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Review Paper

Corrosion inhibition study of Stainless steel in Acidic medium – An Overview

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Abstract

Inhibition of corrosion with different types of stainless steel, medium and inhibitors has been reviewed. Corrosion can be controlled or minimized by the use of inhibitors. Acids are frequently used to remove such scales including hydrochloric acid (HCl), sulphuric acid (H_2SO_4), sulfamic acid (H_3NSO_3) and phosphoric acid (H_3PO_4). There is a continuous search for better corrosion inhibitors to meet the need of the industrial expectations. The inhibition's efficiency of inhibitor compounds is strongly dependent on the structure and the chemical properties of the film formed on the metal surface. The adsorption of inhibitors on the metal surface through polar atoms will prevent corrosion. The protection of metals from corrosion is analyzed by many technologies such as weight loss, Open Circuit Potential (OCP), Potentiodynamic Polarization, Electrochemical Impedance Spectra (EIS), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction spectroscopy (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscope (SEM), FTIR, UV-Visible spectra and adsorption study.

Keywords: Stainless steel, acidic medium, corrosion inhibition, SEM.

Introduction

Stainless steel type 304 is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, thermal power plant, chemical cleaning and pickling process, due to their stability, good corrosion resistance, high strength, workability and weldability. Corrosion is the deterioration of essential properties of a material due to reactions with its surroundings. Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel although many other metals may corrode as well. Corrosion damage can cause leakage of fluids or gases. Even more dangerous is a loss of strength of the structure induced by corrosion and subsequent failure. The application of acid corrosion inhibitors in the industry is widely used to prevent or minimize material loss during contact with acid. It has been observed that the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and Π orbital character of donating electrons and also on the electronic structure of the inhibitor. It has been reported that many inorganic, organic and heterocyclic compounds containing hetero atoms like N, O, S and P have been proved to be an effective inhibitors for the corrosion of stainless steel in acid media[1-53].

One way to protect the metal against corrosion is to add certain organic molecule that adsorb on the surface and form a protective layer. The unique advantage of the possibility of adding inhibitors is that this can be done without disruption of the industrial process. Corrosion inhibitors are useful when this addition in small amount prevent corrosion. At higher concentrations of organic compounds added additional testing for environmental impact is required [1-2].

Metals: Different inhibitors have been used to control the corrosion of stainless steel metals with different grade such as 410[3,53], AISI 304[10-13,15,17,18,24-29,31,33,35,42,48,50,52], AISI 304L[14,23,37,45], AISI 316[4,11,20,27,29,43], AISI 316L [14,16,19,22,40,41,44,45,51], UNSS31603[5], 0Cr13[8], 1Cr13[6], 302[30,36], ASTM 420[32], 430[34,38,39], Austenitic stainless steel[47], stainless steel[21,46,49], and iron[12].

Medium: In this overview my research is mainly focused on acidic medium such as sulphuric acid and hydrochloric acid. But few of the works carried out in the medium such as pure water, ground water, sea water, sodium chloride, sodium sulfate and sodium sulfide are used for this purpose.

Additives: Various inhibitors have been used as corrosion inhibitor alone or combination with additive such as HEDP[8], ATMP[8], Zn^{2+} [9,24,53], Tween 80[9,24], Potassium iodide[49]and Potassium thiocyanide[35].

Methods: Different methods have been used to determine the inhibition efficiency of different inhibitors by Weight loss[3,10,17,33,35,36,38,43,48,49,52,53], Gravimetric test[27,29], Potentiodynamic Polarization[3,5,6,8,13-19,21-23,27-31,37,39,40-42,44-52], Potentiostatic Polarization[7,10,33,36], Galvanostatic Polarization [13,25,35,38], Linear Polarization[26,32,47], Cyclic Polarization [15,32], Cyclic voltametry[11,12,14,26,44], Gasometry[7], Current Transient

Analysis[21], Repassivation Potential[21], AC impedance[7,12,33,53], Electrochemical Impedance Spectroscopy[11,16,18,23,27,28,41,45,46,50,52], Open Circuit Potential [11,12,15,30,31,40,44,51], Temperature dependent pitting potential [4] and Synergistic effect[35,49] has been analyzed.

Surface Analysis

A protective film is confirmed by various surface examination techniques such as SEM[3,14,20-24,26,27,29,37,38,40,41,44,45,53], XRD[9,24,45], FTIR[9,24,26], EDX[14,22,27,29,38], XPS[20,21,24,27,32,34,37], X-ray mapping[29], surface reflectance – IR spectroscopy [20], X-ray photo electron [34], AFM[53] and Luminescence spectroscopy [9,24].

Adsorption Study

The adsorption behavior of different inhibitors on the stainless steel surface has been investigated. The following adsorption isotherms have been obeyed such as Langmuir[3,6,8,10,14,17,19,25,28,33,36,39,47,52], Frumkin[7,9], Freundlich[49], Tempkin[30,38,42,48,50] and Dubininradushkevich adsorption isotherm[47].

A list of corrosion inhibition studies performed in different type of stainless steels is shown in table–1.

Table-1
List of Corrosion inhibition studies of Stainless steel

S. No	Metal	Medium	Inhibitor	Additive	Methods	Findings	Ref	Year
1	410 Stainless steel	1 N H_2SO_4	Thiourea, Allylthiourea and n-Phenylthiourea		Weight loss, PotentiodynamicPolarisation, SEM and adsorption study.	It shows better inhibition in the following order n-Phenylthiourea >Allylthiurea> TU. A protective layer is confirmed by SEM and it obeys Langmuir adsorption isotherm.	3	1990
2	AISI 304 and AISI 316 Stainless steel	0.1 M and 0.5 M NaCl	0.01 M and 0.1 M Molybdate		Temperature dependent pitting potential.	It shows better inhibition for both alloys.	4	1991
3	UNS S31603 stainless steel	0.6 M NaCI + 0.1 M Na_2SO_4	Cerium		PotentiodynamicPolarisation, Adsorption study.	It is an excellent inhibitor. Thermodynamic data suggests that the highly stable cerium oxide is responsible for blocking the active sites during cathodic and anodic reactions.	5	1993
4	1Cr13 Stainless steel	0.1 M H_2SO_4	ATMP (aminotrimethylenephosphonic acid), MADMP (methylaminodimethylenephosphonic acid), BADMP (n-butyl-aminodimethylenephosphonic acid) and HEDP (1-hydroxyethylidene 1, 1-diphosphonic acid)		Potentiodynamic Polarization and adsorption study.	It shows Mixed type of corrosion inhibitors, Their adsorption obeys the Langmuir isotherm equation	6	1994
5	AISI 304 Stainless steel	2 M H_2SO_4	2- Methyl benzoazole derivative		Weight loss, Gasometry, PotentiostaticPolarisation, AC impedance and adsorption study.	It shows excellent inhibitor. The stability of film formed was verified and it obeys the Frumkin isotherm.	7	1998
6	0Cr13 Stainless steel	0.1 M H_2SO_4	SADP (N-sulfonic amino-dimethylenephosphonicacid)	HEDP (1-hydroxyethylidene-1, 1-diphosphonic acid) and ATMP (aminotrimethylenephosphonic acid)	Potentiodynamic Polarization and adsorption study.	It was found to be an efficient inhibitor for acid corrosion and it obeys Langmuir adsorption isotherm. The corrosion inhibition efficiency may be high in the following order. SADP>ATMP>HEDP		

7	AISI 304 austenitic stainless steel	Ground Water	3-phosphonopropionic acid	Zn^{2+} and Tween 80 (polyoxyethylenesorbitanmonooleate)	Luminescence, XRD, FTIR and SEM.	It shows Mixed type of inhibitor and a protective layer is confirmed by SEM and FTIR.	9	2002
8	AISI 304 Stainless steel	1.0 M HCl	Rhodanineazosulpha drugs		Weight loss, PotentiostaticPolarisation and adsorption study.	It is a mixed type excellent inhibitor and it obeys the Langmuir adsorption isotherm.	10	2002
9	AISI 316 and AISI 304 Stainless steel	0.5 M HCl and H_2SO_4	PolyanilineandPoly(o-methoxyaniline)		Open Circuit Potential (OCP), Cyclic voltametry, Impedance Spectroscopy (EIS).	Potential value move towards positive direction and it shows better inhibition, a protective layer is confirmed by impedance spectra.	11	2002
10	AISI 304 stainless steel and Iron	0.01 M NaCl	Tungstate		Open Circuit Potential, Cyclic voltametry, AC impedance spectroscopy.	Potential value move towards positive direction and it shows better inhibition.	12	2003
11	AISI 304 Stainless steel	0.5 M H_2SO_4	4-Substituted pyrazole-5-ones		Potentiodynamic and GalvanostaticPolarisation and mechnism of inhibition.	It is an excellent inhibitor.	13	2003
12	AISI 304L and AISI 316 L Stainless steel	0.5 M HCl and H_2SO_4	(MBO) 2-Mercaptobenzoxazole		PotentiodynamicPolarisation, Cyclic voltametry, EDX, SEM, and adsorption study.	It is an excellent inhibitor. It obeys the Langmuir adsorption isotherm and the formation of passive film is confirmed.	14	2004
13	AISI 304 Stainless steel	Pure Water	Oxyanions tungstate and molybdate		Open Circuit Potential (OCP), PotentiodynamicPolarisation and Cyclic Polarisation.	Potential value move towards positive direction and it shows better inhibition at higher temperatures.	15	2004
14	AISI 316L Stainless steel	Acidic Alkaline solution of 0.3 M NaCland pH 4,8 and 10	Indole		PotentiodymanicPolarisation and Electrochemical Impedance Spectra(EIS).	It has proven to be efficient inhibitor. Indole was found to have no significant efficiency on the corrosion of the metal in alkaline solutions.	16	2004
15	AISI 304 Stainless steel	15% HCl	N-[(Z)-1-Phenylemethyleidene]-N-{2-[(2-{[(Z)-1 phenylmethylidine] amino}phenyl)disulfanyl] phenyl} amine		Weight loss, PotentiodynamicPolarisation, Impedance Spectroscopy (EIS) and adsorption study.	It is a mixed type excellent inhibitor and it obeys the Langmuir adsorption isotherm.	17	2005
16	AISI 304 stainless steel	0.5 M H_2SO_4	Thiphene derivatives		PotentiodynamicPolarisation, Impedance Spectroscopy(EIS)	It is a mixed type excellent inhibitor and a protective layer is confirmed.	18	2005
17	AISI 316L Stainels s steel	75 g/L H_2SO_4 + 25g/L HF +	3-Hydroxybenzoic acid		PotentiodynamicPolarisation, and adsorption study.	It is an excellent inhibitor and obeys the Langmuir andFrumkin adsorption isotherm.	19	2005

		30g/L H_2O_2						
18	AISI 316 Stainless steel	0.5 M H_2SO_4	2-thiophene carboxylic hydrazide (TCH)		Surface reflectance IR spectroscopy, XPS and SEM	It is an excellent inhibitor. A protective layer is confirmed by XPS and SEM.	20	2005
19	Stainless steel	0.02 M NaCl	Copper		Current transient analysis, Polarization, repassivation potential measurements, XPS and SEM.	Copper reduces steel dissolution rates in acidic chloride medium and a protective layer is confirmed by XPS and SEM.	21	2005
20	AISI 316L Stainless steel	0.5 M NaCl	2-Mercaptobenzimidazole		PotentiodymanicPolarisation, EDX, SEM and adsorption study.	It is an efficient inhibitor, breakdown potential move towards positive direction, and the negative values of activation energy indicates spontaneous adsorption .	22	2006
21	AISI 304L Stainless steel	1 M H_2SO_4	Cysteine		PotentiodymanicPolarisation, Electrochemical Impedance Spectra and SEM.	It proves better inhibition and it forms a protective layer on the metal surface.	23	2006
22	AISI 304 Stainless steel	Ground Water	(Amino trimethylenephosphonic acid) ATMP	Zn^{2+} along with Tween 80 (polyoxyethylenesorbitanmonooleate)	Luminescence Spectra, FTIR Spectra, XRD, XPS and SEM.	To understand the mode of corrosion inhibition and also the morphological changes on the metal surface	24	2007
23	AISI 304 Stainless steel	0.1 M HCl	Pyrimidine derivatives		GalvanostaticPolarisation, adsorption study.	It is a mixed type of inhibitor and it obeys the Langmuir adsorption isotherm.	25	2007
24	AISI 304 Stainless steel	0.5 M HCl and 0.5 M NaCl	Poly(N-ethylaniline)		Linear Anodic Polarisation, Cyclic voltametry, FT-IR Spectroscopy and SEM.	It is an excellent inhibitor and a protective layer is confirmed by FT-IR, SEM.	26	2008
25	AISI 316 and AISI 304 Stainless steel	30 wt% H_2SO_4	Mo and Mn		Gravimetric test, Polarisation, Impedance Spectroscopy(EIS), SEM, EDX and XPS.	It shows excellent inhibitor, A protective layer is confirmed by SEM, EDX, and XPS.	27	2008
26	AISI 304 Stainless steel	0.1 M H_2SO_4	1,2,3-benzotriazole (BTAH)		Potentiodynamic Polarization curves, Electrochemical Impedance Spectroscopy (EIS) and adsorption study.	It was found to be an efficient inhibitor for acid corrosion and it obeys Langmuir adsorption isotherm.	28	2008
27	AISI 304 and AISI 316 Stainless steel	3.5 wt % NaCl and 6wt % $FeCl_3$	Mn and Mo		Gravimetric tests, PotentiodymanicPolarisation, SEM, X-ray mapping and EDX.	It proves better inhibition. It forms a protective layer on the metal surface and it is confirmed by SEM and EDX.	29	2008
28	302 Stainless steel	1M HCl and 1M H_2SO_4	MPT (1-methyl -3 Pyridine -2-yl-thiourea		Open Circuit potential(OCP), PotentiodymanicPolarisation, Adsorption study.	Formation of passive films, inhibitor follows Tempkin adsorption isothem.	30	2009

29	AISI 304 Stainless steel	1.5% NaCl	Ciprofloxacin andNorfloxacin		Open Circuit potential(OCP), PotentiodynamicPolarisation.	It is a anodic type of inhibitor and a potential becomes positive direction.	31	2009
30	ASTM 420 Stainless steel	3% NaCl	Polyethyleneimine		Linear, Cyclic Polarisation, and XPS.	Proves that it is a very good inhibitor in pitting corrosion and a protective layer is confirmed by XPS.	32	2009
31	AISI 304 Stainless steel	1 M HCl	Bis-N,S-bidentate Schiff base		Weight loss, PotentiostaticPolarisation, AC impedance and adsorption study.	It is a mixed type excellent inhibitor and it obeys the Langmuir adsorption isotherm.	33	2009
32	AISI 430 stainless steel	3% NaCl	polyethyleneimine.		Linear Polarisation, Cyclic Polarisation and X-ray photoelectron spectroscopy (XPS)	It proves better inhibition. It forms a protective layer on the metal surface and it is confirmed by XPS.	34	2009
33	AISI 304 Stainless steel	3.0 M HCl	4-phenylthiazole	KSCN	Weight loss, Synergistic effect, GalvanostaticPolarisation and adsorption study.	It shows that it is an excellent inhibitor also higher temperature. Synergistic role existing between the inhibitors and it obeys Temkin's adsorption isotherm and thermodynamic – kinetic model.	35	2009
34	302 Stainless steel	0.5M H_2SO_4	(BCBD) 2,2'-[bis - N(4-chlorobenzaldimine)-1.1' – dithio, (BAPD) bis - (2-amino phenyl) disulphide		Weight loss, PotentiostaticPolarisation, Adsorption study.	It is a mixed type of inhibitors. It obeys Langmuir adsorption isotherm.	36	2010
35	304L Stainless steel	0.9% NaCl	Poly (Vinyl Alcohol)		PotentiodynamicPolarisation, impedance spectroscopy, SEM, XPS.	PVA act as a good inhibitor and it confirms a stable and uniform thin film formation.	37	2010
36	430 Stainless steel	2 M HCl	Crown ethers		Weight loss, Galvanostatic Polarization, SEM, EDX and adsorption study.	It shows Mixed type of corrosion inhibitors. Protective layer is confirmed by SEM, EDX and obeys the Temkin adsorption isotherm.	38	2010
37	430 Stainless steel	0.1 M HCl	N,N'-diquaternized 4,4'-dipyridinium salts		PotentiodymanicPolarisation, adsorption study.	It is a mixed type excellent inhibitor and it obeys the Langmuir adsorption isotherm.	39	2010
38	316L Stainless steel	0.5 M H_2SO_4	Lysine (α,ε-diaminocaproic acid)		Open circuit potential (OCP), PotentiodynamicPolarisation, and SEM.	Potential value move towards positive direction, Lysine act as a good cathodic inhibitor. A protective film is confirmed by SEM	40	2011
39	316L Stainless steel	0.5 M H_2SO_4	Triazoloisoquinoline derivatives.		PotentiodynamicPolarisation, EIS and SEM.	A very good inhibitor. Hydrogen evolution rate is low by EIS anda protective film is confirmed by SEM.	41	2011
40	AISI 304 Stainless steel	2 N HCl	N-Furfuryl N'-Phenyl Thiourea		PotentiodymanicPolarisation, and adsorption study.	It shows that it is an anodic inhibitor, it follows the Temkin's adsorption isotherm and	42	2011

						the mechanism is followed by Physisorption.		
41	AISI 316 Stainless steel	0.1 M HCl	2-(4-Methyl -3-oxo-2-phenyl-2, 3-dihydro - 1 H- pyrazolo[3, 4-b] pyridine -4-yl) acetic acid butylester		Weight loss and adsorption study.	It proves that it is an excellent inhibitor and it suggests that spontaneous adsorption takes place.	43	2011
42	AISI 316L Stainless steel	0.15 M NaCl	Molybdate and Nitrate		Open Circuit Potential(OCP), Polarisation, Cyclic voltametry and SEM.	A potential value move towards positive direction and shows that it is a good inhibitor. A protective layer is confirmed by SEM.	44	2011
43	AISI 304L and AISI 316 L Stainless steel	Oxygen free Na_2SO_4 + Na_2S at pH 3	H_2S		PotentiodynamicPolarisation, EIS, SEM and XRD.	It is a better inhibitor for both alloys and a potential value move towards positive direction. A passive layer is confirmed by XRD and SEM.	45	2011
44	Stainless steel	1 N H_2SO_4	poly-N-vinylimidazole and N-vinylimidazole		Potentiodynamic Polarization, EIS and adsorption study.	Shows that it is an excellent inhibitor. Thermodynamic data suggests that the highly stable layer is confirmed.	46	2011
45	Austenitic stainless steel	0.5 M H_2SO_4	5-benzoyl-4,6- diphenyl-1,2,3,4-tetrahydro-2-thiopyrimidin (DHPM I) and 5-Benzoyl-6-phenyl-4-p- tolyl-3,4-dihydropyrimidin-2(1H)-one (DHPM II).		Potentiodynamic Polarization, Linear Polarization resistance (LPR), EIS andadsorpion study.	It shows better inhibition, and obeys the Langmuir, Dubinin–Radushkevich adsorption isotherm.	47	2011
46	AISI 304 Stainless steel	2 N HCl	N - (2-mercaptophenyl) -N' - phenyl Thiourea		Weight loss, PotentiodynamicPolarisation andadsorption study.	It is a mixed type of inhibitors. It obeys Temkin adsorption isotherm, and the inhibition is governed by physisorption mechanism.	48	2011
47	Stainless steel	1 M HCl	Decylsulphate sodium salt (SSDS),Dodecylsulphate sodium salt (SSDDS),Hexadecylsulphate sodium salt (SSHDS), Dodecyl benzene sulfonate sodium salt (SSDDBS)	Potassium Iodide (KI)	Weight loss, Synergistic efect, PotentiodynamicPolarisation and adsorption study.	It is a mixed type excellent inhibitor and it obeys the Freundlich adsorption isotherm. Synergistic role existing between the inhibitors.	49	2011
48	AISI 304 austenitic stainless steel	0.5 M H_2SO_4	hexadecylpyridinium bromide (HDPB)		Potentiodynamic polarization, EIS and adsorption study.	It is a mixed type excellent inhibitor and it obeys the Temkin adsorption isotherm.	50	2011
49	AISI 316L Stainless steel	1 M H_2SO_4	AMINIO ACIDS (Arginine. Glycine, Leucine and Valine)		Open Circuit Potential(OCP), PotentiodynamicPolarisation.	Glycine, Valine and Leucine act as corrosion inhibitors but Arginine act as corrosion accelerator.	51	2011
50	AISI 304 Stainless steel	1 M HCl	Extract of Salvia officinalis		Weight loss, Potentiodynamic Polarization, EIS and adsorption study.	It shows Mixed type of corrosion inhibitors and their adsorption obeys the Langmuir isothem.	52	2012
51	410 Stainless steel	Sea water	Sodium Tungstate	Zn^{2+}	Weight loss, AC impedance, SEMand AFM.	It shows that excellent inhibitor and Protective film is confirmed.	53	2013

Conclusion

Corrosion inhibition study on using stainless steel in acidic environment with various inhibitors and additives at room temperature has been reviewed. Electro chemical studies like Polarization, AC impedance and surface morphology such as Scanning Electron Microscope, Atomic Force Microscope and Fourier Transform infrared Spectroscopy have also been analyzed.

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