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Preliminary assessment of the vertical release of liquefied chlorine inside a depression

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Summary

Toxic industrial chemicals (TICs) are used in most places and can pose a threat due to accidents, terror, or sabotage. Many of the most common TICs are gasses at ambient atmosphere, such as chlorine, ammonia, and sulfur dioxide, but are stored and transported as liquids in pressurized containers. This study addresses the release of chlorine from such a container.

There exist a considerable knowledge gap and lack of reliable predictive models for calculating the dispersion and transport of dense gasses such as chlorine when released into the atmosphere. Existing models have a general tendency to severely over predict the hazard areas and very large differences in the predictions are obtained using well established approaches. These differences are believed to be primarily related to poor source modelling, especially for large scale releases. It therefore exist a need to improve our fundamental knowledge of the physical processes involved and to develop improved and reliable predictive models for large scale releases of dense gasses. This study constitutes a part of a recently initiated joint effort between the US Department of Homeland Security/Chemical Security Analysis Centre (CSAC), Naval Surface Warfare Centre Dahlgren Division (NSWCDD), and FFI with the objective to address these issues and in particular consider large scale releases of liquefied chlorine. The work consists of both theoretical and computational modelling of dense gas dispersion and transport supported by a large scale field test in which two tons of liquefied chlorine will be released. These experiments are planned to be conducted in the USA in the second half of 2009.

The objective of this study is to aid the planning of these field tests. The study focuses primarily on the necessary size and geometry of the depression for a release as large as this. The following recommendations are made:

- The shape of the depression used in this study seems a viable geometry to contain the initial cloud and prevent spill-over of liquid chlorine
- It is recommended that in order to contain the initial cloud resulting from the release of chlorine from a pressurized tank, the depression should have a radius of minimum 18 - 20 m and a depth of 1.5 – 2.0 m. The lateral and vertical dimensions stated above must be regarded as a minimum.
- A concrete slab (approximately 1 m diameter) e.g. should be placed directly beneath the release point in order to prevent significant erosion which adversely would affect the experiment.

Sammendrag

Toksiske industrikjemikalier (TICs) er i utstrakt bruk de fleste steder og kan utgjøre en fare ved uhell, terror eller sabotasje. Mange av de vanligste TIC er gasser ved normal atmosfære, slik som for eksempel klor, ammoniakk og svoveldioksid, men lagres og transporteres ofte som væsker i trykksatte tanker. Denne rapporten adresserer utslipp fra slike tanker.

Det eksisterer et betydelig kunnskapsgap og mangel på pålitelige modeller for å beregne spredning og transport av tunge gasser ved utslipp i atmosfæren, slik som klor. Eksisterende modeller har generelt en tendens til å overpredikere fareområdene, og veldig store forskjeller oppnås ved bruk av etablerte metoder. Forskjellene er antatt i hovedsak å være relatert til mangelfull kildemodellering, spesielt for store utslipp. Det er derfor et behov for å forbedre den fundamentale kunnskapen om de fysiske prosesser som inngår og utvikle bedre og mer pålitelige modeller for storskala utslipp av tunge gasser. Denne studien er en del av et nylig startet samarbeid mellom US Department of Homeland Security/Chemical Security Analysis Centre (CSAC), Naval Surface Warfare Centre Division Dahlgren (NSWCDD) og FFI som har til hensikt å adressere disse spørsmålene, og spesielt se på storskala utslipp av væskeformig klor. Arbeidet består både av teoretisk og beregningsmessig modellering av spredning og transport av tunggass, støttet av storskala felttest der to tonn trykksatt flytende klor skal slippes ut. Disse eksperimentene planlegges utført i USA i andre halvdel av 2009.

Formålet med denne innledende studien er å understøtte planleggingen av disse eksperimentene. Studien fokuserer spesielt på hvilken form og størrelse en slik forsenking bør ha for et utslipp av denne størrelse. Forstudien konkluderer med følgende:

- Den geometriske utformingen av forsenkingen brukt i denne studien ser ut til å være hensiktsmessig for å holde på den inisielle klorskyen og hindre at klor i væskeform spres over kanten.
- Anbefalt størrelse på forsenkingen er en radius på 18 – 20 m med en dybde 1,5 – 2,0 m.
- For å forhindre signifikant erosjon bør det for eksempel plasseres en betongplate (1 m i diameter) rett under utslippspunktet.

Contents

Preface

This study constitutes a part of a joint effort between the US Department of Homeland Security/Chemical Security Analysis Centre (CSAC), Naval Surface Warfare Centre Dahlgren Division (NSWCDD), and FFI with the objective to address the knowledge gap between source and transport modeling for large scale releases of liquefied chlorine into the atmosphere.

1 Introduction

Numerical simulations of the release of liquefied chlorine from a pressurized tank have been conducted. These simulations constitute a preliminary assessment of the near source dispersion characteristics set up to assist in the planning of large scale field tests presently undertaken by Dr Shannon Fox, US Department of Homeland Security (DHS)/Chemical Security Analysis Center (CSAC) and Mr Timothy Bauer, Naval Surface Warfare Center Dahlgren Division (NSWCDD). These field tests are tentatively planned to be conducted in late fall of 2009. The present study will be followed up by a thorough numerical investigation that will be conducted at FFI using a considerable more advanced computational approach. The experimental data collected during the field tests will ultimately be used to verify these computations. Figure 1 displays a schematic of the experimental setup. It should be noted that the field test setup will include an external cross-wind atmospheric boundary layer. For the purpose of this study, however, the external wind field can be ignored.

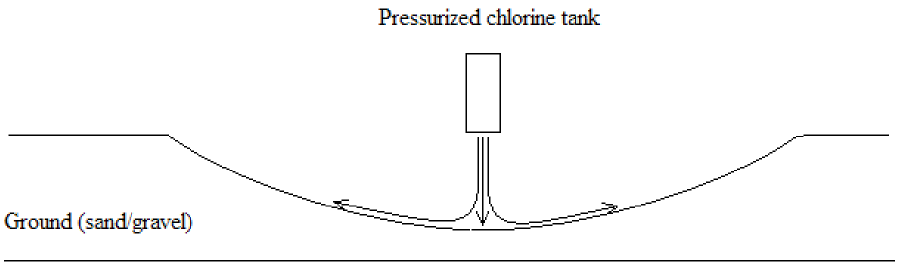

Figure 1: Schematic of the experimental setup.

The objective of the present study is two-fold: Firstly, to determine the horizontal extent and other characteristics of dispersed chlorine dispensed vertically downwards from a pressurized tank located inside a symmetric depression. The output from the simulations primarily provides an estimate of the required physical size of the experimental setup in order to contain the initial chlorine cloud without an external wind field. The second objective of this study is to determine simulations parameters relevant for the second phase of the computational modeling effort. These include e.g. temporal and spatial scales of the flow field.

This study is based on a full three-phase time-dependent computational approach using the Volume of Fluid (VoF) approach. The RANS approach is employed to account for the effects of the averaged turbulent advection on the mean flow field. The three phases are: chlorine liquid, chlorine vapor, and air. Due to the assumption of no external wind field the computational domain can be considered as statistically axisymmetric which in this case implies that it can be treated as a time-dependent and two-dimensional case. To further reduce the computational effort only a simple two-equation RANS model has been used.

2 Mathematical model

The simulation has been conducted with the commercially available CFD-code Fluent and the computational mesh was generated using Gambit. The standard $k-\varepsilon$ RANS model was used. Although this model has a well-known deficiency for impinging turbulent flows (Durbin & Pettersson Reif, 2001) it was chosen out of convenience and mainly because of its diffusive character whereby the numerical stability is enhanced. Its excessive diffusive character stems from an exaggerated generation of turbulence kinetic energy in the impingement region but as compared to the envisioned experimental setup this weakness is not believed to significantly affect the results because the ground characteristics in the experiments are dominated by surface roughness (sand grain size) while in the computations the ground is assumed to be perfectly smooth. This particular weakness of the model is thus believed to account for at least some of this difference. The simplified approach adopted in the study is judged to be of sufficient accuracy to provide reasonable estimates of the global parameters of the experimental setup although it should be kept in mind that the excessive production of turbulence kinetic energy at the stagnation point also reduces the mean flow kinetic energy.

The interaction between the three phases is modeled by the volume-of-fluid approach. One set of mean momentum transport and mass conservation equations are shared by the three phases;

$$\frac{\partial U_i}{\partial t}+U_k\frac{\partial U_i}{\partial x_k}+\frac{\partial}{\partial x_k}\langle u_k u_i\rangle=-\frac{1}{\rho}\frac{\partial P}{\partial x_i}+\nu\frac{\partial^2 U_i}{\partial x_k \partial x_k}+g_i+F_i\,, \tag{1}$$

$$\frac{\partial U_k}{\partial x_k}=0\,. \tag{2}$$

Here, **g** and **F** denote the gravitational acceleration and the force associated with the surface tension, respectively. The correlation of fluctuating velocity components, $\langle u_k u_i\rangle$, represents the ensemble averaged effect of turbulent advection on the mean flow field **U** and this a priori unclosed term is modeled by the $k-\varepsilon$ model. The interface between the phases are tracked by the continuity equation

$$\frac{\partial \alpha_q}{\partial t}+U_i\frac{\partial \alpha_q}{\partial x_i}=S_{\alpha_q}+\sum_{p=1}^{3}\left(j_{pq}-j_{qp}\right) \tag{3}$$

where α_q and S_{α_q} are the volume fraction of and source term to phase *q*, respectively, whereas j_{pq} denotes the rate of mass transfer from phase *p* to phase *q*. The continuity equation (3) is only solved for the secondary phases; the volume fraction for the primary phase are calculated from the constraint

$$\sum_{p=1}^{3} \alpha_p = 1. \quad (4)$$

The mass transfer from the liquid to the vapor phase is computed through the enthalpy balance

$$\Delta m = C_p m_{liq} \left(T_{mix} - T_{boil} \right) / L, \quad (5)$$

where C_p is the liquid specific heat capacity, m_{liq} the liquid mass, and T_{mix} and T_{boil} are the cloud and chlorine boiling temperature, respectively. L denotes the latent heat of vaporization of chlorine. The energy equation

$$\frac{\partial(\rho E)}{\partial t} + U_k \frac{\partial}{\partial x_k}(\rho E + P) = \frac{\partial}{\partial x_k}\left(k_{eff} \frac{\partial T}{\partial x_k} \right) + U_k \frac{\partial \tau_{eff}}{\partial x_k} + S_h \quad (6)$$

is finally solved to close the set of governing equations.

3 Computational results

In the simulation, the chlorine was released 3 m above ground, whereas the computational domain extended vertically 7 m above the release point in order to diminish any influence of the boundaries. The shape of the ground is curved with a monotonically increased slope until it reached the height of the release (3 m), at a radial distance 22 m from the release point. The geometry is depicted in figure 2 and it is believed to relatively closely resemble the depression planned to be used during the field tests. A non-uniformly distributed grid consisting of approximately 0.5 million computational cells was used. The cell size varied form 1 *x* 1 cm^2 near the ground and in the vicinity of the release point. The grid was monotonically stretched up to 10 *x* 10 cm^2 far away from the ground (away from the most densely gridded regions).

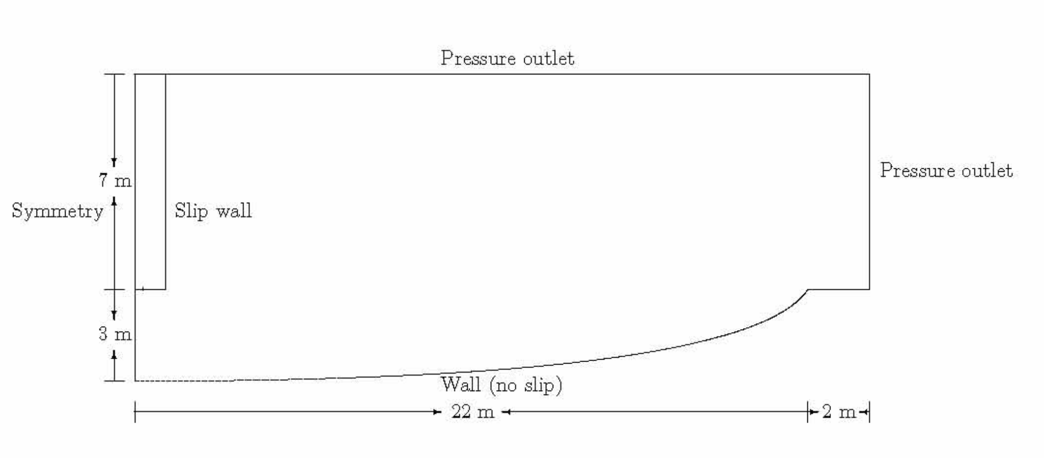

Figure 2: Schematic of the large-domain axisymmetric geometry (x and r plane). The symmetry edge corresponds to the axis of symmetry of the circular shaped mass inlet (with radius 0.03m).

The flow field is confined only by the ground (lower edge). The pressure outlet edges do not constrain the flow in any way. The pressurized tank is included in the domain (although having exaggerated dimensions) and the surface of the tank is assumed to be slip-velocity walls which ease the grid requirement significantly in this otherwise less important area.

The initial characteristics of the jet were specified by Mr Timothy Bauer (NSWCDD). A circular chlorine jet was released vertically downward with a mass flow rate of 67.2 kg/s, (mass fraction of 82.38 % liquid and 17.62 % vapor), and with a radius of 24.5 cm. This radius corresponds to the state immediately downstream the adiabatic expansion, but before air entrainment takes place, outside the tank upon release from a hole with radius 3 cm. Both the liquid and vapor phases were assigned the boiling temperature of chlorine, 239.18 K, and the ambient temperature was set to 293.15 K.

A time-step of 0.001 s was used, and between 10 and 20 sub-iterations per time-step was needed to achieve numerical convergence. The simulation was conducted for 32.9 s real-time which corresponds to a total release of approximately 2000 kg chlorine.

An estimate of the vertical distance can be given by energy conservation. If the only sources of energy are the energy from the motion of the jet and potential energy from motion in the gravitational field, energy conservation gives: $\frac{1}{2}\rho U^2 = \rho g h$. With the velocity of the jet in the horizontal direction directly after the release point, approximately 12 m/s, the vertical distance is $h \approx 8$ m. However, ground frictional forces and conversion to turbulence kinetic energy will reduce the mean velocity efficiently. As will be shown below, the released chlorine only reaches approximately 0.7 m in the vertical direction inside the depression. Figure 3 displays contours of the velocity magnitude throughout the depression. The figure shows the full physical domain; the computational result is mirrored about the vertical symmetry axis. The high velocity magnitude of the chlorine jet is fairly quickly damped out. Still velocities of 4-5 m/s are induced even at distances of more than 20 meters away from the jet in the lateral directions. Also high above the initial jet, velocities of such magnitudes are found.

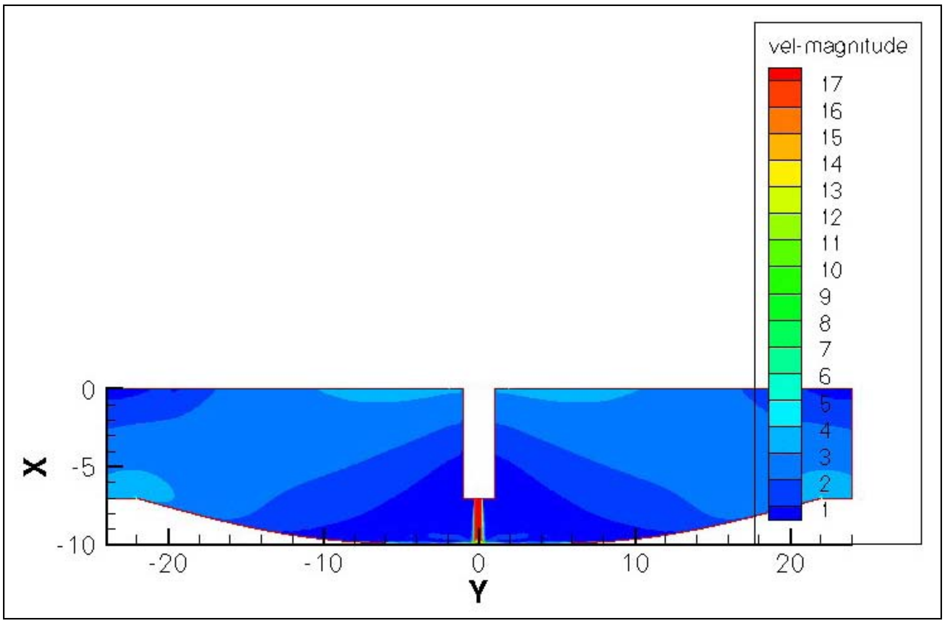

Figure 3: Instantaneous mean velocity contours after 32.9 seconds

From thermo dynamical considerations, the liquid and vapor mixture should achieve a temperature below the boiling point of chlorine. This is because the evaporation of chlorine by air and water results in a cloud with the boiling temperature of chlorine and ambient pressure. The chlorine vapor however, can not be at the vapor pressure at one atmospheric pressure with air entrained, and thus the liquid-vapor equilibrium is no longer valid. As there is no way to raise vapor pressure, the only option is to lower the temperature until the chlorine vapor pressure equals the chlorine vapor partial pressure. The energy to cool the cloud comes from evaporating yet more liquid, and results in a cloud with temperature beneath the boiling temperature. The temperature for the simulation, shown in figure 4, is not below the boiling temperature for chlorine, and is thus too high. However, the primary motivation for this simulation is to determine the extent of the lateral and vertical dispersion of the released chlorine and the initial cloud size, and this is therefore not so important for this case.

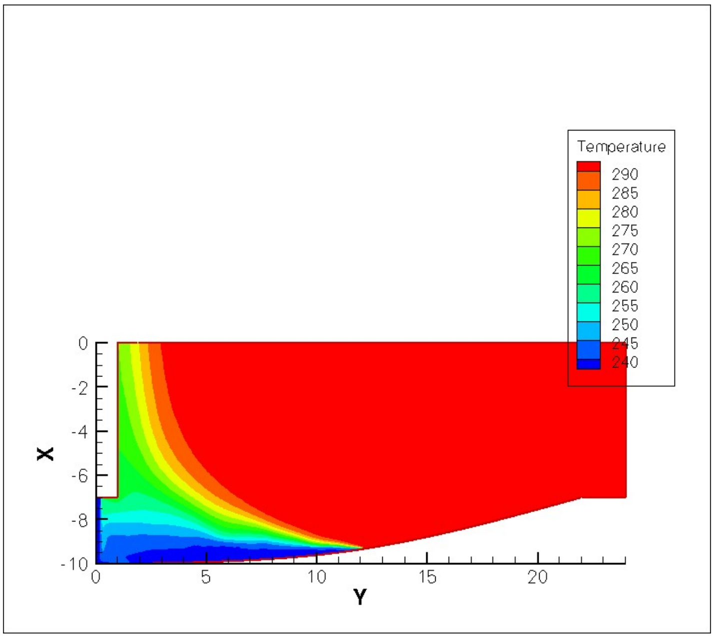

Figure 4: Instantaneous temperature contours at 32.9 seconds.

Figures 5 and 6 show contours of the chlorine vapor and chlorine liquid fraction, respectively, at discreet instances in time. The vapor and liquid transport is closely correlated as expected since there is no side wind imposed. The maximum radius and height predicted by the model is approximately 13 m and 0.7 m, respectively. This point is reached approximately 4 seconds after the initial release. The liquid phase is in this simulation essentially continuous with no, or very little, large scale break up. In reality, the liquid in the jet would be dispersed into larger droplets and aerosols. But since there is no side wind imposed in the present case, this difference is believed to be minor.

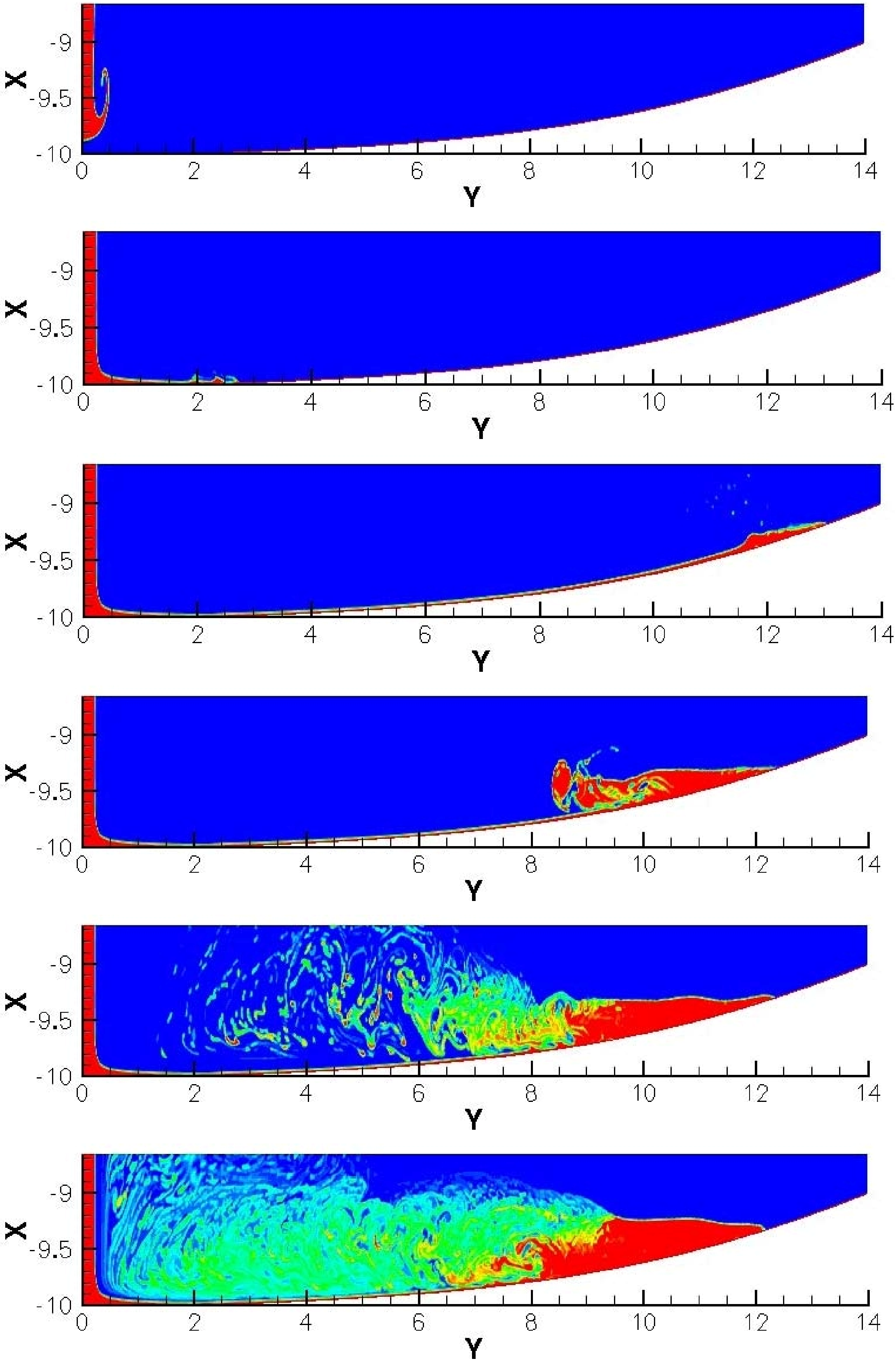

Figure 5: Contours of chlorine vapor at (a) 0.2 s; (b) 0.4 s; (c) 4.0 s; (d) 10.1 s; (e) 20.1 s; (f) 32.9 s. Red: high concentration; blue: low concentration. Close-up view.

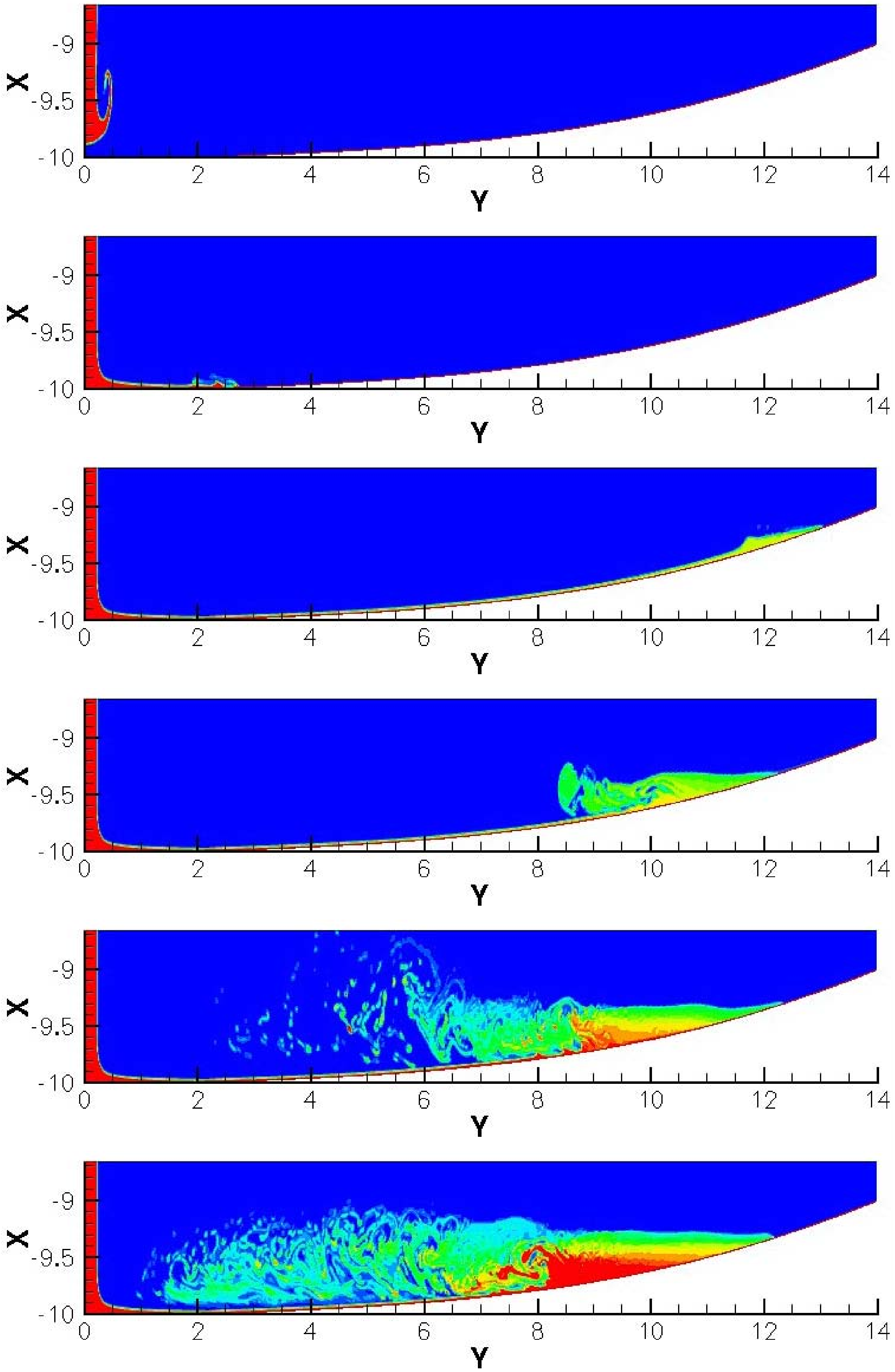

Figure 6: Contours of chlorine liquid at (a) 0.2 s; (b) 0.4 s; (c) 4.0 s; (d) 10.1 s; (e) 20.1 s; (f) 32.9 s. Red: high concentration; blue: low concentration. Close-up view.

The chlorine jet directed towards the ground will yield a pressure force on the ground. Immediately after the jet reaches the ground, between time steps at 0.2 and 0.4 s in Figures 4 and 5, the computed ground pressure force is approximately 1190 N. This force will be sufficient to locally erode the sand ground beneath the release point significantly and adversely affect the experiment. This can be avoided by placing a small circular concrete slab (approximately 1 m in diameter) directly beneath the release point.

In order to determine important parameters for the forthcoming Large Eddy Simulation (LES) effort, relevant statistical scales have been extracted form these simulations. Firstly, the Kolmogorov scales have been estimated. These scales define the smallest turbulent scales, where turbulence is dissipated by molecular viscosity. The Kolmogorov length scale, η, and time scale, η_τ, are given by:

$$\eta = (\tfrac{\nu^3}{\varepsilon})^{1/4}, \ \tau_\eta = (\tfrac{\nu}{\varepsilon})^{1/2}$$

where ν is the kinematic viscosity and ε the rate of dissipation of turbulent kinetic energy. In the vicinity of the jet, the Kolmogorov length scale is of the order: $\eta \sim 10^{-5}$, and the time scale of the order: $\tau \sim 10^{-3}$. In the regions far away from the jet, both the length and the time scale are of an order of magnitude greater. The large-scale, energy containing length scales (also referred to as integral scales) have also been estimated by using the relation $k^{3/2}/\varepsilon$. The distribution of integral length scale is shown in Figure 7 and it varies from less than 0.1 m up to scales greater than 3 m in areas with low turbulence kinetic energy.

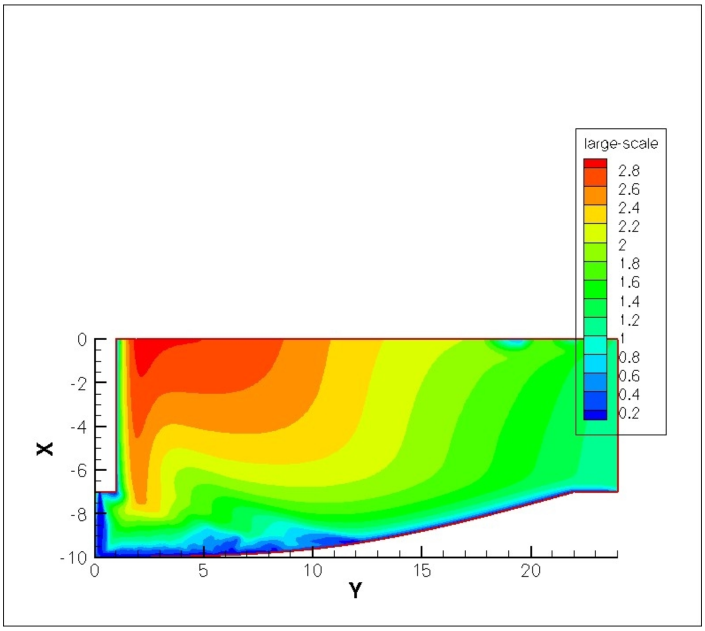

Figure 7: Instantaneous contours of the turbulent integral length scale (in meters) at 32.9 seconds.

4 Summary and recommendations

A numerical simulation of the release of chlorine from a pressurized tank has been performed. This is a preliminary study in order to determine the dimensions needed to construct an experiment in which two tons of chlorine is to be released into a depression. This work will be continued by performing more quantitatively accurate simulations, and by comparing the results from these simulations with the experimental results.

The turbulence model used in this simulation, the standard k-ε model, is known to exaggerate the production of kinetic energy, and thereby drain too much energy from the mean velocity fields. This weakness is believed to be accounted for, at least partially, by the fact that the simulation has been performed with a smooth surface, while the ground characteristics for the experiment will be rather rough. Still, these results should be considered to give a minimum of the dimensions needed for the depression to contain the initial chlorine cloud.

<u>The main results from this preliminary assessment are:</u>

- The chlorine reaches a lateral distance of approximately 13 m and a height of 0.7 m inside the depression.
- The dissipative length and time scales in the vicinity of the chlorine jet are of the order of 10^{-5} m and 10^{-3} s, respectively.
- The energy containing length scales are in the order 0.1 m of in the vicinity of the jet, and increases rapidly away from it.

<u>Recommendations concerning experiments:</u>

- The shape of the depression used in this study seems a viable geometry to contain the initial cloud and prevent spill-over of liquid chlorine.
- The lateral and vertical dimensions stated above must be regarded as a minimum. It is recommended that in order to capture the initial cloud resulting from the release of chlorine from a pressurized tank, the depression should have a radius of minimum 18 - 20 m and a depth of 1.5 – 2.0 m.
- A concrete slab (approximately 1 m diameter) e.g. should be placed directly beneath the release point in order to prevent significant erosion which adversely would affect the experiment.

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