HEAT TRANSFER ANALYSIS OF STORAGE CONDITIONS FOR HEAT SENSITIVE SUBSTANCES IN SUMMER WEATHER

Giovanni Cocchi
g.cocchi@forensicexperts.it
Forensic Experts S.r.l. Via Zannoni 58, 40134, Bologna

Abstract
Heat sensitive substances, like propellants and organic peroxides, may experience severe self accelerating decomposition reactions, if stored or transported in conditions which expose them to exceedingly high ambient temperature. In this work a methodology for transient thermal analysis of storage depots is discussed in detail, including the use of appropriate natural and forced (due to wind) convection coefficients and a procedure for predicting diurnal time dependent air temperatures and solar radiation heat fluxes. Time dependent boundary conditions enable a better analysis of thermal conditions inside the depot, effetively including the effect of diurnal cycle. This may prove useful for both accident investigations and safety assessments.

Introduction

Substances liable to self accelerating decomposition processes are indeed heat sensitive, since the kinetic of decomposition reactions, including those which may be regarded as auto –catalytic, is strongly influenced by temperature of the reacting system. In fact, commonly an increase in temperature results in an exponential rise of the reaction rate. Since thermal runaway happens when the heat generated by the decomposition reactions is greater than heat losses to the surrounding environment, an increase of the reaction rate may renderer unstable and thus trigger supercritical behaviour in a package of heat sensitive substance. This is a relevant safety concern in storage and shipping of such substances. In the scientific literature it is widely accepted that the best risk mitigation measure is the control of the temperature at which liable substances are being transported or stored. The UN regulations on the transportation of hazardous substances are based on temperature control rules and state that only products with self accelerating decomposition temperature greater than 55°C may are suitable for uncooled transport. The relationship between reactivity of a substance (represented by its heat of reaction, by the activation energy and by the frequency factor of the decomposition reaction(s)), critical temperature, package size and heat transfer conditions (represented by internal and external heat transfer coefficients and by the thermal properties of the substance itself) may be elicited by means of the well known Semenov and Frank Kamenetskii theories, or with the Gray Wake approach. Examples of heat sensitive substances may be easily found among explosives, propellants and organic peroxides. Such products are commonly stored and shipped all around the globe and thus may be exposed, sometimes for small amount of time, sometimes for longer periods, to extreme weather conditions and thus to challenging thermal conditions. This may be especially true for ship transportation across the tropical regions and the historical data by Bowes (Bowes 1966) and the more recent work by Steensma et al. (Steensma et al. 2008) are the most important literature reference on the topic. According to Bowes (Bowes 1966), ship's deck temperatures as high as 60°C were recorded in the Caribbean, Panama Canal and Guayaquil harbor and a value of 70°C is quoted for the voyage of another ship vessel, while according to Steensma et al. during a sea voyage of 2 month through the tropics temperatures as high as 63°C were recorded as the air temperature of the grey top of a container, but only for 1 hour. In the same voyage, the highest recorded air temperature in the air space of one of the container's compartment was 50.7°C, but recorded liquid temperature of the top packages was only 32.3°C and the most inward packages even did not followed the day-night temperature cycle. Similar statement may be found in Bowes. According to Steensma et al., in the same voyage, the worst day the 24 h average temperature of the roof of the sea container (a grey coloured ISO container sized 20'x8'x8'6'') was 8.5°C higher than the average ambient temperature. The average temperature of the sun exposed side was 7.5°C higher than the average ambient temperature, while on the other side, which remained in the shade, the average temperature was almost equal to the ambient average. Similar values are reported by Bowes, which for safety reasons rounds the average deck temperature excess to 10°C above the ambient average. Steensma et al. concluded that even taking into account adverse temperatures conditions (which are undoubtedly at the upper bound of the values recorded in ship holds), the question *"Are transport incidents always due to bad quality products or bad handling practices?" Must also be answered by "yes, if there is a transport incident there has been something wrong with the product quality"*. In fact, Steensma et al. argument that even liquid organic peroxides having an of SADT 55°C can be safely transported in uncooled sea containers, validating the previously cited UN criterion. Summer weather conditions in many European countries like Italy may, in principle, prompt similar concerns, even if it is clear that less extreme conditions are expected respect those found in tropical areas.

The diurnal cycle of air temperature and solar irradiance according to UNI10349

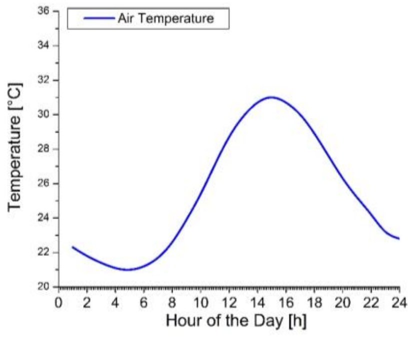
On average, excluding episodic meteorological phenomena like storms, the temperature of air will vary along the day and the night according to a cyclic or periodic law. The maximum and minimum values, along with the characteristic time constant of the air temperature cycle depends from the geographical location and from the period of the year. The standard UNI10349 provide a simplified relationship, in tabular form, which give a reasonable estimation of the summer air temperature cycle, if maximum and minimum air temperatures of the site are available, as well as solar irradiance as a function of the position on the globe and of the day of the year. Figure 1 and 2 report an example of summer air temperature cycle and solar irradiance for a location in central Italy, estimated according to UNI10349. This data are the inputs for the following calculations. Maximum and minimum air temperatures were obtained by a local weather station.

Heat transfer from the external surfaces of a building or of a container

The sun irradiance provide an incoming heat flux which impinge the external surfaces of the storage building or of the container used for shipping or for temporary storage, raising their temperature above those of the surrounding environment. Convective heat transfer between the external surfaces of the building and the surrounding air is indeed a relevant contribution to the energy budget of the building envelope or of the container used for shipping or for temporary storage. Heat transfer coefficients may be estimated by means of empirical correlations like those proposed by Jurges,(Defraye et al. 2010) which include the effect of wind and are extensively used for building applications. The external surface will also lose heat through radiation toward all the other solid surfaces which are within its field of view (the terrain, other buildings, vegetation etc etc). Emissivity factor of 0.9 may be assumed as a rough estimate of the emissivity of real world gray bodies.

Therefore, the net heat flux from the exterior, as a function of time and surface's orientation may be estimated as:

$$\dot{q}''_{net,ext} = \dot{q}''_{sun\ irradiance} + h(T_{amb} - T_{wall}) + \sigma\varepsilon({T^4}_{amb} - {T^4}_{wall}) \quad (1)$$



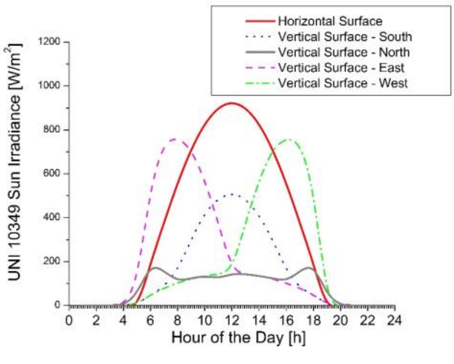


Figure 1 and 2: The daily cycle of air temperature, estimated according UNI 10349 and the daily cycle of sun irradiance at 44° latitude

The thermal environment inside a building or inside a container used for temporary storage

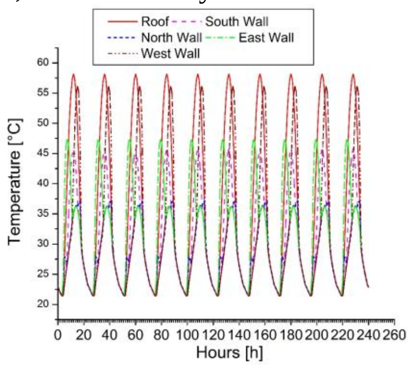
The wall and the roof of any enclosure exchange heat also with the air and with the objects inside. According to Steensma et al. (2008), values between 4 to 8 W/m2K give a reasonable representation of free convection heat transfer. Radiative heat transfer contribution may be accounted as well, assuming appropriate values for the view factor between the enclosure walls and the object surfaces.

$$\dot{q}''_{net,int} = h(T_{wall} - T_{air}) + \sum F_{wall,j}\, \sigma\varepsilon\left({T^4}_{wall} - {T^4}_{object\ j}\right) \quad (2)$$

For thermally thin walls, temperature gradient across it will be negligible and the diurnal temperature variation will closely follow the diurnal variation of the sun irradiance and, during the night, the hourly variation of air temperature. The energy balance equation for a thermally thin wall is:

$$\delta\rho Cp \frac{dT_{wall}}{dt} = \dot{q}''_{net,ext} - \dot{q}''_{net,int} \quad (3)$$

Since the net heat flux from the external environment is explicitly time dependent, this equation must be solved by means of numerical method. Since the internal heat exchange of the wall with the internal air and the internal objects depends on the temperature difference with air and objects itself, the energy balance of the walls must be solved along with their energy balance equations. In the present case, a simple Euler method was implemented, adopting a 60 s time step, which is adequate to simulate a week of daily long cycles. Further refinement of the time discretization led to the same numerical result. The above equation must be written for each wall and for the roof, while heat transfer through the bottom of the container, when lying on the ground, may be neglected. Since during summer terrain temperature is lower than that of air or of any sun exposed surface, and thus the ground may act as a heat sink, this choice may be considered to be conservative.



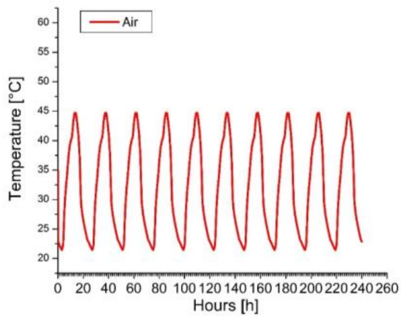


Figure 3 and 4: The daily cycle of the wall temperature and the daily cycle of the air temperature inside a 27 m^3 metallic enclosure.

Figure 3 shows the results of the transient heat transfer analysis applied to a 3m x3m x 3m enclosure used for storage (as it may be a container used for temporary storage). The walls and the roof are 3 mm thick steel plates and are exposed to sun irradiance, whose intensity and diurnal variation is given by the functions plotted in Figure 2. The enclosure is aligned along the N-S axis. Air temperatures are those plotted in Figure 1. Wind velocity is assumed to be 14 km/h (i.e. 7 knots). The surface of the roof reaches 58.2°C at midday, while its average value is around 35°C, which is 9 °C higher than average temperature of ambient air. This result is indeed in excellent agreement with the experimental result of Steensma et al. (Steensma et al. 2008) and with the simple rule proposed by Bowes (Bowes, 1966). Figure 4 shows the results of the calculation of the air temperature inside the 3m x3m x 3m enclosure. Even if the surface of the roof reaches 58.2 °C, the maximum predicted air temperature inside of the enclosure is 44.7°C. The average air temperature is estimated to be 31°C.

The temperature of a package of reactive substance

Let us consider a package of a liquid reactive substance, like the organic peroxide considered by Steensma et al., stored inside the above described metallic enclosure, for which the thermal environment has been already characterized as described in chapter 4 of the present work. The thermochemical and kinetic parameters of the liquid organic peroxide adopted in the present work are the same of Steensma et al. (Steensma et al. 2008). With this set of thermochemical parameters a 25 kg package of liquid organic peroxide will exhibit a SADT equal to 55°C, which is the highest SADT for which uncooled transport and storage may be allowed per UN regulations. The same calculations of chapter 4 have been redone including 1 m^3, 4 m^3 and 12 m^3 packages of the above mentioned self reactive substance. It is assumed that the liquid is perfectly stirred and thus the temperature of the package is assumed to be homogeneous. The energy balance equation for the package, which is assumed to be exchanging heat with the surrounding air through convection and with the surrounding walls through radiant heat transfer, is:

$$mCp\frac{dT_{package}}{dt} = \sum A_i h_i\left(T_{air} - T_{package}\right) + \sum A_i F_{package,i}\sigma\varepsilon\left({T_{wall,i}}^4 - {T^4}_{package}\right) + mQ_0 exp(-E/RT) \quad (4)$$

Figure 5 shows the results for the two package size considered. It is found out that even the biggest package considered in the present work remains subcritical (i.e. do not experience thermal run away) and that the bigger the package, the lower is the effect of diurnal **variations**. The maximum liquid temperature do not exceed 35°C and the liquid average temperature are close to 33°C. This value is quite close to the values predicted by Steensma et. al.., which used experimentally determined values for the wall temperature, but used directly the 24 hour averaged values. In order to assess the effect of the organic peroxide reactivity, the calculations have been repeated assuming that the liquid be inert (setting equal to zero the pre exponential factor). It is found that the average temperatures predicted for the reactive liquid are 1.4 K or less higher than the values predicted for the inert liquid: this is the same results obtained by Steensma et al..

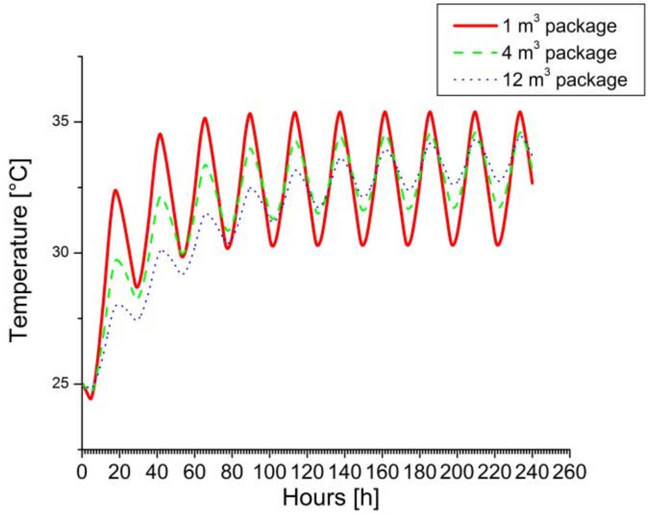


Figure 5: The daily cycle of the temperature inside a liquid organic peroxide stored in a 27 m^3 metallic enclosure.

Conclusions

This work presents a method to predict the thermal environment that develops inside sun exposed storage depots or containers during summer period in Italy. This method has been applied to a metallic enclosure with thin walls, to estimate the temperature of packages of various size of reactive substance stored inside the sun exposed metallic enclosure, in Central Italy. It has been found that even if the maximum temperature of the metallic walls may reach 58.2°C, its average temperature do not exceed 35°C, while **t**he maximum temperature in the package of liquid organic peroxides is around 35°C and the average temperatur**e** of the liquid organic peroxides are close to 33°C. Therefore, even a reactive substance with SADT equal to 55°C may be stored uncooled inside such enclosure. The results of this work confirms the conclusion reached by Steensma et..

References

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