

Corrosion Behavior of Ferritic Steel, Austenitic Steel and Low Carbon Steel Grades in Sugarcane Juice

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ABSTRACT

The objective of the present study is to evaluate the corrosion behavior of ferritic grade AISI 444 and to compare its performance with the austenitic grade AISI 304 and low carbon steel AISI 1010 in the corrosive medium of raw sugarcane juice. General corrosion and pitting corrosion behavior of AISI 444, AISI 304 and AISI 1010 steels in sugarcane juice was investigated using traditional weight loss method and cyclic polarization scan. Crevice corrosion tests were also conducted, as per ASTM standard G 78. It is observed that the corrosion performance of AISI 444 as compared to AISI 1010 is far superior and comparable to that of AISI 304 grade steel.

Keywords: Stainless steel, polarization, pitting corrosion, crevice corrosion

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1. INTRODUCTION

In sugar industry most of the equipment parts used are made from mild steel [1]. Mild steel is extensively used mainly because of its low cost, good mechanical properties, and ease of fabrication. Hence it is used as construction material of machinery and equipment in Indian sugar industry. However, it has a poor corrosion resistance in that environmental condition. Sugar industry is plagued by high maintenance, replacement and repair of equipment due to corrosion and abrasion. Due to this reason, the industry is gradually switching over to components made

of/fabricated with stainless steel, mainly for excellent corrosion resistance, better hygiene, fewer breakdowns of the plant, etc. Most sugar mills across the world have switched over to use the components made of various grades of stainless steel [2]. Among the various grades, most commonly used is the conventional AISI 304 grade, due to its all-round performance in most environments. But, with the prices of 304 soaring (due to high volatility of nickel prices), ferritic stainless steel has been proposed as a prospective replacement material for the sugar industry. It has been reported that, stainless steel depends on the formation of a

thin passive film to maintain low corrosion rates in aqueous solutions [3]. Any breakdown of this film is likely to result in localized corrosion, at pits and crevices. It is, therefore, essential that corrosion resistance of steel in the sugarcane juice environment be evaluated to enable the machine designer to choose the proper materials.

Sugarcane juice is acidic with a pH value of around 5.6 when freshly extracted and is known to vary depending on the geographical region of its cultivation [4]. This acidic property is due to the presence of various acids in the sugarcane juice namely, aconitic, citric, malic, oxalic, glycolic, mesaconic, tartic, succinic, fumaric and syringic acids. The sugarcane juice that was used as electrolyte in this investigation was obtained from Allahabad region of the state of Uttar Pradesh in India.

Sugarcane juice contains a high level of chlorides (approximately 1300 ppm). Pitting corrosion is caused by the breakdown of the passive film which occurs in the presence of aggressive anionic species. The presence of oxidizing agents in a chloride-containing environment is usually extremely detrimental and further enhances localized corrosion [5]. Numerous investigations have been reported in the literature on the corrosion of materials

in the sugarcane industry [6–9]. Bajpai et al. [10] have conducted experiments to investigate the effects of pH, temperature, brix (solid concentration in the juice) and dissolved oxygen content on the corrosion rate of mild steel in sugarcane juice. They reported an increased rate of corrosion below a pH value of 7 of the sugarcane juice and more sharp increase below the pH value of 4. Up to a juice temperature of 70 °C, no significant change in the corrosion rate was observed, but above this temperature the rate increased sharply. The corrosion rate linearly increases with decrease in brix and corrosion rate increases with dissolved oxygen content. Ramkumar et al. [11] found that corrosion of mild steel and brass depended mainly on pH and the juice flow rate and that the corrosion rate was maximum with mixed juice and minimum in case of final molasses.

S.K. Gupta et al. [12] reported the finding of a definite relationship between iron content in processed liquors and the color development of sugar. The reaction between iron and polyphenols alone increased the color values of clear juice by 5–7%, which in turn on crystallization enhanced the sugar color by corresponding value. S.K. Gupta et al. [7] have reported that the corrosion rate of mild steel was more in raw juice than clarified juice and water. Therefore, the

investigations carried out by us were done using the freshly crushed sugarcane juice as the corroding medium.

Corrosion testing also serves multiple functions in equipment design, manufacture, and service life extension. The weight loss corrosion technique is the simplest of all corrosion estimating techniques for general corrosion. Electrochemical scanning techniques indicate the ability of a material to resist a given environment or repassivate after corrosion sets in [13]. Cyclic potentiodynamic polarization test is widely used to study the pitting susceptibility of stainless steel in chloride-containing environments. An anodic polarization curve is measured by a cyclic potentiodynamic polarization method using a specific scanning rate, from which breakdown potential and protection potential can be determined. The multiple crevice assembly technique, using a serrated washer to create many crevice sites on each side of a test panel, has become commonplace in the investigation of crevice corrosion.

Though numerous research studies are made on stainless steel in different corrosive mediums including sugarcane juice, investigations on the comparative study of corrosion of ferritic and austenitic stainless

steel in the sugarcane juice environment is meager. The aim of the present investigation is to probe the feasibility of replacing AISI 304 steel and low-carbon steel with AISI 444 as the fabricating material in the manufacture of machinery and equipment in a sugar mill.

2. MATERIALS

Ferritic steel AISI 444, austenitic steel AISI 304 and low carbon steel AISI 1010 were received as rolled sheets of 1.5 mm thickness and were subjected to the weight loss corrosion test, potentiodynamic cyclic polarization scan and crevice corrosion tests with sugarcane juice as corroding medium. Table I provides the details of their chemical compositions as subjected to spectrometric analysis. Table II lists the density, yield strength and Vickers hardness properties of these materials.

3. METHODOLOGY

3.1. Weight Loss Corrosion Test

ASTM G 31 was followed as a guide for weight loss immersion tests [14]. Three specimens of each material were prepared to rectangular size of 25 mm × 50 mm × 1.5 mm and a 2-mm diameter hole was drilled at the top edge of

Table I: Chemical Composition (% wt) of the Tested Materials.

Grade	AISI 444	AISI 304	AISI 1010
Fe	78.34	70.6	99.21
C	0.011	0.03	0.09
Si	0.64	0.46	0.04
Mn	0.23	1.42	0.52
P	0.014	0.018	0.019
S	0.005	0.014	0.034
Cr	17.9	18.11	--
Mo	2.01	0.29	--
Ni	0.13	8.49	--
Al	0.01	--	0.047
Co	0.02	0.13	--
Cu	0.042	0.287	0.008
Nb	0.39	0.03	--
Ti	0.16	0.01	--
V	0.09	0.08	--

Table II: Density, Yield Strength and Hardness Properties of the Tested Materials.

Grade	Density (g/cc)	Yield Strength (MPa)	Hardness (HV)
AISI 444	7.75	354	188.02
AISI 304	7.97	350	188.65
AISI 1010	7.83	265	80.49

each specimen to enable suspension. After the specimens were polished with 0, 00 and 000 grit abrasive papers, they were thoroughly rinsed in water and degreased in acetone. The specimens were weighed prior to immersion in sugarcane juice test solution on an electronic balance with an accuracy of 0.1 mg. When each of the specimens was placed separately in 250 ml conical flasks, it was ensured that they were completely

immersed in cane juice. To avoid fermentation, the test solution was sterilized in an autoclave for 30 min at a steam pressure of 1.03 bar. The specimens were suspended using a nylon thread in the corrosive medium for predetermined time duration of 1250 hr. After the corrosion test, the specimens were cleaned by placing them in the ultrasonic cleaner for 15 min. The specimens were then rinsed in acetone, dried

and weighed. According to ASTM standard practice G 31, the corrosion rate may be expressed in the following form [14].

$$\text{Corrosion rate} = (K \times W)/(A \times T \times D) \quad (1)$$

Where K is a constant whose value is 8.76×10^7 when corrosion rate is desired in $\mu\text{m}/\text{yr}$, T is the time of exposure in hours, A the area of the specimen in cm^2 , W the mass loss in grams, and D the density in g/cm^3 . Of the three specimens that were exposed for each type of steel, the average values of nearest two corrosion rates have been considered.

3.2. Cyclic Polarization Scan

Samples for cyclic polarization were cut into 2 cm diameter circular discs and abraded through 1200 grit abrasive papers in accordance with ASTM G 61 [15] cold mounted so as to get 5 cm diameter discs with both flat faces of the specimens exposed. The polished face was exposed to the electrolyte and the other exposed face enabled to give electrical connection with the help of a screw tightened against it. The specimens were degreased in acetone and washed in water. These specimens were used as the working electrode giving an exposure area of 3.14 cm^2 .

Cyclic polarization was carried out using PC4 potentiostat of GAMRY instruments

Inc., Warminster, PA, USA with DC 105 software according to the standard ASTM G 5 [16]. The electrolytic cell was made of a 1000 ml Pyrex glass flask with five entrances for reference electrode, working electrode, counter electrode, temperature measurement and aeration/ deaeration. A saturated calomel electrode (SCE) was used as a reference electrode. The counter electrode was a graphite rod. Measurements were done at ambient temperature using freshly crushed sugarcane juice as the electrolyte. The juice was replaced for each test. Before the actual run of the cyclic potentiodynamic polarization scan, the specimens were immersed in the electrolyte at least for 30 min to stabilize at the open circuit potential (OCP). Cyclic polarization curves were measured at a scan rate of 5 mV/s starting from -500 mV with respect to OCP up to 1500 mV before reversing. A plot of $\log I$ versus E is plotted. A scanning electron microscope (SEM) model Jeol JXA 8100 was employed to reveal the types and morphologies of the pits on the surfaces of the corroded specimens after the polarization scan.

3.3. Crevice Corrosion Test

Carbon steels do not suffer crevice corrosion in acidic solutions because of the absence of a passive film, but do suffer crevice

corrosion in alkaline solutions when there is a passive film [12]. As sugarcane juice is acidic in nature crevice corrosion of AISI 1010 steel is ruled out. Therefore, only the stainless steel specimens were subjected to the crevice corrosion test. The specimens were evaluated for their crevice corrosion resistance using the standard ASTM G 78 method. Flat, rectangular-shaped specimens of dimension 50 mm × 25 mm × 1.5 mm with a 6 mm diameter hole at the center were

cut from the sheets of the candidate materials. The surfaces were mechanically polished progressively to 1200-grit level. Hastelloy C-276 fastener was employed for each assembly comprising a threaded bolt and nut plus two washers. Two non-metallic multiple crevice washers made of nylon were pressed onto the specimen using the Hastelloy nuts and bolts as shown in Figure 1.

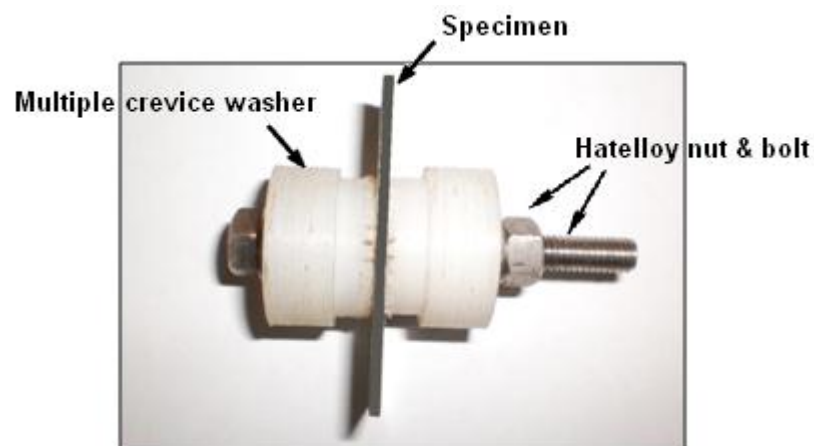


Fig.1: Photograph of Multiple Crevice Assembly for Crevice Corrosion Test according to ASTM G 78.

All crevice assemblies were tightened to the same torque of 8.5 N-m. In this manner, 24 small crevice sites were formed on each side of the specimen. The immersion test was carried out using the crevice assemblies similar to the one shown in Fig. 2. The assembly was immersed in an artificial

sugarcane juice which simulated the industrial sugarcane juice at ambient temperature for 30 days. The specimens were weighed before and after the test using an electronic balance. After exposure of the materials, the surfaces were characterized for the extent of localized corrosion attack

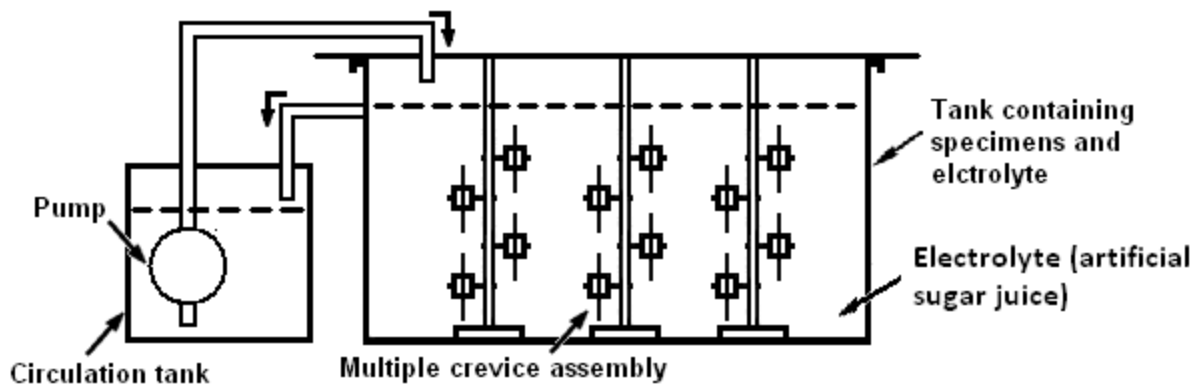


Fig.2: Schematic of Crevice Corrosion Test Setup.

The composition of the electrolyte simulating the industrial sugarcane juice was adapted from the work of E. Zumelzu, et al. [17].

4. RESULTS AND DISCUSSION

4.1. Weight Loss Corrosion Test

The corrosion behavior of the steel grades in freshly crushed sugarcane juice was studied for a duration of 52 days amounting to 1250 hr. Figure 3 shows corrosion rates of the tested materials in micrometers per year.

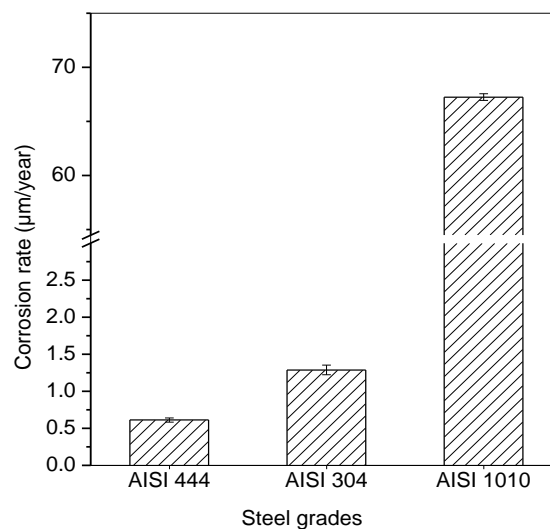


Fig.3: Test Results of Weight Loss Corrosion Test.

As anticipated, the carbon steel AISI 1010 fared badly and its corrosion was one to two

orders of magnitude higher than the stainless steel grades. Due to the porous and non-

adherent nature of the oxide layer formed on the carbon steel, corrosion continues without passivating. The ferritic steel AISI 444 exhibited better corrosion resistance than the austenitic steel AISI 304. Though both these steels have similar chromium content in their chemical composition, 444 steel contains higher niobium content due to which it may have performed better. H. Demiroren [18] reported that the presence of niobium improved the corrosion resistance of the ferritic steel 444 due to the stable surface

layer it forms. The type 444 was the most resistant in this test, and the carbon steel the least resistant.

4.2. Cyclic Polarization Scan

The cyclic potentiodynamic polarization scans in the Figures 4 and 5 show the relative relationships among potentials. Figure 4 shows the potentiodynamic polarization curve for AISI 304 and AISI 444 steels. Table III gives the values of E_{corr} , E_{br} and E_{prot} potentials obtained by the scans.

Table III: Potentials of Cyclic Potentiodynamic Polarization Test

Steel	E_{corr} (V-SCE)	E_{br} (V-SCE)	E_{prot} (V-SCE)
AISI 444	- 0.654	0.327	0.845
AISI 304	- 0.625	0.506	- 0.125
AISI 1010	- 0.809	N/A	N/A

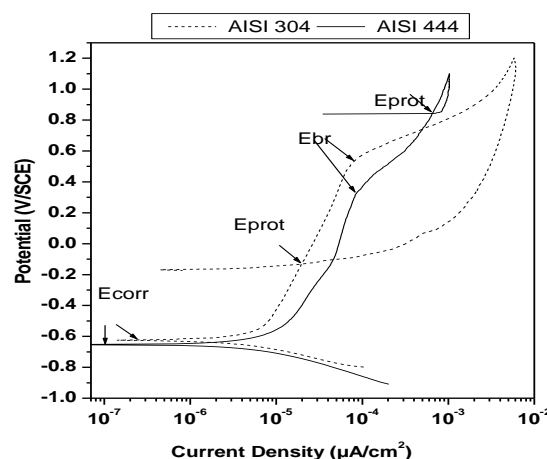


Fig.4: Potentiodynamic Polarization Curve for AISI 304 and 444 Stainless Steel in Sugarcane Juice.

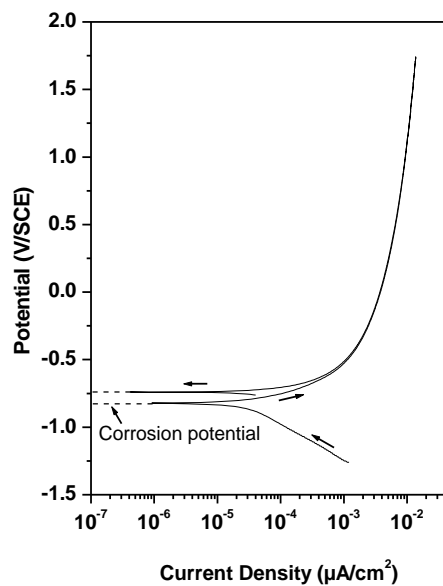


Fig.5: Potentiodynamic Polarization Curve for AISI 1010 Low Carbon Steel in Sugarcane Juice.

The evaluation criterion is that the more noble the breakdown potential, the less susceptible the alloy to the initiation of pitting [12]. The more positive the potential at which the hysteresis loop is completed, the less likely that localized corrosion will propagate. Additionally, the difference in potential between E_{corr} and E_{prot} , ($E_{\text{prot}} - E_{\text{corr}}$) is often taken to indicate relative resistance to local corrosion. The larger the hysteresis, the more likely a localized corrosion site will propagate once initiated.

Both the stainless steels have almost identical corrosion potentials, though 304 steel has a more noble breakdown potential. The breakdown potential E_{br} is one at which

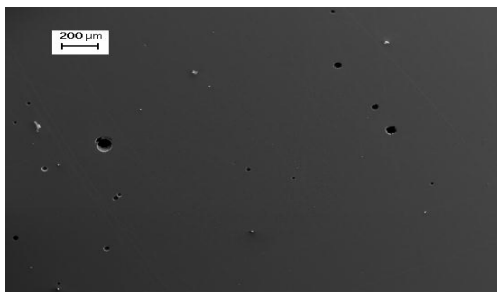
the forward portion of the cyclic potentiodynamic polarization scan changes from a relatively slow rise in current with respect to voltage to a rapid rise in current with respect to voltage. Above the breakdown potential, pits can initiate and propagate. The E_{br} potentials of 444 and 304 lie about 0.327 V-SCE and 0.506 V-SCE respectively with respect to the potential of the reference electrode and the curves then move on to the transpassive region. The nobler the breakdown potential, the nobler is the alloy in localized corrosion. The protection potential of AISI 444 is more anodic to that of the AISI 304 which gives us the idea that soon after the initiation of

pitting the 444 steel repassivates and the pitting is inhibited. The 444 steel shows a small clockwise hysteresis during the reverse scan whereas the hysteresis loop of 304 steel was larger, indicating greater susceptibility of 304 steel for propagation of localized corrosion in the sugarcane juice electrolyte.

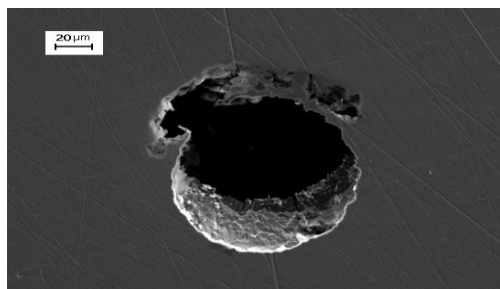
Figure 5 shows the behavior of AISI 1010, and the curve has neither the breakdown and protection potentials nor any hysteresis loop. This indicates that the transpassive region for low carbon steel is beyond the parameters used for the test. As expected, the alloy has much more negative E_{corr} value of -0.809 V-SCE indicating higher corrosion rate than the stainless steel alloys. Due to the more active

corrosion potential of carbon steel, it corrodes preferentially when used in contact with the stainless steels.

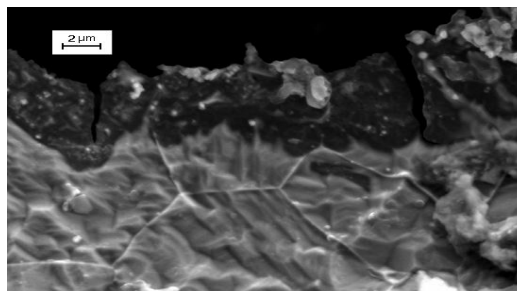
The SEM image of the corroded specimen in Figure 6(a) shows large number of pits on the surface of the 304 steel. Pits of various sizes are visible on the surface of the 304 specimen surface from few micrometers to $100 \mu\text{m}$ diameter. Figure 6(b) shows the extent of the depth of the pits formed which are almost equal to the diameter of the pit. Figure 6(c) shows the SEM image of a single pit at a magnification of $3000\times$ revealing clearly the austenitic grains and the cracks in structure.



a) AISI 304 Coupon at $40\times$.



b) AISI 304 Coupon at $500\times$.



c) AISI 304 Coupon $3000\times$ (View Inside a Pit).

Fig. 6: SEM Images of the Corroded Specimens after the Cyclic Polarization Scan.

The surface of 444 specimen does not reveal any pitting attack. S. J. Doh et al. [19] have studied the influence of chromium and molybdenum on the passivation of AISI 444 with borate buffer solution and have suggested that the alloy exhibited improved passivity mainly due to the substitution of chromium oxide by molybdenum oxide in the passive film. The better performance of 444 steel in the cyclic polarization scan is possibly due to the 2% molybdenum in its composition and the molybdenum substitution of chromium oxide by molybdenum oxide when the passive film breaks down.

4.3. Crevice Corrosion Test

Only the ferritic AISI 444 and austenitic AISI 304 coupons were subjected to this test. After the crevice corrosion test, the coupons were subjected to visual inspection of the surface which did not show any sign of pits for the duration of the test. The test did not appear to have deteriorated the specimens, showing the excellent corrosion resistance of these stainless steel alloys. The weight loss measurements were made prior to and after the test and the results are given in Figure 7. The difference in the weight loss is not significant for the candidate materials, though AISI 304 steel performed marginally better than AISI 444 steel.

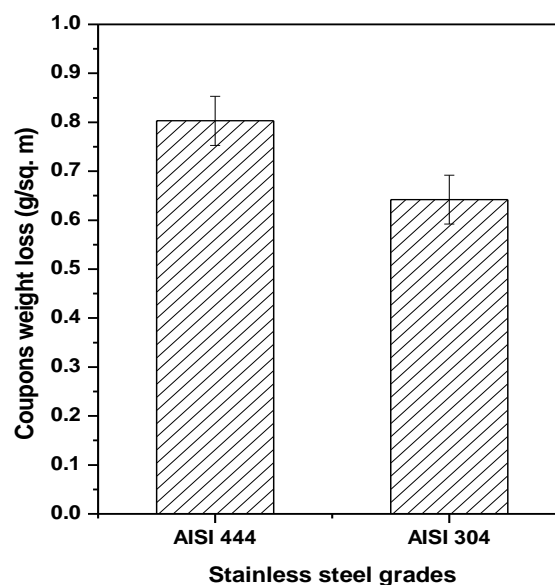


Fig.7: Weight Loss in Crevice Corrosion Test.

Scanning electron microscopy examination of the coupons was done. It was observed that no surface damage had taken place and pits had not formed under the surfaces which were under multiple crevice washers. The images only show some pre-existing flaws on the coupon surfaces. Both AISI 444 and AISI 304 may be considered to perform equally well with regard to crevice corrosion in the corrosive environment of sugarcane juice.

5. CONCLUSIONS

The conclusions that can be drawn from this investigation are:

- (i). The type AISI 444 steel shows better resistance to general corrosion in sugarcane juice environment.
- (ii). Tenacious oxide film formed by niobium on the surface of the 444 steel could possibly have resulted in better general corrosion resistance.
- (iii). AISI 444 and AISI 304 steels underwent localized corrosion as evident by the hysteresis loops in the cyclic potentiodynamic polarization scans. The AISI 304 steel had a larger hysteresis loop than AISI 444 steel indicating that the alloy experiences greater pitting susceptibility. The SEM images show the pitting caused on the 304 electrode. The transpassive region for low carbon steel could not be reached by the parameters used for the test.
- (iv). The better performance of AISI 444 steel as shown in the cyclic polarization scan is possibly due to the 2% molybdenum in its composition and the molybdenum substitution of chromium oxide by molybdenum oxide when the passive film breaks down.
- (v). No surface damage was observed on 444 and 304 steel coupons in the crevice corrosion test. Both AISI 444 and AISI 304 may be considered to perform equally well with regard to crevice corrosion in the corrosive environment of sugarcane juice.
- (vi). The performance of AISI 444 as compared to AISI 1010 is far superior and comparable to that of AISI 304 steel. Owing to the low-cost advantage of AISI 444 as compared to AISI 304, it can be recommended for use in sugar industry.

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