|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. xxx, 2025*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: Bruno Fabiano, Valerio Cozzani  Copyright © 2025, AIDIC Servizi S.r.l. **ISBN** 979-12-81206-xx-y; **ISSN** 2283-9216 | |

Bridging Analytical Models and CFD: Advancing Ammonia Spill Dispersion Predictions

Filippo De Rosaa, Pablo Giacopinellia,\*, Felicia Tanb, Alexandre Lebasa, Christophe Mabilata

aMES, One Springfield Drive, Leatherhead, Surrey, KT22 7AJ, UK

bBP, ICBT, Sunbury Business Park, Sunbury-on-Thames TW16 7BP

\*pablo.giacopinelli@mes-international.com

The dynamics of pool spreading, evaporation, dissolution and dispersion of refrigerated ammonia spills are highly complex, with no readily available models capable of accounting for all relevant thermochemical properties, and their interactions with varying terrains and environmental conditions. To address this gap, this study presents a novel modelling approach to predict accurately ammonia behaviour during accidental releases. The methodology integrates an analytical model for pool spreading and evaporation (on both land and water), advanced Computational Fluid Dynamics (CFD) simulations for the ammonia dispersion in air, and the coupling of analytical and CFD models to ensure accurate predictions.

This novel analytical-CFD coupling approach enhances the accuracy in predicting dispersion patterns while maintaining practical computational demands, thereby providing valuable insights for industrial safety planning and risk mitigation.

* 1. Introduction

Accidental releases of refrigerated ammonia present significant hazards due to the complex interactions between pool spreading, evaporation, dissolution, and atmospheric dispersion. Accurate modelling of ammonia dispersion is crucial for industrial safety, yet existing models face limitations in capturing key phenomena, lacking the capability to fully integrate all relevant thermo-chemical properties across varied terrains and environmental conditions. Traditional 2D consequence modelling tools provide validated solutions for flat terrain but struggle to capture the full complexity of ammonia behaviour when interacting with complex surrounding geometrical features and for water releases by simplifying dissolution mechanisms.

Several studies have leveraged CFD to simulate ammonia dispersion under different environmental conditions. Liu et al. (2024) analysed ammonia leakage during ship-to-ship bunkering, emphasizing the impact of ship structures on dispersion but neglecting ammonia pool spreading and evaporation dynamics. Skarsvåg et al. (2024) introduced an evaporation-dissolution model for ammonia spills, highlighting humidity and evaporation effects (ammonia-water fog formation), but without integrating a full thermodynamic pool model neither extending the study to gas dispersion. Kiša and Jelemenský (2009) validated CFD dispersion models using FLADIS field experiments, focusing on urban terrain effects but excluding detailed pool evaporation and spreading processes. Similarly, Namboothiri and Soman (2018) applied CFD-probit analysis to assess ammonia dispersion threats but did not incorporate liquid-phase pool formation.

Zárate et al. (2024) and Kjørsvik-Abbedissen (2018) further explored CFD-based gas dispersion models, with the former studying generic toxic gas dispersion without ammonia-specific thermodynamic interactions and the latter analysing ammonia dispersion in an industrial setting without considering pool evaporation. While these studies demonstrate the effectiveness of CFD in gas dispersion modelling, they lack integration with analytical models for ammonia pool behaviour, leading to gaps in accurately predicting ammonia behaviour in complex environments.

* 1. Methodology

The methodology consists of three main phases: (i) an analytical model to simulate pool spreading and evaporation, (ii) CFD simulations to model atmospheric dispersion, and (iii) coupling of the analytical and CFD models for improved accuracy.

Modelling pool spreading and evaporation is complex and, whilst there are some models available in advanced computational tools such as CFD, these models have many limitations (e.g. limit on pool height, no dissolution, simplified physics, strong constraints on mesh and timestep) and are computationally demanding.

As a result, a pool spreading model based on mass and heat balance using reliable and well documented correlations for mass and heat transfer was developed. The model is resolved using a 2nd order discretisation method for stiff problems. This allows the pool dynamics to be easily computed and assessed prior to the subsequent CFD dispersion, whilst keeping the computational requirements in terms of model size and runtime manageable for the purpose of the project. A schematic of the quantities considered and how they affect the model for land and water releases is presented in Figure 1.

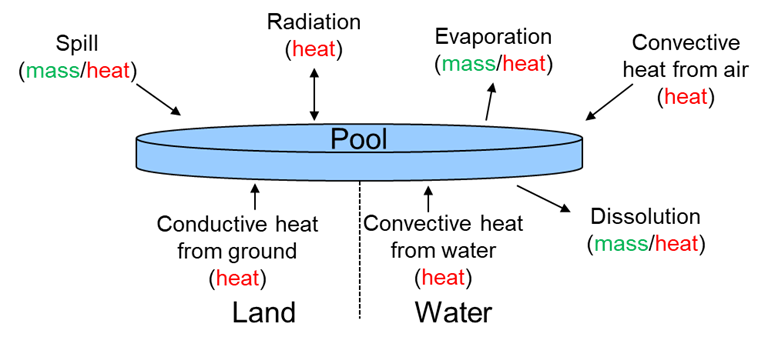


Figure 1: Schematic of the quantities considered for the pool spreading model.

The main assumptions associated with the pool spreading model are:

* The mathematical model is derived considering perfect mixing inside the pool (i.e. CSTR model) therefore the differential equations are descriptive of the dynamics where all variables, at each timestep, are constant throughout the volume of the spreading pool both on land and on water.
* The fluid properties of the pool including density, specific heat capacity and vapour pressure are assumed to be constant over the entire volume of the pool at each time step. This is the underlying assumption in all integral pool models which handle average properties across the pool volume.
* The pool is cylindrical in shape and axisymmetric, with the spill source located in the centre of the pool. Therefore, only fluid flow in the radial direction is considered.
* The height of the pool is uniform across its surface. The pool is assumed to be sufficiently thin so that its temperature is constant in the vertical direction.
* At each timestep, the dissolution of ammonia in liquid water is assumed to be instantaneous as the solution is assumed to be at the thermodynamic equilibrium.
* Ammonia evaporation from the release (i.e. breaking point to sea surface) is assumed negligible.
* All material properties were temperature-dependant including specific heat, density, vapour pressure, heat of vaporisation, and solubility. The vapour above the pool behaves as an ideal gas.

A timestep sensitivity was carried out to ensure that the time discretisation of the model had no impact on the prediction of the pool dynamics. Time profiles of pool radius, height, temperature, ammonia evaporation and dissolution rate were the outputs of the model.

* + 1. Analytical Model for Pool Spreading and Evaporation

The main modelling equations to describe the behaviour of the pool are:

* + - 1. **Mass Balance**

The pool is modelled as a collapsing cylinder spreading over a thin film of height, , equal to the average surface roughness length. The spreading law used in this model to calculate the evolution of the pool radius is given by (Shaw and Briscoe, 1980):

|  |  |
| --- | --- |
|  | (1) |

For pool spreading on land surface, a global mass balance has been derived to calculate the height of the pool:

|  |  |
| --- | --- |
|  | (2) |

For pool spreading on sea surface, Eq (2) was modified as follows to also consider that a fraction of the pool is lost in dissolution into water:

|  |  |
| --- | --- |
|  | (3) |

* + - 1. **Evaporation and Dissolution**

The evaporation rate, , from an evaporating pool can be expressed in the general form (Brighton, 1985):

|  |  |
| --- | --- |
|  | (4) |

Similarly, the dissolution rate is computed as per Eq (5):

|  |  |
| --- | --- |
|  | (5) |

The interface concentration is estimated using saturation properties of ammonia at pool temperature according to the following equation derived from the ideal gas state:

|  |  |
| --- | --- |
|  | (6) |

For pool spreading on water, the interface mass fraction between pool and water has been computed using Eq (7) below:

|  |  |
| --- | --- |
|  | (7) |

Where represents the mass solubility of ammonia in water and it has been derived from solubility values as detailed in Green and Southard (1971). It should be noted that the temperature range does not covers temperature lower than 0°C therefore the maximum solubility (1g of ammonia per 100g of water) was considered outside of the range.

The friction velocity is estimated using the logarithmic wind profile equations in line with the atmospheric boundary layer setup while carrying CFD simulations:

|  |  |
| --- | --- |
|  | (8) |

According to Dodge et al. (1985), the boundary layer is formed in the liquid by the transfer of momentum to the water by the wind. Since the shear stress across the interface is assumed to be continuous, then the friction velocities in air and water are related according to Eq (9) below.

|  |  |
| --- | --- |
|  | (9) |

An expression for the evaporation mass transfer coefficient, , has been derived from the solution of the advection-diffusion equation (Kunsch, 1998):

|  |  |
| --- | --- |
|  | (10) |

Where is a semi-empirical equation detailed in Kunsch (1998) for hydrodynamically smooth surfaces:

|  |  |
| --- | --- |
|  | (11) |
|  | (12) |

Similarly, the mass transfer coefficient between the liquid pool and the sea has been computed according to Eq (14) reported below as per Dodge et al. (1985):

|  |  |
| --- | --- |
|  | (13) |

Where:

|  |  |
| --- | --- |
|  | (14) |
|  | (15) |

* + - 1. **Energy Balance**

A global mass balance has been derived to calculate the Temperature of the pool:

|  |  |
| --- | --- |
|  | (16) |

For pool spreading on sea surface, Eq (16) was modified as follows to also consider that a fraction of the pool is lost in dissolution into water

|  |  |
| --- | --- |
|  | (17) |

The heat transferred to the pool due to external environmental factors is reported below:

|  |  |
| --- | --- |
| *+* | (18) |

It should be noted that the term was only considered for the pool spreading on land surface while the was only considered for the pool spreading on sea surface. The formulation of the two terms, however, remains the same as detailed in Eqs (19) and (20).

Perfect thermal contact between the pool and the ground’s surface is implied. The analytical expression for the heat exchange between the pool and the ground is derived from (Shaw and Briscoe, 1980):

|  |  |
| --- | --- |
|  | (19) |
|  | (20) |

The heat provided by air convection can be generally written as:

|  |  |
| --- | --- |
|  | (21) |

Where the heat transfer coefficient was estimated using Eqs (22), (23), and (24) according to Fleischer(1980):

|  |  |
| --- | --- |
|  | (22) |
|  | (23) |
|  | (24) |

* + 1. Computational Fluid Dynamics Simulations

The CFD dispersion modelling was carried out using Siemens Star-CCM+, a state-of-the-art commercial software widely validated for a wide range of problems. The CFD code solves the Reynolds Averaged Navier-Stokes (RANS) equations for momentum, enthalpy, turbulence energy, turbulence dissipation rate and scalar concentration, using the buoyancy modified standard two-equation (k- ε) closure model and standard numerical schemes. A finite-volume approach to the discretisation of the equations is used with well-defined boundary and initial conditions, and simulations were run transiently with high order time and temporal discretisation schemes.

To build the model, the first step was to create a suitable geometrical representation of the domain of interest, including all relevant obstructions that could affect the dispersion. Figure 4 shows the geometrical model representing an onshore storage terminal connected to a bunkering loading arm. Given the practical constraints of a real-world project, a pragmatic approach was adopted for mesh generation. A 3D unstructured (‘trimmed’) grid was created to represent the full domain and geometry, with local refinement near the release source, pool, and major obstructions. A 2-stage adaptive mesh refinement technique was implemented to track regions of high ammonia concentration and regenerate the grid every 10 seconds of simulated time, ensuring accurate plume resolution throughout the simulation. Near-ground resolution was achieved with four prism layers across the first 2 meters, starting at 30 cm and growing at a 1.2 ratio. An all-Y+ wall model was used to manage near-wall turbulence within the constraints of a large domain and long transient run time. The mesh design was carefully refined around key geometries and terrain features, while adaptive meshing maintained a 1 m resolution in high concentration regions. This approach balances accuracy with computational feasibility for a two-hour transient simulation with varying source terms over a large-scale domain.

A close-up of a computer

Description automatically generated

Figure 4: 3D geometrical model representing an onshore storage terminal and details of the 2-stage adaptive mesh refinement design implemented for the CFD modelling.

* + 1. Coupling of Analytical and CFD Models

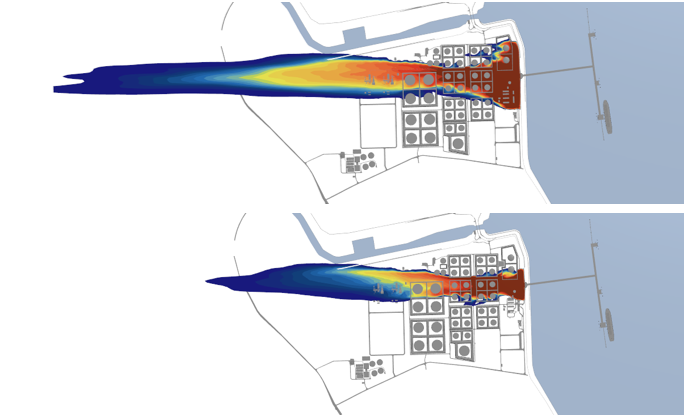
To ensure seamless integration, the analytical model provides the initial pool spreading and evaporation data, which are dynamically incorporated into the CFD domain. The CFD model then tracks ammonia vapor dispersion, accounting for terrain effects, atmospheric conditions, and local obstructions.

The ammonia was released using mass, momentum and energy source terms in the layer of cells directly above the pool. In order to adequately release ammonia in the CFD model, it was necessary to dynamically modify the computational cells that were used as source terms. This would ensure that the mass of ammonia released would match the outcome of the analytical model and that the concentration build-up above the pool would be consistent with the evolution of the pool radius.

Direct toxic probit calculations were performed considering real time concentration of ammonia across the whole simulation domain, in contrast with more simplified approaches which would only provide these at specific monitoring locations.

* 1. Results and Discussion

Figure 5 show a variety of release conditions and locations for different weather conditions modelled with the developed analytical model coupled with CFD simulations.

A blue and red plane

Description automatically generated with medium confidence

Figure 5: Dispersed Ammonia gas concentration contours for 10 minutes (top) and 2 minutes (bottom) isolation times: 2F weather condition on land pool release (left) and 5D weather condition on water pool release (right).

By improving initial conditions accuracy, this coupled approach provides accurate predictions, overcoming the limitations of standalone CFD models. The results highlight some of the following observations:

* Land vs. Water Releases: Ammonia pools on land tend to spread further, leading to higher evaporation rates and larger dispersion extents. Water spills result in ammonia dissolution, removing ammonia from the pool and subsequently in a smaller pool extent. Heat released during the dissolution process led to additional evaporation, keeping the pool at boiling temperature and affecting evaporation dynamics.
* Impact of Weather Conditions: Lower wind speeds (e.g., 2F) lead to larger pools and prolonged evaporation, whereas higher wind speeds (e.g., 5D) enhance dispersion but reduces pool size. Furthermore, larger pool radius combined with lower evaporation rate means that the concentrations near the pool for a 2F scenario would be lower than in the 5D case.
* Isolation Time Effects: Faster leak isolation significantly reduces both the overall ammonia release, limiting pool growth and dispersion extent, as well as the exposure time and therefore the toxic probit.
  1. Conclusions

Existing CFD-based ammonia dispersion models excel in predicting gas-phase behaviour but fail to capture ammonia’s complex interactions with land and water surfaces. Conversely, empirical models address pool evaporation and spreading but lack detailed gas dispersion accuracy. This novel methodology bridges these gaps overcoming the limitations of standalone CFD or empirical models, providing a more reliable tool for ammonia spill risk assessment and industrial safety planning by integrating:

* A robust analytical model for ammonia pool spreading, evaporation, and dissolution.
* High-resolution CFD simulations to track atmospheric dispersion under varying conditions.
* A fully coupled hybrid approach that ensures accurate and computationally efficient predictions.

This model not only improves dispersion prediction but also provides detailed insights into thermochemical interactions that influence ammonia evaporation and dissolution, making it a significant advancement over traditional methods while maintaining computational efficiency. These findings provide valuable insights for industrial safety planning and risk mitigation in ammonia storage and transportation facilities.

Nomenclature

, , - Dissolution, Evaporation & Spilled rates, kg/s

- Heat of dissolution, j/kg

- Heat transfer coefficient between air and pool, W/(m2K)

, - Minimum height & Height of the pool, m

- Vapour concentration at the pool surface, Kg/m3

- Molecular weight of ammonia, kg/kmol

- Vapour pressure of ammonia at pool temperature, Pa

- Short wave incident solar radiation, W/m2

- Overall heat transferred from environment, W

, - Ambient & Ground Temperatures, K

, , – Pool, Spill & Water Temperatures, K

, - Sensible heat (air) & Sensible heat, j/(kgK)

- Mass solubility of Ammonia, -

, - Mass trans coeff. (Evap.) on land & water, Kg/(m2s)

- Pool Radius, m

, - Pool Surface Water & Wind Friction Vel, m/s

- Wind speed reference value at 10m elevation, m/s

– Ammonia interface fraction at ammonia/sea interface, -

, - Surface roughness & Reference height, m

, - Ground & Water thermal diffusivity, W/(mK)

, - Semi-empirical corr. for Diss. & Evap., -

- Latent heat of vaporisation, j/(kg)

- Viscosity (air), m2/s

, , – Air, Liquid Ammonia & Water Densities, kg/m3

, , – Nusselt, Prandtl & Reynolds Numbers (Air), -

- Ideal Gas Constant, j/kmol

, - Schmidt numbers for Ammonia & Water, -

, - Napier & Von Karman Constants, -

Acknowledgments

The authors would like to express their gratitude to bp project (Christian Schovsbo, Marco Giannelli) and central engineering team for their feedback and technical expertise, which contributed to the development of this work.

References

Brighton, P., 1985. Evaporation from a plane liquid surface into a turbulent layer. J. Fluid Mech., 159, 323-345.

Dodge, F., Park, J., Buckingham, J., and Magott, R., 1985. Revision and experimental verification of the hazard assessment computer system models for spreading, movement, dissolution, and dissipation of insoluble chemicals spilled onto water. Report: CG-D-35-83. Washington.

Fleischer, F., 1980. SPILLS: An evaporation/air dispersion model for chemical spills on land. Houston, Texas: Shell Westhollow Research Centre.

Green, D. W., & Southard, M. Z. (Eds.), 2018. Perry's Chemical Engineers' Handbook (9th ed.). McGraw-Hill Education.

Kiša, M., Jelemenský, Ľ., 2009. CFD Dispersion Modelling for Emergency Preparedness. J. Loss Prev. Proc. Ind., 22,97-106.

Kjørsvik-Abbedissen, R., 2018. A Numerical Study of Ammonia Dispersion in an Industrial Area with the CFD Tool FLACS. Master’s Thesis, University of Bergen.

Kunsch, J., 1998. Two-layer integral model for calculating the evaporation rate from a liquid surface. J. Hazard. Mater., 59, 167-187.

Liu, Y., Harikrishnan, B., Kolluru, R., Mastorakos, E., 2024. Computational Fluid Dynamics Simulation of Ammonia Leakage Scenarios During Ship-to-Ship Bunkering. Ocean Eng., 297, 114139.

Namboothiri, N.V., Soman, A.R., 2018. Consequence Assessment of Anhydrous Ammonia Release Using CFD-Probit Analysis. Process Saf. Prog., 37 (1), 84-96.

Shaw, P., and Briscoe, F., 1980. Spread and evaporation of liquid. Prog. Energ. Combust., 6 (2), 127-140.

Siemens, Star-CCM+. www.plm.sw.siemens.com/en-US/simcenter/fluids-thermal-simulation/star-ccm/

Skarsvåg, H.L., Fyhn, E.H., Aasen, A., 2024. Influence of Ammonia-Water Fog Formation on Ammonia Dispersion from a Liquid Spill. arXiv preprint, arXiv:2404.17285.

Zárate, L.G., Cordero, M.E., Ponce, A., Escartín, A.E., 2024. Simulation of Toxic Substance Dispersion Using CFD. Strategy Technol. Soc., 9 (2), 87-101