Compatibility of Metals & Alloys in Neat Methanol Service

There are about a dozen classes of alloys that are appropriate for neat methanol service. Some alloys are appropriate for a variety of applications; others are suitable for a narrow range of service. Service applications are:

- storage- tanks, totes, drums 5 gallon buckets, and 1 gallon cans;
- transportation- ships, barges, rail cars, tanker trucks, totes, drums, and cans;
- processing- pressure vessels, columns, shell and tube heat exchangers, plate and frame heat exchangers, piping and fittings, valves, process sensors and transmitters; and
- transfer (machinery)- compressors, pumps, and fans.

A large number of the alloys listed in the Table 1, "Metals and Alloys Compatibility Table," are suitable as pump and valve trim, and as bellows, gaskets, and seals to contain pressurized fluids. By comparison, a list of alloys suitable for fabrication of Process Flow Diagram (PFD) and Piping and Instrument Diagram (P&ID) tag-numbered equipment items is short. Brief descriptions of commonly used alloy groups are presented below. Examples of alloys used in a variety of applications and their compatibility ranking for applications involving neat methanol are presented in Table 1.

Physical properties such as yield strength, ultimate tensile strength, elasticity, toughness, etc., and chemical compatibility (i.e., corrosion resistance) of metals and alloys is determined by selection of a particular base metal (aluminum, copper, iron, lead, and titanium), and relative abundance of specific alloying elements within the base metal: i.e., argon (Ar), aluminum (Al), boron (B), carbon (C), columbium (Cb), cobalt (Co), chromium (Cr), copper (Cu), cesium (Ce), magnesium (Mg), manganese (Mn), molybdenum (Mo), nitrogen (N), niobium (Nb), nickel (Ni), lead (Pb), antimony (Sb), silicon (Si), tin (Sn), tellurium (Te), titanium (Ti), vanadium (V), tungsten (W), zinc (Zn), and zirconium (Zr). Base metal elements in one group of alloys may be alloying elements in a second group, or contaminants in a third group.

Materials Selection for Neat Methanol Service (cont.)

Alloy composition, method of manufacture, thermal history, post solidification heat treatment, etc. determine crystal lattice structure, atomic packing density, grain size, phase abundance, and microstructure. Grain size and microstructure dictate physical properties, and in combination with circumstances of application, determine useful life, and failure mode (e.g., stress cracking, hydrogen embrittlement, fatigue, creep, etc.). Failure mode is determined by a combination of stress loading, alloy properties, uniformity of alloy composition near the grain boundaries, relative phase abundance, and chemical compatibility within the service environment. It is not always possible to presuppose how a particular alloy will perform in a particular application. For this reason, experience is a fundamental determinate in predicting when and how alloys will fail. Typically, experience is determined by a combination of testing and reviewing prior service experience. The one certainty is that given sufficient time, all metal alloys will fail.

Carbon Steels

Iron is the base metal for carbon steels. Carbon (0.12-2.0 C)is the primary interstitial alloying constituent in carbon steels, along with no minimum content specified or required for chromium (Cr), cobalt (CO), molybdenum (Mo), nickel (Ni), niobium (Nb), tungsten (W), vanadium (V) and zirconium (Zr). Maximum contents for copper (Cu), manganese (Mn) and silicon (Si) are 0.60, 1.65, and 0.06 wt/percentage respectively. Two fundamental conventions relative to alloying, melting, solidifying, cooling, tempering, and aging metals are too little of a good thing is a bad thing, and too much of a good thing is a bad thing. Because multiple factors determine a particular set of alloy properties, it is necessary to control alloy composition and each stage of the production process in order to produce product with the desired properties. The ultimate success is determined by chemical analysis, micrographic inspection, and mechanical testing to verify that the desired properties are achieved. Alloy formulation, thermal history, and property verification is stipulated in standards such as those published by American Society of Testing and Materials International (ASTM). In selecting metals and alloys it is necessary to specify the alloy (e.g., American Iron and Steel Institute (AISI) 1020 carbon steel, 304 stainless steel, nodular cast iron, etc.), and the code that is appropriate for your application.

Molten iron and molten steel contain dissolved gases, which cause boiling of liquid metal during pouring, solidification, and cooling. These steels are termed “unkilled” or

Materials Selection for Neat Methanol Service (cont.)

"wild" steels. Addition of oxygen scavengers, (e.g., Si, and/or Al) to the molten metal removes the gases, thereby preventing boiling and allowing the molten liquid to solidify with fewer defects and smaller grain size. So-called "killed" steels are cleaner, exhibit superior mechanical properties, and are therefore generally used in preference to unkilled steels. ASTM A106 pipe, A105 forgings, and A516 plate are examples of "killed" steel. Unkilled and semi-killed steels are permitted in benign services. ASTM A53 and American Petroleum Institute (API) 5L pipe and ASTM A36 structural steel are examples of "semikilled" steels. Unkilled versus killed steel continues to be important in terms of code compliance; however, as a practical matter, more than 95% of world steel production uses continuous casting and all continuously cast steels are "killed" as an inherent aspect of the process.

In order to resolve issues of recognized equivalence between coding systems, metal alloy products can be stenciled to indicate compliance with multiple codes. For example, American Society of Mechanical Engineers (ASME) dictates use of ASTM A106 Grade B seamless pipe. In recognition of code equivalence, seamless pipe can be code stamped as API 5L Grade B/API 51 Grade X42/ASTM A106, and ASTM A53 Type S Grade B.

Low Alloy High Temperature Chrome-Molybdenum Carbon Steels

Low alloy steels are defined as iron-based alloys that contain less than 12% of intentional alloying element. Low alloys of Cr-Mo such as 1Cr-½Mo and 1¼Cr-½Mo are used for temperatures above 800^{o}F (425^{o}C). Enhanced strength plate steels are used in pressure vessels. Refer to ASTM A302, A537,A542, and A543 for examples of plate materials in this class. Alloys containing Cr ≥5% are used for resistance to sulfidic corrosion in high temperature service. Series 1¼Cr-½Mo, 2¼Cr-1Mo, and 3Cr-1Mo alloys and their vanadium enhanced counterparts are used in high pressure, high temperature $H_{2\,(g)}$ service. ASTM A213 T5 5Cr-0.5Mo is used in steel tubes for boilers and ASTM A335 5Cr-0.5Mo alloys is used within the petrochemical industry as tube material.

Low pressure production of methanol involves three principal process steps: 1.) *reforming*, in high temperature reforming furnaces and catalyst bed converter reactors of Cr-Mo Steels, 2.) *synthesis,* separation of methanol from un-reacted gases, and 3.)

Materials Selection for Neat Methanol Service (cont.)

distillation, separation of methanol product from high boiling and low boiling impurities. Equipment components in the synthesis and distillation sections are fabricated from austenitic, ferritic, and duplex stainless steels.

3% Nickel Carbon Steel

Ni-Mn alloys with either 3½ or 9% Ni are used for low temperature applications such as storage of LPG and LNG storage where service temperature ranges from -50 to -320^oF (-46 to -195^oC). Addition of nickel eliminates issues associated with ductile to brittle transition temperature failure of unalloyed carbon steels.

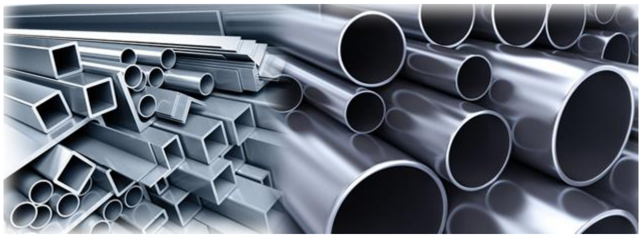
300 Series Austenitic Stainless Steels

The 300 series austenitic stainless steels are the workhorses in applications that require corrosion resistance. These alloys are available in regular carbon and low carbon grades. The low carbon grades are preferable for welded construction. Alloy 304 is a so-called 18-8 (18Cr-8Ni) with no Mo alloying agent. Alloy 316 is an 18-8 alloy containing Mo alloying agent. Addition of molybdenum increases maximum allowable working stress and improves resistance to chloride-induced pitting and crevice corrosion. Alloys containing greater amounts of chrome and nickel such as type 310 (25Cr-20Ni) are available in cast and wrought form and are used in high temperature heater applications.

A major difficulty with conventional austenitic stainless steels is susceptibility to stress chloride cracking (SCC), also termed stress corrosion cracking. Regular carbon grade austenitic stainless steels are subject to sensitization, which is the selective precipitation of chromium carbide at the grain boundaries, thereby creating adjacent narrow zones of chromium enrichment and depletion. The chromium enriched and depleted zones act as a local galvanic couple that accelerates corrosion at the grain boundary, particularly in the presence of chloride ion. Imposed or even residual stress can cause component failure by cracking along the weakened grain boundaries. Ferritic alloy types such as 430 stainless steel (14-18Cr), nickel-copper alloys such as Monel 400 (67Ni-30Cu), superaustenitic alloys with high chromium and nickel plus 2-6 % Mo, nickel alloys such as titanium stabilized Alloy 825 (22Cr-42Ni-3Mo), and duplex austenitic-ferritic alloys such as Alloy 2205 (22Cr-5Ni-3Mo-N) are selected in place of 316 to avoid the sensitization issue.

Materials Selection for Neat Methanol Service (cont.)

400 Series Ferritic and Martensitic Stainless Steels



All 400 series stainless steels are subject to grain coarsening in weld heat-affected zones. The air hardenable martensitic grades also have very brittle heat-affected zones. Consequently, straight chromium stainless steels are not recommended for pressure vessel service. Major uses are heat exchanger tubing, valve and pump internals, pressure vessel internals, and as clad and weld overlay linings in pressure vessels and heat exchangers. All 400 series stainless steel alloys are essentially immune to chloride stress corrosion cracking, but are subject to chloride pitting. Superferritic stainless steels such as 25CR-4Ni-4Mo demonstrate satisfactory resistance to chloride pitting and chloride stress corrosion cracking. Higher chromium grades such as Type 430 are susceptible to embrittlement at temperatures over 750^{o}F (400^{o}C). Standard practice is to avoid using straight chromium stainless steels in pressure applications above 650^{o}F (345^{o}C). All ferritic and martensitic stainless steels are susceptible to hydrogen stress corrosion cracking, to hydrogen-induced cracking, and to transition temperature low temperature embrittlement.

Duplex Stainless Steels

Microstructure of duplex stainless steels is a mixture of both ferrite and austenite in approximately equal amounts. Typically duplex stainless steels contain >17% chromium and <7% nickel, plus 2% molybdenum in the more corrosion resistance types. Duplex steels are stronger than austenitic steels, and have greater resistance to chloride SCC. Microstructure consisting of 50% ferrite makes these alloys susceptible to hydrogen embrittlement. Because manufacturing and fabrication are more difficult for duplex steels, their use is usually more costly than for conventional austenitic stainless steels.

Precipitation-Hardening Stainless Steels

Precipitation-hardening alloys are denoted with the suffix “PH” (i.e., Precipitation Hardening). Alloy 17-4 PH (17Cr-4Ni-4-Cu) is an example of this type alloy. These alloys are hardenable by heat treatment and are relative easy to fabricate. Common applications are springs, valve stems, and internals for rotating equipment. They are characterized by high strength and superior corrosion resistances compared to 12Cr

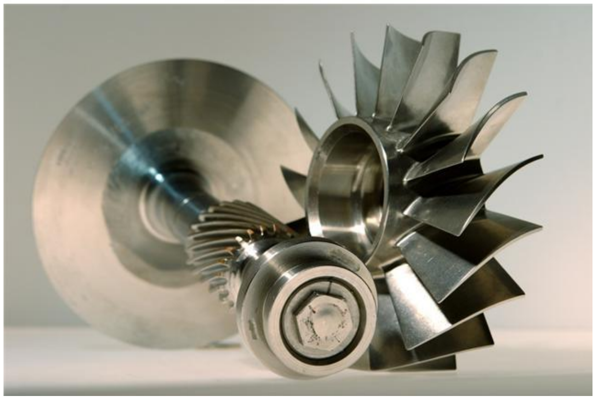
Materials Selection for Neat Methanol Service (cont.)

steels, but are inferior to Type 304 stainless steel. Precipitation hardening alloys can be susceptible to chloride SCC and hydrogen induced cracking (HIC).

Electroless Nickel Plated Alloys

A technique known as "electroless nickel plating" is used with carbon steels to avoid product contamination, prevent galling, and to enhance tight sealing in valve closures.

Nickel and Nickel-Based Alloys



Monel 400 alloy in precipitation-hardenable form is used in high strength applications such as pump shafts. The family of nickel cast irons containing 13 to 35% Ni with copper and chromium alloying additions are widely used for wear resistance, corrosion resistance, and service at both low and high temperatures. Nickel-chromium-molybdenum alloys such as Hastelloy C-276 (15Cr-54Ni-16Mo) and its derivative alloy containing 3% tungsten are premium alloys for harsh corrosion environments. Nickel alloy failure mechanisms for this family of alloys include high-temperature intermetallic phase embrittlement, stress corrosion cracking, and various other forms of cracking. Cracking threshold values are alloy specific.

Cast Iron Alloys

Cast irons differ from cast carbon steels in the amount of carbon content. Cast irons contain at least 2% carbon; cast carbon steels typically used for plant construction contain less than 0.35% carbon. Two types of cast iron are commonly used: 1.) gray cast iron (ASTM A48) is plain cast iron with no intentional alloying elements, and 2.) Ductile cast iron, known as nodular or spheroidal cast iron, which contains small amounts of magnesium alloying element to improve ductility and toughness (ASTM A536). Nodular cast iron is used in valve bodies, pumps, and large reciprocating compressors. Malleable cast iron (ASTM A47) is a nodular cast iron in which the graphite nodules form as a result of heat treatment rather than solidification. Three

Materials Selection for Neat Methanol Service (cont.)

specialty cast irons are used in fabrication of equipment components: 1.) corrosion-erosion resistant silicon cast irons (ASTM A518) containing up to 25% chromium, 2.) white cast irons (ASTM A532) containing up to 25% chromium used in pumping abrasive slurries, and 3.) nickel-rich cast irons (Ni-Resist, ASTM A436) are used in low and high temperature applications requiring wear resistance and resistance to seawater corrosion. Cast irons are used in many services for internal components such as pump impellors and valve components.

Aluminum Alloys

Aluminum alloys are available in a large number of variations, emphasizing properties such as strength, fatigue resistance, toughness, and enhanced corrosion resistance. Aluminum alloys are used for storage and transportation of many refined chemicals such as methanol, and fuels such as gasoline and diesel. Care should be taken since methanol can vigorously attack some aluminum alloys. Aluminum alloys offer a favorable strength to weight ratio, but are susceptible to chloride pitting, and crevice corrosion in chloride contaminated methanol service.

Copper and Copper Alloys

Copper and its alloys are attacked slowly in methanol service. Copper and copper alloy plating and cladding over carbon steel is aggressively attacked and is not recommended for methanol service.

Copper alloys are used primarily for heat transfer in methanol service (titanium alloy Ti-6Al-4V, a superior tube material in sea water and hydrocarbon applications, is incompatible in methanol service). Copper alloy designations are listed below using the Unified Numbering System (UNS) for Metals and Alloys. Unlike ASTM, UNS is not a specification. Various categories of copper family of alloys are listed as follows:

- *coppers and high copper alloys*: [C 10100 - C 19600; C 80100 - C 82800] Metals which have a designated minimum copper content of 99.3% or higher are termed “high coppers”.
- *zinc brasses*: [C 20500 - C 28580] Wrought alloys comprise three main families of brasses: copper-zinc alloys; copper-zinc-lead alloys (so-called leaded

Materials Selection for Neat Methanol Service (cont.)

brasses); copper-zinc-tin alloys (tin brasses). Binary copper zinc alloys are the most widely used group of copper alloys. Alloys above 15% zinc may experience dezincification, a condition in which zinc alloying agent is selectively leached from the copper-zinc metal matrix.

- *tin brasses*: [C 40400 - C 49800; C 90200 - C94500] Additions of tin significantly increase corrosion and dezincification resistance of some brasses.
- *aluminum brasses*: [C6640 - C69900] Aluminum oxide is an important constituent of the corrosion film on brass containing several percent aluminum. Presence of aluminum oxide increases resistance to impingement attack in turbulent high-velocity applications.
- *aluminum bronzes*: [C 60600 - C 64400; C 95200 - C 95810] Broadly speaking, bronzes are copper alloys in which the major alloying element is not zinc or nickel. Originally “bronze” described alloys with tin as the only or principal alloying element. The term “bronze” is no longer used by itself, but is accompanied by a modifying adjective. Aluminum bronzes contain 5 to 12% aluminum, which provides excellent resistance to impingement corrosion, cavitation resistance and high-temperature oxidation. Nickel-aluminum bronzes have greater resistance to dealloying and to cavitation erosion in methanol service. Aeration can result in accelerated corrosion in some media that appear to be compatible.
- *cupro-nickel alloys*: [C70600 (90Cu-10N)i; C71500 (70Cu-30Ni)] The cupronickels are solid solutions of nickel in copper which are available as plate, sheet, bar, and pipe and tube. These alloys are used in desalination, seawater piping systems, and cooling loops, and heat exchanger service.

Lead and Lead Alloys

Lead is an amphoteric metal, subject to chemical attack by both acids and alkalis. It has substantial corrosion resistance in environments that produce an insoluble film of corrosion products. Common lead (L50045) has more corrosion resistant, harder and stronger variations in chemical lead (L51120), antimonial lead (L52605) and tellurium lead (L51123). Primary use of lead alloys in methanol service is as metal gaskets and seals.

Titanium and Titanium Alloys

Materials Selection for Neat Methanol Service (cont.)

Titanium alloys exhibit rapid and catastrophic stress corrosion cracking if the methanol contains insufficient water to passivate the titanium. Use of titanium in methanol service requires between 2 and 10% water depending on service conditions. *Avoid use of titanium alloys in dry anhydrous methanol service.*

Graphite

Although not classified as a metal, graphite is most appropriately included with metal and alloy sealing applications. Graphite can be used in place of elastomer and rubber compounds and provides a much wider operating window with better service life.

Operating temperatures and pressures are the primary selection criterion of synthetic elastomer and rubber compound valve O-ring and packing types. Use of graphite as a sealing material in place of elastomers and rubber compounds covers a wide operating window with two packing types: dye-formed graphite and braided graphite yarn. Graphite has the advantage of being a noble material with respect to methanol and is compatible with neat methanol at all temperatures. When packing longevity is an issue, aging behavior of packing materials becomes important. Graphite has good longevity, which can be increased by use of high purity graphite. Good practice is to prescribe an 'industrial grade' graphite of at least 98% purity with no more than 2% ash. Service temperatures above 750^{o}F (400^{o}C) require 99% nuclear grade purity graphite.

Compatibility of Metals and Alloys in Neat Methanol Service

Information presented in Table 1 is gathered from trade association publications (American Society of Metals (ASM), American Petroleum Institute (API), NACE International, American Society of Mechanical Engineers (ASME), from journals, and from metals and alloy suppliers. Readers will notice that nearly all of the listed metals and alloys are ranked as being excellent, good, or suitable for methanol service, regardless of application, and with almost no regard for service temperature, equipment type, corrosion form, or failure mode. Most of the rankings in Table 1 are extracted from supplier compatibility charts available on the internet. A very few of these tables provide specific information. As a result, rankings are inconsistent. For example, the FMC Technologies "Compatibility Manual for Liquids, Metals, Elastomers, and Plastics",

Materials Selection for Neat Methanol Service (cont.)

Bulletin AB0A002 ranks suitability of aluminum alloys in methanol service as D, "Not Recommended," with a cautionary note "avoid dissimilar metals" in methanol service. Methanol is electrically conductive. Hence, galvanic corrosion is always a concern in selecting dissimilar alloys that have electrical continuity with methanol and each other. Parker Seals, "Metal Seals Catalog 5135 USA" ranks aluminum as "satisfactory" for methanol service. Crane Valves, "Engineering Data," © 1995 does not rank aluminum, presumably because aluminum alloys are not used for valves in chemical service.

Rankings presented in Table 1 provide a starting point for materials selection.

TABLE 1.

Compatibility of Metals and Alloys for Applications in Methanol Service

A = recommended, resistant under normal conditions
B = conditional, consult supplier, consider modifying process parameters
C = not recommended, investigate modifying process parameters
Generalized corrosion metal thickness removal rate = 0.0# in/yr
*Compatibility ratings indicated in this table are derived from published compatibility charts available on the internet. Neither the author nor Methanol Institute makes any warranty, explicit or implied regarding their accuracy or applicability to specific applications in methanol service.

Alloy Group	Application	Designation	Compatibility Rating*
Carbon Steels	Piping	ASTM A53 Grade B, or A106 Grade B seamless pipe	A
	Valves	ASTM A216-Grade WCB Cast; ASTM A105 Forged; ASTM A352-Grade LCB Cast	A <0.02 in/yr
	Process Controls		A
	Tanks	(Mild Steel/Carbon Steel Plates) ASTM A36 S275JR, IS-2062 GR. A/B, Fe 410WA, Fe 410WB; ASTM A36 - GOST 08KP/3 PS SP – SAE 1006/1010/1020	A <0.02 in/yr
	Pressure Vessels	(Alloy Steel Plates 387 & Pressure Vessel Chrome Molybdenum Alloy Steel) ASTM A387 GR. 11 CL. 1/2; ASTM A387 GR. 12 CL. 1/2; ASTM A387 GR. 22 CL. 1/2; ASTM A387 GR. 5 CL. 1/2; DIN 17175 15Mo3; ASTM A387 GR.2 CL. 2/204 GR. A/204.B (Boiler Quality Plates designed to withstand the internal pressure of pressure vessels, boilers, and valves) ASTM A516 GR. 60; ASTM A516 GR. 70; ASTM A515 GR. 70; IS 2002 GR. 1/GR.2 (Quenched & Tempered Steel Plates) ASTM A514 GR. B; ASTM A517 GR. F; ASTM A537 CL. 1 & CL. 2	A <0.02 in/yr
	Gaskets		Satisfactory
Low Alloy,	Piping	1 Cr-½Mo; 1 ¼Cr-½ Mo; 2¼Cr-½Mo; 3Cr-1Mo; 5-Cr;	A

Materials Selection for Neat Methanol Service (cont.)

TABLE 1.

Compatibility of Metals and Alloys for Applications in Methanol Service

A = recommended, resistant under normal conditions
B = conditional, consult supplier, consider modifying process parameters
C = not recommended, investigate modifying process parameters
Generalized corrosion metal thickness removal rate = 0.0# in/yr
*Compatibility ratings indicated in this table are derived from published compatibility charts available on the internet. Neither the author nor Methanol Institute makes any warranty, explicit or implied regarding their accuracy or applicability to specific applications in methanol service.

Alloy Group	Application	Designation	Compatibility Rating*
High Temperature (>800°F; 425°C) Chrome-Molybdenum Carbon Steels		9Cr-1Mo[1]	
	Pressure Vessels	1 ¼Cr-½ Mo; 2¼Cr-½Mo; 3Cr-1Mo with Vanadium enhancement Product forms: ASTM A 182, A 199, A 217,A335, A336, A387,A 541, and A 73	A
3% Nickel-Iron Steel Alloy	Valves	ASTM A126-Class B Modified	A
Austenitic Stainless Steels (300 series alloys)	Piping	ASTM 304; ASTM 304L; ASTM 316; ASTM 316L (ASTM 321; ASTM 309; ASTM 310; ASTM 317L are not generally used for piping in methanol service, but may be used in chemical plant service involving methanol as a feed stock.)	A; A <0.02 in/yr <0.02 in/yr <0.02 in/yr
	Valves	ASTM A276 Type 316; ASTM A351-Grade CF-8M; ASTM A564 Type 630	A <0.02 in/yr
	Worchester Controls	ASTM 316; Alloy 20;	A; A <0.02 in/yr 0.002-0.02 in/yr
	Tanks	ASTM 304; ASTM 304L; ASTM 316; ASTM 316L (ASTM 321; ASTM 309; ASTM 310; ASTM 317L are not generally used for methanol storage tank service. ASTM 316L may be used in water treatment service where methanol is added as carbon for denitrification.)	A;A <0.02 in/yr <0.02 in/yr
	Pressure Sensors diaphragms, Transmitters, Flange Adaptors	ASTM 316; ASTM 316 SST	B; A <0.02 in/yr
	Isolating	ASTM 316; ASTM 316 SST	B; A

Materials Selection for Neat Methanol Service (cont.)

TABLE 1.

Compatibility of Metals and Alloys for Applications in Methanol Service

A = recommended, resistant under normal conditions
B = conditional, consult supplier, consider modifying process parameters
C = not recommended, investigate modifying process parameters
Generalized corrosion metal thickness removal rate = 0.0# in/yr
*Compatibility ratings indicated in this table are derived from published compatibility charts available on the internet. Neither the author nor Methanol Institute makes any warranty, explicit or implied regarding their accuracy or applicability to specific applications in methanol service.

Alloy Group	Application	Designation	Compatibility Rating*
	Diaphragms,		
	Metal Gaskets	ASTM 304; ASTM 316; ASTM 347	Satisfactory
Ferritic & Martensitic Stainless Steels (400 series alloys)	Valves	ASTM B582 Type 416 Wrot; ASTM A217-Grade CA-15; ASTM A276 Type 410 Wrot	A
		3 commonly used generic Martensitic stainless steels: 13Cr; 13Cr-4Ni; 17Cr-4Ni	
Duplex Stainless Steels			
Nickel-Based Alloys	Worchester Controls	Hastelloy C276 (54Ni-16Mo-15.5Cr-5.5Fe-3.75W-2.75Co) Plate, Sheet, & Strip: ASTM B 575; ASTM B 906; ASME SB 575; ASME SB 906; ISO 6208' DIN 17750; VdTUV 400/12.98 Pipe and Tube: ASTM B 622; ASTM B 829 & ASME SB 622;; ASME SB 829 (seamless tube); ASTM B 6276; ASTM B 751 & ASME SB 626; ASME SB 751 (welded tube); ASTM B 619; ASTM B 775 & ASME SB 619; ASME SB 775 (welded pipe); ISO 6207 (seamless tube); DIN 17751; VdTUV 400/12.98 Fittings: ASTM B 366 & ASME SB 366 Welding Filler Metal: C-276 – AWS A5.14/ERNiCrMo-4 Welding Electrode: C-276 – AWS A5.11 /ENiCrMo-4	A <0.002 in/yr
	Pressure Sensors Transmitters-Flange Adaptors	Cast Alloy—Monel 400 (67Ni-33Cu); Hastelloy Cast Alloy C-276 (54Ni-16Mo-16Cr); Nickel Plated Carbon Steel	A; A; B <0.02 in/yr <0.002 in/yr <0.02 in/yr
	Pressure Sensors	Cast Alloy—Monel 400 (67Ni-33Cu); Cast Alloy C-276 (54Ni-16Mo-16Cr); Tantalum	A; A; A <0.02 in/yr

Materials Selection for Neat Methanol Service (cont.)

TABLE 1.

Compatibility of Metals and Alloys for Applications in Methanol Service

A = recommended, resistant under normal conditions
B = conditional, consult supplier, consider modifying process parameters
C = not recommended, investigate modifying process parameters
Generalized corrosion metal thickness removal rate = 0.0# in/yr
*Compatibility ratings indicated in this table are derived from published compatibility charts available on the internet. Neither the author nor Methanol Institute makes any warranty, explicit or implied regarding their accuracy or applicability to specific applications in methanol service.

Alloy Group	Application	Designation	Compatibility Rating*
	Transmitters-Isolating Diaphragms		<0.002 in/yr
	Worchester Controls	Monel 400 (67Ni-33Cu)	A <0.02 in/yr
	Metal Gaskets	Nickel; Monel	Satisfactory
Cast Iron			
	Valves	Gray Cast Iron ASTM A 126 Class B	A <0.02 in/yr
	Valves	Ductile (nodular) Cast Iron ASTM A 395 Heat Treated; ASTM 536 As Cast	A <0.02 in/yr
	Worchester Controls		B <0.02 in/yr
	Pumps Valves	High Silicon Cast Iron	<0.002 in/yr
	Valves	Ni-Plated Ductile Cast Iron ASTM B 320 Plating	A <0.02 in/yr
Aluminum Alloys	Storage Tank floating Roofs	5454; 6061	B 0.02-0.05 in/yr
	Geodesic Tank Covers	6061; 6063; 6082	B 0.02-0.05 in/yr
	Rail Tanker Cars	EN 485-2 & EN 14286: alloys 5059, 5083, 5086, 5088, 5182, 5186, 5383, 5454 H38, 5754, 6061 & 6082	B 0.02-0.05 in/yr
	Tanker Trailers	EN 485-2 & EN 14286: alloys 5059, 5083, 5086, 5088, 5182, 5186, 5383, 5454 H38, 5754, 6061 & 6082	B 0.02-0.05 in/yr
	Totes	EN 485-2 & EN 14286: alloys 5083, 5454 H38, 5754, 6061 & 6082	B 0.02-0.05 in/yr
	Metal Gaskets		Satisfactory

Materials Selection for Neat Methanol Service (cont.)

TABLE 1.

Compatibility of Metals and Alloys for Applications in Methanol Service

A = recommended, resistant under normal conditions
B = conditional, consult supplier, consider modifying process parameters
C = not recommended, investigate modifying process parameters
Generalized corrosion metal thickness removal rate = 0.0# in/yr
*Compatibility ratings indicated in this table are derived from published compatibility charts available on the internet. Neither the author nor Methanol Institute makes any warranty, explicit or implied regarding their accuracy or applicability to specific applications in methanol service.

Alloy Group	Application	Designation	Compatibility Rating*
Copper	Valves	ASTM B75 Wrot; ASTM B88	A <0.02 in/yr
	Shell & Tube Heat Exchanger Tubes		No Data
	Metal Gaskets		Satisfactory
Bronze	Valves	ASTM B 61 Cast; ASTM B 62 Cast; ASTM B 584; Alloy 844	A <0.02 in/yr
Silicon Bronze	Valves	ASTM B 98 Alloy B; ASTM B 3781 Wrot	A
Aluminum Bronze	Valves	ASTM B 148 Cast; ASTM B 150 Rod	A <0.02 in/yr
Tin Bronze			<0.02 in/yr
Brass	Valves	ASTM B 16 Wrot; ASTM B 124 Forged	A 0.02-0.05 in/yr
	Process Controls		B
Lead	Gaskets		<0.02/yr
Titanium Alloys	Piping	UNS designations: R50250 Grade 1, unalloyed; R56400 Ti-6-4, Ti-6Al-4V; R56260, Ti-6-2-4-6, Ti-6Al-2Sn-4Zr-6Mo; Ti-3-8-6-4-4, Ti-3Al-8V-6Cr-4Zr-4Mo	C SCC
Graphite	Valve Packing	Industrial grade with >98% graphite and < 2% ash for Temperatures ≤ 750°F (400°C)	A
	Valve Packing	Nuclear Grade with purity > 99% and density > 1.50 g/cm^3; Temperatures > 750°F (400°C)	A

Generalizations regarding suitability for methanol service should not be relied upon without thoroughly analyzing the specific circumstances of the application. The material may or may not be appropriate, depending on the type of equipment (tanks, vessels, piping, machinery, etc.), operating conditions, presence of contaminates such as water and chlorides, and severity of process excursions during abnormal operating conditions.

Materials Selection for Neat Methanol Service (cont.)

Understanding the corrosion mechanism is likewise important (i.e., generalized corrosion, galvanic corrosion, pitting, crevice corrosion, stress corrosion cracking, under deposit corrosion, etc.), and finally, it is essential that the likely failure mode be identified, and consequences of failure assessed, and mitigated to an acceptable level of risk. All of these considerations must be well understood in order to select the optimum material for your application. Materials selection is perhaps the most design consideration for mechanical integrity. Mechanical integrity is in turn an important factor in a facility's ability to sustain "fitness for service."

Information Sources

General Information on Metals and Alloys

- C.P. Dillion: *Materials Selection for the Chemical Process Industries*, © 1992 McGraw-Hill, Inc., 337 pp., ISBN 0-07-016984-5.
- David A. Hansen & Robert B. Puyear: *Materials Selection for Hydrocarbon and Chemical Plants*, © 1996 Marcel Dekker, Inc., 412 pp., ISBN 0-08247-9778-7.
- R.A. White & E.F. Ehmke: *Materials Selection for Refineries and Associated Facilities,* © 1991 National Association of Corrosion Engineers, 183 pp., ISBN 0-915567-45-8.
- J.R. Davis et al: *ASM Handbook® Volume 2: Properties and Selecrtion: Nonferroous Alloys and Special-Purpose Materials,* © 1990 ASM International, 1328 pp. ISBN 0-87170-378-5 (v.-2)
- I.J. Korb, D.L. Olson, et al editors: *ASM Handbook® Volume 13: Corrosion,* © 1982 ASM International, 1415 pp., ISBN 0-87170-007-7.
- Robert H. Perry & Don Green Editors: *50th Anniversary Edition Perry's Chemical Engineers' Handbook,* © 1984 McGraw-Hill, ISBN 0-07-049479-7.
- American Petroleum Institute Recommended Practice 941: *Steels for Hydrogen Service at Elevated Temperature and Pressures in Petroleum Refineries and Petrochemical Plants,* 7th Edition, 2008.
- Crane®: *Engineering Data*, © 1995 Crane Valves, 77 pp.
- Joseph R. Davis: *Corrosion of Aluminum and Aluminum Alloys*, © ASM International, Jan 1, 1999, 313 pp., ISBN: 0-87170-629-6.
- "Corrosion of Aluminum", www.asminternational.org/pdf/XXspotlightsXX/CorrosionOfAluminum.pdf
- "Aluminum Alloys Versus Types of Steel", http://en.wikipedia.org/wiki/Aluminum_alloys_versus_types_of_steel

Materials Selection for Neat Methanol Service (cont.)

- The Aluminum Association: *International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys, Revised February 2009,* © 2009 The Aluminum Association, Inc.
- J. Gilbert Kaufman: *Introduction to Aluminum Alloys and Tempers,* © 2000 ASM International, ISBN 0-87170-689-X.
- R. Dwight Atkinson: "Distribution of Methanol as a Transportation Fuel," EPA Technical Report EPA-AA-SDSB-82-13, June 1982.
- European Aluminum Association: "Aluminum in Commercial Vehicles", www.alueurope.eu/wp-content/uploads/2011/10/Aluminum-in-Commercial-Vehicles_Rev2_Bookmarks1.pdf
- "Silhouettes of Rail Cars, Tank Trucks and Chemical Tanks", www.hazmat101.com/hazmat/docs/silhoutes.pdf
- 49CFR 180.407: "Requirements for Test and Inspection of Specification Cargo Tanks", http://www.law.cornell.edu/cfr/text/49180.407
- "Highway Cargo Tank Emergency Response and Damage Assessment", www.iafc.org/associations/4685/files/haz10_spkr703a-hwycargotankemerg-hand_bill.pdf
- United States Environmental Protection Agency: "Survey of Gasoline Tank Trucks and Rail Cars", EPA-450/3-79-004, March 1979
- Dr.rer.nat Johann Gwenhenberger & Prof. D.-Ing. Klaus Langwieder: *Tanker Trucks in the Current Accident Scene and Potentials for Enhanced Safety*, Road-transport-Technology.org/Proceedings/7%20-%20ISHVWD/Tanker%20Trucks%20In%20The%20Current%20Accident%20Scene%20And%20Potentials%20For%20Enhanced%20Safety%20-%20%20Gwehenberger.pdf
- "Design Guidelines for Stainless Steel Piping Systems", www.nickelinstitute.org/en/TechnicalLiterature/AISI/9024_DesignGuidelinesforStainlessSteelPipingSystems.aspx
- Copper Development Association: "Aluminum Bronze Alloys Corrosion Resistance Guide", Publication No 80, 1981
- CM Key to Metals, the World's Most Comprehensive Metals Database: "Corrosion of Copper and Copper Alloys", www.keytometals.com/Article16.htm
- "Copper and Copper Alloys Weldability of Materials Job Knowledge", www.twi-global.com/technical-knowledge/job-knowledge/weldability-of-materials-copper-and-copper-alloys-023/
- CM Key to Metals, The World's Most Comprehensive METALS Database: "Corrosion of Titanium and Titanium Alloys".
- Siemens Process Instrumentation: Biodiesel – Process Instrumentation for the manufacturing process," www.siemens.com/biodiesel

Materials Selection for Neat Methanol Service (cont.)

- Roth: "Flow Center and Loop Application/Installation Guide," P/N: 2300100909, www.roth-america.com
- James Walker: "Gaskets & Jointings Guide," Issue 7.4
- John E. Edwards: "Design and Rating Shell and Tube Heat Exchangers," MNL 032A Issued 29 August 08, by P&I Design Ltd. Teesside, UK. www.pidesign.co.uk
- Element 1 Hydrogen Generators: "e1 Methanol Handbook," August 2013. www.e1na.com/e1%20Methanol%20Handbook%20v2013.pdf
- Finn Kirkemo, Sealflex a.s.: "Design of Compact Flange Joints-PVP2002-1087," ASME-PVP 2002, Bolted Flange Connections, August 4-8, 2002, Vancover, British Columbia, Canada, 14 pp., © ASME.
- "Technical Supplment 3: Equipment Leak Fugitives," TCEQ Publication RG-360, Revised January 2006.
- Valve Engineering: "Zero Leakage Concept & EN 1779 std". http://www.eng-tips.com/viewthread.cfm?qid=150132
- Global Supply Line Pty Ltd ABN 86 008 1345 512: "Leakage Acceptance Rates Comparison Metal & Soft-Seated Valves API 598/API 6D/MSS SP-61/FCI 70-2
- CG Industrial Specialties Ltd (CGIS): "Sometimes Zero means everything".
- Tyco Valves & Controls: "Vanessa Weries 30,000 Metal Seated Zero Leakage, Rotary Process Valves".
- Realzero Refrigerant Emissions and Leakage ZERO Project: "Illustrated Guide to 13 Common Leaks". www.realzero.org.uk
- Guy A. Jolly, P.E. Chief Engineer, Flowserve Vogt Valves: "Bellows Seal Valves, The Utlimate Solution to Preventing Fugitive Emissions through Valve Packing," FCD VVABR1011-00-01/05. Flowserve.com
- Francisco J. Montero, European Sealing Association (ESA) member: "Tightness in Gasketed flanged unions_ PART III: New Standards for Calculation and Testing. The European Standards." www.europeansealing.com
- Texas Flange: "Product Catalog: ver 4.01". www.texasflange.com
- U.S. Chemical Safety and Hazard Investigation Board: "Methanol Tank Explosion and Fire, Bethune Point Wastewater Treatment Plant, City of Daytona Beach Florida, January 11, 2006," Report No. 2006-03-I-FL March 2007.

<u>Chemical Compatibility and Chemical Compatibility Charts</u>

- Klinger: "Chemical Resistance Table- guide for the resistance to media of all asbestos-free gaskets"
- Little GIANT: "Chemical Resistant Chart- ratings for these materials are based upon the chemical resistance only; added consideration must be given to pump selections

Materials Selection for Neat Methanol Service (cont.)

when the chemical is abraisive, viscous in nature, or has Specific Gravity greater than 1.1"

- CDA Publication No. 106, Copper Development Association Inc.: "Corrosion Resistance of Copper and Copper Alloys",
- Parker Seals: *Metal Seals Catalog 5135, USA,*© 1998, 9 pp.
- FMC Technologies: "Compatibility Manual, Liquids, Metals, Elastomers, Plastics," Issue/Rev. 0.2 (12/96)
- Emerson Process Management: "Material Selection Considerations for Pressure Transmitters," Technical Note 00840-0100-3045, Rev AC, May 2014. www.rosemount.com
- The Hendrix Group Materials & Corrosion Engineers: "Corrosion Resistance of Copper and Copper Alloys," hghouston.com/resources/material-property-data/copper-and-copper-alloys/copper-corrosion-resistance-data.aspx
- "Minseal Flexible Graphite Chemical Compatibility Chart". Minseal.com/chemicalcompat.htm
- Graftec: "Gasket Handbook," www.intermech.net
- Cole-Parmer: "Chemical Compatibility Results". Coleparmer.com/Chemical-Resistance
- ERIKS: Spiral Wound Gaskets | FlangeGaskets. http://flangegaskets.info/en/products/metallic-and-semi-metallic-gaskets/spiral-wound-gaskets/
- Flexitallic: "Gasket Design Criteria," rev. 05-9-14. Flexitallic.com/uploads/files/broDesignCriteria.pdf
- NIBCO: "CHEM-GUIDE, Chemical Resistance Information for Plastic and Metal Valves and Fittings," catalog C-CRG-1011, 30 pp.
- FLOWSERVE, Worcester Controls Corrosion Data: "Selection of materials for corrosive service," FCD WCATB0002-00 (C12-7). www.flowserve.com/files/Files/Literature/ProductLiterature/FlowControl/WorcesterControls/WCATB0002-00.pdf
- BAL SEAL Engineering: "Chemical Compatibility Chart- Metallic Materials Used in Bal Seal Products," Technical Report TR-60C (Rev. 0; 5-28-99). www.balseal.com/sites/default/files/tr60c_020707132612.pdf