

Fabrication of Construction Materials in Urea Manufacturing Plants

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Abstract: Urea is produced from NH₃ (Ammonia) and CO₂ (Carbon dioxide). The reaction involves the formation of intermediate product known as 'Ammonium Carbonate' which further decomposes to Urea and Water. Elevated temperature and pressure is required for the above reaction to occur. The pressure typically varies between 140 and 210 bars and the temperature between 170°C and 200°C, depending on the process technology.

Ammonium Carbonate, which is an intermediate product, is very corrosive. Equipment and Piping of High pressure (HP) synthesis section (where the above reaction occurs), need to be constructed with a corrosion resistant material. Stainless steels are the candidate materials but conventional SS grades such as SS 304, SS 316 do not withstand the corrosion due to carbonate. Earlier, SS 316L UG (urea grade) was used with high amount of oxygen supply. Recent trend for selection of MOC involves application of 25Cr-22Ni-2Mo, Safurex, DP 28W, depending on the process licensors, in HP section.

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. Welding is used as prominent method for fabricating such huge equipment. Though weld ability is not a concern with respect to the above materials, quality of weld obtained during fabrication decides the service life of the equipment. Welding procedures are qualified by optimizing weld parameters in order to meet stringent. The qualification is adopted for job, with appropriate quality checks in production welds also.

Recent developments in construction materials to curb corrosion mechanism operative in HP section is also integrated. The criticality involved in welding these materials, to meet the stringent client specification requirement is discussed in the paper.

Keywords: Urea, Carbonate, Stainless steel, Corrosion, Welding.

I. INTRODUCTION

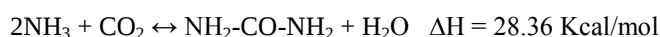
Urea manufacturing involves reaction of CO₂ and NH₃ at high temperature and pressure. Products of this reaction are inherent with unique type of corrosive environment that demands specific material of construction for piping and equipments, in terms of composition and quality. Awareness of the important factors in material selection, equipment design, manufacture and inspection, periodic corrosion inspections are the key factors for safe operation for intended life. This paper describes various corrosion mechanisms operative during urea manufacturing, Material of Construction (MOC) used worldwide for equipments and piping a LK Process Description – UREA.

A. Basic Reactions

In first step, ammonia and Carbon dioxide combine to give ammonium carbonate, which is an exothermic reaction. This is followed by dehydration of ammonium carbonate to yield Urea and Water. This reaction is mildly endothermic. The reactions are given below:



Overall reaction is:



Ammonia and Carbon dioxide are fed at the bottom of the Urea reactor. Urea is produced in the reactor and fed to the stripper at 156 Kg/cm² and 188°C approximately. In stripper, Urea solution is stripped, either by CO₂ or by NH₃ depending upon the licensor technology. Residual carbonate and ammonia present in the urea solution are recovered downstream of the stripper in subsequent decomposition section, operating at lower pressures. From the decomposition section, the urea goes to the third section where the solution is concentrated before the urea is solidified, either by granulation or prilling, to the required size. NH₃ and CO₂ vapours from the stripper top, after mixing with the carbonate recycle solution, are condensed and is fed to the reactor.

Figure 1 shows the process flow diagram of Urea Manufacturing process (Snamprogetti process) and Figure 2 shows the equipments in the high pressure section.

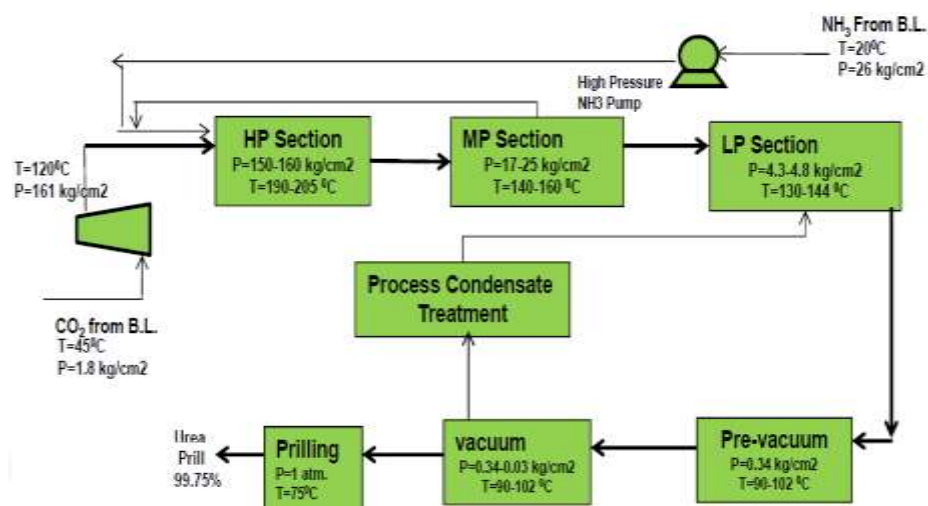


Fig. 1: Process flow diagram of Snamprogetti Urea manufacturing process

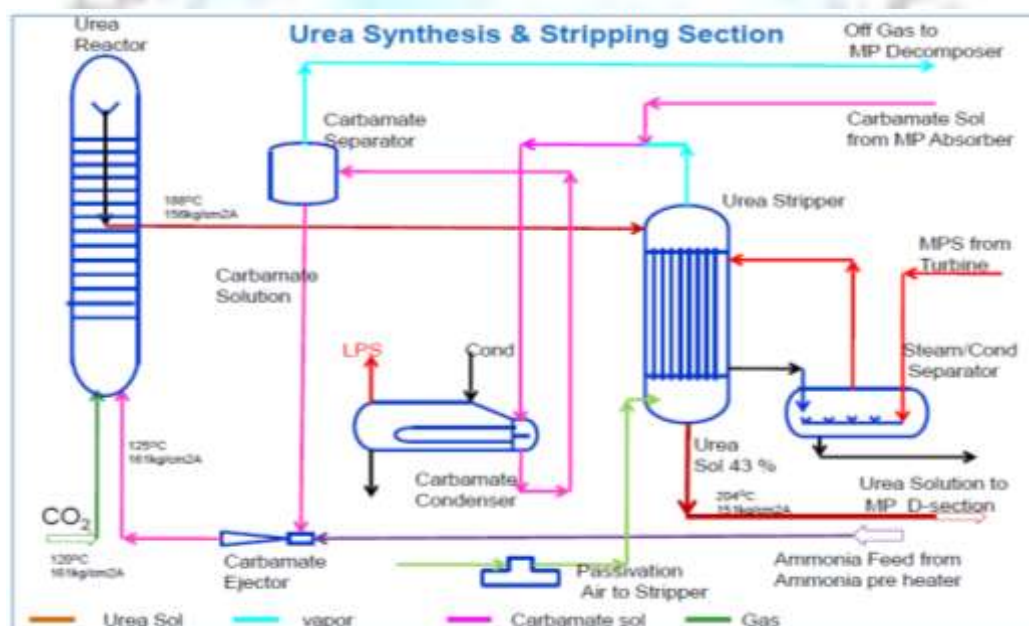


Fig. 2: Urea synthesis and High pressure section of Snamprogetti Urea manufacturing process

II. MATERIAL OF CONSTRUCTION OF EQUIPMENTS & PIPING IN UREA PLANTS

The material of construction essentially affects the reliability, operability and maintainability of urea plant. It means that the urea plant performance through its lifecycle relates closely with the material of construction. Also, in global nitrogen fertilizer business scenario, large size and high performance urea plants are the need of the hour.

When material of construction is discussed, a combination of material factor and environmental factor should be considered. The environmental factors include operating temperature, dissolved oxygen and fluid composition while the material factors cover corrosion and erosion resistance, mechanical property, weldability and cost.

Urea plant operates at high temperature / high pressure and carbonate solution, the intermediate product is extremely corrosive. Ammonium carbonate at approximately 180-250°C and 180bar is extremely aggressive to materials. Candidate MOC for such aggressive environments is Zirconium, Titanium, Duplex Stainless steel (SAFUREX & DP-28W) and stainless steel (25Cr-22Ni-2Mo & 316L UG).

Titanium had been used widely in the synthesis reactor of the total recycle plants till early 1970s and the high pressure (HP) stripper of ammonia stripping process till early 1990s. It has good passivation property with less passivation air. However titanium is susceptible to erosion and it is difficult to weld. Due to this disadvantages, titanium has been gradually taken over by stainless steel.

Stainless steel has been widely used for this equipment in urea plants. Stainless steel is almost immune to erosion and has good weldability but requires large amount of passivation air for urea synthesis equipment compared to titanium. Type 316L UG has been used for a long time in urea plants mainly because of its excellent weldability, fair corrosion resistance and relatively low cost. Requirement of huge amount of passivation air by 316L UG in synthesis and recycle sections restricts its operability.

TABLE I

S.no	MOC	Advantages	Disadvantages
1.	Titanium	1. Good passivation properties with less air	1. Susceptible to Erosion 2. Difficult to Weld 3. Costly
2.	Stainless Steel	1. Immune to Erosion 2. Good Weldability	1. Large amount of passivation air
3.	316L-UG	1. Excellent Weldability 2. Fair corrosion 3. Relatively less cost	1. Large amount of Passivation air
4.	25Cr-22Ni-2Mo	1. Excellent weldability 2. Better Corrosion resistance than 316LUG	1. Susceptible to SCC by chloride 2. Costly
5.	Duplex Stainless Steel (SAFUREX)	1. Good Weldability 2. Excellent Corrosion Resistance 3. Passivation air is not required	1. Costly

Type 25Cr-22Ni-2Mo SS is being used due to its better corrosion resistance than 316L UG and excellent weldability. This has been used in reactor and strippers but it is susceptible by chloride to SCC and costly.

Duplex SS shows excellent corrosion resistance in both Weld metal and HAZ. They possess better resistance to Stress Corrosion Cracking, hence used in chloride environments as well. In oxygen free carbonate solutions, duplex has proved to be more corrosion resistant than much more costly materials such as Titanium and high nickel alloys. Various MOC used in urea plants worldwide, their advantages and disadvantages are depicted in Table 1. Chemical composition of the MOC widely used, is given in Table 2.

TABLE II

Material Grade	C	Cr	Ni	Mo	N ₂	Others
SS 316L	0.03	16.0-18.0	10.0-15.0	2.0-3.0	-	P ≤ 0.045; S ≤ 0.03
SS 316L UG	0.02	16.0-18.0	13% min	2.0-3.0	< 0.10%	P ≤ 0.015; S ≤ 0.01
25 Cr-22Ni – 2Mo (SNAMPROGETTI)	0.02	24-26	21-23.5	2.0-2.6	0.10-0.15	P ≤ 0.02; S ≤ 0.01; B ≤ 0.0015
SAFUREX (STAMICARBON)	0.03	28.0-30.0	5.8-7.5	1.5-2.6	0.3-0.4	Cu ≤ 0.8
DP28W (TOYO)	0.03	27.0-28.0	7.0-8.2	0.8-1.2	0.30-0.40	W: 2.1-2.5

III. CORROSION MECHANISMS OPERATIVE IN UREA PLANT

Due to high operating temperature and pressure as well as the corrosive nature of Urea Carbonate, equipment and piping materials degrade due to corrosion in Urea plants. Various corrosion mechanisms involved are detailed below.

A. Active Corrosion

Stainless steel owes their corrosion resistance to the presence of a protective oxide layer on the surface. As long as this layer is intact, the metal corrodes at a very low rate. If the passive layer in stainless steel is ruptured, active corrosion starts in aggressive corrosive environments. Stainless steels exposed to carbonate containing solutions in urea synthesis section can be kept in a passivated state by adding a given amount of oxygen. If the oxygen content drops below this limit, active corrosion starts after sometime. Adding oxygen and maintaining sufficiently high oxygen content in the various process streams are pre-requisites for preventing corrosion of the equipment and piping. Once active corrosion occurs, the corrosion rate is extremely high (>50mm/year).

B. Erosion / Erosion-Corrosion

Erosion-Corrosion is the acceleration or increase in the rate of deterioration or attack on a metal because of mechanical wear or abrasive contributions in combination with corrosion. The combination of wear or abrasion and corrosion results in more severe attack than would be realized with either mechanical or chemical corrosive action alone.

C. Inter-Granular Corrosion

In Austenitic Stainless steels, the cause of intergranular attack is the precipitation of chromium rich carbides (Cr_{23}C_6) at grain boundaries. These chromium rich precipitates are surrounded by metal that is depleted in chromium; therefore they are more rapidly attacked on these zones than on undepleted metal surfaces.

In Urea plants, this corrosion is caused by the highly oxidizing action of oxygen containing urea carbonate solution, a low NH_3/CO_2 ratio and segregation of impurities, in a sensitized stainless steel.

D. Stress Corrosion Cracking

Stress Corrosion Cracking (SCC) is a cracking phenomenon that occurs in susceptible alloys and is caused by the conjoint action of a surface tensile stress and the presence of a specific corrosive environment. For SCC to occur, three conditions must be met simultaneously, namely, a specific crack promoting environment must be present, the metallurgy of the material must be susceptible to SCC, and the tensile stresses must be above some threshold value. In the presence of chloride, SCC occurs more prominently and termed as Chloride SCC.

Any chloride ingress in the shell side of the stripper/carbonate condenser will initiate stress corrosion cracking on austenitic stainless steel tubes whereas Duplex SS material resists chloride SCC.

IV. FABRICATION OF EQUIPMENTS

High pressure synthesis reactor consists of a carbon steel wall with a protective layer. The function of the carbon steel is to resist the high pressure at which the process operates. The carbon steel wall can be typically a solid wall type, multi wall or a multi-layer type. The total thickness of the carbon steel will be somewhere around 150-300mm.

A protective layer is required to protect the carbon steel from carbonate corrosion. The protective layer can be a liner or an overlay welding or a combination of both. The thickness of the liner/overlay typically varies between 5mm and 10mm depending on the licensor. This liner/overlay on the carbon steel portion is manufactured by welding process.

A. Welding Requirements

Most common cause for failure or leakage is welding faults (fusion defects) in the liner welds or corrosion in the Heat Affected Zone (HAZ) of the welds. Hence, Process Licensors specify stringent requirements for welds (Liner, butt, fillet & overlay welds). Before welding the actual job, Welding Procedures need to be qualified, achieving those stringent specification requirements on the welded coupon. The same set of parameters needs to be maintained during production welds, to achieve quality welds on job. This requires training and education of welders, monitoring and inspecting the job on a continuous basis. Table 3 gives the specification requirement of Process Licensors visa-vis Snamprogetti and Stamicarbon.

B. Welding Parameters

For butt welds, GTAW and SMAW process was used whereas Automatic GTAW shall be used for tube to tubesheet joint (specific licensor requirement). Liner welds was qualified with GTAW. Electro slag strip cladding (ESSC) & SMAW were used for weld overlay qualification.

While qualifying both austenitic (25Cr-22Ni-2Mo) and duplex (SAFUREX) grade, appropriate shielding and purging gas selection, choice of quality consumable supplier, maintaining proper welding parameters plays a vital role in attaining resultant weld metal properties.

While welding, heat input was maintained at 1.5KJ/mm approximately for both austenitic and duplex materials. Interpass temperature employed was 175°C maximum for austenitic grade and 150°C max for duplex SS grade. Shielding & Purging gas was Argon for austenitic grade whereas Argon shielding and Ar+2% N₂ is used as purging gas for Duplex grade. Finally, the procedure qualification coupon was tested at reputed laboratories and the results were found complying with the respective licensor requirements.

TABLE III

Type of Testing	Requirements on Butt, Tube to Tubesheet, Lining & Overlay welds	
	Snamprogetti (25Cr-22Ni-2Mo – AUSTENITIC SS)	Stamicarbon (SAFUREX – DUPLEX SS)
Metallography	Absence of intermetallic phase, Sigma phase and grain boundary precipitate	
Corrosion Tests	a) ASTM A 262 Pr. C – 7 mils/year b) Depth of attack – ≤ 70 microns	a) ASTM A 262 Pr. B – 25 g / m ² . hr b) Depth of attack – ≤ 70 microns
Ferrite content in Weld metal	SMAW Process – $\leq 1\%$ All other process – $\leq 0.6\%$	30-70%
*Crack & Flaw Examination	To be carried out at 0,1,2,3 mm	To be carried out at 0,1,2,3 mm

* Crack & Flaw examination is not required for weld overlay & Butt joints in Snamprogetti qualification

V. CONCLUSION

Ammonium carbonate, the intermediate product in urea manufacturing is extremely corrosive. Material selection plays a pivotal role in combating corrosion in urea plants. Fabrication methods such as welding requires a proper qualification and subsequent implementation and monitoring on the production welds of the job. This will ensure defect free welds, which will assure a safe and long lasting operation of the equipments.

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