

# ioFirst Technical Basis and Assumptions

---

## Introduction

This chapter contains a discussion of the detailed models upon which ioFirst models are based and the correlations used to simplify them for use in ioFirst. An overview of available and included detailed models is given in section 1.3 Models and Scoring, and the accuracy of ioFirst is discussed in section 1.4 Accuracy. ioFirst equations and correlation tables are given in Chapter 2.

The following three sections discuss the hazards considered and the models used by ioFirst for toxic vapor dispersion, fire and flammability, and vapor cloud explosion, respectively. The specific hazard criteria in each category are given. Detailed models and associated assumptions are explained along with the further assumptions made to simplify models for use in ioFirst. The last two sections of this chapter give the basis for the methods used to adjust scores for specific sites and combine scores to obtain an overall site score.

For each of the three hazard categories addressed, the criteria established are fatality based. Simplifying assumptions that introduced uncertainty were made such that the hazard zones are overestimated rather than underestimated. This approach is consistent with the approach taken in the development of the detailed models that are the basis of ioFirst. All the ioFirst algorithms assume a release of the maximum feasible quantity, usually the maximum container capacity or pipeline inventory and a very short release time.

## Toxic Vapor Dispersion Hazard

For chemicals that are inherently toxic, the hazard zones are governed largely by the extent of toxic vapor dispersion. The dispersion hazard zone is primarily dependent on the limiting concentration, the quantity and nature of material released, the storage and release conditions, and the prevailing atmospheric conditions.

The limiting concentration defines the toxic hazard criterion. For ioFirst purposes this criterion could be the LC 50, or the lethal concentration for fifty percent fatalities among the exposed population. LC 50 values based on animal experiments or estimated using other published data are among the required input values for implementation of ioFirst. For screening to comply with regulations, the Acute Toxicity Concentration (ATC) would be more appropriate.

The spreading of a vapor greatly depends upon the material and its conditions before and during release. For example, a highly volatile material stored under pressure and released at a very high rate will lead to a vapor cloud containing the entire mass of material released. A similar situation may develop given a highly reactive material that readily decomposes forming a vapor. In these cases, the release typically disperses in the form of a puff, and the dispersion takes place in the lateral, vertical, and longitudinal directions.

Conversely, for a chemical with a boiling point above ambient temperature that forms a pool upon release, the vapor generation rate is largely governed by the vapor pressure and the spill area. This produces a continuous plume (rather than a discrete puff) as does a vapor released from a tank at a slow rate. In the case of a continuous release, dispersion is assumed to spread only in the vertical and longitudinal directions.

For the purposes of ioFirst the chemical is assumed to spill over a very short duration. The dispersion is dependent on the nature of the released material and is modeled as a puff or plume, accordingly. ioFirst uses the atmospheric boiling point to categorize materials into four different “classes” for dispersion modeling. For each class ioFirst algorithm is based on detailed evaporation and puff or plume dispersion models that were selected and tailored to fit the category.

Class I materials are highly volatile chemicals with boiling points below  $-20^{\circ}\text{C}$ . A release is assumed to vaporize

very quickly and form a puff rather than a plume. For class I toxic vapors a short term release Gaussian puff dispersion model is applied. Liquid hydrogen and other asphyxiants are handled separately since they do not disperse as other vapors in this class.

Liquid hydrogen, when released over a very short duration travels along the ground for a short period and then as a result of the spill momentum, the sudden vaporization of the liquid, and the thermal instability, air is rapidly entrained and the cloud becomes buoyant. Hazards of liquid hydrogen are evaluated on the basis of a liftoff algorithm that estimates the distance at which the bottom of a hydrogen cloud begins to rise above the ground. The algorithm is based on an data reported by Witcofski and Chirvella and by an ADL report to the Air Force Ballistic Missile Division.

Other class I asphyxiants are handled separately since neither of the algorithms discussed above apply for short term spills of materials in this class where very high concentrations are of interest. In such cases the toxic vapor hazard score is set to 50. This value represents the maximum hazard radius in meters given a 1,000,000 lb release of a highly pressurized material with a low boiling point that has a vapor density close to that of air. While this may over-predict zones for smaller quantities, it is a relatively short distance and therefore should not significantly affect ranking results.

Class II materials are those with boiling points between  $-20^{\circ}\text{C}$  and  $0^{\circ}\text{C}$  which, when released over short durations, form pools of boiling liquid. The portion of released material in the vapor cloud is estimated based on a boiling pool model that accounts for the rate of heat transfer from the ground to the pool and the rate of vaporization. Subsequent dispersion is based on a Gaussian plume dispersion model.

Class III chemicals have boiling points between  $0^{\circ}\text{C}$  and ambient temperature and, as class II materials, form pools of boiling liquid when released over short durations. As for class II, a boiling pool model and a Gaussian dispersion model are used. The models are implemented in this class so as to reflect the lower rates of ground heat transfer and vaporization expected for class III materials when compared to class II materials.

Class IV refers to chemicals with boiling points above ambient temperature. For materials in this class the vapor pressure at ambient temperature is an input value and is the only parameter contributing to the evaporation flux. Similar to classes II and III, a continuous dispersion model is used.

The plume model used for classes II, III, and IV is appropriate if the vapor enters the atmosphere over an extended period of time. If the evaporation time is shorter than the time required to establish a steady state plume, the vapor disperses more as a puff. The quantity FLAG checks results of the calculations prescribed for these three classes. FLAG is used to determine when the class I algorithm for discrete puff dispersion should be used for class II, III, or IV materials.

In all of the scoring schemes a point source is assumed for dispersion modeling. Although the geometry of some sources, such as evaporating pools, can be characterized as lines or areas, the deviations associated with the point source assumption are greatest when considering near field dispersion, that is, dispersion within ten times the characteristic source dimension. At farther distances, which are of greater interest for the purposes of ioFirst, the effects become smaller and eventually negligible. Furthermore, use of the point source assumption leads to a modest over-prediction of actual dispersion hazards.

All dispersion calculations assume the vapor to be neutrally buoyant, that is, of comparable density to air. This assumption introduces deviations for materials that produce heavy vapors and for releases that result in dispersion of a mixture of vapor and liquid aerosol with an effective density that is greater than that of air. The latter case may be produced by sudden releases of pressurized liquids. Comparison of results of detailed models for neutrally buoyant and heavy gases has shown that use of the neutrally buoyant model for dispersion of heavy gases produces results that generally overestimate the hazard zones significantly. In some cases hazard zones are slightly underestimated.

Prevailing atmospheric conditions are characterized by wind speed and atmospheric stability class. These two parameters determine the Pasquill-Gifford dispersion coefficients which provide a measure of the turbulence

intensity in the lateral (cross wind) and vertical directions. ioFirst assumes a neutral stability class (class D) and a wind speed of 9 mph as typical weather conditions at all sites. It should be noted that under adverse weather conditions (stable with low wind speeds), the dispersion hazards could be significantly higher.

It should also be noted that the hazard zone is assumed to be at ground level, as is the vapor source. The effects of surrounding terrain are not considered.

Hazard zones predicted using the simplified model in its original form were compared to those predicted by a more detailed model for various quantities of seven different materials that generate toxic vapors. These validations and comparisons can be given out if requested and upon our review.

## **Fire and Flammability Hazard**

The fire and flammability hazard score is an estimate of the hazard distance in the event of a pool fire or a fireball. A pool fire occurs when a spilled flammable liquid is ignited and burns in the form of a large turbulent diffusion flame. Conditions under which a fireball occur often include a large quantity of pressurized flammable liquid or compressed gas becoming engulfed in flames. A fireball may also result when a pressurized material is released instantaneously and ignited. Materials stored under the conditions for which a fireball is feasible are those with low boiling points, particularly those stored in pressurized containers. A fireball consists of a quantity of unconfined vapor burning as an unsteady turbulent diffusion flame that grows larger and moves upward due to buoyancy and typically burns out after only a few seconds.

The hazard criteria for pool fires and fireballs are implicitly included in ioFirst equations. The criterion for a pool fire hazard is expressed in terms of incident flux of thermal radiation, which is a measure of radiant power per unit area. The duration of a fireball is usually only a few seconds, and it is important that the associated hazard quantification account for duration of exposure. For a fireball the hazard criterion is expressed in terms of a thermal dosage, which sums the incident flux quantities over the duration of the fireball.

Experimental data were used in the selection of levels of thermal radiation flux and dosage for an ioFirst hazard criteria. The criterion for a pool fire hazard is 12 kW/m<sup>2</sup> and the corresponding fireball criterion is a thermal dosage of about 160 kJ/m<sup>2</sup>.

The thermal radiation flux from a pool fire can be estimated as the product of the effective emissive power, a transmissivity coefficient, and a view factor. The effective emissive power depends upon the characteristics of the flame, such as its geometry, and the properties of the burning material. The size of the flame will depend upon the spill surface, the quantity spilled, the thermochemical properties of the spilled liquid, and the burning rate. The transmissivity coefficient accounts for the amount of thermal radiation obscured by the smoke generated by the fire and carbon dioxide and water vapor in the intervening atmosphere. The view factor depends upon the observer's distance and orientation to the flame.

Estimating a hazard distance from a fireball involves some similar parameters, such as the effective amount of energy radiated, the material quantity, the heat of combustion, and the effect of the intervening atmosphere. In the case of a fireball, however, the material burning is in vapor form and as it burns it entrains air, grows in size, and gains elevation. The computation of a hazard distance requires taking all of these factors into account and performing an integration over the duration of the fireball to obtain dosages and associated distances.

The hazard zones predicted by detailed models for pool fires were compared to those for fireballs for four quantities of eight materials. The fireball fatality distances were consistently greater than the pool fire fatality distances. Consequently, for materials with low boiling points, less than or equal to 35°C, for which the fireball hazard is feasible, the ioFirst fire and flammability algorithm is based on the fireball model to produce conservative results. For materials with high boiling points, the pool fire model is used.

Simplifying assumptions made for the ioFirst pool fire calculations include:

- ?? The material is released over a 20 second period,
- ?? The pool is circular and spreads on land,
- ?? The pool spreads to its maximum diameter before igniting,
- ?? Ambient temperature is 20<sup>0</sup>C, humidity is 70%, and the atmosphere is free of fog and haze,
- ?? Effects of wind are negligible, thus the flame does not tilt and the radiation field is radially uniform, and
- ?? Both pool fire and observer are at ground level.

Taking these assumptions into account, the effective emissive power, the transmissivity coefficient, and the view factor can be expressed in terms of known parameters. The effective emissive power is estimated using a correlation with the normal boiling point that is based on observed values. This correlation does not apply to materials with very high boiling points, which tend to have lower values for effective emissive power. A minimum effective emissive power of 20 kW/m<sup>2</sup> has been assumed as a conservative lower limit. Using the correlation this corresponds to a boiling point of approximately 154.5<sup>0</sup>C. Thus the effective emissive power is set to 20 kW/m<sup>2</sup> for materials with boiling points greater than 154<sup>0</sup>C.

The transmissivity coefficient can be set to its maximum value, 1.0, which assumes all radiation is transmitted. The view factor can be expressed in terms of the burning pool area and the distance from the pool to the observer. To get the maximum hazard distance the maximum area of the pool becomes the burning pool area.

The product of the three quantities, effective emissive power, transmissivity coefficient, and view factor can be equated to the incident flux, 12 kW/m<sup>2</sup>. Solving for the distance from the pool to the observer gives the quantity of interest, the hazard distance. This has been done separately for materials with boiling points between 35<sup>0</sup>C and 154<sup>0</sup>C and for those with boiling points greater than 154<sup>0</sup>C. Finally a safety factor of 1.2 was incorporated to bring the predictions to the conservative side of detailed model predictions. The resulting algorithm was applied to three quantities of six materials. For the largest quantity, 1,000,000 lbs, the ioFirst algorithm overpredicted the hazard distance by 8% to 25% when compared to the detailed model. More discussion on accuracy appears in section 1.4.

Simplifying assumptions made for the ioFirst fireball calculations include:

- ?? the fireball initially contains no air,
- ?? the fireball is initially at ground level,
- ?? ambient temperature is 20 C and humidity is 70%, and
- ?? the effects of wind are negligible.

Taking these assumptions into account, the remaining variables of significance for a fireball calculation are:

- ?? the heat of combustion,
- ?? the vapor density,
- ?? the fraction of combustion energy radiated,
- ?? the quantity, and
- ?? fireball duration.

The first three parameters are material dependent and since the heat of combustion and fraction of combustion energy radiated are closely related, only one of these is required as a user input. The quantity and fireball duration are also closely related, allowing the duration to be implicitly incorporated into an algorithm including quantity.

In obtaining predictions from the detailed model for ioFirst development purposes, fireball hazard zones involving six quantities of three representative materials with varying heats of combustion and vapor densities were studied.

The hazard zones were correlated to mass and heat of combustion. Although vapor density is not explicitly included, the correlation's deviation from the detailed model is less than 15% for hazard distances greater than 140 m for the representative materials which have vapor densities ranging approximately from neutrally buoyant to three times the density of air.

## Vapor Cloud Explosion Hazard

The Overpressure Hazard Score (OHS) is an estimate of the distance to the hazards associated with a ground level unconfined vapor cloud explosion (UVCE). An UVCE may occur when a flammable vapor cloud is ignited. The overpressure hazard associated with an explosion refers to the danger posed by a pressure wave in excess of atmospheric pressure.

The criterion selected for an ioFirst overpressure hazard is 3.0 pounds per square inch in overpressure (psig), which is based on measurements taken during TNT explosions and correlated to expected damages. Although fatalities due to direct effects of an explosion require levels of up to 29.0 (psig) or higher, significantly lower levels result in building damages that would likely lead to fatalities. An overpressure of 3.0 to 4.0 psig would destroy a frameless steel panel building, 5.0 would snap wooded utility poles and severely damage plant structures, and 5.0 to 7.0 psig would cause nearly complete destruction of houses.

A flammable vapor cloud may travel a considerable distance before encountering an ignition source. The rate of travel depends on the material and the atmospheric conditions. ioFirst estimates a hazard distance from the center of the cloud without indicating the location of the cloud center.

The distance to a given overpressure can be determined by representing the vapor cloud by an equivalent quantity of TNT and implementing the TNT model for which extensive data have been collected. Comparison of UVCE incidents and the TNT model show good agreement except in the near field, where TNT overpressures are in excess of 15 psig. Close to the center of the explosion the TNT model predicts overpressures that are significantly higher than those experienced during vapor cloud explosions. However, for ioFirst, the region of interest is of 5 psig, which occurs in the far field.

To adapt the TNT model for application to vapor clouds the mass of flammable vapor is converted to an equivalent amount of TNT using two material dependent factors. The first factor is the ratio of the heat of combustion of the vapor cloud material to that of TNT and it adjusts the mass based on the amount of energy released during combustion. A second adjustment is needed since only a fraction of the total available energy contributes to the explosive effect in an UVCE. This fraction is given by an empirical yield factor which is material dependent and is usually between 0.02 and 0.20.

The ioFirst version of this model includes these factors in a somewhat simplified manner. The heat of combustion of the material of interest is a required input value and the ioFirst algorithm incorporates the heat of combustion of TNT in its coefficient. Since the yield factor may not be readily available for all materials, a default value of 0.1 can be used. Use of the default value can over-predict a hazard zone by up to 49% for materials that have low yield factors or under-predict by up to 19% for materials that have high yield factors.

Another consideration for the ioFirst model is that the quantity in the flammable vapor cloud may be less than the quantity released. For example, consider the release of a liquid resulting in an evaporating pool. Vapor is produced and subsequently diluted and carried downwind by air. If a vapor cloud explosion occurs, the material involved would be that which is in the cloud where the vapor concentration is between the material's flammable limits. For pressurized liquids, a release often results in immediate vaporization, or flash, of a fraction of the release quantity. The violence of the vaporization forces an additional quantity into the air in the form of fine liquid droplets, of which some become entrained in the cloud and some fall to the ground. The remainder forms an evaporating pool.

The Evaporation Fraction (EF) estimates the fraction of the pool mass that evaporates and contributes to the flammable vapor cloud. EF has been correlated to the normal boiling point on the basis of results of detailed models

applied to a variety of quantities of seven materials with a wide range of boiling points, molecular weights, and lower flammability limits. This correlation assumes that the pool is at ambient temperature, which is taken to be 20<sup>0</sup>C, or the normal boiling point, whichever is lower.

For pressurized liquids stored at temperatures above their normal boiling points, the Flash Fraction (FE) is determined to account for the portion of the total mass that vaporizes upon release. In such cases the pool mass is taken to be the total mass released less the mass flashed. The amount that flashes can be estimated based on equilibrium considerations where the important parameters are the normal boiling point, the storage temperature, the liquid specific heat capacity, and the heat of vaporization. The normal boiling point and the storage temperature are required input values and the remaining parameters have been combined into a single quantity, the Indicator for Flash (IF). Examination of 1023 pure compounds in terms of IF showed that a value of 160 provided an accurate or conservative estimate of IF for compounds with normal boiling points above -173<sup>0</sup>C, which included most of the compounds under consideration. For the remainder of the compounds, IF can be set at 80.

Explosions occurring near the ground tend to have further reaching impacts than those occurring above the ground due to the energy reflected by the ground. The ioFirst algorithm includes a factor of 1.26 to account for ground level effects.

## **Exposed Population Score**

The Exposed Population Score (EPS) reflects surrounding population for the site and is used to weigh hazard zone scores in consideration of the potential impact involved for comparison of scores for different sites. The impact of an episodic chemical release event is primarily related to the number of individuals who may be adversely affected. It follows that the population densities inside and outside plant perimeters play an important role in determining overall risks. This approach is to some extent also an indicator of property damages as well, since higher population densities usually correlate to larger numbers of potentially vulnerable building structures.

The point assignment scheme used to determine the EPS takes into account the surrounding population and facilities and their proximities to the site. Points for numbers of people working at the site and residing within one mile of it are similarly assigned according to specified population ranges. Since the effects of a hazardous material incident are generally much more severe closer to the origin, points are added for the presence of a residence or industrial facility within half and one mile radii from the site.

For sensitive target, such as hospitals, nursing homes, and schools, within one mile of the plant facility a point value is assigned that is consistent with that prescribed for the other populations within one mile, that is, it is equal to the point value assigned for a residential population of 100 to 1000 within one mile. Populations residing at greater distances from the site are assigned points on different scales to incorporate an adjustment that reflects the greater importance of nearer populations.

## **Age Score**

The Age Score (AS) reflects the thinking, that as plants age, they become more vulnerable to mechanical failures. However, experience also tells us that very new plants are also somewhat vulnerable until some operating experience with the equipment is obtained. The AS is designed to penalize facilities that are less than two years old and greater than 20 years old. The AS is used to adjust the Process/Activity Ranking Score (PARS).

## **Incident History Score**

The Incident History Score (IHS) is another adjustment factor to the PARS, to reflect the quality of safety

management systems at the facility. The metric used to gauge this quality is the number of incidents in the prior five years which required activation of the emergency response organization. Even though the incident may have been a “near miss” instead of a major event, the fact that it occurred, is an indication that some fundamental root causes are not being addressed.

## **Process/Activity Ranking Score and Site Ranking Score**

The Process/Activity Ranking Score (PARS) is the product of the greatest single hazard score associated with a process or activity, the Age Score (AS), the Incident History Score (LHS), and the Exposed Population Score (EPS). While it does not directly give a physical measure, it is important to note that it does represent a site specific hazard value that is directly comparable to other site scores. In using a single hazard score it is recognized that while many hazards are possible, only one could prevail in a release. The maximum hazard score gives the worst case outcome.

The Site Ranking Score (SRS) combines all the PARS associated with a site and is used for comparison of sites. Since both the number of processes or activities and the hazards of each contribute to the level of concern, the PARS are summed. The logarithm (base 10) of the resulting sum is then taken in order to provide a range of scores that is convenient and appropriate for ranking purposes.

## **References**

Arthur D. Little, Inc. (1960), *Final Report on an Investigation of Hazards Associated with the Storage and Handling of Liquid Hydrogen*, Report to Air Force Ballistic Missile Division, Cambridge, MA.

Arthur D. Little, Inc. (1988), *CHEMS-PLUS Version 1.0 Reference Manual*, Cambridge, MA.

Chirivella, Dr. Jose E. and Robert D. Witcofski (1986), “Experimental Results from Fast 1500-Gallon LH<sub>2</sub> Spills,” *Cryogenic Properties, Processes and Applications 1986, No 251, Vol 82*, New York.

Edeskuty, F. J., J. J. Haugh and R. T. Thompson (1986), “Safety Aspects of Large-Scale Combustion of Hydrogen,” *Hydrogen Energy Progress VI, Vol 1*, New York.

Koopman, R. P. (1986), “Atmospheric Dispersion of Large Scale Spills,” *Cryogenic Properties, Processes and Applications No 251, Vol 82*, New York.

Society of Fire Protection Engineers and National Fire Protection Association (1988), *SFPE Handbook of Fire Protection Engineering*, Quincy, MA.

Witcofski, Robert D. and Dr. J. E. Chirivella (1982), “Experimental and Analytical Analyses of the Mechanisms Governing the Dispersion of flammable Clouds Formed by Liquid Hydrogen Spills,” *Hydrogen Energy Progress IV, Vol 4*, New York.

Van Buijtenen, C.J.P. (1979), “Chapter 7, Dispersion,” *Dispersion*, Rij’swijk, The Netherlands.