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LATEST DEVELOPMENTS IN POLLUTION CONTROL OF UREA PLANTS¹**F. Granelli**

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RESUME

The problem of pollution from fertilizer plants, and particularly from urea plants, has become more serious in the last few years and the same trend will be valid for the future. The limits allowed for the pollutants are not uniform, differing from one country to another, and sometimes, within a country from one region to another.

There are instances in which a country establishes the maximum allowable limits for pollutants but regions, on the basis of the local situation and often on the basis of the local specific needs of the inhabitants, request different values that can be much lower than the national standards.

The present paper describes the possible sources of pollution from a urea plant and the contribution of Snamprogetti to reduce the values sometime even lower than those allowed by the most restrictive regulations.



Le problème de pollution par les usines d'engrais, et particulièrement les unités d'urée, s'est aggravé ces dernières années et cette tendance se poursuivra dans l'avenir. Les limites de polluants autorisées ne sont pas uniformes et diffèrent d'un pays à l'autre, et parfois à l'intérieur du pays d'une région à l'autre.

Il arrive qu'un pays établisse des limites maxima autorisées à ne pas dépasser pour les polluants, mais les régions, en fonction des situations locales et souvent selon les besoins spécifiques des habitants, imposent des valeurs différentes qui peuvent être bien plus basses que les normes nationales.

La communication décrira les sources possibles de pollution dans un atelier d'urée et la contribution de Snamprogetti à la réduction des valeurs parfois même au-dessous de celles autorisées par les réglementations les plus strictes.

¹ *The full paper will be published in the volume of the discussions.*

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RESUME

Le problème de pollution par les usines d'engrais, et particulièrement les unités d'urée, s'est aggravé ces dernières années et cette tendance se poursuivra dans l'avenir. Les limites de polluants autorisées ne sont pas uniformes et diffèrent d'un pays à l'autre, et parfois à l'intérieur du pays d'une région à l'autre.

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1. INTRODUCTION

We quote the following sentence from the paper we had the opportunity and the pleasure to present at the IFA Conference held in Kuala Lumpur during December 1994: « Antipollution requirements can be expected to be more severe in future and we believe that the solution of the relevant problems will determine the choice of the urea technology ».

This is true today and it will be even more so in the coming years, towards and after the 2000's, for urea plants as well as for any other industrial plants, although a good technology, including all the up-to-date steps for minimizing pollution, is not sufficient: good engineering, plant operation and maintenance play an important role in preventing pollution. Essential is in any case the mentality of the plant owner who has to maximize the benefits minimizing the social costs. The most economical method of running a plant is not necessarily the best one in the long run.

Frequently, in the past, environmental considerations were overlooked, but even today sometimes pollution regulations are not fully respected, also because in some cases they are not clear and often contradictory.

Anyway, today the problem of air and water pollution produced to some extent by every human activity is becoming more and more keenly felt. The problem is of course particularly marked in large-sized industrial plants, specially if located in the vicinity of large towns.

This is the case of the large capacity ammonia and urea plants: at the present time we are designing ammonia and urea plants having capacities of 2500 and 3000 T/D respectively, in one line. But, although with lower capacity, in some factories 3-4 urea lines in parallel are already in operation with a total production around 6000 T/D.

Figure 1 indicatively shows the enormous increase in the urea worldwide production in the last decades, while Figure 2 shows the capacity increase for a single line urea plant in the same period of time.

Such industrial growth in the production of urea was associated with an increase of problems caused by the effluents in gaseous as well as in liquid form.

The polluting elements from urea plants are represented by gaseous ammonia and urea dust in the gaseous effluents and by ammonia and urea in solution in the liquid effluents.

The importance of these problems varies from one country to another depending on many factors and, in the same country, from one area to another depending on the perception of the problem by the nearby population, being in general more acute in those areas that are more densely populated.

So every country has different allowable legal limits for the pollutants, in any case becoming more severe with time. These limits require measures involving considerable amounts of money (particularly for the existing plants), in order to reach the required limits.

Some industrial plants have been shut-down forever due to pollution problems: as far as we know this is not the case of urea plants. Anyway, for some of them, air pollution due to ammonia and urea dust from the prilling tower was considered important enough to compel the plant owner to reduce the plant capacity or to switch the finishing section from prilling to granulation or to produce urea solutions.

2. ENVIRONMENTAL REGULATIONS

In the 1950's and in the 1960's no great attention was paid to the pollution problem by ammonia and urea from urea plants, discharged into the air or into the water.

The consumption of ammonia per ton of urea, that theoretically is around 566 kg, was much higher than 580 kg, which means that at least 14 kg of ammonia (as ammonia or urea) were lost as pollutant to the environment for each ton of urea.

In these years such loss (about 2.5% of the consumption) was tolerated due to the low urea production, but in the 70's and the 80's the enormous increase in the urea production made it unacceptable. Today for a plant having a rather common capacity of 2000 T/D, such loss would be about 28 T/D.

Apart from the pollution consideration this amount of loss means a higher cost of the urea production, having the cost of the ammonia an impact of about 80-90% on the plant battery limit cost of urea. This consistent amount of loss justifies the efforts made to reduce it, not only from the point of view of pollution: easy to say that those antipollution systems leading to the recovery of ammonia would be preferable.

In the 70's the regulations began to set limits that became more restrictive during the 80's. Let us see some allowable legal limits.

2.1. Gaseous effluents

2.1.1 EEC countries

EEC authorities provide the general rules and recommendations. Each country fixes the maximum emission levels which must not be exceeded.

For the urea plant the Italian national rules are as follows:

- urea dust : 100 mg/m³
- ammonia : 200 mg/m³

Inside the EEC countries each region has the possibility to reduce the national limits depending on several parameters, viz.:

- density of population
- density of already existing emissions
- climate (particularly wind)

For example in the Italian Lombardia region (high population density and low wind) the values are as follows:

- urea dust : 20 mg/Nm³
- ammonia : 20 mg/Nm³

The values of three other Italian regions are here given (mg/m³):

		REGION		
		Emilia	Umbria	Puglia
-	urea dust	20	50	80
-	ammonia	35	50	80

while in Germany and Austria they are:

- urea dust : 75 mg/Nm³
- ammonia : 20 mg/Nm³

2.1.2 U.S.A.

In USA the regulations procedure is similar to the European: E.P.A. (Environmental Protection Agency) fixes some maximum emission levels and each State of the Union (as the regions in EEC) can reduce the limits.

Anyway E.P.A. ignores the NH_3 emission to the atmosphere. This is probably due to the fact that ammonia is not so hazardous for human health as other pollutants from fertilizer plants like SO_2 , NO_2 and HF. Moreover ammonia is lighter than air and is therefore dispersed in the atmosphere, for example from an adequate vent stack or from the top of the prilling tower.

Ammonia is contemplated only in the TLV (threshold limit value) list indicated by ACGIH (American Conference of Governmental Industrial Hygienists). TLV's represent the limit concentration in air inside the Battery Limits of the plant, i.e. « the conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect ».

The value for ammonia is:

TLV-TWA (time weighed average)	:	18 mg/m^3
TLV-STEL (short time exposure level)	:	24 mg/m^3

Figure 3 indicates the above values and others.

2.2. Liquid effluents

2.2.1 EEC countries

Also in case of liquid effluents EEC authorities give only general recommendations (precise figures for the maximum levels are given only for very toxic emissions). For the most common pollutants each EEC country had rather strict laws since the 70's: regional authorities are just entrusted with the task of getting them complied with.

The national Italian values for nitrogenous pollutants are:

- total ammonia as NH_4^+	:	15 mg/l
- nitrous nitrogen as N	:	0.6 mg/l
- nitric nitrogen as N	:	20 mg/l

EFMA indicates the following values of pollutants in the discharged water:

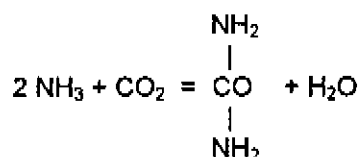
- Urea	1 mg/l
- Ammonia	5 mg/l

2.2.2 U.S.A.

E.P.A. regulations are already rather strict, but any State of the Union can increase or decrease the limits after evaluating all the factors at plant site. Anyhow any increase in emission limits is subject to approval by E.P.A.

3. SOURCES OF POLLUTION FROM UREA PLANTS

All industrial urea production plants are based on direct synthesis between ammonia and carbon dioxide according to the following reaction, represented in Figure 4.



$$\text{i.e. } 566 + 734 = 1000 + 300$$

In fact this reaction leads to a urea solution at about 70% by weight, containing a small quantity of the reactants, NH_3 and CO_2 , and must be followed by a finishing step by which solid urea (prilled or granular) is produced from the solution.

Figure 5 represents the two above steps: the reaction from NH_3 and CO_2 that leads to the urea solution and the solidification of urea from said solution.

During the process of urea production there are continuous losses and discontinuous losses. The points of continuous losses are indicated in Figure 5 at point 1, 2 and 3:

1. Ammonia losses in the « Inerts »
2. Ammonia and urea dust losses from prilling towers or granulation stacks
3. Ammonia and urea losses in the process water.

The discontinuous losses are represented by leakages, drainages and spillages.

In Figure 6 all these losses, continuous and discontinuous, as ammonia or as urea, are summarized. In the following paragraph we examine all of them and we indicate the minimum values that can be reached with the Snamprogetti technology.

4. MINIMUM POLLUTION VALUES ACHIEVABLE WITH SNAMPROGETTI UREA TECHNOLOGY

4.1. Continuous losses

4.1.1 Ammonia losses in the "Inerts"

« Inerts » are the so called components contained in the CO_2 (and partially also in the NH_3), like H_2 , CH_4 , CO , Ar , etc., that enter a urea plant and do not participate to the reaction that forms urea. It is also well known that in all industrial urea plants some passivation oxygen, mainly as air, is introduced in a urea plant just for the protection of the stainless steel surfaces, in contact with the process fluids, against corrosion.

When the « inerts » and the passivation air release the urea plant to the atmosphere they contain some NH_3 , that is a loss and represents a pollutant and at the same time, as all the pollutants, a process inefficiency. The lower the amount of passivation air is, the higher the efficiency of the ammonia recovery may be, without incurring the well-known problem of the explosive mixtures. Those processes are therefore favoured that require (like the Snamprogetti one) a lower amount of passivation air. The ammonia content in the « inerts », plus the passivation air, released to the atmosphere is generally about 1% in volume in this effluent.

As already said in the last years authorities and citizens themselves have become more aware to ammonia pollution problems, especially in case of those plants that are close to crowded areas. In these cases there is the request to strongly reduce the emission of ammonia.

Snamprogetti has already in operation plants in which the ammonia content in the « inerts », leaving the plant to the atmosphere, is reduced to about 10 ppm, totally avoiding the formation of explosive mixtures. Such a result is reached by the addition of an inert gas before the final washing with water to recover ammonia. This inert gas may be nitrogen or, more conveniently, synthesis or natural gas. This inert gas can be added to the « inerts » before their final washing with water in order to recover practically all the ammonia they contain. The resulting ammonia solution is sent back to the urea plant and any problem of explosion is completely avoided. The principle of this deep and safe washing of ammonia is represented in Figure 7.

As well known the composition of the gas mixture leaving a urea plant to the atmosphere can be represented by a triangular diagram, having at the apexes O_2 , N_2 and a flammable mixture made of H_2 , CH_4 , CO , NH_3 . In this triangle the dotted areas represent all the possible explosive mixtures. Supposing that the gas mixture leaving the urea plant is represented by point A in Figure 7.1, after a washing with water in order to recover NH_3 and to reduce pollution, the composition of the mixture, after washing, can be represented in the same Figure 7.1 by point B, i.e. inside the area of the explosive mixture. But if, before washing, an inert gas (like natural gas) is mixed with the mixture represented by previous point A, the new representative point is point C in Figure 7.2.

Washing by water the new mixture, represented by point C, ammonia can be totally recovered and the new composition of the « inerts », plus passivation air, leaving the plant is represented, in Figure 7.3, by any point on the straight line between the apex representing 100% flammable mixture and point D, i.e. for example, according to the quantity of added natural gas, by point E, that is completely out of the composition of explosive mixture.

The gas mixture can be sent to burn in a burner or in a reformer.

In Figures 7.1, 7.2, 7.3 the explosive area has been considered, for simplicity, as constant. In fact it changes with the composition of the flammable mixture.

The flow sheet of said solution is represented by Figure 8 that does not need clarification. The quantity of ammonia in the « inerts » can be limited to 10 ppm.

4.1.2 Ammonia and urea losses from prilling towers and granulation stacks

The air pollution problem due to ammonia and urea dust in the air from a prilling tower is very uneasy to eliminate due to the large volume of air, the extremely low partial pressure of ammonia in the air and to the small size of the particles of urea to be caught.

The effect of the emissions of urea dust on the environment is not very clear: in the vicinity of a plant the effect on vegetation can be even considered as beneficial, but the prevailing winds can concentrate the dust in a small area to cause scorching on vegetation.

Normally from our prilling tower (natural raft) the quantity of urea dust is about 40 mg/Nm³.

In some plants Snamprogetti has installed a dedusting system that can reduce the urea dust emission to 15 mg/Nm³.

If such efficiency does not seem too brilliant, it must be reminded that a large part (80%) of the urea dust has a size lower than 3 µm.

In Figure 9 we have indicated this size and the quantity of air involved. As a comparison we have also indicated the same values for a granulator, Hydro Agri fluidized bed granulator.

It appears clear from this figure that the urea dust pollution from granulation is lower than from a prilling section.

As regards ammonia in the air from the prilling towers it is only in the last decade that authorities, due to the claims of the nearby population, have issued more severe limits. As above said these strict limits made some plant owners to install a granulation section in a urea plant already supplied with a prilling tower.

Apart from a better product achieved, in some cases the granulation section was installed just to reduce pollution problems.

In fact from a granulation section it is easier to catch the urea dust, but it is also possible to reduce the quantity of ammonia sent to the atmosphere.

In order to reach the low values of ammonia, as indicated in Figure 3 (20-30 mg/Nm³), it is necessary a scrubbing with a mildly acidified solution.

Due to the fact that even traces of ammonium nitrate cannot be tolerated in the final urea product, this acid can be used only if the recovered ammonium nitrate is sent to a UAN or DAP/NPK plant.

If sulphuric acid is used for scrubbing, the obtained ammonium sulphate can be recycled to the urea plant if the product is used as fertilizer.

In the 1650 T/D urea granulation plant of Ferrara (Italy) utilizing the double falling curtain drum granulation technology of Snamprogetti, in operation since 1990, a double scrubbing is installed: in the first one urea dusts are scrubbed by means of water, and the obtained solution is recycled to the urea plant, while in a second scrubbing by mildly acidulated water (with sulphuric acid) ammonia is scrubbed and the obtained ammonium sulphate solution is sold separately by the factory.

In the same plant, anyway, for the first 4 years of operation only one scrubbing was installed with acidified water (with sulphuric acid) and the obtained solution of urea and ammonium sulphate was recycled back to the urea plant.

The final urea product contained about 2500 ppm of ammonium sulphate with no detrimental effect on the urea used as fertilizer.

Figure 10, that does not need any clarification, represents the double scrubbing of the granulation plant of Ferrara, while Figure 11 indicates the values of the pollutants in the emission, that are much lower than those reported by Italian as well as by regional laws (Ferrara is in the Emilia region).

As regards the double contemporary scrubbing of ammonia and urea dust on top of the prilling tower there are very few examples in the world, always by scrubbing with a mildly acidified water.

Snamprogetti has tested a different method to reduce the quantity of ammonia in the air from the prilling tower.

The tests have been made, in a urea plant of 360 T/D, by dosing a moderate quantity of sulphuric acid in the molten urea upstream the prilling bucket of the prilling tower. This method, which is simple to implement, has a modest investment and operation cost, ensures easy operability and has reached both the set goal of an appreciable reduction of ammonia emission in the air released to the atmosphere and, unexpectedly, a second result consisting in a remarkable reduction of the free ammonia present in the prilled product, with considerable environmental benefits in the product transportation and storage system.

However, it should be specified that this treatment produces prilled urea with about 2000/3000 ppm of ammonium sulphate.

As already said, this does not restrict in any way the use of urea as a fertilizer, but it can be a limitation for many of the technical uses of the product.

We are still continuing these tests and the results will be the object of the future paper.

4.1.3 Ammonia and urea losses in the process water

As indicated in Figure 4, the theoretical quantity of water produced for every 1000 kg of urea is 300 kg. In fact, due to some injection of steam and water for flushing or washing or for the vacuum ejectors, the amount of the process water can be even as high as 600 kg/T of urea, i.e. for a 2000 T/D urea plant it means 1200 T/D of water.

Unfortunately this process water (also called process condensate or waste water) contains some 4-5% wt of NH_3 and 0.5-1% wt of urea when it leaves the urea plant.

The presence of ammonia is due to the residual ammonia in the 70% wt urea solution sent to the evaporation section, while the presence of urea is attributable to some entrainment of liquid particles from vacuum separators.

Undoubtedly the major problem is toxicity of ammonia to aquatic organisms.

Among the first attempts to reduce ammonia was to strip it out from water and to send it to the atmosphere. Useless to say that the pollution problem is transferred from water to air unless ammonia is fixed as an ammonium salt.

Later on, recovery of the ammonia (as water solution) was introduced.

Today it is possible to strip ammonia to an extremely low value, to recover it, and to couple such stripping with a thermal hydrolysis where also urea can be completely decomposed to NH_3 and CO_2 , which are completely recovered to the urea plant.

The flow sheet of the Snamprogetti process water treatment section is indicated in Figure 12 and Figure 13 represents the values of pollutants in the discharged water:

- Urea : 1 ppm
- NH_3 : 1 ppm

By this treatment three targets are contemporarily achieved:

- ammonia specific consumption reduced
- pollution practically zero
- possibility of reusing process water as B.F.W.

With the values of pollutant contained in the three above examined sources of pollution the specific consumption of ammonia per ton of urea is very near to the theoretical value.

Figure 14 indicates in details such specific consumption of ammonia per ton of urea (565.69) which corresponds to a plant efficiency higher than 99.7%.

4.2. Discontinuous losses

If good antipollution systems can lead at the same time to low specific consumption of ammonia and to low contents of pollutants in the emissions as indicated above, it must be pointed out that these values remain targets to be reached.

In fact they depend not only on the process, but also on engineering proper operation and maintenance of the plant, awareness of hazards of pollution, control by the factory management and authorities, lack of legislation.

Process fluids containing ammonia and urea may be released into the environment due to leakage, spillage, drainage or other accidents which can be even more polluting specially if they are concentrated in pollutants. It is during start-up and shut-down and during other periods of irregular operation that losses from the plant are most likely to occur.

At such time transients the storage of solution in large quantity may present serious problems, which can be alleviated by:

- less frequent plant stoppage
- less frequent plant emptying
- lower inventory of process solution

Obviously good maintenance of flanged joints, pump glands, etc. is important.

But more than that, the very design principles and design details make the most important contribution to a pollution free urea plant.

5. CONCLUSIONS

There are processes available in order to reduce emissions of pollutants from urea plants.

We can supply such process, regarding the continuous losses and we can design the plant in order to reduce emissions during plant irregular operations.

But a great contribution must come also from the plant owner who should have the correct mentality to avoid problems, even in the areas where regulations do not exist or are contradictory.

6. REFERENCES

1. F. Granelli, *Ways to revamp urea units*, Hydrocarbon processing, June 1989
2. F. Granelli, *An improvement in technology has accompanied the enormous growth of urea production in the last four decades*, IFA Conference of Kuala Lumpur, December 1994
3. F. Granelli, A. Cavallaccio, R. Botti, *The Granular urea in the world and the experience of the granulation unit at the Ferrara factory (Italy)*, IFA Regional Conference for Asia and the Pacific, Perth (Australia), December 1995

Figure 1 - Urea world production

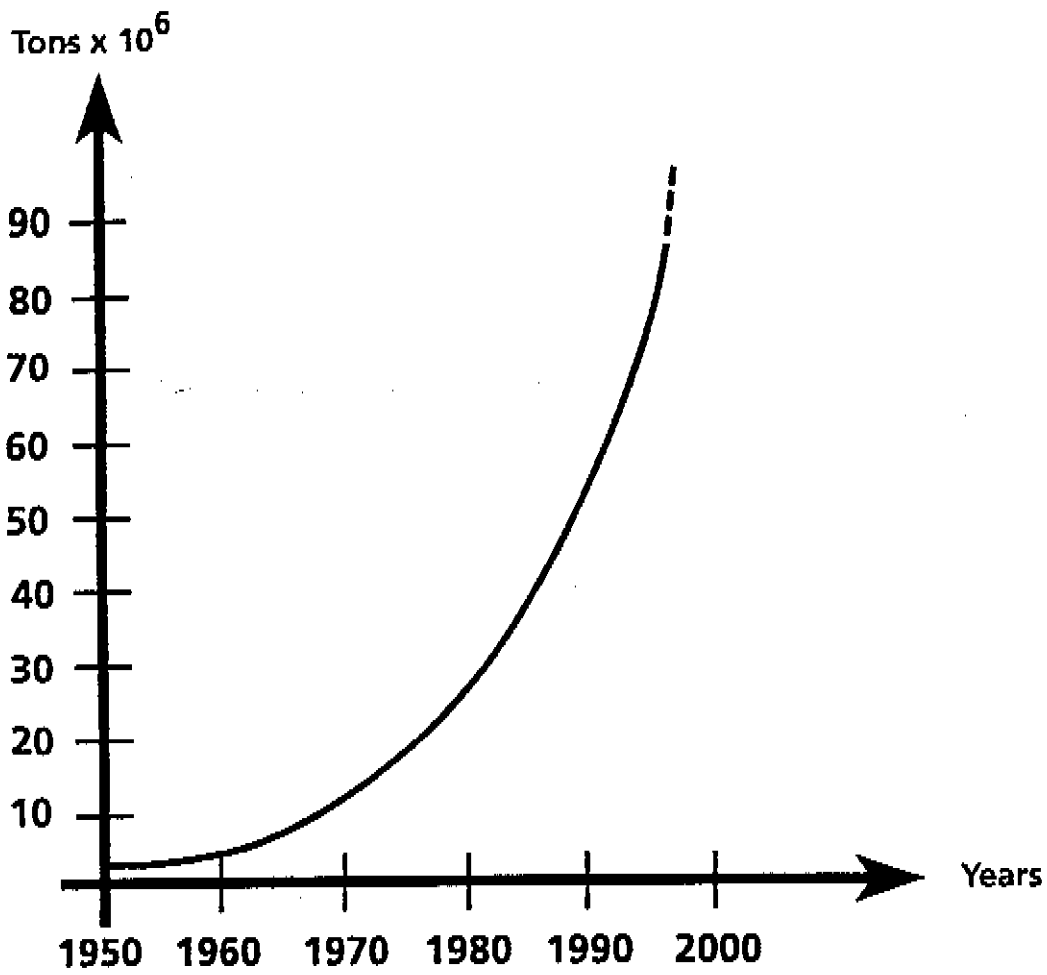


Figure 2 - Single line urea plant capacity

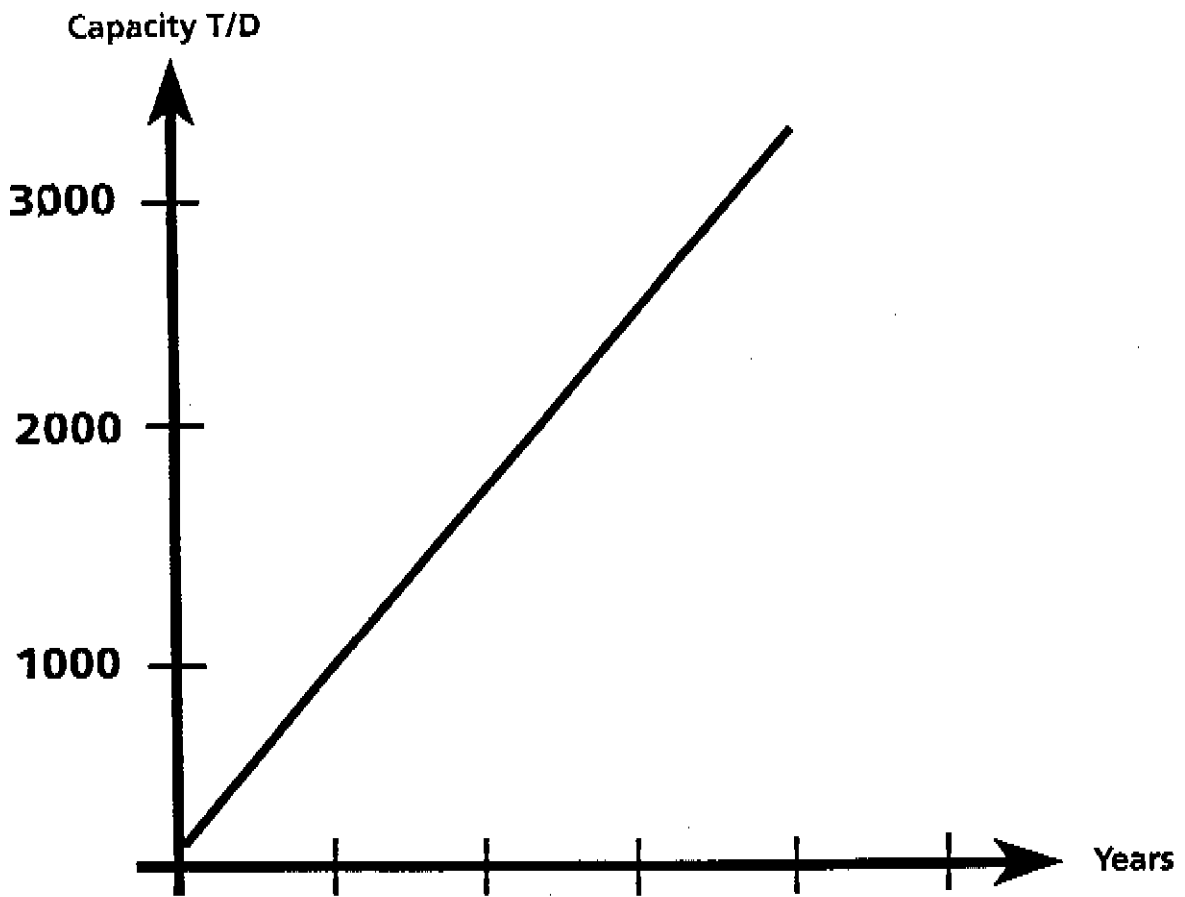


Figure 3 - Urea plant gaseous effluents pollutants limits

		UREA DUST	AMMONIA
ITALIAN NATIONAL LIMITS:	mg/m ³	100	200
ITALIAN REGIONAL LIMITS:			
- LOMBARDIA:	mg/Nm ³	20	20
- EMILIA:	mg/m ³	20	35
- UMBRIA:	mg/m ³	50	50
- PUGLIA:	mg/m ³	80	80
GERMAN VDI 3453 LIMITS:	mg/Nm ³	50	60
AUSTRIAN LOCAL LIMITS:	mg/Nm ³	30	30
EFMA⁽¹⁾:	mg/Nm ³	50	50
WORLD BANK:	mg/Nm ³	50	35
TLV- TWA⁽²⁾ (ACGIH)⁽³⁾:	mg/m ³ ⁽⁵⁾		18
TLV- STEL⁽⁴⁾:	mg/m ³ ⁽⁵⁾		24

(1) European Fertilizer Manufacturer Association

(3) American Conference Governmental Industrial Hygienists

(2) Threshold Limit Value - Time Weighted Average

(4) Threshold Limit Value - Short Time Exposure Value

(5) At 25° C

Figure 4 - Urea synthesis reaction

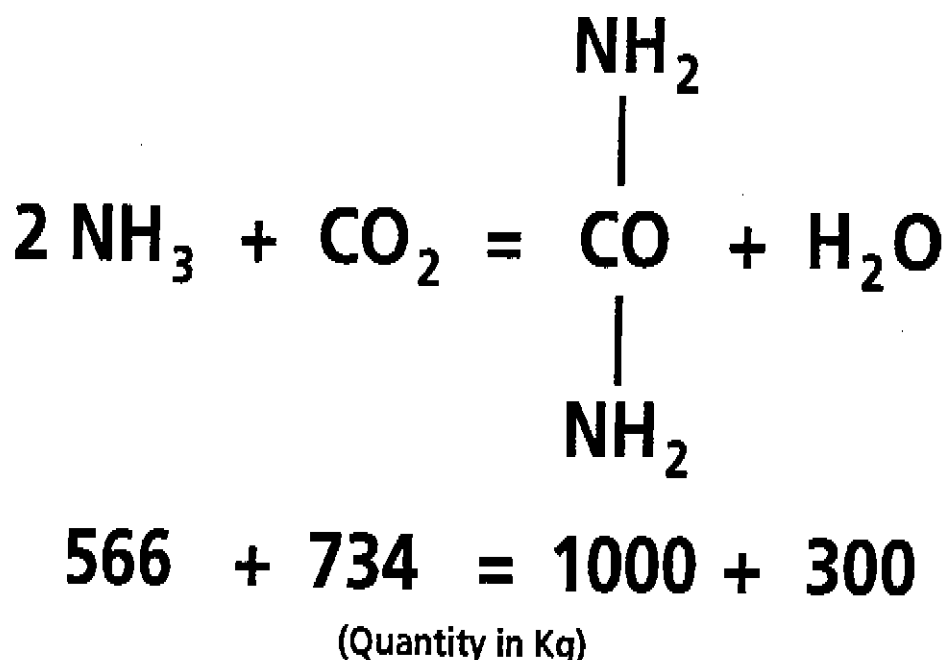


Figure 5 - Block diagram of urea production and sources of pollution

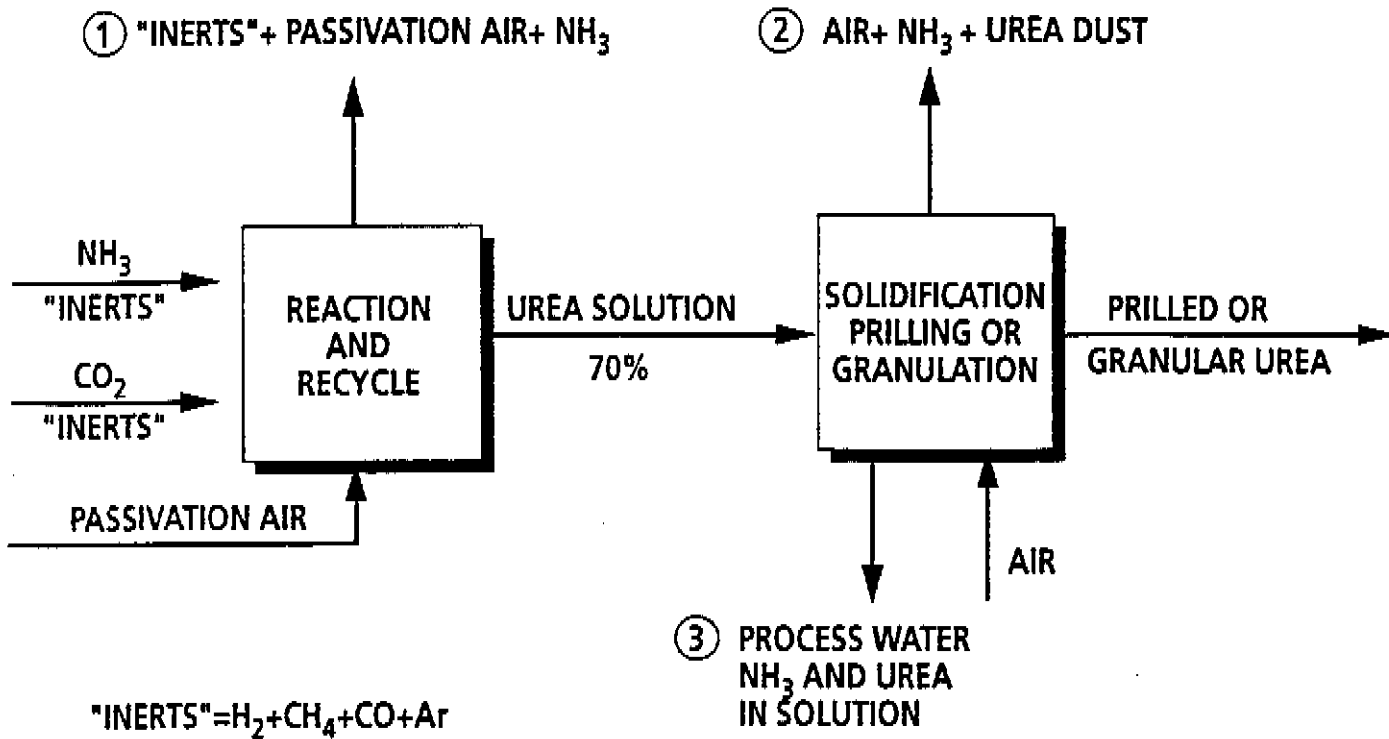


Figure 6 - Losses from urea plants

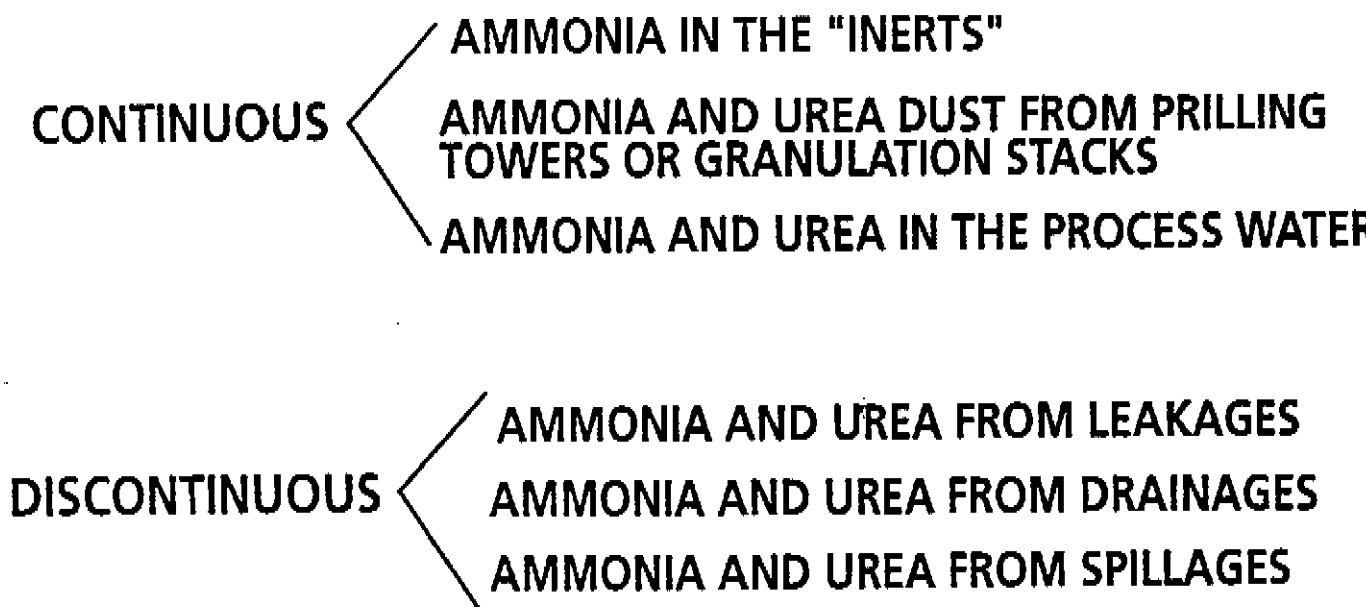


Figure 7 - Total absorption of ammonia from the « inerts ». No explosive mixtures

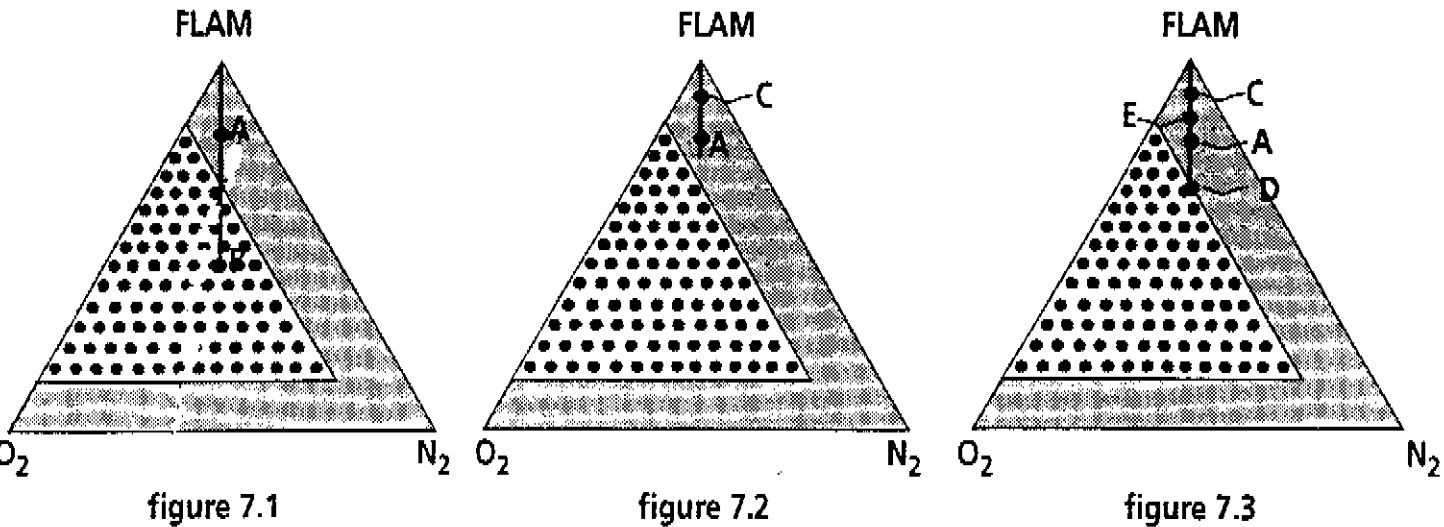


figure 7.1

figure 7.2

figure 7.3

FLAM (flammable)= H₂+CH₄+CO+NH₃ etc

NB. for simplicity the explosive area has been considered constant, while in fact it changes with the composition of the flammable mixture

Figure 8 - Total absorption of ammonia from the « inerts ». No explosive mixtures

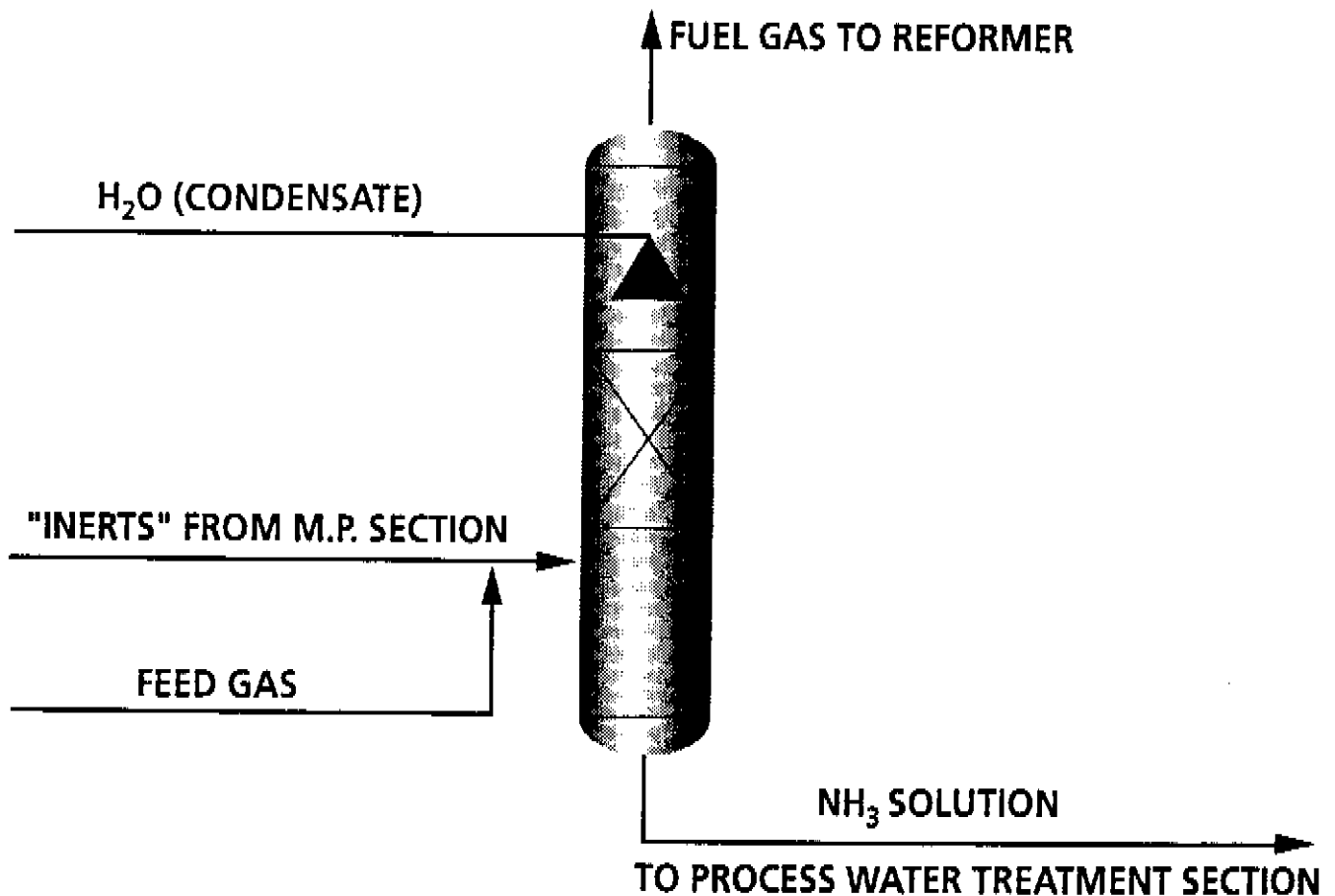


Figure 9 - Urea dust emission characteristics

		PRILLING ⁽¹⁾	GRANULATION ⁽²⁾
AIR QUANTITY	Nm³/T of UREA	8,000	5,500
DUST EMISSION	mg/Nm³	40	25
TOTAL DUST	Kg	0.32	0.14
DUST SIZE MICRON (10⁻³ mm)			
	> 3	18	97
	1 ÷ 3	66	2
	< 1	16	1

(1) Natural draft, without dedusting

(2) From Hydro Agri fluidized bed, not from cooler.

Figure 10 - Separated air washing system for urea dust and ammonia

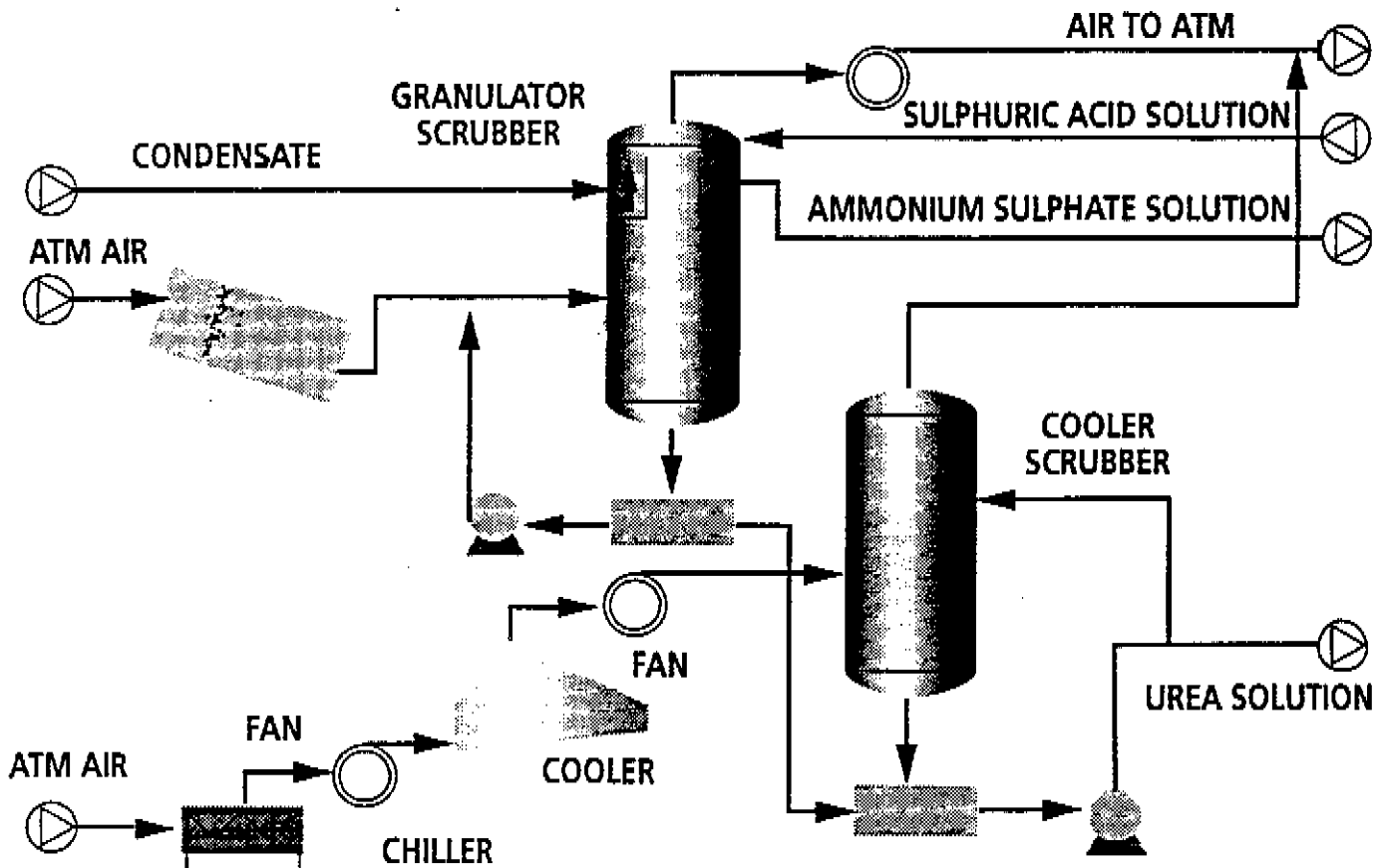


Figure 11 - Values of urea and ammonia in the air to the atmosphere

UREA DUST	15 mg/Nm³
AMMONIA	20 mg/Nm³

Figure 12 - Process water treatment section

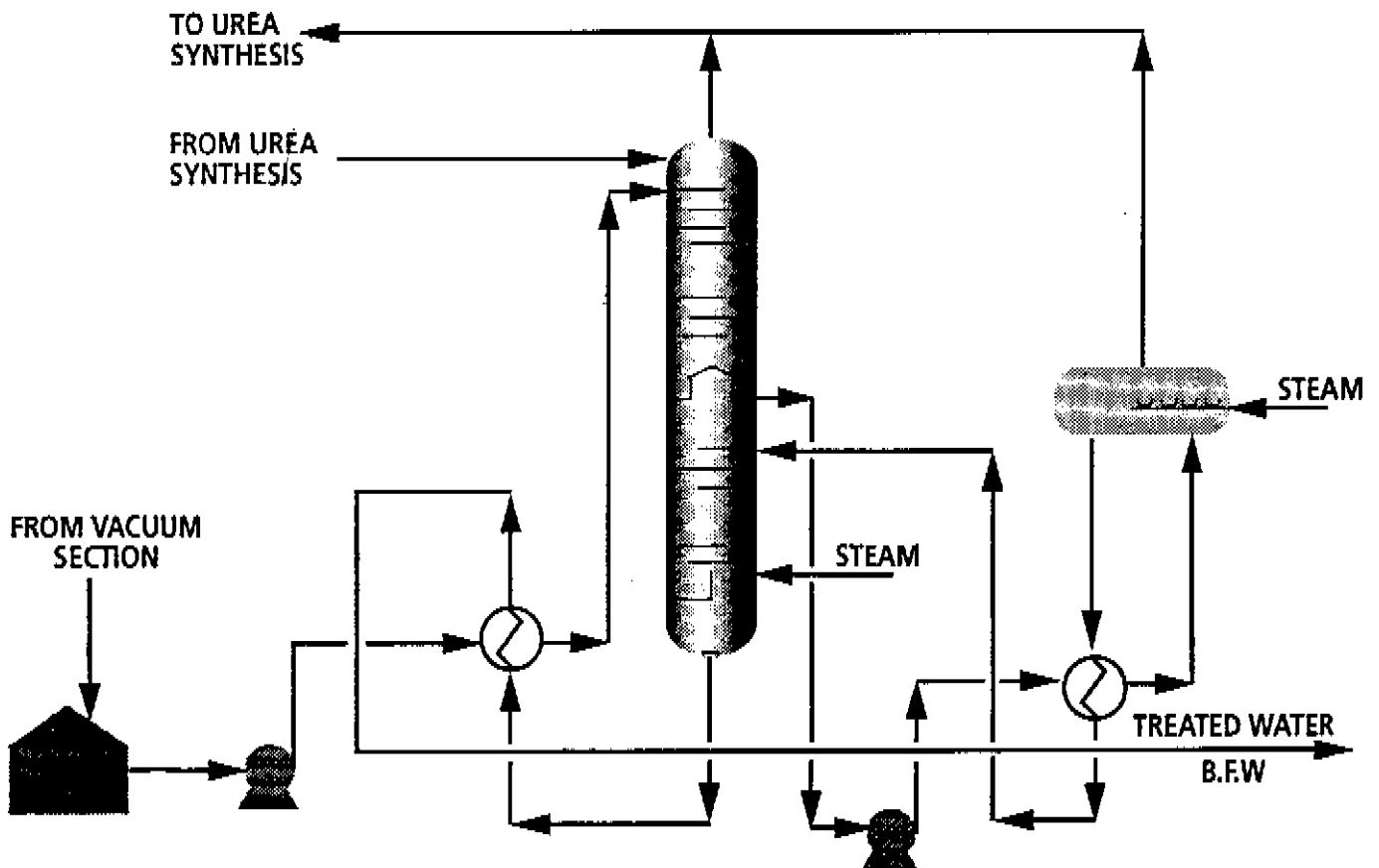


Figure 13 - Process water. Value of pollutants in the discharges process water

UREA: 1 ppm

NH₃: 1 ppm

Figure 14 - Ammonia specific consumption

BASIS:	UREA BIURET MOISTURE	98.8% wt 0.9 % wt 0.3% wt	100% wt	WITH UREA DEDUSTING IN THE PRILLING TOWER	kg/MT
	AS UREA IN THE PRODUCT				559.87
	AS BIURET IN THE PRODUCT				4.46
	FREE IN THE PRODUCT (150 ppm)				0.15
	IN VENTS (10 ppm)				neglig.
	IN TREATED WATER FREE AND AS UREA (1 ppm UREA, 1 ppm NH ₃)				neglig.
	FREE IN AIR FROM PRILLING TOWER (120 ppm)				1.13
	AS UREA DUST IN AIR FROM PRILLING TOWER (15 mg/Nm ³)				0.08
	TOTAL				565.69
	EFFICIENCY				99.7%