

The hazards of oxygen and oxygen-enriched mixtures

Most people who use pure oxygen are aware of the hazards of and special precautions for handling this material. Unfortunately, fewer are aware that these hazards extend to oxygen mixtures. This Safetygram reviews how to distinguish between the various mixtures of oxygen, the hazards of pure oxygen and oxygen mixtures, and how to safely handle these products. The Safetygram concentrates on mixtures above 23.5% oxygen and pure oxygen because operationally they should be treated with the same precautions and requirements.

Oxygen-enriched classification

Oxygen-enriched mixtures or atmospheres are defined as those containing more than 23.5% oxygen by volume. In oxygen enriched atmospheres, the reactivity of oxygen significantly increases the risk of ignition and fire. Materials that may not burn in normal air may burn vigorously in an oxygen-rich environment. Materials that burn in normal air may burn with a much hotter flame and propagate at a much greater speed. Fires can be started with much lower ignition energy, and sparks normally regarded as harmless may cause fires.

Oxygen mixtures are classified, labeled and valved differently. As with all gases, the primary method of product identification is the label.

Hazards of oxygen and mixtures

One of the challenges in educating individuals about the dangers associated with oxygen is their perception of the product. When one thinks about oxygen, medical applications usually come to mind. Doctors, dentists, nurses, paramedics and first aid teams administer oxygen to people when they are sick or injured. These professionals would not allow us to intentionally inhale a hazardous material. This perception can downplay or at least minimize respect for the hazards of oxygen. But let's look at oxygen from a different perspective.

Oxygen and its mixtures are packaged as compressed gases. They are supplied at pressures up to 4500 psig (300 barg). In addition to pressure, oxidizers carry other hazards. To fully understand these hazards, we must first understand some of the terms used:

- **Adiabatic compression:** A process in which there is loss of heat from the system while undergoing pressurization. With respect to this document, it is the heat generated in the gaseous oxygen from a rapid pressurization of the system.
- **Autoignition Temperature:** The lowest temperature required to ignite or cause self-sustained combustion in the presence of air and in the absence of a flame or spark.
- **Flammable Range:** The range of concentration in volume percent of flammable gas or vapor between the upper and lower flammability limits.
- **Kindling Chain:** The promotion of ignition from materials of low ignition energies to materials of higher ignition energies.
- **Limiting Oxygen Concentration:** The minimum oxygen concentration in volume percent (at a given temperature) in a gaseous mixture containing a fuel below, which a flame will not propagate.
- **Lower Flammability Limit:** The minimum fuel mixture in volume percent with air through which a flame will just propagate.

- **Upper Flammability Limit:** The maximum fuel mixture in volume percent with air at which a flame will just propagate.
- **Ignition Energy:** The minimum amount of energy that can ignite a mixture of a specified flammable material with air or oxygen.

In an oxygen-enriched environment, fire chemistry starts to change. Materials become easier to ignite because their flammable ranges start to expand, and their autoignition and minimum ignition energies temperatures begin to drop. This includes the materials of construction used in oxidizer systems, such as metals. This reactivity continues to increase not only with the concentration of oxygen, but also with pressure and/or temperature. In other words, oxygen contacting a material at 2000 psig (138 barg) is more likely to react with the material than at atmospheric pressure. In the case of a contaminant in a system, the contaminant may react and generate enough heat to start another material reacting. This is called the kindling chain. When temperature increases, it can lower the amount of energy required to initiate a reaction.

Let's look at the basic fire triangle. All three legs of the triangle must be present to produce a fire—a fuel, an oxidizer, and an ignition source. If asked to name some fuels, materials like wood, coal, oil, and gas would be mentioned. But would anyone list materials like aluminum, steel, stainless steel? What is the primary reason we can light a piece of wood with a match but not a steel rod? The ignition temperature of the wood is much lower than that of the steel rod, and the heat from the match is sufficient for ignition. Remember what we said about fire chemistry and oxygen—as the oxygen concentration increases, the autoignition temperature decreases. So materials that cannot be ignited in normal air may burn readily in oxygen-enriched atmospheres. With this in mind, it is easy to see that in an oxidizer system we have two legs of the fire triangle present. All that is required for an ignition is an energy source.

Now let's consider ignition sources. Typical sources of ignition would be fire, open flames, sparks, or cigarettes. But that is in the world of normal air, not oxygen-enriched atmospheres. Remember the definition of autoignition temperature—the lowest temperature required to ignite a material in the absence of a flame or spark. Could gas velocity, friction, adiabatic heat, or contamination provide ignition sources? Yes.

In the case of gas velocity, a particle that has been propelled by the gas and impacts the system with sufficient force can have sufficient energy to ignite materials. The heat generated by particle impact may be sufficient to start a fire, depending on the material impacted. Friction from a component malfunctioning or operating poorly can generate heat. Friction between two materials generates fine particles, which may ignite from the heat generated.

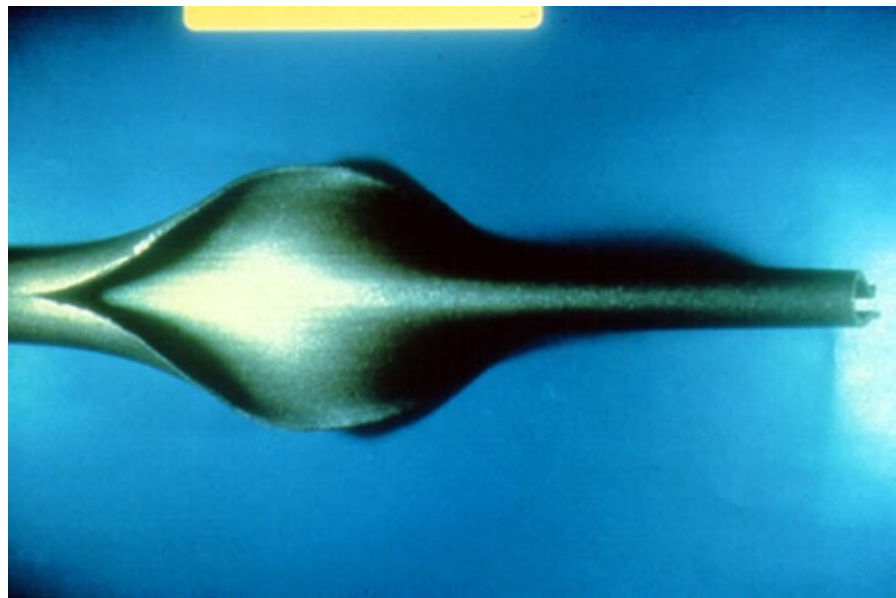
Another common cause of ignition is adiabatic compression. Adiabatic compression occurs where there is a rapid pressurization of a system and the heat of compression is unable to be absorbed or conducted away by the system. Heat of compression causes the temperature of a system to rise. An example would be a tire pump. The barrel or compression chamber builds heat as the pump compresses air. This process occurs relatively slowly, and the system is able to conduct away the majority of the heat. In adiabatic compression, the gas absorbs the majority of the energy and the gas temperature rises rapidly. This heating occurs at the point of compression or the point where the flow of gas is stopped, such as at a valve or regulator seat. Depending on the material in use where the hot gas impinges, the heat may be sufficient to ignite the material.

All of these energy sources can be enhanced by the presence of a contaminant. Contaminants are typically easier to ignite than the components of the system. If they react with the oxygen, they may generate sufficient heat to propagate a reaction to the system. Or as in the case of the pipe in Figure 1, they may react so strongly as to compromise the system.

Figure 1 depicts a section of an oxygen pipeline that ruptured. Here's how this happened. The oxygen supply line at an installation needed to be extended an additional 150 feet (45.7 meters). The line was solvent washed, but shop air was used to dry the line rather than clean, dry nitrogen. Most shop air is compressed with a hydrocarbon compressor, and in this case, the compressor did not have a cleanup system to remove any trapped oil. When the line was purged, a thin film of hydrocarbon oil coated the interior of the pipe. The pipe was put into service, and the operation went smoothly until at the end of the shift when a valve at the downstream end was closed. This stopped the flow, and the oxygen heated as it compressed against the valve seat. The adiabatic compression provided enough heat to raise the gas temperature enough to react with the hydrocarbon oil, and a deflagration occurred. The speed of the pressure wave was such that it duplicated the line rupture, as depicted in Figure 1, every 15 feet (4.57 meters). This is a very good example of how materials that burn in normal air can react more intensively in oxygen.

It is critical to keep nontypical ignition sources in mind when designing systems for oxygen use. Some applications are very vulnerable to ignition. For example, the elastomers used in valves and regulator seats have lower ignition energies than metals. Since particle impingement or adiabatic compression can be directed at these valves and regulators, they are particularly susceptible to ignition.

Figure 1



Let's take a look at a carbon steel pipeline used to provide oxygen to a customer. Because most of these pipelines have large diameters, economy and availability make carbon steel the material of choice. Carbon steel is an excellent fuel when used in oxygen service. To prevent fires in these pipelines, ignition sources must be considered. Since these lines are underground, external sources are usually not a problem. However, carbon steel is prone to rust, which can generate particles. If a particle is picked up in the flow of oxygen, the particle may impinge on part of the system. If the impingement generates sufficient heat, it may provide a source of ignition energy. Carbon steel pipelines in oxygen service must be designed and operated to minimize the potential hazard. This is accomplished by following the gas velocity limitations set forth in CGA publication G-4.4 and in EIGA Doc 13. By limiting the velocity, the particle impact energy is reduced, which minimizes the chance of an

ignition.

The above examples show how contamination in a system can enhance the potential for a reaction. It must be stressed that systems must not only be cleaned for oxidizer service requirements on initial construction but must be maintained in that condition of cleanliness. Contamination with materials like hydrocarbons or contaminants that may be in the form

of particles can initiate a system fire.

These are potential problems in oxidizer systems, but what happens when oxygen enters the atmosphere? If oxygen leaks or escapes into the air as part of a normal process, oxygen enrichment may occur if the ventilation is insufficient. If the surrounding air becomes oxygen-enriched, the same changes in fire chemistry take place. In other words, materials become easier to ignite because their autoignition temperatures and ignition energies begin to decrease, and their flammability ranges increase. Remember that materials which do not ordinarily burn in air may ignite, and materials that do burn in air will burn hotter and faster. Most areas where enrichment is known to be a possibility are posted with signs warning about smoking or open flames. The real danger is if oxygen enrichment occurs and people carry the hazard with them when leaving the area.

Clothes can trap and hold the oxygen enriched atmosphere in the countless air spaces within the weave of the fabric. Hair poses the same problem. If someone comes in contact with an enriched atmosphere, it is extremely important to isolate the person from any source of ignition, particularly smoking, and move them to a well-ventilated area for at least 30 minutes. Think about how easily cloth and hair burn in air, and then try to imagine how they would burn in an oxygen-

Figure 2



Figure 3



enriched environment.

Figure 2 shows a normal cotton work shirt, stuffed with paper and saturated with oxygen. Inside the shirt is a simple ignition device. The results of the ignition are shown in Figure 3. Individuals must be aware of the hazards of oxygen enrichment, since oxygen is not detectable by human senses. It is colorless, odorless, taste-

less and nonirritating. Likewise, they must be aware where oxygen enrichment is possible, such as at a vent, a leak, or failure of a ventilation system. Sometimes a worker may intentionally saturate themselves with oxygen without recognizing the danger. Think about the person who may use the flow of oxygen from an oxyacetylene torch to blow off dirt or to cool down.

Safe handling of oxygen and mixtures

It is important that all personnel handling oxygen and its mixtures be aware of its hazards and trained in the use of proper procedures and personal protective equipment. The SDS is the primary source of hazard data. All personnel handling a material should be thoroughly familiar with the SDS, including personal protective equipment recommendations.

As mentioned earlier, oxygen mixtures are classified, labeled, and valved differently. The primary method of product identification is the label. Mixtures with oxidizing potential will have a yellow oxidizer hazard class diamond in addition to the green nonflammable gas diamond. Do not let the presence of the green nonflammable label lessen the warning of the oxidizer hazard.

The valve connections provided may prevent the possible connection of an incompatible material, but they must not be relied upon for identification of the mix. If the mixture label and valve connection do not comply with the above-mentioned classifications, DO NOT use the cylinder until consulting with the supplier. NEVER use adapters or change connections to accommodate the connection of a cylinder to a system. If a cylinder does not connect easily, do not force; put the cylinder aside, label as to the problem, and contact the supplier.

From an operating perspective, areas of possible oxygen enrichment must be identified and plans implemented to address these potential hazards. These plans should consider safety systems including but not limited to training, signage, monitoring, and ventilation. Systems using mixtures of oxygen 5% and greater at high pressure (greater than 450 psig/30 barg) should be cleaned for oxygen service. Most compressed air systems use compressors that are hydrocarbon lubricated. However, the pressures at which they operate do not pose reaction problems and cleaning these systems is not practical because they are self-contaminating from the compressor oil. However, materials of construction and system design requirements for enriched oxygen concentrations must be specially cleaned to very high standards.

Plant systems must be designed with the special considerations required for the safe handling of oxygen. There are several documents available to help design systems and equipment for the safe handling of oxygen. They include but are not limited to Compressed Gas Association publication G-4.4, "Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems," and the ASTM International Standard G 88, "Designing Systems for Oxygen Service." The European Industrial Gas Association and the International Standards Organizations also publish related documents, including EIGA Doc 13, "Oxygen Pipeline and Piping Systems."

Designing and building these systems requires an intimate knowledge of oxygen and how it reacts with the materials it contacts. Basic design considerations include but are not limited to control and avoidance of unnecessarily high temperatures and pressures; cleanliness; elimination of particles; minimization of heat of compression; avoidance of friction and galling; minimization of resonance with direct flow paths; use of hardware that has a proven history in oxygen service; minimizing available fuel and oxygen through materials selection and system volume; anticipation of indirect oxygen exposure from system failures; and design of systems to manage fires, using techniques such as fire stops and automatic extinguisher systems. The first step in constructing any system for oxygen should be to consult your supplier.

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