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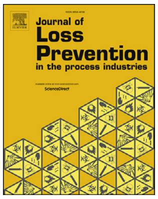

Small-scale field spill experiments of liquid nitrogen, oxygen and their mixture on concrete surface

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ABSTRACT

This paper presents the findings of small-scale experiments (5–15 kg) of cryogenic liquid spills on a representative industrial grade diking concrete. Physical properties of the substrate, *i.e.*, the thermal conductivity (k) and heat capacity (Cp) of the concrete were measured in the range of −160 °C to 50 °C using guarded hot plate and differential scanning calorimeter (DSC), respectively. Vaporization rate of liquid nitrogen (LN_2), liquid oxygen (LO_2) and a mixture of 80% v/v LN_2 and 20% v/v LO_2, (*i.e.*, liquid air - LAir) were studied on the same concrete. Convective and radiative heat transfers were limited by insulation. The contribution of conductive heat transfer from the concrete substrate for the vaporization of cryogenic liquids was studied. The effect of preferential boiling was observed when the liquid air was spilled.

1. Introduction

In the case of an accidental spill of cryogenic liquids, vapor will form due to the heat transferred from substrates (conductive), atmosphere (convective) and (/or) from radiation sources (*e.g.,* the sun, fire). Different cryogenic materials may cause similar or different types of hazardous situations, owing to the nature of formed vapor cloud. For example, liquefied natural gas (LNG) vapor cloud may cause many hazardous situations, such as – (a) an asphyxiating environment when the cloud stays closer to the ground at low temperature, (b) An early ignition of LNG vapor may result in flash fire and/or pool fire, (c) a late ignition may increase the severity of the event by causing a vapor cloud explosion in a highly congested space. Liquid nitrogen (LN_2) vapor cloud may result in an asphyxiating environment. An individual exposed to such conditions may suffer from irreversible health condition when the oxygen concentration goes below 19.5% (Crowl and Louvar, 2011). Liquid oxygen (LO_2) and its vapor are very reactive and promote violent burning or oxidizing flammable and combustible materials.

Industrial standards such as NFPA 59A (NFPA, 2013) specified the use of dikes or impoundment area around the LNG containers to prevent uncontrolled dispersion of LNG and its vapor. The most common dikes floor material is concrete. If LNG containment tank fails, the cryogenic liquid will boil up due to heat transferred from dike floors and the walls. The severity of a spill event would depend on the size of the vapor cloud. Therefore, it is important to study the vaporization rate to predict the risk in the cryogenic processing facility.

The experimental study suggests that conductive heat transfer from the solid substrate to the liquid pool is the main mode of heat transfer during pool vaporization (Drake and Reid, 1975). Other studies suggest convection and solar radiation can be accounted for less than 5% of the total mass vaporization (Burgess and Zabetakis, 1962; Cavanaugh et al., 1994; Webber and Ivings, 2010; Woodward and Pitblado, 2010). Some argue whether convective heat transfer is so negligible heat transfer to the pool (Véchot et al., 2012). Nevertheless, it is well accepted that conduction heat transfer from the substrate is a major heat transfer source in cryogenic pool vaporization, at least at the beginning of the spill. Briscoe and Shaw developed a model based on the assumption that the conductive heat transfer from the ground is the dominant heat transfer mechanism (Briscoe and Shaw, 1980). A proper use of such model requires the thermophysical characteristics of the ground material

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(Drake and Reid, 1975). A theoretical vaporization models, whether simple as unidirectional (1-D) Briscoe & Shaw model or advanced as CFD study by (Ahammad et al., 2016a, b), experimental investigations are still necessary to validate the aforementioned theoretical models (Mannan et al., 2016).

Understanding the importance of LNG vaporization “source-term” in determining the severity of loss of primary containment, Reid and Wang (1978) have studied this parameter for LNG on insulated dike floors. In their study, pure methane was considered as LNG. As a result, the effect of mixture boiling on vaporization rate was left uninvestigated. Industrial practice includes addition of an insulating lining on the spilled concrete surface made by incorporating numerous small bubbles into the dike floor, adding insulating material into the concrete mix, using polystyrene foam board between concrete pours *etc*. These approaches can significantly reduce the thermal conductivity of the substrate. Knowing the thermal conductivities and heat flow characteristics of the regular concrete will help in designing insulation needs. Thus, the study of the cryogenic source-term on a non-insulated concrete ground remains an important area for research. The source-term investigation results will be helpful in determining a spill consequence severity and the risk of the processing facility.

An early review of cryogenic spill data was conducted by (Prince, 1983) and a recent one by (Thyer, 2003). They have reviewed 39 cryogenic spill experiments reported in the literature. Their analysis showed that seven of these experiments were lacking in capturing detail information to be usable. A concrete substrate was used in 7 instances among the 32 hazardous material spill studied. Chlorine, hydrogen, oxygen, and water were used in three studies. In the remaining 4 studies, pure methane was used by referring as LNG, and the insulated concrete floor was used for three cases. This might result in some prediction error as the literature suggests that multi-component mixtures may have a significant influence in vaporization (Conrado and Vesovic, 2000). The remaining one study did not characterize the substrate concrete. Therefore, we have concluded that vaporization of cryogenic mixtures on concrete requires more investigation.

Recently, Olewski et al. (2013). have studied liquid nitrogen vaporization when spilled (up to 19 kg) on a concrete block with dimensions of 0.5 × 0.5 × 0.4 m, however, it was with pure liquid nitrogen only.

This study focuses on the vaporization of liquid nitrogen (LN_2), and liquid oxygen (LO_2) spills on concrete. Literature suggests that influence of multi-component mixtures can be significant for other cryogenic liquids such as LNG and LPG (Conrado and Vesovic, 2000). Thus, to understand the influence of multi-component, a mixture of the initial composition of 80% LN_2 and 20% LO_2 (v/v) is used to contribute in generating experimental knowledge of cryogenic vaporization source-term, which in turns will help the existing models in validating their assumptions. In this study, the liquid mass vaporization, temperature, and heat flux profiles inside the substrates were investigated. Thermo-physical characteristics of the concrete substrate were determined at cryogenic temperatures.

2. Experimental work

A series of experiments were performed in a wind tunnel of Qatar Petroleum's Fire Station 2 at Ras Laffan Industrial City, Qatar. Experiments were performed in April and May 2014. The first day included the spill of liquid nitrogen (LN_2) only and was performed on April 22nd, 2014. The second experiment included the spill of liquid nitrogen and liquid oxygen mixture (LN_2-LO_2) and was performed on April 28th, 2014 and the third experiment included the spill of liquid oxygen (LO_2) only and was performed on May 13th, 2014.

2.1. Experimental setup

Three cryogenic liquids, *i.e.,* liquid nitrogen (LN_2), liquid oxygen (LO_2) and liquid air (LAir), which was a mixture of 80% liquid nitrogen and 20% oxygen (volume by volume, v/v), were poured onto a concrete pad of area size 400 by 400 mm and depth of 650 mm. Steel plates were used to construct a containment (400 mm × 400 mm x 300 mm) on the top of the concrete to hold a liquid above a concrete pad. The walls of the pad and containment were insulated using 3-inch polystyrene foam to reduce a horizontal heat transfer. This horizontal heat flux was also measured by two heat flux plates installed between concrete and polystyrene and was found to be negligible in comparison to heat flux provided to the pool from the concrete. The open top of liquid containment was partially covered with polystyrene during the experiments to reduce convective heat transfer from air to the liquid pool. A 30 feet long insulated connecting hose, with a vapor and liquid separator at the open end, was used to transfer the liquid from the cryogenic liquid tank to the experimental setup. A schematic diagram of the experimental setup is shown in Fig. 1 and some pictures in Fig. 2.

Eleven thermocouples of type N and two heat flux measuring sensor plates of Hukseflux, HF-01 type, with a sensitivity of ± 1084 $\mu V/W/m^2$, were placed at four layers inside the concrete substrate. The exact locations of the thermocouples (TC) and heat flux sensors (HF) are given in Table 1. TC-110, TC-111, TC-113, TC-115 thermocouples and HF-284 heat flux sensor were placed in the first layer beneath the boiling liquid at an approximate depth of 25 mm. Heat flux sensor was located almost in the center of the block cross-section, whereas thermocouples were located several centimeters off the center (see Table 1 for exact locations). In 2nd layer, TC-108, TC-114, TC-106 thermocouples and HF-285 heat flux sensor were placed at an approximate depth of 110 mm. In the 3rd layer, at a depth of 220 mm, TC-107, and TC-109 thermocouples were placed. Finally, in the 4th layer, at a depth of 620 mm, TC-112, TC-116 thermocouples were placed. It should be noted that the heat flux plate sensors measure both the temperature and the heat flux at its location. This whole instrumented set-up was connected to a data acquisition system.

2.2. Thermo-physical properties of the concrete

Industrial grade concrete, which was used in the construction of Testing Prop-5 at Ras Laffan Emergency Safety College in Qatar, was also used to construct the concrete substrate of this experimental setup. The concrete was made out from the aggregate of limestone rock, washed sand and dry Portland cement with the ratio of 3/2/1, respectively. The water content in the concrete was 6.4%. The average density of the concrete was determined as 2335 kg/m^3. The thermal properties of the concrete were experimentally obtained at NETZSCH Instruments Testing Laboratory, Burlington, MA, for a temperature range from -160 to 50 °C. Standard procedures (ASTM C 177-10), steady-state heat flux measurement and thermal transmission properties by means of guarded hot plate apparatus, utilizing a Holometrix Model, were followed to measure the thermal conductivity. Two concrete slabs, of the same composition and dimensions of 305 by 305 mm square with a thickness of 43 mm were used to test for thermal conductivity. Fig. 3 shows the dependence of thermal conductivity on the mean temperature between the top and bottom surfaces. The reported results have the uncertainty of lower than 7%. It is observed that thermal conductivity increases linearly between -161 and -66 °C with a rate higher than at a temperature range from -41 °C to 50 °C (Fig. 3). Thermal conductivity slightly decreased between -66 and -41 °C.

Four additional small concrete samples were prepared to determine a concrete, specific heat capacity. The mass of the