HONEYWELL BW™ FLEX 4 SERIES

A Guide to Exotic Gas Sensing

Honeywell

EXOTIC GAS SENSING INTRODUCTION

> Exotic gases play important roles in a many different industries. However, their use can also result in the possibility of risk to equipment and facilities and potentially hazardous working conditions for workers. Effective detection and monitoring are key to their safe use.

OVERVIEW

Although they're called exotic, to say that exotic gases are used in a wide range of applications is an understatement. These gases play important roles in industries as diverse as semiconductor manufacturing, sewage and waste water treatment, mining, fire and rescue operations, underground mining and construction, oil and gas refining, and food and beverage processing.

In this guide, we'll review the properties of the most frequently used exotic gases to understand why they can pose significant risks to operations as well as the health and safety of workers. We'll also go into detail about many of the common applications of these gases in the types of industries outlined above.

Companies that work with exotic gases include not only the gas producers themselves, but those who service the producers' facilities; equipment manufacturers who supply storage vessels, portable tanks, valves, vaporizers, pumps, and associated processing and handling equipment; and transporters of the gases. Gas sensors are often important to help all of these companies meet their safety specs.

As you'll see throughout the e-book, Honeywell has broad experience and understanding of where and how exotic gases are used, so when your business relies on working with them, you can rely on us to help you work with them safely. Our Honeywell BW™ Flex, for example, offers you a choice of 12 different sensor types to protect facilities and workers from multiple gas hazards, in a small, rugged, and easy to use device that also makes safety compliance for your business easy to achieve.

Exotic gases can pose challenges. With Honeywell, choosing the right sensors to monitor and manage them isn't one.

How to use this guide.

This guide may be read through in its entirety. Or, if you prefer to discover more about a specific gas or the Honeywell solution, please click on a specific icon.

CO_2
HCN
NO
NO2
Cl2
CO
-H
H

CARBON DIOXIDE GAS SENSING

> Carbon dioxide is a commonly encountered but often misunderstood gas, and as such, the potential hazard it poses to human health is often disregarded. As applications involving the use or possible exposure to CO_2 are on the increase, however, the need for dedicated personal carbon dioxide monitoring has never been greater.

GAS OVERVIEW

At standard temperature and pressure, carbon dioxide is a colorless, odorless, heavier-than-air gas. CO_2 is produced by all aerobic organisms during respiration, during the processes of decay of organic materials and during the fermentation of sugars in bread, beer, and wine making. It is produced by the combustion of wood and other organic materials and fossil fuels such as coal, peat, petroleum, and natural gas.

CO_2 is high solubility in water, forming carbonic acid, gives it a sour "soda water" like taste at high concentrations, which may also cause irritation to the body's mucous membranes such as eyes, nose, and lungs. It is naturally present in air at just over 400 ppm and is completely harmless at these concentrations. At higher concentrations, however, as well as being a simple asphyxiant gas, it has a pronounced toxic effect upon the human body. These effects, including increased breathing rate, tiredness, confusion, and eventually unconsciousness, occur at concentrations much lower than those required for suffocation. This toxic effect has led most regions to impose Occupational Exposure Levels (OELs) for carbon dioxide of around 5000 ppm TWA and 15000 ppm STEL[1].

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[1] Consult local regulatory bodies for specific relevant OELs

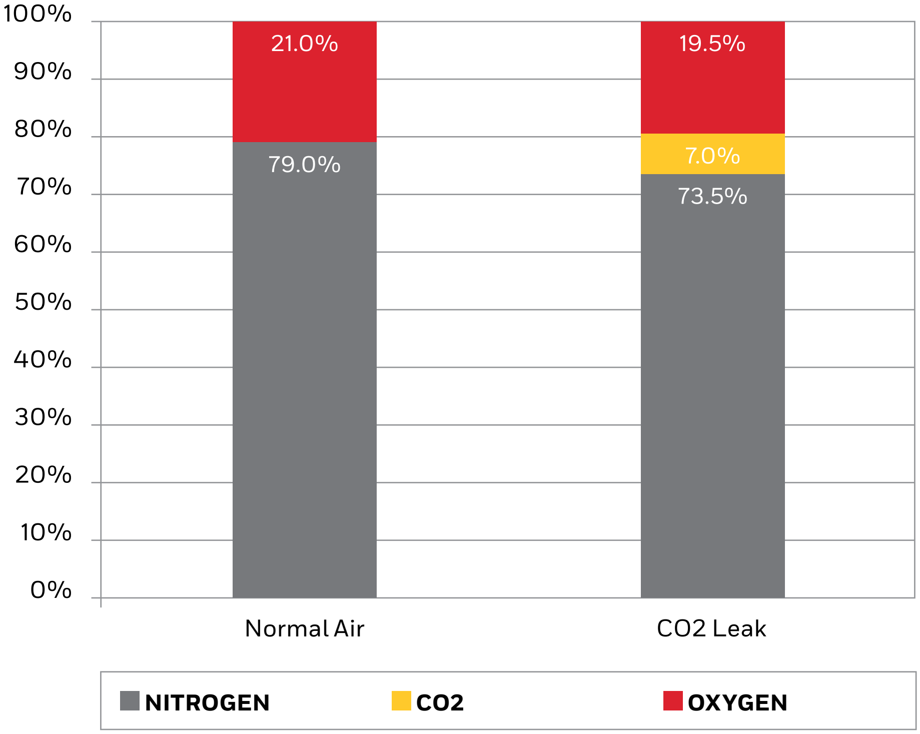
WHY ARE DEDICATED CO2 SENSORS IMPORTANT?

The ever-increasing number of applications and processes involving potential human contact with dangerous levels of CO_2 means that dedicated gas detection can make the difference between life and death. We are often asked the question; “but surely, I’m safe to use a simple oxygen sensor to warn me of dangerous levels of carbon dioxide like I would for any other displacing gas such as nitrogen?”

Were CO_2 only an asphyxiant gas, then the above statement may well be true but, unfortunately, it also has a significant debilitating toxic effect on the human body at far lower concentrations than are safely detectable using a simple oxygen sensor alone.

To displace enough oxygen from normal air to trigger a low alarm on a standard oxygen gas detector, the CO_2 concentration would need to be in the region of 7 %V/V or 70,000 ppm. This value is 14 times higher than the standard EU Occupational Exposure Limit (TWA) of 5000 ppm, meaning employing an oxygen detector alone would be a wholly insufficient method of protection against this gas.

Using a dedicated CO_2 sensor also gives us the ability to offer both Instantaneous Alarm Thresholds as well as the Time Weighted Average (TWA & STEL) alarms usually required by local national legislation. Above 5 % (50,000 ppm), the effects on the human body quickly become very serious, leading to tiredness, confusion, hyperventilation and, eventually, to unconsciousness and potentially death. Typical 8-hour time weighted average Occupational Exposure Limits sit at around one tenth of this value, and represent the average allowable exposure over an 8-hour standard work shift period and would apply to all workplaces.



APPLICATION OVERVIEW

CO$_2$

THE DRINKS INDUSTRY

This industry has numerous processes dependent on the use of CO$_2$ or which themselves produce this gas as a byproduct. On top of this, a global upturn in the emergence of the smaller craft or microbrewery segments is reaffirming the need for better CO$_2$ safety practices in the workplace.

We can identify three major subcategories within this industry, each with its own unique set of circumstances and potential risks: beer & wine production, distilleries, and the wider hospitality industry such as pubs, bars, and restaurants.

Beer Brewing and Wine Making

It's widely understood that the conversion, by yeast, of certain sugars during the anaerobic fermentation process produces alcohol and, as a byproduct, releases substantial volumes of carbon dioxide. A portion of this CO$_2$ may be allowed to remain in solution giving the characteristic "fizz" in beers and sparkling wines, but much is released as a by-product. Traditionally with smaller breweries and winemakers, this excess CO$_2$ is simply vented to the immediate environment, which can lead to considerable fluctuations in the local environmental CO$_2$ levels, potentially exceeding the local Occupational Exposure Limits. Due to its heavier than air property, there is also potential for this gas to collect in low-lying spaces such as pits and drains, leading to serious oxygen depletion. In modern high volume brewing facilities, this excess CO$_2$ from the fermentation process may be captured and stored for later use in the carbonation process. This introduces the risks associated with the storage and management of large volumes of compressed CO$_2$. Cleaning of the fermentation vessels, which may still contain the CO$_2$ byproduct, is often a very manual process involving the brewer/winemaker fully entering these confined spaces, usually without proper ventilation or SCBA.

Distilling

The process of distilling begins with a very similar fermentation process to create an alcoholic "wash" and so distilling liquor such as whiskey, gin, and rum introduces the same risks of CO$_2$ exposure as beer and wine making. The exception with this application is that the process of distillation also includes further gas hazards that the user should be fully aware of. Distillation requires a strong heat source which is more commonly powered by natural gas. As well as this, the product of the distillation process is a strong alcoholic liquor of up to 65 % to 70 %ABV. With alcohol being itself a potentially flammable Volatile Organic Compound (VOC), this gives the distiller two further potential gas hazards to monitor for. Portable multi-gas detection, which includes both CO$_2$ and flammable gases as a minimum, would be the preferential choice in this application.

The Hospitality Industry

The modern hospitality industry incorporates many applications, but the use of compressed CO_2 to carbonate drinks, or as a propellant to disperse them, is widespread, and so are the risks. The market for carbonated and draught drinks includes not only bars, restaurants, and pubs but hotels, cinemas, fast-food restaurants, and more. This also means that the area at risk has diversified away from the classic pub/restaurant cellar to a wide variety of purpose-built storage areas acting as confined spaces. All these spaces should be risk assessed with the same rigor as the traditional pub cellar commonly is, ensuring the most appropriate personal CO_2 protection is employed where necessary.

Other Gases to Consider: Sulfur Dioxide

It's not just CO_2 that is of concern in the drinks industry, Sulfur Dioxide (SO_2) is often used in this industry as a preservative and antioxidant. Usually harmless to healthy individuals when kept in recommended concentrations, it can induce asthma when inhaled or ingested by sensitive individuals, even in high dilution. In high doses, it can be very dangerous. Exposure to sulfur dioxide may also occur when manufacturing or preparing food and drink in factory, restaurant, and home settings.

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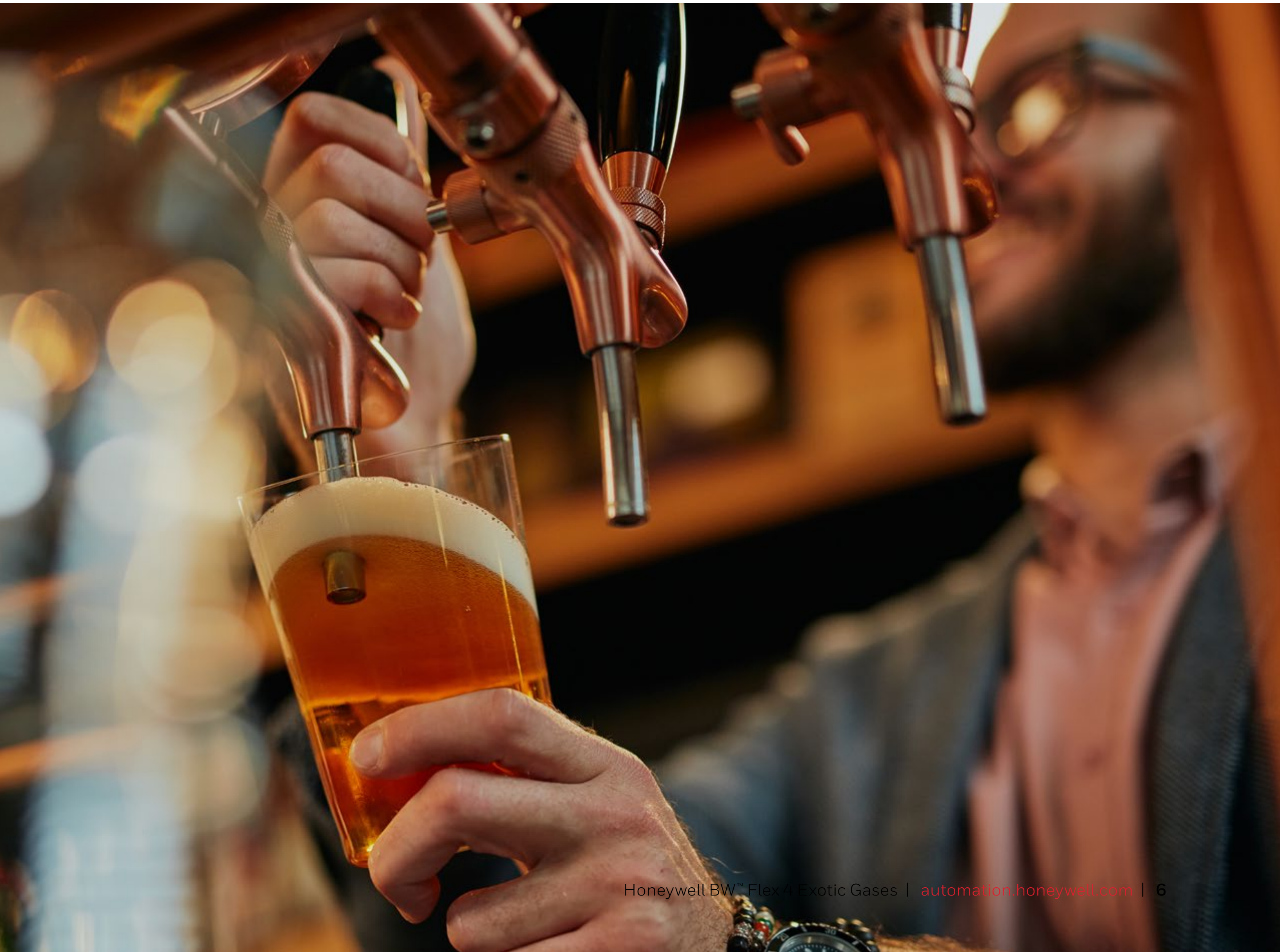
2. http://www.nationalarchives.gov.uk/doc/open-government-licence/version/3/

   https://www.hse.gov.uk/carboncapture/assets/docs/major-hazardpotential-carbon-dioxide.pdf



CARBON CAPTURE

Carbon capture and storage (CCS) is the process of capturing waste carbon dioxide from bulk industrial processes such as power generation, steel, and cement and sequestering it away, so it never re-enters the atmosphere and doesn't contribute to further climate change. These vast quantities of CO_2 are injected deep into the earth, often in oil and gas fields or unmineable coal seams, where the rock formations are stable enough to safely absorb and contain the waste carbon dioxide.

CCS will result in CO_2 being handled in quantities much greater than it is today. For example, a coal-fired power station consuming 8000 te (metric ton) a day of coal (in the region of one GW power generation) will produce up to 30 000 te/day of CO_2 to be captured and transported to long-term storage facilities. Whereas in existing CO_2 handling facilities, an inadvertent release of CO_2 may have created a small-scale hazard, potentially only affecting those in the local vicinity; a very large release of CO_2 from a CCS scale operation has the potential to produce a harmful effect over a significantly greater area and as such it would be likely to affect a significant number of people. CCS scale of CO_2 operation, therefore, has the potential to introduce a major accident hazard (MAH) where currently one does not exist[2].

SEWERS AND WASTEWATER

The aerobic digestion of sewage sludge is known to produce up to 30 %V/V carbon dioxide as well as other waste gases such as methane. This aerobic digestion may be harnessed as part of the wastewater treatment process, and the risk of exposure to this CO_2 to a degree may be limited to the waste treatment sites themselves.

However, as aerobic digestion is a naturally occurring process, CO_2 is commonly formed throughout the sewer system. Unlike other waste gases from this process, such as methane, CO_2 is a heavier than air gas which can potentially remain trapped within the subterranean sewage network leading to toxic atmospheres.

Other Gases to Consider: Oxygen, Hydrogen Sulfide, and Flammable

Hydrogen Sulfide (H_2S) is a common sewer gas released from waste material as it begins to decompose. This can cause both toxic and flammable hazards. H_2S is highly poisonous and can cause death within minutes. Exposure to concentrations as low as 10 ppm can affect personnel. In addition, H_2S, with an LEL of 4.3%, is highly flammable. Confined space environments can rapidly become explosive due to the lack of ventilation and low percentage flammability.

Oxygen (O_2) is also considered a sewer gas, especially when monitoring O_2 depletion. There is constantly a 20.9 % volume of Oxygen in the air; the volume must stay within this percentage to keep personnel healthy and alive. As individuals work in confined spaces - like sewers and wastewater plants, O_2 can be replaced by CO_2 as humans breathe. Even a 3 % change in volume can be hazardous; therefore, monitoring is vital.

OTHER APPLICATIONS

Only a few applications involving possible exposure to CO_2 at toxic levels have been covered in this document, but there are many other environments known to contain similar potential hazards.

- Landfill
- Biogas
- Mining
- Horticulture
- Refrigeration
- Food production

HYDROGEN CYANIDE GAS SENSING

HCN

> **Hydrogen cyanide (HCN) is one of the most hazardous gases used throughout industries today. It not only causes serious internal organ damage if adequate protections are not provided, but exposure can be fatal. As such, accurately and reliably detecting its presence is critical in applications where it plays a role.**

GAS OVERVIEW

Hydrogen cyanide (HCN), also known as prussic acid, is a colorless gas with a bitter, almond-like odor. It is extremely poisonous; exposure interferes with the body's use of oxygen and as a result may cause harm to the brain, heart, blood vessels, and lungs or even be fatal. As with most toxic gases, harm depends on the dose, duration, and work being done.

As a liquid, it boils only slightly above room temperature (25.6 °C or 78.1 °F, below which it is a pale blue liquid). Above that temperature, it exists in gaseous form, which is more toxic than solid cyanide compounds due to its highly volatile nature. It is weakly acidic and ionizes partially in water. The gas is lighter than air and rapidly disperses into the atmosphere; in air, it is explosive at concentrations above 5.6%.

Whether hydrogen cyanide is an organic compound or not is a topic of debate among chemists, and opinions vary. Commercially, HCN is produced by the reaction of ammonia, methane, and air over a platinum catalyst or from the reaction of ammonia and methane. HCN is also obtained as a by-product in the manufacture of acrylonitrile and may be generated as a by-product in a number of other manufacturing processes as well.[1] HCN is present too in vehicle exhaust and smoke from burning nitrogen-containing plastics.[2]

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1. https://www.ncbi.nlm.nih.gov
2. www.britannica.com

WHY ARE DEDICATED HCN SENSORS IMPORTANT?

There is probably no more impactful way to emphasize why dedicated HCN sensors are critical wherever this gas is employed than to briefly describe how it has been used as a poison.

Hydrogen cyanide is highly toxic through inhalation, ingestion, or skin contact because it inhibits cellular oxidative processes. Most adults can withstand 50–60 parts of hydrogen cyanide per million parts of breathing air for an hour without serious consequences. Exposure to concentrations of 100–200 ppm in breathing air, however, will kill a human within 10 to 60 minutes and 200–500 parts per million of air for 30 minutes is usually fatal. At a concentration of 2000 ppm (about 2380 mg/m^3), death will usually result in just one minute.

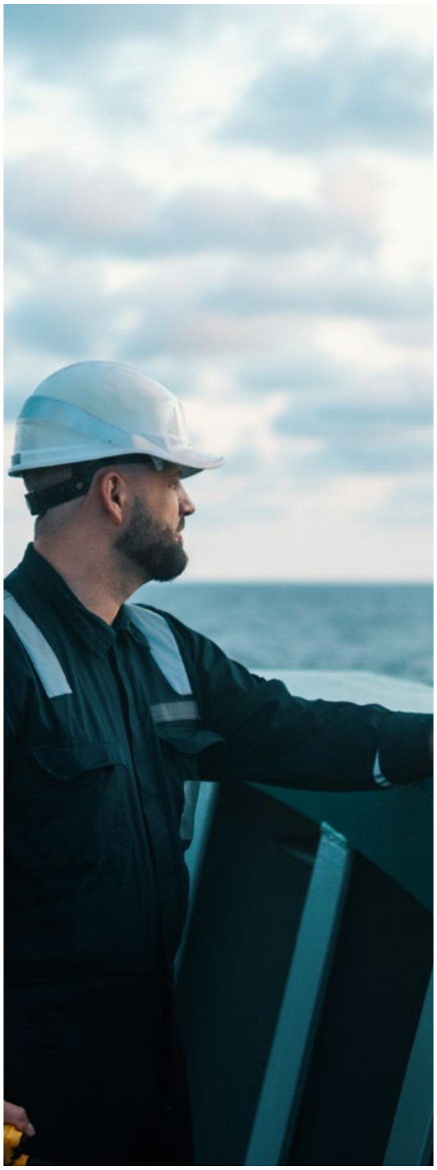
The time weighted average (TWA) for HCN as mandated by OSHA is 10 ppm, its lower explosive level (LEL) is 5.6 %, and is immediately dangerous to life or health. The airborne concentration value (IDLH) as developed by the National Institute for Occupational Safety and Health (NIOSH) is 50 ppm.

As it relates to other signage, warnings, and limits, the following is also applicable for HCN.

TABLE 1. REGULATION LIMITS

Limit/Level	Type	Organization
1.0 ppm	AEGL-1 (8 hrs)	EPA
2.5 ppm	AEGL-2 (8 hrs)	EPA
6.6 ppm	AEGL-3 (8 hrs)	EPA
10 ppm	TWA (8 hrs)	OSHA
4.7 ppm	ST	NIOSH

Source: EPA, NIOSH, and OSHA



APPLICATION OVERVIEW

MARINE ENVIRONMENTS

The marine industry is growing as more vessels enter the market every year. These ships transport vast quantities of hazardous materials, including highly regulated fumigation products and insecticides for food production. Stringent safety standards govern the industry, and marine workers need portable and fixed gas detection systems to help protect them from toxic and flammable gases in a wide variety of settings including merchant ships, ferries, Coast Guard vehicles, fishing boats, frigates, submarines, drill rigs, shipyards, and even some manufacturing facilities for products sold to these types of customer, such as lifeboat and fiberglass boat manufacturers.

Because of the tight quarters on most marine vehicles, internal ventilation is often relatively poor, making sensors important to warn against dangerous gas concentrations. Sewage and most waste products from cleaning or engine servicing are also often retained on board, resulting in a significantly increased risk of dangerous gas accumulation that can be exacerbated by bad ventilation. Besides protecting personnel, gas detection also protects onboard equipment and cargo.

In addition to frequently insufficient ventilation, marine environments are usually harsh, and gas detectors should have appropriate resistance against moisture and corrosion (fixed gas detectors are often stainless steel). Equipment is also subject to vibration[3].

Another challenge for instruments in marine environments is the fact that vessels can remain at sea for weeks at a time with limited or no access to spare parts or service support until their next berthing. As such, gas detectors for these applications need to be durable, reliable, and easy to maintain.

An everyday activity that exposes marine workers to the risk of toxic and flammable gases is confined space entry. Workers enter confined spaces, often around tanks, to perform routine tasks like inspection and cleaning. During this activity, they could be exposed to any of the gases listed below.

TABLE 2. COMMON MARINE GASES

Category	Gas	Sources	Potential Risk
Toxic	H_2S	Crude oil and petroleum products	Toxic to humans
	CO	Exhaust gases	Toxic to humans
	O_2	AEGL-3 (8 hrs)	Need a minimum level for breathing
	CO_2	Exhaust gases	Toxic to humans
	HCN	Fumigation	Toxic to humans
	PH_3	Insecticide	Toxic to humans
Flammable	Flammable gases	LNG, LPG, Natural gas, solvents	Fire or explosion
Toxic & Flammable	VOCs	Crude oil and petroleum products	Fire or explosion Toxic to humans

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[3] https://www.noventis.com.au/application-marine-gas-detection

Container vessels account for more than 3,000 of the marine vehicles and require several types of specialized gas detection sensors in addition to sensors that monitor other gases found on most types of vessels regardless of the vessel's purpose, such as the standard LEL and O_2 sensors to clean, repair and inspect the fuel and ballast tanks.

HCN is an important gas for several different types of gases encountered in marine applications, as there are often fumigants onboard container vessels so additional gas-specific sensors are needed to detect methyl bromide, phosphine, and a potentially broad range of other chemicals used to control pests or other cargo contaminants.

Fumigants can affect the commodity; or the nature of the commodity itself may affect the efficiency of a fumigant. Methyl bromide and phosphine may reduce seed viability, and methyl bromide can taint some products. Absorption of methyl bromide in oilseeds and other high oil content materials can reduce or even stop penetration of this gas into a bulk quantity of materials. In these conditions, hydrogen cyanide is the fumigant of choice for:

- Vertebrate pest control in enclosures (confined-space entry);
- Where a rapid treatment is required and germination must be preserved;
- Where a rapid treatment is required and the equilibrium relative humidity of the commodity is less than 60 % and methyl bromide may lead to taint or excessive residues.

In any fumigation operation, detection of gaseous concentrations is an essential prerequisite for both operational and safety reasons. Because HCN has minimal environmental impact compared to fumigants like methyl bromide or sulfuryl fluoride, when properly controlled it is often a fumigant of choice where environmental impact is important, including on marine vessels where onboard contaminants could be accidentally released into bodies of water.

Another primary application for marine gas-detection monitors is tank inspection. These confined-space tanks can be divided into four different groups:

- Cargo tanks (only on tankers and supply vessels)
- Slop tanks that carry water to clean the cargo tanks (only on tankers and supply vessels)
- Fuel tanks
- Ballast tanks that use seawater drawn from outside the vessel – and usually full of plants, mussels and even fish that will start to rot inside the tank

These tanks are generally being monitored for

- Sufficient oxygen
- Explosive gases
- Toxic gases based on the regulated limits

FIRE AND RESCUE

Another market where accurate HCN detection is critical is in fire and rescue operations. Because of building materials and materials used in home furnishings, the risk of poisoning associated with HCN-poisoning in fires that occur in closed spaces like buildings or mass transport has increased substantially.

CO (carbon monoxide) poisoning as a cause of serious poisoning or death in smoke-filled environments has long been recognized but beginning in the 1960s, HCN poisoning started to become a major cause of serious or fatal smoke inhalation victims. Unfortunately, firefighters are routinely exposed to dangerous levels of hydrogen cyanide at fires without even realizing it.

In addition to being present in fighting active fires, overhauling is a high-risk environment for HCN exposure. Overhauling is the late stage in a fire-suppression process during which the burned area is carefully examined for remaining sources of heat that may re-kindle the fire. This activity often coincides with salvage operations to prevent further loss to structures or their contents, as well as fire-cause determination and preservation of evidence.

During this stage of firefighting, there is no fire and little to no smoke in the environment, and firefighters are likely to work without their self-contained breathing apparatus (SCBA). In overhauling, the smoldering fumes of a recently controlled fire can be filled with dangerous and toxic gases and vapors that threaten the life and health of firefighters as they sift through piles of materials or take down rafters and walls to eliminate falling hazards.

As they do so, poisonous gases such as carbon monoxide, sulfur dioxide, hydrogen cyanide, nitrogen oxides, formaldehyde, benzene, and phosgene are released from the materials or are churned and become airborne particles that can be inhaled. Direct exposure to these dangerous aerosols and particles presents a real risk for immediate harm or acute and longer-term chronic health problems.

Two of these can be especially harmful when combined: HCN and CO. According to the NIOSH publication, “Preventing Fire Fighter Fatalities Due to Heart Attacks and Other Sudden Cardiovascular Events,” HCN is formed in a fire incident by incomplete combustion of any substance that contains carbon and nitrogen (both naturally occurring and synthetic), such as laminates, synthetics, foams, and plastics, as well as treated and untreated wood. It cannot be readily ascertained with a sensing device and although it can be relatively safe in non-gaseous form, when it heated it can become a lethal concern. It targets the central nervous system, cardiovascular system, thyroid, and the blood, causing firefighters to lose focus and become disoriented and agitated.

Carbon monoxide (CO), on the other hand, causes tissue hypoxia when inhaled and is also impossible to distinguish through human senses alone. When inhaled it prevents the blood from carrying sufficient oxygen and can cause dizziness, nausea, headache and, at higher concentrations, convulsions, tachycardia and death from suffocation.

Breathing these gases together is one reason firefighters can suffer further harm when they take off their masks once they’re out of air from their SCBA or if they feel they’re out of immediate danger from active flames. When inhaled together, the synergistic effect of these so-called “toxic twins” can cause even more harm than concentrations of either toxicant alone:

- HCN is 35 times more toxic than CO
- HCN can enter the body by absorption, inhalation, or ingestion and targets the heart and brain
- HCN often incapacitates the victim within a short period of time
- HCN is again produced after the flame is out and the materials continue to off-gas when no smoke may be visible

HAZMAT

As reviewed earlier, HCN can be present in a wide variety of situations, both fire-related and otherwise. HCN has been known to be used in terrorist attacks on food, water, and environmental resources as well as in direct contact with targeted victims. Since the gas is very hard to accurately detect without specific sensors, most hazardous materials (HAZMAT) training programs recommend that such sensors are readily available in HAZMAT response vehicles.

Personal protective equipment is also required to combat harm from HCN gases in HAZMAT incidents. PPE is rated from A to D in terms of protection levels, with A being the highest and most dangerous. HCN exposure has an A rating, requiring that first responders wear a completely encapsulated suit with respiratory protection provided by a positive-pressure self-contained breathing apparatus[4].

Anyone whose clothing or skin is contaminated with cyanide-containing solutions can secondarily contaminate response personnel by direct contact or through off-gassing vapor. This applies to potential victims as well as first responders, who operate on the principle that a person exposed to a lethal amount of cyanide will die within 5 to 10 minutes of exposure. Because it can be difficult to clearly identify when first exposure occurred, confirming the presence of HCN via reliable sensors is critical to quick response and positive health outcomes.

Sensors are also important in decontamination efforts to ensure that victims and responders are cleared of any lingering traces of HCN[5].

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4. https://remm.hhs.gov/ppe_classification.htm
5. https://chemm.hhs.gov/cyanide_prehospital_mmg.htm
6. https://www.firehouse.com/tech-comm/atmospheric-monitoring/article/21274295/oxygen-and-lel-metering-by-firefighters

Don’t forget oxygen!

The need to accurately measure oxygen levels in firefighting applications – and fire prevention applications too – is also clearly important. As threats to first responders have increased with the amount and variety of chemicals they encounter when fighting fires, the ability to detect the gases produced by those chemicals has also increased.

The most common sensor configuration of a four-gas meter is oxygen, lower explosive limit, carbon monoxide, and hydrogen sulfide. The oxygen sensor is arguably the most important because sensor readings are based on normal oxygen levels in clean air.

Most oxygen sensors have two alarms: low (19.5 %) and high (23.5 %). These alarm levels are considered IDLH (immediately dangerous to life and health) atmospheres and even at low, SCBAs should be worn to protect against possible toxicity, flammability or hypoxia hazards. At 23.5 %, there’s also an increased fire risk.

Firefighting gas detection equipment also includes LEL sensors, which usually use a catalytic bead technology, to alert to the presence of methane[6].

Preventing fires in the first place is also a role for oxygen sensors. Oxygen-deficiency is a threat to life, leading to unconsciousness and death. In industrial locations where nitrogen or other inert gases are in use, undetected gas leaks can displace oxygen from the air, resulting in respiratory difficulty.

However, in areas where pure oxygen is used, an oxygen leak is equally dangerous. As the percentage of oxygen in air increases above the normal 20.9 %, the air is said to be enriched, which can cause fires burn hotter and more readily than normal, including causing many materials to burn with almost explosive force.

Related to these two potential problems, oxygen reduction systems represent a fire prevention technology used with increasing frequency, particularly in information technology (IT and server rooms), warehouses (including small-load carrier, hazardous material and deep freeze stores) and archives. These systems reduce the oxygen content of the air to levels that will prevent the outbreak of fire, based on the materials being stored or the equipment being protected.

METAL ORE REFINING

As the demand for metals has increased with the demand for new types of batteries for applications like solar power stations and electric vehicles, mining companies are finding new ways to get more metals out of “old” mines. Rather than extracting metals from tons and tons of rock, biomining is much more efficient, cost-effective, and when done properly, less invasive for the environment.

This is where cyanide comes into play, because of its ability to bond well with gold and a wide variety of other metals as well. It is one of the main substances used in a process called cyanide leaching or cyanidation.

The use of cyanide to chemically extract metals from rock has proven to be both commercially acceptable as well as cost-effective. As might be expected, though, safety is critical when working with the types of chemicals that are required.

These operations depend on effective gas sensors, particularly hydrogen cyanide (HCN), for safe, ongoing operation. In leaching, the alkaline cyanide solution used in this extraction method is stable and generally safe. However, if the solution’s pH drops below a certain point, it can emit HCN.

As described earlier, HCN can cause death by asphyxiation. The severity of the reaction depends on the exposure time as well as the concentration of HCN. In addition to potentially fatal consequences, long-term effects are also possible, including chronic headaches, ongoing weakness, permanent changes in taste and smell, and continual eye and throat irritation, vomiting, abdominal colic, excessive salivation, nervous instability, and thyroid gland swelling.

Confined spaces without adequate ventilation, which can be common in mining and mining-related operations, are often risk areas and require continuous HCN gas detection. High-risk zones of HCN release can also be monitored to warn the staff of potential hazards before entering a specific area in order to increase their awareness of danger and improve use of protective personal equipment (PPE) where appropriate.

While the smell of hydrogen cyanide can be detected from 0.58 ppm – which is lower than the ceiling value (10 ppm), the IDHL (50 ppm) and the LEL (5.6 % or 56,000 ppm) – not all people can detect it and using human smell as the only detection for HCN is both unreliable and irresponsible. Only by using quality HCN sensors can operations ensure that they are relying on the best possible HCN detection technologies[7].

Best practices in cyanide usage are regulated by “The International Cyanide Management Code” with a goal of protecting mine workers as well as the flora and fauna of mining environments. There are multiple steps in the process outlined in the code ranging from handling and storage all the way through mine decommissioning[8].

Another relatively new method of extracting metals that are commonly bound up in solid minerals uses the concept that some microbes (microorganisms) can oxidize those metals, allowing them to dissolve in water to make them more easily recoverable than trying to extract them from solid rock. Another biomining technique for metals which are not dissolved by microbes uses microbes to break down the surrounding minerals to recover a metal directly from the remaining rock. Biomining is also used to clean up sites that have been polluted with metals.

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7. https://www.spi.com/en/blog/respiratory-protection/mining-gas-detectors-protection-against-no2-and-hcn?setContextLanguageCode=en
8. https://www.sciencedirect.com/science/article/abs/pii/S016745280515008X

Most current biomining operations target valuable metals like copper, uranium, nickel, and gold that are commonly found in sulfidic (sulfur-bearing) minerals.

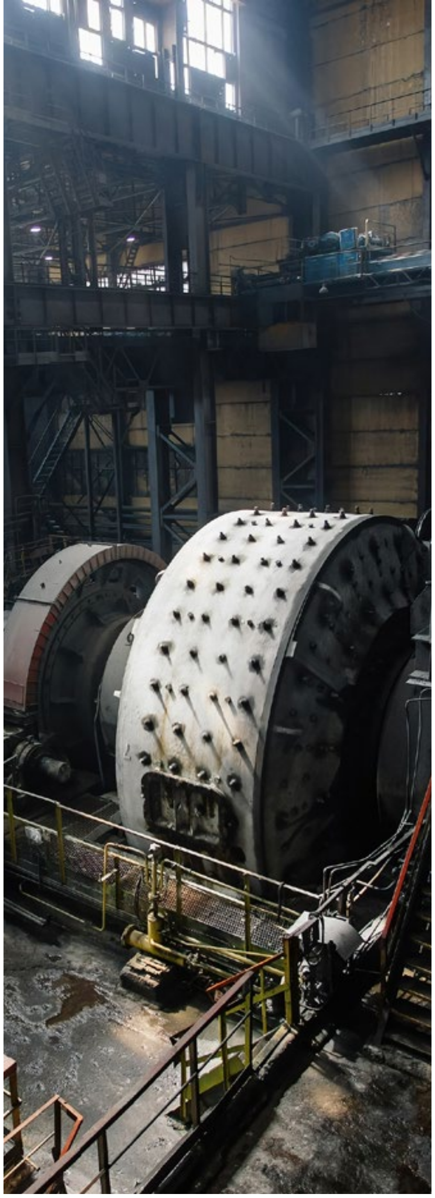
The most common processes used in biomining are:

- Heap leaching: freshly mined material is piled into heaps that are then bioleached
- Dump leaching: low-value ore or waste rock is placed in a sealed pit and then bioleached to remove valuable metals from the waste
- Agitated leaching: crushed rocks are placed into a large vat that is shaken to distribute the microbes and material evenly and speed up the bioleaching process

Leaching times vary from days to months, making this process slower than conventional mining, and most current biomining operations use naturally occurring microbial communities, making environmental risks relatively small.

Just because the leaching is being done with microbes instead of chemicals does not mean that effective sensing of off-gases is not needed or important: depending on the type of metal being leached, the type of rock in which it exists, and the biological process(es) that occur when the two are put together, appropriate sensing is still important for worker safety as well as ensuring efficiency and environmental protection.

Biomining is currently only a small part of the overall mining industry, but it is growing. Worldwide, 10-15 % of copper is extracted using bioleaching. Biomining is also important in the gold industry, where roughly 5 % of global gold is produced using bio-oxidation[9].



OTHER APPLICATIONS

Hydrogen cyanide and its compounds are used for many other chemical processes beyond those outlined here, including:

- Fumigation in other industries beyond marine operations
- Case hardening of iron and steel
- Electroplating
- Preparation of acrylonitrile, which is used in the production of acrylic fibers, dyes, synthetic rubber, and plastics
- Insecticide production
- Jewelry making
- Photographic processes
- Agricultural applications

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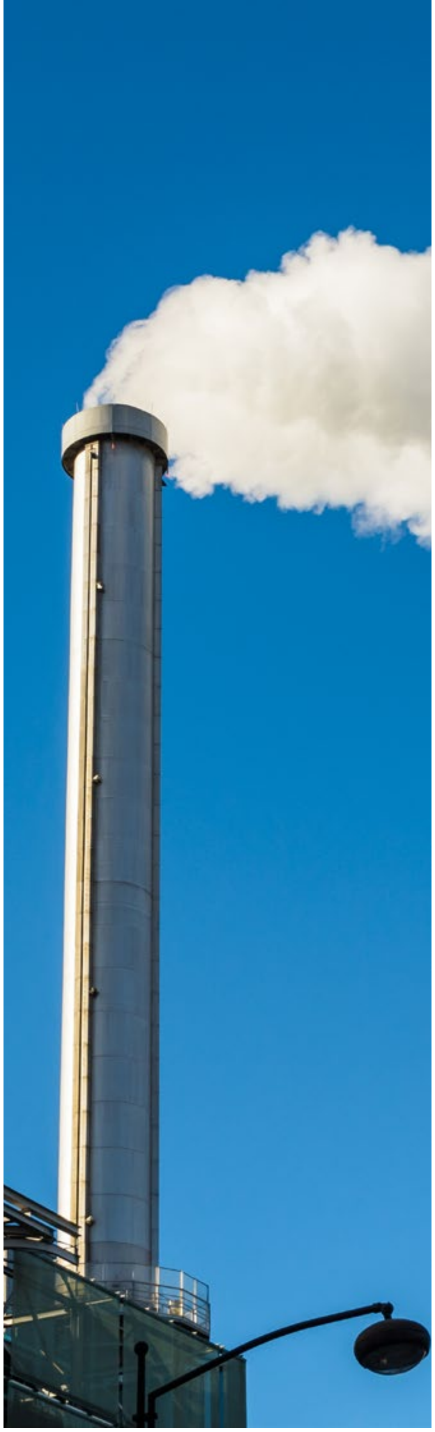
[9] (https://www.americangeosciences.org/critical-issues/faq/what-biomining

NITRIC OXIDE & NITROGEN DIOXIDE GAS SENSING



> Nitrogen oxide (NOx) can be found in applications ranging from tunneling, power generation, and manufacturing chemicals to the development of rocket fuels. Inhalation incidents are on the rise as these types of applications increase: the National Occupational Exposure Survey (NOES) estimates that more than one million U.S. workers are likely at risk for pulmonary irritants each year. While not explosive by itself, NO$_2$ can accelerate the burning of combustible materials, resulting in explosions caused by other chemicals or materials. Detection is key to minimizing accidents that can result in asset destruction to say nothing of impacting organization reputation and worker safety.

GAS OVERVIEW

While they are two different gases based on their elemental structure, nitric oxide (NO) and nitrogen dioxide (NO$_2$) are usually referred to together using the term "nitrogen oxides." Nitric oxide is a colorless, odorless gas; nitrogen dioxide is a reddish-brown gas with a sharp, sweetish, pungent odor.

Confusing? The explanation is simple but there is a difference. "O" is elemental oxygen while "O$_2$" is a molecular form of oxygen, often called dioxygen, that occurs when two atoms of oxygen chemically bind together to form an oxygen molecule. Both elemental oxygen and dioxygen have different chemical and physical properties: Nitrogen dioxide is formed when nitric oxide reacts with ozone. So, NO can exist by itself only in environments that do not include ozone, and NO + ozone = NO$_2$. NOx is often used as shorthand for both types of gases.

NO is a deadly air pollutant generated by fossil fuel-powered engines in any number of markets and applications as well as by power plants. When a mixture of air and hydrocarbon fuel is burned in an internal-combustion engine or a power plant, the ordinarily inert nitrogen in the air combines with oxygen at very high temperatures – or when exposed to electric sparks – to form nitric oxide. More readily, NO can result from the interaction of diluted nitric acid with copper or mercury.

The nitric oxide and hydrocarbon vapors that are then emitted undergo complex photochemical reactions in the lower atmosphere to form various secondary pollutants called photochemical oxidants, which make up photochemical smog. Nitric oxide combines with water vapor in the upper atmosphere to form nitric acid, one of the components of acid rain (rain occurs when air rises into the upper atmosphere and cools, causing water vapor to condense into water droplets that fall from clouds as rain when the air becomes saturated).

Heightened levels of atmospheric nitric oxide resulting from transportation and industrial activity have also been shown to be one of the causes of gradual depletion of the ozone layer in the upper atmosphere. Sunlight causes nitric oxide to react chemically with ozone (O_3), thereby converting the ozone to molecular oxygen (O_2) and creating NO_2[1].

Occupational hazards can be elevated in indoor spaces and as NO_2 exists in gaseous form both indoors and outdoors, inhalation is generally the primary route of exposure. Direct contact may occur in industrial settings with high gaseous NO_2 concentrations, which can lead to direct eye contact and irritation[2].

Interestingly, NO occurs naturally in humans and acts a “chemical messenger” that can help assist in internal bodily functions such as neurotransmission (information sharing between neurons), which is important in nervous system functions like digestion and memory. It may also encourage the release of hormones, including growth hormones and insulin. It can act as vasodilator in medical applications, where it is commonly used with a ventilator, often to treat newborn babies with respiratory failure caused by pulmonary hypertension. When inhaled, NO works by relaxing the smooth muscles to widen the blood vessels in the lungs[3].

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1. https://www.britannica.com/science/nitric-oxide
2. https://www.ncbi.nlm.nih.gov/books/NBK138707/
3. www.mayoclinic.org

WHY DEDICATED NO_2 SENSORS ARE IMPORTANT

Because it is present both indoors and outdoors and its sources are not always readily apparent, NO_2 exposure can be a problem even in industries such as construction and agriculture where many operations are performed out in the open air. It can be widely present even in everyday air and its odor is not always immediately detected, making it easy to encounter and inhale. So dedicated sensors to alert humans in the vicinity to its presence are very important.

NO_2 is toxic at varying levels, depending on the health and age of the person breathing it into their lungs. Inhalation may cause lung injury, asphyxiation, or chronic systemic effects. Once in the body, it can damage internal organs as well as unborn fetuses because it reacts with blood to form methemoglobin, which cannot bind to oxygen and results in a lack of oxygen to tissues and organs.

Low levels can cause a slight cough, mild fatigue, and nausea and eye, nose, and throat irritation are also common. At high concentrations, NO_2 can cause coughing, choking, headaches, abdominal pain, and shortness of breath. Workers may be unaware of ongoing exposures and longer exposures allow a higher concentration of nitrogen oxides to reach the lower airways, leading to delayed lower respiratory tract injury. These types of symptoms may linger for varying lengths of time after exposure, especially if the concentration was high, but even when exposure was relatively limited. This makes it necessary to measure not only the presence of NO_2 but its concentration levels as well[4].

TABLE 1. NO2 REGULATION LIMITS

Limit/Level	Type	Organization
0.5 ppm	AEGL-1 (8 hrs)	EPA
6.7 ppm	AEGL-2 (8 hrs)	EPA
11 ppm	AEGL-3 (8 hrs)	EPA
5 ppm	C	OSHA
1 ppm	Short term	NIOSH

Source: EPA, NIOSH, and OSHA
AEGL: Acute Exposure Level Guideline

Personal protective equipment (PPE) requirements by the U.S. Occupational Safety and Health Administration (OSHA) for exposure to NO and NO_2 are Level C, which means that on-site contaminants are unlikely to contact and/or affect the skin. However, as described earlier these are dangerous gases and therefore the requirements for respiratory protection against these chemicals are still quite rigorous; while optional, a two-way communication system and escape-hardened self-contained breathing apparatus (SCBA) are recommended:

TABLE 2. PPE RECOMMENDATIONS[5]

Category	Potential Risk
Respiratory Protection	Positive-pressure, full-face piece self-contained breathing apparatus (SCBA) or Positive pressure supplied air respirator (SAR) with SCBA-type auxiliary escape respirator
Clothing	Totally encapsulating chemical- and vapor-protective suit
	Chemical-resistant inner suit (e.g., Tyvek coveralls)
	Long underwear
	Hard hat (worn under suit)
Gloves	Inner and outer chemical-resistant gloves
Boots	Chemical-resistant boots, with steel toe and shank

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[4] https://www.ncbi.nlm.nih.gov/books/NBK554539/

[5] https://remm.hhs.gov/osha_epa_ppe.htm

The legal airborne permissible exposure limit (PEL) is 5 ppm as defined by OSHA, not to be exceeded at any time. NIOSH's recommended airborne exposure limit is 1 ppm, also not to be exceeded at any time.

The ACGIH (American Conference of Governmental Industrial Hygienists) recommends a TWA (time-weighted average) of 3 ppm for nitrogen dioxide and 5 ppm STEL (short-term exposure limit). NIOSH (National Institute for Occupational Safety and Health) recommends a PEL (permissible exposure limit) of 5 ppm.

The U.S. Environmental Protection Agency (EPA) maintains a national ambient air quality standard (NAAQS) for nitrogen oxides of 1-hour maximum daily concentration of 100 ppb and an annual standard at a level of 53 ppb[6].

TABLE 3. NO REGULATION LIMITS

Limit/Level	Type	Organization
1.0 ppm	AEGL-1 (8 hrs)	EPA
2.5 ppm	AEGL-2 (8 hrs)	EPA
6.6 ppm	AEGL-3 (8 hrs)	EPA
10 ppm	TWA (8 hrs)	OSHA
4.7 ppm	ST	NIOSH

Source: EPA, NIOSH, and OSHA

AEGL: Acute Exposure Level Guideline

As it relates to worker safety, it cannot be overemphasized that while not combustible itself, NO_2 can enable and accelerate the ignition of materials – including other airborne gases or particles – that are flammable, leading to serious fires, especially in oxygen-rich environments.

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[6] https://www.ncbi.nlm.nih.gov/books/NBK554539/

APPLICATION OVERVIEW

NO

NO2

While NO and NO_2 can be present in a wide variety of industrial applications, we'll take a look at a few specific ones as examples, and then present a summary of the many other industries where effective detection of these gases is important to worker safety and asset protection.

TUNNELING AND UNDERGROUND CONSTRUCTION

OSHA has issued a number of regulations related to the construction of underground tunnels, shafts, chambers, and passageways. As technologies advance, so do both the opportunities for improvement and the overall number of potentially dangerous situations to arise. Working under reduced light conditions, difficult or limited access and egress, and with the constant potential for exposure to air contaminants and the hazards of fire and explosion, underground construction workers face many dangers[7].

A 2023 study on the presence and impact of nitrogen monoxide (NO) and nitrogen dioxide (NO_2) levels in mining and tunneling operations discussed concerns about compliance. The study focused on the use of a tunnel-boring machine (TBM) and Tier 3 emission locomotives in a recent tunneling project. (Tier 3 is an emissions standard recently developed by the US Environmental Protection Agency [EPA]; it establishes more stringent standards that require covered locomotives to have essentially zero fuel vapor emissions, new test procedures, and a new fuel/evaporative system leak emission standard over a useful life of 150,000 miles or 15 years, whichever occurs first[8].

As explained earlier, nitric oxide (NO) is inherently unstable in the air and can spontaneously oxidize to NO_2. In tunnels, it originates primarily from diesel engines burning fuel that react with airborne water vapor. TBMs are also equipped with emergency that are only used in power supply failures or for high voltage (HV) cable extensions, both of which are potentially hazardous situations when NO_2 is present.

TBMs are used in mining operations for many minerals, including tungsten, magnesium, dolomite, iron, and others, and they are also important when constructing underground tunnels for transportation purposes. They are preferred because their implementation does not require explosives, which are a major source of NO_2 emissions in tunneling construction activities.

A TBM's cutting wheel excavates the soil while also serving as support for the tunnel face to prevent settlement. Additives are then used to condition the excavated material for conveyance above ground. As the TBM advances – up to 50 feet per day – it places concrete segments that fit together to form a tunnel ring that will form the wall of the tunnel. The TBM also uses the rings it builds as traction to keep moving forward, pulling with it all essential equipment including a control room, grout, ventilation equipment, and other tools. At any given time, there are 8-10 people in the TBM to keep it operational.

Gas levels are indicated on the operator control cabin display and a horn signal is given when a limit value is exceeded to warn all personnel working with the TBM. Gas monitoring systems include electrochemical sensors for NO_2 gas detection with specific linearity, range, and resolution information. The TBM stores the average gas concentration during the excavation cycle, and every time the TBM operator presses the ring-built button, the average gas concentration per ring is recorded.

7.https://www.osha.gov/sites/default/files/publications/osha3115.pdf

8. https://dieselnet.com/standards/us/loco.php

As with any industrial operation, continuous productivity improvements are important in underground construction and tunneling operations. It's no surprise, then, that a clear relationship can be observed between the TBM's production and an increase in NO_2 levels. As production increases, the number of locomotives required for transporting rings, grout, and other materials increases, leading to higher NO_2 emissions. Additionally, the study showed a correlation between the planned tunnel length and NO_2 levels. As the tunnel length increases, the TBM's performance improves, but this improvement is accompanied in NO_2 levels. A decrease in air flow rate further contributes to safety challenges.

All told, the study provided new data on the complexity of NO_2 emissions in tunnel construction projects and proved important in emphasizing the necessity for the meticulous management of TBM production, locomotive usage, and ventilation to mitigate the impact on air quality and safeguard worker health, preferably prior to the time that the length of the tunnel begins to change any requirements for updated standards. When emission standards from TBM equipment and locomotives is not optimal, there are repercussions of a significant decrease in occupational exposure limit (OELV) levels, especially concerning NO_2 concentrations.

NO
NO2

With growing populations and the need for efficient transportation solutions, cities are increasingly turning to TBMs to expedite the construction of subway tunnels for urban metro systems. Notable examples include the London Crossrail project and the New York City Second Avenue Subway, both of which have utilized TBMs for construction.

TBMs have also been instrumental in the development of hydropower projects and complex underground energy storage facilities for the efficient generation and storage of renewable energy. For instance, TBMs have been employed in the construction of hydropower tunnels in China's Three Gorges Dam project, the world's largest hydropower plant.

As innovations for new TBMs and types of locomotives (Tier 4 and 5) become more prevalent, tunnels will be able to be constructed bigger, better, and longer. They already have improved worker safety through automating and speeding up many of the process steps in creating a tunnel and are also "greener" due to fewer emissions overall as well as not necessitating as much traffic re-routing above ground, which can lead to more emissions from vehicles on roads.

Autonomous TBDs and robotic equipment may result in even greater improvements but the necessity for effective measurement of NO_2 will still exist as long as NO_2 does, which is to say, for the foreseeable future of tunneling and mining[9].

And always remember...oxygen!

It takes just 30 seconds of oxygen withdrawal for an individual to lose consciousness and at atmospheric levels as low as 5 % to 15 % methane becomes highly combustible and even explosive. In addition, carbon monoxide levels as low as 0.1 % can be fatal after only a few minutes of exposure.

So while monitoring NO_2 is obviously very important in tunneling operations, oxygen is its twin in terms of protecting assets and workers. As oxygen decreases, the potential for increased concentrations of noxious gases and other contaminants such as dust or flying debris also increases the potential for hazardous conditions.

Continuous air quality monitoring can never cease in order to alert workers of increased toxic conditions, be those from more noxious fumes from increased production or leaks or less oxygen – or both. Workers should have access to personal protective equipment (PPE) including not only hard hats and safety goggles but self-contained breathing apparatus (SCBA) as conditions warrant.

Effective ventilation is necessary to ensure a safe and healthy work environment underground. Proper airflow helps control dust, fumes, and other harmful particles. Dust control measures such as water sprays or dust collection systems can minimize respiratory problems and enhance worker safety as well as helping to reduce flammable conditions since even though not combustible on its own, NO_2 can exacerbate combustion of flammable materials such as methane that are often found in underground applications[10, 11].

POWER GENERATION

The presence and concentration of toxic gases both within power plants and their emissions from those plants are important to the power generation industry.

Inside power plants, their complex operations include high-voltage equipment, flammable materials, and hazardous chemicals. Even a split-second lapse in safety protocols or equipment failure can have catastrophic consequences, resulting in environmental damage, significant infrastructure damage, worker injuries, and even fatalities.

No one understands the significance of power plant safety better than those doing the job and reporting on their challenges: according to the Bureau of Labor and Statistics, the power generation industry had 18 fatalities and more than 5,000 reportable injuries and illnesses between 2019 and 2021. Additionally, OSHA reports that power generation, transmission, and distribution workers face a fatality rate almost three times higher than the national average for all industries.

Most injuries occur as the result of fires, electrical accidents, exposure to hazardous materials, or falls. Highly flammable materials and the potential for electrical sparks create conditions for fires, and coal dust, hydrogen gas, and other materials pose high explosion risks. The high-voltage electrical systems in power

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[9] https://utilitiesone.com/advances-in-tunnel-boring-machines-for-efficient-underground-construction

[10] https://utilitiesone.com/essential-safety-guidelines-for-workers-in-underground-construction-tunnels

[11] https://www.mining-technology.com/sponsored/the-importance-of-atmospheric-monitoring-in-tunnels/

plants not only contribute to igniting fires but also electrical shocks and power outages and their associated hazards if circuits are disrupted. Fuels, lubricants, and chemicals must be labeled, stored, handled, and disposed properly to avoid gas leaks. In short, power plants are inherently dangerous workplaces that benefit substantially from proper use and placement of sensors that monitor and provide alerts when conditions escalate[12].

Outdoors, as power plants emit waste products from their operations into the environment, their interactions with those environments is also important to monitor and improve.

As previously noted, nitrogen dioxide (NO_2) is one of the common toxic air pollutants. The LC50 (Lethal Concentration for 50 % of those exposed) for one hour of NO_2 exposure for humans has been estimated as 174 ppm. The most common air pollutant, sulphur dioxide (SO_2), is mostly found as a mixture of sulfur oxides (SO_x). It is an invisible gas with an unpleasant, sharp smell and the maximum concentration for SO_2 exposures of 30 min to an hour has been estimated as 50 to 100 ppm. The main sources of SO_2 include burning of fossil fuels in power stations, oil refineries, other large industrial plants, motor vehicles and domestic boilers although it is also produced from natural sources like active volcanoes and forest fires.

As with NO_2, when SO_2 is released into the atmosphere it can cause harm to eyes, lungs and throats. It is also toxic to some plants, inducing visible injury and reducing yields. When combined with moisture in the air, SO_2 causes gradual damage to some building materials, such as limestone. SO_2 can readily dissolve in the water droplets in clouds, causing acid rain that affects the natural balance of rivers, lakes and soils, resulting in damage to wildlife and vegetation[13].

While that may seem like a lot of hazards, clear paths to improvement have been demonstrated. The COVID pandemic, for example, presented a lot of challenges but at the same time, some remarkable opportunities. For example, relevant to NO_2, take a look at the impact of reduced NO_2 gas concentrations as a direct result of less vehicle emissions…

Improvements continue to be made. From 2022-2023, emission rates at coal facilities for sulfur dioxide (SO_2) and nitrogen oxides improved by 7 % and 3 %, respectively. Roughly half of this improvement resulted from units more effectively operating their existing controls and half resulted from increased utilization of more highly controlled units.

NO
NO2

12.https://hsi.com/blog/power-plant-safety

13.https://www.mdpi.com/1424-8220/19/4/905)

Compared to 2022, the 2023 data show a 15 % decrease in NOx emissions, a 24 % decrease in SO_2 emissions, a 7 % decrease in carbon dioxide (CO_2) emissions, and a 17 % decrease in mercury emissions. Additionally, ozone season (May 1 to September 30) NOx emissions decreased by 9 % nationwide and 18 % for the ten states implementing the Good Neighbor Plan[14].

Between 1990 and 2023, annual emissions of SO_2 from power plants fell by 96 % and annual emissions of NOx from power plants fell by 90 %. In 2023, sources in both the Cross-State Air Pollution Rule annual program and the Acid Rain Program together emitted 0.65 million tons of SO_2, a reduction of 11.2 million tons from 1995 levels. Additionally, in 2023, sources in these programs together emitted 0.64 million tons of NOx, a 5.2-million-ton reduction from 1995 levels. While complying with programs to reduce SO_2, NOx, and mercury, power plants reduced their CO_2 emissions by 28 % between 1995 and 2023[15].

In order for scrubbers and other mitigating equipment to maximize their cleaning potential before emissions are released into the environment, power plant emissions have to work as effectively as possible. In comparison to gas detection techniques like optical, acoustic, and gas chromatographic methods, electrochemical sensing is the most popular technique for ambient toxic gas monitoring. The key advantages of electrochemical detection are having low energy linear output with high resolution, good selectivity and repeatability, ppm level detection with high accuracy, and being more inexpensive than other techniques. In the past, electrochemical sensors have been overly sensitive to temperature fluctuations but that problem has essentially been minimized in advanced sensing materials being used in more recent devices.

The future development of toxic gas detection methods is expected to be a vital technology for the emerging Internet of Things (IoT) era, where gas sensors will need to be ultra-low power, low cost, long lifetime, integrable into electronic circuits, mini-sized and often wireless gas sensors for remote air quality monitoring and enhanced automated systems[16].

NO

NO2

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[14] https://www.epa.gov/newsreleases/epa-announces-final-good-neighbor-plan-cut-harmful-smog-protecting-health-millions

[15] https://www.epa.gov/newsreleases/epa-releases-2023-power-plant-emissions-data

[16] https://www.mdpi.com/1424-8220/19/4/905

OTHER APPLICATIONS

NO_2 is used in many other markets and applications in addition to those reviewed here. A classic example of nitrogen dioxide toxicity is found in agriculture and is known as “silo filler’s disease.” Silo filler’s disease occurs when the nitrogen dioxide that forms during the decomposition of agricultural organic matter silage (typically corn or other grains) is inhaled. The most significant risk of overexposure occurs within the first month after the silos are filled. Oxides of nitrogen are heavier than air and gather on top of the silage so exposure occurs when a worker enters a silo or opens the hatch without proper respiratory protection. This can result in shortness of breath, cough, or even symptoms consistent with acute respiratory distress syndrome (ARDS).

In a more unusual example, NO_2 can be produced by ice-resurfacing machines (so-called “Zamboni machines”) in their emissions as they combust propane. In enclosed spaces without enough ventilation, such as indoor ice-skating rinks, this can be dangerous. This happened in 1987 when 116 people attending an ice hockey game in Minnesota reported various symptoms from cough to coughing up blood due to significant nitrogen dioxide exposure. So, hockey arenas can be added to a list of NO_2 sensor applications[17].

NO and NO_2, as well as SO_2, are used in many other ways beyond those outlined here, including:

- Underground mining
- Agriculture
- Fertilizer production
- Underground parking garages
- Construction and demolition sites that use diesel or gasoline fueled trucks, excavators, loaders, bulldozers, mobile cranes, off-road machinery , and static engines such as pumps and electricity generators
- Wastewater treatment plants
- Electroplating
- Electric arc welding
- Engraving,
- Petroleum production and refining
- Pulp and paper processing
- Distilleries
- Where used as a nitrating agent for organic compounds, oxidizing agents, rocket fuel, and flour bleaching agents
- Indoor kerosene or gas space heaters and gas stoves

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[17] https://www.ncbi.nlm.nih.gov/books/NBK554539/

CHLORINE GAS SENSING

Chlorine gas (Cl_2) is one of the ten most-manufactured chemicals in the United States. Between 13 and 14 million tons are produced commercially each year by electrolysis of sodium chloride brine. At room temperature Cl_2 is a yellow-green gas, used to disinfect water and in sanitization facilities for sewage and industrial waste as well as in the preparation of chlorides, chlorinated solvents, pesticides, polymers, synthetic rubbers, and refrigerants. Due to its extensive use in industrial and commercial locations, widespread exposures could occur from accidental spills. Exposure is usually from inhalation although when oxidized it also can form dangerous acids, making effective use of appropriate gas sensors important wherever Cl_2 is used.

Cl2

GAS OVERVIEW

For storage and transportation, Cl_2 is pressurized and cooled to change into an amber liquid; when liquid chlorine is released, it quickly turns into a gas that is 2.5 more dense than air and consequently stays close to the ground and spreads rapidly.[1]

At room temperature, Cl_2 is a yellow-green gas with a pungent, unpleasant odor similar to bleach that is relatively detectable by humans at low concentrations. This feature can provide early warning of its presence but also causes olfactory fatigue or adaptation that can reduce awareness with prolonged low-concentration exposure.

Cl_2 is not flammable by itself but when combined with many common substances – including acetylene, ether, turpentine, ammonia, natural gas, hydrogen, and many petroleum-based substances – it can form explosive compounds, some of which can spontaneously combust.

Health issues arising from chlorine exposure begin in only seconds or minutes. Because it reacts with water – including moist body tissues like those in nasal passages, mouths, throats and lungs – exposure can cause the formation of hypochlorous acid (HClO) and hydrochloric acid (HCl), both of which are very dangerous.[2]

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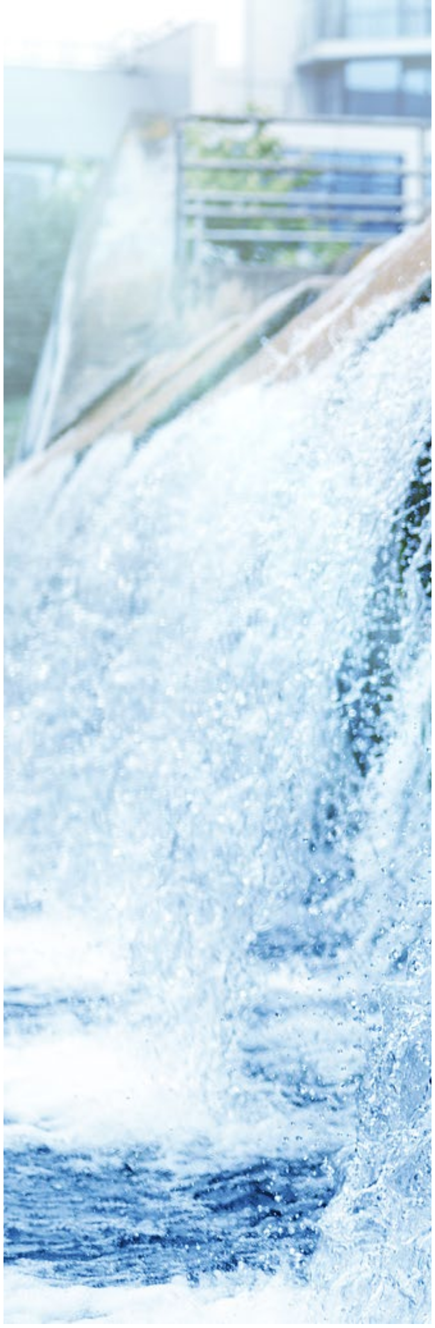
1. https://www.cdc.gov/chemicalemergencies/factsheets/chlorine.html
2. https://www.health.ny.gov/environmental/emergency/chemical_terrorism/chlorine_tech.htm

Most of the chlorine used in the United States plays a role in the manufacture of organic chemicals (e.g., vinyl chloride monomer, ethylene dichloride, glycerin, chlorinated solvents, glycols). The second highest use is for the production of vinyl chloride, an important building block for poly vinyl chloride (PVC) and a number of petrochemicals (see Figure 6-1). The remainder is used in the pulp and paper industry and the manufacture of inorganic chemicals, disinfection of water, and production of hypochlorite, which is used in disinfecting and bleaching paper products and fabrics.[3]



WHY DEDICATED CL2 GAS SENSORS ARE IMPORTANT

As with other hazardous industrial gases, Cl_2 is highly toxic. There's no better way to drive that home than to note that it was the first poison gas to be used as a weapon in WWI. The American Association of Poison Control Centers has reported chlorine as the most common inhalational irritant in the United States.

Because it is a gas at room temperature and stays pretty close to the ground since it's more than twice as dense as air, the probability of inhaling Cl_2 as the result of a leak or spill can be relatively high. Additional danger arises when it reacts with other substances commonly found in industrial and commercial applications – such as ammonia, natural gas, hydrogen, and petroleum-based products like gasoline, diesel, oil, and solvents – which can render it highly explosive and making it important to detect leaks or spills as quickly as possible.

Low-level exposures will cause eye and skin irritation, and higher exposure may result in severe chemical burns or ulcerations. Chronic exposure, usually the result of continuous risks in workplace settings, can even cause noncardiogenic pulmonary edema and corrosion of the teeth. Exposure to compressed liquid chlorine can cause frostbite of the skin and eyes.[4]

Cl2

Symptom severity varies depending on the amount, route, and duration of exposure, and the level of corrosive tissue damage can lead to the destruction of cell structure in extreme cases. At concentrations of 1 to 3 ppm, Cl_2 will irritate eyes and oral mucous membranes; at 15 ppm, there is an onset of pulmonary symptoms, and when inhaled at concentrations greater than 30 ppm, it reacts with water within the lungs, which as noted earlier produces hydrochloric acid (HCl) and hypochlorous acid (HOCl), both of which can cause severe burns.[5]

Cl_2 is detectable with sensors in concentrations as low as 0.2 ppm, and by smell at 3 ppm. The IDLH (immediately dangerous to life and health) concentration is 10 ppm. Coughing and vomiting may occur at 30 ppm, lung damage at 60 ppm, death can occur within 30 minutes at 430 ppm, and at about 1000 ppm, just a few deep breaths of the gas can be fatal.[6]

TABLE 1. CL2 WORKPLACE EXPLOSURE LIMITS

Agency	Description
OSHA	The legal airborne permissible exposure limit (PEL) is 1 ppm, not to be exceeded at any time
NIOSH	The recommended airborne exposure limit (REL) is 0.5 ppm, which should not be exceeded during any 15-minute work period
ACGIH	The threshold limit value (TLV) is 0.5 ppm averaged over an eight-hour workshift and 1 ppm as a STEL (short-term exposure limit)

Since Cl_2 is a gas at room temperature, ingestion is much less likely, but if it occurs at dangerous levels in drinking water it can corrode internal tissues so the ability to detect fumes that could arise from its presence in water may be important in some facilities. Importantly, while most people recover following exposure to chlorine gas, there is no antidote for chlorine poisoning. Treatment of inhaled Cl_2 may include administration of humidified oxygen, bronchodilators and airway management.[7]

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[3] https://www1.eere.energy.gov/manufacturing/resources/chemicals/pdfs/profile_chap6.pdf

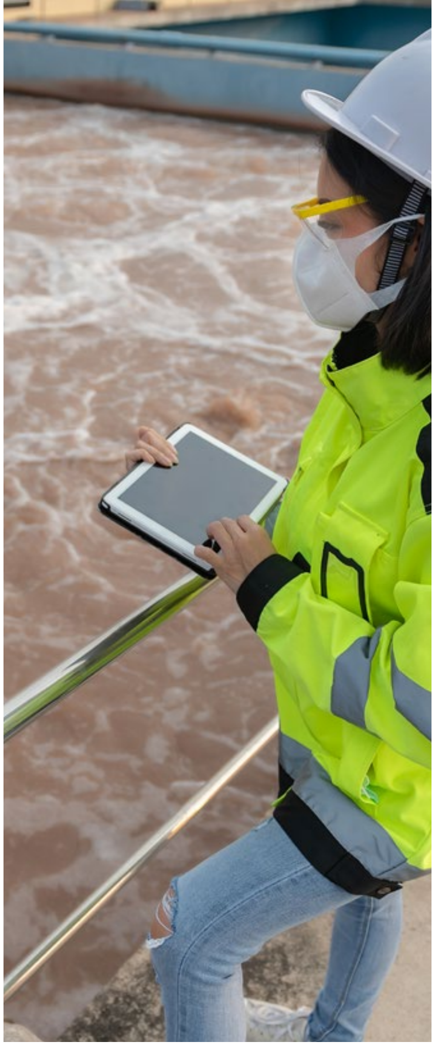
[4] https://www.cdc.gov/chemicalemergencies/factsheets/chlorine.html

[5] https://www.ncbi.nlm.nih.gov/books/NBK537213/

[6] https://en.wikipedia.org/wiki/Chlorine

[7] https://www.health.ny.gov/environmental/emergency/chemical_terrorism/chlorine_tech.htm

APPLICATION OVERVIEW



Cl2

Cl_2 is used in many industrial and commercial applications, so let's take a look at a few good examples where its effective detection is mandatory for worker safety and asset protection.

WATER TREATMENT

Water is a critical resource for many industries, but the presence of contaminants can substantially limit its usability. Chlorine in different forms has been used for centuries to address this issue.

Undesirable organisms in domestic wastewater include enteric bacteria, viruses, and protozoan cysts. Chlorine destroys these target organisms by oxidizing cellular material. It is less expensive to obtain and less complicated to apply than ozonation or ultraviolet (UV) disinfection (except when dichlorination is required and fire code requirements must be met), and more compatible with a high percentage of existing purification processing facilities.

While highly corrosive, chlorine has a long history as an effective disinfectant and is common enough that good procedures have been developed for safe and easy handling, storage, and shipping. It is not known to produce any toxic residuals or carcinogenic compounds.[8]

The types of organisms that can be eliminated with chlorine include:

TABLE 2. INFECTIOUS AGENTS POTENTIALLY PRESENT IN UNTREATED DOMESTIC WASTEWATER[9]

Organism	Disease Caused
Bacteria	
Escherichia coli	Gastroenteritis
Leptospira (spp.)	Leptospirosis
Salmonella typhi	Typhoid fever
Salmonella (=2100 serotypes)	Salmonellosis
Shigella (4 spp.)	Shigellosis (bacillary dysentery)
Vibrio cholerae	Cholera
Protozoa	
Balantidium coli	Balantidiasis
Cryptosporidium parvum	Cryptosporidiosis
Entamoeba histolytica	Amebiasis (amoebic dysentery)
Giardia lamblia	Giardiasis
Viruses	
Enteroviruses (72 types) e.g., polio echo and coxsackie viruses)	Gastroenteritis, heart anomalies, meningitis
Hepatitis A virus	Infectious hepatitis
Norwalk agent	Gastroenteritis
Rotavirus	Gastroenteritis

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[8] https://nepis.epa.gov/Exe/ZyPDF.cgi/200044E0.PDF?Dockey=200044E0.PDF

[9] https://nepsis.epa.gov

Detection systems are required at water treatment plants to activate emergency services and confirm that any spilled or leaked chlorine that has resulted in Cl_2 has been effectively decontaminated.

Sensors should be installed at strategic locations in the plant area, including chlorine injection areas, cylinder storage areas, cylinder off-load site, and other locations where canisters, hoses, or other gas-containing equipment might leak so that odors can be detected and alarms activated at levels as low as 0.1 ppm (0.289 mg/m^3). The sensors should function in on-line as well as off-line mode for continuous safety monitoring.[10]

PULP AND PAPER MANUFACTURING

Chlorine in the pulp and paper industry is used in the process that bleaches and whitens paper products ranging from copy paper to paper towels. The demand for unbleached, less-processed paper products has increased in recent years, but bleached paper is still in wide use within the publishing industry as well as paper products for home and commercial use.

The chlorine used by the paper industry during the bleaching process combines with organic molecules from the wood to form organochlorine compounds, which are then discharged in the mill's effluent. Waste is typically processed in a secondary treatment plant before release to surface waters or to industrial sewers leading to municipal sewage treatment plants where the water is treated as described earlier in the water treatment section. Prior to more stringent EPA regulations, organochlorine compounds were commonly found in fish and sediments downstream from paper mills.[11]

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10. Emergency Response Center, Safety Guidelines for Water Treatment

11. http://pdf.wri.org/bell/case_1-56973-133-0_full_version_english.pdf

A number of gas hazards exist in the pulp and paper processing industry, so careful monitoring and handling of these substances is a must. The toxic gases found in any typical plant vary based on the end products being produced, which could include everything from cereal boxes and paper towels to books and magazines, and can often include:

- Hydrogen sulfide (H_2S)
- Carbon monoxide (CO)
- Chlorine (Cl_2)
- Chlorine dioxide (ClO_2)
- Sulfur dioxide (SO_2)

These chemicals are used in various steps in the paper-making process, which starts when the wood is stripped of bark and ground into chips. Those wood chips are then broken down with steam, pressure, and chemicals in digester units. As the wood is broken down, the pulp is separated out: this is where gas exposures may occur.

Once the pulp has been separated out, it can go through several bleaching processes where chlorine is used to transform what starts out as a brown slurry into the bright white associated with paper. Excess chlorine must then be removed, generally by using sulfur dioxide to wash the pulp and help maintain the color in the paper after it is bleached. Chlorine is also used to help remove inks from post-consumer paper waste in paper recycling processes.

Cl2

All of these substances – hydrogen sulfide, sulfur dioxide, chlorine, and chlorine dioxide – can be respiratory hazards, even in relatively low concentrations. Also, like many other industrial processes, paper making also requires boilers that power the operation—and any time there is combustion, there is potential for carbon monoxide as well as interactions with other substances that can result in explosive materials or general fire hazards.

Gas sensors for the parts of the process and areas of the plants where gas exposure is possible are important safety precautions. It should be noted that in processes such as this, it is not always a matter of “just” spills or leaks that can be problematic: since gases can result from the processes themselves, continuous process monitoring is important to ensure that the necessary gases stay within safe operating parameters.[12]

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[12] https://www.indsci.com/en/blog/what-you-need-to-know-about-gas-hazards-in-pulp-and-paper-mills

REFRIGERANTS AND CL_2

While Cl_2 is not used as widely in refrigeration systems today as it has been in the past, it is still commonly utilized in many parts of the world. There are two types of refrigerants that include Cl_2: CFCs and HCFCs.

Chlorofluorocarbon- or CFC-based refrigerant is capable of changing its state from a liquid state to a gas state and back again. In a gas state, CFC-based refrigerant will dissipate into the atmosphere where it can contribute to the breakdown of the ozone layer. Additionally, CFC-based refrigerant is less efficient than its R-410A counterpart, so more of it is required to reach the same desired temperature.

In 1992, the U.S. Environmental Protection Agency (EPA) announced plans to phase out the use of CFC-based refrigerants for environmental reasons. As a result, the EPA no longer allows new systems to use CFC-based refrigerants. Instead, they must use an alternative type of refrigerant, such as R-410A.

However, it's important to know that because CFC-based refrigerant is only prohibited in new refrigeration products and systems, many older systems still use CFC-based refrigerants. For owners of these systems, monitoring Cl_2 is an important safety measure.

Hydrochlorofluorocarbons, or HCFCs, were developed as a transitional alternative to CFCs. Although not as harmful as CFCs, they still contain chlorine/CLl2. R-22, R-123, and R-124 are examples of HCFC refrigerants. In addition to being used in refrigerants, air conditioning, foam blowing, solvents, aerosols, and fire suppression products also contained HCFCs.

As with CFCs, HCFCs have mostly been phased out in developed countries, making it illegal to have new production or import new products or systems that contain HCFCs. But as is the case with CFCs, HCFCs are still used in existing refrigeration equipment. Phase-out in the U.S. is to be complete by 2030.

Because so many older units still utilize Cl_2 gas, especially in lesser-developed parts of the world, Cl_2 sensors are important to ensure their safe operation. Without effective monitoring and alarm systems, workers and other occupants in the area of Cl_2 use may be exposed to the harmful effects of spills and leaks outlined earlier, in addition to the potential for explosive interactions with common substances leading to fires and other explosion-related incidents.

HYDROGEN PRODUCTION

As of the end of 2021, almost 47 % of the global hydrogen production came from natural gas, 27% from coal, 22 % from oil (as a by-product) and only around 4% from electrolysis.[13] Chloralkali, which utilizes Cl_2 in its process, is in the electrolysis category.

The chloralkali process (also chlor-alkali and chlor alkali) is an industrial process for the electrolysis of sodium chloride (NaCl) solutions. It is used to produce chlorine, hydrogen, and sodium hydroxide (caustic soda), commodity chemicals required in many industries.

This process has been in use since the 19th century and is a primary industry in the United States, Western Europe, and Japan, becoming the principal source of chlorine during the 20th century. There are three methods, two of which have been in use for over 100 years and are not environmentally friendly. The membrane cell process, the third and last developed (in the mid-20th century), is a superior method that does not rely on harmful chemicals and offers significantly improved energy efficiency.

Usually the process is conducted on a brine (an aqueous solution of NaCl), which results in sodium hydroxide (NaOH), hydrogen, and chlorine. Because the process yields equivalent amounts of chlorine and sodium hydroxide, it is necessary to find a use for these products in the same proportion. For every mole* of chlorine produced, one mole of hydrogen is produced. Much of this hydrogen is used to produce hydrochloric acid, ammonia, hydrogen peroxide, or is burned for power and/or steam production. The process, for which the overall chemical equation is $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$.

As noted earlier, only about 4 % of global hydrogen production came from electrolysis, which utilizes Cl_2 as part of its process.

Electricity had a global average renewable share of about 33 % in 2021, which means that only about 1% of global hydrogen output is produced with renewable energy (electrolysis). Electrolytic hydrogen from dedicated production has mostly remained limited to demonstration projects adding up to a total capacity 0.7 gigawatts (GW) in 2021. In contrast, the 1.5°C Scenario[14] would need 4-5 terawatts (TW) by 2050, requiring a faster rate of growth than that experienced by solar photovoltaic (PV) and wind to date.[15]

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13. https://www.irena.org/Energy-Transition/Technology/Hydrogen

14. https://www.ipcc.ch/sr15/

15. https://www.irena.org/Energy-Transition/Technology/Hydrogen

* A mole is defined as 6.02214076 × 1023 of some chemical unit, be it atoms, molecules, ions, or others. The mole is a convenient unit to use because of the great number of atoms, molecules, or others in any substance (https://www.britannica.com/science/mole-chemistry).

With those numbers as a backdrop, an interesting new process currently under study is seawater electrolysis that would electrochemically split seawater to simultaneously produce Cl_2 and H_2 gases. With seawater making up over 90 % of the earth's water supply, this could be an exciting new development in hydrogen production.

OTHER APPLICATIONS

Chlorine is used in many industries. Some examples of where workers could be at risk of being exposed to Cl_2 include the following:

- Chemical production
- Healthcare
- Pharmaceutical
- Hazmat
- Livestock facilities, such as dairy farms
- Swimming pool facilities
- Janitorial processes
- Bleach manufacturing
- Plastics manufacturing
- Antiseptic manufacturing
- Insecticide manufacturing
- Paint and other petroleum products manufacturing
- Textile engineering and production
- Mining processes

CARBON MONOXIDE GAS SENSING

> Carbon monoxide (CO) is one of the most dangerous and widespread industrial hazards. Present in many industrial and commercial applications, to say nothing of being a hazard to anyone working around motor vehicles, the primary danger with carbon monoxide is that it is colorless, odorless, and tasteless and so cannot be easily detected through human senses alone: sensors specifically designed to alert to its presence are necessary.

CO
-H

GAS OVERVIEW

Carbon monoxide (CO) is colorless, odorless, and tasteless and therefore, almost undetectable without sensors developed to be specifically sensitive to its presence. The poisonous gas consists of just two elements, one atom each of carbon and oxygen, is slightly less dense than air, and mixes readily with air. Poisoning occurs from inhalation and can be fatal quickly. When mixed with air, large quantities of carbon monoxide can sometimes be highly flammable and explosive.

CO is derived from the incomplete burning of gasoline, wood, coal, oil, propane gas, or anything else that contains carbon. While the exhaust from internal combustion engines powered by fossil fuels is the chief source of workplace exposure to CO in many industries (trucks, material handling equipment, some conveyor systems, etc.), smelting operations, furnaces, and ovens also produce large amounts of the gas, especially when they are not properly maintained.

Truck drivers, forklift operators, or anyone working near such equipment are potentially exposed. Facility environments that may be particularly dangerous include enclosed areas such as manholes, splicing vehicles, garages, tunnels, loading docks, warehouses, and vehicle repair shops.[1]

Of course, carbon monoxide is also produced by humans and other oxygen-breathing creatures when exhaled, so technically we are also a CO source!

Carbon monoxide enters the bloodstream through the lungs and combines with hemoglobin, the red pigment in the blood that carries oxygen. Although carbon monoxide follows the same path as oxygen, the poisonous gas combines with hemoglobin 210 times faster than does oxygen. This means that even though there may be ample oxygen in the surrounding atmosphere, carbon monoxide will get into the bloodstream first. High blood-level concentrations of the compound will prevent sufficient amounts of oxygen from reaching the heart and brain, which can lead to suffocation, capillary hemorrhaging, permanent damage of nerve tissues and brain cells, and even death .[2]

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1. https://cwa-union.org/national-issues/health-and-safety/health-and-safety-fact-sheets/carbon-monoxide-and-workplace
2. https://cwa-union.org/national-issues/health-and-safety/health-and-safety-fact-sheets/carbon-monoxide-and-workplace

Once within the body, CO combines with hemoglobin in the blood to produce carboxyhemoglobin, which potentially affects gas exchange and can quickly be highly toxic. Concentrations as low as 667 ppm may cause up to 50 % of the body's hemoglobin to convert to carboxyhemoglobin and may result in seizure, coma, and fatality. In the United States, OSHA limits long-term workplace exposure levels to 50 ppm.[3]

The initial symptoms of carbon monoxide poisoning can easily be confused with other possible causes or health conditions. Low-level exposure can cause headaches, dizziness, drowsiness, or nausea. Further exposure will aggravate these symptoms and can accelerate to include rapid pulse, confusion, loss of coordination, or collapse. The long-term effects of low-level exposure have not been confirmed but should be avoided.

High exposure can lead to convulsions, coma, or death and even if recovered, highly exposed victims may still suffer permanent damage of the brain or nerve tissue. Sudden exposure at high levels can kill in just a few minutes. During World War II in Italy, over 500 persons were killed almost instantly when their overloaded train became stuck in a steep, icy tunnel and toxic gas from the burning coal suffocated them[4]

WHY DEDICATED CO GAS SENSORS ARE IMPORTANT

CO exposure is dangerous enough that many communities require detectors in homes. Unfortunately, this can also lead to the use of home CO detectors in business environments or even industrial facilities. This is not appropriate and can lead to hazardous conditions.

Home CO detectors are typically designed using Underwriters Laboratories Inc. Standard UL2034 alarm points for these concentration levels of carbon monoxide:

- 400 ppm – Alarm between 4 and 15 minutes of exposure
- 150 ppm – Alarm between 10 and 50 minutes of exposure
- 70 ppm – Alarm between 60 and 240 minutes of exposure

The OSHA personal exposure limit (PEL) for CO is 50 ppm. The threshold limit value (TLV) from the American Conference of Governmental Industrial Hygienists (ACGIH) for CO is 25 ppm. NIOSH has established an instantaneous 200 ppm ceiling level. So in workplaces, it is possible to exceed all of these limits without a peep from a detector made for residential use. Even models with digital readouts often won't display concentrations below 30 ppm, and calibration is nearly impossible.

When using proper sensors for workplace settings, alarms often trigger more than sirens: because CO cannot be detected with human senses, a first reaction is sometimes that the sensor is wrong, it's not powered correctly, or someone accidentally triggered it. This is especially the case where there are no combustion sources, not a lot of fueled vehicles currently running or present, or when most vehicles in an area have been converted to battery power. However, this can be a critically wrong reaction.

Many CO sensors are not CO-specific, and there are a lot of other gases that can create interferences and set off your detector. When further exploration shows that CO was not the trigger, workplaces may develop a skeptical reaction to future alarms and of course that can be deadly.

Hydrogen gas is a particularly frequent culprit in setting off detectors that are not single-gas devices or not able to be set up to always alert to the presence of CO.

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3. https://en.wikipedia.org/wiki/Carbon_monoxide
4. https://cwa-union.org/national-issues/health-and-safety/health-and-safety-fact-sheets/carbon-monoxide-and-workplace

Also important in the selection of CO-specific detectors is the ability to calibrate it for a specific workplace environment. This calibration should include knowing reaction times to alarms (in other words, how quickly can personnel be evacuated and assets secured, if necessary), specific concentration levels, potential for CO interference with any other gases or materials in the area, and so on.

With the information above in mind, here is a look at the acceptable levels of workplace exposure to CO from a number of national and international health and safety organizations[5]:

Physical Symptoms
physical symptoms may include headache, fatique, dizziness and/or nausia.

0 ppm	**Recommended Safe Level**	
6 ppm	WHO 24 Hour Average	
9 ppm	ASHRA 8 Hour Average EPA 8 hour 8 Hour Average NAAQS 8 Hour Average WHO 8 Hour Average	
25 ppm	ACGIH 8 Hour Average	
30 ppm	WHO 1 Hour Average	
35 ppm	NIOSH 8 Hour Average NAAQS 1 Hour Average	Physical symptoms after 6-8 hours.
50 ppm	OSHA 8 hour Average (PEL)	
30-69 ppm	UL 30 Day Alarm	
87 ppm	WHO 15 Minute Average	
70-149 ppm	UL 1-4 Hour Alarm	
200 ppm	NIOSH 15 minute STEL	Physical symptoms after 2-3 hours.
150-399 ppm	UL 10-50 Minute Alarm	
400+ ppm	UL 4 Minute Alarm	Physical symptoms in 1-2 hours. Life threatening 3 hours.
		Physical symptoms in 45 minutes. Unconscious in 2 hours. Fatal in 2-3 hours.
800 ppm		Physical symptoms in 20 minutes. Fatal within 1 hour.
1,600 ppm		Physical symptoms in 5-10 minutes. Fatal within 25-30 minutes.
3,200 ppm		
6.400 ppm		Physical symptoms in 1-2 minutes. Fatal within 10-15 minutes.
12,800 ppm		Fatal within 1-3 minutes.

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5. https://www.co2meter.com/blogs/news/carbon-monoxide-levels-chart

In the U.S., the Occupational Safety and Health Association (OSHA) personal exposure limit (PEL) for CO is 50 parts per million (ppm) and exposure to more than 50 parts of CO gas per million parts of air averaged during an 8-hour time period is prohibited. The 8-hour PEL for CO in maritime operations is also 50 ppm. Maritime workers, however, must be removed from exposure if the CO concentration in the atmosphere exceeds 100 ppm. The peak CO level for employees engaged in short-term roll-on roll-off operations during cargo loading and unloading is 200 ppm.

As shown, standards are a bit tighter for entities governed by the National Institute for Occupational Safety and Health (NIOSH), which is the US federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness. NIOSH recommends no more than 35 ppm time weighted average (TWA) exposure limit and no more than 200 ppm short-term exposure limit (STEL) for 15 minutes.

While short- and long-term carbon monoxide levels recommended by the organizations differ somewhat, there is consensus that…

- 9 ppm (parts-per-million) is the maximum indoor safe carbon monoxide level over 8 hours
- 200 ppm or greater will cause physical symptoms and is fatal in hours
- 800 ppm of CO or greater in the air is fatal within minutes

Personal protective equipment (PPE) in cases of CO exposure include a full-face piece pressure-demand self-contained breathing apparatus (SCBA) certified by the National Institute for Occupational Safety and Health (NIOSH), or a combination full-face piece pressure demand supplied-air respirator with auxiliary self-contained air supply[6].

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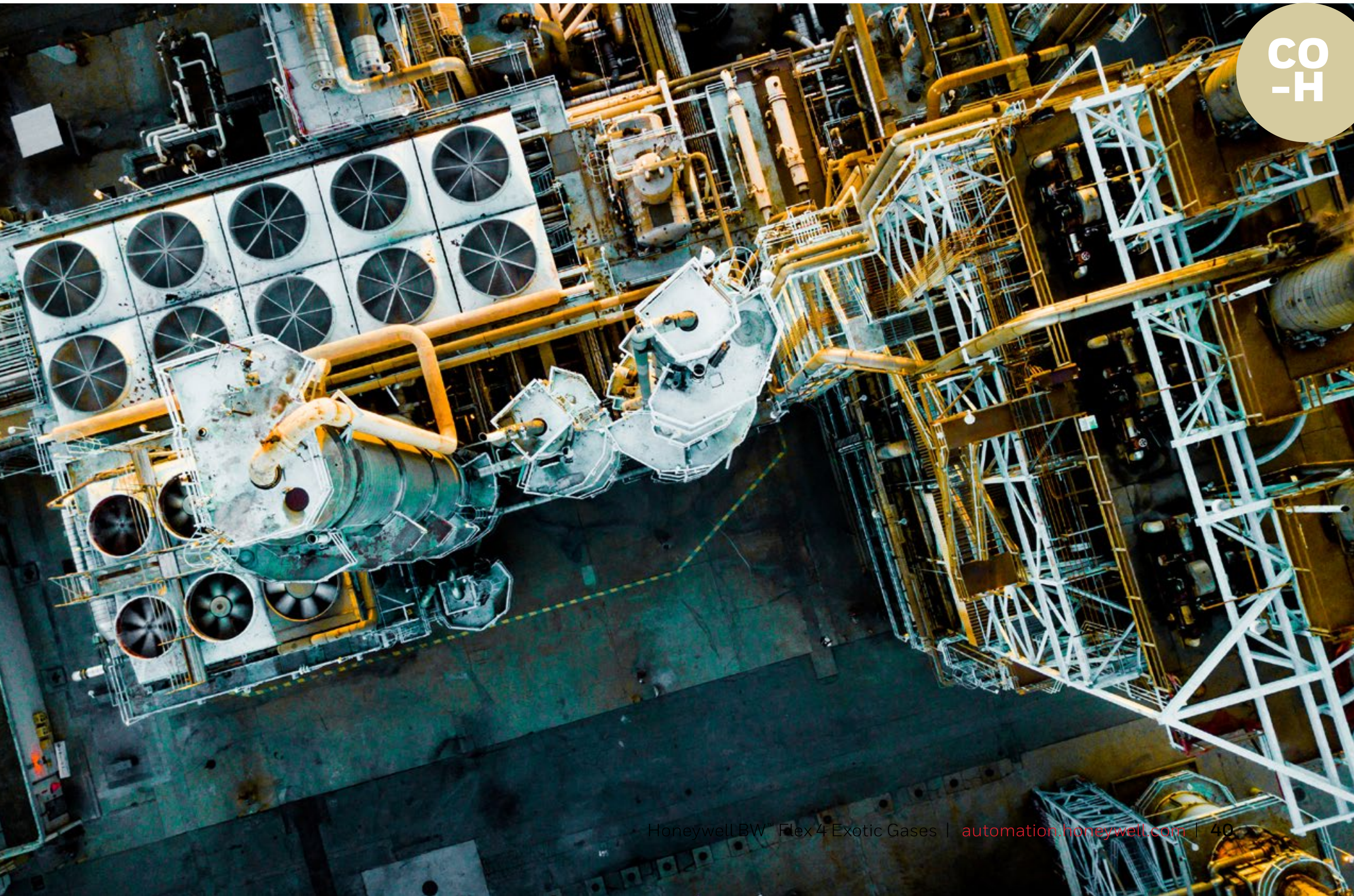
[6] https://cwa-union.org/national-issues/health-and-safety/health-and-safety-fact-sheets/carbon-monoxide-and-workplace



APPLICATION OVERVIEW

Carbon monoxide is present and/or produced in many industrial processes including metal manufacturing, electricity supply/power generation, mining metal ore and coal, food manufacturing, oil and gas extraction and refining, and production of chemicals, cement lime, plaster and concrete. It's also a significant hazard in mining, where it is known as "whitedamp" or the "silent killer" – it can be found in poorly ventilated areas in both surface and underground mines (of note, the low-temperature oxidation of coal can lead to CO being present even in less confined areas).

Let's take a look at two of these, steelmaking and refining of oil and gas.

STEEL PRODUCTION

Steelmaking is a melting, purifying, and alloying process carried out at approximately 1,600°C (2,900°F) in molten conditions. Various chemical reactions are initiated throughout the process, either in sequence or simultaneously, and many of the chemicals, materials, or elements (such as fire) can or should interfere with one another. These interactions necessitate close monitoring of environmental conditions to ensure worker and asset protection. There are numerous toxic and combustible gas hazards present in steel production, including:

- CO
- CO_2
- Combustibles
- H_2S
- NH_3
- NO_2
- SO_2
- VOCs

A very important chemical reaction during steelmaking is the oxidation of carbon. Its gaseous product, carbon monoxide, goes into the off-gas and is eventually emitted out of the facility. CO is generated during the smelting process, where heat and chemical agents decompose the ore and leave the metal behind. Risky areas for CO exposure include blast furnaces, coke ovens, and boiler rooms, and many other work areas in steel plants involve working in and around confined spaces, such as tanks, furnaces, and pipes.

Only a few of breaths of CO can be enough to inflict permanent damage to the heart and nervous system or at high enough concentrations, even cause death. But while CO is one of the most prevalent gases in steel production, many others, including potentially hazardous gases such as carbon dioxide (CO_2) as well as explosive gases such as methane (CH_4) are also released.

While CO_2 is considered minimally toxic by inhalation, exposures above 10000 ppm can begin to have negative effects such as headaches and drowsiness and breathing oxygen-depleted air caused by extreme CO_2 concentrations (over 50000 ppm) can lead to death by suffocation. In the steel industry, CO_2 may be used as an inert gas in welding and fire extinguishers, as a pressurizing gas in air guns and oil recovery, and as a supercritical fluid solvent in supercritical drying.

This means that the atmosphere must be permanently monitored using highly reliable, durable, and precise gas detection devices for CO, CO_2, and any other gases that could cause even minimal harm. In the case of CO, as noted earlier, the simultaneous presence of hydrogen (H_2) can contaminate CO sensors and lead to false alarms.[7]

With methane and other explosive and highly flammable gases that are always present in some form in steel production facilities, it is important to ensure that oxygen levels are within safe parameters and also that gases with known explosive interactions amongst themselves are also carefully monitored and controlled to minimize fires and associated damages and injuries.

It should be noted that as climate considerations become more important, many steel-making facilities need to find ever-more efficient and cost-effective ways to "scrub" CO and CO_2 from their emissions. Equipment and processes to accomplish this require high-quality CO detectors as exposure is often to high concentrations on a continual basis and CO_2 detection may be more important as well since emission concentrations are likely higher in these applications.

One option that is being reviewed is so-called "green steel" manufacturing in which hydrogen replaces coal in the manufacturing process. The 2022 Inflation Reduction Act in the U.S. and additional infrastructure bills passed by Congress are seen as instrumental in exploring and implementing these innovative technologies[8].

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7. https://www.britannica.com/technology/steel/Primary-steelmaking
8. https://www.marketplace.org/2023/05/22/the-steel-sector-is-carbon-intensive-green-steel-could-be-a-game-changer/

OIL AND GAS REFINING

As one of the biggest industries that involves combustion of fossil fuels as an actual product, it's easy to see why the oil and gas refining industry is a major producer of CO and therefore its presence in the workplace must be carefully monitored.

Products produced through oil and gas refining include gasoline, kerosene, liquified petroleum gas (LPG), distillate fuels, residual fuels, coke, asphalt, solvents, petrochemicals, lubricants – in other words, products that incorporate in many ways and are nearly ubiquitous in everyday life.

The largest sources of greenhouse gas (GHG) emissions at petroleum refineries, most of which include CO or other toxic gases to some degree, are stationary fuel combustion units such as steam boilers, process furnaces, and process heaters. Additional process emissions come from catalytic cracking units, fluid coking units, delayed coking units, catalytic reforming units, coke calcining units, asphalt blowing operations, heat exchangers, cooling towers, vacuum distillation units, blowdown systems, storage tanks, equipment leaks, compressor engines, loading operations, flares, and sulfur recovery plants.

As with steelmaking, the oil and gas refining process can also involve many chemicals. Common refinery chemicals include:

- Leaded gasoline additives
- Oxygenates
- Caustics
- Sulfuric acid and hydrofluoric acid

Again, as with steelmaking, the potential for chemical interactions is a constant source of potential hazards in oil and gas refining. The need to carefully monitor individual gases both for their individual toxicity as well as the potential for toxic or flammable interactions with other gases cannot be underestimated.[9]

Getting raw materials for oil and gas refining to the refinery and then out to customers after they have been rendered into saleable products presents another application for effective detection of CO and other toxic gases. As noted earlier, logistics such as barge or ship loading and gasoline loading racks specifically located at petroleum refineries represent potentially hazardous situations.

Hydrogen sulphide (H_2S), for example, is a potential problem in the transport and storage of crude oil as the cleaning of storage tanks is a highly hazardous process. Many confined-space entry problems can occur here, including oxygen deficiency from previous inerting procedures, rusting, and oxidation of organic coatings.

Inerting is a safety step that reduces the oxygen levels in a cargo tank to remove the oxygen element required for ignition, but carbon monoxide (CO is often present in the inerting gas. In addition to H_2S, depending on the characteristics of the product previously stored in the tanks, other chemicals that may be encountered include metal carbonyls, arsenic, and tetraethyl lead. All of these require careful monitoring to avoid toxic levels of concentration.[10]

Like steel-making, this industry is also being critically reviewed for its role in climate pollution and as such, the need to clean and/or reduce emissions is a high priority. As refineries work to develop new ways of handling their toxic waste products, the ability to manage those wastes through process improvements, will lead to the need for ever-more effective monitoring through the use of efficient gas-sensing devices to better protect both the environment and facility workers.

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[9] https://www.epa.gov/sites/default/files/2016-11/documents/refineries_2013_112516.pdf

[10] https://www.crowcon.com/blog/the-importance-of-gas-detection-in-the-petrochemical-industry/

OTHER APPLCIATIONS

The risk of carbon monoxide poisoning exists in many industries and applications, requiring early detection for worker safety. CO is used by the chemical industry, for example, for the synthesis of many compounds such as acetic anhydride, polycarbonates, and acetic acid. It is also used as a reducing agent in metallurgical operations, in the manufacture of metal carbonyls, and in organic synthesis. Carbon monoxide is also used in the manufacture of zinc white pigments.[11]

More Applications include:

- Warehouses
- Boiler rooms
- Pulp and paper production
- Loading docks
- Shipyards
- Blast furnace applications
- Welding
- Automotive repair garages
- Firefighting
- Carbon-black production
- Diesel equipment operation
- Refueling stations for aircraft and marine vessels
- Forklift and other material handling operations
- Marine terminal equipment
- Toll booth or tunnel maintenance
- Taxi operations (drivers, maintenance, garages)
- Vehicle occupations and operations (cars, trucks, boats, planes)
- Commercial restaurants or food processing (stoves, ovens, grills)
- Fireplace and furnace maintenance/repair
- Gas-powered portable generators maintenance/repair

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[11] https://www.ncbi.nlm.nih.gov/books/NBK153697/

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