

Emission Control in Urea Plants During Normal Operating and Upset Cases – Why So Many Different Solutions?

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Several technical solutions for the reduction of ammonia emissions in urea plants have been discussed during the last ten years. Legal requirements for continuous emissions are mostly well known; EFMA and IFC provide clear guidelines. For emissions released intermittently or as a result of upset conditions, the picture is less clear. The limit values depend on the customer's rules and on the regulations stipulated by local authorities. These are influenced by a number of factors, including the type of surrounding area. Consequently, local requirements for non-continuous emissions differ significantly from plant to plant.

It may be necessary to determine the different kinds of protection layers needed to reduce the likelihood or impact of a severe emergency emission for each individual situation.

Several options are available to minimise emissions. Guidance to make sound decisions based on local, environmental and economical aspects is provided.

INTRODUCTION

During the past two decades ammonia emissions in urea plants, and the reduction of these emissions, have become an increasingly challenging issue. Of immediate concern were the continuous emissions, but emissions resulting from upset plant operation, as well as accidental emissions, have also entered the spotlight. It seems logical to look for a solution which covers all emissions regardless of their frequency with one particular system. However, to find the most economical and sustainable solution, a proper analysis of actual requirements, laws and regulations, as well as local conditions and the customer's own rules, is

advisable. The purpose of this paper is to provide information about the available technologies along with the pros and cons for each set of individual circumstances.

The most logical way to start the analysis of the various ammonia abatement systems is to focus on the frequency of emissions.

NORMAL OPERATION EMISSIONS

The requirements for normal operation are usually set by local or international standards. According to World Bank standards (IFC / International Finance Corporation of the World Bank Group) and EFMA (European Fertilizer Manufacturer Association), continuous ammonia emissions should not exceed a maximum of 50 mg/Nm³ during normal operation of a newly built urea plant.

There are generally three emission points in a urea plant producing granules (see Figure 1): Although emissions from the two absorbers in the synthesis part of the plant total approx. 4 - 6 kg/h ammonia only, the concentration limits are greatly exceeded due to a very low overall flow rate. Emissions from the granulation stack amount to approx. 80 - 90 kg/h, however, the huge amount of air dilutes the concentration to approx. 100 mg/Nm³.

All figures in this paper refer to a state-of-the-art capacity of 3,500 mtpd urea granules based on Stamicarbon's Urea 2000 plus process for the synthesis part and a fluid bed granulation process.

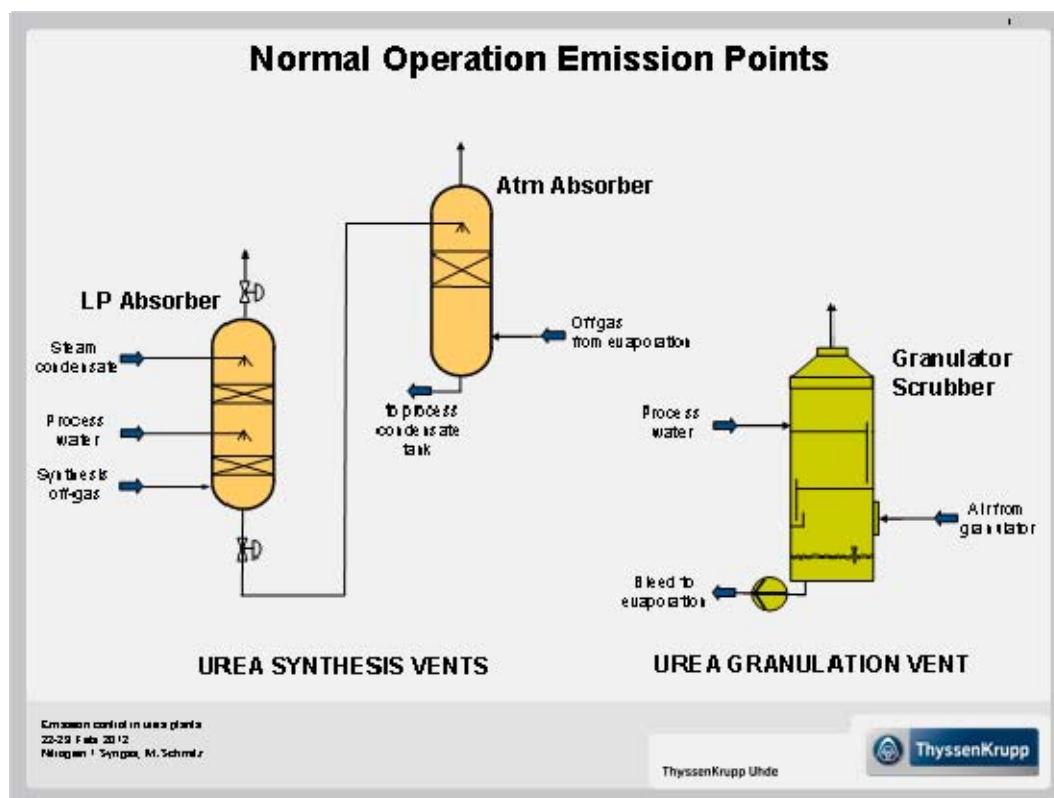


Fig 1: Emission points of a urea and granulation plant in normal plant operation

Usually, water scrubbing is used to reduce dust emission in granulation and prilling plants to adhere to the urea dust emission limits of 50 mg/Nm³. Consequently, acidic scrubbing is the most economical way to reduce ammonia emissions to the required limit. Flaring is not an option for reducing ammonia emissions from the off-gas of a granulation/prilling plant due to the low concentration of ammonia and the high water content in the off-gas from the preceding dust abatement. Generally, an acidic scrubbing unit is stacked on the dust scrubbing unit so that the off-gas is first freed from dust and then from ammonia (see Figure 2).

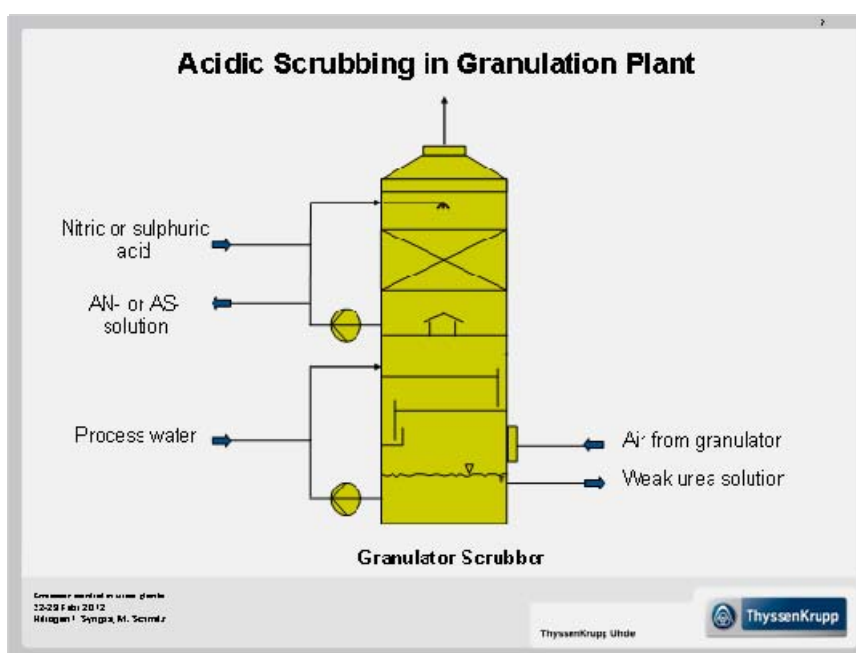


Fig 2: Acidic and Dust Scrubbing in Granulation Plant

If acidic scrubbing is used to reduce ammonia emissions in the solidification part of the plant, it is most economical to use it on continuous emissions in the synthesis part of the urea plant as well, since the infrastructure installations, such as storage tanks and the respective pumps, are already available. Only one additional absorber, including circulating pumps, is required to handle the off-gas from both existing absorbers (see figure 3).

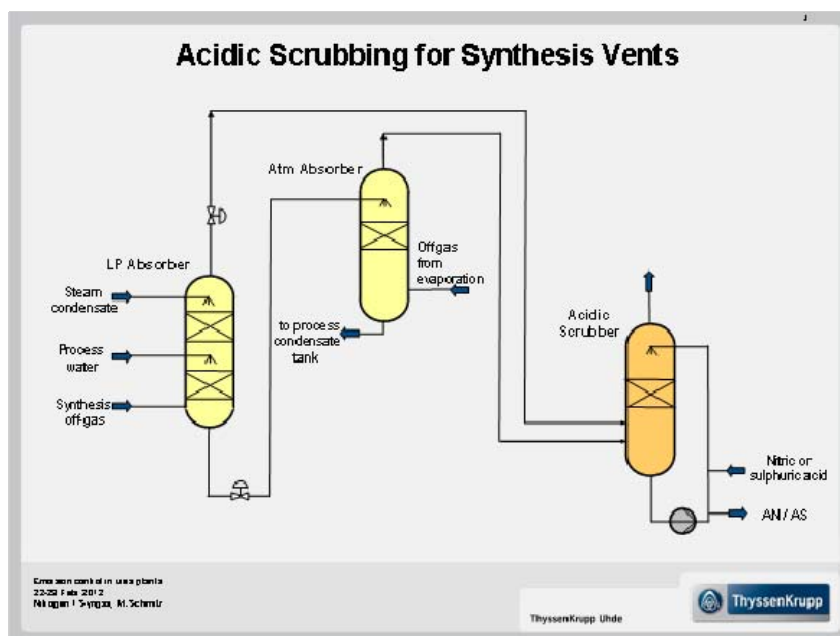


Fig 3: Acidic Scrubber in urea synthesis

Acidic scrubbing changes the emission of ammonia from an air issue to an effluent issue. Consequently, the salt solution produced needs to be disposed of. Two commonly available acids can be used for ammonia abatement; sulphuric or nitric acid. Depending on the acid used, either AS (ammonium sulphate) or AN

(ammonium nitrate) solution is produced, both of which need to be disposed of. Approx. 33 kg/h nitric acid (60 wt-%), or 16 kg/h sulphuric acid (98 wt-%) is required for the acidic scrubbing of the absorber vents.

Two disposal methods are available: The first involves concentrating the solution and adding it to the melt being sent to the granulator. This process is offered by Uhde Fertilizer Technology. It is known as Ammonia Convert Technology and can be used for AS solution. A dedicated evaporation stage, including a condensation/vacuum section, is required for this disposal method; the granules produced will maintain the quality required for fertilizer grade, but not for technical grade. Since granules are rarely used for technical applications, and only about 10 to 15 % of all urea produced is used in the non-fertilizer industry, this constraint is minimal [4].

Alternatively, AS can be crystallized and finally formed into pellets by Rotoform, if required,

Using nitric acid as an abatement aid, AN solution is produced. This cannot be added to the urea melt, but can be used to produce UAN solution. If this option is chosen, the dust and ammonia scrubbing can be combined in one stage. However, not all customers are in a position to avail themselves of this option.

Both solutions, AS and AN, can also be sold as liquid fertilizer, if the required logistics are available.

The investment in acidic scrubbing for the synthesis absorbers is clearly less than that required for a flare system, provided the infrastructure detailed above already exists. If tanks and pumps need to be added, then the investment is approximately the same.

In the case of standalone urea synthesis plants, i.e. without a solidification unit on its tail, flaring the ammonia emission from the absorber vents presents an alternative to acidic scrubbing. However, in this case the vent lines need to be purged with nitrogen to ensure positive flow and avoid oxygen ingress which could lead to an explosive mixture in the plant. The off-gas to be flared typically contains less than 1 mole-% ammonia and about 99 mole-% nitrogen, oxygen and water which leads to an extremely low heating value. This means that a substantial amount of support gas is required to combust the ammonia reliably. Furthermore, it is reasonable to assume that NO_x is formed during the combustion, which contributes much more to global warming, tropospheric ozone-forming potential and ozone-depletion potential than ammonia does [3]. The acidification effect is also assumed to increase as a result of the nitrogen purging and the amount of support gas required when flaring the ammonia from the synthesis vents. It can, therefore, be concluded that flaring the process vents in urea synthesis worsens the environmental balance and cannot be seen as an equitable alternative to scrubbing from an environmental point of view. Flaring is also questionable in view of the considerable consumption of nitrogen (about 2000 Nm³/h) [3] and natural gas (9,000 – 10,000 Nm³/h) [3, 6] and the consequent economical impact.

EMISSIONS FROM VENTS AND SAFETY VALVES

In addition to normal operation emissions, fugitive emissions of ammonia are also released during normal operation, e.g. through tank vents, and occasionally through safety valves. EFMA proposes to lead the pure ammonia emissions from pump safety valves to a flare system and the emissions from the tank vents to a safe location, e.g. via the stack. The IFC requirement of 50 mg/Nm³ only applies to 95 % of the time that the plant is operating; this limit does not need to be observed for emissions occurring less than 5 % of the operating time. Despite the fact that there are no strict international requirements for these emissions, local rules may need to be observed. In all cases where people live in the vicinity, the ammonia smell should be minimized.

In steady operation the fugitive emission from the tanks is extremely low; however, it increases during load changes or when granulation is stopped. According to the above points, flaring is the second-best method in terms of environmental and operating cost factors. If acidic scrubbing is already in use in the plant, this option is preferred in terms of investment cost.

Emissions from safety valves can be quite significant; critical safety valves are typically the ones around the HP pumps, reactor and rectifying unit, where flow rates of 50 to 100 t/h ammonia is released during the opening of the safety valve. Whereas pure ammonia releases can be easily combusted, either by a dedicated

flare in the urea plant or by a flare system in the ammonia plant, the mixture of carbamate, CO₂, water, urea and ammonia requires additional consideration to avoid crystallisation.

The preferred option for all emissions is, of course, avoidance by preventing the safety device from blowing. Installing pressure switches to trip the plant before blowing the safety valves (PSV) is one option. Installing 2003 SIL classified pressure switches with a set pressure well below the set pressure of the safety valve is beneficial and does not affect the availability of the plant. This arrangement has been used in a number of plants in the last few years for the PSVs on the reactor and the recirculation unit. It is reliable and works well. It can also be a solution for existing plants if there is scope between the set pressure of the safety valve and the operating range.

Another way of preventing emissions from blowing safety devices is to select the design pressure accordingly. For economical reasons this mainly applies to safety valves protecting installations from overpressure caused by centrifugal pumps.

Other safety valves also emit ammonia-bearing fluids. Usually their blow-offs run to the vent stack, but flaring is also an option for these intermittent emissions. Since continuous gas purging is not required and the continuous pilot only consumes a few Nm³/h of flare gas, the negative impact on the environment is less critical compared to the continuous flaring of the sources discussed above.

EMERGENCY RELEASES

Emergency releases are examined as a final issue. No international requirements are imposed for this kind of release, but public authorities may define limit values depending on local conditions. Areas with frequent emissions and/or neighbouring inhabitants may have different requirements to those in grassroots area.

Emergency releases may occur if a tube ruptures in the HP heat exchangers of the synthesis. In this case nearly the entire content of the synthesis will be released to the environment.

Since this scenario is extremely rare, but the impact can be serious, it is good practice to first evaluate the risk before deciding on any measures necessary. First the severity of the impact and the likelihood of the accident should be analysed. In fact, a Qualitative Risk Analysis should be carried out. This can be done using a HAZOP [7] procedure or by using a semi-quantitative risk ranking. Risk is defined as the product of frequency (likelihood) and severity (consequence). If the risk level is higher than deemed acceptable, measures to decrease the frequency or the severity need to be developed. If it is not possible to decrease the severity by adding sufficient protection layers, or the required measures are not acceptable for one reason or another, measures to reduce the frequency are required, or vice versa.

One method to evaluate measures influencing the frequency or severity of occurrence is the Layer of Protection Analysis (LOPA). This analysis considers the evaluation of all available safeguards, including all layers of protection.

Example:

The QRA shows that the risk of tube rupture in a urea plant is not acceptable due to the nearby neighbourhood and adjacent chemical plants.

The severity will be reduced by separating the fluid emitted from the tube rupture; the liquid content is sent to a tank and the gas release point is run up to a level above the highest platform. The risk of harming people is decreased due to the high release point for ammonia and the safe containment of the liquid phase. The resulting severity can be assessed using a dispersion calculation showing the ammonia concentration in the proximity. A separator downstream of the blow-off lines from the various safety devices can be used for this purpose and has been used in one of the Uhde urea plants built in Qatar.

If this measure is still not sufficient, the ammonia emission can be reduced by absorption or flaring. Systems with absorption have been installed twice in Uhde urea plants, both in The Netherlands (see figure 4); a flaring system is currently being installed in Abu Dhabi.

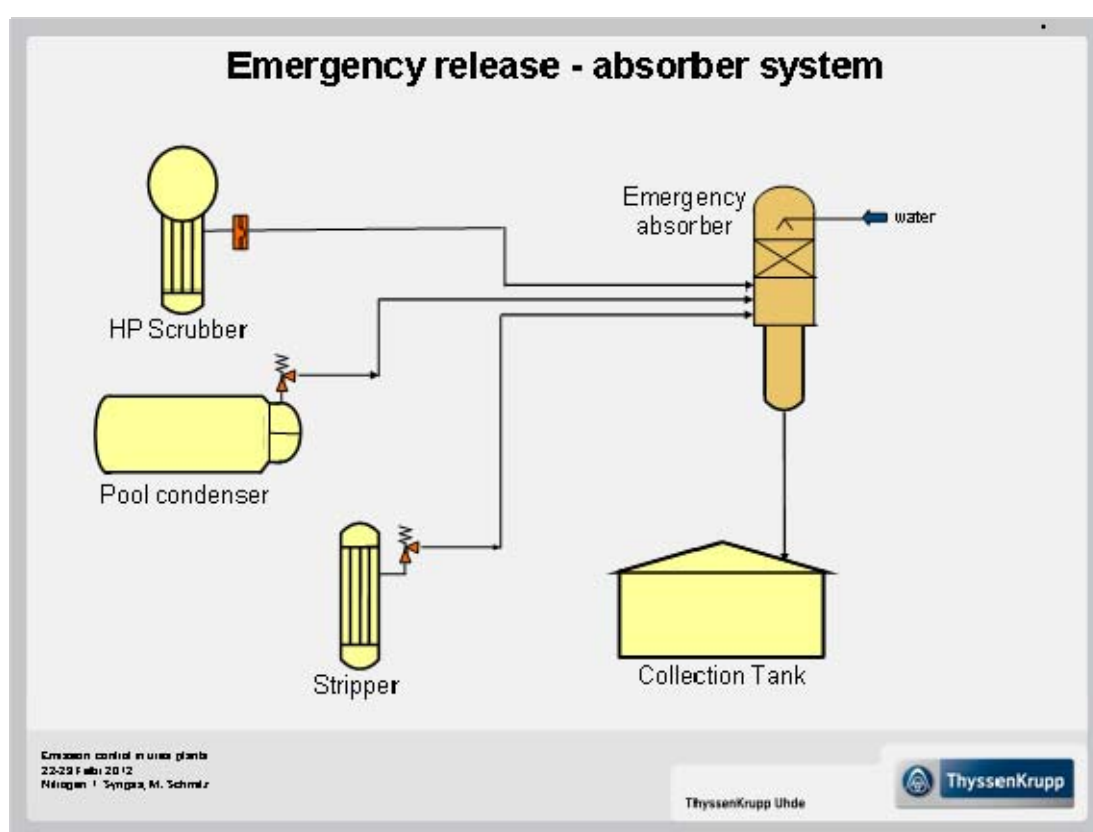


Fig 4

If the risk is still assessed to be too high, measures to reduce the frequency also need to be considered. If corrosion is the reason for a tube rupture, improved materials with a higher resistance to corrosion can reduce the expected frequency of occurrence. All modern Uhde urea plants use Safurex, a duplex material specially developed for application in the synthesis section, and no tube rupture has been recorded since it was first implemented more than 15 years ago.

Analysing the chance of reducing the risk is not actually a stepwise procedure. The choice of provisions is arbitrary and if the risk can already be decreased to an acceptable limit by a number of alternative measures, the most economical one will probably be chosen. However, other aspects like reputation or ethics may also influence this decision.

CONCLUSION

The most appropriate solution will be chosen based on the frequency and severity of ammonia emissions. According to today's reference situation, ammonia emissions from a urea granulation plant can only be reduced to international requirements economically using acidic scrubbing. With this technique already on site, it is more economical and clearly more environmentally friendly to use it for the emissions from the absorber vents in the synthesis as well, and for the tank vents if required.

Since international limit values for emergency releases are not currently available, risk analyses should be based on local authority requirements or the customer's safety policy to find the optimum solution for these emergency scenarios. This may involve investing in improved materials or in secondary safety measures, such as collection or absorber systems.

References and notes

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