GUIDELINE FOR SMALL SCALE HYDROGEN PRODUCTION

AIGA 125/23

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Preface

As part of a program of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has issued this publication AIGA 125, *Guidelines for Small Scale Hydrogen Plants,* jointly produced by members of the International Harmonisation Council and originally published by the Compressed Gas Association (CGA), CGA H-17, *Guideline for Small Scale Hydrogen Production and Deliveries.*

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 Nm^3/hr to 10 000 Nm^3/hr; 40 MSCFD to 9000 MSCFD; or 1070 Nm^3D to 241 000 Nm^3D).

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 m^3) 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);

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[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.

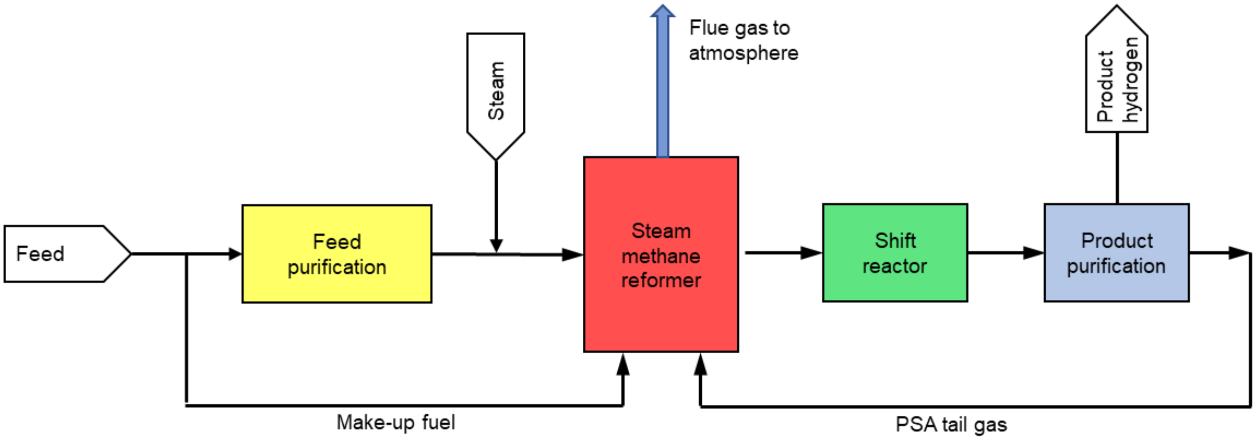

Figure 1—Steam methane reforming process with PSA purification

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 ($CH_4 + H_2O + \text{Heat} \leftrightarrow CO + 3H_2$); and
- water gas shift ($CO + H_2O \leftrightarrow CO_2 + H_2$).

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.

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[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 ($CH_3OH + H_2O + Heat \leftrightarrow CO_2 + 3H_2$);
- methanol decomposition (cracking) ($CH_3OH \leftrightarrow CO + 2H_2$); and
- water gas shift ($CO + H_2O \leftrightarrow CO_2 + H_2$).

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.

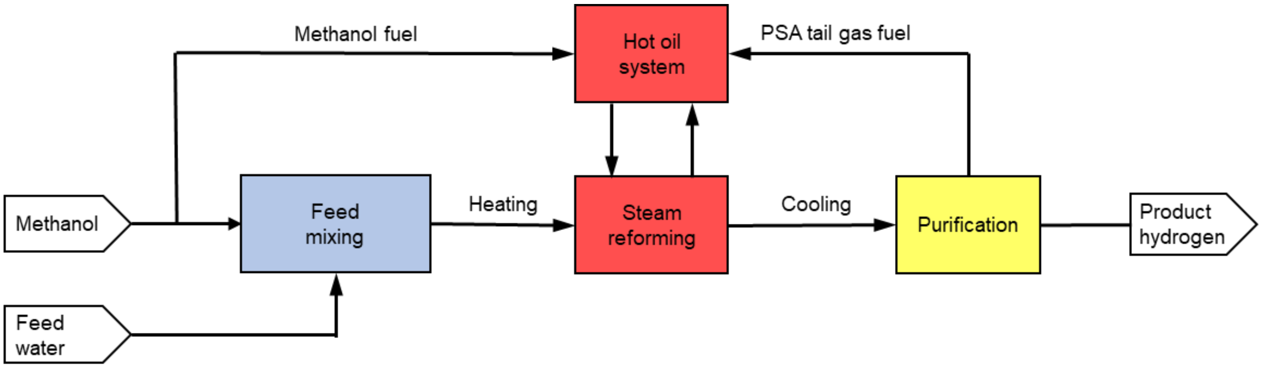


Figure 2—Hot oil heated methanol cracking process

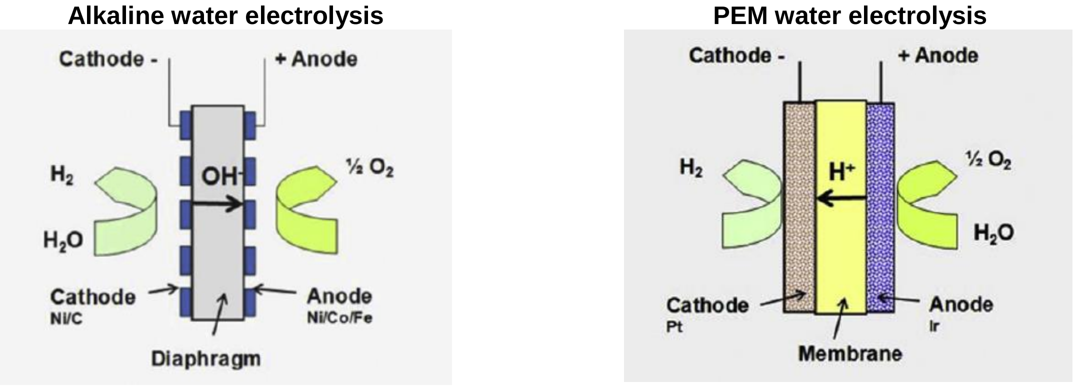
5.3 Hydrogen production via electrolysis of water

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.



Anode	$2\ OH^- \rightarrow ½\ O_2 + H_2O + 2\ e^-$	Anode	$H_2O \rightarrow 2\ H^+ + ½\ O_2 + 2\ e^-$
Cathode	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$	Cathode	$2\ H^+ + 2\ e^- \rightarrow H_2$
Total reaction	$H_2O \rightarrow H_2 + ½\ O_2$	Total reaction	$H_2O \rightarrow H_2 + ½\ O_2$

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.

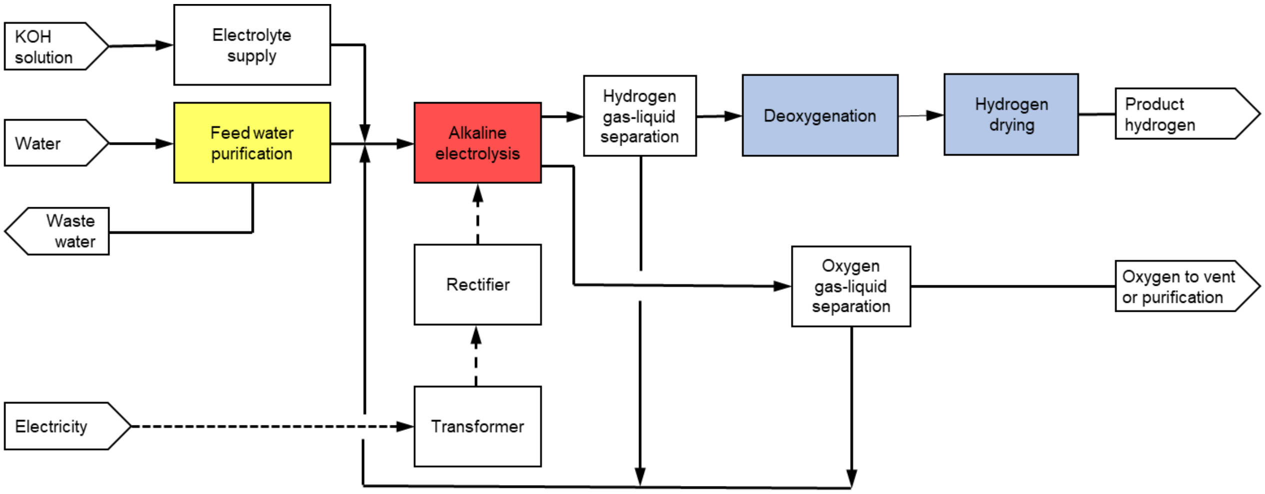


Figure 4—Block flow diagram of a typical alkaline water electrolysis system

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.

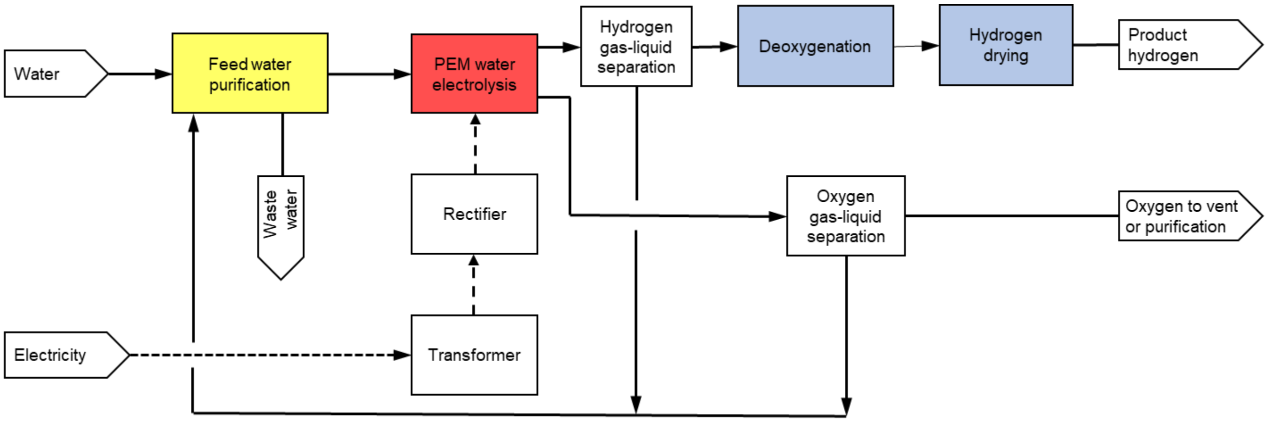


Figure 5—Block flow diagram of a typical PEM water electrolysis system

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 Nm^3/h hydrogen consisting of 320 cells in a single stack with a cell area of 1000 cm^2 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 of oxygen deficiency, its effects on humans can vary from physiological changes to actual illness or even to death. See CGA P-76, *Hazards of Oxygen-Deficient Atmospheres* [11].

An oxygen deficient atmosphere can occur if large amounts of nitrogen are used during purging and then vented into the work area. An oxygen deficient atmosphere cannot readily be detected by the senses. Victims are usually unaware of the danger and can even have a feeling of wellbeing. A person working in an area where the air has become enriched with nitrogen or other inert gases can become unconscious without sensing the lack of oxygen.

The risk of asphyxiation can be elevated in a small hydrogen plant, because they can be sited within a building or enclosure. 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.

The risk of asphyxiation is also elevated in congested areas where nitrogen can leak and accumulate and where access/egress is limited (e.g., high concentration of flanged piping where operators could be present). Fixed or portable %oxygen monitors shall be used to detect this condition and warn personnel.

6.1.5 Alkaline electrolyte corrosivity

Potassium hydroxide is normally used as the electrolyte in alkaline water electrolyzers. Potassium hydroxide solution (about 30% concentration in deionized water) is a strong caustic that is prepared either by diluting a higher strength solution or by dissolving a solid form of potassium hydroxide in water. When an aqueous solution is being prepared, an exothermic reaction takes place. Due to the presence of potassium hydroxide, the pH values of the gases (due to entrainment) and liquids inside the electrolyzer lines, water locks and drains can rise to pH14 even under normal operating conditions. The impact of high pH shall be managed during maintenance and normal operation to maintain safety and to prevent exceeding wastewater permit limits.

Potassium hydroxide is one of the strongest alkalis known. Improper handling of potassium hydroxide is very dangerous because it reacts quickly with moisture to produce heat and to dissolve all types of body tissues. The risk is elevated in the electrolysis process by the nominal operating temperature 140 °F to 195 °F (50 °C to 90°C) and potentially elevated operating pressure.

While potassium hydroxide is not as dangerous in solid form as it is in liquid form, either form of potassium hydroxide in contact with moisture in the skin will result in chemicals burns. The burns happen slowly and are not noticed at first, but these burns are very penetrating.

Important safeguards regarding potassium hydroxide include:

- Wear the correct PPE including footwear, rubber gauntlets, eye protection (goggles and/or face shield), rubber aprons, and heavy clothing;
- Wear long sleeved shirts and long trousers. Potassium hydroxide is very dense and splashes further than other liquids. Therefore, spills that hit the ground tend to spray on bare legs or arms;
- Wash hands and face thoroughly after handling a potassium hydroxide solution;
- Avoid inhalation; and
- Safety shower and eyewash station should be readily accessible. The SDS should be consulted to determine if additional safeguards are required.

6.2 Burn exposure

The human body faces a burn hazard if it is in direct contact with surface temperatures higher than 140 °F (60 °C). Any thermal-based hydrogen production plant or electrolysis plant will contain hot surfaces. Insulation shall be provided to protect personnel from exposure per company standards. Where insulation cannot be applied, barriers or other means of protection shall be provided.

An operator also faces a burn hazard if exposed to leaks of high temperature fluids from the process. The risk is particularly acute in a thermal-based hydrogen production plant because hydrogen burns with an invisible flame during daylight, and superheated steam (steam greater than its boiling point) is invisible.

The operator shall wear heat resistant gloves and flame-retardant clothing with long sleeves when working around high temperature equipment to prevent burns in case of accidental contact. For certain tasks, thermal protection for the face could be required (see CGA H-10) [5].

6.3 Pressurized gas and liquid hazards

Parts of both electrolysis and thermal production plants operate at elevated pressure. High pressure gas contains huge amounts of potential energy that is trapped within equipment and/or piping. If the equipment and/or piping ruptures or leaks, the energy is quickly released and can result in significant damage to plant, equipment, and people. There is also a risk of injury when a person comes into contact with high velocity gas.

High pressure liquid also contains a high level of potential energy trapped within equipment or piping. This applies to the methanol water mixture in methanol crackers and to the boiler feed water/makeup water in SMR plants. There can be other high pressure liquid streams in these plants, as well. The caustic electrolyte solution in pressurized alkaline electrolysis units presents a spraying corrosive liquid hazard in addition to the potential energy hazard.

6.4 Electrical hazards

The incoming power supply to the plant from the local utility could be at 4160 volts AC (VAC) or higher. Associated equipment such as switch gear and transformers are used to distribute this power to equipment within the facility.

Thermal-based hydrogen production plants use high voltage equipment. Motors in these plants are typically 480 VAC and can be 4160 VAC. Water electrolysis plants use a high current electrical power supply to provide power to the cells. This power supply consists of an AC to DC rectifier. The rectifier output typically ranges from 100 VDC to 600 VDC and supplies current to a single cell stack at up to 4000 A or more. An electrolyzer unit with multiple cell stacks would require current that can exceed 20 000 A (depending on the production capacity).

These power sources are potentially dangerous and can cause severe electric shock to anyone who comes into contact with them. Equipment operating at these voltages and currents requires maintenance to be performed by qualified personnel following proper procedures. This type of equipment can produce arcing in the event of a short circuit. This can expose personnel to shock or arc flash injury (e.g., burns, nerve damage, blindness, hearing loss, and cardiac arrest). Fatal burns can occur when the victim is several feet from the arc. An arc flash study provides information on the level of PPE required to work on electrical equipment and power systems. The high current density in the rectifier produces a large electromagnetic field which can damage electronic devices (e.g., a pacemaker) or damage magnetic storage media (e.g., credit card data strip).

The electrolysis cell stack holds a considerable residual voltage after shutdown such that the danger of electric shock persists. Care shall be taken when performing maintenance on the cell stack. Always check for residual voltage using a voltage tester.

Electrical equipment can cause sources of ignition either by sparks from shorts in electrical connections or from static electricity. All equipment shall be adequately earthed or grounded so that a source of ignition is not available.

Electrical equipment that exists in a location where flammable process materials could be present shall comply with the requirements of NFPA 70®, *National Electric Code®*, Article 500 (Hazardous Locations) [12]. This article covers the requirement for classification of hazardous locations and the resulting mitigations to prevent the ignition of flammable materials by the electrical equipment that is present.

Electrical equipment that is installed in such classified locations shall be specially designed and tested to ensure it does not initiate an explosion due to arcing contacts or high surface temperature of equipment. Hazardous locations are classified based on class (material present: gases, dust, fibers), division (probability of material quantity being sufficient for ignition or explosion), and Groups (flammability and ignitability). For example, Class 1, Division 2, Group B is the classification for areas that could contain hydrogen in the event of an upset. Class 1, Division 1, Group B is the classification for areas that will contain hydrogen. Electrical equipment installed in a classified location (including instruments) shall be rated for the specific classification.

6.5 Combustion safety

Combustion is necessary for thermal-based hydrogen production. Oxygen (air), fuel, and an ignition source are required for combustion to occur. Combustion reactions involving fuel and oxygen take place according to stoichiometric combustion principles. Complete combustion occurs when all of the fuel is burned. Air is the source of oxygen (21% by mole or volume). Thermal hydrogen production units operate with excess oxygen in the flue gas leaving the reformer firebox to ensure complete combustion.

Basic combustion hazards (including flame instability, flame lift off, back burning, after burning, and exposure to hot gases) and the critical process safety controls and interlocks for a SMR are described in detail in CGA H-10 [5]. Some of these controls and interlocks also apply to the fired heater in a methanol cracker. The combustion hazards shall be controlled by a burner management system (BMS).

6.6 Hazards of thermal production units co-located with liquid fuel dispensing equipment

In addition to a hydrogen production unit being a hazardous location, as defined in NFPA 70, due to the potential presence of flammable gases in the atmosphere (i.e., due to leaks), a thermal hydrogen production unit itself is a source of ignition [12]. The flue gas/fuel side of the furnace or fired heater will have air intakes and one or more burners where air and fuel are combusted to generate heat. Flammable liquid or vapor ingress shall be prevented to avoid serious safety consequences.

When co-locating a thermal hydrogen production unit next to a liquid fuel dispensing facility (e.g., a gas station), the risks associated with nearby sources of liquid flammables shall be considered. If a liquid spill can occur in sufficient quantity such that the liquid can migrate into the thermal hydrogen production unit, ignition of the liquid (liquid pool fire) could cause overheating, weakening, and subsequent rupture of the hydrogen process equipment, causing injury or further damage due to the resulting overpressure wave. When this equipment is co-located with a liquid fuel dispensing facility, a pool fire migrating from the liquid fuel dispensing facility shall be considered during the hazard analysis for the hydrogen production unit. Air intake vents can be raised to mitigate the hazard of liquid fuel vapor intake, but this could impact the location of any flammable gas vents.

If a liquid pool fire were to occur in the liquid fuel dispensing facility, the first action required is to shut down the operation of the hydrogen production unit, either automatically or manually. Once the production unit is shut down and secured, additional plant emergency protection systems may be used during a liquid pool fire to prevent the fire from causing further damage to equipment or injury to personnel within the plant or third parties.

6.7 Hazards of bulk storage of gases or liquids co-located with liquid fuel dispensing equipment

When co-locating a hydrogen bulk storage facility next to a liquid fuel dispensing facility (e.g., a gas station), the risks associated with nearby sources of liquid flammables shall be considered. If a liquid spill can occur in sufficient quantity such that the liquid can migrate into the bulk storage facility, ignition of the liquid (liquid pool fire) could cause overheating, weakening, and subsequent rupture of the storage equipment, causing injury or further damage due to the resulting overpressure wave. When this equipment is co-located with a liquid fuel dispensing facility, a pool fire migrating from the liquid fuel dispensing facility shall be considered during the hazard analysis for the bulk storage facility.

When ultra-high pressure storage is used for a hydrogen fueling application, the likelihood of ignition in the event of a high-pressure hydrogen leak is high. Hydrogen has a low ignition energy, and hydrogen leaks can easily ignite due to static sparks generated by flow friction. This shall be taken into account when determining the risks associated with co-locating the storage facility near a liquid fuel dispensing facility and when selecting the emergency protection systems required for such co-location.

If a liquid pool fire were to occur in the liquid fuel dispensing facility, the first action required is to shut down the operation of the hydrogen storage and dispensing facility, either automatically or manually. Once the unit is shut down and secured, additional plant emergency protection systems may be used during a liquid pool fire to prevent the fire from causing further damage to equipment or injury to personnel within the plant or third parties.

6.8 Additional material hazards

In addition to feeds and products, other substances used or produced in the hydrogen production process can create safety hazards, and appropriate precautions shall be taken. When developing a safety plan associated with material handling, the relevant SDSs shall be consulted and required PPE shall be specified.

6.8.1 Water treatment chemicals

Water treatment chemicals are often acids or bases. Water treatment chemicals are used to mitigate against fouling, scaling, and corrosion in process equipment and piping. In plants with cooling towers and boilers, there can be both cooling water chemicals and boiler feedwater chemicals. Boiler feedwater chemicals differ from cooling water chemicals because of the higher temperature and pressure at which the boiler equipment operates.

Personnel working with water treatment chemicals shall familiarize themselves with the safety guidance provided by the associated SDS documents. They shall wear the PPE prescribed in 4.2. In addition, goggles, face shield, and chemical resistant gloves typically are required; and additional PPE could be required based on the guidance in the SDS documents. Because water treatment chemicals typically are acids and bases, they are corrosive to some extent. See 6.1.5 for details on a special water-based solution used in alkaline electrolysis.

The primary first aid remedy, if human skin comes into contact with these chemicals, is flushing the affected area with clean water. Therefore, a safety shower and eyewash station shall be available near the area where these chemicals are handled.

6.8.2 Catalysts and adsorbents

Catalysts, chemisorbents, and adsorbents are required in thermal-based hydrogen plants. These materials can require periodic replacement, and it is during this replacement activity that operators can come into contact with the materials. It is also during replacement that the catalyst can come into contact with air, which creates a risk of overheating and potential fire with self-heating catalysts. Adsorbents exposed to atmosphere can degas any adsorbed constituents (e.g., hydrogen sulfide, carbon monoxide), and the dust from many catalysts is toxic if inhaled (e.g., catalyst dust of nickel-containing catalysts) or can cause damage to organs through prolonged or repeated exposure. In addition, hazardous components (e.g., nickel carbonyl and iron carbonyl) can form over the catalyst if the process is not purged properly during shutdown. Catalysts can also have environmental impacts with long-lasting effects. All of these hazards associated with catalyst handling are covered in CGA H-15, *Safe Catalyst Handling in HYCO Plants* [13]. Note that CGA H-15 was written for large SMR plants, and the catalysts used in small plants can differ [13].

7 Guidance on the siting of small scale units

There are two aspects to risk analysis, consequences within the unit and resulting effects on neighboring facilities. Individuals working within the operating unit are trained on the risks inherent to the unit, while individuals working in neighboring facilities might not be aware of the risks. This is particularly true if the neighboring facility is nonindustrial or a public space. Both types of risks, those contained within the unit and those affecting neighboring facilities, shall be evaluated and addressed. The risk analysis shall consider the risks of overpressure, toxicity, and fire (e.g., jet fire). At a minimum, a consequence analysis shall be performed. These analyses require specialized knowledge of vapor cloud explosion overpressure effects and therefore can require a qualified individual to develop.

7.1 General siting considerations

Current codes and standards primarily address how to prevent the propagation of fire from one section to another within a facility (for example, by providing physical distance between process units). Adding process units which contain a reactive gas like hydrogen presents a risk of vapor cloud ignition, which under certain conditions can transition to detonation. Typical code-specified distances between process units do not account for the additional potential for overpressure resulting from hydrogen ignition in a congested area. Additionally, the production of hydrogen often produces carbon monoxide as a byproduct.

Prevention of ignition is one of the primary means to mitigate the risk of fire. Compliance with the mandatory requirements for area classification in NFPA 70, Article 500 and its referenced documents provide methods to control the exposure of flammable materials to ignition sources [12]. Small production units such as a reformer or electrolysis unit contain multiple ignition sources that trigger the requirements for area classification. The owner shall perform the required preventative maintenance on equipment to maintain adherence to electrical classification guidelines.

Siting risks of small production units are exacerbated if there are bulk storage containers co-located as a back-up supply. These may be in the form of high-pressure gaseous storage (2500 psi to 15 000 psi [17 200 kPa to 103 000 kPa]) or cryogenic liquid storage in a vacuum insulated tank. In the event of a leak, high pressure can increase the length of a jet fire. Cryogenic liquid greatly increases the stored volume in a location, and cold vaporized gas behaves quite differently in a leak scenario. At a minimum, separation distances approved by the authority having jurisdiction (AHJ) shall be established and maintained. If there is an associated ambient vaporizer or an array of vaporizers, the congestion density of the vaporizer and the flame propagation from one to the next shall be accounted for in the overpressure model.

NFPA 2, *Hydrogen Technologies Code,* addresses the separation of hazards related to hydrogen [14]. Separation may take the form of physical distance or the presence of a barrier such as a wall or enclosure. CGA H-5, *Standard for Bulk Hydrogen Supply Systems (an American National Standard)*, provides additional detail for gas and liquid hydrogen supply systems provided by the industrial gas industry [15]. The separation distances specified in these documents are the minimum requirements for the prevention of fire propagation. A hazard analysis process shall be used with appropriate overlapping scenarios when small scale hydrogen facilities are located in and around other industrial or commercial facilities to determine if these distances are sufficient to mitigate an overpressure event.

Small production units typically do not contain enough volume of gas to bring them under the OSHA PSM [2], although the presence of a cryogenic liquid storage unit for backup could result in sufficient material on-site to trigger the threshold for PSM. Even if the volume of material is such that PSM does not apply, the risks are serious enough that they should be managed in a holistic and systematic approach to ensure the integrity of the operating facility. As noted in 4.1, CGA P-86 introduces a framework that can be adopted to manage process safety risks [1]. CGA P-28, *OSHA Process Safety Management, and EPA Risk Management Plan Guidance Document for Bulk Liquid Hydrogen Supply Systems* provides guidance for regulatory compliance for hydrogen supply systems with more than 10 000 lb (4563 kg) of stored hydrogen [16].

7.2 Siting of hydrogen bulk storage

Small scale hydrogen production facilities will generally require a backup supply of hydrogen. Thus, the hydrogen production unit can be co-located with a bulk hydrogen supply system that can consist of gaseous high pressure storage and/or a liquid hydrogen system.

The gaseous hydrogen system may include any of the following:

- high pressure storage vessels;
- compressor(s); and
- pressure control system including regulators, valves, and instrumentation.

The liquid hydrogen system may include any of the following:

- cryogenic liquid hydrogen storage tank;
- heat exchanger, generally in the form of ambient air vaporizers;
- cryogenic pump(s);
- compressor(s); and
- pressure control system including regulators, valves, and instrumentation.

Siting of the bulk hydrogen storage systems in relation to all setback distances and electrical systems is critical. In the case of siting near a small scale hydrogen production facility, air intakes, vents, buildings and/or enclosures, electrical systems, as well as the available space to install the back-up system all pose challenges to properly locating the system. CGA H-5 shall be used for siting, equipment selection, and overall design of the bulk hydrogen system [15].

CGA H-5 contains minimum requirements for locating/siting, selecting equipment, installing, starting up, maintaining, and removing bulk hydrogen supply systems [15]. The standard covers gas supply systems, liquid supply systems, and hybrid supply systems where liquid is either pumped and vaporized or vaporized and compressed. In a hybrid system, the high pressure gas is stored in gas receivers. CGA H-5 provides all the details necessary to meet the requirements of NFPA 2 [15, 14]. CGA H-5 covers free-standing hydrogen supply systems located at customer sites [15]. Back-up supply systems have some differences from free-standing supply systems. The owner of the integrated system (hydrogen production unit plus back-up system) should consider the following points:

- Free-standing bulk hydrogen systems are typically unstaffed. Service technicians who work on the system usually take the system offline and purge the system to minimize exposure to hydrogen. A co-located hydrogen production unit might require more personnel on-site and more work while the back-up hydrogen system is online. Conversely, it might be necessary to work on the back-up system while the hydrogen production unit is operating. The owner should locate the two systems with enough separation distance to minimize exposure of personnel working on either or both systems. The owner should also develop administrative procedures that reflect the use of both systems;

- Bulk hydrogen systems use the standard NFPA 2 separation distances for locating the system relative to offsite exposures [14]. The owner should determine whether to use the NFPA 2 distances or to develop more stringent ones based on a qualitative risk analysis or a quantitative risk analysis [14].

- Bulk hydrogen systems use one or more vent stacks for directing hydrogen releases to a safe location. CGA G-5.5, *Standard for Hydrogen Vent Systems*, provides requirements for the vent systems [17]. Vent stacks typically are not purged with nitrogen, and the vent stack can have an ignition of released hydrogen at the top of the stack. The owner should use the CGA G-5.5 recommendations to locate onsite equipment and personnel to minimize exposure to thermal radiation from the top of the vent stack [17];

- Neither CGA H-5 nor NFPA 2 require continuous hydrogen monitoring or installed fire protection systems [15, 14]. Personnel working on the system typically use personal monitors. The bulk hydrogen system is located to reduce impact of a fire on surrounding equipment and personnel. The typical approach is to let the fire burn itself out and have the local fire department protect surrounding equipment. If the fire is extinguished without shutting off or otherwise eliminating the fuel, there is a risk of delayed reignition leading to unexpected fire or energy release. If the hydrogen production unit has a fire protection system, its design shall be such that it cannot send water into vent stacks used for cold hydrogen vapors. Water ingress into vent systems should be avoided and is of particular concern with cold hydrogen systems since the cold vapors could freeze the water and plug the vent stack, preventing the tank from venting and creating potential for a tank rupture. Indications of leaking relief valves (i.e., ice ball around the relief valve) on liquid hydrogen tanks should be addressed promptly, as the hydrogen vapor is cold enough to freeze air, which could impede the performance of the relief valve;

- In accordance with CGA H-5, liquid hydrogen tank product (supply) gas or liquid lines leaving the tank, except relief valve line(s) and fill line(s), shall have remotely operated emergency shutoff valves for shutting off the flow of fluid [15]. The shutoff valves are air operated and fail closed;

- Liquid hydrogen storage tanks are typically vacuum insulated. This insulation is not perfect and therefore there is a finite heat leakage into the tank (due to ambient temperature and insolation). This results in an amount of liquid boiloff produced gas. In the case where the liquid tank is being used for back-up of a hydrogen production unit, there is normally no flow out of the tank, and this boiloff gas generation will cause the tank pressure to rise. This pressure rise shall be controlled by an automated pressure control path leading to a vent or some other suitable location. The impact of the vent including expected flow during tank filling and other high venting activities shall be considered when siting the hydrogen production unit. The impact of weather (e.g., high wind) shall also be considered. A dispersion study is recommended to identify minimum spacing (horizontal and vertical) between vents and air intakes;

- Liquid hydrogen storage tanks have two pressure relief valves for safe venting of overpressure conditions such as loss of vacuum insulation integrity. These pressure relief valves shall not be used as a primary pressure control for controlling pressure produce by boiloff; and

- NFPA 2 defines the electrically classified areas around bulk gas and liquid hydrogen storage [14]. For sites where the classified areas for the hydrogen production unit and the backup system are close to each other, the owner should consider combining the classified areas and modifying the area boundaries to avoid gaps.

7.3 Location in or adjacent to an existing industrial facility

If the hydrogen production unit is located adjacent to an industrial facility, the risk assessment shall address the effects of the surrounding industrial facilities on the new unit and vice versa. It could be necessary to place occupied buildings associated with the new unit outside the larger facility perimeter at quite some distance from the new unit and/or to install blast-resistant (overpressure rated) buildings.

Most small scale thermal-based hydrogen production units will have predominately Class 1, Division 2 areas, although some Division 1 areas can exist. The presence of hydrogen requires the adherence to Group B; Group C & D are required for hydrocarbon feeds. If the unit is enclosed, the interior is deemed Class 1, Division 1 unless other mitigations as defined in the code are applied.

Electrolysis units are often enclosed. The interior will be deemed Class 1, Division 1 unless other mitigations as defined in the code are applied. Since electrolysis units do not have hydrocarbon feeds, they would be subject to Group B.

Safeguards to mitigate the ignition risks address the lighter than air density of hydrogen. Leaking hydrogen is not visible as it is a clear odorless gas at ambient temperatures and pressures. Additionally, the flame is nearly invisible during the day and very difficult to extinguish. Small thermal hydrogen production units may have an atmospheric vent or a flare. Electrolysis based hydrogen production units have a hydrogen vent and an oxygen vent. A hydrogen bulk storage system will have a hydrogen vent. The location of all process vents and the air intakes for ventilation or combustion air shall be sufficiently separated, and the potential impact of vented oxygen on surrounding processes shall be taken into account. Although oxygen is nonflammable, it increases the flammability of other substances; and any resulting fire is faster and more intense. Hydrogen is lighter than air and oxygen is nearly the same density as air, which greatly affects dispersion of the gas discharging through a vent. Therefore, wind direction and dispersion shall be accounted for in vent location. The vent design should include provisions for weather proofing.

CGA G-5.5 covers requirements for the design of hydrogen vent systems [17]. Some of the design considerations include:

- If the gas leaving the vent has delayed ignition, the vent is at a high enough elevation to mitigate the impact of the blast wave and fireball on the surrounding equipment and personnel travel paths;

- If the gas leaving the vent ignites, the flame is upward and at a high enough elevation to mitigate the heat radiation hazard on the surrounding equipment and personnel travel paths; and

- Location of a vent or flare point is situated far enough away from any air intakes such that no significant amount of gas is ingested. Downdrafts caused by neighboring structures and density variation due to cryogenic liquid vaporization are taken into account.

Siting of a small unit can cause surrounding preexisting equipment such as area lighting and security cameras to fall into a classified area. Any affected equipment shall be upgraded or relocated so as not to provide an unmitigated ignition source.

7.4 Co-location with vehicle fueling station

The public can perceive a hydrogen production unit or hydrogen storage facility to be a dangerous industrial process located in their neighborhood. Risk assessment and mitigations are required, most likely with local jurisdiction involvement.

The requirements for area classification for a traditional vehicle fueling station are referenced in NFPA 30A, *Code for Motor Fuel Dispensing Facilities and Repair Garages*, which calls out NFPA 70 [18, 12]. Both Class 1, Division 1 and Division 2 areas will exist and will most likely be Group C & D. This is due to the ignitability of the various fuel vapors (e.g., gasoline, diesel). Safeguards to mitigate these ignition risks address the heavier than air density of the common motor fuel vapors. Spills are visible since these fuels are liquid at ambient temperatures and pressures. Burning fuel of this type is visible (yellow flame & black smoke) and relatively easy to extinguish.

The addition of a hydrogen vehicle fuel dispensing unit and its associated hydrogen source (production and/or storage) to an existing vehicle fueling station (e.g., dispensing gasoline) presents an additional layer of complexity. The requirements for area classification for a hydrogen vehicle fuel dispensing unit are referenced in NFPA 2, which calls out NFPA 70 [14, 12]. The requirements for electrical area classification for hydrogen supply systems are covered in CGA H-5 [15]. A hydrogen vehicle fuel dispensing unit will have both Class 1, Division 1 and Division 2 areas, but they will be Group B due to the presence of hydrogen.

Most small scale thermal-based hydrogen production units have predominately Class 1, Division 2 areas, although some Division 1 areas can exist. The presence of hydrogen requires the adherence to Group B; Group C & D are required for hydrocarbon feeds. If the unit is enclosed, the interior is deemed Class 1, Division 1 unless other mitigations defined in the code such as ventilation are applied in which case the enclosure may be deemed Class 1, Division 2.

Electrolysis units may be enclosed, in which case the interior will be deemed Class 1, Division 1 unless other mitigations as defined in the code are applied. Since electrolysis units do not have hydrocarbon feeds, they would be subject to Group B. A byproduct of the electrolysis units is oxygen, which is generally vented to the atmosphere, but still needs to be addressed as a hazard within an enclosure. Typically, gas analyzers with alerts are installed to detect high levels of oxygen and hydrogen.

A typical bulk storage facility will have predominately Class 1, Division 2 areas although some Division 1 areas can exist. The presence of hydrogen requires adherence to Group B. If the unit is enclosed, the interior is deemed Class 1, Division 1 unless other mitigations as defined in the code are applied. Safeguards to mitigate the ignition risks associated with the lighter than air density of hydrogen are addressed in 7.3.

Gas station fires can occur due to spills from tank overfill, broken fueling hoses, and broken delivery hoses. A thermal-based hydrogen production unit co-located with a typical vehicle fueling station adds additional fuel and ignition sources. In order to mitigate the risks of an event in the vehicle fueling station causing a subsequent event in the hydrogen production unit:

- Hydrogen production units shall have one or more layers of protection to mitigate the risks of vapor from a liquid fuel spill migrating into the combustion air inlet. For example, it could have a means of flammable gas detection within the combustion air inlet system that will safely shut down the firing in the event of the detection of a significant percentage of the LFL and/or could be tied into the emergency shut off switch that the vehicle fueling station is equipped with;

- Dispersion analysis that considers all potential vents (e.g., oxygen, hydrogen, syngas, natural gas), combustion intake systems, and fuel spills is recommended; and

- Owner should consider the risk of reverse flow from the flue gas stack drawing flammable vapor (from a liquid spill) backwards into the firebox after a shutdown where ignition could occur. Depending on the firebox, flue gas stack, and air inlet configuration, reverse flow (post shutdown) could also result in hot gases venting from the air inlet. This could result in delayed ignition of the resultant vapor cloud outside of the unit or exposure of individuals to hot, flammable, and/or asphyxiating gases.

Unlike a fired thermal-based hydrogen production unit, electrolysis units or bulk storage facilities are not in themselves an ignition source. If the area classification requirements are met, they do not present a propagation risk.

The owner shall assess any security barriers for the potential of causing congestion or confinement of a flammable gas cloud, particularly if the gas is hydrogen. Sufficient confinement or congestion can result in an ignited cloud of hydrogen transitioning from deflagration to detonation. The resulting high overpressure could cause significant damage to the surroundings.

The owner should consider a means of detection of flammable gases within the area of the security barrier that will safely shut down the firing in the event of the detection of a significant percentage of the LFL.

The owner should consider linking the e-stop system of the small production unit with the e-stop system in the associated vehicle fueling station. Activation of e-stop in either facility would shut down both.

7.5 Perimeter security

Hydrogen vehicle fueling installations can be co-located with existing motor fuel distribution and retail locations. This will bring a process, which is historically only found in heavy industrial areas, into direct contact with the public.

Typical access restrictions such as signage reading DO NOT ENTER, AUTHORIZED PERSONNEL ONLY could be insufficient due to the principle of an attractive nuisance. Sufficient security barriers (e.g., fence or container) shall be in place to deter an interested party or a party with malicious intent from gaining access to the hydrogen production unit and bulk hydrogen supply system. Additionally, the equipment in the hydrogen production unit and bulk hydrogen supply system shall be protected from vehicular impact by bollards or equivalent.

The owner should consider means of detecting an intruder that will safely shut down the hydrogen production unit in the event of the detection of unauthorized access.

7.6 Permitting

Multiple permits will be required to build and operate a hydrogen production unit and/or bulk hydrogen storage system. These are typically issued by the city or county where the unit is being planned. Required permits include, but are not limited to, demolition, excavation/grading, building, electrical, mechanical, fire, and noise. Depending on the jurisdiction these permits can be discretionary, so it is important to identify if that is the case and, if so, consider taking steps to coordinate closely with the city or county. Consider utilizing local, external resources (e.g., environmental consultants, engineering firms, etc.) to facilitate obtaining the required permits.

Depending on the process, site, etc., other permits can be needed for things such as underground storage tanks and certain pressure vessels. These permits are typically issued by the state. Jurisdictions can require permitted pressure vessels to be inspected periodically.

One or more environmental permits, typically issued by the federal government or the state, will be required. These are discussed in Section 8.

8 Environmental considerations

There are federal, state, and local environmental considerations, including planning, permitting, licensing, operational and reporting requirements, that could apply to small scale hydrogen production units. If the production unit is sited within a larger chemical or refinery plant, a customer site, etc., the environmental permitting requirements may be covered under the existing permits for the larger facility. In cases of co-located units, the permit compliance responsibilities of each party should be clearly defined.

Environmental considerations include but are not limited to the following.

8.1 Planning

8.1.1 Environmental due diligence

Depending on where the production unit will be located, due-diligence steps (e.g., an environmental site assessment) should be considered to ensure owner protection against future environmental liabilities (see CGA P-90, *Guideline on Due Diligence Considerations for the Compressed Gas Industry* for further details/explanation) [19].

8.1.2 Environmental strategy

A documented assessment of the environmental impacts can be used to identify the various environmental impacts and/or requirements that would apply for the proposed project, including any special permitting requirements. This document can carry important information for project development/execution staff's awareness and will ensure any environmental aspects are being properly and adequately addressed.

8.2 Air quality

8.2.1 Combustion-related emissions

For thermal hydrogen production units involving the combustion of fuel and/or waste gas, air permitting is likely required to account for potential pollutants generated from associated reforming combustion and to identify and address applicable regulations covering emissions standards, monitoring and measurement, testing, reporting, etc. The most commonly regulated pollutants are nitrogen oxides, carbon monoxide, particulate matter, and sulfur oxides. Depending on the level of greenhouse gas (e.g., carbon dioxide, methane, nitrous oxide) emissions, additional federal and/or state greenhouse gas reporting can be required. Flares for emergency/upsets/maintenance, power generators, emergency engines, supplemental-fired equipment also contribute to this category.

8.2.2 By-product pollutants

For thermal hydrogen production units involving the processing of gaseous feedstock(s), methanol, ethanol, and ammonia by-products (MeOH, EtOH, NH_3) will form in the reformer and CO-shift reactors. These byproducts are soluble in water and will end up in the process condensate that is separated from the syngas stream prior to product purification. Depending on how this process condensate stream is managed (i.e., to sewer, to steam system), different actions and requirements would apply.

For reuse as steam, process condensate would be sent through a deaerator/degasifier that is typically vented to atmosphere. It should be noted that there would still be trace levels of these byproduct pollutants in the steam, so any atmospheric steam vents can be regulated.

8.2.3 Miscellaneous emissions from vents, ancillary equipment, etc.

Depending on process variations, integration with other processes, site-specific factors, etc., there can be other processes subject to environmental permitting/regulations including but not limited to emissions from atmospheric vents and cooling towers. Leaking flanges, bleed valves, valve packing, etc., are sources of fugitive emissions. The most commonly regulated pollutants from these locations are volatile organic compounds (VOC).

8.3 Water quality

8.3.1 Wastewater management

Depending on the size of the unit (including whether it is a part of a larger site with other operations) and to where the wastewater will be discharged (e.g., publicly owned treatment works or to a river, lake, or ocean), permits and associated requirements can apply (i.e., monitoring, reporting, inspections, treatment costs, etc.). The requirements should be understood, and the wastewater assessed for compliance with any applicable pollutant standards and limits (e.g., pH, conductivity, metals, soluble sulfides, etc.). Water treatment plant waste streams, boiler blowdown, and cooling tower blowdown are typical sources of wastewater. Sanitary wastewater can also be combined with process wastewater as it leaves the site.

If process condensate from a thermal hydrogen production unit is sent to drain, the wastewater treatment system (whether off-site, on-site, or municipal) should be capable of dealing with the biological oxygen demand it will cause. Condensate typically contains ammonia, and this can upset the balance in the treatment system. The condensate will contain other dissolved process gases (e.g., carbon monoxide and carbon dioxide) and could create a toxic hazard as the dissolved gases disengage.

8.3.2 Storm water management

Construction of some standalone facilities can disturb enough land to require a construction stormwater permit and accompanying stormwater pollution prevention plan; however, for most small and micro sites, especially in cases in which hydrogen production is being added to an existing facility, it is expected that the land disturbance would be insufficient to require such a construction stormwater permit.

Depending on the size of the unit (including whether it is a part of a larger site with other operations), a general or site-specific industrial storm water permit can be required that would regulate discharge of storm water to a local body of water either directly from the site or via a local storm sewer system. Associated requirements can apply (e.g., monitoring, reporting, inspections, etc.) and should be understood and the site assessed for compliance with any applicable pollutant standards and limits (e.g., pH, oil and grease, total suspended solids, metals, etc.). Typical sources of pollutants in this category are machine oil and spillage from liquid transfer.

Note that some general industrial discharge permits cover both process water and storm water.

8.3.3 Spill prevention, control, and countermeasure

Depending on the amount of total site aboveground oil (oil is broadly defined by the EPA) storage or the location (adjacent to receiving waters), the operation can be subject to spill prevention, control, and countermeasure (SPCC) requirements, including use of secondary containment, SPCC plan development and implementation of other generic, advanced and/or specific best management practices. If the site is subject to SPCC, secondary containment for machinery or for hydrocarbon storage (e.g., methanol or naphtha) could be required to contain any spills.

8.4 On-site materials impacts

8.4.1 Hazardous materials storage and use

Depending on the process and unit, there could be various hazardous materials that are utilized on-site including, but not limited to, in-process feedstock/fuels/gases, electrolyte solution, water treatment chemicals, adsorbents/catalysts, and lubrication/transformer oils. The management of these materials, including handling, storage, and transportation, will need to follow federal, state, and local regulatory requirements. In addition, for emergency planning and community right-to-know (EPCRA) purposes, depending on the material and associated reporting thresholds, some or many of these materials might need to be reported as part of a hazardous materials inventory and response program typically regulated by the EPA, state, or local city or county.

8.4.2 Waste management

Most of the considerations described in this section are essentially the same as would apply to larger scale production units but, due to their size and/or process variations, reduced or less stringent requirements can apply. For more information, refer to CGA P-37, *Good Environmental Management Practices for the Compressed Gas Industry* [20].

Nonhazardous and hazardous wastes could be generated from these units including, but not limited to, lubrication oils (itself, from maintenance activities on rags, as a spill cleanup in absorbents, in drained oil filters), hazardous materials spill cleanup, spent electrolyzer cell and cell components (electrodes & separators), used potassium hydroxide electrolyte solution, spent adsorbents and catalyst, and miscellaneous items (E-waste, light bulbs, batteries). The handling, storage, transportation, and disposal of these wastes is subject to very complex federal, state, and local regulations. Depending on the type (nonhazardous, hazardous, or universal) and quantity of the wastes generated, there will be requirements around managing the waste when on-site (e.g., labeling, inspections, accumulation periods, etc.) as well as requirements for transportation and/or disposal (e.g., characterization, profiling, manifesting, land disposal restrictions). Note that management and disposal of certain spent catalyst can involve stabilizing the catalyst to prevent self-heating. Refer to CGA H-15 for additional information and guidance [13].

8.5 Emissions control

The main source of emissions in a thermal production plant is the flue gas stack. Proper burner design and excess oxygen control are critical in limiting pollutant emissions from the stack. Limiting atmospheric venting is also important for controlling emissions. Flares are a means of emissions control and a source of emissions but are not normally required in small plants.

9 Best practices for operation

An effective operating and maintenance program is essential to maintaining safe, efficient, and reliable plant operation. While the efficiency and reliability requirements for small hydrogen plants can be less stringent than those for large hydrogen plants, the same principles apply.

This section addresses best practices for operation, including on-line operator rounds/inspections, while Section 10 addresses offline maintenance for small hydrogen plant generators. CGA H-5 provides guidance for the operation and maintenance of bulk storage equipment [15].

Operating procedures or site work instructions shall, as a minimum:

- Address all regulatory requirements;
- Address normal startup, operation, and shutdown operation;
- Address emergency operation/action or shutdown, including startup following an emergency shutdown;
- Address nonstandard temporary operation (e.g., unusual customer demand, changes in feedstock, quality, etc.);
- Identify the alarm and shutdown setpoints, which define the safe operating limits (temperature range, pressure range, analytical result, etc.);
- Identify the key hazards and associated risks based on workplace risk assessment or job safety analysis techniques;
- Identify required routine inspections and any plant data that need to be collected; and
- Consider human factors, ergonomics, and PPE requirements.

Although many small hydrogen production plants are configured to be able to operate without operator intervention, including plant load change, it is important for operators to understand the primary process control loops, particularly those that provide protection against unsafe conditions or equipment damage.

9.1 Operating procedures

All documents required for safe operation and maintenance of the hydrogen plant shall be provided by the original equipment manufacturer (OEM) or developed by the operating company. Three key documents typically provided by the OEM are the process flow diagram (PFD), a detailed process description, and the piping and instrumentation diagram (P&ID or PID). The PFD and detailed process description help the operator understand how the plant functions in normal operation. The P&ID provides a more detailed view of the process controls for the facility as well as all interconnecting piping, valves, and instruments. When preparing for maintenance, it is critical to have an accurate view of the plant piping and instrumentation to ensure proper isolation of piping and equipment.

Operating procedures for individual unit operations or equipment items could be part of the OEM instruction manual, or the operating company could develop them from the OEM instruction manual.

An alarm and trip summary shall be developed or provided, listing the setpoints of all alarms and trips/shutdowns. This table may include a column that documents the basis for the alarm/trip setpoint, which is a helpful addition. The alarm and trip summary could be documented within the basic process control system (BPCS) configuration, but updates to either or both (table and/or BPCS) shall be managed via management of change (MOC). A consequences of deviation table is another helpful document, which explains to the operator the consequences that could occur as the result of a process deviation and any actions they should take to avoid further consequences. A shutdown table or interlock matrix shall also be developed or provided, listing all trips/shutdowns, the trip initiators, and the actions taken on a trip/shutdown.

9.1.1 Startup and shutdown procedures

The need to specifically consider and address the startup and shutdown of industrial processes is well recognized as a cornerstone to safe operation. For hydrogen production units that contain sufficient volume of flammable/toxic fluids, requirements to address startup and shutdown safety in operating procedures are included in process safety regulations in 29 CFR Part 1910.119, and in Europe, Seveso III Directive 2012/18/EU [2, 3]. Other local codes can have additional requirements. For plants that do not contain sufficient volume to be governed by regulatory requirements, CGA P-86 identifies a subset of guidelines for operating procedures (including startup and shutdown) [1].

Guidelines for the safe startup and shutdown of industrial production units are technology specific. Industry-wide publications addressing startup and shutdown practices exist for many technologies. CGA H-11, *Safe Startup and Shutdown Practices for Steam Reformers* provides guidelines specific to SMR [21]. Although these guidelines were developed around large scale hydrogen production plants, many of the same principles apply to small SMR plants.

Some of the general principles around preparation for startup and shutdown apply to all hydrogen production facilities (more details are included in H-11) [21]:

- Review all necessary procedures prior to startup or shutdown to ensure procedures are available and sequence is understood;
- Ensure all materials and equipment required for startup or shutdown are available (e.g., hoses for purging, burner ignition equipment);
- Review the bypass log and remove all hardwired and software bypasses unless authorized under management of change. In particular for startups following a maintenance outage, temporary bypasses could have been used for testing and calibration of mechanical equipment, electrical equipment, etc.;
- For startup, remove equipment lockout/tagout and confirm the position of valves, permanent blinds, and spool pieces. Confirm that lock open and lock closed valves are locked in position according to the P&ID. Confirm all instrumentation is functioning and ready for operation;
- Remove temporary hose connections other than those authorized via the bypass log or under management of change and required for startup or shutdown;
- Verify all safety work permits are closed prior to startup, unless work is ongoing and does not impact startup or shutdown;
- For startup, ensure applicable utilities and auxiliary services are placed in service (e.g., flare or vent system, instrument gas, cooling system);
- For startup following a maintenance outage, ensure process piping and equipment have been adequately purged into service to remove oxygen. The P&ID should be used to confirm that all sections of the plant, including dead legs, have been purged/tested; and
- For startup following an outage, the plant should be leak-tested following purging to ensure it is leak-tight. After startup, and during startup as pressure is increased (if applicable), leak testing should be repeated to ensure leaks don’t form as pressure or temperature increases.

Some (typically smaller) hydrogen plants are configured with a single push-button for startup, shutdown, or rate change. For plants that are not configured this way, the operator should adhere to any guidelines associated with the rate at which the plant is ramped up or down. In alkaline electrolyzer plants, this is done to avoid the electrolyte being carried over into the hydrogen and oxygen product streams, which can be caused by the increase in temperature of the electrolyte and by the “bubbling” effect of electrolysis. In thermal production units, exceeding the maximum rate of temperature change can result in mechanical damage of the reformer or other equipment.

It is also important in SMR hydrogen plants to maintain the flow of nitrogen and steam through the reformer while heating up to operating temperature, or the reformer tubes and downstream equipment could be damaged.

9.1.2 Additional operating procedures

In addition to startup and shutdown procedures, site-specific operating procedures should exist to address applicable utility and auxiliary systems, including those listed below. This list might not be all inclusive due to the individual design of plant equipment, and this list does not include generic instructions like handling of temporary connections (e.g., hoses to purge equipment for maintenance). In addition, some procedures might not be applicable because of the highly automated nature of some small hydrogen generation units.

9.1.2.1 Thermal hydrogen production

Procedure on how to start up, operate, and shut down includes:

- rotating equipment;
- steam and boiler feed water (BFW) systems;
- cooling water system;
- product purification (e.g., PSA);
- feed and fuel system;
- ammonia system (if applicable);
- nitrogen system;
- flare or vent system;
- demineralized water (water purification) system;
- electric power and uninterruptable power supply (UPS);
- BMS; and
- instrument air.

Procedure for lineup includes:

- piping and equipment (normal operation); and
- piping and equipment (shutdown/maintenance)

9.1.2.2 Electrolysis

Procedure on how to start up, operate, maintain standby, and shut down includes:

- cooling water system;
- demineralized water (water purification) system;
- nitrogen system;
- instrument air system;
- electric power and UPS;
- vent system;
- electrolyte (e.g., potassium hydroxide) or water system;

- rotating equipment; and
- product purification.

Procedure for lineup includes:

- piping and equipment (normal and standby operation); and
- piping and equipment (shutdown/maintenance).

NOTE—Some electrolyzers have a standby mode in which the rectifier is turned off, the PLC remains on, the electrolyte/water circulation remains on, and the nitrogen purge may be turned on or off depending on the nature of the standby configuration.

9.1.2.3 Common procedures

Procedure on how to start up, operate, and shut down:

- process analyzers; and
- freeze protection.

Procedure on testing and proper operation of safety devices.

9.2 Primary process control loops

Although small hydrogen generation plants may be designed to operate without intervention, operators should understand how the plant is designed and configured to operate. This section describes the purpose and function of the primary process control loops associated with SMR, methanol cracker, and electrolyzer plants. Operators should consult the OEM instruction manual of their specific equipment to understand other process control loops.

9.2.1 Steam methane reformer

The main control loops of a SMR may include plant load change (master rate control), steam to carbon ratio control, reformer temperature control, reformer pressure control, hydrogen product purity control (PSA cycle time), and PSA tail gas pressure control. Relevant trip initiators (e.g., steam to carbon ratio, steam drum level, excess oxygen) shall never be bypassed during normal operation.

9.2.1.1 Master rate control

The function of the master rate controller is to control the product hydrogen flow by adjusting the hydrocarbon feed to the reformer. As feed flow is adjusted, other process parameters (e.g., fuel to the reformer) may be adjusted automatically to keep the process within design parameters.

9.2.1.2 Steam-to-carbon ratio control

The steam-to-carbon ratio is typically defined as the moles of steam divided by the atoms of organic carbon in the feed (i.e., the number of carbon atoms in all carbon species except carbon monoxide and carbon dioxide). The ratio cannot be directly determined by dividing the steam flow by the gas flow. Typically, there is a fixed factor built into the control system to account for the feed composition. Higher steam-to-carbon ratio, higher tube exit temperature, and lower pressure favors higher conversion of hydrocarbons in the reformer tubes.

Steam-to-carbon control can be active (controlling steam flow to maintain a specific steam-to-carbon ratio) or passive (directing all generated steam to the process). In the latter case, the steam to carbon ratio will vary with rate because steam production varies with production rate.

The steam-to-carbon ratio is kept above a minimum value to prevent carbon (coke) formation on the reformer catalyst and potential overheating of the reformer tubes. At the inlet of the reformer, the steam is well in excess of the amount required for reaction in order to minimize carbon formation within the reformer tubes and to prevent damage to the shift catalyst. It is critical to ensure that the amount of steam generated by the process is sufficient to meet the needs of the reformer and shift catalysts. If the steam-to-carbon ratio drops below a plant-specific minimum value, an interlock will cause the plant to trip to avoid reformer catalyst damage.

9.2.1.3 Combustion air flow and reformer pressure control

The amount of air to the reformer should always be high enough to ensure complete combustion (typically 10% to 15% excess), which is both a safety and environmental requirement. This can be achieved by designing the equipment to achieve the required flow for the maximum rate case and accepting increased excess air at turndown; or the air flow can be adjusted to maintain a minimum oxygen level leaving the reformer. With either design, the stack oxygen level varies as the PSA cycles due to the changing composition and flow of the PSA tail gas.

The air flow to the reformer also controls the reformer operating pressure, which can be positive or negative depending on the reformer configuration. Most reformers have one or more fans to achieve flow and pressure control, although some reformers only use stack draft. The reformer should be operated within the design pressure limits of the equipment. To keep the reformer within design limits, interlocks to shut off the fuel based on reformer box pressure, air flow, fan status, and/or oxygen content can be present (some or all).

9.2.1.4 Reformer temperature control

The make-up fuel to the furnace is adjusted to maintain either the temperature of the process gas exiting the reformer catalyst tubes or the flue gas temperature exiting the reformer (often referred to as the bridgewall temperature). This is important to avoid overheating the reformer tubes and downstream equipment. The plant is interlocked to trip in the event of high reformer exit temperature.

9.2.1.5 Burner management system

The BMS is designed to protect operating personnel and fuel-fired equipment by ensuring the proper execution of a safe, and orderly operating sequence during the startup and shutdown of the reformer. The BMS startup sequence is divided into four major steps:

- Purge residual combustible fuel and flue gas from the reformer firebox and convection section;
- Check the operating integrity and initial closed state of all fuel valves (automatic and manual, as applicable);
- Introduce make-up fuel to the burners to permit burner startup; and
- Introduce PSA tail gas fuel to the burners to increase reformer firing rate in order to increase production rate.

A failure of any step in the BMS startup sequence will prevent startup from continuing. Refer to CGA H-10 and NFPA 86, *Standard for Ovens and Furnaces* for details [5, 22].

9.2.1.6 Steam drum level control

It is important to maintain a minimum level in the steam drum to avoid overheating the tubes of the steam generator. The water flow to the steam drum is adjusted to maintain the steam drum level. The plant is interlocked to trip in the event of low-low level in the steam drum.

9.2.1.7 Pressure swing absorption and PSA tail gas tank pressure control

The PSA is automatically adjusted based on the inlet flow and the PSA (capacity) factor. Operator control of the PSA typically is limited to adjusting cycle time (either directly or indirectly through the PSA capacity factor) and, in larger plants, triggering reduced bed operation in the event of a valve failure (or following valve repair) in the PSA system. Decreasing cycle time has the effect of improving product purity. As flow to the PSA increases, cycle time decreases to achieve the same product purity.

Flow to the PSA tail gas tank varies as the PSA operates across its cycle, and the tail gas tank pressure and tail gas flow to the reformer can be controlled in different ways. The tail gas flow or pressure control valve opens or closes (sending more or less flow to the reformer) to try to maintain a constant tank pressure or constant flow to the reformer. Any change in flow with time affects the reformer exit temperature, while any change in tail gas pressure can affect PSA recovery. If the tail gas tank pressure gets too high, an additional pressure controller will open to vent tail gas to atmosphere or flare to prevent overpressure of the tank and to prevent too high a flow of tail gas to the reformer. Tail gas venting should be minimized for both environmental and efficiency reasons.

Interlocks exist in the PSA control system and in the BMS that will shut down the PSA and/or plant based on parameters in this system.

9.2.2 Methanol cracker

The main control loops of a methanol cracker plant may include master rate control (plant load change), water-to-methanol ratio control, combustion air flow and fired heater pressure control, BMS, reactor outlet temperature control, and PSA and PSA tail gas tank pressure control. Relevant trip initiators (e.g., water flow, methanol flow, flow ratio) shall never be bypassed during normal operation.

The composition of the reactor effluent stream is closely related to the operating pressure and temperature of the reactor and the water-to-methanol ratio at the reactor inlet.

9.2.2.1 Master rate control

The function of the master rate control is to control the product hydrogen flow by adjusting the methanol feed flow to the reactor. As feed flow is adjusted, other parameters of the process (e.g., make-up fuel to the fired heater) will be adjusted automatically to keep the process within design parameters. As the plant rate is changed, the reactor temperature should be maintained at the same temperature.

9.2.2.2 Water-to-methanol ratio

The most important control loop in the plant is the water-to-methanol ratio. The water-to-methanol ratio is typically defined as moles of water to moles of methanol and is calculated by measuring the density of the mixed feed (water and methanol), applying pressure and temperature compensation to determine the methanol concentration, and finally calculating the water-to-methanol ratio. These calculations are done within the control system.

The water-to-methanol ratio is controlled automatically, with the set point adjusted automatically to correspond to plant load. Insufficient process steam (water) causes carbon (coke) formation and possible damage to the reactor catalyst. In a severe case (e.g., loss of process water), the catalyst tubes could rupture.

As the water-to-methanol ratio at the reactor inlet is increased, residual methanol from the reformer/cracker decreases. Periodically, the water-to-methanol ratio should be validated manually during plant operation. This can be done by taking the flow controllers out of master rate control and validating the ratio manually with the indicated flows. The water-to-methanol ratio influences the efficiency of the process as well as the amount of make-up fuel required in the fired heater. If the water-to-methanol ratio drops below a plant-specific minimum value, an interlock will cause the plant to trip to avoid reactor catalyst damage.

9.2.2.3 Combustion air flow and fired heater pressure control

The amount of air to the fired heater should always be high enough to ensure complete combustion (typically 10% to 15% excess), which is both a safety and environmental requirement. This can be achieved by designing the equipment to achieve the required flow for the maximum rate case and accepting increased excess air at turndown; or the air flow can be adjusted to maintain a minimum oxygen level leaving the fired heater. With either design, the stack oxygen level varies as the PSA cycles due to the changing composition and flow of the PSA tail gas.

The air flow to the fired heater also controls the heater operating pressure, which can be positive or negative depending on the configuration. Most fired heaters have one or more fans to achieve flow and pressure control, although some only use stack draft. The fired heater should be operated within the design pressure limits of the equipment.

Interlocks exist to shut off the fuel to prevent unsafe conditions. Typical interlocks are low air flow, loss of fan status, low flue gas oxygen content, low or high fuel pressure, low hot oil flow, and high flue gas or hot oil temperature.

9.2.2.4 Burner management system

The BMS is designed to protect operating personnel and fuel-fired equipment by ensuring the proper execution of a safe and orderly operating sequence during the startup and shutdown of the fired heater. The BMS startup sequence is divided into four major steps:

- Purge residual combustible fuel and flue gas from the fired heater;
- Check the operating integrity and initial closed state of all fuel valves (automatic and manual, as applicable);
- Introduce make-up fuel to the burners to permit burner startup; and
- Introduce PSA tail gas fuel to the burners to increase firing rate in order to increase production rate.

A failure of any step in the BMS startup sequence will prevent startup from continuing. Refer to NFPA 86 for details [22].

9.2.2.5 Reactor outlet temperature control

As the reactor outlet temperature is increased, methanol slip from the reactor decreases as the methanol steam reforming reaction is driven towards hydrogen. However, the methanol decomposition reaction is also favored by the higher temperature, which increases the quantity of carbon monoxide in the effluent stream. The water gas shift reaction is favored by lower temperatures and, therefore, the conversion of carbon monoxide to hydrogen is adversely affected by the higher temperature. As the plant rate changes, the fuel flows will change due to changes in the heat load requirement of the reactor. The plant is interlocked to trip in the event of low reactor outlet temperature.

9.2.2.6 Pressure swing adsorption and PSA tail gas tank pressure control

The PSA is automatically adjusted based on the inlet flow and the PSA (capacity) factor. Operator control of the PSA typically is limited to adjusting cycle time (either directly or indirectly through the PSA capacity factor) and, in larger plants, triggering reduced bed operation in the event of a valve failure (or following valve repair) in the PSA system. Decreasing cycle time has the effect of improving product purity. As flow to the PSA increases, cycle time decreases to achieve the same product purity.

Flow to the PSA tail gas tank varies as the PSA operates across its cycle, and the tail gas tank pressure and tail gas flow to the fired heater can be controlled in different ways. The tail gas flow or pressure control valve opens or closes (sending more or less flow to the fired heater) to try to maintain a constant tank pressure or constant flow to the fired heater. Any change in flow with time affects the fired heater exit temperature, while any change in tail gas pressure can affect PSA recovery. If the tail gas tank pressure gets too high, an additional pressure controller will open to vent tail gas to atmosphere or flare to prevent overpressure of the tank and to prevent too high a flow of tail gas to the fired heater. Tail gas venting should be minimized for both environmental and efficiency reasons.

Interlocks exist in the PSA control system and in the BMS that will shut down the PSA and/or plant based on parameters in this system.

9.2.3 Electrolyzer controls

The main control loops of an electrolyzer include liquid level control, electrolyte composition and flow control, monitoring of product and byproduct purity, and monitoring of electrolyzer temperature and/or pressure, voltage, and current. Relevant trip initiators (e.g., hydrogen in oxygen, oxygen in hydrogen) shall never be bypassed during normal operation.

9.2.3.1 Product flow control

The production rate of hydrogen is controlled by adjusting the amount of load or current that is applied to the electrolyzer. The electrolyzer’s internal pressure is typically controlled by a gasholder or by a back pressure valve that modulates and maintains a constant internal pressure. The applied current can be adjusted based on production demand (demand control) or based on availability of power (load control). Pressure downstream of the electrolyzer’s pressure control valve or gasholder can be used as an indication of production versus demand, and the amount of current being sent to the electrolyzer can be modulated to match capacity to demand. Alternatively, based on the availability of power (e.g., when running on renewable power dependent on sunlight or wind profile), the applied load can be ramped up or down.

Alkaline electrolyzers typically operate at near atmospheric pressure but can operate at elevated pressure. Elevated pressure operation is primarily performed in a balanced mode, where the differential pressure between the anode and cathode is kept very small.

PEM electrolyzers can operate at near atmospheric pressure or at elevated pressure. Elevated pressure operation can either be in a balanced or in a differential pressure mode. In balanced pressure mode, the differential pressure between the cathode and the anode is kept to a minimum. In differential pressure mode, the cathode might operate at elevated pressure, while the anode operates at lower pressure.

9.2.3.2 Liquid level control (electrolyte or feed water)

The gas-liquid separators are designed to collect the produced hydrogen and oxygen separately. To keep the electrolysis cells flooded and prevent mixing of oxygen and hydrogen, the gas-liquid separators are half filled with electrolyte in an alkaline electrolyzer and with feed water in a PEM electrolyzer.

Control of the liquid level in both separators is critical. It is necessary to maintain a liquid level in both separators to prevent hydrogen or oxygen gas from exiting the separator through the liquid line and possibly creating an explosive atmosphere when the liquid is recirculated. As water is consumed in the production of hydrogen, makeup water is added to maintain level.

9.2.3.3 Raw gas contaminant monitoring

Hydrogen and oxygen cannot be allowed to create an explosive mixture (either in the pipe work or in the atmosphere). Instrumentation is installed 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 if an unsafe composition is detected in either gas stream.

For safe operation, the hydrogen in the oxygen byproduct shall be continuously monitored. The analyzer is mounted on the oxygen outlet of the electrolyzer and measures percent hydrogen in oxygen. The analyzer senses high hydrogen content and shuts down the electrolyzer at predetermined impurity shutdown levels, between 25% and 50% of LFL (typically less than 1% to 2% hydrogen in oxygen), well before an explosive gas mixture occurs in the system. In this case, the control system will initiate a nitrogen purge to the cells.

There is a similar configuration on the raw hydrogen product, except oxygen content in the hydrogen is monitored. The analyzer is mounted on the hydrogen outlet of the electrolyzer and measures parts per million (ppm) levels of oxygen in hydrogen. The analyzer senses high oxygen content and shuts down the electrolyzer to prevent overheating of the deoxo unit or formation of an explosive gas mixture. The shutdown limit depends on the deoxidizer unit design.

9.2.3.4 Electrolyte composition control (alkaline electrolyzer)

The level control in the tanks (which controls the addition of makeup water) is used to maintain the electrolyte composition, as the potassium hydroxide itself is not consumed. The potassium hydroxide electrolyte will be replaced at a supplier-specified interval (e.g., 1-4 years).

9.2.3.5 Monitoring of product purity

Some units will have an analyzer monitoring oxygen in the product hydrogen (usually when a deoxidizer unit is supplied). These analyzers will measure parts per million (ppm) oxygen. On plants that do not have an on-line product analyzer, this stream purity shall be checked at least once per day using a portable analyzer. If the hydrogen purity is below design, it should be reported to the plant manager for further review.

Another analyzer that may be deployed is for water/moisture in the hydrogen. This will also measure in ppm and will be located downstream of the dryer.

9.2.3.6 Monitoring of electrolyzer temperature, pressure, and voltage

For optimal operation, the cells need to be operated at a specified temperature. Under applied load, heat is generated within the cells and is removed from the stack by the electrolyte/feed water circulation and the coolant loop. The temperature of the product gas exiting the electrolyzer and/or the electrolyte may be monitored and utilized for controlling the operating temperature at the desired level.

The differential pressure between the anode and the cathode chamber and the pressure in the electrolyzer and header tanks should be monitored and interlocked as needed to prevent mixture of hydrogen and oxygen gases. The voltage of the electrolyzer may be monitored and in certain configurations, individual cell level monitoring may also be available or manually measured to assess performance of the electrolyzer.

9.3 On-line inspections/rounds

All hydrogen production plants require a preventive maintenance, testing, and inspection program to keep them in a safe and reliable working condition; and an important part of that program is on-line inspections or operator rounds. Regular inspections during plant operation are one means of identifying damage and/or deterioration of equipment, and routine equipment maintenance can be required. The list of on-line maintenance requirements should be developed from the OEM instruction manual. The operator should maintain a list of required maintenance based on findings from on-line inspections/rounds. Some of these findings can be resolved during plant operation; others need to be deferred until the plant is shut down for maintenance.

Hydrogen production plants shall have a permit to work system in place to ensure that work is conducted safely. A list of routine operator tasks that do not require a work permit should be developed.

If a leak is detected during operator rounds, the operator shall follow appropriate emergency response procedures based on the size and composition of the leak. See CGA H-14 for more information on leak detection and response guidelines [4].

Inspection and on-line maintenance intervals can vary depending on the task, and the operator should consult the OEM instruction manual for required inspections and recommended inspection intervals. On-line inspection and maintenance intervals typically vary from daily to quarterly or annually and will depend on the size and design of the plant, whether it is co-located with a fueling station or not, and what kind of remote monitoring capabilities are in place. Off-line maintenance intervals can be dictated by local or national codes, vendor recommendations, site environment, or equipment condition.

On-line inspection should also include comparison of plant operating conditions relative to historical readings. Any changes in operating conditions indicate a potential plant issue, although performance of some equipment is expected to degrade with time (e.g., CO-shift reactor catalyst, electrolyzer cell performance). The OEM instruction manual should indicate how performance will degrade from “start of run” to “end of run.”

9.3.1 General plant leak checking

Leaks can be identified by either an operator on rounds using their senses or by a fixed or portable monitor. Quite often leaks are detected based on the hissing sound the gas makes as it changes pressure from high to low. If external piping is inspected in darkness, a blue or orange flame can be present if the leak has ignited. Leaks can also be detected based on changes in process parameters. If a leak is detected, the operator shall follow appropriate emergency response procedures based on the size and composition of the leak. See CGA H-14 for information on basic leak response [4]. The plant emergency response manual shall address leak response in general including, at a minimum, the following elements:

- plant-wide alarm notification protocol with required action by site employees;
- emergency response and control procedures;
- procedure for emergency shutdown of operations;

- internal and external emergency contact information (first responders and neighboring facilities); and
- required authority and regulating agency notification requirements and timing based on the regulations for the site.

If a leak is detected and a temporary repair is implemented (e.g., a clamp is installed around a defective component), the permanent leak repair shall be added to the plant outage maintenance list. Leak repair devices such as clamps are temporary mitigations for loss of containment of a process fluid. These devices will degrade over time and should be removed and the underlying condition repaired at the first scheduled opportunity.

9.3.2 Electrical equipment monitoring

New electrical components begin to deteriorate as soon as they are installed. Vibration, fatigue, and aging cause the loosening of electrical connections and deterioration of components, and environmental conditions can hasten this process. Loose or corroded connections result in increased resistance, with a resulting increase in temperature. Similarly, overloaded or failing components also result very often in higher temperatures. Thermal imaging can detect these developing faults before they result in failure.

Some types of electrical equipment that are suitable for thermal monitoring include:

- transformer, termination boxes, and bushings;
- motor control centers (MCCs);
- motors (including bearings);
- distribution boards (DBs);
- fuses and fuse boards;
- wiring, including power cables; and
- circuit breakers.

9.3.3 Steam methane reformer plant; on-line inspections and monitoring

This section covers some of the more common on-line inspections that should be conducted on SMR hydrogen production plants. Not all of the inspections will be applicable to all plants, and the OEM instruction manual should be consulted.

9.3.3.1 Leak checks

The areas where leaks most commonly occur are at the inlet and outlet of the reformer and at the pressure swing adsorber unit if present. Leaks can occur more frequently at the inlet of the reformer if multiple flanged connections exist. Leaks can occur more frequently at the outlet of the reformer due to the high temperature operating conditions and the aging/degradation affect that high temperature has on the reformer outlet system (see CGA H-12, *Mechanical Integrity of Syngas Outlet Systems)* [23]. Leaks can occur more frequently at the pressure swing adsorption unit due to multiple flanged connections (typically) that cycle from high pressure to low pressure on a frequent basis and due to the presence of many valves that can develop packing leaks. Note that leaks that occur in piping or vessels subject to cyclic service (i.e., cycle from high to low pressure) can escalate rapidly. Temporary leak repair devices such as clamps shall be inspected at regular intervals, and their fitness for continued use should be regularly assessed. See 9.3.1 for more information.

9.3.3.2 Temperature monitoring

Thermal imaging (thermography) should be used for monitoring the surface temperature of static equipment to provide early indications of underling issues that could be present. The routine inspection and monitoring of certain key areas and equipment throughout the plant is an important task.

The hot static equipment in an SMR can be externally insulated, internally insulated or non-insulated, dependent on the location in the process and the process design. Regular inspection and monitoring of the surface temperature of the following items is recommended in order to determine the integrity of the insulation and whether the material design temperature might be exceeded leading to early onset of failure mechanisms:

- reformer box and furnace;
- reformer tubes;
- reformer outlet system; and
- syngas heat recovery.

This monitoring should be completed with an infrared thermometer and/or infrared thermography, typically on a monthly or quarterly basis, depending on the risk review. Results from inspections should be compared to previous results. Although temperatures can change with operating and weather conditions, significant or abnormal changes in temperature should be investigated.

9.3.3.3 Reformer catalyst and tubes

Status of the reformer catalyst can be monitored by regular syngas sampling for methane, hydrogen, carbon monoxide and carbon dioxide content in the syngas as prescribed in the OEM instruction manual or preventive maintenance (PM) list. An increase in methane slip (methane value) can indicate reformer catalyst deactivation. If regular syngas sampling is not conducted, plant performance should be monitored for indications of degradation; and any indications of degradation warrant further investigation. As the reformer catalyst deactivates, the amount of feed required to produce a fixed amount of hydrogen increases, the recovery of the PSA decreases, and the make-up fuel consumption also decreases (because the PSA tail gas flow increases). Because the PSA could be configured to run conservatively (i.e., more pure hydrogen than required), changes in performance could first manifest as changes in product purity, which initially could go unnoticed. Catalyst deactivation leads to a temperature rise of the catalyst tube wall temperature, as the endothermic reforming reaction is reduced and does not provide the same degree of cooling as fully active catalyst.

Carbon deposits on the catalyst can cause increased pressure drop across the catalyst tubes as well as increased tube temperatures. Pressure drop should be monitored as prescribed in the OEM instruction manual or PM task list. A potential cause of tube temperature variation can be carbon formation, which will first show up as increased tube wall temperatures.

The reformer tubes and outlet system are operated at high temperatures close to the limit of metallic materials. The result is that the tubes undergo a permanent deformation with time called creep. The reformer tubes are designed for a given operating life (e.g., 100 000 hours operation) at conditions equal to or less severe than design. Operation in more severe conditions (higher operating pressure or higher operating temperature) is possible for short periods but will decrease the reformer tube or outlet system life.

The temperatures of the high-alloy reformer tubes and gas manifolds should not be increased beyond the design limit for the operating pressure. Excessive temperature considerably reduces the service life of these parts. In case of doubt, the steam reformer operating temperature should be reduced until the situation has been clarified.

The reformer outlet system should be inspected periodically. If the outlet piping is of a high alloy material with no internal or external insulation, visual checks are recommended. If the outlet piping has internal or external insulation, it should be visually examined as well as inspected with a thermal camera to check for hot spots. See CGA H-12 for more information [23]. The reformer tubes, outlet system, and catalyst may not be designed to last the contract life of the plant. Long-term maintenance planning should include replacement of the catalyst and tubes if required based on expected life and/or results of inspections.

9.3.3.3.1 Reformers that operate at positive pressure

Some reformers that operate at positive pressure have glass viewports that enable some internal inspection, but many reformers that operate at positive pressure on the flue gas/fuel side cannot be inspected via viewports during normal operation. Instead, periodic inspection of the external surface of refractory-lined equipment (e.g., with a thermal camera or infrared thermometer) should be considered as a means of identifying hot spots, although this will not detect problems with the reformer tubes. It is important to monitor for changes in operating conditions and plant performance as indicators of potential problems.

If possible, based on the reformer configuration, the reformer burners should be visually inspected on a regular basis via the reformer viewports. The burners are assessed to determine if the flames are impinging (touching) on the reformer tubes and to assess the flame color, stability, and shape. Flame impingement is one of the major causes of damage to a reformer tube. If impingement is noticed, the burner should be adjusted or turned off without delay.

Operators should be aware of the appropriate flame shape and color for the burner that is in use. This information should be part of the OEM instruction manual.

9.3.3.3.2 Reformers that operate under vacuum

Some reformers that operate under a slight vacuum on the flue gas/fuel side can be inspected internally via viewports while the plant is in operation. If the viewports have to be opened to conduct furnace monitoring, the operator can be exposed to hot flue gases from the inspection ports if the furnace pressure goes positive while performing these tasks. To reduce the hazards, personnel:

- Shall be equipped with the appropriate PPE; and
- Should stand to the side of the opening while slowly and carefully opening the inspection port to avoid exposure to hot combustion gases and heat radiation.

See CGA H-10 for more guidance on on-line reformer inspections [5].

Where possible, tube wall temperatures should be monitored regularly, and tube temperatures should be logged or recorded along with the corresponding operating plant data. Visual inspections of the reformer tubes should be conducted on a regular basis (e.g., as part of operator rounds), as tube wall temperature can be inferred from the tube color: the hotter the metal, the lighter/brighter the color. There is typically a gradual change in tube color from top to bottom of the furnace, and all tubes should exhibit similar coloration. Infrared pyrometers are a good way to check and record temperatures. Discoloration patterns such as mottling, banding, striping, and localized spotting are indicative of local hot spots. The visual inspection also should assess the mechanical condition of the tubes, such as bending or leaking. A tube leak can be identified by sound or by observing an unusually bright spot (possibly with visible flame). If there is a severe imbalance in the reformer tube temperatures, the situation should be analyzed by qualified personnel.

Table 1 summarizes how tube appearance allows one to make conclusions regarding the cause of catalyst deactivation or other issue.

If possible, based on the reformer configuration, the reformer burners should be visually inspected on a regular basis via the reformer viewports. The burners are assessed to determine if the flames are impinging (touching) on the reformer tubes and to assess the flame color, stability, and shape. Flame impingement is one of the major causes of damage to a reformer tube. If impingement is noticed, the burner should be adjusted or turned off without delay.

Operators should be aware of the appropriate flame shape and color for the burner that is in use. This information should be part of the OEM instruction manual.

Table 1—Reformer tube appearance, causes, and remedies

Tube Appearance	Causes	Remedies
Hot bands Clearly defined hot bands	• Catalyst activity has decreased by poisoning and/or the surface has become coated by a thin layer of carbon • Catalyst is too old for further use	• Increase steam-to-carbon ratio • Steam the catalyst • Discharge and refill catalyst at a suitable opportunity
Tiger tailing Clear and well-defined hot rings, alternating with cooler rings	• Voids in the catalyst bed • Catalyst bridging due to improper loading	• Vibration or careful hammering of catalyst tube; potential need to add catalyst for proper filling to the top • Discharge and refill catalyst at a suitable opportunity
Giraffe necking Random hot zones or patches	• This is generally the first sign that catalyst activity is declining due to age or poisoning (sulfur is most common)	• Steam the catalyst • Discharge and refill catalyst at a suitable opportunity
Hot tubes The whole tube is overheated	• Extensive carbon deposition • Catalyst breakage or material in inlet header restricts the gas flow and the tube gets overheated • Flow distribution issues causing low flow	• Catalyst in hot tubes should be discharged and replaced at the next opportunity • When all tubes are hotter than expected, visual inspection should be confirmed with infrared pyrometer or other method
Hot tubes The top section (less than 1 m) is overheated	• Settling of catalyst bed during operation; top section of tube not filled with catalyst due to improper loading or breakage	• Add catalyst to fully load the catalyst tube

9.3.3.4 Feed pretreatment (desulfurization)

The expected life of the desulfurizer catalyst (adsorbent or chemisorbent) will vary with the amount and type of sulfur in the feed, and the volume of the adsorbent or chemisorbent would have been determined based on an assumed feed composition and design life. Some (typically larger) hydrogen plants are configured with lead/lag desulfurizer beds such that the chemisorbent can be changed on-line; otherwise, the design life of the desulfurizer adsorbent or chemisorbent typically is set based on the maintenance turnaround interval. It is possible to use one or more reactor vessels and install one or multiple layers of catalyst and absorbent (e.g., hydrotreating catalyst, chloride guard bed, sulfur absorbent).

A breakthrough of sulfur will damage the reformer catalyst. Therefore, it is recommended to monitor the level of sulfur compounds in the incoming feed gas and to check for the breakthrough of sulfur compounds both partway through the desulfurizer bed (if applicable) and downstream of the desulfurizer bed as prescribed in the OEM instruction manual or PM task list to check for breakthrough. The life of the adsorbent/chemisorbent will vary nearly linearly with the sulfur content in the feed.

Specific gas sample tubes can be used for streams containing sulfur to get an indication of the sulfur level. Precautions should be taken during sampling since the gas is flammable and, depending on the sulfur level, could be toxic. In many cases the gas to be sampled is also hot, and a sample cooler should be used following plant procedures.

If sulfur compounds are detected at the desulfurizer outlet, the adsorbent or chemisorbent should be replaced. If sulfur is detected partway through the desulfurizer, the remaining life of the adsorbent or chemisorbent should be estimated based on the sulfur level in the feed and plans made accordingly. Guidance on safe catalyst handling is available in CGA H-15 [13].

9.3.3.5 CO-shift reactor

When the CO-shift catalyst is working per design, the temperature increase over the catalyst bed will be within the range given by the supplier. For a fixed inlet temperature, the temperature rise will decrease with time as the catalyst deactivates, so the expected temperature rise typically is given as a range rather than a fixed value. If the temperature rise is lower than the given span, the inlet temperature of the CO-shift reactor should be checked against the design value. The inlet temperature of this catalyst bed is usually adjustable by manipulation of a bypass in the syngas cooler upstream. If the inlet temperature has been adjusted to its maximum and the temperature rise is below target, then further investigation is warranted; and the catalyst could require change-out.

Status of the shift catalyst can be monitored (or confirmed) by regular syngas sampling for methane, hydrogen, carbon monoxide, and carbon dioxide content as prescribed in the OEM instruction manual or PM task list. An increase in carbon monoxide in the PSA feed can indicate shift catalyst deactivation.

9.3.3.6 Boiler feed water/boiler water chemistry

The boiler feed water treatment system (to produce high purity water) should be inspected periodically as prescribed in the OEM instruction manual or PM task list. Potential areas of interest include the raw/treated water storage tanks, filtration systems, reverse osmosis or demineralization systems, analyzers, etc., cleaning, repairing, or replacing as necessary.

High-purity BFW and steam drum water should be analyzed periodically as prescribed in the OEM instruction manual or PM task list. A dedicated sample stream with a sample cooler should be used. Periodicity depends on the number of online analyzers available for monitoring the water chemistry in these two locations and on other factors such as variation in source water quality or plant load. The water chemical dosing system flow rate is adjusted based on the test results (e.g., conductivity, hardness, oxygen content, pH-value).

Steam drum blowdown (continuous and intermittent) is adjusted based on steam drum water conductivity. If the conductivity is too high, the blowdown flowrate or frequency needs to be increased.

It is recommended to have a consequences of deviation table or technical assurance document specific to boiler water chemistry that defines the parameters to be monitored, the normal operating range, actions to be taken if outside of the normal range, and potential adverse effects when outside of the normal operating range.

9.3.3.7 Cooling tower/cooling water chemistry

Based upon the design of the plant, there may be cooling water supplied from outside the battery limit, a cooling tower, or a closed loop cooling system. Regardless of the type of system, the circulating cooling water should be monitored for treatment chemical content and biological activity.

Cooling water chemistry should be checked regularly per the site OEM instruction manual or PM task list to verify that key physical and chemical parameters are within the expected range. These checks could be conducted by the water treatment provider. Typical parameters that are checked are both chemical properties (e.g., free chlorine, halogens) and physical properties (e.g., total dissolved solids, pH, conductivity). The “cycles of concentration” of the cooling tower should also be evaluated. Biological activity should be monitored and controlled by the addition of biocides. There can be local regulatory requirements regarding the monitoring and treatment of legionella.

It is recommended to have a consequences of deviation table or technical assurance document specific to the cooling water chemistry that defines the parameters to be monitored, the normal operating range, actions to be taken if outside of the normal range, and potential adverse effects when outside of normal operating range.

If the site includes a cooling tower, it should be inspected regularly per the OEM instruction manual or PM task list. Typical on-line checks include an assessment of general system cleanliness, fill material condition, water level, water distribution system operation, and fan operation. It is also advised to check periodically for combustible gases at the cooling tower. If combustible gases are detected, it could indicate a leak in one of the process gas exchangers.

If the unit is fitted with a closed loop cooling system, the following inspections can be made. The pipework should be visually inspected for the presence of leaks, and the specially fitted bleed points should be checked for the presence of entrapped air. In addition, the operator should listen to the piping for any audible indications of the presence of vapor in the lines. A visual inspection of the control panel should be made to confirm proper operation. It should be verified that the system is operating at the recommended pressure.

9.3.3.8 Water purification system

Depending upon the incoming water purity, various purification systems may be employed to meet vendor specifications. Typically, a conductivity analyzer is used to confirm quality, and this should be periodically checked. Leak tightness should be checked with a visual inspection for leaks. Supply water pressure should be checked. Pressures and flows should be compared to values supplied with the system at commissioning.

9.3.3.9 Pressure swing adsorption

The PSA vessels and piping between the PSA vessels and the switch valves cycle between high pressure during adsorption and low pressure during desorption. As such, the piping and vessels in this section of the PSA are in cyclic service and are subject to fatigue damage mechanisms. The sections of piping used to equalize pressure between vessels during the cycle also can be in cyclic service and subject to fatigue damage mechanisms. The control valves and associated components are subject to high cycle wear and tear. See CGA H-13, *Hydrogen Pressure Swing Adsorber (PSA) Mechanical Integrity Requirements* for more details [24].

The PSA system shall be included in periodic rounds. Rounds observations should include gas detection to determine if there are any gasket or packing leaks as well as listening to operation for abnormal sounds such as the whistling of leaking gas. Due to a variety of factors such as weather, significant leaks can remain undetected by fixed gas monitors. Note that leaks that occur in the piping or vessels subject to cyclic service can escalate rapidly.

9.3.4 Methanol cracker plant; on-line inspections/monitoring

This section covers some of the more common on-line inspections that should be conducted at methanol cracker hydrogen production plants. Not all of the inspections will be applicable to all plants, and the OEM instruction manual should be consulted.

9.3.4.1 Leak checks

The areas where leaks most commonly occur are the methanol feed system (e.g., storage, pumps, preheater, vaporizer, fuel, etc.), outlet of the reactor/process gas cooler, and the pressure swing adsorber unit. Leaks generally occur more frequently wherever multiple flanged connections exist, wherever valves are present that could develop packing leaks, and whenever there are frequent startup/shutdown cycles that cause the unit to cycle from hot to ambient. Leaks in cyclic service piping or equipment can escalate rapidly.

Temporary leak repair devices such as clamps shall be inspected at regular intervals, and their fitness for continued use should be regularly assessed. See 9.3.1 for more information.

9.3.4.2 Reactor catalyst and tubes

Status of the reactor catalyst can be monitored by regular sampling for methanol, hydrogen, carbon monoxide and carbon dioxide content in the syngas as prescribed in the OEM instruction manual or PM task list. An increase in methanol slip (methanol value) can indicate reactor catalyst deactivation. If regular syngas sampling is not conducted, plant performance should be monitored for indications of degradation; and any indications of degradation warrant further investigation. As the reactor catalyst deactivates, the amount of methanol required to produce a fixed amount of hydrogen increases, the recovery of the PSA decreases, and the make-up fuel consumption also decreases (because the PSA tail gas flow increases). Because the PSA could be configured to run conservatively (i.e., more pure hydrogen than required), changes in performance could first manifest as changes in product purity, which initially could go unnoticed. Temperature indication across the length of the catalyst tube can be used to monitor the condition of the catalyst. The temperature probe, where fitted, has measurement points along the length and when trended over time gives an indication of the transient front moving through the catalyst tube, and hence when the catalyst is nearing end of life.

Carbon deposits on the catalyst can cause increased pressure drop across the catalyst tubes as well as increased tube temperatures. Pressure drop should be monitored as prescribed in the OEM instruction manual or PM task list. A potential cause of tube temperature variation can be carbon formation, which will first show up as changes in the temperature profile.

9.3.4.3 Fired heater

If possible, based on the equipment configuration, the fired heater burner(s) should be visually inspected on a regular basis via the viewports. The burners are assessed to determine if the flames are impinging (touching) on the tubes and to assess the flame color, stability, and shape. Flame impingement is one of the major causes of damage to a tube. If impingement is noticed, the burner should be adjusted or turned off without delay.

Operators should be aware of the appropriate flame shape and color for the burner that is in use. This information should be part of the OEM instruction manual.

Many fired heaters operate under a slight vacuum on the flue gas/fuel side and can be inspected internally via viewports while the plant is in operation. If the viewports have to be opened to conduct monitoring, the operator can be exposed to hot flue gases from the inspection ports if the pressure goes positive while performing these tasks. To reduce the hazards, personnel:

- shall be equipped with the appropriate PPE; and
- should stand to the side of the opening while slowly and carefully opening the inspection port to avoid exposure to hot combustion gases and heat radiation.

See CGA H-10, portions of which are applicable to fired heaters, although the publication was developed for reformers [5].

9.3.4.4 Hot oil system

Hot oil quality has a significant effect on heat transfer efficiency. The expected life of the hot oil will vary with the design and actual operating conditions. The oil should be sampled and analyzed periodically to ensure the quality is within recommended working condition and specifications. The most important parameters include acid number, viscosity, flash point, and carbon residue (refer to the OEM instruction manual). If the hot oil has degraded and the oil parameters are outside of the allowable range, replacement could be necessary.

9.3.4.5 Reactor feed water chemistry

The reactor feed water treatment system (to produce high purity feed water) should be inspected periodically as prescribed in the OEM instruction manual or PM task list. Potential areas of interest include the raw/treated water storage tanks, filtration systems, reverse osmosis or demineralization systems, analyzers, etc. The equipment should be cleaned, repaired, or replaced as needed based on inspection.

The high purity feed water should be analyzed periodically as prescribed in the OEM instruction manual or PM task list. A dedicated sample stream should be used. Periodicity depends on the number of online analyzers available for monitoring the water chemistry and the variation in source water quality. The water chemical dosing flow rates are adjusted based on the test results (e.g., conductivity, hardness, oxygen content, pH-value).

It is recommended to have a consequences of deviation table or technical assurance document specific to feed water chemistry that defines the parameters to be monitored, the normal operating range, actions to be taken if outside of the normal range, and potential adverse effects when outside of normal operating range.

9.3.4.6 CO-shift catalyst

See 9.3.3.5 for discussion and recommendations.

9.3.4.7 Cooling tower/cooling water chemistry

See 9.3.3.7 for discussion and recommendations.

9.3.4.8 Water purification system

See 9.3.3.8 for discussion and recommendations.

9.3.4.9 Pressure swing adsorption

See 9.3.3.9 for discussion and recommendations.

9.3.5 Electrolyzer; on-line inspections/monitoring

This section covers some of the more common on-line inspections that should be conducted at alkaline water electrolysis and PEM water electrolysis hydrogen production plants. Not all the inspections will be applicable to all plants, and the OEM instruction manual should be consulted.

9.3.5.1 Leak checks

The integrity of the water supply system should be checked regularly as prescribed in OEM instruction manual or PM task list, as leaks can allow the growth of algae and affect the purity of the water supply.

In alkaline electrolysis plants, frequent checks of electrolyte or water leaks in the piping, valves, pumps, heat exchangers, the header tanks and other equipment used in the process are critical for safe operation of the electrolyzers. Beneath each cell stack a collecting tray may be used for catching any aqueous potassium hydroxide solution that leaks from the system. A visual inspection of this and the pipework above and below the cell stack can catch leaks before they become a problem such that plans for repair can be incorporated into the maintenance schedule. A check should be made not only for liquid but also for the white crystalline staining that is left behind when the water from aqueous potassium hydroxide has evaporated.

In PEM water electrolysis systems, similar checks for hydraulic fluid and water leaks in the piping, valves, pumps, heat exchangers, header tanks, and other equipment are also critical for safe operation and should be conducted regularly as prescribed in the OEM instruction manual.

Temporary leak repair devices such as clamps shall be inspected at regular intervals, and their fitness for continued use should be regularly assessed. See 9.3.1 for more information.

9.3.5.2 Water purification system and auxiliaries

Depending on the incoming water purity, various purification systems may be employed to meet vendor specifications. Potential areas of inspection include the raw/treated water storage tanks, filtration systems, reverse osmosis or demineralization systems, analyzers, etc., cleaning, repairing, or replacing as necessary. Supply water pressure should be checked, and pressures and flows compared to values supplied with the system at commissioning. The remaining run time for the (on-line) filter bed should also be checked.

The high purity feed water should be analyzed periodically as prescribed in the OEM instruction manual or PM task list. A dedicated sample stream should be used. Periodicity depends on the number of online analyzers available for monitoring the water chemistry and the variation in source water quality. The calibration of the conductivity sensor and any other online analyzers should be checked as prescribed in the OEM instruction manual or PM task list.

It is recommended to have a consequences of deviation table or technical assurance document specific to feed water chemistry that defines the parameters to be monitored, the normal operating range, actions to be taken if outside of the normal range, and potential adverse effects when outside of normal operating range.

9.3.5.3 Vent lines and water seals

A visual inspection of the vent lines should include the water seals at the base of each vent stack confirming the presence of water and the integrity of the overflow. The temperature of the lines should be checked, as a hot vent line can indicate problems with gas cooling. The external section of the vent lines should also be checked for the possibility of blockage or freezing and to ensure no damage has occurred. If a leak is suspected, a closer inspection can be made with a leak detection fluid.

9.3.5.4 Hydrogen to oxygen and oxygen to hydrogen analyzers

The hydrogen to oxygen (HTO) analyzer measures the hydrogen in oxygen because it is faster reacting for control purposes, and the oxygen to hydrogen (OTH) analyzer (if present) measures the hydrogen purity to the deoxo unit. The HTO (and OTH, if present) analyzer and its associated pipework should be visually inspected for damage, blockage, or leaks as prescribed in the OEM instruction manual or PM task list. It should also be verified that the HTO (and OTH, if present) analyzer is receiving the correct flow and that no water vapor or condensation is present in the sample line. An in-line replaceable desiccant unit is typically installed in the sample line. The condensation pot in the system should remove the unwanted water droplets, but this needs to be checked to prevent the drying agent from being used up. The drying agent will change color when it is saturated with moisture. The desiccant should be replaced when this is noticed or when an online indicator indicates that the drying agent is at end of life.

9.3.5.5 Dryer systems

The drying systems (deoxo dryer and/or dehydro dryer), if present, should have the following visual inspections made whenever possible.

The flow of gas to the regenerating bed of the dryer should be checked during the appropriate phases of the dryer operation. Adjustments can be made using the regulating valve on the flow meter.

The pressure of the regenerating bed of the dryer should be checked during the appropriate phases of the dryer operation. Pressure in the regenerating bed should be just above atmospheric pressure. Adjustments can be made by adjusting the hand valves to drain on the system.

9.3.5.6 Auxiliaries—closed loop cooling (cooling tower/cooling water chemistry)

See 9.3.3.7 for discussion and recommendations.

9.3.5.7 Auxiliaries—chiller

If a chiller unit is present in the system, pressure in the system should be checked and maintained at the recommended value as prescribed in the OEM instruction manual or PM task list. The pipework should be visually inspected for the presence of leaks, and the specially fitted bleed points should be checked for the presence of entrapped air. In addition, the operator should listen to the piping for any audible indications of the presence of vapor in the lines. A visual inspection of the control panel should be made to confirm proper operation. Any malfunctions are typically displayed in the control system.

9.3.5.8 Water purification system

See 9.3.3.8 for discussion and recommendations.

9.4 Remote operation and observation

Remote operation of a production plant offers several advantages over local operation but does not remove the requirement for certain local operations or inspection. New plants may be designed for remote operation (and potentially remote start), and existing plants may be modified for remote operation if those capabilities do not initially exist.

There are a few situations where local manpower is required at site and the exact details of these will vary location by location. The below list is not intended to be all-inclusive:

- In response to multiple or specific plant trips or alarms;
- During startups following an extended shutdown, the plant requires at least one operator at the plant. This is to do pre-start checks (e.g., check for flange leaks), operation of nonautomated valves, and clearing of all work permits;

- During commissioning, additional personnel (e.g., experienced operator, supervisor, plant engineer, instrument technician, etc.) shall be present or available until unit is operational and site staff are adequately trained;

- During normal plant operation, certain routine operations need to be carried out at the plant (e.g., checks for leaks, hot spots, unusual audible noise for machinery, etc.); and

- Routine monitoring, operations, and on-line maintenance all require periodic plant visits.

Remotely operated plants are designed such that important controllers operate in automatic or cascade mode, requiring minimal supervision. This ensures that the plant is operating as efficiently and safely as possible during normal operation.

Monitoring of multiple remotely operated plants can be conducted from one location, allowing much more efficient operation through consistent application of operations best practices, and rapid application of new ideas to all plants that are controlled centrally.

However, unless additional monitoring devices are installed, remote operators might not detect the noise or visual indicators that could be associated with a mechanical equipment failure (such as tube rupture or heat exchanger leaks); nor can they develop the experience and knowledge gained through regular plant rounds. The remote operation system totally relies on the plant's automatic trip and interlocking systems. Other issues can include a longer time lag between a plant failure and when the plant trips or the longer time that it takes to attend and inspect the failure. Therefore, there shall be a carefully considered assessment of the risk associated with remote operation before remote operation can go ahead.

During normal operation, the plant operates steadily, and less attendance is required. There are enough alarm and trip systems to alert the operator well in advance before the plant operation becomes hazardous. In addition to regular monitoring of key parameters via the control system, the most common procedures that can be done remotely during normal operation are:

- changing plant load (if not done automatically by the control system);

- changing compressor operation;

- changing plant operating modes;

- monitoring the plant during startup or shutdown;

- startup and shutdown of the plant (where designed for this purpose).

10 Maintenance considerations

To ensure safe operation of the hydrogen generation plant, regular maintenance is required, both on-line and off-line. Maintenance recommendations should be part of the documentation package provided by the equipment and/or plant supplier. Maintenance can be performed both on-line when the unit or part of the unit is running and off-line when the entire unit is shut down.

In some cases, the plant does not need to be shut down to conduct a repair or maintenance (e.g., replace a temperature element in a thermowell, replace a fire eye, conduct thickness checks on a section of piping or vessel). Leak repair is another possible online maintenance activity and may consist of a temporary remediation such as a clamp or a permanent repair such as replacing a control valve while the control valve is isolated and bypassed (see CGA H-14 for more information) [4]. For cases where on-line maintenance is considered, it shall be evaluated whether the plant can continue to operate safely (e.g., with a faulty or missing instrument reading) and whether the maintenance can be conducted safely (e.g., process and piping does not have to be opened to atmosphere, or a section of the plant can be adequately isolated from the rest of the plant).

Off-line maintenance can include catalyst replacement, cell stack replacement, mechanical integrity inspections, regulatory inspections, equipment cleaning, equipment repair or replacement, modifications to improve performance or change plant capacity, etc. Mechanical integrity inspections should take into consideration corrosion mechanisms, metallurgy, and operating conditions, including conditions during turndown, startup, and shutdown. The inspection method used to detect or monitor corrosion should be appropriate to the corrosion mechanism(s), which could be present in a given section of the plant. CGA H-12 provides guidance for corrosion and failure mechanisms associated with different reformer outlet systems [23]. CGA H-13 provides guidance for corrosion and other failure mechanisms associated with PSAs [24]. CGA H-13 also provides guidance on inspection techniques applicable to the corrosion/failure mechanisms associated with PSAs [24].

Prior to conducting off-line maintenance, the plant or system shall be shut down, isolated, and prepared for maintenance. It is a good idea to record key operating parameter values prior to shutting down the plant (e.g., take screen shots from the plant control system) if not automatically done as part of plant datalogging. These can be used when the plant is starting up and to compare performance before and after maintenance. All maintenance shall be conducted under the plant's permit to work system. Activities that involve confined space, high-voltage electricity, or hot work typically require an additional special permit. Other nonstandard activities (e.g., crane work, excavation) could also require an additional, activity-specific permit.

Some parts or equipment (e.g., thermocouples, transmitters, fire eyes) can have a relatively short life span. These items should be available in spare parts inventory to facilitate more rapid replacement. Spare parts recommendations should be part of the maintenance documentation package received with the equipment or plant. Additional spare parts or materials could be required depending on the planned offline maintenance activities.

If any part of the plant has to be replaced, it should be replaced in kind, or the plant's MOC process shall be followed. Adequate reviews of the proposed change shall be conducted by knowledgeable individuals of the appropriate disciplines (e.g., process, mechanical, electrical, controls, materials, etc.) to ensure that the proposed change does not have any unintended consequences.

See CGA P-91, *Plant Integrity Management*, API 510, *Pressure Vessel Inspection Code*, and API 570, *Piping Inspection Code* [25, 26, 27].

10.1 Maintenance planning

One of the initial steps in planning for maintenance or for a maintenance turnaround is to develop the list of maintenance tasks. Some of these will come from the recommendations in the documentation package provided by the equipment and/or plant supplier. Others will have been identified during on-line inspections/rounds. Still others will be to effect permanent repairs of previous temporary repairs (e.g., leak repair devices). This last category of tasks is often overlooked but is extremely important to address.

Once the maintenance list has been developed, the operator can develop the maintenance schedule and identify the resources required. Certain tasks (e.g., high voltage electrical work) require specially trained personnel. Other tasks (e.g., confined space entry) require additional personnel in order to conduct them safely.

Prior to shutting down the unit for maintenance, the operator should plan to have the required parts, equipment, tools, utilities, and procedures required to complete the maintenance tasks. Some of the other maintenance planning considerations are listed here. This list might not be all inclusive due to the individual design of plant equipment, and some procedures might not be applicable for all small hydrogen generation units:

- schedule of work to avoid interference between different maintenance activities;
- consideration of potential impacts on adjacent surroundings, such as businesses, homes, or roadways;
- adequate lighting for nighttime work;
- accessibility to equipment, (e.g., platforms, scaffolding, or personnel lift);
- cranes and lifting equipment, lift procedures;
- utility availability (compressed air, power, nitrogen for inerting, water, calibration gases);
- confined space entry preparations;

- portable office and utility trailers (see CGA P-64, *Guideline for the Location of Occupied Buildings in Industrial Gas Plants*, for guidance on siting [28]);
- supply of backup hydrogen (gas/liquid);
- assessment of potential impact of sections of plant that were not inerted, or electrically isolated (made safe) for maintenance;
- notification of customers;
- storage of equipment and spares prior to the work commencing and during work;
- safety training for personnel not based at site; and
- waste handling (see Section 8).

10.2 Plant preparation for maintenance

Prior to conducting maintenance work on the plant, the plant shall be prepared for maintenance. The relevant section of the plant shall be isolated, and it shall be verified that the relevant equipment cannot be put into operation. This is handled through the lockout/tagout work process (see 4.5). If the equipment or piping will be open to atmosphere during maintenance, systems containing flammable or toxic material shall be purged with nitrogen to remove the flammable or toxic material and replace it with an inert material. Oxygen piping shall be similarly purged. After depressurization, the system may be opened, allowing exposure to air. It is the operator's responsibility to take all measures to ensure that maintenance can be safely conducted and that the plant or equipment system cannot be put into operation automatically or by mistake.

The lockout/tagout process is also used for electrical equipment. For medium and high voltage equipment there are specialized requirements for the addition of temporary grounding. This grounding is a form of personnel protection and provides a safe path for current that has erroneously been introduced into the work area. All electrical switching (low, medium, and high voltage) and temporary grounding (medium and high voltage) operations require specially qualified personnel and special PPE for arc flash protection. See NFPA 70E, *Standard for Electrical Safety in the Workplace*® for details on this PPE requirement [29].

For more details on the requirements of purging out of service, consult NFPA 56, *Standard for Fire and Explosion Prevention During Cleaning and Purging of Flammable Gas Piping Systems* [30]. Even though some portions of a small hydrogen production unit are outside of the scope of NFPA 56, it is recommended that all cleaning and purging be done in accordance with NFPA 56 [30]. Any purging or venting activity shall consider ignition sources (e.g., engine-driven equipment, nonclassified electrical equipment, temporary equipment) in and around the hydrogen production unit or adjacent units or facilities (e.g., vehicle fueling stations). Flammable gas shall be vented to a safe location so that the vented gas does not come into contact with any ignition source.

10.3 Maintenance of individual components

Maintenance requirements for the overall plant and for individual components should be specified in the documentation package provided by the supplier, including any sub-supplier documentation. CGA H-12 provides guidance on maintenance requirements of syngas outlet systems, some of which could be applicable to the outlet systems of small thermal-based hydrogen production units, although H-12 was written around large SMRs [23]. CGA H-13 provides guidance on maintenance considerations for pressure swing adsorption units, which could be applicable to PSAs associated with small thermal-based hydrogen production units [24].

It is recommended to create a detailed maintenance plan based on this information which defines what type of checks need to be done, on what equipment or item, and at what frequency. This is particularly important for safety-critical equipment (e.g., ambient air monitors, steam drum level instrumentation, safety valves, electrolyzer HTO and OTH analyzers, etc.), and maintenance plans shall be developed for all safety-critical devices.

An example maintenance plan/chart is provided in Table 2. This can also be programmed in an electronic maintenance planning system. When maintenance is conducted, the date of maintenance and any findings should be recorded. These records can be used for future maintenance planning (e.g., identify timing of replacement of components) and to identify systemic or ongoing issues.

Depending on the size of the plant, component inspection could require confined space entry into a vessel or other equipment item, or inspection could be conducted externally or via borescope or other inspection method or device. If confined space entry is required, appropriate precautions shall be taken when preparing and isolating the equipment for entry and during the equipment entry.

Table 2—Sample maintenance plan

Item	Type of check	Daily or shift	Weekly	Monthly	Every 3 months	Every 6 months	Yearly	Other
On-line checks	Plant walkaround, calibrations	Per plant or equipment supplier						
Safety-critical instrumentation	Function checks	Per plant supplier						
Pressure vessels	Regulatory inspections	Based on regulatory/local authority requirements						
Boiler/steam generator	Regulatory checks	Based on regulatory/local authority requirements						
Rotating machinery	Lubrication/vibration	As per machinery suppliers' recommendations						
Safety valves	Regulatory inspection, refurbish/replace as required	Based on regulatory requirements or on service conditions						
NOTE—This list is incomplete and used as an example. Extend and revise as required								

10.3.1 Steam methane reformer plant; maintenance of individual components

As noted in 10.1, a maintenance list should be developed based on guidelines in the OEM instruction manual and any maintenance defects identified during online inspections. Maintenance required for some of the more technology-specific components are summarized here. CGA has developed safety guidelines associated with some of these, but these guidelines were written for large hydrogen production units and could require adaptation for smaller thermal units due to differences in materials of construction and plant configuration:

- Reformer firebox—The interior of this unit runs at high temperature and components are subject to creep and other damage mechanisms. Check major components and refractory and insulation for signs of wear or damage. See CGA H-10 for more information [5]. The reactor tubes and collection headers could require replacement during plant lifetime. Condition monitoring and remaining life estimates are recommended in order to adequately plan for this major maintenance activity;

- Catalyst—Any of the reactors or adsorbers could require catalyst or chemisorbent replacement at regular intervals. See CGA H-15 for more information [13]. Condition monitoring and remaining life estimates are recommended in order to adequately plan for this major maintenance activity;

- Reformer outlet systems—The outlet system is subjected to high temperature and pressure. Hot outlet systems are externally insulated, and the piping (pressure boundary) operates at the syngas outlet temperature. Cold outlet systems are internally insulated, and the piping (pressure boundary) operates at low temperature. Externally insulated components can be subject to creep damage. Internally insulated (refractory lined) components can be subject to high temperature hydrogen attack, and the refractory will degrade (cracking and spalling) with time. Because of the severity of the service, regular inspections are required, and periodic repairs can also be required. These components can have a defined service life (less than plant design life) that is influenced (positively or negatively) by the operating conditions of the plant. See CGA H-12 for more information [23];

- Boiler feedwater, steam generating, and steam transport systems—Typically, the water in these systems contains enough chloride to induce stress corrosion cracking in stainless steel. The BFW system between the deaerator and the steam drum can be susceptible to flow accelerated corrosion. Control valves can be subject to erosion. BFW pumps can be subject to cavitation. Scheduled maintenance activities and mechanical integrity program inspections should consider these failure mechanisms when planning work;

- Cooling water system—Open loop cooling systems (those with a cooling tower) are subject to dirt and foreign object intrusion. Heat exchangers containing cooling water should be opened on a periodic basis to check for fouling or accumulated debris. Cooling performance (heat exchangers and tower) should be monitored in order to adequately plan for scheduled maintenance activity. Cooling towers require basin cleaning and packing replacement on periodic intervals. During scheduled maintenance, the cooling tower structure (particularly if wood) should be inspected and repaired as required; and

- PSA—PSA vessels and piping are in cyclic service and subject to fatigue failure; therefore, periodic inspections for defects in the adsorber vessel welds are typically required. These components should be covered by a mechanical integrity program. See CGA H-13 for more information. Valves and other instrumentation (e.g., limit switches) require periodic replacement [24].

10.3.2 Methanol cracker; maintenance of individual components

As noted in 10.1, a maintenance list should be developed based on guidelines in the OEM instruction manual and any maintenance defects identified during online inspections. Maintenance required for some of the more technology-specific components are summarized here. CGA has developed safety guidelines associated with some of these, but these guidelines were written for large hydrogen production units and could require adaptation for smaller thermal units due to differences in materials of construction and plant configuration:

- Reactor/fired heater—The interiors of these units run at high temperature, and components can be subject to creep and other damage mechanisms. Check major components and refractory and insulation for signs of fouling, wear, or damage. Check burner and ignition electrode for condition, fouling, coking, orientation, and carbon deposition, etc. See CGA H-10 for more information [5];

- Catalyst—Any of the reactors could require catalyst replacement at regular intervals. See CGA H-15 for more information [13];

- Reactor outlet systems—The interior of the outlet system is subjected to high temperature, pressure, and hydrogen attack, while the outside is subjected to ambient conditions. Because of the severity of the service, periodic inspections and replacements can be required. These components can have a defined service life (less than plant design life) which is influenced (positively or negatively) by the operating conditions of the plant. See CGA H-12 for more information [23]; and

- PSA—PSA vessels and piping are in cyclic service and subject to fatigue failure, therefore periodic inspections for defects in the adsorber vessel welds are typically required. These components should be covered by a mechanical integrity program. See CGA H-13 for more information. Valves and other instrumentation (e.g., limit switches) require periodic replacement [24].

10.3.3 Electrolysis; maintenance of individual components

As noted in 10.1, a maintenance list should be developed based on guidelines in the OEM instruction manual and any maintenance defects identified during online inspections. Maintenance required for some of the more technology-specific components are summarized here but this list is not all inclusive due to differences in materials of construction and plant configuration.

10.3.3.1 Alkaline water electrolysis system

- Electrolyzer—Check piping, fittings, valves, and connections to the electrolyzer for leaks and presence of dried caustic. Perform analysis of the electrolyte for concentration and for presence of other impurities. Check insulation and isolation integrity. Replace cell components as needed or based on manufacturer recommendations;

- Header tanks (anolyte/catholyte)—The header tanks are exposed to caustic solution and oxygen at higher temperatures. Perform required mechanical integrity inspections;

- Filters (electrolyte and product gases)—Filters may be present in the electrolyte loop and/or product gas stream to remove any mist and to prevent carryover of electrolyte or other foreign matter to the downstream compression and purification. Perform inspections as specified by the manufacturers;

- Product compression and drying—Perform inspections as specified by the manufacturers;

- Purification equipment (deoxygenation and oxygen purification, if present)—Perform inspections as specified by the manufacturers;

- Heat exchangers (electrolyte and product gases)—Perform required mechanical integrity inspections;

- Pumps—Inspect for leaks; perform periodic overhaul per OEM instruction manual;

- Hydrogen and oxygen vents—Check vents for blockages;

- Electrical (transformer/rectifier, busbars, cabinets, isolators)—Check for ground faults, inspect heat exchanger loop and equipment, inspect isolators, insulation, and electrical connections. Clean or replace cabinet filters as necessary;

- Instrumentation—Inspect analyzers (gas/water/electrolyte) for leaks or blockages in the sampling loop and perform process analyzer calibration and/or overhaul per OEM instruction manual. Inspect and calibrate other instruments per manufacturer's recommendations;

- Demin water system—Perform inspections as specified by the manufacturer. Periodic replacement of the ion exchange resin can be required; and

- System enclosure (if applicable)—Check or function test ventilation system, atmospheric gas sensors, heat sensors, and any other safety monitoring equipment as applicable.

10.3.3.2 Proton exchange membrane water electrolysis system

- Demin water system—Perform inspections as specified by the manufacturer. Periodic replacement of the ion exchange resin can be required;

- Hydrogen and oxygen vents—Check vents for blockages;

- Filters—Perform inspections and replace filter elements periodically as specified by the manufacturers;

- PEM cell stack—Check piping, fittings, valves, and connections for leaks. Check insulation and isolation integrity. Replace cell components as needed or based on the OEM instruction manual;

- Instrumentation—Inspect analyzers (gas/water) for leaks or blockages in the sampling loop and perform process analyzer calibration and/or overhaul per manufacturer's recommendation. Inspect and calibrate other instruments per the OEM instruction manual;

- Purification equipment (deoxygenation and oxygen purification, if present)—Perform inspections as specified by the manufacturers;

- Pressurized vessels and equipment—Perform required mechanical integrity inspections;

- Heat exchangers (water and product gases)—Perform required mechanical integrity inspections;

- Pumps—Inspect for leaks; perform periodic overhaul per the OEM instruction manual;

- Electrical (transformer/rectifier, busbars, cabinets, isolators)—Check for ground faults, inspect heat exchanger loop and equipment, inspect isolators/insulation/electrical connections. Clean or replace cabinet filters as necessary; and

- System enclosure (if applicable)—Check or function test ventilation system, atmospheric gas sensors, heat sensors, and any other safety monitoring equipment as applicable.

10.4 Preparation for return to operation

Once maintenance has been completed, the system can be returned to the condition it was in prior to maintenance. See 9.1.1, which covers some of the general considerations for startup preparation. Where practical, leak check the system up to operating pressure while purging to detect leaks before startup. Locks and tags that were installed as part of the work permitting process shall be removed. In most cases, valves will be returned to the positions specified in the normal operation or plant startup valve lineup procedure (see 9.1.2). If any portion of the plant was disassembled and reassembled, checks shall be conducted to make sure that components have been installed in the correct direction (e.g., check valves, orifice plates, control valves, machinery rotation, etc.). In preparation for operation, piping and equipment that will contain flammable gas shall be purged (typically with nitrogen) to remove air/oxygen from the system. Subsequently, the system may be put into service by introduction of the process fluid.

The lockout/tagout process shall also be reversed for electrical equipment. For medium and high voltage equipment the specialized temporary grounding shall be removed. Once the grounding is removed, the circuit integrity shall be tested to confirm it is ready for energization. There is a finite probability that any piece of electrical equipment will fail on initial energization. It is imperative that all unnecessary personnel are removed from the area and that personnel carrying out the ground removal and energization wear the appropriate PPE. All electrical switching (low, medium, and high voltage) and temporary grounding (medium and high voltage) operations require specially qualified personnel and special PPE for arc flash protection. See NFPA 70E for details on this PPE requirement [29].

Placing the control system back in service may require confirmation/testing of interlocks. If there was an MOC executed, any associated interlocks shall be tested prior to startup. Interlock testing is also typically required at defined intervals and shall be completed prior to startup. Any temporary bypasses, jumpers, or value simulations that were used for the purposes of testing or troubleshooting shall be removed prior to startup. Similarly, any hoses or other temporary connections other than those authorized via the bypass log or under management of change and required for startup shall be removed.

Prior to and during restart of the plant following maintenance, leak tests shall be performed on all pressurized equipment and piping, especially those containing high temperature, flammable, or toxic fluids. For thermal processes, this can require repeated leak checks as the plant is heated up and joints expand. As flanged or threaded joints heat up, connections that did not leak at low temperature and pressure can begin to leak.

When gases and liquids are first brought into the plant following maintenance, checks should be done to confirm instrumentation and controls are responding appropriately, confirm gases or liquids are flowing through the system appropriately and machinery is operating appropriately (temperature, vibration, pressure). These checks are part of the plant recommissioning process. Other checks could be required depending on the process.

For more details on the requirements of purging into service, consult NFPA 56 [30]. In addition, CGA H-11 provides details on purging, leak checking, and other pre-startup checks that are applicable to thermal production plants [21]. See CGA H-14 for additional information regarding leak detection [4].

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