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Oxygen consumption in confined environments: seawater in contact with stainless steels

Zehbour Panossian
Tarcisio H.C.
Carlos Alberto da Silva
Giuliano Mouza Alcântara Prearo
Emerson Simão Pereira
Flavia M.F. Guedes
Ilson Palmieri Bapatista

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Instituto de Pesquisas Tecnológicas do Estado de São Paulo S/A - IPT
Av. Prof. Almeida Prado, 532 | Cidade Universitária ou
Caixa Postal 0141 | CEP 01064-970
São Paulo | SP | Brasil | CEP 05508-901
Tel 11 3767 4374/4000 | Fax 11 3767-4099

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Zehbour Panossian - IPT

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Tarcisio H. C. Pimentel (SENAI-CIMATEC)

Carlos A. da Silva (IPT)

Giuliano M. A. Prearo (IPT)

Emerson S. Pereira (IPT)

Flavia M. F. Guedes (CENPES-Petrobras)

Ilson Palmieri (CENPES-Petrobras)

Oxygen consumption in confined environments in seawater in contact with stainless steels

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Motivation

- ✓ Hibernation (submersing in seawater and filling with seawater) of flexible pipes and umbilicals occurs when they remain inactive for long periods.
- ✓ In this conditions, a special confined environment is established: low volume of seawater (V) and the large area of metallic surface (A).
- ✓ Under these conditions, rapid oxygen consumption occurs.
- ✓ There are doubts about the reasons for the rapid oxygen consumption:
  - some authors attribute this consumption to the formation of the passive layer over a large surface area of the metal alloys used (stainless steels AISI 304, AISI 316, and duplex steel SAF 2205).

Objective

Understanding the causes for the rapid consumption of O_2 during hibernation with natural seawater, focusing on the metal materials normally used in flexible pipes, and considering the variations of:

- ✓ **material**: AISI 304, AISI 316, and duplex steel SAF 2205;
- ✓ **temperature**: 5 ^{o}C, 15 ^{o}C, and 25 ^{o}C;
- ✓ **medium**: natural and synthetic seawater (sterilized and non-sterilized).

Test Matrix

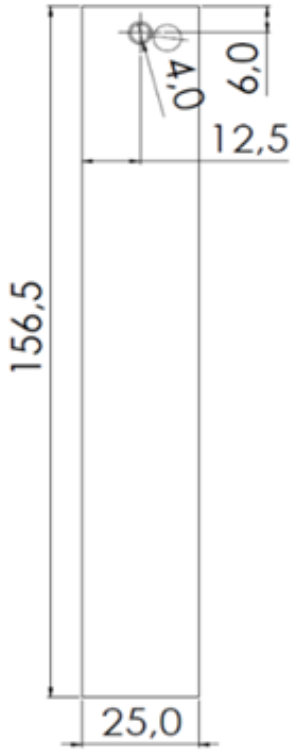
Steels	Natural seawater			Sterilized synthetic seawater			Sterilized natural seawater		
AISI 304	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C
	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C
	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C
AISI 316	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C
	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C
	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C
SAF 2205	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C	5 °C
	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C	15 °C
	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C	25 °C

Total possible tests: 81
Selected tests: 34

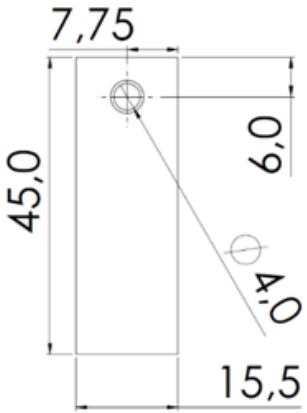
Methodology

The total area of coupons was fixed to achieve a V/A of 1.7 mL/cm²:

- ✓ five coupons with dimensions 156.5 mm x 25 mm x 1.4 mm;
- ✓ two biocoupons with dimensions 45 mm x 15.5 mm x 1.4 mm;
- ✓ surface finishing:
  - as received;
  - special treatment:
    - immersion in 10 % nitric acid at 60 °C;
    - washing with water;
    - immersing in 70 % ethanol;
    - dried (inside a microbiological hood);
    - immersed in the test vessel inside a microbiological hood.



Cupom



Biocupom

Test environment

Four types of test medium were used:

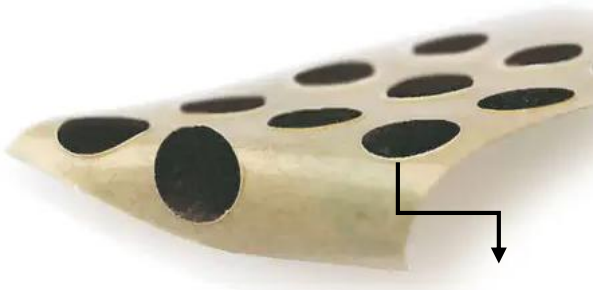
- ✓ **natural seawater** collected from the São Sebastião canal, transported on the same day of collection, filtered with a 50 µm filter, and preserved at 5 °C until the start of the test, which occurred within 48 h after collection;
- ✓ **natural seawater** (the same as cited above) **sterilized**;
- ✓ **sterilized synthetic seawater** according ASTM D1141, without heavy metals;

Sterilization: autoclave at 121 °C ± 5 °C under 1.1 atm for 15 min

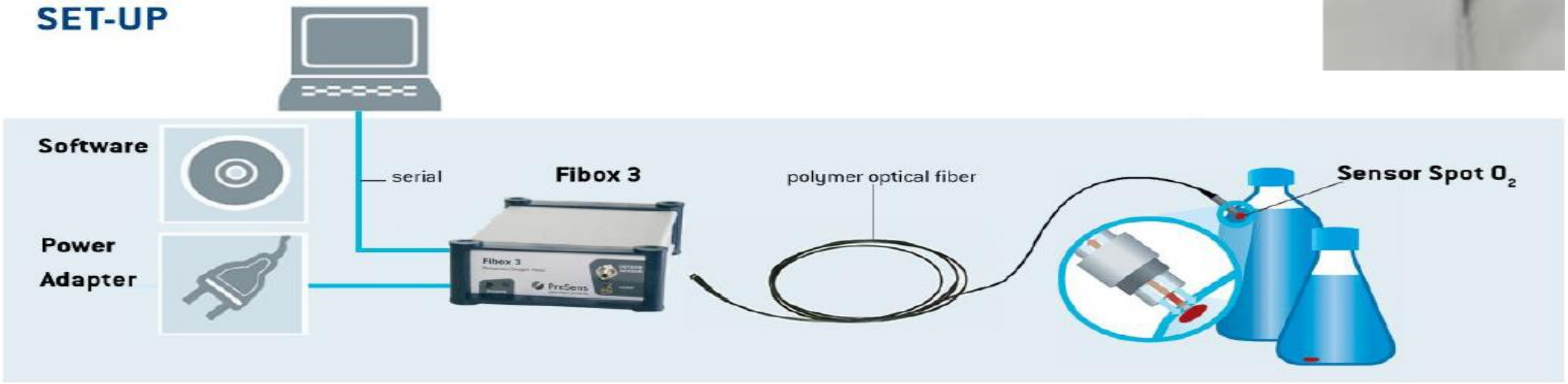
Determination of the O_2 content

Adhesive optical sensors (PSt3 - Presens Precision Sensing):

- ✓ sensors glued to the inner wall of the test vessel;
- ✓ a small glass tube was glued to the external wall in front of the sensor to insert the reading sensor.



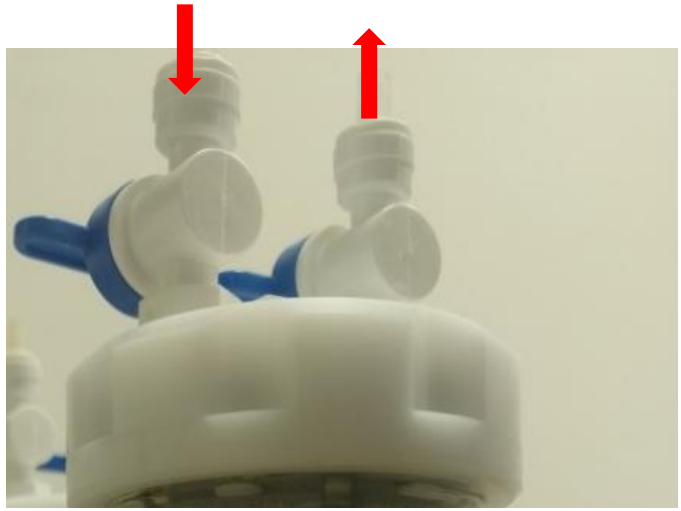
Black discs are adhesive optical sensors!
Optical luminescence O_2 sensors

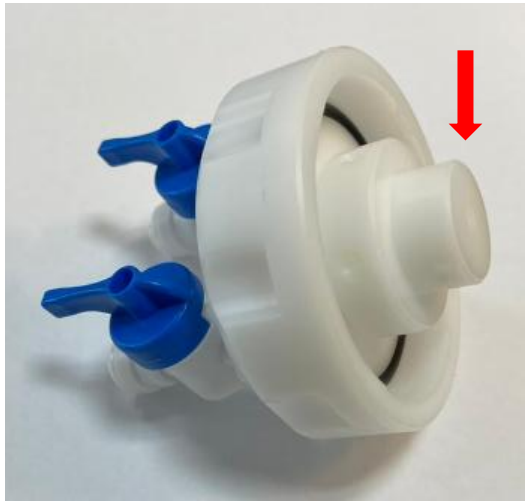


Preparation and sterilization of the test devices

The test vessel and its lid were specially prepared:

- ✓ threaded glass cylinder 16 cm high and 8 cm in diameter;
- ✓ a Teflon lid:
  - at the top side, provided with one gas inlet and one gas outlet (N_2 or O_2);
  - at bottom, adapted for a device for installing test specimens.





Sterilization by rinsing with 70 % ethanol or exposing to UV light.

Assembling

Steps:

a) installation of the specimens and biocoupons in the lid and closing of the test vessel;

b) transfer of test medium to test vessel;

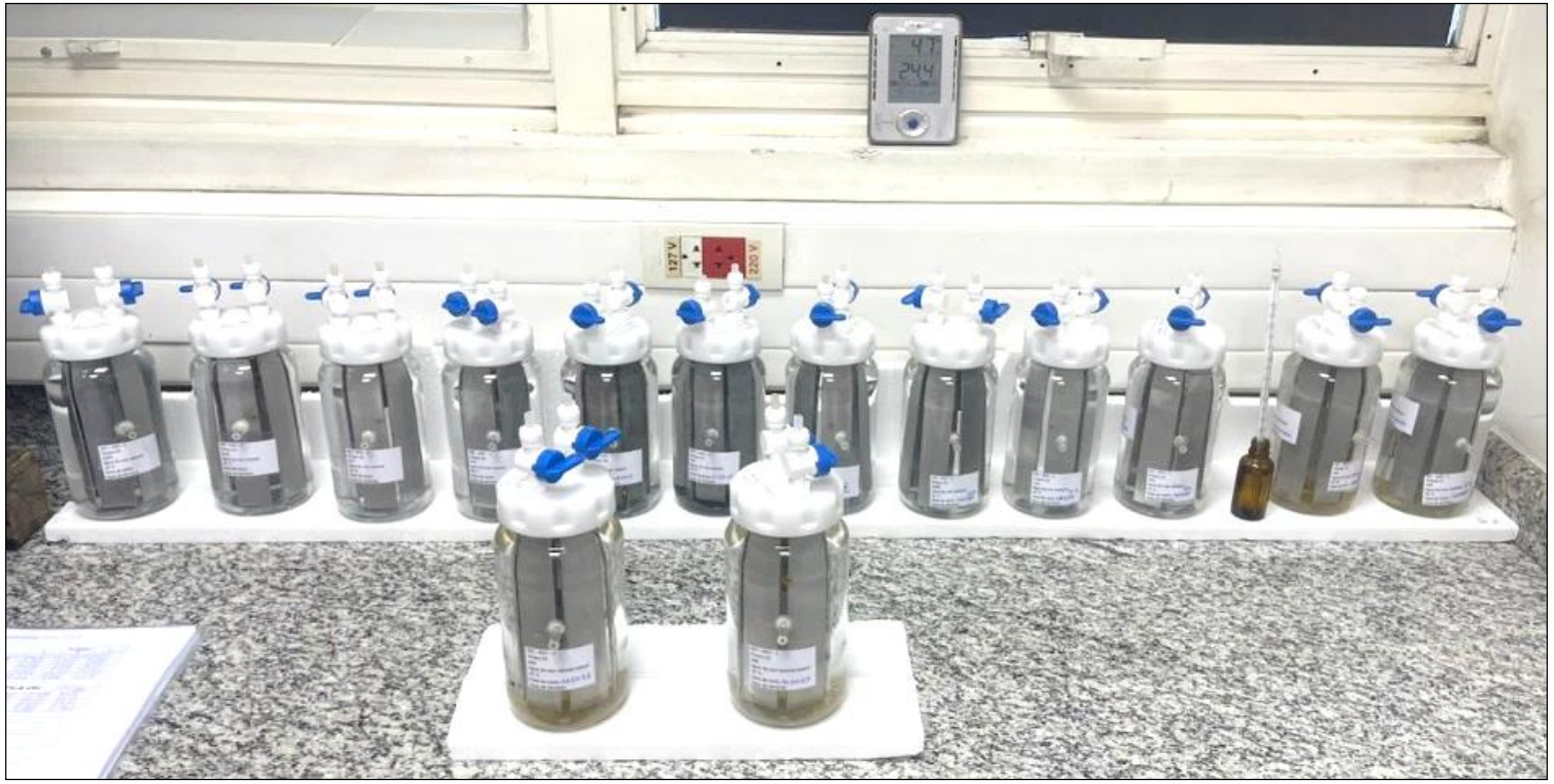
c) adjusting the desired temperature;

d) bubbling with pure hospital-grade O_2 gas until reaching a content just above 8 mg/L;

e) Monitoring the O_2 contente for 60 days.

Monitoring the Temperature and the O_2

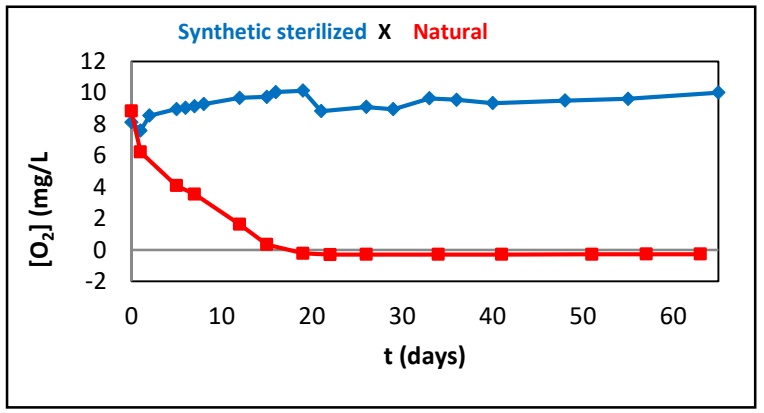
5 ºC e 15 ºC

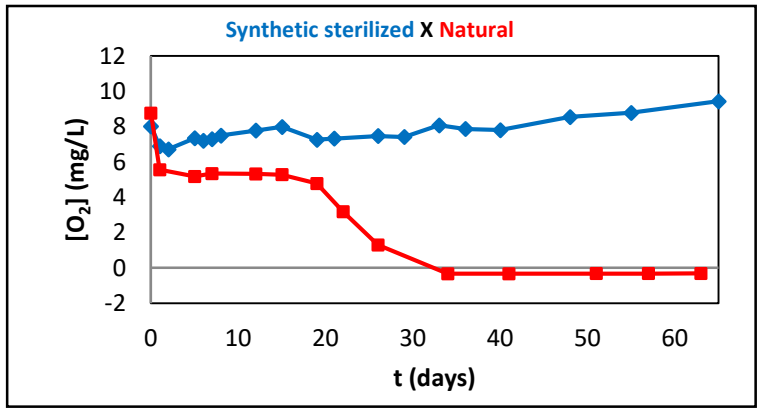


25 ºC

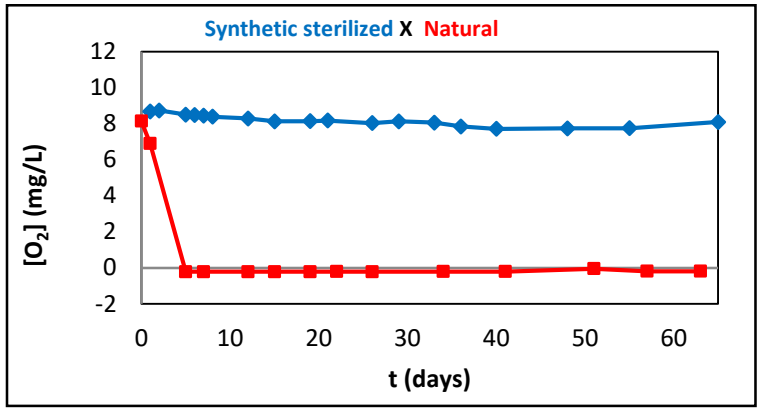
AISI 304

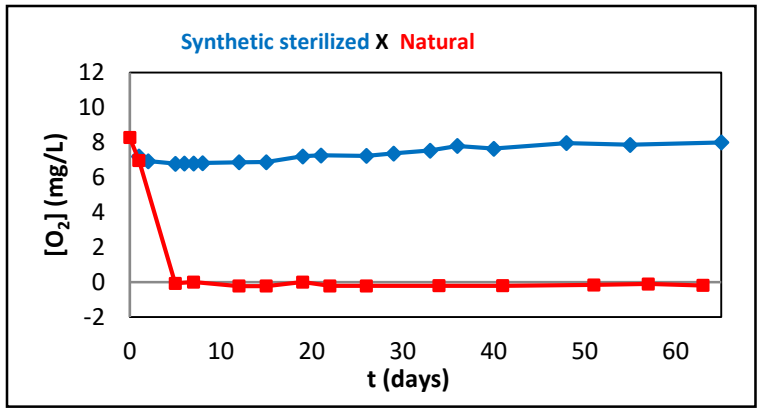
5 °C



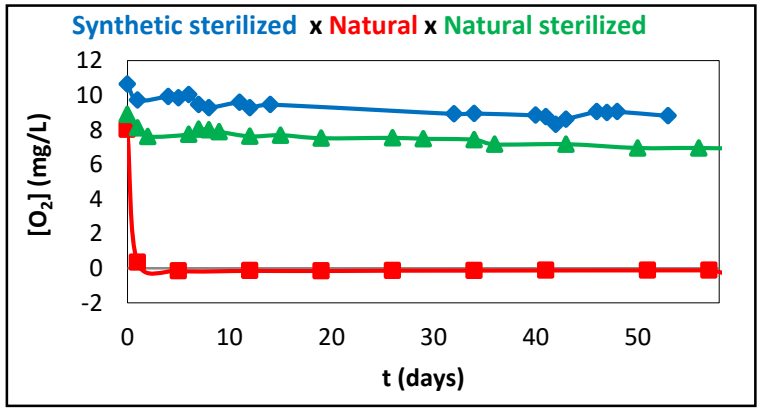


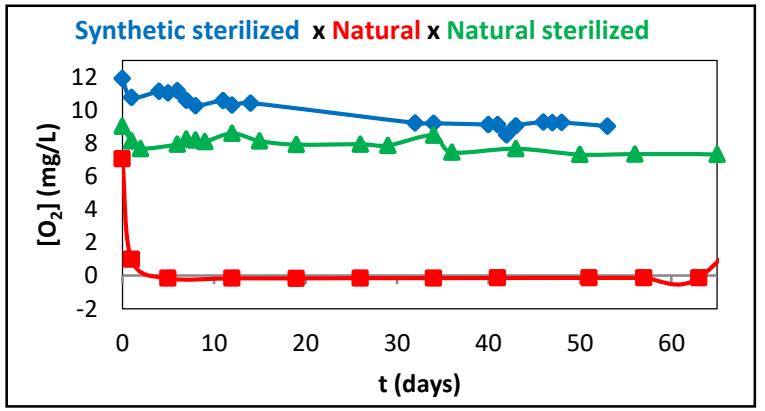
15 °C





25 °C





■ **Rapid consumption of O_2 in natural seawater**: the faster the consumption, the higher the temperature.

◆ **No O_2 consumption in synthetic sterilized seawater** at 5 °C and 15 °C

◆ ▲ **Slight O_2 drop in sterilized seawater** at 25 °C

Pitting corrosion – AISI 304

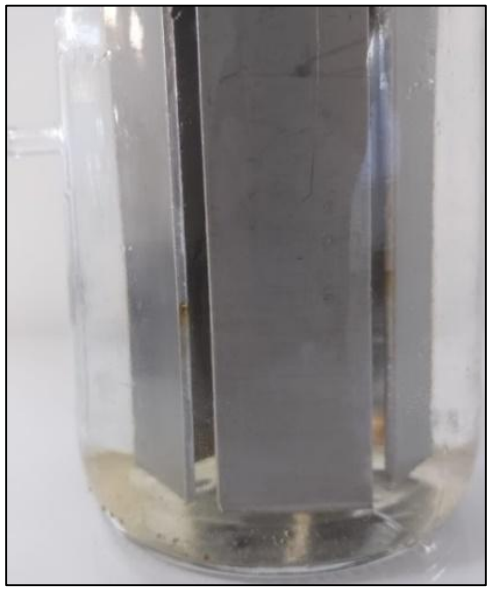
Consumo de O_2

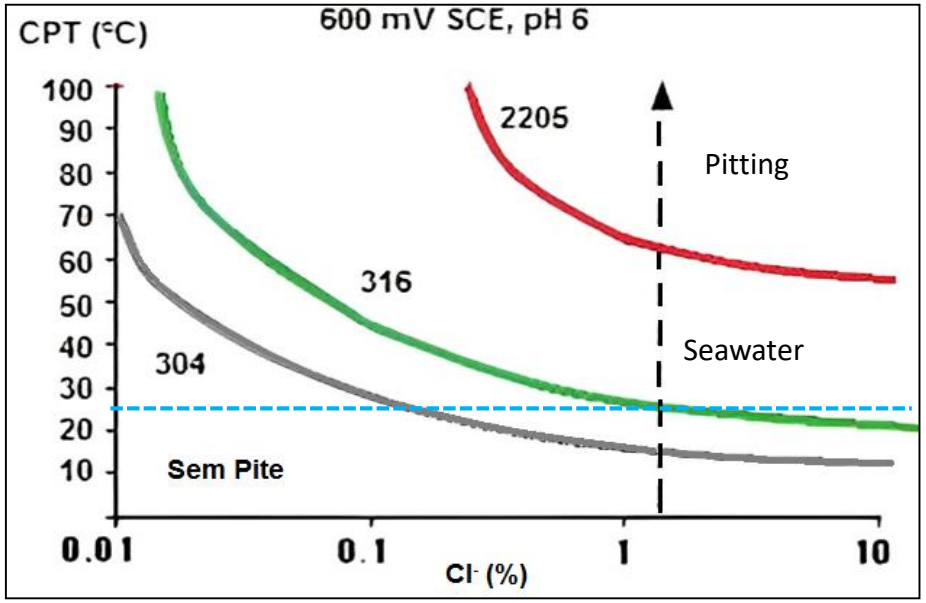
Synthetic sterilized 25 ºC

Natural sterilized 25 ºC

Synthetic sterilized 15 ºC

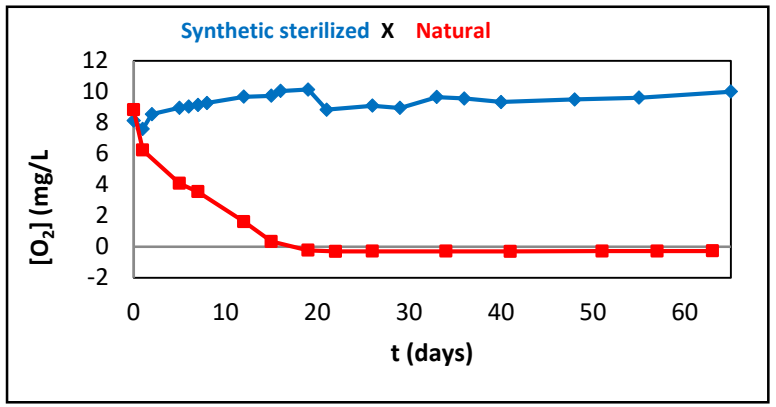
Natural sterilized 25 ºC

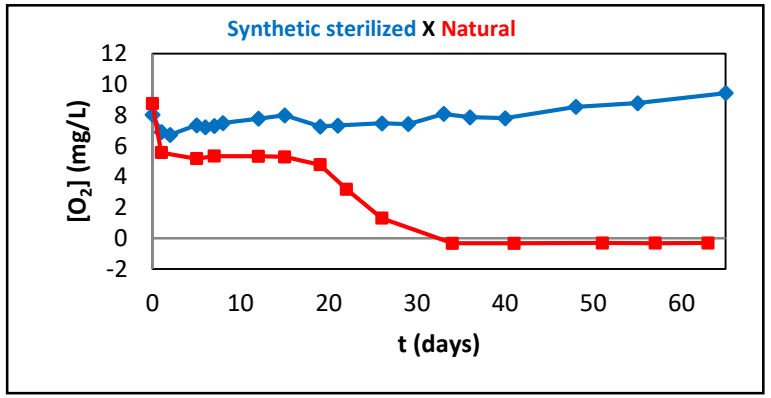




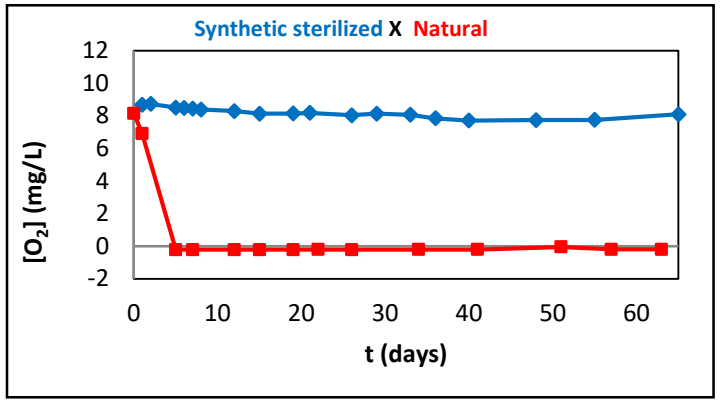
AISI 304

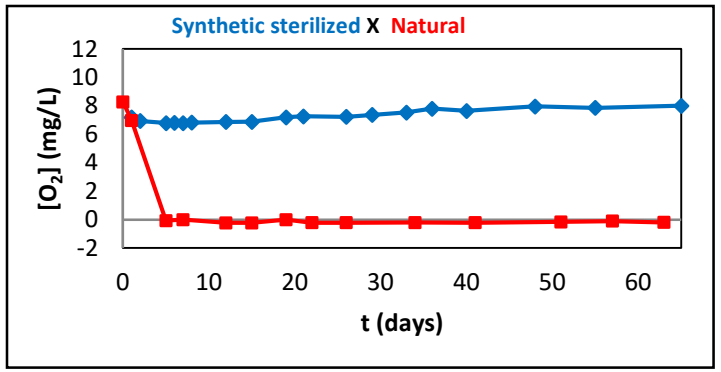
5 °C



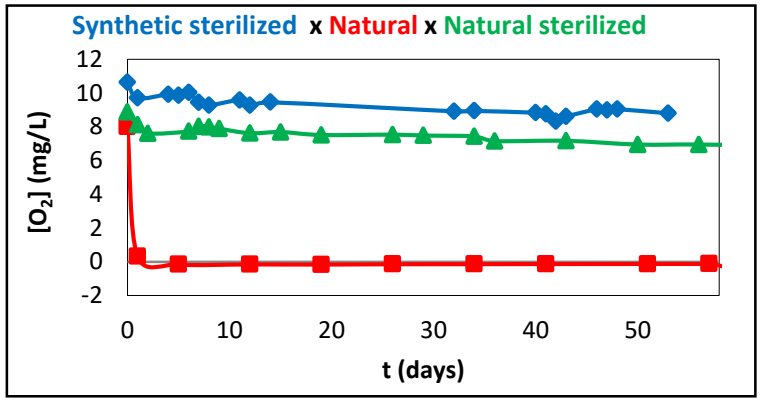


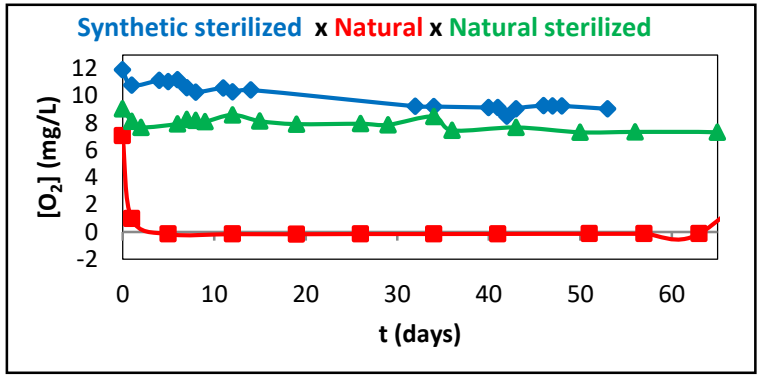
15 °C





25 °C





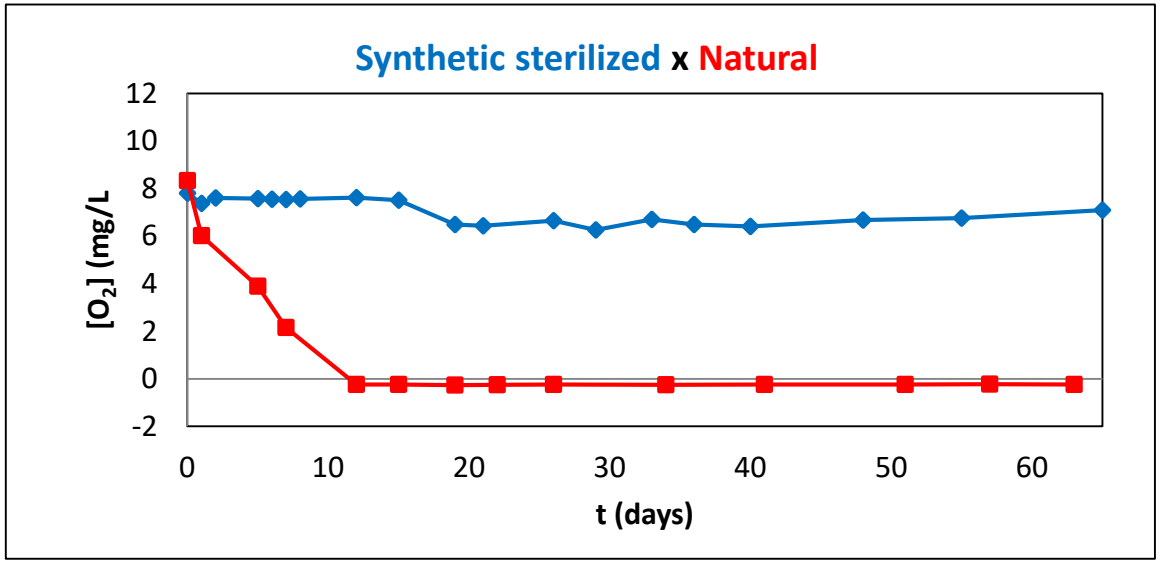
- **Rapid consumption of O_2 in natural seawater**: the faster the consumption, the higher the temperature.
- **No O_2 consumption in synthetic sterilized seawater** at 5 °C and 15 °C
- **Slight O_2 drop in sterilized seawater** at 25 °C

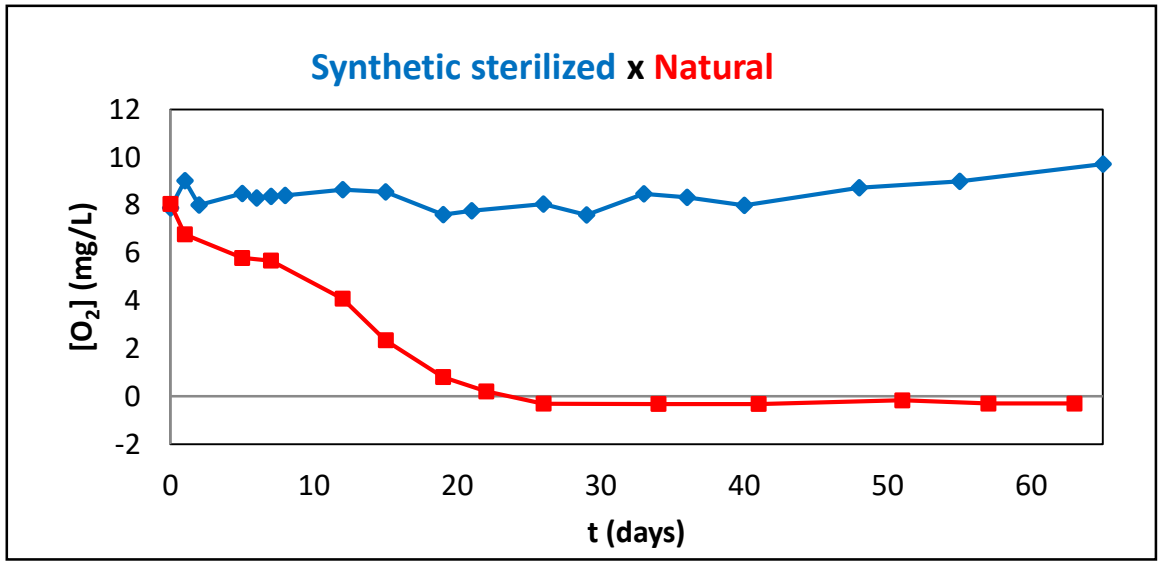
Conclusion

O_2 consumption is associated with the presence of microorganisms present in non-sterilized seawater and not with metal passivation as mentioned in the literature.

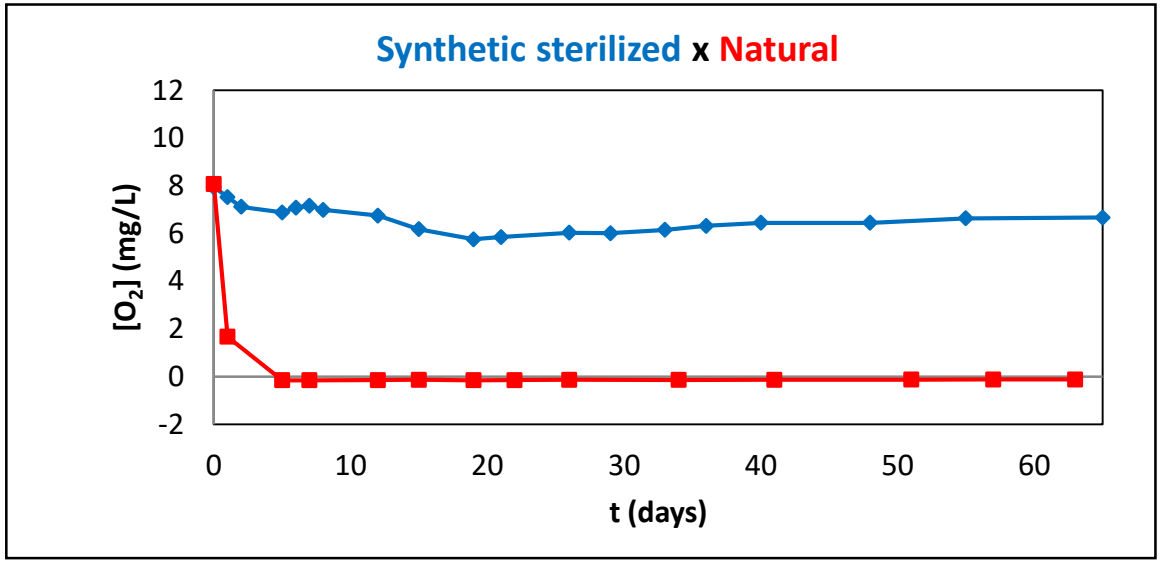
Results – AISI 316

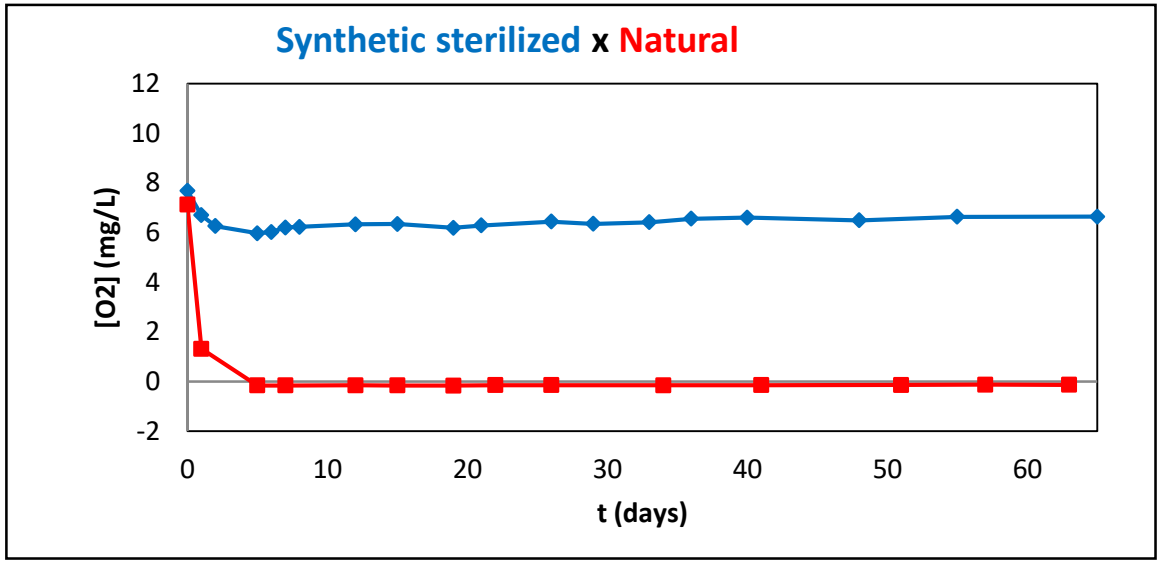
5 °C





25 °C

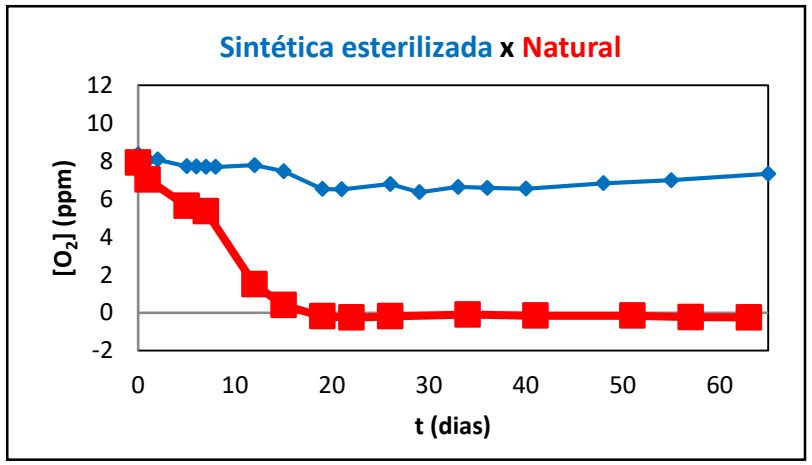


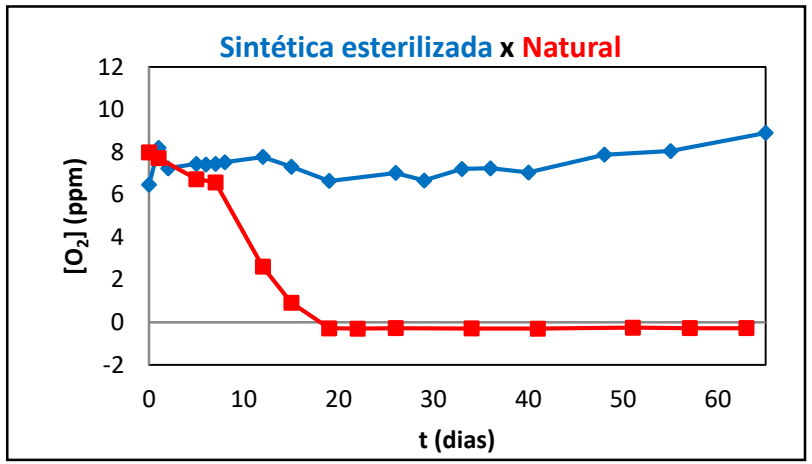


Resultados – SAF 2205

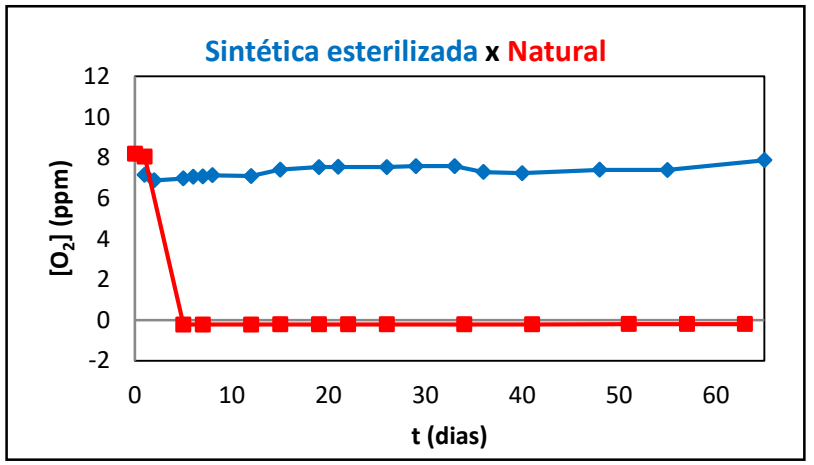
Consumo de O_2

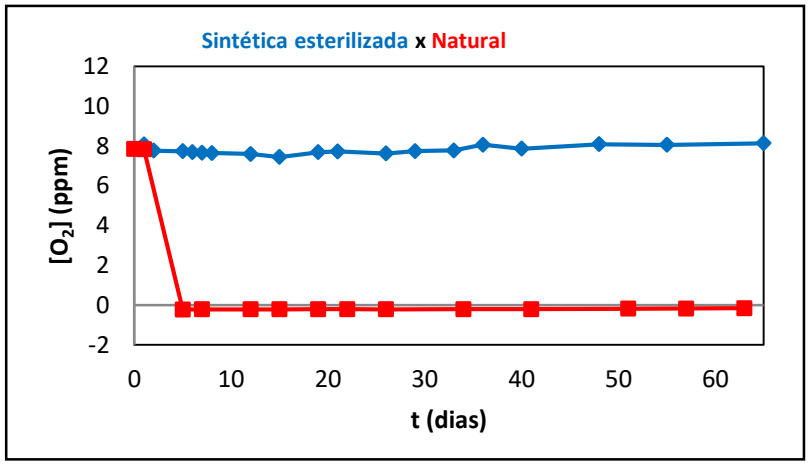
5 °C



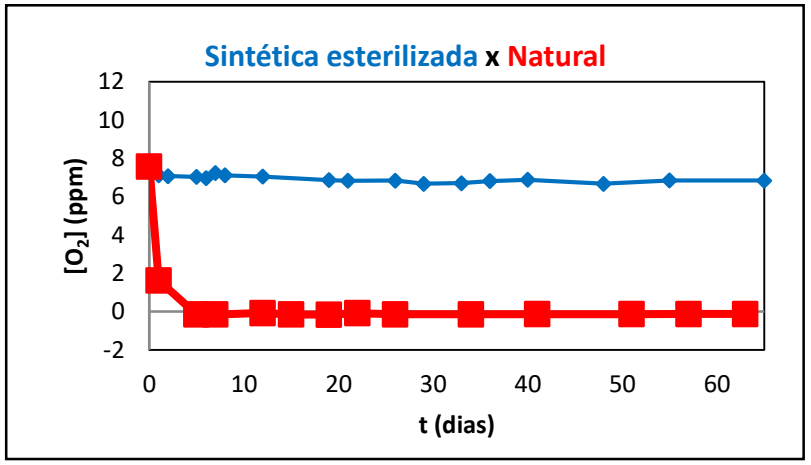


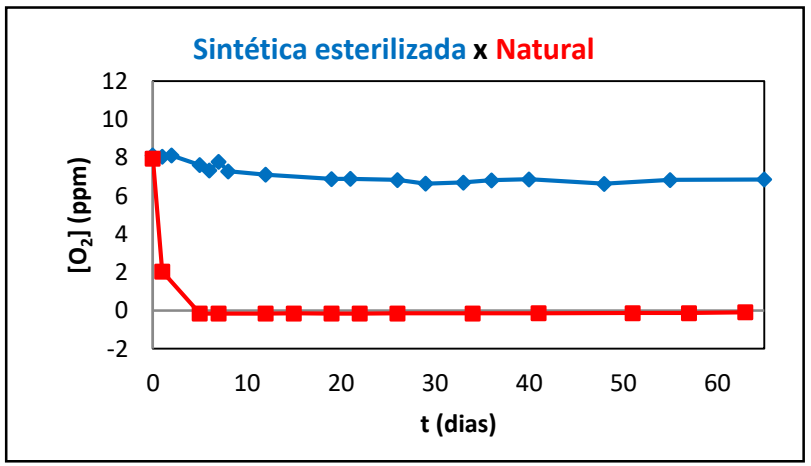
15 °C





25 °C

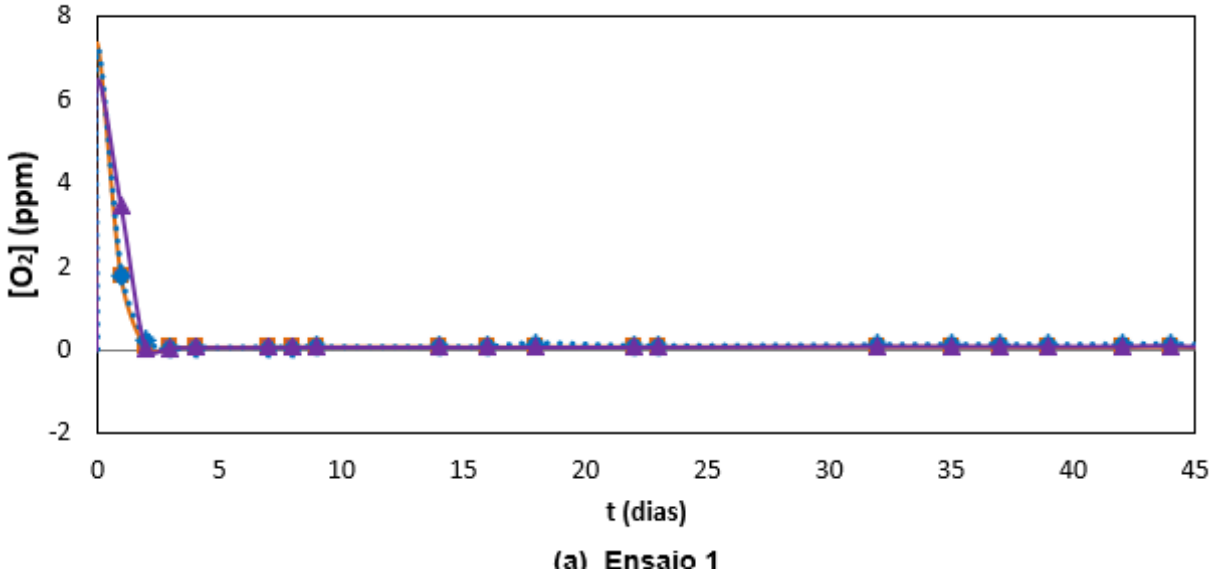




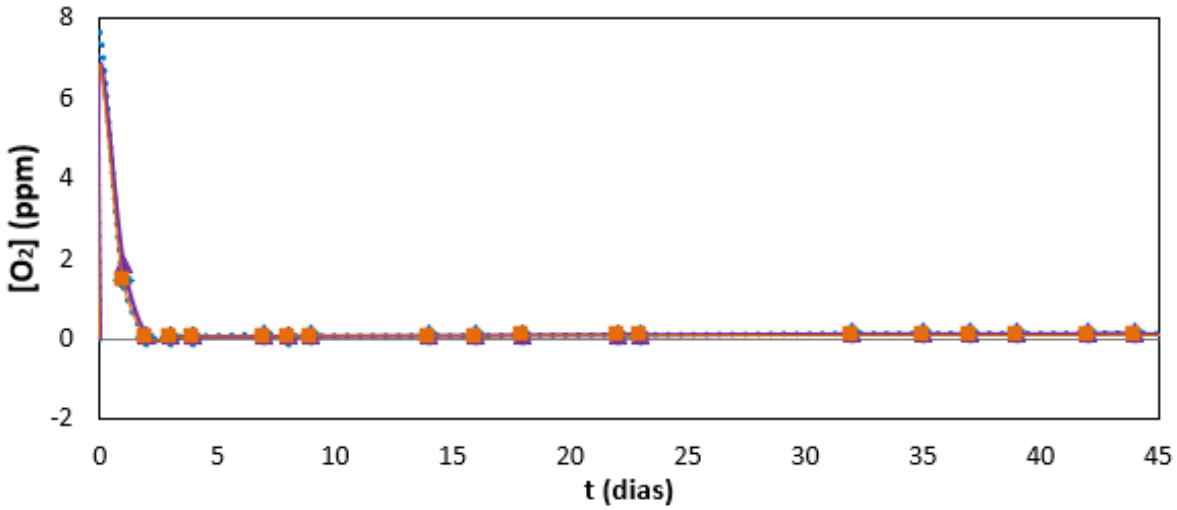
Tests performed adopting different V/A

SAF 2205 25 ºC

Natural sea water: V/A = 1,7 mL/cm², V/A = 6 mL/cm² e no metal



(a) Ensaio 1



(b) Ensaio 2 (Repetição)

✓ Oxygen is consumed in a few days, regardless of the V/A ratio and even in the absence of metal, confirming once again that the rapid consumption is due to the microbial activity present in natural seawater.

Microbiological analyses

No micro-organisms´ growing were detected on the test biocupons after the tests

Conclusions

- ✓ The optical luminescence O_2 sensors proved to be quite suitable for monitoring the dissolved O_2 content at the temperatures adopted in the present study (5 °C, 15 °C and 25 °C), presenting adequate durability for tests of up to 60 days, without presenting any type of failure.
- ✓ At 25 °C, O_2 consumption is rapid in non-sterilized natural seawater and practically zero in sterilized natural and synthetic seawater, indicating that O_2 is consumed by microorganisms present in natural seawater and not due to metal passivation as cited in the literature.
  - ✓ Most likely the amount of O_2 consumed by steel passivation is so small that it is not detected by dissolved O_2 content monitoring.
- ✓ O_2 consumption decreased with lowering the temperature in all conditions studied, most likely due to the decrease in bacterial activity with temperature.

Conclusões

- **AISI 304**
  - The critical pitting temperature of AISI 304 steel in seawater is close to 15 °C. For this reason, this steel showed significant localized corrosion on the cutting edges at 25 °C, slight localized corrosion at 15 °C, and did not show any pitting at 5 °C.
  - The O_2 consumed due to localized corrosion of AISI 304 was detected by the O_2 sensors.

- In future studies on dissolved O_2 consumption, it is recommended that only steels that are not susceptible to localized corrosion be used.


thank you!