POOL EVAPORATION OF HAZARDOUS SUBSTANCES IN INDUSTRIAL STORAGE DIKES: A STUDY ON SPATIAL AND TEMPORAL TEMPERATURE VARIATIONS AND ITS CONSEQUENCES

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ABSTRACT

Storage of hazardous products requires utilizing containment systems such as diking against the unintended release of these materials. In case of volatile compounds, the liquid contained by the dike will offer a large surface for evaporation. It is of major importance to calculate the evaporation rate since evaporation may create a toxic or flammable cloud. This study aimed to study the temperature distribution in a liquid pool during evaporation. Vertical and horizontal temperature distributions were recorded by a series of thermocouples and an infrared camera. Evaporation experiments were performed with acetone in a wind channel facility. Vertical experimental data highlight a thin cold liquid layer at surface which remains during the evaporation and the liquid level decrease. This influences strongly the evaporation rate. On the horizontal consideration, surface gradients were observed when cavity flow occurs. These gradients are not believed to influence significantly the overall evaporation rate. A focus was done on the error induced when considering only mean liquid temperature instead of a distributed profile on several correlations from literature.

INTRODUCTION

One of the major accident scenarios in industrial safety deals with hazardous product release following a loss of containment. In order to minimize the consequences of a release, all chemical or petrochemical facilities over a certain size or that handle over a certain amount of hazardous products are required to utilize containment systems such as diking and loading pads to protect against the unintended release of these materials. Diking is affected by legislation requirements and is defined in order to recover a certain amount of the product in case of catastrophic release. Generally, dikes are made of concrete, earth or clay, with a sealing system sufficiently impervious to contain the hazardous substance. Containment walls have to be high enough to contain all hazardous substance on a small area, but may not be too high in order that workers can easily see and step over the walls. A one meter (three feet) wall is considered as a good compromise. A significant release of hazardous product may therefore fill the dike on a significant height. In case of volatile compounds, the liquid contained by the dike will offer a large surface for evaporation. It is of major importance to calculate the evaporation rate since evaporation may create a toxic cloud, or a flammable cloud that can lead to worse domino effects in case of cloud ignition (fire, explosion). Many studies were performed in order to predict the evaporation rate of any volatile substance. The evaporation kinetics depends mainly on two parameters which are wind velocity and substance volatility. Since evaporation is an endothermic phenomenon, the temperature of the liquid pool will decrease with time until reaching a thermal equilibrium state [1]. To calculate the temperature drop and equilibrium state, it is frequently assumed that the liquid pool is perfectly mixed during evaporation and that the temperature is uniform. But no previous experimental focus was done on this assumption to demonstrate the hypothesis.

This study aimed therefore to study the vertical and horizontal temperature distribution in a liquid pool during evaporation in a cavity.

NOMENCLATURE

c	[g/m^3]	Mass concentration
D	[m^2/s]	Diffusion coefficient
k	[m/s]	Transfer coefficient
M	[g/mol]	Molar mass
m	[g]	Mass of liquid
P	[Pa]	Pressure
R	[J/K.mol]	Ideal gas constant
t	[s]	Time
T	[K]	Temperature
J	[J/m^2.s]	Heat flux
C_p	[J/g.K]	Heat capacity
A	[m^2]	Liquid surface area

Special characters

α	[m^2/s]	Thermal diffusivity
ϕ	[g/m^2.s]	Evaporation mass flux
ΔH	[J/g]	Evaporation enthalpy

Subscripts

0	At intial time
m	Related to mass
th	Related to heat
p	Related to pressure
sat	At saturation
∞	At infinite distance

evap	From evaporation (endothermic)
rad	From sun (radiative)
floor	From floor (conductive)
conv	From air (convective)

THEORY OF EVAPORATION

Evaporation rate is commonly defined as the mass flow rate from the liquid spilled substance to its gaseous phase. Evaporation mass flux is usually preferred and corresponds to the evaporation rate per surface unit. The phenomenon is described by two linked mass and heat balance equations.

Mass balance equation

The mass balance equation links evaporation mass flux Φ_m with liquid and vapor properties, air hydrodynamics and geometric properties. In most previous works [3], authors consider a boundary layer flow at the liquid surface and suppose a diffusion phenomenon with three different contributions:

- Mass diffusivity of vapor in the air or Fick's law, D_m, linked with concentration gradient;
- Thermal diffusivity of vapors in air D_{th}, linked with thermal gradient;
- Diffusivity of vapors linked with pressure gradient (D_p).

The global formulation is described as:

$$\Phi_m = -[D_m grad(c) + D_{th} grad(\ln(T)) + D_p grad(\ln(P))] \quad (1)$$

When dealing with evaporation from an open air liquid pool, the term linked with Fick's law becomes preponderant, and thus equation (1) becomes:

$$\Phi_m = -D_m grad(c) \quad (2)$$

Considering a linear concentration profile in the boundary layer equation (2) can be expressed as:

$$\Phi_m = k_m(c_{sat} - c_\infty) \quad (3)$$

Many empirical mass transfer coefficients k_m can be found in the literature[3], in different configurations:

- No wind [4][5]. This case corresponds to pure diffusion case in case of cold liquids;
- Boundary layer conditions [6][7][8]. This is the most studied case. Correlations involve either regression versus experimental data or heat and mass transfer analogies;
- Cavity flow. No empirical correlation could be found in the literature. Shehata and al. [9] present some general considerations about the local evaporation rate as a function of the wind velocity just before the pool and of the ratio between the length of the pool and the depth of the cavity.

In case of evaporation of a liquid into open space (assuming that air is renewed and do not get enriched with vapour), a common way to express the mass transfer equation is the following:

$$\Phi_m = k_m \frac{P_{sat}M}{RT} \quad (4)$$

The saturation pressure P_{sat} is a function of the liquid properties and temperature. P_{sat} may vary by several orders of magnitude and is a key parameter of evaporation. Liquid temperature results of a heat balance between the heat consumed by evaporation (endothermic phenomena) and the heat exchanged with the environment. However, most of the heat required for the evaporation is taken from the liquid itself, decreasing its temperature and by the same way the evaporation rate. An energy balance is therefore required to calculate the liquid temperature.

Heat balance equation

Heat balance equation describes enthalpy variation of the pool versus different heat fluxes exchanged with its environment and the energy consumed by evaporation. From Van den Bosch [3]:

$$mC_p \frac{dT}{dt} = A.(J_{floor} + J_{rad} + J_{conv} + J_{evap}) \quad (5)$$

The heat flux consumed by evaporation J_{evap} can be computed from the evaporation mass flux:

$$J_{evap} = \Phi_m.\Delta H_{evap} \quad (6)$$

The different contributions to heat exchange have to be computed separately. It is generally assumed that the heat flux from floor overrides the other contributions [3]. It is a transient heat flux quantified from the knowledge of the thermal properties of the floor (concrete, soil or other), the initial temperature profile of floor and liquid. It can be determined thanks to Fourier's law. Assuming the floor is a semi-infinite solid, the heat flux is quantified by:

$$J_{soil} = \frac{\lambda_{floor}(T_{0,floor} - T_{liq})}{\sqrt{\alpha_{floor}\pi t}} \quad (7)$$

This hypothesis is true while $\sqrt{\alpha_{floor}\pi t}$ is lower than the thickness of homogenous top layer of the floor. If not, the floor temperature must be computed through depth by finite differences near the surface in order to characterize the heat flux.

The radiative heat flux J_{rad}, is mainly due to solar radiations when the spillage occurs outside. In order to predict this heat flux, geographical coordinates of the location of the spillage, date and hour of the day and some weather characteristics are required [3].

The convective heat flux is a function of the temperature difference between the liquid surface and the air above it. The convective heat transfer equation between a fluid and a surface is employed:

$$J_{conv} = k_{conv}(T_{liq} - T_{air}) \quad (8)$$

Several correlations tend at expressing the heat transfer coefficient, linking this temperature difference to the heat flux, as a function of Reynolds and Prandtl numbers. Some authors consider the heat-mass transfer analogy to calculate k_{conv} from k_m, which is relevant in certain circumstances in boundary layer driven phenomena [3].

Evaporation rate prediction

Evaporation flow rate prediction requires computing equations (4) and (5) simultaneously. However, several points are tricky to estimate and entail a large uncertainty in the prediction.

The first point to consider is hydrodynamics above the liquid. Several previous authors focused their efforts on the hydrodynamic aspects of the problem of evaporation into a turbulent medium under varying degrees of turbulence. Two problems were investigated: (i) the variation of the rate of evaporation with the size and shape of the evaporating surface; and (ii) the variation of the rate of evaporation with the mean wind velocity in air streams possessing varying degrees of turbulence. But most authors considered the natural evaporation from a plane horizontal surface and neglected any dike effect. One of the most used equation to compute equation (4) is the equation of Mackay and Matsugu [7]. This empirical equation was proposed on the base of experiments performed at small scale without any dike. However, Forestier at al [2] showed that the hydrodynamics involving a dike differs significantly with the experiments performed my Mackay and Matsugu. Therefore a significant shift in evaporation flow rate is likely to occur.

Next, the heat balance was scarcely studied since the uncertainty relies more on the knowledge of the surroundings parameters of the evaporating pool than on theoretical considerations. On most cases, the floor temperature, composition and humidity are roughly estimated. Convection and radiation may be neglected in a first approach. Eventually, overestimating values are used in risk analysis to provide conservative values of evaporation rates.

Another issue concerns the crude hypothesis of perfect mixing in the liquid. Since evaporation takes place at the surface of the liquid, the top thin layer of liquid will cool quickly entailing natural convection cells into the bulk of the liquid. For this reason, some authors consider the liquid temperature as homogenous. A first objective of this paper is to check if this assumption is realistic, by measuring the vertical temperature gradient occurring in the liquid.

Another issue is the horizontal temperature distribution. Since surface temperature is tightly linked with local evaporation rate, a difference in local air hydrodynamics could lead to inhomogeneity in surface temperatures. Natural convection cells in the liquid could also create hot and cold zones at the surface of the liquid. Some works studied that point, in the case of water evaporation in natural environment. These studies are relevant to oceanography and limnology, where evaporation at the air/water interface can drive natural convection in the water bulk. The authors [10-13] measured the velocity and temperature in an evaporative convection flow. Temperature measurements were obtained at a point on the water surface, and velocity measurements were obtained at locations beneath this point. The author measured the root mean square of surface temperatures and observed a difference versus the wind velocity. However, the degree of correlation between these velocity and temperature measurements was investigated and revealed that there is no clear correlation between surface temperature distribution and air velocity. Other

parameters have to be considered, especially in case of dike effects.

As a consequence, this work focused on an experimental study in order to investigate the horizontal temperature distribution at the surface of the liquid and in a vertical axis depth. Experiments were performed with acetone at small scale.

EXPERIMENTAL SETUP

The different experiments involved a liquid pool evaporating under constant wind profile. Seven experiments were performed twice with two different setups. The wind velocity ranged from 3 m.s^{-1} to 4m.s^{-1} and the initial liquid temperature ranged from 277 K to 295 K. The first setup involved a thin layer of liquid (2cm) with a concrete floor under the liquid (5cm) (Figure 1). In tests 1;2;5;6 the floor was heated at 60°C (to simulate a liquid spill in summer midday), in test 3 and 4 the floor was cooled at 4°C (to simulate a liquid spill in winter), in test 7 there was no floor: the liquid was contained in a deep tank with wall insulation (Figure 2). In order to keep a constant wind velocity profile, the experiments were performed in a wind channel. Table 1 presents the summary of experiments.

Table 1 Summary of experiments

Experiment	1	2	3	4	5	6	7
Setup	1	1	1	1	1	1	2
Initial liquid temperature (°C)	22	22	22	4	4	4	15
Initial floor temperature (°C)	60	60	3	3	60	60	No
Wind velocity (m.s^{-1})	3	4	4	3	3	4	4
Air temperature (K)	288	288	288	288	288	288	288
Initial thickness (cm)	2	2	2	2	2	2	70
Evaporated mass (g)	311	358	264	248	278	333	170
Experiment duration (min)	96	70	101	150	73	47	302

No = no floor, insulated system

Instrumentation aimed at characterizing mass balance equation, thus, measurements focused on the different variables introduced in equations 4 and 5: mass measurements, liquid temperature, liquid surface temperature, wind velocity and distance between liquid surface and top edge of the bund.

- Mass measurements were performed thanks to laboratory scale (Kern 100S0.5, static error 0.5g)
- Liquid temperature measurements were performed with different thermocouples combs. These sensors are welded and calibrated in lab, their static error being 0.5 K. The spatial resolution reaches 0.2 cm for thin liquid pools (15 probes) and 2 cm in case of thick pools. (34 probes)
- A sonar sensor (Siemen BERO M18) measured step height between liquid surface and bunds.

In order to get a common wind profile between the experiments, the distance between top edge of the bund and wind channel floor is similar for every experiment and reaches 13cm. There is no cavity effect in setup #1 since the vessel was initially filled with liquid at wall level. On the opposite hand, setup #2 enabled to have a strong dike effect. Indeed, when the liquid level lowered, a cavity was created above the liquid and wind recirculation cells appeared. This point was controlled by particle image velocimetry [2].
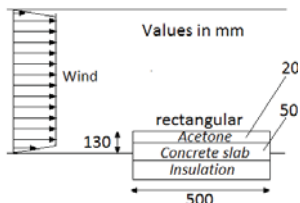
Figure 1 Configuration #1   **Figure 2** Configuration #2
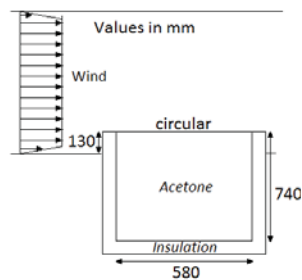
Many observations can be drafted from the experimental data. However, only the data about temperature distribution are presented and discussed in this work. Table 2 summarizes the different configurations that were analysed.

Table 2 Summary of configurations

	Initial time	Final time
Setup #1	No cavity effect	No cavity effect
	Thin liquid layer (2cm)	Thin liquid layer (2cm)
	Floor influence	Floor influence
Setup #2	No cavity effect	Cavity effect
	Thick liquid layer (74cm)	Thick liquid layer (74cm)
	No floor influence	No Floor influence

RESULTS AND DISCUSSION

Results are presented in two sections, horizontal surface temperature distribution and vertical depth temperature distribution. The influence of the observations is then discussed in a last section.

Surface temperature distribution

Figure 3 and Figure 4 present surface temperature during test 3 measured with an infrared camera. The emissivity of acetone was measured as 0.86. Figure 3 reveals convection cells in the liquid, with puffs of warmer acetone rising to the surface.
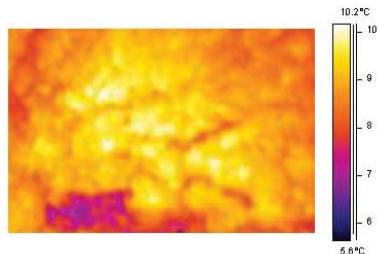

Figure 3 IR picture during test 3

The temperature varied slightly in a range of 5°C. Figure 4 plots temperature on a line across the surface in wind direction at different time steps. Two lines are separated by 5 minutes. The temperature drops by tens of degrees with remain quite homogenous horizontally.
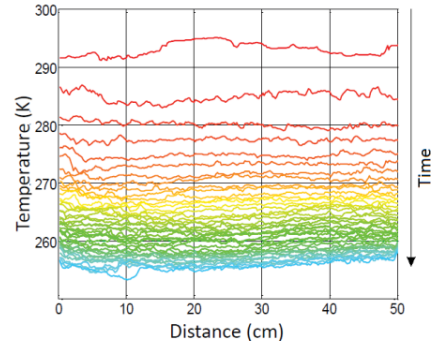

Figure 4 Horizontal temperature profile test 3

A cavity effect was observed in test 7. This cavity was revealed by particle image velocimetry [2] but can also be seen on the infrared picture on Figure 5. Two dark zones can be clearly observed, corresponding to lower surface temperatures. The zones correspond to areas located close to the wall, which was observed previously[14][15]. The surface temperature profile along a horizontal line in the wind direction is drawn on Figure 6. The temperatures vary clearly in both zones, the zone 1 being larger than zone 2. The difference in temperature between the cold zone and the central zone is 3°C.
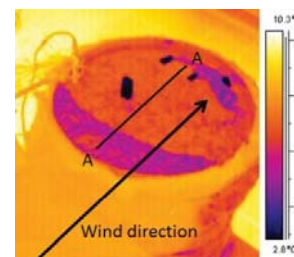

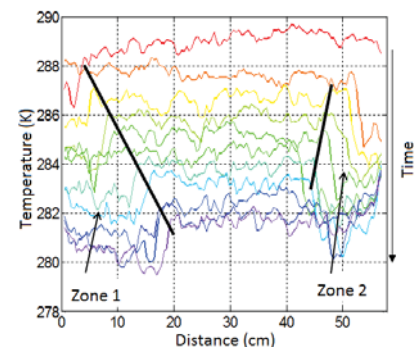**Figure 5** IR picture in configuration #2 setup

Figure 6 Horizontal temperature profile test 7

Vertical temperature distribution

The vertical temperature profile was measured by a comb of thermocouples, separated from 2cm each other. A temperature profile against time is drawn on Figure 7. The temperature

appears to be constant in the bulk of the liquid. However, temperature gradients can be observed at the surface of the liquid.

A focus on upper thermocouples is given on Figure 8. All temperatures follow the same trend except for the upper five (annotated T34 to T30, T1 being at the bottom of the liquid). The temperature of these five thermocouples decreases significantly just before crossing the interface.

It has to be noted that the temperature drop is sharper for the first thermocouple (T34) than for the fifth one (T30). This temperature drop could be explained by three reasons:

- A cold liquid layer reaches the thermocouple, since the level of liquid lowers and since a significant cooling occurs at surface;
- The wet thermocouple get through the interface and is cooled by drying, entailing a temperature drop of the thermocouple;
- The thermocouple gets through the interface and remains in a cold vapour layer above the liquid surface.
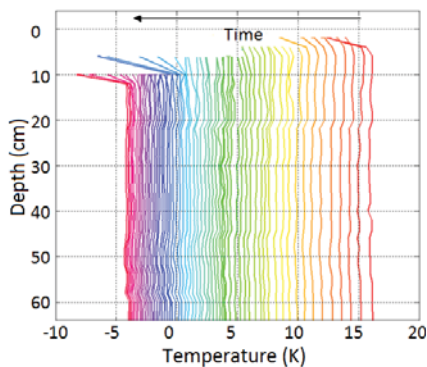

Figure 7 Vertical temper e test 7

Each reason considered alone could explain the temperature drop. However, even if it is likely that the three phenomena occur consecutively and cool the thermocouple with different importance, a parallel study not reported in this work showed that a wetted thermocouple (by acetone) will not follow the temperature drop trend shown on Figure 8. Moreover, when the thermocouple is in vapour phase, it indicates a colder temperature than air temperature (less than 280K instead of air temperature 288K).
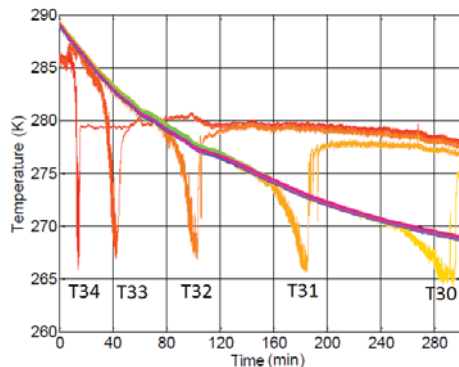

Figure 8 Temperature of upper thermocouples (test 7)

These data indicate that two cold layers exist on either side of the interface. The temperature difference between surface and the bulk of the liquid can exceed 5 or even 10°C. It has to be noted that this cold layer temperature cannot be correctly measured by infrared camera since the thickness is too small for a sufficient emissivity; the measured surface temperature is highly influenced by the bulk of the liquid.

Consequences on evaporation flux prediction

Experimental results show that temperature gradients appear during the evaporation. Temperature is a key parameter in vapour pressure (Equation 4) but also in the mass transfer coefficients k_m (equation 7). Since the measurement of surface temperature is a tricky task and since most authors neglected the liquid cold, most correlations predicting evaporation mass transfer were established from the temperature of the bulk instead of the cold layer surface. This method presents the advantage of being consistent, unlike any attempt aiming to measure the temperature of the cold layer.

Most correlations from literature were established on regression schemes from experimental data. Therefore, these grey box based correlations contain by nature the necessary correction to predict the right flow rate from the temperature of the bulk of the liquid instead from the surface temperature. If the physics of evaporation depends on surface temperature and not on the bulk of the liquid temperature, a right evaporation rate could however be assumed to be computed from the irrelevant temperature of the liquid thanks to the regression scheme.

But this assumes that the temperature distribution and stratification in the liquid is identical in any configuration. Since the physics of the phenomena is incorrectly represented by using the temperature of the bulk instead of the surface, how to consider that the prediction is right whatever the liquid depth and evaporation rate? A sensitivity analysis was performed on most used correlations [7;16-21] in order to check the influence of a wrong estimation of the temperature on the evaporation prediction. Results are given on Figure 9.
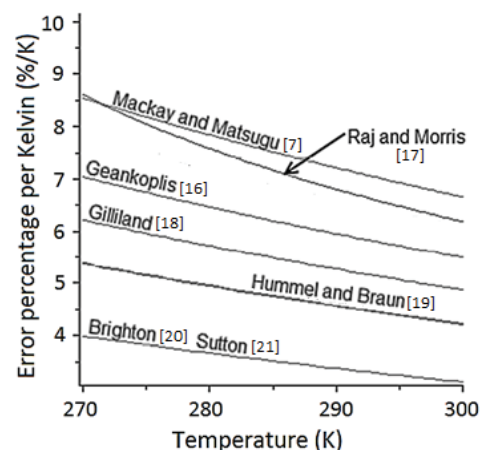

Figure 9 Influence of temperature error on evaporation flow rate

This figure shows the error expected while computing the evaporation rate from a temperature estimation error of 1K, for

temperature varying in the range [270-300] K. This range covers most evaporation temperatures. The correlation of Mackay and Matsugu appears to be the most sensitive to an error of temperature estimation, with an error rising 9% for 1K error.

Figure 8 shows that the difference in temperature between the bulk of the liquid and the surface varies from 15°C at the start of evaporation to only 5°C after 6 hours of evaporation. So, it is unlikely that the Mackay and Matsugu correlation is able to correct the wrong use of bulk temperature with two different temperature differences. By assuming that this correlation was fitted on the first part of the phenomena (first hours), the error in temperature could occur at longer times. A ten degrees Celsius error may entail an error of 70% in the evaporation rate prediction.

About the surface gradient temperature occurring when a cavity flow is created, experiments showed that the temperature gradient is very small, some degrees Celsius. Since the surface involved may be assumed to be small in comparison with the whole evaporation surface, a small effect on the evaporation prediction has to be expected.

CONCLUSION

This study aimed to study the temperature distribution occurring during the evaporation of a liquid contained by dikes. The experimental data showed that a surface temperature gradient may be observed close to the walls of the dike, and entailing a temperature difference of some degrees Celsius.

A cold liquid layer was measured with a maximum value at the early step of evaporation and decreasing with time. Most correlations use the temperature of the bulk of the liquid which is wrong in principle. This assumption could entail a large error on the evaporation rate, but it is not very clear how the existent correlations correct this principle method by regression scheme. Others issues need further efforts to better understand the evaporation phenomena. A cold vapour layer was observed above the liquid surface and could influence the evaporation rate. The cavity effect has a major importance on mass transfer coefficient and is actually poorly understood.

These points are of interest in a scientific consideration. But large scale evaporation experiments should be performed in order to investigate the accuracy of existent models to predict the evaporation and to show if further work will be necessary or not to improve the risk assessment in case of a volatile liquid release.

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