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Metallic corrosion of the tanker "Prestige" in deep seawater(•)

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Abstract In this paper the authors make a worst-case approach estimate of steel durability in the hull of the wreck "Prestige", based on the scarce data published on marine corrosion of steel at great depths.

Keywords Marine corrosion. Deep seawater. Carbon steel. Wreck. Tanker "Prestige".

Corrosión metálica del petrolero *Prestige* en agua de mar a grandes profundidades

Resumen En el artículo los autores realizan un pronóstico sobre la durabilidad del acero que integra el casco del pecio *Prestige*, en base a los escasos datos publicados sobre corrosión marina del acero a grandes profundidades.

Palabras clave Corrosión marina. Agua de mar profunda. Acero al carbono. Pecio. Petrolero *Prestige*.

1. INTRODUCTION

The tanker "Prestige", constructed 26 years ago with single-hull technology and transporting around 77,000 t of heavy fuel-oil in its tanks, split in two and sank on 19 November 2002 off the north-west coast of Spain (Fig. 1). Its sinking led to a pollutant spill of crude oil in the sea with disastrous consequences for this region of the Spanish coastline.

John Whitfield published in Nature[1] a note indicating that the spill produced by "Prestige" was one of the worst ever, due to the quantity of heavy fuel-oil released, its toxicity, and the environmental importance of the damaged coastline.

The volume of fuel-oil transported by "Prestige" was much greater than that transported by other tankers: *Exxon Valdez* in 1989 (34,000 t), *Nakhodka* in 1997 (19,000 t), and *Erika* in 1999 (11,000 t), which also caused major spills. The Scientific Advisory Committee set up by the Spanish government during the crisis estimated on 13 February 2003 that a total of 39,455 t had been spilled[2].

Besides the important economic repercussions of the disaster in Spain, the oil spill has affected an important fishing area of the Spanish coast, contaminated beaches in the Galicia region of Spain and devastated some ecosystem types protected by the European Union's Habitats Directive[1].

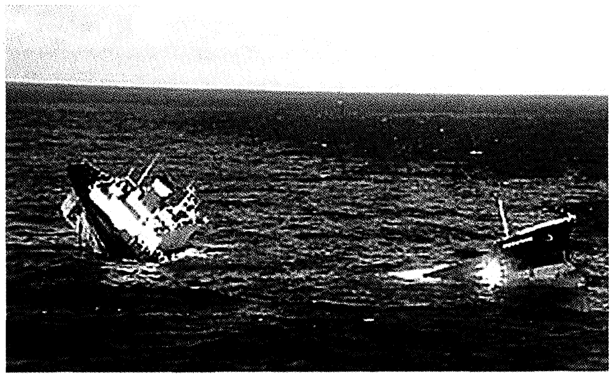

Figure 1. Sinking of tanker "Prestige" on 19 November 2002. (Reproduced with permission of EFE Agency).

Figura 1. Hundimiento del petrolero Prestige el 19 de Noviembre de 2002. (Reproducida con permiso de la Agencia EFE).

The sinking of "Prestige" made a deep impression on Spanish society and was without doubt the major news item of the year. Its important social repercussions stirred up armies of

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volunteers to help clean the beaches and unprecedented acts of solidarity.

The heavy impact of the ship as it hit the seabed caused considerable deformations in various zones of the hull (bow bulb, stern post and sides) and folds and staving in of the deck. The impact also caused the opening of doors and tank hatch covers, as well as the formation of cracks in local structural deformations. With the assistance of the bathyscaph *Nautile*, operated by the French Institute for Marine Exploration (IFREMER) and contracted by the Spanish government, up to 20 fuel-oil leaks were counted, which due to the oil's lower density than seawater, rose up to the surface of the ocean[2].

In several campaigns of the *Nautile* and its robot assistant *Robin*, it was possible to seal most of these leaks (Fig. 2), greatly reducing the volume of discharges which decreased from 125 t/d (10/12/2002) to 2 t/d (30/01/2003)[2].

The two wreck sites of the sunken vessel, partially sunk (0.4-1.4 m) in sediments of the seabed, are situated at depths of 3,830 m (bow) and 3,545 m (stern), where the temperature of the seawater in this zone is 2.5 °C and the dissolved oxygen concentration is 5.4 ml/l (7.7 ppm)[2].

2. DEEP SEA CORROSION. A REVIEW

Even in the event that fuel-oil discharges into the seawater can be cut to zero by sealing all the leaks, the question is whether we can stop worrying and be sure that no new leaks will occur, this time due to the perforation of the cargo tanks by corrosion of the ship's hull's steel plates by seawater. The answer is obviously no. For this reason, the Scientific Advisory Committee for "Prestige" made a worst-case approach estimate of the durability of the ship's hull before its perforation[2].

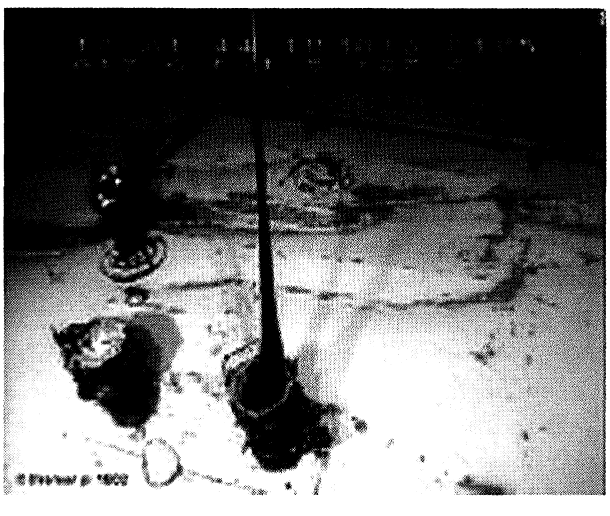

Figure 2. Fuel-oil leaks from the "Prestige" wreck. (Reproduced with permission of IFREMER).

Figura 2. Fugas de petróleo de los restos del Prestige. (Reproducida con permiso de IFREMER).

The first step was to review the literature with regard to data published on corrosion rates for carbon steel –the material of which "Prestige's" hull was constructed– in deep sea environments which may serve as the basis for the prognosis. There is very little published information on the behaviour of construction materials in deep ocean environments. The review takes into account information from field research and regarding real wrecks on the seabed.

The Civil Engineering Laboratory (Port Hueneme, California), conducted between 1961 and 1971 a research programme to determine the effects of deep ocean environments on materials[3]. They considered a seawater environment in the Pacific Ocean at depth of 1,830 m, whose dissolved oxygen concentration was 1.35 ml/l.

Mild and low-alloy steels corroded uniformly (or generally) and corrosion rates increased linearly with the oxygen concentration in the seawater, this being the main variable of the corrosion of steels in this environment. The average corrosion rate found for all the carbon steels after one year of exposure versus the oxygen content and the temperature of seawater was[4]:

$$\text{Corrosion rate (microns per year)} = 21.3 + 25.4\,(O_2) + 0.356\,(T) \qquad (1)$$

where the oxygen content (O_2) of seawater is expressed in millilitres per litre (ml/l) and the temperature (T) in degrees Celsius (°C).

The corrosion rates of the steels exposed in seawater decreased asymptotically to a value approximately three times lower when the exposure time was increased from one to three years. The corrosion of steels was not affected by depth (pressure) and none of the specimens were covered with any visible marine growth (absence of macrofouling). The data obtained on the corrosion of carbon steel at a depth of 1,830 m indicates average values of 57 μm/y (microns per year) for the first year of exposure, decreasing asymptotically as exposure time increases, reaching 17 μm/y after three years of immersion.

Corrosion of the areas of the tanker "Prestige" which are buried in the deep seawater sediment is another situation to consider. It is known that biological cultures are possible to find (for example, sulfate-reducing bacteria) in these sediments and they are capable of promoting a biodeterioration of the metal[5]. Data found in the seawater sediment by Civil Engineering Laboratory[3] showed corrosion rates for carbon steel in the first year (31 μm /y) lower than the values obtained in flowing seawater, decreasing the corrosion rates to 21 μm/y after three years of exposure.

In 1989 the General Electric Company published an interesting study[6] on the corrosion of materials in the deep Atlantic Ocean at depths of 3,000 and 3,700 m, similar to the depth at which "Prestige's" wrecks lie. This study considered a variety of materials in different exposure conditions (flowing, stagnant, semi-stagnant, buried in sediment). The seawater temperature (2.6- 3.0 °C) and the dissolved oxygen content (4.5- 5.2 ml/l) were also very similar to the case of "Prestige". The predicted range found using 90 % confidence intervals for the long term steady-state carbon steel mean corrosion rate was 65 ± 15 μm/y (flowing seawater) and 70 ± 27 μm/y (buried in sediments).

Studies have subsequently been carried out in the Arabian Sea and the Bay of Bengal[7] at depths of 1,000 and 2,900 m and in the Indian Ocean[8] at depths of 3,500 and 5,100 m. Venkatesan *et al.*[8] obtained carbon steel corrosion rates of 54 μm/y at a depth of 3,500 m, similar to the depth at which "Prestige" rests. Also they pointed out the absence of macrofouling at the deep ocean.

Though corrosion rate data has not been found for the many shipwrecks that rest on the ocean floor, it is interesting to consider two real cases for which a certain amount of information on the deterioration of their structures on the seabed is available. We are referring to the Russian nuclear submarine *Komsomolets*, which sank on 7 April 1989 in international waters in the Norwegian Sea[9], and the *RMS Titanic*, one of the great icons of the twentieth century, which sank on 15 April 1912 in the Atlantic Ocean, about 500 km off the coast of Newfoundland[10].

The submarine *Komsomolets* lies at a depth of 1,655 m. It has a double hull of 100 and 9.8 mm thickness respectively, made of a titanium alloy, and was powered by one pressurised water reactor, whose vessel is made of low-alloy steel of 15 cm thickness. The following corrosion rates were used by Gladkov *et al.*[11] as the basis for the prognosis of durabilities of both the hull and reactor vessel: carbon steel (75 μm/y); and titanium alloy (<<1 μm/y). According to the worst-case approach performed, neither the submarine's hull nor the reactor vessel will be destroyed by corrosion for at least 1,000 years.

The *RMS Titanic* lies at a depth of 3,900 m, where the seawater temperature is 1 °C. Several scientific expeditions have been undertaken to determine the rate of its deterioration over time, and unlike the case of *Komsomolets* the *Titanic* shows important signs of deterioration after 91 years of immersion in seawater; it being feared that in time it will cease to be a recognisable structure[10 and 12].

Conspicuous corrosion products in the form of growth, coined rusticles, and resembling stalactites can reach lengths of several tens of cm and grow from various parts of the ship. Their microestructure indicate that bacteria play a major role in their formation[10]. These rusticles, with a high iron content ranging from 24 % to 36 % consisting mostly as complex ferric oxides and hydroxides, are growing larger and denser extracting iron from the steel plating of the ship.

3. CORROSION ESTIMATES FOR "PRESTIGE": A WORST-CASE APPROACH

According to the standards of the International Association of Classification Societies (IACS), we should assume that the thickness of the steel plates on the deck, bulkheads and sides of the sunken ship when the accident occurred had acceptable minimum values of 20.0, 9.6 and 15.5 mm respectively.

On the other hand, the carbon steel plates that form "Prestige's" hull and fuel-oil storage tanks are currently protected with marine paint schemes. However, when considering the most unfavourable conditions in order to estimate the time in which perforation of these plates may occur, leading to the release of the remaining crude oil stored in the tanks, it must be considered that corrosion would initially progress in the zones of the structure that are not protected by paints (blows, scratches, unpainted zones, etc.), and thus for practical purposes it is as if there were no protective coating.

Because of the ocean currents, the corrosion of the hull of "Prestige" is occurring in flowing seawater, with its rest zone partially buried (0.4-1.4 m) in sediments.

From the literature that has been consulted[3, 4 and 6-9], and in view of the depth

(3,545-3,830 m), temperature (2.5 °C) and dissolved oxygen content in the seawater at this depth (5.4 ml/l), the data obtained by Barth and Sheldon[6] in the Atlantic Ocean at depths of 3,000-3,700 m with a seawater temperature of 2.6- 3.0 °C and a dissolved oxygen concentration of 4.5- 5.2 ml/l, very similar to the case of "Prestige", is an excellent reference for our purposes. It is recalled that in the aforementioned situations these researchers obtained long-term mean corrosion rates for carbon steel in the interval of 50- 80 μm/y. This interval also covers the data obtained in the Indian Ocean (54 μm/y)[8] and the figure used by Gladkov *et al.* (75 μm/y) in corrosion estimates for the submarine *Komsomolets*[11]. Even an extrapolation of the long-term data obtained by Reinhart[3] in the Pacific Ocean to the environmental conditions of "Prestige" and applying equation (1) will yield carbon steel corrosion rates of 52 μm/y, also within the aforementioned interval. In a worst-case approach we must consider the highest figure of this interval reported by Barth and Sheldon[6], i.e. 80 μm/y.

However, we must bear in mind that even when the above investigations indicate carbon steel corrosion of a generalised type affecting all the metallic surface exposed to the marine environment, the surface profile always shows irregularities with areas of preferential corrosion where the attack goes deeper than the average penetration. According to studies performed in seawater[13 and 14], the pitting at sites of preferential attack can exceed up to 5 times the average rate of penetration of the generalised attack, which means that in the case of an average penetration of 80 μm/y, the attack may reach penetrations of 400 μm/y at the sites of preferential attack. Considering this maximum rate of preferential attack and assuming that corrosion takes place at a constant rate, the time required for perforations to occur in the bulkheads (9.6 mm), sides (15.5 mm) and deck (20.0 mm) of the oil tanker "Prestige" would be 24, 39 and 50 years, respectively.

On the other hand, it should not be discarded that perforations of the ship's hull in those zones partially buried in the marine sediments can be produced, in which has been indicated previously, corrosion can progress at slightly higher rates, depending on the characteristics and nature of marine sediments.

There is also a possibility that perforations may be initiated after shorter times in the zones of the ship's structure that have been deformed, folded or cracked as a consequence of the impact of the wreck hitting the seabed and of local collapses of the structure originated during the sinking. It is known that these highly deformed zones are more susceptible to marine corrosion. Video footage from the scientific expeditions to the site where the "RMS Titanic" rests in order to determine the rate of deterioration over time shows that all of the decking structures located at the aft end of the bow section, which folded and collapsed during the impact, have now disintegrated away[10].

4. CONCLUSIONS

It may therefore be concluded that even if all the leaks are completely sealed and the volume of fuel-oil discharged from the wreck is reduced to zero, local structural deterioration after 24 years (bulkheads), 39 years (sides) and 50 years (deck) may be sufficient for perforations to appear in the ship's steel plates, causing the spillage of the remaining crude oil stored in the tanks. It should not be ruled out that perforations may occur after shorter times in the zones of the wreck that were deformed due to the impact of "Prestige" hitting the seabed.

In response to the problem the Spanish Government firstly considered two options: extraction of the fuel remaining in the wreck, or, if this was not technically possible, installation of a containment structure to prevent the further spillage of fuel into the seawater. Of the two studied alternatives, on 12 December 2003 the Council of Ministers approved the extraction of fuel by means of rigid aluminium shuttles as the final solution for "Prestige".

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