

Evaluation of the Corrosion Rate at the Bottom of the above – Ground Tank for Storage of Petroleum Products

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Abstract — A study of corrosion in steel fuel storage tanks, which failed after several years of operation highlighted intense pitting and microbiological corrosion. Significantly higher corrosion rates were found than would be expected with normal seawater corrosion. Therefore, the established methodology for predicting the remaining service life of tanks is also questionable. The aim of the study was to evaluate the actual corrosion rates at the bottom of the petroleum product tank. For this purpose, we adapted the established laboratory methods for evaluating the corrosion rate to perform field measurements. The observed corrosion rates in the tank are higher than the currently known values.

Keywords — corrosion rates, linear polarization, microbiological corrosion, pitting corrosion, tank.

I. INTRODUCTION

Corrosion control at the bottom of above-ground storage tanks for oil and its derivatives is one of the most technically, ecologically, and economically demanding areas in the oil industry. Due to the presence of water, water-soluble substances, microorganisms and chemical properties of the stored medium, the bottoms of above-ground storage tanks are highly exposed to uncontrolled corrosion processes. Tank failure due to corrosion of the bottom requires repair or even replacement of the sheet metal, potential contamination of the stored medium and, in the worst case, uncontrolled spillage. Unexpected premature bottom sealing failures have occurred on tanks over the past decade. We detected a leak at the tank after six years of exploration. The extent of corrosion damage at the bottom of the tank required replacement of the upper bottom. This allowed us to study the corrosion problem at the bottom of the tank in more detail.

During the bottom remediation, we performed a detailed inspection of corrosion damage and performed potentiodynamic measurements of the corrosion rate. A sample of corrosion products in the drainage water sediment and sheet metal samples were taken for later laboratory studies and analyses.

We do not have reliable data on the actual corrosion rates at the bottom of the tank. Therefore, we have so far used steel corrosion rates in seawater and estimates of corrosion rates based on linear extrapolation of sheet thickness measurements. The corrosion rate does not progress evenly. At the beginning, corrosion does not take place at all (initiation time), and then the corrosion rate increases

exponentially. Therefore, the current methods used for predictions of corrosion progression are too optimistic.

Measuring the actual corrosion rates at the bottom of the tank would allow us to have significantly more reliable predictions of the corrosion rate. Carrying out measurements in the tank is a great challenge, because in addition to operational limitations, we are dealing with a large measuring system over which we have practically no complete control. It is therefore reasonable to doubt the results of the measurements in the tank. Changing the bottom of the tank allowed us to repeat the measurements of the corrosion rate, in the same places of the sheets, in a controlled environment. In addition to the measurements, we also performed an informative review of corrosion phenomena in the tank and analysis of corrosion products with electron microscopy and X-ray spectroscopy.

II. EXPERIMENTAL PROCEDURE

A. Above-ground Storage Tank

Measurements of corrosion processes were performed at the bottom of the above-ground tank for storage of petroleum products. The tank was built in 2006, the main technical characteristics of the tank are [4], [11]:

- 1) Nominal tank volume: $V = 55.000 \text{ m}^3$
- 2) inner diameter: $d = 57.000 \text{ mm}$
- 3) tank shell height: $h = 22.500 \text{ mm}$
- 4) bottom of the tank: double bottom, two sectors
- 5) corrosion allowance: 1 mm
- 6) stored medium: diesel fuel

The bottom of the tank was made of structural steel S235JRG2 [4], [11].

B. Performing Electrochemical Measurements

At potentiodynamic polarization, the current density through the measuring cell is monitored in a selected voltage interval around the corrosion potential. Due to the operational restrictions of the tank for performing measurements, we determined the corrosion rate, applying linear polarization:

$$E = E_{corr} + R_p I \quad (1)$$

where E is the potential of the metal substrate, E_{corr} is the corrosion potential, R_p is the polarization resistance, and I is

the electric current.

The Tafel slopes, for determining the Stern-Gary coefficient [8], [13], were evaluated by an alternative method of nonlinear optimization:

$$2,3R_p i_i = \frac{\beta_a \beta_k}{\beta_a + \beta_k} \left[\exp\left(\frac{2,3\epsilon_i}{\beta_a}\right) - \exp\left(-\frac{2,3\epsilon_i}{\beta_k}\right) \right] \quad (2)$$

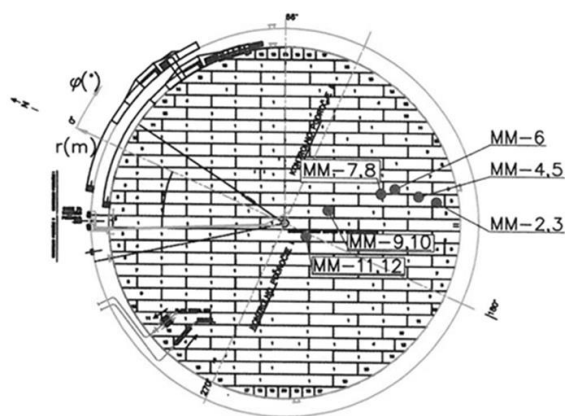
where R_p is the polarization resistance, β_a and β_k are the Tafel anodic and cathodic slopes, i_i is the measured current density and ϵ_i is the measured polarization

The corrosion rate (v_{corr}) is usually given as the loss of material thickness in mm/year:

$$v_{corr} [mm/year] = 3268,42 \frac{i_{corr} \left[\frac{A}{cm^2} \right] M \left[\frac{g}{mol} \right]}{z \rho \left[\frac{kg}{L} \right]} \quad (3)$$

where M is the molar mass of the metal, i_{corr} is the corrosion current density, z is the number of electrons exchanged in the reaction, and ρ is the metal density.

Electrochemical measurements at the bottom of the tank were performed before the upper bottom of the tank was replaced. Before making the measurements, the tank was degassed and the bottom of the tank industrially degreased. During the measurements, we turned off the active cathode protection system. Before installing the measuring cell, the surface was thoroughly cleaned with acetone. Measurements were carried out at eleven measuring points (Fig. 1).



Measurement spot	ϕ (°)	r (m)
2,3	148	24,80
4,5	144	22,10
6	139	18,70
7,8	139	15,50
9,10	139	7,30
11,12	188	3,40

Fig. 1. Tank floor plan – graphical representation of the arrangement of measuring spots.

The electrochemistry of corrosion was evaluated using the BioLogic SP-200 portable potentiostat, upgraded with the SP-300 plate with the option of performing measurements using the electrochemical impedance spectroscopy method. The instrument allows voltage control ± 30 mV to ± 10 V for DC measurements. The uncertainty of the standard voltage source ± 1 mV and the uncertainty in setting the potential $\pm 0.03\%$. The minimum voltage resolution shall be $1 \mu V$. The instrument allows current measurements in the range from $\pm$

100 nA to ± 500 mA. The uncertainty of the measured current $< \pm 0,1\%$ of the measuring range and $\pm 0,03\%$ of the measurement. The maximum resolution for flow measurements $< 0,0033\%$ of the measuring range.

To carry out the measurements, we used a modified Tait cell with an area of $34,21 \text{ cm}^2$. The liquid electrolyte was replaced with a gel prepared with the help of Agar-Agar and 0.1 M NaCl solution. The Tait cell (Fig. 2) allowed us to perform measurements with three electrodes. As a working electrode (WE), it served the steel surface of the bottom of the tank. Instead of a standard reference electrode, we used a mechanically resistant pseudo-reference electrode (RE) of the Haftelloy alloy, which has a potential of $+0.171 \text{ V}$ in the $0,1 \text{ M NaCl}$ gel.

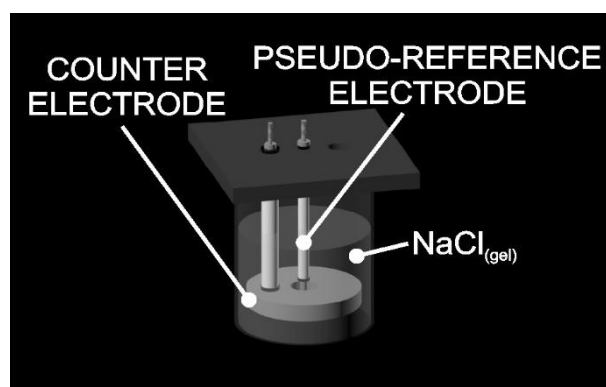


Fig. 2. Tait cell.

The main challenge we encounter when measuring in a tank is to ensure a sufficiently stable configuration of the measuring system. The lower bottom of the tank is protected with active cathodic protection and in direct electrical contact with the abutting upper bottom. To perform the measurements, we had to turn off the cathodic protection system and wait for about 2 hours for the electric potentials to stabilize near the corrosion potential. The cathodic protections of some connecting pipelines that could not be switched off caused a constant slight fluctuation of the measuring cell potential by about 1 mV . However, this did not prevent the stabilization of the open cell potential after about 30 minutes, when the difference between the corrosion potentials of the individual measurements fell below 10 mV . A reliable answer about correctness of measurements in the tank was obtained based on a comparison of the results of repeated measurements on the cut sheets of measuring locations in the laboratory.

The rate of corrosion on the sheet of the bottom of the tank was evaluated by potentiodynamic polarization amperometry. The polarizing curves were performed after stabilisation of the measuring system. In the tank we performed a series of measurements at an interval of ± 50 to $\pm 75 \text{ mV}$ around the corrosion potential at a rate of $0,25 \text{ mV/s}$. The measurements were repeated until the difference between corrosion potentials fell below 10 mV . We performed two measurements at each measuring spot. Each measurement takes about 30 minutes after stabilization of the potential, i.e., approximately 1.5 to 2 hours were spent on each measuring spot (Fig. 9 and 10).

The measuring positions were marked with a coloured spray. When removing the upper bottom of the tank, the sheet

metal was cut out at measuring spots and transported to the laboratory, where we later (30 days after the measurements in the tank) repeated the measurements in the controlled environment. Measurements were made with the same measuring cell, the same measurement parameters and at the same measuring spots on the metal sheet as in the tank. In the laboratory we were able to expand the measurement range up to 300-400 mV around corrosion potential. The narrow range of polarization measurements in the tank did not allow us to determine the Tafel slopes with a reliable determination. Therefore, we determined The Tafel slopes only in laboratory polarizing curves.

Given the narrow voltage range of the polarization curves, we used linear polarization to determine the polarization resistance and corrosion potential. To estimate the Stern-Gear coefficients, an alternative method for determining the Tafel slopes was used in laboratory measurements [6]. Tafel slopes were optimized by the least squares' method using the Newton-Raphson algorithm in the slope range from 120 to 240 mV [6], [7]. The observed values of the Stern-Gear coefficients ranged between 41 and 52 mV. Therefore, we used the maximum value of the Stern-Gear coefficient of 52 mV for the calculations of the corrosion current density in all measurements [3].

III. RESULTS AND DISCUSSION

A. Tank Status Overview

The bottom of the R20 tank was not anticorrosion protected. The bottom surface was covered with a black compact oxide layer, which was taken away and performed a composition analysis. In the vicinity of the drainage shaft, where the bottom of the tank is the lowest, we observed pitting corrosion (Fig. 3). Circular corrosion ulcers with a diameter of 10–20 mm of intense yellow-orange colour was found all over the bottom surface (Fig. 4). These were grouped together, which usually indicate microbial corrosion in tanks. On surfaces with pitting and microbiological corrosion, the depths of ulcers were measured at an interval between 0.4 and 3.5 mm.

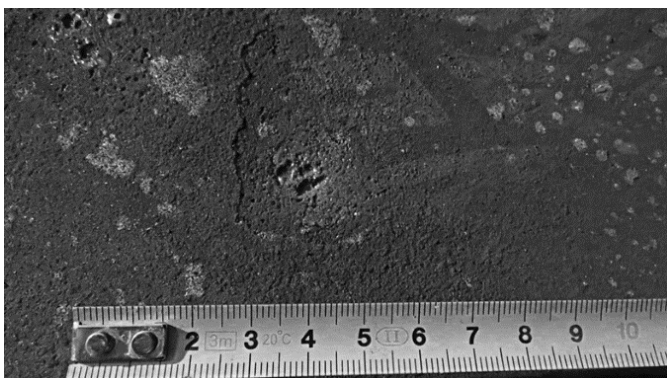


Fig. 3. Pitting corrosion.

B. Laboratory Sample Studies

Electron microscopy (SEM JSM-6500F) was performed on samples of sheet steel taken during bottom replacement. Electron spectroscopy (EDS) showed a large presence of oxygen and chlorine on the surface of the sheet in addition to the expected iron. Oxygen indicates iron oxides and crystal

bound water. The source of chlorine on the surface is seawater, which is found as an impurity in the fuel during transport by tankers (Fig. 5).

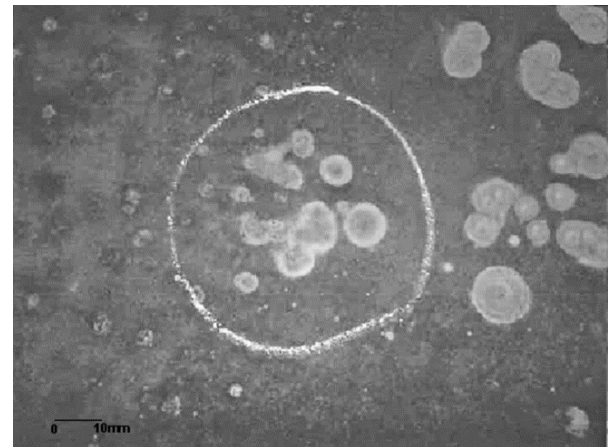


Fig. 4. Microbiological corrosion.

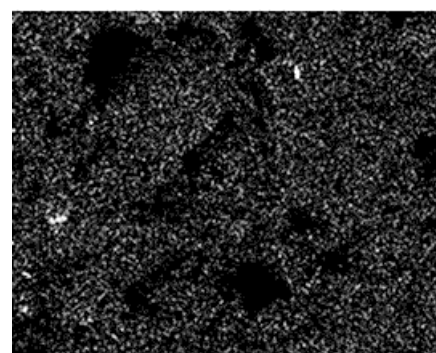
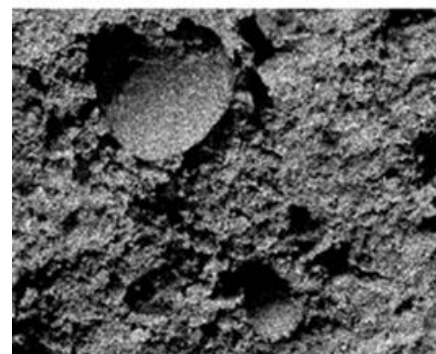
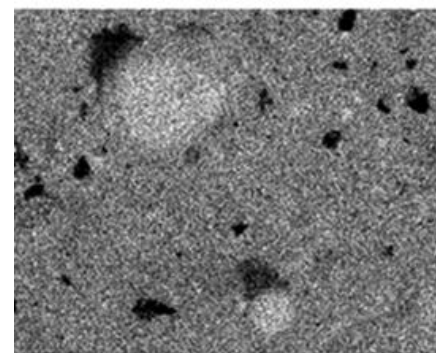


Fig. 5. Surface image with SEM EDS - elementary surface analysis.

Microscopy of the sheet metal cross section from the bottom of the tank showed a thickness of corrosion products of 50–100 μm (Fig. 6).

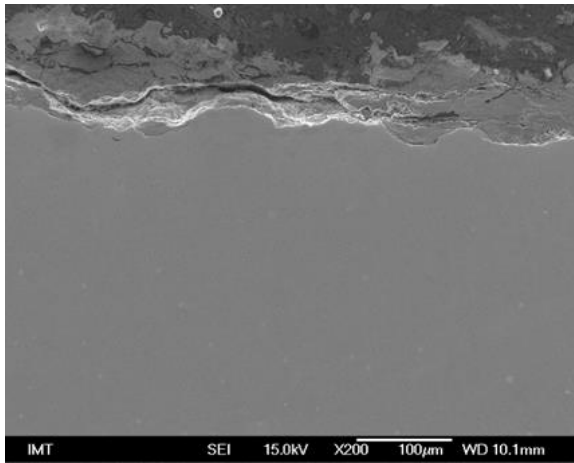


Fig. 6. SEM image of metal cross-section with corrosion products (200x magnification).

Corrosion products from the sediment of drainage water had pronounced ferromagnetic properties. Subsequent analysis of the crystal structure (XRD, Miniflex, II, Rigaku, Nano-Tesla Institute, Ljubljana) showed a high concentration of magnetite, which is typically formed by pitting corrosion [1], (Fig. 7).

C. Corrosion Rates in the Tank

Corrosion at the bottom of the tank takes place in the area

of the aqueous phase area, in the part where the aqueous solution is present. The measurements when the fuel is stored in the tank is of course not possible, so there is doubt about the adequacy of our measurements regarding the actual state of corrosion processes at the bottom of the tank. After emptying the tank and cleaning, practically all organic and inorganic impurities are removed from the bottom of the tank. When the tank dries after washing, the presence of electrolyte on the metal surface is removed. The further course of corrosion is thus stopped. When the measuring cell is placed at the measuring spot on the bottom of the tank, restore the aqueous phase locally, which has a controlled electrolyte chemical composition (0.1 M NaCl). Microbiological corrosion was removed when the bottom was cleaned, while other corrosion processes were restored. Thus, after their stabilization, we measure the corrosion that took place in the tank when it was still filled with fuel, and an aqueous solution was present at the bottom of the tank. The concentration of NaCl in the measuring cell is about 5%, so we believe that our measurements are a good approximation of the actual conditions in the tank, where the composition of the aqueous phase in the worst case corresponds to seawater. The evaluation of the corrosion rate in the tank is particularly important from the point of view of the reliability of the tank seal. Therefore, the least favourable corrosion rates provide a conservative assessment of the effects of corrosion process.

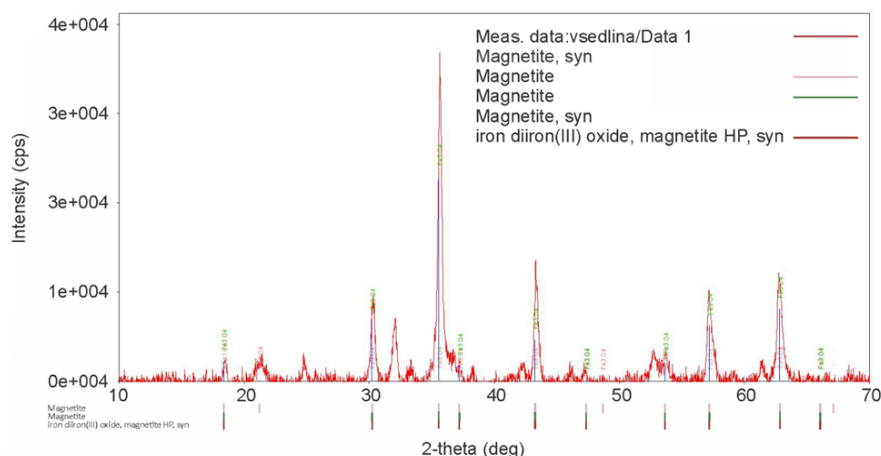


Fig. 7. XRD analysis of corrosion product obtained from drainage water.

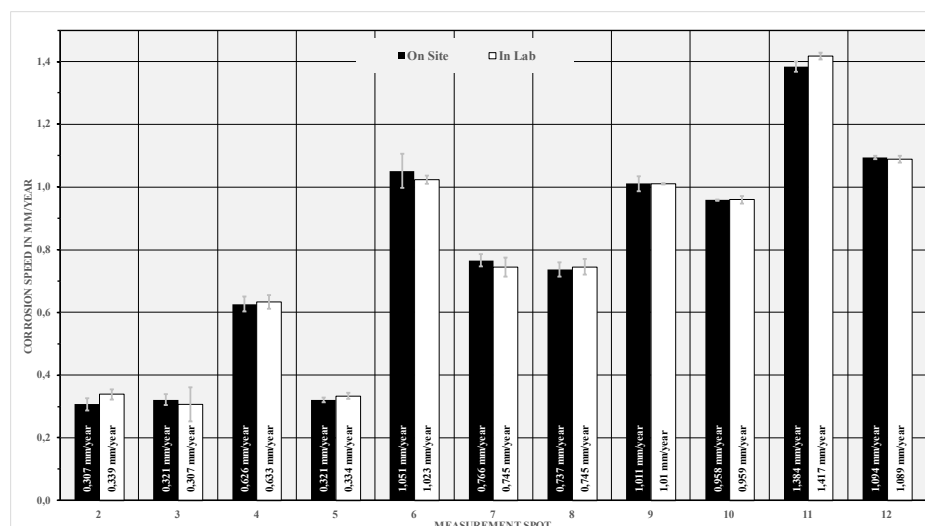


Fig. 8. Evaluated corrosion rates in on-site and in laboratory.

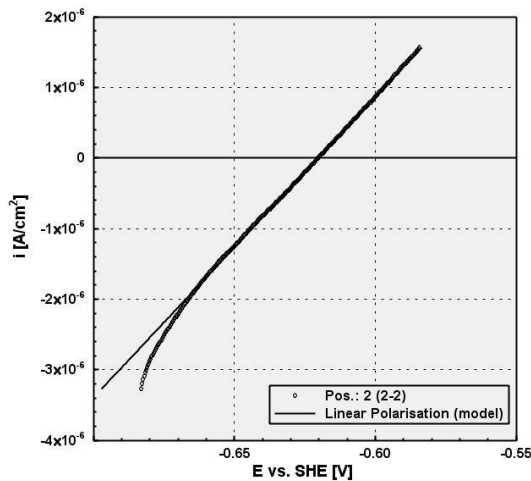


Fig. 9. Linear polarization of measuring point 2 in laboratory.

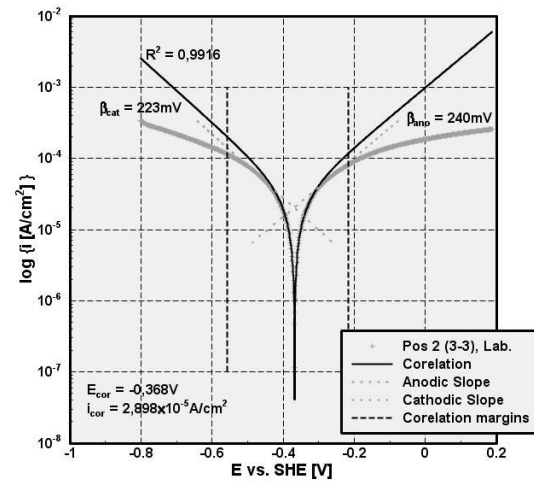


Fig. 10. Determination of anodic and cathodic slopes at the measuring point 2 in-vitro.

A comparison of the evaluated corrosion rates (Fig. 8) shows a good correlation between the results of measurements in the tank and the laboratory. In general, corrosion rates in the laboratory are 0.1 to 0.2 mm/year lower than in the tank. The differences found between the results of measurements in the tank and the laboratory are probably related to the hysteresis of active cathodic protection, which was switched off for the performance of measurements. The tank is also in electrical contact with fire piping, which has a separate active cathodic protection, which we were unable to switch off during the measurements.

The measured corrosion rates range between 0.313 mm/year and 1.589 mm/year (Fig. 8) and show an increasing trend from the circumference (measuring spot 2) towards the middle of the tank (measuring spot 12). This can be explained by the concave shape of the bottom of the tank with the lowest part in the middle and the fact that when fuel is delivered by tankers, a certain amount of seawater usually also arrives with the fuel. The measured corrosion rates are comparable to the available sources in the literature [1], [3], [17], [18] for local pitting and microbiological corrosion.

High measured corrosion rates are important for evaluating the remaining operating time of tanks. Current approaches for estimating the remaining operating time of tank bottoms are based on estimating the corrosion rate by linear extrapolation to a previously determined tank condition. Usually to the initial design state as no other data is available. Such an estimate of the corrosion rate does not take into account the time required for corrosion initiation and the subsequent exponential increase of the corrosion rate with time [19]. Therefore, significantly underestimate the actual corrosion rate at the bottom of the tanks. The estimate of the remaining operating time of the tank [10] is based on the current state of the tank bottom (current sheet thickness, depth of pits) and on the estimated corrosion rate, which is linearly extrapolated to the future. A good match between the corrosion rate measurements in the tank and in the laboratory proves their reliability [11]. The actual measured corrosion rates at the bottom of the tank allow us to predict more reliably the remaining operating time of the tank bottom independently of corrosion types, since we eliminate the unreliability of the corrosion rate estimates based on NDT measurements due to unknown corrosion initiation time.

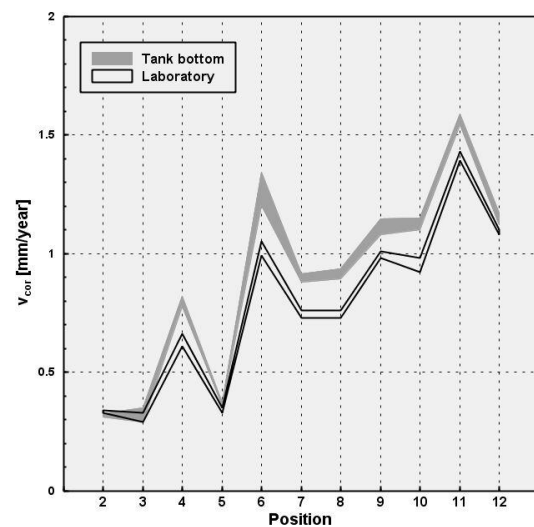


Fig. 11. Comparison of evaluated corrosion rates in-vitro and in-situ.

REFERENCES

- [1] Shreir L.L., Jarma R.A., Burstein G.T. *Corrosion*. Third edition, Butterworth-Heinemann, Boston 2000.
- [2] Groysman A. *Corrosion in Systems for Storage and Transportation of Petroleum Products and Biofuels*, Identification, Monitoring and Solutions, Springer Dordrecht Heidelberg New York London, 2014.
- [3] Uhlig's *Corrosion Handbook*, Second Edition, Edited by R. Winston Revie, CANMET Materials Technology Laboratory Ottawa, Ontario, Canada, 2000.
- [4] *Welded Steel tanks for Oil Storage*, API Standard 650, American Petroleum Institutut, Washington, D.C., 2012.
- [5] Loto C. A. Microbial corrosion: mechanism, control and impact-a review. *International Journal of Advanced Manufacturing Technology*, 2017; 92:4241-4252.
- [6] Ahmad S., Jibran M. A. A., Azad A. Z., Maslehuddin M. A Simple and Reliable Setup for Monitoring Corrosion Rate of Steel Rebars in Concrete, *Scientific World Journal*, Vol 2014,
- [7] Collis G. W. *Fundamental Numerical Methods and data Analysis*, Case Western Reserve University, 2003.
- [8] Mansfeld E. Tafel slopes and corrosion rates from polarization resistance measurements, *Corrosion*, 1973;29(10):397-402.
- [9] *Guidelines for use of statistics for analysis of sample inspection of corrosion*, Research report 016, Health and Safety Executive 2002,
- [10] *Tank inspection, repair, alteration and reconstruction*, API Standard 653, American Petroleum Institutut, Washington, D.C., 2014.
- [11] *Specification for the design and manufacture of site built, vertical, cylindrical, flat-bottomed, above ground, welded, steel tanks for the*

storage of liquids at ambient temperature and above SIST EN 14015:2005.

- [12] *Linings of Aboveground Petroleum Storage Tank Bottoms*, API Recommended practice 652, 4th Edition, API, September 2014.
- [13] Perez N. *Electrochemistry and corrosion science*, Boston 2004.
- [14] Wang W., Jenkins P. E., Ren Z. *Heterogeneous corrosion behavior of carbon steel in water contaminated biodiesel*. Corrosion Science, 53: pp. 845–849, Elsevier Science 2011.
- [15] Cheng Q., Tao B., Song L., Zhang W., Liu X., Li W., et. al. Corrosion behavior of Q235B carbon steel in sediment water from crude oil, *Corrosion science*, 2016;111:61-71.
- [16] Mejfa J. A., Hay J., Mustafa V., Santa Fe J. Aboveground Storage tank Floor Corrosion Condition Assessment. *AVANCES Investigación en Ingeniería*, 2010;12:9-13.
- [17] Mobin M., Malik A. U., Al-Fozan S., Al-Muaili F. Corrosion Failure of bottom plates of Aboveground Storage Tank. *Journal of Failure Analysis and Prevention*, 2007;7(1):18-22.
- [18] Groysman A. Corrosion of Aboveground Fuel Storage Tanks. *NACE International*, 2005;44(9).
- [19] Kowaka M. *Introduction to Life Prediction of Industrial Plant Materials, Application of the Extreme Value Statistical Method for Corrosion Analysis*, Sumitomo Metal Industries, 1994.