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Tianjin Chemical Warehouse Explosions – Never Let A Serious Crisis Go To Waste

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Los Angeles, September 13, 2015

Warehousing hazardous chemicals, on a large scale, is not uncommon, and can be done safely provided the facility is properly designed. The Tianjin explosion (August 12, 2015) highlights the consequences of failing to appropriately store bulk quantities of potentially hazardous chemicals. At about 11:30pm (local time), a series of explosions in Tianjin devastated a chemical warehouse and storage complex and the surrounding area. Tianjin is a port city located about 150 kilometers southeast of Beijing. On September 12, 2015 Chinese authorities ended the search of the eight remaining missing persons, setting the final death toll at 173.

This article offers an overview of the design and operational basis for chemical warehouses. It also presents an explanation for the events of the explosion from a chemical perspective.

Understanding each chemical's hazardous properties, including its toxicity and thermal stability, is a big part of providing a safe storage facility. Getting the design right, including ensuring that it is appropriate to handle in-coming chemicals, is centered around providing satisfactory answers to two fundamental questions:

- What is the nature and extent of the potential hazards posed by each chemical?
- Is the facility designed and managed to minimize the risks of handling these materials?

The first question may be answered by understanding the implications of the health, environmental, and physical and chemical properties of each chemical. For example, chemicals may be classified as:

- *Highly flammable,* such as solvents like acetone, or fuels such as gasoline (butanone, reported present),
- *Water reactive*, or when exposed to air, will give dangerous reaction products (calcium carbide, confirmed),
- *Liable to explode* if surrounded by a fire (ammonium nitrate, confirmed),
- *Strong oxidizers* that can increase the ferocity and spread of a fire (potassium nitrate and sodium nitrate, confirmed),
- *Highly toxic* and therefore dangerous if the containers are compromised by a fire or explosion (sodium cyanide, confirmed).

Although a full inventory of chemicals and the amounts stored at Tianjin has not been released by authorities, the widely reported short-list of chemicals, believed to have been present, include examples of each of the above classes, and in quantities that are in the tens to hundreds of tons.

The **risks** associated with a dangerous event, such as the Tianjin explosion, is governed by the **consequences** if the event happens and the **likelihood** that it will occur. Reducing the risk to an acceptable level requires reducing the likelihood of occurrence to as close to zero as possible, and mitigating the consequences if the event occurs. Mitigation usually includes providing warning and protection systems, using adequate and safe equipment and facilities, and an in-place robust operating discipline that is adhered to. It is also essential that activities having an unacceptable consequence are banned, or handled in a custom designed facility.

Risk reduction activities become a joint effort among the facility owners and operators, the manufacturers and owners of the chemicals to be stored, the local officials including planners and licensing agencies, emergency response teams, and outside experts with wide experience in the management of highly hazardous chemcials.

A properly designed storage facility would have the following characteristics:

- Constructed from non-flammable materials.
- Chemical storage, within the facility, is governed by segregation zones designed to accommodate the various hazard classes. For example, the flammable liquids storage area would be designed differently from the area used to store water reactive chemicals.
- Water-free zones are established where water reactive chemicals can be stored.
- Area alarms are present to detect the initial outbreak of a fire in any area of the warehouse.
- Automated extinguishing systems are in place to douse a fire before it becomes unmanageable.
- Chemical segregation within the warehouse so that, in the event of a fire, emergency responders have knowledge of what and how much of each chemical is stored, and where they are located.
- Segregation also helps to keep chemicals apart that are incompatible, especially in a fire.

The bottom-line is that it is vital, if a fire breaks out, to keep the impacted area will be as small as possible and controlled as quickly as possible. Even though the Tianjin facility was a transit warehouse serving the port, the segregation concept of storage areas should have been part of basic building design, and implemented for each chemical stored. Given this design, an incoming chemical, would be stored according to the segregation plan, based on information in its safety data sheet (SDS). In N. America, Europe and other countries movement and storage of chemicals without an SDS is against the regulations.

Design of the warehouse, the second major question, can be addressed once the necessary physical and chemical property information has been obtained and factored into the design basis. Nine questions arise from this second concern:

- Is the physical location of the storage facility appropriate with respect to the surrounding community?
- Are there particular building design requirements when storing chemicals of varying hazard classes?
- Does the environment of the several segregation zones need to be individually controlled?
- Are there materials of construction to be avoided in a storage facility, or when upgrading an existing one?
- Are fire detection and suppression measures needed, including appropriately rated fire-walls?
- Are there limits on the amounts of particular chemicals that can be stored?
- Are there chemicals or substances that must not be present in a particular storage area?
- Are there chemicals that must not be stored in any part of the facility?
- How should the storage facility be managed on a daily basis?

Location of this type of warehouse, established during the early planning stages, is critical. In the event that a fire becomes unmanageable, the possibility of several, severe explosions, as the fire heats the stored chemicals, greatly increases the risk to area residents. Restricting housing to no closer than a particular distance is the standard approach. The exact distance is based on the proposed use of the warehouse, in terms of the type and quantity of chemicals to be stored. These are derived, in part, on the recommended evacuation distances during an emergency (*2012 Emergency Response Guidebook*, by US DOT) as well as from blast damage calculations.

The risks to local area residents include:

- spread and increasing intensity of the fire,
- explosions of stored chemicals and those susceptible to heat,
- release of toxic gases into the atmosphere from the combustion process,
- release of toxic liquids and solids released due to exploding containers,

- dispersal of toxics to the surrounding area during explosions,
- mixing of water reactive chemicals with water, either from water to fight the fire or from ruptured water systems within the warehouse.

From the Tianjin news reports, it appears that the firemen were faced with the monumental task of controlling and dousing the fire, arriving when the fire appeared to be fully engaged. They were unaware of the magnitude of the hazards.

In Europe and N. America the on-scene incident commander will assess the fire, based on what chemicals are present and their quantities using SDS information and the emergency Response Guidebook. Often the firemen would be pulled back to a safe distance and directed to concentrate on wide area containment and evacuation as needed. An exclusion zone of ½ to 2 mile radius, during fire-fighting, is typical depending on the chemicals involved.

A new US chemical storage warehouse would have to be approved by state and local authorities, subject to Federal regulations and requirements. The community's local fire chief has a key responsibility here. Design considerations include and address:

- proposed floor plan, based on the required segregation zones,
- alarm and fire suppression systems,
- use of non-flammable construction materials throughout each building,
- proximity of warehouse building(s) to populated areas and other structures,
- operating discipline once the facility is functioning.

The safety culture in China is not as comprehensive or thorough as one finds in N. America and Europe and several other countries, where regulatory coverage is the driving force in planning, compliance, and enforcement. Active participation by owners and operators of storage facilities, for example, is crucial to establishing and maintaining an appropriate operating discipline. At Tianjin, the storage of 700 tons of sodium cyanide, when the regulatory limit had been set to 70 tons, is an example of an ineffective and lax safety culture.

The cause of the Tianjin explosions and their consequences may be explained by a sequence of chemical reactions brought on by the fire within the facility.

> *It is emphasized that, without full knowledge of the chemical inventory, this hypothesis is speculation, albeit well-grounded in known chemical reactivity and accident histories, along with what is known at this point.*

The observable facts are that there was a large fire, and at some point, there were a series of explosions. The penultimate explosion was large and generated a sizable explosion flash. The final explosion, some seconds later, was extremely large generating a flash that briefly over-saturated the video cameras' CCD recording devices, resulting in a loss of video for about a second. The following day the extent of the damage was seen to be extensive within the blast zone.

Chinese authoritative sources stated, soon after the explosion, that potassium nitrate (500 tons), sodium nitrate (unknown amount), calcium carbide (unknown amount), and sodium cyanide (700 tons) were present in the warehouse area. Recently, ammonium nitrate (800 tons) was added to this list. There have been unconfirmed reports that butanone (flammable) and toluene di-isocyanate (water reactive and flammable) were also present.

The observable facts and the chemical inventory, known to date, may be linked together:

- **Calcium carbide** reacts vigorously with water evolving acetylene, a highly flammable and potentially explosive gas. This reaction generates more and more acetylene as the temperature increases. Even if water was not used to fight the fire, an intense fire would quickly lead to failure of internal water pipes and headers – there was, most likely, no shortage of water to make acetylene. Eventually, the heat of the fire could increase the acetylene generation rate to explosive levels.
- **Solvents**, in drums or tanks will usually fail quickly providing an explosive fuel to the conflagration.
- **Ammonium nitrate**, exposed to a large fire will begin to melt. Molten ammonium nitrate decomposes and may be easily detonated, if there other explosions close to its storage area. These detonations are devastating, as witnessed by the 2013 explosion of an ammonium nitrate warehouse in West, Texas
- **Potassium nitrate** is a strong oxidizer, that will cause a fire to increase in intensity. Together with sodium nitrate, also reported to have been present, these chemicals will react with many other materials leading to an even more intense and dangerous fire. It is imperative to keep these chemicals, and ammonium nitrate away from a fire and to provide systems, such as sprinklers or deluges, to extinguish any fires before they can become too difficult to control.
- **Sodium cyanide**, while not an explosive chemical, may generate prussic acid that might explode if it is confined and heated. However, since the sodium cyanide was most likely within the impact area of the final explosion, it would be distributed over a wide area by the force the explosion, contributing to a wide area of dangerous contamination. The fish-kills noted a few days after the explosion attest to this assertion.

These five points are derived from the chemical properties of the chemicals believed to have been present and the conditions of the fire. It is therefore reasonable that the contents of the warehouse, and the intense fire conditions, led ultimately to the detonation of all or part of the stored ammonium nitrate, believed to be about 800 tons. This sequence of known chemical reactions and predictable consequences are consistent with the damage seen at Tianjin (video unedited for language: https://www.youtube.com/watch?v=Q04fV4j7A1w).

The publicly available videos (https://www.youtube.com/watch?v=wd2Om4MO6dA Video unedited for language) and pictures of the West, Texas explosion and its aftermath show striking similarities to this accident. Tianjin is simply very much larger in scope. It was estimated that the West, Texas explosion was equivalent to about 20 tons TNT, generated by about 30 to 40 tons of stored ammonium nitrate (Aerial pictures of West, Texas devastation: http://www.news.com.au/news/photos-fn78rwin-1226623466631?page=3). The extent of the devastation area in Tianjin, if ammonium nitrate was the last chemical to detonate, suggests that a great deal more than a 20 TNT equivalent amount of ammonium nitrate was involved in this explosion (Aerial pictures of Tianjin devastation: http://qz.com/481174/photos-high-res-aerial-images-of-the-tianjin-blast-crater-show-devastation-that-words-cant-explain/). This is the TNT equivalency that has been stated by Chinese officials at Tianjin.

Commentary: China has a long road ahead of it to improve their safety record. It could start with a re-evaluation of their chemical management systems including manufacture, warehousing and distribution. History shows, at least in N. America and Europe over the last century, that major disasters of this magnitude often result in a major shift in regulatory oversight, fundamental operating disciplines, and in the safety culture.

Winston Churchill, and latterly Rahm Emanuel, noted that one should "never let a serious crisis go to waste" – valuable advice indeed.