HONEY MELL BW FLEX4 SERIES

A Guide to Cl₂ Gas Sensing



CHLORINE GAS SENSING

Chlorine gas (Cl₂) is one of the ten mostmanufactured 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, 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 Cl₂ is used.

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.

 $\rm Cl_2$ 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



^{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 Cl₂ 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

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

Cl₂ 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

- 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

 $\rm Cl_2$ 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:





Cl2

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/m³). 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

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 (H₂S)
- Carbon monoxide (CO)
- Chlorine (Cl₂)
- Chlorine dioxide (ClO₂)
- Sulfur dioxide (SO₂)

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.

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

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



REFRIGERANTS AND CL₂

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+2H₂O \rightarrow Cl₂+H₂+2NaOH.

As noted earlier, only about 4 % of global hydrogen production came from electrolysis, which utilizes Cl₂ 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 Scenario¹⁴ 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

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

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With a choice of 12 different sensor types, the Honeywell BW[™] Flex protects workers from multiple gas hazards, in a small, rugged, and easy to use device. BW[™] Flex keeps specialists operating in confined spaces, or general workers on a plant, safe from gas hazards while making safety compliance for the business easy.

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- **Reliable** The Honeywell BW[™] Flex can be used in potentiality explosive atmospheres. Indoor, outdoor, onshore or offshore
- Advanced connectivity Using a smart mobile device or PC. operators can fully configure their device using Safety Suite solutions on iOS®, Android™, or Windows[™] platforms
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- **Responsive** Offering instantaneous alarms, with time weighted average exposure levels (STEL/TWA), users are protected all round, from flammable, oxygen, and toxic gases
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For the detection of the most common gas hazards including: Flammable gas (LEL), oxygen (O_2), carbon monoxide (CO), hydrogen sulphide (H_2 S), carbon dioxide (CO_2), sulphur dioxide (SO_2), chlorine (Cl_2), nitric oxide (NO), nitrogen dioxide (NO_2), and hydrogen cyanide (HCN)



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