CHAPTER – III

LITERATURE SURVEY AND SCOPE OF THE PRESENT WORK
CHAPTER – III

LITERATURE SURVEY AND SCOPE OF THE PRESENT WORK

The action of an inhibitor in aggressive media is assumed to be due to its adsorption at the metal – solution interface. If a co-ordinate type bond is formed, the process is termed as chemisorption [1]. This situation can arise if the inhibitor molecule contains lone pair of electrons or multiple bonds on conjugate \( \pi \)-type system, a highly charged center etc [2–3].

Many organic compounds containing N, S, O and P atoms have been widely tried as inhibitors. Among them there has been a growing interest in the use of the thiosemicarbazide derivatives as inhibitors for the aqueous corrosion of metals [4–7]. The inhibiting action of thiosemicarbazide derivatives has been mainly attributed to adsorption of the thiocarbonyl group on the surface of the metal. This adsorption affects the electrochemical behaviour involved in the corrosion process [8].

Synergistic effect, which is the enhanced performance of mixture of inhibitors compared with individual inhibitors on the corrosion of metals, has been reported [9,10]. However the use of mixtures of thiosemicarbazide derivatives has not been systematically explored [11].

The influence of CaO, CaCl\(_2\) and sodium citrate on the electrochemical properties of different grades of commercial aluminium in alkaline medium has been reported [12, 13, 39, 77].
E. Deltombe and Pourbaix [14] have studied the potential – pH diagram of Al – H₂O system and found that aluminium in alkaline range attained highly negative potentials.

D.S. Clark [15] has observed that the increase of corrosion rate of aluminium with increasing temperature as due to increase in the rate of diffusion and ionization of active species in HCl medium.

Subramanyan et al [16, 30, 34] have studied the mechanism of inhibition of corrosion of 2S aluminium in alkali by calcium and citrate ions. The adsorption of radioactive calcium on aluminium from 0.2M NaOH containing radioactive calcium (Ca⁴⁵) was studied. There was a progressive increase in the adsorption (uptake) of Ca⁴⁵ with time. But when sodium citrate was added to the radioactive calcium solution, the uptake (adsorption) was practically insignificant. The discharge characteristics of a cell using aluminium 2S as anode and alkaline citrate electrolyte (4% NaOH + 0.1% Ca(OH)₂ + 5% sodium citrate) was also reported.

J. Bocksite et al [17] have observed that the corrosion of aluminium in NaOH can be considerably reduced by the addition of Ca(OH)₂ and sodium citrate to the solution. It has been reported [18, 19, 21, 23] that alloying of aluminium with other metals, made aluminium free from the passivation in neutral medium.

K. Kapali and J. Subramanyan [20] have reported that a combination of Ca²⁺ and complexing agents like citrate, tartarate can appreciably bring
down the self corrosion of 2S aluminium in 1N NaOH solution and can also improve its anode efficiency for a possible use as a galvanic anode.

Subramanyan et al [22] have shown that the wasteful self-corrosion of aluminium in NaOH solution can be considerably reduced by the addition of Ca(OH)$_2$ and sodium citrate to the solution. Calcium and citrate are synergistic in bringing down the corrosion of aluminium in alkali. Aluminium and its alloys have been found to be useful as anodes in alkaline batteries since they show high energy density and high negative open circuit potential in alkaline solutions. The aluminium–air cells that are capable of producing high-energy density and very high power density have been reported [24, 55, 66, 70].

Gerhard Wild Brett et al [25] have studied the influence of sodium citrate as a corrosion inhibitor for aluminium in alkaline solutions. They found that the addition of silicate is responsible for the film formation on the aluminium surface. Different metals withdraw differing amounts of the corrosion inhibitor from silicate containing solution (in decreasing order Fe, Al, Zn, Cr, Sn, Ni, Cr – Ni, Steel and Cu) depending not only on the specific adsorption of silicate, but also on the corrosion resistance of the various metals.

Subramanyan and Yamuna [26] have found that a combination of calcium ions and sodium tartarate might not be effective as citrate in complexing the aluminium, as it caused greater degree of polarization than citrate and favoured anodic oxidation.
Venkatakrishna Iyer et al [27, 59] have studied the inhibition of self-corrosion of aluminium by adding inhibitors, complexing the agents and some addition agents in the electrolyte. According to Musa Yoshi et al [28] the addition of 0.5M sodium stannate to 5M KOH solutions inhibit corrosion of aluminium.

Ramakrishnaiah and Subramanyan [29, 33, 35, 41] have reported that the effect of calcium combined with various organic compounds like acids, ethers, amino compounds etc act as synergistic inhibitors in reducing the corrosion of 2S commercial aluminium in 1M NaOH solution.

M.N.Desai et al [31] studied that ethylene diamine to be effective short-term inhibitor for corrosion of aluminium in HCl.

E.Heusler and Allgaier [32], Greef and Norman [63] and O.R.Brown and Whitley [69] have reported the formation of a porous protective film on aluminium in NaOH solution at higher positive potentials.

Shenoi et al [36, 67] have reported the binary and ternary alloys of aluminium for use as sacrificial anode in synthetic seawater and in 3% NaCl solution.

S.C.Makawana et al [37] have reported the inhibition efficiency of benzoic acid for the corrosion of aluminium in 1N HCl.
Y.Kordesch Karl [38] has studied the corrosion inhibition of aluminium in alkaline medium by adding a mixture of sparingly soluble mercury complex and soluble stannate and/or Zincate salt.

A.R. Despic et al [40], K.F. Blurton et al [45] Salisbury et al [50], J.F. Copper et al [51], Hori et al [62] and have published papers regarding the advancement of Al – air batteries.

L.K. Moden and G. Perkons [42] have reported with aluminium having less than 0.1% gallium and approximately 1% Mg to show desired electrochemical property, i.e., higher current densities at very negative potentials.

M. Krishnan and M. Subramanyan [43] observed that aromatic compounds are generally more effective than aliphatic compounds in inhibiting the corrosion of aluminium in an alkaline solution. In the presence of calcium, the inhibition efficiency of all the compounds were improved. McMinn and Brans Comb [49] have observed that the alloy containing 0.4 - 0.8% manganese 0.4% iron and 0.04% gallium would provide the required electrochemical performance for aluminium as galvanic anode in alkaline solution.

The dissolution of aluminium in KOH solution is reported in the following stiochiometry [44, 69]

\[
\text{Al} + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{AlO}_2^- + \frac{3}{2} \text{H}_2
\]
and hence the measurement of hydrogen can predict the corrosion rate of aluminium quantitatively.

K.Aramakai [46] observed that the inhibition effects of inhibitors were expected to be closely related to the hard and soft acids and bases principle.

W.Bohnstedt [47] have studied the shift of open circuit potential in the negative direction and the improvement of polarization characteristics simultaneously achieved by mercury and indium ions and even more effectively with gallium ions when alloyed with aluminium.

D.D.Macdonald et al [48, 68, 72–74] studied the mechanism of dissolution of aluminium and its alloys in alkaline media, the effect of hydroxide concentration and applied potential on the metal dissolution and hydrogen evolution rate.

G.C.Wood and W.H.Daker observed that the corrosion of aluminium and zinc initiates as the pit where the flaws associated with the metal substrate and its air formed film are present [52].

Yu.F.Fateev and L.I.Antropov [53] have studied the corrosion of aluminium in KOH solution containing calcium and calcium–containing organic compounds and reported the reaction to be under anodic control.
Fitz Patrick et al and Maimoni [54, 60] have studied the voltaic and coulombic efficiency, which are practically quite important to the design of a cell system.

Sarangabani et al [56] have studied the influence of a few metallic additives, which are added as their oxides to the alkaline citrate electrolyte to assess the performance of aluminium as a galvanic anode. It was found that the incorporation of zinc into the base electrolyte influences favorably the inhibition efficiency as well as the anode efficiency.

B.A. Abd El Nabey et al [57] have reported a gasometric method to determine the rate of dissolution of aluminium in neutral medium.

Tadensz and Zoful [58] reported the benzimidazole derivatives to be effective for non-ferrous metals such as Cu, Al and Zn.

B.A. Abd El Nabey et al [61, 65, 76] observed that thiosemicarbazide and thiosemicarbazones are effective inhibitors for corrosion of iron and aluminium in acid medium. They have also revealed that the protection efficiency increases with increasing π-bonds and phenyl groups. It is reported that introduction of thiosemicarbazide molecule to furfuraldehyde, crotanaldehyde etc. increases the inhibiting power for the corrosion of aluminium and zinc in NaOH solutions.

Sarangapani et al [64] have also studied the performance of the battery having an anode of 2S aluminium and an electrolyte of an alkali hydroxide [2–5N NaOH or KOH] containing sodium citrate and / or
tartarates complexing agent, 5 – 35% conventional additives such as metals (Zn, Sn, U, W, Mo, Al), metal oxides including rare earth oxides, and salts of metalloids 0.4 – 5%. The complexing agent and additives are found to decrease the corrosion of aluminium in alkaline medium.

D. D. Macdonald et al [71] have studied the various oxy anions such as SnO$_3^{2-}$, Ga(OH)$_2$, In(OH)$_3$ and MnO$_4^{-2}$ and their combinations as inhibitors for the corrosion of pure aluminium (99.99%) in 4M alkaline solutions.

E. Khamis et al [77] have proposed an adsorption isotherm of the general form.

\[ F(\theta, x) \exp(-a, \theta) = K_c \]

Where \( f(\theta, x) \) in the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm. ‘\( \theta \)’ is degree of coverage, ‘\( x \)’ is the number of water molecules replaced by inhibitor molecule and ‘\( a \)’ is a mole molecular interaction parameter, which depends upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface.

Kapali et al (78) observed that the alkaline citrate cum stannate solution to be the best electrolyte in terms of electrochemical characteristics and electrolyte management. Aluminium – air battery with this electrolyte can be used safely and effectively at an ambient temperature. The best anode based on 99.8% pure aluminium is a quaternary – alloy containing lead, gallium and indium.
O.F. Offiong and Martelli [79,81] observed the inhibiting efficiency of the mixture of PME (P – 2 – acetyl pyridine -(4- Phenyl thiosemicarbazone), M: – 2- acetyl pyridine - (4-phenyl isomethyl thiosemicarbazone), E:– 2 – acetyl pyridine –iso– ethyl thiosemicarbazone) is greater than the mixture of any two compounds of the above three.

A. Onuchukwu et al [80] have studied the hydrogen permeation through aluminium in alkaline medium. They have reported the influence of some anions and temperature on this process.

K. Khamis et al [82] studied the corrosion inhibition of steel in phosphoric acid by thiosemicarbazide derivatives using chemical and electrochemical techniques. They confirmed that the inhibitor follows adsorption mechanism. They have also reported the influence of exposure time on the performance of CrTSCN.

J. Jeyaraj et al [83] have studied the synergistic inhibition effect of calcium acetate and salicylic acid in aluminium in 0.1 N NaOH and reported that the corrosion is under anodic control.

J. Jeyaraj et al [84] have reported the synergistic inhibition effect of tetra ethyl ammonium bromide and CaO in 4N NaOH for the corrosion of aluminium.

It is reported that [85] on increasing the concentration of either calcium oxide or catechol increases the inhibition of corrosion of aluminium that is under anodic control.
SCOPE OF THE PRESENT WORK

Form the exhaustive survey of the literature it has become clear that large number of references have been encountered with regard to the developments of aluminium alloys and electrolyte composition, which are vital for aluminium – air cells to produce high energy density and very high power. The large-scale self-corrosion of aluminium in alkaline media can be brought down by suitable alloying of aluminium, modifying the battery electrolyte besides the use of some powerful inhibitors. Only limited compounds have been tried as inhibitors for the above purpose and among them some thiosemicarbazones deserve mention. The work of E.Khamis et al is pioneering in this direction. Taking clue from their studies it has been proposed to synthesize a family of thiosemicarbazones to be tried as inhibitors for aluminium – air cell application. The synthesized compounds are to be characterized for structural elucidation through spectral methods. Several alloys of aluminium with varying amounts of lead, over fixed proportion of gallium and indium are to be prepared and tried for their self-corrosion to be chosen as the best alloy composition with maximum corrosion resistance in alkaline media. Instead of the usual 4N NaOH, the alkaline battery electrolyte with Ca\(^{2+}\)-citrate complex added is to be tried in conjunction with the inhibitors in order to achieve the above objective.

The conventional weight loss methods, gasometry, spectrophotometry, electrochemical polarization and impedance measurements are the techniques to be adopted to quantify the corrosion and to understand the corrosion inhibition mechanism by the additives. Using thin aluminium foils as membrane electrode, the hydrogen uptake of the
metal in the medium in presence of the inhibitors are to be evaluated. From
the kinetic and thermodynamic data, a suitable mechanism for the adsorption
process of the inhibitors on the metal surface is to be proposed. The
interference if any by the inhibitors on the reduction reaction of oxygen on
carbon electrode is to be explored. Finally these inhibitors are to be used as
the additives in a proto-type aluminium – air cell and the discharge capacity
of the cell at a specified load is to be monitored.
References

7. B. I. Ita and E. Offiong, Inhibition of steel Corrosion in HCl by Pyridoxal, 4 methyl semicarbazide pyridoxal (4 methyl TSC) and its Zn (II) Complex, Materials Chemistry and Physics, 48 (1997) 64.
14. E. Deltombe and M. Pourbaix, Proceedings of the 9th meeting CITCE
    Paris, 1957 (Butter Worths Scientific Publisher London) (1959) 123.
15. D. S. Clark, Physical Metallurgy of Engineers, Dan Nostrand
16. N. Subramanyan, M. G. Potadar and A. R. Yamuna, Pat Appln. 106,
    (1963) 806.
17. L. Bocksie, D. Trevethan and S. Zaromb, J. Electrochem, Soc. 110
    (1963) 267.
19. T. C. Ramachandar and U. K. V. Unni, Chem. Agent of India 15, 4
    (1964) 543.
20. V. Kapali and N. Subramanyan, Indian patent, 104522 (1966)
22. V. Kapali and N. Subramanyan, Ind. J. Tech. 5 (1967) 230
24. S. Zaromb, Power Systems for Electronic Vehicle a symposium
25. Gerhard Wild Brett, Klaus Von Grundher and Fredrich Kier Merier
    (Tech, Hoehsuch, Mutrich, Ger), Werkst Korros, 18 (1967) 217.
    (1969) 305.
28. K. Musa Yoshi, K. Simizok and J. Katofs, J. Electro Chem. Soc. of


59. K. B. Sarangapani, V. Balaramachandran, V. Kapali, R. Arghode, S. Venkatakrisna Iyer, M. G. Portar and K. S. Raja Gopalan,


79. O. E. Offiong and S. Martelli, Antifungal and Anti bacterial activity of 2- Acetyl pyridine (4-Phenyl thiosemicarbozone) and its Metal II Complexes II Armaco, 47 (1992) 1543.
