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Critical Material Selection for Ethylene

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***Abstract* – The article covers the critical properties of metallurgy to be used in ethylene mainly. Also the different terminology impact is described in detail so that corrosion impact is reduced for the various equipment in the industry. The process conditions are also mentioned as they play a vital role as well under the material of construction. The article covers the materials selection diagram as it's the tool for material selection depending on safety, reliability, process conditions and environmental conditions as well. Also the material selection basis is elaborated which depends on industry practices and again process conditions along with material properties and environmental conditions. Reference material list is indicated with the Table of galvanic series, API, ASME and more others per detailed description. Overall all the information in this article is per the past industrial experiences with better engineering judgement and practices.**

***Keywords* – Metallic, Steel Making, Heat Treatment, Non-Destructive Examination, Erosion.**

I. Introduction

In the production of ethylene, the selection of appropriate materials of construction is crucial to ensure the safe and efficient operation of equipment and to minimize the risk of corrosion. Ethylene is a highly reactive and flammable gas that is commonly used as a building block for a wide range of chemicals, plastics, and other materials. Some of the key properties that need to be considered when selecting materials for use in ethylene processing include:

1. *Corrosion Resistance:*

Materials must be resistant to corrosion from exposure to ethylene, as well as other substances that may be present in the process stream.

2. *High Strength and Durability:*

Ethylene processing equipment must be able to withstand the high pressures and temperatures that are involved in the production process, as well as the constant wear and tear that comes with use.

3. *Thermal Stability:*

Materials must be able to withstand extreme temperature changes without undergoing significant changes in their physical or chemical properties.

4. *Compatibility with Other Materials:*

Materials used in ethylene processing must be compatible with other materials that may be used in the same process, such as catalysts and additives. Some of the most commonly used materials for ethylene processing equipment include:

5. *Stainless Steel:*

Stainless steel is a corrosion-resistant material that is commonly used in ethylene processing equipment. It is particularly effective at withstanding the high pressures and temperatures that are involved in the production process.

6. *Nickel-Based Alloys:*

Nickel-based alloys are also commonly used in ethylene processing equipment due to their high strength and excellent resistance to corrosion.

7. *Titanium:*

Titanium is a lightweight and corrosion-resistant material that is often used in ethylene processing equipment where weight and corrosion resistance are both important considerations.

8. *Plastics:*

Some plastics, such as high-density polyethylene (HDPE), are also used in ethylene processing equipment due to their excellent corrosion resistance and low cost.

The selection of materials for use in ethylene processing equipment must take into account the specific process conditions and other factors, such as the cost of materials and the availability of skilled labor to work with them. It is important to consult with experienced engineers and materials specialists to ensure that the appropriate materials are selected for each specific application.

Environmental factors such as location (near coastal regions or sea), low temperature areas, and possible acid rain areas can significantly impact the selection of materials for equipment and structures. For example, exposure to saltwater or high humidity can accelerate corrosion and affect the performance and durability of materials.

Internal process factors such as stream composition, design/operating conditions (temperature/pressure), fluid state (phases/mixture of phases), and fluid velocity can also impact the selection of materials. Materials with different properties such as resistance to corrosion, erosion, or high temperatures may perform differently under the same conditions, and therefore need to be carefully evaluated.

In addition to material properties, the presence of contaminants or trace elements in the process stream can also influence material selection decisions. The use of protective surfaces (e.g., cladding, coatings, or corrosion products) and inhibitors can also be considered as protective measures against corrosion and other forms of degradation.

Other factors such as cost (including initial cost, expected service life, and product purity/contamination), safety, and reliability considerations (e.g., local code regulations, high reliability areas) are also important considerations in the selection of materials for equipment and structures.

Finally, equipment life considerations also play a significant role in material selection decisions. The expected service life of different equipment types (e.g., vessels, heat exchangers, pumps, piping) can vary, and materials need to be selected accordingly to ensure adequate performance and longevity of the equipment.

II. Materials Selection Diagram (MSD)

A material selection diagram (MSD) is a graphical tool used for selecting materials based on multiple criteria, such as environment, process conditions, cost, safety, and reliability. The MSD typically includes different regions or zones that correspond to specific materials or material families based on their performance and suitability for the specified criteria. The MSD can be used as a quick reference guide to help engineers and designers make informed decisions about material selection for various applications. MSDs can be created for specific industries, such as oil and gas, chemical processing, and aerospace, or for specific applications, such as piping, vessels, or pumps.

- MSD is based on the PFD's prepared by process engineers.
- Special client requirements [1].
  - Ambient local conditions at plant site.
  - Expected equipment life.
  - Special requirements for sour wet service (if any).
  - Listing of expected corrosion species.
  - Materials for major components as in pumps, tower internals etc.
  - (Use of corrosion probes & injection points if required).
- Preparation of MSD's involve special considerations like overhead corrosion control by using excess water for NH_4HS, minimize velocity or select higher metallurgy.
- Advantage is taken from corrosion protection because of coke lay down to use a lower grade material in delayed cokers.
- Intermittent use of equipment affects the materials selected.
- Use of excessive corrosion allowance must be properly balanced by downstream products of corrosion.
- Materials selection must not conflict with the operating manual, especially during shutdown & start up procedures provided for specific technology (by General Industry).
- Intermittent use of an equipment or piping must be taken into consideration to balance the cost of higher grade metallurgy.
- Materials such as carbon steel have many grades and quality and must be specified for specific applications.
- Low temperature operation must be considered for brittle fracture avoidance.
- Sometimes line class index may dictate a different metallurgy because of the temperature-pressure rating.
- Local jurisdictional rules and applicable codes can play important role during materials selection process.
- PFD's must contain [2].
  - Process stream data (S, H_2S, Cl^-, CO_2, Naphthenic acid conc.)
  - Contaminants not shown in material balance data.
  - Operating & design conditions temp / press.

– Upset & regeneration conditions (if any).

III. Materials Selection Basis

- Sour Wet Service ($T< 200^0F$)

– No HIC steels, Limit S to 0.01% max + PWHT of all welds. Limit hardness of welds/HAZ to 200HB max

- Amine Service.

– PWHT of all welds. Hardness of welds/HAZ to 200HB.

- High Temp. H_2 service (hydroprocessing) [3].

– API 941 (2004 edition).

- Presence of S.

– Use McConomy curves based on design temp.

- Presence of H_2S (high temp. sulfidation).

– Couper Gorman curves based on design temp.

- $T < 500^0F$----------------- C.S.
- $> 500^0F < 590^0F$---------5Cr-1/2Mo.
- $> 590^0F < 650^0F$---------9Cr-1Mo.
- $> 650^0F$ --------------------304 SS.
- Presence of Nap. acid (>0.5 TAN+$T>450^0F$ & $< 750^0F$.

– Use 316 SS with Mo>2.5% or 317 SS.

- Presence of wet CO_2.

– Use Dewaard nomogram (or Dewaard Milliam equation) for CS corrosion rates- 304SS O.K for all concentrations.

- Reference Materials List [4] [5].

– Galvanic series: A table that ranks different metals and alloys based on their tendency to corrode in a given environment. It is useful for predicting galvanic corrosion when dissimilar metals are in contact.

– Dewaard CO2 corrosion nomogram: A graphical tool that helps estimate the corrosion rate of carbon steel in wet CO2 environments based on temperature, CO2 partial pressure, and pH.

– McConomy Curve for S corrosion: A chart that helps estimate the corrosion rate of carbon steel in sour service environments with high levels of hydrogen sulfide and elemental sulfur.

– Couper Gorman curves for H2S corrosion: A set of curves that help estimate the susceptibility of different alloys to hydrogen sulfide cracking (i.e., sulfide stress cracking and hydrogen-induced cracking) in sour service environments.

- Caustic Soda service chart: A chart that shows the recommended materials for different concentrations and temperatures of caustic soda (sodium hydroxide) service.
- ASME sec. VIII, div. 1 para UCS 66 for low-temperature brittle fracture avoidance: A code requirement that mandates certain minimum design temperatures and material toughness values to prevent brittle fracture in low-temperature applications.
- API 941 (1999 edition)- materials for high temp. H2 service: A standard that provides guidelines for selecting materials for high-temperature hydrogen service environments.
- API 610 Centrifugal Pumps designation chart: A chart that shows the materials and design features recommended for different pump types and services in the oil and gas industry.
- Miscellaneous photographs showing cracks, etc.: Visual aids that illustrate the different types of corrosion and damage that can occur in materials and structures, such as stress corrosion cracking, pitting, and erosion.

IV. Ethylene

- Purpose.
  - To convert ethane / naphtha into ethylene by thermal cracking.
- Major Equipment.
  - Cracking heater (see Heat Transfer Equipment).
  - Low temperature section.
- Corrosion Issues.
  - High temp. section (see next section on heat transfer equipment)
  - Low temp. section has almost no corrosion issues except low temperature brittle fracture considerations & formation of acetylides with copper bearing alloys, which can be explosive.
- Materials considerations for low temperature section
  - CS capable of meeting low temp. properties.
  - 304 SS where temp. < -55^{o}F.

A. *Heat Transfer Equipment*

- Heat Exchangers
  - General refinery service (process to process)
  - General refinery service (cooling water to process)
- Helichanger Exchangers
- Air Coolers
- High Temperature Special Heat exchangers [6]

– RM Interchanger in SM production.

– Waste Heat Exchangers in SM production.

- Heaters in general refining service.

– Moderate temperature service.

- Feed or charge heaters.
- Temperature range TMT (upto 800^{o}F).

– High temperature service.

- Hydrogen heater in LC Fining service.
- LC Fining Feed heater & delayed cokers.
- Temperature range TMT(1200^{o}F).

– Ethylene cracking & steam superheater type service.

- Temperature range TMT (~ 2000^{o}F range).

B. *Ethylene Crackers & Steam Superheaters*

- General

– Both ethylene cracking heaters & steam superheaters involve use of high temperature material for tubes [7]

- In steam superheaters, the tube materials must withstand high temperature and oxidizing conditions.
- In ethylene cracking tube materials must withstand the carburizing environment in addition to high temperature & oxidizing conditions of the heater box.

– Before going into the actual materials used in these applications, it is important to give a brief description of the basics of high temperature metallurgy.

C. *High Temperature Metallurgy Basics [8]*

- Deformation process.
- Strengthening due to elements in solid solution.
- Strengthening due to precipitation of intermetallic compounds.
- Strengthening due to dispersion of refractory oxides.
- Creep & Rupture strength.
- Oxidation resistance.
- Fuel side corrosion.
- Carburization.
- Metal Dusting.

D. *High Temperature Alloys used in Crackers & Steam Superheaters*

- Basic alloy types

– Alloy type 25Cr / 20Ni (HK).

– Alloy type 25Cr / 35Ni (HP).

– Alloy type 35Cr / 45Ni.

– Alloy type 35Cr / 35Ni / 15Co / 5W.

– Alloy type 28Cr / 41Ni / 5W.

– Alloy type 33Cr /48Ni /16W.

Most of the alloys are modified by additions of Nb, Ti, Si, Th, W and rare earth elements like Zr, Ce, Hf & B. [9].

E. *High Temp. Tubes & Fittings Manufacture and Fabrication*

- Static Casting.
- Centrifugal Casting.

– Casting factor & sound metal thickness.

– Center-less boring for controlling thickness.

- Wrought tube manufacturing by rolling.
- Welding (fabrication).

– Electron beam welding.

– Autogenous welding.

– Automatic welding.

– Manual welding.

F. *Inspection of Tubes, Fittings & Fabricated Coils*

- Inspection.

– Dimensional.

– Visual (boroscope).

– Liquid penetrant (LP).

– Eddy Current.

– X Ray (gamma ray).

Manufacturers of cast high temperature alloy tubes & fittings.

- Manoir (France).

- Schmidt & Clemens (Germany).
- – Centracero, Spain.
- – Villares, Brazil.
- Kubota (Japan).
- Sumitomo (Japan, only wrought tubes).
- Paralloy (U.K.).
- Lloyds Burton (U.K.).
- Metal Tek (Wisconsin).
- Duralloy (Pennsylvania).
- Ultracast (Indiana).
- Manufacturers of weld filler metals for high temperature alloy tubes & fittings.
- Thyssen Krupp (Germany).
- Kobe (Japan).
- Nippon (Japan).
- Special Metals (USA).
- Oerlikon (Sweden).
- UTP (U.K).
- Metrode (U.K).

G. *High temperature cracking heaters [10].*

- Allowable stress values.
- – Creep rupture dependent (API 530).
- – Very low & can compete with weight of the coil depending upon the thickness.
- Tube life & tube replacement criteria.
- Use of ferromagnetic probes.
- Change of physical dimensions like bulging > 5% is a good rule of thumb.
- Weldability.
- Metallurgical examination to check for creep voids & extent of carburization.
- – Replica technique.

  In-situ (surface results only).
- – Boat sample.

Destructive but salvageable (better representation).

V. Conclusion

It’s always critical to consider the properties of material especially for metals as they eventually corrode and reactive to certain services. Design and process conditions need to be evaluated and also lessons learned from the past projects need to be considered so that the equipment or pipe material can last longer and operate considering safety with regular maintenance.

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Ravi Kiran Dasari, Over 15 years of Qualitative experience as a Process / Facilities Engineering Manager in Upstream, Midstream and Downstream industry. Worked on Technologies like Hydrogen; Petrochemicals (Ethylene, Butadiene Extraction, Cumene Phenol); Refinery (Delayed Coking); LNG. Have both Greenfield and Brownfield work experience in Feasibility Study, Pre-FEED, Front End Engineering Design (FEED) and Detailed Engineering (DE). Proven success in creating Process / Facilities Engineering Deliverables including Process Simulations, PFD and P&ID Development, Equipment Sizing, Equipment data sheets, Line Sizing, Line List, PSV Sizing, Process studies, P&ID Walkdown, Mechanical Completion, Pre Commissioning, Commissioning and Start-up. Familiar with Simulation Softwares like Aspen HYSYS, Pro-II, Pro Max, Aspen Plus. Well versed with Process Industry Standards: API 14C, 14E, 520, 521, 610 and ASME B31.3, B31.4 and B31.8. Also hold certifications like PE (TX, LA), PMP. Effective communicator with excellent relationship management, influencing & negotiation skills. Proficient with Microsoft Office Software (i.e., Word, Excel, PowerPoint and Access).