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CASALE GROUP EXPERIENCE FOR REVAMPING UREA PLANTS

by F. Zardi, A. Orlov

UREA CASALE S.A.
Lugano, Switzerland

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FOREWORD

Urea Casale has been active in the urea field since 1985, first as Ammonia Casale and from 1991 as an independent company.
From the very beginning, the activity of the company has been concentrated on revamping existing urea plants.

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

The competitiveness and the success of Urea Casale revamping technologies is proven by the fact that, in the last ten years, 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.

UREA CASALE TECHNOLGIES FOR PROJECTS AIMING SMALL/MODERATE CAPACITY INCREASE AND ENERGY SAVING

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 CO_2 conversion (4 to 5 percentage points) reducing the specific amount of steam required to recycle back the unreacted CO_2.

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 CO_2 and NH_3 stripping plants and for conventional total recycle plants.

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 vapor-liquid heterogeneous reaction system. All along the reactor both the vapor phase (containing free CO_2, NH_3, some water and inerts) and the liquid phase (containing NH_3, ammonium carbamate, bicarbonate, urea and water) are present. The reactants are progressively transferred from the vapour to the liquid phase, where CO_2 reacts with NH_3, producing carbamate and then urea and water with a continuous exchange of CO_2 and NH_3 between the two phases.

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

(1) $CO_{2\ Liq} + 2\ NH_{3\ Liq} \Leftrightarrow NH_4^+ + NH_2CO_2^-$
exothermic – very fast

(2) $NH_4^+ + NH_2CO_2^- \Leftrightarrow (NH_4NH_2CO_2) \Leftrightarrow Urea + H_20_{Liq.}$
endothermic – rate determining step

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

$$CO_{2_{Gas}} \Leftrightarrow CO_{2_{Liq}} \quad ; \quad NH_{3_{Gas}} \Leftrightarrow NH_{3_{Liq}} \quad ; \quad H_2O_{Gas} \Leftrightarrow H_2O_{Liq}$$

In such a heterogeneous reaction system, like the one for the formation of urea, we can identify three regions shown in Fig.1:

- 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

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 vapors 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 vapors containing CO_2 and NH_3 are still present at reactor outlet.

Casale, together with Prof. M. 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 (Fig. 2 A, B), 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 vapors 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.

After having found, as seen above, that heat and mass transfer phenomena are limiting the efficiency of most of the existing urea reactor, new reactor tray designs have been developed (and fully patented) in order to improve heat and mass transfer rates :

- Casale ZigZag tray design
- Casale-Dente tray design.

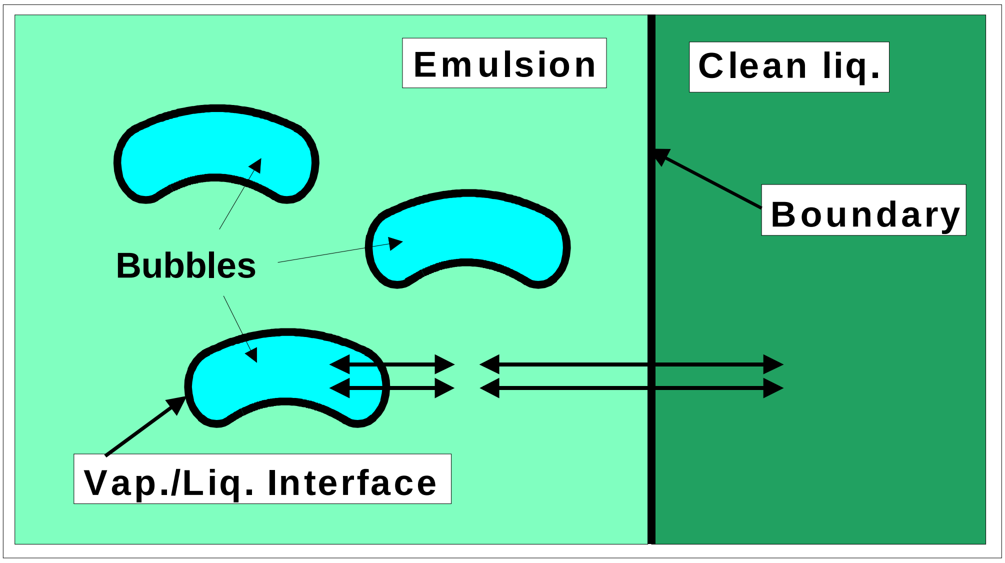

Fig. 1 Regions in urea reacting system

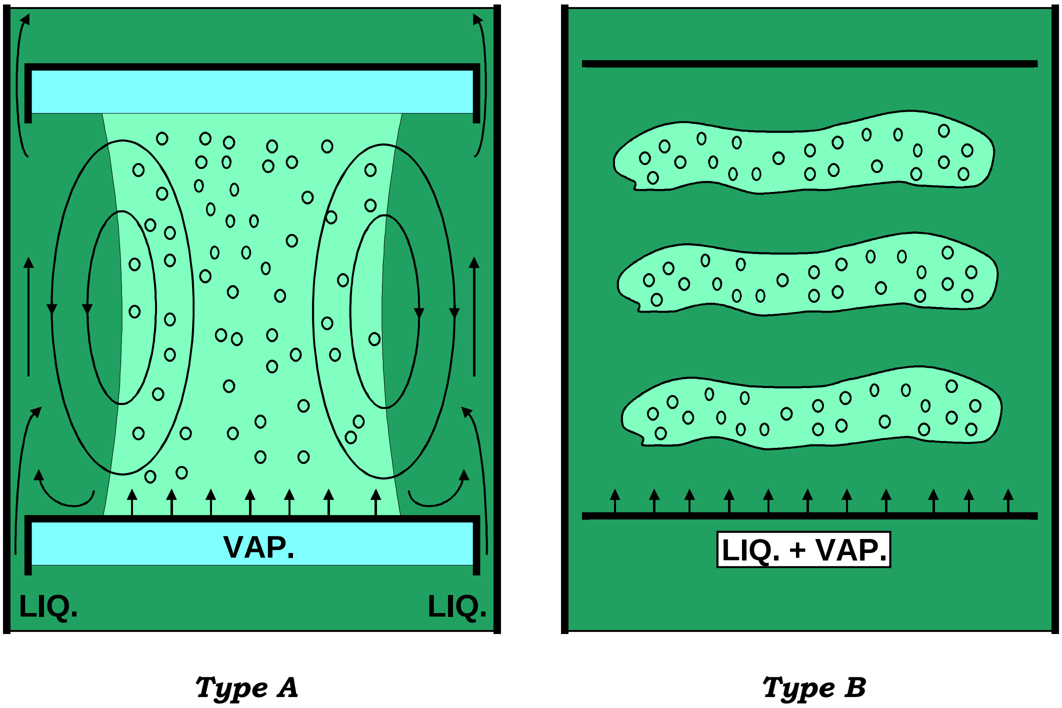

Fig. 2 Standard type of reactor tray

The Casale ZigZag design, is based on forcing the liquid to cross the rising column of bubble as shown in fig. 3. This is obtained with the following modification:

- substantially obstructing the gap between the plate collar and the inner wall of the reactor vessel, enlarging the plate diameter
- forming off-set openings in the plates, causing a zigzag liquid flow from one plate to next one, while vapours are flowing upwardly through the holes of the plate
- a small gap is maintained between plate collar and inner wall of the reactor vessel for minimum liquid flow for reactor wall passivation against corrosion.

In a second version of the method, the perforated zone of each plate is also divided in a plurality of perforated and unperforated sectors side-by-side generating channels through the rising column of bubble.

The improvement obtainable with the ZigZag design are only marginal as this design has still some disadvantages of the classical designs such as very long stream lines, large bubbles, liquid by-passing the bubble column going around it, etc.

The Casale-Dente design is, on the contrary, a complete redesign of the tray achieving a more drastic improvement.

The Casale-Dente design, in fact, improves the tray geometry realising much better contact patterns of the phases, reducing the path length of the eddies' streamlines into the emulsion (mixed phase of bubble and liquid) and drastically increasing emulsion to clean liquid boundary surface.

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 (see Fig. 4) 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.

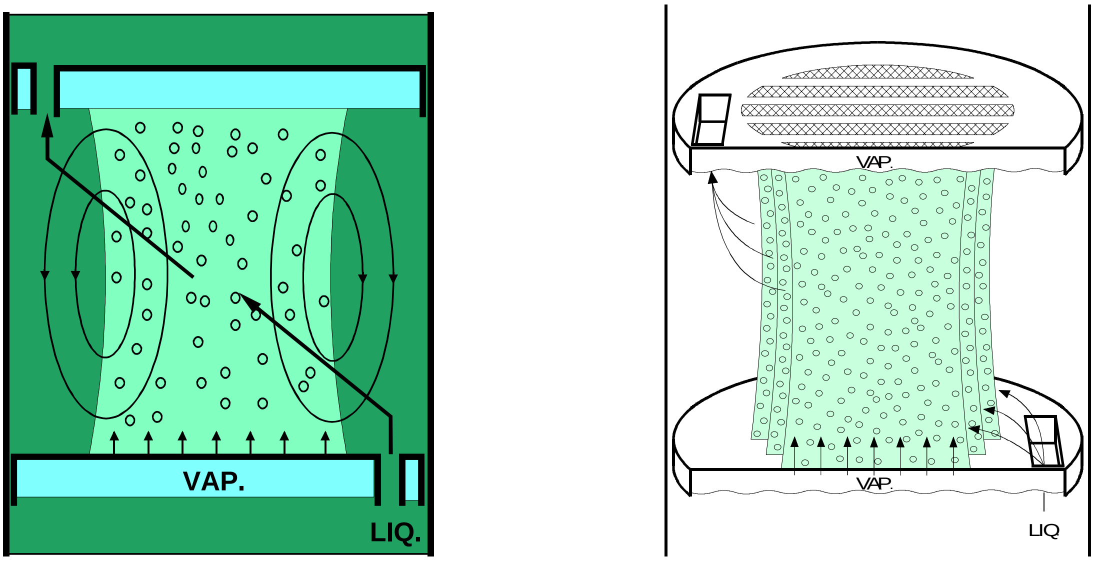

Fig. 3 Casale new ZigZag tray design

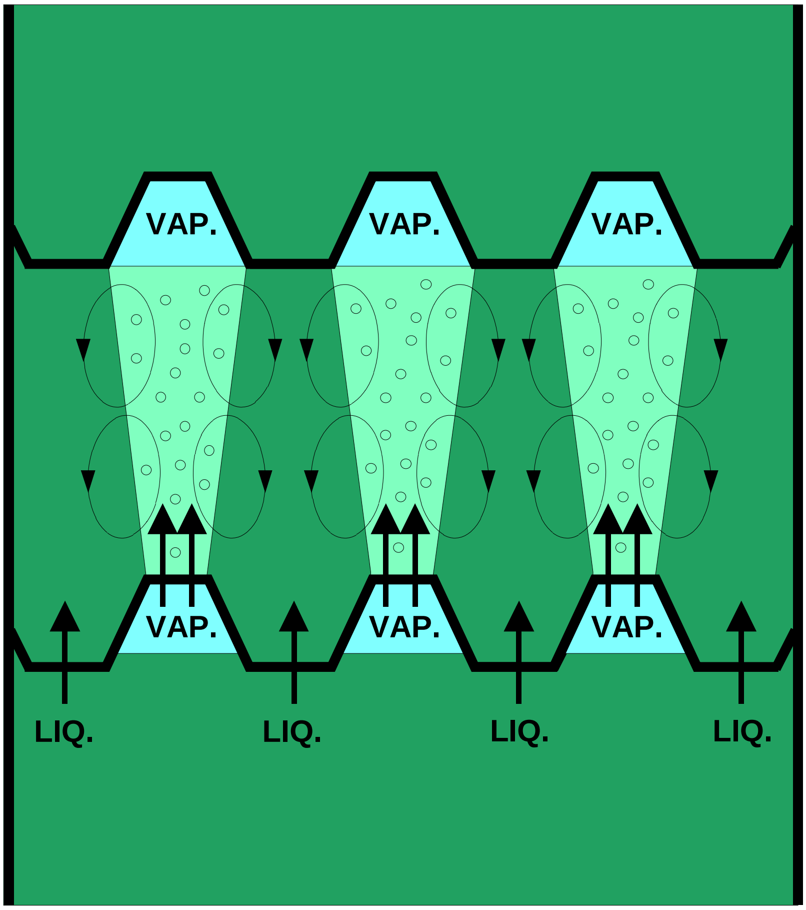

Fig.4 - Casale-Dente High Efficiency trays

Due to the much better performances, Casale has used only the Casale-Dente design in all its implementations.

INDUSTRIAL EXPERIENCE

In the last three years a total of forty (40) projects involving installation of HET have been carried out or are under completion for plants having capacities ranging from 250 to 2100 MTD. Thirty three (33) 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.
(Eight of the plants in operation with Casale trays are located in the CSI).

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.

A TWO-CASE HISTORY WITHIN THE CSI FOR THE APPLICATION OF HET WITH CAPACITY INCREASE

The Toaz project:

At the beginning of the nineties, Toaz asked Urea Casale to study the revamping of the its 1500 MTD Urea plants to increase the capacity by 15 % decreasing the energy consumption and increasing plant reliability.

Casale concluded that the following modifications were required to reach the new capacity:
- installation of Casale High Efficiency trays (HET) to increase reactor efficiency.
- replacement of CO_2 compressor internals to increase its capacity.
- replacement of the internals of the carbamate pumps.
- replacement of prilling bucket.

In order to reduce the energy consumption and the plant reliability, the following was suggested:
- installation of a heat recovery section to recover the heat from the MP evaporator vapours using it to evaporate the water from the urea solution.
- installation of the URS to reduce the urea carry over from the vacuum evaporator.
- installation of the CCPS to reduce the corrosion of the HP carbamate condenser.

It is to be noted that the installation of the Casale HET and the replacement of the CO_2 compressor internals are also contributing to the reduction of the energy saving.
During 1993 and 1994 the above modification for the capacity increase have been carried out in both plants achieving the 15 % capacity increase.

In addition, the following benefits in terms of energy consumption reduction have been obtained:

- the compressor was able to compress 15% more CO_2 with the same amount of steam, this means that the steam consumption of the turbine has decrease by 15%.
- the steam consumption of the stripper has decreased by ab. 200 kg/MT due to the fact that the CO2 conversion in the reactor has increased by ab. 4-5 percentage points.

For the other modifications Casale has completed the supply but the erection has not completed yet.
From previous experience, the following benefits are expected:

- saving of ab 200 kg/MT of LP steam
- decrease of the urea content in the process condensate down to 500 ppm.
- drastic reduction of the corrosion in the HP carbamate condenser and increase of its exchange coefficient allowing to operate the stripper with a lower pressure (few bar) increasing its efficiency.

During the revamping of the urea plants, Casale has also supplied a replacement stripper (of the same size of the existing) for one line were the existing stripper reached the end of life.

Styrol project
In 1997, Styrol asked Urea Casale to study the revamping of its 1000 MTD Urea plant to increase the capacity by 35 % decreasing the energy consumption and increasing plant reliability.

Casale concluded that the following modifications were required to reach the new capacity :

- installation of Casale High Efficiency trays (HET) to increase reactor efficiency.
- Installation of a new CO_2 compressor to increase CO_2 compression capacity.
- modification of the ammonia and carbamate pumps.
- installation of additional heat exchange surface to the cooling water system of the HP scrubber.
- installation of additional heat exchange surface to the LP decomposer and condenser.
- installation of additional heat exchange surface to the vacuum evaporators and condensers.
- installation of the URS to reduce the urea carry over from the vacuum evaporator.
- replacement of trays in the desorbers of the waste water treatment section.
- replacement of prilling device.

During 1997 the HET have been installed in the reactor achieving the energy saving and creating the potential for the capacity increase.
During 1999 the rest of the modifications for the capacity increase were carried out achieving the 35 % capacity increase, and at the same time, with a significant increase of reactor conversion and consequent decrease of steam consumption.

CONCLUSIONS

Urea Casale has developed, since the start of its activity, several technologies to upgrade urea plants.
Some of these technologies have proven to be real "breakthroughs" in the urea field, such as the High Efficiency Trays and the HEC and VRS processes.
Nobody in the field would have imagined, just few years ago, that the CO_2 conversion in urea synthesis reaction sections could be drastically increased even if at the same time the capacity is significantly increased, as Casale proved with the application of its technologies.
Thanks to its HET technology, Casale can offer to the Urea Industry an economical way of significantly incrementing the capacity of urea plants and decreasing energy consumption.
This becomes very competitive versus increasing the capacity by adding new plants.
The Casale concept, in fact, reaches the increment in capacity with an investment, which is a fraction of the cost of a new plant. In addition, as all the new equipment can be erected with the plant running and the modifications to the existing plant are reduced to a minimum, this is obtained with a required shut down time no longer than a major maintenance shut down.
These technologies, therefore, opened new horizons in the field of urea plant modernisation, making the revamp of existing plants possible even when significant capacity increases are required.
This offers the market very competitive and flexible alternatives to the construction of new plants in today's growing demand for fertilisers, also in view of the fact that Casale technologies can be applied to almost any kind of urea process.