International Journal of Advanced Chemistry, 7 (1) (2019) 46-51

International Journal of Advanced Chemistry

Website: www.sciencepubco.com/index.php/IJAC

Research paper

Evolution of the aggressive or scaling character of the water according to the dose of corrosion inhibitor

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Abstract

In the treatment of water to fight against corrosion, there are several techniques that can slow down this phenomenon and thus extend the service life of the pipes. Among these techniques, the use of corrosion inhibitors is one of them. It is in this context that the evolution of the aggressive and turbulent nature of the water of the Lubumbashi River has been studied experimentally through the determination of indicators such as pH, chemical potential, total alkalimetric titre, calcium hardness THCa, free chlorine content, dissolved oxygen content, SO_4^{2-} sulfate ion content and Ryznard and Langelier index. Numerous relationships between the dose of the inhibitor and the physicochemical parameters of water have been established. Similarly, it has also been shown that the dose variation of the inhibitor is related to the Langelier index and the Ryznard index. Thus, it follows that with the dose of 0.30ml / L, an appreciable decrease in dissolved oxygen, which is the main oxidant in basic medium, is recorded. The use of the inhibitor has a positive effect on corrosion because it acts directly on all physicochemical parameters and on all oxidants. Subject to economic analyzes, the dose of 0.30 ml / L is more advisable especially as it would prevent in the cooling circuit degradation of the thermal coefficient and the formation of precipitates in the exchangers occasioned.

Keywords: *Oxidant; Indicator; Langelier Index; Ryznard Index*

1. Introduction

Corrosion is the physicochemical interaction between a metal and its environment, which results in changes in the properties of the metal and may lead to a significant functional deficiency of the metal, the environment or the technical system of which it is a part [1]. In industry, the internal corrosion of plant pipelines causes many aesthetic, sanitary or hydraulic problems [2], which is not without generating high network maintenance costs [3]. As a result, the fight against corrosion becomes a constant concern, from the design of equipment to their daily maintenance. There are many techniques to slow down this phenomenon in order to extend the life of the pipes and the use of corrosion inhibitors is one [4]. The literature gives these products many properties, including the ability to form a protective film on the surface of the pipe wall, which inhibits or slows the rate of corrosion. Thus, several factors can also have an influence on the scaling power of the water, it is among others the calcium hardness, the alkalinity, the temperature, the pH, and the chemical composition of the water which can be determined at from some indices including the Langelier index or saturation index and Ryznard index or stability index given by the study of the carbon balance of a calcareous water [5].
To date, no water study has shown the variation of the corrosion-indicating parameters as a function of the dose of corrosion inhibitors. The few studies that exist have focused more on the synergy of several inhibitory ions, the inhibitory efficacy, the effectiveness of the inhibitory behaviour, the effect of pH on corrosion as well as the impact of water quality on the water corrosion process [1], [5], [6], [7].
Therefore, no recommendation on the influence of the inhibitor dose has been made, yet this information is crucial for the mastery and understanding of the mechanism and processes involved in the treatment of water. This study therefore seeks to determine the action of corrosion inhibitors on the scaling and corrosiveness of water. This makes it possible to verify the hypothesis according to which the variation of the inhibitor dose leads to the increase of the Langelier I_L index and the reduction of the Ryznard index while acting directly on the evolution or the decrease of the physicochemical parameters and oxidants present in water.

2. Study area, material and methods

2.1. Study area

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Located at 1230m altitude, the city of Lubumbashi covers an area of 747 square kilometers. It consists of a slightly hilly plateau is limited by 11 ° 27'-11 ° 47'S and 27 ° 19'-27 ° 40 'E. The city of Lubumbashi is in a dry climate with two seasons that are rainy season from late October to mid-April and the dry season from late April to mid-October.
The city of Lubumbashi is crossed by two large rivers: Kafubu and Lubumbashi. Its watershed is composed of four streams that are: Katuba, Kimilolo, Kiawishi and Naviundu. The Lubumbashi River has its source northwest of the city of Lubumbashi and it is in this river that the society for the treatment of the slag Lubumbashi (STL) and the GECAMINES capture the water they use among others for the cooling of the furnace and transformers.
The STL produces a copper-cobalt alloy and zinc oxide leaving the Lubumbashi slag slag. It uses water for cooling the furnace and transformers, for metal and slag granulation as well as for related uses. This water is captured by means of a submerging pump; it is conveyed through underground pipes of unalloyed carbon steel into the enclosure of the STL. Arrived in the enclosure, part of this water goes to the decanter for the decarbonation, and the other part goes to the filter RO3. After filtration, this water is stored in tanks TKO3 and TKO5 that are open, and it is used for granulation of the alloy, poor slag and in the fire-fighting circuit.

2.2. Methodology

2.2.1. Collection of the sample

The physicochemical parameters were determined from daily samples taken at the STL. The water was taken from a tap after filtration; the sample was transported from the place of collection to the laboratory in sealed 1000 ml flasks. We would like to point out that this study was done during the dry season, from August 08 to August 29, 2015. Conservation and handling of samples were made according to the general guide for the conservation and handling of samples [8].

2.2.2. Analysis of the sample in the laboratory

For carrying out the test, 1 liter of water was taken and introduced into a beaker without adding the inhibitor. After homogenization, the analysis was carried out and repeated adding successively for each test 0.05; 0.1; 0.15; 0.20; 0.25; 0.3; 0.35; 0.40; 0.45 and 0.50 ml of SUDKOR 255.

2.2.3. Experimental procedure

The evolution of the parameters as well as the study of the indices as the volume of SUDKOR 255 was increased was as follows: characterize the water before adding the inhibitor, pour 1000ml of the water to be analyzed in a beaker of 2000 ml, add x ml of SUDKOR 255, shake for two minutes at a speed of 500 rpm to homogenize, take three times 100 ml of the water dosed for the determination of TH, Tca and TAC in following the same procedures.

2.2.4. Materials needed

For water analysis, the following devices were used: an Inolab pH-7310 brand pH meter; dissolved oxygen, total duration THT, calcium time, magnesian hardness: TH Mg, sulfate ions SO_4^{2-} with CIFEC brand photometer PC 7100, the aggressive or water tendency were determined on the basis of the indices of Ryznard and Langelier [9] an electric stirrer for the homogenization of the samples A stopwatch for the respect of the conditioning time of the reagents, A beaker; two pipettes, two burettes; a bottle and an Erlenmeyer flask.

2.2.5. Reagents used

The reagent for dosing water, SUDKOR 255 (NaOH-based molecule) is a corrosion inhibitor with the following characteristics: pH 13.50, electrical conductivity 66.91ms / cm, E-339mv, TDS 34.5g /, density 1.12, vapor pressure 3 mmHg, boiling point 141.7 ° C, reactivity CO, CO_2, Na_2O, proportion of NaOH 40 at 50%, proportion of H_2O 50 to 60%.

2.3. Experimental conditions

As part of our study, we used the following parameters:

- The hydrotimetric titer (TH) or the total hardness; it expresses the concentration of alkaline earth ions in water. It is the sum of the calcium hardness (Ca2 + ion content) and the magnesian hardness (Mg2 + ion content) [10].
- The alkalimetric titer (TA) is the content of hydroxide ions and half of the carbonate ions [10]
- The complete alkalimetric titer (TAC) or alkalinity: it expresses the content of carbonate ions, bicarbonates and hydroxides [10]
- PH: it intervenes in the calculation of the indices of RYZNARD and LANGELIER. It determines the corrosive character (low pH <7.4) or corrosive character (pH> 7.6). It also characterizes the strength of acids and bases, it ranges from 0 to 14 [9]
- Oxidoreduction potential, it characterizes the strength of oxidants and reducing agents (in mV).
- The content of strong acid salt (SAF in mg / l) is mainly SO_4^{2-} ions.

In order to determine the aggressive or tangible character of the water, we have based on the calculation of the RYZNARD and LANGELIER indices. The Ryznard stability index is an empirical index intended to determine the corrosive or scaling character of water [11].
Another method of evaluation to solve this same problem and the Langelier index is the study of the carbon balance of calcareous water; it involves all the equilibria that exist at a given temperature between the ions H^+, OH^-, CO_3^-, H_2CO_3, which amounts to establishing a relation between the pH, the calcium hydrometric title, the alkalinity and the temperature. The Langelier saturation index is equal to the difference between the current pH of the water and the saturation pH (pH at which it is neither scaling nor corrosive). This pH of saturation pHs is obtained from the temperature, the hardness limestone, the alkalinity with the methylorange or the complete alkalinity (TAC) and the content of dissolved total solids [12].

Table 1: Langelier's Parameters

Saturation pH	Binder trend
pH - pHs> 0	Water descaler
pH = pHs	Neutral water
pH – pHs < 0	Corrosive water

3. Results and discussion

According to the analysis of the curves of figures 1 and 2, it is noted that the pH changes rapidly from 8.11 to 8.91 for a dose ranging from 0 to 0.30 and from a dose of 0.30 at 0.50 the latter evolves only very slightly. Similarly, there is a change in the total alkalimetric title from 18.2 to 22.2.

This is due to the fact that the variation of the inhibitor dose causes the variation of the pH and the TAC which in principle should decrease by the fact that there is dissolution of atmospheric CO_2, thus leading to the formation of carbonic acid and that it dissociates in the water by releasing the protons which increase the acidity of the water according to the following reaction:

$$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^- \quad (1)$$

Their increase is justified by the fact that our inhibitor has a basic nature since it is based on NaOH; which means that by adding the dose of SUDKOR255 in the water, the reaction that takes place is practically the reaction observed when neutralizing a weak acid with a strong base and consequently the pH increases according to the addition of the base [13]. Increasing the pH and decreasing the potential bring the water into its stability zone; in addition the increase of pH promotes production of calcium carbonate [5] according to the following reaction [14]

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (2)$$

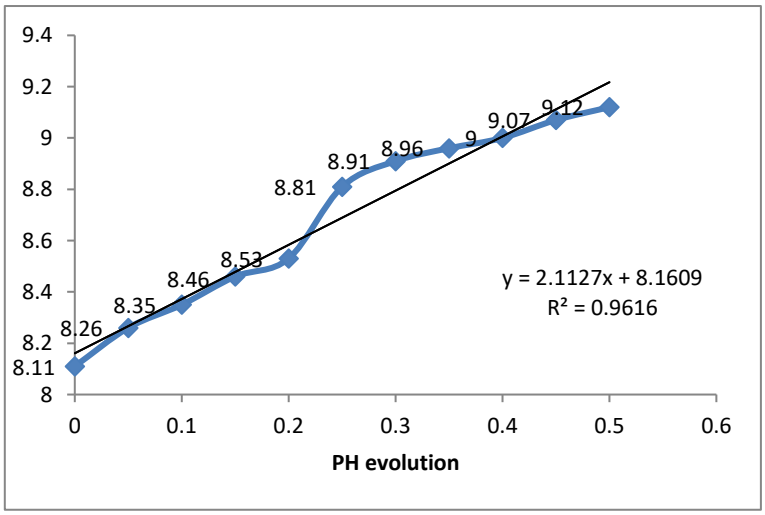


Fig. 1: Evolution of the Ph According to the Volume of SUDKOR255.

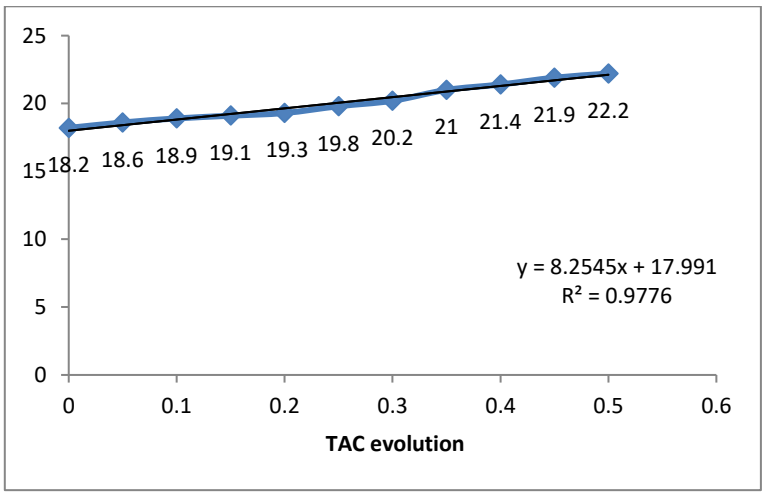


Fig. 2: Evolution of the TAC According to the Volume of SUDKOR255.

The examination of figures 3 and 4 shows that there is a link between the chemical potential E as well as the calcium hardness THCa because the more the dose of the inhibitor increases, the less the chemical potential E as well as the calcium hardness THCa decrease.

The decrease of the potential is explained on the basis of Nernst's law or the more the pH increases, the more the potential decreases, which is in agreement with the literature [1].

The decrease in THCa is a direct consequence of the increase in pH, because the higher the pH, the greater the possibility of formation of calcium carbonate [10].

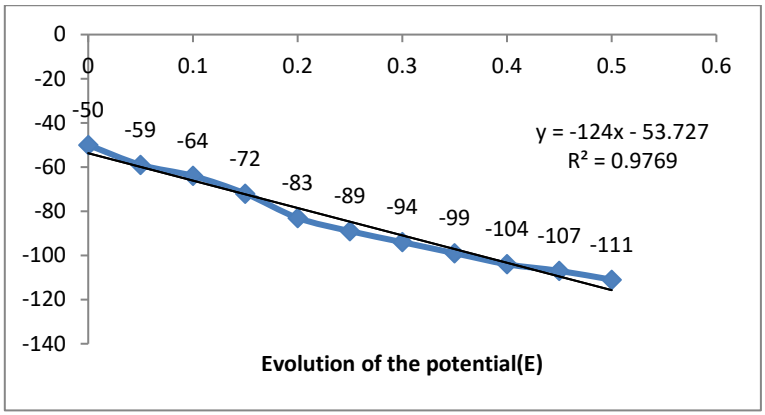


Fig. 3: Evolution of the Electrochemical Potential According to the Volume of SUDKOR255.

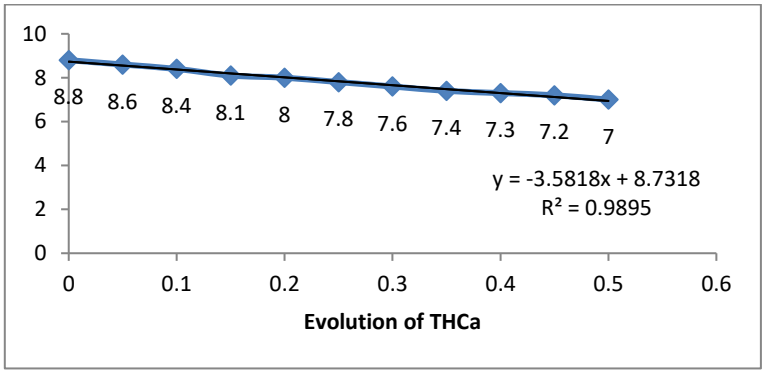


Fig. 4: Evolution of Thca According to the Volume of SUDKOR255.

The examination of figures 5 and 6 shows that, with regard to the RYZNARD and LANGELIER indices, for the doses ranging from 0.00 to 0.20 ml / L the water is in equilibrium with $CaCO_3$. For doses ranging from 0.25 to 0.35 ml / L, the water is always in equilibrium with $CaCO_3$. In contrast, for doses ranging from 0.40 ml / L and thereafter, the water leaves the equilibrium domain with $CaCO_3$ and can lead to a deposition of $CaCO_3$. This justifies the fact that the increase in alkalinity favors the formation of $CaCO_3$. We thus note that the variation of the dose of inhibitor leads to the increase of the index of Langelier I_L and the decrease of the index of Ryznard [10].

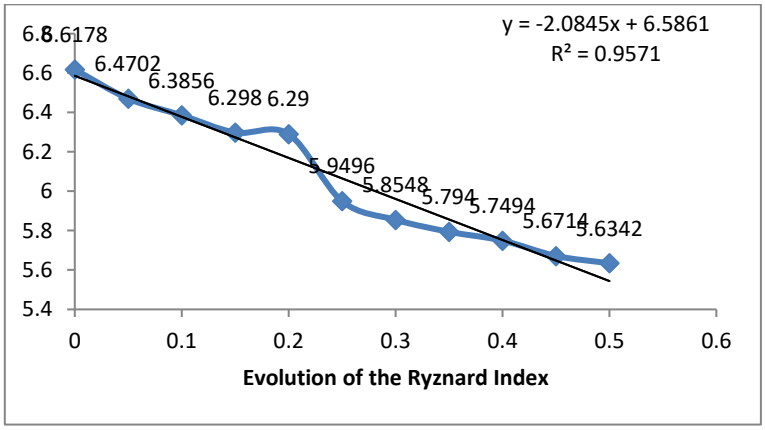


Fig. 5: Evolution of the Ryznard Index According to the Volume of SUDKOR255.

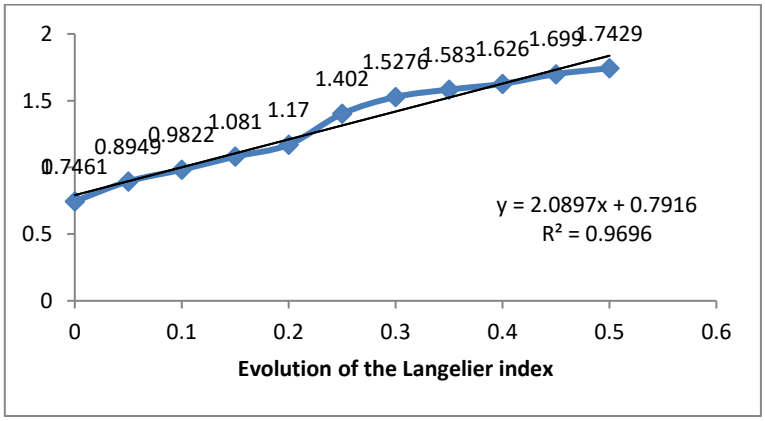


Fig. 6: Evolution of the Langelier Index According to the Volume of SUDKOR255.

Examination of Figure 7 shows that the concentration of the sulfate ion decreases gradually with the addition of the inhibitor. With regard to the sulfate ion, this can be attributed to bacterial corrosion [7]. The sulfate ions are reduced by the bacteria in the presence of hydrogen from the organic compounds present in the water according to the following reaction:

$$SO_4^{2-} + 8H^+ \leftrightarrow S^{2-} + 4H_2O$$

But this can also be due to the fact that the inhibitor is based on sodium hydroxide, once in solution; it releases Na^+ ions which in turn react with the sulfate ions in the water.

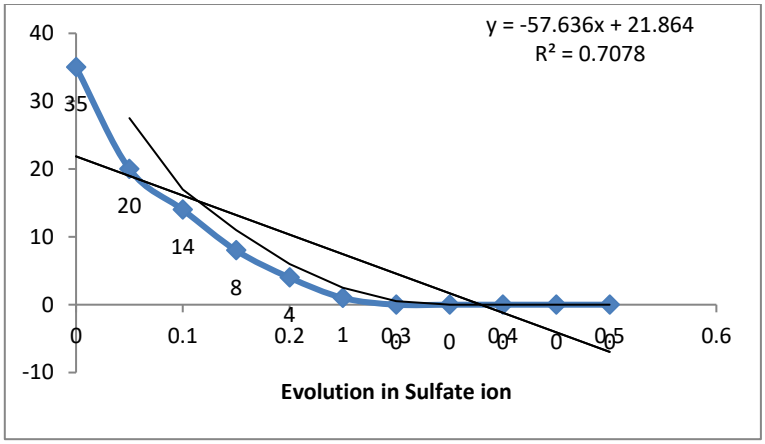


Fig. 7: Evolution of the Sulfate Ion Concentration as A Function of the Volume of SUDKOR255.

Before the addition of the inhibitor, the water is in calcocarbonic equilibrium, although with slight corrosivity and scaliness because IR = 6.6178 and I_L = 0.7461. It is therefore probable that the addition of the inhibitor modifies this equilibrium, which is what directly causes the variation of all the physical and physicochemical parameters of this water. However, there is an increase in pH, TCa, TAC and IL which is justified by the fact that the inhibitor is based on an alkaline solution. Indeed, the latter once added to the water, results in the growth of the hydroxide and Na^+ ion content, which has a direct effect on the TAC, the pH, and the potential E and even on the index from Langelier I_L.

In addition, this study also showed that the sulphate ion content decreased over time, due to the fact that we carried out this study with open vials. This seems to suggest that atmospheric gases have been dissolved, which has a direct consequence on the variation of parameters such as calcium hardness, potential and sulfate ions.

4. Conclusion

The aggressive and turbulent nature of the water of the Lubumbashi River has been studied experimentally through indicators such as pH, chemical potential, total alkalimetric titre, calcium hardness THCa, free chlorine content, oxygen content dissolved, SO_4^{2-} sulfate ion content, Ryznard and Langelier index. After several tests in the laboratory, it has been shown that the variation of the dose of the inhibitor is related to the Langelier index and to the Ryznard index. And it follows that it is at the dose of 0.30ml / L that we have the best results. Under these conditions, we note an appreciable decrease of dissolved oxygen which is the main oxidant in basic medium; we are located in the passivation zone on E-pH diagrams of iron and water superimposed. In addition, the water remains in equilibrium with the calcium carbonate and can neither dissolve nor deposit it. In addition, almost all Cl_2 and SO_4^{2-} ions are eliminated.

These results confirm that the use of the inhibitor has a positive effect on corrosion because it acts directly on all physicochemical parameters and on all oxidants. The dose of 0.30 ml / L avoids in the cooling circuit the degradation of the thermal coefficient caused by the formation of precipitates in the exchangers occasioned. However, it is important to integrate the economic factor, especially since in the industry the water to be treated is very important and to study the relationship between the variation of the dose of the inhibitor and the chlorine content and dissolved oxygen from the water as these are indicators of corrosion that should be monitored regularly.

Acknowledgments

The authors thank Professor Useni Yannick for his comments.

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