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Study of the Corrosion Rate in the Couple of Steels ASTM A-36 and AISI/SAE 304 in a Water-coke of Petroleum System.

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Abstract

In the synergy produced by the action of the percentages of sulfur, sodium, and other elements that comprise chemically Venezuelan petroleum coke in the company of a significant proportion of water in the mixture, generates an environment with corrosive indices important to any metal equipment to have interaction with it, both in the oil industry as in any other that use this fuel as a product or input into their operations. In this work, laboratory tests were conducted to determine the corrosion rate in a system consisting of metal par ASTM-A36 structural steel and stainless steel AISI / SAE 304, commonly found in business management and production of petroleum coke. The study was performed by gravity, which is the common methodology to establish mass loss values in the time using the corresponding international standards and thus be able to determine by experimental simulation, the lifetime of any structure exposed storage corrosion generated by means of this study, taking care preparation for anterior and posterior with the examination of the specimens or "corrosion coupons". For this purpose joined a corrosion test, which produced a series of rectangular specimens previously appointed steels, which were superposed one on another, and subjects using electric resistance welding with non-consumable electrode, guaranteeing so had no material contribution to the double metal welding by another guy that could affect the study in the base metal of the board in question. Were compared to corrosion rates of each of the metals individually and studied together, revealing that it increases when the two (02) steels are interacting together.

1. Introduction

According to Palacios (1985), there are many types of stainless steel and not all are suitable for structural applications, particularly when carried out welding operations. There are five basic stainless classified according to its metallurgical structure: austenitic, ferritic, martensitic, duplex, and precipitation hardening (precipitation

hardening). Valencia (1998) says: stainless steels containing more than 7% nickel, called "austenitic", since they have a metallographic structure in the annealed condition, consists essentially of austenite. Are not magnetic in the annealed condition, and therefore are not attracted by a magnet. These austenitic steels can be hardened by deformation, changing metallographic structure contain "martensite". In this situation become partially magnetic. Are, in general, the groups of stainless steels commonly used in the construction of structures having excellent corrosion properties.

Usually, according to Valencia (1998), the steels commonly used in the construction industry are carbon steels, which in its different concentrations of chemical, mechanical properties are modified in order to be best utility in the different positions. One of the most frequently used steels designation is ASTM-A36, which has characteristics very similar to the 1020 carbon steel, this steel, a member of the "structural series" American Society of Testing Materials, is the most commercialized in the world, including used oil facilities, automotive, etc.

Also can be found in any structure, machine or tool made with either of these two steels, which in the case of stainless austenitic AISI treat / SAE 304, which, in combination with steel are ASTM-A36 studied in this work.

2. Experimental Procedure / Methodology

In this work, a descriptive study of the traces of corrosion specimens ASTM-A36 steel, AISI / SAE 304, and a combination of the metal duo formed by them, through the use of optical microscopy, where the obtaining work and cutting of the specimens was developed in the workshop of company operations Industria Metalúrgica Oriente, CA, Anzoátegui, Venezuela. The materials used were a steel sheet ASTM-A36 with the following dimensions: 1.200 mm x 2.400 mm and 3 mm thick sheet steel and AISI / SAE 304 with the following dimensions: 1.200 mm x 2.400 mm x 1,60 mm thick. To ensure equality in the surface dimensions of the metallic specimens with a pneumatically Guillotine a rectangular pieces of 10 mm x 20 mm were cut, obtaining a 200 mm^2 area both for structural steel to stainless steel. Extensions of corrosion coupons were established retaining contact area ratio, established by Palacios (1985), where being the worst case a larger cathodic area compared to the anodic area, because the current flow is greater in the anodic area, therefore the corrosion rate will be higher. That is:

$$\frac{Cathodic\ Area}{Anodic\ Area} \gg 1\ \ (Unfavorable)$$

(1)

$$\frac{Cathodic\ Area}{Anodic\ Area} \ll 1\ \ (Favorable)$$

(2)

Thickness variation ensures having more anodic mass than cathodic, but retains the same surface between the two metals. According to Avner (1974), in the scheme of electric potential galvanic series, stainless steel AISI / SAE 304, being an alloy steel would be the cathode electrode and the steel ASTM-A36 to resemble the chemical composition of carbon steel would be the anode electrode. Prior to preparation of the samples of each of the materials used in the experiment proceeded to determine a population according to the test, aiming at evaluating five aspects (05) to serve as time points in the graph of Mass difference vs Test time; NACE Standard TM0169-2000 (2000), suggests doubling the test specimens used in ± 10% when the attack with the corrosive medium is uniform in the test , was performed for each test point three (03) mass loss measurements, checking the deviation for each testing time between these measurements. From the above it can be deduced logically that the number of samples to evaluate the metallic pair is fifteen (15) the same number, which was evaluated for each of the steels by individual when exposed to ambient study , giving a grand total of forty-five (45) corrosion coupons.

To achieve optimal results, we performed surface preparation of corrosion coupons, according to the provisions in ASTM G1-90 (1993) and NACE TM0169-2000 (2000), hewn each burrs and deformations caused the pneumatic shear during the cutting of these, to avoid stress concentrators and energy accumulated in each of the samples, which could alter any results, since these are factors favoring increased corrosion rate. The ASTM-A36 steel is carried out a more detailed polished with sandpaper, achieving an area of "bare metal", thus ensuring a specimen clean of any embedding strange as dust, rust prior, dirt, fluids or any agent not innate in this. Taken fifteen (15) pairs of metal coupons, steels formed by ASTM-A36 and AISI / SAE 304, and binding was performed for each of these, which

were superimposed on one another and fastened by the use of welding electric resistance with non-consumable electrode, as shown in Figure 1.
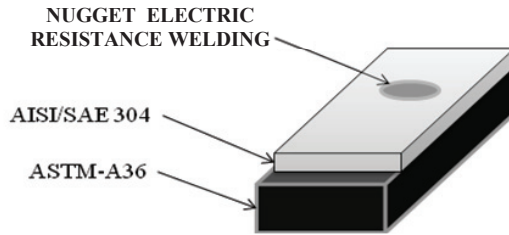

Fig. 1. Schematic representation of the samples formed by the pair metal used in the study.

Each of metal pairs described above, were immersed in a mixture of three (03) parts by volume of a petroleum coke (01) part by volume of white water from the service line from the network, individual fifteen (15) separate containers clearly identified. The same procedure was carried out with fifteen (15) steel specimens ASTM-A36 and fifteen (15) of AISI / SAE 304, thus obtaining three (03) separate test benches for steels in question, leaving uncovered each glass containers of 250 cm^3 capacity of each of the members of the group under study, so that they have interaction with the environment. According to HIDROLÓGICA DEL CARIBE, C.A. (2010), the physico-chemical composition of the white water, and according to EMPRESA MIXTA PETROCEDEÑO (2010), the physico-chemical composition of the petroleum coke used are shown in Tables 1, 2 and 3 respectively.

Table 1. Physicochemical Analysis of White Water used in the experiment.

Physicochemical Analysis	Units of Measure	Concentrations
pH	-	7,50
Turbidity	UTM	0,20
Calcium	mg/l	24,00
Silica	mg/l	10,00
Magnesium	mg/l	6,80
Chloride	mg/l	4,90
Potassium	mg/l	2,00
Density @ 25°C	g/l	997,05
Conductivity	us	114,80

Table 2. Physic Analysis of petroleum coke used in the experiment.

PHYSICAL PROPERTIES				
Property	Unit	Value	Limit	Test Method
Real Density	g/cm^3	2,06-2,10		ASTM D 2638-97
Tapped Density (-28 +48 mesh)	g/cm^3	0,87	min	ASTM D 4292-92
Electrical Resistivity	μohm*m	480-520		ISO 10143-95
Grindability Index	H.G.I.	35-40		ASTM D 409-97
CO2 Reactivity at 1000 °C	%	10,00	máx	ISO 12981-1
Air Reactivity at 525 °C	%/min	0,18	máx	ISO 12982-2

Table 3. Chemical Analysis of petroleum coke used in the experiment.

CHEMICAL COMPOSITION				
Property	**Unit**	**Value**	**Limit**	**Test Method**
Humidity	%	0,10	máx	ASTM D3173-00
Volatile	%	0,30	máx	ASTM D3175-01
Ashes	%	0,30	máx	ASTM D3174-00
Fixed Carbon	%	99,30	min	ASTM D3172-02
Sulphur (S)	%	1,80-2,80		ASTM D4239-02
Iron (Fe)	ppm	300	máx	ASTM D3682-01
Silicon (Si)	ppm	200	máx	ASTM D3682-01
Nickel (Ni)	ppm	220	máx	ASTM D3682-01
Vanadium (Va)	ppm	270	máx	ASTM D3682-01
Nickel+Vanadium (Ni+Va)	ppm	450	máx	ASTM D3682-01
Sodium (Na)	ppm	100	máx	ASTM D3682-01
Calcium (Ca)	ppm	150	máx	ASTM D3682-01

In a large plastic container was prepared a mixture of water-petroleum coke system in the proportions shown in Table 4, temperature conditions in which the experiment was performed were environmental, ranging from 25 ºC as minimum and 36 °C as maximum, with the average temperature of 30,5 ºC. The test was conducted by immersion for three (03) test benches, as established in ASTM G31-90 (1993), suggesting that the minimum ratio of solution volume to the exhibition area of the witnesses to be 40 cm^3/cm^2. For this test was counted for each container with a volume of the mixture that makes up the system water-oil coke 200 ml, thus ensuring that the volume is large enough to prevent corrosion appreciable changes due to depletion of corrosive constituents or buildup of corrosion products which may affect the advancement of the test.

We measured the pH of the solution served as corrosive medium, obtaining 6,4 as a value. Each of the witnesses was identified corrosion as suggested in ASTM G4-68 (1974), and doing so with each of the recipients of the test benches.

Table 4. Quantities and conditions used to prepare the Water-Petroleum Coke System.

SUBSTANCE	QUANTITY
Petroleum Coke	6000 ml
Water	3000 ml
Temperature	27°C

The duration of the test was set as suggested in section 4.10.5 of NACE Standard TM0169-2000 (2000), which coincides with the provisions of ASTM G4-68 (1974), where the minimum duration of the corrosion tests are:

$$Duration\ of\ Test = \frac{50}{Corrosion\ Rate\ (mm/year)}\ or\ \frac{2000}{Corrosion\ Rate\ (mills/year)} \quad (3)$$

According to the DEPARTAMENTO DE QUÍMICA FÍSICA DE LA UNIVERSIDAD DE ALICANTE (2002), for expensive alloys, corrosion rates, greater than 0,1 - 0,5 mm / year are excessive, classifying this as a good range for the relative resistance to corrosion. Therefore took the value of 0,1 mm / year for replacement in Equation 3, and determine the duration of the test, resulting in 500 hours, equivalent to 20 days and 20 hours time minimum duration. Given the above, established a regime for the test duration of 43 days maximum, that is, increasing slightly more than double the exposure time suggested by the standard in order to achieve better results in time, taking in

several intervals a trio of samples of each test, thereby generating a series of graphs for each of the metals in study, with five (05) representative points, depending on the loss of mass over time.

3. Results and Discussion

The results obtained after mechanical cleaning, and measuring the weight loss is shown in Table 5:

Table 5. Data Sheet for the study of gravimetry.

Item	SPECIMEN: ASTM-A36		SPECIMEN: AISI/SAE 304		SPECIMEN: ASTM-A36 + AISI/SAE 304	
	Original Weight Po (g)	Final Weight Pf (g)	Original Weight Po (g)	Final Weight Pf (g)	Original Weight Po (g)	Final Weight Pf (g)
I-1	7,4428	7,4167	2,4211	2,4206	9,4983	9,4942
I-2	7,5074	7,5019	2,4401	2,4395	9,8201	9,8173
I-3	7,2780	7,2612	2,3381	2,3378	9,3885	9,3824
II-1	7,1976	7,1760	2,2772	2,2768	9,2735	9,2685
II-2	7,2120	7,1953	2,2716	2,2707	9,2745	9,2465
II-3	6,6874	6,6622	2,3679	2,3675	9,3681	9,3618
III-1	7,3726	7,3443	2,3209	2,3200	9,3671	9,3263
III-2	7,2739	7,2346	2,3181	2,3173	9,4610	9,4140
III-3	7,1061	7,0641	2,4109	2,4106	9,3012	9,2490
IV-1	7,0142	6,9824	2,3084	2,3078	9,2132	9,1634
IV-2	7,5706	7,4908	2,2891	2,2885	9,1132	9,0637
IV-3	7,1856	7,1498	2,3962	2,3951	8,9140	8,8588
V-1	7,3520	7,2408	2,2779	2,2770	9,2011	9,1081
V-2	7,2538	7,2064	2,2969	2,2961	9,2436	9,2098
V-3	7,0608	7,0054	2,3137	2,3130	9,4905	9,4205

For the above table were obtained different results, which were averaged as the exposure time, as indicated in the following table:

Table 6. Data table average mass loss generated in the study gravimetric.

SAMPLE ITEM GROUP	EXPOSURE TIME (Days)	DIFFERENCE OF AVERAGE WEIGHT LOSS (g)		EXPOSURE TIME (Days)	DIFFERENCE OF AVERAGE WEIGHT LOSS (g)
		ASTM-A36	AISI/SAE 304		PAR METAL: ASTM-A36 + AISI / SAE 304
ORIGINAL	0	0,0000	0,0000	0	0,0000
I	7	0,0161	0,0005	7	0,0043
II	14	0,0212	0,0006	12	0,0131
III	21	0,0365	0,0007	22	0,0467
IV	33	0,0491	0,0008	29	0,0515
V	43	0,0713	0,0008	43	0,0656

From the results shown in table number 6, the following graphs were obtained for each of the steels that made the test.
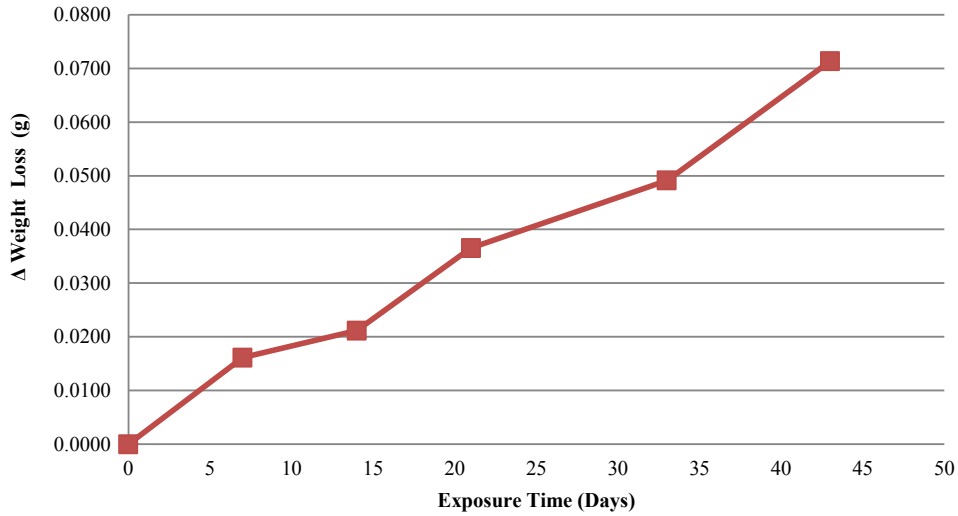

Fig. 2. Graph of the corrosion rate of steel by ASTM-A36 in a System of Petroleum Coke Water.

In Figure 2 shows that the loss of mass over time for steel ASTM-A36 in a System of Petroleum Coke Water is approximately linear, indicating that the corrosion is uniform coupons exposed to the test medium. Now, if we take the average values, identified in Table 6, and divided by the number of days, this will result in a value of the instantaneous speed of corrosion intervals in each studied in the test, as reflected in Table 7.

Table 7. Table corrosion instantaneous velocities and average speed steel corrosion ASTM-A36 and AISI / SAE 304.

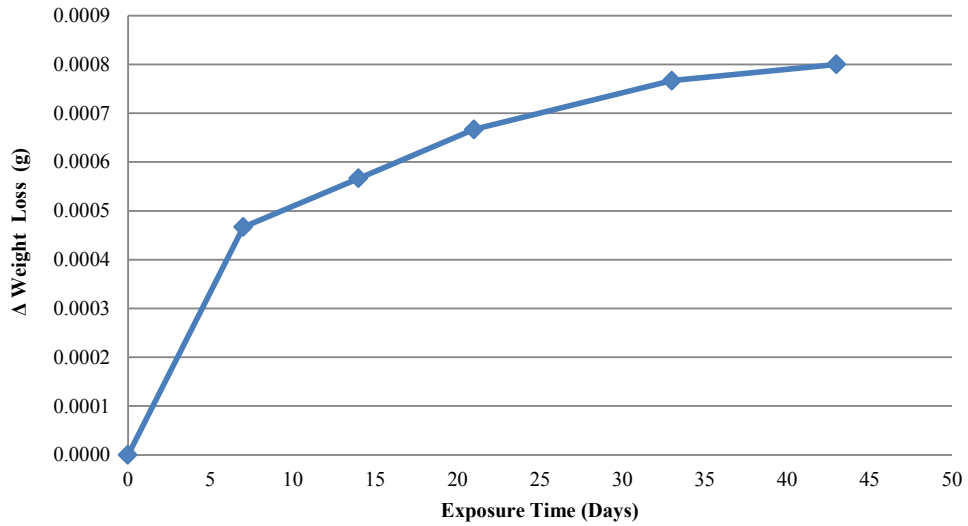| SAMPLE ITEM GROUP	EXPOSURE TIME (Days)	SNAPSHOT OF CORROSION RATE (g / day)	
		ASTM-A36	AISI/SAE 304
ORIGINAL	0	0,000000	0,000000
I	7	0,002305	0,000067
II	14	0,001512	0,000040
III	21	0,001740	0,000032
IV	33	0,001489	0,000023
V	43	0,001659	0,000019
AVERAGE RATE OF CORROSION (g / day):		0,001451	0,000030

Fig. 3. Graph of the corrosion rate of steel by AISI / SAE 304 in a System of Petroleum Coke Water.

The procedure for Figure 2, can also be taken for all the others, since the behavior of these tend to be nearly linear, so it can be added that the value of the average speed of corrosion on steel AISI/SAE 304 is 0,000030 g / day, as expressed in Table 7.
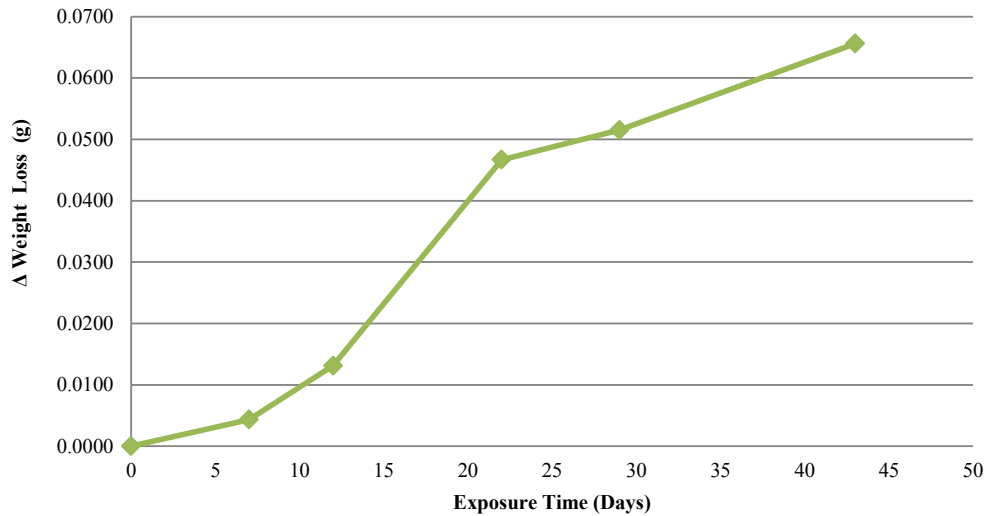

Fig. 4. Graph of the corrosion rate of metallic pair ASTM-A36 and AISI / SAE 304 in a System of Petroleum Coke Water.

Table 8. Table instantaneous corrosion rates and average speed torque Metallic Corrosion: ASTM-A36 + AISI / SAE 304

SAMPLE ITEM GROUP	EXPOSURE TIME (Days)	SNAPSHOT OF CORROSION RATE (g / day) PAIR METALLIC: ASTM-A36 + AISI / SAE 304
ORIGINAL	0	0,000000
I	7	0,000619
II	12	0,001092
III	22	0,002121
IV	29	0,001776
V	43	0,001526
AVERAGE RATE OF CORROSION (g/día):		0,001189

Figure 4, represents the behavior of the pair metal ASTM-A36 + AISI / SAE 304, which has a linear trend with respect to the mass differential with respect to time, therefore, if one follows the procedure described above , and applied to the figures 2 and 3, you get an average speed value 0,001189 corrosion g / day, as shown in Table 8.

Table 9. Loss of thickness per year of test specimens of corrosion

SPECÍMEN	SPECIMEN AREA (cm²)	DENSITY (g/cm³)	AVERAGE SPEED OF CORROSION (g/day):	THICKNESS LOSS PER YEAR (mm/year)
ASTM-A36	2,00	7,86	0,001451	0,336834
AISI/SAE 304	2,00	7,94	0,000030	0,006923
PAR METÁLICO: ASTM-A36 + AISI/SAE 304	2,00	7,90	0,001189	0,274650

The Figure 5 provides a comparison between the behavior of each of the specimens that form the corrosion test, showing that steel AISI / SAE 304 does not suffer almost no damage compared to ASTM-A36 steel and Par metallic comprised steels listed above, if it is also displayed in Table 9, we will pretend that the corrosion rate as shown by test specimens, ASTM-A36 steel behaves very similar to the ASTM-metal duo A36 + AISI / SAE 304, but the latter has a thickness loss per year younger.
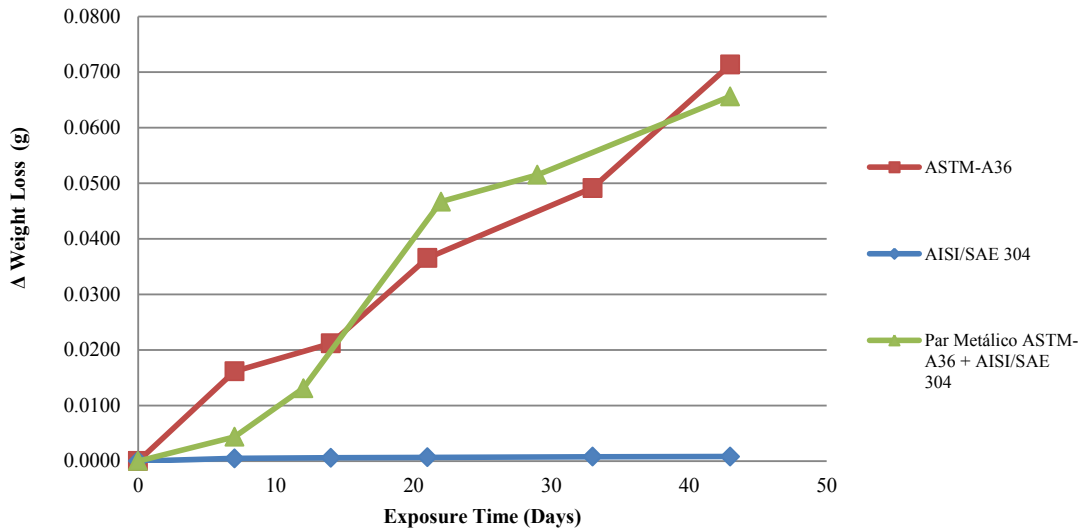
Fig. 5. Graph comparing the corrosion rates of steels ASTM-A36, AISI / SAE 304 and ASTM-A36 Par metallic AISI / SAE 304 in a System of Petroleum Coke Water.

4. Conclusions

- The study of determining corrosion rate found that the metallic pair: ASTM-A36 + AISI / SAE 304, has a thickness loss per year of 0,274650 mm / year, said pair able to resist the environment severity Water System corrosive Petroleum Coke, as it is located within the range of 0,1 - 0,5 mm / year, classified by the DEPARTAMENTO DE QUÍMICA FÍSICA DE LA UNIVERSIDAD DE ALICANTE as good for the relative resistance to corrosion.
- The Dupla Metal: ASTM-A36 + AISI / SAE 304, is subject to the corrosive environment created by the Water System Petroleum Coke, retaining a relationship: (cathodic area) / (anodic area) = 1, indicating a condition of concern when designing, as it is at the limit established by other studies relating cathode - anode, but to see that to be within the range established as good for corrosion resistance, this pair retains a relationship Metallic FAVORABLE having that value.
- You can set a the behavior of the steel AISI / SAE 304, subjected to this environment, individually, was excellent, due to the value obtained from the corrosion.
- The results obtained in this study can be as reference to take preventive measures for the maintenance of computers that have the structural characteristics and the use described herein.

References

ASTM G1-90. "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens". Annual Book of ASTM Standards, Vol. 3.02, ASTM, Philadelphia, 1993.

ASTM G4-68. "Standard Recommended Practice for Conducting Plant Corrosion Test". Annual Book of ASTM Standards. Vol. 3.02, ASTM, Philadelphia, 1974.

ASTM G31-90. "Standard Method for Conducting Corrosion Coupon Test in Plant Equipment". Annual Book of ASTM Standards. Vol. 3.02, ASTM, Philadelphia, 1993.

Avner, S. "Introducción a la Metalurgia Física", 1974, Editorial Mc. Graw-Hill. México.

DEPARTAMENTO DE QUÍMICA FÍSICA DE LA UNIVERSIDAD DE ALICANTE, "Fundamentos de Corrosión", 2002, Fondo Editorial. España.

EMPRESA MIXTA PETROCEDEÑO. "Examen de Laboratorio de la Composición Fisicoquímica del Coque de Petróleo Calcinado", 2010, Planilla de Laboratorio. Venezuela.

HIDROLÓGICA DEL CARIBE, C.A. "Examen fisicoquímico del agua de Planta", 2010, Planilla de Laboratorio. Venezuela.

NACE STANDARD TM0169-2000, "Standard Test Method Laboratory Corrosion Testing of Metals", 2000, Annual Book of NACE Standards, Item No. 2200, NACE International. Houston, TX.

Palacios, C. "Apuntes de Corrosión", 1985, Fondo Editorial UCV. Venezuela.

Valencia, A. "Tratamientos Térmicos de los Aceros", 1998, Editorial Mc. Graw-Hill. México.