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EXPERIENCE OF MATERIAL IN FERTILIZERS INDUSTRIES

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Abstract

Materials plays very important role in any industry. Selection of material is vital at design stage itself ,Wrong selection of material may lead to catastrophic failures and outage of plants & even loss of Human lives, Right selection of material leads to long life of plant. In the latest plants specialty 2 RE-69 materials are used for liner. The actual reactor has been constructed using a variety of materials, e.g. Zirconium, Vessel inside a protective liner. This paper intended study Material in urea plant in different vessels and equipment design. In Primary reformer numbers of materials are modified such as micro alloy are also used in tubes.

Keyword- Corrosion, Duplex, Stainless steel, 2-RE-69, SCC, Titanium, Zirconium

Introduction

National Fertilizers Ltd, (NFL) operates a fertilizer complex at Vijaipur, Distt. Guna (Madhya Pradesh) consisting of two units Vijaipur-I and Vijaipur-II, plants were commissioned in December 1987 and March 1997 respectively. Ammonia Plants are based on M/s. HTAS's Steam Reforming of Natural Gas and Urea plants are based on M/S. Saipem's Ammonia Stripping technology. The Vijaipur unit, which is an ISO 9001:2000 & 14001 certified, comprises of two streams. The Vijaipur have two ammonia plant M/S. Haldor Topsoe Technology, Denmark capacity 1750 & 1864 TPD for Line-I & line-II respectively and urea plant capacity 3030 and 3231 TPD for line-1& Line-II respectively. In urea line-1 & line-2 plant many time shut down taken due to leakage of stripper, Reactor and carbamate condenser. Maximum leakage occurred due to stripper tube leakage. Both unit have bimetallic stripper. Initially line -1 have Titanium stripper and changed by bi-metallic stripper.

History of Urea Reactor Liner

The all four reactors(R-1) of Urea line 1 & 2 plants are 40 meters Height (Tan to tan). The liner of all reactors has SS 316 L (mod) while shell of line 1 & line 2 are differing. The line -1 both reactors are coil layered vessel while 31 unit has multi layered and that of 41 is mono block reactor. Detail as following table N0-1. The all four Urea reactor have 15 number of sieve trays. These have been provided to prevent the escape of gaseous CO2, which must react with NH_3 in the lower portion of the reactor. These trays also help in preventing the internal recycling of the reaction products with higher specific gravity products formed in the upper part of the reactor. Reactor shell is made of CS with a 7 mm liner of SS316L (mod) on the liner surface. In the sixties the convention or non stripping process are used having high pressure, the process based on the 1stprincipal of decrease in pressure and increase in temperature" and then have a series of decomposition stage where the Reactor discharge is treated in successively at lower pressure. In the CPI allied process having 400 kg/cm2 pressure, the reactor liner used Zirconium;

Sr. No.	Material of Construction	Advantages	Disadvantages
1	Titanium	Good passivation properties with less air	Susceptible to Erosion Difficult to Weld Costly
2	Zirconium	Zirconium is extremely well suited to the urea processing environment. No passivation required.	Costly
3	Stainless Steel	Immune to Erosion Good Weld ability	Large amount of passivation require.
4	316L(urea grade)	Excellent Weld ability	Large amount of passivation

		Fair corrosion Relatively less cost	require
5	2RE-69 (Sandvik)	Excellent weld ability Better Corrosion resistance than 316L(urea grade)	Susceptible to SCC by chloride Costly
6	Duplex Stainless Steel (SAFUREX)	Good Weld ability Excellent for stress corrosion cracking Corrosion Resistance Passivation air is not required	Costly

Table-1(Material detail)

This is the first and unique process having Zirconium liner in the reactor. Zirconium has a very tenacious, naturally occurring, passive oxide layer that is virtually impervious to conditions inside a urea process plant. As compared to stainless steel, zirconium does not require any additional oxygen to be added to the process stream to remain resistant to corrosion. Additionally, Zirconium has a much higher temperature capability in the urea process solution compared to other materials. Zirconium is extremely well suited to the urea processing environment; it has a very high tolerance for variable plant conditions and compositions. Very little formal corrosion data has been generated for zirconium in this application beyond the numerous successful applications in operating plants. Numerous in-plant coupon tests have helped to confirm the operating plants' experience. The material of liner in urea reactor essentially affects the reliability, operability and maintainability of urea plant.Zirconium is highly resistant to corrosion in typical urea processing conditions. Sandvik 2 RE 69 is a fully austenitic stainless steel with extra low carbon and impurity contents. Excellent resistance to corrosion in ammonium carbamate excellent resistance to inter granular corrosion, high resistance to pitting and crevice corrosion and good weld ability. Zirconium has a long successful track record in solving very difficult corrosion problems in the urea industry. In an era where urea plants are expanding and "mega" plants with capacities approaching 5000 TPD in Saipem plants are designed and built, plant downtime and corrosion issues in general are greatly magnified in their significance regarding process reliability and operation profitability. Increasing, process designers and operators are looking to zirconium to provide the materials performance necessary for these mega-plants. By using zirconium, existing urea processes can perform at a higher level. Increasingly capacity, energy savings, reduction of corrosion products in the process stream, and elimination of the requirement for additional passivation air, and other environmental benefits in addition to longer equipment life may be possible with the proper application of zirconium. The zirconium also used in Omega Bond Tubing in urea applications developed by Saipem Technology. However, certain impurities are known to be deleterious to zirconium even in relatively low concentrations. Fluoride, in particular can cause rapid general attack on zirconium, especially in an acidic environment. Additionally, some metal ions (i.e., Cu or Fe^{3+}) may promote the initiation of pitting in certain conditions. In MTC process the reactor liner is used Titanium. Titanium is used frequently in urea processing applications due to its passivity in the urea processing environment. However the oxide layer of titanium is not nearly as hard and tenacious as that of zirconium, and it therefore suffers from localized erosion / corrosion on the inside of heat exchanger and stripper tubes, specifically where the fluid velocity is high. Titanium is used in the relatively pure state .It has excellent corrosion resistance but is one of the more costly and difficult alloy to weld. Titanium corrosion resistance is due to the impervious oxide film i.e.100% TiO_2 film on surface. Titanium is resistant to stress corrosion cracking and erosion corrosion, but it is susceptible to crevice corrosion in stagnant chloride solutions. Titanium is not maintenance friendly the difficult in welding Titanium is due to high affinity for Hydrogen, Nitrogen and oxygen in the molten state. Therefore, it must be welded by such inert-gas welding method as the TIG or MIG process. After a weld has been made, the inert-gas protection must be maintained until the welding joint cool below 650^0C, otherwise the Titanium will react with the oxygen, Nitrogen and moisture in the air, resulting in weld embrittlement. The conventional process is generally not economical to maximize the percentage conversion in the reactor since this would require an excessive retention time. The aim therefore is to attain maximum quantity of urea production per unit of time with due regard to the cost of recycling un reacted CO_2 and NH_3 as well as the cost of increased reactor size and corrosion difficulties which increase with temperature and reduction of N/C ratio. Typical operating conditions are: temperature, 180°-210°C; pressure, 140-250 kg/cm^2; NH_3 CO_2 mole ratio, 3:1 4:1; and retention time, 20-30 minutes. The MTC Process having pressure 240-250 kg/cm2 pressure, Liquid NH_3 and gaseous CO_2 are pumped to the urea reactor at 200 atm. The temperature of the reactor is maintained at about 185°C by proper balance of excess NH_3 and carbamate solution recycles feed. About 100%-110% excess ~NH_3 is used; about 70% of the NH_3 and 87% of the $C0_2$ are converted to urea. The remaining 30% of the NH_3 will be recycled back to reactor. Shortly after stamicarbon introduction of the $C0_2$ stripping process, Snamprogetti launched its ammonia stripping technology. In this process stripping gas is ammonia and carbon dioxide is introduced directly into the synthesis reactor. The route is also distinguished by the use of two stage carbamate decomposition, the first operating pressure~ at 17 kg/cm2 g and the second at 3.5 kg/cm2 g. The synthesis conditions are maintained at 185-190°C and 155-166 kg/cm^2. Ammonia corning from M.P section is raised to 230 kg/cm2 g and is used as driving fluid in carbamate ejector where the recycled carbamate is compressed up to synthesis pressure. The reaction products leaving the reactor flow to the steam heated falling film stripper which operates at 150kg/cm2 g .

Sr. No.	Material Grade	C	Cr	Ni	Mo	N_2	Others
1	SS 316L	0.03	16-18	10-15	2.0-3.0	.	P-≤0.045 S-≤0.03
2	SS 316L UG	0.02	16-18	13.0	2.0-3.0	<0.1	P-≤0.015 S-≤0.01
3	2 RE 69(Saipem)	0.02	24-26	21-23.5	2.0-2.6	0.10-1.5	P ≤ 0.02; S ≤ 0.01; B ≤ 0.0015
4	Safurex(Stamicarbon)	0.03	28-30	5.8-7.5	1.5-2.6	0.3-0.4	Cu ≤ 0.8
5	DP28W(Toyo)	0.03	27-28	7.0-8.2	0.8-1.2	0.3-0.4	W: 2.1-2.5

Table-2 (MOC)

The carbon dioxide in the solution is reduced by stripping action of ammonia which in fact boils out of the solution. Overhead gases from the high pressure stripper and the recovered solution from the medium pressure absorber all flow to high pressure carbamate condenser. The drawback of Titanium When the material is heated during welding, oxygen like that found in ambient air can infiltrate and corrupt the weld. The oxide layer of titanium is not nearly as hard and tenacious as that of zirconium, and it therefore suffers from localized erosion / corrosion on the inside of heat exchanger and stripper tubes, specifically where the fluid velocity is high. As compared to stainless steel, zirconium does not require any additional oxygen to be added to the process stream to remain resistant to corrosion. Additionally, zirconium has a much higher temperature capability in the urea process solution compared to other materials. This makes the metal brittle and prone to cracking or premature fracture in service, which is clearly unacceptable in critical-use applications.2RE69 are also used in conventional process. After development since sixties the Stripping or non conventional process became very popular, e.g. Ammonia stripping process and CO_2 stripping Process, To reduce the partial pressure of product by swamping the system by one of the reactant which reduce the partial pressure of other reactant considerable without changing the total pressure either CO_2 or NH_3 or both can be used as a stripping agent."

Design of Urea Reactor

The reactor is a simple vessel with adequate volume to let the reaction progress, but the pressure, the large dimensions and the huge surface to be lined make it a critical construction, where each detail must be designed according to specific features to guarantee the expected reliability. The reactor has been layered with titanium, zirconium, austenitic stainless steels (316L-UG and 25Cr-22Ni-2Mo) and duplex stainless steel. The choice depends on the type of process and the specific experience of the licensor. 25Cr22Ni-2Mo has been the typical choice for modern plant, giving excellent results in terms of reliability and endurance.

Urea reactor is the plug flow type reactor and diameter of the vessel is designed such a way that the solution cannot be come down. A reactor for the synthesis of urea from ammonia and carbon dioxide at elevated temperature and pressure is provided with perforated reactor high efficiency trays in which at least a pair of spaced part perforated reactor trays each have at least one opening at least a distance closer towards the periphery than the center, such as on or near the edge of a perforated reactor tray, and each of such pair perforated reactor trays is provided with a tube with a height of 50-500 mm located on and depending from an underside, e.g. bottom side in a column reactor, of each of such pair perforated reactor tray. The tubes extend to no more than 1/3 of the distance between two adjacent reactor trays. The designed of the vessel according to following table.3.

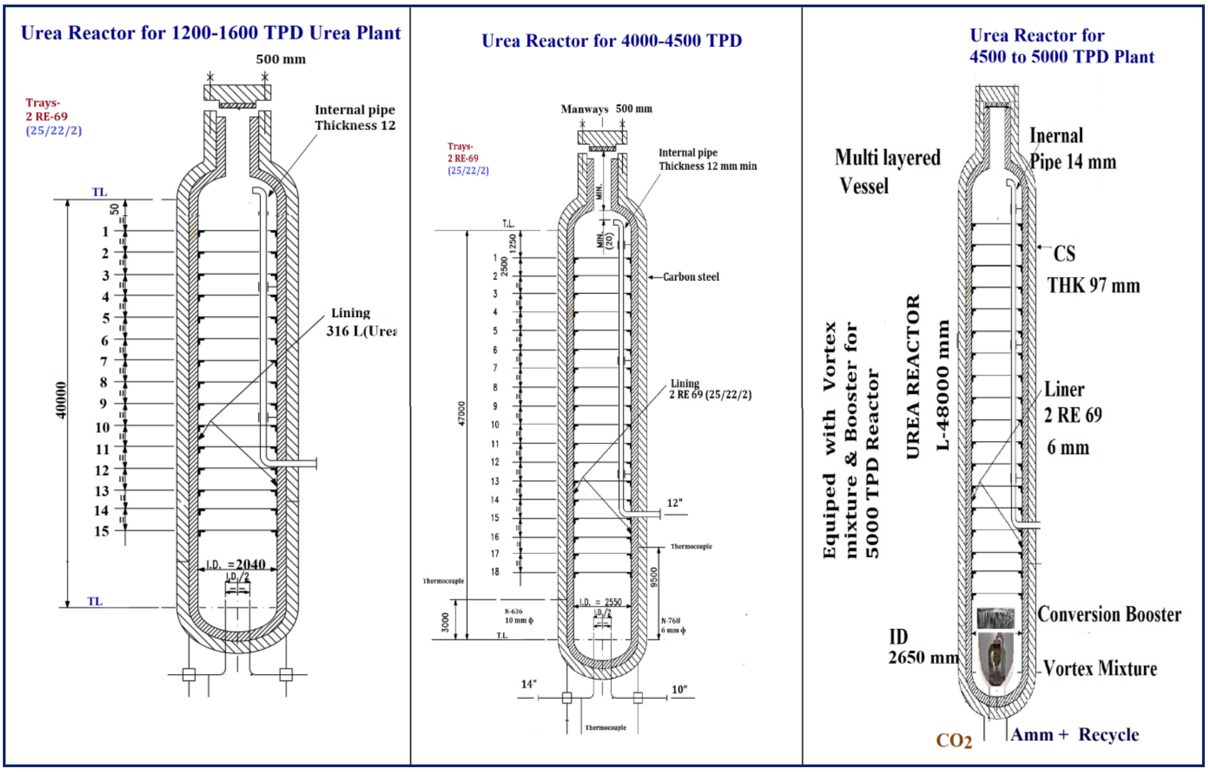

Fig-1

Corrosion is the function of Temperature as well as Corrosiveness of process fluid is not constant owing to effect of start-up/shut-down, fluctuation of temperature and dissolved oxygen content and geometrical flow distribution. For stripper. Passivation air role is principal in this issue The Passivation given in CO2 depends upon the process to process in M/Saipem it is 0.25% and in M/S Stamicarbon it is 0.4-0.6%.This passivation depends upon N/C ratio in Reactors.

Design of Urea Reactor						
Sr. No.	**Urea Production,TPD**	**Reactor ID,Meters**	**Radius, Meters**	**Reactor Height, Meter**	**Reactor Volume.M^3**	**Residence Time, Min**
1	1000-1500	2.04	1.02	40.0	135.2	35
2	1600-2000	2.65	1.33	26.2	154.3	34
3	2100-2500	2.15	1.08	42	157.7	33
4	2600-3000	2.25	1.13	43	177.0	32
5	3100-3500	2.45	1.23	44	215.2	31

6	3600-4000	2.55	1.28	47.0	248.8	30
7	4100-4500	2.6	1.30	48	264.2	29
8	4600-5000	2.7	1.35	49	291.0	28
9	5100-5500	2.8	1.40	50	319.5	27

Table-3

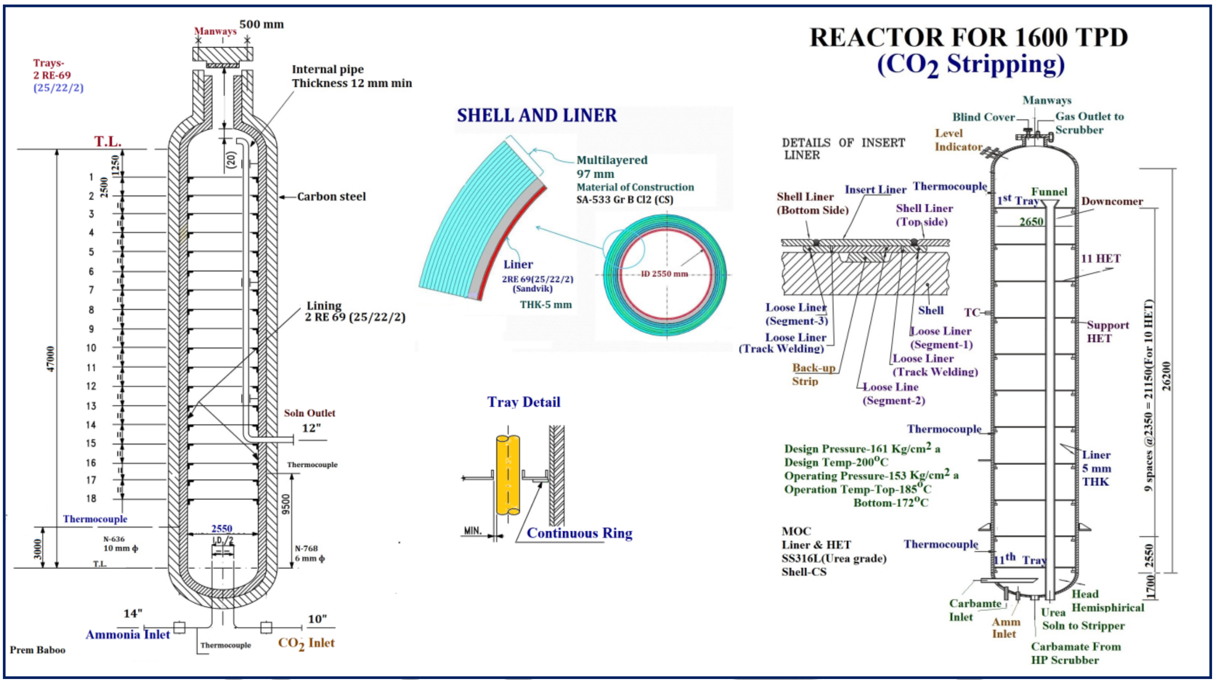

Fig-2

HP stripper

The stripper is possibly the most critical equipment in the urea process. Different process designs have different requirements; that is why so many materials have been used in the past. The equipment itself is generally a falling evaporator, and different details generally related to the different material requirements. Tube material is the most important choice. Reliability is mainly connected to the specific choice that each basic material selection involves. Notwithstanding the general basic material selection, from stainless steel to duplex to titanium imply a specific detailed design, where specific knowledge and experience is the key for a trouble free life of the equipment. Carbamate The design of this eq substantially according to the technology selected. Horizontal or vertical installation with process fluid tube side or shell side are commonly used. Since the reaction heat is usually utilized to generate steam stress corrosion can be a problem. In this case the use of a duplex material for tubes may be advantageous. The stripping of unconverted carbamate from the autoclave effluent is accomplished in the HP stripper by CO_2 feed stock from CO_2 compressor. The stripper is a vertical in tube falling film decomposer in which the liquid, distributed on the heating surface as a film, flows by gravity to the bottom. In practice, it is a vertical shell-and-tube exchanger with the heating medium on the shell side, and an upper head on tube side sheet specially designed to permit the uniform distribution of urea and carbamate solution. In fact, each tube has an insert-type distributor (ferrule or male type) designed to put the feed uniformly around the tube wall in film form. The holes of the ferrule act as orifices and their diameter and liquid head control the flow rate. As the liquid film flows, it is heated and decomposition of carbamate and surface evaporation occur. The carbon dioxide content of the solution is reduced by the stripping action of the ammonia as it boils out of the solution. Generated vapors (essentially ammonia and carbon dioxide) are removed by flowing to the top of the tube. The carbamate decomposition heat is supplied by means of condensing saturated steam at 219 °C. Decomposition in stripper based on Henry Law of partial pressure.Heat transfer area depends upon plant load and depends upon what types of stripping, i.e. ammonia stripping or CO_2 stripping. The exchanger consists of a stainless steel tube bundle with fixed tube sheet and a carbon steel shell with expansion bellow to take up the differential expansion. The top channel houses the liquid distribution ferrules which are extensions of the heat exchanger tubes. Ferrules fixed in each of corrosion of tubes. The CO_2 enters the bottom channel from a gas distributor above the liquid level in the bottom channel to prevent CO_2 flowing to the recirculation section. accurate control of the level is necessary to maintain a liquid seal. The flow of CO_2 to stripper is measured by FR. A low flow of CO_2 will also be indicated by a high temperature of the liquid from the stripper. The radioactive level recorder is provided at HP stripper bottom. The Radar type level transmitters are also provided to maintain the kevel. LRC controls the level in the HP stripper bottom. A high level alarm is also provided for the HP stripper bottom level. A drain and a vent line (each 1") are provided for the .

Titanium & Bimetallic Stripper

Urea Stripper used in Saipem presses is a falling film shell and tube type heat exchanger. The urea solution from reactor outlet carrying unconverted Carbamate, urea, water and excess ammonia enters the vertical tube through ferrules(inserts) mounted on the top of tubes. Ferrules are provided with three (or four) tangential holes at 120^0(or 90^0) angle which allow inside the tubes. The film adheres to the tube surface while flowing down to the bottom of each tube. The film is heated by means of saturated steam at 25 ata. The excess ammonia present in the urea solution evaporates thus reducing the partial pressure of the CO_2 in the vapour phase hence causing stripping of the CO_2 from the Carbamate present in the solution phase.

Advantages of falling film heat Exchanger

1. Higher rate of heat transfer due to high velocity of film and less convective resistance.
2. Reduced biuret formation due to less residence time.
3. Minimum internal pressure drops.
4. Less tube skin Temperature for same solution outlet temperature.

High Pressure Corporation and Passivation method

the tubes have 3-4 liquid holes, each of 2.0-3.0 mm diameters according to plant load . Liquid flows into the tubes wetting the walls. The liquid level above the ferrule in top channel, provides the static head for the liquid flow. Liquid distribution in the tubes is a very important factor as any of the tube starved of liquid flow may tend to overheat and may result in heavy
shell side of the heat exchanger. A bursting disc BD-1202 on the shell relieves CO_2, NH_3 and H_2O mixture to the atmosphere in case of tube failure. A high temperature alarm is installed in the solution outlet line of HP stripper. Saturated steam from 23 ata steam saturator at a pressure of 21.0 kg/cm2 g and temperature of 215.90 C is used in the shell side of the HP stripper for the decomposition of carbamate.

According to plant load the stripper heat transfer area is increases i.e. number of tubes increases as per following table-40. The CO_2 stripping process the stripper size is more than Ammonia stripping process

For the Titanium Stripper the dissolve O_2 in the bottom Stripper solution should be 2.0 ppm even less, whereas for bimetallic stripper, the dissolve O_2 in the bottom stripper solution should be 5.0-6.0 ppm .By increasing the temperature in the stripper bottom (if air is not injected directly), the dissolve O_2 in the bottom solution should decrease as per following data:-

Design feature of the stripper

During initial plant construction, Saipem, used special grade of stainless steel i.e.2-RE69 (25-22-2) as material of construction for tubes, ferrules and tube sheet / channel side lining in plants in the world. It was found that these strippers generally suffered from severe corrosion attack particularly during lower turn down plant operation due to less availability of O_2 for passivation layer.

Bimetallic Tubes

1. Tubes consist of two tubes an external tube of 2 RE-69 and an internal tube of Zirconium.
2. These tubes are fabricated separately according to specification of Saipem.
3. Then they are assembled and drawn together.
4. During drawing operation a proper mechanical bonding is obtained.

Temperature Vs. O_2

Sr. No.	Stripper bottom temperature, ^{0}C	Oxygen in Bottom solution, ppm
1	204	6
2	205	5
3	206	4

4	207	3
5	208	2.5
6	209	2
7	210	2

Table-4

Zirconium in ammonium Carbamate solution is highly corrosive resistance; furthermore it does not show the erosion problems typical of Titanium. When it is in contact with air, the Zirconium is covered by film formed by ZrO_2 that are able to protect the metal up to 300^0C. Only few agent are attack the Zirconium: Floridic acid, copper and iron chloride. The main limitation of the Zirconium use is the high cost of it. To circumvent the above problem, stainless steel as above was replaced by Titanium which was extremely good corrosion resistance and not requires O_2 for passivation. For all plants in India and also around the world, similar construction was followed till recently by Saipem. However, the above change in material of construction unfortunately could not solve all the operation and maintenance problem and the stripper continued to attract greater attention by the plant operators and also of the designer

1. Titanium inherently offers excellent corrosion resistance but being soft as metal has little resistance to corrosion. Due to process/operational reasons the exchanger is subjected to both corrosion and erosion. Therefore, major causes of failures in stripper are attributable to erosion of tubes leading to thickness reduction.
2. Process requirement calls for effective liquid film inside the tube and also stripping of CO_2 by heating along the tube length. To fulfill the above requirements it is desire to have:
3. Good coupling between tube and ferrules to prevent bypassing of liquid through the mating surface.
4. Effective positive pressure on the on the top of the ferrules to secure a leakage free joint (external ferrules).
5. Provision of anti-erosion (Teflon bush) in between ferrule and tube end.
6. To have least erosion damage to tube due to high velocity of fluid leaving at the end (tip) of internal ferrule.
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11. Provision of anti-erosion (Teflon bush) in between ferrule and tube end.
12. To have least erosion damage to tube due to high velocity of fluid leaving at the end (tip) of internal ferrule.
13. It consists of a vertical tube bundle exchanger, with hemispherical head cylindrical channels at top and bottom
14. The heat needed for decomposition of Carbamate, for the separation of vapour and for increasing the temperature is supplied by steam condensing in shell side of stripper.
15. The solution inside the tube falls down along the internal walls of tube to ensure high residence time (to prevent burette formation). and high heat transfer.
16. Passivation air is injected at bottom channel by K-3 compressor along with electric heater for preheating.

Material of Constructions

Sr. No	Part	Material
1	Hemispherical head(Top bottom)	516-GR-60+2-RE-69(LINER)
2	Channel(Top & Bottom)	A266-C12+2-RE-69 A266-C12+2 RE 69 Overlay

Table-5

About 2-Re 69 Materials

1. It is a tailor made grade of Austenitic Stainless Steel ordered according to Licensor's . Specification and also known as 25-22-2.
2. According to Saipem specification CR.UR.G510 1995 material shall meet to following requirement.

Chemical Composition:-

Cr-24-26%,Ni-21-23.5%,Mo-2-2.6%,C-.02,Mn-1.5-2.0,Si-0.4,S-0.015,P-.02,N-.1-.15%

2-RE-69 Vs Titanium

Advantages:-

1. Excellent erosion and corrosion resistance especially in tube due to Zr. Lining.
2. Cost effective.
3. Easy maintenance.

Limitations.-

Stripper bottom temperature is limited to 207^{0}C means less decomposition. High pressure air compressor is required for passivation of bottom part. Plant cannot be run at lower capacity than normal.

1. As per M/S. Saipem, the maximum operating temperature of the Bimetallic Stripper with bottom passivation air is 205^{0}C.
2. It was reported that in Mexico, against the recommendation of M/S Saipem, Bimetallic Stripper was run at 210^{0}C.After 3 years of operation, on inspection, the bottom liner was found totally worn-out.
3. On this experience, M/S Saipem have been recommending the maximum bottom temperature of bimetallic stripper as 205^{0}C.
4. It was reported that minor problem has been faced at Oswal Chemicals (Presently Kribhco Shyam) with Bi-Metallic Stripper.
5. It has been in operation without passivation air at the bottom (on account of non-availability of the air compressor) against the recommendation of M/S Saipem. Now the bottom temperature remains at 206-207^{0}C at 115% plant load.

Metallographic Properties

1. Material in contact with process fluid shall have Austenitic structure.
2. Ferrite content shall not exceed 0.6%except for manual welds for which 1.0% is allowed.
3. Sigma phase shall be absent.
4. Chromium carbide may be present in amount only.
5. Material shall pass Huey Test
6. **Mechanical Properties**

The mechanical properties of the material shall conform to the values indicated in the following tables. The values indicated below should be obtained on each specimen and no averaging shall be permitted.

At room temperature (Specimen in solution annealed condition)

Yield strength E 0.2%, Min. - 220 MPa

Ultimate tensile strength, Min.-525 MPa

% elongation L=5.65 - √A, Min. -45 ,% reduction of area shall be noted for information.

Charpy U-notch impact strength -14 da J/cm^2 (min. individual value), Hardness (maximum) Brinell - 200 , Rockwell-B - 94

At elevated temperature

(Specimen in solution annealed condition)

Minimum strength for 0.2% Permanent off set with 110 MPa at 823 K (550^{o}C)

5 minutes holding time - 110 MPa at 823 K (550^{o}C)

Ultimate Tensile Strength, % elongation & % reduction of area shall be noted for information.

Sr.No.	Urea Production	No. of Tube	Tube Length, M	Tube ID,m	Surface Area one tube, m	Total Heat transfer Area,m^2
1	1200-1600	1677	6	0.0200	0.377	631.9
2	1600-2000	1800	6	0.0200	0.377	678.2
3	2000-2500	1900	6	0.0200	0.377	715.9
4	2500-3000	2670	5.5	0.0200	0.345	922.2
5	3000-3500	3350	5.5	0.0200	0.345	1157.1
6	3500-4000	4370	5.5	0.0200	0.345	1509.4
7	4000-4500	4500	5.5	0.0200	0.345	1554.3
8	4500-5000	4500	5.5	0.0220	0.380	1709.7

Table-6

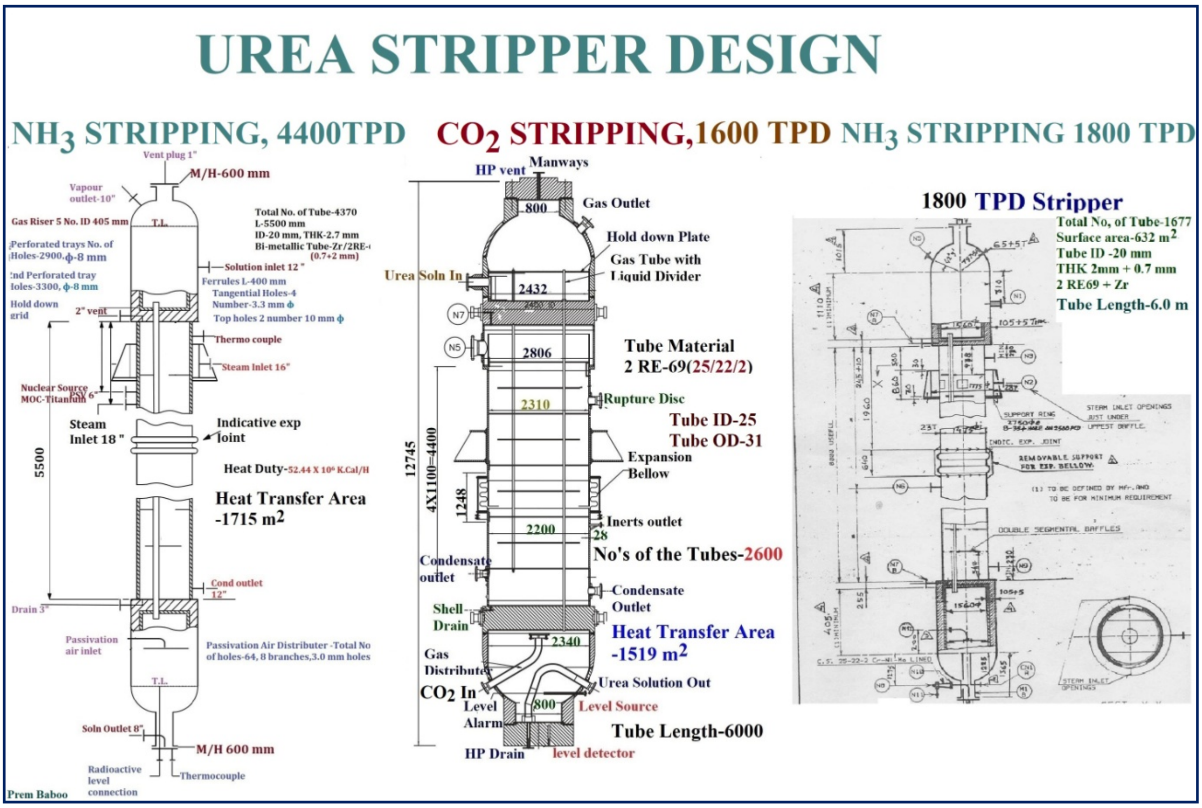

Fig-3

Omega Bond Stripper

Omega bond stripper is the development of M/S. Saipem, it is the best stripper in the Fertilizers industries. First Omega bond stripper installed GPIC complex and second in FFC Pakistan. The omega bond stripper can be operated at higher temperature no passivation is required and boosting plant capacity. Expected life is about 25 years. The return investment projected at the rime of project initiation estimated a payback with 2 years.

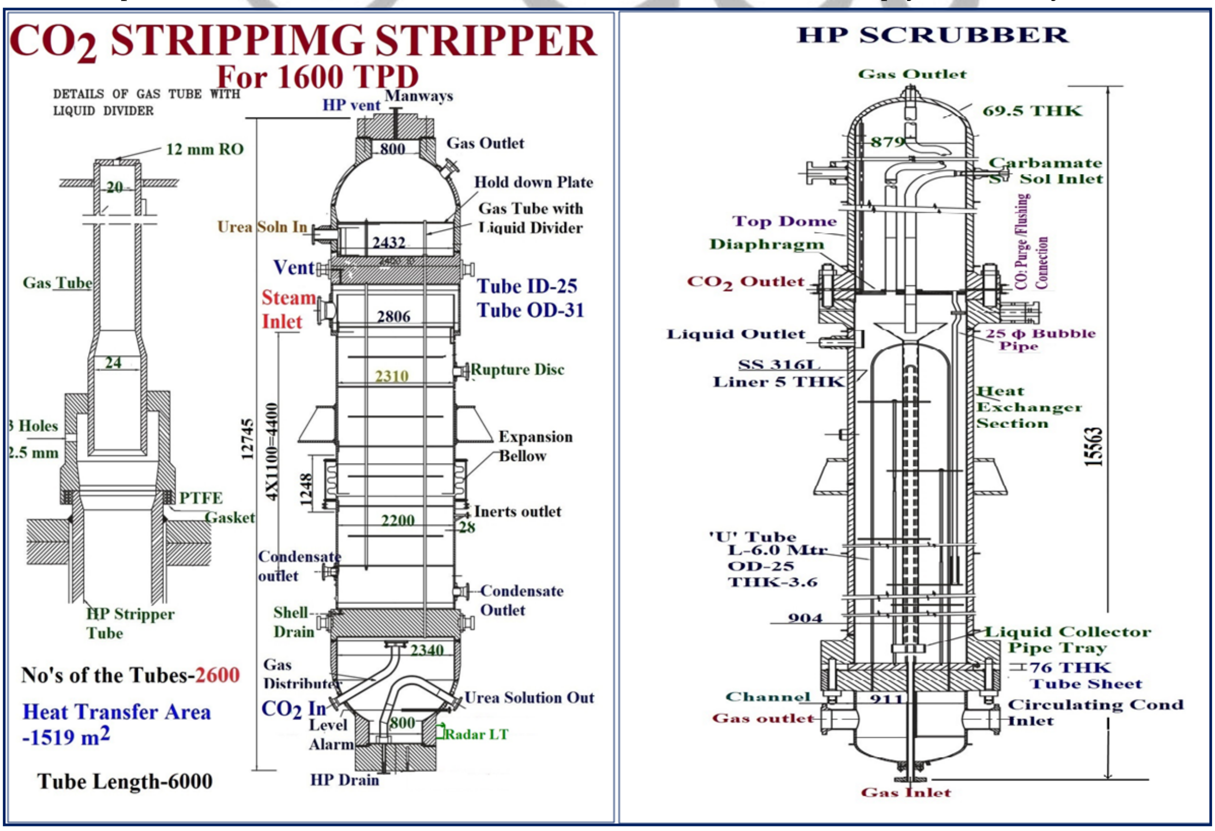

Fig-4

For Stamicarbon Design stripper

Sr.No.	Urea Production	No. of Tube	Tube Length, M	Tube OD, m	Surface Area one tube,m^2	Total Heat transfer Area,m^2
1	1200-1600	2600	6	0.031	0.584	1510
2	2000-2500	3000	6	0.031	0.584	1752

Table-7

Comparison of Stripper for Ammonia & CO_2 Stripping Process

Sr. No.	Parameters	Ammonia stripping Process	CO_2 Stripping Process
1	Surface Area	Less	More in same plant Load because the double load of heating(CO_2 as well as Reactor effluents)
2	Nos of Tubes	Less	About 150 % tubes more
3	Cost	Less	Very Costly at same plant load
4	**In Case of Tube or tube sheet Leakage**	In case of Leakage the pH of Steam condensate is more than 9.0-10.0 because the **ammonia content is higher**, Hence no problem of corrosion, you can run the plant at minor leakage by separate draining of condensate,	In case of minor leakage , take shut down immediately because the pH of steam condensate come down below 7.0 due to **CO_2 contents is higher** and hence corrosion start in CS shell, otherwise equipment will damage and cause major incident.

Table=8

HP Carbamate Condenser (CO_2 Stripping)

The vapours (NH_3, CO_2 and steam) from the HP stripper are condensed in HP carbamate condenser with fresh ammonia from HP ammonia pumps and recycle carbamate (65% of total) from the LP carbamate condensers via HP carbamate pump An overall NH_3:CO_2 mole ratio of 2.8 to 3.0 is maintained so as to condense the gases.

The flow of ammonia is controlled by varying speed (rpm) of ammonia pumps on the basis of N/C ratio in the autoclave liquid outlet. The HP condenser is a shell and tube heat exchanger with the process fluids on the tube side and steam and condensate on the shell side. The shell side constitutes 4.5 ata steam boiler system connected to the steam drum via eight steam risers and four condensate down comers. By controlling the shell side temperature (by controlling the steam pressure), the rate of condensation of carbamate on the tube side of the HP condenser is controlled because the condensation reaction is a function of the rate of exothermic heat removal from the reaction zone. The steam drum is elevated above the HP condenser to provide a natural thermo-siphoning circulation for the steam system. The carbamate solution from LP carbamate separator via HP Pump, and liquid ammonia from the HP ammonia pump enters the HP condenser at the top of the channel and flows down a small packed bed above the liquid distribution tray. The vapours (NH_3, CO_2 and steam) from the HP stripper enter outside the packed section. Some of the vapour enters the packing from the bottom via gas risers. Part of CO_2 and NH_3 in the vapours condenses in the packing section increasing the partial pressure of oxygen. The pressure of this oxygen acts as corrosion inhibitor at the welds between the tubes and the top tube sheet. The liquid from the packing and most of the gas feed flow down the tubes where they condense to form carbamate. Steam temperature on the shell side is controlled such that only about 90% (by vol.) of the vapours condense in the HP condenser . The rest is condensed in the autoclave. TR records the temperature of carbamate outlet from HP condenser going to the autoclave. A bursting disc on the shell side relieves CO_2, NH_3 and H_2O mixture to the atmosphere via vent stack in case of tube failure. One drain and one vent line (25 mm each) are provided for the shell.

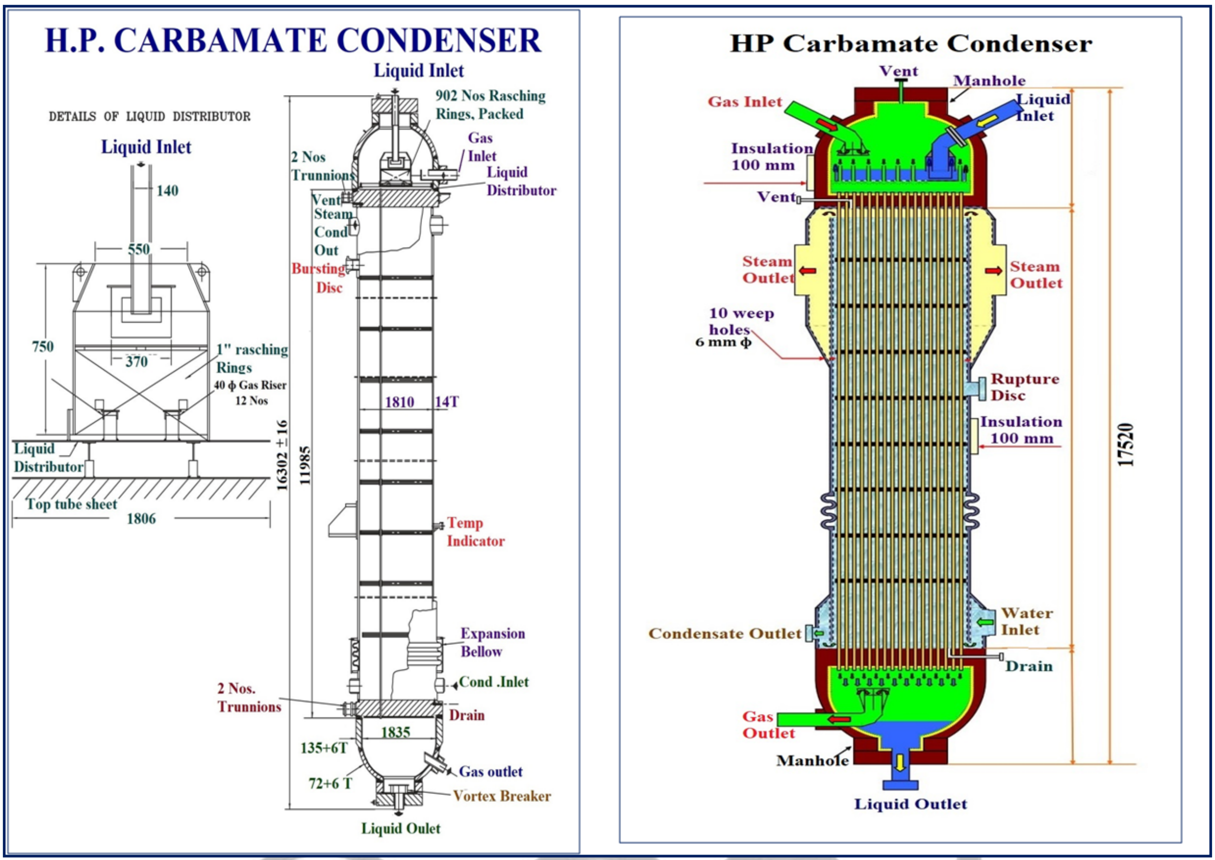

Fig-5

Risky Section of CO_2/NH_3 Stripping

High Pressure Scrubber

HP Scrubber safe operational Conditions

The inerts, unconverted ammonia and CO_2 from the top of the autoclave are condensed in the HP scrubber with carbamate solution formed in the low pressure carbamate condensers. The HP scrubber consists of bundle of U-tubes with circulating condensate from condensate circulation system-II via Pump, flowing through the tubes. The condensate enters the exchanger tubes at a temperature of 120°C and leaves at temperature of 140° C. NH_3 and CO_2 in the off gases from the autoclave are condensed to form carbamate at a temperature of about 152° C in the presence of recycle carbamate from the LP carbamate condensers . Under these conditions, the crystallization of carbamate is not possible thus avoiding the blockage of the HP scrubber However, the circulating condensate temperature must be maintained such that crystallisation of carbamate doesn't take place. . In case of temperature low alarm, both the pre evaporator hot water heat exchanger and CCS-II cooler shall be bypassed with HIC and HICV respectively to maintain CCS-II temperature to HP scrubber.

If for any reason the flow of carbamate to the scrubber is suspended, the circulating condensate inlet temperature is to be raised to 130° C so as to avoid possibility of crystallization of carbamate. To raise the CCS-II inlet temperature to HP scrubber, 9 ata steam jacket on CCS-II cooler condensate outlet line is provided. The 23 ata steam injection to CCS-II pump discharge is provided for initial heating of the CCS-II circuit. The BFW pump discharge is connected to CCS-II pump discharge line for initial make-up of the circuit. The 15 NB off sites BFW coil condensate connection is provided for continuous make-up of the system. The uncondensed vapour and inerts from the top are sent to LP absorber via pressure control valve PRC for further recovery of ammonia. PRCV controls the HP loop pressure. The condensed carbamate overflows back to the autoclave bottom from an overflow nozzle in the heat exchange section so that the U-tubes are always submerged. The gas space over the liquid distribution weir and the gas outlet pipe volume is designed to give a minimum gas volume and one of the features of this design is to prevent process gas finding its way to the top space outside the gas outlet line. The process gas contains H_2 (inerts in NH_3) and O_2 Hence, it is a potentially explosive mixture. In case an explosion, the partition plate between the gas space above liquid distribution will burst and the shock will be taken up by the top space which is at least 20 times the explosion volume. The outer top space is therefore always purged with a small amount of CO_2 from the compressor in order to avoid formation of explosive mixture of NH_3 and air. FI indicates the flow of CO_2 going to the HP scrubber.

The purpose of the HP scrubber is to condense and absorb ammonia and CO_2, present in the off gas from the urea reactor, in a heat exchanger part and an absorber part with help of the carbamate recycle solution from the LP recirculation section.

The HP Scrubber consists of following parts-

1. A blanketing sphere which receives the gases coming from reactor.
2. A Heat exchanging part which is equipped with central down comer which through degasified liquid flow down. A gas distributor installed in the bottom.
3. A scrubbing part in which the remaining gases are scrubbed with the weak Carbamate solution and where the ammonia and carbon dioxide are almost totally condensed.

The carbamate recycle solution sent by the HP carbamate pump passes through the packing section at the absorber part of the HP scrubber and then thrugh the heat exchanger part of the HP scrubber where it reaches the bottom. Here it is mixed with the off gas from the urea reactor, which first passes through the hemisphere and the U shaped line. The mixture thus formed flows upwards through the heat exchanger tubes, during which ammonia and CO_2 in the gas are condensed and absorbed, while the heat is removed by the tempered cooling water on the shell side. Unabsorbed ammonia and CO_2 then contact counter-currently with the carbamate solution sent by the HP carbamate pump in the packing section of the HP scrubber for heat exchange and mass exchange. Inert gases going out of the HP scrubber and a small quantity of ammonia and CO_2 are absorbed in the LP system and then vented to atmosphere. The inert gases origin from the inerts present in the feed plus the air added to the CO_2 feed for the operation of the During the start-up of the HP scrubber, when the temperature of the tempered cooling water is from CO_2.

hydrogen converter and for the passivation of the applied stainless steels in the urea plant. This means oxygen is present in the off gases and like in any other urea process proper attention need to be paid to avoid explosion risks.

Process operation of the HP Scrubber

Most of the personnel operating a newly built urea plant are not so experienced in the process operation of the HP scrubber. Various abnormal situations might occur during the startup, shutdown and even during normal production of the plant. In view of this, the following analyses are made on the process operation of the HP scrubber:

Normal operation mode

Why should the carbamate solution outlet temperature of the HP scrubber be controlled above 155 o C during normal operation? And how to control? Assuming that the carbamate solution at the outlet of the HP scrubber is in equilibrium with the gas stream in the bottom section of the packed bed, the temperature of this carbamate solution is influenced by the percentage inerts present in the gas phase. The higher the percentage inerts, the higher the inert pressure, the lower the system pressure (= partial pressure of NH_3, CO_2 and H_2O) and the lower its boiling temperature. In order to maintain non-explosiveness of the off-gas of the HP scrubber, inert gas content in the off gas should be less than 36%. It can be found from NH3-CO_2-H_2O ternary diagram in terms of temperature, pressure and composition that this means that the partial pressure of NH_3+CO_2 should not be less than 8.29 MPa when the operating pressure is 14.4 MPa, which corresponds to a carbamate solution temperature of 155^0 C. If the H_2O content in the carbamate solution increases, the outlet fluid temperature should be increased accordingly so as to maintain the same partial pressure. Remark UreaKnowHow.com: The carbamate solution temperature can be controlled by means of the HP inert valve. When opening this valve the temperature will increase.

1. Temperature difference of the HP scrubber gradually reduces with zigzag fluctuation
2. The vented quantity of off gases increases.

Temperature of tempered cooling water is too low

controlled too low, the carbamate solution in the tubes of the heat exchanger may crystallize and block the tubes. This again might cause a damage to the cylinder in the hemisphere. Signals are:

1. The tempered cooling water shows no temperature difference between in and outlet of the heat.
2. Exchanger the temperature of the off gas of the HP scrubber rises rapidly.
3. Temperature of the carbamate solution outlet of the HP scrubber drops.
4. The temperature at the outlet of the HP carbamate ejector drops rapidly.
5. CO_2 conversion rate in the reactor decreases.
6. Steam consumption of the HP CO_2 stripper increases.
7. Steam consumption of the first-stage evaporation heater increases.

Start up and shut down operation modes

Blocking U-shape gas line during a blocking in shutdown of the HP scrubber the gas in the U-shaped line from the hemisphere to the bottom of the heat exchanger may crystallize and cause plugging. For example when the power supply of the plant is shut down and the emergency power supply fails to start and the steam supply for the plant is unavailable, etc.). Remark UreaKnowHow.com: or when the tracing and insulation is in bad condition. As a result a large pressure difference between the inside and outside of the cylinder in the hemisphere occurs and might become damaged. Signals are: The pressure of the HP synthesis system rises rapidly

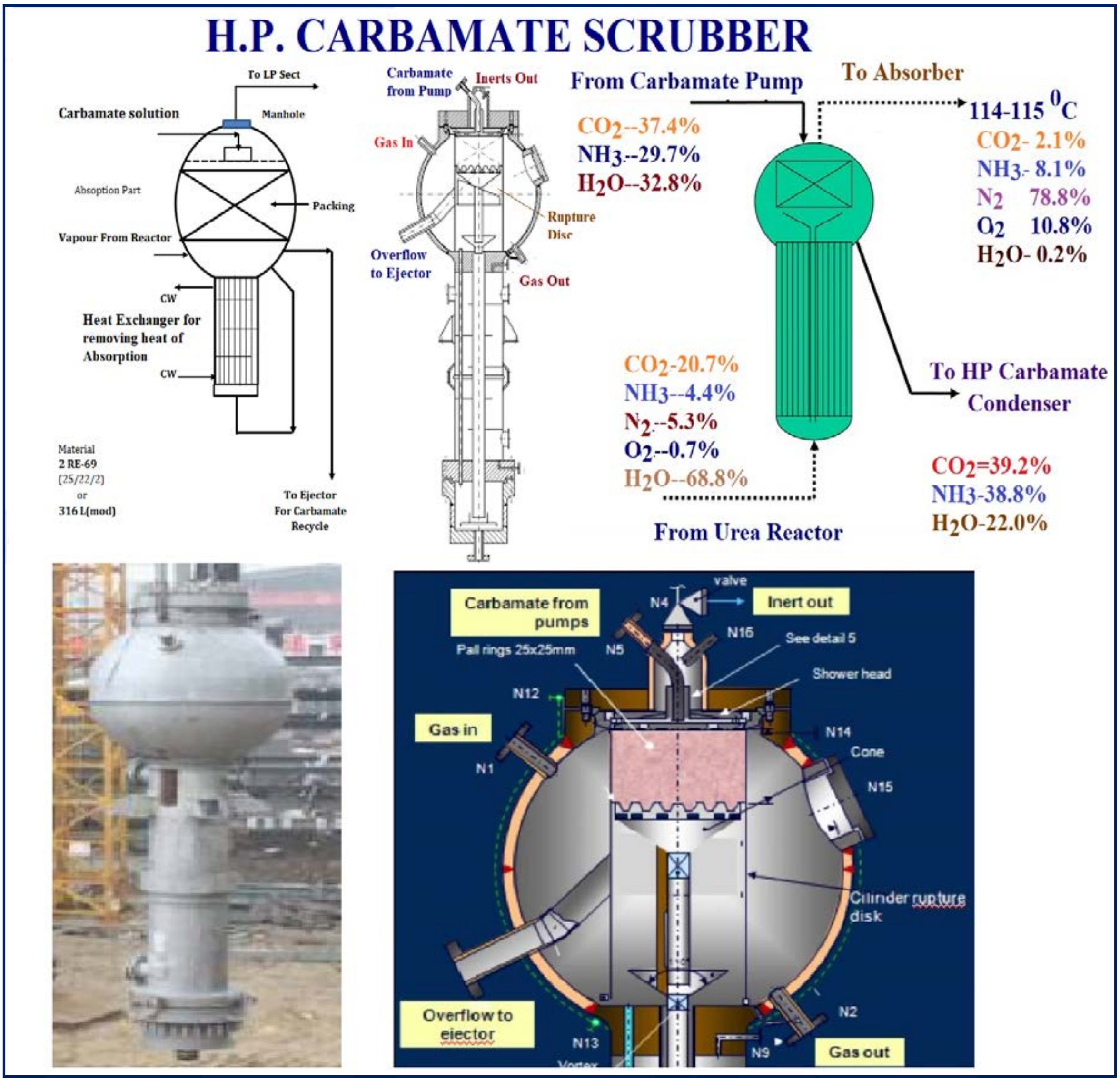

Fig-6

Another problem which may occur when the temperature of the tempered cooling water of the HP scrubber is controlled at a too low level, is that NH_3 and CO_2 are excessively condensed in the HP scrubber, causing that the off-gas may fall into the explosion zone.

Hydrogen Content too high

When the hydrogen converter fails or due to a problem in the ammonia plant too much hydrogen is present in the feed, the off gases of the HP scrubber may fall into the explosion zone. Signals are:

1. Hydrogen content of the hydrogen analyzer increases.
2. N/C ratio increases.
3. CO_2 conversion rate decreases.
4. Steam consumption of the HP CO_2 stripper increases.
5. Temperature of the liquid outlet of the HP carbamate condenser drops.
6. Pressure of the HP synthesis system rises.

Carbamate solution temperature too low

We have observed that all HP scrubber off-gas fires during the start up occur within 10-15 minutes after overflow of the urea reactor. Why would the off-gas become explosive at this moment ? Observations from each plant show that it is caused by a sudden drop of the temperature of overflow liquid from the HP scrubber. We have made a comparison between good operation and bad operation practice. The minimum carbamate liquid overflow temperature of the HP scrubber is above 155 o C in the good operation practice while the minimum temperature drops to 136 oC in the bad operation practice. When the overflow temperature is lower than 150 o C the off-gas may enter into the explosive zone.

Why there is a low point of the temperature of overflow fluid at that moment: the reason why the off gas of the HP scrubber may enter the explosive zone when the urea reactor is at overflow condition is that the temperature of the reactor solution is lower during the overflow. When the temperature of the reactor solution is lower, the NH_3 and CO_2 contents of the off gas of the reactor, which is in equilibrium with the reactor solution, decreases. As the off-gas discharge amount remains unchanged (remark UreaKnowHow.com: as the off gas discharge amount is determined by HP inert valve position), the available NH_3 and CO_2 to be absorbed by the HP scrubber decreases, thus the reaction heat generated from the condensation in the HP scrubber decreases, causing the temperature of the overflow fluid of the HP scrubber to drop down.

Conclusion

The proper selection of the equipments MOC can save the production as well as human life in case of causalities. This is because, there is a limit to how far corrosion resistance can be improved by alloying, therefore investigating how corrosion resistance can be improved by strengthening the microstructure through heat treatment is important. Micro alloy can be used in reformer tubes. We have seen the 2RE-69 for urea reactor liner is the right selection instead of SS316 (urea grade).Omega Bond stripper is the life time equipment. Maximum shut down due to the failure of stripper.

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