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Environmental Diffusion Analysis and Consequence Prediction of Liquefied Ammonia Leakage Accident

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Abstract: The demand for the industry chemicals, which serve as the main material and product of heavy industries, has seen a dramatic increase with the development of industrialization and transportation. Meanwhile, dangerous chemicals accidents such as liquefied ammonia leakage occasionally happen due to operational uncertainty, which will do great harm to people and animals because of their hazardous characteristics. In this study, the overall diffusion process of the hypothesized liquefied ammonia leaking accident is firstly analyzed. Then, source density and flash strength are calculated which proves that the diffusion of liquefied ammonia leakage transforms from heavy gas to non-heavy gas in specified time. Furthermore, influence range of gas cloud, concentration change of some fixed point and flammable and explosive region are predicted based on Aloha. Through the consequence prediction, factors in terms of distance from leakage source, wind speed, stability of environment and ground roughness are compared, according to which it can be inferred that the cloud concentration is split into two centers in initial state and cloud tailing with wind exists.

Key words: Ammonia leakage accident, ALOHA, diffusion analysis, consequence prediction

INTRODUCTION

Along with social progress and the advancement of technology, the use of dangerous chemicals is increasingly frequent. According to European Chemicals Bureau, the current European Inventory of Existing Commercial Chemical Substances (EINECS) contains 100204 kinds, including nearly 2500 high production volume chemicals. However, the risk of production, storage, handling and transporting them can bring huge losses to human, environment and society. According to incomplete statistics from 2002-2004, there are 1091 cases of dangerous chemicals accidents in China, which caused 977 deaths and1477 injuries. Especially, the leakage of liquefied ammonia can cause both explosion and poisoning. So, the environmental risk analysis and prediction of liquefied ammonia leakage in terms of the extent of spread and consequences of accidents are very important.

Arendt and Lorenzo (2000) develop detailed scenarios-based quantitative estimate of impacts of chemicals accidents, while the focus is the consequence variation in terms of hazards of interest, specific accident scenarios, consequence type of interest. Chen *et al.* (2011) uses half sphere and the Gaussian models are used to calculate the hazard scope of liquefied ammonia leak in spherical tank to improve the accuracy of simulation analysis. Hassan *et al.* (2010) combines failure frequency analysis and consequence analysis to assess the risk of transporting dangerous chemicals through populated areas. It assesses the risk results from. Burgess and Murphy (2007) give measurements of the atmospheric dispersion of natural gas to test the applicability of the bivariant Gaussian distribution equation with standard deviations. Bouet *et al.* (2005) measure ammonia concentrations in the plume by test and find that for discharges with identical flow rates the distances corresponding to the same concentration vary a lot according to the configurations. Labovský and Jelemenský provide a comparison of the results obtained by the FLADIS field experiments and those of CFD modeling by Fluent 6.3. FLADIS experiments were carried out by the Risø National Laboratory using pressure liquefied ammonia. Junior *et al.* (2012) use a systemic accident analysis methodology based on some knowledge base containing sociotechnical principle of understanding the real operating conditions in which accidents take place. Sommer *et al.* (2006) give the description and prediction algorithms of ammonia emission processes concerning the transfer of NH3 from the manure to the

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free atmosphere. Bernatik, *et al.* (2008) argues that common software packages such as ALOHA, EFFECTS, TerEx should be augmented with Computational Fluid Dynamics (CFD) models or related physical modelling in order to model transport accident of releases and dispersions of dangerous chemicals. However, the accurate prediction of environment consequence of dangerous chemicals accident is still difficult. In this study, diffusion analysis is conducted by physical and chemical calculation model and consequence is predicted by simulation experiment to provide emergency suggestions.

SCENARIO OF LIQUEFIED AMMONIA LEAKAGE ACCIDENT

We hypothesize that the accident took place in San Antonio Texas (due to the possible function of imbedded database, the ALOHA is able to invoke the real data of the local place) in Texas, the residents are always living in one-story building as a result of the farming and remote area, so it's appropriate to choose "unsheltered single storied" mode at the very beginning. The leaked chemical was ammonia. According to the US AEGLS, the amount of AEGLS-1 is 30 ppm, AEGLS-2 is 160 ppm, AEGLS-3 is 1100 ppm, which refers to the corresponding injury as slight injury, severe injury and the death, the normal boiling point in standard condition is -33.9°C, the above and related data of chemicals have been stored in the database, once we make sure the type of the leaked chemical, the data of which have been known for certain. As for the environment condition, we hypothesize that the accident happened in summer, the south wind at 3 m sec^{-1}, the cloud coverage is 20%, temperature at 32°C, humidity at 50%. We set that the cause of the accident was the leakage from "short pipe or valve", the opening was a circle whose radius was 0.75 m. The tank is a cylinder whose radium is 0.4 m, length 1.65 m, capacity 0.83 m^3, containing 450kg liquefied ammonia, which accounts for 92% of the total capacity.

ENVIRONMENTAL DIFFUSIONANALYSIS OF LIQUEFIED AMMONIA LEAKAGE ACCIDENT

The source strength (Q) is the source release rate of hazardous chemicals, which is one of the most basic physical indexes in a number of gas diffusion model calculation. Its accuracy also determines whether the model calculation is successful to a great extent. The calculation of Q can be written as:

$$Q = C_d A\rho\sqrt{2gh + \frac{2(p - p_0)}{\rho}} \qquad (1)$$

In Eq. 1, Q is leakage flow rate (kg sec^{-1}), C_d is emission factor (usually taken 0.6-0.64), A is leak orifice area, ρ is leak fluid density, p is media pressure in container (pa), p_0 is pressure on the environment (pa), h is the liquid level height (m). Since the minimum design pressure of the liquid ammonia storage tank can be determined by liquid ammonia saturated vapor pressure in the storage temperature, the container pressure under 32°C is 1.23 mpa. In addition, $\rho = 592.136$ (kg m^{-3}), $p_0 = 0.101$ (mpa), $A = 1.77\times10^{-4}$ m^2, $h = 0.3$ (m). So, Q can be calculated as 3.23 kg sec^{-1}.

At this point the quantity of heat released from the leaking liquid ammonia is:

$$Q = W\times C\ (T\text{-}T_0) \qquad (2)$$

In Eq. 2, Q-heat released by liquid ammonia (KJ); W-the total quality of liquid ammonia in the storage tank (kg). In this case, there is 450 kg liquid ammonia in the storage tank. C-average specific heat and the average specific heat of liquid ammonia is 4.6 kJ/(kg°C). T-storage temperature and the storage temperature in this case is 32°C. T_0 boiling temperature of liquid ammonia, i.e.,-33°C. In this way, Q = 134550 kJ. And the evaporation of liquid ammonia is:

$$W = Q/H = 134550/(1.37\times10^3) = 98.21\text{ kg} \qquad (3)$$

In the above expression, $H = 1.37\times10^3$, which means vaporization heat of liquid ammonia.

Because the location of leakage is at the middle of the storage tank, the total time of leakage is:

$$t = (450 - \frac{V\rho}{2})/Q = (450 - 245.43)/3.23 = 63.3s \qquad (4)$$

The evaporation rate of flash *v* can be calculated as:

$$v = W/t = 1.55\text{ kg sec}^{-1} = 93.0\text{ kg min}^{-1} \qquad (5)$$

Part of liquid ammonia which leaks from the tank volatiles into ammonia immediately, so two phase flow (liquid phase and gas phase) should be considered in the whole process of the leakage. The ALOHA software collect a variety of gas diffusion models, so the user can let the software to determine which model should be chosen based on the physicochemical properties of chemicals and can also choose the model all by himself. In this example, the heavy gas diffusion model will be chosen to simulate the diffusion of ammonia preliminarily.

The change principle of the flash strength refers to the change principle over time of the average density of air mass after the liquid ammonia at the leak point flash into air mass. In this case, the result of the variation of flash strength which is simulated in the ALOHA software is showed in the Fig. 1.

As is known from the diagram mentioned above, average density of the air mass decreases gradually as the time goes by, especially, we can see that the density decreases sharply at the point of 2min. We speculate that this phenomenon is resulted from density sharply diluting which is caused by the conversion of air mass from heavy gas to non-heavy gas. The proof is shown as follows:

Richardson number R_i can be used to determine whether the leakage of gas belongs to heavy gas or not. It can be determined by:

$$R_i = (\rho- \rho_a)\, gh\, \rho^2_a v \qquad (6)$$

Here, ρ means the cloud density (kg m^{-3}), ρ_a means air density (kg m^{-3}), v means friction velocity generated from air shearing cloud.

When $R_{10} = 10$, if $R_i > R_{i0}$, the diffusion will be considered as heavy gas diffusion, otherwise it will be considered as non-heavy gas diffusion. Under this threshold (R_{i0} equals 10), $\rho_a = 1.1465$ kg m^{-3} (environmental temperature is 32°C), h = 0.4 m (the vertical distance from the ground to the location of leakage), v = 3 m sec^{-1} and then $\rho = 11.195$ kg m^{-3}. This is critical air mass density when the heavy gas converts into the non-heavy gas.

The liquid ammonia air after flashing is a mixture of liquid-gas, when the average density reaches $\rho = 11.195$ kg m^{-3}, we assume that the volume of the liquid is x, Eq.7 exists as the following:

$$\rho_1 x + \rho_2 (1-x) = \rho \qquad (7)$$

Then x can be derived as 0.018. From this, we can see that heavy gas changes into non-heavy gas when volume fraction of liquid phase is 1.8%.

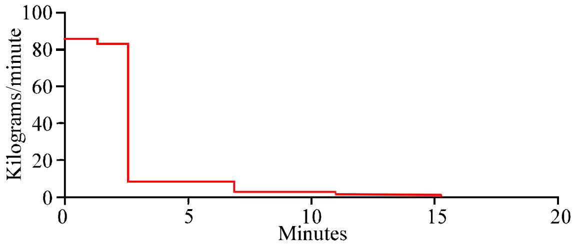

Fig. 1: Flash strength change at the leak point based on ALOHA

In this case, the leakage of liquid ammonia is 450-Vρ_1 2 = 204.26 kg, the flash rate which is calculated above is 93. The time when the air mass reaches the critical state of heavy gas and non-heavy gas is 204.26×(1-0.018)/93 = 2.2 min, which proves that the flash strength of leak point decreasing stepwise substantially after 2min results from the change of air mass diffusion.

CONSEQUENCE PREDICTION OF LIQUEFIED AMMONIA LEAKAGE ACCIDENT

Influence range of gas cloud: After the self-calculation based on the formula widely used in vapor cloud diffusion, the ALOHA drew the different influenced areas according to the AEGL standard, namely, death area (AEGL≥1100 ppm), severe injury area (160 ppm≤AEGL≥1100 ppm), slight injury area (30 ppm≤AEGL≥160 ppm), influenced area (influenced but not injured) and safe area. It can be shown in Fig. 2. If there is no wind at all, the theoretical figure of influenced areas should be circle. But we can see that the final figures are likely the sectors due to the force of wind, while the wings of sectors slightly diffuse. So the speed and the direction of wind are two main factors which worth paying attention.

Concentration change of some fixed point: When faced with the toxic chemicals leakage, it is a challenge that which option residents and animals should take. It really counts for lifesaving and shorten the rescue time to provide a precise prediction. Here we simulate with ALOHA, dividing the situation as indoors and outdoors and predict on how bad the creatures get poisoned based on the AEGL standard and the results are shown later in Fig. 4.

The flammable and explosive region: After the spill, if the leakage chemical is flammable and explosive, a certain area at the periphery of the accident should be determined to ban out smoke fire. Consequently, it is

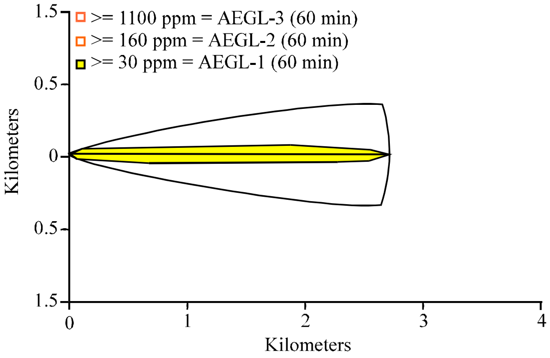

Fig. 2: Influenced area of ammonia leakage

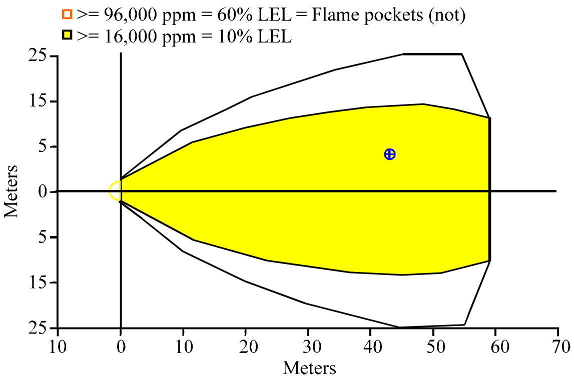

Fig. 3: Marked flammable region

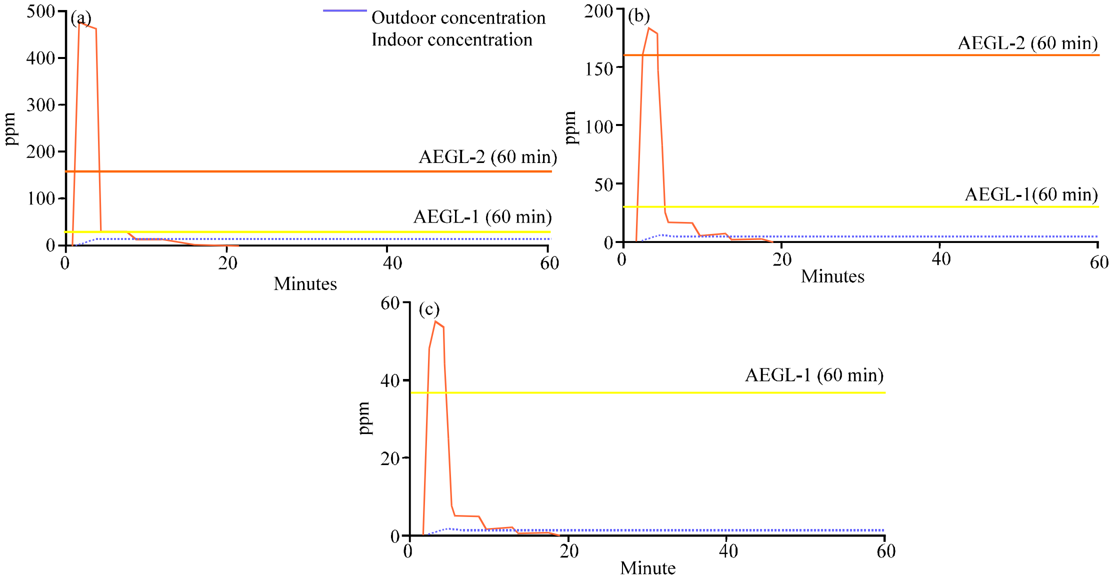

Fig. 4(a-c): Concentration change at some fixed points (a) At point: Downwind: 0.51 km off centerline: 0.024 km, (b) At point: Downwind: 1.00 km off centerline: 0.012 km and (c) At point: Downwind: 2.00 km off centerline: 0.012 km

crucial to accurately predict the explosive areas. Each hazardous flammable has a lower explosion limit LEL (Lower Explosion Limited), which is the lowest concentration of flammable gas in the air in case of fire explosion. For the general monitoring of the gas in the ambient air, gas environment risk is often directly given, that is, the percentage of the content of the gas in the air with its lower explosive limit. Here we use 10% LEL as the flammable region. In this case, the flammable region is given in Fig.3.

ENVIRONMENTAL RISK FACTOR ANALYSIS OF LIQUEFIED AMMONIA LEAKAGE ACCIDENT

It is known that distance from leakage source, wind speed, atmosphere stability, ground roughness, relative humidity and temperature are environmental risk factors of liquefied ammonia leakage. However, the gas diffusion process on some fixed point is comparatively not clearly shown. In this study, the factors effecting consequences are simulated and compared to get some useful hints for rescue planning. For example, the concentration change of 3 fixed points with different distances from leakage source is given in Fig. 4. In this figure, the distances from monitor point to source are 0.5, 1, 2 km separately for (a) (b) and (c).

It can be seen that the changing mode of different points are similar and presents mound-shaped curve. However, there are other two findings. For one thing, the three points all reach peaks at about 7-8 min. We hypothesize that the peaks times at different points without dilution of atmosphere are different under the

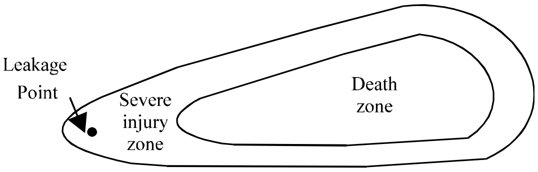

Fig. 5: Contour of cloud passing some point

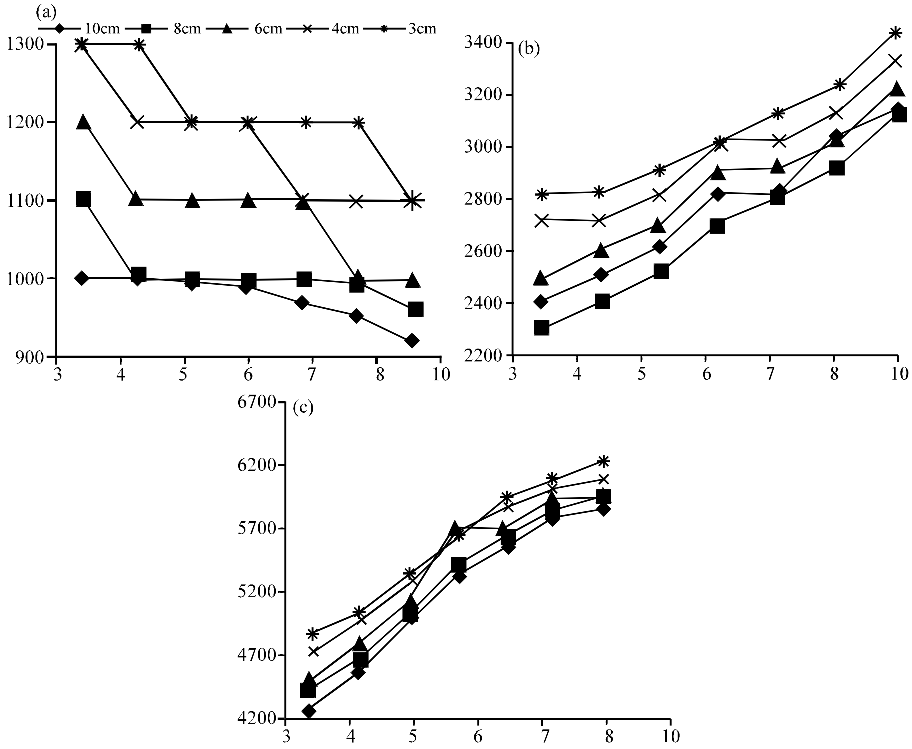

Fig. 6(a-c): Consequence analysis based on wind speed and ground roughness

effect of wind. From Fig. 4, it can be deduced that the ammonia cloud is diluted with air, which causes the effecting area spread and makes the three points arrives at peak simultaneously. For the other, there occur two concentration centers at 0.5 km from source, while there is only one leakage point. For points with distance longer than 2km, the concentration center remains one. It can be inferred that the cloud concentration is split into two or more centers in initial state due to complex environment and this phenomenon gradually disperses.

For some point, the process of usher in cloud striker and the whole cloud is different and this results in cloud tailing due to wind and other environmental factors. Figure 5 shows the contour of cloud passing some point.

In addition, environmental consequence analysis of liquefied ammonia leakage accident with two or more changing factors is worth investigating. By group experiments, the change of accident consequence under two effecting factors is given.

Wind speed and ground roughness: In the case of the same ground roughness, the fastest influence distance of the death zone downwind decreases gradually with the wind speed increasing; then with the increase of land surface roughness, this trend becomes more and more evident. However, the fastest influence distance of the severe injury zone and the slight injury zone downwind gets longer and longer with the increase of ground roughness. This trend also becomes more and more evident, which can be shown in Fig. 6. In Fig.6, x axis means wind speed (m sec^{-1}) and y axis means fastest influence distance.

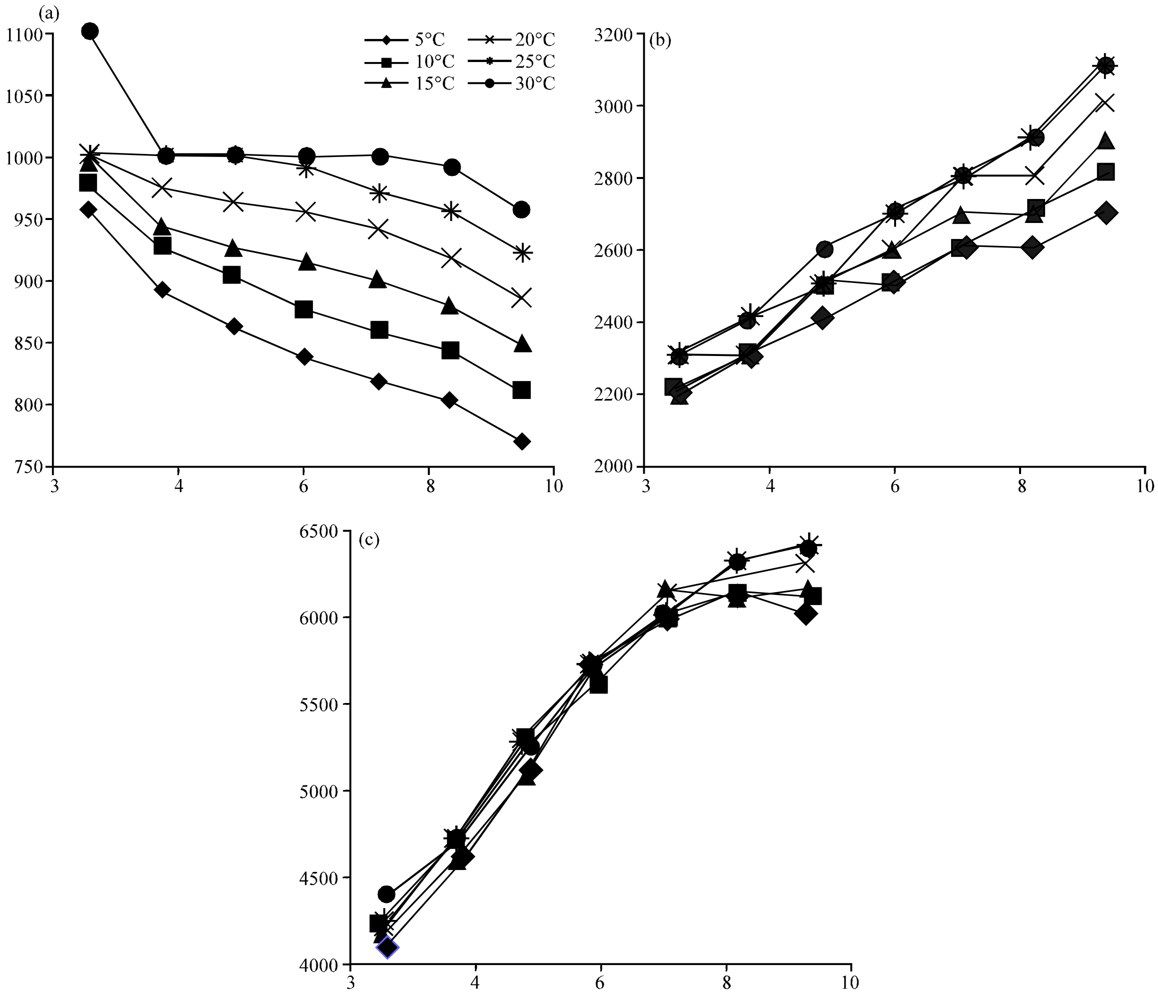

Fig. 7(a-c): Consequence analysis based on wind speed and temperature

Wind speed and temperature: In the case of a constant temperature, the fastest influence distance of the death zone downwind decreases gradually with the wind speed increasing, meanwhile, as the temperature decreases continually, the influence distance decreases continually and decreases faster. However, the fastest influence distance of the severe injury zone downwind increases with the wind speed increasing. At the same time, the higher the temperature is, the longer the distance becomes. Also, the fastest influence distance of the slight injury zone downwind gets longer when the wind speeds up. But the increasing temperature only has a little impact on the fastest influence distance of the slight injury zone downwind. This can be seen in Fig. 7.

Ground roughness and temperature: As shown in Fig. 8, in the case of a constant temperature, the fastest influence distance of the death zone, the severe injury zone and the slight injury zone downwind decreases with ground roughness increasing. With the temperature rising, the fastest influence distance of the death zone downwind decreases much faster than that of the sever injury zone and the slight injury zone and decreases in a larger number.

As for temperature and relative humidity, in the case of a constant temperature, the fastest influence distance of the death zone, the severe injury zone and the slight harm zone downwind remain unchanged as the relative humidity increases. But the rising temperature will result in the fastest influence distance of the downwind death zone increases, while has little influence on the fastest influence distance of the severe injury zone and the slight injury zone downwind.

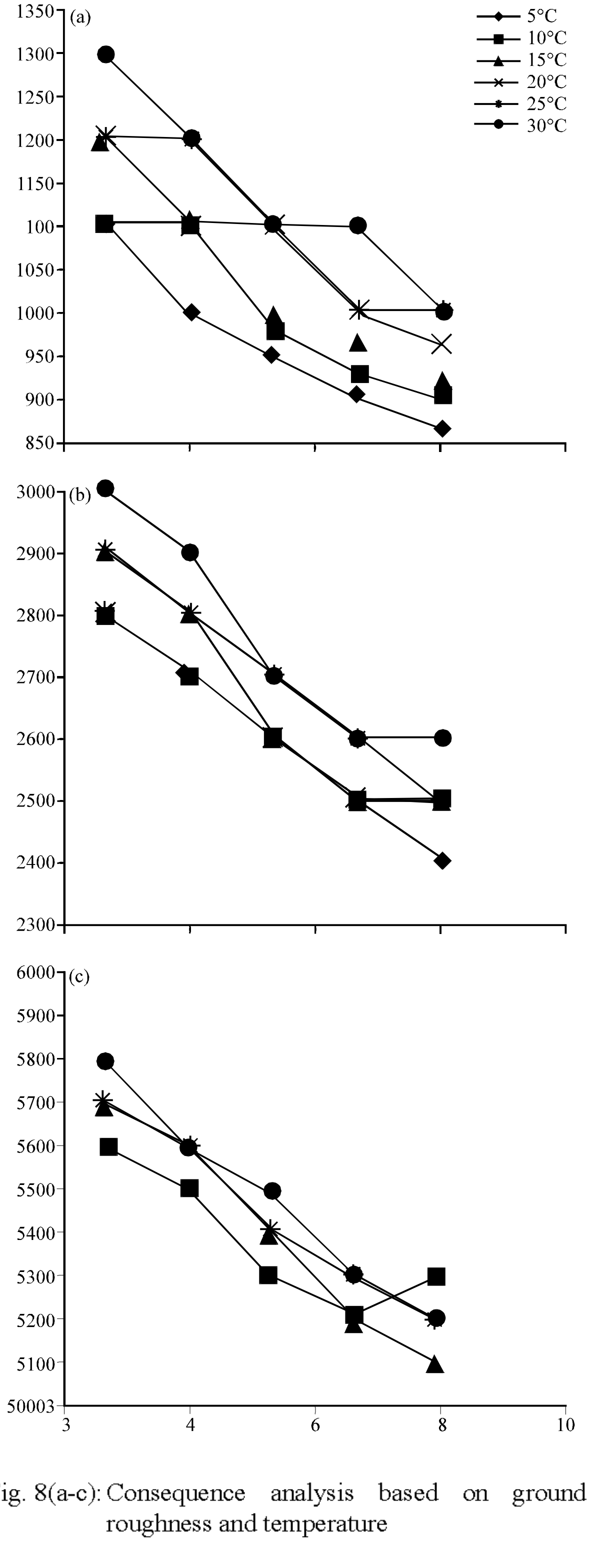

Fig. 8(a-c): Consequence analysis based on ground roughness and temperature

CONCLUSION

The diffusion process of liquefied ammonia leakage accident is studied in this study. According to physical and chemical diffusion model, key parameters such as Richardson number, source intensity and flash strength are calculated and analyzed through a case study, which shows that liquefied ammonia transforms from heavy gas to non-heavy gas in 2.2 min for that case. Also, accident consequences such as influence range, concentration change and flammable and explosive region are simulated based on Aloha, which further explains the cloud diffusion process and principle. Furthermore, the effect of factors including distance from leakage source, wind speed, stability of environment and ground roughness on diffusion are analyzed and some useful hints such as concentration center split, cloud tailing and different factors importance are given.

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