REDUCTION OF PICKLING LOSS BY OPTIMIZATION OF INHIBITION *

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Abstract
In this work we present a study of optimization of a new inhibitor for turbulence pickling line. The efficiency of inhibition was measured and the weight of loss was evaluated in four different materials to optimize the dosage of the inhibitor. In seven months we had 8.7% of reduction in pickling losses.

Keywords: Inhibitor, pickling line, optimization, overpickling.

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1 INTRODUCTION

The segment of flat steels industry needs to remove the iron oxide layer from the strip which is generated in the hot rolling process. This demand is important to enable the subsequent cold rolling process aimed at reducing thickness, in addition to the following processes: annealing, galvanizing, hardening [1].

This layer is formed after the hot rolling process during cooling (550-570 °C), with a thickness of scale ranging between 8-12 µm. In this last stage, after the coiling, the scale is composed of three well defined layers of iron oxide in the forms of wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3) respectively in that order from the base metal. The thickness of the layer is influenced by the cooling temperature, the higher the cooling temperature, the greater the thickness [2].

In the Figure 1 we can see an illustration, where the steel is the metal base.

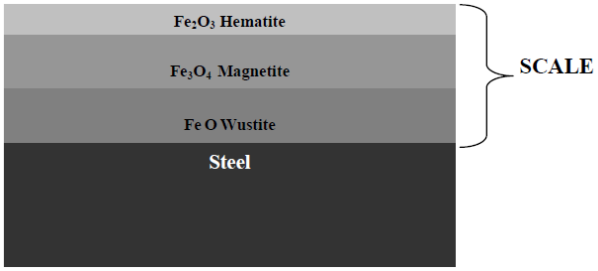

Figure 1. Layers of oxides formed after the hot rolling process. [3]

To removal these layers, the material should be submitted to the pickling process, where the oxides will be removed chemically by acids solutions. In our study we applied the test in a turbulent pickling line which consists in a continuous line where the strip passes through four turbulent pickling tanks with a solution of 18% of hydrochloric acid at a temperature of 80-90 °C [1]. After the chemical reaction in the pickling tanks the strip should pass through the rinses tanks where the exceed solution will be removed.

During the process of pickling line the acid also react with metal base by diffusion through the micro cracks of magnetite and hematite and through the pores that exist in oxidation layer [4] forming hydrogen gas in the anodic region. When these gases reached the surface of the liquid they break violently producing fumes. In high-strength steels the formed gas also causes hydrogen *embrittlement* [5], [6]. This phenomenon leads to a non-uniform pickled or overpickling in the surface causing damage and increasing the acid consumption [3], [7].

In the Figure 2 an illustration of acid attack is shown.

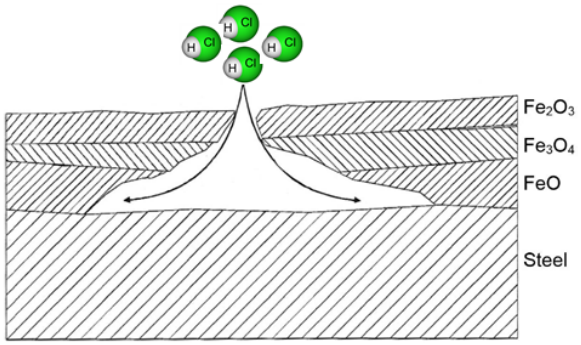

Figure 2. Diffusion of acid through the micro-cracks in the scale of oxides [6].

In order to reduce the metal base attack and avoid weight of mass and overpickling, the use of additives is mandatory. These kinds of additives are known as inhibitors. Inhibitors are mixtures or compounds that can interact with metal base interface creating a barrier that preventing or minimized the acid attack. Diaz [3] mentioned that “according to the ISO norm 8044:1999 a corrosion inhibitor can be defined as a chemical substance that effectively decreases the corrosion rates, when added in small concentration to an environment without having the concentration of the corrosive agent unchanged.”

According Dariva and Galio [8] the inhibitors could be classified by:

- ⇨ the chemical nature as organic or inorganic;
- ⇨ the mechanism of action as anodic, cathodic or anodic-cathodic mix;
- ⇨ by adsorption;

- ⇨ as oxidants or not oxidants.

Lai et al [9] described that the most of effective inhibitors are organic compounds which contains electronegative atoms (such as nitrogen, oxygen, Sulphur and phosphorus), unsaturated bonds and all kinds of aromatic cycles. These structures can interact with metal base and, depending on the chemical structure, in both cathodic and anodic reactions.

Several studies have been conducted with organic inhibitors in order to evaluate the effectiveness of the inhibition with alternative compounds. Lai et al. [9] have studied the inhibition of three different synthesized organic compounds during pickling with hydrochloric acid, were potentiodynamic polarization, weight of loss and SEM of surface were evaluated. Dekmouche et al. [10] have studied the effect of inhibition of steel with an extract of the *pistacia atlantica* in hydrochloric acid and obtained good results of inhibition of cathodic reaction. Arockiasamy [11] has been investigated the effect of inhibition of methanolic extract of *mollugo cerviana plant* in hydrochloric acid with good results of inhibition. Other researchers were conducted studies using inhibitors in acid solutions to evaluate weight of loss and mechanism of inhibition [12], [13], [14]. Were evidenced, in all the studies mentioned before, that the efficiency of inhibition increased with increasing the concentration of the inhibitor and the adsorption of all these compounds on steel surface obeys the *Langmuir isotherm*.

In this work we used a commercial organic base inhibitor derivate of a mixture of amino/alcohol compounds with cycle's structures and unsaturated bounds. The action mechanism of this inhibitor is anodic-cathodic with absorption.

2 MATERIAL AND METHODS

In this section we describe the methods used to evaluate the efficiency of inhibition and the metallic loss in different steel grades varying the inhibitor concentration.

2.1 Efficiency of inhibition (EI)

The efficiency of inhibition measures the inhibitor's ability to protect the base metal.

To quantify the effect of the inhibitor we used the gravimetry test [9], [11], [12] which consists in measuring the mass of sample that were pickled with inhibitor and in its absence.

To run the tests 5 samples of the IF steel were submitted in a solution of 1.5 L of a 190 g/L HCl solution (without inhibitor) at 85 °C for a residence time of 15 min. The acid used was a commercial acid without any contamination.

A second test was also performed with 5 IF's samples under the same conditions as in the previous test, but with 1.0 mL of inhibitor per one liter of HCl solution at 190 g/L.

All samples were previously pickled in a solution of 190,0 g/L of HCl in a residence time of 15 min to remove the scales of oxides. After that the samples were cleaned with demineralized water, dried with absorbent paper and kept in a desiccator with silica gel during 15 minutes.

To evaluate the efficiency of inhibition was used de (Equation 1) described below:

$$EI = \left(\frac{\Delta\text{weight}_0 - \Delta\text{weight}_{inhibitor}}{\Delta\text{weight}_0}\right) \times 100 \quad (1)$$

Where:
EI ➔ Efficiency of inhibition;
Δweight_0 ➔ final mass without of inhibitor;
$\Delta\text{weight}_{inhibitror}$ ➔ final mass with inhibitor;

To perform the tests, we use the following materials and reagents:

500 mL Beaker;
Support for samples;
Heating plate;
Thermometer;
Desiccator;
Soft absorbent paper;
Analytic balance (accuracy in mg);

Pipette;
HCl 190.0 g/L;
Inhibitor;
Demineralized water.

The details of the sample are described in the chapter 3.

2.2 Metallic loss evaluation

To generate the metal loss curves four different types of steels were used: USIBOR, IF, ES and DP780. These samples have been cut 5x5 cm, eight samples per material.
The tests have the object to compare sensitivities to overpickling effect in function of the doses in order to determine the best efficient overpickling inhibitor dose witch should be recommended.
Initial weight of coupons was measured on prepared samples after removing of scale by pickling in order to avoid interferences as was done in the first test.
Each material was submitted in submersion in a beaker of 200 mL of HCl solution of approximately 184,48 g/L and 19,82 g/L of $[Fe]^{2+}$ at 85 °C for a residence time of 15 min. For each sample was applied a specific dosage of inhibitor. All the conditions to run the tests are described below:

Pickling bath:
[HCl]= 184,48 g/L and [Fe] = 19,82 g/L
Pickling conditions:
Temperature = 85°C
Homogenization = 30 minutes
Pickling time = 15 minutes
Beaker volume = 200 ml
Inhibitor doses = 0; 0,1; 0,2; 0,4; 0,6; 0,8; 1 et 1,2 mL/L

To obtain the results two tests were done for each sample using the same procedure.

3 RESULTS AND DISCUSSION

The measurements from samples of the efficiency test are shown in the Table 1:

Table 1. Dimension of the samples used for efficiency tests

Process			Superior area		Lateral area (width face)		Lareral area (tickness face)	
Inhibitor	Time (s)	Sample	Width m	Length m	Tickness m	Width m	Tickness m	Length m
No	900	1	0,032	0,079	0,003	0,031	0,003	0,079
No	900	2	0,031	0,079	0,003	0,031	0,003	0,079
No	900	3	0,031	0,080	0,003	0,031	0,003	0,080
No	900	4	0,032	0,080	0,003	0,031	0,003	0,080
No	900	5	0,032	0,080	0,003	0,032	0,003	0,080
Yes	900	1	0,031	0,080	0,003	0,031	0,003	0,080
Yes	900	2	0,032	0,080	0,003	0,032	0,003	0,080
Yes	900	3	0,032	0,080	0,003	0,032	0,003	0,080
Yes	900	4	0,032	0,080	0,003	0,032	0,003	0,080
Yes	900	5	0,032	0,080	0,003	0,032	0,003	0,080

The Table 2 presents the values of loss of mass and attack for both situations, with inhibitor and with absence of inhibitor.

Table 2. Results of loss of mass in the tests with inhibitor and in absence of inhibitor.

Area m²	Weight inicial (g)	Weight Final (g)	Δweight (g)	Attack (g/m2)
0,0057	56,206	50,788	5,42	955
0,0056	56,171	50,670	5,50	986
0,0056	55,665	49,937	5,73	1020
0,0057	56,197	50,593	5,60	988
0,0056	56,124	50,658	5,47	971
0,0056	54,348	54,213	0,14	24
0,0057	55,650	55,524	0,13	22
0,0057	54,852	54,729	0,12	21
0,0057	54,754	54,613	0,14	25
0,0057	53,683	53,541	0,14	25

We can notice in Table 2 the significant difference in metal loss when we have absence of inhibitor. The attack is much higher too though the time of reaction used in this experience, was higher than the maximum special time we have when processing material with the minimum speed in our line.
The Table 3 presents the results of efficiency of inhibition. The effectiveness of the inhibition was calculated achieving interesting values for this space time.

Table 3. Efficiency of inhibition with a dosage of 1,0 mL of inhibitor per L of acid solution

$\Delta weight_0$ (g)	$\Delta weight_{inhibitor}$ (g)	Efficiency of inhibition %
5,42	0,14	97,51
5,50	0,13	97,70
5,73	0,12	97,86
5,60	0,14	97,49
5,47	0,14	97,39

The Tables 4, 5, 6 and 7 present the results of metal loss for USIBOR, IF, ES and DP780. Two trials were run where for each concentration of inhibitor.

Table 4. Results of loss of weight for USIBOR varying dosage of inhibitor

USIBOR	trial 1		trial 2		Metal loss	
[inhibitor] mL/L	Mass after trial (g)	Δm	Mass after trial (g)	Δm	Average Δm	EI %
0	60,72	2,042	61,909	2,086	2,064	
0,1	62,131	1,406	60,73	1,377	1,392	32,58
0,2	61,165	1,227	60,949	1,196	1,212	41,3
0,4	60,955	0,826	60,847	0,857	0,842	59,23
0,6	60,819	0,503	/	/	0,503	75,63
0,8	62,768	0,295	/	/	0,295	85,71
1	60,167	0,239	61,044	0,242	0,241	88,35
1,2	60,795	0,155	60,886	0,147	0,151	92,68

Table 5. Results of loss of weight for IF varying dosage of inhibitor

IF	trial 1		trial 2		Metal loss	
[inhibitor] mL/L	Mass after trial (g)	Δm	Mass after trial (g)	Δm	Average Δm	EI %
0,0	78,762	2,222	78,831	2,231	2,227	
0,1	80,950	1,413	79,742	1,416	1,415	36,47
0,2	81,049	1,015	81,122	1,044	1,030	53,76
0,4	79,789	0,492	81,104	0,501	0,497	77,70
0,6	76,902	0,291	/	/	0,291	86,93
0,8	78,842	0,191	/	/	0,191	91,42
1,0	79,379	0,169	81,052	0,173	0,171	92,32
1,2	81,012	0,129	80,679	0,121	0,125	94,39

During the experiments with the inhibitor dosage in lab, we can notice, qualitatively, an absence of bubbles of gas hydrogen usually formed when the inhibitor is not added.

Table 6. Results of loss of weight for ES varying dosage of inhibitor

ES	trial 1		trial 2		Metal loss	
[inhibitor] mL/L	Mass after trial (g)	Δm	Mass after trial (g)	Δm	Average Δm	EI %
0,0	49,025	2,104	49,072	2,227	2,166	
0,1	50,582	1,350	51,356	1,474	1,412	34,80
0,2	51,012	1,076	51,071	1,027	1,052	51,44
0,4	50,636	0,521	50,754	0,541	0,531	75,48
0,6	50,489	0,356	/	/	0,356	83,56
0,8	50,966	0,176	/	/	0,176	91,87
1,0	50,913	0,160	50,473	0,166	0,163	92,47
1,2	50,751	0,113	50,663	0,094	0,104	95,22

Table 7. Results of weight of loss for DP780 varying dosage of inhibitor

DP780	trial 1		trial 2		Metal loss	
[inhibitor] mL/L	Mass after trial (g)	Δm	Mass after trial (g)	Δm	Average Δm	EI %
0,0	50,100	0,393	50,180	0,413	0,403	
0,1	50,247	0,334			0,334	17,12
0,2	50,142	0,247			0,247	38,71
0,4	49,566	0,110	50,234	0,106	0,108	73,20
0,6	50,159	0,092	50,179	0,084	0,088	78,16
0,8	50,316	0,086			0,086	78,66
1,0	79,379	0,169	81,052	0,173	0,171	92,32
1,2	81,012	0,129	80,679	0,121	0,125	94,39

The Figure 3 presents the curves of metal loss from the different steel grades.

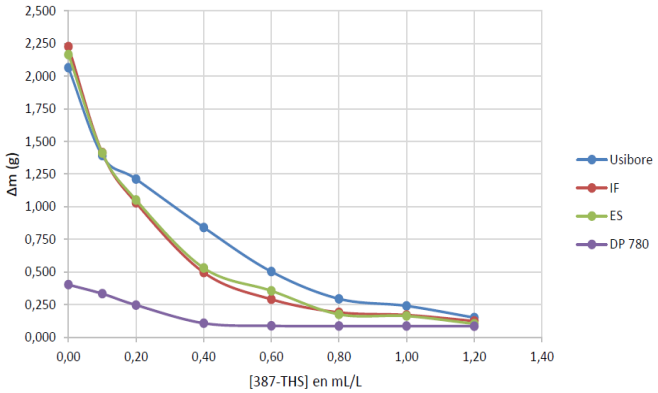

Figure 3. Comparison of loss of weights of different steels grades function

We can see by the Figure 3 the influence of inhibitor dosage in mass loss. The DP780 is less sensitive to the overpickling then the others grades due to the influence of complex oxides formed with silica as

described for Mouayd [15]. USIBOR remains more sensitive to the overpickling compared with IF and ES. From the curves we can obtain the optimized dosages, which in this case, is the range between 0.8 to 1.0 mL/L where the variation of loss is low.

In Figure 2 we can see the evolution of pickling losses after the use of inhibitor.

Applying this dosage in industrial scale and comparing with the results before optimization, we have performed the new pickling loss as showed in Figure 4:

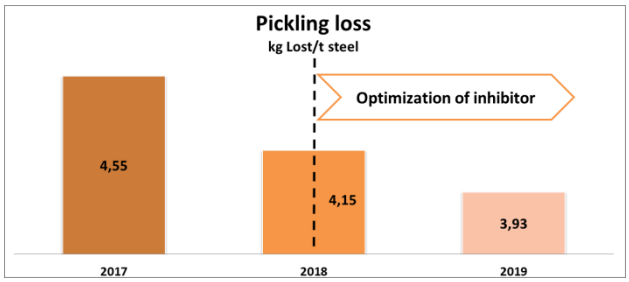

Figure 4. Evolution of pickling loss after addition of inhibitor.

We can notice a significant reduction in a metallic loss. Comparing 2017 with 2018 we have a reduction of 8.7% of metallic loss in seven months with the new presets. Comparing 2018 with 2019 until May, we have a reduction of metallic loss of 5.3%

4 CONCLUSION

The results in laboratory of the inhibition efficiency were shown to be above 97%. This is consistent with the results found in the literature.

Using the range evaluated from the curves of weight of mass we have obtained results in the process which are in agreement with the laboratory results, since the reduction of the metal loss was significant.

Though, we don't have measure of the fumes generated in the process, we expected a reduction of hydrogen generation because of the inhibitor action what result an improvement of safety since inflammable gas represents a risk of firer.

For further studies we suggest an investigation of the influence of this inhibitor on superficial quality, since we had a reduction in the average concentration of iron in the emulsion after the optimization and development of the new inhibitor. By the statistic analyze we have evidenced a reduction in the mean of iron from 72,7 ppm to 50,6 ppm.

The Figure 5 show the statistic dada of iron concentration in the emulsion before and after the application of new presets:

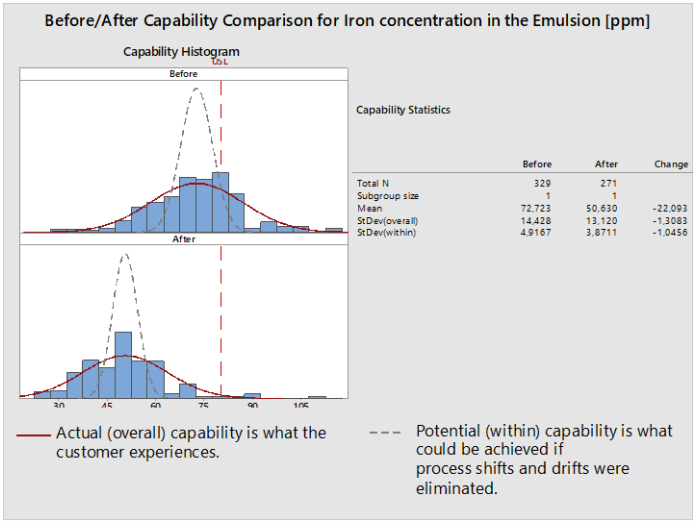

Figura 5. Capability comparison of mean of iron concentration before and after inhibitor dosage implementation

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The improvement of roughness on the steep may reduce the friction during the cold mill and consequentially reduce the concentration of iron in the emulsion.

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