Corrosion Protection of Oil Storage Tank Tops

Efim Lyublinski[1], Yefim Vaks[2], Marcelo Schultz[3],
Joelma Damasceno[4], Ronnie Singh[5]

Abstract

Corrosion rates of oil storage tank roofs are unpredictable. Various references give general corrosion rates in the range 0.1 - 0.5 mm/year and selective corrosion (pitting, crevice, galvanic) up to 10 mm/year. The rate of corrosion depends on the stored products, application condition of the tanks, composition and condition of the vapor space environments, design, material and dimensions of the tank, and any coating used for corrosion protection.

This complicated situation reduces the possibility of finding a simple corrosion protection method. Coatings are not efficient enough and provide a service life of only 3-10 years. Repainting is very difficult and very expensive. The service life of tanks tops, even with using coatings, is typically 5 to 10 years.

This paper provides an outline of corrosion data that collected on the various storage tanks at the Petrobras facilities. These results are very important for evaluating the time for replacement of the tanks roofs and choosing the right corrosion protection method. Final data can be used by different refineries for making decisions of the corrosion problem and choosing the corrosion protection method.

Keywords: tanks roof, environment, crude oil, corrosion, inhibitor, coating, service life

[1] Professor, PhD em Corrosão – Empresa NTIC, EUA
[2] Engenheiro Mecânico – Empresa NTIC, EUA
[3] Doutorando, Mestre em Corrosão, Engenheiro Mecânico – Empresa Petrobras S.A.
[4] Mestre, Engenheira Mecânica – Empresa Petrobras S.A.
[5] MBA, Engenheiro Mecânico, NACE Corrosion Senior – Empresa Zerust Prevenção de Corrosão S.A.

Introdução

The oil storage tanks roofs always have vapor spaces (Figure 1). Depending on the stored product composition and application conditions the corrosion environment can vary significantly. The tank tops atmosphere, for example, can contain the following highly corrosive components (Volume % up to):

SO_2 – 5 CO_2 – 30 H_2S – 10 Cl^- - 5 O_2 –20 H_2O– 3

One of the typical corrosion environments on the top of crude oil storage tanks is shown in Table 1.

It must be taken into consideration that mercaptans create approximately the same corrosion problems as H_2S. This means that for evaluation of corrosion protection efficiency for testing the chosen concentration of H_2S must be higher than it in the tank tops.

The relative humidity (RH) in most cases is from 80 to 100%. The temperature of the gaseous environment can be in the range from -40°C to +50°C. At the same time, the tank tops' surface temperature can be in the range from -40°C to +80°C.

The corrosion in the tank tops occurs when the gaseous corrosion components absorb the layer of water condensed on the surface. In most cases this layer is highly acidic with pH (less than 5 and up to 2) and this creates a very high corrosion rate as it shown in table 2.

This dangerous corrosion happens also in the event when:

- the coating does not have proper properties on some of the metallic surface of the tank tops,
- the coating became permeable and corrosion occurs under the coating surface,
- there some crevice between top and the support of tanks,
- the coating achieved it expected service life.

Typical examples of corrosion on the tank tops are shown in Figure 2.

It creates the following critical situations:

- Dangerous application condition that can cause fire hazard and explosion of tanks in case of lightning for example.
- Loses of product and contamination of environment.
- The necessity to take the tanks out of operations and replace tank roofs every 5-7 years

Today, on average all refineries loose about 10% of the operating life of each storage tank.

The traditional corrosion protection methods (coatings, stainless steel, aluminum, polymeric covers**)** in many cases are not efficient enough, are not cost effective, or they cannot be applied. All these methods cannot be applied without taking the tanks out of operation.

It is obvious that reliable and efficient corrosion protection systems that can be applied for corrosion protection of the new and existing tanks are necessary.

We have now created a new corrosion protection system that delivers the required types, compositions, and concentration of volatile corrosion inhibitors (VCI) directly on the tank tops. It can be applied on both existing and new tanks. The basic test results and advantages of this system are discussed below.

Resultados / Discussão

Creation of a New System

The following stages were conducted that allow creating a system for corrosion protection of oil storage tanks tops:

- Laboratory tests to choose VCI compound and compositions that can be efficient in the most corrosive (predictable and unpredictable) environment available.
- Field trial tests to finalize the efficiency and achieve the required service life of corrosion protection.

The Main objective was to create a system that will increase the service life of tank top up to 25 years, to exclude the necessity to replace tank tops and take them out of operation due to corrosion.

Laboratory Tests

The pretest concerns that included the evaluation of exact tank tops environment and composition of corrosion product samples (Figure 3) allowed us to choose the most corrosive environments and conditions (Table 3) for testing the efficiency of VCI compounds and compositions.

The preliminary tests of a wide number of VCI's allowed us to chose for final testing three of them – VCI for aboveground crude oil storage tanks tops – Volatile Tanks Inhibitors (VTI-1, VTI-2, and VTI-3).

The efficiency of new VCI was investigated after testing according to the following procedures:

- The tests conducted in special assemblies created for these procedures.
- Test specimens (88x25x0.5 mm) were made from mild steel C1010.
- Assembly was closed for 20 hours to allow inhibitor to saturate environment.
- Assembly was placed in corrosion testing chamber. Conditions in chamber were: Gas atmosphere of SO_2 and H_2S, temperature 38^oC, and relative humidity (RH) up to 100%.
- The corrosion rate (CR) was determined by measuring the weight loss of the specimens.

Laboratory Test Results and Discussion

Summary of the tests results shown in Table 4 and Figure 4 gave the possibility to define efficiency of chosen corrosion inhibitors and their combinations. In the environment without inhibitors the corrosion started instantly. After about one hour, the surface of all specimens was fully covered with corrosion products (Figure 4). The specimens tested in environment with inhibitors had some spots only on the horizontal surface areas. All three types of VCI's and their combinations showed approximately the same high efficiency, from 70 to 100% (Table 4). The average corrosion rate of carbon steel in environment without inhibitors was from 0.6 to 4.0 mm/year. The corrosion rate of specimens tested in all environments with inhibitors was from 0 to about 0.1 mm/year (only in certain spots).

The test results allow us to make the following conclusions:

- The selected VCI compositions have high efficiency in the most corrosive environments that contain: sulfur dioxide, hydrogen sulfide, relative humidity up to 100%, and temperatures in a range 25 to 55° C.
- It is possible to achieve the efficiency of corrosion protection above 70% by choosing the exact type, combination, and concentration of VCI's.

Field Trial Tests

The objective of the trial tests was to verify the efficiency of chosen VCI's. For this purpose, a highly efficient system (utilizing VCI dispensers) was created, which allows simultaneous delivery of one or more type of VCI's directly to the tank tops (Figure 5 and Figure 6).

These dispensers have the following advantages:

- The manufacturing and installation is very simple and low cost.
- Can be applied one time for corrosion protection of full time service life of tanks, up to 25-40 years, for example.
- Refilling of inhibitors is very fast and does not require the necessity to take the tanks out of operation. The dispensers on tank with diameter 55 m., for example, can be refilled within one day.
- In the event that the corrosion environment and/or application condition during service life of tank will be change, the required efficiency can be achieved only by changing of VCI's types or compositions.

The trial tests were provided during two years at Petrobras Refinery (Brazil). For testing two tanks with similar properties were chosen:

- same dimensions (diameter 55 m and height 14 m),
- tank tops were replaced approximately at the same time,
- both tanks are used for crude oil storage.

The following procedures were conducted to define the efficiency of the new Corrosion Protection System – VCI Dispensers:

- In both tanks, steel test specimens were installed to define the initial information about the corrosion rate.
- Monitoring of environment conditions (RH, temperature (T), the concentrations of O_2, SO_2, H_2S) in the empty spaces of tops of tanks.
- Measuring of weight loss of test specimens installed in both tanks.
- Measuring of top of tanks' thickness by using Ultrasonic Thickness Gage.
- Monitoring of inhibitor weight loss to define the expected service life of refilling the dispensers' containers.

Field Trial Test Results and Discussions

Environmental conditions. The test results show that the empty spaces of both tank tops have a very aggressive corrosion environment (Table 5). Comparison of the test results shows that in Tank 2 the corrosion environment was much more aggressive than in Tank 1. The concentrations of the most corrosive acidic pollutants (SO_2 and H_2S) in Tank 2 were 3 - 20 times higher than in Tank 1.

Corrosion loss of steel specimens

Summary of tests results showed that in all cases, corrosion of specimens in Tank 2 (with protection) was 2 - 3 times less than in Tank 1 (without protection).

Corrosion loss of tanks tops

The tanks tops were evaluated by ultra-sound technique to define the corrosion loss of thickness. The summary of monitoring tanks tops thickness (Figure7) shows that the corrosion rate is:

- 1.6 mm/year in Tank 1 without protection
- 0.12 mm/year in Tank 2 with applied VCI dispensers

Corrosion loss of tanks tops. The tanks tops were evaluated by ultra-sound technique to define the corrosion loss of thickness (Figure 7). Three areas (1x1m) were chosen for monitoring of the roof thickness In each area, 676 points were measured. The summary of monitoring tanks tops thickness (Figure 8) shows that the corrosion rate is:

- 1.6 mm/year in Tank 1 without protection
- 0.12 mm/year in Tank 2 with applied VCI dispensers

It is necessary to take into consideration that depending on environment and application conditions (wich for tank tops in most cases unpredictable) the corrosion rate by using of VCI can be different from the shown (for example, up to 0.3 mm/year), but in all cases it will be 5-10 times less than without protection. The created system allows increasing the required efficiency by chosen other composition of inhibitors.

System Application

The trial testing allowed starting general application of the Tank Top VCI Dispensers system for protection of internal surfaces of storage tank roofs. Taking into consideration the positive results and experience achieved during trial testing, this system is now being implemented by Petrobras on oil storage tanks with carbon steel roofs. The design of the dispensers was finalized accordingly and the first system was successfully applied at REDUC-Petrobras

Refinery in year 2008 (Figure 9). It is anticipated that this system will be applied on the most of Petrobras tanks.

This system can be applied on new storage tanks and during regularly scheduled maintenance or replacement of tank roofs on existing storage tanks. It does not contain any moving or electrical parts, is hermetically sealed, and can be serviced during operation of the tank. The results of 9 month application of created system (Figure 9) showed it high efficiency. The corrosion rate was up to 0.16 mm/year – more than 5 times less than without protection.

Conclusões

1. Corrosion loss of tanks tops thickness depends on the gaseous composition and concentration of main compounds (SO_2, H_2S), RH, temperature, as well as operation conditions of tanks.
2. The trial protection system (VCI Dispensers) decreased the loss of thickness in the most corrosive environment from 1.60 mm/year to 0.12 mm/year, or more than 10 times. The service life of tanks can be increased at least 5 times.
3. It necessary to take into consideration that depending on environment and application conditions the corrosion rates (with and without protection) can be different from the shown data. But in all cases the VCI system allows to decrease the corrosion rate more than 5 times.
4. The new protection system (Dispensers) can be recommended for the required service life only by replacing VCI containers every 0.5 to 3 years.
5. The trial protection system is very efficient when the tanks are in operation. In case the tanks are taken out of operation, the VCI Dispensers must be turned off. At this time, the corrosion loss of thickness will depend on environment conditions and the duration of tanks being opened (not in operation).
6. The corrosion protection system, utilizing VCI Dispensers, can be applied on new and existing oil storage tanks, making the following advantages possible:
    - Exclude stoppage the tanks (taken out of operation) for replacement of tops or for replacement of coating
    - Exclude the necessity to use very expensive stainless steel, aluminum and plastic instead of carbon steel
7. The composition of the VCI formulation can be chosen to optimize protection for different products, depending on environment and application conditions.
8. Some data can be corrected depending upon the efficiency of coatings used and temperature of the tank surfaces.
9. Tank Top VCI Dispensers system has been successfully applied at one of Petrobras' refineries and allows to decrease the corrosion rate up to 0.16 mm/year - more than 5 times.

Tabelas, Ilustrações e Fotos

TABLE 1
BASIC COMPOSITION OF THE GASEOUS ATMOSPHERE IN THE TANKS TOPS

Components	**O_2**	**SO_2**	**H_2S**	**R-S-H***	**Cl**	**N_2**	**CO_2**	**H_2O**
Approximate volume, %	4.0	1.0	1.0	5.0	0.5	70.0	12.0	0.5

***Mercaptans**

TABLE 2

Type of corrosion:	General	Pitting	Galvanic	Crevice
Corrosion rate (mm/year):	0.1-0.5	0.5-5.0	0.2 – 3.0	0.3-8.0

TABLE 3

CORROSION ENVIRONMENT USED FOR EVALUATION THE VCI EFFICIENCY

Environments	**Source of**	**Type of environment**		
Components		**A**	**B**	**C**
H_2S	$(NH_4)_2S$	+	-	+
SO_2	Na_2SO_3	-	+	+
RH, %	Chamber and Assembly	T = 25 – 55^{O}C and RH up to 100%		

TABLE 4
SUMMARY OF THE 60 DAYS TEST RESULTS

Type of VCI – VTI:*			**Efficiency** of VCI's in different corrosion environments:**		
1	**2**	**3**	**A – SO_2**	**B – H_2S**	**C – SO_2 +H_2S**
-	-	-	0	0	0
+	-	-	95 - 100	90 - 100	85 - 95
-	+	-	85 - 95	80 - 90	80 - 90
-	-	+	80 - 95	75 - 85	75 - 85
+	+	-	80 - 95	75 - 90	75 - 90
+	-	+	80- 95	80 - 90	80 - 90
-	+	+	75 - 85	70 - 80	70 - 80
+	+	+	75- 85	70 - 80	70 - 85

** In all tests used the same weight of inhibitors*
*** Efficiency by weight loses and surface areas covered with corrosion products*

TABLE 5

ENVIRONMENT CONDITIONS IN THE EMPTY SPACES OF THE CONTROL TANK 1 AND TANK 2 WITH INSTALLED VCI DISPENSERS

Basic Parameters		**Monitoring Results**	
		Tank 1	**Tank 2**
Temperature, ^{o}C		20 – 55	
RH, %		40 – 100	
Concentration	O_2 (%)	18-18.9	10 - 21
	SO_2 (ppm)	1.0-7.0	> 20
	H_2S (ppm)	3.0-6.0	> 26

FIGURE 1. Examples of the vapor spaces in the storage tanks with roofs: fixed (a), floating with pontoon (b), fixed and floating with pontoon (c)

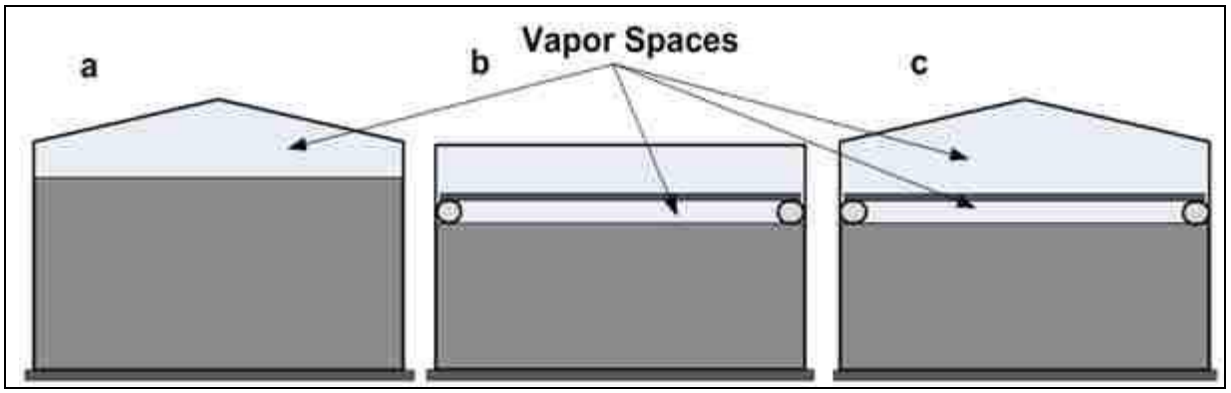

FIGURE 2. Examples of pitting (a-c) and crevice (d) corrosion on the tanks top that had coating for protection from corrosion

FIGURE 3. Corrosion products from top of crude oil storage tank, received from Petrobras (Brazil):
a - Mixed with epoxy coating, b - Behind the coating, c - Free from coating

FIGURE 4. *Specimens after testing in different environments without (a) and with inhibitors (b)*
Samples position (SP) by testing: GS - horizontal, VS – vertical

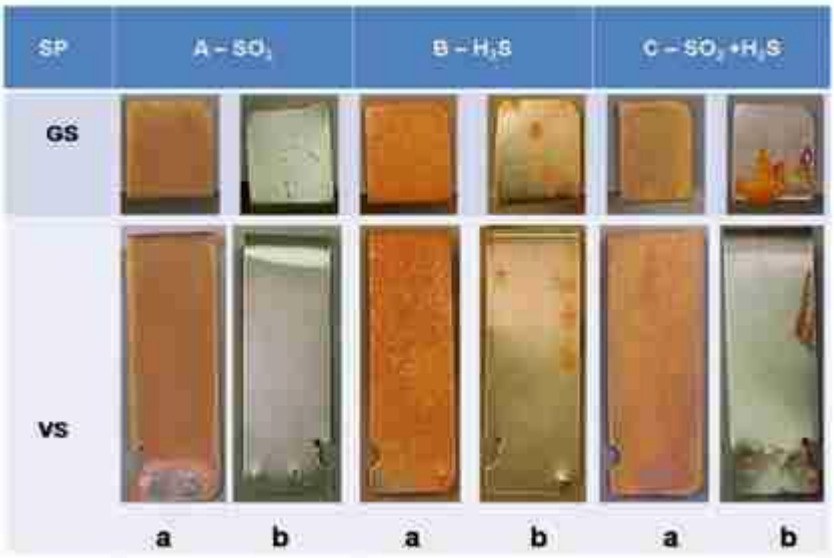

FIGURE 5. VCI's delivery dispensers(a, b) and their installation on the tank tops (c).

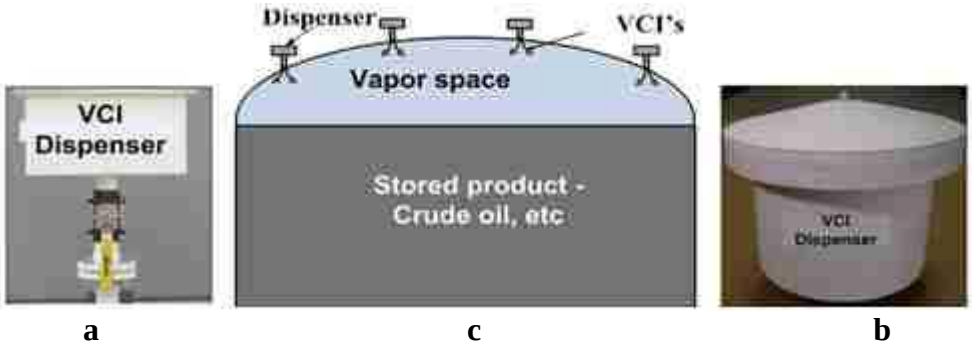

FIGURE 6. Dispensers installed on the tank tops

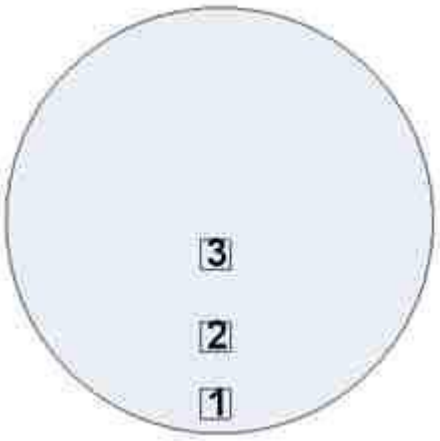

FIGURE 7. The surface areas where the thickness of tanks roofs were measured

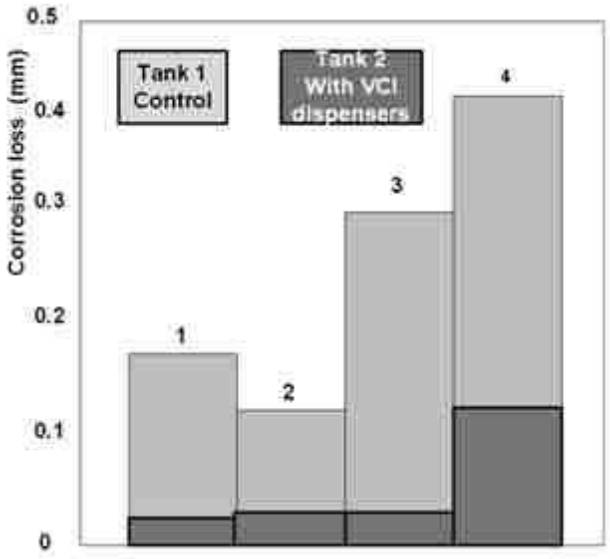

FIGURE 8. Corrosion loss of the tanks tops after 90 (1), 135 (2), 225 (3) days and one year(4) application period

FIGURE 9. Corrosion mitigation system installed on crude oil storage tank roof for long term protection

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