

# COMPARISON, BY ELECTROCHEMICAL MEASUREMENTS, OF THE MICROBIOLOGICALLY INDUCED CORROSION BEHAVIOR IN STAINLESS STEELS

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## ABSTRACT

Many components of floodgates are built in martensitic stainless steels. Different behaviour of these components has been found depending on the river. We have carried out some investigations in order to find the root cause of this phenomenon.

Samples of the usual material AISI 420, together with other possible candidates, were introduced in the typical environment of the components. Simultaneously metallurgical and electrochemical analyses were made, comparing different material heat treatments.

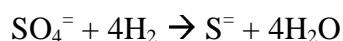
Electrochemical techniques are a very useful tool for determining and compare the corrosion behaviour of metals in a limited experimental period, giving at the same time a very high accuracy.

The results were compared and the material with the best behaviour selected.

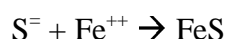
## INTRODUCTION

The influence of the micro-organisms over the corrosion process in metals was suggested at the end of the last century telling about the corrosive action of the  $\text{NH}_3$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  produced by the bacteria over the lead.

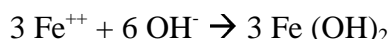
In 1910 it was suggested that ferrous bacteria and sulphate-reducing bacteria were in part responsible of the corrosion in buried metals. Other authors tried to explain the buried corrosion in electrochemical terms by the possibility of the sulphate-reducing bacteria to take  $\text{H}_2$  when the sulphates were reduced following the reaction:



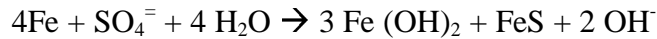
They proposed that this bacterium could use atomic hydrogen from polarised cathode to reduce sulphated compounds. Sulphured ions will react in the anode with part of the ferrous ions in the solution:



The other part of ferrous ions will react with hydroxyl ions:

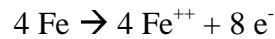


The global reaction is:



Recent works made by King, Miller [1] and Videla [2] have shown that it is more important the action of sulphur ion chemistry produced by the bacteria over the steel than the cationic depolarisation. As the sulphate-reducing bacteria are strictly anaerobic, is necessary a free oxygen environment for its growth. This environment is reached by the symbiosis with ferrous bacteria group which provide an oxygen free place that avoids the sulphydric acid elimination.

Ferrous bacteria and Manganese bacteria take their energy from the ferrous or manganous salts transformation into ferritic or manganic salts. These reactions produce a very high rate of rust formation and break the equilibrium constant of the reaction:



by simultaneous anodic and cathodic depolarisation.

Biologically induced corrosion affects many of kind of industries. Some of our hydraulic power plants have been affected by this phenomenon for years. So, since some year ago our unit has been investigated this kind of corrosion, most resistant materials and protected methods to use [3].

Our work has been based in two simultaneous studies:

On one hand, the different kinds of interesting stainless steels have been subjected to a natural dynamic process, that is, with the specimens in similar conditions in which they usually stayed, for a period of 17 months.

On the other hand, electrochemical measurements have been done to compare these results with the obtained in the other experiments and to see if we could predict metals behaviour with this technique.

The firstly elected materials were: AISI 303, 304L, 310, 316L, 321, 420, 431 in flats and tubes specimens; later we decided to include martensitic stainless steels Cr-Ni 13-4 y 17-4PH on which we continue doing this study, so we can only give partial dates of their behaviour. All of them have been studied in reception state and after a sensitised thermal treatment (700 °C during 1 h. and furnace cooling to precipitate Cr in grain boundary).

## ANALYSIS

The chemical analysis of these metals is shown in the following table:

TABLE 1: STEEL CHEMICAL COMPOSITION

AISI	% C	% Si	% Mn	% S	% P	% Cr	% Mo	% Ni	% Cu
303	0.038	0.24	1.53	0.220	0.033	18.1	0.20	8.0	0.36
304L	0.006	0.41	1.30	0.010	0.027	19.1	0.21	10.0	0.15
308	0.080	1.85	0.66	0.002	0.018	21.0	0.18	10.4	0.09
316L	0.012	0.51	1.60	0.001	0.027	18.1	2.75	12.4	0.20
321	0.040	0.39	1.76	0.001	0.028	18.4	0.12	9.6	0.12
420	0.270	0.88	0.67	0.005	0.021	14.3	0.05	0.0	0.03
431	0.150	0.48	0.54	0.007	0.029	18.0	0.12	1.5	0.05
13-4	0.07	0.57	1.02	0.007	0.026	14.3	0.91	3.36	0.02
17-4PH	0.05	0.72	0.62	0.006	0.025	17.17	0.37	4.18	3.21

Martensitic steel 420 was the originally used material in our plants, so with this study we will obtain information about its comparative behaviour with the others steels.

The water properties where the specimens have been analysed is shown in the following table:

TABLE 2: WATER PROPERTIES OF THE ANALYSIS MEDIA

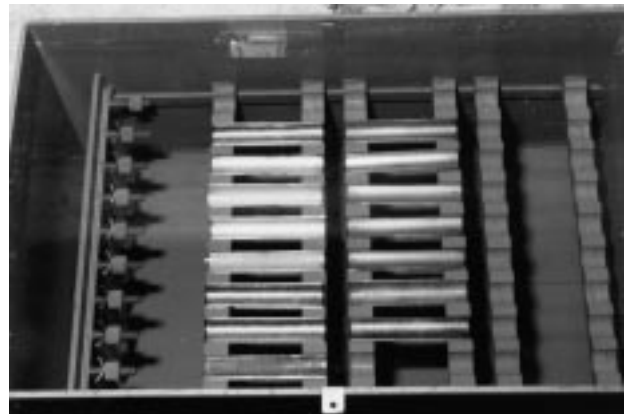
T <sup>a</sup> (°C)	Mat. Sus. (mg/l)	Mat. Sol. (mg/l)	Conductiv. (uS/cm)	Ca <sup>++</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	pH	Total hardness (mg/l CO <sub>3</sub> Ca)	SO <sub>4</sub> <sup>-</sup> (mg/l)	O <sub>2</sub> disolv. (mg/l)
11-19	1.8	358	563	50.6	39.4	7.38	181.6	117.6	0.5

In the figure 1 we can see a general vision of the situation of the dynamic test bed, in the figure 2 we can see the laying of the specimens inside of the test bed.

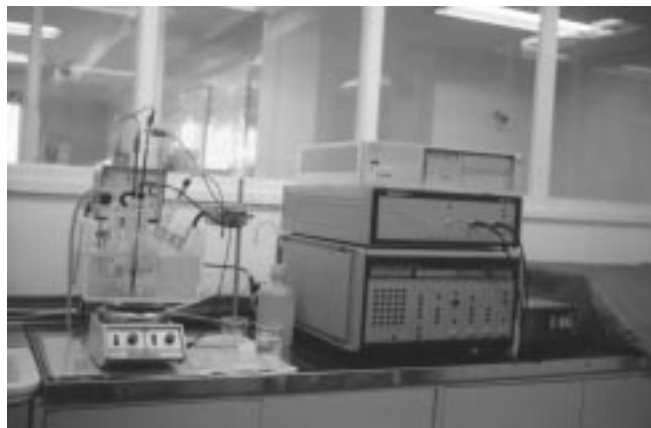
In the figure 3 we can see the system utilised to made the electrochemical measurements.



**Figure 1:** Situation of the test bed



**Figure 2:** Laying of the specimens inside of the bed



**Figure 3:**Equipment for electrochemical measurements

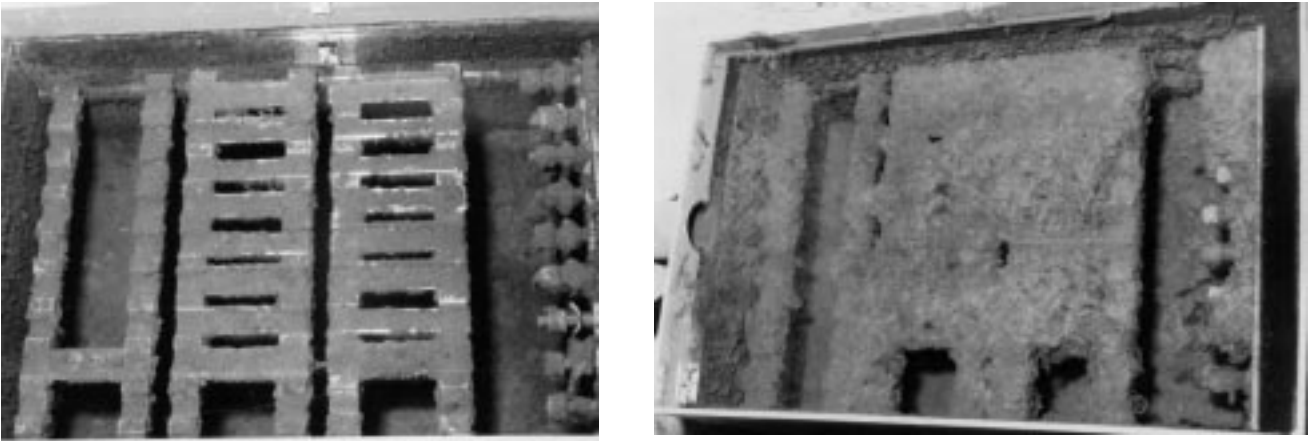
### ***Results of the installed test bed***

The evaluation of the obtained results has been done, firstly by an ocular observation followed by a macroscopic and microscopic examination of the corrosion produced.

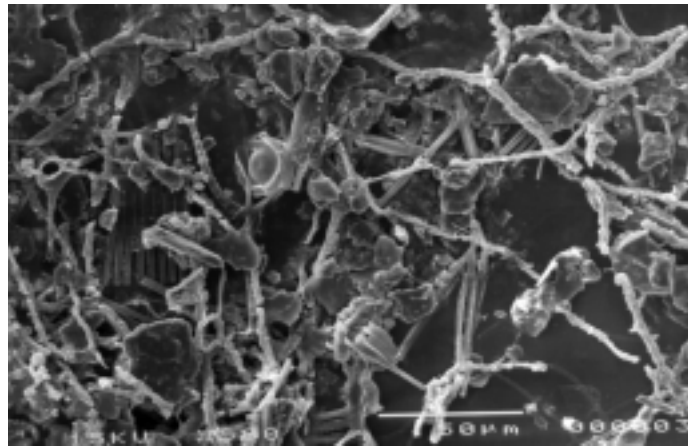
On the other hand chemical and biological tests have been done to confirm the bacterial origin of these kind of corrosion.

In the figure 4 we can see the state of the test bed after 163 days and 17 months.

The specimens ocular inspection showed a thick organic film. The microscopic observation showed that this film was made up by weeds, protozoan and a lot of quantity of bacteria, mainly cells filaments. In the figure 5 we can see a micrography of the fouling founded over the specimens.



**Figure 4:** Test bed after 163 days (left) and 17 months (right).



**Figure 5:** Biofouling founded over the specimens

After cleaning the flat specimens both horizontal and vertical ones, no kind of corrosion was observed in used materials, although when we cut tubular specimens longitudinally, we observed the same layer of biofouling but with less thickness. After cleaning this layer, different kinds of corrosion were found in the following steels:

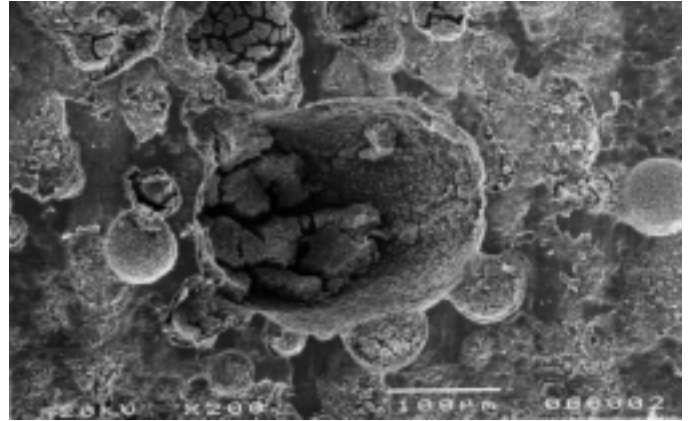
- AISI-308 sensitized: Elongated areas with intergranular corrosion and pitting.
- AISI-321 sensitized: Pitting at the initial part of the tube.
- AISI-420 no sensitized: Pustules at the initial part of the tube, with severe corrosion in areas where the water remained stagnant.
- AISI-420 sensitized: Severe corrosion at the initial part of the tube on the external area. Pitting at the internal surface covered with ferrous pustules. Figures 6 and 7.
- AISI-431 sensitized: General corrosion and pitting with pustules.

In view of the results we can do the following observations.

1. Austenitic stainless steels in reception state showed a good behaviour against biological induced corrosion.
2. Martensitic stainless steels, both sensitized and in reception state, showed great susceptibility to this kind of corrosion, mainly in the first ones.
3. The greater corrosion appears in areas where the water remained stagnant, probably due to a more anaerobic environment than areas with water circulation.



**Figure 6:** Pitting at the internal surface of the tubes



**Figure 7:** SEM photography of the pitting process.

To check the corrosion was produced mainly by sulphate reduced bacteria, we used energy dispersive X-ray analysis to determine the origin of the corrosion products that we found in the pitting process.

The comparison between metal and corrosion products analysis shows clearly the bacteria origin of the last ones, because the great quantity of sulphur that we found (15%). This quantity of sulphur could only come from with this type of bacteria.

### ***Electrochemical measurements***

As we said at the beginning, simultaneously to dynamic tests, electrochemical measurements were done to compare their results and to determine if we can use this technique to predict the behaviour of the metals in their natural environment.

As in the most of the cases microbiologically induced corrosion process is similar to a pitting, we can use the electrochemical technique for localised corrosion to show the susceptibility of the different kinds of steels to this type of corrosion.

This method (cyclic polarisation), based in ASTM G 61-86 rule, consist in the application of a difference of potential from the material corrosion potential to reach a suddenly increase of current density, which indicate the beginning of the pitting process. After that an inversion in the polarisation direction to the corrosion potential show us the area where the material will stay in its passive state against pitting.

By this way we obtain two values, the one hand  $E_b$  or pitting potential, that is the potential over which pitting start, on the other hand  $E_{rp}$  or repassivation potential, that is the potential under which the material remain passive. Between  $E_b$  and  $E_{rp}$  the initiated pitting will continue but new pitting wont start. In figure 8 we can see a typical curve obtained from this technique.

Therefore when pitting potential ( $E_b$ ) is high the corrosion resistant to this type of corrosion is also high and the passive area is as greater as the difference between  $E_b$  and corrosion potential.

In other to accelerate the process, these measurements take place in conditions where pitting corrosion is favoured; in our case the conditions were:

- Electrolyte: NaCl (3,56 % by weight)
- Temperature: 30 °C
- Oxygen free environment

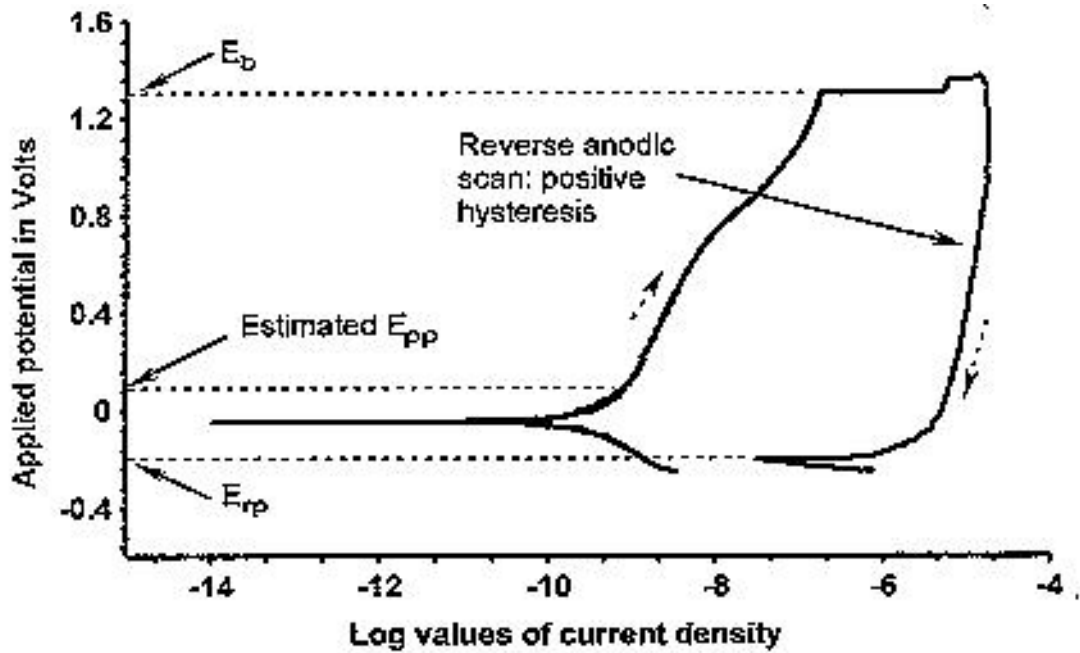


Figure 8: Typical curve of cyclic polarisation technique.

The results of the application of this technique to our specimens are showed in the following table:

TABLE 3: ANALYSIS RESULTS FOR THE MATERIALS ANALYSED

Sample	Pitting Potential range Eb (mV)	Sample	Pitting Potential range (mV)
AISI 321		AISI 303	
Reception	-50-0	Reception	75-100
Sentitized	-100-(-25)	Sentitized	-225-(-175)
AISI 316L		AISI 431	
Reception	550-560	Reception	-150-(-100)
Sentitized	125-200	Sentitized	-200-(-100)
AISI 310		AISI 420	
Reception	150-200	Reception	-200-(-100)
Sentitized	25-75	Sentitized	-300-(200)
AISI 304L		Cr-Ni 13-4*	
Reception	50-75	Reception	100-200
Sentitized	0-75	Cr-Ni 17-4PH*	
		Reception	0-100

\* These materials are being studying by our unit at this time.

From these results we can obtain the following conclusions:

1. Austenitic stainless steels have the best behaviour against microbiologically induced corrosion but with worse mechanical properties for our requirements.
2. Among martensitic stainless steels, without all the dates, Cr-Ni 13-4 and 17-4PH seems to have the best behaviour against this kind of corrosion maintaining mechanical properties.
3. Sensitized materials have worse behaviour than reception ones.
4. The results are very similar to those obtained from dynamic test bed.

## FINAL CONCLUSIONS

The main conclusion is the high influence of ferrous and sulphate-reducing bacteria in the mechanism of corrosion of the metals immersed in environments with these types of microorganisms.

Austenitic stainless steels, both sensitized and in reception state, have a very high resistant to microbiologically induced corrosion.

Martensitic stainless steels have a very high susceptibility to this kind of corrosion, but with the last two metals (Cr-Ni 13-4 and 17-4PH) the behaviour seems to improve.

The results obtained through the two methods are very similar.

Electrochemical techniques seem to be a very useful tool to investigate corrosion mechanisms in a few times and with high accuracy.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. J.D.A. MILLER, "*Microbial aspect of metallurgy*" MTP 1971
2. H.A. VIDELA y R. C. SALVAREZZA, "*Introducción a la corrosión microbiológica*". Librería Agropecuaria. Argentina. (1984)
3. JOSE L. PINTADO y F. MONTERO, "*Proyecto de investigación sobre corrosión bacteriana en aceros inoxidable*" TEMAT. Madrid. 1988.