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Effectiveness of Reacting Spray Curtains Mitigating Toxic Releases of High Solubility Gases

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1. Introduction

Ammonia is one of the most widely chemicals of current concern in hazard control, being amply used in the process industries, e.g., manufacture of nitrogenous fertilizers, explosives, in the textile and fibre industries, in water effluent treatment, as corrosion inhibitor etc. Ammonia-air mixtures are explosives in the range 15.5-27 % by volume, but the primary concern in hazard control is connected to its toxic properties: according to ACGIH following limits were established: TWA = 25 ppm; STEL = 35 ppm; C = 50 ppm. Even if NH_3 molecular weight is nearly 17 $g \cdot mol^{-1}$ and the vapour density at the normal boiling point (t = -33.35 °C) is 0.9 kg m^{-3}, evidence in a number of accident reports demonstrates that ammonia and air can form mixtures that are denser than the ambient air (Griffiths, 1982). The mixing and dispersion of dense gas clouds are often much slower than those of buoyant clouds and consequently it is desirable to increase their natural dispersion by enhancing the dilution rate. In this respect, spray curtains can represent an effective method to control the spreading of an ammonia cloud and mitigate the environmental/toxic effects. The release concentration is reduced by means of two mechanisms: diluting action due to air entrainment by the sprays, particularly effective in case of stable atmospheric conditions and low ventilation; containment action, which extending the "transient phase" reduces the maximum gas concentration, especially when dealing with a release of short duration. The effectiveness of the chemico-physical mitigation of the barrier depends, as well, on the characteristics of the liquid solution and, particularly, on the reagent concentration. Water curtain effectiveness in removing water soluble gas (e.g. ammonia and hydrofluoric acid) was studied theoretically (Fthenakis, 1989; Fthenakis et al., 1993). Dealing with reacting curtains, the authors performed a detailed study at laboratory scale, on the transient behaviour of a chlorine release (Palazzi et al., 2007b). Subsequently, the authors developed a mathematical model of a two-phase jet to evaluate the entrained air rate in connection with the liquid flow rate. The model was successfully compared by means of replicated wind tunnel experimental runs adopting spray nozzles suitable to create a two-blade barrier and taking into account the instantaneous and non-reversible chemical reactions due to chlorine absorption in alkaline solutions (Palazzi et al., 2007a).
The aim of the present study is to verify the generality of the model, i.e. its applicability to gases of different characteristics. To this end, we performed in wind tunnel the abatement of different ammonia releases, either in pure water or in hydrochloric acid solutions. Besides its importance in chemical industry, this gas was chosen in

consideration of the greater solubility and some differences in mechanism of chemical absorption, in comparison with the chlorine, previously studied.

2. Experimental

Method: series of replicated measures of ammonia concentration inside a laboratory wind tunnel (0.9x0.9x5 m), performed at two sampling point, located respectively at a distance from the release 0.70 m (upwind the barrier) and 1.50 m (downwind the barrier). Materials and methods are described in detail in Palazzi et al., 2007a, as concerns experimental runs carried out with a pure chlorine release.
Previous experimental runs, simulating a continuous release with a constant release rate allowed establishing the correct sampling time from the starting of the experiments, so as to obtain significative experimental results in studying stationary performance of the barrier (Palazzi et al., 2007b). We adopted the same geometric and fluid-dynamics conditions used in chlorine treatment, in order to optimize the air entrainment and the release dilution. Ammonia was measured by bubbling air samples through an acidic water trap (pH = 4.0) and by subsequent measurement by means of UV-visible spectrophotometry (Lambda 25, Perkin Elmer) with the Nessler reagent. Optimal operative conditions selected on the basis of preliminary fluid-dynamic and absorption runs, are summarized in the following Table 1.

3. Theoretical

The model, validated by means of replicated experimental runs in wind tunnel, was structured by assembling three sub-models, respectively describing the rate of air entrainment into the curtain, the dilution of ammonia into the circulating air and its physical and chemical absorption in the liquid phase.

Table 1. Range and reference values of experimental parameters.

Parameter			Operating value /	Parameter			Operating value / range
Curtain height	h	[m]	0.61	Release flow rate	$\dot{m}_r$	[l·h^{-1}]	30-170
Curtain length	L	[m]	0.90	Release duration	t_r	[s]	300
Number of nozzles	N	[-]	19	Curtain flow rate	$\dot{m}_l$	[kg·s^{-1}]	0.15
Nozzle pitch	S_N	[m]	0.04	Mean wind velocity	v_w	[m·s^{-1}]	0.1-1
Mean diameter of drops	δ	[m]	$2\cdot10^{-4}$	Concentration of the absorbing solution	C_{HCl}	[kmol·m^{-3}]	0-0.55
Spray angle	ϕ	[°]	110	Temperature	T	[K]	298
Spray exit velocity	v_0	[m·s^{-1}]	9	Mean molar mass of gas phase (NH_3)	M_a	[kg·kmol^{-1}]	17
Liquid phase density	ρ_l	[kg·m^{-3}]		Kinematic viscosity of gas phase	υ_a	[m^2·s^{-1}]	
Gas phase density	ρ_a	[kg·m^{-3}]		Diffusivity of gas in the liquid	D_a	[m^2·s^{-1}]	

Table 2. Nomenclature

A	entrainment constant, -	$k_g p$	mass transfer coeff. in the gas-phase, kmol·m^{-2}·s^{-1}
$\dot{m}_{abs}$	absorption flow rate, kg·s^{-1}	$\dot{m}_{ae}$	air flow rate entrained by the curtain, kg·s^{-1}
$\dot{m}_{au}$	air flow rate induced by the curtain, kg·s^{-1}	$\dot{m}_d$	release flow rate after curtain absorption, kg·s^{-1}
η_{abs}	absorption efficiency, -	η_{dil}	dilution efficiency, -
v_J	liquid velocity at the end of the jet phase, m·s^{-1}	ω_d	conc. of released subst. downwind the curtain, ppm
v_∞	terminal velocity of liquid phase, m·s^{-1}	X_g	single pass absorption efficiency, -

- mass reduction of the toxic/released substance, by means of physical and/or chemical absorption:

$$\dot{m}_d = \dot{m}_r - \dot{m}_{abs} = \dot{m}_r(1-\eta_{abs}) \quad (1)$$

where η_{abs} is the absorption efficiency, defined as follows:

$$\eta_{abs} = 1-(\dot{m}_d/\dot{m}_r) \quad (2)$$

- concentration reduction of the toxic release in downwind immediacy, by means of mixing with air entrained by the sprays. The dilution efficiency may be defined as:

$$\eta_{dil} = 1-(\dot{m}_r/\dot{m}_{a,dil}) \quad (3)$$

The concentration of the released substance, resulting from these two mechanisms may be expressed as

$$\omega_d = \dot{m}_d/\dot{m}_{a,dil} = (1-\eta_{abs})(1-\eta_{dil}) \quad (4)$$

$$\dot{m}_{a,dil} = (\dot{m}_{ae} + \dot{m}_{au})/2 \quad (5)$$

$$\dot{m}_{au} = \dot{m}_l L(v_0/v_j) \quad (6)$$

$$\dot{m}_{ae} = 0.5A\rho_a v_j hL \quad (7)$$

Dealing with chemico-physical absorption of ammonia into water or HCl solution, it results:

$$\eta_{abs} = \frac{2X_g}{1+X_g} \quad (8)$$

where X_g is the intrinsic single-pass absorption efficiency of ammonia either in water or in HCl solution:

$$X_g = 1-\exp\left(-6\frac{h}{\delta}\frac{M_a k_g p}{\rho_l v_0}\right) \quad (7)$$

To the purpose of a correct curtain design, particularly in order to attain a given absorption effectiveness η_{abs} (and therefore X_g), it is necessary to evaluate $k_g p$. Starting from Foust et al. (1980), a theoretical estimate of $k_g p$ was calculated as follows:

$$k_g p = \frac{D_a \rho_a}{M_a \delta}\left[2+0.6\left(\frac{\upsilon_a}{D_a}\right)^{1/3}\left(\frac{v_\infty \delta}{\upsilon_a}\right)^{1/2}\right]$$

By combining previous equations (Palazzi et al., 2007a), the ammonia concentration downwind the curtain can be expressed as:

$$\omega_d = \frac{2\dot{m}_r}{L\left[\frac{1}{2}A\rho_a v_J h + \dot{\bar{m}}_l \frac{v_0}{v_J}\right]\left[2\cdot exp\left(6\frac{h}{\delta}\frac{M_a k_g p}{\rho_l v_0}\right)-1\right]}$$

4. Results and discussion

As already remarked, only the situations of low wind conditions has been extensively examined in the present work. The condition of still air represents the worst case in the proximity of the release, being connected to the highest gas concentration. On the contrary, wind absence can represent an under-estimation of risk for targets at some distance from the release point, in that longer time to intervene with protective actions

are considered. In real world, the condition of still air is not very common, even if can be verified in case of confinement and meteorological stability.

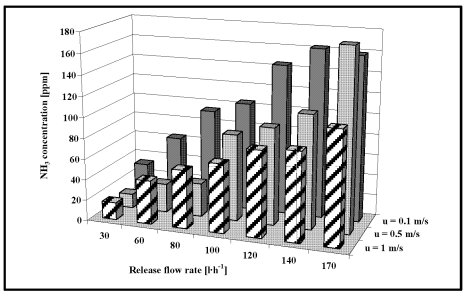

Fig. 1. Measured upwind concentration of NH_3 with a water barrier configuration.

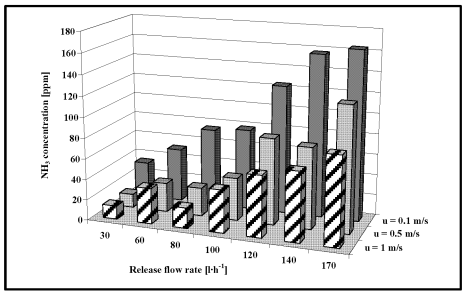

Fig. 2. Measured upwind concentration of NH_3 with with a reacting HCl solution barrier configuration.

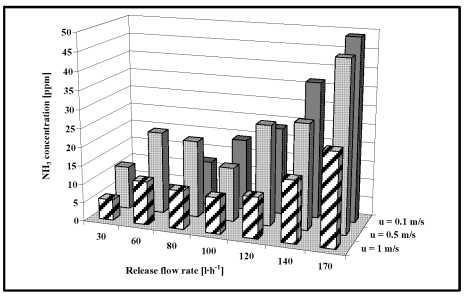

Fig. 3. Measured downwind concentration of NH_3 with a water barrier configuration.

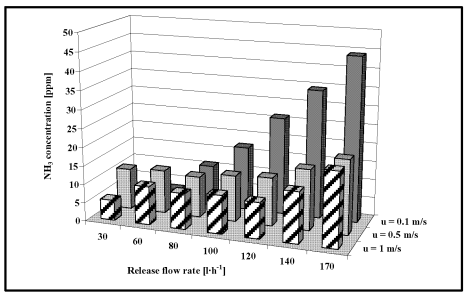

Fig. 4. Measured downwind concentration of NH_3 with a reacting HCl solution barrier configuration.

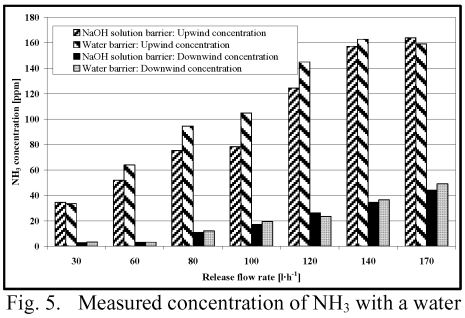

Fig. 5. Measured concentration of NH_3 with a water barrier configuration at wind velocity 0.1 $m \cdot s^{-1}$.

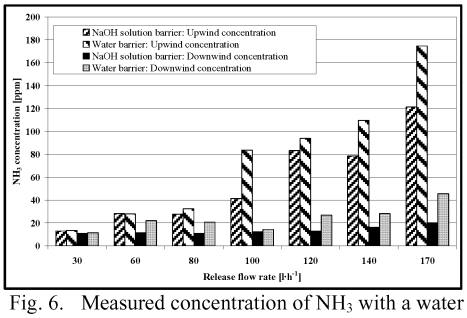

Fig. 6. Measured concentration of NH_3 with a water barrier configuration at wind velocity 0.5 $m \cdot s^{-1}$.

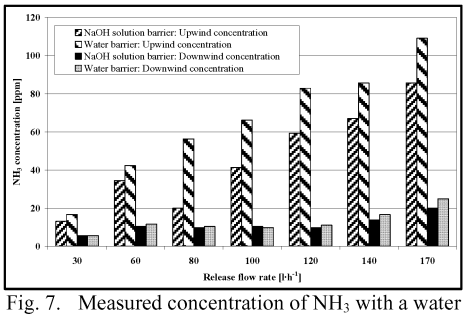

Fig. 7. Measured concentration of NH_3 with a water barrier configuration at wind velocity 1 $m \cdot s^{-1}$.

Table 3. Application of the model: physical absorption and physical-chemical absorption.

Parameter		Water barrier	HCl sol. barrier
Single pass absorption efficiency, -	X_g	0.47	0.61
Absorption efficiency, -	η_{ab}	0.64	0.78
Mass transfer coefficient in the gas-phase, $kmol \cdot m^{-2} \cdot s^{-1}$	$k_g p$	0.006	0.009

Table 4. Comparison ammonia vs chlorine mitigation by pure water and reacting solution.

Release	X_g Water curtain	X_g Reacting curtain	Single pass efficiency enhancement	Absorption efficiency enhancement
Chlorine	0.30 (average value)	0.50 (average value)	67 %	46 %
Ammonia	0.47	0.61	30 %	22 %

The analysis of experimental data obtained in the optimal range, based on, suggests that, according to the physical model of the barrier, the air flow rate induced by the curtain $\dot{m}_{au}$ and the air flow rate entrained by the curtain $\dot{m}_{ae}$ are both nearly 0.45 kg s^{-1}. Figs. 1-2 show the upwind NH_3 concentration obtained respectively with water and HCl solution spray barrier. Figs. 3-4 show the downwind NH_3 concentration obtained respectively with water and HCl solution spray barrier. Figs. 5, 6 and 7 depict the effect of wind velocity on upwind and downwind NH_3 concentration, utilizing both water and HCl solution spray barrier. Application of the model, to both the case of physical absorption and physical-chemical absorption allowed obtaining the results summarized in Table 3. Fig. 8 shows the predicted and measured ammonia concentration ω_d obtained at the different operating conditions utilized in this work, with a water barrier configuration. The corresponding r is 0.847. Clearly agreement between theoretical prediction and experimental measurements is rather good. Fig. 9 shows the predicted and measured ammonia concentration ω_d obtained at the different operating conditions, with a reacting HCl solution barrier configuration. The corresponding r is 0.740. A quantitative comparison with average results obtained in previous experimental runs on chlorine mitigation by pure water and reacting HCl solution, is shown in Table 4. As expected, the adoption of a reacting curtain is relatively less determining in connection with an ammonia release, even if it exerts a significant mitigation effect (ΔX=30%; $\Delta\eta_{abs}$=22%). In order to attain a sharp enhancement of the absorption rate, HCl concentration must by far exceed the stoichiometric ratio, with value of the order of 2% w/w. The mechanism of the reaction appears rather different from the one connected to chemical absorption of chlorine in NaOH solution (non-reversible and instantaneous reaction), as shown by the negligible absorption enhancement obtained in runs carried out with 0.5 and 1% (w/w) HCl solutions. Higher values of the HCl concentration from one side could enhance chemical absorption rate, from the other side could give rise to environmental problems connected to potential acid release into the atmosphere, as well as to technical and economic constraints connected to possible corrosion of the installation. Furthermore, we must notice that, on the basis of field experiments, Dandrieux et al. (2001) reported that even if water barriers are effective in diluting ammonia vapour cloud, the downwind concentrations are still higher than the toxic limit. In this sense, the adoption of a reacting curtain (equipped with a 2% w/w HCl water solution) in order to increase the ammonia dissolution rate can represent a technical option to be considered so as to improve the downwind mitigation, without causing additional problems in environment and/or in the working of the safety device, due to viscosity of solution, pipe corrosion and fouling, and so on.

CONCLUSIONS

This paper presents experimental and theoretical investigations on liquid spray curtains, in the context of the absorption and dispersion of accidental releases of ammonia in air.

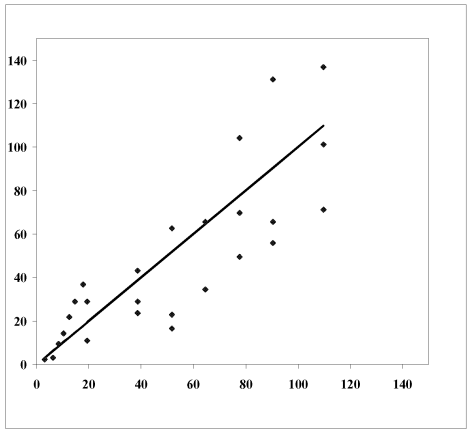

Fig. 8. Predicted and measured NH_3 concentration with a water barrier configuration.

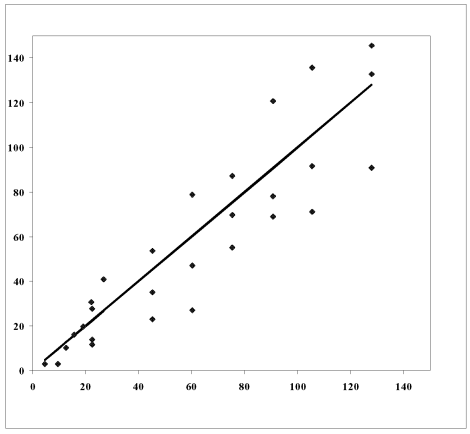

Fig. 9. Predicted and measured NH_3 concentration with a reacting HCl solution barrier configuration.

The model, validated by means of replicated experimental runs in wind tunnel, was structured by assembling three sub-models, respectively describing the rate of air entrainment into the curtain, the dilution of the chlorine into the circulating air and its physical and chemical absorption in the liquid phase. The aim of the present study is to verify the generality of the model, i.e. its applicability to gases of different characteristics. To this end, we performed in wind tunnel the abatement of different releases of ammonia, by a spray curtain either with tap water or with hydrochloric acid solutions feed. Besides its importance in chemical industry, this gas was chosen in consideration of both the higher solubility and some differences in the chemical absorption mechanism, in comparison with chlorine. The experimental results indicate that the curtain model well describes the abatement of ammonia releases, provided that some minor modifications are brought in the kinetics of the absorption sub-model. Another interesting result of this study is the identification of the conditions where the use of a reactive solution significantly increases the efficiency of the release mitigation. In any case, as foreseeable, the relative advantage due to the chemical absorption of ammonia, in comparison to the purely physical one, is lower, with respect to the case of the chlorine, owing to the difference in the solubility of the two gases.

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