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Deposition Time Effect of Dissolved Cow-Bone Powder on Corrosion of Martensitic Stainless Steel in Sea Water

A. G. Asadu[1], C. S. Obayi[1]*, P. S. Nnamchi[1], P. O. Offor[1]
[1]*Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Enugu State, Nigeria.*

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*Corresponding Author:
Camillus Sunday Obayi
Email address:
camillus.obayi@unn.edu.ng

Abstract

Low corrosion resistance is the major drawback of martensitic stainless steel (MSS) in aggressive environments containing chloride ions. A variety of corrosion protection of MSS in such severe media has been attempted using several coating materials that are not only expensive, non-eco-friendly, but difficult to process. This paper is aimed at depositing dissolved CB powder on martensitic stainless-steel surface and determining the effect of deposition time on its corrosion rate in sea water. Cow bone was sourced; washed; dried; crushed; pulverized and sieved to obtain fine powder (≤45-microns) which was later dissolved in Nitric acid using wet digestion technique. The chemical composition of CB was determined using X-ray fluorescence spectroscopy (XRF). The CB powder solution was coated on pre-heated MSS sample surfaces at deposition times of 3, 6 and 9 minutes. Sea water served as the corrosion medium for determination of the corrosion behaviour of uncoated and coated MSS samples using Potentiodynamic polarization testing technique. The corrosion rate of the control MSS sample was 0.0151 gram/hr. The 3-minues, 6-minutes and 9-minutes coated samples had reduced corrosion rates of 0.0075, 0.0058 and 0.0039 gram/hr., respectively. The results indicated that corrosion resistance of MSS improved significantly with increase in deposition time and cow bone can be used as a coating material for improving the corrosion resistance of Martensitic stainless steel in sea water.

1. Introduction

Stainless steels (SS) are an iron-based alloys consisting of high percentage of chromium (11-30 wt. % Cr) and varying amounts of nickel [1]. Stainless steels can be grouped according to chemical composition or into four families based on microstructural characteristics of the alloys as martensitic, ferritic, austenitic or duplex (austenitic + ferritic) [1]. Amidst the groups, martensitic stainless steels (MSS) are cheapest and possess the highest strength [2]. Due to their excellent reproducibility and machinability properties; martensitic stainless-steel alloys are increasingly being used as replacement materials for plain carbon steels and plastics, but have limitation of lowest corrosion resistance in severe environments containing chloride ions [2]. Thus, designing to prevent or mitigate corrosion is a major engineering design criterion in many MSS structures and components.

Furthermore, martensitic stainless steels have found increased industrial applications. MSS are used as turbine-compressor blade materials; tool and cutlery alloys; mining equipment; offshore oil and gas components and in aerospace [2 - 7]. However, MSS has a major drawback of low pitting corrosion and corrosion resistance in confined or severe environments [7]. Previously, several surface treatments have been used for surface protection of martensitic stainless steels. Such surface treatments include use of plasma nitriding [8], organic–inorganic hybrid coatings with different cerium concentrations [7], ZrO_2 coating [9], deposition of Stellite 21 coating [10] and friction surfacing [11]. However, some of these treatments are not only expensive, but toxic and due to environmental concerns, there is the need to find eco-friendly coating materials.

Millions of tons of cow bone (CB) are produced each year in Nigeria [12]. Open-air burning, a common cow bone method forms cow bone ash, which constitutes a serious environmental problem [13-15]. The major component of animal is calcium phosphate (85%) with an approximate chemical formular of $3Ca_3$ $(PO4)_2$ Ca $(OH)_2$ plus calcium carbonate (10%) and traces of calcium fluoride, magnesium chloride, etc [16]. The important ions of the bone salts are calcium, magnesium, phosphate, carbonate, hydroxyl, chloride, fluoride and citrate [16]. A myriad of research has been performed on the synthesis of calcium phosphate for surface modification of medical implants for biomedical applications [17]. Pure calcium phosphate or hydroxyapatite powder synthesized from fish bone and coated on stainless steel 316L prevented the release of metal ions and improved the corrosion resistance of SS 316 L in Ringer's solution [18]. Anhydrous tricalcium phosphate and Hydroxyapatite coatings have also been shown to have a significant inhibitive effect on the corrosion of mild steel in 1M HCl [19, 20], respectively.

This paper is aimed at depositing dissolved CB powder on martensitic stainless-steel surface and determining the effect of deposition time on its corrosion rate in sea water. The use of dry CB powder in this research work is innovative because CB is a waste and readily available material in Nigeria and to the best of our knowledge, the use of CB to mitigate the corrosion of martensitic stainless steel has not been be reported. The use of cow bone will also reduce dependence of surface modification of stainless steels using other expensive chemicals.

2. Materials and methods

2.1 Materials

2.1Sourcing and preparation of materials

The MSS (AISI 410) material having a thickness of 1.2 mm was supplied by Auskan Co. Ltd, Kaduna State, Nigeria. Its chemical composition determined in a previous work using Spark Optical Emission Spectrometer model ARL Quanto Desk rating 350VA, is shown in Table 1 [3].

Table 1. Chemical Composition of AISI 410 Martensitic Stainless Steel

Element	C	Ni	Cr	Mn	Cu	Mo	S	P
Weight %	0.1597	1.0830	13.3300	9.9350	1.2540	0.0344	0.0095	0.0183
Element	Si	Co	Nb	B	Ti	W	V	Fe
Weight %	0.3677	0.1408	0.5166	0.0000	0.0000	0.6169	0.0910	balance

The cow bone (CB) was obtained from an abattoir at Ogige market in Nsukka, Enugu State, Nigeria. The Nitric Acid used for dissolving the cow bone powders was of 70% concentration and 99.90% purity and was purchased from JOECHEM Chemical store, Nsukka, Nigeria. The corrosive medium was sea water, prepared by dissolving analytical reagent grade of 3.5% NaCl in 100 ml distilled water. Other materials were abrasive papers, glass beakers and heat treatment furnace.

2.2 Experiments

2.2.1 Preparation of the Cow Bone

The cow bone was cleaned and sun dried for 14 days to reduce the moisture content and the organic matter therein. The bone was subsequently dried in the heat treatment furnace at 200°C for 2½ hours to further reduce the moisture and organic matter content. The bone was held in the oven for another 1 hour before its removal. The dried cow bone was then crushed followed by pulverization using a grinding machine. The pulverized cow bone was then sieved to obtain finer particle sizes ranging from 0-45 µm and stored to be dissolved later in acidic medium. The chemical composition of the cow bone was determined using X-ray fluorescence spectroscopy (XRF).

2.2.2 Dissolution of the Cow Bone

The pulverized cow bone was gradually dissolved in Nitric acid (HNO_3) until a complete decomposition of the bone was achieved. Fifty millilitre (50 ml) of acid was poured into a beaker. The beaker was placed on a hot plate equipped with magnetic stirrer and heated until the acid boiled at 118°C. Twenty gram (20 g) of the pulverized CB was poured into boiling acid and the continuous stirring of the mixture by the magnetic stirrer ensured complete dissolution of CB in 5 mins. The clear solution was stored to be used for deposition. The steps followed in the preparation of the cow bone are shown in Figure 1 while the forms of the cow bone at each preparatory step is shown in Figure 2.

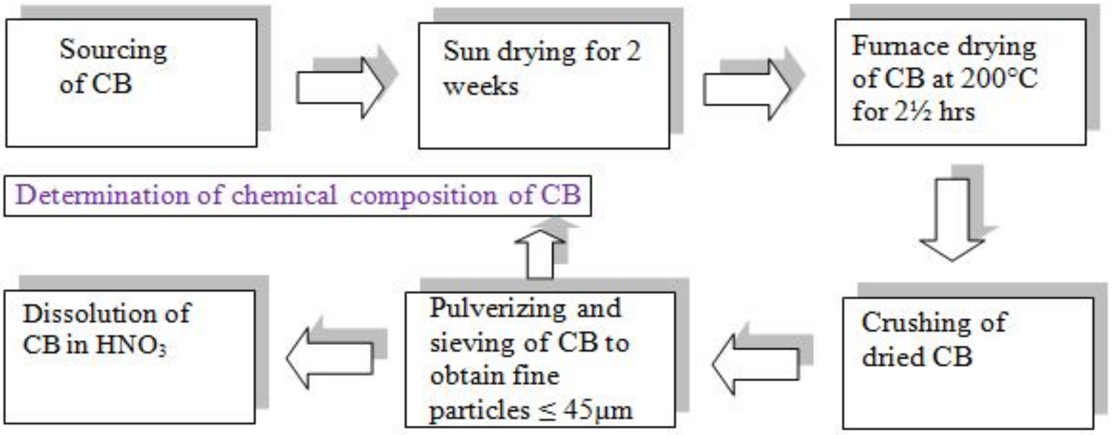

Figure 1. **Cow bone preparation steps**

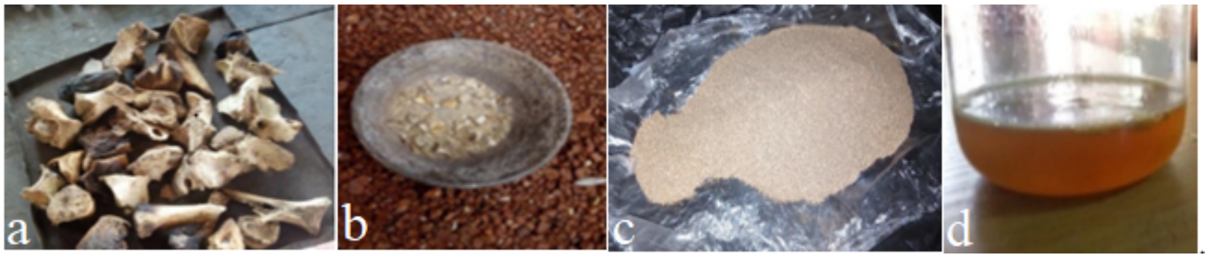

Figure 2: Forms of the cow bone after preparation: (a) Cow bone after drying in the furnace (b) ground cow bone, (c) pulverized and sieved cow bone, (d) dissolved cow bone solution

2.2.3 Spray Deposition of Dissolved CB on the MSS Substrates

Prior to deposition, the stainless-steel sheet was cut into rectangular samples of 10 mm × 10 mm × 1.2 mm. The samples were polished with silicon carbide papers up to 1000 grit, cleaned with ethanol, dried and stored. The polished stainless-steel samples served as substrates for the deposition of the dissolved CB using spray deposition method. Prior to the commencement of deposition, the specimens were heated up to 180°C, followed by deposition of the dissolved CB solution on samples' surfaces using a spray machine designed and used by [21] in their work. The substrates were heated to 180°C because it was observed that the dissolved cow bone could adhere sufficiently on the MSS substrates at room temperature. The carrier gas (air) flow rate was 6 ml/min, the pressure of air was maintained between 25-50 kg/cm^2 while the distance of spray nozzle from the substrate was 20 cm and angle of spray was 45°. The deposition times were 3, 6 and 9 minutes and four specimens each was sprayed for each of the allotted time. The spray deposition steps are depicted in Figure 3.

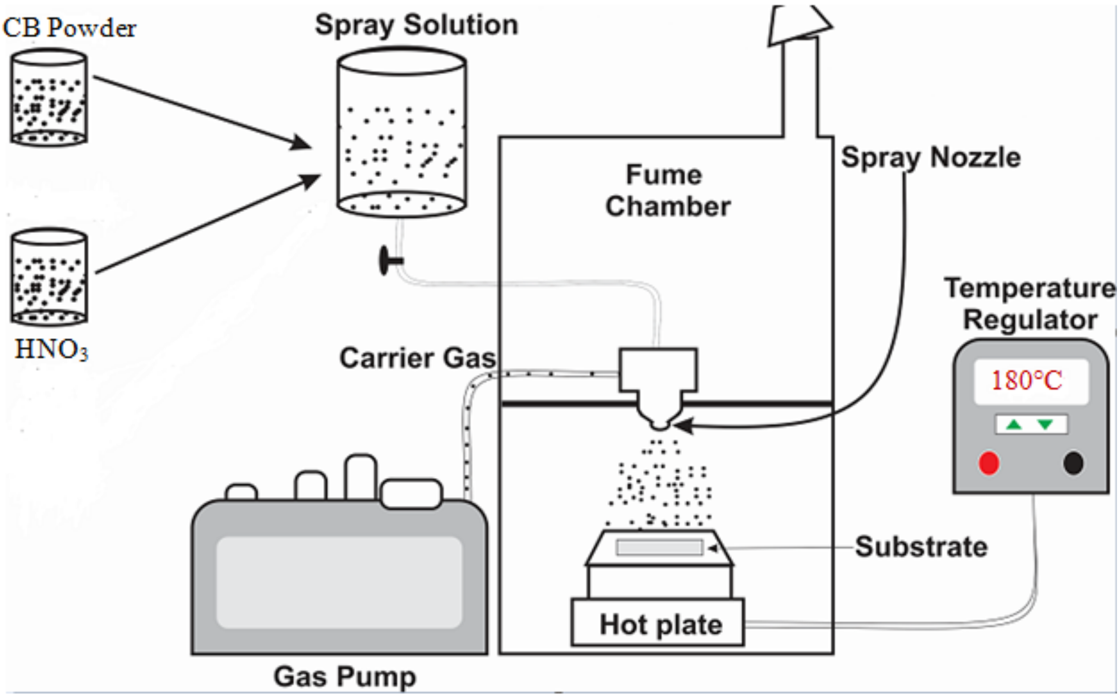

Figure 3. Spray deposition of dissolved CB on the MSS substrates

2.2.4 Corrosion test

Potentiodynamic polarization test was used to assess the corrosion behaviour of both the coated and uncoated samples in sea water. The Potentiodynamic polarization test was performed using a 3-electrode cell, in which a saturated calomel electrode (SCE) was used as a reference electrode, a graphite electrode as a counter electrode and the sample as the working electrode. The 3-electrode measurement system was an Electrochemical Analyzer (CH Instruments, Model CHI604E, USA). Each corrosion test was performed in 250 ml of sea water at room temperature. The working area of 1.12 cm^2 was exposed to the medium. The polarization test was performed at an applied potential in the range of -1500 mV (vs. SCE) to -1500 mV (vs. SCE) at a scanning rate of 0.01 V/s. The corrosion parameters such as corrosion current density, corrosion rate and slopes were obtained from the computer controlled potentiostat. Prior to each corrosion test, the working electrode was allowed to stabilize in the sea water for 1 hr.

3. Results and Discussion

3.1 Chemical composition of the cow bone

The elemental composition of the cow bone which was obtained using X-ray fluorescence spectroscopy (XRF) is shown in Table 2. The result indicates that the cow is majorly composed of Calcium (40.34 wt. %), Oxygen (38.2 wt. %) and Phosphorous (19.07 wt. %), and other elements – Magnesium (0.80

wt. %), Silicon (0.21 wt. %), carbon (0.84 wt. %), Potassium (0.17 wt. %) and Aluminium (0.37 wt. %). These elements exist in combined forms in cow bone as Calcium carbonate ($CaCO_3$), Calcium silicate ($CaSiO_3$), Tricalcium Phosphate $Ca_3(PO_4)_2$ or hydroxyapatite ($Ca_{10}(PO_4)6(OH)_2$). In previous works, cow bone ash was found to contain 10% carbon and 90% of hydroxyapatite [22]; 70 - 76 wt. % of Tricalcium phosphate and 7-9wt % of calcium carbonate [23]. Natural bone is a ceramic composite comprised of calcium phosphate, collagen, and water [24]. Calcium phosphate is present in bones in the form of HA crystals, which provides rigidity to the bone.

Table 2: Chemical composition of cow bone

Element	C	O	Ca	Mg	Si	P	K	Al
Weight%	0.84	38.20	40.34	0.80	0.21	19.07	0.17	0.37

3.2 Corrosion Behaviour of the Uncoated and Coated MSS Specimens

Figures 3 and 4 show open-circuit potential (E_{ocp}) curves and polarization curves of the Uncoated and coated MSS samples, respectively, obtained during Potentiodynamic polarization corrosion tests. An initial decrease in E_{ocp} with time is observed for all samples in Figure 3 due to the dissolution of the uncoated and coated MSS surfaces, after which E_{ocp} maintained almost steady values due to the passivation of MSS surfaces, but the open-circuit potentials of the coated samples were more positive than the uncoated sample. It can be clearly seen in Figure 4 that the uncoated MSS sample displayed pitting in the anodic part of corrosion curve while pitting was not observed on polarization curves of the coated samples. Table 3 lists the corrosion data obtained from Potentiodynamic polarization test. From Table 3, the uncoated sample has a corrosion potential, E_{corr} of -0.612V, followed by the stainless steel coated for 3 minutes with E_{corr} of -0.605V, then by stainless steel coated for 6 minutes with E_{corr} of -0.525V and finally stainless steel coated for 9 minutes with E_{corr} of -0.511V**.**

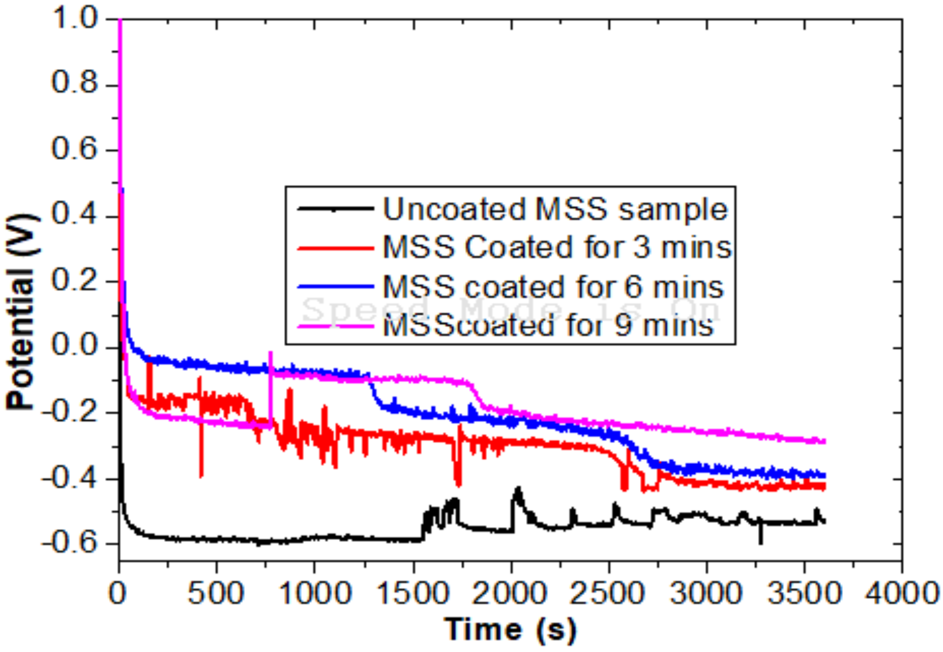

Figure 3: Open circuit potential curves of the uncoated and coated MSS samples.

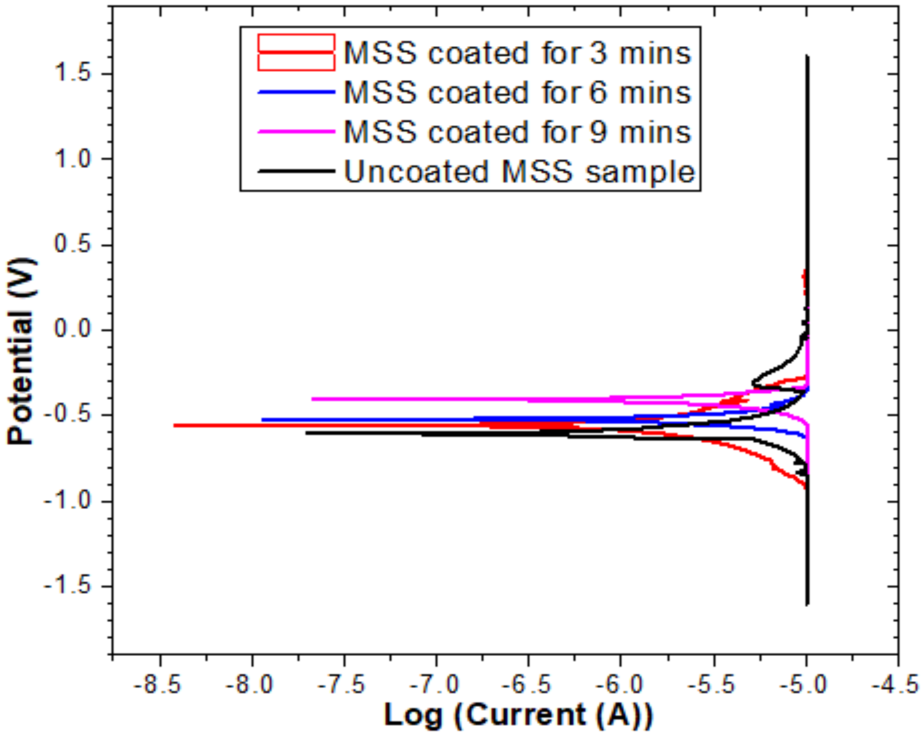

Figure 4: Potentiodynamic polarization curves of the Uncoated and coated MSS samples

Table 3: Corrosion data obtained from Potentiodynamic polarization tests for uncoated and coated MSS samples.

Material	Deposition time (mins)	Potentiodynamic polarization test data		
		Corrosion potential (V)	Corrosion current density (Acm^{-2})	Corrosion rate (g/hr.)
As-received	0	-0.612	0.014877	0.01507
As-coated	3	-0.605	0.012344	0.00747
As-coated	6	-0.525	0.005887	0.00578
As-coated	9	-0.511	0.003883	0.00393

The corrosion potentials of the coated MSS samples became more positive with increase in the time of deposition and this was accompanied by decrease in both corrosion current density (I_{corr}) and corrosion rate. The corrosion potential of the uncoated sample was more negative and had higher corrosion current density and corrosion rate. These could be attributed to the formation of more protective passive films on the coated MSS surfaces due to reaction of the deposited CB powder and sea water. It has long been shown that reaction of hydroxyapatite with seawater is a two-step chemical reaction process [25, 26, 27] that releases calcium and phosphate ions as shown equations (1) and (2).

$$Ca_{10}(PO_4)_6(OH)_2 + 6H_2O \leftrightarrow 4Ca_2(HPO_4)(OH)_2 + 2Ca^{++} + 2HPO_4^- \qquad 1$$

$$Ca_2(HPO_4)(OH)_2 \leftrightarrow 2Ca^{++} + HPO_4^- + 2OH^- \qquad 2$$

Since Calcium is a major constituent of cow bone, Ca^{2+} could diffuse into the passive layer of MSS enabling bonding with the alloying elements and adhesion. It could also enable the formation of a strong metal-ceramic interface, which acting as a barrier obstructs the penetration of chloride ions that initiate pitting attack [28]. This could also be attributed to the blocking of the micropores by the calcium ions, phosphate ions and other ions present in the solution from getting to the surface of the steel [28]. More so, CB contains Si in the form of calcium silicate, a ceramic material that has been found to impede dissolution of steel in sea water [29]. Pure hydroxyapatite powder synthesized from fish bone and coated on stainless steel 316L hindered the liberation of metal ions and improved the corrosion resistance of SS 316 L in Ringer's solution [18].

A fundamental requirement for the reduction of corrosion rate of metals is to reduce the E_{corr} and I_{corr} which is evident in the reduction of the corrosion rates of martensitic stainless-steel samples. The coated samples exhibited an increase in E_{corr} or became more positive with increase in the deposition time, leading to reduction in corrosion current density and increase in corrosion resistance of the samples. It is noteworthy that the uncoated MSS sample displayed pitting in the anodic part of corrosion curve while pitting was not observed on polarization curves of the coated samples, indicating that the CB powder coating could mitigate pitting corrosion of MSS, a major limitation of stainless steels in high chloride containing environment [2, 7].

Conclusion

This paper investigated the effect of deposition time of cow bone powder on corrosion behaviour of martensitic stainless steel (AISI 410) in sea water. The corrosion resistance of the control MSS sample improved from 0.0151 gram/hr to 0.0075 gram/hr (50.33%), 0.0058 gram/hr (61.6%) and 0.0039 gram/hr (74.2%) for the samples coated for 3, 6 and 9 minutes, respectively. The results showed that CB deposition improved corrosion resistance of MSS significantly; indicating that CB, a readily and locally available waste material in Nigeria could be used to improve the corrosion resistance of stainless steels. It is noteworthy that the uncoated MSS sample displayed pitting in the anodic part of corrosion curve while pitting was not observed on polarization curves of the coated samples, indicating that the CB powder coating could be used to mitigate pitting corrosion of MSS, a major limitation of stainless steels in high chloride containing environments.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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