



SAFE CATALYST HANDLING IN HYCO PLANTS

AIGA 114/21

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As part of a program of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has published AIGA 114, *Safe Catalyst Handling in HYCO Plants*, jointly produced by members of the International Harmonization Council and originally published by Compressed Gas Association (CGA) CGA H-15, *Safe Catalyst Handling in HYCO Plants*.

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1 Introduction

HYCO plants utilize a number of catalyst types and catalytic technologies to produce hydrogen, carbon monoxide, or mixtures thereof. These catalysts are comprised of various chemical compounds across a number of support materials and structures, and reaction occurs in tubular, fixed bed, or modular reactors. Most of these catalysts are replaced periodically.

There are safety hazards involved in the storage, loading, unloading, and disposal of these catalysts. These hazards include the handling of self-heating or potentially pyrophoric materials and the presence of toxic metals (e.g., nickel, chromium, etc.), toxic metal carbonyls, and hexavalent chromium. There are also hazards associated with verification of uniformity of catalyst installation, including managing the differential pressure measurements taken during loading of reformer tubes. Development and implementation of safety procedures appropriate to the hazards associated with catalyst handling is required to maintain the exemplary safety experienced of large scale HYCO production facilities worldwide.

2 Scope

This publication applies to HYCO plants that produce hydrogen, carbon monoxide, or mixtures thereof, with a nominal production capacity greater than 9 MMSCFD hydrogen or carbon monoxide/syngas (approximately 10 000 Nm³/hr). Many of the concepts and issues discussed may also apply to smaller HYCO plants depending on the technology used.

This publication covers the safety aspects of all catalysts and chemisorbents such as zinc oxide used in HYCO facilities. Non-catalytic material such as physical adsorbents, for example, those used for pressure swing adsorbers; activated carbon, ion exchange resins, and inert solids (e.g., sand) are excluded from the publication. The publication scope is limited to catalyst and chemisorbent handling, loading, preparation for operation, unloading, and disposal. The publication scope excludes periods when the reactor is in operation (including startup and shutdown). Catalyst-specific instructions related to startup with new catalyst and shutdown prior to catalyst removal are included in the catalyst manufacturer's documentation, which should be consulted. This publication is not intended to replace catalyst manufacturers' operating manuals, handling manuals, or safety data sheets (SDS).

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 container

Industrial-grade container, often cubic in form, designed for the transport and storage of free-flowing dry cargo.

NOTE—The container may be single use or reusable, depending on the material of construction.

3.2.2 Bulk loading process

Catalyst loading technique for fixed vessels that relies on human intervention to distribute the catalyst evenly throughout the reactor.

NOTE—The methodology typically involves an individual directing catalyst addition via a fabric sleeve that is attached to the bottom of a hopper vessel or bulk container.

3.2.3 Catalyst handling service company

Specialized company that deals with the loading or unloading of reactor vessels. Qualified catalyst handling service companies typically have experience in vessel entry, including entry into an atmosphere that is Immediately Dangerous to Life and Health (IDLH), and may offer dense loading techniques/equipment.

3.2.4 Catalyst tube (reformer catalyst tube)

Metallic alloy cylinder used to contain the catalyst in the reformer furnace. Catalyst tubes typically measure 3 in to 5 in (8 cm to 13 cm) across the inside diameter with a vertical orientation and a length spanning the height of the reformer furnace.

3.2.5 Chemisorbent

Solid material that removes an impurity from a process stream by chemically reacting with the impurity.

3.2.6 Dense loading

Catalyst loading technique that relies on a mechanical means to distribute the catalyst evenly throughout the reactor. Dense loading techniques are available for fixed reactor vessels as well as for reformer catalyst tubes.

3.2.7 Flue gas duct

Portion of the reformer, downstream of the furnace, where flue gas passes over heat exchangers and heat transfer occurs via radiation and convection.

NOTE—Also referred to as convection section.

3.2.8 Furnace

Portion of the reformer where the combustion process takes place.

3.2.9 Pyrophoric

Material that will ignite spontaneously when exposed to air. The reaction is sufficiently exothermic such that the material quickly reaches combustion temperature and then incandescence. The material does not rely on insufficient loss of heat to promote the reaction, so any particle size will ignite on exposure to air.

3.2.10 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following globally harmonized standards.

3.2.11 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.

3.2.12 Steam reformer (or reformer)

Processing unit where steam is reacted with hydrocarbons over a catalyst at high temperatures to produce hydrogen and carbon oxides. The reformer includes a furnace/radiant section and a convection section.

3.2.13 Tube hanger

Mechanism that supports the reformer tubes as they move due to thermal expansion or contraction. This may be weights and pulleys, a variable load spring hanger, or a constant load spring hanger.

4 General safety considerations

The catalysts and chemisorbents used in a HYCO facility are potentially hazardous, and all activities involving the materials shall be assessed to identify the potential risks and the necessary safeguards. Some of the hazards involved in catalyst handling are specific to the catalyst composition (e.g., reactivity and toxicity of the material), while other hazards are specific to the catalyst handling activity (e.g., lifting, confined space entry, working at heights). The hazards associated with catalyst and catalyst handling activities shall be addressed through the various elements of a HYCO facility's safety program including training, procedures, personal protective equipment (PPE), work permits, contractor safety, and hazard communication.

4.1 Catalyst composition hazards (SDS considerations)

When developing a safety plan associated with catalyst handling, the relevant SDSs shall be consulted. The SDS includes information on potential short- and long-term health effects due to exposure as well as recommended precautions for safe handling. Many of the catalysts are toxic if inhaled (e.g., catalyst dust of nickel-containing catalysts) or can cause damage to organs through prolonged or repeated exposure. Some catalysts (e.g., zinc oxide) are very toxic to aquatic life, with long-lasting effects.

It should be noted that SDSs apply only to new catalyst. After use, the catalyst can have different chemical and physical properties, which can also vary with the reactor feed and operating conditions. The catalyst supplier should be consulted for the SDS or other information associated with the used catalyst. Laboratory analyses might be necessary to characterize the hazards of used catalyst.

4.2 Pyrophoric and self-heating hazards

Any catalyst in a reduced state can be self-heating. Pre-reduced and stabilized catalyst has an oxide layer on the surface to minimize the potential for self-heating.

Within the scope of this publication, there are no unused catalysts that are pyrophoric. There are materials that can be deposited on and around used catalyst (e.g., on top of the bed) that are pyrophoric (e.g., iron sulphides) or flammable (e.g., coke/carbon). Under certain conditions there is a risk of producing high temperatures and combustion. Because of this risk, some suppliers will refer to self-heating catalyst as pyrophoric.

To mitigate the risks, the catalyst should be cooled to ambient temperature (less than 120 °F [50 °C]) before being put in contact with air. Also, exposure to air/oxygen should be controlled while handling used catalyst and the associated contaminants. Oxygen exposure is controlled by minimizing exposure time to air. The primary method of cooling is flushing the catalyst with cold nitrogen while it is still in the production unit.

After unloading, dividing catalyst among multiple smaller containers prior to exposure to air will limit the overheating risk, as this division provides sufficient surface area to remove the generated heat. The larger the mass of catalyst that is exposed to air, the more likely there will be insufficient cooling. If the rate of heat generation exceeds the rate of cooling, then the temperature will rise and could reach a point that would melt the catalyst and/or damage the container or vessel.

4.3 Nickel/iron carbonyl hazards and safeguards

Nickel carbonyl is highly toxic and formed by the reaction of carbon monoxide with nickel. Nickel carbonyl formation is a potential hazard in HYCO plants containing nickel catalyst. Similarly, iron carbonyl is a toxic compound that can form by the reaction of carbon monoxide with iron from iron-containing catalyst.

Nickel carbonyl is considered to be one of the most toxic chemicals found in industry. The U.S. Occupational Safety and Health Administration (OSHA) Time-Weighted Average–Permissible Exposure Limit (TWA–PEL) for nickel carbonyl is 0.001 ppmv. The TWA–PEL for iron carbonyl is 0.1 ppmv. Regulatory exposure limits can vary by jurisdiction, and the appropriate guidance documents should be consulted [1, 2].¹

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

The formation of nickel carbonyl occurs when carbon monoxide is in the presence of nickel catalyst in the temperature range of 120 °F to 400 °F (50 °C to 204 °C). Its formation is prevented by removal of carbon monoxide by purging equipment prior to reaching the upper formation limit of 400 °F (204 °C). Iron carbonyl is formed when carbon monoxide is in the presence of iron catalyst and is similarly avoided by purging equipment of carbon monoxide prior to reaching a temperature of 400 °F (204 °C). This purging requirement applies to nickel catalysts (e.g., prereformer, reformer and methanation) and iron catalysts (e.g., high temperature shift [HTS]).

If carbon monoxide is not purged prior to reaching 400 °F (204 °C) and there is a possibility that nickel or iron carbonyl has formed, purging at low temperature will not remove it. Reheating the vessel to a temperature greater than 400 °F (204 °C) will cause the carbonyls to decompose.

4.4 Work permits, system isolation, and work planning

All catalyst handling operations shall be conducted under the plant work permit system. Safe loading or unloading operations also require that the system be isolated properly, which is ensured through the plant lockout/tagout program. Things that should be considered when developing the work permit include:

- influence of health and environmental hazards of catalyst on neighboring activities (e.g., dust);
- simultaneous maintenance activities;
- system isolation requirements; and
- purging activities.

When conducting catalyst handling activities, close coordination and communication with the catalyst handling service company is required to prevent conflicts between different maintenance tasks that take place in the same plant area, which often occurs if the catalyst activity will take place during a plant maintenance outage. When loading or unloading reformer catalyst, for example, the loading/unloading activity may occur at the top of the reformer, while at the same time it could be desirable to conduct maintenance activities beneath the reformer. Further, it might not be possible to isolate a reactor from all systems to which the reactor is connected. This is often the case for reformer catalyst tubes, which connect to multiple downstream systems without isolation. If two or more systems cannot be isolated from each other, it might not be possible to work on the systems simultaneously.

In some cases, the plant is configured with two reactors in series or parallel with sufficient isolation valves such that one reactor can be taken off-line and the catalyst replaced while the plant continues to operate. When working on a reactor that is connected to a "live" system, care shall be taken to ensure that the reactor is isolated and deenergized in accordance with company procedure prior to conducting work.

4.5 Personal protective equipment

The catalyst SDS (new or used catalyst) shall be consulted to determine the PPE required for those individuals involved in the direct handling of any catalyst (e.g., loading, unloading, screening, housekeeping, etc.). Additional information and recommendations could be included in the catalyst supplier's documentation. In general, eye protection, gloves and boots are required. Hearing protection, or even double hearing protection, could be required depending on the handling activity. Disposable protective overalls could be required, in particular for individuals handling catalyst within a confined space. Respiratory protection shall be utilized if required to control the inhalation of catalyst dust to a level below the allowable exposure limit. Respiratory protection generally is required for tasks that involve the direct handling of catalyst but might not be required for all tasks. The level of respiratory protection required should be defined for each specific task (e.g., drum handling, hopper loading, screening, vessel entry, catalyst unloading).

4.6 Vessel entry and purging

When loading or unloading catalyst from a vessel, entry into the vessel could be required. Standard confined space entry procedures shall be followed, taking into account the presence of the catalyst and any components that could be present on the catalyst such as contaminants from the process gas or reaction by-products.

If the vessel will be entered under a nitrogen purge, the preferred location for nitrogen introduction is such that the nitrogen flow path is through all or a portion of the catalyst inside the vessel. This reduces the risk for pockets of catalyst to come into contact with air versus a blanketing method supplying nitrogen from the vessel top. When introducing nitrogen with flow through some or all of the catalyst, a test assuring there is not a dangerous pressure differential across the bed of material should be conducted. This test ensures that there is no pocket of high pressure gas that when reached could cause a pressure release that could expel catalyst or personnel. The test, sometimes called a Grubbs' Test, involves flowing nitrogen through the catalyst at the maximum rate that will be used during the confined space entry, then quickly stopping the nitrogen flow and confirming that the pressure at the nitrogen introduction point decreases to atmospheric pressure within 5-10 seconds. If the pressure does not decrease in this time frame, it indicates that there could be blockage within the catalyst bed. In this scenario, consider alternative purge points to avoid the flow blockage, reduce the maximum nitrogen flow needed during entry and retest, or vacuum out the catalyst or blockage without entry into the vessel.

Some of the other confined space hazard mitigations associated with loading or unloading including:

- Catalyst can present an engulfment hazard either due to differences in height or bridging, which can be addressed by using a safety line and by keeping the bed surface relatively flat while vacuuming and never allowing a difference in elevation across the bed of greater than waist-high;
- Appropriate respiratory protection based upon the hazards of the task shall be utilized (dust mask, supplied air, or IDLH-appropriate supplied air);
- Confined space conditions shall be monitored continually because conditions can change due to the reaction of the catalyst with air, which will cause a depletion of oxygen, resulting in asphyxiation risk and temperature increase;
- Due to the reactivity hazards of catalyst, purging with nitrogen can be required throughout the loading or unloading process. Loss of the nitrogen purge can cause a sudden increase in temperature within the vessel;
- If entering the vessel under a nitrogen purge (due to reactivity concerns), then confined space entry protocols applicable to IDLH atmospheres shall be implemented. IDLH entry is an extremely hazardous activity that shall be planned and managed rigorously;
- If there is a potential for the asphyxiating atmosphere to extend beyond the vessel, this shall be taken into account when defining the safety precautions associated with all vessel vent points (e.g., downwind exposure) and with work going on near any of the vessel vent points (e.g., blinding, nozzle disassembly and assembly); and
- If a vessel is purged after catalyst loading is complete (e.g., to prevent moisture ingress or to maintain an inert atmosphere) an area around the vessel outlet sufficient to prevent exposure to an asphyxiating atmosphere shall be roped off or otherwise barricaded.

4.7 Working at heights

Catalyst loading or unloading is typically done from the top of the reactor. In most cases, this means that work is conducted at a significant elevation relative to grade. If permanent platforms are not available, access is often provided by means of temporary scaffolding. Whether working from a platform or a scaffold, precautions should be taken to prevent objects from falling to grade.

The platform or scaffold shall be rated for the maximum combined weight of the equipment, catalyst, and personnel that might be on the platform/scaffold at any one time. Heavy-duty scaffolds typically are required. Permanent platforms should be evaluated depending on the load that they will be required to handle.

4.8 Equipment-related precautions

The equipment used during catalyst loading or unloading shall be considered when identifying the safety protocols required for a particular catalyst handling task such as the following:

- When utilizing vacuum trucks for catalyst unloading, double hearing protection (ear muffs with ear plugs) may be required for individuals working near the vacuum truck. In addition, vacuum trucks should be equipped with a means to instantaneously break or reduce the vacuum in the event that the vacuum either

does not have the suction power to remove something (i.e., is stuck) or in the event that it is pulling on something unintended (e.g., if it is inadvertently placed in contact with an individual). That vacuum break typically takes the form of a tee connection in the hose that may be opened to atmosphere to create a short circuit;

- When cranes are utilized to transport the catalyst, tools, or loading or unloading equipment, then an appropriate lifting study shall be conducted. General safety considerations are covered in Title 29 of the U.S. *Code of Federal Regulations* (29 CFR) Part 1910 [3]; and
- If compressed air that is backed up by nitrogen is used for the catalyst handling activities, then the safety consequences of the nitrogen shall be taken into account, see CGA P-78, *Guideline for the Safe Use of Instrument Air Systems Backed up by Gases other than Air* [4].

4.9 Housekeeping

During catalyst handling activities, workplace housekeeping should be conducted to minimize congestion of the work area. Catalyst spills should be cleaned up promptly and disposed of properly (see 8.3). To avoid formation of airborne dust, sweeping should be avoided. A vacuum cleaner with appropriate filter should be used.

5 Catalyst types and descriptions

Multiple types of catalyst are used in a HYCO facility, each with its own hazards. The following subsections identify some of the unique safety considerations for the most common types of HYCO catalysts. Not all catalysts that are used in HYCO facilities are covered in this publication.

5.1 Hydrogenation

Hydrogenation catalyst is typically a pelleted or extruded catalyst that contains a formulation of chromium/molybdenum or nickel/molybdenum. Its function is to catalyze the reaction between hydrogen and organic sulfur compounds to create hydrogen sulfide, which is removed from the feed by absorption onto zinc oxide. It can also be used to catalyze the reaction between hydrogen and organic chloride compounds to create hydrogen chloride or to hydrogenate unsaturated hydrocarbons. Sulfiding is required to create an active form of the catalyst and to protect it from being reduced to a metallic state. It may be shipped in either unsulfided or presulfided states.

In some cases, the sulfur content in the feed is too low to sulfide the catalyst. A sulfiding agent, such as dimethyl disulfide, may be required to sulfide the catalyst in situ. Dimethyl disulfide is a liquid that is both flammable and toxic. Hence, safeguards and procedures need to be in place when sulfiding hydrogenation catalyst using dimethyl disulfide or other hazardous sulfiding agent.

On-site screening of presulfided material should not be performed unless it can be accomplished in an inert atmosphere. Prolonged exposure to air can lead to an exothermic reaction resulting in high temperature and/or the release of sulfur compounds to the atmosphere, which creates a hazardous condition for personnel in the vicinity. Exposure to air should be minimized at all times.

Hydrogenation catalyst is typically shipped in steel drums or bulk containers. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.2 Purification and ultrapurification

Purification chemisorbents are available for the removal of hydrogen sulfide or chlorides. Sulfur and chloride-containing compounds are poisons for nickel, iron and copper-based catalysts. Standard sulfur removal chemisorbents, which can reduce the sulfur content to a range of 20 ppb to 50 ppb, are typically pelleted materials formulated of zinc oxide with a binding agent. The zinc oxide material may be present as either a layer underneath the hydrogenation catalyst or in a bed downstream of the hydrogenation vessel. Once loaded, there are no special requirements for zinc oxide before use, but there are hazards once the material has been exposed to feed gas.

The primary safety concerns associated with used zinc oxide are the release of hydrogen sulfide and the autoignition of solid carbon on the bed. Prior to removing zinc oxide from the vessel, the bed should be cooled to ambient temperature to minimize the liberation of hydrogen sulfide and to avoid ignition of the carbon.

Ultrapurification chemisorbents that remove hydrogen sulfide to extremely low levels (< 10 ppb) are typically copper-based, pelleted materials. The chemisorbent could be hygroscopic and should not be exposed to excessive moisture during loading. In addition, care should be taken to prevent this material from contacting skin. Ultrapurification chemisorbents are reduced with hydrogen prior to the introduction of feed. The reduction reaction is highly exothermic, and safeguards should be in place to control the reduction and prevent runaway reaction. In their reduced state, ultrapurification chemisorbents can be self-heating. If the temperature becomes high enough, sulfur dioxide can be released.

Chloride guards are pelleted chemisorbents typically formulated of sodium aluminate. The material is installed in a vessel upstream of the zinc oxide bed(s) or as a layer on top of the zinc oxide bed. The material requires no pre-treatment or activation prior to use, and there are no specific safety concerns.

When multiple layers of hydrogenation and/or purification catalysts are present in a single vessel, the risks of all of the individual catalysts are present.

In addition to the single-purpose sulfur removal materials described, there are dual-purpose materials that combine both hydrogenation catalyst and sulfur chemisorbent into one pellet called hydrodesulfurization (HDS) catalyst. The risks associated with these catalysts combine the risks associated with hydrogenation and sulfur-removal materials. Because these materials can contain proprietary components, the manufacturer should be consulted for any specific handling recommendations.

Purification, ultrapurification, chloride guard, and HDS materials are typically shipped in either steel drums or bulk containers. They are typically loaded via a bulk loading process and unloaded with a mobile vacuum truck or by gravity flow from the bottom of the vessel.

5.3 Prereformer

Prereforming catalyst, which may be referred to as catalytic rich gas (CRG) catalyst, is typically a nickel-based, pelleted catalyst. The function of prereforming catalyst is to convert heavier hydrocarbons to methane and hydrogen and to react some of the methane with steam to produce hydrogen. The high nickel content of prereforming catalyst enables the reforming reaction to occur at a lower temperature than in the steam methane reformer. Metal toxicity, temperature increase due to self-heating, and the formation of toxic nickel carbonyl are the safety concerns of prereforming catalyst.

Prereforming catalyst may be supplied in either a pre-reduced or an oxidized state. Pre-reduced catalysts come in a stabilized form in which the top layer of the active material has been partially oxidized, allowing the catalyst to be exposed to air with reduced risk of self-heating at ambient temperatures. Stabilized catalysts can lose their stabilization layer if exposed to temperatures greater than 120 °F (50 °C) or to water and can begin to self-heat when subsequently in contact with air. If there is any possibility that the stabilization layer has deteriorated, a test should be done where only one drum is opened to atmosphere and monitored to ensure that it does not self-heat.

Catalyst supplied in the oxidized state requires reduction prior to the introduction of heavy feeds. The catalyst is self-heating after it has been fully reduced, hence safeguards shall be in place to ensure an inert atmosphere within the reactor after reduction.

Prior to unloading, a controlled passivation procedure may be applied by steaming at elevated temperatures to partially oxidize the surface of the catalyst. During shutdown, the catalyst is purged with steam and/or nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of nickel carbonyl formation. For safe removal, the carbon monoxide should be removed prior to reaching 400 °F (204 °C), and the catalyst should be cooled to less than 120 °F (50 °C) prior to removal.

Prereforming catalyst is typically shipped in steel drums. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.4 Tubular (primary) reforming

Reforming catalyst is typically a nickel-based, pelleted catalyst. Its function is to react steam with hydrocarbons in the feed to produce carbon monoxide, which is subsequently reacted with steam to produce carbon dioxide and hydrogen. The catalyst is supplied in either alkali-promoted or non-promoted formulations. Metal toxicity and the formation of toxic nickel carbonyl are the safety concerns of both formulations.

Unused reforming catalyst is typically stable and non-reactive. The catalyst is reduced in the reformer using hydrogen or natural gas, typically during plant startup. During shutdown, the catalyst is purged with steam or nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of nickel carbonyl formation. For safe removal, the carbon monoxide should be removed prior to the process equipment temperature being reduced to the upper formation limit of 400 °F (204 °C) and the catalyst cooled to less than 120 °F (50 °C).

Reforming catalyst is typically shipped in drums, bulk containers, or socks. It is typically loaded via a dense loading technique and unloaded with a mobile vacuum truck.

5.5 Secondary reforming

Secondary reforming catalyst is similar to tubular (primary) reforming catalyst in that it is typically a nickel-based, pelleted catalyst. Secondary reforming occurs immediately after primary reforming. The function of the secondary reforming catalyst is to react synthesis gas (syngas) from the tubular reformer with either air or oxygen to produce a syngas composition that is more amenable to the specific downstream process (e.g., higher carbon monoxide content). Unlike primary reformers, secondary reforming occurs in a single, refractory lined vessel containing catalyst. The secondary reformer is a fired reactor that operates at high temperature, and protecting the main catalyst with a layer of large catalyst pellets is a common practice. Metal toxicity and the formation of toxic nickel carbonyl are the safety concerns of secondary reforming catalyst.

Unused catalyst is typically stable and non-reactive. The catalyst is reduced in the reactor vessel using hydrogen or natural gas, typically during plant startup. During shutdown, the catalyst is purged with steam or nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of nickel carbonyl formation. For safe removal, the carbon monoxide should be removed prior to the process equipment temperature being reduced to the upper formation limit of 400 °F (204 °C) and the catalyst cooled to less than 120 °F (50 °C).

Secondary reforming catalyst is typically shipped in drums or bulk containers. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.6 Autothermal reforming

Autothermal reforming catalyst is similar to tubular (primary) and secondary reforming catalyst in that it is typically a nickel-based, pelleted catalyst. Similar to secondary reforming, autothermal reforming occurs in a single, refractory lined vessel containing catalyst. The autothermal reformer is a fired reactor that operates at high temperature. Protecting the main catalyst with a layer of zirconium-based ceramic target tiles is a common practice. Unlike secondary reforming, autothermal reforming does not require a primary reformer, although pre-reforming might be carried out before the autothermal reformer. The function of the autothermal reformer is to react air or oxygen with a hydrocarbon feed stream to produce a carbon monoxide-rich syngas stream. Metal toxicity and the formation of toxic nickel carbonyl are the safety concerns of autothermal reforming catalyst.

Unused catalyst is typically stable and nonreactive. The catalyst is reduced in the reactor vessel using hydrogen or natural gas, typically during plant startup. During shutdown, the catalyst is purged with steam or nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of nickel carbonyl formation. For safe removal, the carbon monoxide should be removed prior to the process equipment temperature being reduced to the upper formation limit of 400 °F (204 °C) and the catalyst cooled to less than 120 °F (50 °C).

Autothermal reforming catalyst is typically shipped in drums or bulk containers. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.7 High temperature shift

HTS catalyst is typically iron/chromium-based with a copper promoter and is typically in a pelleted form. The function of HTS catalyst is to further "shift" or react the carbon monoxide in the syngas from the tubular or

secondary reformer with steam to produce carbon dioxide and hydrogen. Metal toxicity and formation of toxic iron carbonyl are the safety concerns of HTS catalyst. Some HTS catalyst formulations are supplied with hexavalent chromium, which will be reduced during activation. Hexavalent chromium can also be formed if the catalyst is oxidized with oxygen/air at elevated temperature, typically before removal.

The catalyst is typically reduced with syngas during initial startup to convert the iron oxide phase from hematite to magnetite. The reduction reaction is exothermic and can lead to a temperature increase, with temperatures exceeding the design temperature of the HTS vessel and piping. If the catalyst is overdried prior to startup, which can occur if the catalyst is held in nitrogen flow for excessive periods, a minor exotherm can occur when the catalyst is rehydrated with steam.

The catalyst can over-reduce due to exposure to excessive hydrogen with insufficient steam during startup. On subsequent exposure to syngas during plant startup, an exotherm can occur due to the methanation reaction, with temperatures exceeding the design temperature of the HTS vessel and piping. End users should refer to the supplier's operating manual for requirements related to water/hydrogen or water/methane ratio to properly reduce the catalyst.

During shutdown, the catalyst is purged with steam or nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of iron carbonyl formation. For safe removal, the carbon monoxide should be removed prior to the process equipment temperature being reduced to the upper formation limit of 400 °F (204 °C) and the catalyst cooled to less than 120 °F (50 °C).

HTS catalyst is typically shipped in drums or bulk containers. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.8 Medium/low temperature shift and isothermal shift

Medium temperature shift (MTS), low temperature shift (LTS), and isothermal shift (ITS) catalysts are typically copper-based (copper oxide), pelleted catalysts supported on a structure containing zinc oxide and alumina. MTS and LTS are fixed bed adiabatic reactors. ITS is a fixed bed reactor operated isothermally by continuously removing heat from the catalyst bed with the use of cooling tubes or jacket. As with HTS catalyst, the function of these catalysts is to react the carbon monoxide in the syngas from the primary or secondary reformer with steam to produce carbon dioxide and hydrogen. MTS and ITS catalysts operate in a similar temperature range, while LTS catalyst operates at a lower temperature. To accommodate the lower operating temperature of LTS catalyst, the copper content is higher. Metal toxicity and temperature increase during reduction and/or as a result of self-heating are the safety concerns of MTS, LTS, and ITS catalysts.

Prior to use, MTS, LTS, and ITS catalysts are reduced with hydrogen to convert the copper oxide to its metallic state. The catalyst reduction reaction is highly exothermic, and controls (automated or procedural) shall be in place to control bed temperature. A carrier gas such as nitrogen is used to dilute the hydrogen during the reduction step. Once reduced, MTS, LTS, and ITS catalysts are self-heating.

During shutdown, the catalyst is purged with nitrogen to remove hydrocarbons. For safe removal, the catalyst should be cooled to less than 120°F (50°C) prior to removal.

Reduced catalysts containing copper will react with water to form hydrogen. Precautions shall be taken to ensure that a flammable or explosive mixture is not created. There should be no sources of ignition in the vicinity.

MTS, LTS, and ITS catalysts are typically shipped in drums or bulk containers. MTS and LTS catalysts are typically loaded via a bulk loading process and unloaded with a mobile vacuum truck. ITS catalyst is loaded and unloaded using different methods depending on the configuration of the reactor.

5.9 Methanation

Methanation catalyst is typically a nickel-based, pelleted catalyst. Methanators are used to purify synthesis gas (i.e., remove traces of carbon oxides) and to manufacture methane by reacting carbon oxides (carbon monoxide and carbon dioxide) with hydrogen to form methane and water. Metal toxicity, temperature increase due to self-heating, and the formation of toxic nickel carbonyl are the safety concerns of methanation catalyst.

Methanation catalyst may be supplied in either a pre-reduced or an oxidized state. Pre-reduced methanation catalyst comes in a stabilized form in which the top layer of the active material has been partially oxidized, allowing the catalyst to be exposed to air with reduced risk of self-heating at ambient temperatures. Stabilized catalysts can lose their stabilization layer if exposed to temperatures above 120 °F (50 °C) or to water and can begin to self-heat when subsequently in contact with air. If there is any possibility that the stabilization layer has deteriorated, a test should be done where only one drum is opened to atmosphere and monitored to ensure that it does not develop an exotherm.

Methanation catalyst is reduced in the reactor using process gas during plant startup. The catalyst is self-heating after it has been fully reduced, hence safeguards shall be in place to ensure an inert atmosphere within the reactor after reduction.

During shutdown, the catalyst is cooled and purged with nitrogen to remove hydrocarbons and carbon monoxide to eliminate the possibility of nickel carbonyl formation. For safe removal, the carbon monoxide should be removed prior to the process equipment temperature being reduced to the upper formation limit of 400 °F (204 °C) and the catalyst cooled to less than 120 °F (50 °C).

Methanation catalyst is typically shipped in drums. It is typically loaded via a bulk loading process and unloaded with a mobile vacuum truck.

5.10 Selective catalytic reduction

The active component of selective catalytic reduction (SCR) catalyst is vanadium and/or tungsten oxides on a structured carrier containing titanium oxide. The structured carrier is constructed of either corrugated fiber-reinforced plates or ceramic honeycomb for low pressure drop in high flow applications. The SCR catalyst bed is constructed of modules stacked inside the flue gas duct of the reformer so that they cover the cross-sectional area of the duct. The purpose of the SCR bed is to reduce the amount of nitrogen oxides in the flue gas exhausted from the reformer stack. Metal toxicity and the large size and heavy weight of the modules are the safety concerns of SCR catalyst.

SCR catalyst is shipped to the site in crates to protect the modules from mechanical damage and for ease of handling. SCR catalyst is stable in air and can be handled safely during loading or unloading.

6 Storage and handling

Correct storage conditions for unused catalyst are an important consideration for ensuring that catalyst integrity and performance are not adversely affected prior to loading activities.

Catalyst can be supplied in several different containers including drums, boxes, bulk containers, small bags or pre-filled polyethylene socks in boxes. If the catalyst is supplied in a metal container, then it usually will be contained within a polyethylene bag. Storage of catalyst shall be executed in accordance with applicable regulations. Catalyst should be kept segregated from incompatible materials. Catalyst should be stored in a dry place, and the containers should be kept sealed to avoid contamination of the catalyst or environment. All containers shall be appropriately labelled.

Certain catalysts are shipped in an inert atmosphere to mitigate reactivity hazards (when exposed to air). Catalyst containers should be inspected for damage when they arrive on site. Catalyst containers should not be opened until they will be loaded into the reactor vessel.

Care should be taken to avoid accidental damage to containers by forklift trucks during storage or transportation. The containers should be stored in a safe location and out of active traffic ways.

Refer to the catalyst operating manuals for specific requirements related to new catalyst storage. Unless otherwise stated, catalysts typically are not affected by extremes of temperature from –60 °F to 120 °F (–50 °C to 50 °C) provided that they are kept dry. Prerduced catalysts should be stored out of direct sunlight, away from sources of heat or flammable materials, because they have the potential for self-heating if they lose their stabilization layer. In extremely humid atmospheres, it could be necessary to store catalysts in an air-conditioned building. Catalysts should always be protected from mechanical impact, crushing and water or moisture (kept dry).

If the catalyst has changed composition or properties during use, the used catalyst storage/shipping containers should be selected based on the applicable transportation and/or waste regulations specific to the used catalyst. Since used catalyst in many instances has less mechanical stability, increased dust formation can occur. If the used catalyst could contain other components (e.g., iron sulfide or coke/carbon), this should be considered during handling and selection of the container.

It is important to follow the safety instructions given by the catalyst supplier (modified as appropriate if the composition or properties of the catalyst have changed due to use) and to ensure that people handling the catalysts are trained and aware of the hazards and correct handling of the catalyst. Appropriate PPE shall be used, taking into account the catalyst SDS, product bulletins, and any characterization information of used catalyst. Many of the catalysts are toxic if inhaled (e.g., catalyst dust of nickel-containing catalysts) or can cause damage to organs through prolonged or repeated exposure. Some catalysts (e.g., zinc oxide) are very toxic to aquatic life with long-lasting effects.

6.1 Drums

Drums contain catalyst within a sealed polyethylene liner and are banded together (typically 4 drums) on pallets to stabilize the load and to allow easier movement. Banding shall not be removed while the drums are stored on pallets or the pallet is part of a stack.

The drums should be inspected on arrival to site for damage and shall not be stacked on their sides or stacked more than four drums high, even when held on pallets. Stack heights should be reduced if the ground is not even. Taller stacks are unstable, and the lower drums can be crushed, damaging the catalyst and/or resulting in catalyst spillage.

Drums can be used for long-term storage as long as they are suitably protected. Indoor storage is preferred, but they may be stored outdoors if they are protected from adverse weather conditions and remain dry.

Lids should be left on drums until just before the catalyst is loaded. If the lids are removed for some reason (e.g., inspection), they should be replaced as soon as possible to prevent contamination of the catalyst.

Full drums weigh between 175 lb and 550 lb (80 kg and 250 kg), which should be taken into account when moving them. Fork-lift trucks or mobile cranes may be used to move pallets of drums. A smooth, unobstructed paved area is desirable to facilitate movement. Personnel should stay a safe distance away from drums being moved in the event that the drums become unstable. Pallets of drums should only be moved if the banding is intact.

When lifting an individual drum, a rim or body clamp should be utilized to avoid damage. Standard forklift trucks shall not be used to lift individual drums by placing the forks under the rolling hoops, as this inevitably damages the drum and catalyst.

Drums should not be rolled on their side from one location to another. If manual transport is unavoidable, proper equipment such as drum barrows, upending levers, or skids shall be used.

6.2 Bulk containers

Catalysts may be supplied in bulk containers. These containers may be constructed of metal or fabric. Fabric bulk containers are often referred to as sacks. Sacks may be shipped within a secondary container made from cardboard or wood to provide additional protection during transportation and storage. Sacks are typically made of polypropylene and are commonly referred to as big bags or large bulk bags. Bulk containers should be kept upright and should not be stacked more than one high. If sacks are in a secondary container, they may be stacked up to two high.

Bulk containers may be used for long-term storage as long as they are suitably protected. Indoor storage is preferred, but they may be stored outdoors if protected from adverse weather conditions and they remain dry. Some containers are more susceptible to water ingress than others.

Forklifts may be used to transport bulk containers by the lifting straps or on a pallet. Prior to lifting a sack out of a secondary container, the sack should be inspected for damage and care should be taken to prevent tearing when lifting it. When lifting sacks, spreader bars or extended hooks are required to distribute the weight of the

catalyst and to prevent the sack from splitting or falling. Always use all of the lifting straps (typically four are provided). When using a forklift, care should be taken to avoid accidental damage to the lifting straps; this may be achieved by covering the forks to eliminate sharp edges.

Catalyst may be transferred from bulk containers directly to the vessel. The benefit of this is that the handling of large numbers of smaller containers (such as drums) is eliminated, and the loading of the vessel can be conducted much faster. Application of such a loading technique can depend on the location of the plant and access to the vessels.

6.3 Socks

Reforming catalyst may be supplied in pre-filled polyethylene bags or socks that contain approximately 20 lb (10 kg) of catalyst. Dimensions are such that the sock can be inserted into the reformer tube during loading. Small bags and socks are typically supplied in wooden crates, boxes, or drums for transportation and storage. Boxes should be inspected for damage when they arrive on site. Catalyst can be stored indefinitely, provided the socks are kept dry. Indoor storage is preferred, in a building or warehouse, but it is also acceptable to store outside if water ingress is prevented.

6.4 SCR catalyst

SCR catalyst is provided by suppliers in rectangular prism modules, which consist of multiple catalyst blocks or elements. The modules are typically wrapped in plastic and packaged in a wooden crate or frame or in heavy-duty cardboard. The catalyst is stable in air over a wide temperature range but can be damaged from exposure to liquid water.

The catalyst should be stored in its original packaging, in a warehouse or enclosed building that will provide protection from dust, precipitation, and excessive humidity. The storage location should be clear of vehicle/fork truck traffic and out of the way of other objects that could impact and damage the catalyst. Catalyst modules can be stacked; consult the supplier for recommendations on stacking the modules.

It might be necessary to temporarily store the catalyst outdoors or under an open roof in the facility as part of catalyst replacement staging. During this period, the modules should be well covered with heavy-duty plastic sheets or waterproof tarps to protect against precipitation, exposure to chemicals, and incidental contact. The area should be clear of activities that can cause physical damage to the modules. The modules should not be stored in low-lying areas of the facility that are prone to accumulate water during rain events to avoid the potential for water damage.

Catalyst modules should be moved using a forklift truck or mobile crane. Forklift trucks should properly align the forks under the module pallets and should be rated for the load of the catalyst module. The truck or crane operator should take care to ensure the module is not knocked or dropped (even from small heights), as the catalyst material is rigid and can be fractured or cracked if mishandled or shocked. Crane lifts should be reviewed to ensure proper lifting methods and utilization of the rigging equipment (slings, yokes) that is often provided with the modules.

7 Catalyst loading or unloading

The loading or unloading of catalyst in HYCO facilities are potentially hazardous activities that require appropriate planning, safeguards, and execution. The following sections identify general and reactor-specific safety considerations associated with catalyst loading or unloading.

7.1 General considerations

Catalyst suppliers typically screen catalyst to remove dust and small pieces prior to packaging the catalyst such that additional screening on site is unnecessary. However, extremely rough handling in transit can cause some breakage and dust formation. Prior to loading, a visual inspection of the catalyst is recommended. In cases of questionable catalyst integrity (e.g., odd appearance, unknown age, or unclear storage condition history) consult the catalyst supplier. If significant breakage is evident, additional screening may be done to remove broken pieces and dust. Appropriate PPE should be worn by personnel to mitigate hazards associated with dust exposure.

Prior to loading catalyst, reactor vessels should be clean, dry, and free of contaminants that can react with the catalyst. SDSs are an excellent source for determining reactivity hazards. Reactivity hazards shall be clearly identified and safeguards shall be implemented. Loading or unloading procedures shall be generated. Certain catalysts require that the vessel be maintained in an inert atmosphere while loading or unloading.

Many catalysts look the same (e.g., shape, size, and color), and more than one type may be loaded in a reactor. Procedures should be in place and the loading plan should be reviewed with the catalyst handling service company to ensure that the correct catalyst is always loaded as intended.

Loading is not recommended in heavy rain or high winds. Appropriate waterproof covers should be available for hoppers and the vessel if there is any potential for rain.

Pre-socked reforming catalyst requires no further action before loading. If the socks are filled on site, any broken catalyst and pellet fragments should be removed before socking to minimize uneven catalyst density within the reformer tubes and subsequent pressure drop problems.

Pre-reduced and stabilized catalyst may be safely loaded into the reactor without purging the loading equipment with nitrogen. Once loaded into the reactor vessel, air should be removed and the catalyst should be maintained in an inert atmosphere.

Loading or unloading operations will generate dust. If dust release thresholds could be met or exceeded, these activities will require emissions control, air permitting, local emissions reporting, and/or reporting under EPA's toxic release inventory (TRI) program.

7.2 Tubular reactors—reformers

Reformers and other tubular reactors (e.g., ITS and gas-heated reactors) consist of catalyst-filled tubes mounted within a vessel, cylindrical can, or box. Reformer catalyst tubes typically are 3 in (7.5 cm) diameter or greater. In contrast, catalyst tubes mounted within a vessel typically are less than 3 in (7.5 cm) diameter and are more densely spaced than reformer tubes. Guidance for tubular reactors other than reformers is given in 7.5.

Reformers have catalyst tubes situated within a cylindrical can or box, and burners supply additional heat external to the catalyst tubes. Combustion gases flow on the outside of the tubes, which enables heat transfer to occur simultaneously with the chemical reaction occurring within the tubes. The burners can be located on the sides, bottom, or top of the reformer.

7.2.1 General safety

The loading or unloading of reformer tubes has some unique safety issues due to the configuration and layout of the reformer. Access to the catalyst in the tubes is usually from a flanged connection at the top of the tube. For most box-type reformers, these flanges and their associated inlet piping are housed in a semi-enclosed structure on top of the furnace, commonly referred to as a penthouse or doghouse. The tubes are laid out in rows or circles with narrow access walkways.

All tube loading or unloading operations are performed along these narrow walkways. Due to the limited space and the elevation of the penthouse, recommended safe work practices include:

- maintain good workplace housekeeping to avoid trip hazards due to the congestion of equipment, electrical cords, vacuuming, air lines, and personnel;
- ensure that workers secure and handle all tools properly so that they do not fall over the side of the reformer;
- the penthouse is a partially enclosed area so ensure proper ventilation, that all exits remain clear, and that personnel are aware of all exits;
- where practical, secure all electrical cords and air lines above the working area to eliminate trip hazards;
- limit nonessential personnel from entering the work area;

- cover any floor opening or uneven surfaces that can present a falling or tripping hazard; and
- after unbolting flanges, ensure inlet piping and tube hangers are secured so as not to present hazards if bumped or dislodged.

Large volumes of nickel-containing pelleted catalyst are handled during both the loading or unloading operations. Good practices to perform this safely include:

- Ensure that proper PPE such as an approved dust mask or respirator is worn and that adequate ventilation is available. Catalyst dust is unavoidable, especially during unloading; and
- Cover any grated walkways that are open to levels below with plywood or tarps to prevent catalyst from falling through and striking personnel working below.

The considerations previously noted for reformers apply in general to all tubular reactors, with the exception that the area at the top of the reactor might not be semi-enclosed and movement is not restricted to narrow walkways, although space is still limited.

7.2.2 Unloading

Pelleted catalyst is usually removed from the catalyst tube by vacuuming from the top of the reformer. Main vacuum lines are usually brought up to the penthouse from grade and are split into smaller lines so that more than one tube can be vacuumed at a time. An emergency vacuum breaker mechanism should be on the main line such that on opening, the vacuum will be reduced to all lines at once. Vacuuming reformer tubes is physically demanding and requires repetitive motions. Therefore, ensure proper ergonomics and rotate personnel through the catalyst handling tasks as needed.

If tubes require internal mechanical cleaning with brushes, additional dust is generated and should be controlled during generation and removed.

7.2.3 Loading

As described in 4.7, platforms and scaffolding are rated for a maximum load. Signage should be placed in the area that states the maximum load that can be present at any time. In addition to the people and equipment, the maximum number of drums or sacks that can be stored on the platform or scaffold at any time should be considered as part of the maintenance planning process. If temporary scaffolding is used, the load shall be balanced across the scaffold.

If a dense loading technique is used, the loading apparatus can have moving parts that could present pinch point hazards. If vibrational settling is necessary (e.g., hammering, pneumatic vibration), the ergonomic and safety issues associated with this activity shall be addressed.

After loading, if the final loaded density of the catalyst in the tubes has changed, either because of a change in catalyst type or the loading technique, it is important to determine if the total tube weight is outside of the limits of the tube hangers or other support system components. Depending on the support system configuration, adjustments could be needed, regardless of whether the total weight decreased or increased. A mechanical engineering analysis should be performed so that adjustments to springs and other components of the system can be made before the plant restarts.

7.2.4 Differential pressure drop measurement

To ensure consistent tube-to-tube loading, differential pressure (DP) drops across reformer tubes can be measured at various times during the loading or unloading operations. The differential pressure drops are measured with a DP rig.

A DP rig operates by flowing compressed air, termed tube source air, through a restrictive orifice and then down through the tube (a typical flow schematic is shown in Figure 1). To seal the top of the tube and to force the air down the tube, a bladder is inserted into the top of the tube and inflated, using bladder inflation air, against the tube inner wall. The tube source air then flows through the bladder, down the reformer tube, and out the process gas outlet piping or header system. Under a constant tube source air flow, the pressure is measured downstream

of the restrictive orifice and recorded as the pressure drop of the tube. Once this DP has been recorded, the tube source air is stopped, and the bladder is deflated and removed from the tube.

When tube source air is being flowed through the tube, the tube is pressurized. If for any reason the bladder becomes dislodged, the pressure in the tube could cause the bladder to be ejected at high velocity back out of the top of the tube, possibly causing injury. The following physical safety requirements should be considered for the DP rig to minimize the possibility of any ejections and to prevent personnel injury:

- Both the tube source air and the bladder inflation air should be pressure regulated;
- Bladder shall not be inflated past its design pressure, and a pressure relief valve should be installed downstream of the bladder inflation regulator if the bladder is not rated for the maximum incoming air pressure;
- To minimize the chance of bladder ejection, a pressure relief valve should be installed on the tube source air downstream of the pressure regulator to limit the maximum air pressure;
- In case of a blockage in the tube, the DP rig should have a tube bleed valve to safely allow residual pressure in the tube to be reduced;
- If there is evidence that a tube could be partially or totally blocked, consider reducing the tube source air pressure to a lower value to first test the tube for air flow. If the tubes are clear, then the pressure can be returned to its original value;
- Latch locking valve should be used for the bladder bleed valve to avoid inadvertent depressurization while tube source air is flowing, which can result in ejection of the bladder;
- When in the tube, the bladder shall be constrained to limit movement if ejected. The bladder should be attached to the upper tube flange at two locations that are 180 degrees apart;
- Safety perimeter is determined by the bladder constraint method. All personnel should stay outside of that safety perimeter when the bladder is pressurized. There shall be enough hose length between the DP rig valves and the tube inlet to allow the DP rig operator to be outside of the safety perimeter; and
- Compressed air should be used to perform the DP checks. Due to its asphyxiating potential, nitrogen should not be used. If nitrogen must be used, the associated risks shall be mitigated.

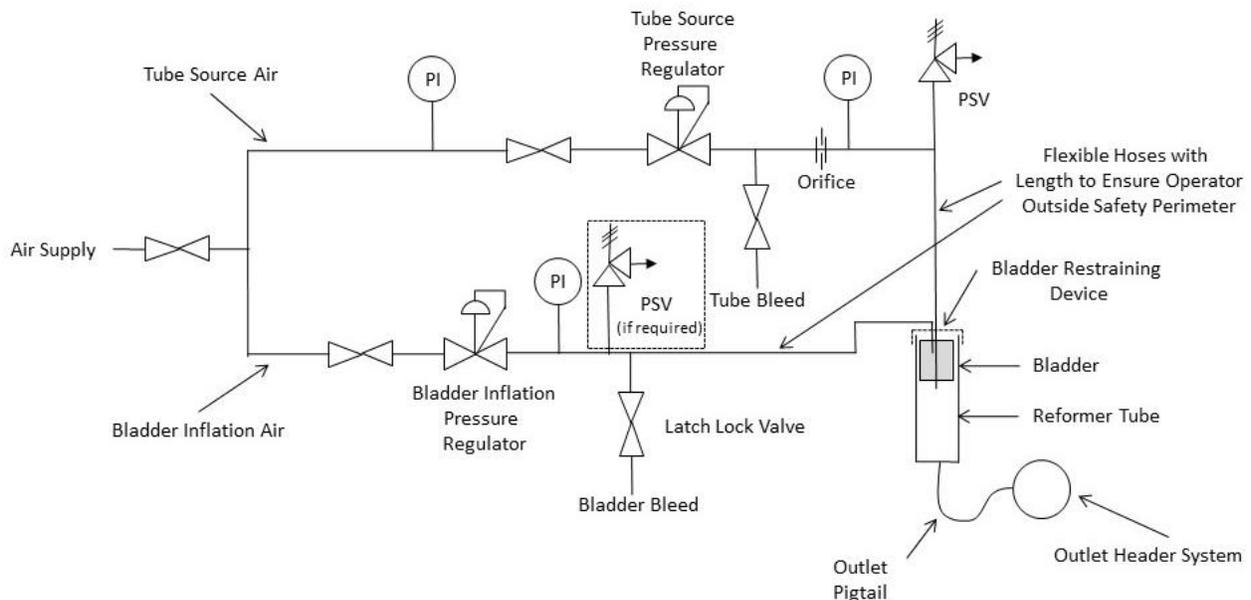


Figure 1—Key components of a differential pressure rig

7.3 Fixed vessel reactors

In general, fixed vessel reactors are simply vessels filled with catalyst through which process fluid flows and reactions occur. Specialized versions may include internals to allow for flow distribution or for other operations such as heat exchange.

7.3.1 General safety

The primary safety considerations regarding fixed vessel catalyst loading or unloading center around confined space entry and the presence of catalyst (e.g., dust generation, self-heating, combustible materials, desorbed gases). Vessel entry in fixed vessel reactors is at times necessary for loading, unloading, or maintenance activities. Entry into this type of vessel shall be handled under a confined space permit. Consideration shall be given to vessel internals that can restrict movement within or exit from the vessel. In addition, work inside the vessel requires ropes, power cables, hoses, ladders, loading sleeve, etc., that will restrict the opening in the manway and thus restrict personnel exit.

When there is a possibility of catalyst self-heating, the reactor interior shall be continuously monitored for temperature increase. The following methods may be used:

- Installed thermocouples—If the bed has installed thermocouples that are online during the maintenance, monitoring these can give indication of temperatures at points not yet measurable by manual means. Further, these can be trended and have alarms. However, since these are fixed points without the normal fluid flow of operation, these temperature indication points are not a representative indication of the temperature of the entire catalyst bed; and
- Manual readings—Monitoring of the top of the catalyst bed by the use of a contact thermometer or a handheld infrared thermometer to measure the surface temperature of the catalyst.

Depending on the catalyst and the reactor, air ingress can lead to the initiation of a temperature increase. Air can enter the vessel due to natural convection or diffusion. Therefore, nitrogen may be used to prevent oxygen from reaching the catalyst, first by having a nitrogen atmosphere inside the vessel before opening and then by providing a continuous source of nitrogen to the vessel. The amount of nitrogen provided to the vessel will depend on catalyst reactivity and unloading method (e.g., overcoming the loss to vacuum). If it is critical that oxygen level remains near zero, recycling the nitrogen from the vacuum truck is not recommended due to the potential for leaks and air ingress. If recycling nitrogen cannot be avoided, additional care should be taken to avoid the buildup of oxygen (for example, additional monitoring and leak checks).

Vessel entrants should have respiratory protection. For a nitrogen purge condition, the vessel entry is covered by IDLH protocols, and both entrants and personnel on platforms at the loading nozzle need to have supplied breathing air.

Preparations shall be made to address potential catalyst temperature increase. If self-heating is observed, steps may include exit of personnel from the vessel, increase of nitrogen purge, stopping of vacuum, and cooling/suppression via steam or water. A hot spot could be uncovered during unloading if the bed was insufficiently cooled prior to catalyst removal, and any of the above self-heating response actions are suitable. When entering any vessel from the top, consideration should be given to preventing the undesired flow of gas (e.g., air) due to the chimney effect (either from induced vacuum or temperature/buoyancy effects). This can occur when the vessel is open to the atmosphere at the bottom (for example, if the nitrogen purge hose is removed).

Maintenance work for fixed vessel reactors typically involves access to the reactor via a top nozzle accessed from a platform or scaffold. Care should be taken on these platforms as they are at the top of a tall vessel and they have limited access or egress. Good workplace housekeeping should be applied to avoid tripping hazards, and the area should be limited to necessary personnel.

7.3.2 Unloading

Three methods are available for vessel unloading: vacuum, dump nozzle, and manual. Vacuum and manual unloading frequently require confined space entry, which has specific hazards relating to the unloading operation. Engulfment is a possibility if vacuuming is done in a non-uniform way such that the surface of the catalyst bed is

uneven. The maximum height differential across the catalyst bed surface should be no more than waist height of the vessel entrants. If a jackhammer or other mechanical or manual means of loosening catalyst agglomeration is required, safeguards appropriate to the task shall be put into place through the normal work permit process.

7.3.2.1 Vacuum

The most common method (especially for larger reactors) of unloading is the use of mobile vacuum trucks. These trucks are equipped with vacuum generators, cyclone separators, and dust filters. Hoses are connected to the system and used to vacuum the catalyst from the reactor. The catalyst is separated in the cyclones and is typically dumped into metal bulk containers (commonly referred to as flow bins) or other storage receptacles.

For small reactors, the vacuuming may be done from outside the reactor by guiding the hose without vessel entry. For large reactors, vessel entry is typically required to guide the vacuum hose.

The vacuum can have difficulty with fused catalyst or large support balls. Fused catalyst usually can be broken by hand or with simple tools and then vacuumed. Removing heavy support balls can be too slow via vacuum unloading, and bucket unloading can be required.

Vacuuming (especially the cyclone separation) will typically break a large portion of the catalyst and result in considerable dust, which will load the filters quickly. If the catalyst is self-heating, precautions shall be taken as the dust is more likely to heat up, which could melt plastic hoses or ignite paper/fabric filters.

7.3.2.2 Dump nozzle

Some vessels are equipped with dump nozzles near the bottom of the catalyst bed. These nozzles are angled to allow the catalyst to free flow from the vessel. This method allows for fast unloading with minimal equipment and no entry into the vessel.

Dump nozzles will often leave catalyst and/or support media inside the vessel. This may be considered acceptable, or entry for cleaning can be required.

If the catalyst is fused or bound in areas within the vessel, dump unloading will not fully unload the vessel. This partial unloading can lead to a potentially dangerous scenario in which there is bridging of the fused catalyst above a void. If personnel enter the vessel to break up the catalyst, the bridge can collapse.

Dump nozzles are difficult (sometimes impossible) to control, and the receiving container can be overfilled during unloading. If it is desired to obtain samples from specific locations within the vessel or if it is desired to separate different layers (e.g., support from catalyst), then unloading via a dump nozzle might not be suitable.

7.3.2.3 Bucket unloading

The simplest method of unloading is to use buckets with personnel inside the reactor. However, the access point for unloading will often slow the bucket removal considerably. The safety considerations of manual unloading are similar to those of vacuum truck unloading with entry.

7.3.3 Loading

Loading of fixed vessel reactors is a process that might not require vessel entry. Catalyst typically flows into the vessel through a canvas sleeve integrated with a bulk container or connected to a hopper. The same method may be used when loading inert support balls. The size and density of the material being loaded should be considered when determining the loading rate.

Because many bulk containers or drums of catalyst can be required to fill a vessel, each should be inspected prior to loading to ensure that it is the correct material. The vessel and internals should also be inspected for readiness prior to catalyst loading. The catalyst should not be allowed to freefall excessive distances (approximately 3 ft [1 m] is ideal) due to potential for mechanical breakage and dust formation. This applies to both loading and transfer of material (e.g., drums to hopper or bulk container).

When loading tall vessels, a hopper with an extended canvas sleeve is required. In this case, someone usually enters the vessel and directs the flow to ensure even loading. Care should be taken to avoid filling the sleeve to

prevent rupture and potential injury of the individual inside the vessel. Due to the fragile nature of many catalysts, standing directly on the surface of the catalyst is not recommended. Use of wood planks to distribute weight is common, but care should be taken to ensure the planks are removed.

Dense loading is an alternative technique for catalyst loading that does not require vessel entry during loading, but dust formation and any equipment-specific safety concerns should be considered.

7.4 Selective catalytic reduction catalyst

The SCR catalyst bed is constructed of modules stacked inside the flue gas duct of the reformer so that they cover the cross-sectional area of the duct. The SCR catalyst can be installed in either horizontal or vertical flue gas ducting.

7.4.1 General safety

The SCR catalyst can be an irritant to the respiratory system. When handling unused SCR catalyst (outside of the furnace or in a new furnace), avoid inhalation of catalyst dust. Under normal circumstances, large amounts of dust formation are not expected, as the catalyst remains relatively protected within the framing of the modules. Minimize activities that will result in dust generation and accumulation. Provide appropriate exhaust ventilation at places where dust is formed. Personnel should wear appropriate respiratory protection when catalyst dust is present.

When handling used SCR catalyst (installation, removal, or cleaning), employees can be exposed to other potential respiratory hazards. Refractory dust (potentially containing refractory ceramic fibers) can accumulate in the flue gas duct around the SCR catalyst and on the SCR catalyst modules. This dust can contain trace amounts of heavy metals from upstream equipment. Personnel shall wear appropriate respiratory protection while working in the area until the refractory dust has been cleaned up. If required based on task-specific safety concerns, personnel shall wear disposable protective clothing. Used catalyst can also contain trace amounts of heavy metals such as chromium, and arsenic.

7.4.2 Unloading

The catalyst modules are typically removed through an opening in the flue gas duct. Removable panels in the flue gas duct are typically provided for this purpose.

This activity requires a confined space entry into the flue gas duct so that the mounting hardware can be disconnected from the catalyst modules. For vertical duct configurations, there is a potential fall hazard while working inside. Additional precautions, such as barricading and/or fall protection, shall be considered.

The area around the SCR catalyst should be cleaned and vacuumed prior to catalyst removal. This will minimize the generation of dust during unloading. A vacuum cleaner with appropriate filter should be used.

Removal of the modules shall be carefully coordinated between the people working inside the flue gas duct and the crane operator lifting the modules out of the flue gas duct. The crane operator cannot see the inside of the flue gas duct. Use of radios and/or a spotter located outside the opening of the duct is recommended to ensure adequate communication between the crane operator and the workers inside the flue gas duct.

The modules are removed one by one, and hardware could need to be removed prior to lifting the next layer. The modules need to be guided through the opening in the flue gas duct as they are lifted out. Removal of the hardware should not be conducted during lifting operations to minimize risk to personnel. Guiding the modules requires that an individual is working inside the duct, close to the module, during the lift. Individuals working around the modules are at risk for crushing and pinching injuries, in particular during lifting operations, due to the weight of the modules and hardware.

7.4.3 Loading

Typically, the modules are lowered into the flue gas duct through an opening in the duct. The modules are stacked and secured in place. This usually involves having a crane lower the modules into the duct one at a time. As each module is put into place, workers inside the flue gas duct secure it.

Activities are similar to those associated with the removal of used catalyst, but in reverse. The same hazards exist and similar precautions should be taken.

7.4.4 Cleaning

During operation, dust and other foreign material can collect on the front face of the module layers and inhibit performance. Vacuuming the surface can reduce pressure drop through the modules and improve flow distribution. This activity involves making confined space entry into the flue gas duct. The necessary precautions shall be taken and the required work permitting shall be completed prior to entry. For vertical duct configurations, there is a potential fall hazard while working inside. Additional precautions such as barricading and/or fall protection should be considered.

The debris being removed from the face of the modules is a mixture of dusts and fibers that have migrated from upstream. Employees shall wear appropriate respiratory protection, and use of disposable protective clothing should be considered. A vacuum cleaner with appropriate filter should be used.

7.5 Other tubular reactors

There are several types of tubular reactors, aside from reformers, used in HYCO plants and processes. Such reactors include ITS that utilize a shell and tube exchanger vessel where the shift reaction (with catalyst) can occur inside or outside the tubes. Additional examples include shell and tube or tube-in-tube vessels that utilize reformer catalyst in the tube(s) with a hot syngas or hot flue gas as the shell side heat transfer fluid.

Reactors in this category have specialized designs and are not common in HYCO plants. Catalyst handling safety guidance and procedures should be sought from the reactor technology providers, catalyst suppliers, and catalyst handling services company. However, many of the safety principles provided in 7.1 through 7.4 can be applicable to the reactors in this category.

8 Stabilization and disposal

Disposal of used catalyst involves stabilizing the catalyst to prevent self-heating, identification of hazardous components, and transportation/disposal.

8.1 Stabilization

Catalyst with the risk of self-heating should be stabilized prior to disposal so that it does not heat during transportation or reclamation. Stabilizing the catalyst consists of oxidizing the catalyst in a controlled manner. There are multiple methods for stabilization of catalyst, all of which have advantages and disadvantages.

The following steps should be followed:

- a) Catalyst is moved into non-flammable containers with lids. After filling, the lid is immediately closed. A piece of dry ice (i.e., frozen carbon dioxide) is added on top to displace any air in the container. The lid should not be so tight as to prevent pressure buildup or vacuum formation;
- b) Temperature of the container is monitored, typically by infrared thermometer;
- c) When the container cools to ambient temperature the lid is opened for a short time (e.g., 10 seconds) re-exposing the contents of the container to air;
- d) Continue to monitor the temperature of the container, which can increase due to reaction of the catalyst with air; and
- e) Once the container returns to ambient temperature, repeat the lid opening process until there is no temperature rise after exposure to air. When the material no longer shows signs of heating, the material has been stabilized.

This process should be carried out in an open area away from flammable material. Water should be available to spray on containers in the event of overheating. Avoid contacting the catalyst directly with water. There can be metal dusts, carbon dust, and soluble metal salts (e.g., hexavalent chromium) on the catalyst, which if suspended

or dissolved in water can produce a personnel safety hazard and a hazardous waste management issue (including capture and treatment or disposal of contaminated water).

In the event that the catalyst is heating quickly and there is a concern that the design temperature of the vessel will be exceeded, the container may be filled with water. This action will cool and further oxidize the catalyst. Additional care should be taken for disposal of the container, catalyst, and contaminated water (e.g., transport in an overpack). If water filling is used for LTS catalyst, care should be taken because this catalyst can react to form hydrogen even with cold water when reduced. Applicable regulations should be consulted to determine any requirements that exist regarding this activity.

Certain catalysts, if they overheat, can release toxic gases once they have been exposed to process gas. For example, zinc oxide chemisorbent, in its reacted state of zinc sulfide, can release hydrogen sulfide and sulfur dioxide. Controlled stabilization of these catalysts is particularly important.

Other stabilization methods include:

- spreading out the used catalyst on a concrete pad;
- filling the vessel or discharge containers with water;
- exposure to air in the vessel; and
- exposure to air in the discharge containers.

Methods that rely on exposure of the catalyst to water create waste disposal issues, potential waste treatment permitting issues (depending on jurisdiction), and personnel exposure concerns as previously noted. Methods that rely on exposure to air create an increased potential for overheating of the vessel or discharge containers.

8.2 Labelling

Labeling shall be applied on each container with an indication of its content. Any applicable hazard communication Globally Harmonized System (GHS) pictograms appropriate to the hazards of the waste catalyst shall remain or be placed on the waste container. Waste catalyst shall be properly identified and characterized in accordance with applicable solid and hazardous waste management regulatory requirements. Any hazardous waste shall be appropriately marked, packaged, managed onsite, and shipped according to both environmental and transportation requirements.

Hazard and emergency response information shall be provided to the transport and final waste management contractors. The SDS of new catalyst may fulfill this requirement but it might not fully represent the actual used catalyst composition. Contaminants can be present, or the material could have reacted during normal operation (e.g., zinc oxide desulfurization chemisorbent is converted to zinc sulfide). Hazard information of these contaminants or of additional components should be included in the documentation.

8.3 Transportation and disposal

Used catalysts contain metal materials and possibly other hazardous substances with potential consequences to the environment and human health. As such, to minimize the impact on the environment, disposal of used catalyst should be part of any existing plant waste management procedures. Refer to AIGA 006, *Good Environmental Management Practices for the Industrial Gas Industry*[6] and CGA P-37, *Good Environmental Management Practices for the Compressed Gas Industry* [5].

There are two primary methods used for final disposal of used catalyst, disposal in a landfill or reclamation/recycling to recover valuable base metals. Whichever method is selected, approved contractors that are in compliance with all applicable regulations on waste treatment shall be used. Transportation to the landfill or reclamation site shall follow applicable local, regional, national, and international regulations.

9 References

Unless otherwise specified, the latest edition shall apply.

- [1.] *NIOSH Pocket Guide to Chemical Hazards*, National Institute for Occupational Safety and Health, Center for Disease Control and Prevention. www.cdc.gov/niosh
- [2.] European Chemicals Agency. www.echa.europa.eu
- [3.] *Code of Federal Regulations*, Title 29 (Labor), Superintendent of Documents. www.gpo.gov
- [4.] CGA P-78, *Guideline for the Safe Use of Instrument Air Systems Backed up by Gases other than Air*, Compressed Gas Association, Inc. www.cganet.com
- [5.] CGA P-37, *Good Environmental Management Practices for the Compressed Gas Industry*, Compressed Gas Association, Inc. www.cganet.com
- [6.] AIGA 006, *Good Environmental Management Practices for the Industrial Gas Industry*, Asia Industrial Gases Association, www.asiaiga.org