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Informational uncertainties of risk assessment about accidents of chemicals

ZHANG Yi-xian

(Suzhou Institute of Urban Construction and Environmental Protection, Suzhou 215011, China)

Abstract: An analysis system of informational uncertainties for accidental risk assessment of chemicals is introduced. Statistical test methods and fuzzy sets method can do the quantitative analysis of the input parameters. The uncertainties of the model can be used by quantitative compared method for the leakage accidents of chemicals. The estimation of the leaking time is important for discussing accidental source term. The uncertain analyses of the release accident for pipeline gas (CO) liquid chlorine and liquid propane gas (LPG) have been discussed.

Key words: uncertainty; risk assessment; accident; chemicals; pipeline gas; liquid chlorine; LPG

Introduction

The accidental risk assessment of the chemicals is a frontier science and technology referred to both environmental science and safety technology. In recent years many research workers in this field have done it. The analysis of chemical accidents mainly included that the leakage of chemical substances, the physical properties of chemical substances after accidental release, the process of air diffusion, fire and explosion and so on. In the process of analyzing accidental risk there exist uncertain factors in the system models and input parameters. And it is largely affected to the results of the risk assessments. Therefore the reliabilities of the processes and the results for risk assessments of chemicals should be discussed by using uncertain analysis methods (Quantified, 1998; OECD, 1989; Thomas, 1991).

There is a great deal of variability in quantitative risk assessments and it leads to uncertainty in the estimation of risk. The sources of uncertainty may be in two areas: natural or intrinsic uncertainty, and informational uncertainty. Natural uncertainty is due to the fact that many systems have substantial variability in their characteristics over space or time. Informational uncertainty may be subdivided into two parts: model uncertainty which is due to a lack of complete understanding of whole cause and effects in the processes/systems under study; and parameter uncertainty which is due to the shortage of large sample records of the process. Model uncertainty is the most difficult to characterize because it is based on our incorrect assumptions about the system. Because it cannot be realistically quantified, the important of model uncertainty should be considered during risk management for reducing the extent of environmental risk. Parameter uncertainty springs from the shortage of totally accurate and complete data.

The analyzing systems of uncertainties for accidental risk assessments of the chemicals are composed of four parts, such as (1) introduction of system application; (2) database and data management of the chemicals; (3) modeling system for estimating chemical dangerous sources; (4) modeling system for uncertain analysis. The design of interface can be realized by multilevel structure computer-model frame, which is an open system with self-adaptability. The software system is realized by using Visual FoxPro 5.0 on Window 98 operational platform. It is systematic, dynamic and interactive requiring iterations or feedback loops in order to be effective. The general database for chemicals depends on the national classification standard of chemicals, which is defined as (1) explosive; (2) oxidizing; (3) compress gas and liquefied gas; (4) ignition chemicals; (5) water-ignition chemicals; (6) flammable liquid; (7) flammable solids; (8) toxicants; and (9) corrosive and radioactive chemicals.

The general model of accidental source term for the chemicals piled up various types of accidental models. It is important to select correctly the model. But it is more or less different that

the model is corresponding to actual situation of chemical accidents. Therefore it will introduce the uncertainties in the processes of selecting model and affect directly the results of the risk assessments. By using mathematical statistics method the parameters and input variables of A type uncertain degree, which showed statistical characteristics, can be treated effectively and reliably. The statistical test methods usually include Monte Carlo method, LHS method and random sampling method and so on. Fuzzy sets method can be considered a probability distribution which is not definite in statistics and can be treated as the parameters which is B type uncertain degree and the uncertainties introduced by non-data factors such as expert idea, subjective decision and model uncertainty and so on (WHAZAN-Ⅱ, 1993; Quelch, 1994).

1 The quantitative calculations of the parameter uncertainties

There are many model parameters such as the physical and chemical properties of the leaking chemicals, the total storage capacity of the chemicals, the storage temperature and pressure and so on. Among these parameters the leaking time of the chemicals, the shape and the area of the leaking orifice and the flux factor regard as uncertain parameters in this paper.

1.1 The model for the leakage of pipeline gas (CO)

Assuming leaking gas outflow through an orifice from pipeline or container, the process is adiabatic expansion change using Bernoulli equation and adiabatic equation. The equation of the mass flux for jet gas (WHAZAN-Ⅱ, 1993) is as follows:

$$Q = C_d A \frac{P_1}{(RT)^{0.5}} \left(\frac{2rM}{r-1}\right)^{0.5} \left[\left(\frac{P_2}{P_1}\right)^{2/r} - \left(\frac{P_2}{P_1}\right)^{\frac{r+1}{r}}\right]^{0.5}, \quad (1)$$

in which Q is outflow rates or mass fluxes; A the area of the leaking orifice; C_d the flux factor; P_1 the gas pressure before outflow; P_2 the environmental pressure. When the kinds of gas and the parameters P_1, T_1, A and fixed before jetting, the mass flux will depend on the pressure ratio (P_2/P_1). Hence there is the maximum value Q in case $0 < P_2 < P_1$.

1.1.1 The range of uncertaintive parameters A and C_d values

The area of outflow, which is damage dimensions, may be an uncertain parameter in the risk assessments of the leakage release accidents. Different position of the leakage and different reasons of the damages for different containers bring about different shape and size of the damages. Generally the leakage dimension made from corrosion is less than 20% pipe diameters. Dimension of the mechanic damages which were made of outside mechanical damages or external loading to produce crackle, perforate, snap etc. for container and pipeline are bigger generally as 20%—100% pipe diameters. Because of ascending inside pressure, which is introduced for example by interior explosion, the dimensions of the leaking damage are also bigger. The area of outflow, which made from mis-operation and mis-effect, is about 0—100%.

The flux factor or the outflow coefficient C_d may affect directly the calculated results of the outflow rate of gas. In the jet processes of gas from an orifice or narrow crack, the neck-contracted phenomena occurred in the entrance of the orifice. Thus the actual area of the outflow is smaller than that of the leaking entrance. Due to the difference between theoretical flux and actual flux, it is necessary to introduce C_d for revision. Generally the range of flux factor value is 0.6—1.0.

1.1.2 The example of the leaking source item calculated by using random sampling method for pipeline gas (CO)

The example is the converter gas (CO) outflow from the reduced pipeline in the iron and steel factory. The range of C_d values is 0.6—0.9. A values are about 0—20% area of the pipe cross-section (the pipe diameter $D = 1.4$m). The input parameter are $r = 1.4$, $\rho = 1363$ kg/m^3, $M =$ 28 g/mol, $P_1 = 400$ kPa, $P_2 = 100$ kPa. Random sampling for C_d and A from 25 sets data, the range of the leaking rate value Q is 0.37 kg/s—126.71 kg/s according to Formula (4), in which the average value Qa is 59.08 kg/s and the standard error is 35.71. By using χ^2 statistical test the leaking rate of the accident can be considered normal distribution N (59.08, 35.70) where the credible degree is 95%. Therefore the leaking rate of pipeline gas (CO) is within the normal

probability density distribution. Integrated probability distribution function is Equation (2). It requires 90% to creditable degree in environmental risk assessment. When $F(q) = 0.9$ or the effective rate of statistic deductive method is 90%, the leaking rate of the pipeline gas (CO) Q is 104.79 kg/s.

$$F(q) = \frac{1}{35.71(2\pi)^{0.5}} \int_{-\infty}^{q} \exp\left[-0.5\left(\frac{q - 59.08}{35.71}\right)^2\right] dq. \tag{2}$$

By using latin hypercube sampling (LHS) method the leaking rate Q in 95% creditable degree is 117 kg/s. This value is closed to the above Q value.

1.2 The model for the leakage of liquid chlorine

The leaking rate of the liquid can be obtained by using Bernoulli equation

$$Q = C_d A \rho \left[\frac{2(P_1 - P_2)}{\rho} + 2gh\right]^{\frac{1}{2}}, \tag{3}$$

where ρ is the liquid density, P_1 and P_2 the storage pressure and atmosphere pressure respectively, h the water head of the liquid. The limited condition is that no flashing occur in the entrance of the orifice. The input parameters ρ, P_1, P_2, g, h are fixed in Equation (3), in which $P_1 = 2000$ kPa, $\rho = 1395.5$ kg/m^3, $h = 1.0$m. The flux factor C_d and the area of the leakage A are uncertain parameters. The ranges of C_d values are from 0.6 to 1.0 and the range of A value is from 0.01 to 0.10 (m^2). By using Monte Carlo random sampling and Equation (3) a set of data for C_d, A and Q can be obtained. The range of the leaking rate Q value is from 487.3 to 3598.4 (kg/s). Through testing the hypothesis of the leaking rate Q and its standard error the normal distribution function of the leaking rate will be given. The forecasting value of the leaking rate Q is 2195 (kg/s) for the effective rate 0.9.

1.3 The model for two-phase outflow of the chemicals

In the case of storage of pressurized liquefied gas, venting induces flashing of the superheated liquid; in the case of thermal runaway reactions, gassy reaction products can be released with the liquid phase. Releases involving two-phase flow exhibit specific characteristics, which can significantly influence the dispersion process.

For a liquid, the fraction F_v of the flashes is calculated in thermodynamics by assuming that the entropy is constant during this idealized initial phase, there is

$$F_v = C_{p(l)}[T_1 - T_b]/\Delta H_v, \tag{4}$$

in which T_b is the temperature of the boiling point of the liquid at atmosphere pressure. The average density of the two-phase mixture can be calculated as follows:

$$\rho_m = \frac{1}{F_v \rho_g^{-1} + (1 - F_v)\rho_l^{-1}}.$$

The releasing rate of the two-phase fluids from Bernoulli equation is then:

$$Q = C_d A[2\rho_m(P_1 - P_2)]^{0.5}. \tag{5}$$

Because of flashing atomization, the fragmentation results from the violent boiling and bursting of bubbles in the superheated liquid, the liquid droplet may be mixed with evaporated cloud and formed aerosol effect. Hence the flashed fraction F_v is an uncertain factor that is relative to the aerosol fraction in the evaporated cloud.

1.3.1 The example of liquid propane gas (LPG) accidental release

A 12.4m-diameter sphere vessel contains 400000 kg of liquid propane. The pressure P_1 is 1000 kPa and the temperature is 298K, $\Delta H_v = 429$ kJ/kg, the boiling point $T_b = 231$K, $C_p = 2.45$ kJ/kg. Hence the flash fraction is 0.38 from Equation (4). But the actual flash fraction is an uncertaintive quantity. It is proved that the range of the flash fraction is from 0.38 to 0.76. Assuming the width of the crack for LPG leakage is 0.01m. The range of the area of the leakage is 0.0778—0.389 m^2 according to 20%—100% area of the crack. The value for C_d is 0.6—0.9. By using Monte Carlo sampling method and Equation (5) the random Q value including 25 sets data of

F_v, A and C_d. The range of the LPG leakage is from 208.39 kg/s to 723.71 kg/s. By using χ^2 statistical test the leaking rate of the LPG from the vessel can be considered as normal distribution N (387.70, 138.67), in which the average value Q_a is 387.70 kg/s and the standard error σ is 138.67. The credible degree is 95%. When the effective rate or the reliability degree is 90%, the release rate of LPG leakage is 565.20 kg/s. Hence the average time of that the flash liquids outflow completely from the sphere vessel is about 12 min.

1.3.2 BLEVE and Fireball model for LPG accidents

When there is a sudden loss of containment of a pressure vessel containing a superheated liquid and liquefied gas, a boiling liquid expanding vapor explosion (BLEVE) occurs. It is impossible to describe accurately the physical and chemical state on accidental scene and to obtain a great of data for risk analysis and emergency management. The Fuzzy sets approach with little information may be used to evaluate the uncertainty of nonstatistical parameter for accidental sudden release. The Fuzzy set A defined on the set of all real numbers R has a membership function. The vagueness could mathematically be represented by allowing the grades of membership of each element $x \in X$ in A and the largest membership grade is 1.

For example, the BLEVE of the boiling liquid formed Fireball; the best-known type of BLEVE involves LPG. The uncertainties of the explosion-forming fireball may be considered the fireball duration (s), the rate of the energy released and the heat flux at a radius r from the fireball center. Using the relationship of Morose *et al*. (WHAZAN-Ⅱ, 1993). The maximum fireball radius is:

$$R_f = 2.665M^{0.323}, \tag{6}$$

where M is the initial mass of the releasing flammable liquid (kg), which is an uncertain parameter. The rate of the energy released by combustion at efficiency η is:

$$Q = \eta \Delta H_c M/t, \tag{7}$$

in which the efficiency of combustion is input uncertain parameter, ΔH_c is the heat of combustion (kJ/kg). The fireball duration $t(s)$ is:

$$t = 1.089M^{0.327}. \tag{8}$$

The heat flux I at a radius r from the fireball center is calculated assuming a point source for the energy and thus by the inverse square law relationship:

$$I = TQ/4\pi r^2, \tag{9}$$

in which T is a transmitting factor that is also an uncertain parameter.

The Fuzzy triangular sets of the uncertain parameter for fireball model have been shown in Table 1. It can be known that the M value affects greatly both the values of Q and I which error is almost 300% as much. When the degree of the membership is 1, the value of Q and I are separately 63270 kJ and 5037.4 W/m^2.

Table 1 The quantitative uncertainty of the fireball model (r = 100 m)

Membership degree	0	0.5	1.0	0.5	0
η	0.13	0.185	0.24	0.295	0.35
T	0.90	0.925	0.95	0.975	1.00
M, 10^3 kg	360	370	380	390	400
t, s	71.44	72.08	72.71	73.33	73.94
Q, 10^7 J	3.035	4.790	6.327	7.913	9.550
I, W/m^2	2631.4	3813.7	5037.4	6300.2	7603.5

2 The discussion of the model uncertainty

2.1 The uncertain relationship between the leaking time and the selection of the model

To define the leaking time is difficult in the risk assessment of the chemical hazardous sudden release. The leaking times not only decide the leaking flux Q, but also directly affect the selecting analysis method of the leakage source. When the accidental release completed immediately it is treated as immediate source. For the leakage from the hole the leaking time is larger and it is treated as continuous source. The division between immediate source and continuous source has been taken according to the following definition: (1) When the leakage time is smaller than 10

seconds, it is considered on immediate source. (2) When steady leakage is more than 10 minutes continuously or $t > X_c/u$ it is continuous source in which X_c is the largest distance for concerning concentration. But it is more complicated for calculation with above-mention definition and the X_c value calculated by diffuse modeling is not reasonable. Thus the best method for discussing leaking time is to make a concrete analysis of concrete conditions.

The leakage of pipeline gas can be divided into two stages: (1) The beginning stage is before partition valve being closed. The leakage rate is not variable constantly before closed partition valve. The leakage time is concern with the reacting time of warning equipment, the effective performance of partition valve and operating time and so on. (2) The decay stage is after partition valve being closed. The leakage rate decays with the time after partition valve closed depending on the leakage area, pressure and container volume and so on. Generally the warning time of the accident is about 3—5 minutes. And the normal closed time of the stop valve is 30 seconds. Therefore the time of the beginning stage is the addition of the both terms of the above-mention. If the stop valve cannot be cat efficiently, the leaking time will be prolonged. So it need be modified according to the conditions of the equipment and management. The leaking time of the decay stage may be calculated step by step. First it calculates the flux of the leakage M in the decay stage. For example $M = LS\rho_g$ for the leakage from the pipeline. Then under the constant temperature and constant volume in the pipeline the pressure is directly proportion to the mass of gas (CO). Thus if decreasing pressure 1%, meantime the mass of gas (CO) in the pipeline decrease to $\Delta m = 1\% M$. (3) Because the outflow rate Q of gas which flows through an orifice on the pipeline under the pressure P can be obtained by using Equation (1), the leaking time $\Delta t = \Delta m/Q$. Reaping above calculation for each decreasing pressure 1% and the total leaking time is $T = \sum \Delta ti$. For example the estimation of the leaking time for gas (CO) in 200m ($D = 1.4$m) pipeline is about 3.1 second in the decay stage.

2.2 The uncertainty of gas release dispersion model

The uncertainties of gas release dispersion process include uncertainties of both diffuse parameters and modeling. There were better descriptions about uncertainties of diffuse parameters. Thus the main discussion is the uncertainties of the release dispersion model in this paper. There are two aspects of the uncertainties made of models. First the model is not consummated itself now and can be consummated by researching and developing model in the future. Second for the model that was selected it is not suitable but is very important and disputatious for people who engage in risk assessment.

The diffusion process after gas release can be divided into two stages: (1) The outflow of gas is from an orifice to atmosphere which include jet diffusion, adiabatic expansion and so on. (2) Gas diffusion occurs in the atmosphere which include gas smoke cloud model or plume rise model and so on. Any ignorance for above stages will affect the reliabilities of accidental risk assessment.

In gas release accidents it is difficult to define the leaking time. Therefore the more uncertainties exist in the treatment of the release source term whether is a continuous source or an immediate source. An example for pipeline gas leakage, assuming the degree of atmosphere stability is D and the wind rate is 1.5 m/s, the leaking time is the addition of the starting stage time and the decay stage time i.e. $T_d = 303$ sec. If the gas (CO) end with outflow in the pipeline that is long 200m and diameter 1.4m, the release flux Q is 37200 kg. The calculation compared with the smoke cloud model and the plume rise model as Table 2. From Table 2 the concentration of any point in the space is not changeable for the plume rise model during the leaking time. When $t = 600$s the leakage had stopped at 303 second actually and the concentration is obviously higher (10.07 g/m^3) in downwind distance 1000m according the smoke cloud model. But it is more reasonable for the concentration (6.63 g/m^3) of the smoke cloud model. When $t = 300$s the concentration of the smoke cloud model (45.9 g/m^3) at the distance 400m is higher unreasonably, due to the part of release gas cannot arrive at this distance. Hence the concentration (35.02 g/m^3)

of the plume rise model is more reasonable.

2.3 The uncertainties of the position of imagine source

The atmosphere diffusion model in most use is Guassian type dispersion. But actually a great of gas mass concentration distribution did not accord with Guassian distribution. Thus the calculations of imagine source is often using for Gaussian type dispersion model. In circumstance of jet diffusion such as gas jet from the container or pipeline TNO model can be used, in which the diluted rate of jet diffusion is greater than diluted rate of mid concentration diffusion. The jet rate changes small along with axis distance. Once the jet rate equals to wind rate at the point of the axis, the leakage at this point is never the jet behavior and Guassian dispersion occurs. Therefore the results of calculation that use the simple actual outflow rate for the point source may be on the high side. Thus the imagine source against the wind which have the same as actual outflow rate can be used for the estimation.

Table 2 The comparative results of the calculation between the smoke cloud model and the plume rise model

Type of model	Concentration, g/m^3			
	Plume rise model		Smoke cloud model	
Release time, s	300	600	300	600
Distance of down wind (X = 400m)	35.02	35.02	45.9	0.0
Distance of down wind (X = 1000m)	10.07	10.07	0.0	6.63

If the way of the gas outflow is immediate adiabatic expansion model the outside radius in the end of the expansion may be the sidewinder width. Due to the rate of adiabatic expansion is very fast, there is no time to move for the gas mass. Hence the position of the actual release source can use directly for calculation. In the same time because the thermal exchange between the gas mass and atmosphere environment is ignored for adiabatic expansion model, the error must exist in the results of the calculation for the actual circumstances. Generally the instantaneous release (within 10 seconds) for a great amount of gas in the large range can employ adiabatic expansion model. The continuous release of gas (over 600 seconds) can adopt jet diffusion model. When the release time of gas is from 10 to 600 seconds, to determine the using model needs a specific analysis.

3 Conclusions

The uncertainties of the input parameters for risk assessment about accidents of chemicals can be treated quantitatively by statistic method and fuzzy sets method. The uncertainties of the model can be analyzed by comparative method for different model. It is important to estimate the leaking time for chemicals. Generally if the leaking time is within 10 seconds it is immediate source, and if the release time were over 600 seconds it would be continues source.

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