

Corrosion of Water Pipes

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Abstracts- Corrosion scales play an important role in modifying water quality in drinking water distribution systems. The corrosion scales from old water pipe lines were analyzed for their structure and composition. Use of corrosion inhibitors in solid form promotes the development of a new technique for internal corrosion protection of oil & gas pipelines and operations of oil wells acidification, because the controlled dissolution of the corrosion inhibitor forms a surface on metallic parts, a protective film that prevents or minimizes undesirable reactions to corrosion. In addition, this technique has important social and environmental benefits, ensures the operator has a lower risk of contamination when handling the product, changes the type of industrial packing, facilitates transportation, reduces solvent use and consequently reduces the waste that normally results from the use of inhibitors. The purpose is to present a class of solid corrosion inhibitor tested in the laboratory and offer proposals for its application in industrial pipes such as gas and oil pipelines.

I. INTRODUCTION

The water distribution system is key public health battlefield of the 21st century. Iron and steel pipes have been used in water distribution systems for over five centuries. The water distribution network cannot be considered as inert system but a reactor interacting with the interior aqueous environments. During interaction the formation of unwanted deposits takes place. The main source of deposit are particulate matter transported by water, dissolved oxygen, microbial activity, chlorides, sulphates and physicochemical reactions both at the pipe wall interface and within the water bulk. Most water distribution systems have build up of iron corrosion products inside the iron pipes. Corrosion scale/deposits not only restrict the flow of water but also degrade the quality of water. The scales are porous deposits that are comprised of iron hydroxide phases.

The study of the modification of polymers obtained by condensation or addition is of growing interest in

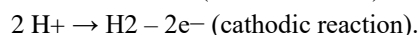
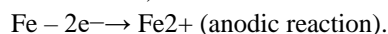
several industrial segments because of the function of the reactive groups present in the polymers' structure. In general, this type of modification targets the synthesis of polymers with physico-chemical properties for industrial application as in the formulation of corrosion inhibitors. Obtaining the polymer: poly (2-vinyl-2-oxazoline), PEOX, in solid form is such an application. The solid characteristics of this substance make possible its use in acidification (stimulation) in oil wells and could result in benefits in terms of controlled dissolution and ease of packaging and transport packaging. Corrosion inhibitors aim at the protection of metals and alloys, preventing or retarding corrosion reactions through formation of a monomolecular film-adsorbed surface exposed to corrosive medium. The modified polymers in the form of solids can be used as corrosion inhibitors, but they must possess, inter alia, the following features: anti-corrosion protection capability, proper consistency to use controlled dissolution rate and chemical compatibility with the material, corrosive medium and other additives used in petroleum industry operations. This work aims at presenting a corrosion inhibitor in solid form for use in the hydrochloric acid solutions commonly used in oil well stimulation and proposing solid inhibitor application techniques for use in segments of the petroleum industry such as oil and gas pipelines.

II CHARACTERISTICS OF CORROSION INHIBITOR BASED ON THE POLY (2-VINYL-2-OXAZOLINE)

The polymer poly (2-vinyl-2-oxazoline) was obtained by the reaction of polyacrylonitrile with 2-amino-ethanol, in the presence of catalyst cadmium acetate, [(Ac)₂Cd], under reflux to 150°C for 25 hours. After reflux, the reaction mixture was distilled to eliminate excess amino-ethanol, filtered, purified and dried under vacuum.

This polymer has oxazolinic rings hanging on the main chain in place of nitrile groups and, consequently, the polymer thus formed will have the characteristics of a paraffin-like appearance associated with the properties of oxazoline-2-substituted. This substance was dark brown, solid, and elastic and its molecular weight was valued at 1000.

When a steel plate is immersed in a solution of hydrochloric acid the preferential reactions (anodic and cathodic) that occur on the metallic surface are:



The Fe^{2+} ion formed by the attack of the acid on the carbon steel leaves the metal (Fe) for the solution, and consequently there is a migration of H^+ ions from the concentrated acid to the metal surface to form atomic hydrogen (H) and, soon afterwards, molecular hydrogen (H_2). The addition of an organic inhibitor-type system non-oxidizing acid reaction can lead to partial or even total with the H^+ ions dissociated in acidic solution, having spontaneously captured the positive charges by the inhibitor molecule, a process called protonation. Consequently there is intense competition between H^+ ions and protonated inhibitor molecules moving into areas where they can accumulate cathode electrons. Although the ionic mobility of the H^+ ions is much greater (because of the smaller size of the ion) than that of the protonated molecular inhibitor, there is an adsorption of the stable inhibitor on the metallic surface, which forms a barrier that prevents migration of H^+ ions to capture the electrons, thus preventing the formation of atomic hydrogen (H) and detachment of molecular hydrogen (H_2).

The adsorptive inhibitors or films are generally organic substances of high molecular weight that form a

monomolecular film on the metal surface, preventing the development of electrochemical reactions.

Considering the protonation in acid medium the most likely mechanism is the adsorption of the oxazolinic rings

on the metallic surface which forms a protective film and reduces or prevents the cathodic reactions.

III. APPLICATION OF CORROSION INHIBITORS IN OIL PIPELINES, GAS PIPELINES AND ACIDIFICATION SYSTEMS

The use of corrosion inhibitors in internal protection of pipes is a technique widely used in the production and

transportation of oil and its derivatives. Applications are usually in liquid or emulsion form, and are organic and

inorganic substances, or both. The solvent has is physicochemistry characteristics of each inhibitor formulation. Solvents used for organic substances are toluene, glycols, alcohols (from methanol to hexanol) and kerosene. In the case of inorganic substances water is generally the solvent although alcohols are also used.

These formulations may also be associated with the demulsifying agent, antifoaming, dispersant, etc. The literature

over the years has shown that most substances used are potentially toxic and the use of aromatics such as benzene has carcinogenic potential. Therefore less toxic substitutes are desirable.

In the case of pipelines, gas pipelines and acidification systems the injection of corrosion inhibitors for internal

protection is in liquid form with solvents such as the BTX family (benzene, toluene and xylene). The idea of

using a solid corrosion inhibitor is to reduce or minimize the risk of contamination to humans (during packaging or operation) and the environment, as it requires no solvent.

Dissolution tests performed with the solid substance poly (2-vinyl-2-oxazoline) presented in order of efficiency of 87%.

Consequently the following proposals for the application of a corrosion inhibitor in solid form are made:

- Small spheres, pellets or soluble capsules injected into the pipe with special equipment;
- Compressed cylindrical rod, consumable and adapted equipment

Small Spheres, Pellets or Soluble Capsules Injected with Special Equipment

Corrosion inhibitors can be manufactured in spherical or oval form or packaged in soluble capsules and injected

by a gun into a gas pipeline, oil pipeline or acidification system. The mechanism shows that the small spheres dissolve in the flux to form a film adsorbed on the metallic surface parts for the necessary corrosion resistance.

Another way to use the inhibitor is to pack its solid particles in soluble capsules, in such a way that it will form a protective film on the metallic surface.

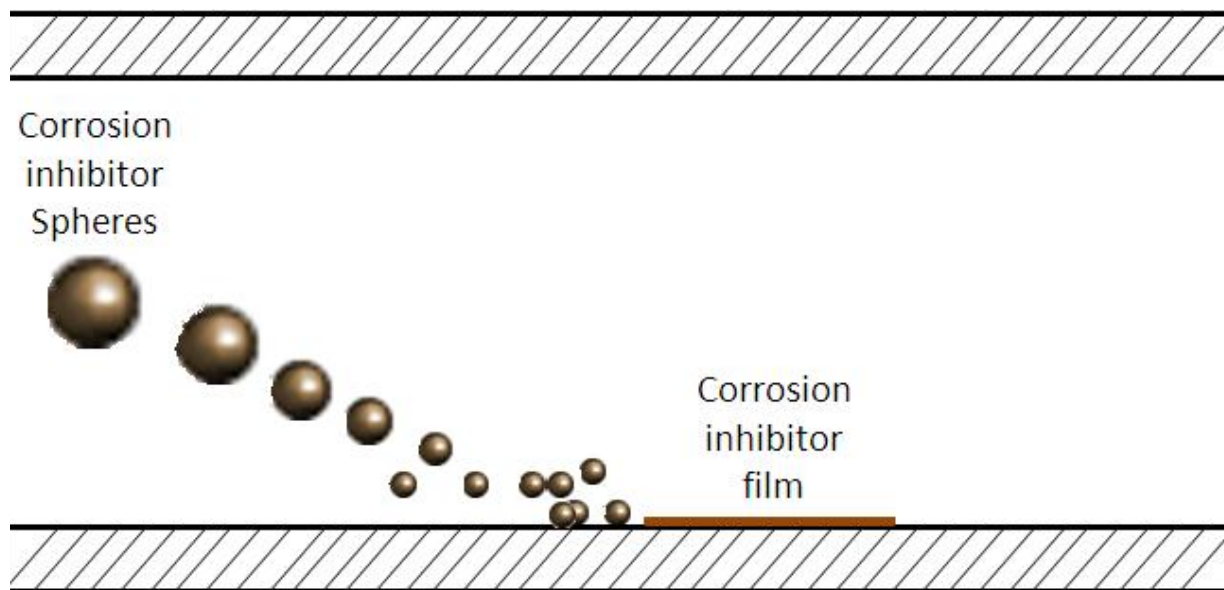
The injection system consists essentially of a pressurized tank attached to a valve and welded to a

pipe flange. The pressurized reservoir containing the spheres or capsules of the inhibitor is controlled and programmed to release mode, so gradually the spheres or capsules adhere to the inside of the pipe.

Pressed Cylindrical Rod, Consumable and Adapted Equipment

This is a simple system, consisting essentially of a cylindrical rod which is introduced inside the pipe through a

flange welded on the outside. The cylindrical rod dissolves and releases particles as a function of flow of the corrosive medium. The cylindrical rod is compressed continuously and controlled for the interior of the pipe as if wearing.



IV. CORROSION LABORATORY TEST AND RESULTS

The corrosion coupons to represent the pipeline were made from an AISI 1020 steel sheet measuring $45 \times 15 \times 1.2$ mm. They were prepared with three different sandpapers: 150, 320 and 400, in that order. Then they were degreased with acetone, washed with deionized water and anhydrous alcohol and were finally dried with hot air and stored in desiccators for use in the tests. They were then weighed to the nearest 0.0001 g.

In laboratory experiments hydrochloric acid solution 10% (% mass) was used as a corrosive medium. The

basic substances used as corrosion inhibitors were poly (2-vinyl-2-oxazoline) concentrations of 1000 mg/L, 2000mg/L, 3000 mg/L and 4000 mg/L. Gravimetric assays (weight loss) were performed in a glass vessel resistant to temperature variation with a capacity of 300 mL. The corrosion coupons were completely immersed in 150 mL of acid solution, leaving the remaining capacity of the vessel for the evolution of hydrogen (H₂) resulting from acid attack. The glass vessel was kept at the correct temperature via a thermostatically controlled bath. The temperature was set at 60°C. The time for testing was 1 hour after exposure. Immediately after completion of the test, the corrosion coupons were

removed from the corrosive medium, rinsed in water and alcohol and quickly dried in hot air, before being weighed with the same accuracy. The weight loss was determined according to ASTM G31 - 72.

The corrosion rate (CR) and the efficiency of corrosion inhibitors (E %) are defined by the following expression:

$$\text{Corrosion rate} = \text{CR} = (W_o - W_i)/S.t \text{ (mg/cm}^2\cdot\text{h)}.$$

$$\text{Efficiency} = E \% = 100 (W_o - W_i)/W_o.$$

where:

W_o and W_i are the weight loss in the absence and presence of the inhibitor;

S = area (cm^2);

t = exposure time, h.

The results of the laboratory tests carried out on four carbon steel coupons immersed in hydrochloric acid solution

10% (% mass) and corrosion inhibitor poly (2-vinyl-2-oxazoline) in concentrations of 1000 mg/L, 2000 mg/L, 3000 mg/L and 4000 mg/L.

Big Pipe Sample

The EDS measurement on powder sample (brown deposit) from the big pipe identified that iron was the major component element of the scales besides carbon and oxygen.EDS analysis showed that iron was present 30.29% (atomic percent), Carbon at 8.86%, oxygen at 59.99%, while trace amount of other element such as Aluminium, Silicon, and Chlorine (See Table-2). The corrosion products are analysed by XRD and the results are shown in Fig.1.Goethite, $\alpha\text{-FeOOH}$, $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (Hydrated ferric oxide), hematite $\alpha\text{-Fe}_2\text{O}_3$, Magnetite, Fe_3O_4 and lepidocrocite, $\gamma\text{-FeOOH}$, $\text{FeO}_3\cdot\text{H}_2\text{O}$ (hydrated ferric oxide).

Medium Pipe

The EDS measurement on powder sample (brown deposit) from the medium pipe identified that iron was the major component element of the scales besides carbon and oxygen. EDS analysis showed that iron was present 36.09 % (atomic percent), Carbon at 10.18 %, oxygen at 53.14 % while trace amount of other element such as Silicon and Chlorine (Table-4). The corrosion products are analysed by XRD and the results are shown in Fig.5. Goethite, $\alpha\text{-FeOOH}$, $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (Hydrated ferric oxide),

Magnetite, Fe_3O_4 and akaganite, $\beta\text{-FeOOH}$, $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (hydrated ferric oxide). It is confirmed from XRD Spectrum of medium pipe sample (Fig.5) that the corrosion product consist of maximum amount of Goethite, probable amount of akaganite and least amount of maganite.

Small Pipe

The EDS measurement on powder sample (brown deposit) from the small pipe identified that iron was the major component element of the scales besides carbon and oxygen. EDS analysis showed that iron was present 34.45 % (atomic percent), Carbon at 5.86 %, and oxygen at 59.70 %. (See Table-4). The corrosion products are analysed by XRD. Goethite, $\alpha\text{-FeOOH}$, $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (Hydrated ferric oxide), and Iron Matrix. It is confirmed from XRD Spectrum of small pipe sample that the corrosion product consist of maximum amount of Goethite,rest of the amount was iron matrix.The composition of grain like substance is already confirmed in previous saction.The SEM mophology of small pipe sample shows that goethite was stalactite –like on the surface of iron pipe .The grain of goethite was tiny and needle shape this was confirmed. Lot of cavities or gaps are seen and iron matrix is exposed on local surface.

These are description of each size of pipe.

V. CONCLUSIONS

The analysis of deposit in water distribution pipes revels that the predominance of brown deposits. Organic matter was also found to present. Brown deposits in big pipe sample contain aluminosilicates compounds. Tubercles are formed by electrochemical and microbiological activity. They are composed mainly of goethite, Lepidocrocite, hematite and magnetite. Similarly medium pipe composed of Goethite, Akaganite and magnetite while small pipe sample composed of Goethite and iron matrix. FTIR analysis could be used as indication of the formation of organic material in the sample and therefore, as indicator of the presence of biofilm. An interference of spectra has been observed due to mixture of organic and inorganic mixture in the sample.

1. Laboratory testing with hydrochloric acid solution showed that the inhibitor constituted of poly (2-vinyl-2-oxazoline) presented 87% efficiency in corrosion protection of carbon steel coupons. It is an excellent example of a corrosion inhibitor in solid form.
2. The use of a corrosion inhibitor in solid form opens the door to new uses as there is no need for toxic organic solvents. This technology increases the operational safety of the worker handling the product and reduces environmental contamination.
3. The use of a corrosion inhibitor in solid form as small spheres, packaged as a soluble capsule in the form of a compressed cylindrical rod, provides a new anti-corrosion technique that is easy to operate, particularly in gas and other pipelines and acidification systems.

- [9] O.M. Zachus, M.J. Lehtola, L.K. Korhonen and P.J. Martikainen, (2001) *Water Research* Monteiro, A.P., Guimarães, P.I.C. and Mainier, F.B. (1993) Synthesis and Application of Poly (Ethylene-2-oxazolina). *Brazilian Congress of Polymers*, 2, São Paulo, 5-8 October 1993 (in Portuguese)
- [11] Rodríguez, S., Abreu, A. and Cepero, A. (2003) Comparative Study of Three Oxazolines as Corrosion Inhibitors (Part II). *CENIC Journal. Ciencias Químicas*, **34**, 15-20 (in Spanish).
- [12] Cruz, J., Martínez, R. and Genesca, J. (2004) Experimental and Theoretical Study of 1-(2-Ethylamino)-2-methylimidazoline as an Inhibitor of Carbon Steel Corrosion in Acid Media. *Journal of Electroanalytical*, **566**, 111-121.
- [13] Bentiss, F., Trisnel, M. and Lagrenee, M. (2000) The Substituted 1,3,4-Oxadiazoles: A New Class of Corrosion Inhibitors of Mild Steel in Acidic Media. *Corrosion Science*, **42**, 127-146.

REFERENCES

- [1] Heryong Jung, Unij Kim, Gyutae Seo, Hyundong Lee and Chunsik Lee, (2009) *Environmental Engineering Research*, Vol.14, No.3, 195-199.
- [2] T.S. Rao, T.N. Sairam, B. Vishwanathan and K.V.K. Nair, (2000) *Corrosion Science*, Vol.42, No.8, 147-131.
- [3] P. Sarin, V. L. Snoeyink, J. Bebee, W. M. Kriven and J. A. Clement, (2001) *Water Research*. Vol. 35, no. 12, 2961–2969.
- [4] Benjamin M.M.Sontheimer H. and Leroy P.(1996) Corrosion of Iron and Steel in Internal Corrosion of Water Distribution Systems, Cooperative Research Report, AWWA Research Foundation, Denver Co.
- [5] Lechevallier M.W.Lowry C.D., Lee R.G. and Gibbon D.L.(1993) *Journal of AWWA*, 85(7), 111-123.
- [6] S,A, Imran, J.D. Dietz, G. Mutoti, J.S. Taylor, A.A. Randall and C.D. Cooper, (2005) *Journal AWWA*, Vol.97, No.9, 93-100.
- [7] Zhe Zhang Janet E.Stout Victor L. Yu, Radisav Vidic, (2008) *Water Research*, Vol.42, 129-136.
- [8] Aieta E.M. Berg D.J.A (1986) *J.AWWA*, Vol.78(6), 62-72.