

## Hydrocarbon processing

### Loss Prevention/Process Technology

#### **Control corrosion factors in ammonia and urea plants**

**Processing conditions for ammonia and urea are highly corrosive; using metallurgical advancements can mitigate such forces**

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**M. P. Sukumaran Nair** Travancore Cochin Chemicals Ltd., Cochin, India

In the hydrocarbon processing industry (HPI), the manufacture of ammonia and urea holds a prominent role. These petrochemicals have sustained the growth of agricultural production with new technologies and processes. This industry uses many different feedstocks such as coal, liquid petroleum, natural gas, and refinery residues. These feeds are processed under extreme pressure and temperatures in a highly corrosive environment.

Despite these processing challenges, large-scale fertilizer plants are built worldwide to meet the growing fertilizer demand. A major factor contributing to this achievement is the industry's success in combating corrosion. Adopting modern corrosion-abatement techniques and applying new generation/improved materials of construction have effectively mitigated process corrosion factors.

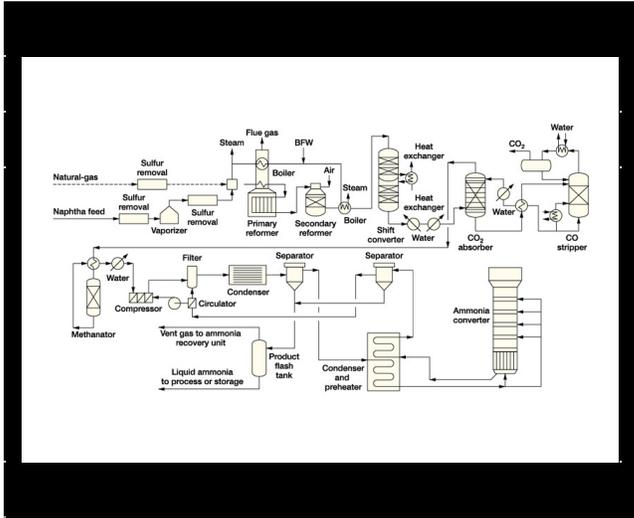
**Better materials of construction.** Over the past two decades, the ammonia and urea industry have witnessed spectacular metallurgical developments for process equipment. For example, stainless steels, modified with special materials, can improve high-temperature creep rupture resistance. Using duplex stainless steels and modern corrosion abatement techniques are other methods that improve plant-operating performance.

Urea or carbamide—a source of nitrogen—is the major fertilizer material and is produced from ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ). Current global production is approximately 100 million tpy. Urea manufacture consumes nearly 90% of all ammonia produced.

Ammonia is produced by the synthesis of elemental hydrogen and nitrogen; it is an energy-intensive process. The most cost-effective ammonia synthesis reaction uses fossil fuels. Thus, ammonia synthesis uses feedstocks such as coal, naphtha, fuel oil, natural gas, etc. Such processing routes involve severe operating environments that are highly corrosive. Special materials are needed to fabricate process equipment and pipelines.

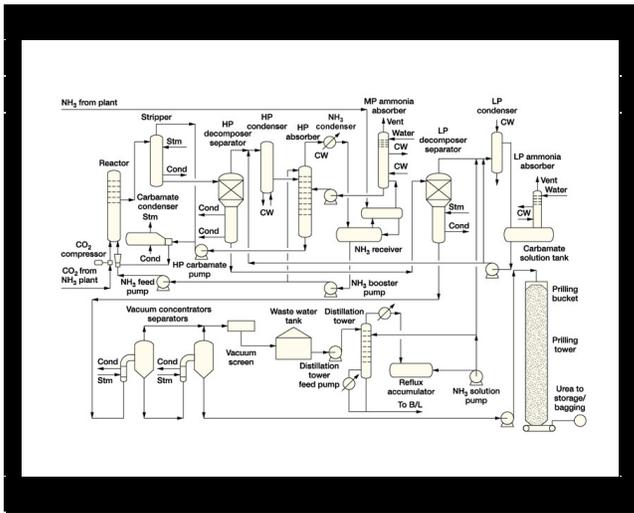
**Technology for production.** Two prominent technologies to process ammonia are: the partial oxidation of heavy hydrocarbons, vacuum residue and coal, and steam reforming of lighter hydrocarbons and natural gas. In partial oxidation, the feedstock along with steam and oxygen react in a gasifier to produce carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ) at  $1,200^\circ\text{C}$ . After cooling and cleaning the gas,  $\text{CO}$  is converted to  $\text{CO}_2$ , which is later stripped off to yield a  $\text{H}_2$  stream. It is then washed with liquid nitrogen to condense and

remove impurities and yield an ammonia-synthesis gas containing hydrogen and nitrogen in the 3:1 ratio.



**Fig. 1. Steam-reforming ammonia process.**

In the reforming process (Fig. 1), steam reacts with a vaporized sulfur-free feedstock (naphtha or natural gas) in an externally fired-tubular reformer to produce CO and H<sub>2</sub>. Hot process air is added to the secondary reformer to introduce nitrogen. The reformed gas—containing mostly CO, H<sub>2</sub> and nitrogen—is cooled. The CO is converted to CO<sub>2</sub> by the water-shift reaction in two stages. The CO<sub>2</sub> is subsequently stripped off to produce the ammonia synthesis gas. Synthesis gas is compressed to 140–200 bar and passed over iron (Fe) catalyst at 500°C to produce NH<sub>3</sub>, which is condensed and separated from the gas stream.



**Fig. 2. Urea process flow diagram.**

In the urea plant (Fig. 2), liquid NH<sub>3</sub> and CO<sub>2</sub> react to form urea at 200 bar pressure and at 190–200°C. The urea solution is concentrated and prilled; unconverted NH<sub>3</sub> and CO<sub>2</sub> are recycled back to the reactor as ammonium carbamate. These plants have various associated utilities, such as, cooling towers, water treatment plants, inert gas plants, boilers, instrument-air units and pollution-control facilities.

The different types of corrosion encountered in NH<sub>3</sub> and urea plants are uniform corrosion, galvanic corrosion, acid attack, crevice corrosion, intergranular corrosion,

cavitation corrosion, high-temperature corrosion, hydrogen embrittlement, metal dusting, etc. (Fig. 3). Most NH<sub>3</sub> plants being constructed are based on the steam-naphtha or natural-gas reforming route; thus, this discussion is focused on these processes.

**Desulfurization.** Petroleum feedstocks, used in synthesis gas generation, contain sulfur as an impurity. It is stored and handled under ambient conditions in carbon-steel tanks and pipelines where the corrosion attack by sulfur is less severe. In the desulfurization stage, vaporized feedstock is handled around 400°C in presence of hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS)—both are highly corrosive in nature. Stainless Steel (SS) 304, 316

or 321 (for fired heater) are used as the material of construction for various process equipment in this section. Equipment failures are attributed to external corrosion and thinning of fired-heater coils and interior deposition of carbon from coking and, consequent, overheating. Fuel-gas lines, containing hydrocarbon vapors and H<sub>2</sub>S should be constructed of SS 304 material and heat traced to avoid condensation.

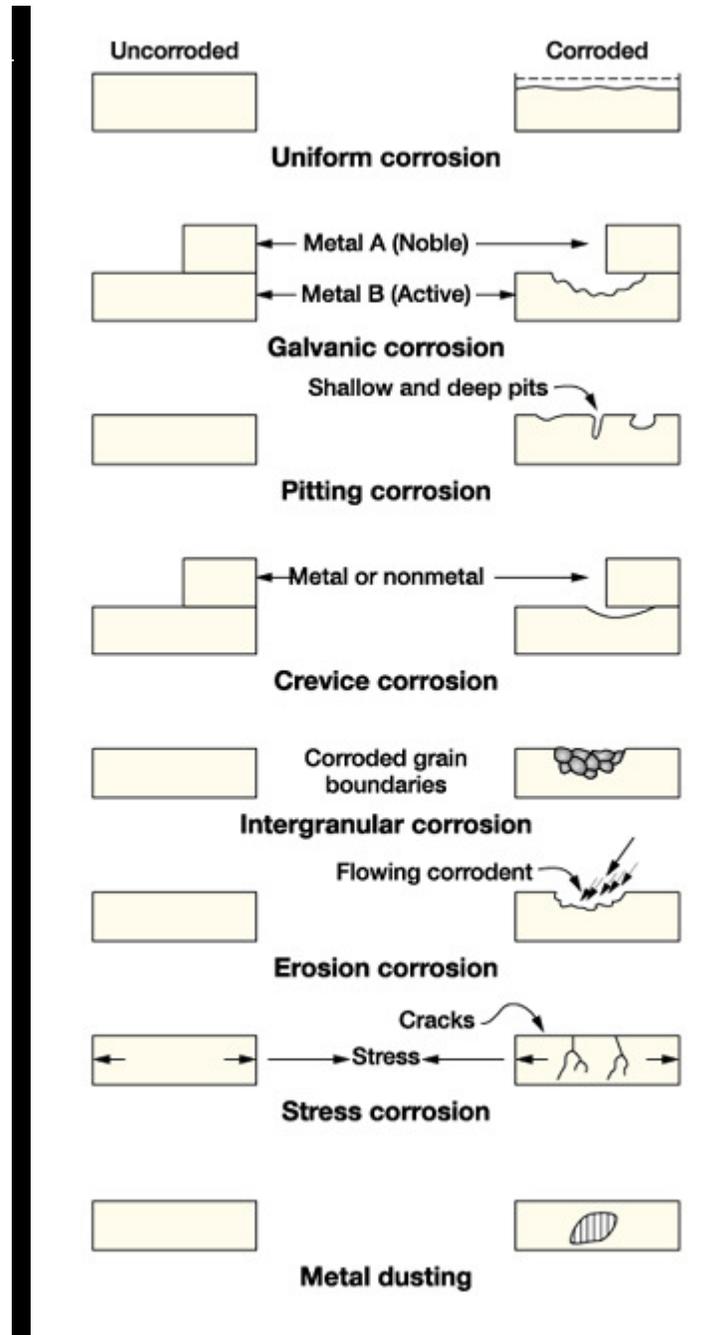


Fig. 3. Various forms of process corrosion.

**Primary reformer.** Steam-hydrocarbon reforming, over nickel (Ni) catalyst, produces H<sub>2</sub> and CO by an endothermic reaction. Tubular furnaces are typically used and are externally

fired at 25–35 bar and 780–820°C on the process side. The reformer tubes function under an external heat flux of 75,000 W/M<sup>2</sup> and are subject to carburization, oxidation, overheating, stress corrosion cracking (SCC), sulfidation and thermal cycling. Previously, SS 304, SS 310 and SS 347 were used as tube materials; however, these materials developed cracks that very frequently led to premature tube failures (Table 1). In the mid-'60s, HK 40 alloy (25Cr/20Ni) was developed and proved to be a good material for vertical reformer tubes. Consequently, plant capacities were extended to 600 tpd with this tube material. Although this alloy had a design service life of 100,000 hrs, overheating considerably reduced tube life. A 55°C excursion above the design temperature could lower tube service life to 1.4 years (Fig. 4).

Stainless steel	Composition, %										
	Designation	C	Mn	Si	Cr	Ni	P	S	N	Mo	Others
SS 304	0.08	2	1	18–20	8–10.5	0.045	0.03	–	–	–	–
SS 310	0.25	2	1.5	24–26	19–22	0.045	0.03	–	–	–	–
SS 316	0.08	2	1	16–18	10–14	0.045	0.03	–	2	–	–
SS 316L	0.03	2	1	16–18	10–14	0.045	0.03	0.1–0.3	2–3	–	–
SS 321	0.08	2	1	17–19	9–12	0.045	0.03	–	–	–	0.4 min Ti
SS 347	0.08	2	1	17–19	9–13	0.045	0.03	–	–	–	0.8 min
											(Nb+Ta)

Overheating can be due to flame impingement, local hot spots, carbon formation or catalyst bands. Hence, meticulous temperature control by conscious burner adjustment is needed to achieve uniform tube-metal temperature. Yet, tube failure will still occur due to various reasons—longitudinal cracking from overheating; weld cracking from lower strength of the weld compared to the parent alloy and stresses from thermal cycling during startup, shutdown and maloperations.

In the '80s, HP (25Cr/35Ni) modified alloys were developed and used certain metals, such as, molybdenum, (Mo), niobium (Nb) or tungsten (W) (Table 2). These metals increased resistance to creep rupture and offered good ductility and weldability. With stronger alloys, wall thickness of tubes could be reduced. Thinner tube walls offered benefits such as using lighter tubes and tube supports, improved heat-transfer, resistance to thermal cycling and increased production capacity. Thinner tubes reduced operating and maintenance costs, and also extended the service life of the reformer. Several plants worldwide were revamped with HP modified tubes in the primary reformers. In some cases, plant capacity rose by 30% after the retrofit.

Furnace alloys	Composition, %					
	C	Mn	Si	Cr	Ni	Others
HK 40	0.4	1.5	1.5	25	20	–
HP 25/35 (Mod)	0.4	1.5	1.5	25	35	1.5 Nb
HP Micro	0.45	0.7	1.5	25	35	Nb, W, present
Alloy 800	0.05	0.75	0.35	20	32	Al + Ti □ 0.7
Alloy 800 H	0.1	0.75	0.35	20	32	Al + Ti □ 0.85

A more recent development is the HP micro alloys that are applied during casting with traces of titanium (Ti), zirconium (Zr) and rare earths. The micro alloys enhanced carburization resistance and improved high-temperature creep-rupture resistance (Fig. 5).

For reformer outlet manifolds the normal metallurgy choice is a wrought type of Alloy 800 H. It has sufficient ductility and thermal-stock resistance during startup and shutdown. The cast version of Alloy 800 H provides a cost-effective, alternate material with a higher creep-rupture strength, low tendency for embrittlement and good ductility. Hot reformed-gas-transfer lines are usually refractory lined with an interior of Alloy 800 sheathing.

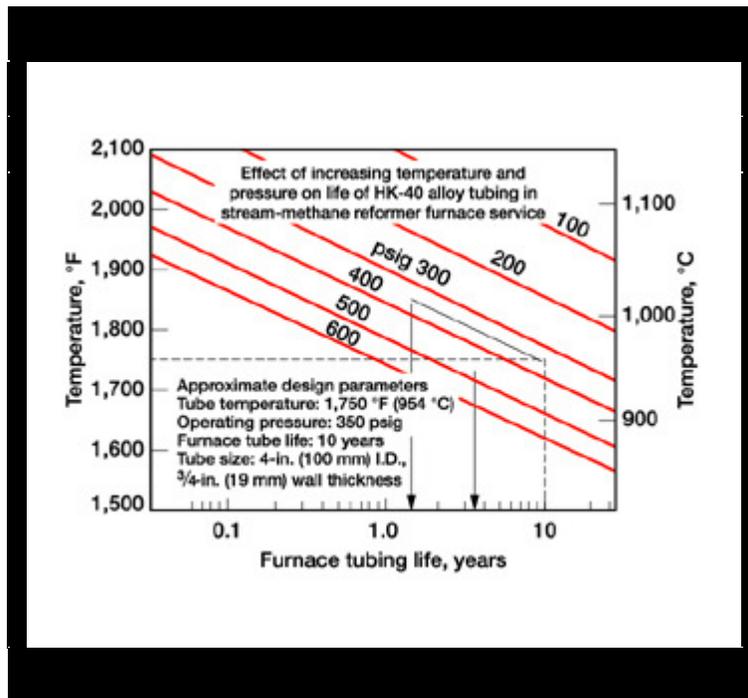
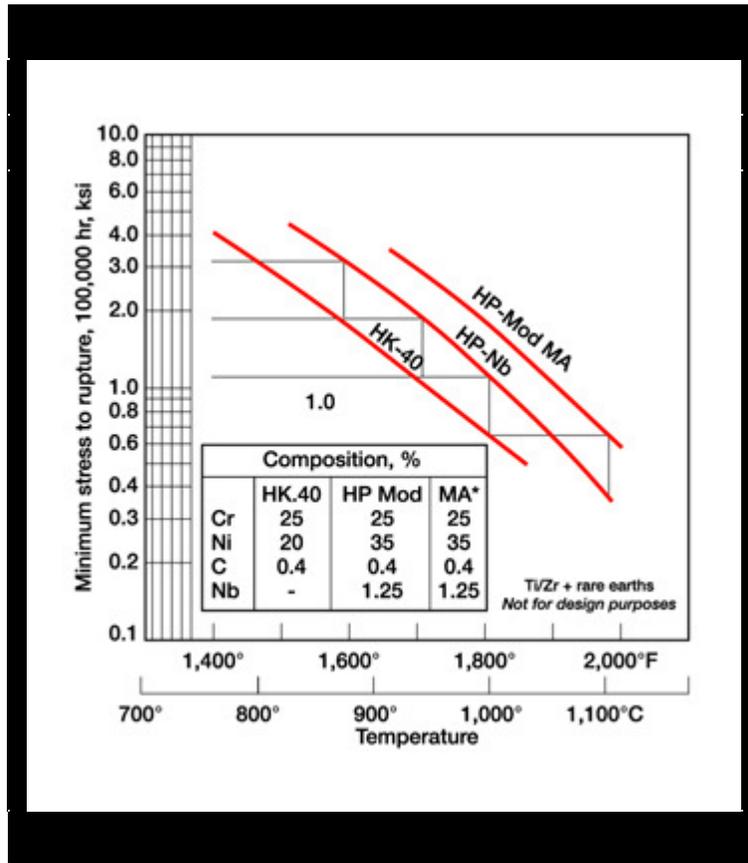


Fig. 4. Overheating shortens tube service life.



**Fig. 5. Generalized comparison of allowable creep-rupture stress for HK-40, HP-Nb and HP-Mod micro alloys.**

**Secondary reformer.** In this unit, air is added to the process stream at operating conditions of 28–30 bar and 957–1,025°C. The refractory-lined vessel has an outer shell of a low-alloy steel containing 0.5 Mo. A typical phenomenon—metal dusting—occurs in the secondary reformer outlet sections. With hot gases containing higher CO content, strong carburizing reactions occur, and carbon will diffuse into the Fe-Cr-Ni alloy. This phenomenon can lead to local mechanical fracturing of surface layers and, subsequent failures, by pitting.

Material such as SS 304 and Alloy 800 are very much susceptible to metal dusting (Fig. 6) in the temperature range of 500–800°C. Besides temperature, carbon activity (ratio of CO/CO<sub>2</sub> in the gas) and gas partial pressure also affect metal dusting. Severe attacks occur when the carbon activity is in the range of 3–10. Recirculating CO<sub>2</sub> into the primary reformer along with feedstock can maintain a low CO/CO<sub>2</sub> ratio and avoid the severity of this attack. Other mitigation efforts are maintaining a high oxidizing potential of the gas (steam/hydrogen ratio) and properly controlling temperatures.

Hydrogen embrittlement is another important corrosion problem that is encountered in reformed-gas pipelines. Usually, the piping material, used downstream of the feed-water heaters where the gas temperature is less than 400°C, is a low-alloy steel. Internal carburization and fissuring of steel is caused by hydrogen permeating the steel and forming methane. The formed methane cannot diffuse out and accumulates in voids formed at the grain boundaries. This condition contributes to high stresses that ultimately fissure and crack the metal.

The Nelson curves (Fig. 7) list the operating limits to avoid de-carburization and fissuring for steel in hydrogen service. Consider these conditions when selecting metallurgy for equipment and pipelines downstream of the reformed-gas boiler and the low-temperature converter.

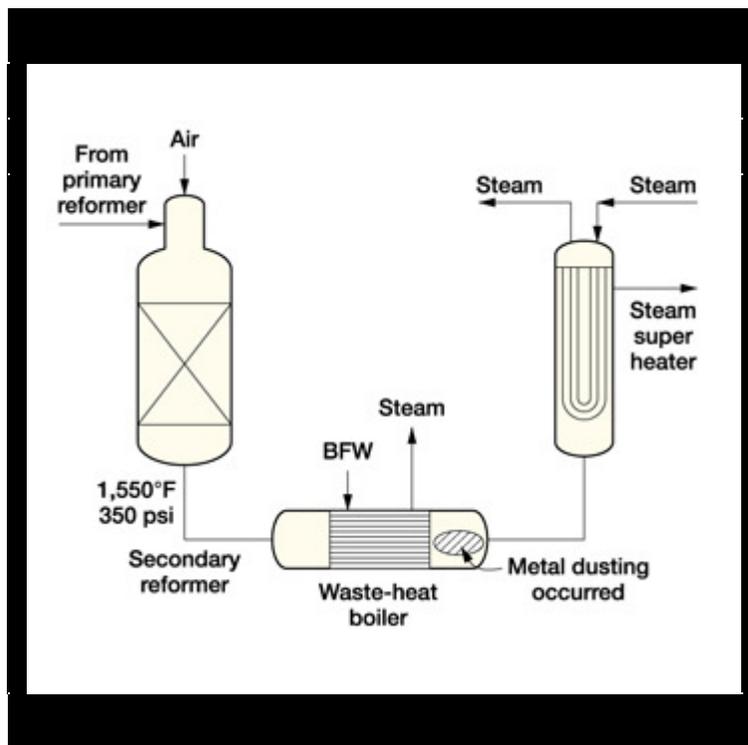
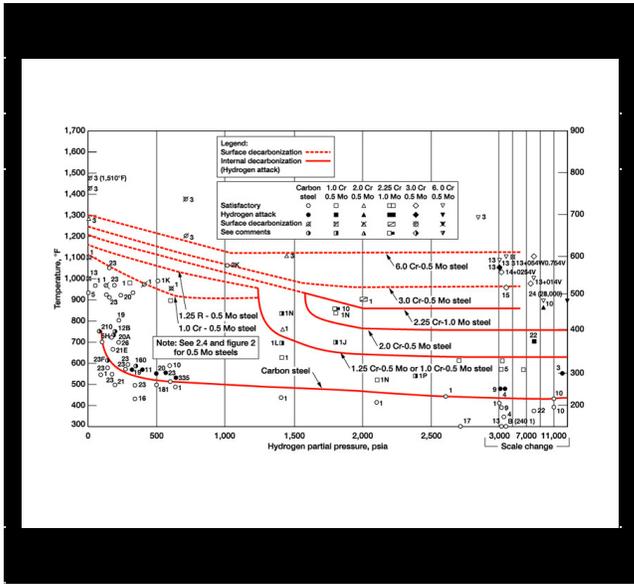


Fig. 6. Metal dusting in waste-heat boilers.

**CO conversion.** The high-temperature converter, where CO in the gas stream is converted to CO<sub>2</sub> by the water-shift reaction, operates at 25–28-bar pressure and 350–450°C temperature. Usually, low-alloy steel with 1Cr-0.5Mo is used as the material of construction. In converted gas pipelines, acid gas (CO<sub>2</sub> and H<sub>2</sub>S) are dissolved in the steam condensate, and often contribute to corrosion. This condition can be avoided by using SS 304 material.

**CO<sub>2</sub> removal.** Choosing the metallurgy in the CO<sub>2</sub>-removal system depends on the solvent used in the process. SS 304 and SS 316 are the preferred materials of construction. Carbon steel, fully stress relieved after metalworking, is also used for piping and

equipment in this section. Iron in the circulating solution can cause erosion corrosion in pipeline bends, pump impellers, pump casings, etc. In plants where amines are used to absorb CO<sub>2</sub>, formation of amine carbamate adducts also contribute to corrosion.



**Fig. 7. Operating limits for steels in hydrogen service.**

With modern alkanolamines—methyl diethanolamine (MDEA)—the carbamate adducts are less heat stable and, thus, do not accumulate in solution. Additives in the solution render the carbamate harmless by converting them into carbonates. In potassium carbonate processes, arsenic and vanadium salts are used to suppress corrosion. A passive layer of magnetite on steel surfaces is maintained by adding small amount of air.

In the CO<sub>2</sub>-removal system, SCC is caused by the combined effects of tensile stress and corrosion. It is a major problem. The caustic environment for carbon steel and the presence of chlorides for austenitic

stainless steel both aggravate SCC. This combined action of tensile stress and corrodant result in either transgranular or intergranular cracking of the metal or both. The overall stress corrosion process is initiated by corrosion damage; these cracks propagate due to joint electrochemical mechanical action and ultimately fail. SCC can be prevented by: better material selection, reduced stress of the metal by proper heat treatment, eliminate chloride solutions, remove oxygen from chloride-containing solutions, apply corrosion inhibitors, etc. Ferritic and duplex (austenitic/ferritic) type of stainless steel show marked resistance to stress corrosion cracking

**Waste-heat recovery.** The waste-heat-recovery system is associated with flue gas from the reformer furnace and process gas from the secondary reformer. It generates high-pressure steam in specially designed boilers. These boilers and steam superheaters operate under very high heat flux on the one side and corrosive water on the other. Consequently, meticulous care is needed to avert failures. Proper material selections and stringent water quality are two proactive loss prevention methods. Various material grades of SA 213, ASTM A312, ASTM A335 and ASTM A351 provide useful service life in this section.

The cooler part of the combustion air preheater—the tail end of the flue-gas-heat-recovery train—more likely to corrode due to sulfur dioxide (SO<sub>2</sub>) condensing from the flue gas. In this area, cast iron or glass will resist the acid attack. Carbon steel preheater tubes, joined with 1.5 to 2 m of SS 304 tubes at the cold end of the tube sheet, can ensure reasonable service life. Typically, the flue-gas temperature to the stack is maintained above the dew point of SO<sub>2</sub> to prevent condensation. During startup and shutdown, condensation of SO<sub>2</sub>

will occur.

The high-pressure, feedwater heaters are prone to leaks at the tube-to-tube sheet joints. Lining or overlaying the tube sheet with material, such as, Alloy 600 and using tube materials with 1 Cr-0.5 Mo can mitigate this risk considerably.

**Ammonia synthesis.** If the synthesis gas contain traces of carbon oxides, upon mixing with the  $\text{NH}_3$  in the recirculating gas from the synthesis loop, ammonium carbamate will form, and clog and/or corrode downstream equipment. To avoid this condition, consider controlling the carbon oxides level with fresh makeup gas to less than 5 ppm.

The compressor interstage coolers are usually constructed of carbon steel and use water as the cooling medium. Low-velocity areas in the water passage are prone to scaling and under-deposit microbial corrosion. These factors may lead to tube failures. Improved design of exchangers can eliminate low-velocity areas; proper cooling-water treatment program can control under-deposit microbial corrosion.

Startup heaters—electrical or direct-fired types—are used to heat synthesis gas for the converter during startup. Hydrogen-induced tracks, overheating and flame impingement, thinning at the bends, furnace explosions, etc., are several problems encountered with this equipment piece. Normally, SS 321 is used for startup heater coils and downstream pipeline.

The ammonia-synthesis converter operates at 150–200 bar pressure and around 515°C. Under these service conditions, nitriding and hydrogen embrittlement can occur. The pressure shell is a multi-layer or multi-wall carbon steel vessel. The internal catalyst baskets, contained in the shell, are constructed from SS 321 material.

Nitriding of pipes and catalyst-support grids are encountered in ammonia plants. The nitriding effect is more pronounced in low-alloy steels above 450°C; austenitic steels with a high-Ni content offer considerable more resistance. Alloys of the Cr-Ni-Mo-type—containing 12–25% Cr, 5–25% Ni, Mo, vanadium (V) and W—are usually used for the gas side. SA 213, T22 material—2.25 Cr-1Mo type or their improved versions—are used for the boiler. Due to the high pressure and temperature in the reactor, atomic hydrogen is absorbed by diffusion; the subsequent reaction with carbon in the steel results in blistering and cracking from decarburization.

**Ammonia storage.** Carbon steel, such as, BS1515, BS1511-213, ASTM A516, etc., are the conventional construction materials for ammonia storage—bullet, Hortonsphere or atmospheric storage. For refrigerated (atmospheric) storage, low-temperature carbon steel is used. A major problem encountered in the storage and transport of anhydrous liquid ammonia is SCC of carbon steel equipment. Cracks occur mostly at weld joints where the left over stress is the greatest. The hardness of the material and presence of impurities and oxygenates in  $\text{NH}_3$  aggravate SCC. Complete stresses relief, operating without air contact and adding small quantities of water (0.2%) as an inhibitor can effectively mitigate SCC. Low-temperature carbon steels have considerable more resistance to SCC than normal

carbon steels; it is the preferred construction material for large atmospheric liquid NH<sub>3</sub> storage tanks, operating at -33°C.

**Urea plant.** Corrosion from ammonium carbamate—an intermediate product formed during the conversion of NH<sub>3</sub> and CO<sub>2</sub> to urea—is a major problem. The intensity of corrosion is greatest in the reaction section and the first recycle, where pressures, temperatures and concentrations are higher than downstream. The reactor liner, pumps, decomposers, strippers and condensers are more vulnerable to attack by ammonium carbamate.

The urea reactor is a multilayered vessel of carbon steel with corrosion-resistant interior liner. Reactor-liner materials are usually SS 316 L (urea grade) with a lower ferrite content ( 0.6 % for pipes and < 1% for forging). SS 316 L and SS 316 L (urea grade) have significant difference (Table 3). American Society for Testing and Materials (ASTM) allows a large tolerance range for composition of 316 L. For example, 316 L—urea grade—is produced to a well-defined composition, which enables maximum corrosion resistance.

<b>Name, %</b>	<b>C(max)</b>	<b>Cr</b>	<b>Ni</b>	<b>Mo</b>	<b>Mn</b>	<b>P</b>	<b>S</b>	<b>Si</b>
316	0.08	16–18	10–14	2–3	2	0.045	0.03	1
316 L	0.03	16–18	10–14	2–3	2	0.045	0.03	1
316L (urea-grade)	0.03	16.5–17	13–15	>2.3	2	0.045	0.03	1

Titanium and zirconium are used to line urea reactors. The liner is continuously passivated with oxygen to resist corrosive action by adding air (0.5–0.8%vol oxygen) in the CO<sub>2</sub> feed.

In urea plants, corrosion failures include erosion, pitting, weld embrittlement and cracking, crevice corrosion and SCC. In the reactor, the liquid/vapor interface is a corrosion-prone area. Attaching a sacrificial plate to the liner can strengthen this section. The multi-layer vessel may also undergo severe corrosion damage from the reactor contents when the liner becomes defective and leaks. Zirconium-lined reactors have good corrosion resistance and do not require passivation.

Reactor-outlet piping and let-down valve are subjected to erosion corrosion from the pressure reduction across the valve and high fluid velocities in pipelines. For the low-pressure downstream equipment, SS 316L and SS 304 are good construction materials. Aluminum alloys and piping are quite resistant to the corrosive attack by urea due to the protective oxide film. These alloys are used in low-pressure piping, floor gratings, hand rails, etc. Dead spots and crevices—where equipment parts are not continuously wetted by oxygen-containing liquids—are prone to severe corrosion. Accordingly, fabrication of this equipment should be done to avoid such vulnerable spots. The probability of process

contamination with corrosive agents, such as, sulfur (through oil in liquid  $\text{NH}_3$ ),  $\text{H}_2\text{S}$  (along with  $\text{CO}_2$ ) and chloride (from cooling water) should be minimized.

Pitting and crevice corrosion occur by the local-cell action on exposed surfaces and weak points on the surface. In threaded or flanged connections where the passivating effect of oxygen is low, this phenomenon can occur and is aggravated by chlorides and higher temperatures. Pitting resistance index (PREN)—a means of comparing corrosion resistance of stainless steel—may provide a useful guideline for material selection in such environments. Pitting resistance equivalent number (PREN) or Pitting resistance index =  $\%Cr + 3.3X\%Mo + 16X\%N$

Duplex stainless steel alloys are a mixture of ferritic (400 series) and austenitic (300 series) microstructure of approximately equal volume fraction after final water-quenching-heat treatment during metalworking. Using this material has become popular because of its resistance to stress corrosion and fatigue, pitting resistance, suitability for a wide temperature range of industrial applications ( $-50^\circ\text{C}$  to  $280^\circ\text{C}$ ) and cost effectiveness. In the urea plants, duplex stainless steel is used to construct strippers, decomposers, condensers and pipe lines.

Cavitation corrosion occur in pumps where the flow conditions form bubbles on surface of impellers. These bubbles, upon formation break with enough force to rupture the protective film of the stainless steel. The above situation can be corrected through design that prevents bubble formation, polishing rotating parts to remove bubble formation sites and by using alloys with greater corrosion resistance and strength.

Besides selecting corrosion-resistant materials, chemical agents can inhibit the corrosive action in the  $\text{NH}_3$  process. Different corrosion inhibitors are used for  $\text{CO}_2$  removal, boiler and cooling water, plant effluents, petroleum products, etc. Using biocides in cooling-water treatment can control microbiological organisms and, thereby, mitigate corrosion in these units. In the feedwater and boiler systems, an alkaline pH is maintained to minimize corrosion. Caustic dosing should be controlled to maintain boiler pH control and avoid embrittlement of boiler steels.

Epoxy-resin-based coatings are used to protect both metallic and nonmetallic structures. Deaerators, naphtha storage, raw-gas pipelines, effluent channels, prilling towers, flooring of bagging plants, silos and conveyor gantries are areas where extensive usage of epoxy coatings provides corrosion resistance.

Many issues arise over material selection and corrosion abatement in modern fertilizer plants. With developments of metallurgy, and usage of newer corrosion-prevention techniques, it is possible to cost-effectively and, more important, safely operate and maintain large-scale plants. Changes to the ammonia/urea processes have reduced harsh environments. New generation materials, such as, ceramics, are resistant to the rigors of processing. Life-cycle analysis and costing are also gaining acceptability as the basis of material selection. **HP**

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## **Nomenclature**

C = Carbon

Cr = Chromium

Fe = Iron

Mn = Manganese

Mo = Molybdenum

Ni = Nickel

Nb = Niobium

N = Nitrogen

P = Phosphorous

Si = Silicon

S = Sulfur

Ti = Titanium

W = Tungsten

Zr = Zirconium



**M. P. Sukumaran Nair** is the managing director of the state-owned Travancore-Cochin Chemicals Ltd., Cochin. He was with the process engineering department of FACT Engineering & Design Organization (FEDO), the design and consultancy division of the Fertilizers and Chemical Travancore (FACT) Ltd. Mr. Nair holds BS degrees in chemistry and chemical engineering and a post-graduate degree in ecology and environment. Mr. Nair also holds an MBA from the Indira Gandhi National Open University, New Delhi. He joined FACT in 1971 and is well experienced in operation, management, process design and troubleshooting of chemical plants. He is a fellow of the Institution of Engineers (India), a member of the AIChE and is listed in the Marquis, Who's Who in the World. He may be reached by email: [mpsn@vsnl.com](mailto:mpsn@vsnl.com).