Materials Selection for Neat Methanol Service

Preface

This is the first of several technical bulletins addressing materials selection of metals, alloys, elastomers, rubber compounds, polycarbonates, and composites in methanol service. This first bulletin focuses on the overall materials selection process. The second and third bulletins address selection of metals and alloys, and elastomers and rubber compounds in anhydrous (neat or M-100) methanol service. The fourth bulletin addresses selection of polycarbonates (plastics) and composite materials for blended fuel service, specifically M-10, M-15, and M-85.

Readers who have researched articles, references, and the many chemical compatibility charts that are available on the internet, know there is inconsistency from one source to another regarding which materials are and are not suitable for methanol service. The diversity of answers is largely due to differences in assumptions regarding specifics of the intended application. This series of four Technical Bulletins addresses this issue by emphasizing materials selection relative to materials application.

Bulletin numbers 2 through 4 organize published information into a table format that enables evaluation of available choices with guidance on compatibility for specific applications. Additional investigation beyond information presented in these four bulletins is needed to arrive at final choices and to write specifications necessary for facility design, and materials procurement. The intent of these bulletins is to provide a structured starting point within a variety of possible choices.

Methanol is manufactured, transported, stored, processed and utilized in a wide variety of purposes and applications including chemical feed stock, hydride control in oil and gas production, motor fuel additive, primary motor fuel (M-100), source of carbon for waste water de-nitrification, manufacture of bio-fuels, methanol-based hydrogen fuel cells, and many others. The array of operating parameters and circumstances is equally wide ranging. Each application has unique material requirements. Guidance in these bulletins is not a substitute for knowledgeable engineering evaluation of process-specific applications. Understanding your application in normal and abnormal operating conditions is essential. Abnormal operation includes all situations and circumstances other than those that are normally intended, and are within
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designated design limits. Pressure testing and startup are examples of abnormal conditions. Materials selection must consider both normal and abnormal conditions.

About Materials Selection

Materials selection is a complicated process that occurs as an iterative progression of considerations that emerge throughout the design process. The first step of materials selection uses a Process Flow Diagram (PFD) and associated process parameter envelopes and assigns Material Safety Data Sheets (MSDSs) for process fluids that comprise unit operations within the PFD. The second step characterizes basic design parameters for the types of equipment that comprise unit operations: e.g., above-ground storage tanks (ASTs), reactors, vessels, columns, towers, furnaces, heat exchangers, piping and components, pumps, compressors, control elements, and their associated trim. The third step identifies design, fabrication, and construction codes and standards that must be followed in order to ensure that process fluids are confined within the equipment. This includes consideration of accepted engineering practices for mechanical integrity and sustained fitness-for-service. This also includes safety requirements for joint tightness and leak prevention.

A ‘standard’ is a document that applies collectively to codes, specifications, recommended practices, classifications, test methods, and guides, which have been prepared by a standards developing organization, and published in accordance with established procedures. Standards can be voluntary, consensus, or mandatory.

‘Voluntary standards’ are developed by private sector bodies and are available for use by any person, company, or governmental organization. ‘Industry’ and ‘consensus’ standards are voluntary unless they become mandatory as a result of use, reference, or adoption by a regulatory authority, or when invoked in commercial instruments such as contracts and purchase orders. Industry standards are developed by trade organizations for use within a particular industry through cooperation of all parties who have an interest in participating in development and use of the standards. Industry standards are voluntary consensus-type standards.

‘Mandatory standards’ require compliance as a matter of governmental statute, regulation, organizational internal policy, or contractual requirement. Failure to comply with mandatory standards implies sanction, such as criminal or civil penalties. ‘Codes’ are standards, which have been codified by governmental authority, and are law within the jurisdiction of that authority. Standards are designated as regional, national, or international.

‘Regional standards’ are those developed, adopted, or promulgated by regional organizations [e.g., European Committee for Standardization (CEN), and Pan American Standards Commission (COPANT)]. Regional standards are generally voluntary in nature. ‘National standards’ are those adopted by a national standards body [e.g., American National Standards Institute (ANSI), Standards Council of Canada (SCC),
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British Standards Institution (BSI)] and made available to the public. As a practical matter, a national standard is any standard that is widely used and recognized within a country. Within this context, even governmental standards such as those issued by the U.S. Occupational Health and Safety Administration (OSHA) can be considered national standards.

Although there is discussion and disagreement regarding what constitutes an ‘international standard’, there is some agreement that international standards must be used in multiple nations, and the development process must be open to all countries. Examples of well-known international standards are the International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC). Some international standards are promulgated by organizations that originated as national industry associations, professional societies, and standards developers. Over time, standards from some of these bodies have gained global presence [e.g., ASTM International, SAE International, NFPA International, NACE International, American Society of Mechanical Engineers (ASME), and the American Petroleum Institute (API)]. Countries are not required to adopt international standards. Rather, they may adhere to their own national standards, adopt another country’s national standards, or adhere to recognized international standards as a matter of treaty such as a trade agreement, or as a matter of convenience.

Because methanol is a toxic material, leakage from pressurized service equipment poses a toxic hazard to persons near methanol equipment. Two aspects of the ASME International codes for process piping and unfired pressure vessels reference design measures such as joint tightness as a means of controlling leakage of contained toxic fluids: B31.3, Chapter VIII, “Piping for Category M Fluid Service” and ASME Boiler and Pressure Vessel Code Section VIII Division 1 section UW-2 (2007 edition), vessels that contain lethal substances (i.e., so-called lethal service applications). The manner in which ASME defines “M Fluid Service” for piping, and “Lethal Service” for vessels is dissimilar. Therefore, it is necessary to review classifications and protective measures in both codes. Further complicating code design considerations involving toxicity, the manner in which “fluid service” and “harmfulness” are designated in the ASME standards is very different from the manner of designation in other widely used national and international standards. For example, Australian and European pressure equipment codes and standards (respectively, Pressure Equipment Hazards Levels, AS4343:2005 and European Union Pressure Equipment Directives, PED 97/23/EC) are very different from each other, and from the ASME piping and pressure vessel standards. Because of this, different standards for pressure equipment arrive at different results for the level of quality assurance and the necessary level of protection. Compliance with ASME in no way implies compliance
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with any other national or international standard for pressurized equipment that contains toxic material.

The process of determining what is required, what is necessary and what is appropriate begins by understanding the nature and severity of the toxicity hazard. Hazardous properties of neat methanol are described in the next section. Once toxicity characteristics are understood, it is possible to refer to the governing codes and standards to determine an appropriate ‘harmfulness’ classification, and then to select methods of protection. Harmfulness of the toxicity hazard is easily determined for neat methanol; however, it may not be easily determined for methanol mixtures. When dealing with mixtures, it may be necessary to enlist a team of specialists consisting of 1.) a process engineer to characterize an operating envelope, 2.) a process chemist to establish chemical composition in a particular piece of equipment, 3.) a toxicologist to determine harmlessness for code-designated exposure pathways, 4.) a Certified Industrial Hygienist to calculate the projected environmental concentration and likely exposure dose, and 5.) a materials engineer to select ‘best’ materials and trim components.

Regulations

The National Fire Protection Association (NFPA) 69 (www.nfpa.org) is the standard on explosion prevention systems. The NFPA addresses MOC but uses the term limiting oxidant concentration (LOC). The limit for methanol is 10%. However, Air Liquide’s practice is to inert flammable systems to half the LOC value.

Methanol Toxicity

Methanol is a toxic material. Ingestion of approximately two tablespoons of neat methanol can be lethal unless recognized and treated within hours of exposure. Methanol exposure can occur by vapor inhalation, by contact and absorption through the skin, and by liquid ingestion. The following occupational exposure limits issued by the U.S. Occupational Safety and Health Administration (OSHA), and the American Conference of Governmental Industrial Hygienists (ACGIH) provides information on methanol’s toxicity:

- OSHA Permissible Exposure Limit (PEL) for 8-hour exposure: 200 parts per million (ppm) equivalent to 260 milligrams per cubic meter of air (mg/m³) Time Weighted Average (TWA)
- ACGIH Threshold Limit Value (TLV): 200 ppm (260 mg/m³) (TWA)
- ACGIH Short Term Exposure Limit (STEL-skin): 250 ppm (325 mg/m³)
- In addition, the National Research Council’s [NRC 1985] Emergency Exposure Guidance Levels (EEGLs) for short-term exposure are:
  - 10-min EEGL: 800 ppm
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- 30-min EEGL: 400 ppm
- 1-hour EEGL: 200 ppm
- 24-hour EEGL: 10 ppm

The National Institute for Occupational Safety and Health (NIOSH) established an acute toxicity concentration of methanol that is Immediately Dangerous to Life and Health (IDLH) at 6,000 ppm, which is based on acute inhalation toxicity data in animals.

Coincidentally, the IDLH value of 6,000 ppm is also 10% of the Lower Explosive Limit (LEL) of 6 vol. %; a typical flammability alarm point of 6,000 ppm and the IDLH are the same. If flammability is the only method of monitoring, then airborne methanol vapor is at the IDLH concentration when a flammability alarm initiates, and the detected vapor concentration exceeds the PEL of 200 ppm by 29 times. Methanol concentration that is safe for fire is not safe for health. Best practice is to monitor and alarm health and fire concentrations separately.

Methanol has poor warning properties. Methanol vapor is invisible; methanol liquid is clear, colorless, and easily mistaken for water or ethanol; methanol flames are invisible in bright light; and the odor threshold of methanol vapor is high, meaning that the presence of methanol vapor may not be detectible below 5,900 ppm. By the time a person detects the odor of methanol vapor, they have already incurred an acute IDLH exposure. A final consideration is that acutely irreversible exposure can occur without symptoms beyond irritation of the nose, throat and airways, and a feeling of fatigue and disconnected discomfort similar to drunkenness.

Onset of acute methanol exposure symptoms is delayed by 8 to 24 hours following exposure; the body metabolizes methanol slowly. The period of delay between the time of exposure and the time at which health critical symptoms manifest is extended if a victim has consumed alcoholic beverage (ethanol) several hours prior to and after exposure. The human body metabolizes ethanol, an alcohol which is poisonous when ingested in large doses, in preference and prior to metabolizing methanol, an alcohol which is poisonous when ingested, inhaled, or contacted in small doses. The effects of ethanol mask the effects of methanol. If exposure is unrecognized and untreated within the first 12 to 24 hours due to poor sensory warning and/or delayed onset of toxic symptoms, then blindness, brain damage, or even death may occur within 48 to 60 hours.

Category M Fluid Service

The American Society of Mechanical Engineers Process Piping Code, ASME B31.3, assigns facility owners responsibility for determining and designating whether their process is Category M Fluid Service. That is, owners must determine whether the toxicity of the fluid and the manner in which the fluid is received, stored,
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transferred, and processed needs ‘joint tightness’ protections for valves, pump seals, flanges and the like, above and beyond those indicated in Chapters I through VII of the ASME Code.

The intent of the Category M Fluid Service designation is to reduce likelihood and rate of fluid leakage through joints from a hazardous to a non-hazardous concentration within the environment surrounding pressurized piping and equipment. Provisions that accompany designation as Category M fluid service increase health protection of those working in and around methanol equipment. Substitution of protections in lieu of measures presented in Chapter VIII of the Code is permitted providing a Process Hazards Assessment (PHA) of unintended leakage is confirmed to cause non-detrimental exposure. The PHA is essentially a qualitative/semi-quantitative risk-based analysis that uses methods, principles and technology applied in Risk-Based Inspection (RBI) and Levels of Protection Analysis (LOPA) to assess the likelihood and consequences of methanol leakage.

The next section addresses methanol toxicity relative to Category M Fluid Service classification and exposure protection.

Owner Responsibilities

The ASME B31.3 piping code defines *Category M Fluid Service* as service in which the ‘potential’ for personnel exposure to toxic fluids is judged ‘significant’. The Code identifies toxicity as exposure by breathing, or bodily contact to even a very small quantity of such fluid caused by leakage, but not by ingestion. If measures listed in Chapters I through VII for “Normal Service”, do not prevent leakage capable of serious irreversible harm to persons in and around pressurized equipment, even when prompt restorative measures are taken, then the service is *Category M Fluid Service*. However, Category M Fluid Service designation is avoidable if sufficient protections beyond those indicated in Chapters I through VII are adopted in lieu of provisions described in Chapter VIII.

Leakage and fugitive emission in methanol service are subject to either of two controls: 1.) designation as M fluid service in which case provisions listed in Chapter VIII are invoked, or 2.) addition of protections not listed in Chapter VIII, which provide equivalent health protection. It is good practice to understand how provisions in Chapter VIII relate to your application before specifying joint, seal, and diaphragm trim tightness. Depending on circumstances, it may be advisable to indicate a maximum allowable fluid leakage rate within valve, flange, and pump seal specifications. Requirements for joint tightness may drive selection of seat, packing, and gasket materials. Maximum fluid leakage rate for valves should consider leakage across the valve seat, through, and across valve trim. Flange connection tightness for piping and equipment such as tanks, vessels, distillation columns, heat exchangers etc. will almost certainly dictate flange gasket material and the method and pattern of bolt tensioning.
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In summation, considerations for Category M fluid service are:

“A fluid service in which the potential for personnel exposure is judged to be significant, and in which a single exposure of a very small quantity of a toxic [poisonous] fluid [liquid or vapor], caused by leakage, can produce serious irreversible harm to persons on breathing or bodily contact, even if prompt restorative measures are taken.”

It is important to understand that determination of Category M designation considers fluid properties and protections in combination. Owners have the option of following provisions of Chapter VIII, or implementing measures that provide equivalent or superior protection.

Chapter VIII leak tightness provisions are unnecessary IF

1. application of multiple protections beyond those prescribed in Chapters I through VII of B31.3 sufficiently protect personnel from exposure to very small quantities of the fluid leaking into the environment,

AND

2. occurrence of severe cyclic conditions and/or severe abnormal operating circumstances can be prevented by design.

Considerations of Materials Selection

A commonly held misconception of materials selection for methanol service is that compatibility (i.e., corrosion resistance) is the major factor in assessing and choosing materials, and that selection of the most corrosion resistant material is de facto the best practice for meeting organizational expectations for health, safety, equipment service life, and equipment life cycle cost. Corrosion resistance as a measure of compatibility is an important consideration. However, other factors also determine the most appropriate material for a particular application. For example, cost, availability, mechanical properties, physical properties, form, mechanism and rate of deterioration, failure modes, consequence severity upon failure, and life cycle cost are all significant considerations.

Corrosion deterioration assumes many and varied forms depending on the alloy group, the type and amount of alloying agent, and thermal history during manufacture, solidification, cooling, and heat treatment. Operating conditions and environmental circumstances associated with an application are likewise important determinates of deterioration rate. Corrosion may occur as generalized metal loss, accelerated metal loss due to galvanic or bi-metal corrosion, localized metal loss due to pitting and crevice corrosion, corrosion erosion, selective removal of an alloying agent (e.g., de-zincification in brasses) and under-
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deposit corrosion. Degradation can also be by chloride stress corrosion cracking (SCC), and by hydrogen-induced cracking (HIC).

Aluminum Alloy Floating Roof and Geodesic Dome AST Tank Covers

As an example of the importance of application in determining suitability of alloys, a quick read of published information indicates aluminum alloys are unsuited for methanol service because methanol is electrically conductive and aluminum alloys are subject to galvanic corrosion when electrically coupled to more noble alloys such as carbon and stainless steels. This information is correct; however, considered in a context of wide ranging applications, this guidance does not necessarily eliminate aluminum alloys from consideration as floating roof and as geodesic dome tank covers.

Carbon steel, or 300 series austenitic stainless steels such as ASTM 304, 304L, 316, or 316L are preferable choices in terms of structural strength, corrosion resistance, the form of corrosion, and life cycle cost. Although suitable choices for tank fabrication materials, steels are not necessarily best choices for tank covers. Properly designed aluminum alloy components have high strength-to-weight and stiffness-to-weight ratios compared to steels. Density of commonly used 5000 series wrought Al-Mg alloys is 0.10 lb/in\(^3\) (2660 kg/m\(^3\)); the density of steel is 0.28 lb/in\(^3\). Density of steel is a factor of three greater than density of aluminum alloys. The high strength-to-weight ratio and stiffness of aluminum alloys, the lower relative buoyancy of steel, and the fact that floating roof service is static, non-flowing service make aluminum a candidate material for floating roofs, particularly if the floats are coating protected. Geodesic dome covers on methanol storage tanks are moist air and methanol vapor service, with condensate liquid service. Padding with dry nitrogen gas eliminates moisture, and reduces partial pressure of methanol vapor, and substantially reduces the rate of corrosive attack. Aluminum 5000 and 6000 series alloys are appropriate applications for floating roof and geodesic dome tank covers, providing measures are taken to control dissimilar, bi-metal, galvanic corrosion.

Service life of carbon steel tanks in methanol service is \(\approx 20\) years (\(\approx 30\) years for 300 series austenitic stainless steel tanks), depending on factors such as inspection frequency, maintenance, and effectiveness of cathodic protection. Life of a 5000 or 6000 series aluminum alloy floating roof/ geodesic dome cover is between 7 and 10 years. Using carbon or stainless steel for tanks and aluminum for floating roof and geodesic dome tank covers is appropriate as long as galvanic corrosion is controlled. The cost and expected life of the tank is greater than costs associated with periodically repairing/replacing an aluminum alloy floating roof or geodesic dome cover. Aluminum
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alloy floating roof and geodesic dome covers are in use at some Gulf Coast methanol marine terminals.

However, if an aluminum floating roof is not electrically isolated from electrochemically cathodic tank material, or if the roof remains in service beyond its useful life without inspection, testing and repair, then wetted surfaces of the floats can develop pinholes, lose buoyancy, and sink. Rate of metal loss on a submerged roof is much higher than metal loss rate on a floating roof. Unless recovery is timely, then the roof may be reduced to undissolved remains, which may or may not be repairable. Furthermore, a large open air floating roof tank is a major fire and toxicity hazard.

As this example illustrates, the issue of whether aluminum alloy is an appropriate material of construction for methanol service depends on specifics of application, and assumptions regarding inspection, maintenance, projected life, and life cycle cost.

Aluminum Alloy Tanker Trucks and Rail Cars

Neat methanol (> 98.5 vol. % purity), also known as M-100 in the alternate fuels industry, is routinely transported in ISO 9001/MC306/DOT406 certified 5454 H38 alloy aluminum tanker trailers and DOT 111A100ALW1 rail tanker cars. Alloy 316L stainless steel is more corrosion resistant and more heat resistant in the event of rollover or derailment and subsequent fire. However, stainless steel has a much lower strength-to-weight ratio and higher capital cost than aluminum alloy, which make 316L stainless steel a less advantageous choice for long distance hauls, but arguably a safer choice for short haul delivery of fuel in congested, densely populated, high traffic areas such as New York City. Because of the lower heat resistance of aluminum alloys compared to steel alloys, some municipalities have considered prohibiting use of aluminum fuel tankers and trailers.

Mechanical integrity and fitness for service of tanker trailers and rail car tankers are important to public safety. The U.S. Department of Transportation (DOT) has rigorous design, fabrication, and inspection requirements for tanker trucks, trailers, and rail cars. The National Transportation Board (NTSB) investigates and reports rail and road accidents involving transport of fuels and hazardous chemicals. These organizations consider safety of aluminum tankers and rail cars adequate for continued service.

Choosing a “suitable” material for methanol service depends on codes, generally accepted good engineering practice as defined by industrial standards, circumstances of intended use (especially pressurized applications), and
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inspection, testing, and maintenance of methanol equipment. Look first to the circumstances of application, and then proceed with materials selection.

This advice applies to all materials in methanol service: metals, alloys, elastomers, rubbers, polycarbonates and composites.

References

- In Society for Standards Professionals, SES-1, “Recommended Practice for Standards Designation and Organization”.
- ANSI's “Standards Management: A Handbook for Profit”.
- ANSI/FCI 70-2: Control Valve Seat Leakage.
- ANSI/ISA Standard SD75.01.01; MSS SP-061: Pressure Testing of Steel Valves.
- API Standard 598: Valve Inspection and Testing.
- www.researchgate.net/publication/228844168_Tightness_of_Bolted_Flange_Connections_what_does_that_mean
- mycommittees.api.org/standards/ecs/sc17/Items%20to%20Review/deesigncfj.pdf.
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- ASME Boiler and Pressure Vessel Code, Section VIII Appendix BFJ: *Bolted Flanged Joint Design*.
- Becht.com/blog/when-should-category-m-fluid-service-be-selected-for-asme-b31-3-piping-systems [C. Becht is principal in Becht Engineering, and is a long serving member and present Chairman, of the ASME B31.3, Process Piping Committee.]
- becht.com/key-contact/Charles-becht-iv-phd-pe
- API Recommended Practice 580: *Recommended Practice for Risk-Based Inspection; Best practice for risk based inspection as a part of plant integrity Management*.