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Corrosion and application of stainless steel in Petrochemical and chemical Industries

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ABSTRACT— Stainless steel finds wide range of corrosion free or high temperature applications in Petrochemical and Chemical industries. This paper presents the details of the two upcoming projects from India: Thal III – New Ammonia Urea Plant at Thal and Integrated Coal Gasification and fertilizer and Ammonium Nitrate Complex at Talcher with the corrosion and application of stainless steel in these plants.

Keywords: Stainless Steel, Corrosion, Chemical Plant, Ammonia Urea Plant Thal, Ammonium Nitrate Complex Talcher

1. Introduction

Over the years since the start of the development of stainless steels the number of grades has increased rapidly. Stainless steel does not readily corrode, rust or stain with water as ordinary steel does. However, it is not fully stain-proof in low-oxygen, high-salinity, or poor air-circulation environments. There are different grades and surface finishes of stainless steel to suit the environment the alloy must endure. Stainless steel is used where both the properties of steel and corrosion resistance are required.

Stainless steel differs from carbon steel by the amount of chromium present. Unprotected carbon steel rusts readily when exposed to air and moisture. This iron oxide film (the rust) is active and accelerates corrosion by forming more iron oxide; and, because of the greater volume of the iron oxide, this tends to flake and fall away. Stainless steels contain sufficient chromium to form a passive film of chromium oxide, which prevents further surface corrosion by blocking oxygen diffusion to the steel surface and blocks corrosion from spreading into the metal's internal structure. Passivation occurs only if the proportion of chromium is high enough and oxygen is present.

Stainless steel categories	Properties
Ferritic Stainless steel	➢ Low carbon and nickel content ➢ Good corrosion resistance ➢ Good weldablility and toughness ➢ Magnetic
Austenitic Stainless Steel	➢ Good to excellent corrosion resistance ➢ Good weldability and formability ➢ Good creep resistance ➢ Non-magnetic
Martensitic Stainless Steel	➢ High strength ➢ High wear resistance ➢ Limited corrosion resistance ➢ Magnetic
Duplex Stainless steel	➢ High strength and toughness ➢ Very good corrosion resistance ➢ Good weldability ➢ Lightweight ➢ Magnetic
Precipitation hardening steels	➢ High strength ➢ High wear resistance ➢ Limited corrosion resistance ➢ Magnetic

2. Corrosion and corrosion properties

Scientists and engineers have categorized corrosion into specific groups. However, many of these involve overlapping properties that may influence or control initiation or propagation of a specific type of corrosion. The most familiar categorization of corrosion based on visual characteristics of morphology of attack is: uniform attack, crevice corrosion, pitting, intergranular corrosion, stress corrosion, erosion corrosion and hydrogen damage.

When we particularly talk about corrosion in chemical and petrochemical industries, we can classify it on the basis of the mechanisms of attack involved. These corrosion types are: general corrosion, localised corrosion, metallurgically assisted degradation and environmentally induced cracking. This categories are not distinct or inclusive and do not necessarily represent the only mode of attack that may be observed.

3. Upcoming New Projects

Today, Chemical and Petrochemical Industries are one of the globally booming economic sectors. There are manifold upcoming projects seeking for potential applications of stainless steel. Acknowledging to its performance characteristics, it has already gained reputation in the market. It has wide applications in transportation and storage tanker, high temperature exchanger and chemical reactor.

4.1. Thal III – New Ammonia Urea Plant at Thal

4.1.1. Project Details

Introduction

- The Rashtriya chemicals and Fertilizers (RCF) is establishing its brownfield expansion of its urea-ammonia plant at Thal in Maharashtra.
- Present capacity of RCF Thal is 1300 MTPD of Ammonia and 2210 of Urea.
- RCF proposed to set up 3850 MTPD Urea and 2200 MTPD Ammonia Plant.
- A gas based captive power plant (CPP) of 30 MW is also coming up along with 2×1000 kva diesel generator.
- As per the proposal. An ammonia-urea plant will be set up with capacity of 1.27 million tonnes per annum at the company's current manufacturing location.
- The plant could be commissioned by 2018.
- The total estimated cost of the project is around Rs.5400-crore.

Nature and Scope of the Project

The general scope of the project is flow (pump/compressor size, pipe size, pressure drops through equipment), reactor design/reaction engineering, heating, cooling, refrigeration, heat transfer, materials (polymers, metals, ceramics, catalysts) synthesis and/or selection, separation (reactants, final products) by many methods (distillation, absorption, adsorption, crystallization, etc.) .

For ammonia-urea plant, the scope of using of the stainless steel is as follow.

- Vacuum concentrator
- Ammonia condenser
- Ammonia receiver
- Reactor feed pump
- Passivation air blower
- Compressor turbine
- Carbon dioxide compressor
- Urea reactor
- Carbomate condenser
- Stripper

4.1.2. Corrosion in Ammonia and Urea synthesis planets

High Temperature Hydrogen Attack, which in an Ammonia plant typically occurs in areas such as secondary reformers, waste heat boilers/exchangers, high temperature shift converters, methanator and synthesis loop equipment. Hydrogen assisted cracking, which has also been detected in Ammonia plants vessels, in particular where the component had not been adequately post weld stress relieved during fabrication. There have been numerous instances where

equipment incorporating this design has suffered from cracking at the interface between the austenitic layer for a period of time.

In the presence of hot ammonia atmosphere, above a certain temperature depending on the type of steel, ammonia reacts with iron to form a hard and brittle Fe-N inter-metallic layer. This phenomenon is called Nitriding. Nitriding develops on low alloy steels and on stainless steel, however, on the latter at much reduced rate and higher temperatures compared with low alloy steels. On pressure equipment this layer does not cause any problem until it remains compact and does not crack, but since a brittle material will reach more easily its rupture limit, in areas of stress concentration cracks can occur, exposing further surface to the nitriding atmosphere. This propagation, cycle after cycle, can lead to the component failure. Nitriding occurs also on stainless steel usually above 400^0C, but considering the high ductility of stainless steel and their low nitriding rate, their use guarantees an acceptable reliability in this situation.

All the equipment is critical in the synthesis section, but the most critical ones are the ammonia converter and downstream exchangers, because the reaction occur at the highest temperatures and the highest ammonia content. In particular reliability is essential for the ammonia synthesis converter, which is the reactor with the longest run between catalyst changes. In general, since the use of stainless steel or higher alloy steels would be too expensive, hence these items are made from low alloy steel to resist hydrogen attack.

The corrosion behaviour of A106 carbon steel absorber for CO2 removal in amine is promoted hot potassium carbonate solution (Benfield solution). A typical Benfield solution contains hot potassium carbonate K2CO3, potassium bicarbonate KHCO3, diethanol amine (DEA) as a promoter and potassium metavanadate KVO3 as corrosion inhibitor. K_2CO_3 with CO_2 purging showed that stress corrosion cracking readily occurred in this system. The stress corrosion cracking of carbon steels in carbonate solutions occurred by the dissolution process of metal at the crack tips. Magnetite passivity, however, may be vulnerable to process conditions such as loss of inhibitor, flow accelerated corrosion and chemical breakdown in the presence of aggressive ions, particularly chlorides. Magnetite films may also have a duplex structure and thick scales which may form when corrosion inhibitor management practices are poor.

The urea process is characterized by the presence of quite aggressive process fluids like ammonium carbamate, ammonium carbonate and urea solution, which require the use of special stainless steels, especially under synthesis conditions (high pressure and high temperature). In the principle, all urea processes utilize stainless steel, but while the low-pressure, evaporation, vacuum and waste water treatment sections use commercial stainless steels(AISI-304L or AISI-316L), the synthesis loop is manufactured with special steels properly studied for urea application.

The most common type of special material for the Urea synthesis is 316L 'urea grade' (UG). This material is widely used in urea plants, mainly because of its excellent weldability, fair corrosion-resistance and relatively low cost. However, the large amount of passivation air required and limited corrosion resistance in harsher conditions prevent its application for the most critical components.

4.1.3. Application of Stainless Steel

The selection of the right alloy must take into account a number of factors like operating temperature conditions: maximum and minimum temperature of working and cycling parameters, thermal gradients of the components, thermal expansion of alloy, mechanical stress and the environment of operation. Condensation and evaporation of nitric acid in heat exchangers in nitric acid plants cause severe corrosion on conventional stainless steel grades. Low impurity in combination with high chromium content has proved to result in stainless steel with improved corrosion resistance.

In desulpurization process, for most operations carbon steel is satisfactory material of construction of the pressure vessels and related piping. For the grating and the mesh screens which support te activated carbon bed, AISI Types 304, 321 or 316 stainless steels are used. Types 304 and 316 are also used in other applications were freedom from corrosion and corrosion products is essential, suc as on-stream instrumentation and valve trim. In certain piping system, no corrosion particles are allowed to enter inside the system. In such cases where extreme cautions are required, stainless steel are preferred over carbon steel. Carbon steel are commercially used on wide scale tan stainless steel because of cost factor. But there are several sectors were life cycle cost increases if we prefer carbon steel over alloyed materials.

For petrochemical applications above 660^0C, heat resistant alloy (HRA) casting (centrifugal tubes) must be used. It as creep resistance, corrosion resistance, and even withstand the effects of cyclic operational changes. These tubes are used to contain the nickel-base catalyst in the primary reformer. Manaurite XM 36 are used for the tubes to withstand high temperature creep. This is an austenitic alloy. Nickel is particularly important in forming and stabilizing the austenitic structure, ye HRA can contain up to 80% carbon. Carbon is also an important element for HRA as it forms carbides which oppose the metal deformation at high temperature.

CO_2Removal Unit uses the Benfield process where CO_2 is absorbed in a Potassium Carbonate solution which is regenerated using steam. Carbon steel is used with passivation of vanadium pentoxide or stainless steel (SS 316) can be used. Potassium metavanadate KVO_3 act as corrosion inhibitor. Types 304 and 316 have been specified for original vessels tubes and tube supports. Effective and economical use is made of austenitic stainless steel, primarily Types 304 and 316 throughout this system because of resistance to hot aqueous solution containing CO_2.

4.2. Integrated Coal Gasification and fertilizer and Ammonium Nitrate Complex at Talcher

4.2.1 Project Details

Introduction

- Talcher Fertilizer Unit is located about 126 kms away from Bhubaneswar, the capital of Orissa State and in the district of Angul. The Unit was established at Talcher due to abundance of coal that was being used as feedstock.
- After a series of CCEA decisions in August 2011, May 2013 regarding revival of FCIL, the Cabinet decided to revive Talcher Unit on 'nomination basis' by a consortium of GAIL, RCF, CIL & FCIL for setting up Urea plant.
- RCF, Coal India Limited (CIL), GAIL and FCIL have signed a Memorandum of Understanding (MOU) to put up a fertilizer complex at Talcher. It is proposed to set up a

3850 MTPD Urea and 2200 MTPD Ammonia plant along with Offsite facilities. JV Agreement has been signed amongst consortium partners. JV Company "Rashtriya Coal Gas Fertilizers Limited" (RCGF) has been incorporated. Selection of technology supplier and allocation of coal block is underway.

- The project promoters RCF, GAIL, CIL (and FCIL) would among themselves form two Joint Venture(JV) Companies JV-1 and JV-2. JV-1 will be primarily responsible for setting up the Upstream Coal Gasification and Gas Purification section on Lump sum turnkey (LSTK) basis after pre-qualifying technology supplier. GAIL will have majority stakes in JV-1 and will be the nodal agency for implementation. The combined stake of PSUs shall remain above 51% at all times. JV-2 would be responsible for setting up Ammonia-Urea, Nitric Acid-Ammonium Nitrate plants. Majority stake shall be held by RCF & CIL. RCF will be nodal agency for implementation of the downstream plants and off sites & utilities.

- Upstream consortia**:** The plant will be built by the two joint ventures the upstream consortia for converting coal into synthetic gas or syngas, and the downstream plant to manufacture urea and other fertilizers. GAIL will hold 35 per cent in the upstream venture, called GAIL Coal Gas (India) Ltd. FCIL will take 11 per cent interest while RCF and CIL will pick up 3 per cent each. The balance 48 per cent will be given to technology provider and financial institutions.

- Downstream venture**:** The downstream venture, Talcher Chemicals and Fertilizers Ltd., would be led by RCF and CIL with 40 per cent stake each while GAIL and FCIL will take 10 per cent each. The plant would manufacture 1.3 million tonnes of urea and other fertilizers annually, the Minister said.

- The JV would produce 11.20 lakh tons of urea and 3.3 lakh tons of Ammonium Nitrate per annum. It would be a Coal-based project.
- The project would have its own captive power plant of around 30 MW. However, construction power would be sought from the State Government.
- Water requirement of the project would be fulfilled from Brahmini River flowing nearby.
- Coal will be made available by CIL from nearby coalfields of its subsidiary, Mahanadi Coal fields. Land and certain facilities needed for the project will be provided by FCIL.
- The quality of Coal processed is:

  i. Coal with Ash content of 35%–40% (Dry Basis) or

  ii. Blended Coal with Ash content of 30%-35% (Dry Basis)

  and the combined Coal throughput achieved in Gasifiers is 1200 MTPD

- The estimated project cost is around 9,000 Crore.

Nature and Scope of the Project

For this plant, the scope of using of the stainless steel is as follow.

- Coal slurry pump

- Compressor
- Gas turbines
- Gasifier
- Syngas coolers
- Refractory lined vessels
- Hot gas cleanup systems

4.2.2. Corrosion in coal gasification process unit

The use of various coals under differing combustion conditions, ranging from wide variations in the coal combustion/conversion gas chemistry to wide variations in the nucleation, growth, and condensation of particulates, can have a direct effect on material degradation in these systems. Contaminants such as alkali, chlorine, and sulfur vaporize during gasification and combustion and eventually condense on metal surfaces and the remove the protective layer from those surfaces by chemical reaction, fluxing, or fracture. Because processing conditions (temperature, pressure, air/fuel ratio, etc.) involved in the conversion of coal to gas are diverse, we need a thorough understanding of the influence of various gaseous species and particulates on material degradation to enable the selection of corrosion-resistant materials for a reliable system.

The major corrosion mechanism in syngas coolers is sulfidation. Due to the low PO_2 and relatively high PS_2 of the raw syngas, the sulfidation rate of carbon and low alloy steels is too high to allow the use of these low cost materials. The corrosion rate of low alloy steels appears largely independent of the chlorine content of the coal. If the sulfur pressure in the gas phase exceeds the metal/metal sulfide equilibria of the base-metal elements, sulfides of these elements are formed at the oxide scale/gas interface. As the sulfide grows, stresses develop in the oxide scale, which eventually is breached and sulfidation occurs at the oxide scale/substrate interface. Because the transport rates of cations and sulfur through the sulfide phase are orders of magnitude higher than the transport rates through the oxide scale, the sulfidation attack continues in an accelerated manner. At longer exposure times, the oxide is virtually destroyed and a massive sulfide scale develops, a condition that represents breakaway corrosion of the alloy. The same sequence of steps is operative in alumina-forming alloys, probably at a much slower rate than in chromia-forming materials.

Due to the unacceptably high corrosion rates of low alloy boiler steels, stainless steel heat exchanger tubes, coatings or claddings must be used to provide low corrosion rates. When HCl is present in the syngas the corrosion mechanism changes considerably. Syngas coolers are generally used to recover the sensible heat from raw gas; they are very large (especially when compared with the gasifier) and are fabricated from metallic materials. The temperature of the metal in the syngas system is 300-500°C and the metal is exposed to a highly reducing atmosphere in the presence of hydrogen sulfide, the concentration of which is determined by the sulfur content of the coal feedstock. In addition, the environment contains hydrogen chloride. The gas temperature in the cooler is 1100-1300°C and the cooler experiences on/off service, which results in a contribution to corrosion during downtime.

Aqueous corrosion during downtime can further increase overall corrosion rates in the presence of chloride containing deposits. During downtime hygroscopic chlorides can migrate through cracks in the scale to the scale/metal interface and form an $FeCl_3$ rich layer beneath the scale. During heat up the $FeCl_3$ layer causes spalling of the protective Cr_2O_3 rich scale and a new outward growing FeS rich scale and inward growing Cr_2O_3rich scale is formed. This sequence repeats itself during each thermal cycle. The high temperature corrosion of stainless steels in syngas environments is complex and not readily predictable from simple gas/solid reaction mechanisms, especially when HCl is present in the gas and/or chlorides in the deposit.

4.2.3. Application of Stainless Steel

For applications in coal gasification plants, for raw gas heat exchangers in the temperature range 400-700°C, chromia forming iron or nickel based materials are the usual choice. Stainless steel must have alloy contents greater than 17%. Ni-Cr alloys should have Cr contents greater than 20% to form a protective laye. A popular Fe-CrNi material is Alloy 800 (Fe-20Cr-32Ni-Al-Ti)… At temperatures between 900-1200°C, alumina forming alloys are preferred as chromia becomes volatile at this temperature.

Boilers and heavy wall components of supercritical plant (above 538°C and 3400 psi) require special materials. Austenitic stainless steels have high thermal expansion that lead to thermal fatigue in thick sections. Ferritics are preferred for that reason. The requirements for those materials including looking at issues including creep, thermal fatigue, ability to weld, ability to fabricate, toughness, fireside corrosion, steam-side oxidation, and exfoliation. Alloys suggested for these applications include SAVE12 (12CrWCoVNb), NF12, TB12, P122, HCM12A, T23, T91 and EM12. In these alloys, Cr content is for corrosion control; V, Nb and N are for creep reduction; W, Mo and low carbon assist welding, and Si is for toughness. Below 593°C, P91 is recommended. At 620°C, P92, P122, or E9U is recommended.

The water-wall within a boiler is exposed to extreme conditions and often requires additional measures to prevent failure through corrosion. Weld overlays are used to add additional oxidation and sulphidation resistance. Testing has shown that FeCrAl alloys make good weld overlay materials. Chromium oxides and aluminum oxides that form are stable and resistive. The balance of chromium and aluminum in the alloys depends on weldability and the propensity for hydrogen cracking. The acceptable alloys form a triangle with one leg being the concentration of chromium between 0 and 12wt%, and the second leg being the concentration of aluminum between 5 and 14wt%. Too much aluminum and the weld cracks. The optimum alloy was determined to be Fe10Al5Cr. Molybdenum is kept out of the alloy as molybdenum sulfide forms instead of the preferred chromium oxide.

Waste-to-energy boiler systems have higher corrosion resistance requirements due to high concentrations of alkalai metal, lead, sulfates and chlorides in their fuels. Up to 20% os ash deposited on superheater tubes may be liquid salt deposits. Superheater tubes up to 450°C may be of 310SS or Incoloy 825. Between 450 and 500°C, Inconel 625, JHN24, or MAC-F are recommended. Water-wall weld overlay alloys may be NiCrSiB or an Inconel 625 spray.

4. Conclusion

The high reliability of plants is a choice and it can obtained through proper application of materials . Equipment such as Urea reactor, Urea stripper, Carbonate condenser, Carbonate ejector are constructed with Carbon steel lined or overlaid with a protective layer of the above mentioned Stainless steel materials instead of using pure stainless steel. The key factors for safe operation for intended life are awareness of the important factors in material selection, equipment design, manufacture and inspection and periodic corrosion inspections

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