Pneurop White Paper EN 1012-3 possible Extension regarding Hydrogen

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To support climate targets as defined, the global hydrogen business is emerging. At the same time process gas compressors are considered an essential part of the related value chain, including transport, storage and downstream utilization of hydrogen and hydrogen products.

Unless process gas compressors have been applied to Hydrogen Services in traditional market areas like fertilizers and refineries before, application areas are extended, additional boundary conditions are under consideration and resulting technical demands for process gas compressors apply.

Therefore, the Pneurop PN18 process compressor committee of the Pneurop association supports an addendum to EN1012-3 to detail out specifics for hydrogen compression, potential risks and additional safety requirements related to those services. This topic could be later added as a new chapter 5.7.6 in EN1012-3 and therefore already uses a corresponding chapter numbering.

The requirements and information of the addendum (shown below) are based on existing knowledge and experience regarding safety- and design relevant aspects with process gas compressors in hydrogen- / hydrogen rich services providing guidance during product-development and product-application.

The addendum contains sub-chapters as shown below:

- Hydrogen Characteristics
- Material Properties in Hydrogen Services
- Explosion and Flammability
- Consideration for Product Design for Hydrogen Services
    - Mutual reactions with different media
    - Sealings
    - Leak Tightness

Thereby, the addendum is considered an extension of already existing safety requirements. Effective regulations and limits are to be considered in addition.

5.7.6 →Hydrogen

This chapter describes the additional safety requirements for a compressor if hydrogen is present in the compressed gas.

Hydrogen or fluids with a high hydrogen concentration are covered by EN 1012-3. Safe handling of hydrogen is only possible with knowledge of its properties and appropriate safety measures. This chapter is a supplement to the previous binding safety regulations; all applicable legislation, guidelines and limit values shall still be acknowledged. The following section describes the specific features that arise when handling hydrogen.

5.7.6.1 →H2 properties

The following properties of hydrogen must be taken into account in the risk analysis/assessment:

- Hydrogen is a combustible gas with low ignition energy and a wide ignition range.
    - Odourless,
    - Easily flammable,
    - High ignition temperature of 585°C,
    - Combustion rate approx. 10 times higher than with hydrocarbons,
    - Deflagration: Flame pressures at containment 8-10 bar, propagation velocity up to 975 m/s,
    - Explosive,
    - Detonation: Detonation pressures 15-20 bar, propagation velocities 1500 to 3400 m/s, spatial wave-like propagation, depending on concentration, pressure and temperature,
    - Any blend of H2 from 4% to 74 % in air and from 4% to 94% in oxygen is flammable,
    - invisible (colourless) to almost invisible flame,
    - very volatile gas,
    - lighter than air → volatile, escapes through smallest openings, s. also respective chapters in EN1012-3,
    - diffuses in and through materials,
- An explosion hazard begins with a concentration of 18%,
- As soon as around 75 % hydrogen in air is present, ignition and thus explosions are no longer possible, as the amount of oxygen is insufficient for this. Since hydrogen is 14 times lighter than air and thus quickly evaporates in the open air, the explosion hazard of hydrogen is further reduced,
- Joule Thomson Effect,
  The Joule Thomson effect is describing the temperature change of a real gas following an isenthalpic expansion. This change of temperature is defined by the Joule Thomson coefficient, which is given by the differential of the temperature along the pressure at constant enthalpy. The sign of this coefficient is changing at the specific inversion line for each real gas. Because of the very specific characteristic of hydrogen, this will lead to an increase in gas temperature for most of the hydrogen compression applications, which needs to be considered during the design of a hydrogen compressor solution,
- Hydrogen creates water in gas phase (steam) when contacting with oxygen on burning related temperature, resulting in expansion with very large volume respectively pressure when enclosed,
- Brittle effect on some materials (see also section 5.7.6.2),
    - can lead to a reduction of strength (hydrogen embrittlement or 'HIC-hydrogen induced cracking').

5.7.6.2 →Material properties ´

The specific application of the machine defines the selection of suitable materials and their properties. The materials for the compressor and the associated components must (at least) fulfil the special requirements of hydrogen applications. When assessing the materials, the position of the materials in the compressor and the anticipated contact with hydrogen must be taken into account. The following factors and their interactions must be taken into account:

1. Load,
2. Material,

3. Environment.

To prevent hazards and safety risks due to hydrogen, the selected materials must correspond to the mechanical properties and metal behaviour:

1. Reduced ductility,
2. Reduction in notched impact strength and breaking strength,
3. Increased material fatigue.

Depending on the process conditions, hydrogen gas can severely embrittle construction materials. In components, the significant reduction in ductility and fracture toughness can cause spontaneous failure.

Hydrogen attack leads to material separation inside the metal which takes the following forms.

- Surface bubbles,
- Internal cracks without the effects of internal or external stresses,
- Stress corrosion cracking in the presence of tensile stresses.

The following conditions must be fulfilled:

- Existence of phase boundary reactions that supply atomic hydrogen,
- Presence of a driving force that favours the absorption of hydrogen atoms into the material,
- Susceptibility of the metallic material to hydrogen-induced corrosion.

Atomic hydrogen can be produced from the gas phase or from aqueous electrolyte solutions during electrochemical reactions.

The risk of embrittlement of the materials of construction under the influence of hydrogen requires special precautions if the following operating conditions are exceeded:

- Hydrogen content in the gas greater than 90 % and/or,
- Hydrogen partial pressure in the process greater than 8 bar absolutes.

At temperatures above 220 °C, chemical reactions of hydrogen gas with carbon steels and low-alloy steels are also possible (High Temperature Hydrogen Attack). The mechanical characteristics of the steels deteriorate which can also lead to the failure of components.

The following is a detailed description of the component damage mechanisms of e.g.:

- Hydrogen embrittlement,
- Hydrogen induced cracking (HIC),
- Hydrogen-induced stress corrosion cracking (HSCC),
- H-induced corrosion,
- Delayed brittle fracture.

Hydrogen can be absorbed by reaction with aqueous solutions or from gases. In any case, hydrogen can only penetrate the material in atomic form, as only atoms are diffusible in metals.

The resulting damage can be divided into three types:

1. Chemical pressurised hydrogen damage at elevated temperatures,
2. Physical hydrogen damage,
3. Electrochemically induced hydrogen damage.

Re. 1. chemical hydrogen pressure damage

Chemical pressurised hydrogen damage occurs at high pressures (from approx. 100 bar) and above approx. 200°C.

There is a limit temperature for each steel at a given hydrogen pressure and a corresponding limit pressure at a certain temperature, below which no hydrogen-related damage is to be expected during the service life.

For the suitability of steels and other materials, it has generally proved useful to analyse them in a Nelson diagram. Nelson diagrams show the application and limit ranges of materials. In the Nelson diagram, partial pressure is assigned to the right-hand axis and temperature to the vertical axis.

Note: API 941 "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants" contains Nelson diagrams for materials for hydrogen applications.

Above the limit conditions (temperature and partial pressure see Nelson diagram), the balance between atomic and molecular hydrogen changes towards larger proportions of atomic hydrogen. This can lead to increased material attack.

Re. 2. physical hydrogen damage

Physical hydrogen damage can occur in high-purity pressurised hydrogen even at room temperature if mechanical alternating loads with plastic deformation of the material or as a result of slow flow processes at localised surface areas cause expansion processes with low deformation rates. The occurrence of physical hydrogen damage is strongly dependent on the degree of purity of the hydrogen.

Re. 3. hydrogen damage as a result of electrochemical corrosion

Electrochemically induced hydrogen damage is caused by the adsorption and absorption of atomic hydrogen, which can occur during corrosion reactions, e.g. with H2S. This is possible in the metal/electrolyte solution system and therefore only below the dew point of the electrolyte solution (see compressors for gases containing H2S are described in chapter 5.7.5 of EN1012-3:2013).

5.7.6.3 →Explosion and flammability

5.7.6.3.1 → Limits for explosion and flammability

The requirements of clause 5.8 Fire and Explosion of EN1012-3:2013 and any other legislative requirements for explosion protection apply.

Hydrogen is colourless and odourless and burns with an almost invisible flame. The required minimum ignition energy of 0.019mJ is extremely low (one order of magnitude below propane), making hydrogen highly flammable. For example, even the smallest particles whirled up by the escaping medium are sufficient to generate an ignitable spark through electrostatic charging or contact with an obstacle. This high reactivity is often misunderstood as the ability of hydrogen to self-ignite spontaneously.

Compared to other known flammable gases, considerably larger ranges of mixture ratios are flammable:

- In air, any mixture between 4% and 74% hydrogen by volume is flammable (explosion limits),

- In oxygen, any mixture between 4% and 94% hydrogen by volume is flammable.

Explosive concentrations must be avoided; it must be ensured that leakage rates and accumulations of large quantities of the medium in operating facilities are avoided.

Further information can be found in the section on handling explosions and flammability.

5.7.6.3.2 → Handling explosion and flammability

As indicated in the chapter above, it is essential to avoid large quantities of hydrogen accumulating in the vicinity of the compressor, which can cause potentially explosive concentrations. On the one hand, this can be prevented by the design and, on the other hand, monitored by gas measuring devices. Manufacturers and operators are required to coordinate preventive and defensive measures to ensure fire and explosion protection. Both constructive and organisational measures can be used to ensure fire and explosion protection.

5.7.6.4 → (Notes for) component design

With H2 compressors, particular attention must be paid to the following areas:

- Lubrication system,
- Seals,
- Tightness and leakage rates.

The material selection according to section 5.7.6.2 must be taken into account accordingly when designing the component.

5.7.6.4.1 → Interaction with other media

If a mixture of hydrogen and lubricant is to be assumed, a potential and possibly spontaneous outgassing of H2 in the lubrication tank must be taken into account in the design in order to prevent an explosive atmosphere in the oil tank.

The Nelson diagrams mentioned under 5.7.6.2 clearly show that the partial pressure of hydrogen is one of the two essential variables for damage caused by hydrogen. The partial pressure is the product of the amount of substance (‘concentration’) and the total pressure. Under certain circumstances, high total pressures can occur locally. In these cases, critical partial pressures already occur at low H2 concentrations. High total pressures exist, for example, in lubricating oil in the contact area between rolling elements and bearing rings.

5.7.6.4.2 → Seals

When sealing H2 compressors, the gas properties under the existing operating conditions must be taken into account. With hydrogen, the increased volatility and diffusivity must be taken into account in particular (see 5.7.6.1 H2 properties). Inert or non-reactive gases must be used for the sealing gases.

Chapters 5.7.8 and 5.7.9 on seals of EN1012-3:2013 and Chapters 5.8 and 5.7.6.3 on explosion and flammability of EN1012-3:2013 must be taken into account as a basis. In addition, the compatibility of the seals with hydrogen must be checked (see section 5.7.6.2 on material properties and 5.7.6.4.1 on interaction with other media).

The special features of H_2 in discharges (safe location) and rapid depressurisation, for example, must be taken into account.

5.7.6.4.3 → Tightness and leakage

In deviation from section 6.2, helium must be used for leak tightness test of pressure containing parts, as no safe gas with a comparable molecular mass is available for hydrogen or gas mixtures with a molecular mass significantly smaller than 4 g/mol.

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