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Corrosion protection of tank product side bottoms

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Abstract

Corrosion of storage tank product side bottoms and tanks of tankers is one of the most critical problems worldwide in oil and gas industry. The protection methods currently in use include cathodic protection systems (CPS) and soluble corrosion inhibitors (SCI). Crude oils contain water and various soluble inorganic and organic compounds. During the storage and transportation of crude oil, the sediment aqueous solutions (SAS) contains high concentrations of H_2S, Cl^-, SO_4^{2-}, *etc*. The corrosion rates of storage tanks and tanks of tanker bottoms can vary from 0.05 to 3.0 mm per year. The service life of tank bottoms is unpredictable and can range from 2 to 20 years. In many cases, traditional corrosion protection systems (cathodic protection, coatings, and inhibitors) are not efficient enough, have short service life, or cannot be applied. This paper describes a new multistage corrosion protection system that combines different types of soluble corrosion inhibitors and cathodic protection systems. Together they achieve synergistic effects that can decrease the inhibitor protection concentration 3- to 6-fold and the current density 2- to 5-fold. This results in an increased service life of the corrosion protection method.

Key words: *corrosion, inhibitor, cathodic protection, storage tanks, efficiency, service life.*

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Introduction

Corrosion is one of the biggest worldwide problems in the oil and gas industry. In 1996, the total corrosion-related costs in USA refineries were about $3.7 billion [1]. In 1997 the estimated cost of corrosion was about $0.4 per barrel of oil produced [2]. In this case, the corrosion losses per barrel in 2012 show that the top oil production countries are losing from 0.4 to 4.2 million dollars per day (Fig. 1). Due to the increased cost of crude oils, the cost of corrosion per barrel now is much higher.

Many non oil production countries have oil storage tanks and refineries. Their corrosion cost is not included in the data shown. The cost of oil production increases continuously and the related corrosion costs increase as well. About 60% of all maintenance costs are related to corrosion [1, 2].

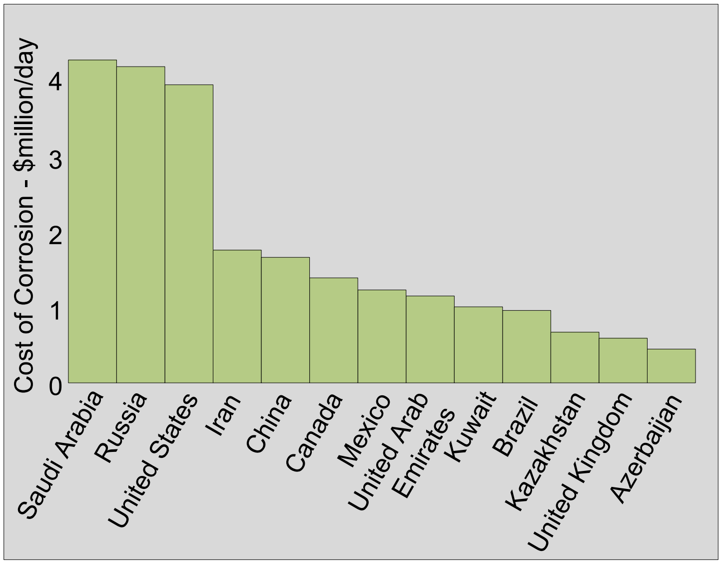

Fig. 1. Estimated corrosion cost in top oil production countries in 2012 taking into consideration the corrosion-related losses of 0.4$ per barrel.

This short introduction shows the importance of creating high-efficiency, long-term corrosion protection methods now and for the future. In this paper, a corrosion protection method for the bottoms of crude oil storage tanks is described.

Crude oils contain water, as well as different water soluble inorganic and organic compounds. During the storage and transportation of crude oil, the aqueous solutions settle to the bottom of the tanks. The composition of the aqueous sediment layer depends on many factors, such as the properties of the oil, extraction technology, *etc*. (Table 1).

The level, composition, concentration, and pH of the water solutions are unpredictable in most cases. In some countries the crude oil stored in tanks contains from 10 to 90% water. After dewatering and desalting, most storage tanks contain up to 2% water. The level of SAS in production storage tanks increases with time, depending on the tank design. The level of SAS can reach 1 m.

The corrosion rate of tank bottoms depends on the composition, concentration, and pH of the aqueous solutions. In a typical aqueous solution (Table 1), corrosion rates can vary from 0.05 to 0.30 mm per year (Table 2). If sediment water contains sulfide, sulfur dioxide and carbon dioxide components, the pitting corrosion rate can increase to 5 mm per year [3–19].

The service life of tank bottoms is unpredictable and is up to 10 years in most cases [13]. Replacement of tank bottoms is very difficult and expensive. Replacement or application of additional tank bottoms, or repairing holes, is necessary every 2 to10 years. The time it takes to replace a tank bottom depends on many factors, and can be 3 to 18 months. Total replacement time can reach 10% of the life time of a tank. In many countries the corroded bottoms were replaced with double bottom or tanks were originally made with double bottoms. However, it did not solve the corrosion problems. In many cases, this approach aggravated the corrosion problems and made corrosion protection technologies more difficult to apply.

Table 1. Typical composition of sediment aqueous solutions (SAS[†]).

Type	Contents of Compounds[††] (g/L)					Total (g/L)	pH
	NaCl	$CaCl_2$	$MgCl_2$	$NaHCO_3$	Na_2SO_4		
1	2.8	0.3	0.07	0.2	0.2	3.5	7.7
2	31.1	0.8	0.5	1.6	0.9	35	6.8
3	187.5	6.4	2.7	2.0	1.4	200	6.9
4	29.1	0.3	1.0	4.2	0.01	35	8.5
5 – SW[†††]	27.1	1.1	2.4	0.2	–	35	7.6
6	30.2	1.2	1.3	1.7	0.07	35	7.6
7	219.9	8.1	11.4	10.6	0.06	250	7.0
8	27.4	4.3	1.2	0.3	1.8	35	7.6
9	185.1	37.6	25.9	0.2	1.2	250	6.7

[†] Some SAS contain up to 1.0 g/L of H_2S and CO_2 (each), do not contain O_2, and can have pH 4–5

[††] Concentration of O_2: up to 20 mg/L

[†††] SW – Sea Water

Table 2. Examples of corrosion rate of carbon steel in the SAS on the tank bottom.

Type of Oil	Corrosion Rate (mm per year)	
	Average	Pitting
Crude	0.1 – 0.5	1.0 – 3.0
Light	0.05 – 0.3	0.4 – 0.8

The danger of corrosion in many cases is created by wide-ranging and unpredictable application conditions. Typical examples of different types and forms of corrosion are shown in Fig. 2.

In many cases, this situation excludes the possibility of achieving the predicted efficiency of existing corrosion protection methods:

- Initially, in oil (Fig. 2a) the corrosion is close to zero. Crude oil works as a lubricant. It explains why the corrosion on the wall is insignificant.

- In a short time, depending on the water contents in crude oil, a sedimented aqueous solution begins to form (Fig. 2b). On the way, it dissolves the inorganic salts. The concentration and corrosiveness of the aqueous solution is initially very high. The level of aqueous solution increases, for example, to 1 m (Fig. 2c) and the concentration of salts can decrease in some cases. Again, it depends on the oil composition.
- Frequent draining does not exclude some level of aqueous solution and corrosion continues for approximately 100% of the time.
- In some cases, the sludge that contains an aqueous solution settles on the tank bottom (Fig. 2d) and in many cases it is the reason for pitting corrosion.

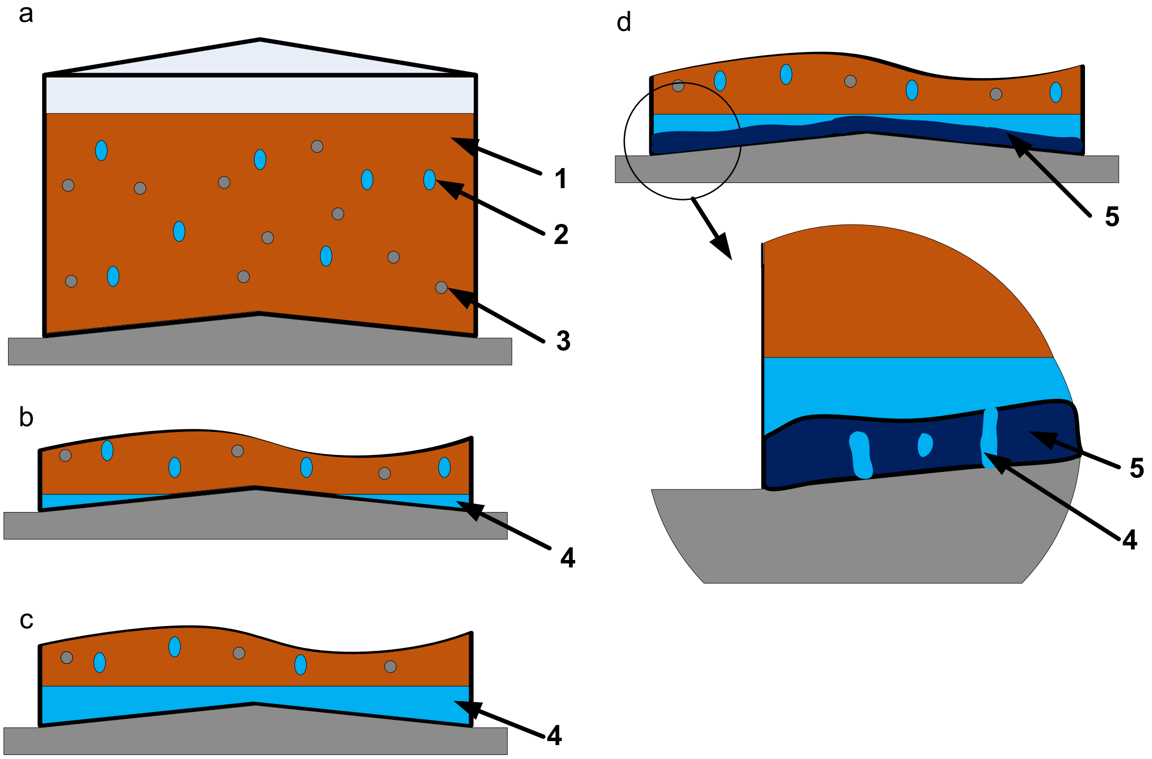

Fig. 2. Examples of the corrosion environments in the tank bottom: 1 – crude oil, 2 – water, 3 – salt, 4 – aqueous solution sediment, 5 – sludge.

Examples show that it is very important to create a corrosion protection technology that will be efficient under all unpredictable application conditions.

The traditional corrosion protection systems (cathodic protection, coatings, and inhibitors) can be efficiently used. In many cases, they are not efficient enough, are not cost effective, or cannot be applied. It is obvious that reliable and efficient corrosion protection systems are necessary. Such systems can use coatings or cathodic protection systems (CPS), or their combinations [9–19]. For 20 to 50% of time the level of aqueous solution sediment (SAS) is low (less than 0.1 m) and CPS cannot work. At this period the concentration of SAS is high and corrosion rate is higher than when the level of SAS increases and CPS start to work (Fig. 3).

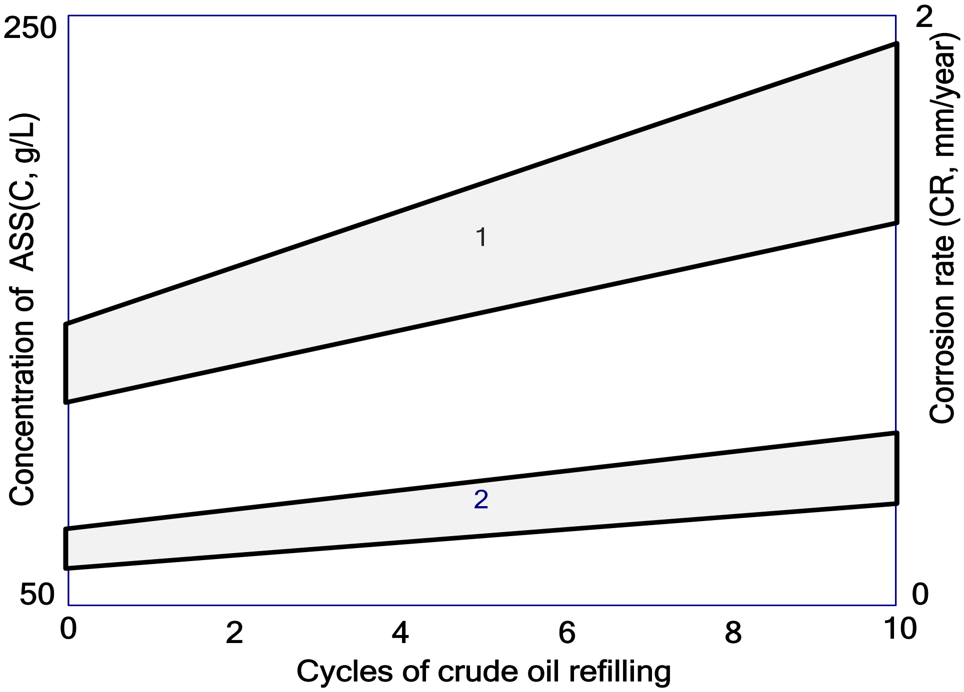

Fig. 3. Schematic example of the relationship between the CR (*1*, *2*) and concentration of sediment aqueous solution (*1*, *2*) when its level is 0.1 m (*1*) and 1.0 m (*2*).

In many cases, periodical draining of water creates the same problems as those shown in Fig. 2. In all these cases, the efficiency and service life of these systems are inadequate. It is impractical to repair the coating because of the high cost.

The efficiency of CPS in combination with SCI for corrosion protection of tanks with seawater is well documented [7, 8]. We have now created a new multistage corrosion protection system, which combines CPS and soluble corrosion inhibitors. This achievement is possible with a newly created special system for delivery of inhibitor directly to the tank bottoms. The basic test results of this system are discussed below.

Creation of the new corrosion protection system

Experimental

The specimens (50×20×1 mm) were produced from strips of mild steel containing, mass%: 0.11 C, 0.94 Si, and 0.71 Mn. They were sand blasted, degreased in alcohol, cleaned by water flushing, dried in a stream of air, and stored in a glass cell with a desiccant at room temperature.

The following aqueous solution was used as the corrosive medium (g/l): 27.7 NaCl, 0.2 $NaHCO_3$, 3.4 Na_2SO_4, 1.1 $CaCl_2$, 2.4 $MgCl_2$, 0.5 H_2S, and 0.5 CO_2. The temperature was 20–25°C. This electrolyte creates one of the most active corrosive environments in seawater, soil, and the aqueous sediment in oil tanks [8]. The pH was 6–8 during the experiments. The results obtained in this medium can be used to choose the corrosion protection methods for all types of oil storage tanks and for other structures containing aqueous solutions.

Various SCI mixtures, including inorganic compounds (for example, NaH_2PO_4, $ZnMoO_4$, $ZnSO_4$), organic acids, and compounds containing nitrite, phosphate, and chloride (for example, $C_{17}H_{30}NCl$) [6, 8, 10, 13, 19] were tested as corrosion inhibitors. The concentration of inhibitors was varied from 5 to 300 mg/L of the aqueous solution.

The electrochemical properties were investigated by potentiostatic cathodic polarization in the potential range from 50 to 300 mV with respect to the corrosion potential (E_C). A platinum-titanium electrode was used as the counter electrode (anode) and a silver/silver chloride electrode was used as the reference electrode (RE). In this paper, the potentials were converted to the hydrogen reference electrode (HRE) scale. The corrosion rate (CR) was determined by measuring the weight loss (W) of the specimens after immersion in an electrolyte without corrosion protection (W_c), with only SCI or CPS (W_{cp}), and with their combination (W_{cpm}). The efficiency of corrosion protection was calculated as: $\eta = (1 - W_p/W_c)\times 100\%$, where: $W_p = W_{inh}$, or $W_{cp,}$ or W_{cpm}.

Results and discussion

The maximum CR (pitting corrosion) occurs rarely and on less than 1% of the surface at the bottom (Table 2). The maximum corrosion rate can be very detrimental. It is well-known that pitting corrosion occurs in the majority of crude oil tanks. The inhibition of medium and high corrosion rates is possible at the same time. That is why the medium corrosion rates are of concern.

The summary of the results shown in Table 3 makes it possible to determine the efficiency of various corrosion protection methods.

The average corrosion rate of unprotected carbon steel is 0.21 mm per year in the aqueous solutions used for testing (Table 3). After addition of 100 or 250 mg/L inhibitor (SCI) solution, the corrosion rate of mild steel decreases to 109 and 21 μm/year with an efficiency of 48 and 90%, respectively. Cathodic polarization is more efficient.

At a current density of 200 mA/m^2, the efficiency increases to about 95%. In most cases, CPS have j = 100−120 mA/m^2 by design, which gives an efficiency of 80%. This method is cheaper and results in an efficient corrosion protection system.

The advantages and the possibilities of SCI, CPS, and their combination are shown in Fig. 4. It is possible to choose the required properties by using various types of inhibitors and their concentrations. Figure 4 shows two different mechanisms of corrosion protection with inhibitors and cathodic polarization. Inhibition decreases the corrosion rate due to the effect of passivation changing the corrosion potential from –500 mV to –400 or –200 mV, for example. The corrosion potential depends on the inhibitor type and concentration. On the other hand, by using cathodic polarization, it is possible to decrease the corrosion rate of steel by decreasing its corrosion potential from –500 mV (j = 0 mA/m^2) to –600 mV (j = 100 mA/m^2) or to –800 mV (j = 200 mA/m^2).

Table 3. Efficiency of SCI, CPS, and their combination (CPM).

Protection method	Concentration of inhibitors (mg/L)	Cathodic current density (mA/m^2)	Average efficiency* (%)
SCI	30	0	5
	100	0	48
	250	0	90
CPS	0	10	25
	0	120	80
	0	200	95
CPM	10	20	48
		50	65
	30	20	70
		50	90
	50	20	80
		50	90
	100	10	80
		30	90

According to NACE and international standards, a cathodic protection criterion is a required cathodic shift of potential of 100 mV, and maximum cathodic shift of 300 mV. Figure 4 shows that cathodic protection criteria in aqueous solution with inhibitor are achieved at smaller current densities. This data explains the parameters described in Table 3.

The goal of this presentation is to show the principle of attaining highly efficient protection systems by combining low concentrations of inhibitor and using low current density cathodic protection. In this case, the synergistic effect allows a decrease in inhibitor concentration by 3 to 6 times and in the current density by 2 to 5 times.

Many inhibitors increase the corrosion rate at low concentrations. The the comparative properties of inhibitors, cathodic protection and combined methods are shown in Table 3 and Fig. 4. A combined corrosion protection method (30 or 50 mg/L inhibitor and 50 or 20 mA/m^2 current density) is optimal. This is only one example of synergistic effect. Further, test results demonstrated the decrease in inhibitor concentration and current density by selection of different types and compositions of inhibitors.

The results shown here are very important for choosing highly efficient and inexpensive corrosion protection methods. However, it is necessary to define the dependence between inhibitor concentration and current density. The combined method is efficient only when inhibition and CPS work simultaneously. On turning off cathodic polarization, corrosion increases and efficiency of the system decreases. Normally, after some time without cathodic polarization, pitting corrosion will start and efficiency will decrease to 5% (Table 3). This system cannot be used without an inhibitor, mainly because the current density is low (for example 10 mA/m^2) and in that case, the efficiency of the cathodic corrosion protection is less than 25% (Table 3).

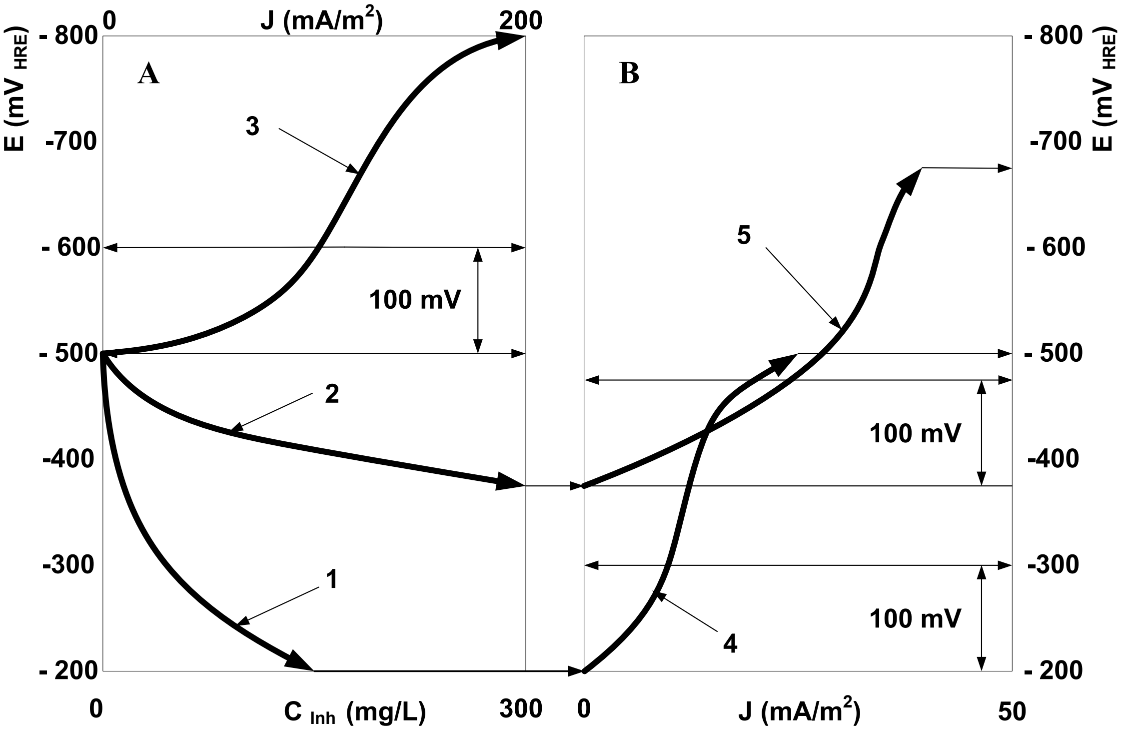

Fig. 4. Relationship between: *A* – corrosion potential (*E*) and concentration (C_{Inh}) of two types of inhibitors (*1*, *2*); *B* – cathodic polarization potential of steel and current density in SAS without inhibitor (*3*) and with inhibitor of type 1 (*4*) or type 2 (*5*).

The test results allowed us to create a multistage protection method for corrosion protection of oil storage tank bottoms. It has a specific operation condition. After filling up the tank with crude oil, an SAS starts to settle. The SAS level, concentration, composition, and time until the maximum SAS level is reached depend upon many factors, including the concentrations of water and mineral compounds in oil. The highest corrosion rate occurs when the level of aqueous solution sediment is very small. At this time, cathodic protection cannot work until the level of aqueous solution increases enough to achieve the radius of protection of the anodes. Inhibitors are efficient only when the level of aqueous solution is low and the concentration of inhibitor is high. As shown in Table 3, the needed concentration of inhibitors is very high and this method is not cost effective. The multistage combined protection method created (Fig. 5) allows us to achieve a high efficiency of corrosion protection when the aqueous solution sediment begins to form and when the volume of the solution increases to the maximum level.

How does the multistage corrosion protection system work?

1. Apply the cathodic protection system with sacrificial anodes on the tank bottoms. Numbers, material, type and dimensions of anodes chosen depend on the required service life and protection radius.
2. Before filling or immediately after filling the tank with crude oil, SCI needs to be delivered to the bottom. The weight of the SCI must be chosen to achieve the concentration, 30 mg/L for example, when the volume of aqueous solution increases to the maximum level.
3. High efficiency of corrosion protection is achieved in the following three stages:

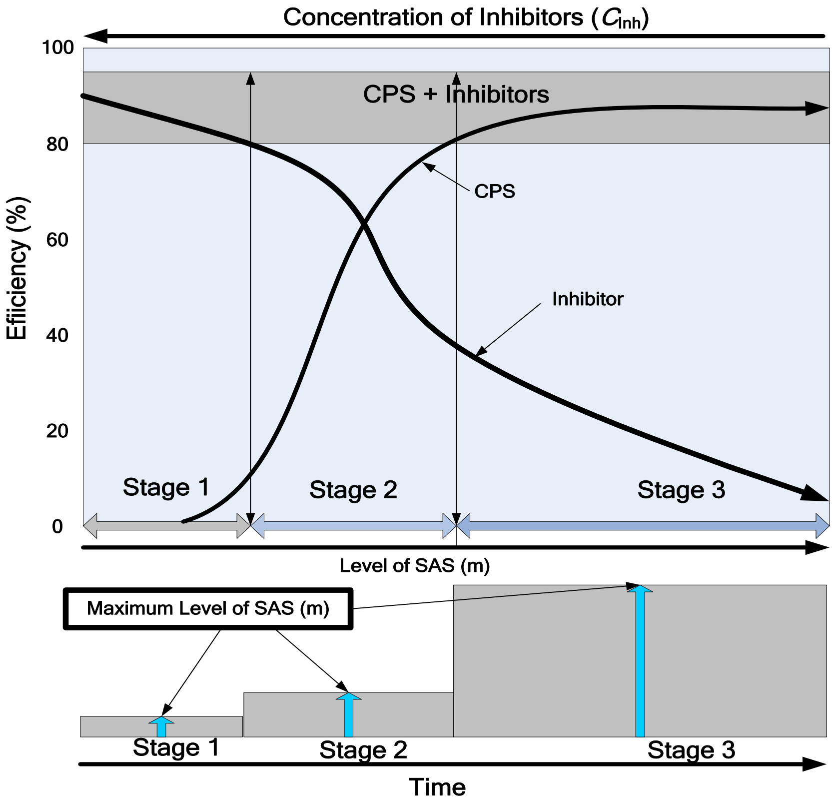

Fig. 5. Efficiency of CPS or/and inhibitor depending on the level of SAS and concentration of inhibitor:

Stages	**1**	**2**	**3**
C_{inh} (mg/L)	> 200	> 100	> 30
J (mA/m^2)	0	10 – 30	30 – 50

Stage 1 occurs when the aqueous solution begins to sediment and dissolves the SCI. The volume of SAS increases and the concentration of SCI decreases to 200 mg/L. In this first stage, the aqueous solution does not cover sacrificial anodes; cathodic protection cannot work properly and the corrosion protection is only achieved due to inhibitors. The efficiency of protection is 80 to 90% (Fig. 5, Table 3).

Stage 2 occurs when the level of the SAS increases and the inhibitor concentration decreases to 100 mg/L. At this time, CPS begins to work with a current density of 10 to 30 mA/m^2. This combination allows efficiency of corrosion protection of 80 to 90% (See Table 3) to be achieved. In this stage, the efficiency is due to inhibitors and CPS.

Stage 3 occurs when the volume of the SAS increases to the maximum level. The SCI concentration decreases to 30 mg/L and CPS achieves a current density of 30 to 50 mA/m^2. This combination allows an efficiency of corrosion protection of 80 to 90% to be achieved (See Table 3). In this stage, the efficiency is due to CPS.

It is necessary to make the following very important remarks. This system is efficient only in combination. Inhibitors (at the concentrations shown) without CPS, CPS in combination with inhibitors, and CPS without inhibitors have the following efficiency (%):

Stages	**1**	**2**	**3**
Inhibitors without CPS	80–90	< 35	> 5
CPS without inhibitors	< 10	< 80	> 80
CPS with inhibitors:	> 80	> 80	> 80

High efficiency (80–90%) of protection systems is achieved due to the synergistic effects observed in Stages 2 and 3. This data explains why the CPS by itself is not efficient enough to exclude the necessity of replacing tanks bottoms.

Multistage corrosion protection systems can be applied on new tanks, or on existing tanks, after replacing or repairing the tank bottoms. In our design, inhibitors can be delivered to tank bottoms without interfering in their operation.

Conclusions

1. A multistage technology for corrosion protection of storage tank bottoms has been created.
2. It is now possible to use soluble corrosion inhibitors in combination with cathodic protection systems. The combined action of inhibition and cathodic polarization results in a synergistic effect. It decreases the needed concentration of inhibitors and the cathodic protection current density.

3. It is possible to supply CPM (SCI + CPS) for corrosion protection of mild steel with an efficiency of 80–90% in aqueous solution sediments.
4. It is possible to choose several inorganic and organic soluble corrosion inhibitors for corrosion protection of steel and other metals.
5. The combined protection system is 2−3 times more cost effective than coating, CPS, and inhibitors by themselves.
6. The created system achieves the required efficiency of corrosion protection on the internal surfaces of oil storage tank bottoms in unpredictable environments and application conditions.

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