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Inhibition and co-adsorption behaviour of *Alkylbenzyldimethylammonium chloride* on carbon steel in potable water system

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ABSTRACT

The synergistic inhibitory action of Alkylbenzyldimethylammonium chloride and zinc ion on the corrosion inhibition of carbon steel in potable water distribution system has been analyzed using Tafel polarization curves, Nyquist impedance plots, scanning electron microscopy (SEM) and weight loss method. The obtained results indicated that the studied inhibitor formulation were good inhibitor. A synergistic effect was also observed for the studied inhibitor formulation.

Keywords: Corrosion of potable water system, Electrochemical studies, SEM, Weight loss

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INTRODUCTION

Carbon steel is employed widely in most industries in due of low cost and its availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, etc. Fouling and corrosion are the two important operational discrepancies in heat exchangers and associated cooling water system pipelines. The problems include flow blockage of pipes, pipe punctures and unacceptable corrosion rates of the system components. For controlling fouling and corrosion, continuous addition of inhibitors as well as the addition of biocides every week or once in a fortnight is explored. Hence, the phenomenon of studying the effect of inhibitors and biocides is quite essential.

Corrosion in potable water systems may be caused by either in inherent factors or design, construction or operational deficiencies. Most materials used potable water systems are susceptible to corrosion. The properties of the material and the composition of the water are interactive in the occurrence or inhibition of the inherent corrosion.

Corrosion susceptibility is also influenced by the many other factor including temperature, local flow rate, pH, alkalinity, carbon dioxide, dissolved solids, minor chemical constituents of either the water or corroding materials.

Cast iron pipes have been used to transport potable water for over 500 years [1] and iron pipe corrosion has been a problem for just as long. The American Water Works Association (AWWA) estimates that it will cost US water utilities $325 billion over the next 20 years to upgrade water distribution systems [2]. This AWWA value is built on the U.S. Environmental Protection Agency (USEPA) estimate of $77.2 billion for service and replacement of transmission and distribution system lines over the next 20 years [3].

The majority of distribution system pipes are composed of iron material: cast iron (38%), ductile iron (22%), and steel (5%) [4]. Moreover, a 1997 survey of the 100 largest American Water Works Association Research Foundation (AWWARF) member utilities found that “the most common distribution system problem is corrosion of cast iron pipe [5].

Corrosion of iron pipes in a distribution system can cause three distinct but related problems. First, pipe mass is lost through oxidization to soluble iron species or iron-bearing scale. Second, the scale can accumulate as large tubercles that increase head loss and decrease water capacity. Finally, the release of soluble or particulate iron corrosion-by-products to the water decreases its aesthetic quality and often leads to consumer complaints of "red water" at the tap. The water industry must be concerned with all three of these aspects of corrosion. The presence of chloride ions, solely or mixed with some other ions, in the nearly neutral aqueous solutions may provoke very dangerous localized corrosion of various iron alloys [6-9]. Effective corrosion inhibitor in combination with metal ions like Zn^{2+}[10-13]. The present work was designed to study the corrosion inhibition of carbon steel in potable water by alkylbenzyldimethylammonium chloride and zinc ions as corrosion inhibitors using three different techniques: weight loss, electrochemical studies and scanning electron microscopy, hoping to get some general ideas to guide the composing of inhibitor in reality.

MATERIALS AND METHODS

Materials

The composition of carbon steel used for corrosion inhibition studies was (Wt %): 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and balance being Fe. The specimens of size 1.0cm×4.0cm×0.2cm were press cut from the carbon steel sheet, were machined and abraded with a series of emery papers.

This was followed by rinsing in acetone and bidistilled water and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors alkylbenzyldimethylammonium chloride, Zn^{2+} ions were used as received. A stock solution of 1000ppm of alkylbenzyldimethylammonium chloride was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of alkylbenzyldimethylammonium chloride used for the study ranges from 10 to 150ppm. All solutions were prepared using potable water (Tiruchirappalli, Tamil Nadu, India). The study was carried out at room temperature. The molecular structure of alkylbenzyldimethylammonium chloride is given in Fig 1.

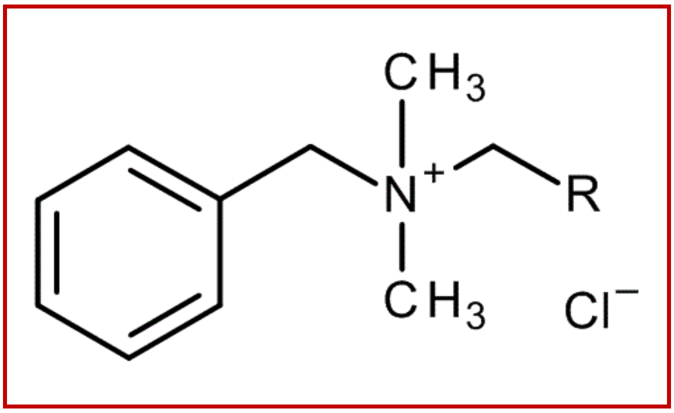

Figure 1. Molecular structure of Alkylbenzyldimethylammonium chloride(ABDAC)

Weight - loss Measurements

The freshly prepared carbon steel specimens were suspended in 150ml beakers containing 100ml of test solution maintained at room temperature with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the specimens. The measurements were carried out for the uninhibited solution and the solution containing ABDAC and ABDAC - Zn^{2+} mixture. Weight loss experiments were performed for the duration of seven days. The specimens were immersed in triplicate and the average corrosion rate was calculated. These uncertainties or RSD for three replicate measurements were less than 5%. The corrosion rates (C_R) were determined using the equation:

$$CR\left(\frac{mm}{y}\right) = \frac{87.6 \times w}{a\,t\,D}$$

where
w = corrosion weight loss of carbon steel (mg)

a = area of the coupon (cm^2)
t = exposure time (h)
D = density of the carbon steel (g cm^{-3}).

The inhibition efficiency (IE) of ATMP - Zn^{2+} mixture was calculated by using the following equation:

$$\%IE = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \times 100$$

where
C_{Ro} = corrosion rate of carbon steel in the absence of inhibitor
C_{Ri} = corrosion rate of carbon steel in the presence of inhibitor

Electrochemical studies

Both the potentiodynamic polarization studies and electrochemical impedance spectroscopic (EIS) studies were carried out using the electrochemical workstation model CHI- 760d and the experimental data were analysed by using the electrochemical software (Version: 12.22.0.0). The measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode as reference electrode.

The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1cm^2 was the only surface exposed to the electrolyte. The three electrodes set up was immersed in control solution of volume 100ml both in the absence and presence of the inhibitors formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solution were adjusted to 7.0 and the solutions were unstirred during the experiments.

Polarization curves were recorded in the potential range of -750 to -150 mV with a resolution of 2mV. The curves were recorded in the dynamic scan mode with a scan rate of 2mVS^{-1} in the current range of -20mA to +20mA. The Ohmic drop compensation has been made during the studies. The corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots. The inhibition efficiency (IE_p) values were calculated from the I_{corr} values using the equation.

$$IE_p(\%) = \frac{1 - I'_{corr}}{I_{corr}} \times 100$$

Where I_{corr} and I'_{corr} are the corrosion current densities in case of control and inhibited solutions respectively.

Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60 KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) were obtained from the Nyquist plots. The inhibition efficiencies (IE_i) were calculated using the equation,

$$IE_i(\%) = \frac{1 - R_{ct}}{R'_{ct}} \times 100$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

Scanning Electron Microscopy

The surface morphology of the corroded steel sample surface in the presence and absence of the inhibitors was studied using SEM (Model: TESCAN vega3 USA). To study the surface morphology of carbon steel, polished specimens prior to initiation of any corrosion reaction, were examined in optical microscope to find out any surface defect, such as prior noticeable irregularities like cracks etc.

Only those specimens, who had a smooth pit-free surface, were subjected to immersion. The specimens were immersed for 24h at 30^0C. After completion of the tests specimens were thoroughly washed with bidistilled water and dried and then subjected to SEM examination.

Energy Dispersive Analysis of X-ray (EDAX)

EDAX (Model: BRUKER Nano Germany) system attached with Scanning Electron Microscope was used for elemental analysis or chemical characterization of the film formed on the carbon steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that, a detector was used to convert X-ray energy into voltage signals. This information is sent to a pulse processor, which measures the signals and passed them into an analyzer for data display on the analysis.

RESULTS AND DISCUSSION

Weight loss measurements

Alkylbenzyldimethylammonium chloride and Zn^{2+} were tested and their corresponding weight loss data are shown in Table 1. The corrosion rate is decreased markedly even by the increases in inhibitor concentrations. The corrosion rate decreased considerably with an increase in concentration of ABDAC and reached the maximum value in the (5ppm Zn^{2+} + 150ppm ABDAC) inhibitor formulation has 72% inhibition efficiency. 5ppm of Zn^{2+} alone has 8% (I.E) and 150ppm of ABDAC alone has 22% (I.E) and combined with these two get 72% inhibition efficiency this increased I.E due to the synergism.

Table 1. Corrosion Inhibition efficiency of carbon steel in potable water system in the absence and presence of inhibitor formulation obtained by the weight loss method

Concentration of (ppm)		Corrosion rate (mmy^{-1})	Inhibition efficiency (%)
Zn^{2+}	ABDAC		
Blank	-	311.1	-
5	-	283.9	8
5	10	342.2	-10
5	25	297.5	4
5	50	264.4	15
5	75	219.7	29
5	100	161.4	48
5	125	124.4	60
5	150	87.51	72
-	150	243.0	22

Potentiostatic polarization technique

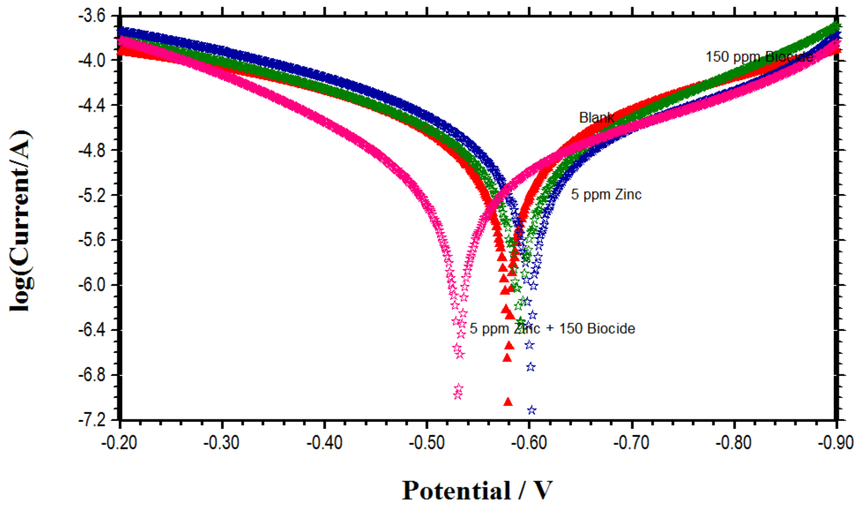

Fig 2. Tafel plots for carbon steel immersed in the absence and presence of inhibitor formulation obtained by polarization measurements

Potentiodynamic polarisation parameters of carbon steel immersed in potable water for all four systems are given in Table 2 and the corresponding polarisation curves are shown in Fig. 2. Addition of 5ppm of Zn^{2+} to the blank solution, the corrosion potential were shifted towards cathodic region, 150ppm of ABDAC to the blank solution, the corrosion potential shifted towards the cathodic region and 5ppm of Zn^{2+} + 150ppm of ABDAC to the blank solution. The corrosion potential towards the anodic region according to Ferreira and W.H. Li if the displacement in

corrosion potential is more than 85mV with respect to the corrosion potential of the blank, the inhibitor can be seen as cathodic or anodic type [14-16]. The maximum displacement was < 49mV which indicated that the studied inhibitor and the effect is more evident at higher concentrations. These results suggest that the studied formulation can be classified as mixed type inhibitor. The inhibitor formulations control the both anodic and cathodic reaction.
From the polarisation curves, the corrosion current density (I_{corr}) was determined by Tafel extrapolation method. The corrosion current density was decreased considerably in the presence of inhibitor. Inhibition efficiency was 71.57%. Zn^{2+} +ABDAC may attributed to the increased electron density leading to electron transfer mechanism from functional group to metal surface, producing greater coordinate bonding with a greater adsorption and inhibitor efficiency. Similar explanation has been sought out the classical work of Khamis and Atea [17].

Table 2. Corrosion parameters for carbon steel immersed in the absence and presence of inhibitor formulation obtained by potentiostatic polarization technique

Concentration (ppm)		Tafel parameters				IE_p (%)
ATMP	**Zn^{2+}**	**E_{corr} mV vs SCE**	**I_{corr} A/cm^2×10^{-5}**	**β_a mV/decade**	**β_c mV/decade**	
Blank	-	-579	1.583	201.2	198.6	-
-	5	-602	1.475	186.0	218.5	6.82
150	-	-590	1.275	203.4	183.1	19.45
150	5	-530	0.450	163.7	202.5	71.57

Analysis of impedance spectra

Impedance spectra for the inhomogeneous films on the metal surface or rough and porous electrodes. Nyquist plot is shown in Fig 3 in the absence and presence of inhibitor solution. The impedance spectra were characterised by two slightly distorted capacitive loops behaviour, one at high frequency and the other at low frequency.

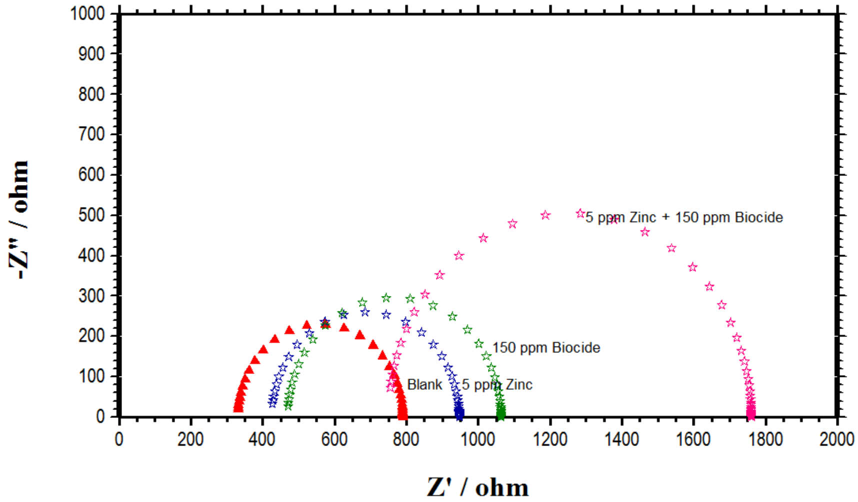

Fig 3. Nyquist plots of carbon steel immersed in various test solutions

Deviations from the ideal semicircles can be attributed to the inhomogenities of the surface as well as due to mass transport process [18]. Charge transfer resistance and the double layer capacitance were calculated from the equivalent circuit fitting (Fig 4) of the Nyquist plot. Charge transfer resistance increased with the inhibitor formulation and became approximately three times higher than the blank value. The increased in charge transfer resistance and the decrease of double layer capacitance were attributed to the enhanced adsorption of the inhibitor molecule on the metal surface [19,20]. Increased in charge transfer resistance resulted in the decrease of metal dissolution reaction. Charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency were calculated from the equivalent circuit fitting of the Nyquist plot are shown in Table 3. The decrease in the C_{dl} value in the presence of inhibitor and biocide show the coverage of metal surface with reaction product that result in decrease double layer thickness [19]. Increased in polarisation resistance resulted in the decrease of metal dissolution reaction.

Scanning electron microscopy

SEM images provides a supported the adsorbed film onto the carbon steel surface. To know the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM images of the surface are examine.

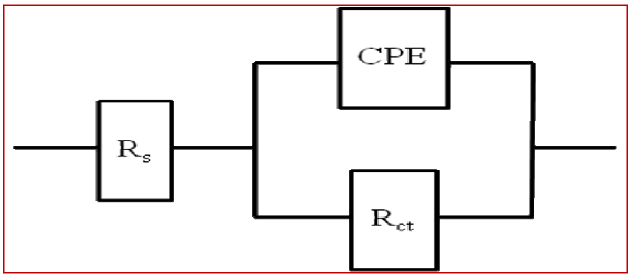

Fig 4. Nyquist curves equivalent electrical circuit

Table 3. Electrochemical impedance parameters for carbon steel immersed in the absence and presence of inhibitor formulation obtained by A.C. impedance spectra

Concentration (ppm)		Charge Transfer Resistance R_{ct} (Ω)	Double layer capacitance Cdl CPE (μF/cm^2)	I.E$_{im}$ (%)
ATMP	Zn^{2+}			
Blank	-	350.09	2.543	-
-	5	375.61	2.108	6.79
150	-	433.14	1.698	19.17
150	5	1213.54	0.209	71.15

Scanning electron microscopy

SEM images provides a supported the adsorbed film onto the carbon steel surface. To know the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM images of the surface are examine.

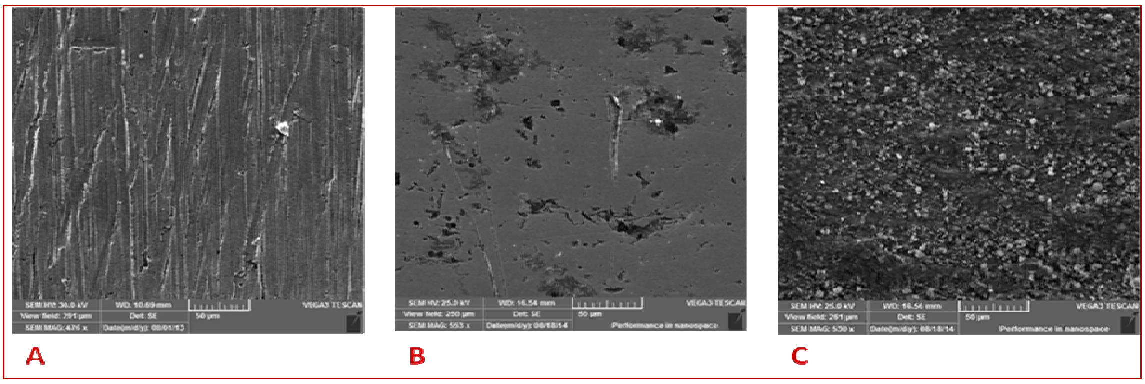

Fig 5. SEM image of A) Polished carbon steel surface B) After immersion of potable water system (blank) C) After immersion of solution containing (5ppm Zn^{2+} + 150 ppm ABDAC)

The SEM images of polished carbon steel surface in Fig 5A show the smooth surface of the metal. This show the absence of any corrosion products or inhibitors complex formed on the carbon steel surface. The SEM images of carbon steel surface immersed in potable water in Fig 5B show the many holes in metal surface, fault of the metallic properties and roughness of the metal surface which indicates the corrosion of carbon steel in potable water. Fig.5C show the SEM images of the carbon surface immersed in potable water containing 5 ppm of Zn^{2+} + 150 ppm of ABDAC creates a thin adsorbed film, which inhibits carbon steel dissolution in potable water distribution system.

Energy dispersive X - ray analysis

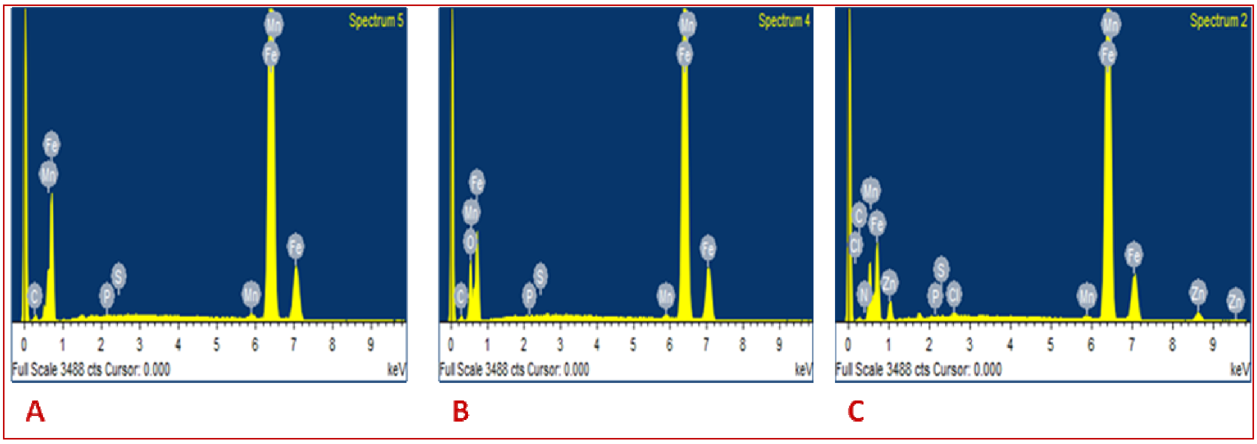

Fig 6. EDAX spectrum of A) Polished carbon steel B) After immersion of potable water (blank) C) After immersion of solution containing (5ppm Zn^{2+} + 150 ppm ABDAC)

It is significant to take into consideration the percentage of the elements present on the surface of the carbon steel surface. The EDAX spectrum of polished carbon steel sample shows good surface properties (Fig 6A). Fig (6B) the presence of the peaks of O and Fe is indicates the formation of iron oxides and other corrosion products formed onto the carbon steel surface. Fig. 6C the peak appeared at C, H, N, Cl and Zn are present in the inhibitor formulation due to confirm the adsorbed film onto the metal surface and suppressed metal corrosion rate.

CONCLUSION

Alkylbenzyldimethylammonium chloride inhibit the corrosion of carbon steel in potable water distribution system.

- ABDAC – Zn^{2+} exhibits excellent synergism in the corrosion of carbon steel in potable water distribution system by weight loss measurements.
- From the corrosion point view, ABDAC with zinc ions acts as good-mixed type inhibitor system.
- Binary inhibitor system is found to affect both the anodic and cathodic processes and its inhibition efficiency increases with the inhibitor concentration and good agreement in weight loss, polarization studies and impedance spectra.
- The formulation consisting of 5 ppm of Zn^{2+} and 150 ppm of ABDAC had 72% corrosion inhibition efficiency.
- Corrosion inhibition may arise from the formation of protective film consists of Fe–ABDAC complex.
- The low Cdl value obtained in the presence of inhibitor formulation indicate the formation of thicker inhibitor film on the metal surface.
- SEM and EDX studies supported the surface adsorbed film formation over the surface of carbon steel by the inhibitor formulation.

REFERENCES

[1] Gedge, G. Corrosion of Cast Iron in Potable Water Service. Proc. Corrosion and Related Aspects of Materials for Potable Water Supplies, *Proceedings of the Institute of Materials Conference. London*, UK **(1992)** .
[2] AWWA. AWWA Report: $325 billion for Pipes. *AWWA Mainstream*, **(1999)** February:3.
[3] Davies, C.; Fraser, D.L.; Hertzler, P.C. & Jones, R.T. USEPA's Infrastructure Needs Survey. *Journal AWWA*, **(1997)** 89:12:30.
[4] American Water Works Association. *WATER:\STATS* **1996** Survey.
[5] Bray, A.V. *Personal communication*. **(1997)**.
[6] T. Szauer, A. Brandt, *Corros. Sci.* **(1983)** (23) 473.
[7] C.A. Acosta, R.C. Salvarezza, H.H. Videla, A.J. Arvia, *Corros. Sci.* **(1985)** (25) 291.
[8] N. Cui, H.Y. Ma, J.L. Luo, S. Chiovelli, *Electrochem. Commun.* **(2001)** (3) 716.
[9] M. Safira, A. Srhiri, M. Keddam, H. Takenouti, *Electrochim. Acta*, **(1999)** (44) 4395.
[10] J. Telegdi, M. M. Shaglouf, A. Shaban, F. H. Karman, I. Betroti, M. Mohai and E. Kalman, *Electrochimica Acta*, **(2001)** Vol. 46, pp. 3791-3799
[11] H. S. Awad, *Anti-Corrosion Methods and Materials*, Vol. 52, No. 1, 2005, pp. 22-28.
[12] J. Jaworska, H. V. Genderen-Takken, A. Hanstveit, E. Plassche and T. Feijtel, *Chemosphere*, **(2002)** Vol. 47, pp. 655-665.

[13] B. V. Appa Rao, M. Venkateswara Rao, S. Srinivasa Rao and B. Sreedhar, *Chemi- cal Engineering Communications*, **(2011)**Vol. 198, pp. 1505-1529

[14] Ferreira, E.S., Giacomellic, C., Giacomellic,F.C., and Spinelli, A., *Mater. Chem. Phys*, **(2004),** 83 (1), 129-134.

[15] Li, W.H., He, Q., Pei, C.L., and Hou, B.R., J. Appl. Electrochem, **(2008)**, 38 (3), 289 – 295 .

[16] T. Asokan and C. Thangavelu., *j. Advances in chemistry*, **(2014)**10 (3), 2369

[17] E. Khamis, M. Atea, *Corrosion*, **(1994)** 50 (2) 106.

[18] K. Juttner, *Electrochim. Acta*, **(1990)**, 35, 150.

[19] E. Mcfferty, N. Hackermann, *J. Electrochem. Soc.* **(1972),** 119, 146.

[20] M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, *Corrosion Sci.* **(2002),** 44 573.