

PhD Thesis entitled:
**“Investigation of Environmental Impacts from Major Accidents
in Chemical Installations”**

EXTENDED ABSTRACT

Summary

The research work implemented in this PhD thesis belongs to the scientific field of *Process Safety Engineering* and aimed at investigating the possibility of three-dimensional modeling and simulation of major industrial accidents, as well as the validation of the numerical models developed through the comparison of the computational results with experimental data from large scale trials. At the same time, inter-comparison studies between numerical and simpler semi-empirical models were made, in order to conclude about the relative accuracy of their predictions. Eventually, one of the validated numerical models was applied to the design of explosion overpressure relief systems in tunnel configurations for the limitation of the impact of the resulting shock waves. The numerical models developed for the simulations were setup in the computational fluid dynamics (CFD) code CFX, which provides a powerful tool for pre-(geometry and mesh construction) and post-processing.

Problem addressed, state of the art and results

In the beginning, several semi-empirical models were used in consequence analysis case-studies of real situations. Their application in quantitative risk assessment of hazardous materials installations (storage units and marshalling yards at Ikonio harbor, Piraeus), as well as fuel gases piping systems (natural and petroleum gas pipelines) existing in Greece, led to useful conclusions for their safety. In particular, the installations confirmed to be highly hazardous for the adjacent population in the former

case, while in the latter, quantitative diagrams for the prompt estimation of safety distances in the vicinity of pipelines transferring either natural or petroleum gas were made.

Thereinafter, the possibility of utilizing CFD techniques in consequence analysis studies was investigated, which was the main part of the thesis. The purpose was to develop specific numerical models able to predict quantitatively the impact of certain accident types and to validate them with experimental data found in the literature. Initially, the Thorney Island trials involving large-scale release and dispersion of heavy gas in obstructed terrain were successfully simulated. Simulation results were found in very good agreement with the experimental data, which concerned the temporal variation of gas concentration at certain positions within the dispersion field. Since the dispersion of a gas is highly affected not only by the atmospheric, but also by the turbulence generated, due to the intercession of solid obstacles in the flow field, the results reproduced from four different turbulence models ($k-\epsilon$, $k-\omega$, SST and SSG) were compared. The comparison showed that all models gave reliable estimations of a series of parameters (peak gas concentration, gas cloud arrival time, gas cloud passage duration); however, $k-\epsilon$ and SST models demonstrated comparatively better accuracy in their predictions.

Cryogenic releases is an important safety issue for light gaseous fuels like natural gas and hydrogen, since storage and transport processes usually imply their liquefaction under very low temperatures for economical reasons, due to their very low density in normal conditions. In case of accidental release and dispersion of a liquefied gas, its dispersion is mainly affected by the low temperature that dominates within the cloud and leads to a denser-than-air fluid. On the basis of available experimental data from large-scale trials that involved cryogenic release and dispersion of liquefied fuel gases, two series of experiments were simulated: the first one concerned the cryogenic release and non-isothermal dispersion of liquefied natural gas that performed in 1980 at China Lake (USA, California) from Lawrence Livermore National Laboratory (LLNL) in cooperation with the USA Naval Weapons Center (NWC). The second concerned the cryogenic release

and non-isothermal dispersion of liquefied hydrogen that performed in 1980 at White Sands (USA) from NASA's Langley Research Center. The main outcome figured out through the results was that fuel gases such as natural gas and hydrogen disperse as heavy rather than light gases during a cryogenic release, despite their positive buoyancy in normal conditions. This conclusion is of major importance from the safety viewpoint concerning chemical installations that handle liquefied gases, given that gravity driven dispersion of flammable gases increases the risk of ignition and hence of accidental fire or explosion. Thus, the behavior of the released gas in these cases should be considered similar to that of a heavy gas when selecting the appropriate dispersion model for application in industrial safety studies. The comparison between the computational gas concentration histories and the corresponding experimental gas histories showed a very good agreement, whereas the application of certain statistical measures showed that gas concentration estimations can be considered as statistically valid. Indeed, it was revealed that the concentration variation at a certain position within the dispersion field may be directly correlated with the temperature variation at the same position through a decreasing linear expression, namely the concentration varies with temperature in an opposite way.

Especially for hydrogen, the usage of which may be not widely spread yet, but the perspective of introducing it as a general-purpose fuel in the world energy market in the near future exists. Thus, it is necessary to highlight common hazards arising from hydrogen storage and distribution systems, as well as to reveal potential accidents that hydrogen may yield under certain conditions. As a result, a hazard analysis was performed based on the Event Tree Analysis Method and the possible outcomes of an accidental hydrogen release were examined. The output of this analysis was that hydrogen may lead to a series of accident types that may pose a severe threat for property and public safety. Moreover, computational estimation of the dispersion resulting from liquefied hydrogen spills showed that the resulting cloud initially behaves rather as a heavy than as light gas remaining for some time in flammable concentrations at low heights and

increasing, therefore, substantially the risk for accidental fires and explosions.

The validity of the numerical model developed for estimating the dispersion of a cryogenic release was further checked by the computer simulation of the Coyote series trials, which conducted in 1981 by Lawrence Livermore National Laboratory (LLNL) and involved large-scale release and dispersion of huge amounts of liquefied natural gas. The experimental data were used for checking the validity of the results obtained through the numerical model, and in addition for performing a comparative evaluation of the performance between the numerical model and two popular box-models (SLAB and DEGADIS), through the estimation of specific statistical performance tests. The statistical treatment revealed that box-models may also give acceptable results even for the complex case of non-isothermal gas dispersion. Nevertheless, the numerical model unambiguously demonstrated considerably better accuracy in providing local gas concentration predictions.

In fact, the purpose of Coyote trials was to study the ignition of the dispersing flammable cloud and the evolution of its combustion into the atmosphere. The experimental data-set was the basis for validating a separate numerical model built in CFX code for the simulation of cloud fires in unconfined space (the so-called flash fires) and hence the quantitative estimation of resulting thermal radiation emissions and overpressure. Computational thermal radiation histories were compared with experimental data from four trials showing a reasonably good agreement for several locations in the field. Discrepancies concern overestimation of the thermal load received at a certain location, yet within a factor-of-two of the observed values. Moreover, positive peak overpressures were sufficiently low to indicate that the combustion of the cloud yielded a flash fire rather than a gas cloud explosion.

As far as explosion events are regarded, the possibility of simulating the resulting shock wave propagation and the imminent impulse development in large-scale obstructed terrain, in addition to tunnel

configurations, was also investigated. A numerical model was developed and validated against experimental data for its ability to predict a series of critical explosion parameters, namely the positive and negative peak overpressure, the arrival time, the positive and negative phase duration, plus the specific explosion impulse at certain positions. In the former case, the data-set from Health and Safety Laboratory (HSL) explosion trials was exploited, whereas in the latter, the data-set from the lab-scale explosion experiments of NC Spiez Laboratory was utilized. The reasonably good agreement between the computational results and the experimental observations confirmed the suitability of the numerical model to provide explosion effects estimation. Consequently, a new tool for application in explosion accident scenarios was investigated. This is able to reproduce reliable overpressure predictions for eventual explosions in the vicinity of installations that possess explosion hazards, as well as for the prediction of the consequences of an explosion in underground stations in case of sabotage. Regarding tunnel explosions, it was found that blast waves propagate preserving supersonic speed along the tunnel for a long distance accompanied by high overpressure levels. This indicates that space confinement favors the formation and maintenance of a shock rather than a weak pressure wave, due to minimization of lateral energy losses.

Furthermore, the numerical model developed for the simulation of explosion phenomena was utilized for the design of effective explosion protection systems against confined explosions. In particular, the quantitative estimation of the protective effect of explosion relief vents in the case of confined explosions inside tunnels was addressed. A series of virtual experiments performed by computer simulation, revealed how the number of vents, their diameter, as well as the angle between the vents and the tunnel, influence the blast wave attenuation. The computational study was performed considering a complicated large scale tunnel configuration with branches on its half portion. The purpose was the calculation of the attenuation effect due to the presence of vents by comparing the total explosion specific impulse developing at anti-diametric positions inside the tunnel. Computer results showed that the use of branch

vents provides an effective method for shock wave attenuation following an explosion, whereas the statistical elaboration of the results revealed that the attenuation is significantly affected by the number of vents and their diameter. In contrast, the angle between the side vents and the main tunnel appeared to slightly affect the pressure wave weakening. Eventually, the quantitative influence of the above parameters was effectively illustrated in functional diagrams, so that the total attenuation effect can be promptly estimated, if the design variables are known. In addition, two multiple regression models with reasonable fitting to the calculated data were constructed. These prediction models demonstrate the attenuation effect as a dependent variable of the design variables and their interactions.

Key innovations

The innovations of this thesis, as can be seen from the relevant published work, consist of:

1. The application of well-established semi-empirical models for quantitative consequence analysis in certain cases not included in the SEVESO II directive (marshalling yards, pressurized gas transmission pipelines), which showed that these models should be subsumed in the regulation concerning the development and establishment of emergency response planning.
2. The development and validation of a number of CFD-based models aiming at the simulation of certain types of major accidents with the perspective of their application in reliable safety studies.
3. The comparison between estimations from semi-empirical dispersion models and the corresponding simulation outputs from a CFD code, finally validated with experimental data.
4. The innovative quantitative approach of the protective effect of explosion relief vents in the case of confined explosions inside tunnels and the construction of suitable regression models for use in practice.

References

The following publications have resulted from this PhD:

In International peer-reviewed journals:

1. Fotis Rigas and Spyros Sklavounos (2002). Risk and consequence analysis of hazardous chemicals in marshalling yards and warehouses at Ikonio/Piraeus harbor, Greece. *Journal of Loss Prevention in the Process Industries*, 15, p. 531-544.
2. Spyros Sklavounos and Fotis Rigas (2004). Validation of turbulence models in heavy gas dispersion over obstacles. *Journal of Hazardous Materials*, 108, 9-20.
3. Fotis Rigas and Spyros Sklavounos (2004). Major hazards analysis for populations adjacent to chemical storage facilities. *Process Safety and Environmental Protection*, 82, 341-351.
4. Spyros Sklavounos and Fotis Rigas (2004). Computer simulation of shock waves transmission in obstructed terrains. *Journal of Loss Prevention in the Process Industries*, 17, 407-417.
5. Fotis Rigas and Spyros Sklavounos (2005). Experimentally validated 3-D simulation of shock waves generated by dense explosives in confined complex geometries. *Journal of Hazardous Materials*, 121, 23-30.
6. Fotis Rigas and Spyros Sklavounos (2005). Evaluation of hazards associated with hydrogen storage facilities. *International Journal of Hydrogen Energy*, 30, 1501-1510.
7. Spyros Sklavounos and Fotis Rigas (2005). Fuel Gas Dispersion under Cryogenic Release Conditions. *Energy and Fuels*, 19, 2535-2544.
8. Spyros Sklavounos and Fotis Rigas (2006). Estimation of safety distances in the vicinity of fuel gas pipelines. *Journal of Loss Prevention in the Process Industries*, 19, 24-31.
9. Spyros Sklavounos and Fotis Rigas (2006). Simulation of Coyote series trials – Part I: CFD estimation of non-isothermal LNG releases and comparison with box-model predictions. *Chemical Engineering Science*, 61, 1434-1443.
10. Fotis Rigas and Spyros Sklavounos (2006). Simulation of Coyote series trials – Part II: A computational approach to ignition and combustion of flammable vapor clouds. *Chemical Engineering Science*, 61, 1444-1452.

11. Spyros Sklavounos and Fotis Rigas (2006). Computer aided modeling of the protective effect of explosion relief vents in tunnel structures. *Journal of Loss Prevention in the Process Industries*, 19, 621-629.

In international books

1. Rigas F. and Sklavounos S., "Computer Simulation in Consequence Analysis and Loss Prevention" in "New Research on Hazardous Materials", F. Columbus (Ed.), Nova Science Publishers, Inc., New York, USA, 2007.
2. Rigas F. and Sklavounos S., "Hydrogen Safety" in "Hydrogen Fuel: Production, Transport and Storage", CRC Press, Taylor & Francis, Boca Raton, Florida, USA, 2008.

In Greek Journals:

1. Sklavounos S. and Rigas F. (2003). Safety distances from petroleum and natural gas pipelines. *Modern Technical Review*, Greek Mechanical Engineers Association, 113, 28-30.
2. Rigas F. and Sklavounos S. (2003). Environmental consequences estimation from accidents in hazardous chemicals installations based on SEVESO II directive. *Technical Reviews*, Technical Chamber of Greece, 3, November-December 2003, 1-31.
3. Rigas F. and Sklavounos S. (2004). The toxic incubus of Ikonio. *Prime Journal*, 7, 66-69.
4. Sklavounos S. and Rigas F (2005). Hazards due to the release of combustible gases from pressurized gas pipelines. *Technical Reviews*, Technical Chamber of Greece, May-June 2005, 1-21.

In Greek Conferences with referees and meetings:

1. Rigas F. and Sklavounos S. (2003). Environmental consequences of major accidents in hazardous chemicals storage installations at Ikonio, Piraeus port. Proceedings, 4th Panhellenic Scientific Conference in Chemical Engineering, pp. 1124-1127 (oral presentation).
2. Sklavounos S. and Rigas F (2003). Safety distances from pipelines transferring liquefied natural and liquefied petroleum gas. Proceedings, 4th Panhellenic Scientific Conference in Chemical Engineering, pp. 1128-1132 (oral presentation).
3. Sklavounos S. and Rigas F (2003). Hazard identification in installations handling hydrogen. Proceedings, 1st National Conference

of Greek Hydrogen Company: Hydrogen Technology, Research, Development and applications (oral presentation).

4. Rigas F. and Sklavounos S. (2004). Hazards associated with natural gas transportation system: Safety distances in case of pipe rupture. Meeting organized by the Technical Chamber of Greece: Penetration of natural gas in energy market – technical problems, aspects, safety (oral presentation).
5. Sklavounos S. and Rigas F (2005). Computation of heavy gases atmospheric dispersion in real conditions. Proceedings, 5th Panhellenic Scientific Conference in Chemical Engineering (oral presentation).
6. Rigas F. and Sklavounos S. (2005). Simulation of shock waves transmission in tunnel configurations and in the open-field in the presence of barriers. Proceedings, 5th Panhellenic Scientific Conference in Chemical Engineering (oral presentation).
7. Sklavounos S. (2008). Occupational hazards assessment for hospital workers. Meeting organized by the General Hospital of Attica: Health and Safety in Hospital Work Environment, Athens (oral presentation).
8. Sklavounos S. (2008). Risk assessment and management in hospital workplaces. Proceedings, 5th Panhellenic Scientific Conference: Quality in Health Services, Athens (oral presentation).