of the valve was grounded to the inlet and outlet fittings and lines, and the Teflon seat was surrounded by metal parts that were grounded to one another. *Electrical arc* was ruled out because the 3-way vent valve was not powered electrically. *Chemical reaction* was eliminated from consideration because no other chemical process was ongoing in the oxygen-enriched product flow stream. *Thermal runaway* was considered not possible because there were no external heaters or heat-generating processes in the vicinity of the 3-way valve. *Resonance heating* was eliminated because the burned 3-way valve had no configurations known to generate acoustic oscillations. Finally, there were no sources of *external heat*, eliminating that as a source of ignition.

Most Probable Ignition Scenario

After careful and extensive examination of the evidence (which included the burned hardware, photographs, witness statements, and lab analyses), the following was selected by the team as the most likely scenario to have caused the fire in the 3-way valve.

- Cellulose particles were deposited at the entrance point to the leak path in the valve as indicated in Fig. 5.

- The temperature of the particle deposit, the Teflon seal, or the silicone grease was increased to as high as 81 °C (177 °F) by the heat of rapid pressurization, as indicated previously.

- The warm cellulose particle/silicone lubricant deposit began to self-heat via the oxidation process. Fresh oxidizer was supplied and the products of oxidation were moved away by the leaking oxygen-enriched product gas.

  Note: At this point in the process, the only macroscopic observation that one could have made was that the valve was leaking. Since a fire event ultimately occurred, it is reasonable to attribute this fire event to the valve leaking gas past a polymer seal at the time of the fire (i.e., flow friction was occurring). However, while that leak was necessary for the ignition scenario described herein, it was not sufficient to cause the fire event on its own.

- The cellulose particles/silicone lubricant accumulation self-heated to its autoignition temperature and ignited (spontaneous ignition).

- The burning cellulose particle and silicone lubricant ignited the Teflon seat packing surrounding the leak path, producing the damage illustrated in Fig. 8 and pictured in Fig. 9. The burning progressed to the side ring improperly located at the CLOSE position of V-9.

- The burning cellulose particles, Teflon seat, and silicone ignited the sharp edge of the stainless steel ball at location A in Fig. 8 and Fig. 9, sending a jet of burning stainless steel/particles/Teflon/silicone across the hole in the ball to far side (Location B in Fig. 8 and

Fig. 9). As the fire consumed more of the edge of the stainless steel ball, the hole increased in size with an accompanying increase in the flow of oxygen and a subsequent change in direction of the flame jet. The flame jet ignited, burned, and eroded the inside of the ball (see Location C in Fig. 8 and 9) and the fire flowed out of the ball, consuming the inside diameter of the valve body at the outlet port.

Discussion

The proposed ignition mechanism is a combination of the heat from pressurization of the product gas, spontaneous heating of very small cellulose fibers and particles, and the effects of the very small flow associated with the product gas leak across the valve seat. Admittedly, this proposal is derived from an unverifiable set of circumstances; but in its defense, this theory matches with all the observed and verifiable evidence. All other ignition mechanisms considered, on the other hand, can be dismissed based upon the known facts related to the configuration of the burned 3-way valve, the system operational configuration, and the witness statements. As one sleuth asked his faithful assistant, "How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, must be the truth?" (Sherlock Holmes in *The Sign of Four* by A.C. Doyle). Perhaps that sentiment applies here, as well.

Estimation of Critical Radius of Small Cellulose Particles in Flowing Oxygen

In order for the proposed ignition scenario to be plausible, it is necessary to demonstrate that small cellulose fibers and particles can undergo spontaneous heating in the configuration at the inlet of the leak path between the stainless steel ball and the unsupported Teflon seat annotated in Fig. 5. To do so, the critical radius of cellulose particles in oxygen-enriched, high pressure, flowing gas would need to be in the range of 0.1 to 0.2 cm. This amounts to approximately a two-order-of-magnitude decrease in the critical radius for white pine sawdust as shown in Fig. 1. The authors propose that three additive factors will produce this decrease in critical radius: 1) higher oxygen

concentration (purity and pressure) compared to ambient pressure air, 2) forced convection (from a

leak) as compared to natural convection, and 3) small cellulose particles compared to white pine

sawdust.

Effect of Oxygen Purity and Pressure—Considering an accumulation or pile of cellulose

particles, as the temperature of the pile increases, the rate of heat generation can increase

exponentially according to the Arrhenius equation (Eq. 1).

$$\dot{q} = Q\rho A e^{-\frac{E}{RT}} \tag{1}$$

Where:
- $\dot{q}$ is the heat generation rate per unit volume (J/s·m^3)
- Q is the heat of reaction (kJ/g)
- ρ is the bulk density of the material (kg/m^3)
- A is the pre-exponential factor (s^{-1})
- E is the apparent activation energy (J/mol)
- R is the universal gas constant (= 8.314 J/mol·K)
- T is the temperature (K) of the particles within the pile

The Frank-Kamanetskii model for spontaneous ignition describes a Damkohler number (δ) as an

estimate of the heat generation within an accumulation of combustible material [10] (Eq. 2).

$$\delta = \frac{\rho Q A}{\lambda} \frac{E r^2}{R T_o} e^{-\frac{E}{RT}} \tag{2}$$

Where:
- λ is the thermal conductivity of the pile of particles (W/(m·K))
- r is the characteristic length of an accumulated pile (radius for a sphere) (m)
- T_o is the flowing gas temperature (K)

Another calculated value, known as delta critical, is derived from heat loss mechanisms. If

the Damkohler number is less than delta critical, the rate of heat loss is greater than the rate of heat

generation and spontaneous ignition cannot occur. If heat generation is greater than heat loss

(Damkohler > delta critical), the temperature can rise exponentially to ignition.

Rearranging Eq. 2 produces Eq. 3:

$$\delta = Q\rho A e^{-\frac{E}{RT}} \cdot \frac{Er^2}{\lambda RT_o} \tag{3}$$

Substituting the first group with $\dot{q}$ yields (Eq. 4):

$$\delta = \dot{q} \cdot \frac{Er^2}{\lambda RT_o} \tag{4}$$

Setting the radius of the pile of accumulated particles to the critical radius makes δ equal to the Damkohler number (Eq. 5).

$$\delta_c = \dot{q} \cdot \frac{Er_c^2}{\lambda RT_o} \tag{5}$$

Carras and Young [11] found that in the early stages of carbonaceous material oxidation, the reaction proceeds as follows:

$$\text{Carbonacous material} + O_2 \rightarrow CO_2 + \text{heat}$$

The rate of the reaction can be expressed as (Eq. 6):

$$r' = [O_2] A e^{-\frac{E}{RT}} \tag{6}$$

Where:
r' is the rate of change in the concentrations of the reactants and products (kmol/(m^3 second)
$[O_2]$ is the oxygen concentration (kmol/m^3)

Therefore, the rate of reaction is proportional to the rate of heat production and can be substituted into Eq. 5 to yield (Eq. 7):

$$\delta_c \propto [O_2] A e^{-\frac{E}{RT}} \cdot \frac{Er_c^2}{\lambda RT_o} \tag{7}$$

Since δ_c, A, E, λ, R, T, and T_o are constants, they can be ignored in the proportionality and Eq. 7 becomes (Eq. 8):

$$r_c \propto \frac{1}{\sqrt{[O_2]}} \tag{8}$$

Equation 8 shows that for a collection of combustible particles that is on the tipping point of spontaneous heating and ignition, if the rate of heat production is quadrupled by increased oxygen concentration, the critical radius will only decrease by a factor of two.

The critical radii data shown in Fig. 1 are postulated assuming air at ambient conditions. The ratio of oxygen partial pressure at 2200 psi (15.2 MPa) and 95 % purity divided by the oxygen partial pressure at ambient conditions results in a 677 fold increase in oxygen concentration. Applying this increase to Eq. 8 predicts a 26 fold decrease in critical radius due to this increase in oxygen concentration.

Effect of Forced Convection—Fig. 10 [12] shows the temperature sensitivity of a packed bed of fine (< 45 µm) carbonaceous material to air flow. The vertical axis describes a runaway temperature which is defined as the temperature increase through the packed bed above the inlet temperature of 493 K. The plateau at approximately 1 L/min translates into a linear velocity across the bed particles of approximately 27 in/s (69 cm/s).

The ratio of outlet temperature to inlet temperature in air is approximately 1.28. Assuming this ratio applies to enriched oxygen and applying it to cellulose at 353 K (177 °F) yields an estimated flowing oxygen exit temperature of 451 K. Substituting the rate of reaction for the oxygen concentration in Eq. 8 yields (Eq. 9):

$$r_c \propto \frac{1}{\sqrt{r'}} \tag{9}$$

Using Eq. 1 with an apparent activation energy of 87,900 J/mol for cellulose [10] to calculate a ratio of reaction rates at the two different temperatures, and applying the results to Eq. 9, yields an estimated decrease in critical radius of 26 fold.

Effect of Characteristic Particle Dimension—Fig. 11 [12] shows the temperature sensitivity of a packed bed of carbonaceous material to various particle sizes. The vertical axis describes a runaway temperature which is defined as the temperature increase through the packed bed above the inlet temperature of 493 K. The assumed characteristic dimension or particle size of white pine sawdust is in the range of 200 to 800 µm, and the measured fiber and particle diameters of the cellulose in the fire event oxygen system is 30 to 60 µm.

The ratio of outlet temperature to inlet temperature is approximately 1.54. Applying this ratio to cellulose at 353 K (177 °F) yields an estimated flowing oxygen exit temperature of 543 K.

Using Eq. 1 with an apparent activation energy of 87,900 J/mol for cellulose [10] to calculate a ratio of reaction rates at the two different temperatures, and applying the results to Eq. 9, yields an estimated decrease in critical radius of 188 fold.

Combined Effects of Factors—The combined effect of oxygen concentration (26 fold), forced convection (26 fold), and particle dimension (188 fold) is a 240-fold decrease in the critical radius. Therefore, the critical radius for white pine sawdust (which is cellulose and thus comparable to the cellulose fibers in the damaged oxygen system) at 177 °F (81 °C) in Fig. 1 will be reduced from 15 in. (38 cm) to 0.062 in. (0.16 cm), as shown in Fig. 12. This dimension fits well within the dimensions of the inlet of the valve as indicated in Fig. 5. It is reasonable to conclude that the ignition scenario presented herein is plausible.

Conclusion

The "flow friction" ignition mechanism is a postulated ignition mechanism that is unsubstantiated by direct test data. Even so, significant circumstantial evidence that ignition events have occurred in oxygen-enriched atmospheres can be attributed to oxygen-enriched gas leaking past polymer seats and seals. The spontaneous ignition of accumulations of small particulate and fibrous debris in a leak path has been postulated as a contributing ignition source in a stainless-steel-

body hand valve with a Teflon seal and silicone lubricant known to be contaminated with small cellulose particles. It was surmised that the leaking oxygen-enriched gas provided the physical transport mechanism to remove oxidation products and supply fresh oxidizing gas to the accumulated deposit of cellulose particles. This adds an important aspect to the discussion of the "flow friction" ignition mechanism in oxygen-enriched atmospheres.

Recommendation for Future Tests

It is recommended that the values of critical radii as a function of surface temperature in Fig. 12 be validated by testing.

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TABLE 1— *List of possible ignition mechanisms in oxygen-enriched environments [1].*

Ignition Mechanisms	Description
Particle impact	Heat generated when particles strike a material with sufficient velocity to ignite the particles and or the material.
Heat of compression	Heat generated when a gas is rapidly compressed from a low pressure to a high pressure.
Flow friction	Heat generated when oxygen flows across or impinges upon a nonmetal (usually a polymer) and produces erosion, friction, and/or vibration.
Mechanical impact	Heat generated as a result of single or repeated impacts on a material.
Mechanical friction	Heat generated as a result of friction and galling at the rubbing interface as two or more parts are rubbed together.
Fresh metal exposure	Heat generated by oxidation when metal is exposed to oxygen.
Static discharge	Heat generated as a result of static discharge that is sufficient to ignite proximate materials.
Electrical arc	Heat generated by an electrical arc that is sufficient to ignite proximate materials.
Chemical reaction	Heat generated between a combination of chemicals sufficient to ignite surrounding materials.
Thermal runaway	Some materials, notably certain accumulations of fine particles, porous materials, or liquids, may undergo reactions that generate heat.
Resonance	Heat generated by acoustic oscillations within resonant cavities.
External Heat	Heat generated by any external heat sources such as lightning, explosive charges, personnel smoking, open flames, shock waves from tank rupture, fragments from bursting vessels, welding, and exhaust from internal combustion engines.
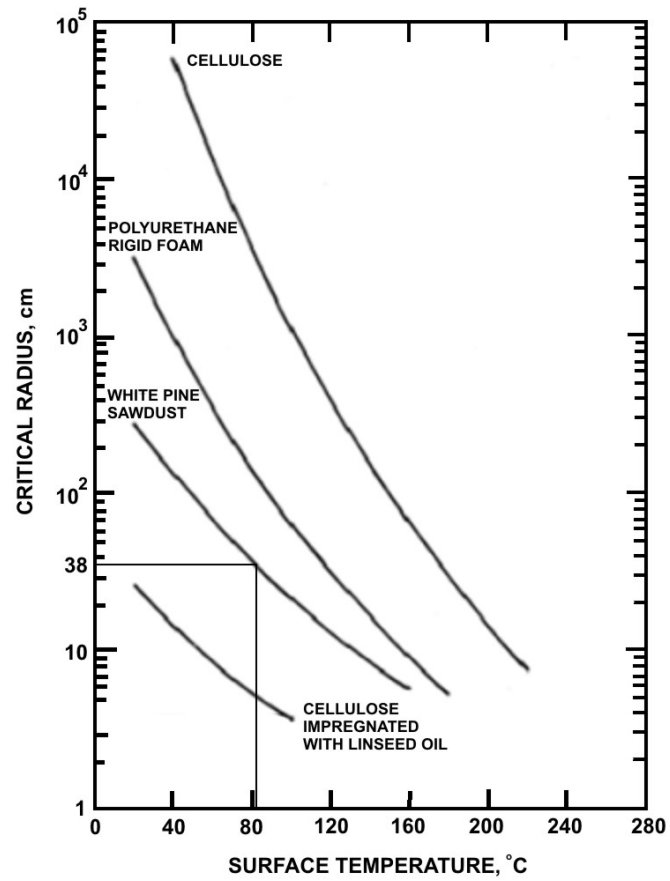
FIG. 1— *Surface temperature vs. critical radius in spontaneous ignition [9]*.
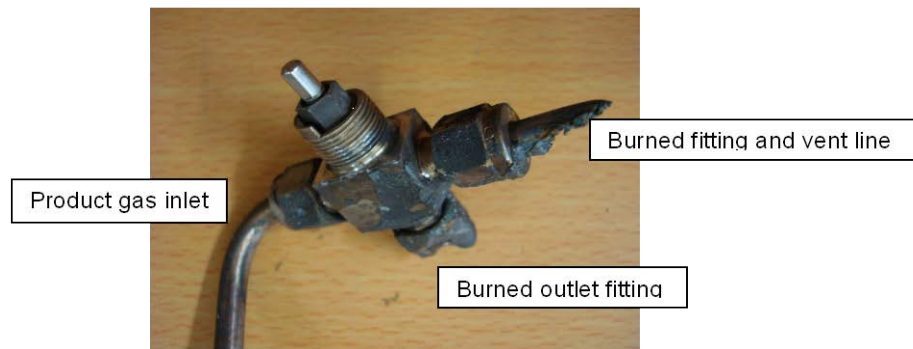
FIG. 2— *Damaged three-way valve shown with valve handle removed.*

FIG. 3— *Damaged 3-way valve with valve stem/Teflon seat assembly removed and located on top of the valve body.*
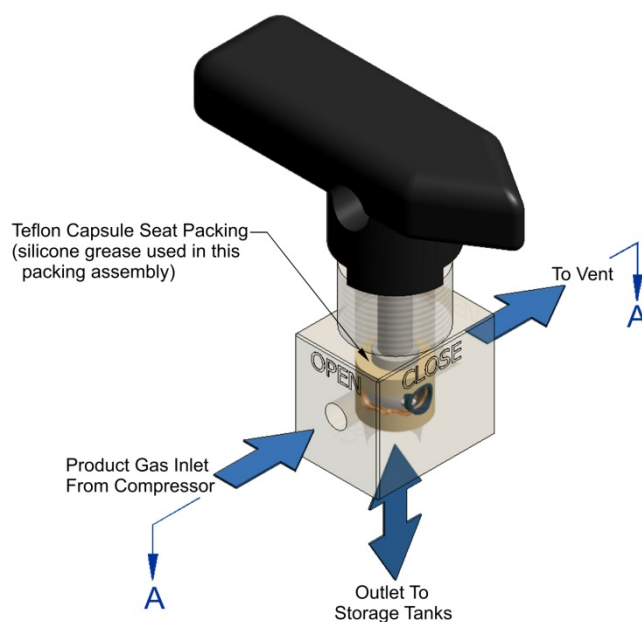
Teflon Capsule Seat Packing
(silicone grease used in this
packing assembly)

To Vent

A

OPEN   CLOSE

Product Gas Inlet
From Compressor

A

Outlet To
Storage Tanks

FIG. 4— *Schematic representation of 3-way vent valve.*
(See Fig. 5 for cross-section A-A.)

0.09cm (0.04in)

Valve shown in the
CLOSE position

0.4cm (0.16in)

OPEN port (from PRV-4
and RIX compressor)

VENT port

Probable particle accumulation
point at entrance to leak path

Particles in flow from
PRV-4 and RIX at
elevated pressure

Probable leak path
with silicone grease

Section A-A
from Figure 4

Silicone grease sealed
between stem and seat
at assembly (cannot be
disassembled)

Unsupported
Teflon

Teflon Seat

Improperly located Side
Ring at CLOSE position

Stainless Steel
Valve Body

FIG. 5—*Section A-A of damaged 3-way vent valve showing expanded view
of improperly configured valve and possible leak path.*
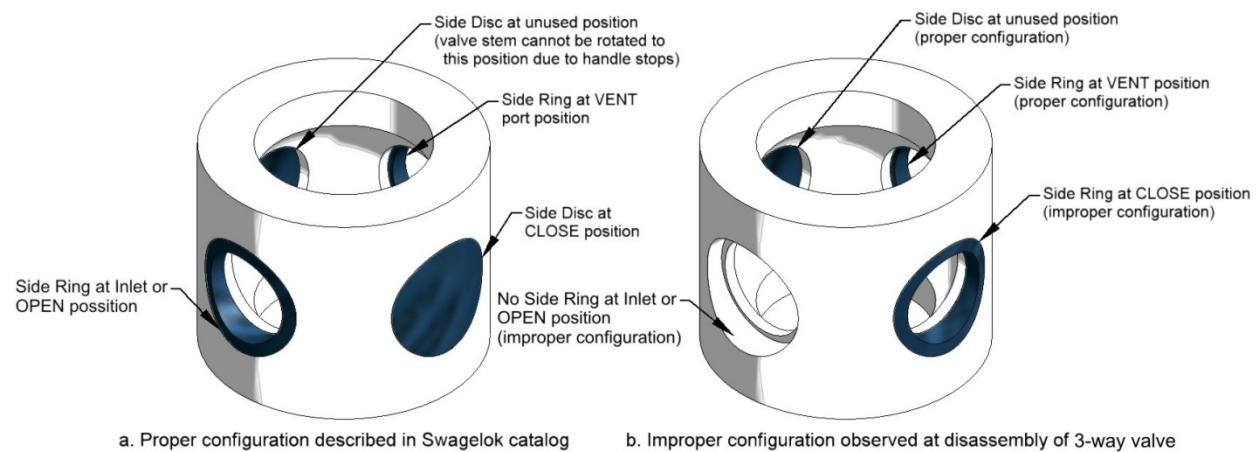
FIG. 6—*Proper (a) and improper (b) configuration of Teflon valve seat and support discs.*
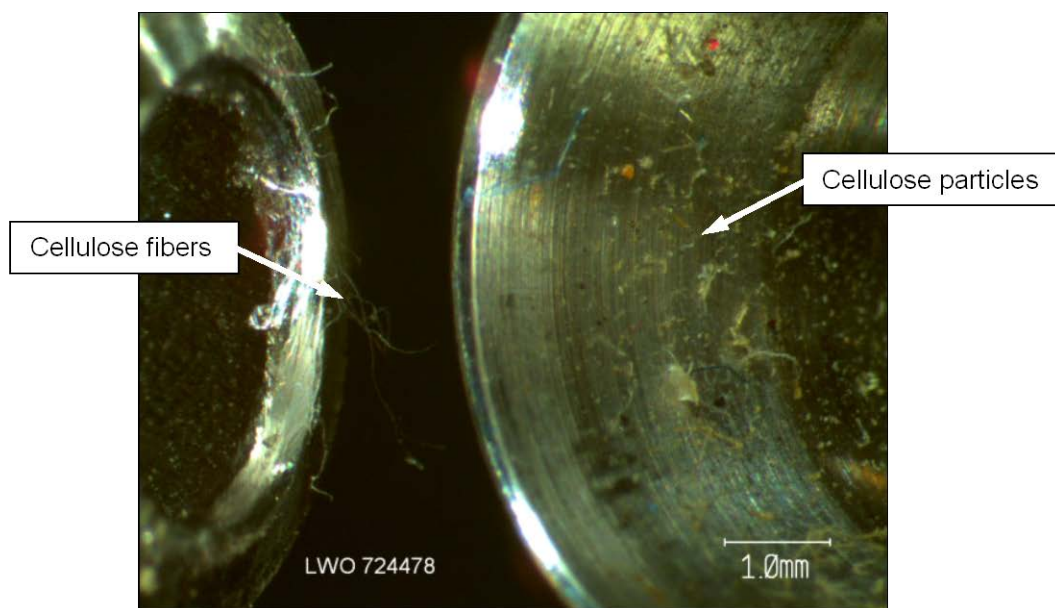
FIG. 7—*View of cellulose fibers and particles observed in high-pressure portion of the system. The fiber and particle diameters range from 30 to 60 μm.*
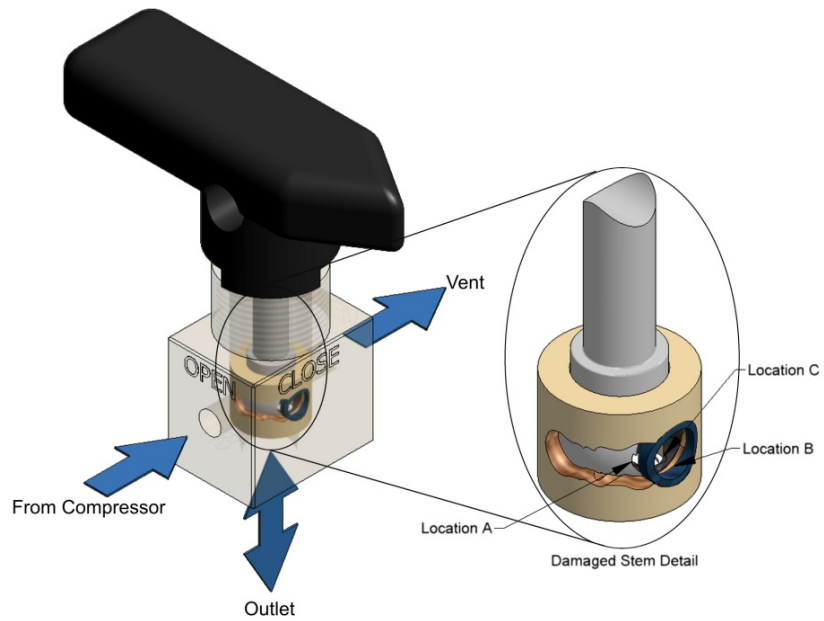
FIG. 8— *Illustration of the damaged valve stem/Teflon seat assembly.*
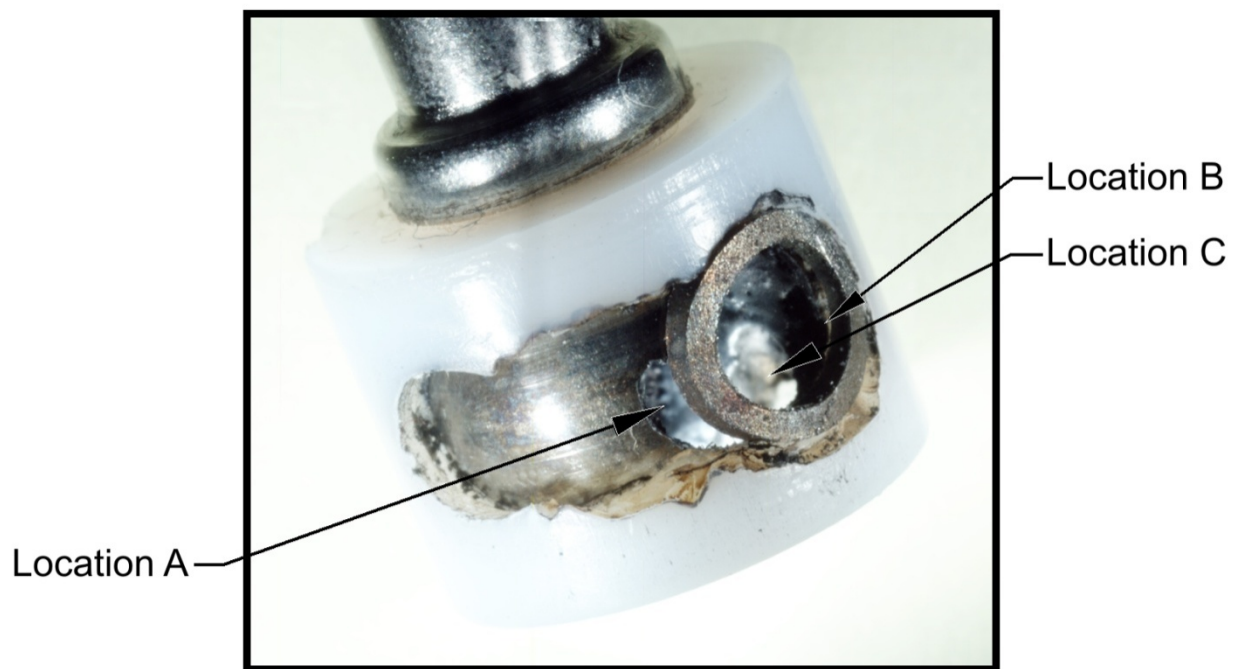
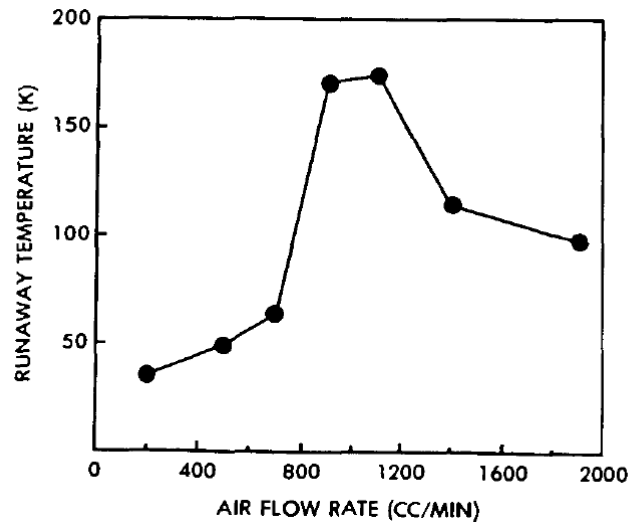FIG. 9— *Close-up view of the damaged valve stem/Teflon seat assembly.*
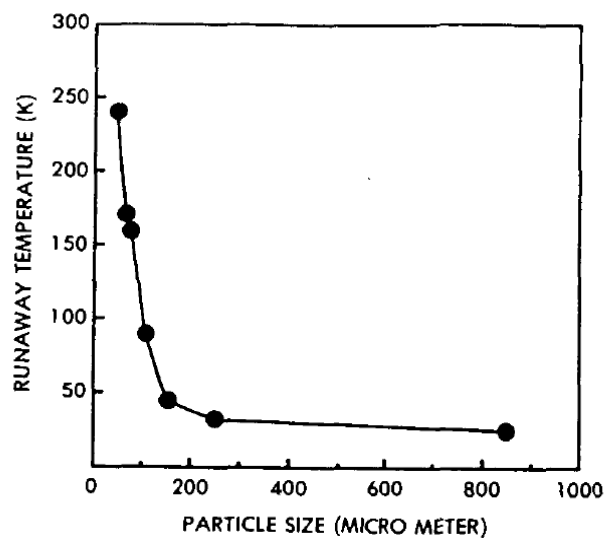
FIG. 10—*Runaway temperature as a function of airflow [12].*

FIG. 11—*Runaway temperature as a function of particle size [12].*
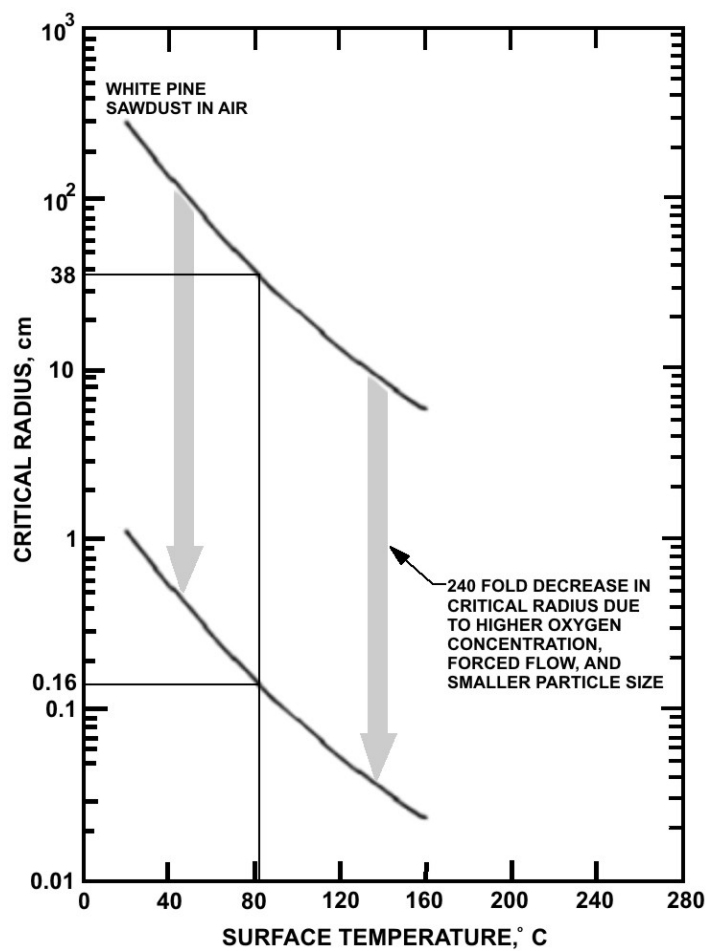
FIG. 12—*Projected surface temperatures vs critical radius in spontaneous ignition of very small cellulose particles in elevated oxygen concentration with forced flow.*

Flow Friction or Spontaneous Ignition?

September 2012

Authors:
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Presenter: Kyle Sparks

Background

- Description of Fire Event Hardware
  - Portable pressure-swing-adsorption system
  - Supplies ~95% O_2
  - Max pressure 2250 psia (15.5 MPa)
  - Fire initiated in 3-way valve
- Operations in which Fire Occurred
  - Recently serviced system
  - Decided to refill tanks to 2250 psia (15.5 MPa) from ~1900 psia (13.1 MPa)
    - Swing-adsorption system turned on
    - Low pressure and purity reached and compressors turned on
    - Pressure was built up downstream of compressor
    - A valve was opened to allow tank fill
    - Fire occurred in a closed valve on a separate leg of the system

Fire Investigation

- Ignition Mechanisms Considered
  - Particle impact
  - Heat of Compression
  - Flow Friction
  - Spontaneous Ignition
  - Fresh Metal Exposure
  - Resonance Heating
  - Static Discharge
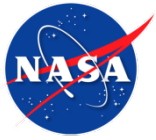 - Electrical Arc
  - External Heating
  - Etc.

Fire Investigation

- Ignition Mechanisms Ruled Out
  - Particle impact
    - Valve not being operated under pressure and was closed
  - Heat of Compression
    - Based on witness statements and knowledge of system operations calculated maximum temperature of 81 °C (177 °F) at seat
  - Others
    - Fresh Metal Exposure
    - Resonance Heating
    - Static Discharge
    - Electrical Arc
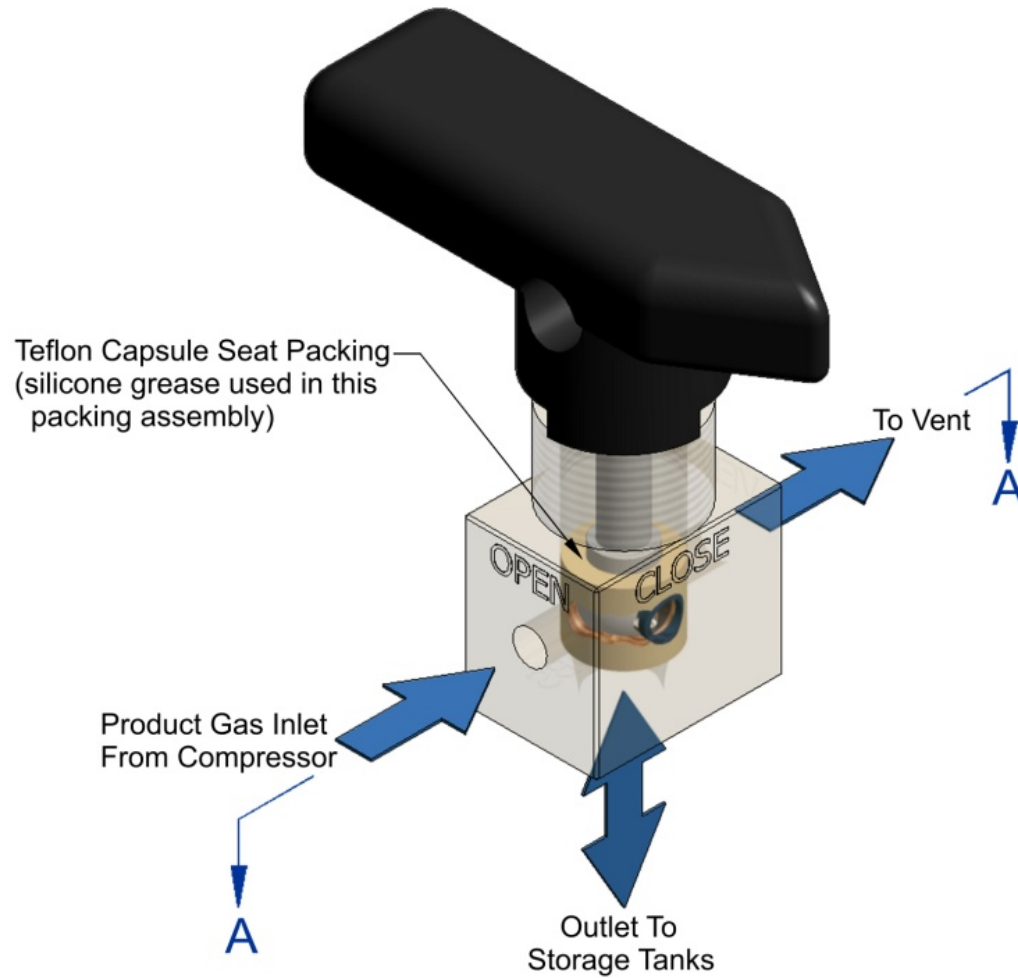   - External Heating
    - Etc

Fire Investigation

- Remaining Plausible Ignition Mechanisms
  - Flow Friction
    - Currently understood as heat generated when oxygen flow across or impinges upon a nonmetal and produces erosion, friction, and or vibration
  - Spontaneous Ignition
    - Spontaneous heating is the slow oxidation of an element or compound which causes its bulk temperature to rise without the addition of an external heat source
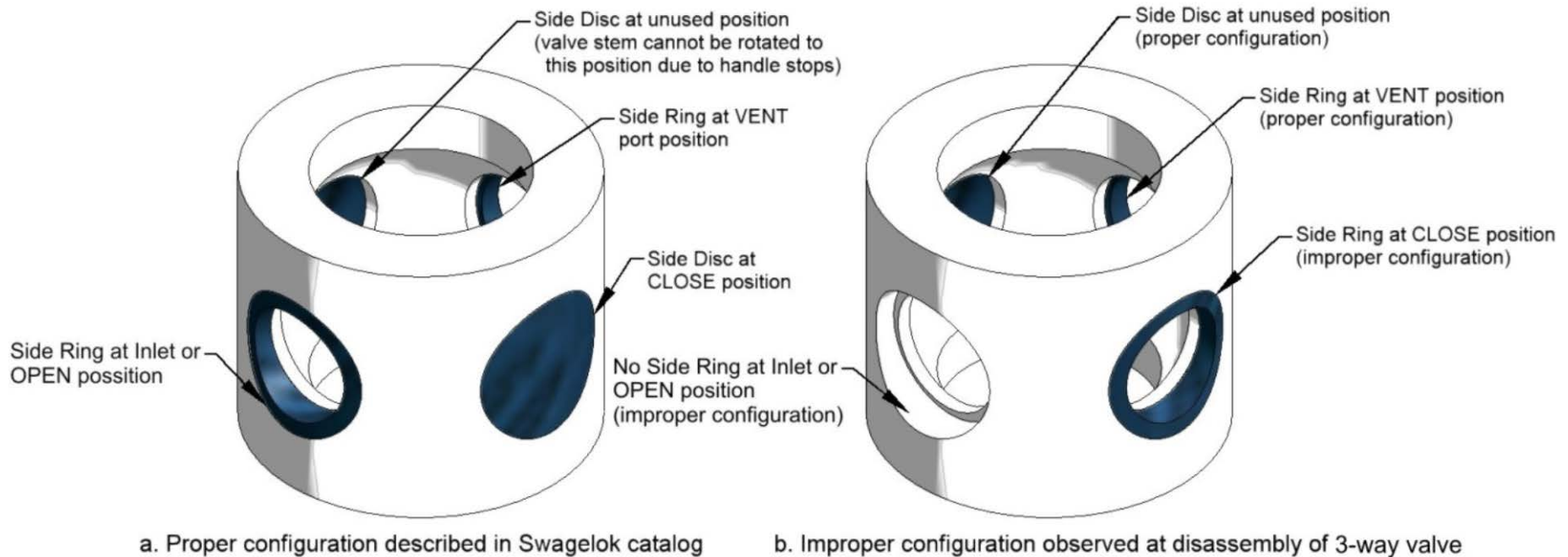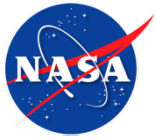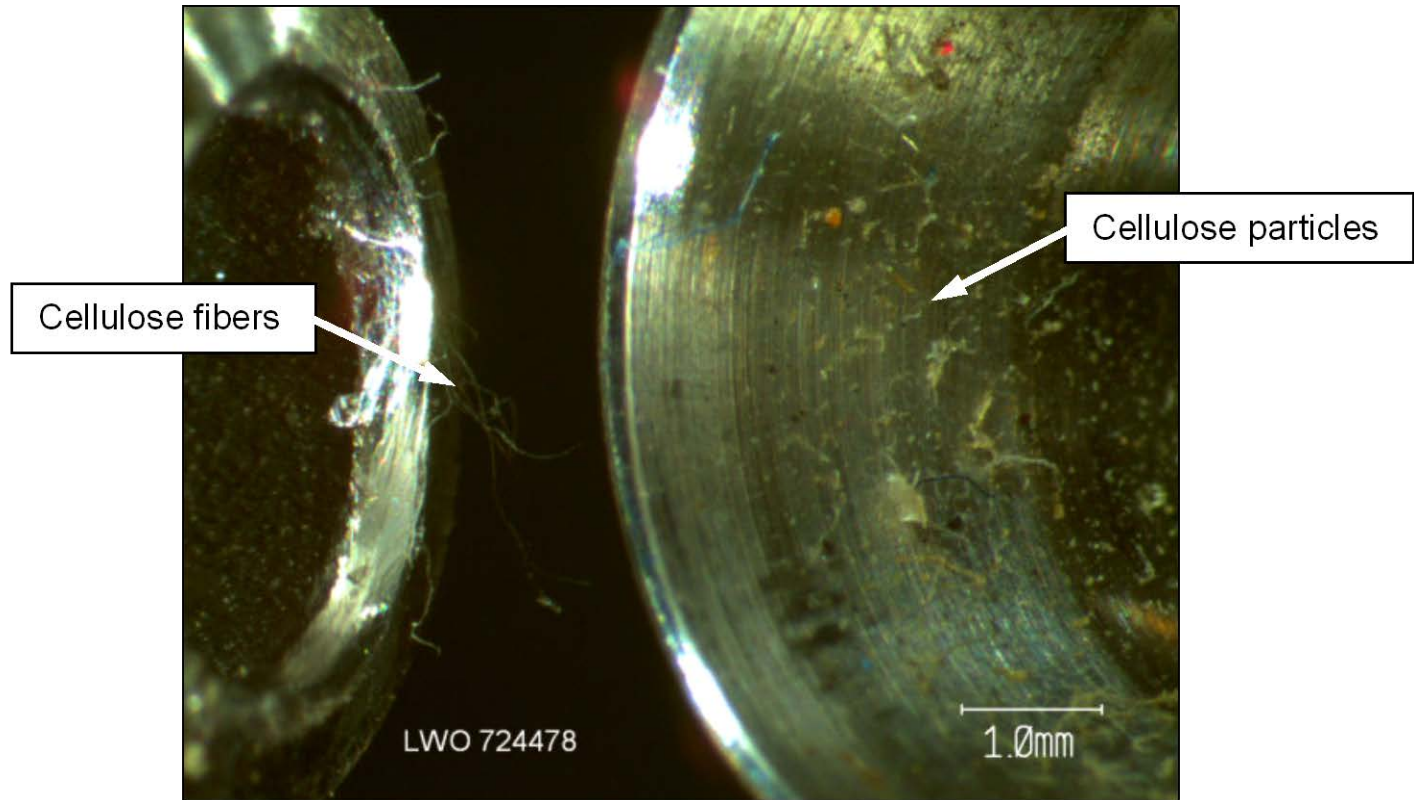 - Combination of the two?

Hardware

Teflon Capsule Seat Packing
(silicone grease used in this
packing assembly)

To Vent

A

OPEN   CLOSE

Product Gas Inlet
From Compressor

A

Outlet To
Storage Tanks

Improper Seat Configuration – Known Leak

a. Proper configuration described in Swagelok catalog

b. Improper configuration observed at disassembly of 3-way valve
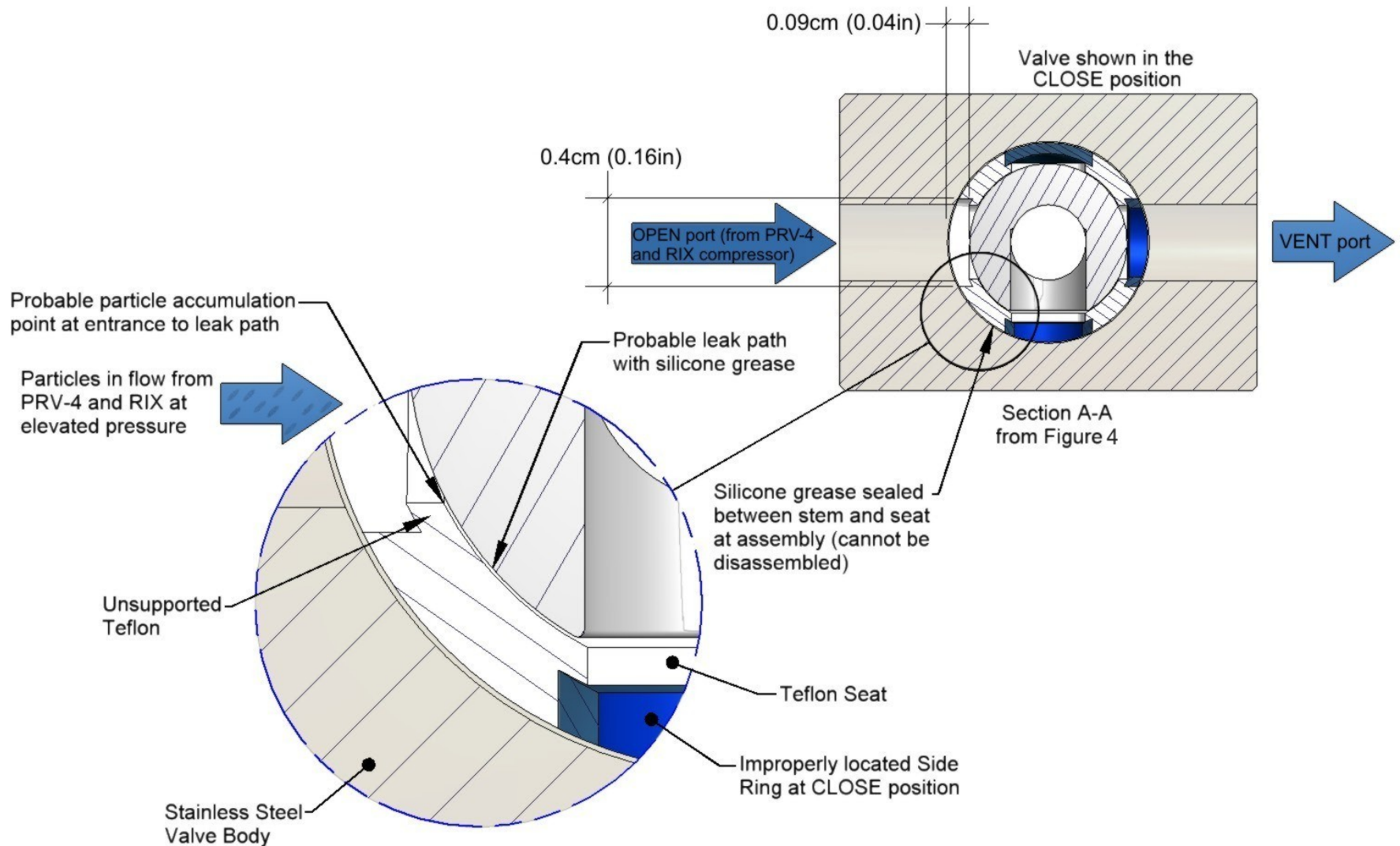
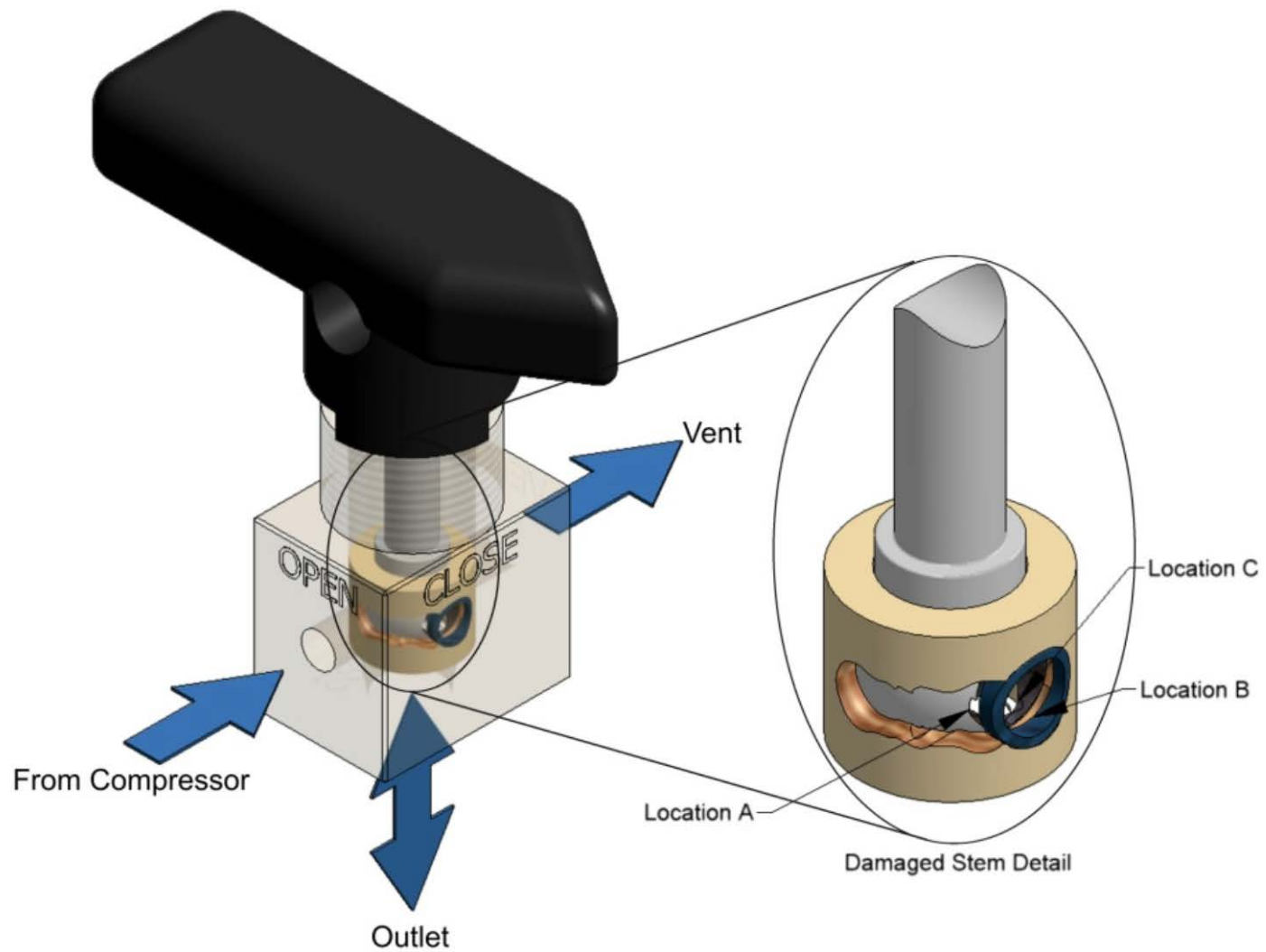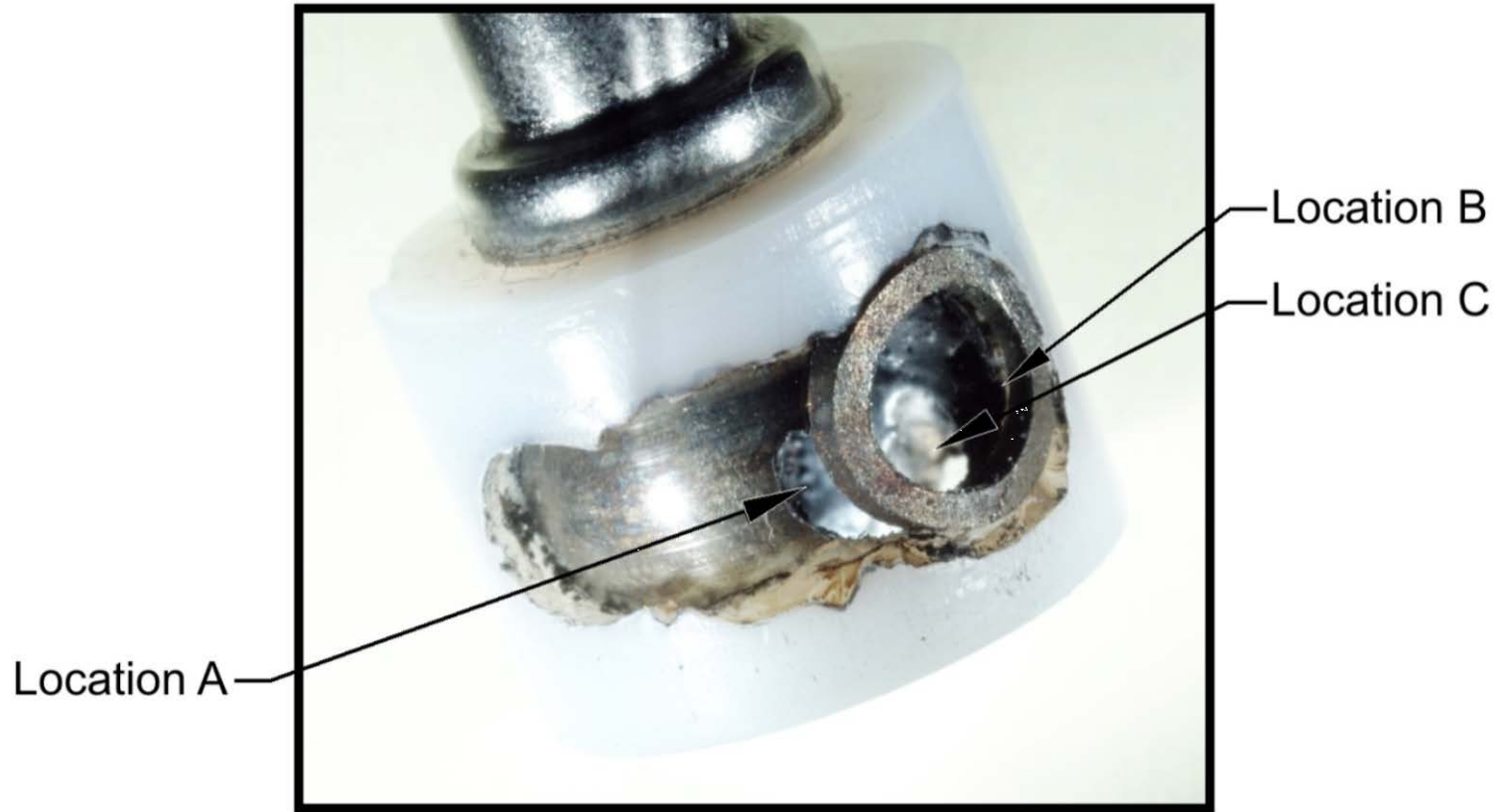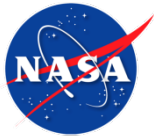# *Contamination Found in Upstream Fitting*

Most Probably Ignition Scenario

- Particles deposited at valve compressor inlet
- Particle deposit, PTFE seal, and or silicone grease heated by rapid pressurization 81 °C (177 °F)
- Warmed cellulose/silicone begins to self-heat via oxidation process
- Fresh oxidizer supplied via small leak path in valve as oxidation products moved away
- Self heats until autoignition temperature reached
- Burning cellulose/silicone/PFTE kindles to sharp edge of stainless steel ball
- Flame jet produced, impinged on bulk of valve and burns through

0.09cm (0.04in)

Valve shown in the CLOSE position

0.4cm (0.16in)

OPEN port (from PRV-4 and RIX compressor)

VENT port

Section A-A from Figure 4

Probable particle accumulation point at entrance to leak path

Particles in flow from PRV-4 and RIX at elevated pressure

Probable leak path with silicone grease

Silicone grease sealed between stem and seat at assembly (cannot be disassembled)

Unsupported Teflon

Teflon Seat

Improperly located Side Ring at CLOSE position

Stainless Steel Valve Body

10

Vent

From Compressor

Outlet

Location C

Location B
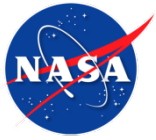
Location A

Damaged Stem Detail

Discussion

- Proposed ignition mechanism is a combination of the heat from pressurization of the product gas, spontaneous heating of very small cellulose fibers and particles, and the effects of the very small flow associated with the leak across the valve seat.

- Derived from an unverifiable set of circumstances

  – Theory matches with all the observed and verifiable evidence.

  – All other ignition mechanisms dismissed based upon the known facts related to the configuration of the burned valve, the system operational configuration, and witness statements.

"How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, must be the truth?"

— Sherlock Holmes

Spontaneous Heating and Ignition

- Fibrous and finely divided materials are more susceptible to spontaneous ignition due to their lower thermal conductivity than solid materials and their increased surface area
- When finely divided materials form a "large" pile, self-heating is a common issue
- Heat generation is proportional to the volume of the pile by the 3rd power of the radius
- Heat loss is proportional to the surface area of the pile by the 2nd power of the radius.
- The critical size, above which spontaneous ignition can occur and below which spontaneous ignition does not occur, is called the "critical diameter" or "critical radius."
- The critical temperature, above which spontaneous ignition can occur and below which it does not occur, is called the "critical surface temperature."

## *Critical Ambient Temperature vs. Critical Radius in Air*
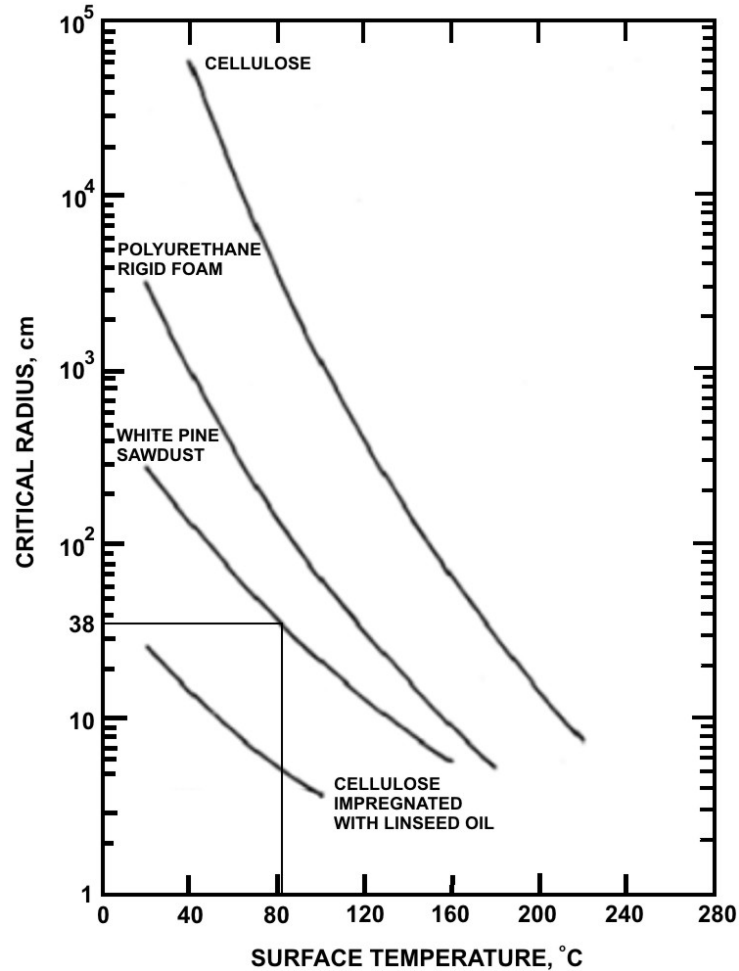
Plausibility

- Estimation of Critical Radius of Small Cellulose Particles in Flowing Oxygen
  - Effect of Oxygen Purity and Pressure
    - Ambient air to 95% O_2 at 2200 psia (15.2 MPa) predicts 26 fold decrease in critical radius
  - Effect of Forced Convection
    - Yields an additional 26 fold decrease in critical radius (based on assumptions of temperature increase via air flow tests on coal)
  - Effect of Characteristic Particle Dimension
    - Yields an additional 188 fold decrease in critical radius (based on assumptions of temperature increase tests on various particle sizes of coal)
- Combined Effects of Factors Yields 240 Fold Decrease in Critical Radius

Critical Ambient Temperature vs. Critical Radius in Oxygen
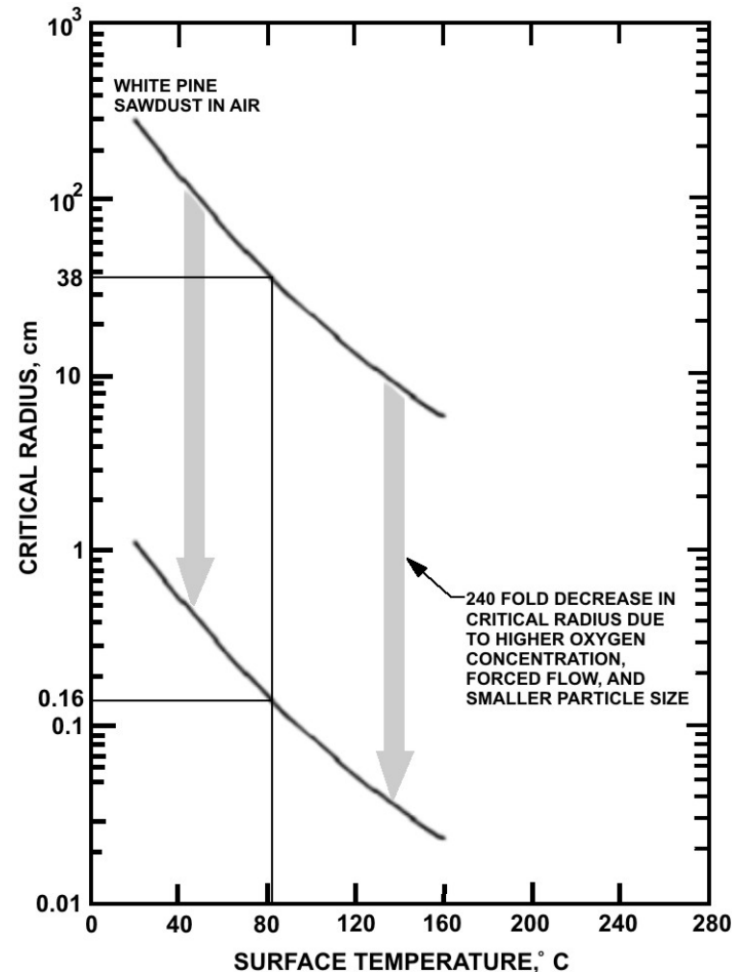
Conclusion

- The "flow friction" ignition mechanism is a postulated ignition mechanism that is unsubstantiated by direct test data. Even so, significant circumstantial evidence that ignition events have occurred in oxygen-enriched atmospheres can be attributed to oxygen-enriched gas leaking past polymer seats and seals

- Spontaneous ignition has been proposed and theoretically shown to be a plausible ingnition mechanism in the discussed fire scenario

- Adds an important aspect to the discussion of the "flow friction" ignition mechanism in oxygen-enriched atmospheres