CHEMICAL ENGINEERING TRANSACTIONS

VOL. 53, 2016

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Valerio Cozzani, Eddy De Rademaeker, Davide Manca

ISBN 978-88-95608-44-0; **ISSN** 2283-9216

DOI: 10.3303/CET1653058

Experimental Study of Submerged Leakage from a Shipwreck Involving Floating Chemicals Cargo

Laurent Aprin*[a], Frederic Heymes[a], Miriam Cosenza[b], Pierre Lauret[a], Pierre Slangen[a], Stephane Le Floch[c]

[a]LGEI, Ecole des Mines d'Alès, avenue de Clavières, 30319 Ales Cedex, France
[b]Università degli Studi di Roma "La Sapienza", Piazzale Aldo Moro 5, 00185 Roma, Italia
[c]Cedre, Centre de Documentation, de Recherche et d'Expérimentations sur les pollutions accidentelles des eaux, 715 rue Alain Colas, 29200 Brest Cedex 2, France
laurent.aprin@mines-ales.fr

The aim of this study was to characterize a chemical release from a submarine breach by quantifying the flow and defining a representation of the dispersion of the chemical leaving the breach. Experimentations carried out consisted in gravity release of chemical in a water column. To achieve this, two different experiments campaign were performed. A small test bench with a double chamber focused on the submerged liquid flow through the orifice. The second experimental apparatus consists of an immerged Plexiglas tank in the large water column (CEC) to study the draining mass flow rate and the fluid flow at the breach level. Silicone oils with different physical properties and di (2-ethylhexyl) adipate were tested to simulate the chemical discharge. Mass flow rate and draining time were measured and a simply model based on Reynolds number power law was proposed to characterize the discharge coefficient. The second experimental phase focuses on the flow behaviour in the water column. Droplet size distribution is evaluated by optical technique and two distributions laws are bring out.

1. Introduction

Hazardous and Noxious Substances (HNS) are "any substances other than oil". HNS covers a wide range of chemical substances that have diverse intrinsic qualities (such as toxicity, flammability, corrosiveness, and reactivity with other substances or auto-reactivity) and behaviours in the marine environment acting as evaporators, sinkers, floaters or dissolvers. More than 2,000 HNS are regularly carried by sea either in bulk or packaged form. In addition to pipelines, the constantly growing fleet of chemical tankers, bulk carriers and container ships, whose ever-increasing size is cause for concern, exacerbates the risk of accidents and spills into the marine environment. The efforts made by IMO (and EMSA) towards greater consideration of this situation testify to this. In fact, given the importance and complexity of the matter, all European Regional Agreements, DG ECHO and EMSA have recently jointly identified the issue of improving preparedness and response to HNS spills as a key priority issue and area of concern. For the European zone and France in particular, the Channel and the Mediterranean Sea are two zones of intense maritime traffic. However, since 1990, the number of accidents with chemicals increases and involves new risks (explosion, toxic releases…). The Ievoli Sun sank about 16.7 km from north Casquets by 70 m deep with chemicals including 3998 tons of styrene, 1 027 t of methyl ethyl ketone (MEK) and 996 t of isopropyl alcohol (IPA) (Law et al., 2003). In addition, the ship contained propulsion fuel (160 t of Intermediate Fuel Oil (IFO) and 220 t of diesel). The release quantities from vessel were 400 t of Styrene, 100 t of MEK and 996 t of IPA. This wreck is not the only example of a chemical loss, in 2001 the Balu sank with 8000 t of sulfuric acid in the Bay of Biscay at 4,600 m of depth; in 2006, the Ece discharged 10,000 t of phosphoric acid by 70 m deep

When ship sinks with a breach both in the hull and in the tank containing floating chemicals, leakage causes an ascending plume of substances toward the surface regarding the volume mass of the bulk. The release of a floating liquid from a vessel aground on the seabed generally corresponds to a release without injection speed and depends only on the fluid properties. Then, during accident, stakeholders have simple questions as quickly manage the crisis and how long will submerge tanks of chemical leak. The experience clearly shows that for shipwreck, a large amount of chemical is typically released into the sea, but some product remains on board and continues to leak at very slow rate. Due to the multiple parameters (shape and position of breach on the vessel, physical and chemical properties of the chemical) it is extremely difficult to determine how long a submerged vessel will leak. Observations on wrecks show that chemical is leaking from along the ship's piping, out vents or simply from cracks or holes in the vessel. If the product's density is very close to seawater, this process can occur very slowly. The second question concerns the duration for chemical to reach the surface. The droplets velocity depends on the relative density of the chemical to the seawater, water turbulence, droplet size and shape. It is noticed that sinking ships can also release air bubbles that rise quickly to the surface. If chemical is pushed with the air bubbles, the chemical droplets can rise much faster. In droplets plumes, there is a slip velocity between rising fluid particles and the surrounding liquid within the plume area. The most used law to calculate this slip velocity is based on the Stokes' law but it approximates only small droplets considered as perfect spheres. Clift et al. (1978) showed that the shape of fluid particles could be approximated as a sphere for the small size range (smaller than 1 mm), an ellipsoid in the intermediate size range (1 mm to 15 mm), and a spherical-cap in the larger size range. They also demonstrated that shape has an important impact on the particle terminal velocity. For spherical particles the terminal velocity is influenced by the viscosity of the ambient fluid; for ellipsoidal droplets the interfacial tension is the key factor, while neither the viscosity of the ambient fluid or interfacial tension influence spherical-cap bubbles.

2. Literature survey

2.1 Breach leakage modelling

As mentioned by Fthenakis and Rohatgi (1999), the discharge rate of a liquid only driven by buoyancy can be calculated by the Bernoulli's relation, assuming a steady behaviour and a perfect fluid.

$$p + \frac{1}{2}\rho V^2 + \rho g H = constant \tag{1}$$

Applying this equation on the discharge of a liquid into air gives the Torricelli's law (2) and the corresponding volumetric flow rate (3).

$$V = \sqrt{2gH}\ ;\ Q = S\sqrt{2gH} \tag{2}$$

With V the ejection velocity at the orifice, g the acceleration due to gravity, H is the height of liquid in the tank, Q the volumetric flow rate and S the orifice surface. As fluids are not perfect, the expressions should be corrected with the discharge coefficient C (Beek et al. 1999)

$$Q = CS\sqrt{2gH} \tag{4}$$

This coefficient fits the equation from the contraction of the jet (contraction coefficient C_c) and from the energy losses due to friction (speed coefficient C_v). The discharge coefficient C is defined as the product of speed and contraction coefficients $C=C_c\ C_v$. It depends mainly on the thickness and rupture profile of the breach (Van den Bosch and Weterings 1997; Beek et al. 1999). The shape of the breach (circular, rectangular) has little influence on the discharge coefficient: according to the differences between the coefficients for a circular orifice of diameter d and a square hole of side equal to d is less than 1%. Also, (Brater et al. 1996) studied the influence of the orifice orientation (vertical or horizontal) and concluded that is has few effect on the coefficient.

These simple equations only consider the release of a liquid into air. In literature, most studies about liquid leakages in another liquid only considered the case of a water leak in water (e.g. flood barriers, locks) or submarine pipelines ruptures (oil in seawater). In the first topic, (Brater et al., 1996) concluded that the immersion of the breach does not affect the discharge coefficient and the volumetric flow rate Q can be deduced by equation (3). In the second case, (Baptista et al., 2007) proposed an empirical model to predict it, depending on geometric considerations and interfacial tension of the liquids. This phenomenological model can however only be used in case of oil release in seawater.

2.2 Liquid release fragmentation

The released liquid leads to the formation of drops directly at the orifice or at the end of a cylindrical jet. The knowledge of the droplets size distribution is necessary to determine their fate in the water column (rising and solubilisation velocity). Droplets diameters depend on their mode of formation, which directly depends on the liquid ejection velocity of the liquid at the breach level. Grant and Middleman (1966) observed three different modes of droplets rupture which depend on flow rate and system properties. The dripping mode is observed

for very low ejection speeds, the drops are formed at the orifice, with a homogeneous size proportional to the size of the orifice. As liquid velocity increases, a jet is formed. Surface tension forces are dominant and the surface of the jet undergoes disturbances that form drops of different sizes; the jetting mode. For very high ejection speed, the atomization process is observed. The influence of the surface tension forces decreases, the hydrodynamic forces become dominant: the jet disintegrates into droplets directly at the orifice.
For underwater buoyancy liquid discharge, the jetting mode mainly governs the draining tank. Although size for the dripping mode can be calculated thanks to the work of (Harkins and Brown 1919; Horvath et al. 1978) and for the atomization configuration by (Babinsky and Sojka, 2002), model exists to characterize the droplet size distributions for the jetting mode. It noticed that Clift et al. (1978) give a definition to estimate the maximum diameter of a droplet according to its physicochemical properties (5).

For $\mu_d/\mu_c > 0.5$

$$d_{frag} = 4\sqrt{\frac{\sigma}{\Delta\rho}} \qquad (5)$$

3. Experimental setup

3.1 Breach release experiments

Experiments were developed at two degrees. The first step consisted in evaluating the discharge coefficient through different diameters and shapes orifice for submerged flow. Floating and non-soluble chemical were used to achieve these tests, di (2-ethylhexyl) adipate (DEHA) and three different silicon oils. These commodities have density lower than seawater and various dynamic viscosities. These fluids were tested to put in evidence viscous phenomena during underwater releases. The physico-chemical properties for the different fluids are listed on Table 1.

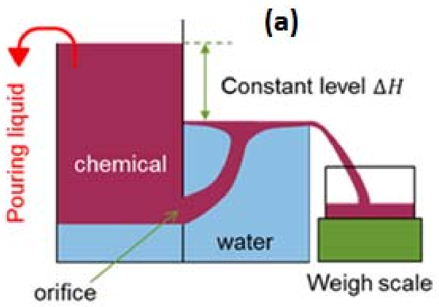
Table 1: Chemicals properties for tested fluids

Chemical	Density (kg.m^{-3})	Dynamic viscosity (Pa.s)
Silicon oil (Rhodorsil 47V5)	910	4.50 10^{-3}
Silicon oil (Rhodorsil 47V20)	950	19 10^{-3}
Silicon oil (Rhodorsil 47V50)	959	48 10^{-3}
DEHA (Bis(2-ethylhexyl)adipate	922	13.2 10^{-3}

The apparatus presented on figure 2a is based on the study performed by Dugdale (1997). A wall with a thin orifice separates two chambers filled for the first one by the chemical and for the other one by water. The liquid remains constants in each compartment with overflow system. A flap system keeps the hole closed and enables to start the test. After spilling over the overflow, chemical mass flow rate is measured by weight scale with 1Hz data rate acquisition. Circular orifices diameters varying between 6mm to 60mm and two rectangular orifices of 10mm x 70 mm and 20mm x 70mm were also tested.

3.2 Seawater column experiments

The second phase of experiments consisted in gravity releases in a water column. The tests were designed to analyze the release hydrodynamics and the droplets size characterization for different configurations and various orifice diameters. di (2-ethylhexyl) adipate (DEHA), was used to achieve these tests. Experiments were performed in the *Cedre* Experimental Column (CEC). A high speed video recording system was used to measure droplets diameters and velocities rinsing in the water column. All the detailed explanations of experimental setup and optical characteristics are presented in previous works (Aprin et al., 2014). The ejection of a liquid from a ship tank corresponds to a gravity release. In order to represent this type of discharge into the water column, a transparent box was immerged in the CEC. This box was equipped with a specific system to perform instantaneous and passive release (Figure 2b). This box is modified to study the influence of the configuration (horizontally or vertically). This tank had three openings (1, 2 and 3 in Figure 2b). The first opening was provided with a guillotine-like valve actuated by cable system. The other two openings allowed testing different scenarios of tank release with several orifices. In this work two configurations were used: a single orifice located in position 1 and a double orifice system with orifices 1 and 2 open. Different orifice shapes and sizes were investigated: five circular orifices (6, 13, 20, 30, 40, 60 mm diameter) and three rectangular holes (70x10, 70x20 and 70x30 mm). The released flow rate was deduced from weighting the immerged tank and considering fluid statics theory. Measurements were performed with an accuracy of 5 g and a sampling rate of 5 Hz.



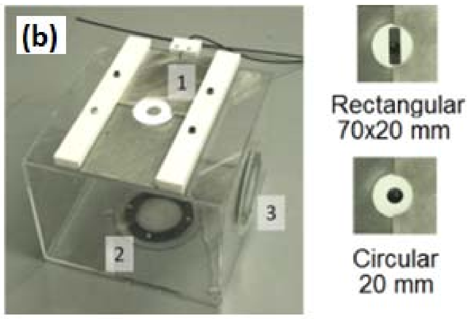


Figure 2: (a) Description of the submerged release apparatus and (b) Illustration of the transparent box to experiment gravity release in the water column

DEHA is a transparent liquid with refractive index close to that of water. Direct visualization with a single video camera is therefore not sufficient to see the DEHA flow in water. Thus an optical technique, the retro-reflective shadowscopy, based on the visualization of refractive index changes was set-in to contrast and highlight drops in water (Slangen et al., 2015).

4. Results and discussion

4.1. Breach leakage modelling

The study of underwater chemical leakage through orifice was studied with submerged release apparatus (Figure 2a). This experimental setup let a constant level of chemical in the left chamber involving a higher hydrostatic pressure than water vessel. The local imbalance due to the different densities of the fluids involves a chemical outflow reaching the water surface and pouring over the wall. The amount of rejected product is then measured by weigh scale. Figure 3a presents the V5 silicon oil mass variation versus time for a various holes diameters. This figure clearly shows a linear variation for the mass of chemical release for all tests and an increase of mass flow rate as the hole diameter increases.

According the Dugdale's approach, the total rate of energy dissipated by the viscous forces in this system can be written by equation (6)

$$p.Q = \frac{C\mu Q^2}{{r_0}^3} \tag{6}$$

Where p is the hydrostatic pressure through the orifice (Pa), Q the volumetric flow rate at breach ($m^3.s^{-1}$), r_0 the orifice radius (m), μ the chemical dynamic viscosity (Pa.s) and C the discharge coefficient. Thus, this approach allows to measure the discharge coefficient through orifice. Figure 3b presents the variation of discharge coefficient according to the Reynolds number (7).

$$Re = \frac{\rho U d}{\mu} \tag{7}$$

Where ρ and μ are respectively the density ($kg.m^{-3}$) and the dynamic viscosity (Pa.s) of chemical, U is the chemical velocity at breach ($m.s^{-1}$) and d the orifice diameter (m). Figure 3b shows the variation of discharge coefficient for all the tested fluids and holes diameter according the Reynolds number. Dugdale's results are also plotted on the Figure 3b. It is clearly observed two different behaviors. For Reynolds numbers less than about 10, viscous forces are dominant and discharge coefficient remains constant (*C~3.2*). For Reynolds numbers higher than 10, inertial forces becomes dominant on viscous forces and the discharge coefficient follows a simply power law ($C=0.14Re^{0.95}$).

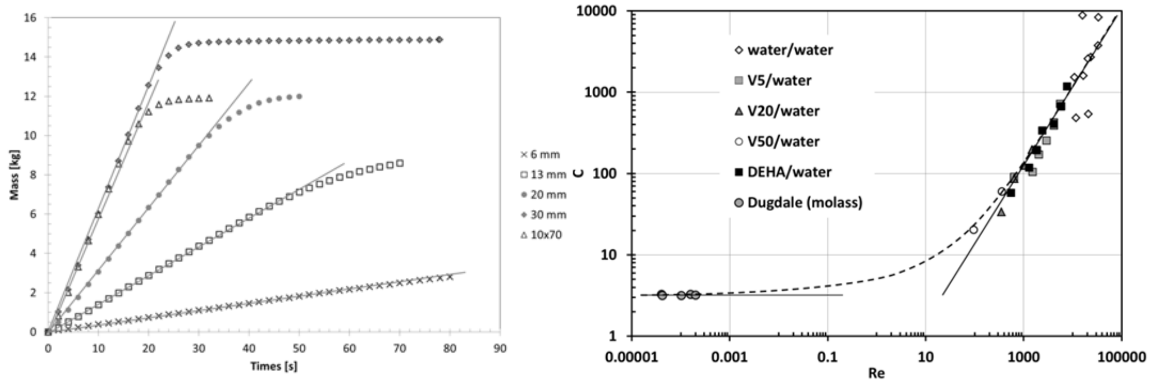


Figure 3: (a) Variation of V5 silicon oil mass vs. time (b) Variation of Discharge coefficient C versus chemical Reynolds number.

4.2. Dispersion in the water column

The analysis of the droplet size was performed on one hundred uncorrelated images acquired at the top of column (Figure 4a). The Figures 4b shows the droplet sizes distributions obtained for all the tests. All the data was concatenated and one or two log-normal distributions fitted on these measures. It noticed the maximum size of the droplets was less than 22 mm, which agrees with the maximum size of 19.1 mm obtained by equation (5) (Clift et al. (1978). For all results, a large proportion, up to 50% in number, of droplets with diameter less than 5 mm was observed. The corresponding log-normal laws for 8 measured distributions are presented in Figure 4b. These distributions are very similar and show two types of distributions following the release rate. For discharge volumetric flow rate less than 10^{-4} $m^3.s^{-1}$, droplets size distribution is well represented by a unimodal law in the range diameter between 4 to 5 mm. For discharge volumetric flow rate up to 10^{-4} $m^3.s^{-1}$, Droplet distribution is represented by bimodal law with two representative droplets size, small droplets of size less than 5 mm and a second droplets class between 10 to 12 mm. Thus these distributions appear to be independent of time and orifice size and can be represented as one or two log normal laws depending on the rate of ejection.

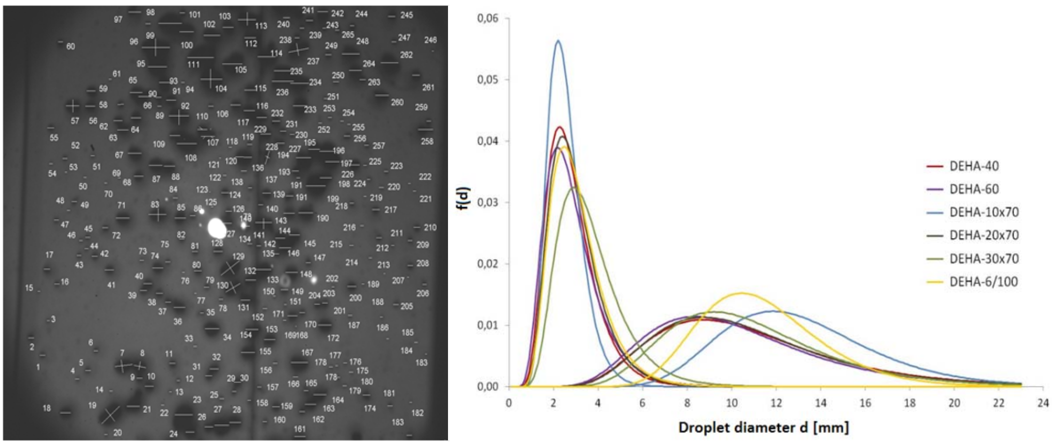


Figure 4: (a) Picture of DEHA droplet at the top of the column and handmade analysis of droplet diameter. (b) Droplet size distribution in the water column.

5. Conclusion

The main purpose of this study was to characterize a chemical release from a submarine breach by quantifying the flow and defining a representation of the dispersion of the chemical leaving the breach. Experimentations carried out consisted in gravity release of a chemical contained in a submerged tank located in a water column. The experimental study of the discharge flow rate from a breach allowed the calculation of the discharge coefficient at the orifice. Two regimes are observed, for low Reynolds number viscous forces are dominant and discharge coefficient is constant. For higher Reynolds numbers, inertial forces are preponderant and discharge coefficient follows a simply power law.

The second part of the present study concerns droplet size distribution in the water column. Two types of distribution are observed: for volumetric flow rate greater than 10^{-4} $m^3.s^{-1}$, the distribution has a single-mode and for smaller flow rate, the distribution presents two modes. These distributions can be represented with one or two log normal laws. Moreover, the maximum droplet size measured for DEHA drop is 22 mm. Future work will focus on finding analytical solutions to predict release flow rates and drops distributions.

Acknowledgments

This project is a part of a European Project entitled “Improving Member States preparedness to face an HNS pollution of the Marine System (HNS-MS)”. This project is supported since 2015 by the European Commission's Humanitarian aid and Civil Protection department (DG-ECHO).

Reference

Aprin L., Heymes F., Fuhrer M., Slangen P., Dusserre G., Le Floch S., 2014, Experimental analysis of n-butanol behavior in seawater due to chemical release from marine shipwreck, Chemical Engineering Transactions, 36, 19-24 DOI: 10.3303/CET1436004

Babinsky, E., Sojka, P. E., 2002, Modeling drop size distributions, Progress in Energy and Combustion Science 28(4): 303-329.

Baptista, R. M., Quadri, M. B., Machado, R. A. F., Bolzan, A., Nogueira, A., Lopes, T. J., Mariano, G. C., 2007, Effective interfacial tension and geometrical parameters relationships for the description of oil leakages from submarine pipelines, Chemical Engineering Transactions, 28: 401-406.

Beek, W. J., Muttzall, K. M. K., Van Heuven, J. W., 1999, Transport Phenomena - Second Edition, John Wiley & Sons.

Brater, E. F., King, H. W., Lindell, J. E., Wei, C. Y., 1996, Handbook of hydraulics, 7th Edition, McGraw Hill.

Clift, R., Grace, J.R., Weber, M.E., 1978. Bubbles, Drops, and Particles. New York, Academic Press

Harkins, W. D., Brown, F.E., 1919, The Determination of Surface Tension (Free Surface Energy) and the Weight of Falling Drops: Surface Tension of Water and Benzene by the Capillary Height Method. Journal of the American Chemical Society 41: 499-524.

Horvath, M., Steiner, L., Hartland, S., 1978, Prediction of drop diameter, hold-up and backmixing coefficients in liquid-liquid spray columns. The Canadian Journal of Chemical Engineering 56(1): 9-18.

Fthenakis, V. M, Rohatgi, U. S., 1999, A model of liquid releases from a submerged vessel, Journal of Loss Prevention in the Process Industries 12 (1999) 437–449

Slangen, P., Lauret, P., Aprin, L., Heymes, F., Lecysyn, N., 2015, Optical characterizations of falling droplets interacting with shock wave, in: 10th Pacific Symposium on Flow Visualization and Image Processing. pp. 1–12.

Van den Bosch, C. J. H., Weterings, R., 1997, Methods for the calculation of physical effects: due to releases of hasardous materials (liquids and gases): Yellow Book (Third edition). The Hague, The Netherlands, Committee for the Prevention of Disasters