# Gas Odorization Technology for Toxic Gas Leak Detection

Hazards are ever-present in the steel plant environment, and a heightened awareness and emphasis on safety is a necessary priority for our industry. This monthly column, coordinated by members of the AIST Safety & Health Technology Committee, focuses on procedures and practices to promote a safe working environment for everyone.

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When steel is made, huge quantities of gas are produced, stored and used as fuel later in the process. For example, coke oven gas (COG), blast furnace gas (BFG), basic oxygen furnace gas (BOFG), and Corex gas can all be utilized when making steel. The majority of these gases are both colorless and odorless, making them undetectable in the case of a leak. The high carbon monoxide (CO) content of these gases causes a toxicity risk in the case of worker exposure.

Many accidents occur every year due to CO leaks. Even though many safety measures have been put in place over the years, gas and asphyxiation remain one of the top five causes of fatality in the steel industry.[1]

Gas odorization is a proven technology and is used globally for the distribution of natural gas and liquefied petroleum gases (LPG), which are highly explosive. It is based on the addition of a powerful warning agent that has a characteristic smell, recognizable to a person's nose in the case of a leak.

In general, a gas can be hazardous because it is flammable and/or toxic. While definitions of flammability (e.g., lower flammability limit), impacts in terms of fire (heat flux) and exclusivity (overpressure) are relatively straightforward, toxicity levels require further definition. CO is colorless, odorless and flammable, but it is also toxic (limits of explosivity 12% to 75%).

Table 1 shows the leading characteristics of the three main steel mill gas streams. All have a significant percentage of carbon monoxide. In the case of BFG and BOFG, both are odorless. In the case of COG, a sulfur odor is present due to the process characteristics, unless it is treated by a desulfurization process.

The health effects of CO are largely the result of the formation of carboxyhemoglobin (COHb), which impairs the oxygen carrying capacity of the blood. Resumption of the normal oxygen supply process takes place once the person is removed from the contaminated atmosphere. However, any damage due to the prolonged loss of oxygen supply to the brain may not be reversible. The extent of impact from toxic exposure depends on the extent of dilution of the substance, the concentration, and the duration of exposure, as seen in Fig. 1.

For instance, exposure to CO at a concentration of 400 ppm (0.04%) will quickly cause a headache; within 3 to 5 hours, exposure to the same concentration can lead to unconsciousness and/or death. Physical exertion, with an accompanying increase in respiration rate, shortens the time to critical levels. Respiratory capacity decreases and

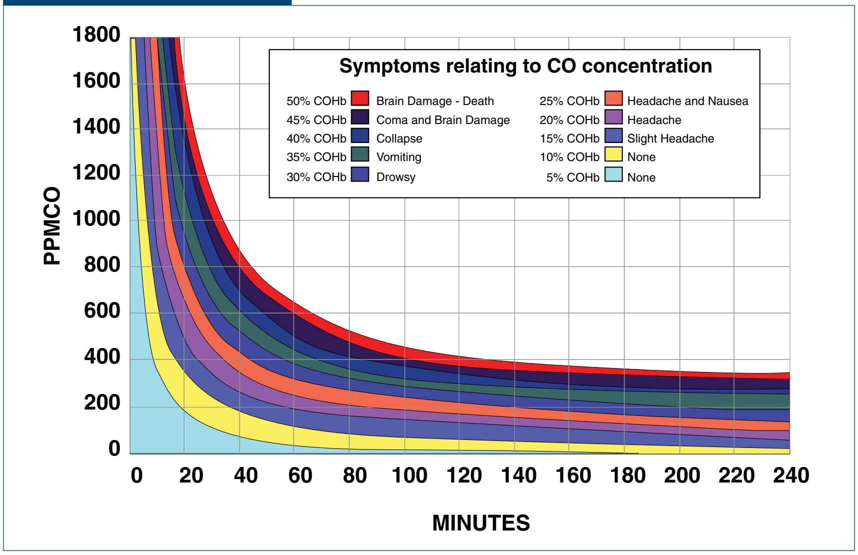
Table 1

*Gas Streams Characterization*[2,3]

| Blast furnace gas | Coke oven gas | Basic oxygen furnace gas |
|---|---|---|
| 20–28% CO | 4–7% CO | 55–80% CO |
| 1,200–1,800 $m^3$/T pig iron | 0.08–0.15 $m^3$/T coal | 55–85 $m^3$/T steel |
| Odorless | Sulfur odor | Odorless |
| LHV 0.9 KWh/$m^3$N | LHV 5 KWh/$m^3$N | LHV 3 KWh/$m^3$N |

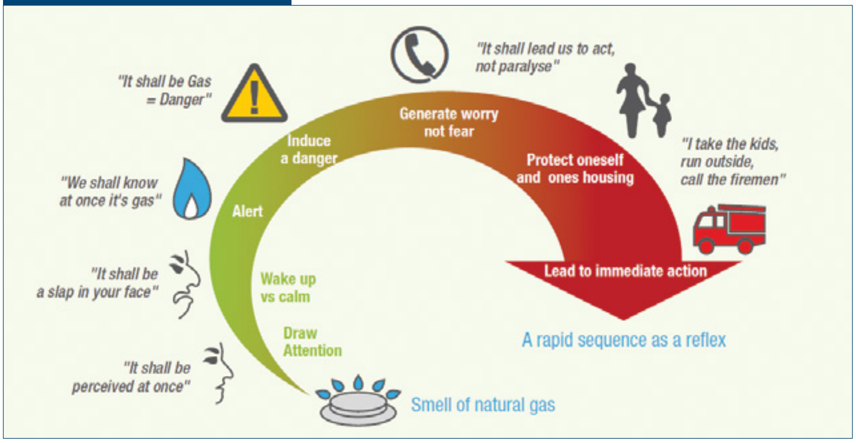
Comments are welcome. If you have questions about this topic or other safety issues, please contact safetyfirst@aist.org. Please include your full name, company name, mailing address and email in all correspondence.

Figure 1




*Symptoms relating to CO concentration. © GV Jones*

Figure 2




*Basic principle for gas odorization.*[4]

the risk of heart attack increases at levels well below 50 ppm.

Incidents related to CO can range from death and poisoning of workers, sub-contractors, visitors and people living in the surrounding areas, to adverse consequences for facilities and the environment. The direct and indirect costs of these incidents are usually measured in millions of dollars, and can affect the business continuity of the plant. These costs can include, but are not limited to, the cost of repair or replacement of damaged equipment, shutdown, a force majeure event due to lost production, lost orders and customers, new investment for health and safety assessment studies, and insurance. There is also civil responsibility associated with these types of incidents, and trust can be lost both internally (i.e., workers and unions) and externally (i.e., customers, the public and relevant authorities).

The current safety measures to prevent the risk of CO leaks in steel plants range from detectors (both fixed and portable) to maintenance operations, pressure monitoring, valve controlling, sealing systems and employee training. In spite of all those measures and plans, incidents are still happening due to equipment failure; critical events such as maintenance, repairs, and commissioning/decommissioning operations; and failure or absence of detectors.

Gas and asphyxiation remains one of the top causes of fatality in the steel industry. Surveys indicate that for fatalities and hazards related to gas and asphyxiation, 15% have no mitigation plan in place, 11% of the mitigation plans are inefficient, and 27% of the hazards are uncontrolled.[1]

This means that there is space for new solutions, such as gas odorization technology, for the reduction of the risk linked to toxic gas in the steel plants.

## Gas Odorization Technology

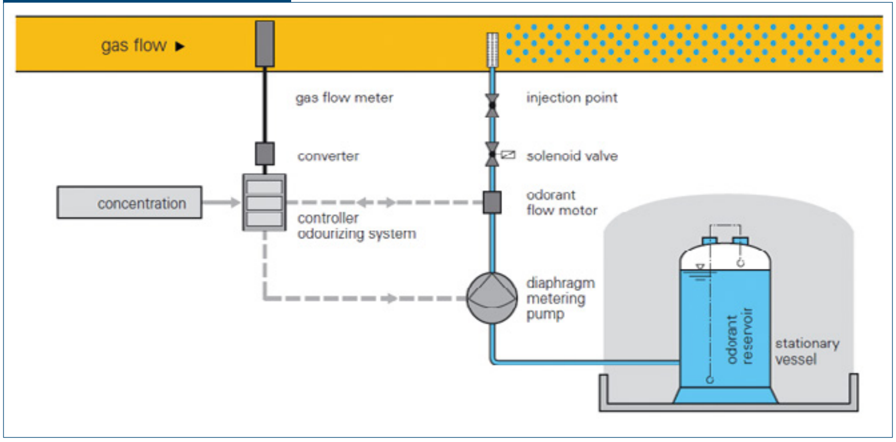
Gas odorization technology has been used worldwide for more than a century for the use and distribution (and sometimes in transportation) of natural gas and LPG. This technology, based on the human sense of smell, is a natural and universal detector against danger and has efficiently helped users to prevent incidents linked to gas leaks.

The principle, as shown in Fig. 2, is that the smell of a natural gas leak is perceived and recognized very quickly, as the human brain almost immediately associates the smell of gas with danger and triggers an instant reaction. For example, in the case of house dwellers, they would open the windows, evacuate the house and call the fire company upon smelling gas.

The purpose of odorization is to prevent the accumulation of gas before it reaches a hazardous level of concentration in the air.

Despite being potentially suffocating, natural gas is considered non-toxic. Its principal danger is its risk of explosion when air/gas mixture reaches the lower explosive limit (LEL). The goal of an odorization system is to alert people before this ratio is reached, at $1/5$ of the LEL. For that purpose, an odorant (warning agent) is added to the gas to convey a characteristic "gassy odor," which is both distinctive and unpleasant, and is readily detectable by a person with a normal sense of smell, before the level of the gas in the air reaches the critical point. This agent doesn't change the physiochemical properties of the natural gas, except its smell.

## Figure 3




*Example of injection system for natural gas.*[5]

In practice, as shown in Fig. 3, the flow of natural gas is measured and a signal is sent to the controller, which regulates the concentration of odorant (in liquid phase). The odorant is then pumped and vaporized into the gas pipe. The properties of the odorant will ensure it is quickly vaporized and dispersed into the gas flow so that a homogeneous dilution is obtained.

In the case of steel plants, gases containing toxic compounds like CO are more toxic than explosive, so the target is to be able to detect a gas leak before it reaches a toxic level in air.

As shown in Table 2, there are two standard limits to measure the exposure while working in CO atmospheres. The time weight average (TWA) is applied for workers that spend 8 hours per day with a risk of CO exposure. In this case, the U.S. Occupational Safety and Health Administration (OSHA) takes into account the long-term exposure limit of 50 ppm. Then for the case of an exposure with a 15-minute reference period (e.g., a leak), OSHA takes into account a short-term exposure limit of 300 ppm.

Given the volumes of gas to be treated, the optimized safety and economic balance for odorization is proposed at the short-term exposure limit (STEL). In this case, the toxic gas pipeline network will be odorized so that people identifying a gas leak will not be exposed to more than 300 ppm of CO and can react immediately seeking self-protection and alert their safety department. This

## Table 2

*Occupational Exposure Limits (OELs) of Some Chemicals*[6]

A. Maximum exposure limits (MELs)

| | Long-term exposure limit (8-hTWA reference period) | | Short-term exposure limit (15-min reference period) | |
|---|---|---|---|---|
| | (ppm) | ($mg/m^3$) | (ppm) | ($mg/m^3$) |
| Acrylonitrile | 2 | 4 | — | — |
| Asbestos | See EH 40 | — | — | — |
| Benzene | 5 | 16 | — | — |
| Buta-1,3-diene | 10 | 22 | — | — |
| Carbon disulfide | 10 | 30 | — | — |
| Ethylene oxide | 5 | 10 | — | — |
| Formaldehyde | 2 | 2.5 | 2 | 2.5 |
| Hydrogen cyanide | — | — | 10 | 10 |
| Isocyanates, all (as NCO) | — | 0.02 | — | 0.07 |
| Lead compounds | See EH 40 | — | — | — |
| Silica | — | 0.4 | — | — |
| Styrene | 100 | 420 | 250 | 1,050 |
| Trichloroethylene | 100 | 535 | 150 | 802 |
| Vinyl chloride | 7 | — | — | — |
| B. Occupational exposure standards (OESs) | | | | |
| Acetone | 750 | 1,780 | 1,500 | 3,560 |
| Ammonia | 25 | 17 | 35 | 24 |
| Carbon dioxide | 5,000 | 9,000 | 15,000 | 27,000 |
| Carbon monoxide | 50 | 55 | 300 | 330 |

proposed odorization positioning can be adjusted by the safety department as needed.

## The Selection of Odorant for the Steel Industry

There are different gas odorants, but in the case of natural gas odorization they all have to comply with ISO 13734 for organo-sulfur compounds.

According to the ISO standard, odorants shall:

- Be unpleasant, distinctive and not confusable with any other odor.
- Display the typical "gassy odor."
- Display a high vapor pressure.
- Be chemically stable, non-corrosive and leave no residue at combustion.
- Be non-toxic for end user at exposure concentrations.

Many factors may influence the choice of an odorant, such as the composition of the gas to be odorized itself, as well as the pipeline network conditions (e.g., material, flowrates, pressure conditions, presence of rust, etc.).

The above requirements for gas odorization are best met by organo-sulfur compounds from two families: mercaptans (RSH), sulfides (RSR) and by blends composed of mercaptans and sulfides.

Gas odorants must comply with the basic requirements of ISO 13734, as well as meet or exceed some specificities of steel industry gases:

- High odor intensity to meet the alert level with low odorant concentration.
- High vapor pressure to be vaporized quickly and readily result in homogeneous concentration in the gas flow.
- A good chemical stability to resist the oxidation reactions that can result in odorant efficiency losses.

There are three different types of odorants that have been used in the steel industry for steel gas odorization: tetrahydrothiophene (THT), ethyl mercaptan (EM) and CoDetect®. All three meet the requirements of ISO 13734. THT belongs to the sulfides group, EM to mercaptans, and CoDetect is a blend of both mercaptans and sulfides.

Table 3 shows the three gas odorants' main properties.

The main parameters for assessing the best odorant are:

- Concentration of odorant in the air to achieve the odor alert level — It is key to define the quantity of odorant that has to be injected in the gas. CoDetect and EM have higher intensity of smell so require lower concentrations in the air for odor alert than THT.
- Vapor pressure — The odorant has to be vaporized from liquid phase. Higher vapor pressure means a quicker vaporization of the gas odorant, which is better for short gas networks. CoDetect and EM both display higher vapor pressure values than THT.
- Reaction of the odorant with the pipes — It is very important that the odorant reacts as little as possible with the pipes, for example with rust. THT and CoDetect both display low reactivity values compared to EM. Indeed, EM gets oxidized quickly into lower odor disulfides, and thus, results in a loss of smell, which increases the risks of incidents.

In Table 4, some examples of estimated injection rates for BFG, BOFG and corex gas for the OEL of 300 ppm.

Around 20 plants in different locations around the world (mainly in China) are already odorizing. Fig. 4 shows an example of a gas odorization unit that uses CoDetect for the odorization of a BOFG line.

**Table 3**

***Tetrahydrothiphene (THT), Ethyl Mercaptan (EM) and CoDetect® Main Properties***

| | THT | EM | CoDetect |
|---|---|---|---|
| Compounds | Sulfides | Mercaptans | Sulfides and mercaptans |
| Concentration in air for alert level | 0.017 | 0.025 | 0.020 |
| Vapor pressure at 20°C (mbar) | 19 | 580 | 400 |
| Reactivity in pipes | Very low | Very high | Low |

**Table 4**

***Required Gas Odorant Concentration in the Gas***

| | Injection rate (mg/m$^3$) | | |
|---|---|---|---|
| | THT | EM | CoDetect |
| BFG (25% CO) | 142 | 21 | 17 |
| BOFG (60% CO) | 340 | 50 | 40 |
| Corex gas (45% CO) | 255 | 37 | 30 |

## Implementation and Feasibility of Gas Odorization Technology in Steel Mills

Every steel plant has a different energy network. When implementing an odorization solution for a plant, a plant should utilize the following processes in order to find the best and optimized service solution:

1. Design — After researching the gas flow, composition, temperature, and pressure for the selected line as well as the piping and instrumentation diagram (PID), the supplier provides a first estimate of the annual odorant consumption, as well as the number and location of the odorant injection points.

2. Technical Visit — The supplier's technical team, together with the process and energy engineers, will go to selected injection points to check the feasibility of these locations as injection points, as well as to have the required technical information to select the best injection system.

3. Pilot Phase — Several factors can have an impact on the efficiency of the odorization. Potential losses of odorant need to be estimated on each network to better calculate the consumption of odorant and optimize the associated costs. A pilot phase should be proposed, in order to verify that this odorizing system is adapted to the steel plant network.

The networks and end uses of steel gases can vary from one steel plant to another. However, these gases are always burned either to generate energy at the power plant or to generate heat in another workshop (coke oven, hot stoves, blast furnace and oxygen converter plants, as well as the hot and cold rolling mills and other furnaces). In all these cases the gas is never in contact with liquid steel, therefore the odorant has no influence on the surface quality of the steel.

4. Installation — The supplier or a local partner installs and provides the injection systems and ensures the commissioning and the odorant supply as well as the maintenance service.

Figure 4

*Odorization unit for BOFG.*

## Safety Awareness

While implementing odorization in the steel factories networks as a complementary safety solution, communication to the workers/stakeholders should be performed in order to increase the efficiency of the protocol.

For steelmaking facilities, specific communication (part of the workers and visitor safety training) should be done internally so that people working or visiting the factory can report any gas leak to the safety department as soon as possible.

In the case of a gas leak going beyond the factory limits, there is a need for local security services to know that the odor could be linked to a CO leak. Accumulation of calls related to gas leak alerts in the vicinity of the factory should help identify and fix the gas leak. Since the odor is perceived as a dangerous natural gas smell by nearby population, it may not be necessary to set up an educational public campaign. However, educating local gas utilities, fire brigades and relevant local authorities on this new odorization practice is recommended.

## Main Benefits for Gas Odorization Technology

As a general conclusion, gas odorization technology can offer multiple benefits compared to other safety measures already in place. It is simple, as it relies on the common sense of smell, which is very efficient and a "maintenance-free" natural detector. This solution is universal, as leaks can be detected by people visiting or living nearby the plant since the "gassy" smell is universally associated with danger. The reliability of this safety measure is linked to the gas, and not to any equipment; so wherever the toxic gas goes, it will be detectable. More importantly, higher safety leads to significant cost savings. CO odorization limits the risk of gas asphyxiation, which can cause deaths, ultimately reducing shutdown times, liability, indemnifications, workers' compensations and general insurance costs.

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