Technically Speaking *- Dr. John Nordin, PhD*

CHLORINE SPILLS

People have asked us, are the models predicting release of a toxic gas release and resulting dispersion any good? Do the models accurately predict the real world situation? We will take a look at chlorine as an example. Chlorine is a highly toxic gas which has many uses. About 40 million tons of chlorine is produced worldwide annually, which includes about 13 million tons produced in the United States and 12 million tons in Europe . Uses include water disinfection, production of plastic products (about 30% of chlorine produced worldwide goes into the production of PVC-based plastic materials), the pulp in paper industry, manufacture of pesticides, liquid bleaches, textiles, manufacture of paints, hydrochloric acid, petroleum products, and various other chemicals.

Chlorine Tank Containing Liquid Chlorine

Chlorine is typically shipped and stored as a liquid in a container under pressure. The maximum-sized container (at least in the United States) shipped by rail is capable of holding 90 tons of liquid chlorine. The maximum size chlorine tank shipped on a barge may have a capacity of up to 1100 tons (more likely, 4 smaller tanks will be shipped on one barge). Tank cars shipped by motor vehicle may have a capacity up to 22 tons.

Under ambient temperature and not under pressure, chlorine is a gas. One pound of this gas at 70^{o}F will occupy 5.45 cubic feet. This is an uneconomical way of shipping and storing chlorine. But if the gas is pressurized, it will liquefy. At a pressure of 86.5 psig (101.1 pounds per square inch absolute) and 70^{o}F, chlorine will liquefy. One pound of liquefied chlorine stored in a tank at 70^{o}F and 86.5 psig will 0.0114 cubic feet rather than the 5.45 cubic feet for gaseous chlorine not under pressure. Clearly, more chlorine can be stored as a liquid under pressure.

Typically, a chlorine tank when full will contain maybe 85% or 90% by volume as a liquid and the rest as chlorine vapor plus a pad of dry air or other non-reactive gas. Chlorine is said to be stored under its own vapor pressure. The system is self-regulating. If the tank temperature increases, the pressure inside the tank will also increase. If the tank temperature decreases, the pressure inside the tank will also decrease. At 0^{o}F, the tank pressure will be about 13.9 psig (or 28.5 psi absolute). But at 100^{o}F, the tank pressure will rise to 140.2 psig (or 154.8 psi absolute). At 120^{o}F, the tank pressure will rise to 201.65 psi absolute. In this example, we are assuming that we are located at an elevation where the ambient air pressure is 14.6 psi.

What happens if the temperature gets too high? Tanks used to store or transport chlorine have pressure release devices designed to vent the tank at the top if the temperature or pressure gets too high. It is better to vent some chlorine to the atmosphere than to have a catastrophic explosion in case of a tank failure.

One-ton chlorine tanks in the United States are equipped with fusible metal pressure release devices (six total, three at each end of the tank) designed to yield or melt at a temperature between 158^{o}F and 165^{o}F. Railroad tank cars have a spring-loaded safety release device set to discharge at a gauge pressure of 225 psig (on cars marked 105A300W) or 375 psig (on cars marked 105A500W). Barge tanks will also have several release devices for each tank, the ones designated 4 QJ are designed to release at 300 psig. Additional details on safety devices are published in “The Chlorine Manual”, published by The Chlorine Institute, Washington , D.C.

Another safety feature on large chlorine tanks is an excess flow valve, which is designed to close automatically if the angle valve which regulates the discharge of chlorine is broken or sheared off. This is not an emergency shutoff valve. The excess flow valve is not activated by pressure or temperature, but is activated if the discharge of liquid chlorine at the exit port exceeds some predetermined value.

What Happens If Liquid Chlorine is Spilled?

The owners of AristaTek while employed by the University of Wyoming Research Corporation (UWRC), d/b/a/ Western Research Institute, made arrangements with the HazMat Spill Center (HSC) located at the Nevada Test Site to spill liquid chlorine in a one square meter pan. Two pans were used. This work was part of a larger contract funded by the U.S. Department of Energy in 1995. The pans were located inside a wind tunnel at the site; the wind tunnel allowed a controlled environment by which measurements and video could be taken without the extraneous complications of sunlight, wind shifts, and precipitation. A large fan at the end of the wind tunnel allowed a controlled wind flow across the pan. There were also turbulence promoters upwind of the pans set in a predetermined pattern as recommended by several consultants familiar with wind flow and atmospheric dispersion studies.

We (the people who later founded AristaTek) had available the HSC for a very short time because of tight scheduling with other clients who also wanted to use the facility; consequently there was time to do only three spill tests (two using ammonia and one using chlorine) on April 4-6, 1995. The major objective of the tests was to see if the pool evaporation rate for spilled cryogenic hazardous chemicals agreed with the pool model evaporation predictions used by ALOHA. The ALOHA model is used in EPA’s CAMEO software.

The chlorine was delivered to the evaporation pan from a one-ton chlorine tank; a vent chamber in line ahead of the pans allowed removal of chlorine gas so only liquid chlorine was delivered to the pan. The system was heavily instrumented (weight sensors, wind speed, temperature, video, etc.), and could be viewed and controlled from the safety of a control room about 1 mile from the test. As the pan was filled, solid chlorine hydrate quickly formed despite the low (10%) humidity. Before the solid chlorine hydrate interfered seriously with the test, we were able to obtain a chlorine pool evaporation rate of 0.7 $kg/min/m^2$, which compares with an ALOHA prediction of 0.85 $kg/min/m^2$. The wind speed for the test condition was 6 m/s. The measured chlorine temperature was -60°C (-76°F).

As the chlorine evaporated, it extracted heat from the chlorine liquid left in the pan. Therefore the pool temperature dropped way below the ambient temperature of 25°C (77°F) even though the temperature inside the one-ton supply tank was also at ambient conditions.

However, the liquid chlorine quickly absorbed water humidity from the air forming the solid chlorine hydrate. The chlorine hydrate fairly quickly coated the temperature sensors in the pan and the sides of the pan. As the pan filled with the solid, the evaporation rate significantly decreased, and the pool temperature increased. The chlorine hydrate could not be pumped.

Liquid ammonia evaporation tests were performed on April 5 and 6, 1995. We were not troubled by the complication of formation of a solid hydrate during evaporation of liquid ammonia. In one test, the evaporation rates were measured at different pool temperatures ranging from -58°C to -67°C at a wind speed of 5.57 m/s. The measured evaporation rates agreed with the ALOHA model predictions. The test was repeated the next day using approximately the same range of pool temperatures except that the wind speed was 3 m/s. Again the measured evaporation rate agreed closely with ALOHA model predictions between 0.11 and 0.22 $kg/min/m^2$ between -70° and -60°C.

There were some differences in the temperature measured within the evaporating pool and the surface. Temperatures at the evaporating skin (as measured using an optical pyrometer) were several degrees lower than the temperature of the bulk liquid. The lowest skin temperature measured was -76°C. It appeared that convection cells may be setting up within the evaporating pool, where the ammonia as it evaporated chilled the surface, and the more dense chilled liquid sank to the bottom of the pan. The sinking of the surface liquid helped mix the liquid ammonia so the bulk temperatures were fairly uniform (within about 2°C) in the pool, but the surface temperature was lower.

The National Oceanic and Atmospheric Administration (NOAA) out of Seattle , WA , sent a representative, Roy Overstreet, to observe the tests. NOAA was responsible for writing the developmental document upon which ALOHA was based[1]. Roy Overstreet concluded that the evaporation test results matched ALOHA predictions. He was able to gather the measurements in the control room while the experiments were underway. We also concluded the same thing after processing the data gathered from the tests.

Because of the test agreement with ALOHA predictions, the founders of AristaTek made a decision when the PEAC tool was developed to use the same evaporation algorithms for pool evaporation that ALOHA used. The pool evaporation algorithms are available in the public domain in peer-reviewed literature.

But there are complications. In the case of chlorine, the chilled liquid extracts moisture from the air forming solid chlorine hydrate, which retards evaporation. The solid chlorine hydrate was observed in other outdoor chlorine field tests at the HSC. The solid hydrate also has been seen in real-world chlorine spill accidents.

Another issue when using an evaporation model is the matter of heat balance. If there were there significant heat input, as what would happen if the chlorine or other liquid were spilled on a hot surface, the evaporation rate would be higher than predictions, at least initially. As the ground becomes chilled, the evaporation rate will become closer to predictions unless there is an extraneous circumstance as in a fire.

Modeling a Chlorine Rail Car Accident.

In this hypothetical example, a 90-ton capacity rail car is involved in an accident, and a strong odor of chlorine is present. As far as first responders can tell, there are no large volumes of liquid chlorine coming from the tank, but the accident scene is obscured by yellowish-greenish gas. Responders can't get near to see what exactly is happening. There is no fire. There are no other rail cars containing flammables or other hazardous substances which might react with chlorine causing an explosion. There are causalities. How should this situation be modeled to estimate a public protective action zone? And how do the models compare in their predictions?

In a real incident, responders rarely have all the necessary information required to do gas dispersion modeling. Reasonable guesses must be made.

On 6 January 2005, at about 2:30AM, three 90-ton chlorine rail cars were involved in an accident at a crossing siding in Graniteville , SC. The resulting chlorine gas leak killed nine people and sent over 350 people to a nearby hospital for chlorine inhalation. About 5400 people were evacuated within a one-mile radius. Initially, responders did not know how many rail car tanks were leaking chlorine. It was established the next day that chlorine was leaking from only one rail car tank, and that perhaps possibly 40% of the chlorine still remained in the tank. The chlorine gas continued to escape from a fist-sized hole in the tank. On January 9, when a temporary patch was used to plug the hole in the tank, it was estimated that 30 tons of chlorine remained in the tank and 60 tons had escaped. More details on the accident are available in an accident investigation report generated by the National Transportation Safety Board that can be viewed or downloaded by clicking here.

There were reports that the ALOHA gas dispersion model was used to estimate a protection action distance for the Graniteville incident, and that this model grossly over predicted concentrations as a function of distance downwind. If the modelers assumed that all of the chlorine were released at once or during a relatively short time period, e.g. 60 minutes, the default time in ALOHA, very large concentrations would be predicted downwind. The chlorine release rate was much slower in the Graniteville incident but still deadly.

The chlorine inside a 90-ton rail car would be shipped as a liquid under its own vapor pressure. Probably about 85% of the volume inside the tank would be liquid and the remaining amount vapor and some nitrogen. Assuming an ambient temperature of 50^{o}F, the pressure (gage) inside the tank would be about 60 psi before the breach. If the hole is at the top of the tank, chlorine gas will be released. The drop in pressure inside the tank would cause the chlorine liquid to boil resulting in more chlorine escaping. As the chlorine boils, the tank will become chilled reducing the evaporation rate. Any air moisture would result in chlorine hydrate formation, which could further reduce the evaporation rate. It will take many days to empty the tank.

On the other hand, if there is a large hole at the bottom of the tank, the pressure will force chlorine liquid out the hole. The tank will empty much sooner. The chlorine liquid on the ground will also evaporate quickly at least initially, but solid hydrate formation will reduce the evaporation rate. Maximum chlorine concentrations in the air will be much greater.

The 2004 Emergency Response Guidebook lists Initial Isolation Zone and Protective Action Distances for hazardous chemicals involved in transportation accidents. This guidebook is published jointly by Transport Canada , U.S. Dept. of Transportation, and Secretariat of Transport (Mexico), and is available at http://hazmat.dot.gov/pubs/erg/erg2004.pdf.

The user need only consider four categories for each chemical when looking up the Initial Isolation Zone and Protective Action Distances in the Emergency Response Guidebook. The categories are (1) small spills, daytime conditions, (2) large spills, daytime conditions, (3) small spills, nighttime conditions, and (4) large spills, nighttime conditions. A breach in a 90-ton railcar is a large spill. The Emergency Response Guidebook lists the Initial Isolation distance for large spills as 0.24 km, and the Protective Action Distance as 2.4 km (daytime conditions), or 7.4 km (nighttime conditions).

What is a large spill and what is a small spill? For most hazardous chemicals, the Emergency Response Guidebook considers anything greater than 55 or 60 gallon as a large spill. A 90-ton rail car is a large spill, but a breach in a one-ton chlorine tank would also be considered a large spill. The information displayed in the Emergency Response Guidebook for chlorine looks like the chart below. The information can be displayed in English or metric units.

Gas dispersion models ask the user basic information such as (1) the chemical itself, or at least information about the chemical such as molecular weight and boiling point; (2) amount of chemical released, (3) information about the terrain, which is usually expressed in terms of a "surface roughness", and (4) meteorology. The user then specifies a location downwind, and the model predicts a concentration at that location. Alternatively, the user may specify a concentration representing a "level of concern", and the model predicts a distance downwind corresponding to that concentration. Information requested on meteorology could include (1) wind speed and direction, and (2) atmospheric stability (time of day, geographical location, date, percent cloud cover, etc.).

What model should the responder use? Some popular models in the public domain are ALOHA and SLAB, Chlorine is a dense gas which tends to "hug" the ground as it travels downwind until either solar heating creates atmospheric instability or turbulence from wind eventually disperses the gas. Therefore any model selected should have a "dense gas" component, which both ALOHA and SLAB have. The model in the PEAC tool also has a dense gas component.

Let us do a model comparison for a chlorine release rate of 1 lb/second under daytime and nighttime conditions. We don't know the release rate but need to proceed with a reasonable guess.

The ALOHA model is available at no cost from the U.S. Environmental Protection Agency. Version 5.3.1 of the ALOHA model can be downloaded at http://www.epa.gov/ceppo/cameo/aloha.htm. The PEAC tool is available from AristaTek, at http://www.aristatek.com/. SLAB is a dense gas model developed by Lawrence Livermore National Laboratories under U.S. Dept. of Energy contract. SLAB is available from a number of sources such as http://www.weblakes.com/lakeepa4.html.

The models shown above were compared at a surface roughness of 0.1 meters (cropland, light residential terrain), and the wind speed was measured at a 2-meter height.

Usually, the Emergency Response Planning Guideline Level 2 (ERPG-2) is used as the Level of Concern for public evacuation distance. The ERPG-2 is also used in the 2004 Emergency Response Guidebook for their Protective Action Distance. ERPG-2 is established by the American Industrial Hygiene Association and is defined as the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. For chlorine, the ERPG-2 is 3 ppm. For the daytime condition at 10 mph wind, the corresponding distance ranges from 0.7 to 1 miles (1.1 to 1.6 km) depending upon what model is used. For nighttime conditions at 2 mph wind, the distances corresponding to 3 ppm varied from 2 to 7 miles (3.2 to 11.3 km) depending upon the model.

The lethal concentration of chlorine (LC50) for a one-hour exposure based on rat studies is just under 300 ppm.

Note that the model comparisons are plotted logarithmically. The level of concern represents the ground level, plume cloud centerline concentration for different distances (in miles) downwind. The models agree fairly close to each other under windy or overcast conditions as represented by the top graph, but depart from each other under the low-wind, clear nighttime condition. The first graph represents a neutral, or “D” atmospheric stability; “neutral” meaning that there is little ground cooling or solar heating resulting in a minimal temperature gradient in the air. The second graph represents a “stable” nighttime atmospheric condition where the cooler air tends to sink to the ground, sometimes referred to as the “F” atmospheric stability. The toxic gas cloud is not readily dispersed under stable, nighttime conditions, and as a consequence, the distances matching up with Levels of Concern are much greater.

Why are the models predicting essentially the same results under “neutral” conditions but depart under the stable, nighttime, “F” stability condition? Models in their development require data sets for calibration. The data sets allow development of algorithms which predict how the chemical cloud will spread and disperse as it travels downwind. For example, the ALOHA model uses Briggs’ dispersion algorithms (called “sigmas”) which were developed from sulfur dioxide releases tests in a Kansas field in the 1960’s. SLAB used some data sets for chemical releases done at the Nevada Test Site near Mercury, Nevada . There are many data sets developed under “D” or neutral stability conditions; the data sets can easily be done in a wind tunnel under controlled conditions. But data sets are few and far between under the stable, nighttime “F” stability condition. Consequently the models differ depending upon what data sets are used.

The Aristatek founders completed a series of chemical releases at the HSC located at the Nevada Test Site under a variety of meteorological conditions ranging from the neutral “D” to the stable “F” stability. The chemical was released and the air concentrations in the chemical cloud were measured by a complex array of sensors placed downwind. Various structures were in the cloud path mimicking conditions which might occur at an industrial complex such as a refinery. Data sets taken under neutral or “D” stability conditions were easy to characterize. The “F” nighttime stability was much more difficult, the data collected was very much dependent upon micrometeorology. There can be a “near F” condition where there was enough local turbulence to disperse the chemical cloud, and a “far F” condition where the chemical cloud remained. Also, meteorological conditions were not uniform as the cloud moved from the source.

Therefore, it should not come as a surprise if available models differ under the “F” stability condition. The discrepancy becomes worse as the wind speed decreases. Available models cannot handle the “zero” wind condition.

A small chlorine release incident occurred in Springfield , MA during June 1988 under calm and overcast nighttime conditions. Based on odor reports, the chlorine cloud appeared to move in all directions from the site, bypassing some locations, with no discernable pattern. People within about ¼ mile from the site were evacuated. A couple of days later, on June 19, the release was much greater with an accompanying fire. Under a daytime 8 mph wind condition, the chemical cloud was described as several miles long and only a few city blocks wide.

The concentrations graphed are maximum, centerline concentrations. If a person moves crosswind from the chemical cloud centerline, the concentrations will usually rapidly drop off. But if conditions are calm or a very low wind speed, especially after sunset, conditions are often unpredictable. If the chemical is a dense gas such as chlorine and there is no fire, the person may be advised to seek higher ground.

What can we conclude from all this?

- In real accidents responders rarely have all the necessary information required to run a gas dispersion model. Reasonable guesses must be made. One of the biggest unknowns is the release rate to the atmosphere. Usually first responders can't even get close to the site to determine exactly what is happening.
- Reasonable guesses must be made as to the release rate and meteorology. If the responders guess too conservatively (e.g. all of the chemical released at once or within a short period of time), critics may say that the model is too conservative.
- The available popular models generally give similar results under "neutral" atmospheric conditions or under light or moderate wind conditions. There may be major differences under low wind, clear, nighttime conditions.
- The pool evaporation model used by ALOHA and which is also in the PEAC tool accurately predict the evaporation rate of liquid chlorine, but there are complications such as chlorine hydrate formation (which reduces pool evaporation) or excessive heat input to the pool (which increases the evaporation rate).

[1] Reynolds, R.M., 1992, ALOHA™ Theoretical Description, Report NOS ORCA-65, National Oceanic and Atmospheric Administration, Seattle , WA .