

Recent Developments in Urea Plant Design

The paper will review the recent Urea Technology developments: a) In Urea synthesis technology for the design of large scale single unit grass root plants, up to capacities of 4,500 MT; b) In the use of new materials with improved corrosion resistance and mechanical strength, offering safe operation, reduction of investment cost; c) In the revamping of conventional urea plants towards big capacity increase and improved efficiency offering attractive investment saving; d) In the Urea Granulation; e) For cooling – conditioning of prilled & granular urea

Pan Orphanides
ORPHANCO Greece

Introduction

Urea plant design and construction in the have been characterized by the following trends in the last years:

- Large single line plants- simplified layout, of a capacity greater than 3500 MTD
- Overcome limits in manufacturing – transportation – erection. For plant capacity of 3500 MTD urea plants reactors 380 tons, pool condenser 300 tons and strippers 230 tons are manufactured, transported and erected in a single piece.
- High reliability - on-stream factor, increased maintainability – operability
- High corrosion resistance – high mechanical strength materials
- New Casale Urea synthesis process
- High quality urea delivered to remote final destinations
- New granulation process of Stamicarbon
- First Hydro granulation revamped to Stamicarbon concept
- Advance of Urea Granulation against prilling

- Refurbishing old plants to high capacity & efficiency increase by obtaining important capital savings.

1. Recent Technology Improvements in Urea Synthesis

In Chapter 1.1 we will discuss developments in the **Urea Synthesis** focusing mainly on the break through opening the way to single line large capacity plants: By **Carbamate Condenser** of a new design first applied by Stamicarbon's Pool Condenser in the 80s. Ten years later Toyo Engineering followed by their Vertical Submerged Condenser and recently Casale with their Full Condenser. The development is continuing with the **Pool Reactor** (Fig.1.1.2a-2), introduced in the late 90s by Stamicarbon in the 1100 MTD urea plant in DSM /Geleen

In chapter 1.2 we will discuss New **Improved materials**.

New Technologies in **refurbishing old, or conventional technology plants** for high capacity increase

and/or efficiency improvement will be discussed in Chapter 1.3.

Developments in Urea Granulation will be discussed in Chapter 1.4 and in Chapter 1.5 Developments and Advanced features in urea cooling are given.

1. 1 High Pressure Carbamate Condenser (HPCC)

1.1.1. Conventional HPCC with carbamate formation on tube side, in spite of recent improvement has many disadvantages:

- even distribution of gas /Liquid load, in each individual tube is not easily achievable, resulting in reduced condensation efficiency
- short retention time, resulting in non complete condensation
- low heat transfer, especially for falling film type condensers
- due to unequal distribution of liquid and gas flows through tubes hot spots are formed creating high corrosion rates, especially in kettle type condensers.

1.1.2. These problems have been radically solved by Stamicarbon's **Pool Condenser** of a new design first applied by in the 80s, and by a further development uniting condenser and reactor introduced in the middle 90s shown in Fig. 1.1.2a-1. The development is continuing with the **Pool Reactor** (Fig.1.1.2a-2), introduced in the late 90s by Stamicarbon in the 1100 MTD urea plant in DSM /Geleen. A few years ago Toyo followed by their **Vertical Submerged Condenser** (Fig.1.1.3b) and recently Casale with their **Full Condenser** shown in Fig. 1.1.3c, Fig.1.3c-1, Fig. 1.3.c-2.

With this development the following has been achieved:

- more than 20 min retention time in the condenser, resulting in important urea conversion of carbamate solution before entering the reactor, allowing by this the conversion efficiency increase in the reactor, close to the equilibrium point
- heat transfer increased substantially, increasing the Condenser capacity
- higher steam pressure steam is generated
- low corrosion due to uniform distribution of liquid and gaseous phase in all tubes, and because hot spots non presence

- simplified synthesis section
- reactor weight reduction for large size plants > 3500 MTD
- further improvements are obtained in CO₂ stripping plants by combination of revamped conventional Falling Film Condenser with split stripper gaseous effluent flow, part directly to the reactor and part only to the condenser, as it is shown and explained in Fig. 1.1.3c, 1.1.3c-1 and 1.1.3c-2. This system is applied by Urea Casale in a conventional CO₂ stripping plant and allowed a substantial capacity increase, without any additional equipment, as it is shown and explained in Fig. 1.3.4.

The new generation HPCC will allow the design of single unit large capacity urea synthesis plants, as well as revamping of existing plants by de-bottlenecking up to factor 2 urea synthesis section and by factor 3 Recirculation. Furthermore capacities up to 4500 MTD will be feasible by re-incorporating in the new HPCC design, the 20 bar Medium Pressure Section in CO₂ stripping process shown in Fig. 1.1.3a. The concept of combining Pool Reactor with 20 bar Re-circulation section is under Construction in DSM Geleen.

The Pool Reactor shown in Fig.1.1.2a-2 operates in the condenser part with NH₃/CO₂ (N/C) ratio of about 2.3-2.6, that means on the top ridge line[1], where the boiling temperature and kinetics are at maximum. 2.5 N/C ratio is close to the top ridge line at the beginning of urea formation>> fast urea formation up to 60% of equilibrium. Then the solution is transferred in the reactor section by NH₃ ejector and N/C becomes 3.1, close again to the top ridge line for conditions prevailing in the reactor part, those increasing urea formation.

Toyo's Submerged type HPCC is applied in Sichuan Chemical Works (China): Improved ACES with the design capacity of 2460 MTPD is under commissioning.

1.1.5 Furthermore, with the application of the new generation Carbamate Condenser in old technology, Total Recycle urea plants, large capacity increase up to

[1] More about stripping process principles & liquid-gas equilibria in a NH₃-CO₂-H₂O system can be read in the paper of P.J.C. Kaasenbrood & Dr. H.A.G. Chermin "Stripping Technology, Phase Equilibria & Thermodynamics", (Proceedings No. 166- December 1977, of the International Fertilizer Society/London

100% and substantial energy saving can be obtained as shown in Fig. 1.3.3, and 1.3.5

1.2 Improved materials: Advantages of 27-28% Cr min. Duplex steels against 25/22/2 L Mn austenitic steels

It is known that balanced ferritic- austenitic content Duplex steels with up to 26.5 –27.5 % Chromium and W addition made it possible to produce urea synthesis components with high mechanical strength and high corrosion resistance in urea-carbamate solutions. Nevertheless passivation by oxygen was necessary in order to maintain corrosion resistance, as it was the case with the high austenitic steel 25/22/2.

- High mechanical strength, good weldability, formability
- Comparably good corrosion resistance in urea-carbamate solution
- Slightly less passivation oxygen resulting in slightly more CO₂ compressor capacity
- Thinner pipes resulting in less weight, less material cost (2.5-3.0 times higher yield strength than 316 Urea grade stainless steel)
- High resistance to stress corrosion cracking in chloride containing environment
- Thermal expansion close to carbon steel
- Duplex steel pipes for 16" HP piping needed for large capacity plants
- Duplex stainless steel is easy to passivate compared to austenitic one, which means duplex steel requires less amount of dissolved oxygen compared with austenitic stainless steel

Additional properties of Special Duplex steel Safurex

The new Duplex steel Safurex with up to 28.5-30 % Cr, developed in co-operation of Santvik and Stamicarbon is promising to eliminate almost entirely the use of passivation air:

- high Cr content, min. 28.5%, excellent corrosion resistance in pilot tests without passivation
- Thinner tubes resulting in more stripping surface for same OD tube, due to higher yield
- Less stripper tubes, resulting in less material, less stripper weight (-16%)
- Almost nil passivation oxygen requirements, resulting in more CO₂ compressor capacity

- Lower inert in reactor resulting in higher conversion efficiency

Safurex for oxygen free urea synthesis?

According to Sandvik – Stamicarbon, so far the only Duplex-Steel quality resisting carbamate corrosion in urea services under almost nil oxygen passivation is SAFUREX (28.5% min. Cr content, Ni 5.8-7.5%, Mo 1.2-3.6%, N 0.3-04%)

As there are All -Safurex synthesis loops under construction, it is expected that a gradual reduction program to lower oxygen values will take place. This will probably be a long term test!

In case oxygen content is near zero and everything is going OK, then the equipment shown in red in Fig.1.1.2a-1 will not be needed, resulting in important savings in investment and operating costs! Stamicarbon claims that savings of up to 10% in investment cost have been achieved.

Finally it is worthwhile mentioning here that a smaller Safurex made stripper ordered for a CO₂ stripping plant was installed as part of an urgent replacement of the failed original stripper in a Snamprogetti large urea plant two years ago. Next inspection will show if Safurex can withstand with similar, or better corrosion resistance rate as bimetallic Zirconium tubes, operating under the conditions typical for a Snamprogetti design urea synthesis and to be a cheaper alternative to a Zr tube and entirely Zr lined stripper.

1.3 Recent efficient revamping Techniques applied for large capacity (40-50%) & efficiency increase

In Fig.1.3.0 the bottlenecks and over-designs, which are usually available in many plants, are given. The right time for improvements is always, when important aged equipment needs replacement: This can save up to 50% investment cost against new plant. In the below given list of Figures, attached to the end of the paper text, the various applied technologies are given and their most important characteristics are commented:.

Fig. 1.1.3a Adding a MP decomposition section. A concept developed by Stamicarbon, as explained in paragraph 1.1.3 above and shown in Fig.1.1.3a. The

concept of combining Pool Reactor with 20 bar Re-circulation section is under construction in DSM - Geleen / The Netherlands

Fig. 1.3.1 Adding a parallel stripper to CO₂ stripping plant: Stamicarbon CO₂ Stripping Revamping by Parallel Stripper of 25% additional stripping surface was successfully applied in a 2000 MTD design capacity urea plant in Saskferco Canada. 40- 50% capacity increase has been obtained. For this revamping a relatively large reactor volume was available and the existing conventional HPCC has been stretched to the maximum of its potential. In order to obtain this high capacity boost HETs have been provided and passivation air has been replaced by oxygen-enriched air.

Fig. 1.3.2 Adding an HP condenser & decomposer and a small 160 bar reactor to a conventional TR plant: Urea Casale HEC process for large capacity increase.

Fig. 1.3.2a Adding a 240 bar small reactor, HP condenser & decomposer to a conventional stripping plant: Urea Casale HEC process

Fig. 1.3.3 Adding a pool condenser and a CO₂ stripper to conventional TR plant: Stamicarbon in Petro China Ningxia Petrochemical Company a Pool Condenser for a 2610 MTPD final capacity Urea Revamp

Fig. 1.3.4 Revamping a falling film vertical HPCC to a submerged thermosyphon type Full Condenser by Casale, First Reference in the 1100 MTD Styrol urea plant in Gorlovka –Ukraine where Capacity was increased to 1500 MTD

Fig. 1.3.5 Adding a Toyo VSCC and a CO₂ stripper for a retrofitting of conventional TR plant, increasing its capacity to 2460 MTD

Fig. 1.3.6 Adding an HP decomposer to decompose recycled carbamate >>>Reactor operates at high conversion due to low H/C ratio: Casale VRS concept for revamping stripping urea plants. This concept has been applied in the Agrium's Carseland, Alberta, Canada and plant capacity has been increased from 1920 to 2350 MTD in 1997

Fig. 1.3.7 Use enriched in Oxygen Air for passivation, (for small capacity increase, when applied alone).

1.4 Urea Granulation Developments

1.4.1 Most important features:

- Melt water content from 1.0 to 6%: merits – demerits: finally Hydro granulation by 95% urea melt represents an overall optimum in terms of investment –operating cost and product quality
- Dispersion of melt to fine droplets, or to melt film: to evaporate humidity from 95% melt it is apparently necessary to atomize it to fine droplets. The consequence is dust formation and aerosols in the granulator and necessity to increase formaldehyde content, to act as crystallization retarder and keep dust formation under control.
- Water evaporation effect on cooling, on granulator size, on final water content in product, and on spraying energy: the penalty of high concentration melt is the need for higher fluidization-cooling air flow, the bigger size of granulator- scrubber
- High content Crystallization Retarder (Formaldehyde) needed to allow fine droplets to stick on seeds: the main advantage of the Stamicarbon process requiring almost 50 % less Formaldehyde to achieve good quality granules.
- Avoid entrapment of dust on seeds by too high fluid air temperature and too low formaldehyde content, if melt is dispersed to fine droplets
- Developments to achieve grain classification inside or at granulator out-let granulator not yet applied industrially (Hydro, Casale, Bayer patents) for urea granulation.

1.4.2 Established Urea Granulation Technologies:

More and more urea granulation plants are built in the last years, with capacities of more than 3500 MTD. This trend is expected to accelerate in the year to come. In the listed below Figures, attached at the end of the paper, the most important characteristics of the various Granulation Technologies are given:

Hydro Agri (Figs.1.4.2a-1/2)

Toyo (Fig.1.4.2b-1)

New Stamicarbon FBG Process (Fig. 1.4.2c-1)

Hydro Agri, Toyo are well-established Urea Granulation technologies with many plant references and large number of technical literature. In the attached Figures only the main characteristics of these processes

are given for comparison to the new Stamicarbon Urea Granulation.

Stamicarbon Urea Granulation Technology is, to date, in industrial operation in only two relatively small-capacity (280 and 650 MTD) revamped plants. In 2004 three plants of 2000 MTD each are in design phase and will be in operation in 2006, all three in Egypt. In Fig. 1.4.2c-1 the main features of the Granulator are given and in Fig. 1.4.2c-2 a Delta operating and investment cost comparison between Stamicarbon and Hydro Granulation process is given.

Single line granulation units up to 4500 MTD and above should be possible without restrictions imposed by design, or manufacturing /erection. Possibly, in order to reduce equipment size and layout requirements it will be preferable to combine air fluidization –cooling in the granulator with indirect water-cooling and /or replace conventional voluminous Fluid Bed Coolers (FBC) with Bulk Flow Coolers (BFC).

1.5 Advanced features for urea cooling

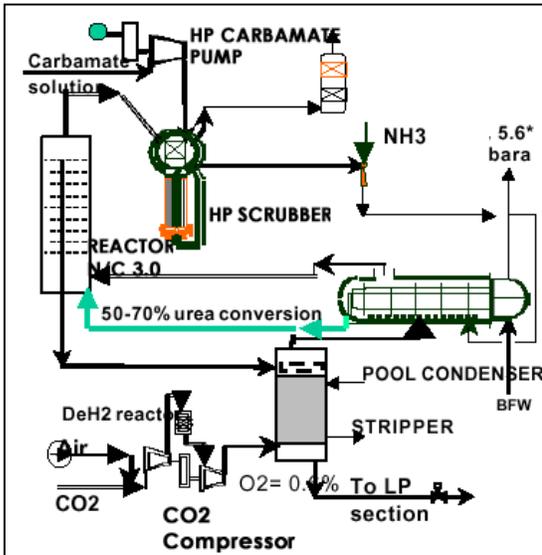
For the cooling of urea (prilled or granular), as well as for other nitrogenous fertilizer grades, the most common method of cooling is by a Fluidized Bed Cooler (FBC), where the method of cooling by Bulk Flow Cooler (BFC) has found a relatively restricted application only, although cooling by FBC has some important disadvantages:

- High investment cost: FBC, Scrubber, blowers, air chiller, large ductwork, important civil works- instrumentation
- High operating cost: about 1.8 MW are required for a 2000 MTD nitrogen fertilizer granulation plant for cooling by FBC, against 200 kW for cooling by BFC
- Extended lay-out required to accommodate voluminous equipment and duct work
- Complex Design in which many vendors are usually involved
- Interference with process by recycling ammonia –process condensates. If treated process condensates containing formaldehyde are used as boiler water in HP boilers, risk of corrosion is imminent.
- For prilled urea, the use of FBC for dedusting, allows only partial urea cooling, not entirely

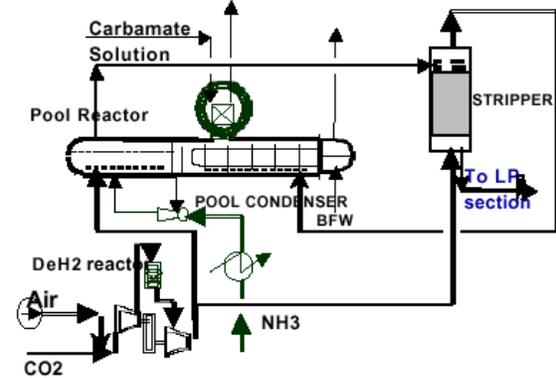
eliminating caking problems in bulk storage. This can be achieved by the use of an improved prilling device, in connection with a simplified BFC, as described in Fig. 1.5.1 & 2

- In case that due to screens disoperation, or granulation upset conditions, a dusty product is fed to the FBC, most of the fines and all the dust would have blown to the scrubber, blocking its operation. For the same as above case with BFC, if proper provisions, described in Fig. 1.5.3 / 4, are taken to avoid condensation, the operation could continue without any blockage.

As shown in Fig. 1.5.4, urea with 0.20 - 0.25% Formaldehyde content behaves differently as freshly granulated urea with 0.55%-0.60% F, in terms of moisture absorption, due to extra hygroscopicity of Urea - formaldehyde pre-condensate in the molten liquor solution phase being in equilibrium with solid crystalline phase and due to the extra surface activity in the porous structure of granular urea with high F content. That means Granular urea from the new Stamicarbon Granulation process, with only 0.25% F, could be cooled in the final, as well as in the primary cooler more efficiently by the use of BFC, in terms of investment and operating cost.

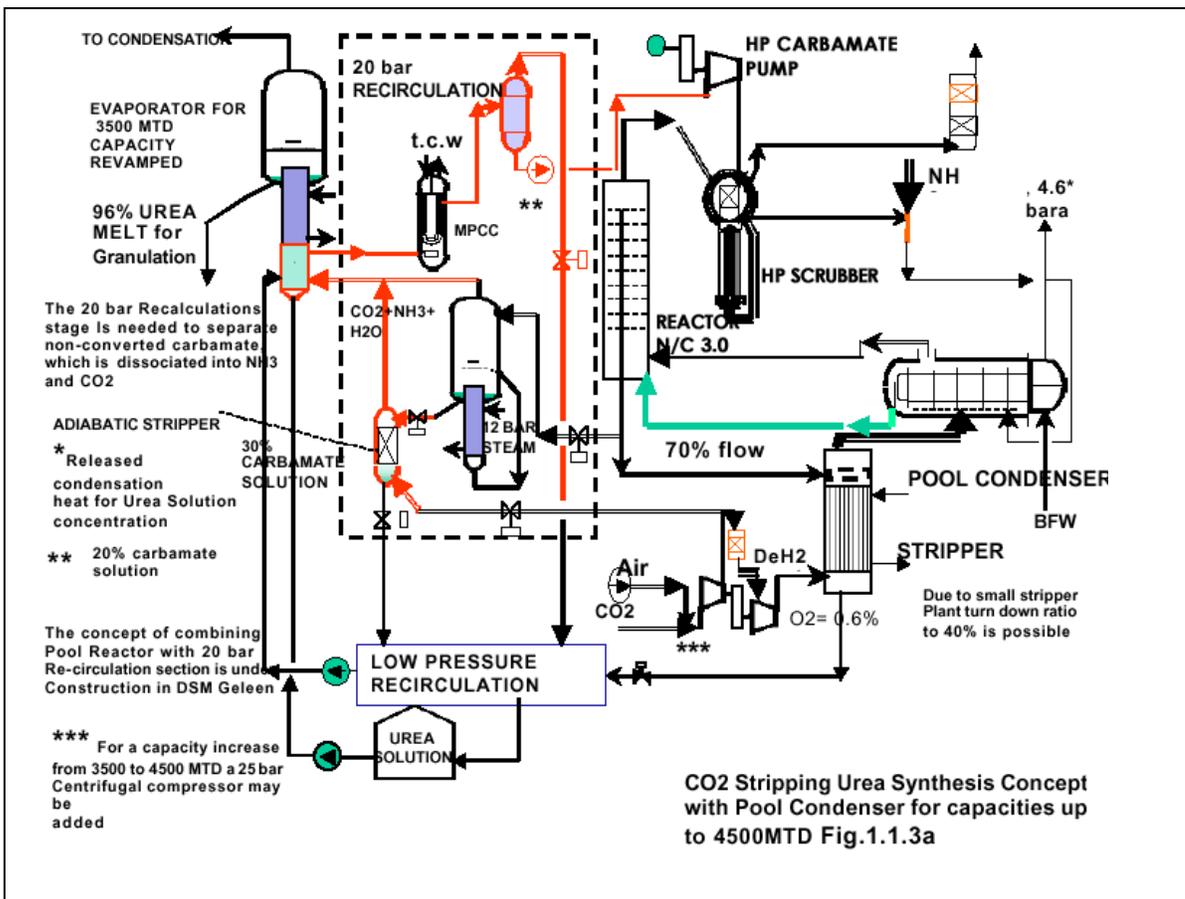


CO2 Stripping Urea Synthesis with Pool Condenser for capacities up to 3500MTD
Fig.1.1.2a-1

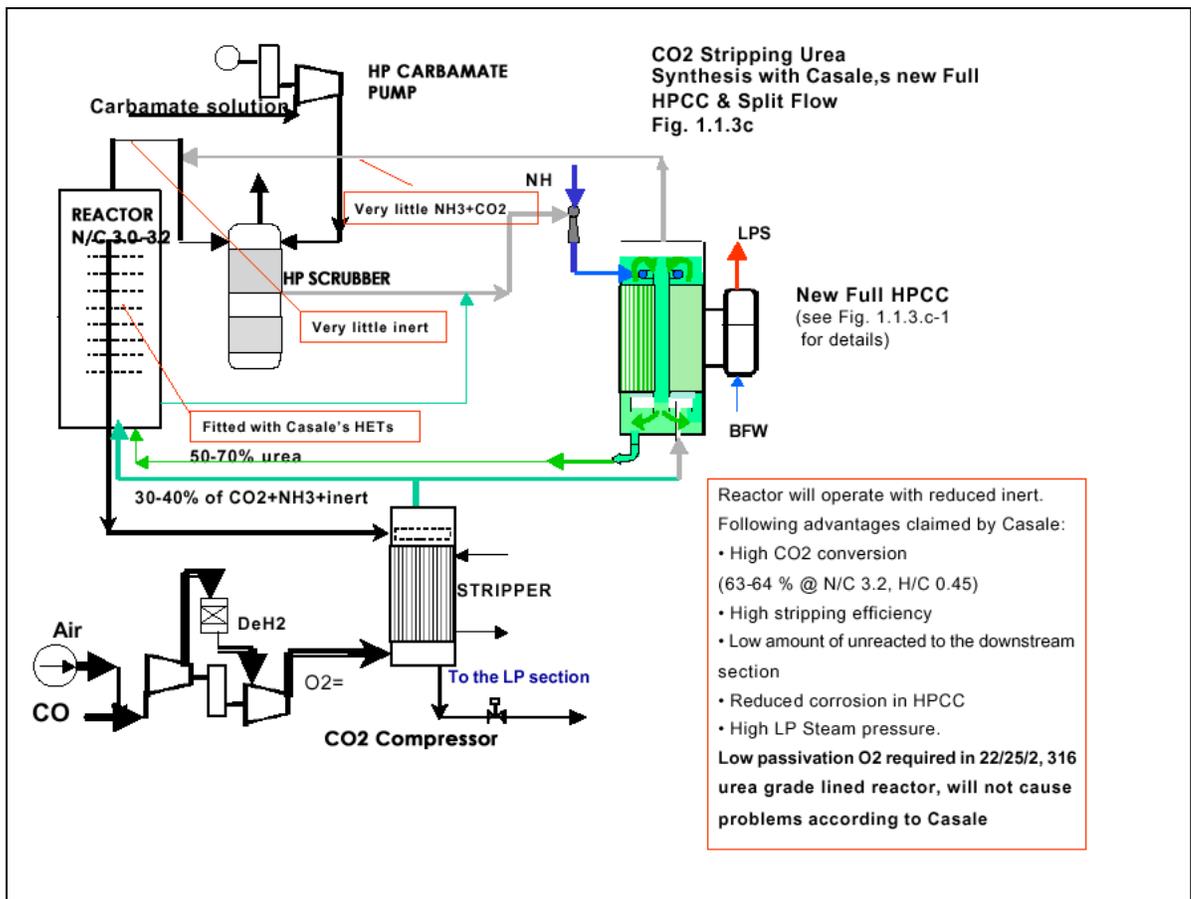
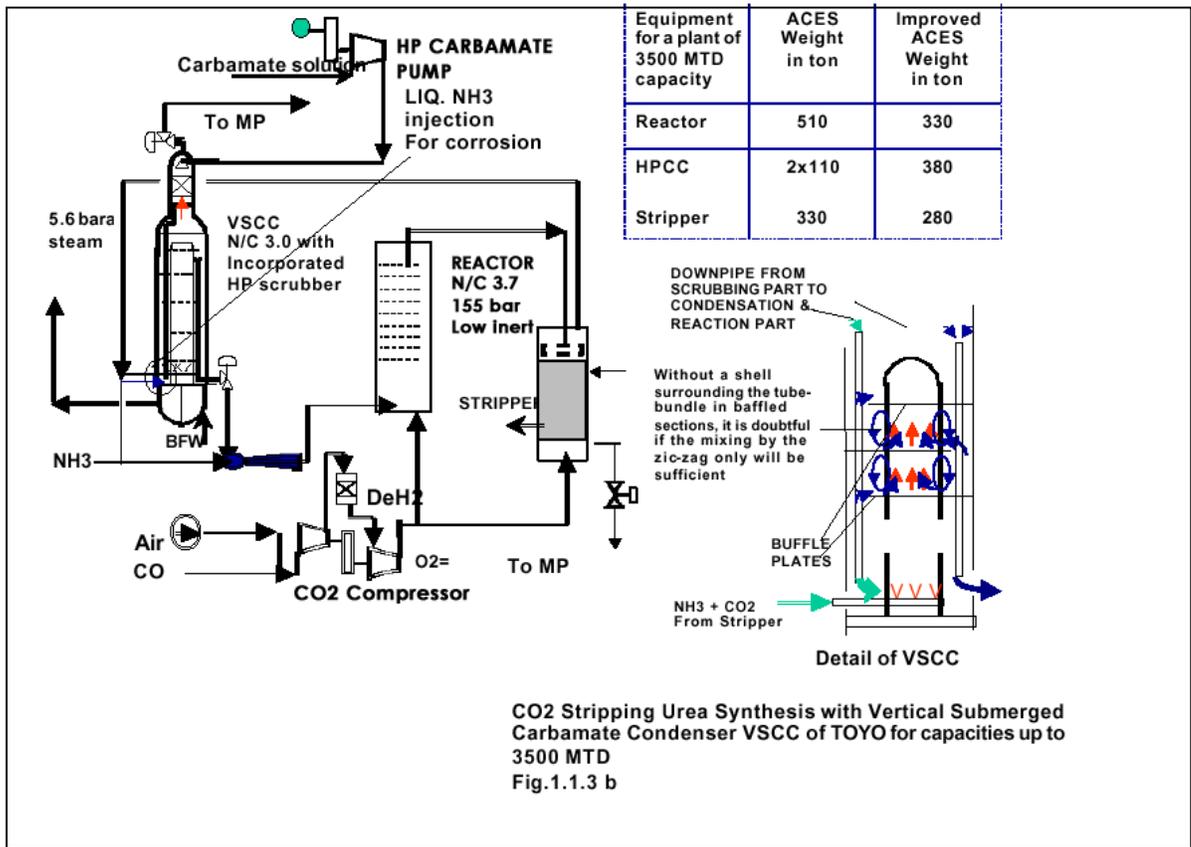


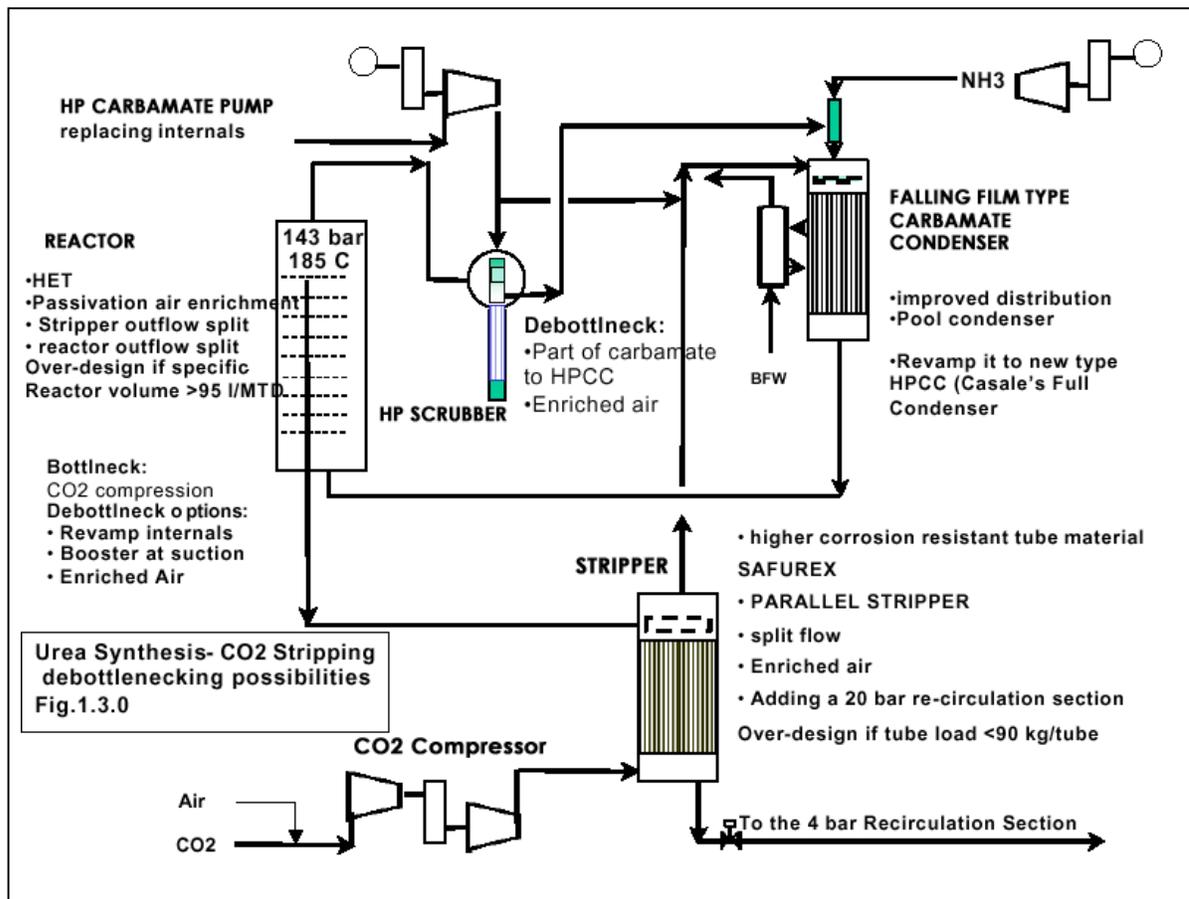
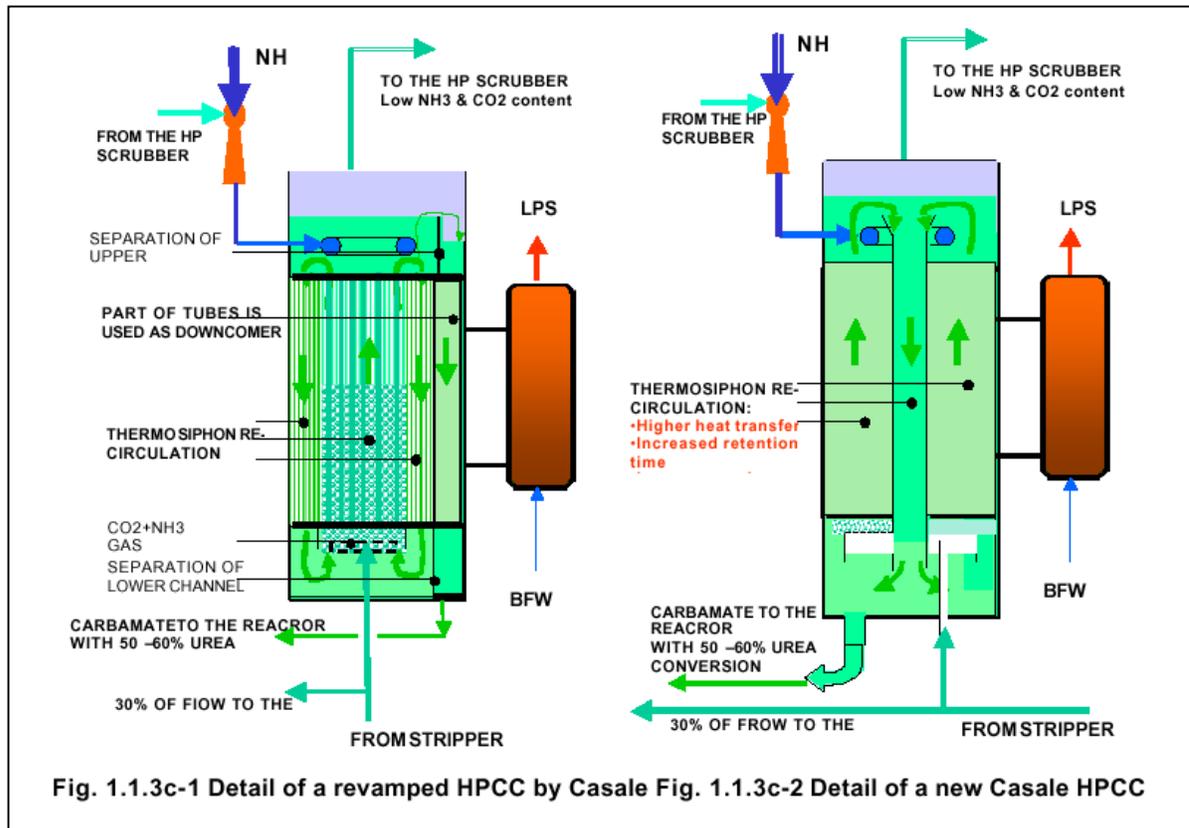
In the condenser part N/C ratio is about 2.3-2.6: on the top ridge line the boiling temperature and kinetics are at maximum. 2.5 N/C ratio is close to the top ridge line at the beginning of urea formation >> fast urea formation up to 60% of equilibrium. The solution is transferred in the reactor section by NH3 ejector and N/C becomes 3.1, close again to the top ridge line for conditions prevailing in the reactor part, those increasing urea formation.

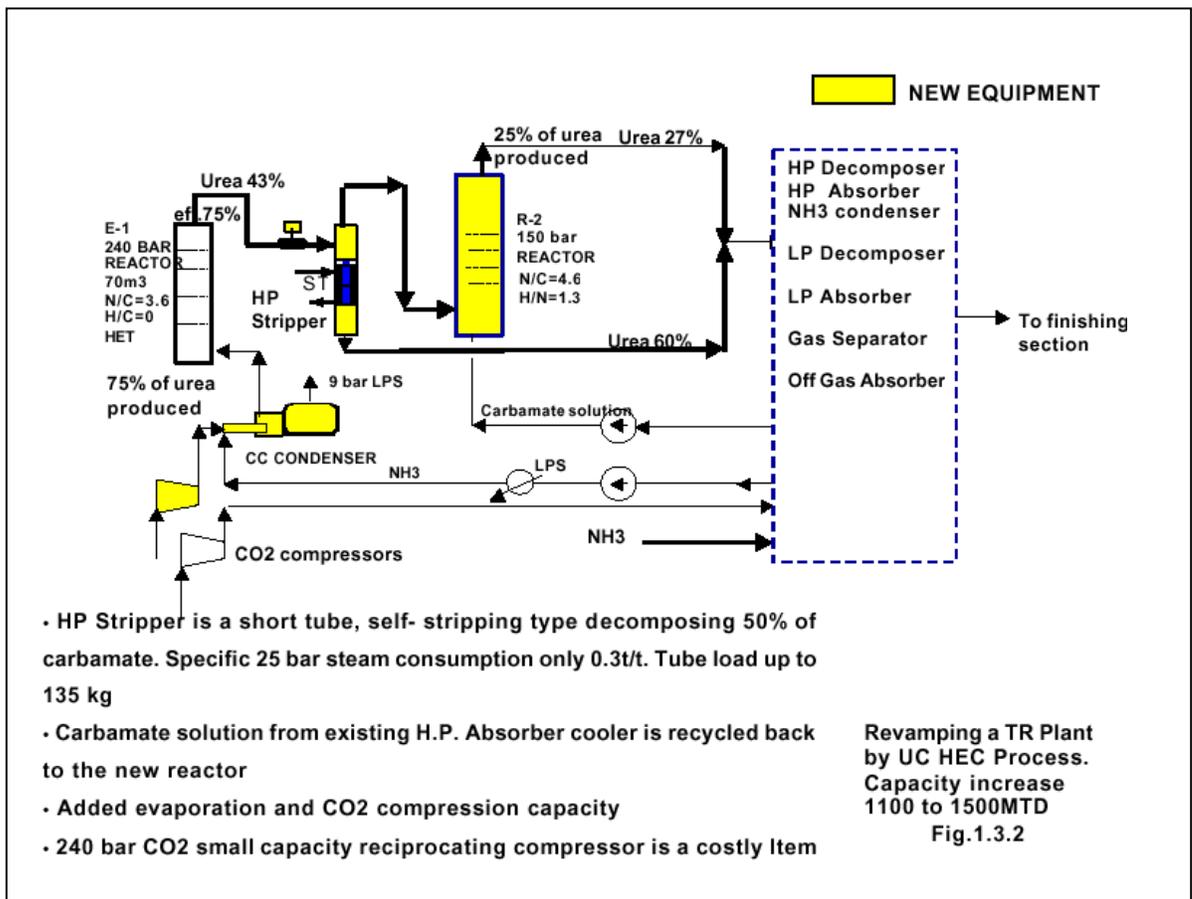
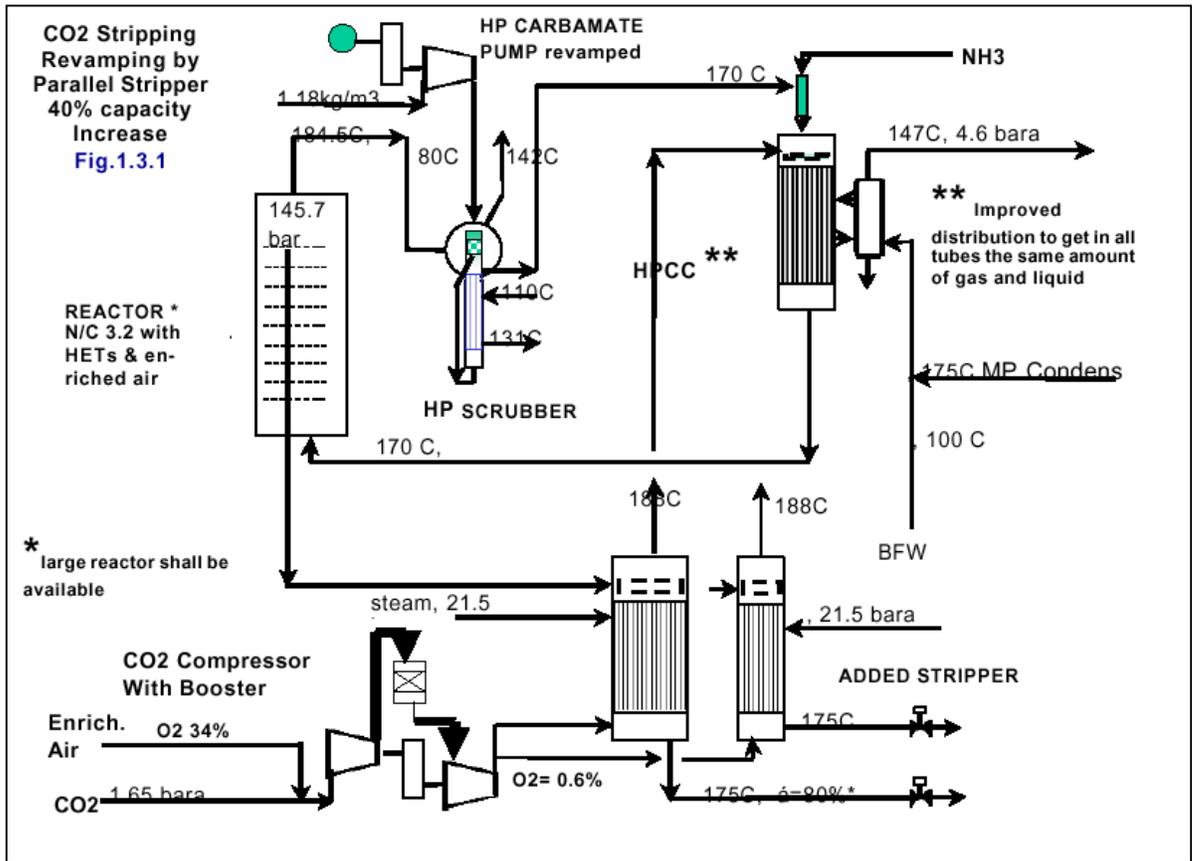
CO2 Stripping Urea Synthesis with Pool Reactor for capacities up to 3500MTD
Fig.1.1.2a -2



CO2 Stripping Urea Synthesis Concept with Pool Condenser for capacities up to 4500MTD Fig.1.1.3a

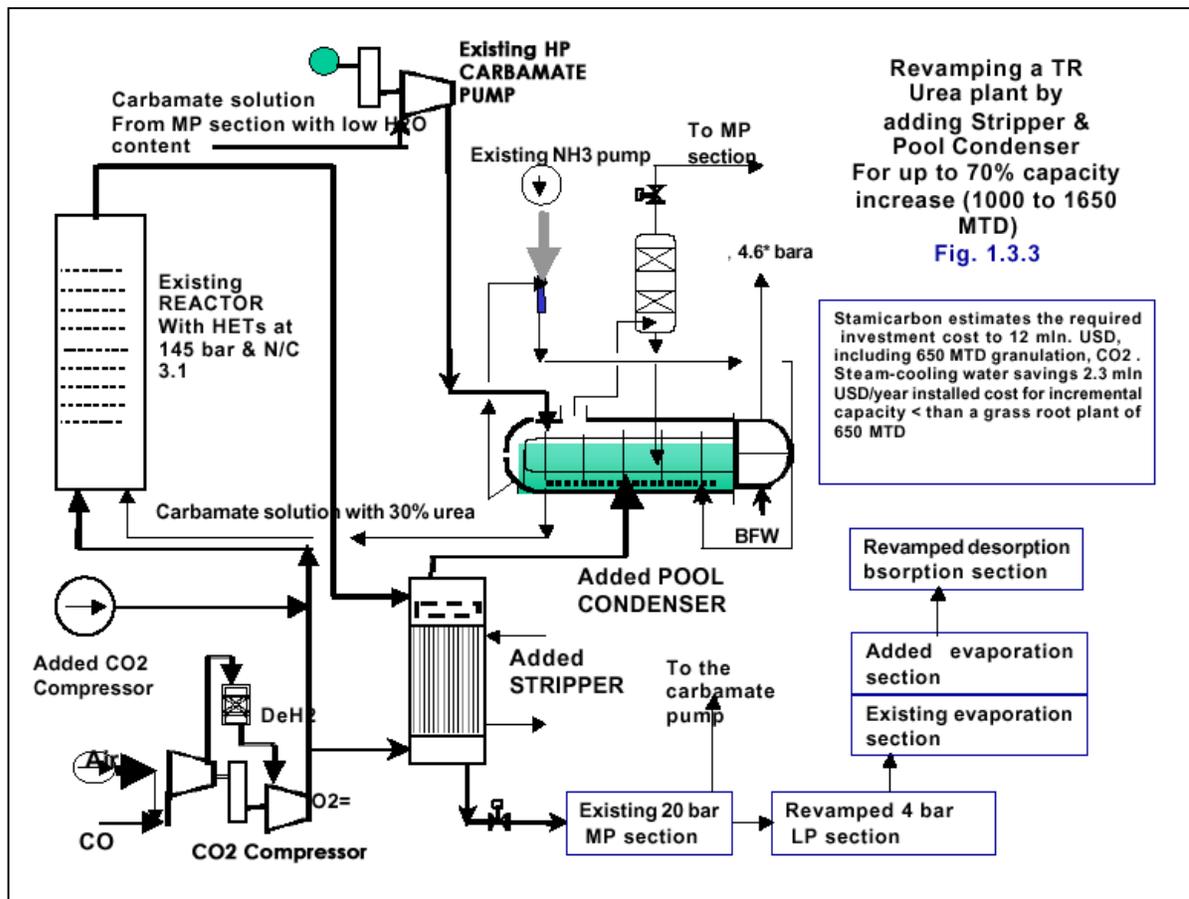
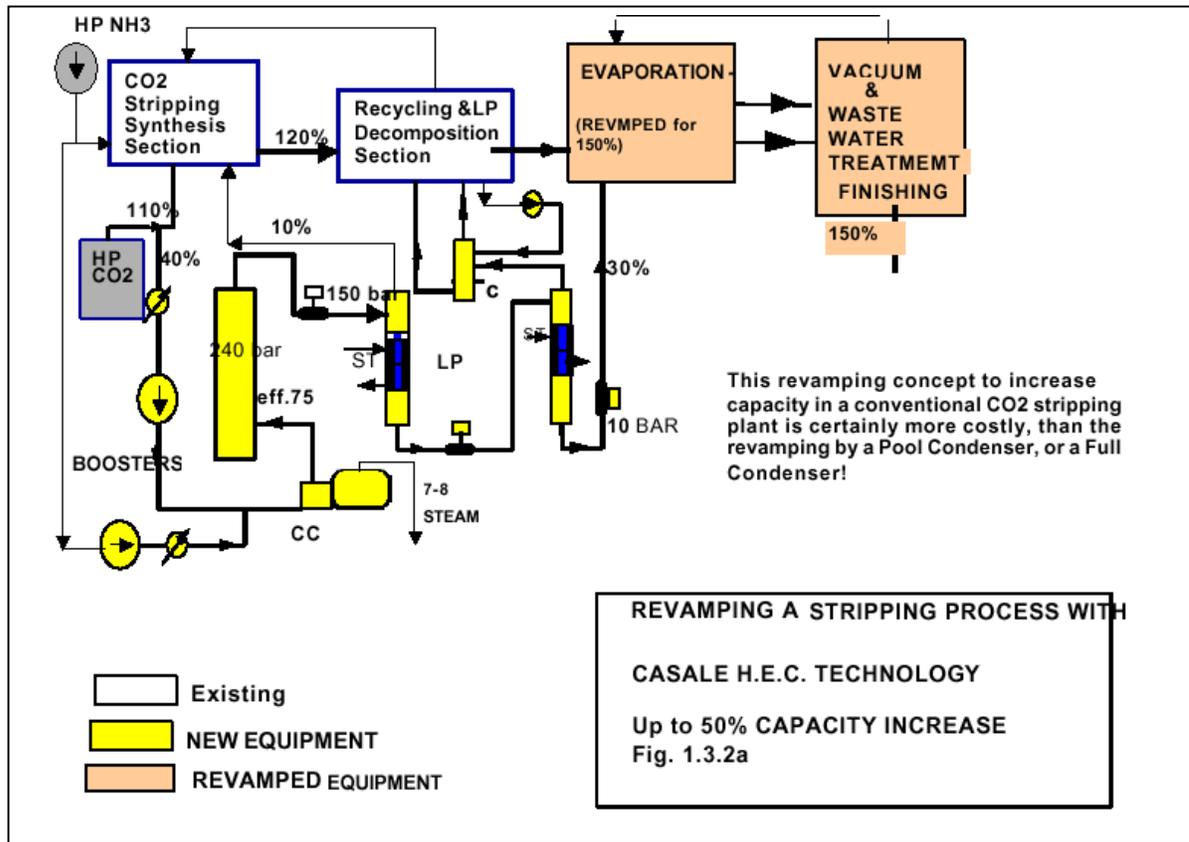


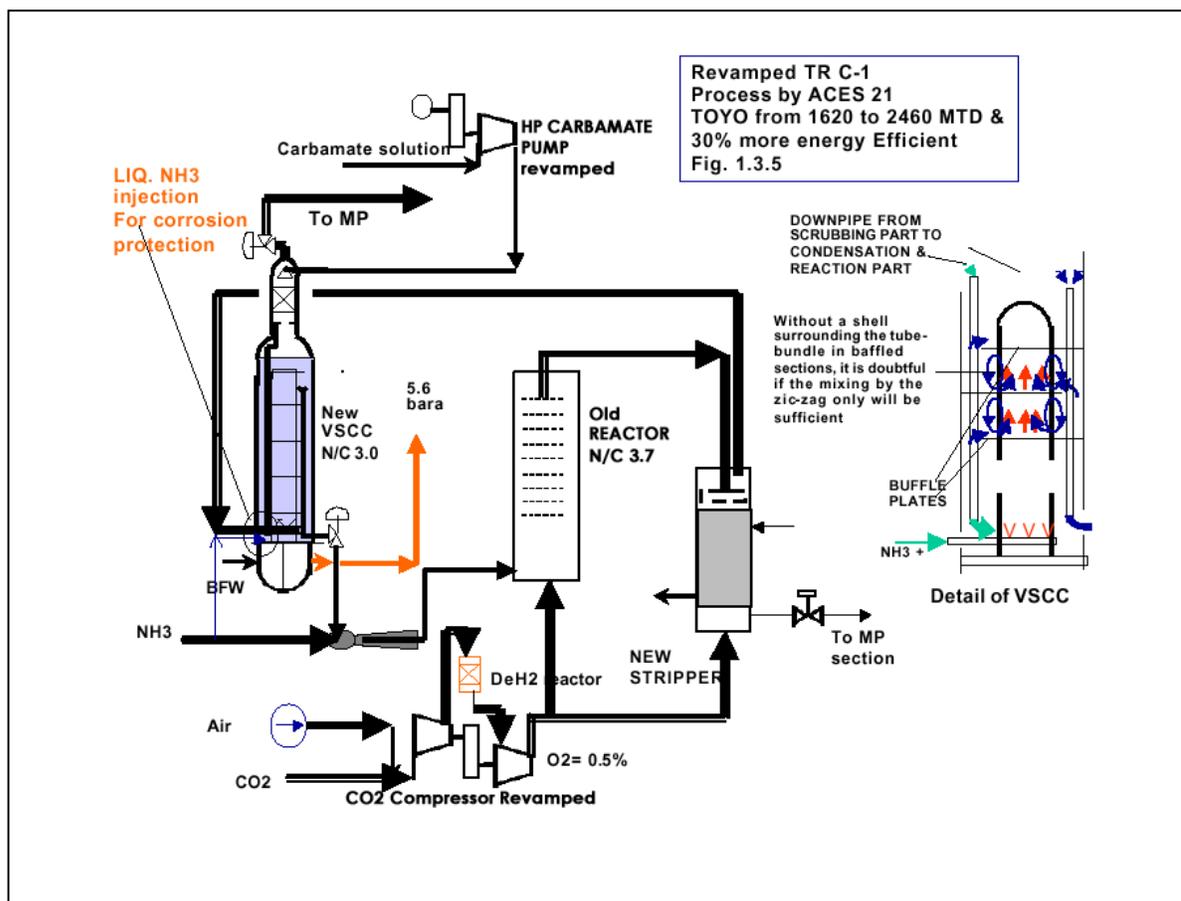
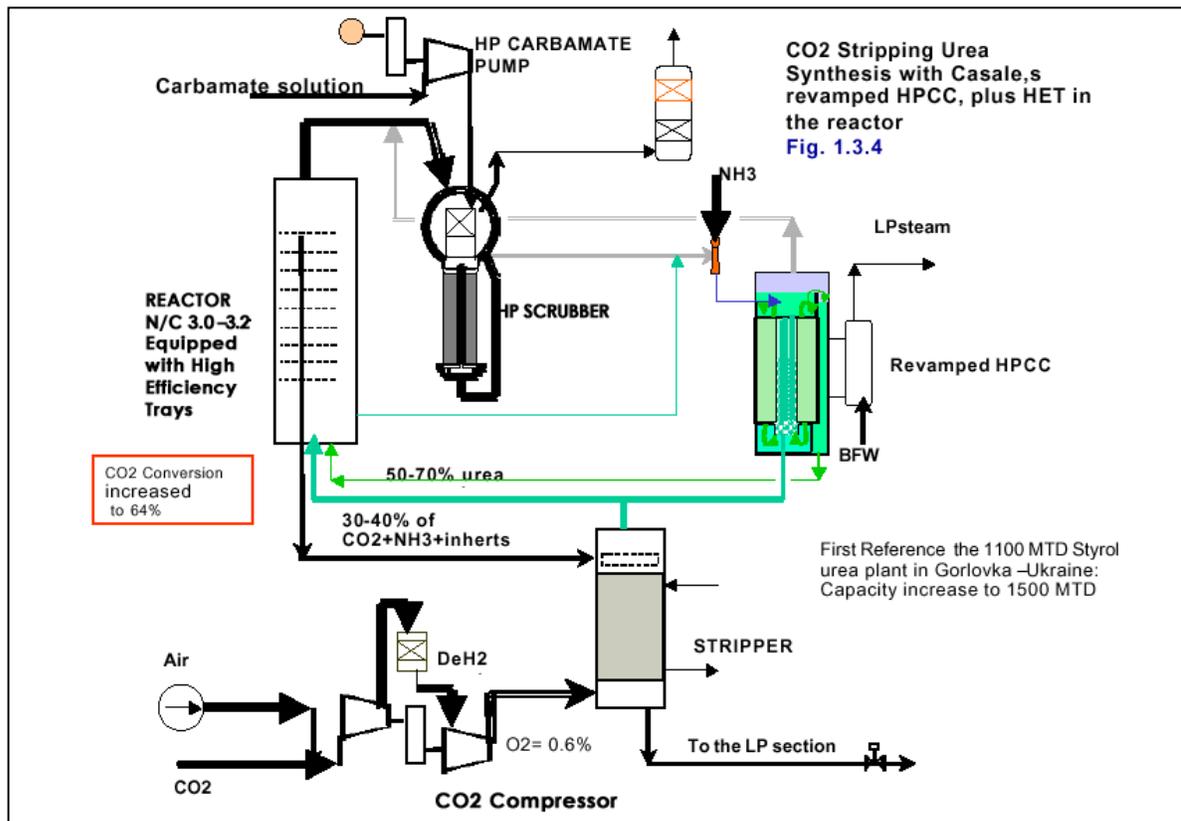


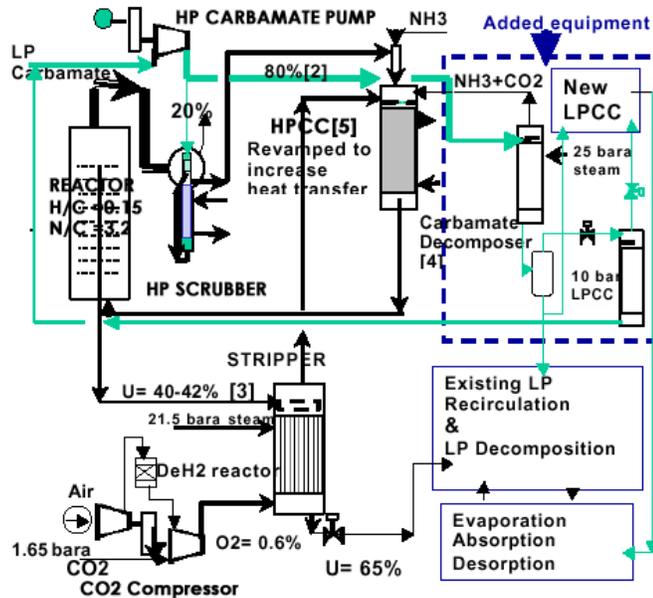


- HP Stripper is a short tube, self- stripping type decomposing 50% of carbamate. Specific 25 bar steam consumption only 0.3t/t. Tube load up to 135 kg
- Carbamate solution from existing H.P. Absorber cooler is recycled back to the new reactor
- Added evaporation and CO2 compression capacity
- 240 bar CO2 small capacity reciprocating compressor is a costly Item

Revamping a TR Plant by UC HEC Process. Capacity increase 1100 to 1500MTD Fig.1.3.2





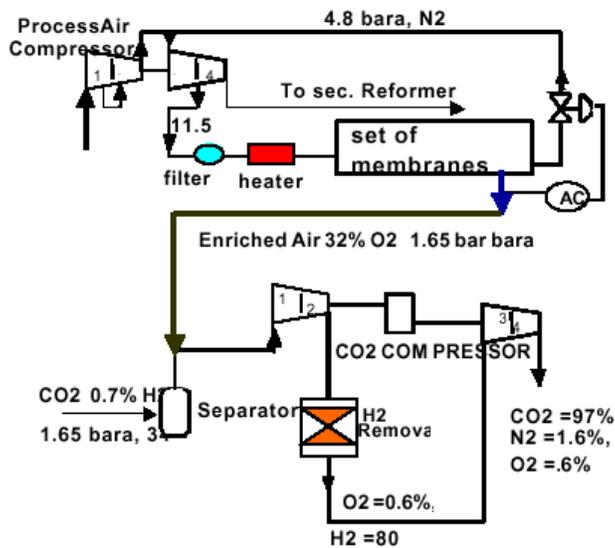


- [1] This concept has been applied in the Agrium's Carseland, Alberta, Canada and plant capacity has been increased from 1920 to 2350 MTD in 1997
- [2] Due to small percentage only of carbamate solution recycled back to reactor, H/C ratio is low (0.25%). CO2 conversion efficiency high, 66% as claimed by Casale and Agrium in the paper #4G (1998 AIChE Ammonia Safety Conference, Charleston, SC).
- [3] The low H/C ratio and the high urea content at the inlet of the stripper allowed to utilize the existing HP stripper and the existing HPCC, as well as the existing LP & evaporation section. Casale and Agrium claim that the system was very stable at high rates immediately after start up.
- [4] In the carbamate decomposer abnormally high corrosion rates have been observed (material 25/22/2) due to lack of dissolved oxygen in the carbamate solution to passivate the tube material operating under severe conditions. HP Air has to be injected. Improved corrosion resistance possible by use of Super duplex steel (min. 26.5% Cr)

Separate circulation of recycle water and recycle NH₃ and CO₂:

- Only NH₃ and CO₂ from recycled carbamate are sent to the synthesis section.
- Water is re-sent to back-end of the plant
- Quick elimination of water from plant start up and upsets

Revamped CO₂ Stripping Plant by UC's VRS process [1]
Fig. 1.3.6



The use of oxygen enriched air for passivation has several benefits:

- higher partial pressure of reactants, due to lower inerts, resulting in a higher urea conversion
- lower NH₃ & CO₂ vent losses via the HP scrubber
- lower recirculation flow
- less compression energy for inerts, giving higher CO₂ throughput
- the membrane system to produce oxygen enriched air is much more safe than the injection of pure oxygen, as any dangerous overdosing of oxygen is absolutely avoided
- Although Stamicarbon disapproves the use oxygen for air enrichment, a safety study conducted in the specific case concluded that the developed process is safe
- Prism separators have been used producing a permeate stream containing 32-40% mol oxygen at about 50% of the feed air rate.
- oxygen enriched air is produced at 40 C and 1.75 bara, directly introduced at CO₂ compressor suction
- the retentate stream containing 7-12% oxygen at a pressure of 4.8 bara is reinjected into the process air compression 3rd stage suction to balance the O₂/N₂ needed for the ammonia synthesis.

To eliminate the risk of Explosion, fully degassed NH₃ is used in the urea Synthesis and H₂ removal System monitoring has Been upgraded

Passivation by Oxygen Enriched Air in a CO₂ Stripping plant
Fig. 1.3.7

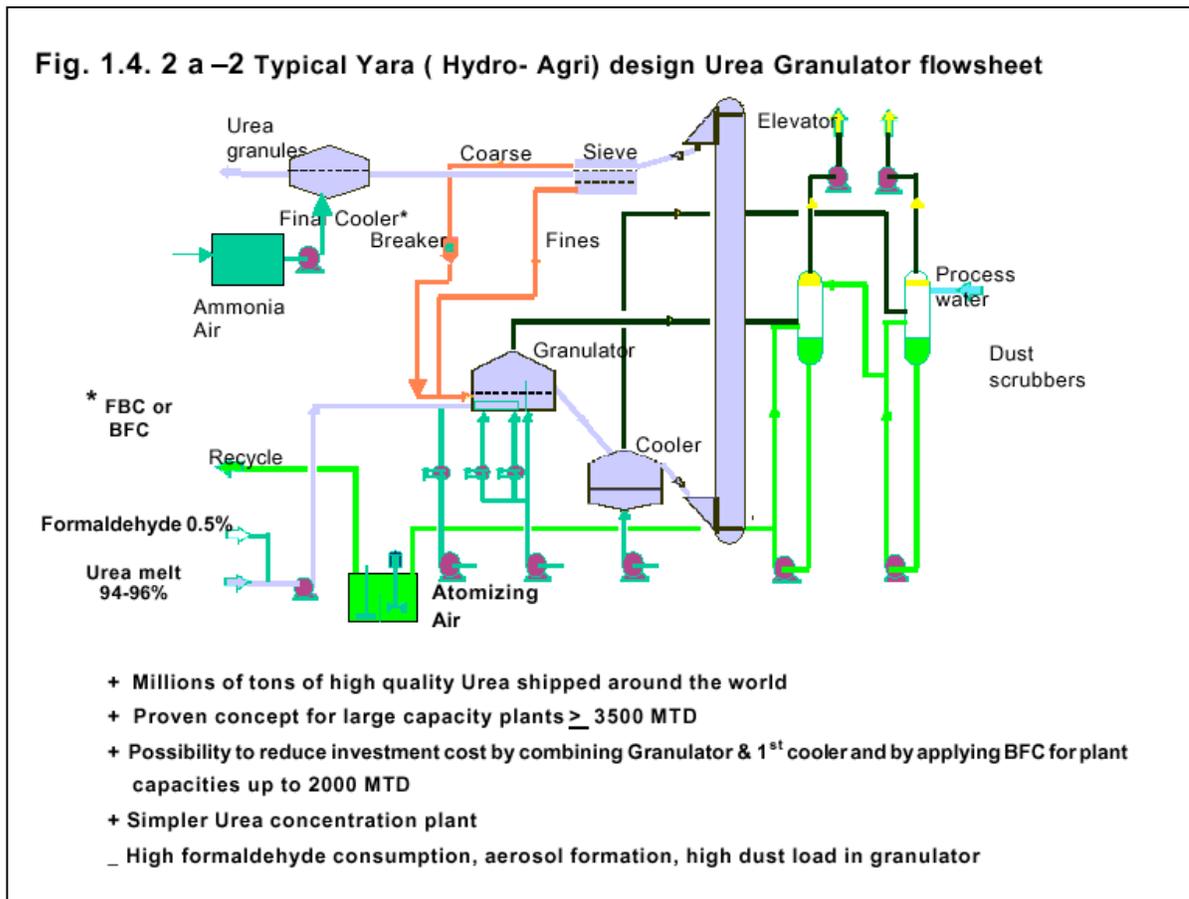
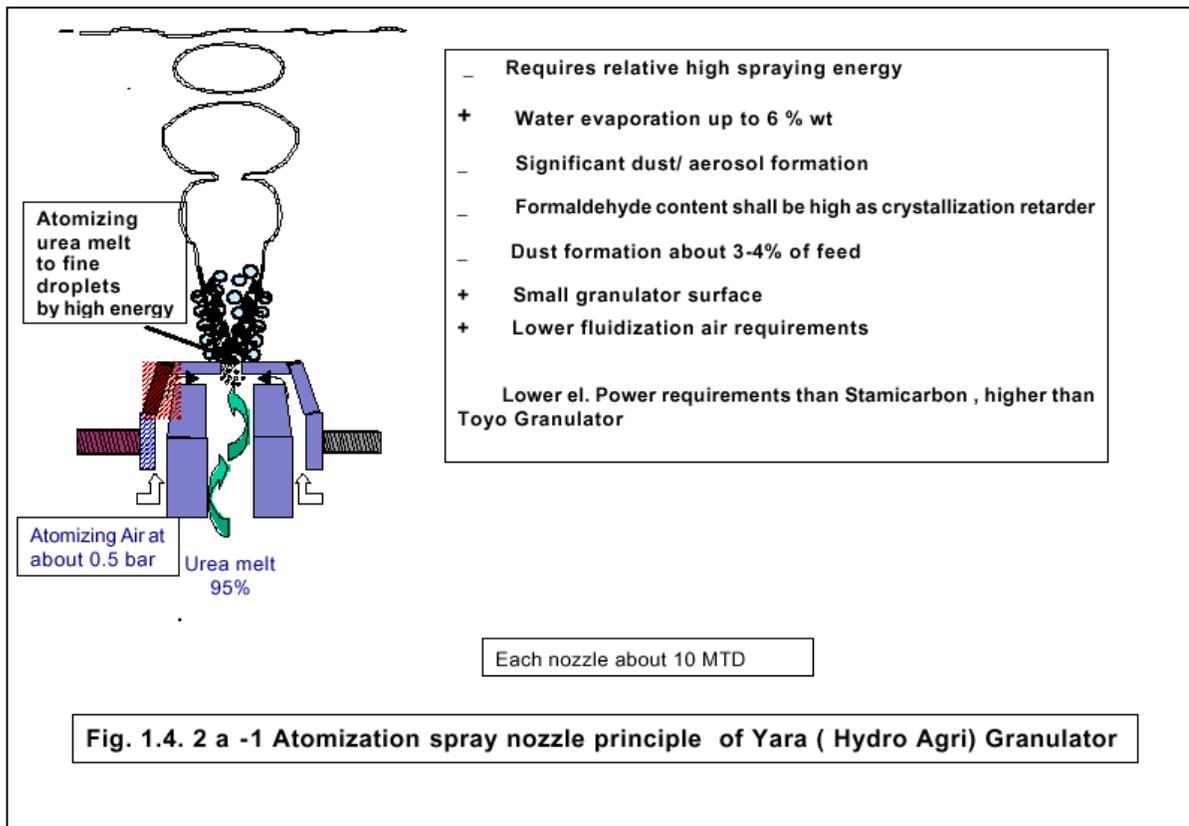
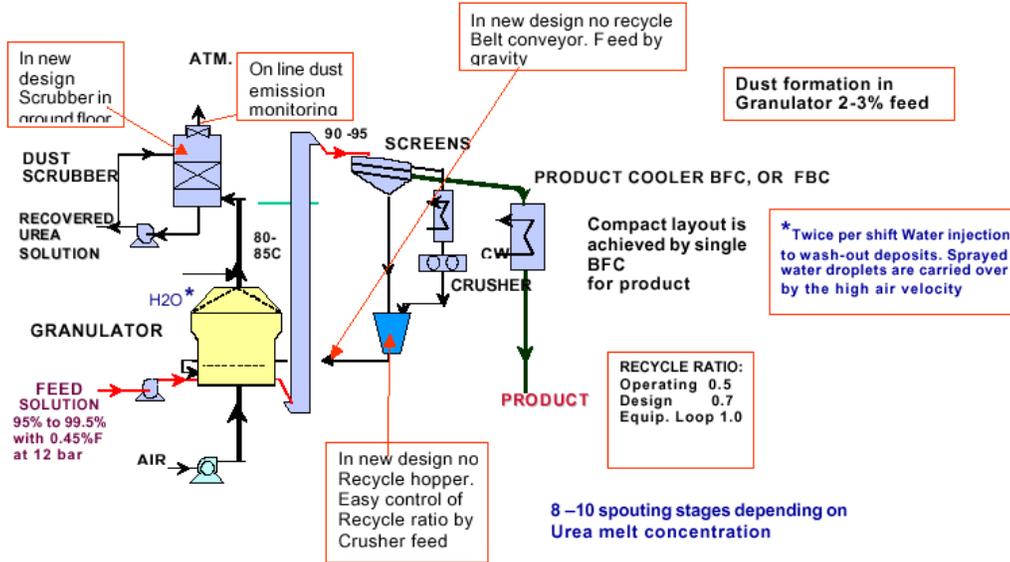
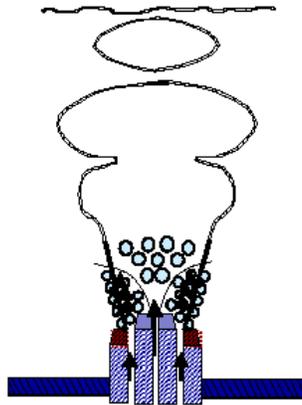


Fig. 1.4.2b -1 Toyo Advanced Urea Granulation Process



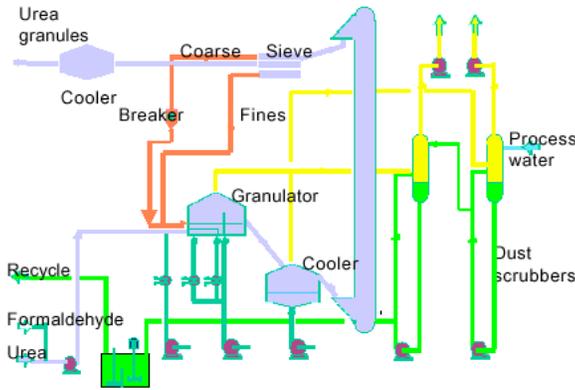
Toyo is using various urea melt concentrations from 96% to 99.5%
 Best performing reference the plant in Piesteritz with 99.5% urea melt. Urea melt by crystallization, otherwise biuret content 1.1-1.2%
 Up to 2000 MTD single scrubber with BFC type coolers for final product and oversize: compact plant, low investment -operating cost



Stable cone of liquid urea
 Grow in size by layering

- ± Spraying energy is low, but overall el. power high
- + Water evaporation 1.5% wt: low granule humidity,
- + Very little dust /aerosol generation: simple Scrubber design
- + Formaldehyde content is low < 0.3%. Less hygroscopic product !!!
- Limited References
- ± Dust formation 1.0-1.5% of feed, but ducting & scrubber big
- Small nozzle capacity (about 4.5 MTD each)
- High Dp perforated plate
- + No high pressure Atomizing air blower required

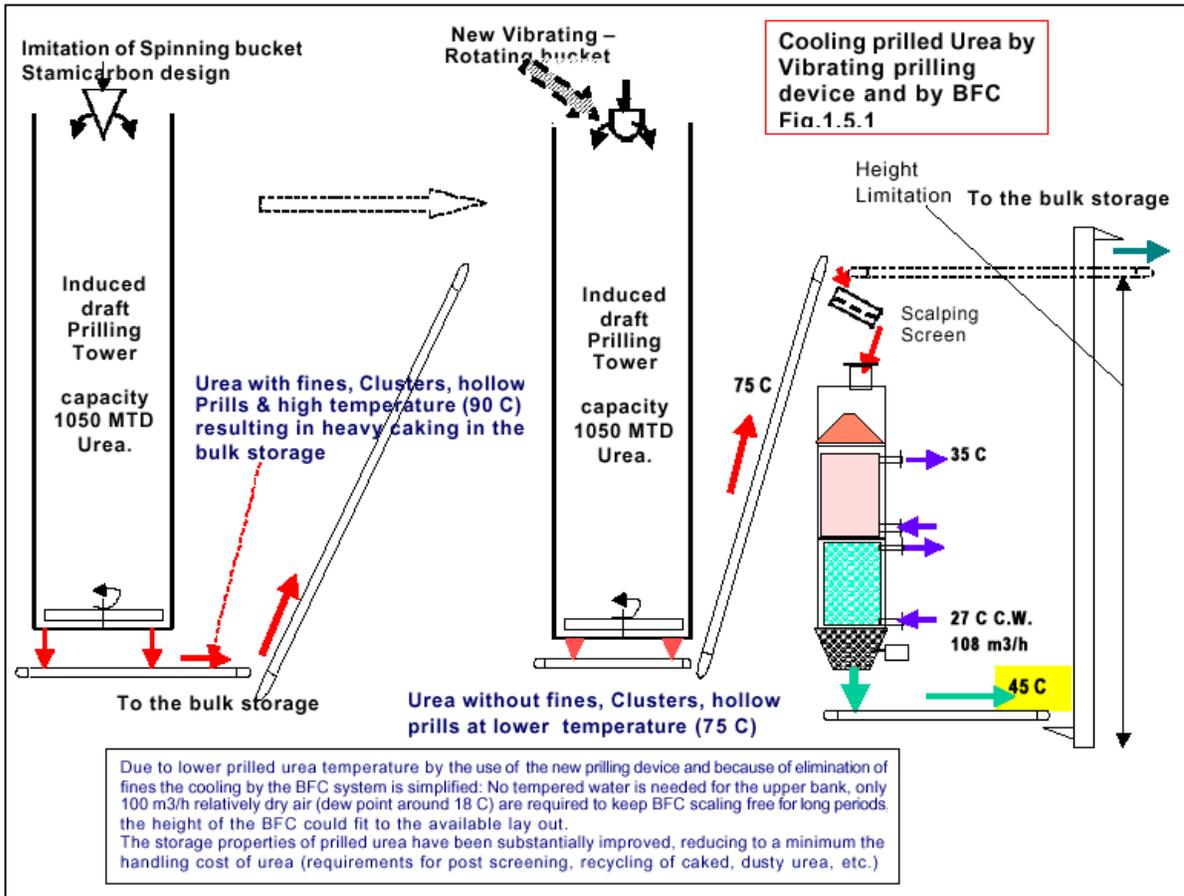
Fig. 1.4.2c-1 Stamicarbon's liquid film nozzle

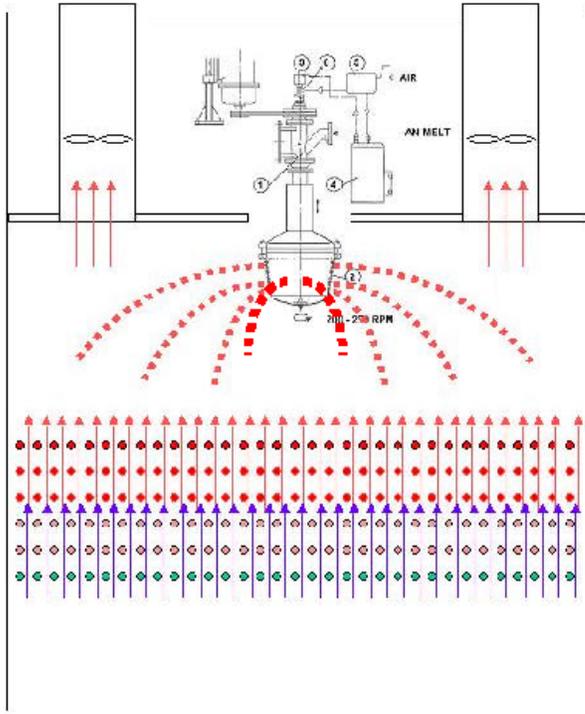


- Stamicarbon:**
- Higher investment cost, bigger plant size than Toyo and Hydro concept
 - Higher energy consumption than Hydro –Toyo concept
 - **Lower formaldehyde content: 0.25%**
 - Higher investment cost and higher energy consumption partly only off-set by low formaldehyde content (see table below)
 - **low dust /aerosol formation in granulator >>**
 - **Potential of design simplification by BFC as primary / final coolers, by lower Dp requirements in fluidization air, by simple design, low Dp scrubber**

Yara Granulation 2000 MTD	Stamicarbon Granulation 2000 MTD
Investment Cost Zero Basis	<u>Delta Investment cost:</u> • 1.3 mln \$ for additional final evaporator • 2.2 mln \$ for bigger granulation plant (Granulator, Scrubber, ducts, Blowers, Headers)
Operating Cost: Zero Basis	<u>Delta Operating cost:</u> • El. Energy 1.2 MWx50 \$x8000= +480000 \$ • Steam 15x10\$x8000= +1200000 \$ • Formaldehyde reduction by 60% - 1500000 \$

Fig. 1.4.2c-2 Operating / Investment cost comparison Yara / Stamicarbon design



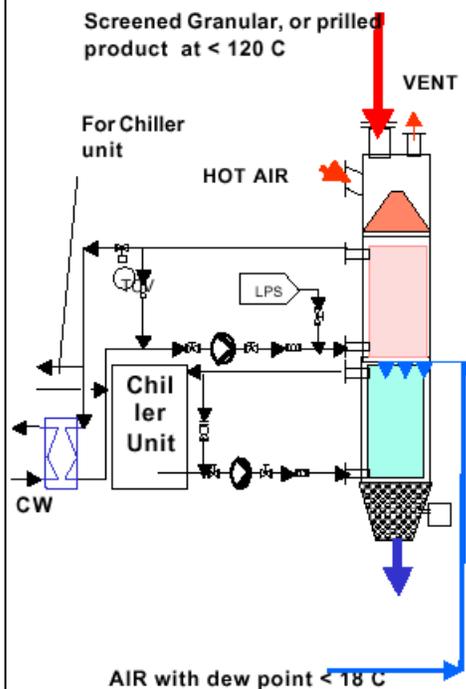


- almost calibrated prills
- less emission
- no fines, no dust
- no oversize, or clusters
- even prill distribution
- self cleaning >> long run
- better product cooling by 10 to 15 Centigrade:

Due to uniform distribution of prills in the entire Prilling Tower crosssection and because of the non formation of clusters & oversize, prills are cooled more efficiently.

The lack of fines and dust reduce the risk of scaling in the downstream BFC and so low cooling water temperature can be selected resulting in smaller size BFC

Fig. 1.5.2 Improved Prilling device

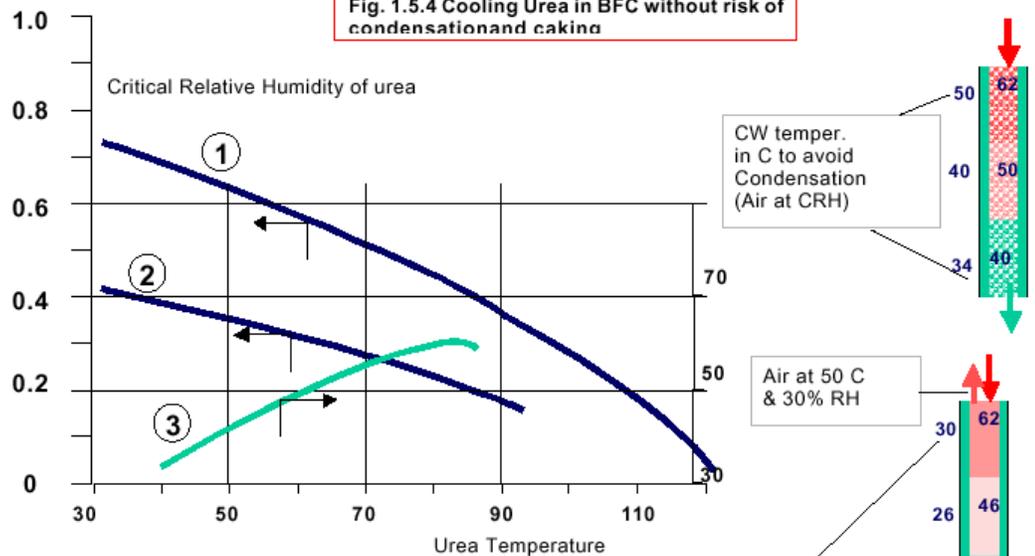


BFC to cool urea as primary or secondary cooler Fig.1.5.3

To avoid scaling, or fouling on plates, even for cases when, due to screens disoperation, or granulation upset conditions, a dusty product is fed to the BFC, the arrangement shown in the picture shall be considered:

1. Multibank cooler with top banks operating with tempered water to avoid condensation.
2. Preferably independent closed cooling circuits to be provided to be able to control water temperature and to avoid long term scaling /corrosion on water side
3. Provision of a sealing flow of hot air at the inlet hopper during humid days and after water washing of BFC
4. Provision of few 100 n3/h air of low dew point (<18C): to purge and to blow BFC during operation to keep air in RH lower than CRH and far from dew point.
5. Provision of LPS injection during start up to warm banks.
6. Provision of an efficient chiller unit (installed power 12-25 kW) to be used when CW temperature is above 24 C, or when final product temperature shall be < 40 C.

Fig. 1.5.4 Cooling Urea in BFC without risk of condensation and caking



- ① Prilled urea 0,2% F, 0,2% H2O
- ② Freshly granulated urea 0,55% F, 0,2% H2O
- ③ Min. Cooling water temperature in BFC plates to avoid Condensation when cooling prilled urea and with air surrounding

CW temper. in C.
 No Condensation! Result low cooling water temperature, smaller FBC, Lower investment—operating cost
 The effect is more attenuated in granular urea cooling.
 BFC as primary cooler in Stamicarbon Granulation process is less prone to scaling due to low Formaldehyde content (less hygroscopic)

Stream of low dew point (15-18C) air at 30 -35 C