

## Risk Assessment of Severe Accidents Involving Atmospheric Dispersion of Anhydrous and Hydrus Ammonia Mixtures

### Abstract

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Accidental events involving sudden, instantaneous and/or continuous releases of anhydrous ammonia ( $\text{NH}_3$ ) to the ambient atmosphere are quite hard to assess, especially when a thorough, realistic, risk assessment is required.

The thermodynamic properties of ammonia, being a major building-block and key component in the manufacture of many products, as well as being widely used as a most efficient refrigerant gas, have been extensively investigated. Thus, the behavior of ammonia during *early stages* of its emission into the atmosphere, following initial interaction with ambient air, such as evaporation from puddles, instantaneous releases during flash accidents (due to e.g. a sudden collapse of a storage tank), dual phase releases from holes in storage tanks etc., has been modelled and can be quantified relatively easily. However, the actual *environmental fate* of ammonia is determined by its dispersion characteristics, which may turn out to be quite complex. Basically,  $\text{NH}_3$ , being much lighter than air ( $M_{\text{NH}_3}=17$  compared to  $M_{\text{AIR}}=29$ ) is expected to undergo significant plume rise processes, prior to its downwind aerosolic diffusion/dispersion *as a gas*. On the other hand, rather vigorous hydrolysis reactions with ambient air humidity can create ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) liquid droplets (or solid icicles), which are expected to behave as particulate matter, i.e. as particles, deemed to either *diffusional dry deposition*, if having aerosolic mean aerodynamic diameters (AMADs) smaller than few tens of a micron, or *gravitational settling*, if having AMADs greater than, say, 50 microns. The  $\text{NH}_4\text{OH}$  particles, which can possibly be produced at very close proximities to the point/surface of release and due to their mass/volume characteristics, will remain close to the release point and start (and continue) their dispersion from rather low altitudes, compared to the light, gaseous  $\text{NH}_3$ . Thus, while due to its height of release,  $\text{NH}_3$  does not seem to cause significant downwind air concentrations, air concentrations of  $\text{NH}_4\text{OH}$  should be carefully analyzed, due to its initial potential of “close to surface” dispersion.

In other words, from point of view of possible downwind air concentrations, determining the potential adverse health effect to public receptors (and hence, the Risks), the fractionation of anhydrous Vs. hydrus ammonia within the bulk of released material, as well as the expected heights of release of both compounds, can turn out *critical* for any risk assessment of ammonia accidents in general, and for risk-assessment-based decision making processes, in particular.

An innovative approach to overcome the above risk assessment difficulties, especially for spills on water and solid surfaces, is proposed. In this approach, (a) Rates of releases of anhydrous ammonia from puddle surfaces as function of initial ammonia temperatures as well as ambient air and surface temperatures are calculated; (b) Rates of creation of  $\text{NH}_4\text{OH}$

close to the evaporating surface are calculated as function of relative humidity (i.e. air water content) assuming rates of reaction between  $\text{NH}_3$  and “water in air”, up to 100% successful hit probabilities of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules;(c) Plume rise and elevated dispersion of  $\text{NH}_3$  (heights of release – a few hundred meters); (d) Dispersion of  $\text{NH}_4\text{OH}$  particles with heights of release  $< 20\text{m}$ ; (e) Consideration of the *significantly different inhalation dose-effect relationships* of  $\text{NH}_3$  as compared to those of  $\text{NH}_4\text{OH}$ ; and finally (f) Fitting the atmospheric dispersion model to the relevant type of release, i.e. instantaneous or continuous, as derived, *inter alia*, from the accident analysis and ambient chemical/physical conditions.

Preliminary results show that conservative assumptions concerning  $\text{NH}_4\text{OH}$  creation from instantaneous “cold”  $\text{NH}_3$  spills on water surfaces followed by consequent vigorous evaporation, do not lead to significant, life threatening, air concentrations at distances as close as 1000-2000 m from the release point; depending, *inter alia*, on prevailing meteorological stability conditions during accident occurrence.