

# HOW TO UTILIZE EXCESS OF $\text{NH}_3$ TO INCREASE UREA PLANT CAPACITY: $\text{CO}_2$ RECOVERY FROM FLUE GAS



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Author(s)	Prayagraj Dhruv, Veronica Rivas, Hans van den Tillaart and Amit Gupta
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# 1 ABSTRACT

Urea production capacity in ammonia–urea complexes is determined by the availability of both ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ). In many natural gas–based plants, urea output is constrained by limited  $\text{CO}_2$  availability despite surplus  $\text{NH}_3$  being available for conversion. Conventional capacity expansion typically requires modifications to the ammonia plant or  $\text{CO}_2$  recovery section, which entails substantial capital investment.

This paper presents a novel  $\text{CO}_2$  capture concept in which  $\text{CO}_2$  from flue gas is converted into an ammonium carbamate solution suitable for direct use in a urea melt plant. The process employs  $\text{NH}_3$  as the reactant for  $\text{CO}_2$  capture, eliminating the need for solvent regeneration and high-pressure  $\text{CO}_2$  compression. As a result, the recovered  $\text{CO}_2$  can be efficiently integrated into urea synthesis.

Application of this concept enables an increase in urea plant capacity of approximately 15–20% while utilizing existing excess  $\text{NH}_3$ . In addition to improved plant economics, the high  $\text{CO}_2$  capture efficiency of the process contributes to a lower overall carbon footprint for urea production. The proposed approach offers a practical and sustainable alternative for debottlenecking and revamping existing urea plants.

## 2 INTRODUCTION

Urea synthesis requires a stoichiometric supply of ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ). In integrated ammonia–urea complexes based on natural gas feedstock, the production rates of these two components are not always balanced. While  $\text{NH}_3$  capacity can often be increased or is already available in excess, the amount of  $\text{CO}_2$  accessible for urea synthesis is limited by the configuration and operating conditions of the ammonia plant. Consequently, urea plant throughput is frequently restricted by  $\text{CO}_2$  availability rather than  $\text{NH}_3$  production capacity.

Historically, this imbalance has been addressed by modifying the ammonia plant or its associated  $\text{CO}_2$  recovery systems to increase  $\text{CO}_2$  generation. Such modifications are capital-intensive and may require significant plant downtime. An alternative approach is to supplement the urea plant with an external  $\text{CO}_2$  source that can be effectively integrated into the synthesis process without disturbing existing ammonia operations.

Flue gas streams within ammonia complexes constitute a readily available source of  $\text{CO}_2$ ; however, their direct use in urea synthesis is impractical due to low operating pressure, dilution with inert gases, and the presence of impurities. Established  $\text{CO}_2$  capture technologies relying on physical or chemical solvents can recover  $\text{CO}_2$  from flue gas, but these systems require regeneration and subsequent compression to urea synthesis pressure. In many existing plants, the lack of spare capacity in the high-pressure  $\text{CO}_2$  compressor represents a major limitation for such solutions.

To overcome these constraints, this paper introduces a process concept in which  $\text{CO}_2$  is captured from flue gas via chemical conversion with  $\text{NH}_3$  to produce an ammonium carbamate solution (hereafter referred to as “carbamate”). This carbamate can be directly routed to a urea melt plant, providing an effective pathway to increase urea production while avoiding conventional compression and revamp limitations.

## 3 CARBON DIOXIDE RECOVERY

### 3.1 Limitations of existing methods

Existing CO<sub>2</sub> capture technologies utilizing Hot Potassium Carbonate (HPC) solutions or amines involve the absorption of CO<sub>2</sub> and subsequent regeneration of the solvent. The recovered CO<sub>2</sub> is produced at low pressure and therefore must be compressed (to around 150 bara) using a high-pressure (HP) CO<sub>2</sub> compressor before it is fed into the synthesis section. In most urea plants, the HP CO<sub>2</sub> compressor has no spare capacity. As a result, capacity revamp projects often require the installation of an additional HP CO<sub>2</sub> compressor, leading to high capital expenditure (CAPEX) and operating expenditure (OPEX).

The uniqueness of Stamicarbon CO<sub>2</sub> capture technology is that CO<sub>2</sub> is captured in the form of a medium-pressure (MP) carbamate solution, which can be injected directly into the MP section of the urea plant, eliminating the need for additional capacity in the HP CO<sub>2</sub> compressor section. This translates to low CAPEX and OPEX.

### 3.2 The challenge

To expand the capacity of a urea plant, additional CO<sub>2</sub> feedstock is often required. The most readily available source of CO<sub>2</sub> is flue gas, also referred to as stack gas. However, this flue gas is not suitable for direct utilization in a urea plant due to its composition, impurities and process conditions (temperature and pressure).

### 3.3 Proposed solution: description and operation

The proposed solution involves the capture of CO<sub>2</sub> using NH<sub>3</sub> to form a carbamate solution, which can be directly utilized in the urea plant for capacity enhancement. Among others, the process includes the following sections (Figure 1):

- **Compression:** The gas containing CO<sub>2</sub> (e.g., flue gas) is compressed to a pressure where the resulting carbamate can be used directly in the MP section of a urea plant, considering both pressure and water content. If the flue gas is already sufficiently pressurized, this step can be omitted.
- **Main Absorption Section:** The compressed gas is introduced into the main absorption section, where CO<sub>2</sub> is absorbed with a slight excess of NH<sub>3</sub> to ensure high CO<sub>2</sub> capturing efficiency. The heat of absorption is removed by circulating the carbamate over a cooler. The outlet product of the absorption column is exported directly to the MP section of the urea plant. A portion of it is recycled back to the absorption section after cooling.
- **Circulation Scrubber Section:** The gas from the main absorption section, containing inert NH<sub>3</sub>, CO<sub>2</sub>, and water, is scrubbed in one or more stages. The carbamate solution is circulated and cooled at each stage to reduce the vapor pressure of the carbamate. The temperature profile of the scrubbing section is selected to be sufficiently higher than the crystallization temperature.
- **Final Scrubbing Section:** The gas leaving the column is scrubbed, preferably with chilled water to minimize the NH<sub>3</sub> in vent gas (in ppm level).

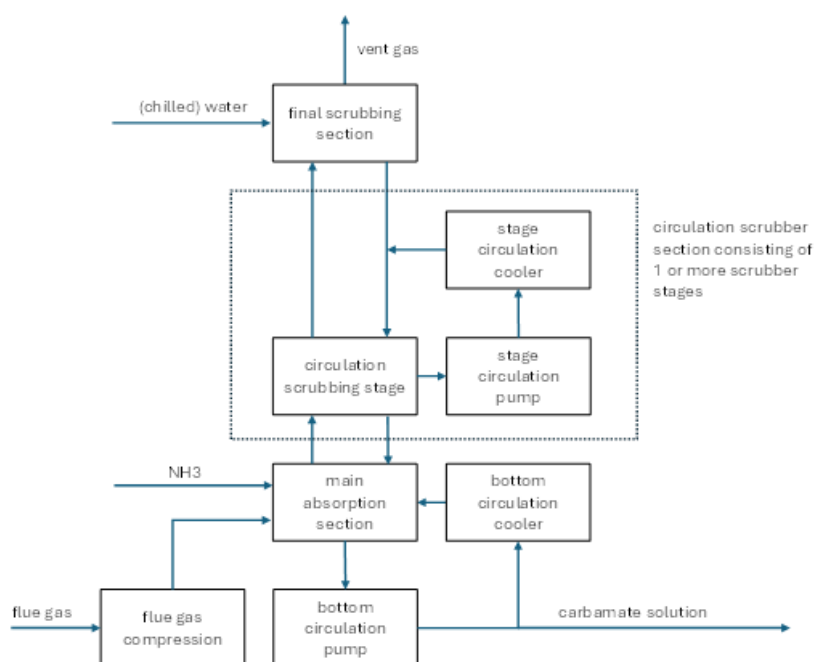


Figure 1. Overall process scheme of CO<sub>2</sub> capturing

The absorption and scrubbing sections can be combined in a single column or separated into multiple smaller columns connected by ducts. The scrubbing stages can be designed as packed beds with structured or random packing, trays, or a combination of these.

### 3.4 Basis of design

The example design basis used for explaining operational aspects further in this paper is given in Table 1.

Table 1. Typical and design flue gas composition of reformer flue gas (ammonia plant)

Components	Typical range, vol.-%	Design composition, vol.-%	Design composition, wt.-%
CO <sub>2</sub>	8.8-13.7	10.2	15.2
H <sub>2</sub> O	15.0-18.0	1.3	0.8
N <sub>2</sub>	69.0-71.0	84.7	80.0
O <sub>2</sub>	2.0-4.0	3.82	4.0

### 3.5 Operating philosophy of the capturing process

The capturing process is operated in a way that produces a fixed quantity of carbamate, corresponding to the revamp capacity chosen. The design capacity increase of the urea melt unit is 12 %, corresponding to 35.4 MTPH of carbamate (30 wt.-% water), based on a plant nameplate capacity of 2000 MTPD.

The amount of flue gas fed to the CO<sub>2</sub> recovery unit is flow controlled, and the NH<sub>3</sub> is controlled such that the quantity of carbamate is produced at optimal N/C ratio (molar ratio of NH<sub>3</sub> to CO<sub>2</sub>), with minimal NH<sub>3</sub> loss.

At a given CO<sub>2</sub> content in the flue gas, the optimal N/C ratio of the carbamate exported to the urea melt plant determines the required liquid NH<sub>3</sub> feed to the CO<sub>2</sub> capture unit. This optimal ratio is governed by the system pressure at the bottom of the absorption column, excluding inert components.

If the N/C ratio is less than optimal, there will be CO<sub>2</sub> slip at the vent of the CO<sub>2</sub> capturing unit. If the N/C ratio is more than optimal, there will be NH<sub>3</sub> slip at the vent of the CO<sub>2</sub> capturing unit.

To ensure high CO<sub>2</sub> capture efficiency, the unit will be operated such that a small amount of NH<sub>3</sub> (ppm level) is always present in the vent gas.

## 3.6 Optimization study

### 3.6.1 Operating pressure

The product stream (carbamate) must be sent to the MP section of the urea melt plant. This section normally operates at around 20-25 bara. The results of a case study, conducted to determine the optimum operating pressure of the unit, are shown below.

The CO<sub>2</sub> capturing efficiency is defined as the CO<sub>2</sub> quantity in the carbamate produced divided by the total CO<sub>2</sub> in the flue gas to the recovery unit.

Figure 2 indicates that CO<sub>2</sub> capturing efficiency improves with increasing pressure up to a point, and then it flattens out. The selected pressure of 25 bara is motivated as an optimum balance between capturing efficiency and CAPEX / OPEX.

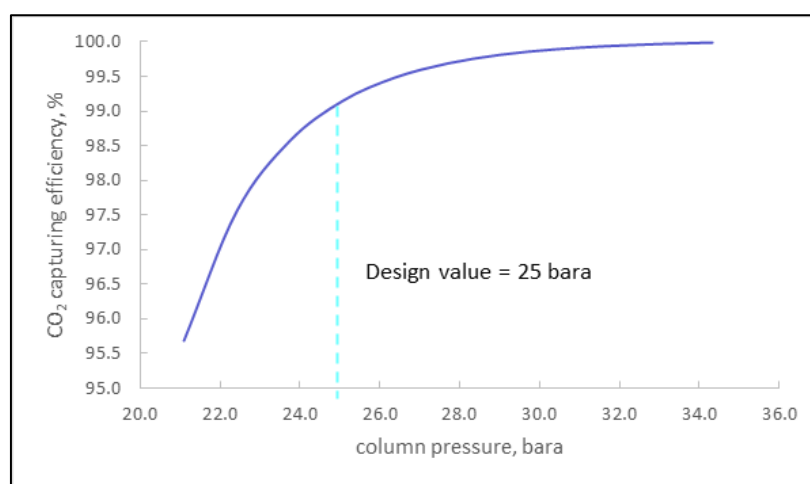


Figure 2. CO<sub>2</sub> capturing efficiency as a function of CO<sub>2</sub> recovery unit operating pressure



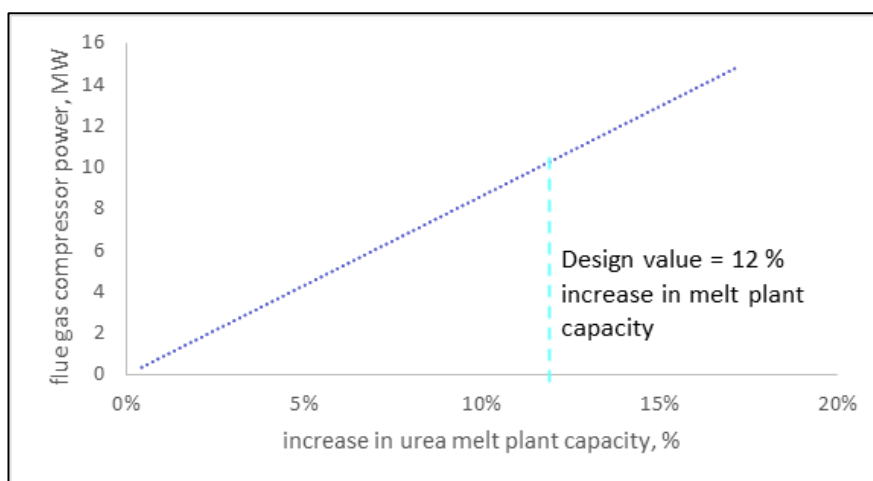


Figure 3. Flue gas compressor power as a function of % increase in urea melt plant capacity (base capacity of 2000 MTPD)

Figure 3 shows that the required flue gas compressor power increases with an increase in melt plant capacity. Based on the chosen design value of a 12 % increase in melt plant capacity, the required compression power for flue gas is around 10 MW (considered suction pressure of compressor is 1.5 bara).

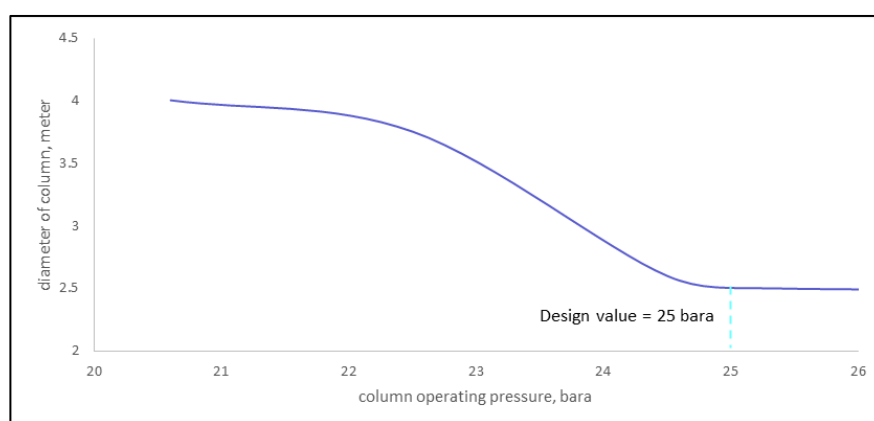


Figure 4. Diameter of column as a function of column operating pressure

Figure 4 indicates the relation between operating pressure and the diameter of the column. The diameter decreases with increasing operating pressure up to a pressure of 25 bara.

### 3.6.2 Effect of CO<sub>2</sub> composition in flue gas

The objective behind this study is to check the robustness of the process with varying CO<sub>2</sub> content of the flue gas. The effects of a surplus amount of CO<sub>2</sub> versus an understoichiometric amount of CO<sub>2</sub> is evaluated. If the CO<sub>2</sub> concentration of the flue gas decreases, the column operating pressure needs to be increased to ensure that the partial pressure of CO<sub>2</sub> in the absorption column is maintained at a sufficiently high level to have the desired capturing efficiency.

If there is NH<sub>3</sub> at the top of the column, no significant CO<sub>2</sub> will slip from the top of the column, i.e., essentially all CO<sub>2</sub> is absorbed. The composition of the flue gas from the stack does not vary much as the burning process is typically precisely controlled. The amount of flue gas to the column is controlled by the speed of the flue gas compressor taking a certain amount of flue gas from the stack. If the system is operating with a fixed amount of NH<sub>3</sub>, flue gas feed and carbamate product, then a small variation in flue gas composition is captured by the NH<sub>3</sub> analyzer installed at the vent gas stream of the absorber. This NH<sub>3</sub> measurement is used for fine-tuning the column operation by controlling the amount of NH<sub>3</sub> feed.

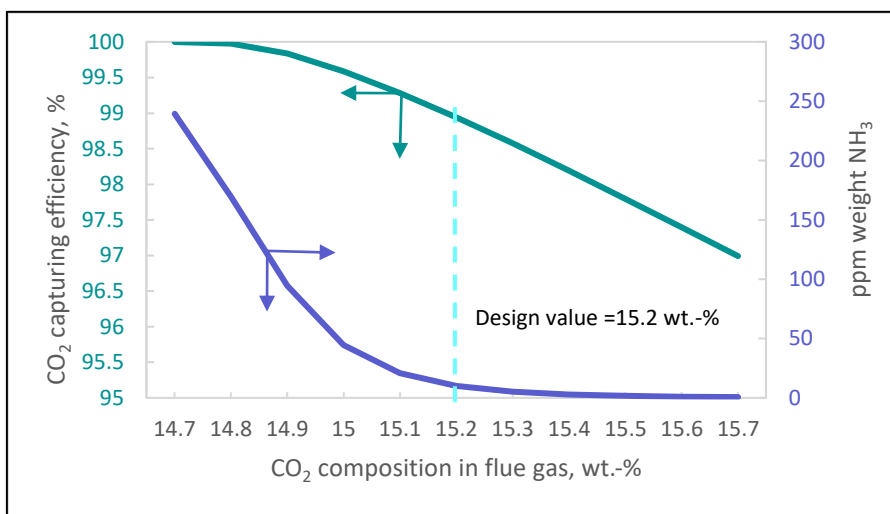


Figure 5. CO<sub>2</sub> capturing efficiency, NH<sub>3</sub> slip in the vent gas as a function of CO<sub>2</sub> composition in flue gas

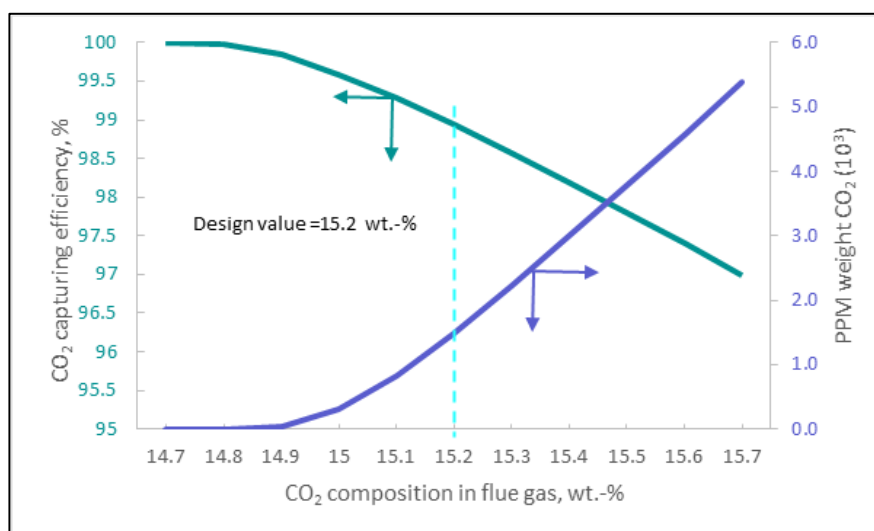


Figure 6. CO<sub>2</sub> capturing efficiency, CO<sub>2</sub> slip in the vent gas as a function of CO<sub>2</sub> composition in flue gas

Figures 5 and 6 indicate the results of sensitivity analysis by varying the CO<sub>2</sub> composition of the flue gas from 14.7 wt.-% to 15.7 wt.-%, keeping all other conditions optimal for the CO<sub>2</sub> concentration of 15.2 wt.-% (design figure).

The effect of variation in the amount of CO<sub>2</sub> is expected to be dampened out in the liquid outlet composition, but will show a more pronounced effect in the gas outlet stream in terms of NH<sub>3</sub>/CO<sub>2</sub> slip. Ideally, the process is controlled in such a way that the outlet NH<sub>3</sub> concentration is between the detection limit and the maximum environmental limit, about 10 ppm-wt.

### 3.6.3 Recirculation ratio of absorption section

Based on Figure 7, if the recirculation ratio increases, the temperature of the carbamate in the column decreases and hence NH<sub>3</sub> slip in that section of the column decreases. This happens because the outlet temperature of the recirculation cooler is fixed at a constant offset to the crystallization temperature of the circulating carbamate. However, a higher recirculation ratio requires higher pump capacity. Reducing the circulation rate decreases capturing efficiency.

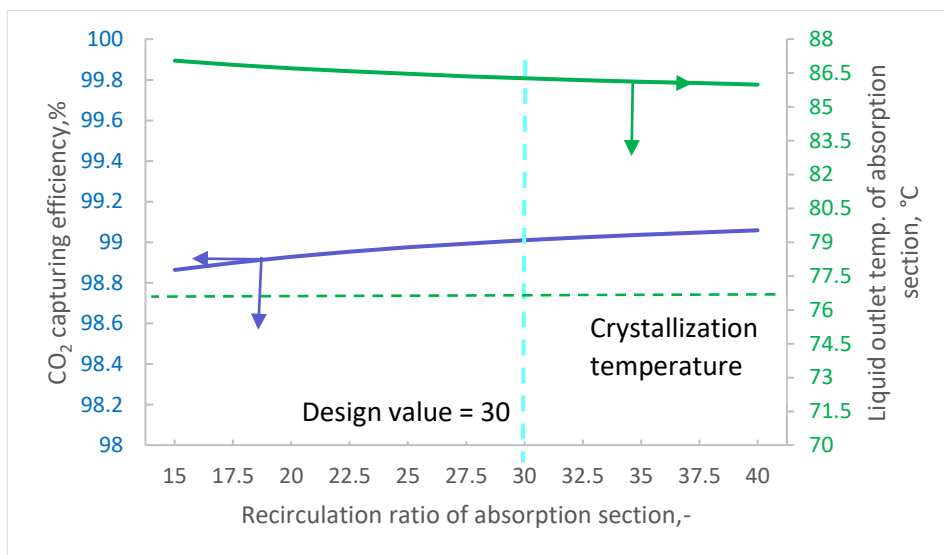


Figure 7. CO<sub>2</sub> capturing efficiency and liquid outlet temperature from the absorption section as a function of recirculation ratio of absorption section

Figure 7 also indicates that on increasing recycle ratio, the export stream from the absorption section gets colder and the offset to crystallization temperature decreases. On the other hand, a colder recycle stream is more effective for the absorption process. To balance these effects, a value of the recycle ratio of 30 is chosen.

### 3.6.4 Recirculation ratio of scrubbing section

On increasing the recirculation ratio of the scrubbing section, the CO<sub>2</sub> capturing efficiency in the CO<sub>2</sub> capturing unit increases (see Figure 8) as the liquid outlet temperature of the scrubbing section decreases. This decrease of temperature leads to a lower NH<sub>3</sub> and CO<sub>2</sub> vapor pressure and hence increases the capturing efficiency.

The amount of recirculation is based on the discharge capacity of the recirculation pump (pump sizing) and the pressure drop across the recirculation line. The pump capacity will be decided based on the required recirculation flow.

For our design, a recirculation ratio of about 20 is selected based on acceptable CO<sub>2</sub> capturing efficiency (>98 %). A higher recirculation rate, although giving higher capturing efficiency, results in higher equipment costs (for the circulation pumps, an increase in the diameter of the absorption column and an increase in the size of the recirculation coolers).

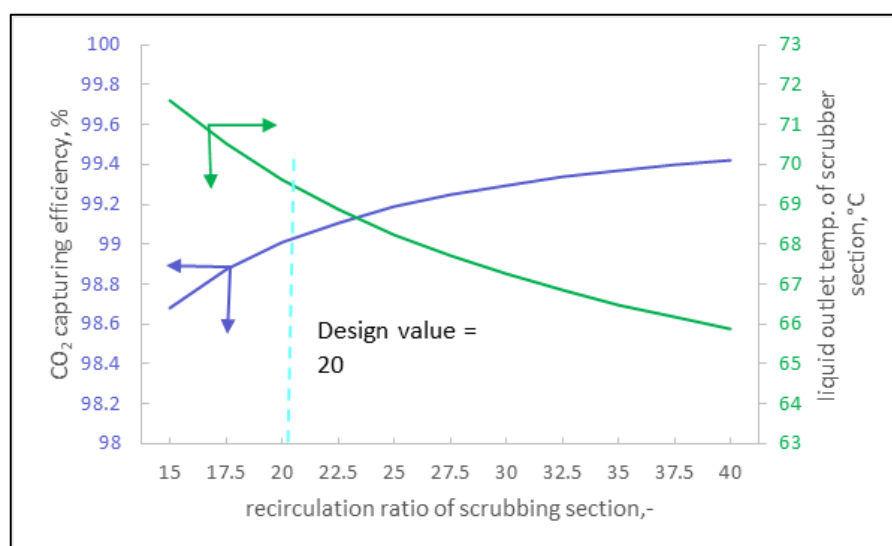


Figure 8. CO<sub>2</sub> capturing efficiency of capturing unit and liquid outlet temperature of the scrubbing section as a function of recirculation ratio of scrubbing section

### 3.6.5 Effect of temperature of water feed at the final scrubbing section

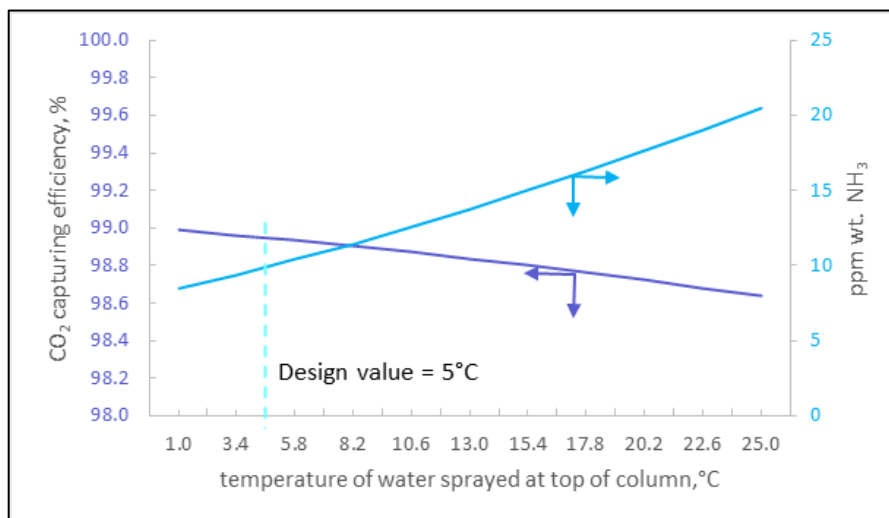


Figure 9. CO<sub>2</sub> capturing efficiency and NH<sub>3</sub> slip in vent gas as a function of temperature of water sprayed at top of the column

Figure 9 shows that as the temperature of the water feed at the top of the column increases, the capturing efficiency decreases and therefore the NH<sub>3</sub> slippage increases. To minimize NH<sub>3</sub> slippage, the temperature of the water feed is selected as 5 °C, which typically requires the use of a chiller. The NH<sub>3</sub> feed to the CO<sub>2</sub> recovery unit can be utilized as a chilling medium in the chiller.

## 3.7 Results

Capturing CO<sub>2</sub> in a single pressure process with two separate scrubbing stages from a typical flue gas (10.47 vol.-% CO<sub>2</sub>) at 25 bara resulted in a carbamate with 30 wt.-% water. The vent gas contained approximately 0.1 vol.-% CO<sub>2</sub> and 10 ppm vol. NH<sub>3</sub> after scrubbing with chilled water at 5 °C in a final scrubbing section. The concentration and temperature profile across the stages are indicated in Table 2.

Table 2. Water concentration and temperature profile along the absorption process

Stage	Water concentration, wt.-%	Temperature, °C
Bottom absorption	30	86
Circulating scrubbing	70	45
Final scrubbing	99.6	37

The process operates at temperatures just above the crystallization temperature. As indicated in Figure 10, at each location throughout the column – from the bottom section to the top – the actual temperature is above the crystallization temperature.

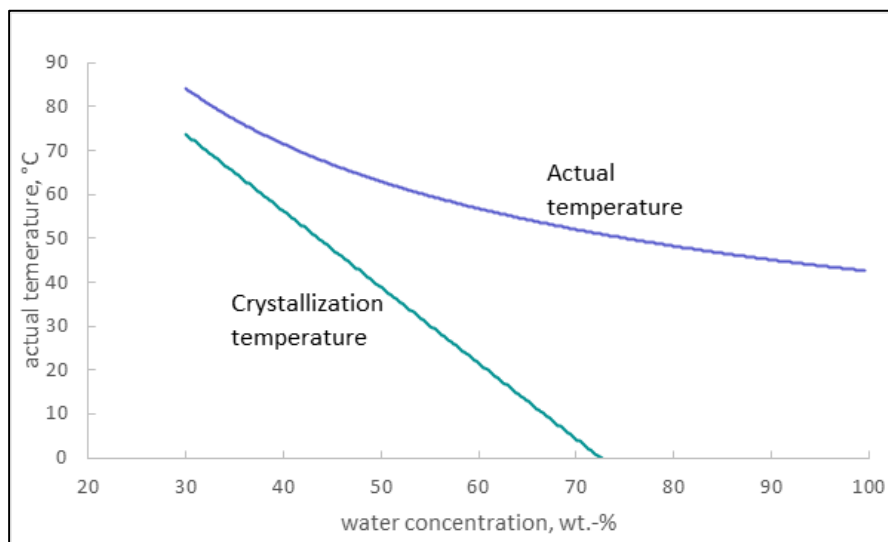


Figure 10. Actual temperature and crystallization temperature as a function water concentration in the CO<sub>2</sub> absorption process

In the following section, a detailed analysis of the utilization of the recovered MP carbamate into the urea production plant is presented.

## 4 UTILIZATION OF THE CARBAMATE SOLUTION IN THE UREA PLANT

Stamicarbon has extensive experience in processing external carbamate streams into urea production including, for example, melamine integration with a urea plant.

This expertise is extended to integrate the carbamate solution from the new CO<sub>2</sub> recovery technology as explained above. The resulting carbamate stream from the CO<sub>2</sub> recovery unit is directly utilized for urea production. The key advantage lies in eliminating the need for dissociating columns, along with the potential to avoid costly modifications to the existing CO<sub>2</sub> compressor to cope with the additional capacity or the addition of a small HP CO<sub>2</sub> compressor.

Furthermore, Stamicarbon has designed an optimal integration that ensures that the specific steam consumption remains comparable before and after the implementation. This is achieved by revamping a Stamicarbon Urea 2000+ plant utilizing Stamicarbon MP flash technology.

### 4.1 Process description

The basis of this process is a typical Stamicarbon CO<sub>2</sub> stripping plant with pool reactor combined with a prilling finishing unit, where the specific steam consumption is typically 891 kg/ton urea (at 23.5 bara and 300 °C).

The carbamate solution from the CO<sub>2</sub> recovery unit at MP will be directed to the newly added MP section of the MP flash technology. The main advantage of this new MP section is that it enables the reduction of the stripping efficiency of the HP stripper, which reduces the import of the HP steam requirement of the urea plant. This saving of steam can be utilized effectively to process the additional CO<sub>2</sub> from the absorption column in the form of a carbamate solution.

By implementing MP flash technology, as shown in Figure 11, the HP steam consumption is typically reduced by about 150 kg/ton urea. This well-proven technology has been in stable operation over a decade. In the process, urea solution from the HP stripper is flashed adiabatically at a pressure of about 25 bara in the newly added MP flash separator. The vapors from the HP scrubber, combined with those generated in the adiabatic MP flash separator, are directed to the shell side of the pre-evaporator / MP carbamate condenser. The heat of condensation released in the shell side (MP carbamate condenser) is used to concentrate the urea solution in the tube side (pre-evaporator). As mentioned previously, the carbamate solution from the CO<sub>2</sub> recovery unit is introduced into the shell side of the combined pre-evaporator / MP carbamate condenser, further facilitating condensation. Finally, the resulting MP carbamate is transferred to the synthesis loop by means of the HP carbamate pump, ultimately increasing the capacity of the urea melt plant.

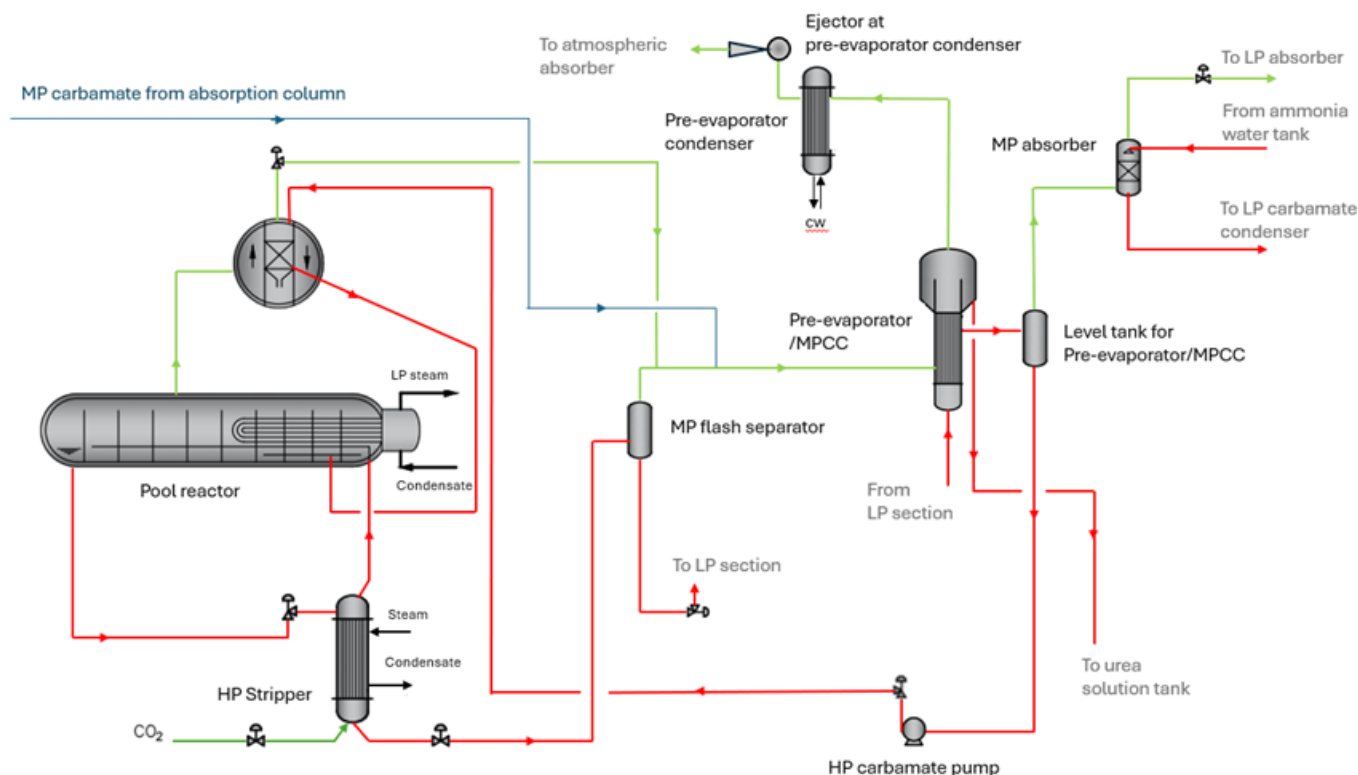


Figure 11. Implementation of MP flash technology and MP carbamate solution from CO<sub>2</sub> recovery unit

Various alternatives have been considered and rejected. The addition of MP flash technology has been identified as the most feasible revamp solution.

One option considered was the addition of Stamicarbon's MP add-on technology, which could handle the increased plant capacity but would result in high steam consumption. This is because the stripping efficiency would remain the same, and there would be extra MP steam required in the MP rectifying column.

Another option considered was directing the MP carbamate from the CO<sub>2</sub> recovery unit to the existing LP section. However, this approach would result in wasted compression energy from the MP compressor at the CO<sub>2</sub> recovery unit, along with increased steam consumption.

A third possibility was to send this stream directly to the HP scrubber, e.g. by supplying this directly to the suction side of the HP carbamate pump.

Ultimately, the addition of an MP flash section makes it possible to effectively translate the steam saving directly into more production, next to other advantages, which are discussed in the next chapter.

## 4.2 Consequences of utilizing the carbamate solution in the urea plant

For the CO<sub>2</sub> stripping urea plant there are three main effects following the introduction of the carbamate import from the CO<sub>2</sub> recovery unit.

1. The effect of the additional water import in the urea plant
2. The effect of the additional CO<sub>2</sub> import in the urea plant.
3. The effect of the additional liquid load on the HP stripper.

These effects are discussed below.

#### 4.2.1 Effect of the additional water import in the urea plant

Since CO<sub>2</sub> has been absorbed in NH<sub>3</sub> and process condensate, forming a carbamate solution, additional water is inevitably introduced into the urea melt plant.

Figure 12 illustrates the impact of introducing carbamate solution with different water concentrations on the HP steam consumption (23.5 bara and 300 °C), based on MP flash technology.

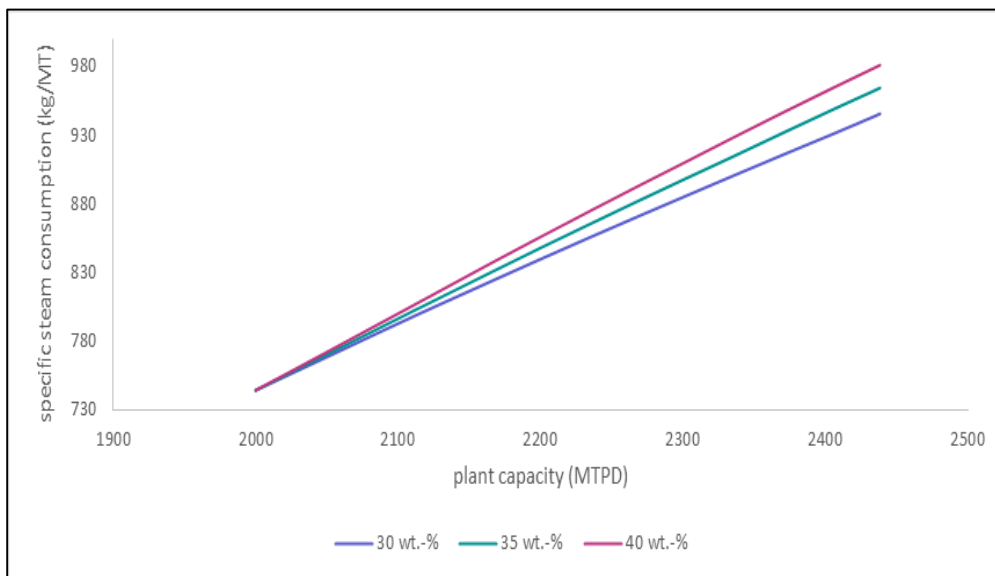


Figure 12. Specific steam consumption versus plant capacity at different carbamate water concentrations for plant with original capacity of 2000 MTPD

A higher water content of the carbamate recycle to the synthesis increases the H/C<sup>1</sup> ratio in the pool reactor, which reduces the urea conversion there. As a result, the urea concentration achieved in the synthesis decreases, leading to increased vapor generated in the stripper at the same stripping efficiency, at the cost of increased HP steam consumption in the stripper.

The effect of additional water on the H/C ratio can be seen below in Figure 13, as well as the urea concentration at the outlet of the pool reactor (shown as concentration urea (U) + biuret (B)). It can be observed that when more water is added, the H/C increases while the urea plus biuret concentration at the outlet of the pool reactor decreases.

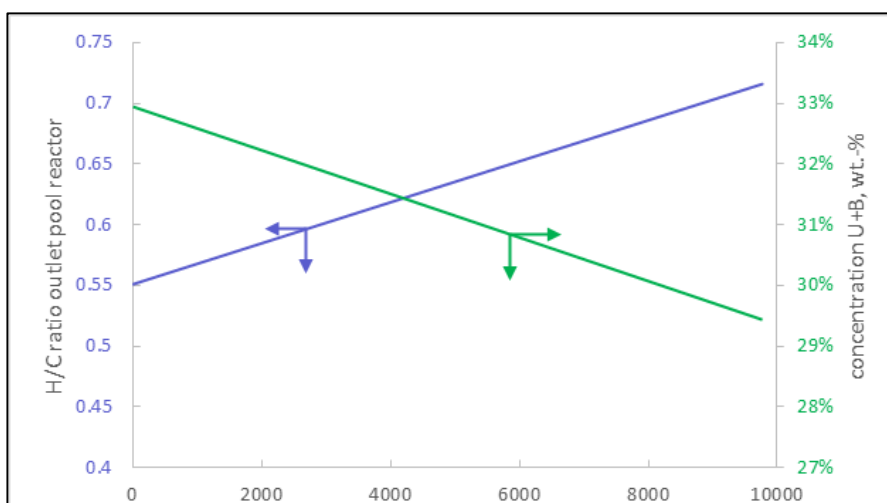


Figure 13. H/C ratio and U+B concentration, both in outlet pool reactor, as a function of additional water by introduction of carbamate from CO<sub>2</sub> recovery unit by increasing the capacity from 2000 MTPD to 2450 MTPD

<sup>1</sup> H/C definition: H<sub>2</sub>O/CO<sub>2</sub> (mol/mol) in the mixture



The primary goal of this integration is therefore to increase the urea plant capacity, enabling higher urea production while maintaining the same specific steam consumption as before, admitting CO<sub>2</sub> from the CO<sub>2</sub> recovery unit.

Figure 14 shows the capacity increase of the urea plant while utilizing the carbamate solution stream from the CO<sub>2</sub> recovery unit.

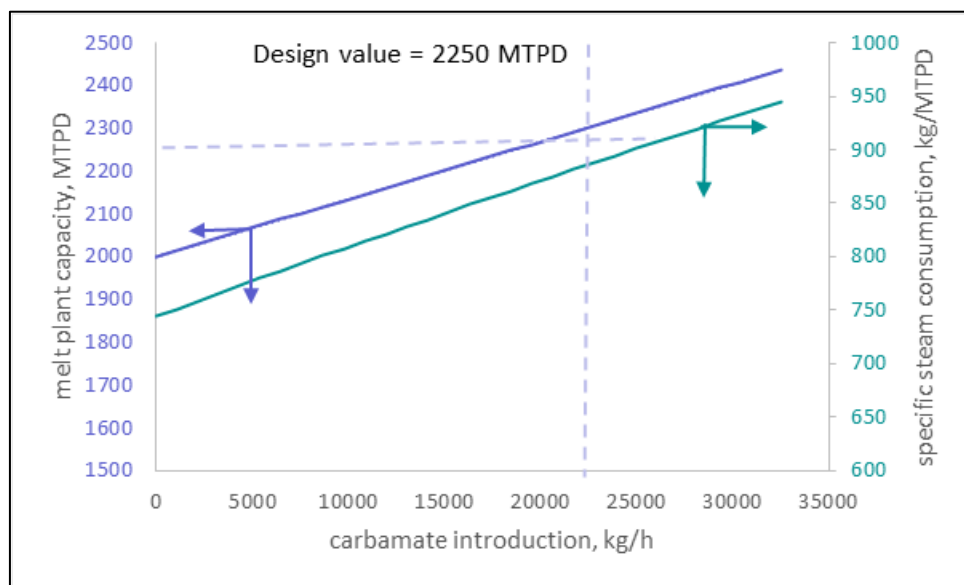


Figure 14. Capacity and specific steam consumption versus the amount of additional carbamate from the CO<sub>2</sub> recovery unit imported to the urea melt plant

By implementing MP flash technology and introducing the MP carbamate from the CO<sub>2</sub> recovery unit, the plant capacity can be increased by up to about 12 % with similar specific steam consumption compared to the original situation. Processing the additional carbamate from the CO<sub>2</sub> recovery unit in the urea plant requires approximately 110 kg of extra HP steam per ton of urea, which is compensated by the MP flash technology implementation. This means that the urea melt plant capacity can be increased by up to about 12 % as shown in Figure 14.

#### 4.2.2 Effect of the additional CO<sub>2</sub> import in the urea plant

One consequence of introducing carbamate from an external source into the urea melt plant is the relative decrease of the CO<sub>2</sub> supplied to the HP stripper, relative to the amount of urea produced, from the CO<sub>2</sub> compressor (the absolute amount from the compressor remains the same), as can be observed in Figure 15.

In general, when only the relative CO<sub>2</sub> feed to the stripper is decreased, the shell side steam pressure needs to be increased for the same stripping efficiency. The resulting higher skin temperature of the inside of the stripper tubes adversely affects the lifetime of the stripper. In this concept, due to the introduction of the MP flash technology, this is not the case, according to the experience of Stamicarbon. The lower stripping efficiency for the MP flash technology counters the effect of the reduced relative CO<sub>2</sub> feed. The ultimate skin temperature of the inside of the stripper tubes will remain about the same.

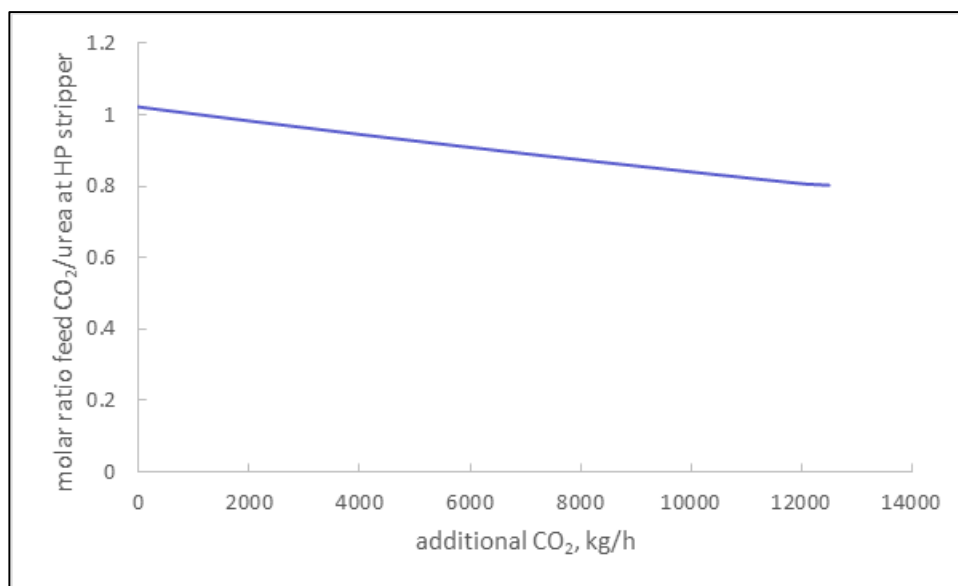


Figure 15. Molar feed ratio of CO<sub>2</sub>/urea at HP stripper as a function of additional CO<sub>2</sub> via carbamate

#### 4.2.3 Effect of the additional liquid load on the HP stripper

After the revamp, the effect on the process side of the existing HP stripper is two-fold.

1. The liquid load at the top of the stripper tubes increases, mainly due to increased capacity.
2. The vapor load at the top of the stripper tubes per kg of liquid feed decrease, due to a decreased stripping efficiency - from approximately 78 % to 68 %.

The top of the stripper tubes is the most sensitive part with respect to flooding, with vapor load being the most critical parameter.

Importantly, the revamped stripper continues to operate with a sufficient margin from the flooding point. This has been verified for the revamp case, where the reduction in vapor load has a stronger (positive) effect than the increase in liquid load.

## 5 CONCLUSIONS

As described, the proposed process illustrates advancements made in CO<sub>2</sub> recovery technology in conjunction with urea manufacturing. This paper demonstrates the effectiveness of the process, and the outlined steps provide a clear pathway for implementation in industrial settings.

The proposed process for capturing CO<sub>2</sub> from flue gas offers several advantages over existing methods. By utilizing NH<sub>3</sub> to form a carbamate solution, the process is very efficient, specifically in the case of the capacity revamp of a urea plant. The resulting recovered CO<sub>2</sub> can be directly integrated into urea production for a 15-20% plant capacity increase. This innovative approach with a high CO<sub>2</sub> capturing efficiency contributes to the sustainability and the reduction of the CO<sub>2</sub> footprint of the manufacturing of urea.

As the demand for sustainable solutions in the chemical industry continues to grow, this process represents a promising development in the field of carbon capture and utilization.

Stamicarbon B.V.

REGISTERED OFFICE

Mercator 3, 6135 KW Sittard,  
The Netherlands  
P.O. Box 53 - 6160 AB Geleen  
P +31 46 4237000  
F +31 46 4237001

p.dhruv@nextchem.com  
v.rivas@nextchem.com

stamicarbon.com



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