

ADVANCED UREA CASALE

TECHNOLOGIES

FOR UREA PLANTS



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PART 1. **UREA CASALE PROFILE**

Urea Casale S.A. is a sister company of Ammonia Casale S.A., established in 1991 to carry on the **urea technology** activities started by Ammonia Casale S.A. in 1985.

It is well known that urea is one of the most important agricultural fertilizers. A large part of the ammonia produced in the world is transformed into urea in plants installed downstream to ammonia producing units. Activities in the urea field have, therefore, become a logical diversification for Ammonia Casale.

Since the beginning, efforts were mainly directly to the revamping of existing plants, with more than 60 plants being revamped since 1985.

Through its revamping activities and thanks to its capability of developing innovative technologies, Urea Casale was able to acquire a considerable share of the market. Today, about 24% of the world production of urea is made by using some part of Urea Casale technology.

Urea Casale has become, in a very short time, a leader in urea plant revamping, having its own technologies to upgrade all types of urea plants.

<u>TOTAL PLANTS</u>	<u>62</u>
NH ₃ Stripping	12
CO ₂ Stripping	37
Toyo	6
Weatherly	1
Vulcan	1
Various	5

**Urea Casale Plant Upgrading
between ,’85 and ‘01**

Capacity increase, energy consumption, corrosion control, pollution abatement and product quality are the key areas for upgrading plant performance.

Several urea-producing reactors have been modernized by installing Casale High Efficiency Trays (HET) with the result of increasing conversion and consequently also plant capacity with a reduction of specific energy consumption.

Several urea plants are operating according to the Casale HEC and VRS processes after their capacity was increased by 50% or more.

Like its mother company Ammonia Casale, the main strength of Urea Casale lies in licensing its technologies. Most of the technologies are, therefore, developed in-house by a team of very specialized and experienced people.

Following the trend set by Ammonia Casale, Urea Casale invested and is still significantly investing in technology development.

Since the very beginning, Urea Casale has also put a lot of effort into developing the right process design tools, process design is now supported by sound insight into the chemistry of the processes, kinetic data, heat and mass transfer phenomena, fluid mechanics, science of construction materials, and cost analysis.

Urea Casale technical Services avail themselves of specialists in all the above fields, and of sophisticated tools for investigating, analyzing and picturing complex phenomena in a way unachievable with skilled manual calculations, including such tools as computer-aided techniques with applications ranging from chemical process design to fluid dynamics evaluations and mechanical stress analysis.

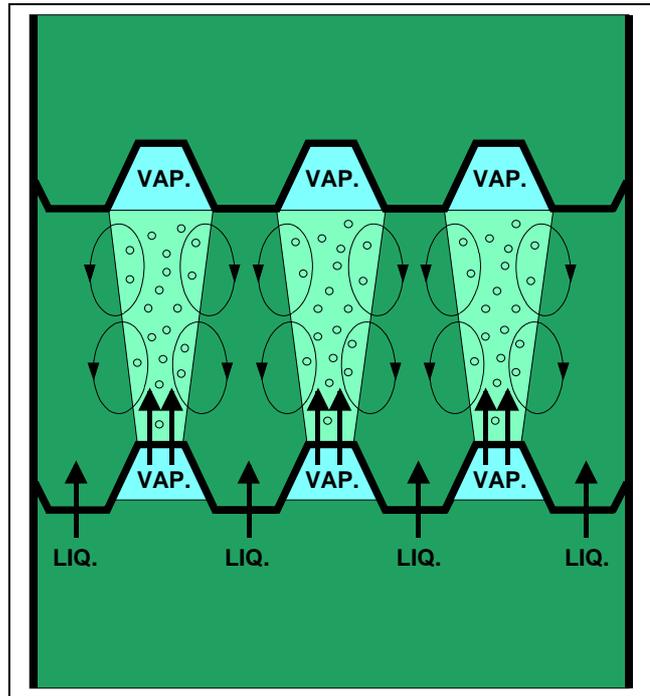


Fig. 1- Urea Casale High Efficiency Trays

In addition to the technology, Urea Casale can also provide all services required for the completion of a project, from engineering right down to construction, start-up and operation of the plant.

The world has changed a lot since the industrial pioneers started out on their paths. New problems are at the forefront and press us for solutions; new needs urge to be fulfilled, often dramatically, such as the quest for a more efficient and environmental-conscious use of natural resources.

Urea Casale has taken up the same spirit of commitment to excellence and achievement as Ammonia Casale and its founders, and offers to the world the most advanced state-of-the-art technology and expertise.

PART 2. **UREA PLANT REVAMPING**

A urea plant revamp can touch different areas and is, generally, aimed to improve the performance of an existing plant.

One can identify the following main goals, which can drive a urea plant revamping project:

- increase plant capacity
- reduce energy consumption
- reduce NH₃ consumption
- reduce emissions to the environment (pollution control)
- increase product quality
- increase corrosion control

In the next sections, an overview is given of the technologies that have been developed by Urea Casale for revamping urea plants in the most efficient way in order to reach one or a combination of the above mentioned goals.

The description will first touch what can be reached with the Casale technologies, and then it will describe with some details these technologies and their industrial applications.

With the application of the above technologies, a wide experience has been acquired by the company in the modernisation of urea plants designed according to different technologies, including TEC Total Recycle, Stamicarbon conventional and CO₂ Stripping, Snamprogetti NH₃ Stripping and other technologies.

The competitiveness and the success of Urea Casale revamping technologies is proven by the fact that, in the last ten years, more than 50 urea plants, with capacities ranging from 250 to 2400 MTD, have been or are being revamped utilising these technologies. Of these plants, 70% were originally designed according to stripping technologies.

As an independent company, Urea Casale S.A. disposes of its own technology as well as third party technology to combine optimised schemes that best fit with project requirements.

PART 2.1.

UREA PLANT REVAMPING: WHAT CAN BE ACHIEVED

Thanks to a team of very skilful people, most of them with a long experience in the urea field, Urea Casale developed several innovative and very competitive technologies to revamp urea plants to achieve:

- large capacity increases
- energy saving
- pollution control
- improvement in plant reliability

Among these technologies we have:

- new reactor trays to reduce steam consumption and increase capacity.
- new urea production processes (HEC, VRS) for drastic capacity increase

Casale has identified the following main classes of revamping that can be made using its technologies:

- reduction of energy consumption
- small to moderate capacity increase, and in some cases up to 30÷35%
- large capacity increase, that means normally up to 50% or more
- pollution control reducing the emissions from the plant

All that concerns plant reliability and special maintenance for critical equipment involves the Urea Casale know-how in the urea field, but not any particular technology.

Urea Casale can supply also this type of revamping, but this presentation will not touch upon this part, that is a more a case-by-case approach.

For each class of revamping, Casale applies its own technologies as follows:

- **High Efficiency Trays (HET)** and **H₂O₂ Passivation System** for small to moderate capacity increase and energy saving for which it is important to achieve an increase in the synthesis section keeping the investment low.

With the HET and the H₂O₂ Passivation System alone it is possible to reduce the energy consumption of practically any urea plant (conventional total recycle and stripping of any designers) with very low investment.

If a small to moderate capacity increase is required, in addition to the HET and the H₂O₂ Passivation System some more modifications are required limited to the non-HP equipment.

In this way the capacity of any urea plant (conventional total recycle and stripping of any designers) can be increased by 15÷20% (and in some cases by 30÷25%) with a relatively low investment.

- **Vapour Recycle System (VRS)**, in combination with the HET, for large capacity increase in stripping plants.

With the VRS it is possible to obtain very big increases in the efficiency of the synthesis section allowing a debottleneck of the plant to increase the capacity by 50%.

The additional equipment required is kept to a minimum but the addition of HP equipment is required. All kinds of stripping plants can be revamped with the VRS.

- **HEC Process**, in combination with the HET, for large capacity increases in conventional total recycle plants.

Like the VRS, a drastic increase in the synthesis section can be obtained, and this is the key point to reach the large capacity increases with only a minimum number of additional pieces of HP equipment.

All kinds of conventional total recycle plants can be revamped with the HEC obtaining capacity increase of 50% or more.

- **High Efficiency Hydrolyser and Urea Recovery System** for pollution control reducing the emission from the plant.

The application of the above technologies is always tailor-made to the actual plant configuration and to the different client requests.

All the equipment in the plant is checked in the new conditions and the necessary modifications are suggested.

If required, third parties technologies for the revamping of the finishing section are used and the best way to revamp the machinery is identified together with the original manufacturer.

PART 2.2

SMALL/MODERATE CAPACITY INCREASE AND ENERGY SAVING: CASALE HIGH EFFICIENCY TRAYS AND H₂O PASSIVATION SYSTEM

The starting point for any Casale urea plant revamping project aiming at increasing the plant capacity, and/or at decreasing the steam consumption, is the installation of Casale High Efficiency Trays (HET) in the reactor (see description in the following sections).

In fact, this new type of reactor tray significantly increases the CO₂ conversion (4 to 5 percentage points) reducing the specific amount of steam required to recycle back the unreacted CO₂.

This allows, for the stripping plants, to reduce the specific load of the equipment in the HP loop, and, for the total recycle plants, to reduce the specific load of most of the equipment in the plant.

If the required capacity increase is not too high, it is, therefore, enough to install the HET to de-bottleneck the HP section, eliminating the need for additional HP equipment and thus maximising the capacity increase with minimum investment.

It is, in fact, very important to avoid, for small capacity increase projects, any change in the HP section, which would drastically increase the return time of the investment.

Through a complete check of the downstream section, the few changes /additions necessary to eliminate the bottlenecks that would still be present after HET installation are determined.

With this approach, i.e. installation of HET and few changes/additions in the downstream section, an increase in capacity up to 30÷35% can be obtained.

This approach can be applied for both CO₂ and NH₃ stripping plants and for conventional total recycle plants.

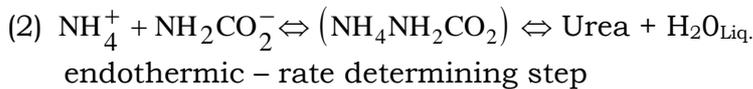
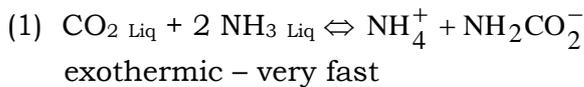
For such plants that are operating with high amount of oxygen for passivation, the H₂O₂ passivation system is also suggested (see description in the following sections). This system replaces most of the passivation oxygen with H₂O₂ reducing in this way also most the inerts introduced with the oxygen. This system helps to increase the reactor efficiency further, reducing the necessary changes/addition to the existing plant.

In case only a reduction of specific steam consumption is required, the installation of HET alone is suggested.

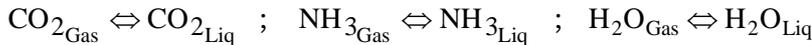
Urea Casale High Efficiency Trays

Urea synthesis reactor is a vapour-liquid heterogeneous reaction system. All along the reactor both the vapour phase (containing free CO₂, NH₃, some water and inerts) and the liquid phase (containing NH₃, ammonium carbamate, bicarbonate, urea and water) are present. The reactants are progressively transferred from the vapour to the liquid phase, where CO₂ reacts with NH₃, producing carbamate and then urea and water with a continuous exchange of CO₂ and NH₃ between the two phases.

Urea is produced into the liquid phase according to the following reversible main chemical reactions:



Since the reacting system is heterogeneous, one has to consider also the following vapour-liquid phase equilibria that are established at the vapour-liquid interface:



In such a heterogeneous reaction system, like the one for the formation of urea, we can identify three regions shown in Figure 2:

- the vapour present in the bubbles that can rise up the reactor in columns or in intermittent swarms
- the liquid emulsion, which is the liquid region through which the bubbles are flowing
- the clear liquid, which is the liquid region outside the liquid emulsion

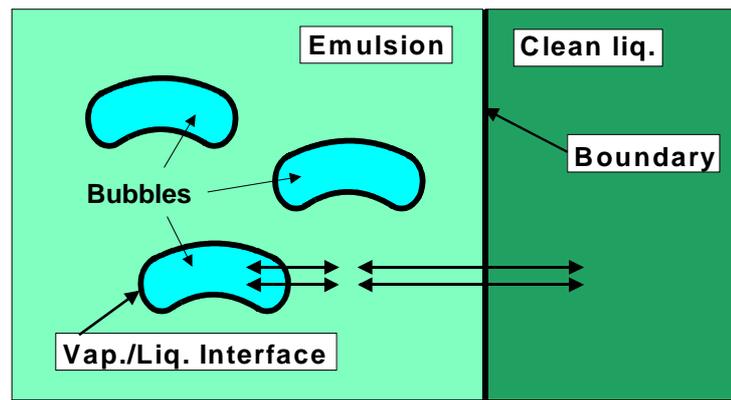


Fig. 2 – Regions in Urea Reacting System

We can also identify the global reaction rate for the formation of urea as being the sequence of the following steps:

- mass transfer from the bulk of the bubble to the vapour-liquid interface (through the vapour-liquid interface area)
- formation of carbamate (and heat) at the vapour-liquid interface
- mass and heat transfer from the vapour-liquid interface to the bulk of the emulsion
- transfer from the bulk of the emulsion to the bulk of the clear liquid (through the emulsion-clear liquid boundary)
- formation of urea from carbamate in both the clear liquid and emulsion

(It is very important to have a good transfer of mass and heat, otherwise local concentration of carbamate and heat, especially at the vapor-liquid interface, would tend to slow down the formation of carbamate and urea).

Looking at the above steps, it becomes clear that the formation of urea is not only controlled by the chemical kinetics and thermodynamics, but also by factors that affect the physical elementary processes, i.e.:

- mass and heat transfer coefficients
- fluid-dynamics and flow patterns of the two phases
- interface areas between vapor and liquid and boundary areas between the emulsion and the clean liquid
- average distance between the bulk of the emulsion and the bulk of the clear liquid
- total recirculated flowrates

Most of the above factors are influenced by the geometry of reactor vessel and its internals (i.e. trays).

A significant part of the total residence time into the reactor is, therefore, justified by the necessity to reach the maximum amount, compatible with the operating conditions, of vapours transported into the liquid phase. The optimum conversion to urea, in fact, could be obtained only on the basis of that condition.

On the basis of the general concepts exposed above, it can be deduced that a majority of the existing urea reactors cannot reach the complete equilibrium, as there is strong evidence that an excess of vapours containing CO_2 and NH_3 are still present at reactor outlet.

Casale, together with Prof. Dente, has supposed that in the design of urea reactors, the fluid-dynamics and transport phenomena aspects could have been, in the past, underestimated (or even neglected). The supposition has also a very macroscopic self-commenting proof: the experimental liquid temperature profile in any existing type of reactor is always monotonically increasing from the bottom to the top of the reactor. On the contrary, if the mass and produced heat transfer of the reactants into the liquid phase would be a process extremely faster than the chemical reaction (as was a diffused opinion in the field), then, considering that the carbamate formation is very exothermic, whilst the dehydration of carbamate to urea is endothermic, a maximum of the temperature near the reactor inlet would have to be observed (and then, hypothetically, the temperature should decrease up to reactor top).

Looking at the standard type of trays present in urea reactors, two main types of reactor trays are presently in use (See the figures 3 and 4), each one characterised by a different geometrical configuration and consequently by a different behaviour:

- **Type A:**

Under each tray the vapours and the liquid are separated; the liquid is then forced to go through the outer annular space between the tray

edge and the reactor inner wall while the vapours are forming a column of bubbles. The clean liquid is generating big eddies. The exchange between the liquid and the vapour, however, is not optimal for the following reasons:

- the transport among clean liquid and the continuous column bubbles can take place, is limited by the extension of its boundary surface
- especially in large reactors, the length of the streamlines path into the emulsion region, is very large, so increasing the transport resistance
- part of the liquid crossing the external annular space may by-pass to the next tray without having being thoroughly mixed with the emulsion phase
- the velocity in the streamlines of the eddies crossing the internal part of the emulsion can be very low causing low convective transport efficiency and the bigger the eddy, the larger the low velocity region is.

- **Type B:**

In this case, the simultaneous passage of gas and liquid through the holes is impossible. The cocurrent gas/liquid flow through the tray holes becomes intermittent; a certain layer of gas builds up below the tray deck, releasing a large swarm of bubbles which is then followed by a continuous slug of liquid flow until the gas build-up releases the next swarm.

Also in this case, the mixing between the liquid and the vapours is not optimal as :

- the bubbles are quite large and can coalesce into larger ones well before reaching the next tray, so further reducing the gas-liquid interface
- the swarms of bubbles substantially remain segregated from the liquid phase, and so recirculation cannot take place into them.

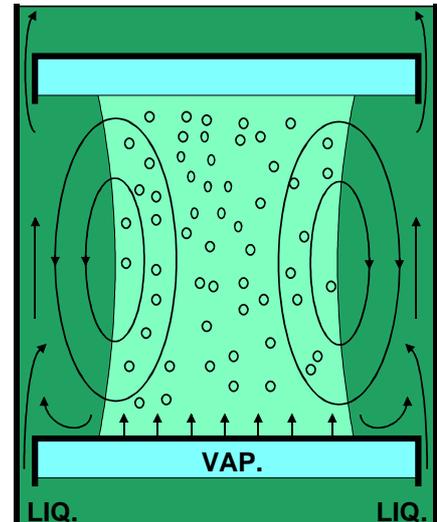


Fig. 3. – Standard type of Reactor Tray – Type A

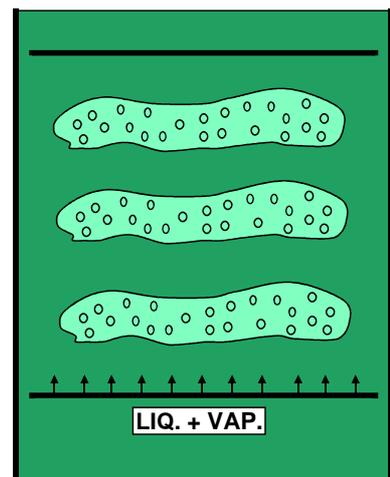


Fig. 4. – Standard type of Reactor Tray – Type B

The new trays are, in fact, designed so that:

- Separate and distributed paths through the tray are provided. They guarantee a steady state flow of the two phases and better approach an even uniform flow of the two phases throughout the whole reactor.
- These separated paths through the tray are chosen so that a very high mixing efficiency between vapour and liquid is obtained. Consequently a very high mass and heat transport within the liquid phase is realised.
- With an appropriate design, the diameter of the generated vapour bubbles is smaller than in any previous design. By consequence, the interfacial surface, for mass and heat transfer, is increased.
- A much larger surface of exchange between emulsion and clean liquid is created.
- The quite shorter path length of recirculation streamlines into the emulsion phase significantly decreases the transport resistances.

The trays are made up by several inverted U beams with large perforations for liquid passage on the bottom wings, and small perforations for gas passage on the sloping and top sections. With this unique design, very small bubbles are generated, and by consequence, very high specific surface for the mass and heat transfer is obtained. This advantage is combined with a very high efficiency in the mixing between vapours and liquid.

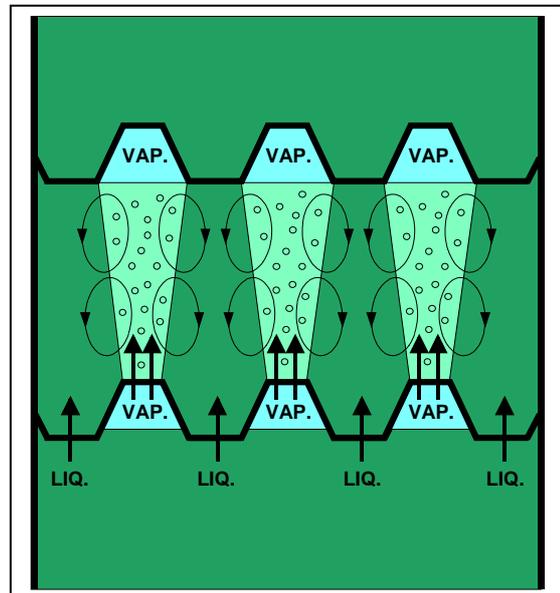


Fig. 7. – Casale-Dente High Efficiency Trays

H₂O₂ Passivation System

The stainless steel equipment of urea plants is protected from corrosion by a thin, compact layer of chromium oxide. In order to form and maintain this layer a small amount of air is added to the CO₂ feed. The use of air as oxidiser is effective, but presents some disadvantages, such as the introduction in the reactor of a large amount of inert nitrogen and the possibility of forming explosive mixtures upon mixing the residual oxygen with the hydrogen carried into the plant as impurity by the reactants.

A few years ago a different technique was successfully tested in industrial plants, in which most of the air is substituted by a cheap and safe liquid oxidiser, hydrogen peroxide.

CASALE found out that the above technique could be applied advantageously to the processes using a lot of oxygen for passivation, like the CO₂ stripping processes.

The System provides considerable protection of critical equipment, such as stripper, carbamate condenser and inerts scrubber, limiting the use of air to an amount of 2,000 p.p.m. O₂ on the CO₂ feed.

This is thanks to the combined action of air and H₂O₂ water solution, which is added upstream the equipment to be protected.

The figure 8 shows how the H₂O₂ passivation system applied to a CO₂ stripping plant.

The quantity of H₂O₂ as 100% to be used is in the order of 0.1 kg/MT urea.

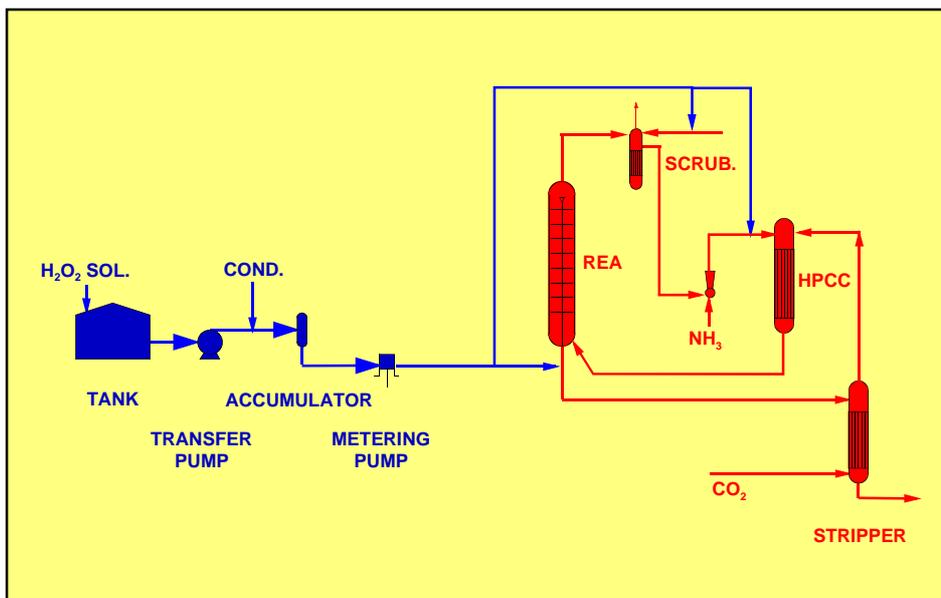


Fig. 8 - H₂O₂ Passivation System Applied to a CO₂ Stripping Plant

Industrial Experience

In the last three years a total of thirty-four (35) projects involving installation of HET have been carried out or are under completion for plants having capacities ranging from 250 to 2100 MTD. Thirty one (31) plants are already successfully operating with Casale HET obtaining increases in conversion up to 5÷6 percentage points and reductions of specific steam consumption up to 200÷250 kg/MT.

Of the total, nine (9) projects are in connection with moderate and large capacity increase projects, while the rest are in connection with energy reduction or small capacity increase projects.

Three major projects have been carried out :

- Togliatti - Russia : two 1500 MTD production lines originally designed according the NH₃ stripping process have been revamped increasing the capacity by 17 %. The installation of HET together with the modification of the CO₂ compressor (new internals) were the only modifications carried out to reach the new capacity. A significant reduction of the steam consumption was obtained.
- Yunnan - China : one 1630 MTD production line originally designed according the CO₂ stripping process was revamped increasing the capacity by 15 %. The only changes necessary to reach the increase in capacity were the installation of the HET and of the URS and the modification to the CO₂ compression system. The steam consumption has been reduced by 150 MTD.
- Arcadian - Trinidad : two 1700 MTD production lines originally designed according the NH₃ stripping process were revamped increasing the capacity by 9 %. In this case the sole installation of HET was necessary to reach the required capacity. The steam consumption was reduced by 180 kg/MT.
- Stirol - Ukraine: one 1000 MTD production line originally designed according to the CO₂ stripping process was revamped increasing the capacity by 35%. In addition to the HET, a few modifications were required in the LP and vacuum sections and to the existing HP pumps (some new internals) in order to reach the new capacity. A new prilling bucket and a refurbished CO₂ compressor have also been supplied.

PART 2.3

LARGE CAPACITY INCREASE STRIPPING PLANTS: **CASALE VRS CONCEPT**

If the required capacity increase were too high, the addition of the HET alone would not be enough to avoid the need for modification in the HP equipment. In fact, due to the overly high decrease in the residence time in the reactor, its efficiency will not increase, if not even decrease, even with the HET.

In this case, Urea Casale proposes different approaches with an even more drastic upgrade of the synthesis section which could guarantee to minimise the addition of HP equipment, and by consequence, the investment as well.

For this purpose, a new technology has been developed for the revamping of stripping plants, namely the Vapour Recycle (VRS) which is described herebelow.

As it is well known, in all "total recycle stripping" urea production plants, the residuals NH_3 and CO_2 at the H.P. loop outlet are recycled to the loop itself, after being separated from urea in the decomposition and finishing sections, in the form of carbamate aqueous solution. Water is, in fact, the essential carrier of such substances (in some cases, part of the NH_3 is also recycled in the form of pure liquid NH_3).

This recycled water is evidenced by the fact that the $\text{H}_2\text{O}/\text{CO}_2$ molar ratio at reactor inlet is higher than zero (generally in the range of 0.5 to 0.8).

The recycle of the H_2O heavily affects all the process phases, namely, the higher the amount of H_2O :

- the lower the conversion in the reactor is
- the lower the decomposers (i.e. stripper, M.P. and L.P. decomposer) performance is
- the higher the quantity of H_2O to be treated is.

Our new VRS concept foresees a separate circulation of recycle water and recycle NH_3 and CO_2 , i.e.:

- The carbamate solution obtained in the downstream process sections instead of being sent the H.P. section, is distilled in an H.P. decomposer working in parallel to the existing stripper.
- The vapours thus obtained (containing NH_3 , CO_2 , and little water) are sent to the H.P. Section (H.P. Carbamate Condenser), while the distilled solution (enriched in water) is sent back to the back-end of the plant.

In this way, practically only the NH_3 and CO_2 contained in the carbamate are sent back to the synthesis section, while the water is almost totally sent back to the recycling and waste water treatment sections.

As a consequence, the H.P. synthesis loop will operate with very low water content with the following advantages:

- very high CO₂ conversion is obtained in the reactor (up to 70%)
- very high stripping efficiency
- lower amount of water to be treated in the existing decomposition, vacuum evaporation and waste water treatment sections.

Revamping of Stripping Plants with VRS

The existing plant is modified according to the VRS concept adding a new decomposition section in parallel to the existing plant.

The HP carbamate is sent to the new section where it is decomposed.

The released vapours, rich in NH₃ and CO₂, are sent to the synthesis section, while the purified solution is sent back to the back-end of the plant.

As the existing reactor will be working with a low water content (H₂O/CO₂ molar ratio of 0.2 ÷ 0.25), a high CO₂ conversion is obtained (66 ÷ 70%).

The figures 9 and 10 respectively show the CO₂ and NH₃ stripping plants revamped according to the VRS concept.

Due to the fact that, in the existing plant, the new conversion is much higher and the water content much lower than the ones before the modification, the existing plant can, again, be re-utilised at higher capacity with only minor modification.

Casale, however, studies the behaviour of all the existing equipment in the new operating conditions and determines the minor changes necessary. A detailed check of all the instrumentation and piping is also done.

With this approach, an increase in capacity up to 50 ÷ 60 % can be obtained.

After revamping, the following consumptions can be obtained :

- raw materials almost stoichiometric
- MP steam ab. 800 kg/MT.

(The above values are based on actual experience and studies performed and can vary depending on the capacity increase required).

One of the big advantages of the approach just described is that the required additional section can be installed while the plant is still running, and just a few tie-ins are necessary to interconnect them with the existing plant minimising in this way the shut down time for the modification.

Furthermore, the solutions generated by plant upsets or shutdown can be recovered very quickly.

The VRS concept offers also big advantages when the urea plant has to treat the off-gases from a melamine plant. The increase in water caused by the integration between the melamine and urea plant can be eliminated by the VRS without causing decrease of efficiency of the synthesis section.

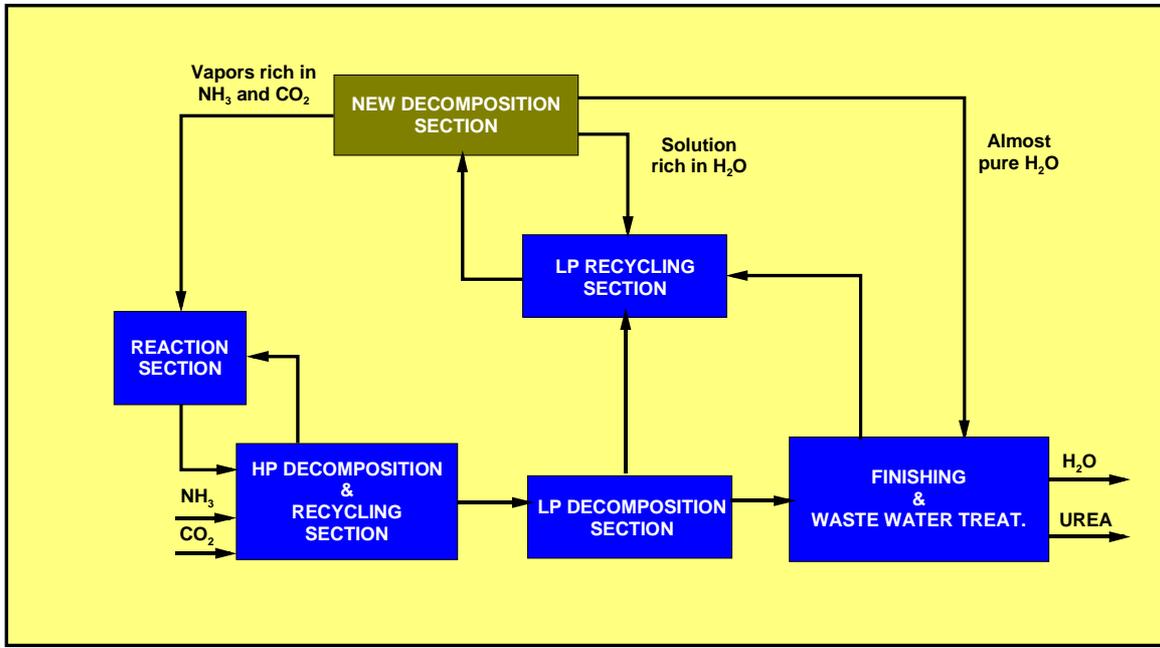


Fig. 9 - CO₂ stripping plant revamped according the VRS concept

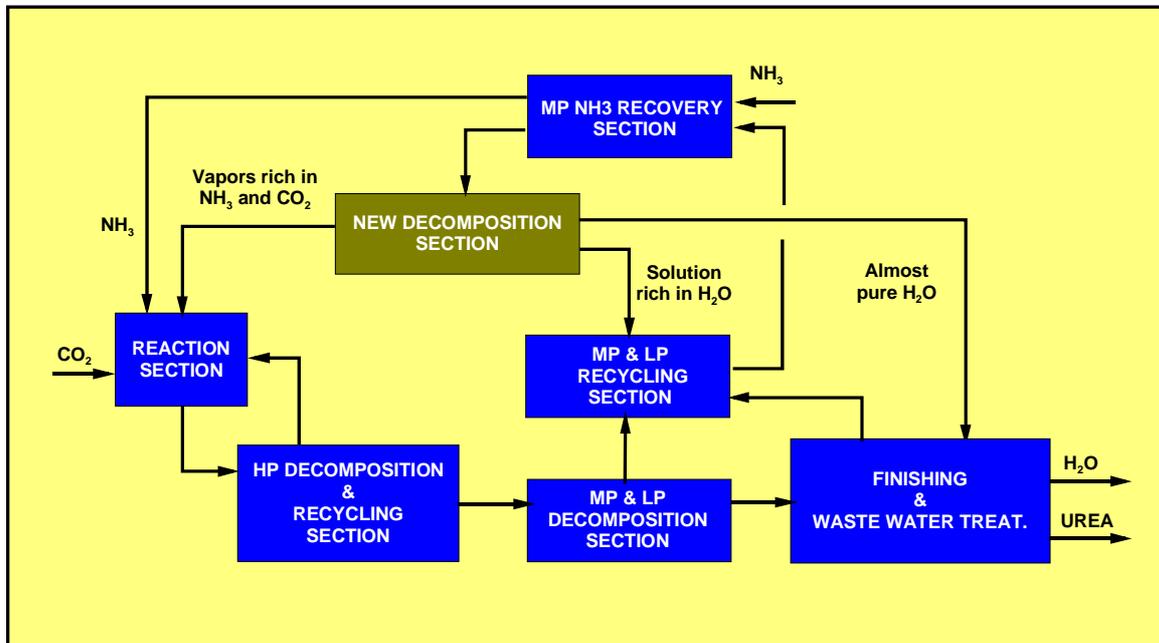


Fig. 10 - Stripping Plant Revamped according the VRS Concept

From 1900 MTD to 2400 MTD with VRS for CO₂ Stripping Plant

Agrium's Carseland, Alberta, Canada, Nitrogen Operations were commissioned in 1977. The Operation included a 1,043 mt/d Kellogg Ammonia Plant and a 1,350 mt/d Stamicarbon Urea Plant plus the design was such that was a zero discharge of effluent water to any water course. All process waters were either irrigated or evaporated on site.

Over the years, the Urea and Ammonia Plants had been expanded to produce 1,250 mt/d Ammonia and 1,825 mt/d Urea. It was decided to look at what the maximum that the Ammonia Plant could be deployed to and match that to an increase in the Urea capacity. Indications were that we could take the Ammonia plant to 1,600 mt/d and the Urea to 2,350 mt/d.

Several methods of expansion were evaluated and in the Urea Plant, Carseland chose to use a novel approach referred to by Urea Casale as the "Vapour Recycle System (VRS)".

Casale proposed its VRS concept in order to fulfil all the requirements in the most economical way. With this concept it was, for instance, possible to avoid any addition of reaction volume and practically no other modifications to the existing plant were needed other than the addition of a couple of vacuum condensers, some surface to the second vacuum evaporator and few trays in the desorber.

The VRS concept was applied adding a kit to the existing plant consisting of:

- a new HP decomposer
- a new LP decomposer
- a new MP separator and condenser

The de-bottleneck of the raw material feed equipment and of the finishing section was carried out directly by the owner. Due to maintenance reasons, the HP condenser was changed with a slightly larger one.

The designed capacity of the revamped plant is 2400 MTD.

The project was first proposed in March of 1995, with a target start-up date of June, 1996. Due to equipment delays the start-up took place in October, 1996. Because of project fast tracking requirements a team of Agrium personnel, along with the engineering companies Fluor Daniel and Urea Casale was put together. The project was designed, equipment procured and construction completed in just 14 months from actual approval to proceed.

Much of the construction occurred while the Plant was running in order to facilitate project tie-ins and completion during a three week turnaround.

This was for the most part, accomplished and with the knowledge gained by this team improvements could be made in this area.

The results are that the Plant is presently running at 1,485 MTD on the Ammonia side and 2,300 MTD on the Urea side.

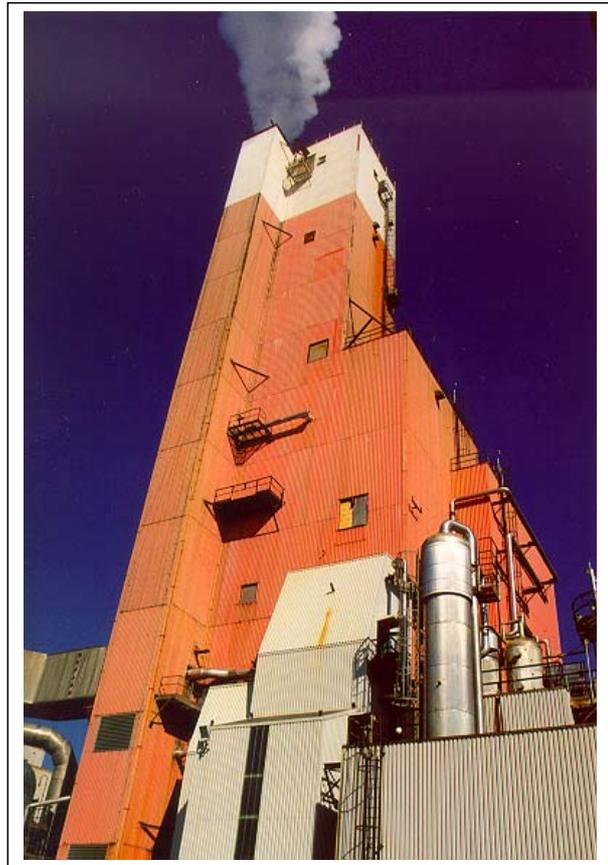
The expected performances of the VRS system have been also confirmed by the plant operation. The main features obtained can be summarised as follows :

- low H_2O/CO_2 molar ratio at reactor (about 0.25)
- high CO_2 conversion even at high capacity (64 %)
- high stripping efficiency
- high Ur concentration at stripper and LP decomposer exit

As expected, the lower H_2O content (due to the low H_2O/CO_2 molar ratio) and the lower CO_2 content (due to the higher CO_2 conversion) allowed not only to reutilize the existing HP decomposition section without changes, but also to achieve a higher efficiency in the decomposition. This de-bottlenecked not only the LP section, but also the first vacuum evaporation stage, which is now fed by a more concentrated solution.

The Urea Plant use of the VRS system resulted in several operational surprises other than the tonnage gains. One was the quickness of eliminating water from the high pressure synthesis loop during start-up or upset conditions.

The second is the stability of the operation at the high rates. These two items alone have the operators putting the unit on line as soon in the start-up as practical.



**Fig. 11 - North American Plant
Revamped according to the
VRS Concept**

PART 2.4

LARGE CAPACITY INCREASE FOR CONVENTIONAL TOTAL RECYCLE PLANTS: CASALE HEC PROCESS

Urea Casale has recently developed a new urea process named HIGH EFFICIENCY COMBINED Process. This process, based on the combination of a very efficient "once-through" reactor and a conventional total recycle one, presents the unique feature of having a very high average CO₂ conversion and by consequence a low energy consumption.

An interesting characteristic of this new concept is that it can be very conveniently applied to the revamp of existing plants achieving the following:

- capacity increase by 50% or more
- energy consumption reduction
- minimum investment
- minimum modification to the existing plant
- minimum shut-down time

The main concept of the HEC process is to obtain most of the urea product in a "once-through" reaction section. In the absence of recycle water, the conversion of carbamate to urea is favoured and a high conversion of CO₂ to urea in single pass (75 to 80%) is obtained. The small amount of residual carbamate is decomposed, condensed and recycled as aqueous solution to a second reaction section (operating at lower pressure) which converts it to urea at a lower conversion efficiency (typically 55).

Now, by feeding all the fresh reactants to the high-pressure reactor without any aqueous recycle, most of the product (75÷80%) is obtained at high conversion efficiency and only a small amount (20÷25%) at reduced efficiency. The weighted average conversion efficiency results in the 70-76% range, a value much higher than the one obtained even in modern urea plants. Consequently, the amount of steam required by the decomposition section is greatly reduced.

The Figure 12 shows a schematic representation of the HEC process.

The "once-through" reaction section designed by CASALE for the HEC process consists of the following items in series:

- The carbamate condenser, a U-tube, kettle type heat exchanger where part of the ammonium carbamate is formed and part of reaction heat is taken out, generating steam (with a pressure as high as 9 ata), in order to control the temperature of the primary reactor.

- The primary reactor, fitted with Casale High Efficiency Trays operating in the following conditions:

NH ₃ /CO ₂	=	3.6
H ₂ O/CO ₂	=	0
Outlet temperature	=	195 °C
Pressure	=	240 ata
CO ₂ conversion	=	77 %

The second reaction section (secondary reactor) is also fitted with Casale High Efficiency Trays and operates in the following condition:

NH ₃ /CO ₂	=	4.5
H ₂ O/CO ₂	=	1.3
Outlet temperature	=	190 °C
Pressure	=	155 ata
CO ₂ conversion	=	55 %

All the CO₂ feed enters the "once-through" reaction section it reacts with NH₃ that is sent in the quantity necessary to keep the desired ratio.

About 77 % of the total production is obtained in this section where steam is also generated (up to 9 ata).

The solution from the top of the primary reactor is flashed down to a pressure of 157 ata and enters the high pressure decomposer where carbamate is decomposed increasing the temperature of the solution up to 205°C by means of MP saturated steam (20 to 25 ata).

The high-pressure decomposer top vapor enters the secondary Reactor to supply part of the heat necessary to control the outlet temperature.

The solution outflowing the secondary reactor joins the solution outflowing the high-pressure decomposer and together they feed the MP decomposer first, and then the LP decomposer and a two-stage (operating at 0.3 and 0.03 bar) vacuum concentration section to obtain the urea melt which feeds the finishing system.

The MP and LP decomposer overhead vapours are condensed respectively into the MP and LP condensers.

The two-phase mixture, from the MP condenser enters the NH₃ recovery section where the total amount of CO₂ is condensed and the resulting carbamate solution is recycled to the secondary reactor.

The pure ammonia is obtained from NH₃ recovery section and recycled to the primary reactor.

The urea melt obtained from the vacuum concentration section can be sent to any conventional finishing section.

The process condensate obtained from the vacuum concentration section is treated in a process condensate treatment section where NH_3 and CO_2 are recovered.

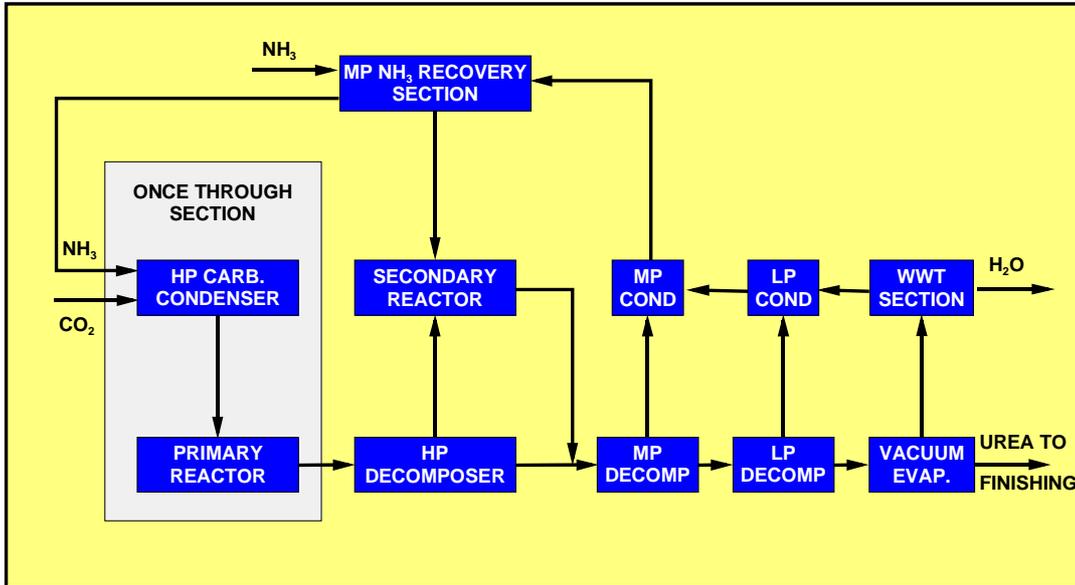


Fig. 12 - HEC Process

Features of HEC Process

Thanks to the utilization of the Casale High Efficiency reactor trays and to the fact that the main reactor is of "once-through" type, the HEC process has the following unique features:

- very high (average) CO_2 conversion, i.e. ab. 72%
- very low $\text{H}_2\text{O}/\text{CO}_2$ ratio, i.e. 0.3.

Thanks to these features, the HEC process has the following performances:

- low specific steam consumption, i.e. 900 kg/MT
- small-size of all the decomposition and recycle equipment (In particular, the size of HP decomposer and condenser is much smaller than in the most advanced processes.

Revamping of Conventional Total Recycle Plants with HEC Process

Thanks to the above features, the capacity of conventional total recycle plants can be drastically increased applying the HEC concept, and this with the addition of just few pieces of equipment.

In order to increase the capacity of conventional total recycle plants up to 60 %, Casale proposes to install its HET in the existing reactor and to apply its HEC concept as follows:

- the existing reactor (fitted with Casale HET) is used as primary reactor

- a section consisting of the secondary reactor, an HP carbamate condenser and an HP decomposer is added (see Fig. 13).

The existing synthesis section will, therefore, be transformed in a HEC synthesis section.

Due to the much higher conversion obtained with the HEC synthesis section, the existing back-end of the plant can be re-utilised at higher capacity with only minor modification.

Casale, however, studies the behaviour of all the existing equipment in the new operating condition and determines the minor changes necessary. A detailed check of all the instrumentation and piping is also done.

With this approach, the highest possible utilisation of the existing equipment is reached, keeping the investment as low as possible.

Increases even higher than 60% can be obtained if, instead of the secondary reactor, the primary reactor is added, together with the HP condenser and decomposer. In this case the existing reactor will be used as secondary reactor.

After revamping, the following consumption's can be obtained:

- raw materials almost stoichiometric
- MP steam ab. 900 kg/MT

(The above values are based on actual experience and studies performed and can vary depending on the capacity increase required).

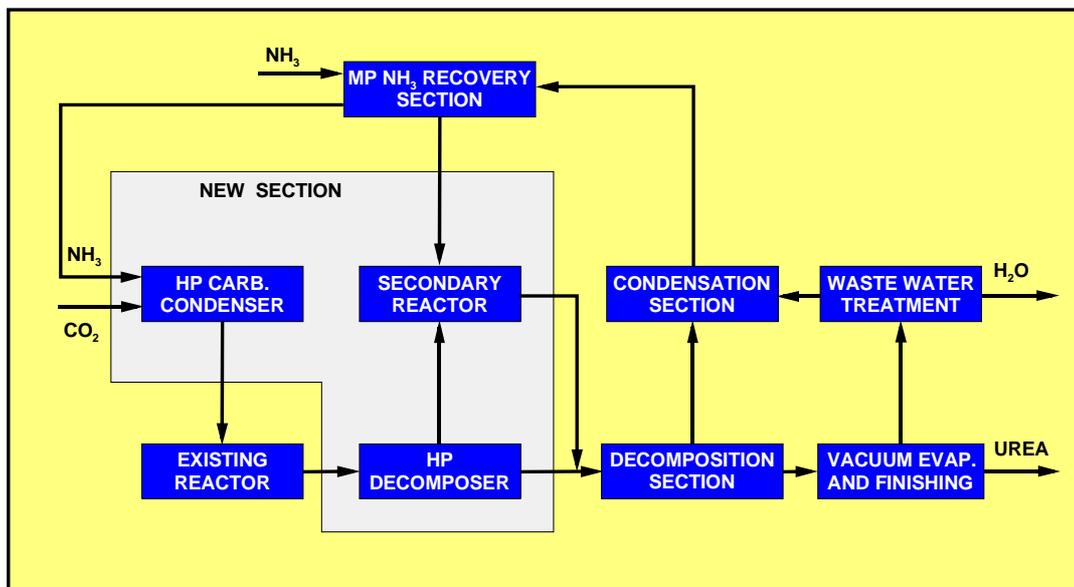


Fig. 13 - Conventional Total Recycle Plant revamped with the HEC Concept

From 270 MTD to 750 MTD with HEC for Conventional Total Recycle Plants

The way conventional total recycle plants are revamped using the HEC concept is illustrated using the revamping of a North American plant carried out by Casale as an example.

In 1993, Casale was asked to study the revamping of a 465 MTD Toyo conventional plant in order to reach a capacity of 750 MTD. The urea was produced in two existing lines having the following capacity :

- No 1, 195 MTD
- No 2, 270 MTD

Line No 1 was a partial recycle line with a one-stage decomposition / recycling section and the NH₃ recovery section.

Line No 2 was a total recycle line with a three-stage decomposition / recycling section and the NH₃ recovery section. A one-stage vacuum evaporation section was producing the urea solution of the desired concentration.

It was desirable to shut down line No 1 and to have only one line for the new capacity. Due to the extremely high capacity increase required from line No 2 (almost three times higher), a drastic increase in the efficiency of the synthesis section was necessary in order to avoid a very complicated approach with a lot of parallel equipment.

Casale, therefore, suggested to retrofit line No 2 using a new front end, designed by Casale according to its High Efficiency Combined Process Technology (HEC), sized for 75% of the final capacity and consisting of :

- a new “once-through” reactor, working at 240 bar, 197°C
- a new HP carbamate condenser generating 6.5 bar steam upstream the “once-through” reactor.
- a new HP decomposer working at 157 bar fed by the once-through reactor outlet stream.

In this way, it was possible to keep the same equipment down stream the existing reactor and to minimize the modifications to it.

Line No 1 was idled and some equipment used, namely the NH₃ condensation section and the machinery for NH₃ and carbamate compression. The CO₂ compression as well as the finishing section capacity were also increased. No other new equipment was needed other than two condensers and an additional vacuum section.

This was also possible, because the stream feeding the decomposition sections then had a CO₂ conversion efficiency of almost 80 %.

The revamped plant was started up in December 1995 and operated at 550 MTD until June 1996 due to an unforeseen bottleneck in the existing NH₃ recovery section. In order to overcome this bottleneck, in July 1996 an idled NH₃ absorber from Line no. 1 was used and a NH₃ absorber pre-condenser and a vent scrubber were added.

From July 1996, the plant has been running with a capacity up to 800 ÷ 810 MTD. All guaranteed values have been met.

The expected performances of the HEC system have been also confirmed by the plant operation. The main features obtained can be summarised as follows:

- high (average) CO₂ conversion: 70%
- low (average) H₂O/CO₂ molar ratio: 0.3%.

Other Applications of the HEC Process

A second plant revamped by Casale using the HEC technology is in operation since December 1996 in New Zealand. This plant was originally designed to produce 480 MTD in a single line according to the Toyo conventional total recycle technology.

The revamped plant is designed to produce 750 MTD. All guaranteed values have been met.

A third plant revamped by Casale using the HEC technology is in operation since 1998 in Canada.

This plant was originally designed to produce 316 MTD in a single line according to the Weatherly conventional partial recycle technology. The revamped plant is designed to produce 655 MTD. All guaranteed values have been met.



Fig . 14 - North American Plant revamped according to the HEC Concept

A fourth plant revamped by Casale using the HEC technology is in operation since 2001 in India.

This plant was originally design to produce 1000 MTD in a single line according to the Tecnimont conventional partial recycle technology.

The revamped plant is designed to produce 1650 MTD.

All guaranteed values have been met.

In addition to the just described projects, it is worth mentioning the following projects which are under implementation by Casale using the HEC for large capacity increase of conventional total recycle plants :

- Petrobras (Brazil) plant
800 MTD single line Toyo plant revamped to 1500 MTD – under optimization.
- Razi Petrochemical (Iran) plant
500 MTD single line Vulcan plant revamped to 875 MTD – under start-up.

PART 2.5

CAPACITY INCREASE OF WWT SECTION POLLUTION AND CORROSION CONTROL: CASALE HIGH EFFICIENCY HYDROLYSER AND UREA RECOVERY SYSTEM

The emissions of a urea plant to the environment are either the excess process condensate, which has to be discharged to keep the water balance, or the vent where the inerts are discharged to avoid accumulation. Both these emissions are contaminated with compounds involved in the urea synthesis and have to be purified to the most possible extent in order to satisfy environmental regulations, which are becoming more and more severe.

The process condensate stream generally contains NH_3 , CO_2 , and Urea. The majority of plants treat the condensate to recover CO_2 and most of the NH_3 in order to minimise raw material losses. Many plants, however, do not have the capability of either completely eliminating NH_3 and Urea or reducing their content below the accepted values.

In order to reduce the liquid emissions, Casale has developed a new hydrolyser of increased efficiency, called High Efficiency Hydrolyser (HEH), which allows to completely eliminate Ur from the process condensate.

In order to obtain also a complete elimination of NH_3 , the HEH is used in a high efficiency waste water treatment section as shown in Fig. 15.

The process condensate is first sent to a desorbition column where most of the NH_3 and CO_2 is eliminated.

The condensate is then sent to the HEH to completely eliminate the Ur and finally to a stripping column where the NH_3 is eliminated.

The recovered NH_3 and CO_2 are sent back to the synthesis.

A water with about 3 ppm of UR and NH_3 can be obtained and can be used as boiler feed.

If it is not required to completely eliminate the Urea in the condensate, Urea Casale can reach a value of 400÷500 ppm by washing the vapours coming from the vacuum separators with its Urea Recovery System (URS).

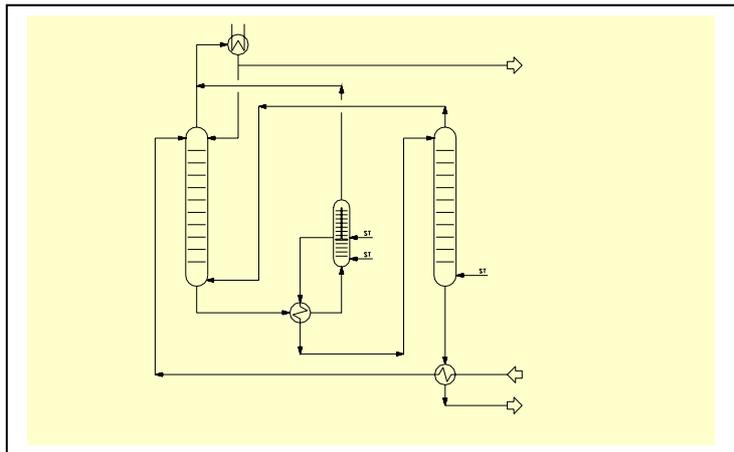


Fig. 15 - High Efficiency Waste Water Treatment Section

In order to reduce the emissions from the vent, the H₂O₂ passivation system can be conveniently used for those plants working with high amount of oxygen for passivation. With this system, the amount of inerts discharged through the vent is drastically reduced, as described in the previous chapter, and by consequent, also the NH₃ and CO₂ emission.

In case of capacity increase, the HEH can be very conveniently utilised to debottleneck existing hydrolysers adding it in series to the existing one. The existing desorbers can be conveniently revamped by changing the trays with one of improved design.

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In case of capacity increase, the HEH can be very conveniently utilised to debottleneck existing hydrolysers adding it in series to the existing one. The existing desorbers can be conveniently revamped by changing the trays with ones of improved design.

High Efficiency Hydrolyser

With the help of Urea Casale's new High Efficiency Hydrolyser (HEH - see description below), adding, if necessary, one or two stripping columns, it is possible to completely eliminate NH₃ and Urea from the process condensate reaching residual values lower than 3 ppm. This value meets the requirements for boiler feed water; the treated condensate can, therefore, be used as boiler feed with economical advantages.

The High Efficiency Casale Hydrolyser (see Fig. 16) makes efficient use of the stripping action of steam to remove the NH₃ and CO₂ from the treated urea plant waste water condensate in order to maximise the hydrolysis of the urea content. The efficiency is enhanced by the fact that the hydrolyser is divided in two zones in order to keep the driving force for the NH₃ and CO₂ removal as high as possible. It is, in fact, very important to eliminate NH₃ and CO₂ from the liquid as much as possible as, since the NH₃ and CO₂ are products of the hydrolysis reaction, their presence tends to slow down the hydrolysis.

Both zones are provided with High Efficiency Casale Trays, which divide them in compartments. In each compartment the liquid is separated from vapours (containing NH₃ and CO₂), creating a multiplicity of streams of vapours, which are injected again into the liquid in form of column of small bubbles maximising the mass and heat transfer. The two zones have the following characteristics:

First Zone

The first zone, fed by the waste condensate to be treated, is operating in “co-current” with injection of steam in the bottom. At the top of the first zone the vapours are finally removed from the liquid which is then treated in the second zone.

Second Zone

The second zone, fed by the liquid coming from the first zone, operates in “counter-current” with liquid going downward and vapour going upward. Fresh steam is injected again in the bottom of this second zone. The driving force for the extraction of NH₃ and CO₂ is, in this way, increased, allowing to reduce urea content to less than 3 ppm.

The vapours are separated from the liquid at the top of the zone and exit the hydrolyser together with the vapours coming from the first zone. Steam at pressure lower than 25 bar can be conveniently used.

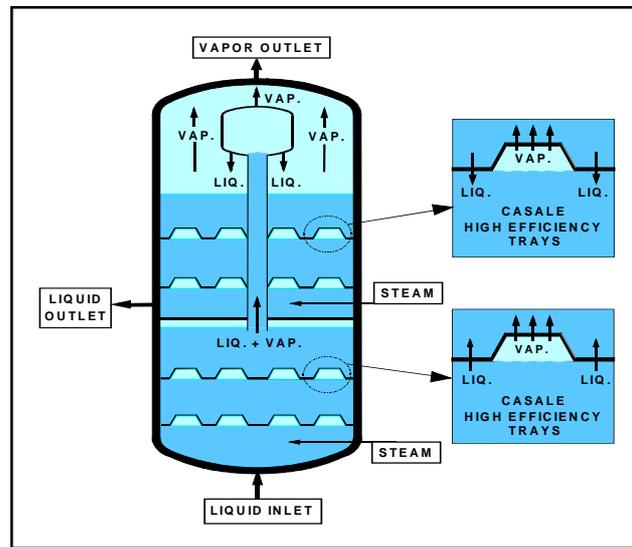


Fig. 16 - High Efficiency Hydrolyser

Urea Recovery System (URS)

A combined system can be offered for the recovery, from vacuum vapours, of 96-97% of urea carry-over as 35% urea solution that is directly reprocessed in the vacuum evaporators.

With this system the urea content in the process condensate going to the waste water treatment section is brought down to 400÷500 ppm.

Two washing systems are installed on the vapour line leaving the first and the second vacuum separators, and washes the vapours leaving the separators using res. 35% and 15% urea solutions.

The 15% solution is recycled from the second vacuum separator washing system to the first one, while the 35% solution is recycled to the vapour evaporators.

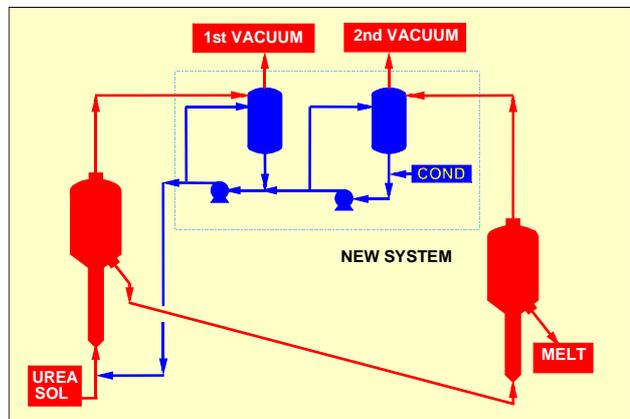


Fig. 17 - Urea Recovery System

Corrosion Control: Carbamate Condenser Passivation System

The passivation of HP critical equipment in a urea plant is guaranteed by the oxygen, which forms an oxide protection layer. Some equipment, however, may not have an optimal distribution of the oxygen to the whole surface to be passivated.

In the case of horizontal carbamate condensers, for instance, under certain fluid-dynamic regimes the presence of dead spots impedes the oxygen to reach certain zones causing corrosion problems which decreases the life of the equipment.

Moreover, in this kind of condenser the relative low velocity causes segregation between liquid and vapour phase, enhancing the chance of corrosion. The low velocity also causes a poor heat transfer.

The above drawbacks may be eliminated by installing one ejector near the heat exchanger head which circulates the vapour-liquid mixture, several times the fed carbamate flow. The ejector uses the fed weak carbamate solution, which is pumped with an extra pressure of about 10 bar, as driving force.

The purpose of the ejector is to maintain the equipment completely full of liquid and avoid "dead spots" which are very dangerous from the corrosion point of view.

This system, called the Carbamate Condenser Passivation System (CCPS), can, therefore, eliminate the dead spots increasing the corrosion control and, therefore, the reliability and the life of the equipment.

Furthermore, the CCPS also increase the performances of the condenser as it increases the heat exchange coefficient.

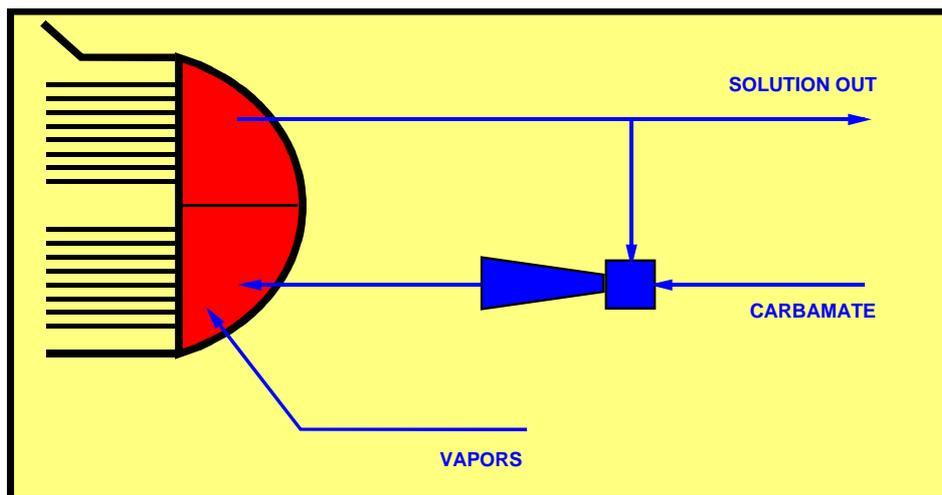


Fig. 18 - Carbamate Condenser Passivation System

Industrial Application of High Efficiency Hydrolyser

The High Efficiency Hydrolyser is currently running in four plants, revamped by Casale according to the HEC technology, obtaining boiler feed grade water and one plant where the waste water treatment section was revamped in order to obtain boiler feed water. In all cases, the treated water reached boiler feed water grade.

Industrial Application of URS and CCPS

The URS is running in three (3) large plants originally designed according to the CO₂ and NH₃ stripping technology obtaining reductions of the urea content in the process condensate down to 300 ppm.

The CCPS is currently running in two large plants originally designed according to the NH₃ stripping technology (both plants are located in India). After one year of operation, after the tube thickness had steadily decreased in previous years, no appreciable reduction in tube's wall thickness was observed. An additional big advantage of this system, which was proven in the first installation, is that the heat transfer coefficient of the condenser is greatly increased, thus debottlenecking the equipment.

PART 3. **NEW UREA PLANTS**

Casale proposed the VRS Process described in the previous sections for the construction of new urea plants.

At present, the most advanced processes for the urea synthesis are the so-called processes introduced about thirty-five years ago.

The common feature of the stripping processes is to have a first separation and recycle of unreacted NH_3 and CO_2 before starting lowering the pressure. This first recycle is made in the so-called high-pressure synthesis loop (HP loop).

All the equipment of the HP loop are, of course, operating at practically the same pressure.

The HP stripper is partially decomposing the carbamate (unreacted NH_3 and CO_2) coming from the reactor obtaining a flow of NH_3 and CO_2 in the vapour phase containing NH_3 and CO_2 coming from the stripper is recycled to the reactor through the carbamate condenser, after being partially or totally condensed.

Thanks to the HP recycle, a big part of the unreacted NH_3 and CO_2 is recycled to the reactor with very little water but still a significant amount of water is required to recycle all the unreacted NH_3 and CO_2 at stripper outlet, even if this amount is less than the one required in the processes prior to the stripping process.

The Casale VRS process, suited for new plants construction, is an improved CO_2 stripping process.

The main concept of the VRS process is to separate the NH_3 and CO_2 contained in the carbamate solution formed downstream the loop, and to send them to the reactor with practically no water. This is achieved with the following steps:

- The carbamate solution obtained in the downstream process sections is distilled, instead of being sent to the HP Section, in an HP decomposer working in parallel to the existing stripper.
- The vapours thus obtained (containing NH_3 , CO_2 , and a little water) are sent to the HP Section (HP Carbamate Condenser), while the distilled solution (enriched in water) is sent back to the back-end of the plant.

The main steps of the VRS Process are the following (see block diagram below):

- The solution from the reactor is first treated in a stripper, operating at the same pressure of the reactor, where, using steam and CO_2 as stripping agent, most of the unreacted NH_3 and CO_2 are recovered and then recycled back to the reactor through a condenser.

- From the stripper, the urea solution, still containing unreacted NH_3 and CO_2 in form of carbamate, is sent to a low-pressure single decomposition/condensation stage where practically all the remaining unreacted NH_3 and CO_2 is recovered in form of a carbamate solution.
- The urea-water solution, containing only small quantities of NH_3 and CO_2 , is then further treated in a two-stage vacuum evaporation section to obtain a urea melt for the prilling tower or the granulator.
- The process condensate, obtained from the vacuum condensers is purified with two columns and one hydrolyser in order to eliminate all the NH_3 , CO_2 , and Urea.
- The carbamate solution obtained in the LP section is treated in a carbamate decomposer working in parallel to the existing stripper, instead of being sent directly to the reaction section as in all the other urea processes.
- The vapours thus obtained (containing NH_3 , CO_2 and little water) are sent to the reaction section, while the distilled solution (enriched in water) is sent back to the back-end of the plant.

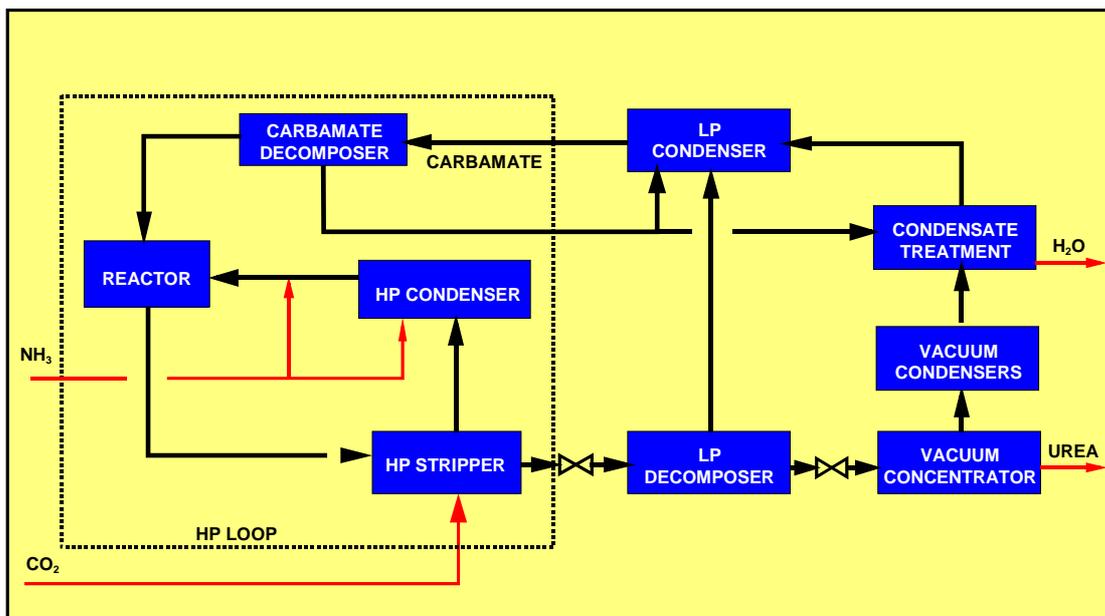


Fig. 19 – VRS Process Block

In this way, practically only the NH_3 and CO_2 contained in the carbamate are sent back to the synthesis section, while the water is almost totally sent back to the back-end of the plant.

As a consequent, the synthesis section operates with very low water content with the following advantages:

- Very high CO_2 conversion in the reactor (up to 70%);
- Very high stripping efficiency
- Low amount of water has to be separated from the solution coming from the stripper.

For this reason, the Casale VRS process is a process with high efficiency requiring, for a given capacity, equipment of smaller size with low investment costs.

In addition, due to the fact that the carbamate is not sent back to the reaction section, the operation of the later is very stable. A plant designed according to the VRS process can, therefore, operate more smoothly than other conventional designs.

As far the operating costs are concerned, the VRS process has values as low as the most advanced processes.

The Casale VRS process is, therefore, suited for plants of very large capacities. The most critical pieces of equipment are, in fact, smaller, for a given capacity, than in most conventional processes.

A plant with a capacity of 2300 MTD is operating in Canada according to the VRS Process since 1996.



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