# Proposal of the use sodium silicate as a corrosion inhibitor in hydrostatic testing of petroleum tanks using seawater

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**Abstract** —*Hydrostatic tests with water are used to evaluate leaks in welds and possible cracks and failures that may have occurred during construction in petroleum storage tanks and derivatives. Defects and cracks in the concrete foundations that support the tank on the ground are also observed in these tests. The use of seawater as a fluid for hydrostatic testing of petroleum storage tanks and derivatives can be a good option in areas lacking fresh water, especially when these tanks are near the sea. The use of seawater is economically attractive; on the other hand, corrosion by seawater is much more aggressive toward carbon steel than corrosion by treated fresh water. The potential advantages of the use of a mixture of silicates and zinc sulphate as a corrosion inhibitor are the effective protection of carbon steel, especially in saline fluids, low cost, and non-aggressive behaviour toward the environment. Gravimetric and electrochemical laboratory tests were carried out using synthetic seawater with the addition of a mixture of sodium silicate ($Na_2SiO_3$) and zinc sulphate ($ZnSO_4.7H_2O$). Gravimetric testing with an immersion time of 40 days using 1000 and 2000 mg/L of $Na_2SiO_3$ and 150 mg/L of $ZnSO_4.7H_2O$ gave a good performance and can be used for hydrostatic testing with seawater.*

**Keywords — *corrosion, hydrostatic testing, silicate, corrosion inhibitor, petroleum tanks, failures.***

## I. INTRODUCTION

It is always good to remember the important critical reflections of Michel Llory [1] and Moacyr Duarte [2] on industrial accidents considering human factors, projects, industrial assemblies, mechanical emergency repairs, and specific and localized environmental conditions, which may consequently result in spills, explosions, evacuations of communities, environmental contamination, poisoning, associated diseases, and loss of life.

According to Mainier [3] all of the above mentioned facts are intended to show those responsible for large industrial complexes the need to respect the integrity of equipment standards and directives regarding environment preservation. In addition, it is essential to develop clean and secure technologies to avoid environmental disasters with the goal of increasing safety and reducing pollution of the planet. Therefore, it is very important to articulate the integration of environmental agencies, public health, safety and industrialization with a society organized to establish standards and procedures in order to ensure real quality of life.

Research conducted by Chang and Lin [4] based on 242 accidents with storage tanks showed that 74% of accidents occurred in petroleum refineries and petroleum storage terminals, with fires and explosions accounting for 85% of accidents. In addition, it was reported that other causes were identified such as equipment failure, sabotage, cracks and ruptures, leakage and rupture lines, static electricity, fire, and so on, with the conclusion that most of these accidents could have been avoided if the principles of good engineering, project, installation, inspection, maintenance, and monitoring had been practiced.

Some authors found that hydrostatic testing on oil storage tanks is relatively effective in the detection of possible defects that can cause failures during routine operations [5–7]. Hydrostatic testing is universally known and accepted as a means to demonstrate the fitness of a pressurized component for service.

According to the Brazilian standard NBR 7821 NB 89 [8], after industrial assembly of large tanks for oil storage, hydrostatic testing must be carried out in order to check the tightness of the welds, possible cracks or fissures, defects of construction, and the state of the foundations (reinforced concrete) that hold the tank on the ground, as shown in Figure 1.
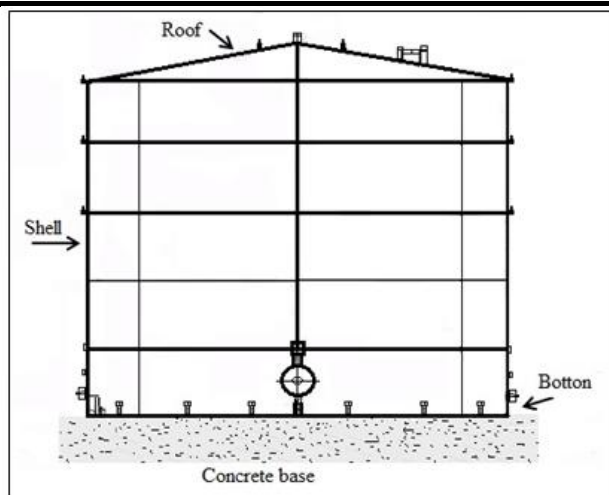
*Fig. 1: Schematic of oil storage tank*

Hydrostatic testing consists of a sequence of filling with water, first halfway, then up to three quarters of the total volume, and finally up to two inches above the top of the mounting bracket. Generally, fresh water is used, but due to the difficulties of obtaining a freshwater supply when the cost of treated water is prohibitive, or when the facilities are located in sea areas, it is possible to use seawater. The test time depends on the criteria of inspection, disposal of the large volume of water from the test and the environmental standards.

When the tanks are near to seawater, it is valid to say that the low cost is attractive; however, due to the severe corrosivity of seawater toward carbon steel (the material from which tanks are manufactured), it is obligatory to use corrosion inhibitors. Corrosion inhibitors can be defined as substances added to the corrosive medium to slow down or inhibit the corrosive process [9, 10].

Sodium silicate is advertised as a corrosion inhibitor, is widely used in industrial applications intended for protection of metals and alloys, and is known as a "green inhibitor" because it does not have an environmental impact. Other compelling factors are the low cost and industrial availability of this inhibitor. Sodium silicate can be prepared by melting sodium carbonate ($Na_2CO_3$) with silica sand ($SiO_2$) in an electric oven at a temperature of 1400 °C, as shown by the following reaction. The product is dissolved in hot water under pressure and filtered to remove insoluble materials. The proportions of the constituents ($xSiO_2$ and $yNa_2O$) in the final product depend on the initial dosages used in the preparation of the mixture.

$$Na_2CO_3 + SiO_2 \xrightarrow{1400\,°C} CO_2 + Na_2SiO_3 \ (xSiO_2.yNa_2O)$$
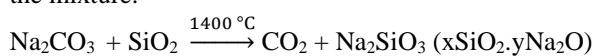
Based on these assumptions, laboratory tests of mass loss and electrochemical tests with specimens of carbon steel and additions of sodium silicate and zinc sulphate were performed to allow the use of synthetic seawater in hydrostatic tests.

## II. MATERIALS AND METHODS

### 2.1 Gravimetric test

The material evaluated in this work was AISI 1020 carbon steel (0.20% carbon, 0.34% Mn, 0.35% Si, 0.011% S, and 0.009% P) used in the confection of the coupons. The coupons used in the gravimetric tests (weight loss) had the following dimensions: an outside diameter of 2.17 cm, an internal diameter of 0.80 cm, and a thickness of 0.19 cm.

The metal surface was prepared with sandpaper of grades 100 to 500. The test coupons were cleaned with acetone and ethanol and dried with hot air. They were then weighed with precision of up to four decimal places using a digital electronic balance.

Gravimetric assays (weight loss) were performed in glass containers with a capacity of 100 mL. The coupons were completely immersed in 80 mL of synthetic seawater containing 3.5% (mass %) NaCl, 800 mg/L of $MgCl_2$ and 600 mg/L of $CaCl_2$.

Sodium silicate ($Na_2SiO_3$) containing 50.90% $SiO_2$ (mass %) and 25.30% $Na_2O$ (mass %) with a $SiO_2/Na_2O$ ratio of 1.95 was used as the anodic corrosion inhibitor. Concentrations of 250, 1000, and 2000 mg/L were used and were referred to as silicate ions ($SiO_3^{2-}$). A cathodic corrosion inhibitor (zinc sulphate – $ZnSO_4.7H_2O$) was also added to the saline solution at a concentration of 150 mg/L, respectively, referenced as 33 mg/L of zinc ions ($Zn^{2+}$).The exposure times of the coupons were 2, 15 and 40 days of immersion and the temperature was held at 25 °C. The pH in the laboratory tests ranged from 7.2 to 8.5 as a function of the addition of sodium silicate and zinc sulfate.

The final mass of each coupon was obtained after the exposure time stated. Each coupon was washed with water, pickled with Clark solution for 40 seconds according to ASTM G 31-72 [12], cleaned with anhydrous ethanol, and dried with hot air. Three coupons were used to check the reproducibility of the results. From the average weight loss results, the corrosion rate (CR) and the percentage corrosion inhibition efficiency (IE %) were calculated using the following equations.

**Corrosion rate = CR = K ($W_o - W_i$)/ρ. S. t (mm/year);**

**Inhibition efficiency = IE% = [($W_o - W_i$)/ $W_o$] × 100;**

where:

K is a constant of $8.76 \times 10^4$ (value to mm/year);

$W_o$ and $W_i$ are the mass losses in the absence and presence of the inhibitor;

S = area of the coupon (cm$^2$);

$\rho$ = density (g/cm$^3$); $\rho$ = 7.8 g/cm$^3$ for carbon steel;

t = exposure time (h).

The evaluation of average corrosion rates of carbon steel coupons was based on NACE-RP-07-75 [13], as shown in Table 1.

*Table 1: Average corrosion rate [13]*

| Average corrosion rate, mm/y | Corrosiveness |
|---|---|
| <0.025 | Low |
| 0.025-0.12 | Moderate |
| 0.13-0.25 | High |
| 0.25 | Severe |

## 2.2    Electrochemical tests

Samples of AISI 1020 carbon steel for the polarization measurements were cut so as to obtain an electrode surface of 0.20 cm$^2$. The metal was then embedded in a polyester resin and polished with no. 600 emery paper. Next, the samples were degreased with acetone and washed in distilled water before being inserted in a conventional polarization cell as shown in Figure 2. The polarization curves were recorded using a Type III Autolab potentiostat by varying the potentials at a rate of 60 mV/min. All measurements were carried out at a constant temperature of 25 °C under aerated conditions and without agitation.

The inhibition efficiency (IE %) was calculated as follows:

$$IE\% = (I_{corr} - I'_{corr}/I_{corr}) \times 100,$$

where $I_{corr}$ and $I'_{corr}/I_{corr}$ are the uninhibited and inhibited corrosion current densities, respectively.
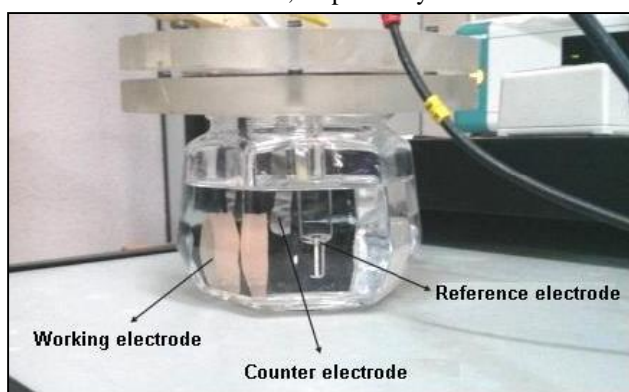


*Fig. 2: Conventional polarization cell*

## III.    RESULTS AND DISCUSSION

### 3.1 Gravimetric test

Figure 3 shows the corrosion rate of carbon steel coupons in synthetic seawater with and without corrosion inhibitor. The exposure times were 2, 15, and 40 days of

immersion and the temperature was kept at 25 °C. Table 2, below, shows the addition of sodium silicate and zinc sulphate as corrosion inhibitor in synthetic seawater in which carbon steel coupons were immersed for an exposure time of 40 days. The results refer to the average of three carbon steel coupons, and pitting and crevices were not observed on the metallic surface. Based on Table 1 [12], the average corrosion rates can be considered to be low.
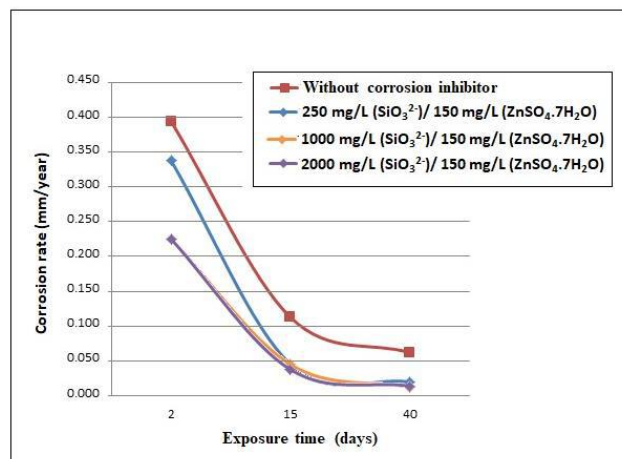


*Fig. 3: Corrosion rate of carbon steel coupons in synthetic seawater with the addition of a mixture of sodium silicate and zinc sulphate as corrosion inhibitor*

Table 2 – Yield of addition of sodium silicate and zinc sulphate as corrosion inhibitor in synthetic seawater in which carbon steel coupons were immersed for an exposure time of 40 days.

| Silicate, $SiO_3^{2-}$, mg/L | $ZnSO_4.7H_2O$ mg/L | Corrosion rate, mm/y | Yield, % |
|---|---|---|---|
| 250 | 150 | 0.020 | 68.00 |
| 1000 | 150 | 0.013 | 79.55 |
| 2000 | 150 | 0.014 | 77.27 |

From the results obtained through the assay, it was possible to verify that during the immersion time, the corrosion rate of carbon steel decreased until it reached a constant value. It is important to note that during the gravimetric assays (mass loss), precipitation and the formation of colloidal mixtures of calcium silicates and magnesium hydroxide (considering the presence of concentrations of Ca$^{2+}$ and Mg$^{2+}$ ions in the saline solution) occurred.

When the process is static and there is no bubbling of air, the absence or low concentration of oxygen dissolved in the saline solution makes the metal corrosion process slower because of its polarizing action. In saline solution that is not aerated, the hydrogen (H$_2$) can be adsorbed on the surface of the cathode, polarizing the reaction formed,

with consequent reduction of the corrosive process [14, 15].

## 3.2 Polarization measurements

The polarization curves for carbon steel in synthetic seawater solutions in the absence and presence of different concentrations of corrosion inhibitor constituted of a mixture of sodium silicate and zinc sulphate are shown in Figure 4. These polarization curves demonstrate, at first view, that in the presence of a mixture of silicate and zinc sulphate the cathodic and anodic branches of the polarization curves are shifted towards lower currents to a similar extent, possibly as a consequence of the blocking effect of the adsorbed inhibitor substance. The polarization curves show that there is a clear reduction of both the anodic and the cathodic current in the presence of corrosion inhibitor compared with those without inhibitor (blank solution). The addition of 250 mg/L of sodium silicate and 150 mg/L of zinc sulphate did not have a good yield, while the yield increased with the addition of 1000 or 2000 mg/L of silicate.
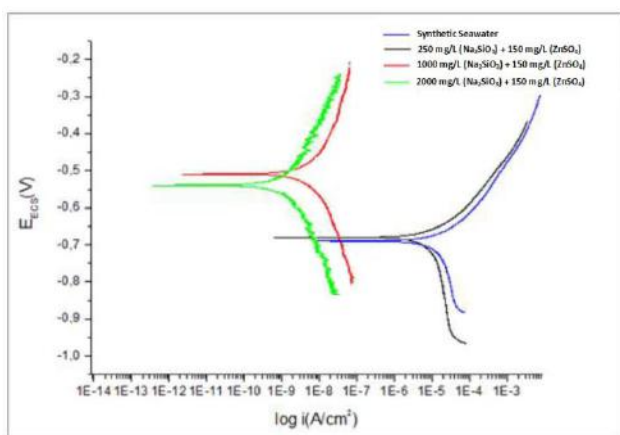


*Fig.4 –Anodic and cathodic polarization curves in the absence and presence of corrosion inhibitor*

Table 3, below, shows the electrochemical kinetic obtained by the Tafel polarization technique for carbon steel in synthetic seawater in the absence (blank) and presence of additions of mixtures of $Na_2SiO_3$ and $ZnSO_4.7H_2O$. The parameters were $E_{corr}$ (mV), Icorr ($A/cm^2$), and IE%.

*Table.3: Polarization parameters for the carbon steel in synthetic seawater in the absence and presence of corrosion inhibitor*

| Corrosion Inhibitor, mg/L | | $-E_{corr}$ (mV), | $I_{corr}$ ($A/cm^2$) | IE % |
|---|---|---|---|---|
| $SiO_3^{2-}$ | $ZnSO_4.7H_2O$ | | | |
| 0 | 0 | -690 | $2.0 \times 10^{-5}$ | ---- |
| 250 | 150 | -680 | $1.0 \times 10^{-5}$ | 50.0 |
| 1000 | 150 | -539 | $8.0 \times 10^{-9}$ | 99.9 |
| 2000 | 150 | -509 | $2.0 \times 10^{-9}$ | 99.9 |

Figure 5 shows the micrographs of the carbon steel coupons that were electrochemically tested with synthetic seawater, revealing the possibility of pitting that may occur on the surface of the steel. Rare pitting occurred at concentrations of 1000 mg/L of silicate and 150 mg of zinc sulphate, while no incidence of pitting was observed at concentrations of 2000 mg/L and 150 mg, respectively
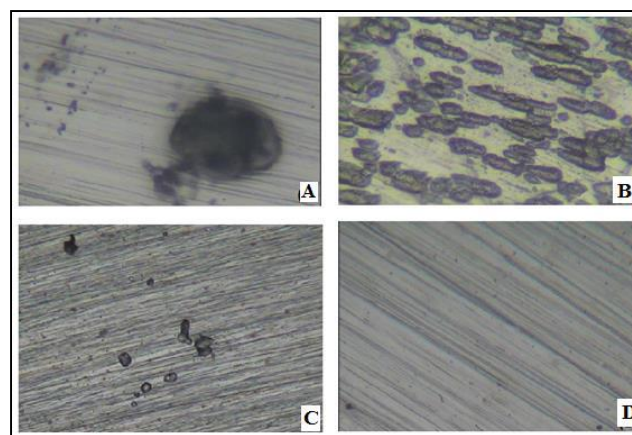


*Fig. 5: Surface micrographs of samples obtained by optical microscopy to investigate the formation of pitting in synthetic seawater: (A) without corrosion inhibitor; (B) with the addition of 250 mg/L of Na₂SiO₃ and 150 mg/L of ZnSO4; (C) with the addition of 1000 mg/L of Na₂SiO₃ and 150 mg/L of ZnSO4; (D) with the addition of 2000 mg/L of Na₂SiO₃ and 150 mg/L of ZnSO4; Magnification: 40x.*

## 3.3 Proposed mechanism of barrier

Many authors referenced have discussed the mechanism of formation and the nature of the protective film formed on a metal surface in solutions of sodium silicate. The differences in the proposals regarding the mechanism of protection and the conclusions may be due to the variation in the concentration of the sodium silicate solution, temperature, ratio of $Na_2O$ to $SiO_2$, experimental conditions, pH, contamination of certain ions in the saline solution that can form precipitates and colloids, presence or absence of dissolved oxygen, and addition of zinc sulphate, considering that $Zn^{2+}$ ions act as a cathodic inhibitor [16–19].

Sodium silicate has anodic inhibition capacity in alkaline medium, meaning that the $SiO_3^{2-}$ ions migrate to the anode region of the metal surface where they react with $Fe^{2+}$ ions, forming a protective film of iron silicate ($FeSiO_3$). The $Zn^{2+}$ ions that are present as a type of cathodic inhibitor migrate to the cathodic region, forming a protective film of zinc hydroxide, as can be seen in Figure 6.
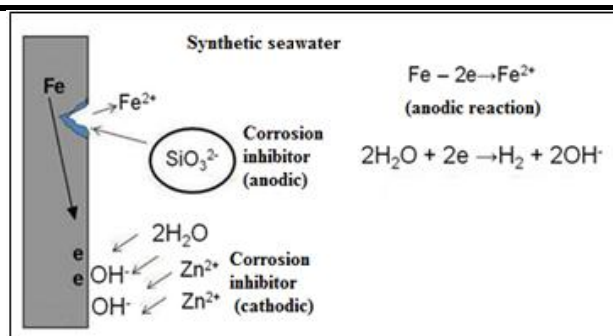
*Fig. 6: Silicate formation on a metal surface in synthetic seawater with additions of corrosion inhibitor*

The proposals regarding the mechanisms of the formation of the protective film are based on research by the previously referenced authors and are presented as models in Figure 7. The $Mg^{2+}$ and $Ca^{2+}$ ions present in the synthetic seawater may migrate to the cathodic area, find the $OH^-$ ions, and form a protective film of $Mg(OH)_2$ and $Ca(OH)_2$. Over time, it is possible to obtain a uniform protective film on the metal surface by adsorption in an alkaline medium by inhibiting the anodic and cathodic reactions, providing excellent protection of carbon steel against corrosion in a saline solution.

This film is made up of iron silicate ($FeSiO_3$), calcium silicate ($CaSiO_3$), magnesium silicate ($MgSiO_3$), and silica ($SiO_2$), which are associated with calcium hydroxide and magnesium hydroxide as well as the zinc hydroxide from the additions of $Zn^{2+}$. Over time it is possible to obtain a uniform protective film on the metal surface by adsorption in alkaline medium by inhibiting the anodic and cathodic reactions, providing excellent protection of carbon steel against corrosion in seawater.
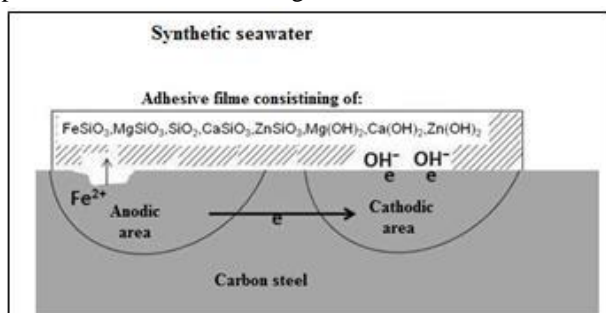


*Fig. 7: Proposed barrier mechanisms provided by silicate in the synthetic seawater*

## IV.    CONCLUSIONS

Based on tests conducted with synthetic seawater without air bubbles, the following conclusions can be drawn:

- Through gravimetric static testing without air bubbles, it was observed that the addition of sodium silicate and zinc sulphate resulted in the formation of a protective film (barrier) on the surface of the carbon steel coupons, which provided a reduction in the corrosion rate;

- The concentrations of inhibitor that showed better performance in gravimetric static testing were 1000 mg/L of $Na_2SiO_3$ and 150 mg/L of $ZnSO_4.7H_2O$, which led to a corrosion rate of 0.013 mm/year and inhibition efficiency of 79.55% for an immersion time of 40 days;

- The electrochemical tests showed that at concentrations of 1000 and 2000 mg/L of $Na_2SiO_3$ together with 150 mg/L of $ZnSO_4.7H_2O$, the efficiency of corrosion inhibition was almost 100%;

- The mechanism proposed for the corrosion protection of carbon steel is based on the formation of a uniform and transparent film with a gelatinous aspect on the steel surface, constituted of iron silicate, calcium silicate, magnesium silicate, and silica, which are associated with calcium hydroxide, magnesium hydroxide, and zinc hydroxide;

- Considering the good results of carbon steel corrosion protection obtained with the addition of sodium silicate and zinc sulphate in synthetic seawater, it is valid to propose its use in hydrostatic testing.

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