

Electrochemical Corrosion of Steels in Distillery Effluent

A. K. Singh, Chhotu Ram

Abstract—The present work relates to the corrosivity of distillery effluent and corrosion performance of mild steel and stainless steels SS304L, SS316L, and 2205. The report presents the results and conclusions drawn on the basis of (i) electrochemical polarization tests performed in distillery effluent and laboratory prepared solutions having composition similar to that of the effluent (ii) the surface examination by scanning electron microscope (SEM) of the corroded steel samples. It is observed that pH and presence of chloride, phosphate, calcium, nitrite and nitrate in distillery effluent enhance corrosion, whereas presence of sulphate and potassium inhibits corrosion. Among the materials tested, mild steel is observed to experience maximum corrosion followed by stainless steels SS304L, SS316L, and 2205.

Keywords—Steel, distillery effluent, electrochemical polarization, corrosion.

I. INTRODUCTION

DISTILLERIES, in India, are mostly molasses based and are considered highly water polluting [1]. Alcohol manufacturing process in these distilleries includes three main steps; namely, raw material preparation, fermentation, and distillation. Among these, the distillation process releases largest amount of effluent [2]. This effluent is then treated anaerobically before it is discharged to the nearby water body. The untreated effluent from distillation stage is expected to be more corrosive due to its lower pH, higher temperature, and its constituents, e.g. chloride, total dissolved solids, chemical constituents responsible for its colour. The literature survey reveals scanty work done related to corrosion in distillery effluent. One study is on the determination of corrosion rate of steels during evaporation of distillery spent wash in incineration system. It was observed that mild steel experienced significant corrosion, whereas stainless steel 316 showed negligible corrosion [3]. Another work suggests the possibility of corrosion in distillery due to various factors. Thus, high concentration of sulphate in distillery effluent was found to be responsible for causing sulphide corrosion in presence of sulphate reducing bacteria in biodigester. Other factors responsible for higher corrosivity were low pH (< 4.5), high chloride, and the other chemical constituents in the effluents [4]. In another study, the material of construction of ethanol producing plant for acid hydrolysis has been suggested to be corrosion resistant alloys. Non-resistant alloys in the

form of pipes, tank and heat exchangers corrode and may leach metal ions into the feedstock. Use of these alloys also limits the useful life of process machinery [5]. Thus, the conditions in distillery plant appear to be highly corrosive for materials of construction. Keeping this in view, a program was initiated to investigate (i) corrosivity of effluents and (ii) performance of material of construction against corrosion in distillery effluents. In two previous studies of the present authors, electrochemical corrosion investigation on steels in anaerobic treated distillery effluent [6], and in-plant corrosion tests of steels in distillery effluent treatment plant [7] were reported. Next, it was planned to investigate (i) the effect of various constituents of distillery effluents on its corrosivity and (ii) the performance of steels against corrosion in these effluents. The work presented here relates to the corrosivity of untreated effluents. The work includes performing corrosion tests on mild steel and stainless steels, candidate materials for plant construction, in effluents prepared synthetically and those obtained from distillery. On the basis of these tests, influence of various constituents of the effluents on its corrosivity was examined. In addition, the performance of the tested steels against corrosion in effluents was also studied.

II. MATERIALS AND METHODS

A. Materials

Mild steel, austenitic stainless steel SS304L and SS316L and, duplex stainless steel 2205 were considered for corrosion tests in the present work. Stainless steel samples were supplied by Avesta Sheffield AB, Sweden, and mild steel was obtained from local market. Chemical composition of these steels is shown in Table I. For electrochemical tests, 1 cm² of the steel sample was embedded in epoxy resin, and an electrical connection was made via a copper wire. Surface preparation to mirror finish of steel specimens was done by abrading them using emery papers from coarse to fine (up to 1000 grit) and then then subjecting to final finishing using 4/0 polishing paper as per the ASTM standard [8]. Polished samples were ultrasonically degreased in acetone before the measurements were undertaken.

B. Characterization of Distillery Effluents

Untreated distillery effluent was collected from effluent treatment plant (ETP) of a nearby distillery unit. It was stored at 4 °C to minimize compositional changes, if any. Characterization of effluent was done by determining biochemical oxygen demand (BOD) and chemical oxygen demand (COD) by BOD bottle method and closed reflux titrimetric method respectively. Chloride and sulphate were

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estimated by argentometric titration and gravimetric method respectively. Total dissolved solids (TDS) and total suspended solids (TSS) were estimated by gravimetric method. Concentration of Fe^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , and Mn^{2+} were measured by atomic absorption spectrophotometer (GBC, model Awanta, Australia), while amount of K^+ and Ca^{2+} was measured by flame photometer. The amount of nitrate and nitrite ions was measured by UV-vis spectrophotometer, whereas that of phosphate ions was determined by stannous chloride method. In all the cases, the methods adopted were as

per APHA standard [9]. The composition of distillery effluent is observed to be in accordance with effluents from molasses based Indian distillery [10]. To analyse the effect of chemicals on corrosivity of the effluent, the laboratory solution was prepared by adding inorganic chemicals in an amount similar to those observed in distillery effluent. Table II shows the composition (as ppm by weight) of distillery effluent and composition of actual compounds added in case of laboratory prepared solution.

TABLE I
COMPOSITION OF STEEL SAMPLES (WEIGHT%)

Sample	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	N
Ms	1.35	0.80	1.87	--	--	--	--	--	--	--
304L	0.025	0.344	1.619	0.027	0.001	18.214	0.294	8.258	0.269	0.074
316L	0.029	0.298	1.652	0.028	0.001	16.919	2.174	10.332	0.373	0.044
2205	0.020	0.52	1.450	0.020	0.002	22.25	3.08	5.48	--	0.150

C. Electrochemical Test

Electrochemical polarization tests were carried for investigating (i) the corrosivity of effluents and (ii) the performance of steels against corrosion. These tests were performed at 25 ± 1 °C in a corrosion cell consisting of a saturated calomel electrode (SCE) as a reference electrode, graphite rods as auxiliary, and the test specimen as working electrode all immersed in the test solution. These electrodes were connected to "Voltalab" Radiometer (Electrochemical Laboratory Model PGZ301) for recording the polarization curves, as per ASTM standard [8], using software Voltmaster 4. To estimate open circuit potential (OCP) of steels, its variation with time was measured for 2 hours. Corrosion rates of the steels in test solutions were obtained from tafel polarization tests. Anodic polarization curves were recorded for estimating pitting potential and passivation range while cyclic polarization curves were recorded for estimating repassivation potential of the tested steels in test solutions. All the polarization curves were measured with a scan rate of 0.166 mV/sec as per ASTM standard [8]. Potentiostatic tests were carried to recheck pitting potential of the tested steels in test solution as per the ASTM standard Each electrochemical test was repeated to check variation in the corrosion parameters. All the potentials referred in paper have been measured with respect to saturated calomel electrode.

III. RESULT AND DISCUSSION

A. Corrosivity of Distillery Effluent

Figs. 1 (a)-(d) represents open circuit potential vs. time curve, tafel plot, and cyclic polarization and potentiostatic curves in the distillery effluent. Electrochemical parameters obtained from these curves are shown in Table III. Lowest value of OCP in case of mild steel and highest value in case of SS 2205 indicate, respectively, poor corrosion resistance of former and better corrosion resistance of the latter steel. This is supported by the observation of maximum corrosion rate of mild steel and minimum of duplex stainless steel 2205 (Table III). The extent of uniform corrosion of mild steel in distillery

effluent (corrosion rate 190.5 $\mu\text{m}/\text{year}$) and in laboratory prepared solution (corrosion rate 227.83 $\mu\text{m}/\text{year}$) suggest that distillery effluents are corrosive. Thus, use of mild steel to handle these media does not appear to be a viable option. Corrosion rates experienced by mild steel in distillery effluent during the in-plant test and immersion test [7] were observed to be 141.47 and 163.3 $\mu\text{m}/\text{year}$ in accordance with the present results on corrosion rate. It was planned to test stainless steels to check their suitability as alternate materials of construction. However, stainless steels have tendency to experience localized corrosion. It was, therefore, thought necessary to check resistance of stainless steels against localized corrosion in the test media. Accordingly, cyclic polarization and potentiostatic tests were also performed on stainless steels (Figs. 1 (c)-(d)). Thus, pitting potential, obtained from cyclic polarization curves, is found to be minimum for 304L and maximum for 2205 indicating lowest resistance against pitting of former and maximum of latter stainless steel. This is further confirmed by the results obtained from potentiostatic test (Table III). Similar conclusions, regarding relative corrosion resistance of the tested stainless steels, can be drawn on the basis of values of passivation range and passivation current density (Table III). Repassivation potential, showing resistance of metal against crevice corrosion, is observed to be maximum for 2205 followed by those of 316L and 304L (Table III). Area of hysteresis loop in cyclic polarization curve indicates the amount of localized corrosion. Size of hysteresis loop is observed to be quite low in 2205 and high in case of 304L (Fig. 1 (c)). Thus, stainless steel 304L demonstrates minimum resistance, while 2205 demonstrates maximum resistance against localized corrosion in distillery effluent. One can compare these results with those obtained after exposure of stainless steel samples in in-plant test and in immersion test. Thus, SEM photographs of the corroded stainless steel samples (Figs. 2, 3) show extent of pitting. Maximum pit depth is observed as 19, 14, and 8 μm on the corroded steel samples after the in-plant test exposure and as 27, 21, and 12 μm on the corroded steel samples after the immersion test exposure in case of SS304L, SS316L, and

2205, respectively [7]. These results are in accordance with the results of electrochemical tests. From these results, it can also be apprehended that, with slight increase in Cl⁻ content and in concentration of oxidants in the effluent, its corrosivity may enhance to a level such that stainless steels 304L and 316L start experiencing localized corrosion.

TABLE II

COMPOSITION OF DISTILLERY EFFLUENTS AND AMOUNT OF ACTUAL COMPOUNDS ADDED TO MAKE LABORATORY PREPARED SOLUTION

S.No.	Parameter	Distillery Effluent	Laboratory prepared solution
1.	pH	4.16±0.03	4.16±0.02
2.	Chloride	5500±60	5500±60 as NaCl
3.	Sulphate	5050±90	5050±50 as Na ₂ SO ₄
4.	Phosphate	250±15	250±10 as H ₂ PO ₄
5.	Potassium	12100±30	12100±25 as KOH
6.	Calcium	650±20	650±15 as CaCl ₂
7.	Nitrate	225±18	225±8 as NaNO ₃
8.	Nitrite	130±12	130±10 as NaNO ₂
9.	Zn ⁺⁺	33±4	33±5 as ZnO
10.	Fe ⁺⁺	214±12	214±10 as FeOH ₂
11.	TDS	81000±150	33880±80
12.	TSS	6855±120	38±5
13.	COD	110000±180	--
14.	BOD	47100±250	--
15.	Ni ⁺⁺	0.98±0.05	--
16.	Cd ⁺⁺	0.112±0.02	--
17.	Mn ⁺⁺	6.18±0.02	--
18.	Cu ⁺⁺	6.85±0.04	--
19.	Colour	Dark brown	--

TABLE III
CORROSION PARAMETERS OF STEELS

Metals	Distillery effluent	Laboratory prepared solution
Open Circuit Potential (V _{SCE})		
Ms	-0.630±0.005	-0.667±0.002
304L	-0.452±0.005	-0.215±0.009
316L	-0.444±0.003	-0.201±0.007
2205	-0.432±0.007	-0.153±0.007
Corrosion Rate (µm/year)		
Ms	190.5±2.54	227.83±11.9
304L	2.997±0.076	3.406±0.310
316L	2.895±0.051	2.743±0.178
2205	2.489±0.050	1.295±0.127
Pitting Potential (Cyclic polarization test) (V _{SCE})		
304L	0.285±0.028	0.195±0.014
316L	0.370±0.025	0.300±0.012
2205	1.075±0.015	0.950±0.016
Pitting Potential (Potentiostatic test) (V _{SCE})		
304L	0.250-0.300	0.200-0.250
316L	0.350-0.400	0.300-0.350
2205	1.000-1.050	0.950-1.000
Repassivation Potential (V _{SCE})		
304L	-0.110±0.025	-0.190±0.00
316L	-0.040 ±0.030	-0.115±0.016
2205	1.050± 0.025	0.860±0.020
Passivation Range		
304L	0.735±0.020	0.540±0.030
316L	0.843±0.016	0.630±0.028
2205	1.520±0.025	1.330±0.015

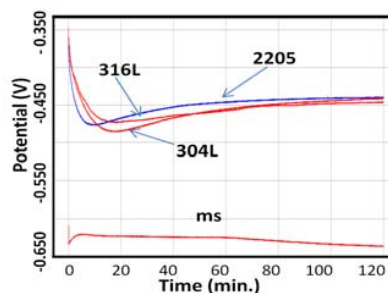


Fig. 1 (a) OCP vs. time curve of SS304L in distillery effluent

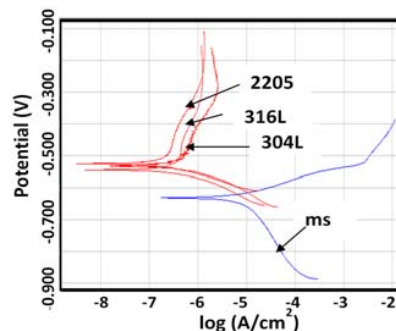


Fig. 1 (b) Tafel plot of tested steels in distillery effluents

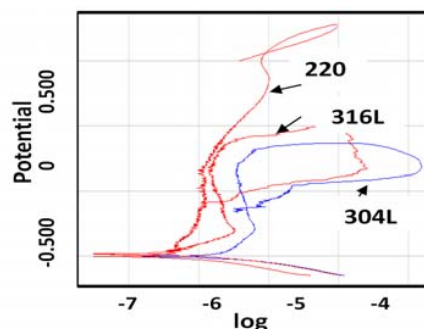


Fig. 1 (c) Cyclic polarization curves of stainless steels in Distillery effluent

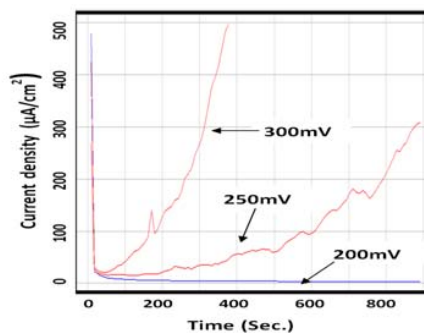


Fig. 1 (d) Current vs. time curve of stainless steel 304L in distillery effluent

To investigate dependence of corrosivity of distillery effluent on its components, measurements were also carried in laboratory prepared solutions of pH 4.16 and having chloride,

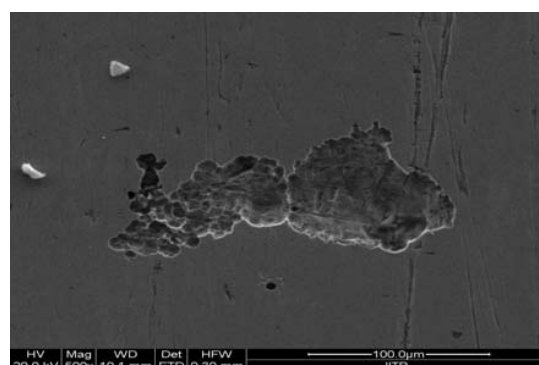
sulphate, phosphate, potassium, calcium, nitrate, nitrite, zinc, and iron in the amount as observed in distillery effluent. Influence of nickel, cadmium, manganese, copper ions on corrosivity was not studied due to their comparatively very low amount in the distillery effluent (Table II). Anodic polarization curves of stainless steel 304L recorded in these solutions are shown in Fig. 4, and respective pitting potentials are given in Table IV. One thus observes that 304L has very low pitting potential in pH 4.16 solution having Cl⁻ only (Fig. 4, curve 1) indicating aggressive character of Cl⁻ in acidic solutions, as observed earlier also [11]. It has been suggested that Cl⁻ ions substantially decrease the effectiveness of passive film by penetrating through the film, due to its small size, and combine with metal cations [12]. Addition of SO₄²⁻ in the solution increases pitting potential (curve 2 in Fig. 4 and Table IV). Hence, inhibitive action of sulphate was observed on stainless steel at concentration present in the distillery effluent. Earlier investigation [13] also suggests inhibitive action of sulphate in the chloride solution by affecting pit initiation as well as pit growth rate on SS304. Addition of phosphate in present solution reduces pitting potential (curve 3 of Fig. 4 and Table IV) so increasing the risk of pitting. This observation is in accordance with an earlier study [14] which exhibits dissolution of passive film in the presence of phosphate at low pH. From curve 4 of Fig. 4 and Table IV, one observes increase in pitting potential due to addition of potassium. This observation is supported by an earlier finding on corrosion of carbon steel in acidic media [15] where inhibition efficiency was observed to increase with thiocyanate concentration.

TABLE IV
PITTING POTENTIAL OF SS-304L IN LABORATORY PREPARED SOLUTION
(ALL VALUES ARE GIVEN IN PPM BY WEIGHT EXCEPT PH)

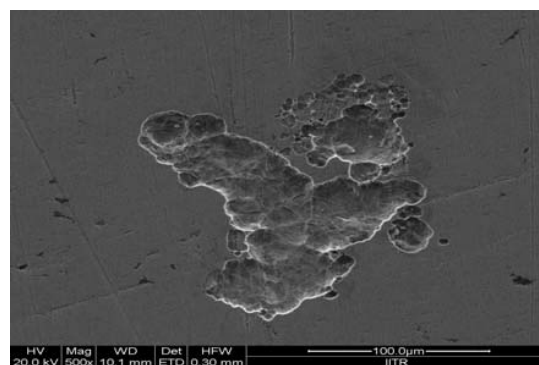
Curve	Laboratory prepared solutions	E _c (mV _{SCE})
1	pH4.16+Cl ⁻ 5500	210±20
2	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050	285±15
3	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050+PO ₄ ³⁻ 250	120±10
4	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050+PO ₄ ³⁻ 250+K ⁺ 12100	385±15
5	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050+PO ₄ ³⁻ 250+K ⁺ 12100+Ca ⁺⁺ 650	245±25
6	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050+PO ₄ ³⁻ 250+K ⁺ 12100 +Ca ⁺⁺ 650 +NO ₃ ⁻ 225 +NO ₂ ⁻ 130	210±20
7	pH4.16+Cl ⁻ 5500+SO ₄ ²⁻ 5050+PO ₄ ³⁻ 250+K ⁺ 12100 +Ca ⁺⁺ 650+NO ₃ ⁻ 225 +NO ₂ ⁻ 130+ Zn ⁺⁺ 34+ Fe ⁺⁺ 214	215±5

In another work, potassium iodide was suggested as corrosion inhibitor of stainless steel in acidic solution [16]. The effect of calcium (curve 5) is observed to reduce pitting potential. Ding et al. [17] have concluded that corrosion of X65 steel in oil field simulated water is enhanced if amount of Ca⁺⁺ ions in them is lying between 256 to 512 mg/L. This has been proposed to be due to grain growth and resulting destabilization of the scale formed on steel. Addition of nitrate and nitrite (curve 6) shows slight increase in the corrosivity of synthetic solution. As per an earlier investigation [18], role of nitrate strongly depends upon pH and it stimulates corrosion of carbon steels in acidic solutions. Addition of zinc and iron in synthetic solution does not exhibit significant effect on corrosivity of the effluent at the studied concentrations.

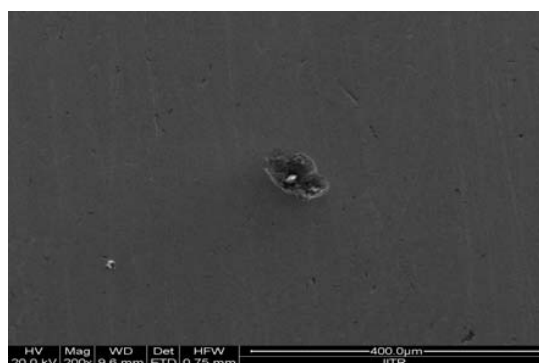
Therefore, presence of chloride, phosphate, calcium, nitrate and nitrite at acidic pH appears to play an important role in enhancing the corrosivity, while sulphate and potassium seem to inhibit corrosion in distillery effluent.



(a)



(b)



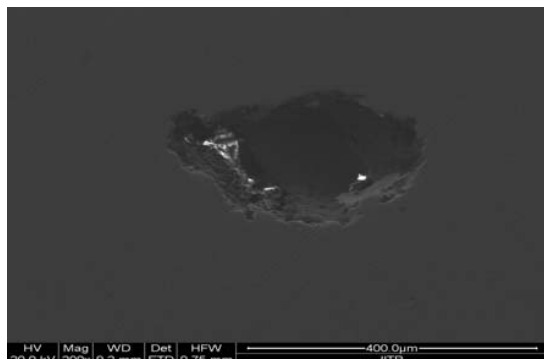
(c)

Fig. 2 SEM micrograph of corroded stainless steels after in-plant test in tank having untreated distillery effluent: (a) 304L (100x), (b) 316L (100x), (c) 2205 (200x)

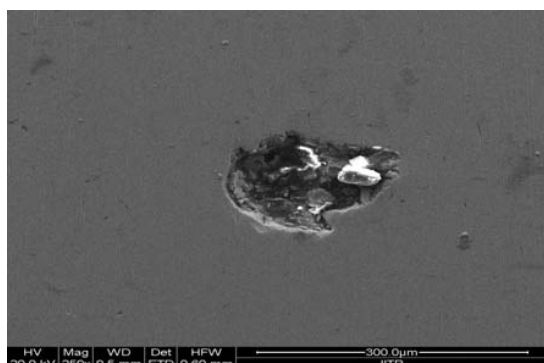
B. Corrosion Performance of Mild Steel and Stainless Steel

The results from electrochemical test (Table III) indicate much higher corrosion rate for mild steel in comparison to stainless steels as such necessitating the use of later steels in handling these liquors. However, stainless steels may undergo localized corrosion, and therefore, one needs to compare their

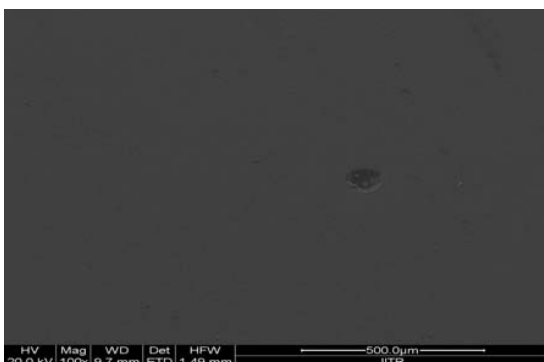
resistance against pitting and crevice corrosion. So, a comparison of parameters (Table III) showing their comparative resistance against pitting and crevice corrosion, in laboratory prepared solution as well as distillery effluent was done.



(a)



(b)

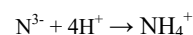


(c)

Fig. 3 SEM images of stainless steels after immersion test in untreated distillery effluent: (a) 304L (200x), (b) 316L (250x), (c) 2205 (100x)

Higher OCP, pitting potential, passivation range, and repassivation potential for 2205 exhibit its maximum corrosion resistance, whereas lowest values of these parameters indicate minimum corrosion resistance of SS304L in distillery effluents among the tested stainless steels. SEM

images of corroded stainless steel coupons exposed in in-plant test (Fig. 2) and in immersion test (Fig. 3) also show minimum pitting in case of SS 2205 and maximum in case of SS304L. Further, lower corrosion rate was observed for stainless steel 2205 followed by 316L and 304L. Hence, tested stainless steels may be put in the following order of increasing resistance against localized and uniform corrosion: 304L < 316L < 2205. A comparison of composition of stainless steels indicates (i) maximum amount of Cr, Mo, and N in 2205 (ii) 304L has higher amount of Cr and N than those in 316L and (iii) amount of Mo is higher in 316L than 304L. Stainless steels owe their corrosion resistance primarily to the presence of Cr(>12%) in them. Presence of chromium results in formation of Cr(OH)₃/Cr₂O₃ which acts as passive layer and therefore provides corrosion resistance [19]. This is manifested in terms of shifting of the corrosion potential to nobler direction and reduction of active/passive current density [20]. Presence of Mo in 316L, on oxidation, leads to formation of MoO₂ in addition to Cr₂O₃, both of which are protective type; hence, 316L shows better resistance against localized corrosion than 304L [21]. In the presence of N and Mo, molybdenum nitride forms, which helps to retain molybdenum ion in the passive film by acting as inhibitor to dissolution of molybdenum ion [22], [23]. According to another hypothesis [24], N in solid solution on dissolution produces NH₄⁺ by reaction given below



which raises pH of the electrolyte presence in the pits and stabilises them. These results suggested better resistance against localized corrosion in case of N bearing stainless steels. Consequently, duplex stainless steel 2205 shows maximum resistance against localized corrosion, while 304L shows poorest corrosion resistance among the tested stainless steels.

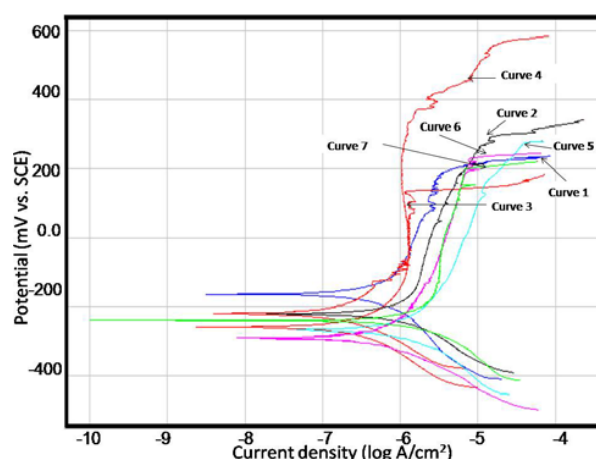


Fig. 4 Effect of addition of Cl⁻(curve 1), SO₄²⁻(curve 2), PO₄³⁻(curve 3), K⁺(curve 4), Ca²⁺(curve 5), NO₃⁻+NO₂⁻ (curve 6) and Zn²⁺ + Fe²⁺ (curve 7), on anodic polarization curves of stainless steel 304L in laboratory prepared solutions

IV. CONCLUSION

The present paper deals with the corrosivity of distillery effluent and corrosion performance of mild steel and stainless steels exposed to the effluent. Role of distillery effluent chemistry on corrosivity was investigated by electrochemical polarization tests conducted in distillery effluent and synthetic effluent. Thus pH, chloride, phosphate, calcium, nitrate, and nitrite are observed to play a role in increasing, whereas sulphate and potassium are observed to inhibit the corrosivity. In these effluents, mild steel shows unacceptably higher corrosion rate, thereby necessitating the testing on stainless steels. Among these stainless steels, 2205 is observed to have higher corrosion resistance than 316L, whereas 304L shows minimum resistance. The presence of alloying elements, i.e. Cr, Mo, and N in stainless steels is found to exhibit important role in imparting corrosion resistance of stainless steels.

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