

## POSSIBILITIES OF EMISSIONS REDUCTION IN NITROGEN-BASED FERTILIZER PLANTS

Lucian Gavrila<sup>(1)</sup>, Daniela Gavrila<sup>(2)</sup>,  
Andrei Ionuț Simion<sup>(1)</sup>, Alberto Javier Granero Rodríguez<sup>(3)</sup>

(1) - University of Bacău, Depollution Engineering Laboratory, Calea  
Mărășești 157, 600115 Bacău, ROMANIA, e-mail: [lgavrila@ub.ro](mailto:lgavrila@ub.ro)

(2) - SC SOFERT SA Bacău, Str. Chimiei 1, 600289 Bacău, ROMANIA

(3) - Universidad de Valladolid, Escuela Universitaria Politécnica,  
C/ Francisco Mendizábal n° 1, 47014 Valladolid, SPAIN

**ABSTRACT:** The paper compares from the standpoint of harmful emissions typical nitrogen-based fertilizer plants producing ammonia and urea with hypothetical plants using the best available technologies. The critical emission points are established and analyzed. Several possible actions to be taken in order to minimize the emissions are presented.

**KEYWORDS:** *fertilizers, environmental impact, pollution abatement, wastewater treatment, ammonia, urea*

### INTRODUCTION

The nitrogen-based fertilizer plants existing in Romania have an important environmental impact. Being based on technologies from the late seventies of the 20<sup>th</sup> century or even elder, they do not meet the most recent regulations concerning the environmental discharge. As a matter of fact, from the nine nitrogen fertilizer plants existing in 1989 [1] only a few are still in operation, and are often confronted with pollution problems. Among the operating units, those belonging to Amonil SA Slobozia, Azomureș SA Târgu Mureș and Sofert SA Bacău are in the most favored position due to criteria such as: location, level of technology, market. These advantages

have to be completed by meeting the environmental criteria required by the European Union legislation.

The paper analyzes one of the typical Romanian nitrogen based fertilizer plants from the emissions standpoint. The typical plant consists of a Kellogg type ammonia plant based on natural gas (single train unit with a nameplate capacity of 300,000 t/yr anhydrous ammonia) and a Stamicarbon urea plant (CO<sub>2</sub> stripping technology, with a nameplate capacity of 450,000 t/yr prilled urea). On the industrial platform there are also sulfuric and phosphoric acid plants, an ammonium phosphates plant, a natural gas based power plant and several minor installations producing calcium and sodium phosphates of different grades.

## AMMONIA PLANT EMISSIONS

The ammonia production is based on the natural gas reforming in two steps with steam and air, followed by catalytic conversion of carbon monoxide to carbon dioxide, carbon dioxide removal using activated hot potassium carbonate solutions, methanation of CO and CO<sub>2</sub> traces, compression and synthesis at about 15 MPa (figure 1) [2 - 4].

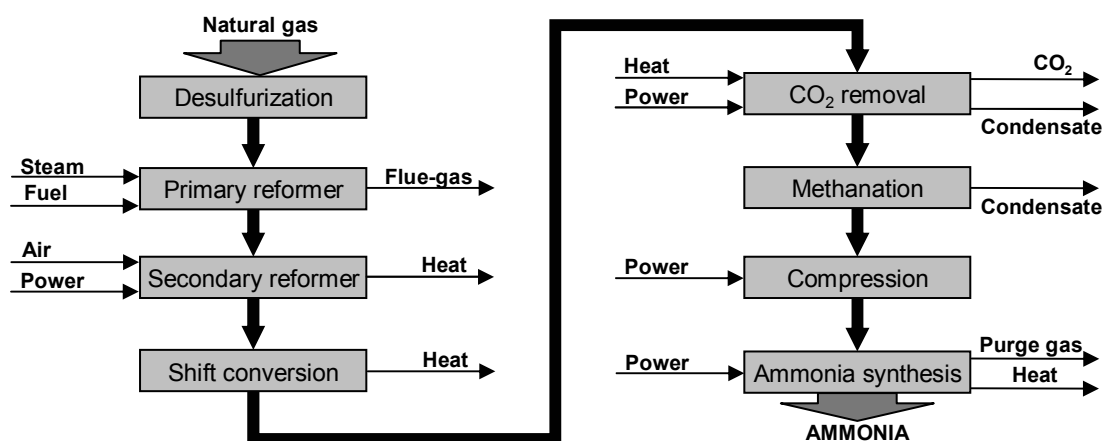


Fig. 1. Block diagram of the Kellogg process for ammonia production

The emissions of the plant may be permanent, transient (during start-up and shut-down) or accidental. The emissions may also be grouped according to the type of environment in: air emissions, water emissions and solid wastes. While permanent and transient emissions are relatively easily quantifiable, the accidental emissions are difficult to predict and evaluate.

The main permanent emissions of the plant are summarized in Table 1. Flows and concentrations are values measured and/or calculated as averages for several years of operation.

Table 1. Permanent emissions from the ammonia plant

Type of emission	Emission / Source	Quantity	Composition
Gaseous	Flue-gas / Primary reformer	120,000 Nm <sup>3</sup> /hr	8% CO <sub>2</sub> ; 3% O <sub>2</sub> ; 88% N <sub>2</sub> (dry gas); 0.12 mg/Nm <sup>3</sup> SO <sub>2</sub> ; 500 mg/Nm <sup>3</sup> NO <sub>2</sub> ; 8 mg/Nm <sup>3</sup> CO
	Vent gases / CO <sub>2</sub> removal	25,000 Nm <sup>3</sup> /hr	99.7% CO <sub>2</sub> saturated with water vapors
	Purge gas / Synthesis loop	3,500 Nm <sup>3</sup> /hr	51% H <sub>2</sub> ; 22.5% CH <sub>4</sub> ; 5.1% NH <sub>3</sub> ; 10.2% Ar; N <sub>2</sub>
Liquid	Process condensate / Shift conversion	55 m <sup>3</sup> /hr	0.8 g/L NH <sub>3</sub> ; 0.1 g/L CH <sub>3</sub> -OH; 0.05 mg/L Fe; 0.175 mg/L SiO <sub>2</sub>
Solid catalysts	Hydrosulfurization	1.3 m <sup>3</sup> /yr	2.5% CoO; 11% MoO <sub>3</sub> / Al <sub>2</sub> O <sub>3</sub>
	H <sub>2</sub> S adsorbent (ZnO)	3.1 m <sup>3</sup> /yr	99% (ZnO + ZnS)
	Primary reforming	12.7 m <sup>3</sup> /yr	10% NiO / Al <sub>2</sub> O <sub>3</sub>
	Secondary reforming	7.4 m <sup>3</sup> /yr	10% NiO / Al <sub>2</sub> O <sub>3</sub>
	High temperature shift	12.5 m <sup>3</sup> /yr	74.25% Fe <sub>2</sub> O <sub>3</sub> ; 7.5% Cr <sub>2</sub> O <sub>3</sub>
	Low temperature shift	25 m <sup>3</sup> /yr	30% CuO; 45% ZnO; 13% Al <sub>2</sub> O <sub>3</sub>
	Methanation	2.2 m <sup>3</sup> /yr	19.5% NiO / Al <sub>2</sub> O <sub>3</sub>
	Ammonia synthesis	12.3 m <sup>3</sup> /yr	60% Fe <sub>2</sub> O <sub>3</sub> ; 32.5% FeO; 3.5% Al <sub>2</sub> O <sub>3</sub> ; 3% CaO

## UREA PLANT EMISSIONS

The block diagram of the urea CO<sub>2</sub> stripping process is presented in figure 2 [3, 5]. The main permanent gaseous and liquid emissions are also shown in the diagram.

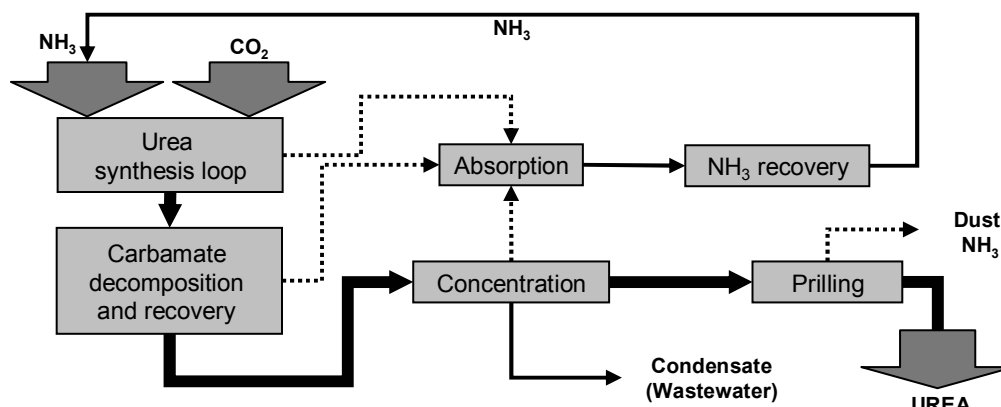
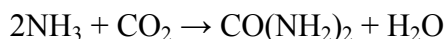


Fig. 2. Block diagram of the Stripping Stamicarbon process for urea production

The main source of process water is the urea synthesis reaction:



where 300 kg of water are formed per tonne of urea. A urea plant of 450,000 t/yr generates theoretically about 410 m<sup>3</sup> water/day (~17 m<sup>3</sup>/hr). This water contains 6% NH<sub>3</sub>, 4% CO<sub>2</sub> and 1% urea (by weight). In the analyzed plant, three main wastewater sources were evidenced:

- oily wastewaters from pumps and compressors seals, floor waters;
- wastewaters from ammonia recovery;

c) clean condensate from compression and concentration section (Table 2).

Table 2. Permanent liquid emissions from the urea plant

	Flowrate, m <sup>3</sup> /hr		Ammonia, mg/L		Urea, mg/L	
	Design	Actual	Design	Actual	Design	Actual
Oily wastewaters, floor waters	15	50	7,400	3,300	4,000	8,000
Wastewaters from NH <sub>3</sub> recovery	30	35	100	800	300	8,000
Clean condensate	0	35	0	1	0	5

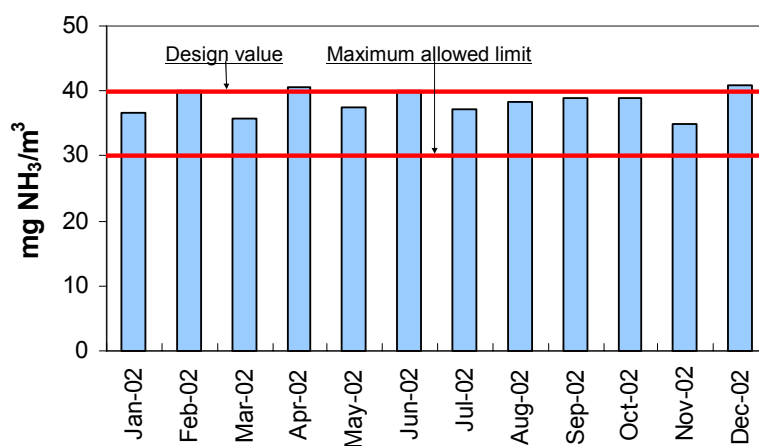


Fig. 3. NH<sub>3</sub> emissions at the prilling tower

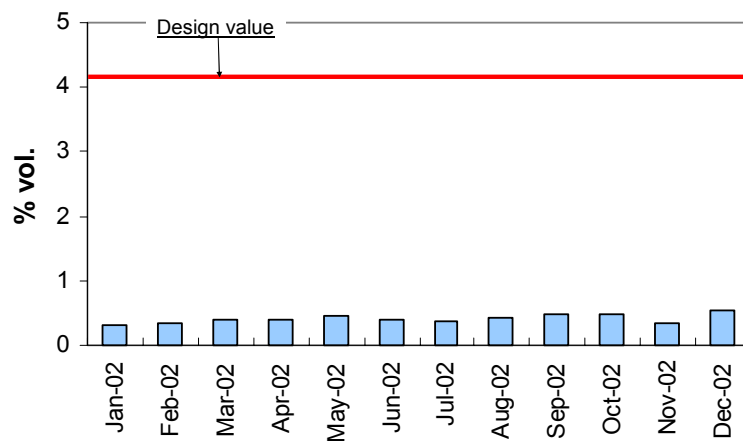


Fig. 4. NH<sub>3</sub> emissions at the absorber

The air emissions consist mainly in ammonia, and they are located in three points:

- the exhausters of the urea prilling tower;
- gas exhaust from the ammonia absorber;
- gas exhaust from the final stack of the synthesis loop.

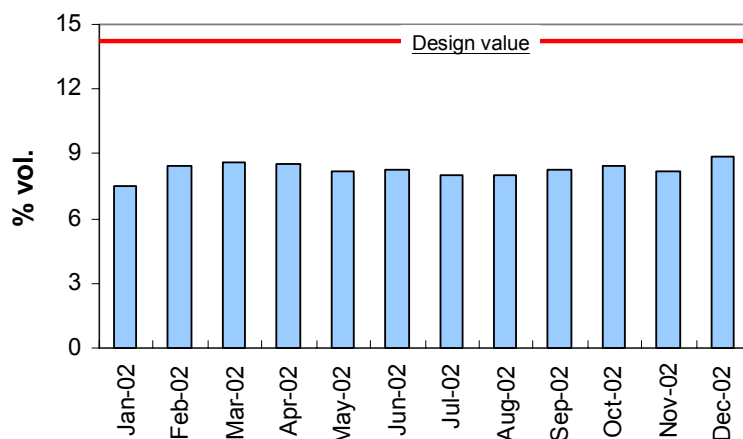


Fig. 5.  $\text{NH}_3$  emissions at the final stack

As shown in figures 3 - 5, all emissions are below the designed value, but they are higher than the maximal allowed concentration,  $30 \text{ mg/m}^3$ , established by legal regulations [6]. The urea dust emitted from the exhausters of the prilling tower has been drastically reduced below  $0.2 \text{ g/Nm}^3$  by scrubbing the exhausted air [7, 8].

## POSSIBILITIES OF AMMONIA PLANT EMISSIONS REDUCTION

Most of the gaseous emissions presented in Table 1 may be avoided: the  $\text{CO}_2$  containing gases from  $\text{CO}_2$  removal unit are used as raw material in the urea plant. The purge gas from ammonia synthesis is water washed in order to recover the  $\text{NH}_3$ , and then is used as reducing agent for the sulfur compounds in the desulphurization unit. The excess remaining gas is used as fuel in the primary reformer.

For the process condensate, which now is dumped to the sewer, there are several potential uses:

- a) for the humidification of the natural gas in order to achieve a proper carbon/steam ratio;
- b) as make up water in the boiler's circuit;
- c) as make up water in the cooling tower's circuit.

In each case, a preliminary purifying treatment is requested, mainly for methanol and ammonia removal. An air stripping unit (for instance an unused forced draft cooling tower) will be sufficient for the removal of over 50% of the contaminants [9], the purified stream containing only  $0.4 \text{ mg/L NH}_3$  and  $0.05 \text{ mg/L CH}_3\text{-OH}$ . For use in the boilers' circuit, or as humidifier for the natural gas, a supplemental ion exchange polishing is necessary for removal of iron and silica. For use in the cooling towers' circuit, no further treatment is required, air stripping being sufficient.

The solid wastes, adsorbents and catalysts that are actually used as landfill may be either returned to the producer, either used for the reclamation of valuable elements such as nickel, molybdenum, cobalt, chromium, copper, zinc [10, 11].

## POSSIBILITIES OF UREA PLANT EMISSIONS REDUCTION

Analyzing the data presented in Table 2, it may be outlined that the actual treatment of oily waters, floor waters and wastewaters is far from the actual target limits of ammonia and urea in wastewaters: 5 mg/L  $\text{NH}_3$  and 1 mg/L urea [12].

The initial desorption - hydrolysis (D-H) unit commissioned with the plant in 1980 consisted in a hydrolyzer, a desorber and a final reflux condenser. The actual D-H unit has two desorbers, equipped with valve trays, the 2<sup>nd</sup> one being installed in the early 90's, in order to reduce  $\text{NH}_3$  emissions. A modern D-H unit uses a counter-current hydrolyzer and two desorption columns equipped with sieve trays (fig. 6). The wastewater leaving this unit contains less than 5 mg/L  $\text{NH}_3$  and 1 mg/L urea [13].

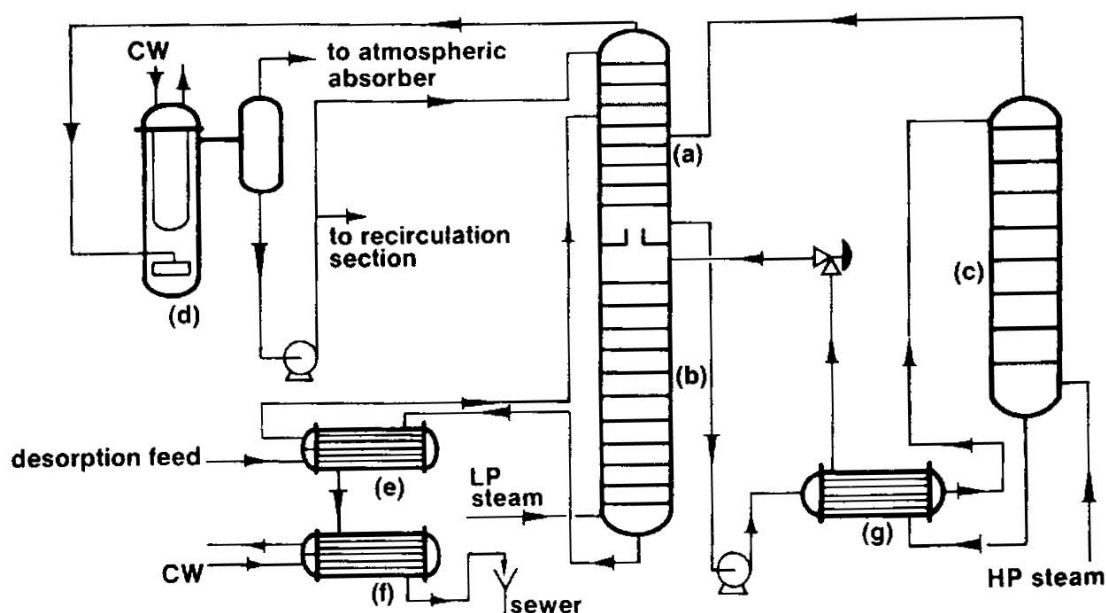


Fig. 6. Modern Stamicarbon D-H unit

*a - 1<sup>st</sup> desorption column; b - 2<sup>nd</sup> desorption column; c - hydrolyzer; d - reflux condenser; e - desorption heat exchanger; f - waste water cooler; g - hydrolyzer heat exchanger.*

Introducing such type of unit or units based on distillation - hydrolysis or stripping - hydrolysis may lead to additional investment costs up to 2.5 M€ [12]. The wastewater from the D-H unit (about 85 m<sup>3</sup>/hr), together with the "clean condensate" from the urea plant (about 35 m<sup>3</sup>/hr) will give 120 m<sup>3</sup>/hr (with 3.8 mg/L  $\text{NH}_3$  and 2.2 mg/L urea) make-up water for the urea and ammonia plants circuits. The make-up necessary depends on the concentration cycles ( $C_C$ ) at which cooling circuits are operated. For the analyzed units,  $C_C$  may vary from 1.1 to 5.0 [14], and the total make-up may vary between 4,400 and 500 m<sup>3</sup>/hr respectively (fig. 7). Thus, 3 to 24% of the fresh make-up may be replaced with recovered wastewater. Assuming that no ammonia desorption and urea decomposition will occur in the cooling circuits, even at high  $C_C$  values, the level of pollutants will be low enough (fig. 8), that nitrifying bacteria cannot develop on a large scale [15].

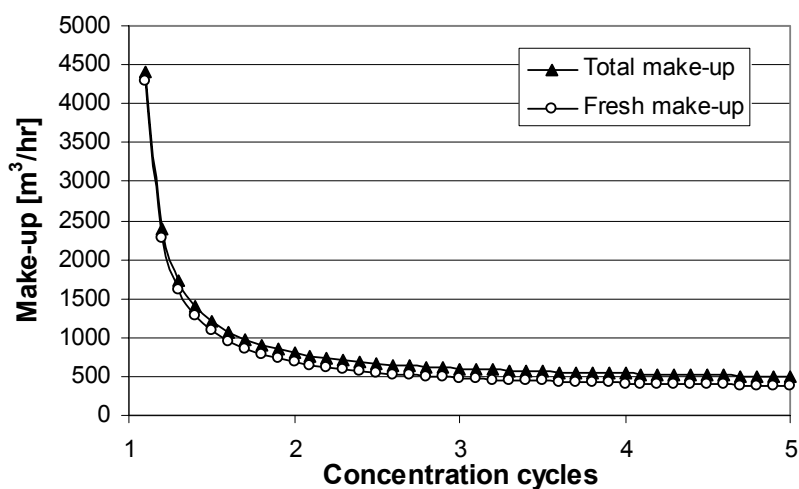


Fig. 7. Make-up water vs. concentration cycles

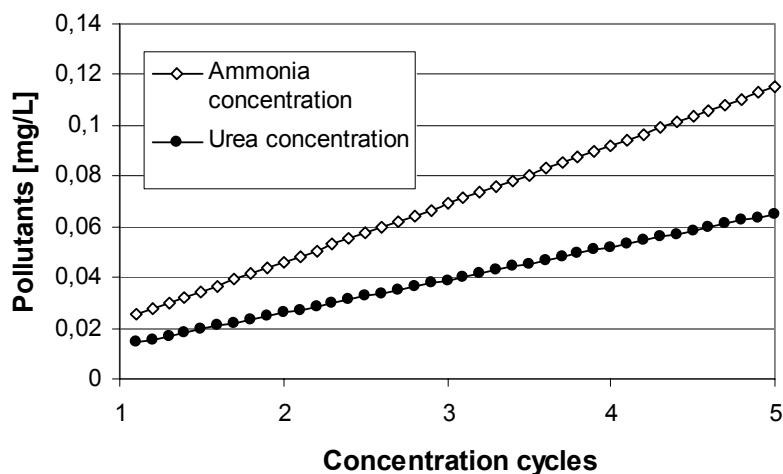


Fig. 8. Ammonia and urea concentration in the cooling circuits

## CONCLUSIONS

The ammonia and urea plants from a fertilizer unit have been analyzed, with regard to the harmful emissions in the environment.

It has been shown that the existing technology do not meet the criteria requested by legal environmental regulations. Major investments have to be done in the urea plant for wastewater processing.

After a proper treatment (stripping, hydrolysis, desorption), the wastewaters may be reused, thus reducing the freshwater consumption and the effluent discharge.

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