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1ST EDITION

GUIDELINE FOR SMALL SCALE HYDROGEN PRODUCTION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has published CGA H-17, *Guideline for Small Scale Hydrogen Production*, jointly produced by members of the International Harmonization Council.

This publication is intended as an international harmonized standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

Large scale hydrogen production has been commercially practiced for decades, and the demand for such production has grown over that period. In response to that demand, industrial gas companies operate and maintain large-scale hydrogen production facilities worldwide and have done so with an exemplary safety record for many years. Most large-scale hydrogen production facilities are based on steam methane reforming (SMR), which is a thermal-based hydrogen production method. Historically, smaller plants have also been based on steam reforming and used in industrial applications. The small facilities typically are sited inside or adjacent to the hydrogen customer's facility.

With the push to include hydrogen as a vehicle fuel, smaller hydrogen production facilities could become more common in order to bring the source of hydrogen closer in proximity to fueling stations and to match the size of the facility with the fuel demand. While some of these production facilities are likely to be based on SMR, other technologies can also be utilized. These plants and the loading facilities associated with them can be more visible and accessible to the public, and end users might have little or no experience in the chemical process industry. In addition, these facilities are more likely than large hydrogen plants to be operated unmanned or partially manned. As a result, there are safety aspects associated with siting and operating small scale hydrogen plants that are not currently addressed in existing publications for HYCO (hydrogen, CO, and/or mixtures thereof) plants and that will be addressed in this publication. Where existing guidelines exist, they will be referenced.

2 Scope and Purpose

2.1 Scope

This publication applies to small hydrogen production units (thermal and electrolytic) that are sited at chemical or refinery plants, as well as those units that are sited at vehicle fueling stations or transfer facilities. For the purposes of this publication, small plants are defined as those with a production capacity between 1666 scfh to 373 000 scfh (45 Nm³/hr to 10 000 Nm³/hr; 40 MSCFD to 9000 MSCFD; or 1070 Nm³D to 241 000 Nm³D).

The thermal hydrogen production methods covered in this guideline are methanol cracking and SMR although some of the guidelines provided can apply to other thermal-based hydrogen production technologies.

2.2 Purpose

This publication will provide a single comprehensive set of safety and operating guidelines to address the multiple hazards associated with the operation of small scale hydrogen production plants. These hazards are particularly acute if the production unit is located next to a liquid fueling station.

This publication will provide information for the end user, whether an experienced industrial user or a first-time industrial or commercial user. This document will reference other related documents and adapt the guidelines of large-scale HYCO facilities to these small scale operations. The following will be addressed:

- best practices for operation of small scale units;
- simplified process descriptions;
- guidance on siting of small scale units, including when next to other flammable material sources. Issues of area classification and vapor cloud explosion (VCE) will be discussed;
- guidelines for how small scale production facilities will interface with a co-located bulk storage facility with compression and high-pressure storage as well as liquid back-up storage and the associated vaporization equipment; and
- high level concerns associated with startup, shutdown, and maintenance.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Bulk hydrogen compressed gas system

Assembly of equipment that consists of, but is not limited to, storage containers, pressure regulators, pressure relief devices (PRDs), compressors, manifolds, and piping, with a storage capacity of more than 5000 scf (141.6 m³) of compressed hydrogen gas that terminates at the source valve.

3.2.2 Bulk liquefied hydrogen system

Assembly of equipment that consists of, but is not limited to, storage containers, pressure regulators, PRDs, vaporizers, liquid pumps, compressors, manifolds, and piping, with a storage capacity of more than 39.7 gal (150 L) of liquefied hydrogen that terminates at the source valve.

3.2.3 Combustion air

Air used to react with the fuel in a combustion process.

3.2.4 Lower flammable limit (LFL)

Lowest concentration of a flammable gas in an oxidant that will propagate when ignited.

NOTE—Also referred to as lower explosive limit (LEL).

3.2.5 Pre-reformer

Reactor, located upstream of the reformer, that primarily converts heavy hydrocarbons (e.g., ethane, propane, butane) to methane.

3.2.6 Pressure swing adsorption (PSA)

Multiple fixed bed gas purification process that uses materials that selectively adsorb one or more gas species from a mixture. Regeneration of the adsorbent is accomplished via pressure reduction or “swing.”

3.2.7 Residual stress

Stress remaining in a solid material/construct as a result of thermal or mechanical treatment, or both. Stress arises in fusion welding primarily because the weld metal contracts on cooling the solid to room temperature.

3.2.8 Self-heating

Material that reacts with air resulting in an increase in temperature. When a sufficient amount of the material is piled in one place, the heat cannot escape fast enough; and the center of the mass will develop an uncontrolled exothermic reaction. The heating will bring the center of the mass to combustion temperature and then incandescence.

3.2.9 Upper flammable limit (UFL)

Maximum concentration in air of a gas, which would burn when ignited.

NOTE—Also referred to as upper explosive limit (UEL).

4 General safety considerations

This section addresses general safety considerations associated with hydrogen production plants, both thermal production and electrolytic. Additional process-specific safety considerations are covered in Section 6.

4.1 Process safety management

The risks associated with hydrogen production facilities are serious enough that they should be managed in a holistic and systematic approach to ensure the integrity of the operating facility. CGA P-86, *Guideline for Process Safety Management* introduces a framework that can be adopted to manage process safety risks, identifying four categories of process safety management elements: process safety leadership, risk identification and assessment, risk management, and review and improvement [1].¹

Small production units typically do not contain enough volume of gas to be regulated under the OSHA Process Safety Management (PSM) Regulations (29 CFR Part 1910.119) or, in Europe, Seveso III Directive 2012/18/EU, although the presence of a cryogenic liquid storage unit for backup could result in sufficient material on-site to trigger the threshold for PSM [2, 3].

The most important elements of process safety management that pertain to small facilities that might not be subject to the full regulation include:

- Leadership commitment and responsibility (Element 1);
- Compliance with legislation and industry standards (Element 2);
- Workforce involvement (Element 4);
- Operating procedures (Element 9);
- Management of change (Element 12);
- Emergency management (Element 14); and
- Work control, permit to work, and task risk management (Element 17).

Some of these process safety elements are touched upon in the sections below.

4.2 Personal protective equipment

Serious hazards to personnel include exposure to toxic releases, fire, asphyxiation, burns, electric shock, exposure to caustic/acidic chemicals, and noise. Safeguards include utilizing personal protective equipment (PPE).

All personnel in the facility shall wear PPE as required by site policies or regulations. A PPE matrix defining task-specific and area-specific PPE requirements should be developed. In areas of the facility associated with hydrogen production or storage, PPE shall include as a minimum:

- safety glasses with rigid side shields;
- hard hats;
- flame-resistant clothing (FRC);
- hearing protection (if required, based upon noise level);

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

- safety shoes or boots; and
- work appropriate gloves.

Wearing portable personal gas monitors is recommended when the risk of a gas leak is present. These monitors can be configured to detect a single gas (e.g., carbon monoxide) or can be multi-sensor monitors (e.g., oxygen, carbon monoxide, flammability). The need for monitoring and the type of monitoring required should be determined based on a site/task-specific risk assessment. Since small plants can be located within a building or enclosure, the impact of any process leak is elevated; and this shall be considered in the site/task risk assessment. More information on this and other types of gas detectors and their use is available in CGA H-14, *HYCO Plant Gas Leak Detection and Response Practices* [4].

For facilities that include a hydrogen vehicle fuel dispenser, PPE requirements in the hydrogen dispensing area will depend on whether the individual is conducting maintenance or is fueling a vehicle. The above PPE is the minimum requirement when conducting maintenance in the hydrogen dispensing area.

Additional PPE could be required for specific operating and maintenance tasks. For example, chemical-resistant gloves or goggles/face shields could be required when working with water treatment chemicals or electrolytes. Thermal protection gloves could be required when working around hot piping or equipment (see CGA H-10, *Combustion Safety for Steam Reformer Operation*) [5]. In alkaline electrolysis plants, the liquid in the cell requires special handling and PPE (e.g., chemical suit). See CGA P-44, *Selection of Personal Protective Equipment* for more information [6].

4.3 Noise control

Hydrogen production plants typically contain operating units that can expose personnel to high noise levels. Personnel shall be aware of the cumulative effects of working in a high noise environment. If the facility is in close proximity to public areas, sound level regulations could be much tighter than in an industrial area. A noise level survey should be completed and shall meet local and regional regulatory requirements. Hearing protection requirements shall meet the relevant local regulations (e.g., OSHA, Directive 2003/10/EC) [2, 7]. Additional sound reduction equipment (e.g., sound barriers, enclosures, sound attenuation insulation) could be required.

4.4 Site safety guidelines

Serious hazards to personnel include exposure to toxic releases, fire, asphyxiation, burns, electric shock, exposure to caustic/acidic chemicals, and noise. Safeguards include limiting exposure by controlling area access to ensure safety of personnel.

Signs stating the potential hazards (e.g., heat, fire, toxicity, anoxia, restricted area, etc.) should be posted visibly in hazardous areas to alert personnel. Personnel who are exposed to these areas shall be trained in the risks and shall wear appropriate PPE to mitigate potential hazards.

Any visitors (non-permanent employees) to the hydrogen production facility should be provided a safety indoctrination prior to entering the facility. The safety indoctrination should describe all the potential hazards and PPE required to enter the unit, and what to do and where to muster in case of any emergency. The indoctrination shall include appropriate response to site alarms, which could be triggered in the event of a significant leak. Hazards associated with materials on-site shall also be covered.

All visitors, including contractors, should sign into and out of the facility.

4.5 Work permits and system isolation

All maintenance shall be conducted under the plant's permit to work system (or work permit system). The safety work permit documents the work that will be completed, the hazards involved, the precautions to take (including PPE requirements and equipment isolation), required authorizations, etc. One copy of the work permit is kept in the control room (or permit office), and the other copy is kept at the work site.

In many cases, maintenance requires that the system be isolated properly, which is ensured through the plant lockout/tagout program. There are three steps to the lockout/tagout process: isolate energy sources, apply locks and tags to each isolation device, and verify that all energy sources are deactivated (e.g., try to start a compressor).

and verify it does not start, verify that flow has stopped from any process bleeds, verify pressure indicators show zero pressure, etc.).

Some of the things that should be considered when developing a work permit include:

- system isolation requirements;
- confined space;
- electrical isolation;
- hot work (work that involves an ignition source such as welding);
- monitoring for potential leaks, particularly for hot work;
- purging activities;
- simultaneous maintenance activities;
- hazardous weather conditions (e.g., heavy rain or wind, extreme heat or cold);
- health and environmental hazards associated with material (e.g., catalyst) handling; and
- activities that involve confined space, high-voltage electricity, or hot work typically require an additional special permit.

4.6 Emergency response

A site emergency response plan shall be developed and shall include, at a minimum, the following elements:

- plant-wide alarm notification protocol with required action by site employees;
- emergency response and control procedures;
- procedures for emergency shutdown of operations;
- internal and external emergency contact information (first aid responders, ambulance, fire department, police, hazardous materials response team, customers, and neighboring facilities); and
- required jurisdictional authority and regulating agency notification requirements.

Some of the most common emergency scenarios that should be addressed are:

- fire;
- medical emergency;
- chemical spill;
- gaseous release with toxicity or ignition/uncontrolled energy release potential;
- security threat;
- weather emergency;
- power outage; and
- earthquake.

Employees and contractors working on the site shall be trained on the site's emergency response plan. Periodic emergency response drills with first responders are recommended.

4.7 Partially staffed or unstaffed operation

Small scale hydrogen plants often are sufficiently automated such that they can be operated by a single individual (lone worker) during routine operation and maintenance. In the case where a single individual is on-site, an effective means shall be established to provide an alert if the operator becomes inactive. The proper means of communication shall be determined by risk assessment. This can be an automated system (lone worker monitoring system) or periodic contact with a designated individual (contact time interval based on risk assessment).

Tasks that are considered highly hazardous based on risk assessment shall require the presence of a minimum of two persons who are routinely in contact with each other.

For unstaffed operation, the hydrogen production facility shall be instrumented such that it is capable of safely shutting down and going to a safe condition. In the case where the facility is unstaffed and remotely monitored, the remote operator should have the capability to monitor all key parameters and shall have the capability to shut the plant down. The owner should consider having an emergency shutdown (ESD) button that is accessible to first responders.

The control system of the hydrogen production facility shall be arranged such that it can safely shut the plant down in the event of significant operational upsets (based on interlock matrix).

5 Hydrogen production processes

The three predominant technologies for small scale hydrogen production are SMR, methanol cracking, and electrolysis. Steam methane reforming and methanol cracking are both thermal-based hydrogen production technologies, while electrolysis uses electricity as the driving force for hydrogen production. This section provides an overview of these processes.

5.1 Steam methane reforming

The term SMR is used for the broader process of steam reforming of hydrocarbons, as the predominant feedstock is natural gas (methane); but the SMR process is suitable for a feedstock range including liquefied petroleum gas, refinery off gas, and light liquid hydrocarbons up to naphtha. The SMR process consists of four basic steps: feed purification, steam reforming, shift conversion, and product purification. Product purification is generally done by pressure swing adsorption (PSA), which produces the hydrogen product stream (up to 99.999% product purity) and a waste stream (PSA tail gas). The SMR process with PSA purification is illustrated in Figure 1. Other methods of product purification besides pressure swing adsorption are possible but are not described in this publication.

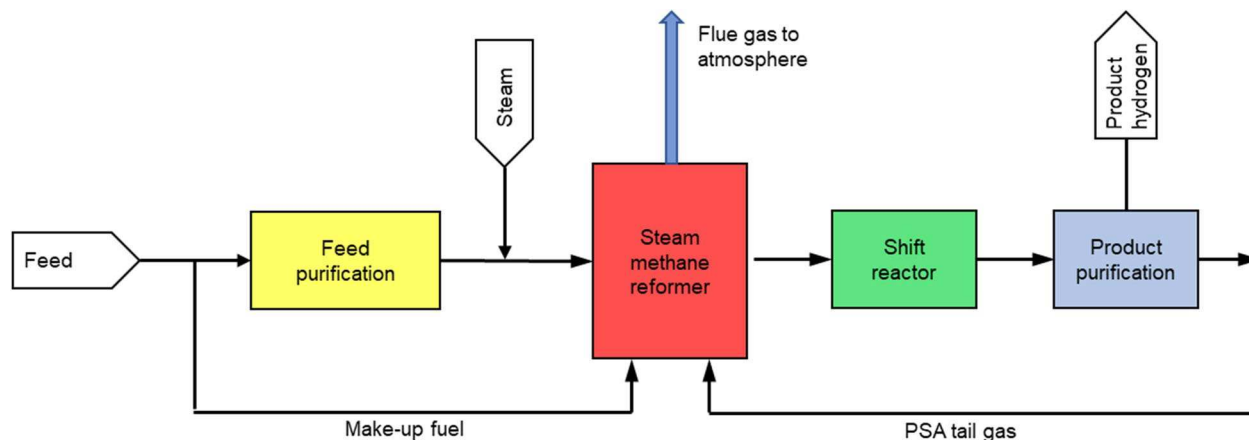


Figure 1—Steam methane reforming process with PSA purification

The first step in the SMR process is feed purification, as most hydrocarbon feeds contain sulfur. Sulfur is a poison to the catalysts used in the process. Sulfur removal can be done at ambient conditions or at elevated temperature. Other contaminants (for example, chlorides) can be present and could require removal. Liquid feeds require vaporization prior to contaminant removal.

Following purification, the feed stream is heated and mixed with steam (produced from boiler feed water) and sent to the reformer where it is reacted to generate syngas (a mixture of hydrogen, carbon monoxide, carbon dioxide, and unreacted components).

The two main reactions taking place in the reformer are:

- steam methane reforming ($\text{CH}_4 + \text{H}_2\text{O} + \text{Heat} \leftrightarrow \text{CO} + 3\text{H}_2$); and
- water gas shift ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$).

Heat for the process is generated by combustion of PSA tail gas and a makeup fuel, typically natural gas, with air (combustion air).

To avoid solid carbon (C) formation in the reformer, the amount of steam added to the feed gas is more than the amount required for the chemical reactions. If the feedstock contains hydrocarbons heavier than methane, they are broken down into methane either before (prereformer) or within the reformer.

Typical conditions at the reformer outlet are 130 psi to 360 psi (900 kPa to 2500 kPa) and at 1560 °F (850 °C), but these conditions can vary by manufacturer.² Due to the severe operating conditions, the reactor is constructed of high alloy materials and heated externally by fuel firing.

After reforming, the syngas is cooled (via heat exchange or quench) and passed to the CO-shift reactor, where carbon monoxide is reacted with residual steam to increase the hydrogen production.

The gas is then cooled further, and the condensed water is removed in a separator after which the gas is fed into the final purification step. Purification is typically conducted in a multibed pressure swing adsorption (PSA) unit, yielding a high purity hydrogen product and a stream of impurities that is used as the main fuel in the reformer. The remainder of heat required in the SMR furnace is provided by make-up fuel.

As practical, the excess heat is recovered from both the syngas and the flue gas (combusted fuel and air) exiting the reformer. The primary method of heat recovery is boiling water to make steam, which is mixed with the feed and used in the reactions. This requires high purity water, which is generated in a water treatment system. Excess heat can also be used to preheat the feed stream, the mixed feed/steam stream, or the combustion air.

5.2 Methanol cracker

A methanol cracker plant produces hydrogen by the catalytic reforming and cracking of methanol and water vapor at elevated temperatures in a reactor heat exchanger. The methanol cracker process consists of three basic steps: feed mixing, reaction, and product purification. Like the SMR process, product purification is generally done by pressure swing adsorption (up to 99.999% product purity). Other methods of product purification besides pressure swing adsorption are possible but are not described in this publication.

Feed mixing is where high purity feed water is mixed with methanol liquid and pumped to high pressure, typically 260 psi to 290 psi (1800 kPa to 2000 kPa), at ambient temperature. Generally, there is no requirement for feed purification, as the methanol liquid does not contain any substances that would poison catalyst. Lower quality methanol could require some form of pretreatment or purification.

The mixed liquid feed is heated to approximately 500 °F to 536 °F (260 °C to 280 °C) and vaporized before entering the reactor, where the gas passes across a catalyst and a syngas stream (a mixture of hydrogen, carbon monoxide, carbon dioxide, and unreacted components) is produced.

² psi, bar, and kPa shall indicate gauge pressure unless otherwise noted as (psia; bar, abs; and kPa, abs) for absolute pressure or (psid; bar, dif; and kPa, dif) for differential pressure. All kPa values are rounded off per CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry* [8].

The conversion chemistry within the reactor is complex but can be represented by the following three reactions:

- methanol steam reforming ($\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{Heat} \leftrightarrow \text{CO}_2 + 3\text{H}_2$);
- methanol decomposition (cracking) ($\text{CH}_3\text{OH} \leftrightarrow \text{CO} + 2\text{H}_2$); and
- water gas shift ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$).

After reaction, the resulting syngas stream is cooled, and the condensed water is removed in a separator after which the gas is fed into the final purification step, typically a PSA adsorption system, to produce high purity hydrogen.

The heat required for the vaporization of the mixed liquid feed and the reforming reaction is provided by a fired heater. The fired heater is fueled by recovered waste gases from the PSA (PSA tail gas), with the remainder of heat required provided by make-up fuel, typically methanol or liquefied petroleum gas. As practical, the excess heat is recovered in the process. The primary methods of heat recovery from the fired heater are to either heat a circulating oil stream that provides the heat for the reactor, or to utilize the fired heater flue gases to provide the heat for the reactor directly. A block diagram representing the hot oil heated methanol cracking process is given in Figure 2.

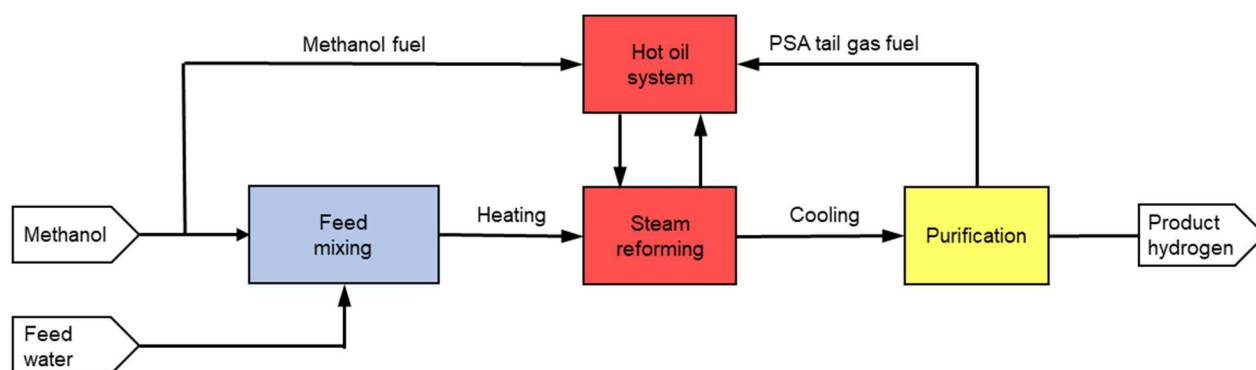


Figure 2—Hot oil heated methanol cracking process

5.3 Hydrogen production via electrolysis of water

A water electrolysis plant produces hydrogen (and oxygen) by the decomposition of water due to the passage of electric current. By passing an electric current between two metal surfaces (“electrodes”) separated by a diaphragm or a membrane, hydrogen gas is formed at the negative electrode (cathode) and oxygen at the positive electrode (anode).

Water electrolysis technologies can be classified according to the electrolyte, which is either added to the water to improve its conductivity or which separates the two half reactions at the anode and cathode of the electrolyzer. The most common water electrolysis technologies are alkaline water electrolysis, proton exchange membrane (PEM) (also known as polymer electrolyte membrane) water electrolysis, anion exchange membrane water electrolysis, and solid oxide electrolysis. Anion exchange membrane water electrolysis and solid oxide electrolysis, also known as high temperature electrolysis, are in the research and development phase and will not be discussed further.

Figure 3 illustrates alkaline water electrolysis and PEM water electrolysis cells and the reactions that occur in each. In alkaline water electrolysis process, an aqueous alkaline electrolyte (e.g., potassium hydroxide) solution is used, and a diaphragm separates the anode and the cathode. The overall reaction and the reactions that occur at the cathode and anode are as indicated in the figure. The name “alkaline water electrolysis” comes from the use of an alkaline electrolyte solution.

In PEM water electrolysis process, deionized water is used; and an ion exchange membrane separates the anode and the cathode. Although the overall electrolysis reaction is the same, the reactions at the cathode and anode differ from the reactions that occur at the electrodes in an alkaline water electrolyzer. The name proton exchange membrane or polymer electrolyte membrane comes from the use of a polymer membrane where protons (H^+) are exchanged from one side of the cell to the other.

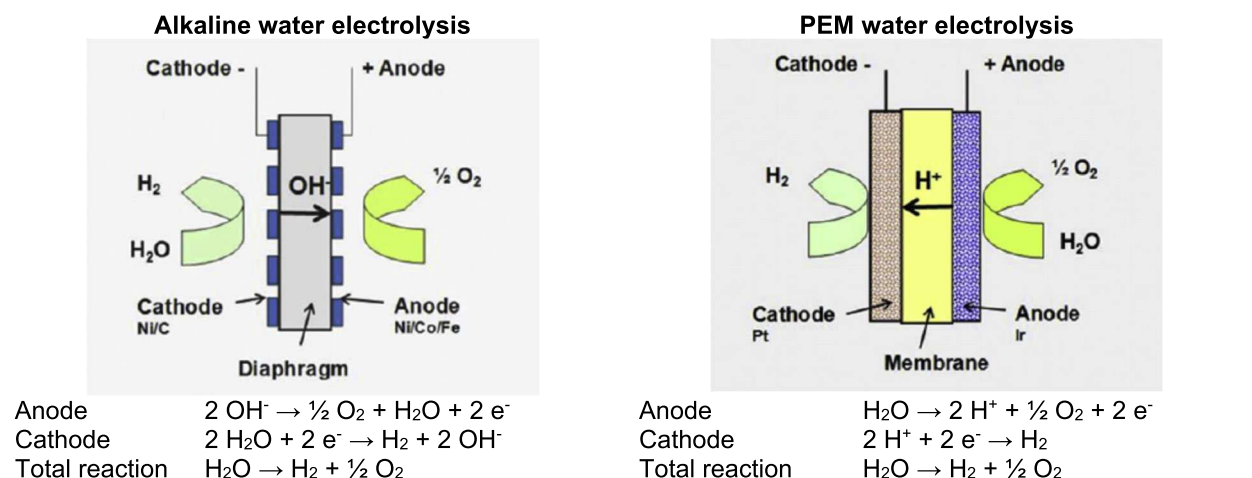


Figure 3—Schematic of the operating principle of an alkaline and PEM water electrolysis cell

5.3.1 Alkaline water electrolysis

As illustrated in Figure 4, there are eight basic units associated with the alkaline water electrolysis process: water purification; electrolyte supply; transformation of medium voltage to low voltage, conversion of alternating current to direct current in the rectifier; electrolysis; gas-liquid separation, deoxygenation, and drying of the product hydrogen.

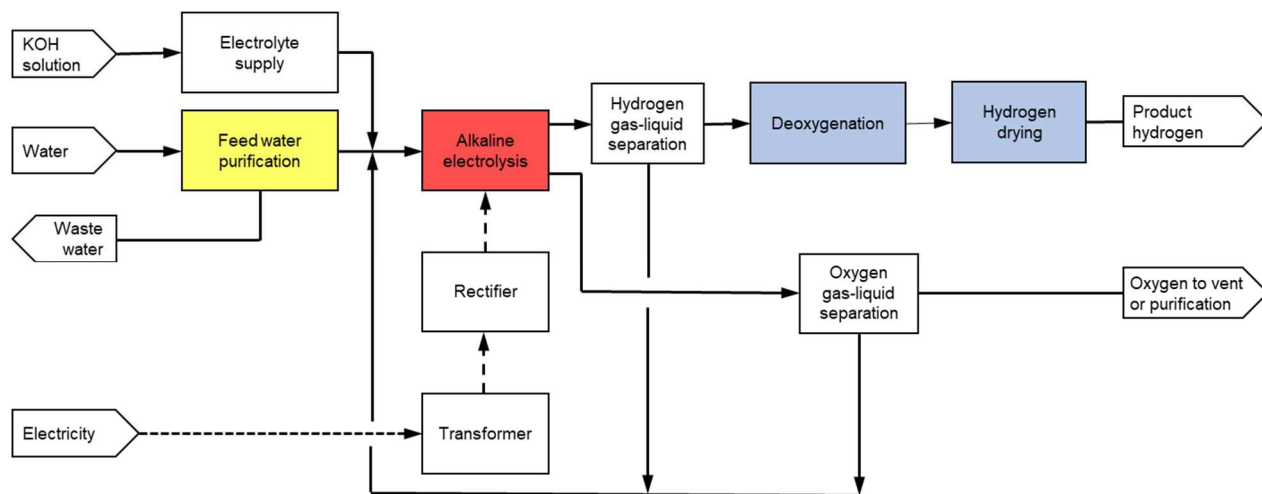


Figure 4—Block flow diagram of a typical alkaline water electrolysis system

The first step of the electrolysis process is feed water purification, because any impurities in the feed water will concentrate inside the electrolysis cells and can cause corrosion and surface deposits. After purification, the feed water is mixed with the electrolyte to improve water conductivity. Deionized water alone cannot be used for water electrolysis, as it is non-conductive. The electrolyte is used only to provide water conductivity; none of it is consumed during the electrolytic process.

Electrolysis of the water occurs in electrolytic cells. The electrodes are immersed in a liquid electrolyte separated by a diaphragm. Older alkaline water electrolyzers can contain asbestos as the diaphragm, but they are being replaced by non-asbestos materials and porous polymers. The electrolyte is usually a 20% to 40% aqueous potassium hydroxide solution. Direct current is passed between two metal surfaces (electrodes) through the water/electrolyte solution, producing hydrogen gas at the negative electrode (cathode) and oxygen at the positive electrode (anode).

Nickel based materials (for example, alloys with metals such as cobalt & iron, mixed metal oxides, etc.) are typically used as electrodes or electrode coatings in the alkaline water electrolysis process. The rate of formation of hydrogen and oxygen is directly proportional to the amount of direct current used. The direct current is generated in a rectifier, which converts alternating current to direct current. The electrolysis of water is performed under low voltage but high amperage. Cell operating voltage is typically 1.8 volts DC (VDC) to 2.4 volts VDC, while the current density is typically 0.2 amperes (A) cm^2 to 0.5 A cm^2 . Amperage will vary based on operating load and age of the cells. The maximum achievable current density of alkaline water electrolyzers is considerably lower than PEM water electrolyzers due to the high ohmic losses across the liquid electrolyte and the diaphragm. Cells are electrically connected in series to form a stack, and the stack operating voltage is proportional to the number of cells. 1400 A applied to 120 cells will produce approximately 70 Nm^3/h hydrogen. 1200 A will produce approximately 60 Nm^3/h . 1400 A and 240 VDC corresponds to about 0.34 MW of DC power.

The electrolyte solution is circulated for the removal of product gas bubbles and heat either by pumps or by natural circulation due to temperature/density gradients. Typically, the nominal operating temperature of alkaline water electrolyzers is between 140 °F to 195 °F (60 °C to 90 °C), and the gaseous hydrogen and oxygen products are water-saturated and carry a small amount of entrained liquid. Entrained liquid (electrolyte solution) is removed from the hydrogen in the hydrogen gas-liquid separator and from the oxygen in the oxygen gas-liquid separator. The resulting liquid streams typically are mixed before being recirculated to the cell stack for reuse. This is done to prevent dilution or concentration of electrolyte, which could occur since water is consumed on the cathode side and produced on the anode side.

The electrolyte solution from the two gas-liquid separators contains dissolved gases (hydrogen in the cathode side, oxygen in the anode side). When the two liquid streams are combined and recirculated to the cell stack (as shown in Figure 4), cross-contamination of the two gaseous constituents occurs. There is an alternate design where the two liquid streams are kept separate and crossfed to the opposite side of the cell. In both cases, the result is that the gas streams leaving the separators are contaminated, the product hydrogen containing a small amount of oxygen and the byproduct oxygen containing a small amount of hydrogen. In a third configuration, the hydrogen-containing electrolyte from the hydrogen separator is pumped back to the hydrogen side of the electrolyzer; and the oxygen-containing electrolyte from the oxygen separator is pumped back to the oxygen side of the electrolyzer. This minimizes cross-contamination, although contamination still occurs due to diffusion of gas from one side of the cell to the other across the diaphragm. To avoid hazardous contaminant concentrations, manufacturers limit turndown of the electrolyzer stack to between 10% to 40% of design load, and the system will shut down based on contaminant concentration.

After gas-liquid separation, any residual oxygen is removed from the raw hydrogen gas in a deoxidizer (sometimes referred to as a deoxo). A deoxidizer is a fixed-bed reactor in which the residual oxygen reacts with product hydrogen over a catalyst to form water.

The water formed in the deoxidizer is removed in the gas drying system. The first step in gas drying is to chill the vapor stream to condense and separate any liquid water formed. The second step is typically a temperature swing adsorption unit consisting of two or more beds of adsorbent. Gas flows through one or more beds, each of which is periodically regenerated by increasing the temperature of the bed to drive off the adsorbed water. The deoxidizer and dryer are designed to achieve the required level of oxygen and water impurities (typically less than 5 ppmv oxygen from the deoxidizer and less than 5 ppmv water from the dryer). Oxygen and water impurity levels are monitored at the outlet of the gas dryer. After drying, the hydrogen is sent to further purification if required and then into the product header or storage.

On older and many current units, the hydrogen product comes out of the electrolysis system at low pressure and, depending on use, probably requires compression. There are newer designs that operate at elevated pressure (up to approximately 500 psi [3450 kPa]). Additional compression can be required for product delivery, depending on final pressure required (e.g., pipe or cylinder). The compression may be located in a variety of places downstream of the deoxidizer or dryer.

5.3.2 Proton exchange membrane water electrolysis

Figure 5 is a block flow diagram of a PEM water electrolysis system. There are seven basic units associated with the PEM water electrolysis process: water purification; transformation of medium voltage to low voltage, conversion of alternating current to direct current in the rectifier; electrolysis; gas-liquid separation, deoxygenation, and drying of the product hydrogen. The main difference between the PEM water electrolysis

system and the alkaline water electrolysis system is that the solid polymer replaces the liquid alkaline electrolyte, so there is no electrolyte supply unit required.

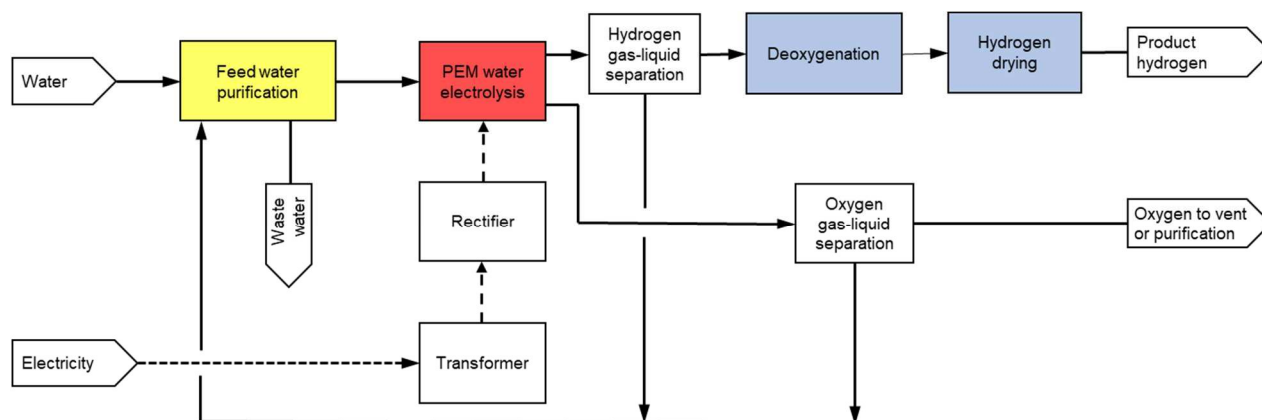


Figure 5—Block flow diagram of a typical PEM water electrolysis system

The first step of the PEM water electrolysis process is to purify the feed water by reverse osmosis, after which it is stored in a dedicated tank. This preliminary step is necessary to remove any contaminants and ions from the water before feeding the process with this ASTM type II deionized water. Any impurities in the feed water will concentrate inside the electrolysis cells and cause corrosion and surface deposits.

As with alkaline electrolysis, electrolysis of the water occurs in electrolytic cells. A proton exchange membrane (polymer electrolyte membrane) separates the two cell halves, and the electrodes are usually directly mounted on the membrane, forming the membrane electrode assembly. Direct current is passed between two metal surfaces (electrodes), producing hydrogen gas at the negative electrode (cathode) and oxygen at the positive electrode (anode). The corrosive acidic regime provided by the proton exchange membrane requires the use of noble metal catalyst coatings on the electrodes. Typically, the anode is coated with a catalytic layer of iridium and the cathode is coated with a catalytic layer of platinum.

The pressure in a PEM water electrolysis unit can be higher than in an alkaline electrolysis unit. The hydrogen gas production section can reach pressure up to 500 psi (3500 kPa) in industrial applications without external gas compression.

Depending on the size of the hydrogen production unit, the input voltage can be single-phase or three-phase power, low voltage (400 V) or medium voltage (10 kV to 30 kV), and 50 Hz or 60 Hz. The rectifier converts incoming alternating current to direct current. The electrolysis of water is performed under low voltage but high amperage. The electric current applied to the stack directly corresponds to the flow rate of hydrogen and oxygen produced. PEM water electrolysis cell operating voltage is typically 1.8 VDC to 2.2 VDC. In comparison to alkaline water electrolyzers, PEM water electrolysis systems can operate at much higher current densities. At the time of this publication, most commercial PEM water electrolysis system available on the market operated in the 1 A cm⁻² to 3 A cm⁻² range.

Cells are electrically connected in series to form a stack, and the stack operating voltage is proportional to the number of cells. For example, a PEM water electrolysis system designed to produce 400 Nm³/h hydrogen consisting of 320 cells in a single stack with a cell area of 1000 cm² per each electrolysis cell will operate at about 640 VDC at approximately 3000 A corresponding to about 2 MW of input power.

A circulation pump feeds water to the anodic side of the cell stack. This water removes heat from the electrolysis cell stack and maintains the stack temperature and liquid level. Part of the deionized water is oxidized into gaseous oxygen at the anodic side of the cell stack, resulting in a gas-liquid mixture (oxygen and water) at the outlet of the stack. Due to the effect of the electric field, protons (hydrogen ions) generated at the anodic side of the cell stack migrate across the PEM to the cathodic side where they combine with electrons from the external circuit to form hydrogen gas. Due to the electro-osmotic effect, water from the anodic side of the cell stack passes through the membrane to the cathodic side resulting in a gas-liquid mixture (hydrogen and water) at the outlet of the cathodic side of the stack. The anodic half of the cell runs at a lower pressure than the cathodic half of the

cell. The resulting differential pressure between the anodic and cathodic cell halves is a driving force for hydrogen permeation across the membrane. In addition to the permeation of the hydrogen, water and dissolved oxygen and hydrogen can be transported through the membrane by convection from the anode to the cathode due to the electrolysis' proton flux, a phenomenon commonly referred to as electro-osmotic drag. Electro-osmotic drag varies with the chemistry of the PEM material and is important since it impacts water management of a PEM water electrolysis system.

With this cross-permeation, hydrogen and oxygen produced at both sides of the electrode permeate through the membrane and then mix in the respective counter electrode compartment. This results in cross-contamination of the oxygen and hydrogen.

Typically, the nominal operating temperature of PEM water electrolyzer systems between 120 °F and 180 °F (50 °C and 80 °C), and the gaseous hydrogen and oxygen products are water-saturated and carry a small amount of entrained liquid. Entrained water is removed from the hydrogen in the hydrogen gas-liquid separator, and from the oxygen in the oxygen gas-liquid separator. The resulting liquid water streams are mixed before being recirculated to the feed water purification unit for reuse in the cell stack. To avoid hazardous contaminant concentrations, manufacturers typically limit turndown to between 5% to 40% of design load.

The water from the two gas-liquid separators contains dissolved gases (hydrogen in the cathode side, oxygen in the anode side). When the two water streams are combined and recirculated to the anodic side of the electrolyzer cell, and from there through the membrane to the cathodic side of the cell, cross-contamination of the two gaseous constituents occurs. This is in addition to the cross-permeation discussed above. Therefore, the gas streams leaving the separators are contaminated, the product hydrogen containing a small amount of oxygen and the byproduct oxygen containing a small amount of hydrogen.

After gas-liquid separation, any residual oxygen is removed from the raw hydrogen gas in a deoxidizer. A deoxidizer is a fixed-bed reactor in which the residual oxygen reacts with product hydrogen over a catalyst to form water.

The water formed in the deoxidizer is removed in the gas drying system. The first step in gas drying is to chill the vapor stream to condense and separate any liquid water formed. The second step is typically a temperature swing adsorption unit consisting of two or more beds of adsorbent. Gas flows through one or more beds, each of which is periodically regenerated by increasing the temperature of the bed to drive off the adsorbed water. The deoxidizer and dryer are designed to achieve the required level of oxygen and water impurities (typically less than 5 ppmv oxygen from the deoxidizer and less than 5 ppmv water from the dryer). Oxygen and water impurity levels are monitored at the outlet of the gas dryer. After drying, the hydrogen is sent to further purification if required and then into the product header or storage. If necessary, the hydrogen product may be compressed.

6 Process-specific safety considerations

This section addresses safety considerations associated with thermal and electrolytic hydrogen production processes. Thermal-based hydrogen production plants operate at high temperature and elevated pressure, utilize flammable feedstock, and produce flammable and/or toxic products. Any flanged or threaded connection is a potential leak point (often of flammable, toxic, or high temperature fluid), and most of the piping in the plant operates at elevated temperature. These risks are particularly acute in a reformer in an SMR-based hydrogen production plant, since it operates at the highest temperature and often has multiple flanged connections that are potential flammable/toxic leak points. Most thermal-based hydrogen production plants require pumps and/or compressors to pressurize feed (hydrocarbon or water) or product streams, and any rotating machinery in the plant presents potential risks of pressure, temperature, and moving parts; and some equipment could require high voltage to operate. This means that most areas of the plant present a risk of personnel exposure to hazards. In addition, since small plants can be located within a building or enclosure, the impact of any process leak is elevated.

An electrolytic hydrogen production unit uses low voltage, high current electricity to drive the disassociation of water. This type of electric current production and transmission presents unique safety hazards not found in typical thermal-based hydrogen production plants. Electrolytic hydrogen production units also produce a pure oxygen byproduct stream, which creates additional hazards that do not exist in a thermal-based hydrogen production unit, and the electrolyte solution is highly corrosive. Other hazards of the process, such as noise, pressure, and high temperature, are similar to those of thermal-based hydrogen production units.

Periodic maintenance of any operating plant is required, which could require working at heights, lifting, confined space entry, or other task-specific hazard. Because of all these factors, awareness of and adherence to safety guidelines is necessary to ensure an injury-free workplace.

6.1 Product and reagent hazards

All personnel should have proper hazard awareness, including familiarity with safety data sheets (SDS) for hydrogen, feedstock, fuel, electrolyte, oxygen, and water treatment chemicals present in the plant. A thermal-based hydrogen production plant typically utilizes a variety of light hydrocarbon gases or liquids as feedstock. These colorless gases or liquids can be flammable and/or toxic. In addition, the catalysts and other materials (e.g., water treatment chemicals, lubricating oil) used in the plant are potentially hazardous. Hydrogen production based on electrolysis can use a corrosive liquid for electrolytes (alkaline process) and produces hydrogen and oxygen gas. The dual production of hydrogen and oxygen presents a reactivity hazard. Key properties (e.g., LFL and toxicity) of some of the more common chemicals found in hydrogen production units (primarily feedstock and products) are summarized in CGA H-14 [4].

6.1.1 Flammability

The hydrocarbon feed/fuel (gaseous or liquid), syngas intermediate, and PSA tail gas from the reforming process are flammable. The hydrogen product from the electrolysis and reforming processes is also flammable. Hydrogen is colorless and odorless and burns with an invisible flame in daylight. Carbon monoxide is similarly colorless and odorless with a pale blue flame.

Hydrogen is one of the lightest substances known and has a specific gravity of 0.069 (at 68 °F [20°C]). Relatively large quantities of hydrogen can flow through a small leak or opening and will diffuse rapidly into the air. Because the specific gravity is less than 1.0, hydrogen in air will rise. Carbon monoxide has a specific gravity near one and will not readily disperse in air.

Depending on the concentration of a flammable gas in air, the vapor cloud can ignite (defined by the gas UFL and LFL). Gases with a low threshold of ignition energy (e.g., hydrogen) can ignite due to static sparks generated by flow friction, which is exacerbated by flow velocity. Vapor clouds ignited in an open area typically burn as a deflagration. However, if the vapor cloud is confined or is in a congested area, the deflagration can transition to detonation.

A portable personal gas monitor with appropriate sensors should be worn in all hydrogen production units. In a thermal-based plant, these sensors should include carbon monoxide, %LFL, %oxygen, and, if required, hydrogen sulfide. In an electrolysis-based plant, these sensors should include %LFL and %oxygen. Fixed monitors may also be used to provide early warning or interlock action. Because small hydrogen plants can be sited within a building or enclosure, the risk of accumulation of flammable gas from a flammable gas leak is elevated. When located in a building or enclosure, appropriate monitoring, alarms, and signage shall be present to detect, alarm, and warn against a potential hazardous atmosphere.

6.1.2 Toxicity

Carbon monoxide and hydrogen sulfide are the two most common toxic substances in SMR hydrogen production plants. Carbon monoxide is produced in the reforming and combustion processes. The syngas produced in the reformer, tail gas from the PSA, and the flue gas all contain carbon monoxide. Hydrogen sulfide can be present in the feed or produced in the feed purification step in SMR plants. Sulfur-based odorants and other toxic substances can be present in the feed.

Carbon monoxide and hydrogen sulfide are both flammable and toxic. When a gas is both toxic and flammable, the toxicity often dictates the severity of the hazard and the behavior requirement in response to a leak. In the case of hydrogen sulfide, odor is one means of detection, but it cannot be relied upon (see CGA H-14 for more information) [4].

In a methanol cracker plant, carbon monoxide (from the reforming process) and methanol are the two most common toxic substances. Methanol is a colorless, volatile flammable liquid, which is miscible with water to any ratio. Methanol vapor is slightly heavier than air and can form explosive gas mixtures. There is a severe danger of poisoning if ingested or inhaled. Skin contact should be avoided.

In terms of relative toxicity, hydrogen sulfide is most toxic, carbon monoxide is next in toxicity, and methanol is third. OSHA's permissible exposure limit (PEL) for hydrogen sulfide is 10 ppm, for carbon monoxide it is 50 ppm, and for methanol it is 200 ppm [2].

In areas where a toxic release or leaks are possible, portable gas monitors with appropriate sensors (carbon monoxide, %LFL, %oxygen, hydrogen sulfide, methanol) should be used. Carbon monoxide monitors should be equipped with hydrogen null sensors to prevent hydrogen cross sensitivity, which is where hydrogen is misidentified as carbon monoxide exposure and results in a false positive carbon monoxide alarm. Fixed monitors may also be used to provide early warning or interlock action. In case of leakage to atmosphere, the operator can be affected. Because small hydrogen plants can be sited within a building or enclosure, the risk of accumulation of toxic gas from a toxic gas leak is elevated. Inadequate purging prior to maintenance can also lead to an elevated risk of exposure. When located in a building or enclosure, appropriate monitoring, alarms, and signage shall be present to detect, alarm, and warn against a potential hazardous atmosphere.

If a vented gas contains a toxic constituent (e.g., carbon monoxide), the vent is located such that after dispersion, PEL are not exceeded where personnel are likely to be present. Dispersed concentration of all vented constituents at ground level should be evaluated. Downdrafts caused by neighboring structures and density variation due to cryogenic liquid vaporization shall be taken into account. If both carbon monoxide and hydrogen are in the vented gas, sensors with cross-sensitivity to hydrogen can be an issue.

6.1.3 Reactivity

The oxygen produced in the electrolysis process is of high purity and creates potential safety issues due to its reactivity. Although oxygen is nonflammable, materials that burn in air will burn much more vigorously and at higher temperatures in oxygen. Some combustible materials such as oil burn in oxygen with near explosive violence if ignited. Concentrated sources of oxygen promote rapid combustion and, therefore, are fire and explosion hazards in the presence of fuels.

Pure gaseous oxygen is colorless and odorless, making leaks difficult to notice. The higher the oxygen concentration in the atmosphere, the greater the hazard and the more likely it is to create an explosive mixture or for objects in the area to catch fire. Oxygen will not readily disperse at ambient temperature because it has a specific gravity near 1.0. In many electrolysis installations, the oxygen is vented to the atmosphere. This vent shall be located such that it accounts for the stream's poor dispersion (conditions are near ambient), is not close to a flammable gas vent, and is not close to a ventilation or combustion air intake.

An important safeguard when dealing with oxygen is to remove all combustible or spark-generating contaminants by thoroughly cleaning all pipe work, vessels and storage tanks before oxygen is produced or introduced.

Never allow hydrogen and oxygen to create an explosive mixture (either in the pipe work or in the atmosphere). As mentioned previously, hydrogen and oxygen produced in the cathode and the anode will permeate through the membrane and then mix in the respective counter electrode compartment, resulting in cross-contamination of the oxygen and hydrogen. These impurity concentrations increase as the applied current or load decreases. Instrumentation is required in the gas piping systems leaving the cells to detect oxygen in hydrogen (in the hydrogen product) and hydrogen in oxygen (in the oxygen byproduct). The unit shall shut down by interlock in the event that an unsafe composition is detected in either gas stream. Another safeguard is that the unit turndown is limited, typically to no more than 10% to 40% of design, to avoid hazardous concentrations. The minimum safe operating load is higher in a pressurized alkaline unit because the liquid can contain more dissolved gases as the pressure increases.

See ISO 22734, *Hydrogen generators using water electrolysis — Industrial, commercial, and residential applications*, and NFPA 67, *Guide on Explosion Protection for Gaseous Mixtures in Pipe Systems*, for more information on safety and design requirements of electrolyzers and associated piping systems [9, 10].

6.1.4 Asphyxiation/anoxia

Asphyxiation can occur in any confined area or insufficiently ventilated location where nitrogen or other asphyxiant can be present. Hydrogen and nitrogen are nontoxic but do not support life. High hydrogen or nitrogen concentration in the surrounding atmosphere will create an oxygen deficiency. Danger begins when oxygen content is less than 19.5% in the air (normal content being 21% by mole or volume). Depending on the degree