

EVAPORATION OF AMMONIA FROM AQUEOUS SOLUTION SPILLS

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ABSTRACT

One of the major accidents that can occur in the process industry or in the transportation of hazardous materials is the spill of a toxic liquid, with the consequent evaporation and atmospheric dispersion. To estimate the possible effects of such an accident, the evaporation rate must be estimated.

Diverse authors have studied the evaporation from pools of pure liquid or of hydrocarbons or oil. However, very few experimental data are available on the evaporation of a volatile substance from an aqueous solution.

In this communication data are given on the evaporation of ammonia from an aqueous solution with an initial concentration of 30% (mass). An experimental set up was devised to study the influence of air speed (ranging between 1 and 5 m s⁻¹) and solution temperature on the ammonia evaporation rate. The variables measured were the speed, temperature and humidity of air, and mass, concentration and temperature of the solution; these variables had to be continuously registered, due their rapid evolution in the first steps of each test, the most important period in the event of an accidental spill.

The weight of solution in the vessel decreased quickly at the beginning, this indicating high evaporation rates, and afterwards the process proceeded more and more slowly as the ammonia concentration in the solution decreased. The solution temperature evolved as follows: initially it decreased significantly, reaching a minimum and afterwards increasing continuously. This behavior has been explained by considering the existence of three steps: I) High ammonia evaporation rate, decreasing the enthalpy of the solution. II) As the temperature and concentration of the solution decreases, the evaporation rate decreases as well and the temperature reaches a minimum. And III) The evaporation rate keeps decreasing, while the transfer of heat towards the solution, from the air and the tray, increases, this rising the temperature. The existence of these different periods can be important from the point of view of analyzing the risk associated to the possible generation of a toxic cloud in the event of a toxic solution spill.

Keywords: liquid spill, release, evaporation, ammonia, aqueous solution, accident, toxic dispersion.

1. Introduction

Major accidents associated to process and storage plants, as well as to the transportation of certain materials, are essentially fires, explosions and toxic releases. In such events, the physical effects of the phenomenon (thermal radiation, blast, concentration/duration of toxic cloud) depend on diverse circumstances: material properties, release condition –liquid, gas/vapor, two-phase flow–, amount released and release type –instantaneous, continuous. As for the consequences, their severity is a function of the effects intensity and duration and of their interaction with the vulnerable elements (people, equipment and environment). Thus, an important aspect when the risk associated to a hypothetical accident is analyzed, is the so-called “source term”, i. e. the amount or flowrate of flammable or toxic material released.

For a given accidental scenario, the source term is usually established according to diverse criteria originated from the expertise; a typical example is the assumption of a given diameter for a hole in a vessel or of a given discharge rate from a relief device.

In the event of a liquid spill, unless if ignition takes place in the first moment, an important issue is the evaporation of volatile compounds. The evaporation flowrate, together with the prevailing atmospheric conditions, will determine the possible formation of a flammable or toxic cloud. And this flowrate will depend essentially on two variables: the spill surface and the evaporation rate.

Several authors have studied the evaporation from pools of pure compounds. A pioneering work (Sutton, 1934) proposed a theoretical model to predict the evaporation velocity from a liquid spill in a turbulent atmosphere. Eckert and Drake (1959) proposed as well an expression to estimate the evaporation rate. Mackay and Matsugo (1973) performed an important experimental work. Later on, Kawamura and Mackay (1987) proposed a new expression. Other equations were also proposed by Brighton (1990) and U. S. EPA (1999). Diverse authors have published experimental results on the evaporation from pure liquids, as well as from hydrocarbon and oil spills (MacKay and Matsugo, 1973; Stiver and Mackay, 1984; Stiver *et al.*, 1989).

However, there are very scarce data on the evaporation of a volatile compound from an aqueous solution, even if accidents have occurred involving this event. Only Mikesell *et al.* (1991) published data on the evaporation of ammonia from aqueous solutions. In this paper experimental results on ammonia evaporation from such solutions are discussed.

2. Experimental set up

An experimental arrangement (Figure 1) was devised to study the influence of the main variables on the evaporation rate: temperature, concentration, air speed.

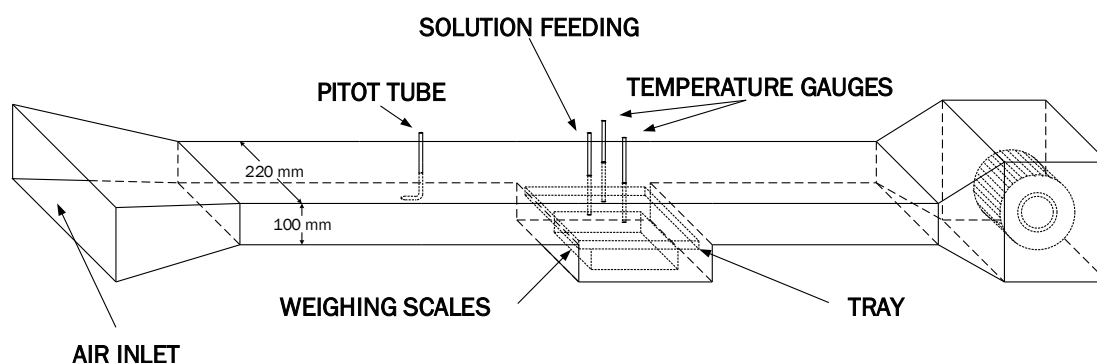


Figure 1: Illustration of the experimental set up.

In the experimental set up (Figure 1), air flowed through a rectangular duct (220 x 100 mm), designed to minimize the turbulence, to the evaporation chamber.

The air was sucked by a fan located downstream. In this chamber (volume: 6.2 l) there was a tray with the ammonia solution. This tray, with a volume of 289 x 190 X 10 mm and thermally insulated, was located on a digital weighing scales; the solution weight, together with the temperatures measured, was continuously registered through a data acquisition system (Field Point, National Instruments). This continuous registration was necessary because of the rapid evolution of the variables in the first steps of each test, the most important period in the event of an accidental spill.

The solution surface was parallel to the air stream and leveled in such a way to minimize turbulences. The tests were performed with an initial concentration of ammonia of 30% in mass. The air speed ranged between 1 and 5 m s⁻¹, a range of special interest from the point of view of risk analysis: at higher air speed the atmospheric dispersion is quite important and the analysis of the toxic impact has no interest, while at lower speeds the influence of wind is almost negligible. The variables measured were the speed, temperature and humidity of air, and mass,

concentration and temperature of the solution. Air temperature varied between 25 and 28 °C and its relative humidity ranged between 53 and 55%. Air speed was measured with a hot wire (TESTO 480) located at the evaporation chamber entrance; its humidity was measured with an electronic hygrometer (TFA 30.5005). The ammonia concentration was determined by refractometry (Atego-Smart I).

The amount of condensed water was determined from the difference between its initial and final mass. The initial mass of water was known and, as the solution mass and concentration were continuously registered, the amount of water in the solution at any moment was also known.

3. Evaporation process

The variation of the percentage of weight loss and the ammonia concentration as a function of time have been plotted in Figure 2 for three air speeds. The weight of solution in the vessel decreases rather quickly at the beginning, this indicating the existence of high evaporation rates (this initial high rate implied a certain difficulty in measuring during the first moments of each test).

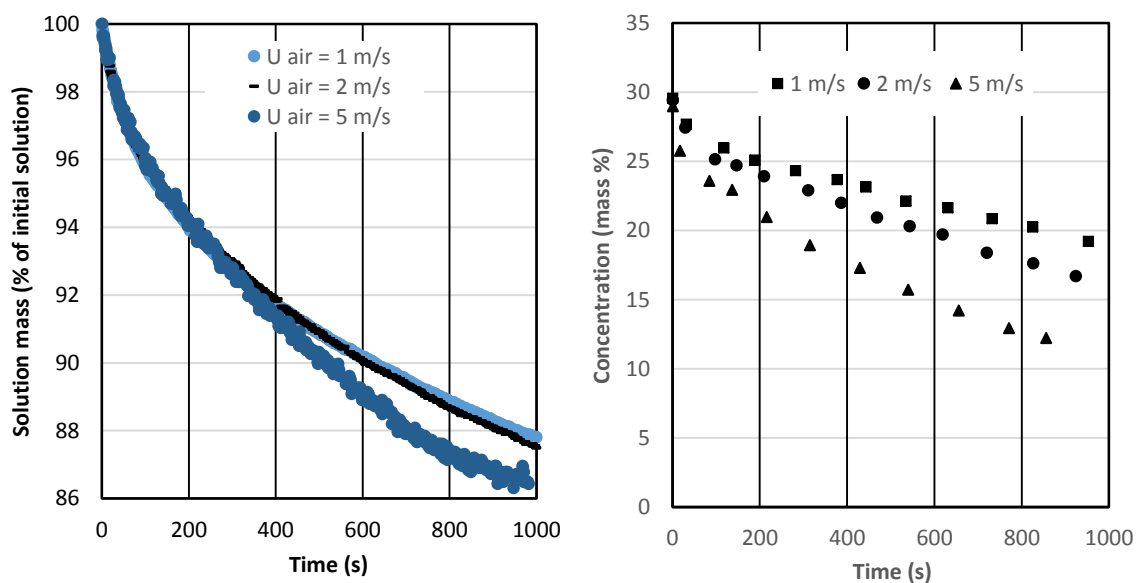


Figure 2: Variation of the relative mass of solution and liquid concentration as a function of time and air speed.

Afterwards, the process proceeds more and more slowly as the ammonia concentration in the solution decreases and the temperature in the liquid upper layer decreases as well. The influence of air speed on the evaporation rate, as can be observed in this figure, is relatively small.

An important aspect is the evolution of the pool temperature; this has been plotted as a function of time in Figure 3 for three air speeds. As ammonia evaporates, it takes the vaporization heat from the liquid, thus reducing the pool temperature; this effect increases with the evaporation rate. However, as evaporation proceeds, the temperature of the solution reaches a minimum and afterwards starts to increase again, the increasing rate depending on the velocity at which air moves above the solution surface.

It can be observed that there is a significant cooling of the liquid pool during the first minutes – corresponding to high ammonia vaporization rates–, reaching temperatures below 0 °C. After reaching a minimum, the temperature gradually increases during the rest of the test. This minimum reaches lower temperatures and appears sooner at higher air rates; this behavior is important as, in a real large-scale spill, it will have an influence on the dynamics of the generation of a toxic cloud.

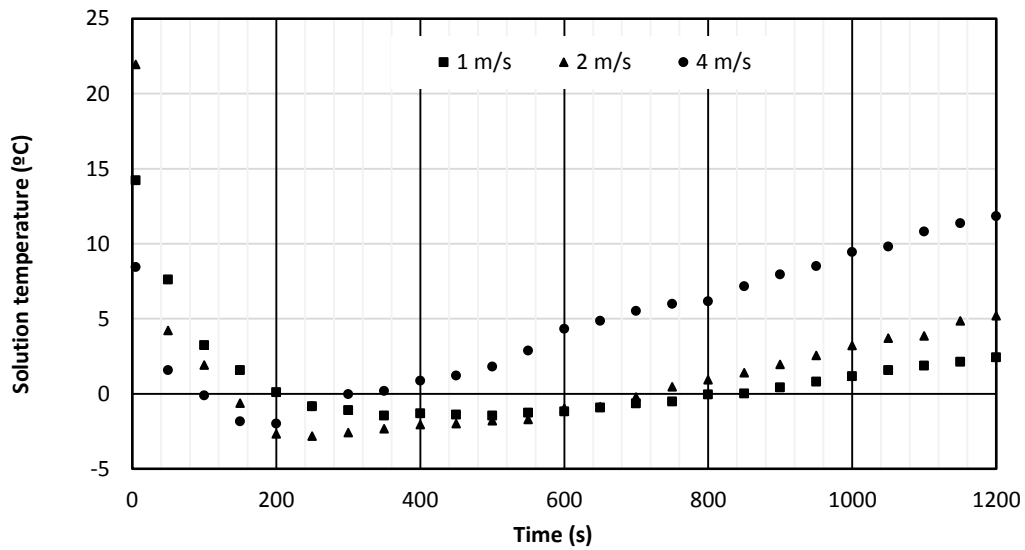


Figure 3: Variation of solution temperature at different air speeds.

4. Discussion

The dynamics of the evaporation process shows clearly the influence of ammonia concentration, with a high evaporation rate during the first period, which decreases then with time. The influence of air speed is also significant.

The evolution of temperature as evaporation proceeds can be explained in terms of three different steps as follows:

Step I) A high ammonia evaporation rate implies a significant decrease in the enthalpy of the solution, with the associated decrease of its temperature.

Step II) The temperature decrease, as well as the progressive reduction of the ammonia concentration in the solution, originates a decrease in the evaporation rate of ammonia; as a result, the cooling velocity of the solution decreases. Simultaneously, due to the low temperature of the solution, the heat transfer rate from the environment to it –from the vessel by conduction, and from the air essentially by convection– increases. This situation leads to a minimum value of the solution temperature (Figure 4).

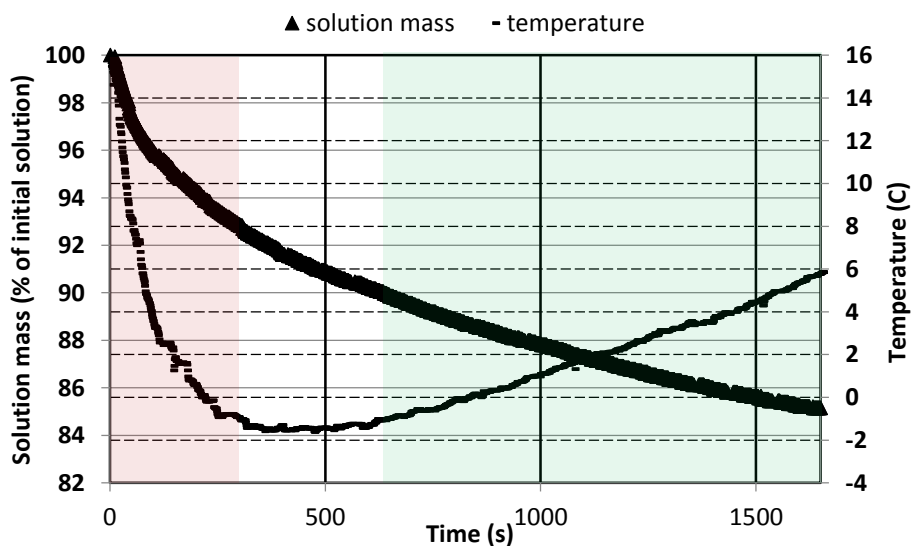


Figure 4: Evolution of evaporation process and temperature with time (air speed: 1 m s^{-1}).

Step III). Ammonia evaporation rate keeps decreasing while the environment heats more and more the solution; as a consequence, its temperature progressively increases towards that of the air stream.

During most of the tests duration, the evaporation of water from the aqueous solution was not possible, as the temperature of the upper liquid layer was lower than the air dew point. However, the inverse process, i.e. the condensation of water from the air humidity due to the low solution temperature, was confirmed; this phenomenon must be taken into account to avoid an underestimation of the ammonia evaporation rate.

The existence of these three different periods can be important from the point of view of analyzing the risk associated to the possible generation of a toxic cloud in the event of a toxic solution spill.

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