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Effect of Passivation Behaviour of various Grades of ASS in Different Acid media: A Review

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Abstract: Passivation means removing the free irons from the surface of the metal by acid solution to prevent rust, to improve corrosion resistance, to remove embedded contaminants, to restore or enhance chromium oxide film on the stainless steel surface. Passivation also used to create shell against corrosion. We can study the effect of passivation on different grades of ASS in different acid environment through potentiodynamic testing. These studies were carried out to obtain polarization curve. By using potentiodynamic test we can find corrosion rate of s.s in different environment & also passivation behaviour of that particular sample.

Keywords: Corrosion, ASS, passivation, potentiodynamic test, Tafel plot, Applications of ASS

I. INTRODUCTION

Stainless steel are very important class of metals. The word stainless is used since cr is added to this composition. Minimum 12 wt% of chromium is necessary to make steel eligible to be classified as “Stainless Steel”. Austenitic s.s (300 series) is the most important group, among all group. Stainless steel is used as substitutional metal for carbon steel in highly corrosive environment.[1-5] From the grades of stainless steel SS304 and SS316 are widely used. SS316 is used for more corrosive environment[6].SS316 is usually known as “marine grade” stainless steel but it can not resist warm sea water because warm chloride environment cause pitting and crevice corrosion[7]. In S.S Ni is added to obtain austenitic structure[8].The austenitic s.s containing 18% or more chromium and sufficient nickel to make fully austenitic metallurgical structure.18-8 S.S is known as the most common group in which 18%cr and 8%Ni. SS316 consist of about 2% Mo to improve the resistance to pitting attack by strengthening the passive film. [7]

Austenitic S.S provides excellent corrosion resistance in many organic, acidic, industrial and marine environments. It has non-magnetic properties & high toughness at all temperatures because of these properties they are used in wide variety of application such as chemical plants, industrial and marine field.[9-10]

Corrosion is a major problem for engineers because of its pervasiveness, corrosion can cause significant damage to engineering structures and products. The estimated cost of corrosion in india is more than $63 billion.[6]

Passivation is a most widely used metal finishing process to prevent corrosion .In stainless steel, the passivation process uses nitric acid or citric acid to remove free iron from the surface. The chemical process ,which form protective oxide layer which less likely to react with air & cause corrosion.

II. POTENTIODYNAMIC TEST

A. Definition of a Potentiostat

A Potentiostat is an electrolyte device that is used to control the potential of a test electrode in an electrolyte. The magnitude of electrode potential changes (polarization) is determined by the amount of electrical current supplied by a potentiostat. Electrode potential is measured as the difference between itself a reference electrode.

B. Potentiodynamic Testing

These studies were carried out to obtain potential (with respect to SCE) v/s log of current density plot which is known as polarization curve. The potential range was selected in a manner so the sample could be polarized both ways i.e. cathodically and anodically.

It is used for

1) Corrosion potential determination
2) Estimate corrosion current
3) Potential region for passivity

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Potentiodynamic polarization test is mainly carried out to find the corrosion rate. Generation of polarization curves continuous to be important in aqueous corrosion research. Potentiostatic method is more time consuming method. However, is has been replaced by potentiodynamic method, in which potential of the corroding metal is automatically varied with time. Potentiodynamic polarization test is most widely used electrochemical test to determine the potential region at which the alloy or metal is passive when exposed to purticular environment. By using potentiodynamic method corrosion properties of passivating metals and alloys are identified. The method estimates the corrosion active region, the onset of passivation, the critical current density, the primary passivation potential, the current in the passive region, the voltage span of the passive region. These method can provide specific information regarding mechanism of corrosion, corrosion rate & susceptibility of particular materials to corrosion in specific environments.

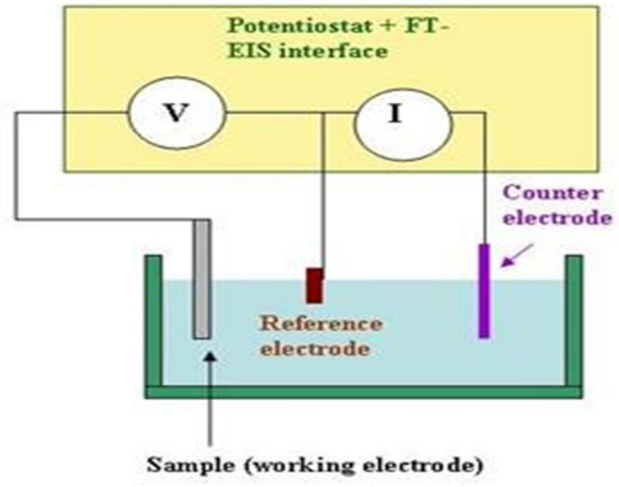

Figure depicts a typical electrochemical corrosion test cell consisting of three electrodes

a) Working electrode (test specimen)
b) Counter or auxiliary electrode (Graphite electrode)
c) Reference electrode (calomel electrode)

Electrical current passing through a potentiostat can make change in a test electrode potential from its OCP is referred to as polarization. In order to maintain electronic equipment & Electrode electrical neutrality , current is supplied to a counter electrode. Difference between potentiostat & reference electrode is test electrode polarization. so it remains at its OCP and provides a 'fixed' reference point for corrosion measurement.The reference electrode provides feedback to the potentiostat so that test electrode potential can be monitored and adjusted to a desired level.

C. Tafel Plot Corrosion Measurement

The Tafel plot corrosion measurement method uses a wide DC potential spectrum (400 to 500 mV) and provides more corrosion information than linear polarization. The Tafel plot has anodic and cathodic branches, corresponding to the anodic and cathodic half reactions for metal corrosion. Tafel plots are generalized in one of two ways:

Method 1 : Tafel plot anodic and cathodic branches are generated from the same test electrode. Polarization is begin approximately say -200mV from OCP and increased until the potential is approximately say +200mV from OCP.

Method 2 : Separate test electrode are used to the same electrolyte to generate Tafel plot anodic and cathodic branches. The cathodic branch is generated by polarizing one of the test electrodes from OCP to approximately -200mV from OCP.

Potential changes are typically 2 mV per step for both methods and potential current data are graphed as applied potential verses log values of current density.

D. Corrosion Rates from Tafel Plots

Corrosion current is read directly from plot without the need for Tafel slope values or use of Stem and Geary equation (i_{corr}= $[1/(2.303R_p)][(\alpha_a * \alpha_c)(\alpha_a + \alpha_c)]$, Figure illustrates how corrosion rates are obtains from both activation and diffusion Tafel plots, respectively.

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Intersection of the anodic and cathodic linear extrapolation at OCP is the corrosion current for an activation controlled Tafel plots, as shown in figure. The corrosion current can be further converted to a corrosion rate in mils/year (mpy), using the following equation;

MPY= I_{corr}(A)(1/n)(a)

Where,

A is combination of several conversion terms and is 1.2866 * 10^5 [equivalents*sec*mils]/[coulombs*cm*year]

Icorr is the corrosion current density & unit is Amps/cm2

n is the density of the metal in grams/cc.

a is equivalent weight in grams/equivalent.

III.LITERATURE STUDY

Table 1: Chemical Composition of Grade 316 Austenitic Stainless Steel

Elements	C	Mn	Si	P	Cr	Ni	Mo	V	Cu	Sn	Al
Wt%	0.08	0.44	0.019	0.009	16.67	9.86	2.09	0.070	0.49	0.013	0.042

Figure 1: Potentiodynamic Polarization Curves 316 Austenitic Stainless Steel in 1 M HCl

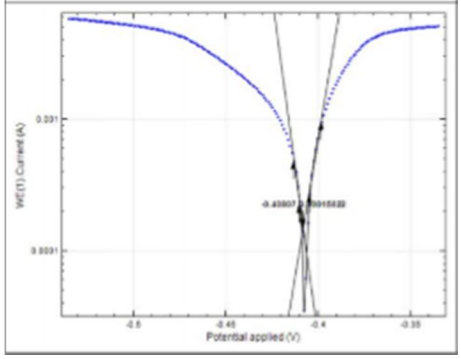

Table 2: Electrochemical Parameters Estimated from the Polarization Tests in 1 M HCl

Conc. (M)	Icorr (A)	Icorr (A/ Cm^2)	bc (V/ dec)	ba (V/ dec)	Rp (Ohm)	Ecorr Reference (V)	Ecorr Calc (V)	Ebegin (V)	Eend (V)	Corrosionrate (mm/year)
1	0.003659	0.003659	0.08779	−1.5819	11.034	−0.4073	−0.4080	−0.4130	−0.3981	42.514

ASS are used as, Construction material for key corrosion resistant equipment. Most major industries due to their strength. Specially in chemically, petroleum, offshore drilling, marine ,shipping, water desalination, processing and power generation plant.

The result showed the more active corrosion reaction in presence of chloride ion results in pitting corrosion observed on the metal surface. Both the pitting potential & protection potential shifted towards the active direction as the potential range of passivity was shortened. The acids at the intermediate concentration show more obvious active corrosion reactions while in the concentrated form they were relatively passive, the passivity is related to the oxidizing nature of the concentrated acid environment.

Electrochemical behaviour of type 316 ASS in acid solution depends on the concentration of HCl. Presence of acid concentration produces & enhancement of metal corrosion through passive layer & reduces passivity break down potential.[7]

Table 3. Test Environments

Sulphuric acid, H_2SO_4	Sulphuric acid + 20g/L NaCl (2%)	Phosphoric acid, H_3PO_4	Phosphoric acid, H_3PO_4 + 20g/L NaCl (2%)
9.1M (48.5%)	9.1 M + 2% NaCl	7.4M (42.5%)	7.4M + 2% NaCl
18.2M (97%)	18.2 M + 2% NaCl	14.8M (85%)	14.8M + 2% NaCl

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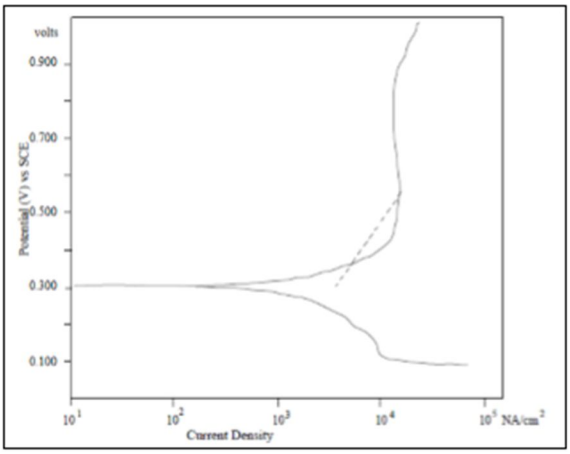

Figure 3. Polarization Curves of 316L S.S in 9.1M H_2SO_4 (48.5%)

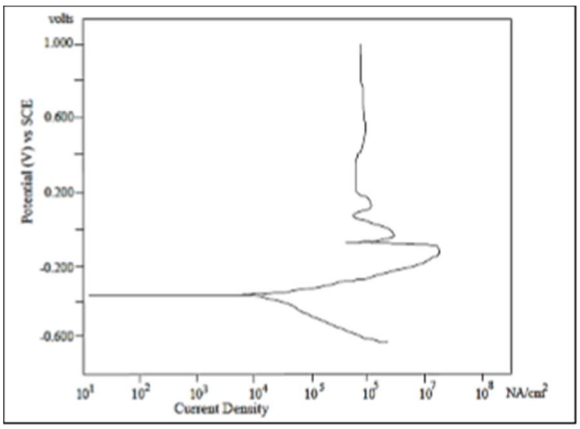

Figure 4. Polarization curves of 316L S.S in 9.1M H_2SO_4 and 20g/l NaCl

Table 4. Summary of Corrosion polarization results for the test specimen in H_2SO_4 media

Sample	i_{corr} (A)	I_{corr} (A/cm^2)	R_P(Ω)	E_{corr} (V)	Corrosion rate (mm/yr)
H_2SO_4 9.1M +NaCl 20g/l	$8.25x10^{-5}$	$1.2x10^{-4}$	$-2.3x10^{-5}$	-0.380	$4.84x10^{-2}$
H_2SO_4 9.1M	$3.56x10^{-7}$	$5x10^{-6}$	$-3.8x10^{-7}$	0.300	$2.09x10^{-3}$
H_2SO_4 18.2M +NaCl 20g/l	$5.69x10^{-5}$	$8x10^{-2}$	$-5.0x10^{-2}$	-0.400	$3.34x10^{-7}$
H_2SO_4 18.2M	$-1.18x10^{-4}$	$-1.66x10^{-3}$	$-3.9x10^{-9}$	0.320	$-6.92x10^{-6}$

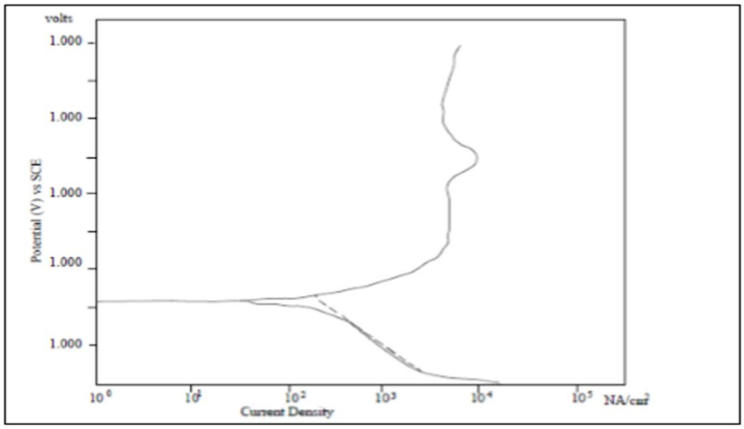

Figure 5. Polarization Curves of 316L S.S in 18.2M H_2SO_4 (97%)

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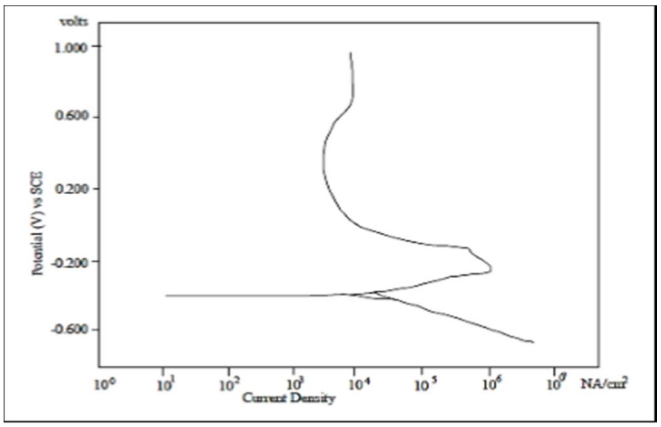

Figure 6. Polarization Curves of 316L S.S in 18.2M H_2SO_4 and 20g/l NaCl

Table 5. Summary of Corrosion polarization results for the test specimen in H_3PO_4 media

Sample	i_{corr}(A)	I_{corr} (A/cm^2)	R_P(Ω)	E_{corr} (V)	Corrosion rate (mm/yr)
H_3PO_4 7.4M +NaCl 20g/l	$1.02x10^{-5}$	$1.2x10^{-2}$	$2.2x10^{-3}$	-0.300	$5.02x10^{-5}$
H_3PO_4 7.4M	$7.12x10^{-7}$	$1.0x10^{-5}$	$2.5x10^{-6}$	0.050	$3.34x10^{-6}$
H_3PO_4 14.8M +NaCl 20g/l	$1.19x10^{-5}$	$1.7x10^{-2}$	$2.4x10^{-3}$	-0.400	$5.59x10^{-5}$
H_3PO_4 14.8M	$1.42x10^{-5}$	$2.0x10^{-4}$	$1.0x10^{-4}$	0.100	$6.67x10^{-5}$

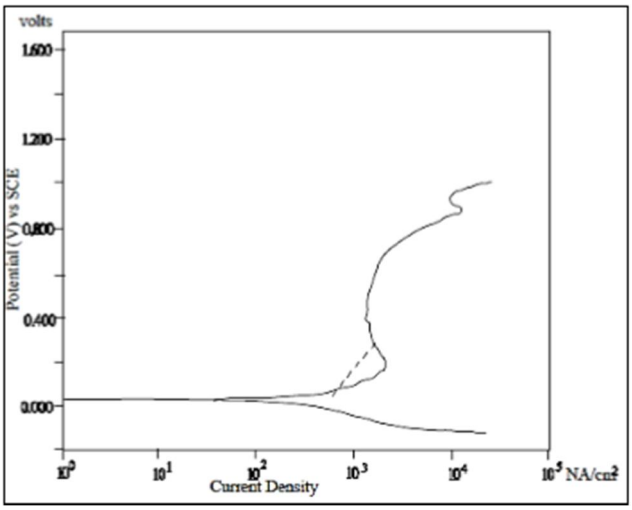

Figure 7. Polarization Curves of 316L S.S in 7.4M H_3PO_4 (42.5%)

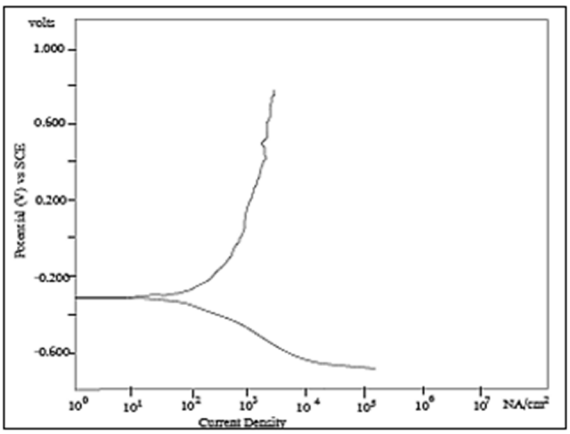

Figure 8. Polarization Curve of 316L S.S in 7.4M H_3PO_4 and 20g/l NaCl

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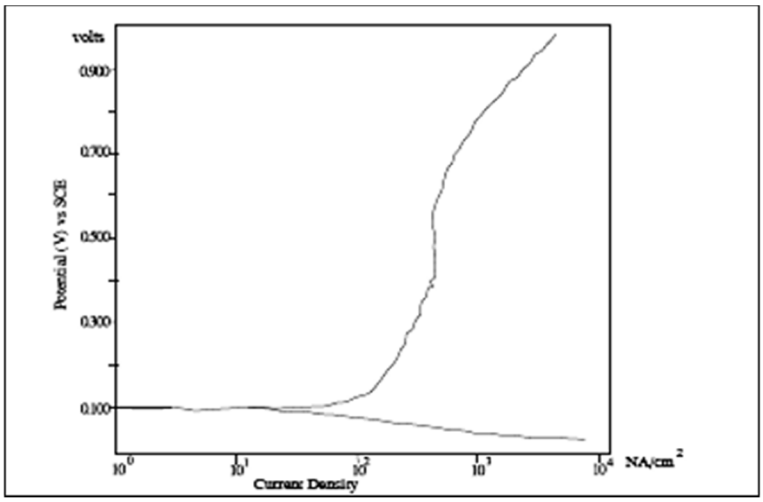

Figure 9. Polarization Curve of 316L S.S in 14.8M H_3PO_4

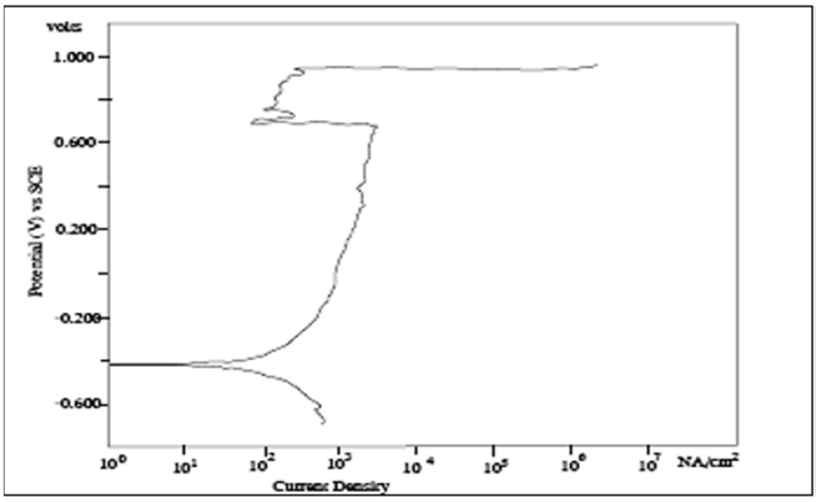

Figure 10. Polarization Curve of 316L S.S in 14.8M H_3PO_4 and 20g/l NaCl

The addition of 2%NaCl to each of the test medium concentration gave increased active corrosion reactions that could be due to the test electrode. The acid test media were contaminated with NaCl to enhance the breakdown of passivity by the chloride ions.

Corrosion polarization behaviour for the test performed in phosphoric acid(H_3PO_3) showed active corrosion reaction behaviour at all concentration. The addition of NaCl gave less corrosion resistance of test electrode[11]

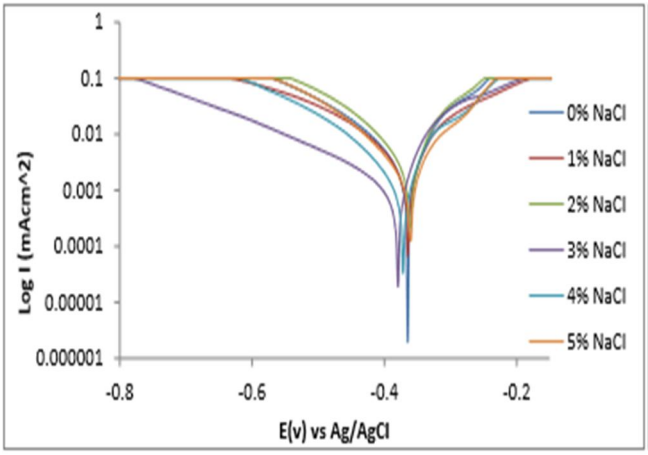

Figure11: Polarization scans for ASS in H_2SO_4 at (1-5) %NaCl concentration

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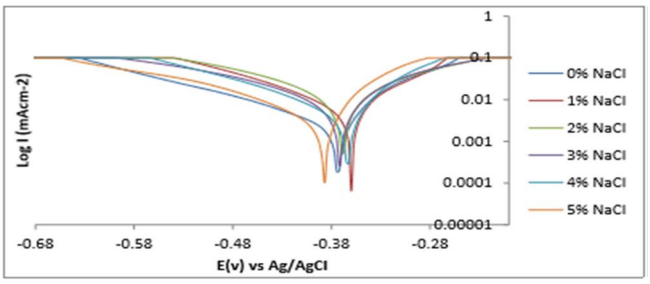

Figure 12: Comparison plot of potentiodynamic polarization curve for ASS in H_2SO_4 with (1-5) %NaCl concentration

SS304 in 2M & 5M HCl with NaCl addition showed that increase in concentration of NaCl caused a proportion increase in corrosion rate in 2M HCl solution coupled with increase in corrosion current density, however at 5M HCl, increase in NaCl concentration initially resulted in instantaneous increase in corrosion resistance before decreasing progressively.[12]

Polarization Studies

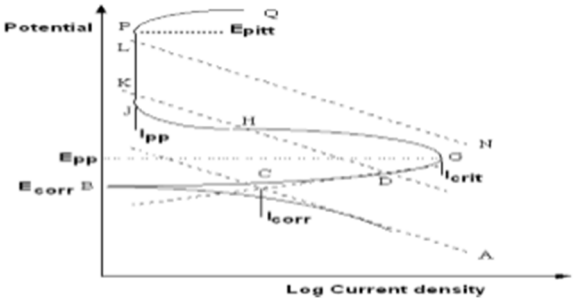

Figure 13 Schematic variation of potential E with log current density

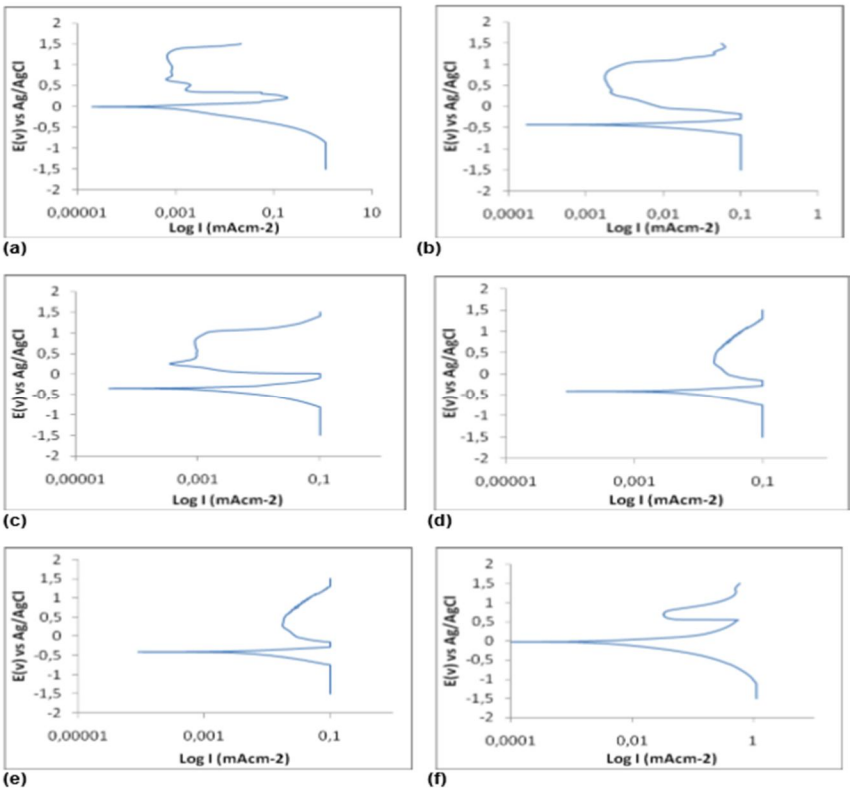

Figure 14:- Polarization Curve of austenitic stainless steel (a) 2M H_2SO_4, (b) 2M H_2SO_4 + 1% NaCl, (c) 2M H_2SO_4 + 2% NaCl, (d) 2M H_2SO_4 + 3%NaCl, (e) 2M H_2SO_4 + 4%NaCl, (f) 2M H_2SO_4 + 5% NaCl

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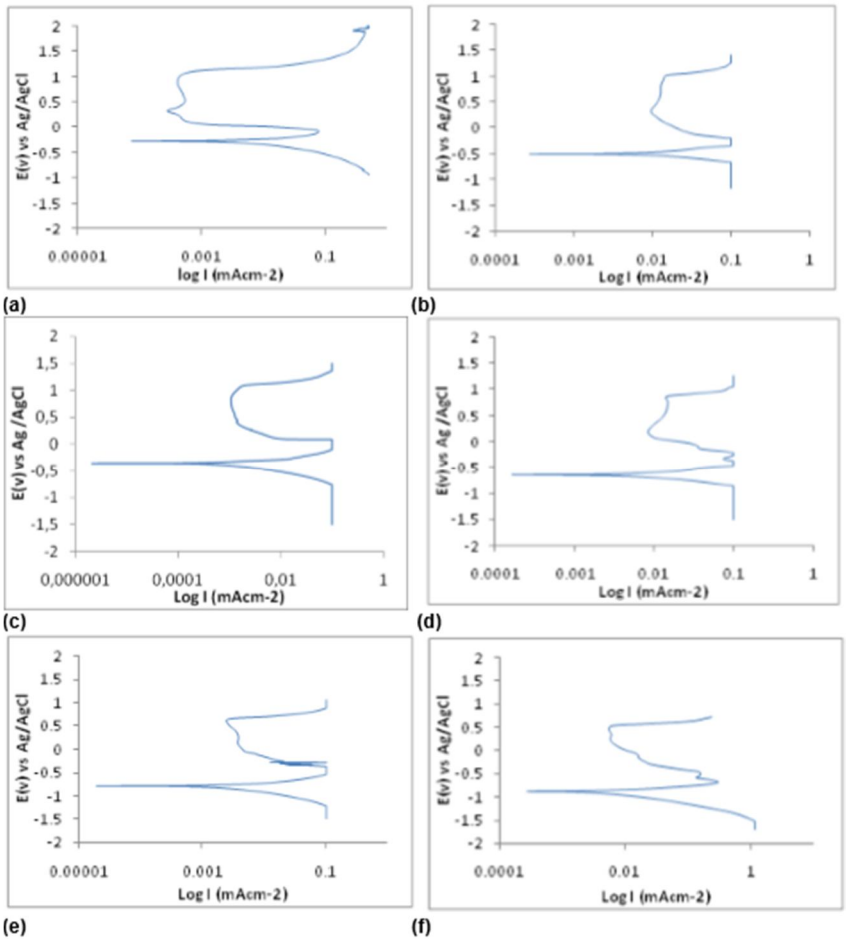

Figure 15:-Potentiodynamic Curve of ASS in different environments in different concentration (a) 5M H_2SO_4, (b) 5M H_2SO_4 + 1% NaCl, (c) 5M H_2SO_4 + 2% NaCl, (d) 5M H_2SO_4 + 3%NaCl, (e) 5M H_2SO_4 + 4%NaCl, (f) 5M H_2SO_4 + 5% NaCl

The S.S in sulphuric acid solution acquired a passive state under anodic polarization, with breakdown at the transpassive region (pitting potential) however, this was greatly reduced with the addition of sodium chloride led to sharp increase in current at potentials (lower than the value that necessitates pitting in the acid environment due to which passive film rapidly break down.
Polarization curves in 2M & 5M H_2SO_4 with those containing NaCl shows that chloride ions significantly reduces the pitting potential. Higher the molarity of sulphuric acid , the greater the potential at which pitting occurs.Increase in the passive regions in the sulphuric acid+chloride media compared to the sulphuric acid solution only due to the break down of the passive film of Cr_2O_3 owing to the high diffusivity of the chloride ions through cracks & film breakage faster than the rate of passivation causing the formation of pits by autocatalyic mechanism.Increaseing the concentration of sulphuric acid only delays the formation of pits but still enhances rate of corrosion.[13]

A. Applications of ASS

1) Sulphuric acid used in industries such as petroleum refinery, steel pickling, extraction of non-metals, paint industries with 304 grade stainless steel.[14]
2) 304 & 316 type ASS are widely used in the pharmaceutical, petrochemical, offshore drilling , marine shipping, water desalination due to being easily handled in very dilute acid at low temperature.[15]
3) ASS steel are widely used in chemical industries in order to producing storage vessels, reactors, pipes, pump bodies & pump shafts which are in contact with acid media.[16]
4) 304 is widely used in desalination plants, thermal power plant, pharmaceutical industry, chemical cleaning in when they contact in acid media.[17]
5) ASS used for the fabrication of equipment components & for construction of industrial plants for chemicals, manufacture of acids due to long life, dependability, safety, reliability & economic viability of plant.[11]

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6) HCl is mainly used for various treatment of materials in industry. The aqeous electrolyte phase in overhead condenser, which is made of ASS.[18]

7) ASS widely ued in industries where high corrosion resistance is required i.e phosphoric acid industries [316L used for their good mechanical properties & corrosion resistance].[19]

IV. SUMMARY

A. In acid media, as molarity increases the corrosion rate decreases, while addition of Cl^- tend to increase corrosion resistance & increase of Cl^- concentration can also increase corrosion resistance.

B. From the research paper,we can say that ASS type 304 shows high corrosion resistance in low molarity acid solution than those of ASS type ,316 that shows much less corrosion resistance in higher molarity acid solution with addition of Cl^- ions.

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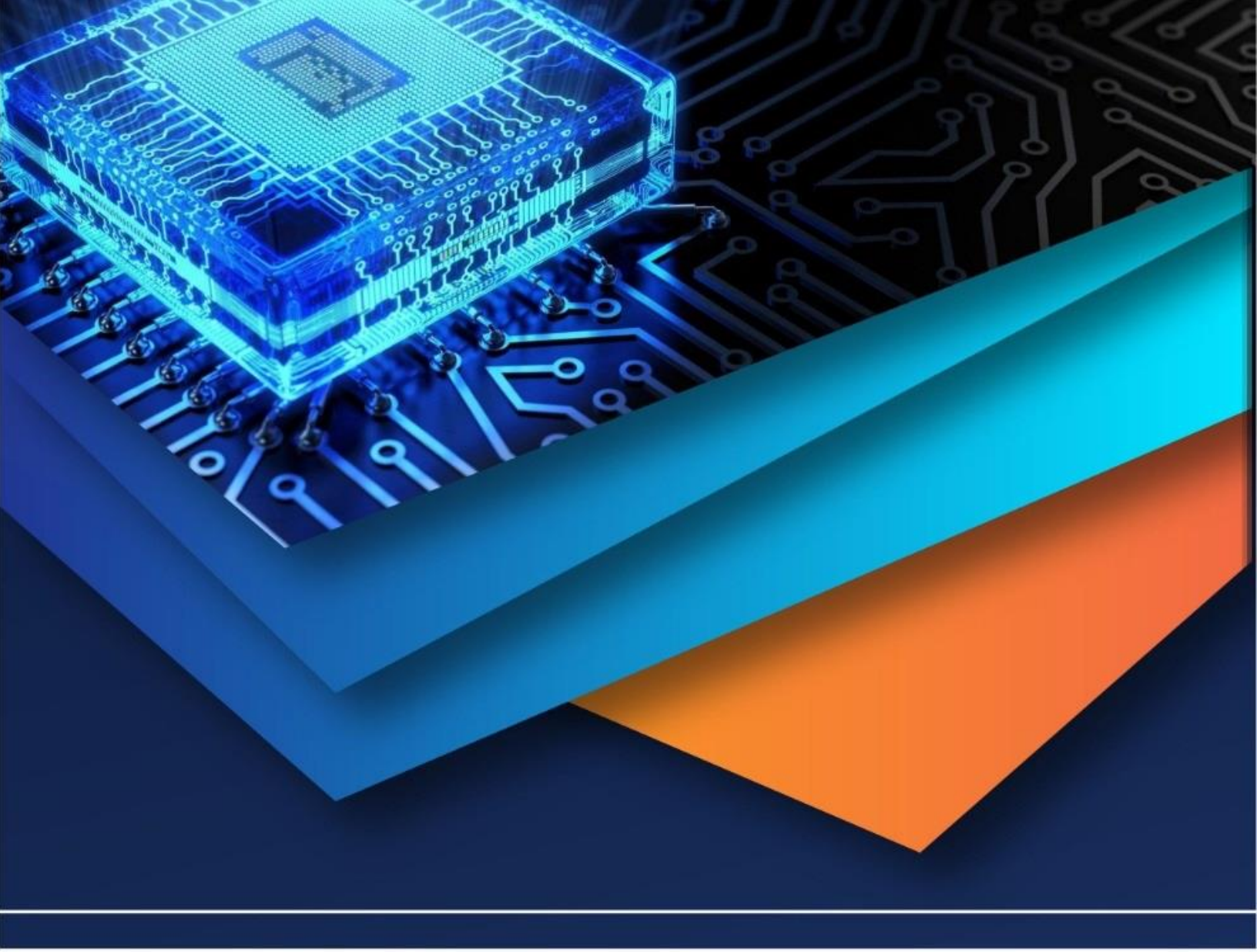

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