Assessment of the behaviour of oil in the tanks of the "Prestige" in the Atlantic deep sea*

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SUMMARY: The sinking of the Prestige supertanker off the coast of Spain in November 2002 led to one of the most devastating oil spills ever worldwide. Between 13,800 and 37,500 tons of oil still remain inside the wreckage. The mid-range and long-term behaviour of oil temperature and leaks were analysed to decide whether the oil could be pumped out in the current conditions. Past and present conditions near the wreckage were analysed, considering depth, water pressure, estimated oil behaviour inside the tanks, and possible future hull corrosion. A similar analysis may be useful in the management of future wreckages.

Key words: oil spill, computational fluid dynamics, deep sea, tanker wreckage, Atlantic Ocean

RESUMEN: ESTUDIO DEL COMPORTAMIENTO DEL COMBUSTIBLE EN LOS TANQUES DEL PRESTIGE EN EL FONDO ATLÁNTICO. – El hundimiento del super-petrolero Prestige frente a las costas españolas en Noviembre del 2002 provocó uno de los vertidos con más consecuencias ambientales entre los producidos hasta la fecha. Entre 13800 y 37500 toneladas de petróleo permanecen aún dentro del pecio. Este trabajo analiza el comportamiento a medio y largo plazo del fuel confinado y del que podría liberarse por una grieta del casco. Se analizaron las condiciones actuales y pasadas cerca del pecio, y se simuló el comportamiento fluidodinámico del petróleo dentro de los tanques y la posible corrosión futura del casco. El análisis permite obtener una serie de conclusiones sobre la viabilidad de un hipotético bombeo del fuel hacia el exterior del casco. Esta clase de análisis podría ser útil en la gestión de posibles pecios futuros.

Palabras claves: vertido de petróleo, dinámica de fluidos computacional, océano profundo, pecios de petroleros, Océano Atlántico.

INTRODUCTION

The 26-year-old single-hull Prestige was carrying more than 77,000 t of heavy fuel oil. It sailed spreading oil from 13 to 19 November 2002 (Serret *et al.*, 2003) before it broke into two pieces and sank 240 km off the northwest coast (province of Galicia) of Spain (Fig. 1) on 19 November 2002. The disaster had devastating ecological consequences for the coastal ecosystem of more than 3,000 km of shoreline. This includes the death of between 65,000 and 130,000 birds (SEO, 2003) and long-term effects on marine mammals due to bioaccumulation of contaminants in the food chain (Mazet *et al.*, 2001). The socio-economic effects are also significant, as 12% of the work in Galicia is directly or indirectly related to the sea (García *et al.*, 2003).

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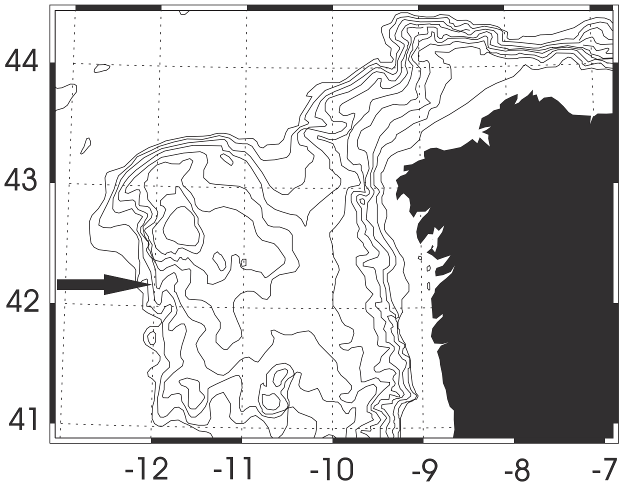

FIG. 1. – Bathymetric map of the sinking location, at 42°10'N, 12º04'W. The first depth isoline corresponds to 200 m; the following ones are displayed every 500 m to 4500 m.

Every year supertankers are the cause of major ecological disasters, such as those caused by the Aegean Sea (Daniel, 1995), the Erika (Cedre, 2002a) and the Exxon Valdez (Harrald, 1995; Hartung, 1995). Due to our energy demands projected worldwide, tanker traffic will nearly double by 2020. Though supertankers are the largest moving structures ever built, the system of constructing, inspecting and certifying them is a relic of the 19th century (Martin, 2002).

Computational fluid dynamics (CFD) models have often been applied to forced and free convection problems in different fields. Here we use a CFD code to approach the Prestige situation with a model in order to estimate the behaviour and evolution of the fuel temperature and leaks.

PROBLEM DIAGNOSIS

Figure 1 shows the position of the Prestige wreck in the North Atlantic Sea off the coast of Galicia. The fore part of the Prestige is situated on a deep-sea plateau at 3,820 m depth. The bow is positioned on the foot of the marine slope at 3,545 m depth at a distance of 4 km (CCA, 2003). For simplification, we approximate the two parts of the wreck as one sunken hull at a depth of 3,700 m. Our focus lays on mid-range and long-term behaviour of the oil remaining in the tanks, which will not be affected by this approximation.

The estimated water pressure on the Prestige's hull is about 380 atmospheres. The hull was designed to resist a pressure of 20 to 30 metres of water column (~2-3 atm). Therefore, the pressures inside and outside the oil tanks have almost certainly equated due to the hull's deformations, structural collapses around the air bags, and water intrusions into the tanks (CCA, 2003).

Oil is released by leaks from the wreck because it is more buoyant than seawater at that pressure (compare 1,012 kg m^{-3} versus 1,045 kg m^{-3}) following the Archimedes principle. The resulting buoyancy pressure is: $P_m = (\rho_f - \rho_w)gh$, where: ρ_f and ρ_w are oil and water densities, respectively; g is the gravity constant and h is the maximum height of the oil in the tank.

Our experiments, performed with actual Prestige oil samples placed in a cooling device and cooled to a temperature of -10ºC suggest that no oil solidification will occur in the tanks under current conditions, as expected (Bohannon and Bosch, 2002), even when the oil cools to the surrounding water temperature.

The oil buoyancy pressure is less than 6,050 Pa (33 kg m^{-3} x 9.8 m s^{-2} x 18.7 m = 6,047 Pa), whereas the hull's resistance is more than 30 times higher (CCA, 2003). The flow rate is dependent on the oil viscosity and the buoyancy force of the oil column which depends, in turn, on the oil volume remaining in the tank. Thus, as the amount of oil decreases due to leaking, the rate of leaking decreases too. From an initial flow rate of 125,000 kg per day, it can be estimated to decrease to 300 kg per day if the initial leaks are present after a ten-year period. Therefore, the preliminary decision to patch the leaks was satisfactory as a short-term solution but fails to take into account the future rusting of the hull. The Spanish Scientific Committee (CCA, 2003) estimated a period of 23 years until the Prestige's hull will rust through and new holes will appear. This does not account for the additional degradation that might be caused by proliferation of the bacterium *Desulfovibrio desulfuricans* inside the tanks. This specific bacterium is a metallivore, producing an acid capable of destroying more than 2 mm of steel per year (Martin, 2002), giving a total time of only 4 years (assumed minimum steel thickness: deck 20.0 mm; bulkhead 9.6 mm; sides 15.5 mm.) until new holes will form. The presence of this bacterium can be determined by taking water samples near the Prestige's hull and measuring the concentration of H_2S (Lloyd *et al*., 1999).

DEVELOPMENT OF THE MODEL

The behaviour of temperature, density, and oil flow through leakages in the tanks of the Prestige was modelled on an ORIGIN 3000 supercomputer using the commercial program FLUENT 6 (Fluent, 2002). This code numerically simulates fluid flow and heat transfer in complex geometries, based on a numerical technique called computational fluid dynamics, or CFD. The solution-adaptive grid capability is particularly useful for accurate prediction of flow fields in regions of large gradients, such as boundary layers. Geometry and mesh were created using GAMBIT, the Fluent companion pre-processor. Boundary conditions, initial flow state and the converged solution were obtained in the form of velocity and temperature fields at different times during the cooling process after specification of material properties.

The simulated flow regime is natural (or free) convection, a term used to characterise a flow induced by density differences in a fluid, which are usually produced by temperature differences. In our case, thermal gradients were caused by oil cooling that would occur due to heat transfer through the tank boundaries to the external water masses. These masses were assumed to flow with a speed of 2.5 cm/s. This value is in the range of values observed recently by the Spanish Institute of Oceanography (Díaz del Río *et al.*, 2003) at a depth of 3700 m: 3.5 cm/s with a standard deviation of 2.4 cm/s. The motion is a result of the imbalance of gravity and pressure forces inside a fluid particle arising from the density differences.

Momentum and heat flow may be calculated by means of a laminar or a turbulent submodel. However, due to the low Reynolds number, the fluid flows in a laminar regime and no turbulent approach is needed. The fluid motion increases the rate of heat transfer above the value that would be expected with only conduction heat transfer in absence of motion. Determination of heat transfer is more difficult due to the nonlinear dependency of fluid flow and heat transfer (Daville and Jaupart, 1993).

The Rayleigh-Bérnard Convection scheme was applied because simulated phenomena correspond to natural thermal convection in highly temperature-dependent viscosity environments (Manga and Weeratne, 2001).

The problem was modelled as a two-dimensional flow in a rectangular cavity (232 x 22 x 10 m).The four tank walls were considered adiabatic at the surrounding water temperature (2.6ºC), and the initial oil temperature was estimated at 50ºC. Thus, two convective flows were generated: one due to the vertical walls and one due to the instability close to the horizontal walls, typically in the form of a series of counter-rotating parallel rolls.

From the linear analysis of Rayleigh, the Rayleigh number can characterise a flow field:

$$Ra = \frac{g\beta \Delta T L^3}{\nu\alpha}$$

where g is the acceleration due to gravity, β the thermal expansion coefficient, ΔT the temperature difference between the wall and the oil, L the walls separation, and ν and α the kinematic viscosity and thermal diffusivity respectively. For low Rayleigh numbers viscous forces in the fluid exceed buoyancy force. Therefore, the fluid is stable and remains stationary. However, at the critical value of the Rayleigh number, buoyancy forces balance the viscous forces, so at Rayleigh numbers above the critical value the fluid layer becomes unstable and convection occurs. For Rayleigh-Bénard convection between solid boundaries, the critical Rayleigh number (*Ra*) was calculated using the linear theory of Jeffreys. The result is 1,707.8. At initial oil conditions Ra is 3.7×10^{13}, so a convective flow is created (Norris, 2000). More details about the convective instability process can be found in the pioneering book of Chandrasekhar (1961).

Computational mesh

The grid used consists of quadrilateral elements in the case of the 2D simulation and tetrahedral ones in the case of 3D simulations. The computational mesh used is shown in Figure 2. The base distance between nodes in the centre of the simulated tank is 100 mm. This distance is decreased by a geometri-

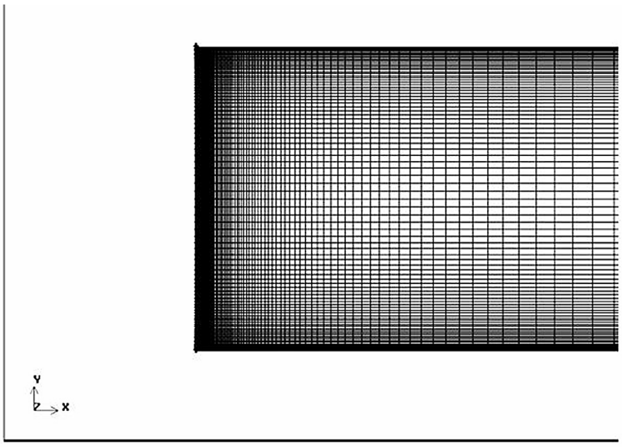

FIG. 2. – Irregular grid of 100,000 nodes used in the 2-D simulation. A succesive dilatation ratio of 1.05 is used in both directions to increase the resolution in the boundary layers close to the walls. The resolution at the centre of the domain is 10 cm.

cal factor of 1.05 towards the tank walls, giving a total of 100,000 nodes to simulate the whole system. In the 3D case we use the same relation, giving a total of 1.5 millions of nodes.

The temporal step of the simulation began by 1 second for the first two hours of evolution with 1,000 iterations per time step. After that we simulated the second hour with different time steps (from 10 s to 20 minutes with 1,000 iterations). Finally, we chose a time step of 15 minutes with 1,000 iterations per step that gives an agreement with the 1 s time step results better than 97%. The same time step (15 minutes) was used to simulate the whole cooling process.

The actual problem is a three-dimensional one with a very complex geometry. We used some approaches in geometry to simplify it. To test our approaches we compared our results with results from a more complex geometry (Hontañon, 2003) and with experimental measurements of fuel temperature and flow rate (CCA, 2003).

OIL PHYSICO-CHEMICAL PROPERTIES

The remaining oil in the Prestige's tanks is a residual product from oil distillation, after visbreaking and cutter stock. The nomenclature is *heavy oil, type M-100* (Russian name), *number 6* (American), and *heavy fuel number 2* (French).

Several institutions have performed oil chemical analysis, and the results in terms of four groups are shown in Table 1. Saturated hydrocarbons, resins, naphthalenes, and nearly 50% polycyclic aromatic hydrocarbons (PAHs) confer the fluid a great stability and toxicity. The light fraction of PAHs tends to change through time due to volatilisation, solubilisation, and photo-oxidation. The heavy molecular weight of PAHs implies that these compounds are hardly biodegradable and display a high teratogene power (IARC). This group of PAHs has the possibility of accumulating in fish and sea food due to their stability (Corina, 2003). From the fluid dynamics point of view, this fraction will not flow in conditions below 5ºC due to the observed percentage of resins and asphaltenes; this corresponds to 20.6 to 34.7% of the fuel.

The physical properties of the oil are those related to the transport and heat transfer inside the fluid. We use 1,717kJ/KgK as the specific heat of heavy oil and 0.123 W/mK as the thermal conductivity.

Oil density variations must be quantified to take natural convection effects into account. Experimental data from Cedre (2002b) were used to obtain the following empirical adjustments that were extrapolated to a pressure of 380 atm. The correlation used for the density is:

$$\rho(kg / m^3) = 1016.3 - 1.4252 \times T,$$

and for oil viscosity is:

$$\mu(kg / m - s) = \\ = 102.8 - 6.6267 \times T + 0.1515 \times T^2 - 0.0012 \times T^3, \\ 50^\circ C < T < 20^\circ C,$$

$$\mu(kg / m - s) = \\ =1000 - 193.95 \times T + 13.114 \times T^2 - 0.2933 \times T^3, \\ 20^\circ C < T < 0^\circ C,$$

where T denotes the oil temperature in ºC.

Fuel density changes from 945 to 1012 kg/m^3 as soon as temperature falls from 50 to 2.6ºC, while viscosity increases by approximately three orders of magnitude from 0.215 to 579 kg/ms. The fluid dynamics are therefore strongly temperature-dependent.

SIMULATION CASES AND RESULTS

Oil temperature, viscosity and density evolutions

The temperature and viscosity evolution were estimated for 450 days (Fig. 3a). The mean temperature in the centre of the tank can be adjusted to the following function of time:

$$T(t) = 2.6 + 47.4 * e^{\frac{-t}{60}}$$

TABLE 1. – Chemical oil analysis (%).

	Saturated hydrocarbons	Aromatic hydrocarbons	Resins	Asphaltenes
Musée National d'Histoire Naturelle	26.6	52.8	8.4	12.2
IFP (original oil)	23	54	12.5	10.3
IFP (emulsion)	21	54	27.7	
CSIC Barcelona	21.6	50.7	34.7	

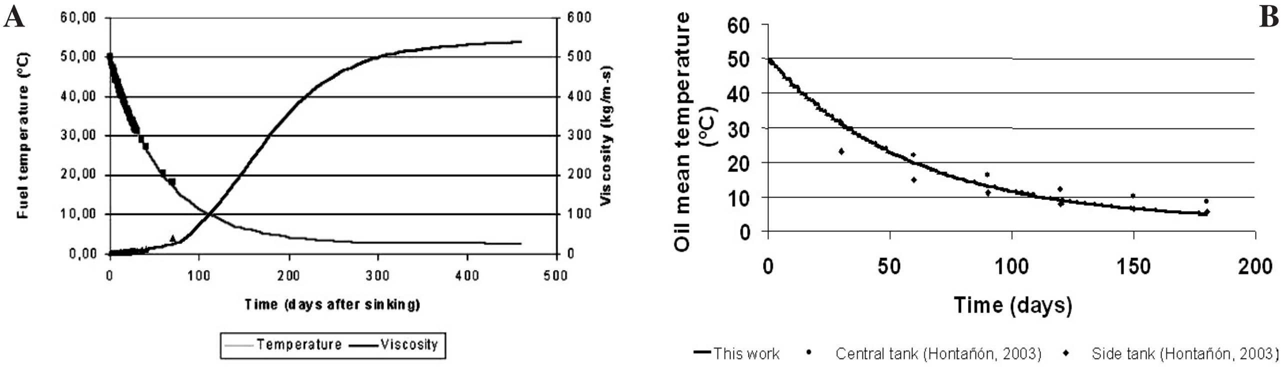

FIG. 3. – **A,** evolution of Oil temperature and viscosity inside the Prestige's tanks. Squares show temperature points simulated by FLUENT code. The clear line shows the evolution temperature best fit. Triangles show corresponding viscosity points. The dark line shows the best-fit viscosity. **B,** comparison of temperature results.

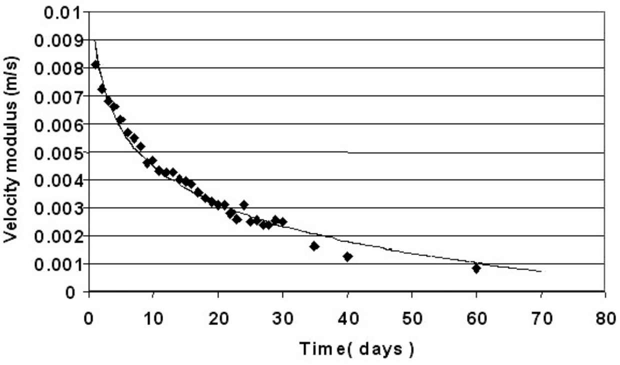

FIG. 4. – Fluid mean velocity modulus as a function of time. The monotonous decrease illustrates the natural decreasing convection process of fluids.

with T in ºC and t in days. The R^2 of the fit is 0.9999.

The cooling rate is initially 0.37 degrees per day and decays exponentially with time, in such a way that more than 4 months are needed to get near the thermodynamic equilibrium.

We estimated the mean whole tank temperature evolution with time. Other authors (Hontañón, 2003) have estimated temperature evolution for a central tank and a side tank. From the comparison of output results (see Fig. 3b) our "mean tank temperature evolution with time" results are between the two curves obtained by Hontañón. This means that temperature evolution prediction is accurate considering the knowledge uncertainties attached to the parameter values which feed the model. It also demonstrates that the spatial and temporal resolution applied in our case to the modelling of the actual problem is sufficient to reproduce the system behaviour.

Both oil viscosity and density increase when temperature decreases. The mean velocity modulus decreases with time (Fig. 4). Cooler oil accumulates at the bottom of the tank. Figure 5 shows the convection and velocity of the oil inside the tank 96 days after the Prestige broke apart and

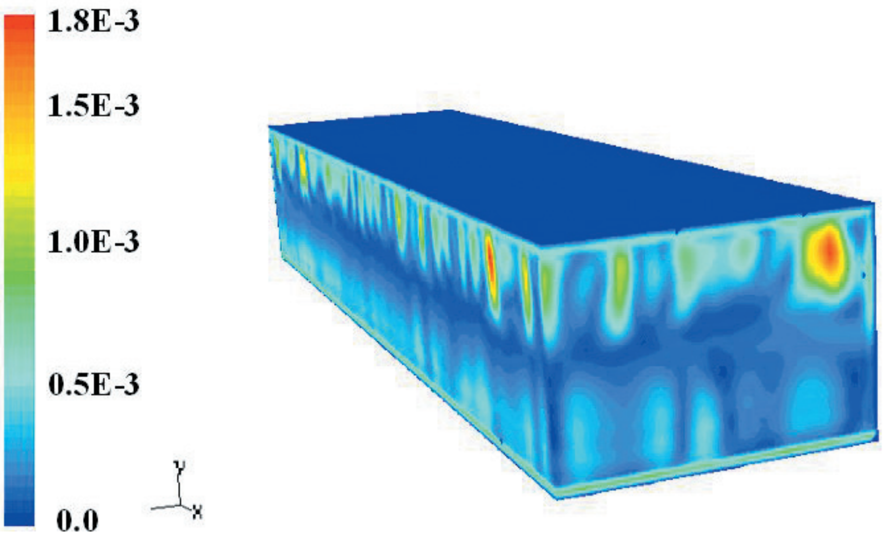

FIG. 5. – Simulation of the oil velocity modulus (m/s) in the tank during the cooling process at day 90.

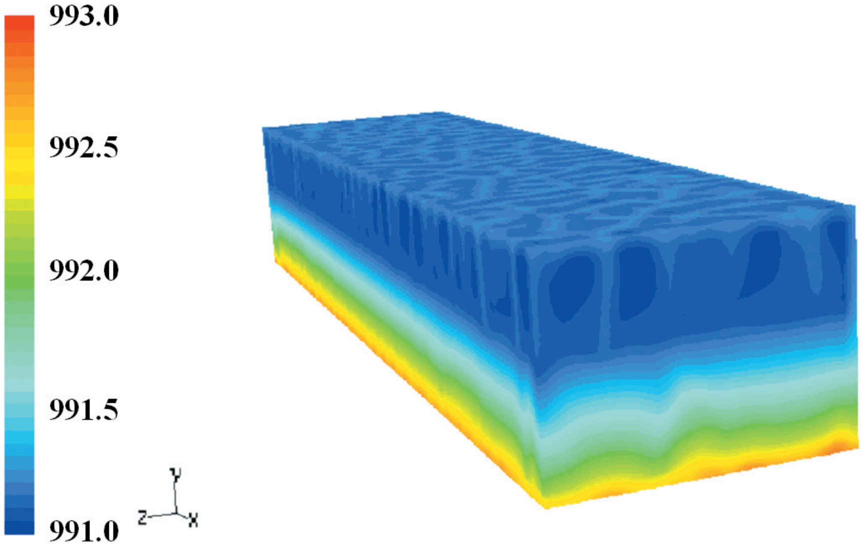

FIG. 6. – Profiles of the simulation of oil density (kg/m^3) at day 90.

sunk. Corresponding density gradients are shown in Figure 6.

Figures 5 and 6 show three different flow regimes: conductive heat transport dominates near the vertical sidewall and causes convection (thermal boundary layer). The oil motion at the top and bottom walls of the tank is dominated by free convection and gravity respectively. Convection cells dominate the vertical motion in the upper half of the tank because the oil temperature is warmer than the bounding tank wall. The lower half of the tank is filled with cooler settling oil, which has a higher density.

Release flow in a typical leaking

The CFD code was used to simulate the oil leaking through a break in the tank wall. A multiphase immiscible fluid was considered, consisting of a body of oil in the tank and a column of seawater above the tank. The Volume of fluid (VOF) model used to track large bubble movement or free surface development, heat transfer with radiation, compressibility, and liquid-solid phase change was employed. In the VOF model, the fluids share a single set of momentum equations, and the volume fraction of the fluid in each computational cell is tracked through the domain.

Considering the oil temperature evolvement and the increasing viscosity and density with time, it is possible to calculate the flow rate of Prestige oil due to the existence of a leak attributed to the initial situation or the present conditions.

Two cases were considered for different initial conditions. The objective of the simulations was to understand the movement of the interface between the two phases and to calculate the flow rate of oil per surface and time unit.

The first case considers a hole in the top of an oil tank, the temperature of the oil being 50ºC. The simulated hole is a square surface with a side length of 0.4 m. According to the first results, the flow rate corresponds to 1.74 kg/s (for 10 m oil depth, at 50ºC). Figure 7 shows the simulated oil leaking at 20, 40 and 60 seconds, considering the conditions on the first day of the sinking. The surface tension was neglected and the droplets obtained are only illustrative. As is apparent from the figure, the oil tends to form ascending filamentary structures that break approximately 1.5 m over the leak. This behaviour was experimentally observed *in situ* from video footage taken by the submarine *Nautile* in December 2003. It is clear that the formation of an umbrella-like descending water mass takes place. Both phenomena are typical of a Rayleigh-Taylor instability process.

The oil flow through the leaks corresponds to the oil closest to the tank walls. It is cooling faster than the oil in the centre of the tanks. The mean temperature estimated by the model after 12 days of cooling is 10.5ºC, which is close to 9.8ºC taken from direct measurements (CCA, 2003, 16-12-02 report). Currently, from the estimations presented in this work, the oil should be at the same temperature as the seawater (2.6ºC), so this is the initial oil temper-

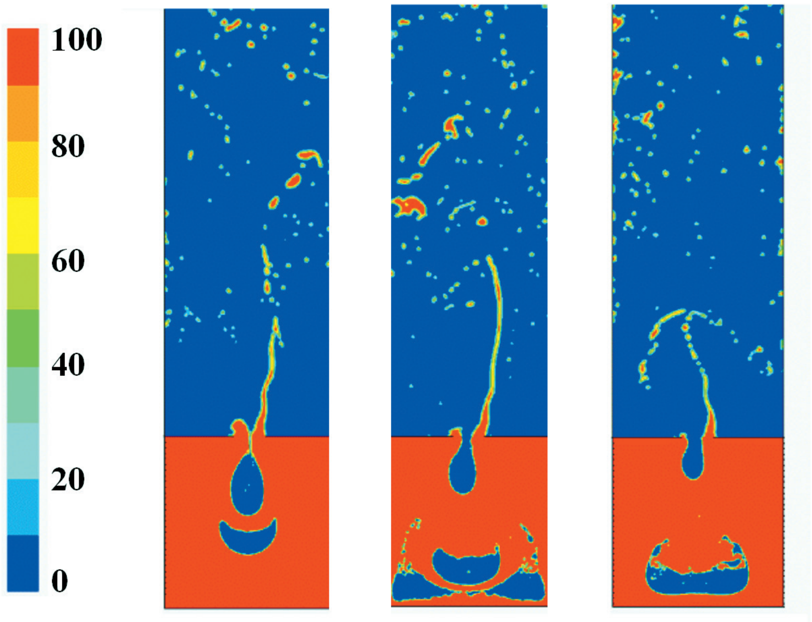

FIG. 7. – Simulation of the behaviour of a leak in the first days after the occurrence of the accident (red colour represents the oil and blue colour represents seawater). Considered oil tank 1 m^3; water column depth 5 m; Leak 0.4 m diameter; oil temperature 10ºC (viscosity: 100 kg/m-s). Oil is substituted by water due to density differences. Shown are the two phases in the water column and oil tank. There is a noticeable dispersion of oil in the water column, after (a) 20, (b) 40 and (c) 60 seconds.

ature that will be used for the simulation of the second case.

For the second case, we simulated the use of large bags to extract the fuel by means of a passive pumping system, taking into account that now the temperature of the oil is 2.6ºC. The effective diameter of the bag valves is assumed to be 0.7 m, oil viscosity 600 kg/m-s, oil density 1,012 kg/m^3 and seawater density 1,042 kg/m^3.

Under the best conditions for extraction, for at least 10 m depth of oil in a tank, filling a bag of 250,000 litre capacity with the calculated flow rate of 0.17 kg/s will require a period of 17 days. This flow rate and the remaining oil in the tank will decrease congruently. With the depth of oil in the tank at 3 m the flow rate is 0.05 kg/s. This means that we need 56 days to fill the third bag.

In this simulation, the fact that this oil is made from different components has not been taken into account. Some of these components should have been decanted now, so the actual viscosity of the fluid part will be less than estimated, making our results a worst-case calculation. An estimation of the behaviour of this multiphase oil is studied below.

Multiphase oil behavior

We have simulated the behaviour of the Prestige oil, considering its composition and its slow cooling process. The values for solidification temperature are related to its composition.

We can distinguish two different phases:

- Phase I, corresponding to light and aromatic hydrocarbons (PAH): Solidification at T<2.6ºC, 70% weight, density (15ºC) 994 kg/m^3.

- Phase II, composed by resins and asphaltenes: Solidification at T > 2.6ºC (6ºC), 30% weight, density (15ºC) 1,002 kg/m^3.

We consider that both phases have the same specific heat, 1,717kJ/KgK, and the same thermal conductivity, 0.123 W/mK.

Density varies with temperature as $\rho(kg\ /\ m^3) = 1016.3 - 1.4252 \times T$ (K), and 100 kg $cm^{-1}s^{-1}$ was utilised as oil viscosity.

As initial conditions, we use our temperature results after 96 days, which correspond to 12.16ºC in the centre of the tank. At this time point, the mean of the fluid velocity modulus is less than 0.001 m/s (see Fig. 4). The cooling process together with low oil velocity permits a settling of the different components. The components with higher density settle to the bottom of the oil tank, where accumulation of the non-fluid phase is observed (see Fig. 8). The initial stage of the oil emulsion is shown in Figure 8A. Figure 8B shows the stratification and nucleation of phase II. Settling of the non-fluid phase caused by higher density is the dominant process shown in Figure 8C.

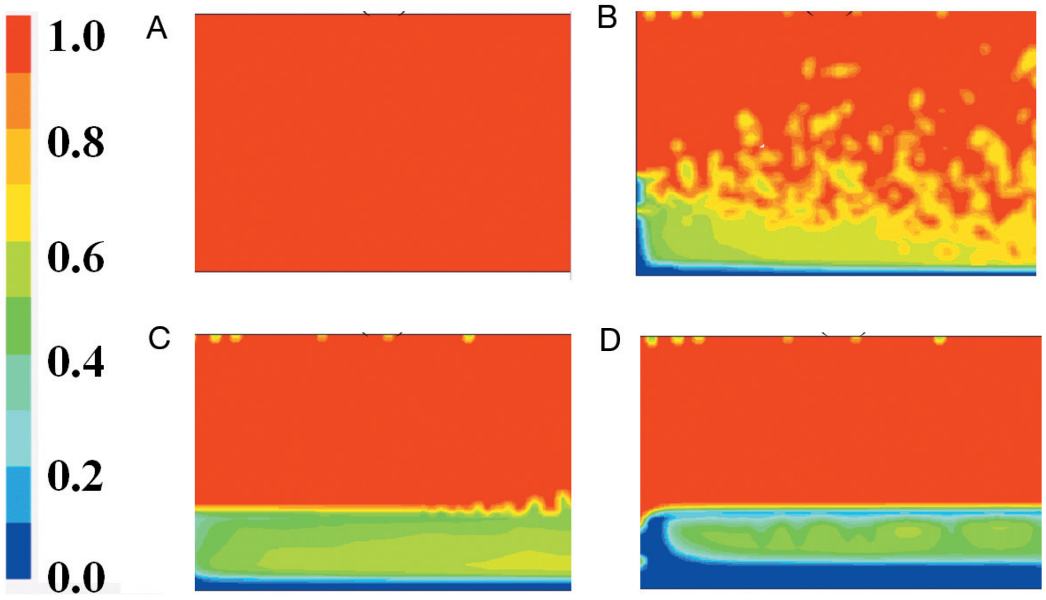

FIG. 8. – Liquid phase fraction per unit of volume in the tank. Two phases are visible in different colours during the cooling process: the fluid phase I (red) and the non-fluid phase II (blue). The components with high density fall to the bottom of the oil tank and accumulation of the non-fluid phase is observed. The pictures correspond to (a) 0, (b) 4, (c) 8 and (d) 18 days after the initial condition.

Figure 8D shows the final equilibrium stage reached approximately 18 days from the start of the simulation case. This accumulates to a total of 114 days following the sinking of the Prestige.

From our results we expect that 30% of the oil will remain inside the tanks after a successful oil extraction by passive (bags), or active (pumping) methods due to the oil composition of the Prestige. This oil will stick mainly to the tank walls. It has to be considered that even after completion of the oil extraction process,10-40% of initial oil amount remains inside the tanks (see Table 2, Cedre, 2002b). Therefore, after hull corrosion, the remainder of the oil will float due to the difference compared to the seawater density. In addition, the temperature in surface seawater, above 6ºC, will liquefy the oil, causing a source of contamination to the marine ecosystem in the future. Therefore, the planning of a neutralisation program will be necessary following the oil extraction.

CONCLUSIONS

The use of direct numerical simulations for leakages under extreme underwater conditions is feasible and helps to understand the interchange of oil and water inside the tanks and also to estimate flow rates. The flow rates are comparable to those measured by the *Nautile*.

Four months after the sinking, the temperature in the centre of the tank is equal to the surroundings (2.6ºC). The cooling process was faster at the beginning due to a greater difference in temperature and low viscosity of the oil. The temperature in the centre of the tank can be approximated by $T(t)=2.6+47.4*\exp(-t/60)$. Our model estimated the oil seeping from the tank to be at a temperature of 10.5ºC (which is near the 9.8ºC measured by CCA) after a period of 12 days.

The modelled behaviour reproduces the form and size of the observed oil filaments quite closely even without considering surface tension.

TABLE 2. – Past successful attempts to remove oil from sunken oil tankers.

Date	Wreck	Wreck location	Sunken cargo (tons)	Sea depth (m)	Oil extraction (tons)	Cost (Million $)
1977	Vöhlen	France	9,800	110	2.500	78
1980	Tanio	France	8,000	90	6.500	100
1995	Cleveco	USA	4,542	21	1.287	3.18
1996	Estonia	Finland	418	70	258	3.96
1998	Yuil nº 1	South Korea	1,400	70	665	7.13
2000	Erika	France	20,000	120	12.280	87.65

A passive pumping method based on rigid bags is currently being tested on the Prestige wreck to extract the oil remaining in the tanks. However, passive pumping is based on the Archimedes principle and will not extract the resins and asphaltenes of the oil. This work suggests that 30% of the oil will remain in the tanks after this kind of operation since the decantation time has been calculated to be 114 days. This conclusion is reinforced by the fact that historically no pumping attempt has ever been able to extract the total sum of oil contained in sunken tanks. Usually, between 10 and 40% of estimated oil cargo remained in the tanks

The passive pumping is a process conditioned by the flow rate from the tank and the time for filling increases as the oil remaining in the tank decreases: 17 days for the first bag and 56 days for the third one. These cases were simulated by assuming the initial non-fractioned state of the oil. With the current oil state, the solid fraction of the decanted oil will not flow and the other part of the oil will take a slightly shorter time to fill the bags.

Since the oil inside the tanks is expected to have been decanted, its solid part cannot flow to the bags though in the future large fractures of the tanks produced by corrosion would expose the oil. These asphaltenes and resins may be transported by ocean currents when the hull is corroded and may become a future environmental problem.

For this reason, an appropriate measure of neutralisation of the remaining oil seems to be recommendable.

The detection of the presence of *Desulfovibrio desulfuricans* bacterium is advised in order to determine whether the hull corrosion will take place sooner than expected, in turn exposing the oil to the open sea.

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