Ammonia and Urea plants upgrading Technologies

by
M. Badano and F. Zardi
Casale Group

Presented at
FMB-NPC/IPCC UREA & AMMONIA CONFERENCE
Tehran, Iran
14-16 September, 2005

**6900 Lugano
Switzerland,
Via G. Pocobelli 6
Tel +41.91.960.72.00
Fax +41.91.960.72.91/2
www.casale.ch
info@casale.ch**

CasaleGroup

◆ FOREWORD

Ammonia and Urea Casale have been very active in the field of ammonia and urea plants revamping for many years and have extensive experience in the design and implementation of complete plant revamping projects with different technologies.

Every ammonia or urea plant revamping project is different from previous ones. The plant owner can have different goals to reach and the plant, even if designed with the same technology, may have different bottlenecks. So every revamping project has to start by identifying the client's goals and the actual bottlenecks in the plant. These may include some or all of the following:

- ✦ Increasing plant capacity
- ✦ Reducing energy consumption
- ✦ Reducing emissions to the environment
- ✦ Improving plant reliability.
- ✦ Reducing ammonia consumption (urea plants)
- ✦ Improving corrosion control (urea plants)
- ✦ Improving product quality (urea plants)

Casale's ammonia and urea plants revamp strategy have always been to develop and apply new, advanced technologies to obtain the best possible improvement in plant performance at the minimum cost.

A plant survey is undertaken to collect actual plant data and information and a base case material and energy balance is developed reflecting actual operating conditions.

After this first phase, Ammonia and Urea Casale propose the technical solution that is considered to reach the required goals with the best return.

Casale observes the following general principles in every project.

- ✦ Always try to upgrade the plant with new technologies
- ✦ Maximise the efficiency of synthesis section
- ✦ Minimise plant shut-downs
- ✦ Minimise modifications to the existing plant
- ✦ Be as simple as possible
- ✦ Keep the return on the project as high as possible

To attain the above objectives satisfying the client's requests, it is essential to identify the most critical items to improve for the best return. Ammonia and Urea Casale have done exactly that in very many projects and have developed and applied a number of proprietary improvements, which are presented below.

For every revamping projects all the equipment and machinery in the plant is checked for compatibility with the new conditions and, if necessary, minor modifications are suggested.

Through its experience in the mechanical design of critical equipment, Casale is also involved, especially for urea plants, in the replacement of critical HP equipment, whenever maintenance requires it. Often such replacement is done by upgrading the original design to the latest standards, used by Casale for the design of new HP equipment installed in its revamping projects.

◆ Part 1 – Ammonia Plants

1.1 PROPRIETARY TECHNOLOGIES

◆ Axial-radial catalyst beds

Casale makes maximum use of the axial-radial bed concept, even in catalytic reactors designed for axial flow. This technology was developed for ammonia converters and later applied to CO shift and pre-reformer reactors, since it was demonstrated as being flexible, economical and efficient. Outside the ammonia field, it has also been applied in methanol and formaldehyde synthesis reactors.

To date Casale has put more than 400 axial-radial beds into successful service.

Fig. 1
Gas distribution in an axial-radial catalyst bed
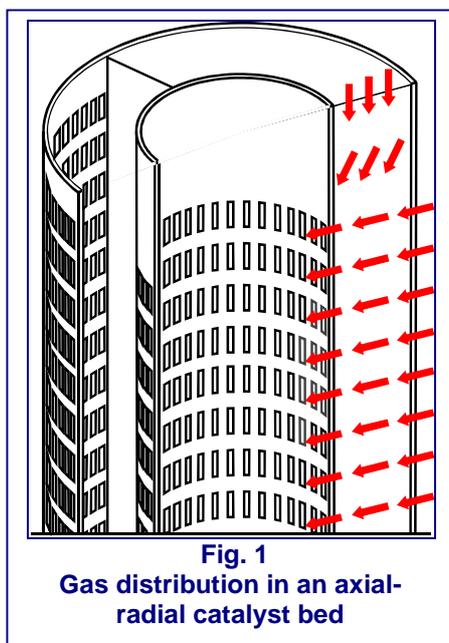
In an axial-radial catalyst bed most of the gas passes through the catalyst bed in a radial direction, resulting in much lower pressure drop than in an axial-flow catalyst bed. The balance passes down through a top layer of catalyst in an axial direction, thus eliminating the need for a top cover on the catalyst bed (Fig. 1).

Mechanically the bed is very simple, being made only of the two vertical perforated walls and of one bottom closure plate. The absence of a top cover greatly simplifies and facilitates the construction of the converter internals.

The materials used for its construction varies according to the application. It can be carbon steel, stainless steel or Inconel, the latter being used for wire mesh only.

The essential advantages of the axial-radial catalyst bed concept are the same wherever in the ammonia plant it is applied, namely:

- low pressure drop;
- use of small-size catalyst, more active and resistant to poisoning.

Application in pre-reforming reactors

Using a pre-reformer enables about 10% of the primary reforming reaction to be carried out outside the primary reformer. This enables the capacity of an existing unit to be raised without increasing the severity of the operating conditions in the primary reforming furnace.

The product of a pre-reformer is a partially reformed gas stream that no longer contains potentially carbon-forming impurities, and therefore can enter the primary reformer at a higher temperature and a considerably reduced steam to carbon ratio.

In short, installing a pre-reformer allows much more even, stable operation of the primary reformer at reduced steam to carbon ratios and higher syngas production.

The axial-radial flow allows the use of small size catalyst much more resistant to poisoning ensuring a longer catalyst life.

INDUSTRIAL EXPERIENCE

Since today, three pre-reformer are already in operation (the first one since 2002) and other two are under engineering/construction.

Application in shift converters

The shift conversion section is often the main bottleneck in an ammonia plant, particularly as the catalyst ages and loses activity. But by applying the combination of the low pressure drop axial-radial bed concept and a smaller-particle catalyst, it is possible to accommodate increased gas flows eliminating the possible constraints imposed by a fixed catalyst volume, which may be insufficient for the higher flow rates and lower steam to carbon ratio necessary by the other elements of the plant revamp.
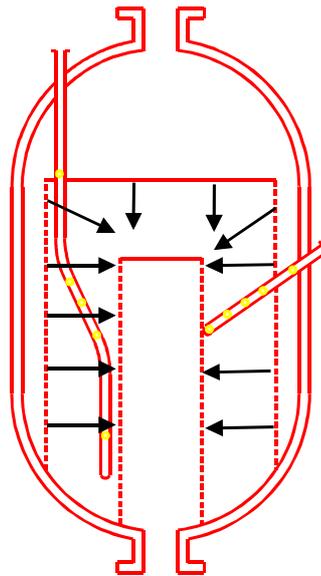
Fig. 2 - Axial-Radial Shift Converter

This catalyst is more resistant to poisons, so has a longer service life with smaller loaded volumes, and gives a lower average CO concentration at the outlet, correspondingly increasing the ammonia production obtained from a given amount of process gas.

An existing shift converter can easily be transformed to the axial-radial design (Fig. 2) by introducing new vertical cylindrical perforated inlet and outlet walls in prefabricated sections, which are assembled inside the existing converter vessel.

The new design has also the following additional features:

✤ the catalyst is protected from water droplets carried over from the secondary reformer heat recovery train or others upstream locations;

✤ different volumes of catalyst can be loaded with no need for mechanical modifications;

INDUSTRIAL EXPERIENCE

Up to now 15 axial- radial shift converters are in operation, the first two since 1995 and other 9 under engineering/construction.

Application in synthesis converters

The ammonia converter is one of the most critical item when planning a revamp to save energy or increase capacity, and in most cases it is the first item to be revamped, thanks to the relatively low cost of doing so and the very high potential return. Ammonia Casale has introduced fundamental innovations such as the "in-situ" modification of bottle-shaped converters of the type found in many Kellogg plants, and a three-bed inter-cooled configuration that Casale has been using for over ten years now.

Casale now has more than 140 converters on stream, The most important ingredients for this success are the axial-radial bed design described above (Fig. 1) and the three-bed configuration, normally with inter-bed heat exchangers for maximum thermodynamic efficiency (Fig. 3). These two elements give the highest utilization of the catalyst volume available, and in combination with 1.5-3 mm size catalyst it is possible to obtain a high ammonia conversion from a minimal catalyst volume with low pressure drop.
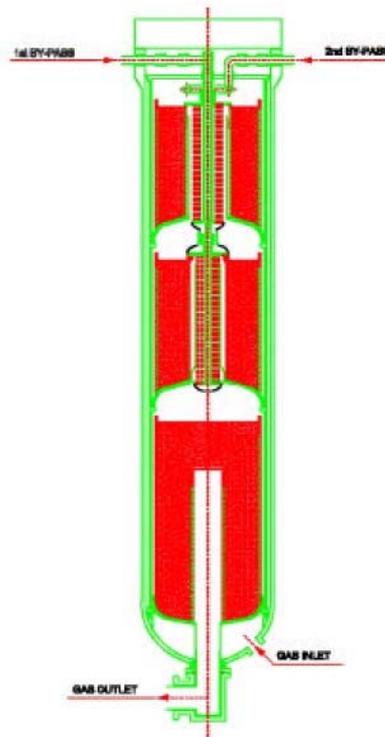
Fig. 3: three bed configuration with inter-bed exchangers

◈ Isothermal ammonia converters

A new technology, developed by Ammonia Casale for the revamping of ammonia converter is the Isothermal Ammonia Converter (IAC) design.

This design abandons the use of multiple adiabatic catalyst beds, commonly used in the ammonia industry for the pseudo isothermal design, and offers a higher conversion per pass. The new design is based on the use of plates immersed in the axial-radial catalyst bed to remove the reaction heat while it is formed. As indicated in the diagram above, the temperature profile achieved in the catalyst bed follows the line of maximum reaction rate, so obtaining the highest possible conversion per pass from a given catalyst volume.
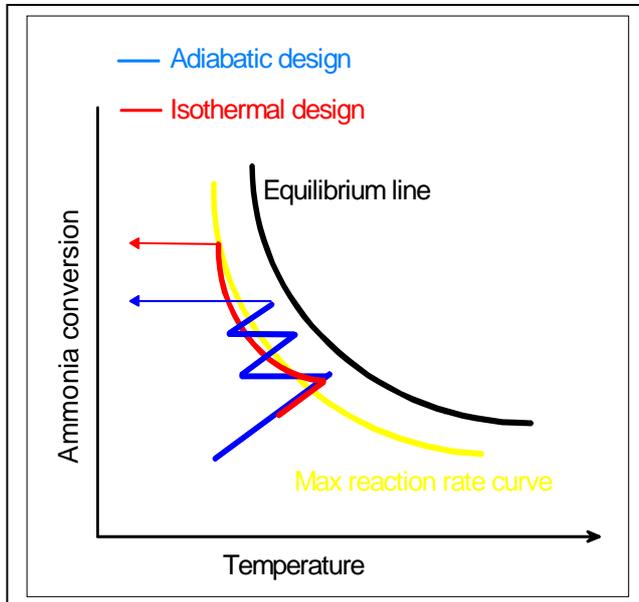
The use of plates for cooling, allows the design of a pseudo isothermal converter without tubesheets, eliminating the size restriction and simplifying the construction of the internals and the operation of catalyst loading and unloading. In addition, the non-adiabatic beds are axial-radial, featuring a low pressure drop and allowing the use of small size, high activity catalyst.

The new IAC is a very efficient design and is also suited for the very high capacity mega-ammonia plants that are becoming popular on the market, with production rates greater than 4,500 STPD.

INDUSTRIAL EXPERIENCE

There are CASALE IAC internals being used in two ammonia reactors for already a few months' time and another one is under construction.

## ◈ Secondary Reformer Burner

Ammonia Casale has developed, through its sister company CASALE CHEMICAL S.A., a new secondary reformer burner design utilizing advanced fluid dynamic simulation techniques. The goal was to develop a simple design capable of withstanding the severe operating conditions in a safe, reliable and cost-effective manner. This has been achieved coupling the Casale experience in burner design with the use of CFD simulations.

The CASALE Advanced Secondary Reformer Burner achieves the following goals:

- low pressure losses
- low temperature of the burner surfaces exposed to the flames;
- superior mixing and reduced flame length;
- protection of the refractory lining from the hot core of the flame

INDUSTRIAL EXPERIENCE

Casale burners are in use in four ammonia plants (one of them in Iran) and two more are being installed.

Figure 4
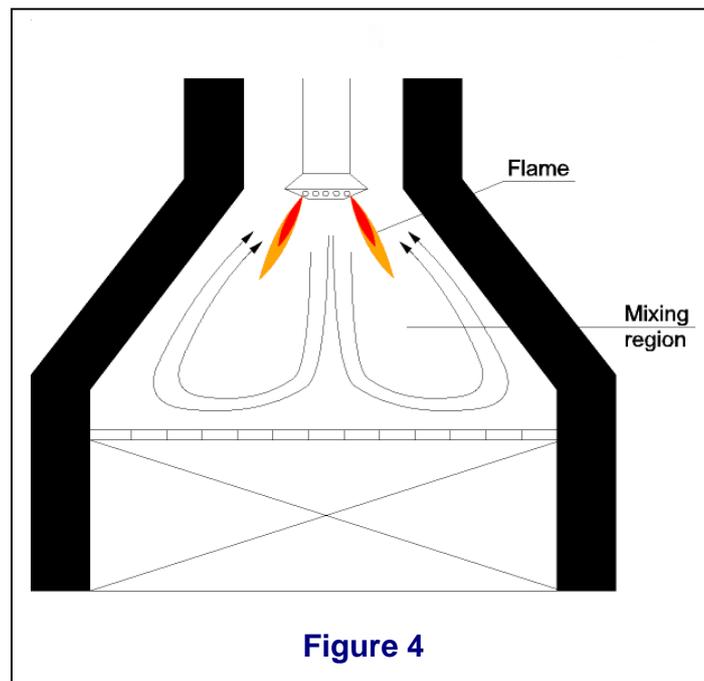
1.2   CASE HISTORY

Al-Jubail Fertilizer Co. – Complete Plant Revamp

In 2002 Ammonia Casale completed the revamp of a 1,000-t/d (original capacity) ammonia plant based on Kellogg technology at the Al-Jubail Fertilizer Company (SAMAD), located in Al-Jubail, Kingdom of Saudi Arabia.

This plant originally started up in March 1983 and it uses natural gas for both feed and fuel with a production capacity of 1'220MTD

The main goal of the project was to increase production capacity to 1,300 t/d. Further targets were energy saving, reducing cooling water consumption and improving reliability.

A second step of capacity increase up to 1,800 t/d was also considered and may be implemented in a short while. All the new equipment had therefore to be designed for the highest capacity.

Since every modification to machinery is very expensive, and because it would have been quite uneconomic to reharp reformer because the existing tubes were almost new, Casale prepared a minimum-investment revamping option according to the following guidelines:

- Main rotating equipment would not be revamped or replaced;
- No modifications would be made to the primary reformer radiant section;
- Modified equipment had to be suitable for the further capacity expansion;
- Possible variations in natural gas quality had to be considered;
- The plant should be able to operate at original capacity when new sections were isolated;
- Possible trips in new sections should not trip the existing plant.

The capacity expansion was limited to 1,300 t/d by the suction capacity of the existing synthesis gas compressor.

The feed gas desulphurization, feed gas compression, secondary reformer and methanation sections were suitable for the new operating conditions and needed no modifications.

The following modifications were implemented:

Pre-reforming and Primary Reforming

The primary reformer of the SAMAD ammonia plant is a typical Kellogg top-fired unit reformer tubes were replaced in 1997, with new HK40 tubes identical in every respect with the original tubes.

Therefore, without upgrading the reformer tubes, the heat flux to the primary reformer could be increased only marginally. To increase the capacity of the reformer up to the level needed for the capacity expansion, the steam to carbon ratio had to be decreased from 3.55 to 3.2. On account of the high concentration of higher hydrocarbons in the natural gas, this could only safely be done by installing a pre-reformer. The pre-reformer feed has to be heated to about 440°C, so a fired heater was installed (Fig. 5).

FIRED HEATER   PRE-REFORMER   PRIMARY REFORMER
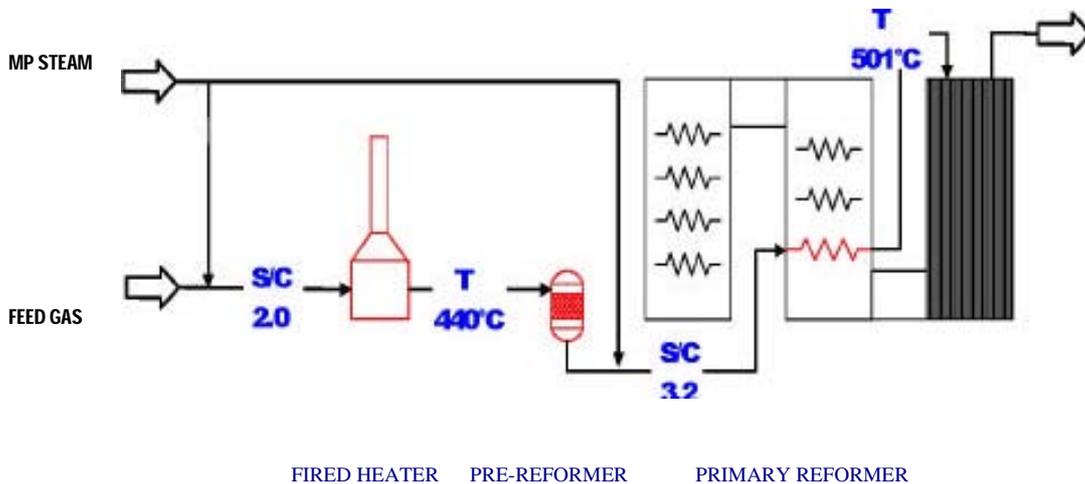
Fig. 5: New fired heater and pre-reformer

The advantages of the use of the pre-reformer and of the fired heater can be summarized as follows:

- the S/C ratio could safely be reduced;
- steam superheating temperature was increased without any change to the superheating coil;
- process air preheating was increased;
- the mixed feed coil did not require replacement, only a mechanically simple tube row removal;
- the BFW preheating level could be maintained;
- every possible change in natural gas composition could be accommodated.

Process air

This section was able to provide sufficient process air for a production of 1,220 t/d of ammonia under winter conditions. Any increase in plant capacity therefore required de-bottlenecking of this compressor.

This was accomplished by installation of a new air booster driven by a back-pressure steam turbine with intake air filter and after-cooler

Shift conversion

The high pressure drop in the shift converters (0.5 bar in the HTS and 0.6 bar in the LTS for new catalysts; and >1.0 bar each for the aged catalysts for both reactors) was due to the

axial-flow design of these converters. Retrofitting with Casale axial-radial internals reduced the pressure drop to about 0.3 bar, correspondingly increasing the suction pressure of the synthesis gas compressor. This pressure increase was very important to allow this machine to achieving the higher capacity without any modification to the make-up stages.

CO$_2$ removal

The carbon dioxide removal system was an inhibited MEA system. The CO$_2$ content of the purified gas was satisfactorily low (around 120 ppm) but corrosion problems were observed. For the revamp the BASF aMDEA© process was adopted by means of a simple solvent swap. None of the equipment needed modification. This change reduced the specific energy consumption from 1'650 to 1'370 kcal/Nm^3 CO$_2$, making it possible to reduce the S/C ratio. This reduction also resulted in a significant saving in the seawater cooling requirement of the stripper overhead condenser.

Synthesis loop

The reduction of the steam to carbon ratio and the revamping of the shift converter internals allowed an increase in plant throughput without appreciably increasing the system pressure drop.

To allow the synthesis loop to handle the increased flow new synthesis converter internals were provided. The existing cartridge was a two-bed inter-cooled design installed in the 1989 revamp. This was replaced by a new three-bed axial-radial cartridge, with one quench inlet between the first and second beds and one interchanger between the second and third beds.

The greater conversion efficiency and lower pressure drop of the new converter internals meant that both the required gas recycle rate and the energy needed to drive it round the system were reduced, so the re-circulator wheel of the main compressor was replaced by a new one designed for the revised flow conditions.

On account of the better converter performance and higher loop operating pressure, not only the ammonia concentration but also the temperature at the converter outlet were higher. The latter was above the design value for the metallurgy of the existing converter outlet pipe and for the boiler feed water preheater, so both were replaced.

The improved performance of the synthesis loop significantly reduced the specific chiller duty, allowing the plant capacity increase to be borne by the refrigeration compressor and its steam driver without any modification.

Table 4 compares the performance of the plant before and after the revamp.

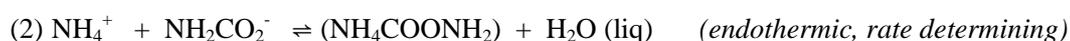| Table 4: SAMAD plant performance before and after revamp		
	Before revamp	**After revamp**
Production, t/d	1170	1312
Specific energy consumption, Gcal/tNH$_3$		about 6 % reduction
Sea water consumption, m^3/tNH$_3$		about 7 % reduction

Part 2 – Urea Plants

2.1 PROPRIETARY TECHNOLOGIES

Casale High-Efficiency Trays (for small or moderate capacity increase / energy reduction)

The starting point for any Casale urea plant revamping project aimed at increasing plant capacity and/or at decreasing the steam consumption is the installation of Casale High-Efficiency Trays (HET) in the reactor. Whether it is a stripping plant or a total recycle process, this new type of reactor tray significantly increases (by 4 to 5 percentage points) the CO_2 conversion, reducing the specific amount of steam required to recycle back the unreacted CO_2. In a stripping plant, that allows the specific load on the equipment in the HP loop to be reduced and, in a total recycle plant, a reduction in the specific load on most of the equipment in the plant. So, if the required capacity increase is not too high, installing the HET may be all that is needed to de-bottleneck the HP section, eliminating the need for additional HP equipment and thus maximising the capacity increase with minimum investment.

In projects resulting in small capacity increases, it is, in fact, very important to avoid any radical change in the HP section, which would drastically increase the time taken to provide a return on the investment. Just by installing HETs and making a consequential changes/additions in the downstream section, it is usually possible to increase capacity by 20-25% and sometimes by as much as 30-35%.

Where only a reduction of the specific steam consumption is required, the installation of HET is suggested alone or eventually in combination with an improvement of the heat integration system.

Urea synthesis is a two-stage reaction sequence in which two essentially gaseous reactants, carbon dioxide and ammonia, combine to produce ammonium carbamate in a liquid phase (equation 1) and the ammonium carbamate then loses a molecule of water to form carbamide (urea) (equation 2). The heat of formation of the ammonium carbamate provides the heat needed for its dehydration to urea.

(1) CO_2 + $2NH_3$ $\rightleftharpoons$ NH_4^+ + $NH_2CO_2^-$ *(exothermic, very fast)*

(2) NH_4^+ + $NH_2CO_2^-$ $\rightleftharpoons$ (NH_4COONH_2) + H_2O (liq)   *(endothermic, rate determining)*

Since the reacting system is heterogeneous, the overall rate of formation of urea depends on more than just the kinetics and thermodynamics of the two reactions. It is influenced by the following mechanisms.

✦ Mass transfer from the bulk of the gas 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 into the liquid phase of the "emulsion" (liquid in the bubble zone)

✦ Transfer from the emulsion to "clear" liquid in the rest of the reactor

✦ Formation of urea from carbamate in both the clear liquid and the emulsion.

Good mass and heat transfer is very important to prevent high localised concentration of carbamate and heat, especially at the vapour-liquid interface, which would hinder the formation of carbamate and its onward conversion to urea. A co-current flow configuration most closely satisfies these requirements, and a significant part of the total residence time in the reactor is needed to ensure that the vapours are absorbed into the liquid phase until equilibrium is reached as nearly as possible under the prevailing operating conditions, otherwise the optimum conversion to urea cannot be attained. Early reactors had no internals, but on the scale of today's plants reactor internals are essential to limit the size of the vessel required. They are essentially there to restrict the rate at which the gas bubbles rise through the reactor and to ensure that the gas is as efficiently dispersed as possible at all levels. But the majority of existing urea reactors still fall short of the ideal, judging from the amounts of CO_2 and NH_3 remaining in the vapours at the reactor outlet.

Casale has developed a new reactor tray type, which is designed to address the shortcomings of the two tray types currently in commonest use.

In collaboration with Professor Dente, Casale has developed a new tray geometry which greatly increases the mixing efficiency between vapour and liquid and, by substantially increasing the liquid boundary interface area between the emulsion and clear liquid zones and reducing
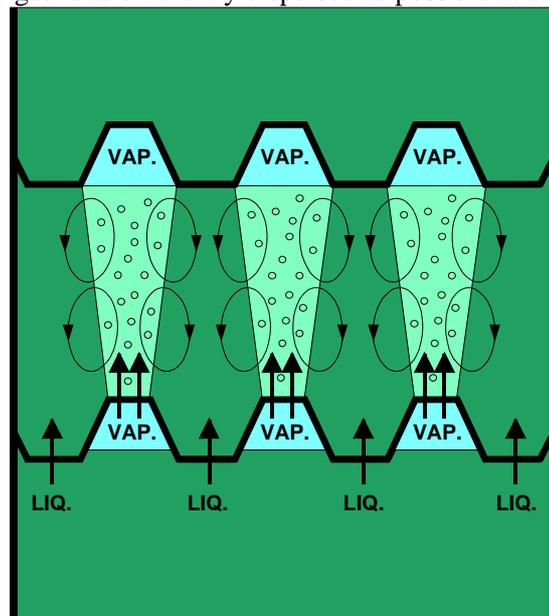

Fig. 6: Casale-Dente high-efficiency trays

the path length of the eddy flows between them, improves the mixing efficiency between the emulsion and clear liquid zones as well. Instead of a flat sieve plate, the new tray has transverse corrugations, with fine perforations through the tops and shoulders of the ridges to permit gas flow and generate copious very fine bubbles and coarser perforations in the troughs allowing liquid to flow through. Figure 2 illustrates the principle. The disposition of the separate gas and liquid flow paths contributes to steady-state, uniform flow of the two phases throughout the whole reactor.

INDUSTRIAL EXPERIENCE

In the last ten years Casale has undertaken a total of 48 projects involving installation of HETs in plants ranging from 250 to 2,100 t/d, some for the purpose of increasing capacity, others solely aimed at energy conservation. Some 44 of these plants are already in successful operation, and the Casale HETs have improved conversion by up to 5 or 6 percentage points or reduced specific steam consumption by 100-150 kg/tonne.

◈ Full-condenser / Split-flow-loop process (for moderate to large capacity increase of CO_2 stripping plants)

The Casale Full-Condenser / Split-Flow-Loop process is a very simple way to debottleneck the HP loop of CO_2 stripping plants to raise their capacity by 25-50% for relatively little investment.

The Full Condenser™ concept increases the heat transfer efficiency (the overall heat transfer coefficient) of the high-pressure carbamate condenser (HPCC) by about 50%. The Split Flow Loop™ concept improves the efficiency of the HP loop, raising the CO_2 conversion in the reactor by 2.5-3 percentage points. In combination with a Casale HET retrofit, this reduces the specific load on the equipment in the HP loop to the extent that, with a few appropriate changes in the downstream sections of the plant but without any further modification in the HP loop, the plant capacity can be increased by 25-40%, occasionally as much as 50%.

Full Condenser™ Concept

This comprises changing the HPCC from a falling-film to a submerged condenser with natural circulation. Casale has used a model based on fluid dynamic simulation to optimise the new design in all its aspects and it has at its disposal all necessary tools to best design any further application of the new concept.

As shown in Fig. 7, the vapour is introduced into the liquid in the bottom compartment of the condenser through a distributor, and a mixture of liquid and bubbles of vapour flows up through all but a very small number of the tubes. Residual gas, mainly inerts, separate from the liquid in the top compartment and leave through the top nozzle. On account of its greater effective density, the liquid returns down the remaining few tubes which do not have any vapour bubbles in them, producing the natural circulation. Incoming liquid (ammonia and carbamate) is introduced into the top of the condenser and merges with the circulating liquid. Liquid overflowing the weir in the top chamber passes down dedicated tubes to an outlet and thence to the reactor.
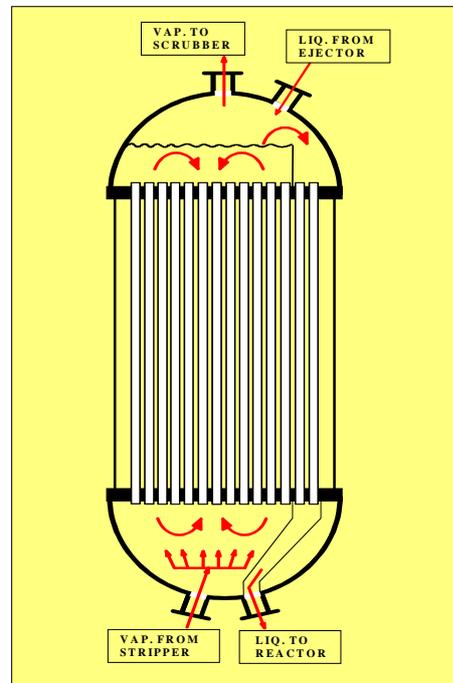

Fig. 7: HPCC modified to the Full Condenser™ concept

The total interface area between liquid and vapour in this bubble flow regime is significantly increased, so the transfer performance of the exchanger is highly improved. Also, the HPCC is better protected from corrosion, as all the tube surfaces are now constantly wetted.

The optimal circulation ratio is determined by Casale in order to achieve optimal condition for the heat transfer in the two-phase upward tubes.

Split-Flow-Loop™ Concept

When the HPCC is converted to the Full Condenser™ configuration it is necessary modify the external piping to fit to the new condenser configuration. Casale's Split Flow Loop™ concept (next Figure) takes advantage of the Full Condenser™ configuration to further increase the efficiency of the loop.

Because the HPCC is practically a total condenser (only inerts and traces of reactant vapours leave the top nozzle), only the amount of vapours that actually needs to be condensed in this equipment go to the condenser. This is about two thirds of the total vapour coming from the stripper. The rest of the vapours, which in the standard configuration would leave the HPCC un-condensed, bypass the condenser and go directly to the reactor. Thus the amount of inerts

entering the reactor is only about one third of what it was previously, so the urea conversion increases.

The liquid from the total condenser is sent to the reactor through a new ejector, driven by part of the ammonia feed that bypasses the condenser, which enhances the driving force for the circulation.

Although only one third as much passivation oxygen reaches the reactor as before, it is still adequate because the amount of passivation oxygen is calculated to guarantee proper

Fig. 8: Split Flow Loop™ configuration

passivation of the stripper, which is the most critical equipment in terms of corrosion, and is much more than is needed for passivation of the reactor.
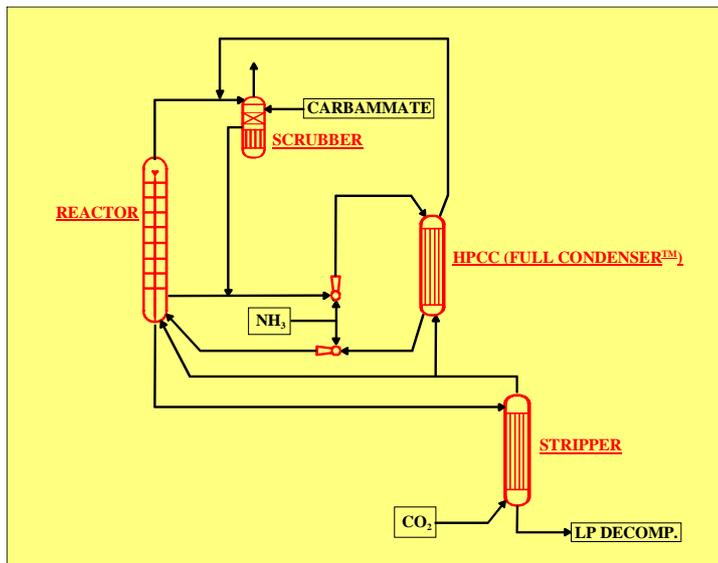

INDUSTRIAL EXPERIENCE

The Full-Condenser / Split-Flow-Loop Process is operating since 2003 in one plant.

◈ The VRS process (for large capacity increase of stripping plants)

A capacity increase greater than what can be achieved by installation of HETs alone normally requires more radical modification of the HP loop equipment. Any increase in mass flow which has the effect of reducing the residence time in the reactor will tend to offset or even outweigh the beneficial effect of HETs on reactor conversion efficiency.

For use in stripping plants Urea Casale has developed a new technology called the Vapour Recycle System (VRS), which not only mitigates the extent of the hardware modifications needed in the HP loop but can be installed while the plant is running and be tied in during a

planned turnaround. VRS reduces the amount of water recycled into the HP loop in the ammonium carbamate solution which is recycled after separation of the urea in the downstream decomposition and finishing sections. Water, being one of the products of the chemical equilibrium in which carbamate is decomposed to urea, has several adverse chemical and physical effects in the HP loop. Specifically, the greater the amount of water, the lower the conversion in the reactor, the lower the performance of the decomposers (i.e. the stripper, and the MP and LP decomposers). VRS separates water from the returned carbamate solution before it enters the HP loop by distillation in an HP decomposer working in parallel to the existing stripper. Figures. 9 and 10 show where VRS is incorporated in CO_2 stripping and NH_3 stripping plants respectively. The vapours thus obtained (comprising NH_3, CO_2 and only a little water vapour) are sent to the HPCC, while the depleted solution (mainly water) is sent back to the waste water treatment section at the back end of the plant.

With the HP loop now operating at a low H_2O/CO_2 ratio, a high CO_2 conversion is obtained in the reactor, stripping efficiency is improved and the existing decomposition, vacuum evaporation and waste water treatment sections do not have to handle as much water. Thus the capacity of the plant can be increased by 50% or more without altering the existing equipment in the HP loop.
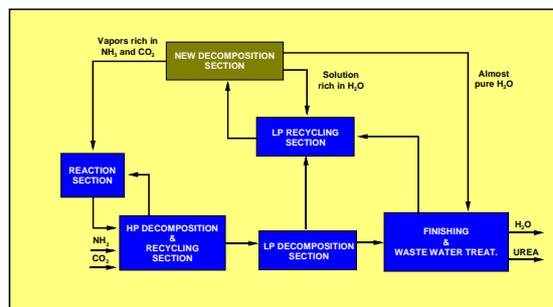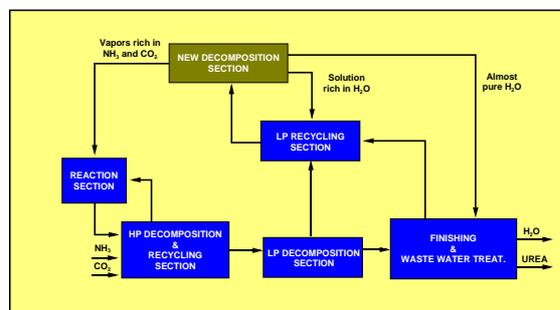

Fig. 9: VRS incorporated in CO_2 stripping plant

Fig. 10: VRS incorporated in NH_3 stripping plant

INDUSTRIAL EXPERIENCE

The VRS Process is operating since 1996 in one plant.

◈ The HEC process (for large capacity increase of conventional total recycle plants)

Urea Casale's new High Efficiency Combined (HEC) urea process, which is based on a combination of a very efficient "once-through" reactor and a conventional total recycle reactor, has a very high average CO_2 conversion and, by consequence, a low energy consumption. When applied as a revamp it can increase the capacity of an existing conventional total recycle plant by 50% or more and reduce its energy consumption for the minimum of investment, entailing minimal modification of the existing plant and the minimum of shut-down time.

Most of the urea is produced in the "once-through" reaction section because, in the absence of recycle water, the conversion of carbamate to urea is favoured and a high conversion of CO_2 to urea in single pass (75-80%) is obtained. The small amount of residual carbamate is decomposed, condensed and recycled, as aqueous solution, to a second reaction section operating at a lower pressure, which converts it to urea at a lower conversion efficiency (typically 55%). The weighted average conversion efficiency is thus in the 70-76% range, which is much higher than is obtained even in modern urea plants. Consequently, the amount of steam required by the decomposition section is reduced to around 900 kg/t. Because of the substantially reduced carbamate recycle, the overall H_2O/CO_2 ratio is only 0.3.

Figure 11 shows how HEC is incorporated into an existing total recycle process.

The new carbamate condenser is a U-tube, kettle-type heat exchanger and generates steam at up to 9 ata. The original reactor, fitted with Casale High-Efficiency Trays, is used as the primary reactor.

Fig. 11: VRS incorporated in NH_3 stripping plant

The secondary reactor is also fitted with HETs.

The solution from the "once-through" reaction section is first decomposed in a high-pressure decomposer, the overhead vapours from which enter the secondary reactor to supply part of the heat necessary to control the outlet temperature, and is then combined with the solution flowing out of the secondary reactor as feed for a two-stage recycling section with an ammonia recovery column.

On account of the much higher conversion obtained in the HEC synthesis section, the existing back end of the plant can be retained with only minor modifications.

INDUSTRIAL EXPERIENCE

Six conventional total recycle plants have been substantially expanded using the HEC technology. Table 5 lists the HEC revamp installations.

Table 5: Revamps using Casale's HEC process					
Company	Country	Original designer	Original capacity	New capacity	Start year
Terra	Canada	Toyo	270 t/d	800 td	1995
Reliance	New Zealand	Toyo	480 t/d	750 t/d	1996
Simplot	Canada	Weatherly	316 t/d	625 t/d	1998
Petrobras	Brazil	Toyo	800 t/d	1,500 t/d	2001
NFL	India	Tecnimont	1,000 t/d	1,650 t/d	2001
Razi Petroch.	Iran	Vulcan	500 t/d	875 t/d	2001

## ◆ High-Efficiency Hydrolyser (for capacity increase of wwt section and pollution control)

Urea plants produce two types of waste stream, both contaminated with compounds involved in urea synthesis. These have to be purified to the greatest possible extent to satisfy environmental regulations, which are becoming more and more severe.

Surplus **process condensate**, which has to be removed from the plant to maintain water balance, is already treated in most plants to recover the carbon dioxide and most of the ammonia it contains so as to minimise raw material losses. But many plants do not yet have the means either eliminate the ammonia and urea they contain completely or at least to reduce their content below contemporary limits, let alone future ones.

Casale's new High-Efficiency Hydrolyser (HEH) can completely eliminate urea from the process condensate and, if it is incorporated in a high-efficiency waste water treatment section, as shown in Fig. 7, ammonia can effectively be completely removed as well.

The process condensate is first sent to a desorption column, where most of the dissolved NH_3 and CO_2 is eliminated. It then enters the HEH, which completely eliminates the urea, 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, while the water, which contains about 3 ppm of urea and NH_3, is pure enough to be used as boiler feed, so the system becomes effectively zero-discharge in respect of liquid effluents.

Figure 12 shows the interior design of the HEH. It makes use of the stripping action of steam to remove the ammonia and carbon dioxide from the treated urea plant waste water condensate. The efficiency is enhanced by the fact that the hydrolyser is divided into two zones so as to keep the driving force for the NH_3 and CO_2 removal as high as possible. Since these are the products of the hydrolysis reaction, removing them to very low levels tends to promote further hydrolysis.
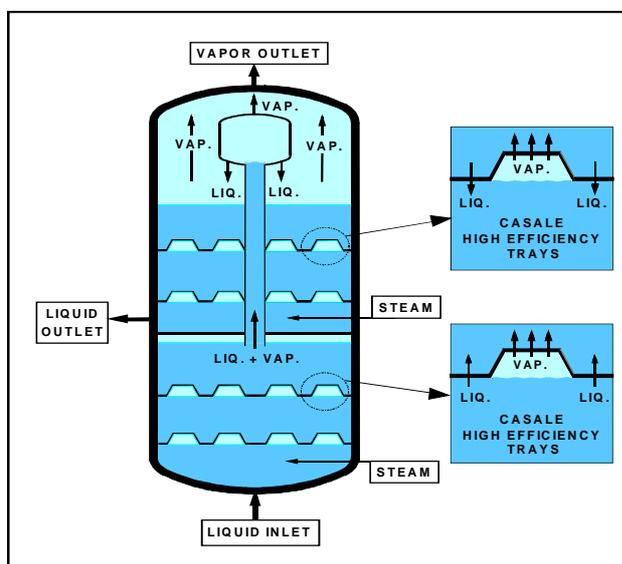
Fig. 12: Casale High Efficiency Hydrolyser

Both HEH zones are provided with Casale HETs, the action of which has been explained earlier. Raw condensate and steam (typically at or below 25 at) are fed in at the bottom of the first zone and rise through it in co-current flow. At the top of the first zone the vapours pass through a sieve plate, while the liquid is forced up into the top of the second zone and falls down through it in counter-current with the rising vapours Fresh steam is fed in at the bottom of this section. The lean condensate leaves from near the bottom of this section while the vapours exit the hydrolyser from the top.

In a capacity-increasing revamp, the HEH can very conveniently be utilised to debottleneck existing hydrolysers by adding it in series with the existing one. Existing desorbers can be conveniently revamped by changing the trays with ones of improved design.

INDUSTRIAL APPLICATION OF HEH

The High-Efficiency Hydrolyser is currently running in six plants, which have been revamped by Casale using HEC technology and one plant where just the waste water treatment section was revamped. In each case the HEH is designed to, and does, achieve boiler feed water grade.

2.2   CASE HISTORY

Concern Stirol – stepwise urea plant revamping

In 1997, a Ukrainian company asked Urea Casale to study the revamping of its 1,000-t/d CO_2 stripping urea plant to increase its capacity by 35%, decrease its energy consumption and increase its reliability.

The desired capacity increase could be achieved with the lowest investment by debottlenecking the HP synthesis section. This was achieved by installing Casale-Dente High-Efficiency Trays without any further modification to the existing heavy equipment in the HP loop. Modifications were, however, made to the HP pumps and CO_2 compression, while additional heat exchange surfaces were required for the LP decomposer and condenser and for the vacuum evaporators and condensers, and some modifications were required in the desorbers in the waste water treatment (WWT) section and in the prilling system.

All the revamp modifications were carried out in a normal shut-down and the plant has been operating successfully at the new capacity since 1999.

Taking advantage of spare capacity in the reactor resulting from the 1999 HET retrofit, a further revamp, commissioned in 2001, focused on debottlenecking the rest of the HP loop, particularly the HPCC, the capacity of which had been diminished by the need to plug a number of tubes. The desired capacity increase to 1,500 t/d was easily achieved at low cost by simply adopting the Casale Split Flow Loop™ / Full Condenser™ concept.

The CO_2 conversion reached in the reactor is three percentage points higher than the value previously obtained with the High Efficiency Trays at 1,350 t/d. A corresponding increase in the stripper efficiency has provided a measure of debottlenecking in the downstream sections without any alterations to the hardware: because of the increase in the heat transfer coefficient, it has also been possible to increase the pressure of the LP steam produced in the HPCC, which improves efficiency in the downstream sections.