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1. Introduction

This document contains specific information on materials selection, design, and construction for the Kharg MEG plant based on Shell MASTER process technology. The experience concerning material problems and the prevention of the formation of impurities is incorporated.

1.1 Definitions

Where applicable, the words “shall” and “required” are to be understood as mandatory while the words “should”, “may”, “can” are to be understood as recommendations. Requirements and recommendations are based on Shell and/or industry best practices.

2. Materials and design aspects for the Kharg MEG plant

The selection of materials for the Kharg MEG plant is based mainly on their resistance to corrosion, product quality requirements, and plant integrity. When applicable, economic considerations have also been taken into consideration during the material selection.

2.1 Nomenclature

Generic names have been used where possible for the materials selections. To avoid potential ambiguity, werkstoff numbers have been given where applicable.

2.2 Design codes

Equipment and piping shall be designed in accordance with design codes for pressure equipment ASME VIII Div 1 or Div 2 for equipment and ASME B31.3 for piping. In addition, countries may require a design in accordance with their own codes.

2.3 Carbon Steel

CS or C-steel refers to carbon- or carbon-manganese steels. These steels are killedⁱ steels that are in normalised condition and have a specified minimum tensile strength less than 500 N/mm². The weld ability and hardness of unalloyed steels depends on the carbon content and the carbon equivalent (Ceq), which should not exceed 0.23%w and 0.45%w, respectively. Example specifications are A516, A285, A106, and A105. If carbon steel is specified, upgrading to (low) alloy steel or higher strength steel is subject to approval.

NOTE:

The **lowest possible metal temperatures** should be defined during further design by

ⁱ completely deoxidised



contractor. Although this is a general requirement, it is most important for piping and equipment that contain pressurised or liquefied gas. The lowest metal temperature takes into account the lowest normal operating temperature, but also exceptional cool-down events such as:

- High rate depressurising resulting in Joule-Thompson cooling or cooling by boiling of liquefied gas.
- Liquefied gas entering space with a low vapour pressure for that gas.
- Ambient conditions.

The design codes specify the requirements to prevent brittle fracture at the lowest possible metal temperature.

2.4 Stainless steels and high grade austenitic Stainless Steels and Ni-base or other alloys

2.4.1 12Cr stainless steels

- a) For internals or cladding, ferritic or martensitic stainless steels like types 405 (Werkstoff nr 1.4002, or equivalent) and 410S (Werkstoff nr 1.4001, or equivalent), although successfully applied in specific cases, are not recommended.
- b) Maximum operating temperatures shall not exceed 350 °C for ferritic or martensitic stainless steels.
- c) If 12Cr casting is applied, CA6NM is the preferred cast version for 12Cr type stainless steels.

2.4.2 Austenitic stainless steels

- a) SS refers to austenitic stainless steels. When austenitic stainless steel has been specified for equipment and line work systems, the following alloys are acceptable:
 - SS 304 (Werkstoff nr 1.4301, or equivalent) but with maximal 0.03%wt C (An exception can be made for non-welded parts)
 - SS 316 (Werkstoff nr 1.4436, or equivalent) but with maximal 0.03%wt C (An exception can be made for non-welded parts)
 - SS 304L (Werkstoff nr 1.4306, or equivalent)
 - SS 321 (Werkstoff nr 1.4541, or equivalent)
 - SS 347 (Werkstoff nr 1.4550, or equivalent)
 - SS 316Ti (Werkstoff nr 1.4571, or equivalent)
 - SS 316L (Werkstoff nr 1.4435, or equivalent)

Note that L-grade steels or stabilised type stainless steels are strongly recommended to ensure adequate corrosion resistance of the welded joints. If adequate corrosion resistance of welded joints and quality of supply of non L-grade steels can be guaranteed, the use of non L-grade stainless steels may be considered for this project.

- b) All austenitic stainless steel base materials shall be solution annealed.
- c) Austenitic stainless steels should be capable of passing the intergranular corrosion test ASTM A262 Practice E or ISO 3651-2 Method A.



- d) Welding procedures should not cause undue weld decay or surface oxidation.
- e) When SS 316(L) is specified, it shall not be replaced by SS 304, SS 304L, SS 347 and SS 321.
- f) For reason of robustness, complicated components (e.g. inlets, distributors, collectors, draw-off trays, structural packing, and schoepentoeters) shall be made of austenitic stainless steel, unless specified differently. Structured packing shall be made of austenitic stainless steel 316.
- g) When austenitic stainless steel is used in column construction, either in the solid or clad form, then internals should be specified in the same type of stainless steel. However, structured packing shall be made of SS 316 (see 2.4.2.f).

2.4.3 Duplex, super austenitic, super duplex stainless steels

- a) When duplex stainless steel is specified for equipment or line work, alloy 2205 (Werkstoff nr 1.4462) or equivalent is meant.
- b) When super duplex stainless steel is specified for equipment or line work, alloy 2507 (SAF 2507) or equivalent is meant.
- c) When duplex SS is specified, super duplex SS may also be used (e.g. when more economic). However, when super duplex is specified, duplex 2205 shall not be used.
- d) For both types of duplex stainless steels the maximum operating temperatures shall not exceed 275 °C.
- e) It is recommended not to mix super-duplex and duplex in one construction.
- f) When super austenitic stainless steel is specified for equipment or line work, corrosion resistant alloys like 254SMO (Werkstoff nr of nearest equivalent grade 1.4529) or more corrosion resistant alloys are to be used.

2.5 Titanium

Titanium is considered for cooling water and sea water applications only. When titanium has been specified, Titanium grade 2 (Werkstoff nr 3.7035) is meant. Titanium grade 12 (Werkstoff nr 3.7105) and Titanium grade 7 (Werkstoff nr 3.7235) are (more corrosion resistant) alternatives.

2.6 Corrosion allowance

For the Shell MASTER technology, the following corrosion allowances shall be taken into account as a minimum:

Equipment

Carbon steel: + 1 mm, unless otherwise is specified (e.g. 3 mm for slightly corrosive conditions).

Piping

Carbon steel: + 1 mm, unless otherwise is specified (e.g. 3 mm for slightly corrosive conditions).



More stringent requirements may be applied by contractor, if specified for this project.

2.7 Flanges and blind flanges in EO service

The hazard of an un-insulated flange in the event of a fire is more serious than the possible consequences of an EO leakage under insulated flanges. Therefore all flanges in EO service with EO concentration exceeding 10 wt% shall be insulated with a closed cell structure, e.g. Foamglass or perlite.

To enable EO leak monitoring at all flanges a vent shall be installed on the flange through the insulation layer as specified in Appendix 2. The insulation shall be covered by either stainless steel or aluminised steel sheeting.

Only raised-face (narrow-faced) flanges shall be used.

2.8 Clad vessels

When austenitic stainless steels are selected for vessels, C-steel with the austenitic stainless steel cladding should be applied.

The minimum thickness of cladding, which meets the specified chemical composition of the cladding material, shall be 3 mm. Cladding is also recommended where stainless steel or a corrosion resistant alloy is specified for part of the wall of carbon- or low-alloy steel equipment. The alternative use of solid material, which would require a dissimilar metal joint, is then subject of approval.

2.9 Corrosion prevention prior to start-up

Adequate procedures are required during fabrication and testing to prevent corrosion damage prior to start-up and reduced corrosion resistance during normal operation. For more details on cleaning refer to section 4 – Cleaning.

2.10 Materials not to be used

Due to the possibility of decomposition of EO in the presence of metallic acetylides, all materials which readily react to form acetylides shall be avoided, i.e. copper and copper alloys, magnesium and magnesium alloys, silver, mercury. Aluminium oxide (Al_2O_3), phosphoric acid and phosphates, iron-oxide, and, under certain conditions, silver, catalyse the isomerisation of EO to acetaldehyde (Ref. 1).

Elastomers generally cannot be used in EO service. For acceptable O-ring materials refer to section 3.5.3 – O-rings. See also section 3.1.3.2 on EO and safety.

Due to their potential for catalyst poisoning, coatings, greases and additives containing arsenic, tellurium, selenium, or sulphur shall not be used.



3. Materials selection aspects for the Kharg EO/EG process

3.1 Factors affecting the material selection

The selection of materials for the Kharg MEG plant is mainly based on their resistance to corrosion, product quality requirements, and plant integrity. Economic aspects have been taken into account during the materials selection. In the following chapters guidelines regarding materials selection for the various process streams are given.

3.1.1 Corrosion / erosion

3.1.1.1 Internal corrosion

Carbon dioxide

The main source of potential internal corrosion within the Shell MASTER process is the carbon dioxide that is generated in the EO reaction section. In the gaseous phase it does normally not present a problem. However, where water condensation can occur or where water is present in the process stream, CO₂ will dissolve to form carbonic acid. Formation of carbonic acid will occur throughout the EO units and most of the EG units wherever CO₂ is present. An acidic aqueous phase is aggressive to normal carbon steel, therefore stainless steel is to be selected for all areas where water could condense in presence of CO₂. Cold branches of main lines operating above dew points should be specified in duplex stainless steel.

Glycols

Acidic by-products in the glycols, mainly formic and glycolic acids, are the main sources of corrosion/erosion within the ethylene glycol section. Although the glycol product is hardly corrosive, the combination of elevated temperature and turbulence induced by high velocities results in corrosion/erosion of carbon steel. The oxidation / degradation products of glycols, caused by air leakages (vacuum), are also known to cause corrosion.

For process streams where both temperature and velocity of the glycol exceed respectively 120 °C and 1.5 m/s, austenitic stainless steel shall therefore be specified. Items that most often experience this combination are pumps, reboiler tubes, inlet devices, column walls opposite the inlet devices and other parts where flashing occurs in equipment and in piping downstream of control valves. Therefore these items are specified in austenitic stainless steel.

Chlorides

Aqueous chloride solutions can cause corrosion of C-steel and localised corrosion (such as pitting, crevice and stress corrosion cracking) on stainless steels. This corrosion risk is mainly determined by the temperature and chloride concentration.

Chloride stress corrosion cracking (Cl-SCC) is a cracking phenomenon that can occur in aqueous chloride containing environments above approximately 50 °C and at almost any chloride concentration. Austenitic stainless steels (Types 304, 316, etc.) and Fe-Cr-Ni alloys with less than about 40% nickel are most susceptible to Cl-SCC. Carbon steel, Cr-Mo steels and 12Cr steel although not



affected, are not recommended as alternative construction material to prevent localised corrosion of austenitic stainless steels. Austenitic alloys with high nickel contents and duplex and super duplex alloys do possess a better to much better resistance towards localised corrosion in chlorides containing environments.

Chlorides can be present in many streams of an EO/EG plant, however, in most cases it is not present in the form of chloride ions in an aqueous environment. There are two areas in which ionic chlorides are typically present in an aqueous environment: the carbonate section and the cooling water system (depending on the CW system type and CW quality). In the carbonate section, chloride stress corrosion cracking of austenitic stainless steels is unlikely under normal operating conditions, as the pH is elevated and provided oxygen ingress into the system is avoided to a minimum.

For the materials selection of all heat exchangers cooled by cooling water in which stainless steel is required for process reasons the guidelines as given in Appendix 4 shall be applied.

Potassium carbonate

Circulating potassium carbonate solution is used as the absorbent in the CO₂ removal section. The carbonate make-up feed as such is not highly aggressive to carbon steel, but corrosivity may increase considerably as the bicarbonate concentration in the absorbent increases.

As carbon steel is susceptible to stress corrosion cracking (SCC) in aqueous carbonate – bicarbonate solutions in the pH range 8 – 11 at temperatures below 100 °C, austenitic stainless steel is applied in this section (for details refer to 3.2.2 – CO₂ removal section).

Other trace components

In the EO Reactor outlet, some trace by-products such as aldehydes (mainly formaldehyde and acetaldehyde) and organic acids (mainly formic and acetic acid) are formed. The formation of these by-products is enhanced by the presence of rust and higher temperatures. Therefore the bottom of the EO reactor and the outlet system up to and including the primary product cooler shall be made of solid austenitic stainless steel or of carbon steel clad with austenitic stainless steel (refer also to 3.2.1 – EO reaction section).

The moderator (ethyl chloride) that is added to the EO reaction section to improve the catalyst selectivity, also gives rise to trace quantities of organic chlorides and hydrochloric acid by decomposition/degradation. As described above, these chloride-ions will accumulate in the carbonate section of the CO₂ removal unit, where they may give rise to chloride induced stress corrosion cracking. The material selection for this part is described in the CO₂ section in 3.2.2.

3.1.1.2 External corrosion

External corrosion of steel is related to local climatic and environmental conditions such as salt laden atmosphere, pollution, humidity at the material surface, and will usually result in general corrosion. Adequate precautions should be taken to reduce the risk of external corrosion.



Austenitic stainless steels are susceptible to external chloride stress corrosion at surface temperatures over 50 °C. When for process reasons, austenitic steel type materials are required adequate precautions should be taken to reduce the risk of external stress corrosion cracking to a minimum.

When insulation is applied, adequate precautions should be taken to prevent underlagging corrosion.

3.1.2 Product quality

3.1.2.1 Glycols

The product quality of MEG, DEG and TEG is adversely affected by the iron content. In order to meet the iron specification in the finished product, all piping handling finished product on plot, downstream the pasteurisation section of the purification columns, shall be handled in austenitic stainless steel, up to and including the product rundown / transfer lines. The final storage tanks (excluded from the scope of this PDP) can be specified in carbon steel, provided a suitable coating is applied (see 3.5.1).

3.1.3 Safety

3.1.3.1 Oxygen system

The danger in the pure oxygen system lies in the fact that many materials, including most metals, once ignited, will burn violently in an oxygen atmosphere. This burning will lead to wall penetration, which in pressurised systems can result in very dangerous situations.

Therefore, the oxygen system shall be absolutely clean, free from oil, rust and metal debris, before going into operation.

Design of the oxygen system and the material selection shall be in accordance with DEP 31.10.11.31-Gen "Gaseous Oxygen Systems" and Appendix 1 "Sealing Materials for Oxygen Service".

For further specification and any details of the oxygen mixing nozzle design not covered by the above mentioned oxygen DEP, please refer to the related equipment data sheets.

3.1.3.2 Ethylene Oxide

In all matters concerning safe handling of EO reference is made to:

- "Ethylene Oxide – Guidelines for bulk handling, (Ref. 1), which is a code of practice developed and distributed by the by the CIA Ethylene Oxide users Group under the responsible care program of the Chemical Industry Safety, Health and Environmental Council

NOTE: The chapters about painting, coating, insulation, and gaskets in the above-mentioned documents are overruled by this Material Selection Guide document for the Kharg MEG plant.



For the insulation of equipment and piping in EO service with concentrations exceeding 10 %wt EO downstream from the EO stripper overhead up to the glycol reactor, an insulation material with a closed cell structure (foamed glass or perlite) shall be used. This is to prevent the insulation material from soaking with EO at possible leaks that can lead to an unsafe situation. For further description see sections 2.7 and 5.

3.2 Materials selection for the Ethylene Oxide section

This chapter contains the materials selection guidelines for the process lines and equipment in the EO section in the Kharg MEG plant.

For the materials selection of all heat exchangers cooled by cooling water in which stainless steel is required for process reasons the guidelines as given in Appendix 4 shall be considered.

3.2.1 EO reaction section

The piping feeding the ethylene and methane to the recycle gas line is made of carbon steel. The oxygen piping, from the oxygen filters up to and including the mixing nozzle, where oxygen is mixed with the recycle gas, is made of austenitic stainless steel. The mixing nozzle is of the concentric ring type, and shall be made of austenitic stainless steel. The injection nozzles themselves shall be made of Alloy 600 (Werkstoff nr 2.4816) or Alloy 400 (Werkstoff nr 2.4360). Alloy 400 is preferred because of easier machining. These materials are required because of their higher ignition temperature in oxygen that allows it to be used at the high gas velocities experienced here. Reference shall be made to the technical specification for oxygen mixing nozzles.

The EO reactor loop piping downstream the mixing nozzle is specified in austenitic stainless steel over a specific length as specified in the data sheet. The remaining part downstream the mixing nozzle up to the EO reactor can be made of carbon steel.

The moderator system (Ethylene Chloride injection) shall be made of austenitic stainless steel.

In this design two reactors are applied. The description below is applicable to both EO reactors.

The ethylene oxide (EO) reactor is a multi-tube reactor where the exothermic EO reaction occurs in catalyst-filled tubes. The water coolant is on the shell side of the EO reactor. Reactor shell and tubes are made of carbon steel. The water used as coolant shall be properly treated and de-aerated boiler feed water. Since the BFW is brought into contact with the catalyst by application of open steam in the Shell MASTER process, additional purity requirements are established, which shall be applied (see Appendix 3 for details). Therefore, the coolant side of the tubes does not need a corrosion allowance. The same is valid for the product side because the EO reaction takes place above the dew point of the mixture, so no corrosion of the carbon steel tubes takes place. However, the coolant lines in the thermosyphon system from the reactor to the HP steam drum shall be provided with at least 3 mm erosion allowance, because of the erosive conditions by the partly evaporated coolant.



The use of high strength steels for the EO reactor shell and heads is restricted to steels with a maximum specified tensile strength not greater than 720 N/mm². Peak stresses at the shell-to-tube sheet joints and at any other location on the waterside shall be limited to 600 N/mm² in order to protect magnetite layers at peak stress locations.

For product quality reasons and to minimise the formation of corrosive by-products the EO reactor bottom shall be provided with an austenitic stainless steel cladding, and the lines up to the EO reactor feed/ product exchanger at the product side, including the product side of the primary product cooler shall be made of austenitic stainless steel. The reactor feed side of the EO reactor feed/product heat exchanger can be made of carbon steel; the tubes shall be made of austenitic stainless steel.

Some condensation is expected to occur locally in the reactor product side of this exchanger. Facilities shall therefore be provided for frequent and proper draining. The reactor product piping downstream the exchanger shall be made of austenitic stainless steel until the MOV. To allow for evaporation of entrained condensate droplets, a minimum of 10 meter of austenitic stainless steel pipe length shall be specified between the EO reactor feed/product exchanger and this downstream MOV as a minimum. However, it is strongly recommended to apply austenitic SS for the full section of reactor product piping up to the secondary product cooler. The secondary product cooler and the piping up to the EO absorber shall be made of austenitic stainless steel.

For dead ends, stagnant branches and cold spots, proper draining facilities shall be installed and all stagnant branches shall be made of super austenite alloys or duplex / super duplex alloys, because operating conditions in stagnant areas will be below dew point and for a large part above 50 °C.

The recycle gas-loop piping from the top of the EO absorber can be made of CS and must be insulated to prevent condensation.

For ethylene and methane containing equipment and lines the lowest possible temperature shall be determined. For equipment / piping that may be subjected to temperatures < 0 °C, materials suitable for the full design pressure at this low temperature (e.g. fine grained, impact tested CS) shall be selected.

3.2.2 CO₂ removal section

The EO absorber overhead, which contains CO₂, CH₄, O₂ and C₂H₄, is partially fed to the CO₂ absorber column. Here the CO₂ is absorbed by carbonate. Austenitic stainless steel is specified in the CO₂ removal section to reduce the potential for stress corrosion cracking due to the aqueous carbonate – bicarbonate solution. Accumulation of chlorides may occur in the reboiler section, but chloride stress cracking corrosion (Cl-SCC) of austenitic stainless steels is unlikely to occur under normal operating conditions, as the pH is elevated and provided oxygen ingress into the system is avoided to a minimum.

Note: It is emphasised that the CO₂ removal unit shall be chemical cleaned to remove oil and grease to prevent foaming problems at start-up. The chemical cleaning method (see also section 4) is to be defined by the chemical cleaning contractor taking into account the specific construction materials used and must



include passivation, if required for the materials used. The applied chemical cleaning method shall be approved by Shell.

The CO₂ product transfer line to OBL shall be specified in austenitic stainless steel, due to potential condensation in this line leading to formation of carbonic acid.

The recycle gas compressor shall be made of austenitic stainless steel. The bottom of the knock-out vessel of the recycle gas compressor, in which condensed and entrained liquid will be collected, shall be clad with austenitic stainless steel.

3.2.3 EO recovery section

Corrosion in the EO recovery section is mainly due to the presence of CO₂ in conjunction with oxygen and water. Also the presence of carboxylic (mainly formic) acids can contribute to corrosion. For this reason the secondary product cooler, where the reactor product is cooled against fat absorbent (product of EO absorber containing dissolved CO₂) shall be made of austenitic stainless steel and the EO absorber column shall be made of carbon steel clad with austenitic stainless steel. Piping from the secondary product cooler to the EO absorber shall be made of austenitic stainless steel (see also section 3.2.1).

The EO absorber overhead recycle gas line contains gases like CO₂, C₂H₄ and CH₄. As no free water phase is present, the medium is non-corrosive and the piping can be made of carbon steel. However, in connected piping, not in continuous service, some water may be present. Therefore these nozzles and stagnant branches shall be made of duplex stainless steel.

The recycle quench liquid line and quench bleed line of the EO absorber contain water with traces of carbonic acid and formates. For this reason the piping shall be made of austenitic stainless steel. The same applies to the quench waterside of the quench cooler and the quench pump.

The quench bleed stripper and overhead piping shall be made of austenitic stainless steel. The pH in the quench bleed stripper bottoms transfer line to the quench bleed flasher shall be strictly controlled between 7-8 with caustic soda.

The quench bleed flasher and the quench bleed flasher reboiler can be made of carbon steel clad with austenitic stainless steel. The reboiler tubes shall be made of austenitic stainless steel. The bottom piping from the quench bleed flasher reboiler up to and including the heavy glycols cooler (product side) and the quench bleed flasher bottoms pump shall be made of austenitic stainless steel 316L (refer also to 3.3.5 Glycol Purification).

Overhead piping and quench bleed flasher condenser shall be made of austenitic stainless steel 316L (product side). Piping downstream from the condenser to the condensate vessel shall be made of austenitic stainless steel.

The lean absorbent is water at ambient temperature, the pH being strictly controlled between 7.5-8.5 with caustic soda. Consequently all equipment and piping in contact with the lean absorbent can be made of carbon steel. Pump



casings in the lean absorbent loop can also be made of carbon steel. The impeller shall be made of SS. If the pH cannot be strictly controlled, stainless steel is advised for all lean absorbent containing lines and equipment.

Equipment and piping downstream the EO absorber (side draw-off), in contact with the fat absorbent containing dissolved CO₂ (pH=4.5-6), shall be made of austenitic stainless steel. For this reason the part of the carbon steel EO stripper column in contact with the fat absorbent, shall be clad with austenitic stainless steel (top section above the feed nozzle from the quench bleed stripper tops). The EO stripper overhead contains EO plus water and residual CO₂, for this reason the overhead piping shall be made from austenitic stainless steel.

The EO stripper below the feed nozzle from the Quench Bleed Stripper tops can be made from carbon steel. However, to prevent corrosion of the EO stripper reboiler tubes, austenitic stainless steel 316L shall be selected as construction material.

3.2.4 Light ends removal

The stripped EO overhead gas from the EO stripper column contains EO, water, and residual CO₂. For this reason the equipment shall be specified in austenitic stainless steel, i.e. the EO stripper tops cooler; EO stripper tops condenser, EO stripper tops vent chiller and EO stripper tops surge drum. The piping in this section of the unit shall be made from austenitic stainless steel as it contains aqueous EO and CO₂.

The top of the light ends column down to 2000 mm below the top of the bed is austenitic stainless steel (clad), the piping to and from the top is also austenitic stainless steel. The rest of the column is made from C-steel. The Light ends (LE) column bottom piping is made of C-steel.

The residual absorber (RA) column is specified in C-steel clad with austenitic stainless steel. The upstream and downstream piping of this column is also austenitic stainless steel.

The pumps in this section of the unit are handling streams that contain residual CO₂ and hence may be acidic. For this reason the pump materials are austenitic stainless steel.

The residual gas compressor and its interstage KO drums and piping shall be made of austenitic stainless steel. The compressor discharge piping can be made of carbon steel since the temperature of the gas is well above the dew point. For cold spots / stagnant points and drains (locations where liquid can be present) duplex austenitic stainless steel shall be applied.

Note: It is emphasised that the LE column must be chemical cleaned to remove oil and grease to prevent foaming problems at start-up. The chemical cleaning method (see also section 4) is to be defined by the chemical cleaning contractor taking into account the specific construction materials used and must include passivation if required for the materials used. The applied chemical cleaning method must be approved by Shell.



3.3 Materials selection for the Ethylene Glycol section

This chapter contains the materials selection guidelines for the process lines and equipment in the EG section in the Kharg MEG plant.

For **glycol containing process streams** at locations with high velocity or turbulence, that is $v > 1.5$ m/s or where flashing occurs, in combination with temperatures above 120 °C, the material selection shall be austenitic stainless steel, due to the presence of acidic by-products.

For the materials selection of all heat exchangers cooled by cooling water in which stainless steel is required for process reasons the guidelines as given in Appendix 4 shall be considered.

3.3.1 Glycol reaction

The EO/water from the EO purification column and/or LE column is mixed with water from the process (dirty) condensate vessel. It has been found that the aqueous EO-feed to the ethylene glycols (EG) reactor is erosive/corrosive to carbon steel because of traces of CO₂. This erosion/corrosion is specifically encountered in the EG reactor and its preheaters. Equipment in contact with the feed is therefore made of austenitic stainless steel. The piping is made of austenitic stainless steel. This material is also used for the glycol reactor outlet piping to the glycol concentrator.

3.3.2 Glycol concentration

Due to the presence of acidic by-products in the glycol streams in the glycol concentration section, most parts of this plant section are made of austenitic SS or austenitic SS clad (even at velocities below 1.5 m/s).

The glycol concentrator column(s) are made of carbon steel with an austenitic stainless steel cladding.

The product side of the reboilers and associated piping shall be made in austenitic stainless steel.

Experience has shown that the acidic by products also cause corrosion in the overhead steam systems of the first, second and third concentrator. The overhead piping and steam side of the concentrator 2 reboiler and concentrator 3 reboiler shall therefore be made of austenitic stainless steel.

The glycol piping between each of the glycol concentrators and dehydrator shall be made of austenitic stainless steel.

The process steam / condensate system originating from process condensate flash drum and 3rd concentrator overhead can be made of carbon steel + 3mm CA. Carbon steel with 3 mm CA is also applied for the process condensate flash drum and water surge drum.

The casing and impeller of both the process condensate recycle pump as well as the process condensate pump are specified in austenitic stainless steel.



3.3.3 Glycol dehydration

Water is removed from the crude glycol in the dehydration unit. This unit is made of carbon steel except in those cases where temperature and velocity of the glycol both exceed 120°C and 1.5 m/s respectively. In that case austenitic stainless steel shall be used.

Measures shall be taken to avoid high velocity/turbulence, especially the areas above the internals supports are sensitive in this respect. Pumps and the product side of the reboilers and its outlet piping shall be made austenitic stainless steel. If high velocity/turbulence cannot be avoided, areas above internals supports shall be clad with austenitic stainless steel.

Further piping from the dehydrator column up to the purification column is specified as carbon steel.

3.3.4 Glycol bleed

The glycol bleed recovery section can be made of carbon steel except in those cases where temperature and velocity of the glycol both exceed 120 °C and 1.5 m/s respectively. In that case austenitic stainless steel shall be used.

Measures shall be taken to avoid high velocity/turbulence, especially the areas above the internals supports are sensitive in this respect. If high velocity/turbulence cannot be avoided, areas above internals supports shall be clad with austenitic stainless steel.

Salts that are concentrated in the bottom section of the glycol bleed flasher may cause erosion corrosion at high concentrations. Therefore the glycol bleed flasher bottoms pump and the product side of the glycol bleed flasher reboiler and its piping shall be made in austenitic stainless steel up to and including the tie-in with the quench bleed flasher bottoms.

3.3.5 Glycol Purification

After dehydration the ethylene glycols are purified (distilled) into various glycols, i.e. mono-, di- and tri-ethylene glycol (MEG, DEG and TEG). For product quality reasons MEG, DEG and TEG purification columns are made of carbon steel clad with austenitic stainless steel at draw-off tray and above, and product piping and rundown pumps are also specified in austenitic stainless steel, i.e. downstream the MEG, DEG and TEG purification columns.

The piping between the MEG, MEG recycle, DEG and TEG column shall be made of austenitic stainless steel after the flow control valve, because of product flashing over control valves and velocities higher 1.5 m/s causing corrosion/erosion at >120°C (especially in elbows and tee pieces). For the same reason tubes/tube-sheets of reboilers and outlet piping shall be made of stainless steel and process pumps in these lines shall also be made of austenitic stainless steel.

Reflux piping and filters for the MEG, DEG and TEG columns are specified in austenitic stainless steel for product quality reasons.



The glycol slops tank can be made of carbon steel with a suitable coating (refer to 3.5.1 – Painting and coating). The glycol rerun pump is specified in austenitic stainless steel, but rerun piping can be specified in carbon steel.

After cooling of the combined heavy glycols stream from the TEG column bottoms, the glycol bleed flasher bottoms and the quench bleed flasher bottoms, carbon steel can be applied provided the pH is strictly controlled in the quench bleed stripper bottoms (refer to 3.2.3 – EO recovery section). The same applies to piping downstream the heavy glycols cooler and the heavy glycols storage tank. The heavy glycols pump casing and impeller shall be made of austenitic stainless steel. If the pH cannot be strictly controlled in the quench bleed stripper bottoms steam, stainless steel is advised for all piping downstream the heavy glycols cooler. In that case a coating is advised for the heavy glycol tank (refer to 3.5.1 – Painting and coating).

3.3.6 MEG/DEG/TEG Storage

For product quality reasons the final glycols product storage tanks (OBL) shall be made of carbon steel tanks with an appropriate coating (refer to 3.5.1 – Painting and coating) or austenitic stainless steel. All transport pumps, filters, loading facilities, and transfer piping both in the product rundown section, as well as the final storage and loading sections shall be austenitic stainless steel.

3.4 Materials selection for Plant Utilities and Supporting Systems

This chapter contains the materials selection guidelines for the supporting utility systems in the Kharg MEG plant.

3.4.1 Plant Utilities – Cooling Water

The required materials selection for cooling water (CW) systems is dependent on the available quality of the water. For the materials selection of all heat exchangers cooled by cooling water in which stainless steel is required for process reasons, the guidelines as given in Appendix 4 shall be considered.

3.4.2 Plant Utilities – Sea Water

Sea water as cooling medium is only applied in the quench cooler and the lean absorbent cooler and the .

For plate and frame exchangers a minimum seawater velocity of 0.8 m/s is advised.

For sea water cooled shell-and-tube exchangers, Titanium tube bundles should be used and the tube-to-tube sheet connection shall be strength welded. The recommended design sea water velocity in Ti tube bundles in a once through system is 2-2.5 m/s. The minimum and maximum velocity in Ti tube bundles is 1.5 and 5 m/s respectively. Velocities below 1.5 m/s due to flow control fluctuations should be avoided as Ti is known to become more susceptible to bio-fouling at low sea water velocities.



3.4.3 Plant Utilities – Clean condensate and Demin water

The clean condensate treating system and demin water system up to and including the deaerator can be in C-steel.

3.4.4 Plant Utilities – Process condensate and Process steam

For the material selection of process steam and process condensate systems CS with 3 mm corrosion allowance is specified as minimum. Based on experience some sections are specified in SS. For details, reference is made to the relevant sections in chapter 3.3 and to material designations on the PFD and the equipment data sheets.

3.4.5 Plant Utilities – Clean steam and boiler feed water (BFW)

For clean steam C-steel with 1 mm CA can be applied, since it is considered to be non-corrosive. Also for clean condensate lines and BFW lines, C-steel with 1 mm CA can be applied because the BFW will be de-aerated.

For Boiler Feed Water and Boiler Water quality control and conditions, reference is made to Appendix 3.

3.4.6 Plant Utilities – Chilled Water

The chilled water used in the Kharg MEG plant originates from demineralised clean condensate. Subsequently it is applied in a closed loop. Air ingress into the circulation loop should be minimized, to reduce the corrosivity of the chilled water to a minimum. Therefore the chilled water tank shall be kept under a nitrogen blanket. For distribution piping, pumps and the chilled water tank C-steel can be selected.

The chilled water quality should be adequately controlled by appropriate oxygen scavengers/inhibitor systems.

3.4.7 Plant Utilities – Nitrogen

The non-compressed nitrogen transport system for purging, blanketing or other services can be entirely made of carbon steel.

The pressurized nitrogen system in the EO reaction section can also be made of CS up to the nitrogen filter. For the nitrogen filter and all piping downstream the nitrogen filter SS shall be applied. The nitrogen buffer and storage vessels can be made of CS.

3.4.8 Pluronic anti-foam agent

To maintain product purity, the construction material of the Pluronic anti foam system in the CO₂ Removal section shall be austenitic stainless steel.

3.4.9 Caustic

Carbon steel is a suitable construction material for the caustic storage tank and piping. A stress relief heat treatment is required for C-steel equipment / piping



containing 20% wt caustic. Electrical tracing shall be applied for the import piping system containing 50% wt caustic solution to prevent the solution from freezing. The temperature in this line shall not exceed 40 °C. If steam tracing is applied in this piping, alloy 600 (Werkstoff nr 2.4816) shall be selected.

Note that the materials selection at the individual caustic injection points shall be compatible with caustic service (20% wt) at the operating temperature of the process line. To be specified by contractor.

3.5 Miscellaneous

3.5.1 Painting and coating

It is recommended to externally paint / coat all carbon steel piping/equipment irrespective the temperature or insulation.

Adequate measures to prevent corrosion under insulation should be in place.

Austenitic stainless steel will not corrode at atmospheric conditions, but is susceptible to chloride stress corrosion cracking at skin temperatures above 50 °C. To minimise the risk for chloride stress cracking in a marine environment all austenitic stainless steel piping and equipment with a wall temperature of 50 °C and above should be coated. A suitable surface pre-treatment in the form of a light blast cleaning with an appropriate abrasive is recommended to ensure proper adhesion of the subsequently applied paint system. Aluminium oxide or other abrasives (free from any chloride or iron / steel contamination should be used for blasting stainless steel.

Structural steel work:

Structural steel should be hot-dip galvanised, in accordance with either ASTM A 123 or BS 729. If hot-dip galvanising is not feasible, steel structures should be adequately painted.

Note:

For potential fire situations, where hot-dip galvanising or zinc-containing coatings are present, any un-insulated (bare) austenitic stainless steel equipment/piping should be specially protected against the possibility of zinc embrittlement failure, which may result in rapid-fire escalation. Such equipment should be located in a shielded position that will reduce the risk of molten zinc falling onto the steel.

Tanks:

The carbon steel **glycol slops tank**, heavy glycols tank, caustic tank, chilled water tank and demineralised water tank should be adequately protected against external corrosion.

To prevent iron pickup of the finished glycols, the OBL glycols rundown and final glycols storage tanks (MEG, DEG and TEG) shall be protected by a suitable



organic or thermal aluminium sprayed internal coating. For quality reasons in the MEG “fibre grade” the preferred coating for these tanks is Amercoat 23. However in case of unavailability, an alternative list of approved coatings for glycol storage is provided in table 1. Note that Ameron has withdrawn the Vinyl, high “volatile organic compounds” (VOC) containing Amercoat 23 coating from their Product Range because of increasing, and more stringent, environmental requirements in many countries. However, on special request from the customer, and for a sufficiently large quantity of coating, Ameron is still prepared to manufacture the Ameron 23 coating.



Table 1: Alternative coating list for storage MEG “fibre-grade”

Coating	Type	Remarks
Plasite 7122 HS	Epoxy - phenolic	Potential requirements for wash down and tight control of humidity and temperature, during application.
Plasite 9062	Epoxy (aliphatic)	Potential requirements for wash down and tight control of humidity and temperature, during application.
Plasite 1002/1010	Inorganic zinc + silicate sealer	Inorganic zinc coatings may impart zinc impurities to the product, e.g. when sealer has been degraded or damaged.
Ameron D9HS/PSX 738 (liquid component of PSX 738 only)	Inorganic zinc + Polysiloxane (sealer)	Inorganic zinc coatings may impart zinc impurities to the product, e.g. when sealer has been degraded or damaged.
Aluminium	Thermal spray	Risk of rust bleed when coating thickness is too low, i.e. less than 150 micron. For MEG storage, a minimum coating thickness of 250 micron should be specified.

For internal coating of the **glycol slops tank**, the following coating systems can be applied (< 60 °C): (i) amine-cured, phenolic epoxy primer (DFT 100 microns), (ii) Amine adduct-cured, phenolic epoxy (DFT 100 microns) Inter-coat, and (iii) high build, amine adduct-cured epoxy (DFT 100 microns).

Application of the selected coating system should be according to manufacturers specification. For optimum paint performance surface to be painted or coated



shall be completely dry and free from burrs, weld spatter, flux, rust, loose scale, dirt, dust, grease, oil and other foreign matter before any paint is applied.

Notes:

- Abrasives for use in blast cleaning carbon steel and low alloy steels are specified in ISO 8504-2. The steel substrate should be grit blasted to at-least Sa 2¹/₂, in accordance with ISO 8501-1.
- Specification of thermal spray aluminium coating should comply with ISO 2063. The steel substrate shall be grit blasted to at-least Sa 2¹/₂, in accordance with ISO 8501-1. Surface roughness (anchor profile) between 60 and 100 micron. Qualification of thermal sprayer should comply with ISO 14918.

3.5.2 Gasket materials

The process stream determines which gasket shall be used.

The following gasket types/materials shall be used for **ethylene oxide service with more than 0.5% wt EO**, which also have to be fire resistant:

- For all temperatures graphite filled SS 316 austenitic stainless steel spiral wound gaskets with an austenitic SS 316 austenitic stainless steel inner and carbon steel outer retaining ring.
- Flanges shall have a finish Ra 3.2 – 6.3 µm
- For heat exchangers at all temperatures graphite filled spiral-wound austenitic SS 316 stainless steel gasket (carbon steel outer ring and an austenitic SS 316 inner ring), shall be used.
- For stuffing boxes of valves at all service temperatures graphite packing shall be used.

Gasket materials for **Oxygen Service** are specified in Appendix 1.

The general gasket material for all other services is spiral-wound type 316, graphite filled.

3.5.3 O-Rings

For O-Rings that are applied in EO service with concentrations >10% wt EO, Kalrez type 6375 and Parker EPR 80A type E515-80 O-rings shall be applied as standard. However, suitable alternatives are Kalrez type 2035, Parker EPDM 90A type E962-90 and Parker EPDM type 75A TYPE E740-75.

4. Cleaning

4.1 Equipment preparation

All columns, vessels and other equipment shall be delivered free of rust. Equipment (e.g. columns, vessels) shall be transported with all nozzles closed and under nitrogen or vapour phase corrosion inhibitor. Corrosion of internal surfaces during construction activities should be prevented. Although sometimes



unavoidable, exposure to air shall be minimised and when possible a nitrogen atmosphere shall be maintained. Nitrogen safety measures shall be taken to protect construction workers and other staff from exposure to nitrogen. Before start-up, the internal surfaces of all Process and Oxygen systems (equipment and piping) shall be free from foreign matter such as welding slag, loose debris, rust, etc.

To ensure trouble-free operation, complete cleaning and testing procedures are required for the initial start-up. All pipelines and equipment should be inspected and cleaned before being tested and placed in operation. No foreign material should enter pumps or control valves. Inspect the plant carefully to determine if equipment and piping have been installed properly. Test and calibrate instruments. Make sure that they are correctly installed and identified. Care should be taken to align and lubricate pumps and drivers in accordance with the manufacturer specifications before operation. As for later start-up, cleaning and testing procedures should be adopted - as necessary - to check the system integrity and prevent possible upsets after any major modification or prolonged shutdown.

4.2 Chemical cleaning

4.2.1 Introduction

Cleaning can be carried out by degreasing and flushing or shot-blasting, or by chemical methods. Shot-blasting should be used for carbon steel equipment and carbon steel piping, which is accessible. For stainless steel equipment/piping and inaccessible pipe-work, acid-cleaning method can be used. **For oxygen systems DEP 31.10.11.31-Gen is also applicable.**

Cleaning of the EO reactors shall be done in accordance with Process Memorandum 101 – Reactor Cleaning and Catalyst Charging.

The following procedure is the recommended method for cleaning of piping and equipment other than the EO reactor and the CO₂ Removal package unit and includes:

- a degreasing stage;
- an acid-pickle stage;
- a passivation stage (when carbon steel is present).

The chemical cleaning method is to be defined by the chemical cleaning contractor taking into account the specific construction materials used and must include passivation, if required for the materials used. The applied chemical cleaning method shall be approved by Shell.

The CO₂ removal unit and the LE column shall be chemically cleaned to remove oil and grease to prevent foaming problems at start-up. Steam detergent cleaning can be used to clean all other columns.

If any column is later repacked, chemical cleaning is needed to remove cutting oils from packing surfaces. If cutting oils are left in the system, they may cause severe foaming.



4.2.2 General considerations chemical cleaning

Chemical cleaning is the process of removing fouling deposits with chemical solutions. The cleaning action may be entirely chemical, using acids or caustics, but may also be assisted by physical means using solvents, steam or hot water. Cleaning operations should be conducted in such a way that they will not lead to unacceptable pollution of the environment.

Cleaning procedures should be available before plant or equipment is started up. The procedure and frequency of cleaning should be noted in a "plant cleaning manual" or similar document and should be reviewed periodically to identify areas of improvement. Specialized contractors should carry out chemical cleaning. The chemical cleaning method is to be defined by the chemical cleaning contractor taking into account the specific construction materials used and must include passivation if required for the materials used. Corrosion rates of materials during chemical cleaning are generally low, but severe damage may still occur if improper procedures are applied, e.g. stress corrosion cracking of stainless steel induced by chlorides. An austenitic stainless steel system should therefore be kept free of chloride ions to prevent localised corrosion (e.g. chloride stress corrosion cracking). The applied cleaning liquids and water must be free of chlorides.

Hydrochloric acid shall not be used for cleaning austenitic stainless steel, e.g. AISI 304, 321, 347, 316, 310, to avoid pitting and/or chloride stress corrosion cracking.

Citric acid is available in crystals. Although corrosion rates are low, effective inhibitors shall be used. Citric acid is typically applied in concentrations of 5% to 6% by weight and cleaning temperatures up to 95 °C can be used to reduce cleaning time. Citric acid is suitable for many materials and should be used when austenitic stainless steel parts are present. For cleaning equipment with internals made of 12% chromium steels (e.g. type AISI 405, 410, 410S) citric acid shall be used only at temperatures below 60 °C.

When acids are used for chemical cleaning, metals will be severely attacked unless a suitable inhibitor is added. Acid velocities affect the effectiveness of inhibitors, which should normally be restricted to 0.5 m/s. There is also a temperature limit above which the inhibitor will decompose and lose its effect. For this reason inhibited acid solutions shall not be heated with live steam. Several types of inhibitor are commercially available, such as Rodine and Armohib (for which chemical cleaning contractors may use their own type description). Manufacturers' prescriptions shall be closely followed for the particular application since the inhibitor is only suitable for one type of acid and metal, and some inhibitors give optimum performance only when added to the concentrated acid.

4.3 Chemical cleaning

4.3.1 Alkaline degrease

Before start-up, oil and grease shall be removed prior to any acid cleaning by alkaline wash to ensure that the acids come into contact with the deposits.



- Using temporary equipment, flush the system with water until the washings are free of suspended solids.
- Establish circulation with good quality water (total hardness <2 mg/l as CaCO_3), check connections, and eliminate any leaks.
- Using low-pressure steam injection into circulating tank or by other available means, raise the temperature of the circulating water to 75-95°C. Add tri-sodium phosphate to give a concentration of 3000-4000 mg/l (as Na_3PO_4) and Synperonic NXr to give a concentration of 1000 mg/l (or 200 mg/l Synperonic NXr).
- Circulate, preferably for 24 hrs, but for a minimum period of 12 hrs. Drain the system and flush with water at maximum available rates until the water is visibly free of suspended solids and contains less than 2 mg/l of tri-sodium phosphate.

As mentioned before, it is crucial for proper performance that the CO_2 removal unit and the LE column are cleaned to remove oil and grease to prevent foaming problems at start-up.

After the above procedure the system shall be acid cleaned.

4.3.2 Citric acid cleaning

- Use feed pumps or temporary equipment, flush with water until the washings are free of suspended solids.
- Fill the system with demineralised water or good quality condensate (chloride content < 1 mg/litre). Establish circulation and eliminate any leaks. Raise the temperature of the circulating water to 75-95°C.
- Add citric acid to give a concentration of 3% in the final circulating solution and a suitable corrosion inhibitor. Both acid and inhibitor should be added at a point of turbulence in the system. The suitability of the corrosion inhibitor (and its concentration) should be established by previous good experience or laboratory testing with materials of construction and procedures that duplicate the cleaning procedure to be used for the system. The continued effectiveness of the inhibitor should be checked during the acid cleaning by periodically immersing wool of the appropriate material in the cleaning solution. The effectiveness of the inhibitor is verified by absence of (hydrogen) bubbles evolved from the surface of the wool. The temperature of the circulating inhibited acid shall not drop below 50°C and the velocity within the system should not exceed 0.5 m/s.

Note:

The solubility of the inhibitor may be temperature-dependent, causing a grey scum to form on the surface of the circulation tank (and loss of protection) if the temperature drops below e.g. 50°C.

Circulate until the rate of increase of dissolved iron concentration or other relevant parameter decreases significantly and continue for a further 2 hrs. If the



dissolved iron concentration reaches a steady state with a maximum of 0.6 wt% drain and continue with the filling of demineralised water or good quality condensate, etc.

4.3.3 Passivation

- For passivation, drain the system, rinse with a solution of 0.1 wt% citric acid in water containing no inhibitor. Refill system with demineralised or good quality condensate. Re-establish circulation, raise the temperature to 40-60°C and add citric acid to give a concentration of 0.5-1.0 wt%. Raise the pH to values greater than 9 by addition of ammonia and then add sodium nitrite to give a concentration of 0.5-1.0%. Circulate the solution through the system for at least 2 hrs. and then drain.
- Carry out the final inspection and put the system into service as quickly as possible or keep it under nitrogen.

Note:

For systems containing no carbon steel equipment the passivation step is not required, however the system shall be flushed with demineralised water or good quality condensate until the pH value of the water to drain is the same as that of the inlet water. Drain and inspect.

Once the system has been flushed clean, it shall be dried by blowing nitrogen or dry air through. Equipment shall be maintained under positive pressure with nitrogen between all stages of the above-mentioned procedure and until ready for start-up.

4.4 Important considerations for the CO₂ removal unit

Gas pressure is needed in the absorber to allow circulation. Natural gas, inert gas or nitrogen is satisfactory. Air may be used only for the initial cleaning. Sufficient pressure is needed to allow circulation at a minimum of 50% of design rates. Gas under pressure is dissolved in the liquid to a small extent and makeup gas is required.

The cleaning solution should be circulated while heating for 2-3 days by supplying heat to the CO₂ stripper reboiler. Check the mechanical integrity of the equipment, including pumps, exchangers, instruments, and control valves. Bring in fresh wash solution and bleed off a corresponding amount of spent solution occasionally. Check foam times by shake test on the cleaning solution each shift and the spent solution to be discarded.

If the final foam times are consistently less than 20 seconds, the cleaning solution can be discarded and the system rinsed with condensate. The system should then be drained through all available blow-down points to flush all lines thoroughly. Also be sure the storage is clean prior to charging the system. If the final foam time exceeds 20 seconds, more circulation or another cleaning is warranted. If severe foaming occurs during cleaning, some antifoam can be applied to facilitate the cleaning process. However, over-injection of antifoam may reduce the cleaning effectiveness and should be avoided.



5. Insulation

Insulation of piping and equipment can be required for:

- heat flux control of processes and product lines
- preventing vapour condensation on the outside surface of the piping and equipment having a temperature below the dew point of the surrounding atmosphere.
- preventing vapour condensation in the piping and equipment.

Adequate measures should be taken to prevent corrosion under insulation.

Insulating materials

Only chloride free (max. 10 ppm.) mineral fibre or cellular glass ('foamed glass'), covered by aluminised or stainless steel sheeting, should be used. Hot dip galvanised steel sheeting should not be used over insulation on or near austenitic stainless steel and/or austenitic nickel alloy piping and equipment because of Liquid Metal Embrittlement (LME) risks.

For flanges in EO service with concentrations > 10% wt EO down stream from the EO stripper overhead and locations where stagnant EO in concentrations > 10% wt may occur an insulation material with a closed cell structure (foamed glass or perlite) shall be used.

For cold ethylene service (-24°C/+10°C) poly-urethane foam with a vapour barrier and a fire protective layer (mineral wool) may also be used.

Alkaline insulating materials, such as magnesia, shall not be used in EO service with concentrations >10% wt, because they lower the EO auto-ignition temperature.



6. References:

1. "Ethylene Oxide – Guidelines for bulk handling"; first edition, 1996. This guide can be obtained through the Chemical Industries Association.

NOTE: The chapters about painting, coating, insulation, and gaskets in the above-mentioned documents are overruled by this Material Selection Guide document for the Kharg MEG plant.



Appendix 1: Sealing material for oxygen service

Note that all non-metallic materials shall be ordered "Suitable for Oxygen Service" and "BAM approved" (see below).

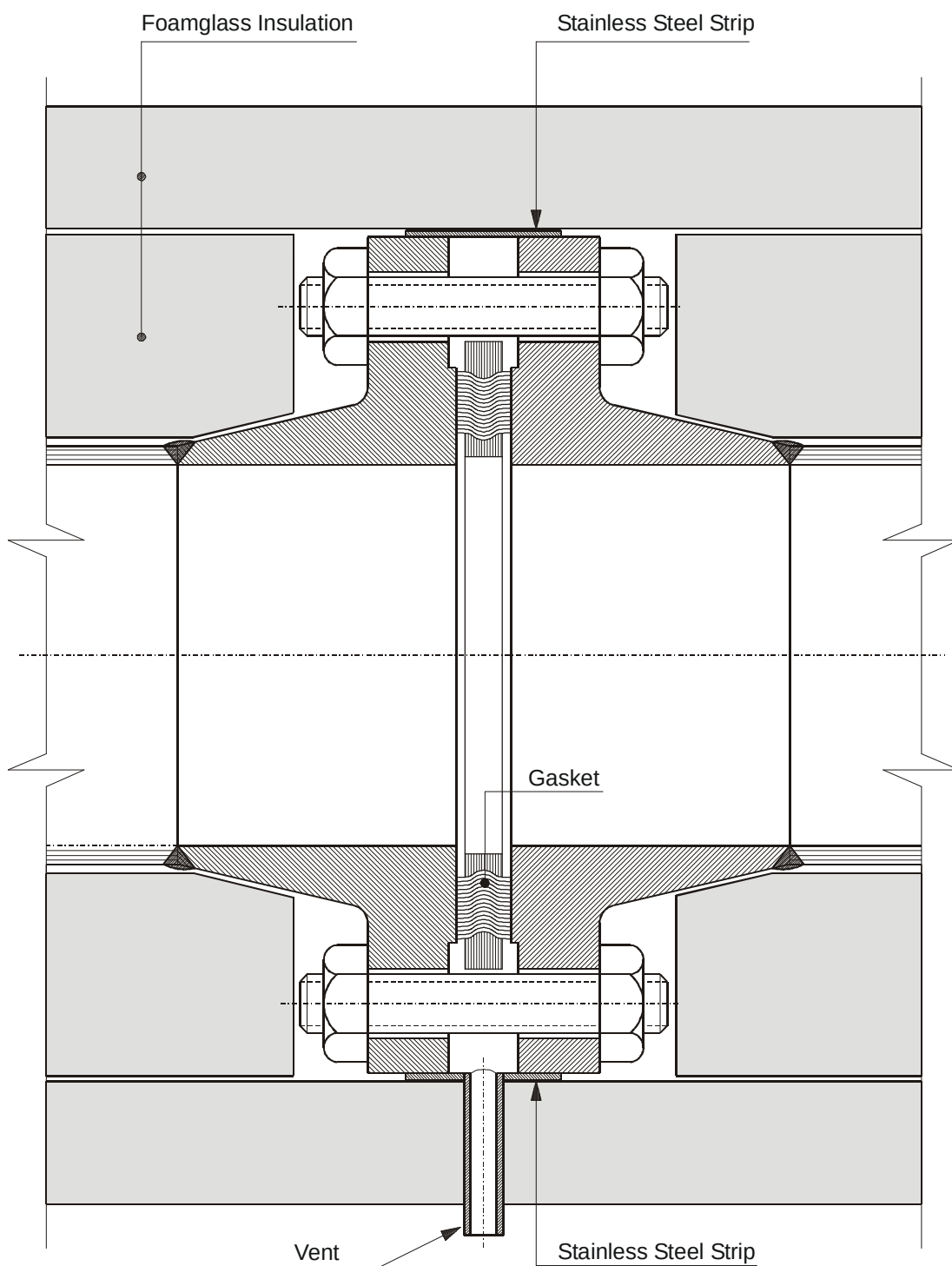
Sealing	Material	Max. Temp °C	Design Pressure Bar
Gasket	NBR bonded non asbestos fibre gasket	80	40
	Graphite fibre	200	40
	PTFE-filled spiral-wound stainless steel with carbon steel external guide ring and 316 stainless steel internal guide ring	200	40
Stuffing box packing	PTFE impregnated-braided non asbestos fibre	200	40
	Graphite fibre	200	40
'O' rings	Viton A	120	40
Seal rings	PTFE	120	40
	PTFE graphite-filled or nickel filled	175	40

BAM: Bundes Anstalt für Materialforschung und -prüfung,
See <http://www.bam.de/ueberuns/wege/wege.htm>

Document: "Liste der nichtmetallischen Materialien, die von der Bundesanstalt für Materialforschung und -prüfung zum Einsatz in Anlageteilen für Sauerstoff als geeignet befunden worden sind. Hinweis: Zusatz für VBG 62"
available from: <http://www.jedermann.de/sites/home/home.html>.



Appendix 2: Flange with vent, for EO service



Appendix 3: Specification for High Purity Boiler Feed Water and for Boiler Water

High Purity Boiler Feed Water Specification to HP steam drum

General requirements	clear and colourless, free from dissolved matter
Conductivity at 25 °C (Note 2)	< 3 μ S/cm
pH value at 15 °C (Note 6)	> 9.5
Oxygen (O ₂) (mg/kg) (Note 5)	< 0.02
Total iron content Fe (mg/kg)	< 0.02
Total copper content Cu (mg/kg)	< 0.003
Silica (SiO ₂) (mg/kg)	< 0.05
Total carbon dioxide content (CO ₂) (mg/kg)	below detection limit
Hardness as CaCO ₃ (mq/kg)	below detection limit
KMnO ₄ consumption (mg/kg)	< 5
Oil Content (mg/kg)	below detection limit
Phosphates	See Note 4
Hydrocarbons	zero

Notes:

1. Feed water specifications and treatment methods shall be decided by the licensee/contractor. Proposed treating chemicals shall be reviewed for process compatibility.
2. With continuous sampling measured after treatment in highly acid cat-ion exchanger (applied exclusively to water that is free from CO₂).
3. Boiler feed water and steam may not contain any hydrocarbons to prevent product quality degradation by contamination via the steam systems of the plant.
4. Phosphates other than Na₃PO₄ should not be used in view of the possible contamination of the EO catalyst. Phosphate is a severe catalyst poison because it promotes the isomerisation reaction of EO to acetaldehyde.
5. Oxygen scavenging by hydrazine or Cor-Trol. Both scavenging agents decompose rapidly and have no influence on EO catalyst performance.
6. For pH control ammonia is preferred. Application of amines on mutual agreement to avoid deactivation of the EO catalyst performance. In case for some reason the pH of 9.5 or higher cannot be maintained for the Boiler water (see Boiler water specification below), Na₃PO₄ may be used for pH control. Application of amines on mutual agreement to avoid deactivation of the EO catalyst.

Boiler Water Specification from HP steam drum (Note 1)

General requirements	clear and colourless, free from dissolved matter
Conductivity at 25 °C (Note 2)	< 150 μ S/cm
pH value at 15 °C (Note 3)	9.5 - 10.5
Silica (SiO ₂) (mg/kg)	< 6
Total carbon dioxide content (CO ₂) (mg/kg)	below detection limit
Phosphates	< 6
Hydrazine	traces

Notes:

1. Only additional requirements or requirements that differ from the high purity boiler feed water requirements are given.
2. Boiler water and steam may not contain any hydrocarbons to prevent product quality degradation by contamination via the steam systems of the plant.
3. For pH control ammonia is preferred. Application of amines on mutual agreement to avoid deactivation of the EO catalyst performance. In case for some reason the pH of 9.5 to 10.5 cannot be maintained for the Boiler water, Na₃PO₄ may be used for pH control. Application of amines on mutual agreement to avoid deactivation of the EO catalyst.
4. The maximum allowable concentration (mg/kg) of phosphates depends on the pressure in the system. For a pressure below 40 barg the maximum allowable concentration is 30 mg/kg.

Appendix 4: Guidelines for application of austenitic stainless steels in heat exchangers with chlorides containing cooling water

1. General introduction to chlorides induced localised corrosion

Pitting corrosion, crevice corrosion and chloride stress corrosion cracking (Cl-SCC) are forms of localised attack that can occur in aqueous, chloride containing environments and at almost any chloride concentration.

1.1 Crevice and pitting corrosion

Depending on pH, chloride concentration, oxygen concentration and possible oxidisers present (e.g. Cl_2 and O_3 concentration), stainless steels can be susceptible to crevice and pitting corrosion even at temperatures lower than ambient. Resistance towards pitting and crevice corrosion increases with increasing molybdenum, chromium, and nickel content of the alloy. Titanium is a good alternative. The likelihood of chloride induced localised corrosion decreases in alkaline solutions.

1.2 Chloride Stress Corrosion Cracking

Chloride stress corrosion cracking (Cl-SCC) is a phenomenon that can occur in aqueous chloride containing environments above approximately 50 °C. The severity of chloride stress corrosion cracking is a function of chloride concentration, tensile stress, temperature, pH, and the presence of oxygen and oxidisers like Cl_2 and O_3 . Cracking is most likely to occur in the presence of oxygen under acidic or neutral pH conditions.

Austenitic stainless steels and Fe-Cr-Ni alloys with less than about 40% nickel are most susceptible to Cl-SCC. Carbon steel, Cr-Mo steels and 12Cr steel are not affected. Austenitic alloys with high nickel contents (e.g., Alloy 825, Alloy 625 and Alloy C-276) are immune up to temperatures > 200 °C. Duplex stainless steels such as Alloy 2205 and Alloy 2507 and high chromium ferritic stainless steels also are very resistant to Cl-SCC. Titanium is a good alternative. For exact temperature / chloride content / pH limits of (super) duplex stainless steels and other alloys to prevent Cl-SCC contact a corrosion engineer.

The result of the cracking is ultimately brittle failure of a very ductile material. Internal claddings and overlays are normally considered to be in compressive stress and much less susceptible to chloride SCC in this form. But, this is not a guarantee of resistance.

Note that the presence of crevices at temperatures above 50 °C can cause Cl-SCC to initiate in the crevices even at very low chloride concentrations in the bulk liquid because inside the crevice, crevice corrosion causes chlorides to concentrate and the pH to decrease. In deep pits (pitting corrosion) a similar mechanism causing Cl-SCC can occur. Furthermore, note that the mentioned SCC resistant alloys can also become susceptible to crevice and pitting corrosion under certain conditions.

2. Guidelines austenitic stainless steels and chlorides containing cooling water

Cooling water systems under consideration are open recirculating systems where the water is:

- Clean and any fine solids are kept dispersed.
- Protected against bio fouling by chlorination, ozonisation, or potentially biocides.
- Chlorination is either continuously or by shock dosing at medium equivalent chlorine level (< 0.4 ppmw continuous and 1-2 ppm by shock dosing)
- Controlled at a pH in the range 7.0 to 8.5
- Inhibited for corrosion of carbon steel, generally by a zinc-phosphate based inhibitor.
- Temperature < 52 °C to prevent scaling.

Because of the corrosivity of the process environment towards C-steel, austenitic SS may have to be selected for the process side of a heat exchanger. Care should be taken to prevent chloride pitting, crevice, and stress corrosion of stainless steel. Below a guideline for the materials selection of austenitic stainless steel in cooling water service.

To prevent galvanic corrosion, the application of different construction materials galvanically connected to each other and all in contact with the cooling water should be avoided. An example is heat exchangers where austenitic stainless steel is required for the product side and the cooling water needs to be on the shell side. Although the recommendation is to select one materials type for all parts in contact with the CW, when a higher corrosion risk is acceptable (possibly reduced life time and possibly higher maintenance costs), it can be decided to select SS 316L (or when needed, a more corrosion resistant material; see sections 2.1 and 2.2. of this appendix) for tubes, solid tube-sheet and the baffle/support plates, and C-steel for the shell and to suppress galvanic corrosion with a suitable corrosion inhibition system. However, it should be noted that inhibitors do not work well in occluded spaces like dead ends, crevices and under deposits. At these unprotected locations accelerated corrosion can occur. Because of the complexity, when the application of dissimilar materials is considered a corrosion engineer should be consulted.

2.1 Shell & tube HE with cooling water (cw) inside SS tubes

If a corrosive process medium is selected on the shell side an austenitic SS shell, tube bundle, tube-sheet, and support/baffle plates can be selected. Application of austenitic SS in cooling water service on the tube side is acceptable provided that:

- a. The chloride (Cl⁻) content of the cooling water is less than:

SS 304 and equivalent steels:

50 ppmw at maximum wall temperature of 75°C and 150 ppmw at a maximum wall temperature of 50°C.

SS 316 and equivalent steels:

50 ppmw at a maximum wall temperature of 80°C and 150 ppmw at a maximum wall temperature of 65°C.

If the equivalent chlorine (Cl_2 eq) content of the cooling water can be reduced sufficiently (from 0.4 ppmw to less than 0.2 ppmw), the maximum allowable wall temperature at mentioned chloride levels can be increased by at least 15°C (up to the inhibitor effectiveness temperature limit of 80 °C). If relevant for the design, a corrosion engineer should be contacted to determine the actual maximum allowable wall temperature at low equivalent chlorine content.

The water should be circulating all the time or the water should be drained from the exchangers, to prevent occurrence of an increased wall temperature under non-flow conditions, that may lead to deposits and chloride-induced corrosion.

Note that at temperatures above 52 °C, scaling may occur. Underneath a scale, chlorides may accumulate up to much higher concentrations than in the cooling water. Therefore, when scaling above 52 °C cannot be excluded, it is recommended to either reduce the skin temperature below 52 °C or apply the guidelines for situations where the presence of crevices cannot be avoided (section 2.2 below).

- b. The tube-sheet on the waterside is of stainless steel and that the stainless steel tubes are welded to the tube-sheet to prevent crevices.
- c. To prevent crevices at front end or rear end flanged connections graphite and 'full density' PTFE gaskets should not be used. Expanded PTFE, e.g. type Gore-Tex, can be used. Only PTFE that contains no free fluoride ions (F^-) is allowed in contact with the metal. Non-asbestos plate gaskets can be used on the waterside in contact with the stainless steel.
- d. Keeping the flow velocity in the range 2 to 4.5 m/s further reduces the risk of fouling inside the stainless steel tubes.

2.2 Shell & tube HE with cooling water on the shell side contacted with SS exchanger parts

If a corrosive process medium is selected on the tube side an austenitic tube bundle and tube-sheet may be selected. The shell and baffle plates on the cooling waterside may still be of carbon steel, although austenitic SS is preferred (see previous discussion of galvanic corrosion).

A design with cooling water on the shell side is NOT recommended and should be avoided as much as possible, because crevices and the formation of deposits on the water side cannot be avoided! This results in an increased fouling and corrosion risk.

If it can not be avoided to have the CW on the shell side, the tube bundle, tube-sheet, shell and baffles (or a part of these exchanger components) may be in stainless steel provided that:

- a. SS 316 or equivalent austenitic stainless steels are selected, equivalent chlorine concentration is sufficiently low (< 0.2 ppmw) and the chloride content of the cooling water is below 50 ppmw at a maximum wall temperature of 60°C. SS 304 or equivalent austenitic stainless steels are not suitable because of less resistance to crevice corrosion at "common" cooling water skin temperature (35-45°C).

The water should be circulating all the time or the water should be drained from

the exchangers, to prevent occurrence of an increased wall temperature under non-flow conditions, that may lead to deposits and chloride-induced corrosion. Note that at temperatures above 52 °C, scaling may occur. Underneath a scale, chlorides may accumulate up to much higher concentrations than in the cooling water.

- b. The tubes are hydraulically expanded over the full width of the tube-sheet to minimize crevices at tube - tube-sheet contact.
- c. To prevent crevices at shell side flanged connections graphite and 'full density' PTFE gaskets should not be applied. Expanded PTFE, e.g. type Gore-Tex, can be used. Only PTFE that contains no free fluoride ions (F⁻) is allowed in contact with the metal. Non-asbestos plate gaskets can be used on the waterside in contact with the stainless steel.

2.3 Plate type heat exchangers

The use of plate & frame type heat exchangers is NOT recommended in cooling water service, because crevices and the formation of deposits (creating crevices) cannot be avoided completely! This increases the risk of occurrence of chloride crevice corrosion.

If the application of a plate type heat exchanger cannot be avoided austenitic stainless steel can be selected, provided that:

- a. SS 316 or equivalent austenitic stainless steels are selected, when chlorine concentrations are sufficiently low (< 0.2 ppmw) and the chloride content of the cooling water is below 50 ppmw at a maximum wall temperature of 60°C. SS 304 or equivalent austenitic stainless steels are not suitable because of less resistance to crevice corrosion at "common" cooling water skin temperature (35-45°C).

The water should be circulating all the time or the water should be drained from the exchangers, to prevent occurrence of an increased wall temperature under non flow conditions, that may lead to chloride induced corrosion and deposits. Note that at temperatures above 52 °C, scaling may occur. Underneath a scale, chlorides may accumulate up to much higher concentrations than in the cooling water.

- b. To prevent crevices at plate / gasket contacts graphite and 'full density' PTFE gaskets should not be applied. Expanded PTFE, e.g. type Gore-Tex, can be used. Only PTFE that contains no free fluoride ions (F⁻) is allowed in contact with the metal.
As alternative welding of the plates can be considered, to avoid crevices at plate contacts.

If mentioned design criteria regarding wall temperature and flow velocities at defined maximum allowable equivalent chlorine and chloride contents can't be realized by sound and economic heat exchanger design an upgrade of the material might be required to a more corrosion resistant alloy (e.g. super austenites, super duplex stainless steels or titanium). But an evaluation should occur to select a preferred solution by either thermal design or material upgrade.