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The Safety aspects/Safety measures for refrigerants NH₃ and CFC/HCFC

Ammonia is good for thermodynamic properties and low ozone depleting potential and is called the best and most cost effective refrigerant by the refrigeration industry. For most large-scale appliances ammonia has become the number one refrigerant.

Safety aspects

On the other hand, ammonia exhibits aggressive and poisoning properties. Considering that appliances and workers may be endangered by ammonia an early warning provided by adequate equipment is indispensable. In most countries directives consequently ask for the installation of ammonia warning systems.

It is recommended for the best interest of the company to install a measurement system even for small ammonia values.

The monitoring of ammonia is divided in two parts:

- Air-/ or area-monitoring
- Monitoring of water-, water-/glycolbrine-circulations

To gain an insight into the different measurement principles that exist on the market we will give an overview about the different principles with their advantages and drawbacks.

Air monitoring

Leak detection in air means monitoring of machine rooms, storage goods, sewers, manholes which have a hazard potential, or rooms in which people work.

The positive thing about small ammonia leakages is that humans recognize these small ammonia amounts by its unpleasant odor. This has however the consequence that concentrations of 100 ppm are sensed so unpleasant that people start to panic. The TLV (Threshold limit value) for ammonia is set to 30 ppm (ppm= parts per million) and indicates the concentration a person can be exposed to on a 8 hours working day without having to face health dangers. Panic during events (e.g. in ice stadiums), health damages, damages of frozen goods and also a severe damage of the reputation of the facility can be affected.

In Europe the installation of gas warning systems is specified by national regulations which will be replaced by the European standard EN 378. Regarding these regulations



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three threshold values have to be monitored. The first alarm calls the technical personnel for attention and turns on ventilation systems (if available). Rising concentrations lead to the shut-down of the appliance and contacting the local fire department. Concerning the German regulations a complete de-energizing has to be provided at 3 Vol.% (30.000 ppm) at the latest to prevent possible explosion of the ammonia. The LEL (lower explosion limit) of ammonia is 17 Vol.%, meaning that at this concentration the mixture is explosive.

Sensor technologies for air monitoring

The following sensor techniques are used on the market for monitoring of different ammonia concentrations:

- Electrochemical sensors
- Semiconductors
- Infrared sensors with sampling system
- Catalytic combustion sensor

The main requirements on the sensortechnique are:

- The sensor used should have low initial and follow-up costs
- The sensor shall only "see" ammonia, so that other substances or temperature conditions will not cause any false alarms
- The sensor should be operational for a wide detection range
- The measurement points should be continuously monitored, to allow for alarm triggering without any delay

Which sensor techniques are offered on the market?

Electrochemical sensors

The electrochemical sensor works like a fuel cell, producing a small current by electrochemically oxidizing the ammonia. Low cross sensitivities prevent false alarms in nearly all applications. The very sensitive sensor may detect concentrations starting at 2...3 ppm, but high concentrations of more than 500 ppm exhaust the sensor rapidly (chemical reaction). Hence, the sensor is suitable for applications where delicate goods need to be monitored and many different gases occur. The lifetime of the sensor depends on the NH_3 amount that it is exposed to and on the ambient temperature at the location (high temperatures of more than 35°C let the sensor dry out).

Advantages of electrochemical sensors:

- High selectivity at small concentrations
- Recommended detection range 0 ... 200/500 ppm

Semiconductors

The semiconductor sensor burns the ammonia on its surface changing the elements resistance. Many other gases



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and vapors (e.g. detergents) may be burned on the sensor surface as well leading to frequent false alarms. Low concentrations cannot be reliably monitored - high concentrations lead to a sensor breakdown (30 000 ppm).

Infrared with sampling system

The infrared system is the most reliable detection principle for monitoring of up to 1 ppm. Due to the high initial costs a sampling system is used to sample the gas from the different measurement points.

This leads to numerous drawbacks:

- The measurement points are not continuously monitored
- The sampling lines need to be wired very precisely (condensation can lead to water damage). Sampling lines are usually made out of plastic, thus they are exposed to pollution and can distort the measurement result
- High initial and follow-up costs

Catalytic combustion sensor

The catalytic combustion sensor uses the heat that is released when ammonia is combusted as a measuring signal. The very low heat that occurs with the combustion of ammonia makes this sensor only suitable for monitoring of the third alarm threshold LEL of 30.000 ppm (3 Vol. %).

Detection principle charge carrier injection (CI)

The charge carrier injection sensor (CI-Sensor) is based on a new detection principle. The shortcomings of the established methods initiated the development of new material adsorbing the ammonia without the need of oxidation. By absorbing molecules the ammonia carriers (charge carrier) are brought into the new sensor material (injection). This changes the resistance of the sensor element and supplies the measurement signal. The basic resistance of the sensor material is so high that it could not be monitored with common sensor elements up to today. Therefore a particular laser structured sensing element had been developed.

The CI Sensor does not depend on the oxidation of the ammonia. Accordingly the cross sensitivities to combustible substances (e.g. alcohol) are remarkably low. The main advantage of the new detection principle is the possible usage of the sensor for small concentrations up to 30 000 ppm. It can be used for all three alarm thresholds, the pre-alarm at 200 ppm, the 1000 ppm alarm and the 30 000 ppm alarm for deenergizing.

Moreover the sensor is not poisoned when exposed to huge ammonia concentrations nor is the lifetime reduced. The



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expected lifetime is more than 5 years. This development is a product of years of research and development carried out by GfG.

Monitoring of water-, water- /glycol-brine systems

If refrigeration systems are cooled with water from public lakes and rivers it is necessary to monitor the refrigerant medium for NH₃-leaks after consumers, condensers or de-heaters.

Many systems are optimized by using water/glycol or brine-mixtures in the secondary circuit. This can lead to dangerous situations when there is a leakage between the primary circuit filled with ammonia and the brine circuit. If the secondary circuit consists of non-ferrous metal the ammonia is bound to the non-ferrous metal leading to an decrease of the wall thickness up to fragmentation. In this case reliable detection is absolutely necessary.

Today technology offers the operator absolute safety by means of ion selective measurement. More than 300 systems have been installed. The measurement technology, for monitoring water circuits (evaporative condensers, deheater, basins etc.) or brinemixture circuits are: ethyl glycol, propylene glycol, tyfoxit, pekazol, marlotherm, therminol, gilotherm, santotherm, talin and many more.

How does ion selective measurement work?

Ammonia is present in water as ion. The escaping NH₃ binds itself to a NH₄⁺ ion and can then be monitored by a NH₄⁺ ion selective electrode. With all direct water measurements, no matter whether in a circuit or basin, the measurement is done selective by means of an electrode, thus only one measurement point after a consumer/condenser is needed. The offered measurement systems are operational up to 6 bar operation pressure, with detection limits of small concentrations 0,2 ppm ...10/100 ppm as detection range. Thereby only the NH₄⁺ ion that escapes into the water is measured.

In water/glycol, brine circuits the ammonia and can not bind itself to the mixture because the displacement of equilibrium of the hydrogen ions are on the one hand inhibitors and stabilizers on the other hand make this impossible. Therefore, brine mixtures ammonia leakages are mainly gaseous as NH₃. Due to this an NH₃ ion-gas selective electrode is used. The interior buffers and the membrane system of the electrode need to adjust to the brine mixture.

Years of experience and research & development have made GfG the market leader for monitoring of water-/water brine mixture circuits.



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Measuring systems can be operated at a pressure of up to 7 bar and temperatures of -45°C ... $+ 90^{\circ}\text{C}$ and are custom installed mainly in closed circuits. A shutting clack can disconnect the measurement unit from the operating circuit to allow for maintenance works or calibration. The shutting clack is included with the packaged measurement system. For higher temperatures and aggressive mediums you can choose variants in POM and PVDF. An automatic ventilator assures that the fitting is permanently ventilated.

Engineers - electricians and end user

Specialized companies consult these people concerning selection, location and the monitoring concept. It is of the utmost advantage if the consultant is provided not only with the experience needed but also the complete range of gas and water monitoring and can offer complete warning controls with respective contact-outputs and schematic diagrams. Thereby interfaces and additional costs through different works and service costs are avoided. This lowers the initial costs as well as the service costs.

The consultant has to notice the country specific regulations as well as the local circumstances and integrate those together with the electrician in a safety concept. Thereby the disconnections (machine disconnections, stop valves etc.) have to be incorporated with refrigeration specific expertise. Moreover the electrician has to mark the machines and valves for emergency measures and describe them in the safety concept.

These extensive measures assure that an operation with ammonia refrigerant is guaranteed to be free from worries and that the operator has well secured his system, this means leakages are detected on time long before the system will be damaged.

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