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Aqueous Corrosion of AA-2024 By Zinc Coated

Steel Fasteners

presented by

Mahesh Rajayya

has been accepted towards fulfillment of the requirements for

Master's degree in Materials Science

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AQUEOUS CORROSION OF AA-2024 BY ZINC COATED STEEL FASTENERS

BY

MAHESH RAJAYYA

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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ABSTRACT

AQUEOUS CORROSION OF AA-2024 FASTENED WITH Zn COATED STEEL FASTENERS

Zinc is more widely used as a protective coating for steel in automotive and aircraft industries, but cadmium has been preferred in aircraft structures for various reasons. However, cadmium has several disadvantages over zinc coating which are environment related. The parts which are made of AA-2024 fastened with zinc coated steel fasteners have been found to suffer from serious corrosion attack. The corrosion behavior of AA-2024 fastened with zinc coated fasteners should be understood properly before choosing the proper coating material. The zinc coating on the fasteners is to anodically protect the aluminum alloy from the corrosion, because the coating is consumed and rapid corrosion of aluminum alloy results.

A cyclic wet/dry exposure test with sodium chloride solutions, galvanic and dripping diectrolyte experiments are conducted to observe the corrosion behavior. The parameters of the experiments are explained, and the performance of the exposed metals are reported in terms of weight loss and galvanic currents observed. Dedicated

to

My Father, Mother and Sister

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1. INTRODUCTION:

This thesis describes the corrosion behavior of aluminum alloy (AA-2024-T3) with zinc- coated steel fasteners, with or without the presence of chloride ion. To evaluate their use as an alternative to cadmium on fasteners, the properties (especially corrosion resistance) of zinc coatings are examined. The plating catholically protects steel bolt and prevents galvanic corrosion at contacts with aluminum alloy. Zinc is the more widely used coating for steel but cadmium has been preferred in aircraft structures for its excellent corrosion resistance. However it suffers from three major draw-backs:

1) Its ions are toxic, the body accumulating the metal from very low dose rates,
 2) Cadmium can embrittle high strength steels,

3) The coating process is costlier, hence electro-plating is put out of business. Hence, in order, to find a substitute for cadmium coatings, zinc coatings are considered. Zinc-coated fasteners used in automotive industries, but these fasteners are inferior to those of cadmium coated ones, with respect to corrosion.

In order to investigate the corrosion mechanism of zinc-coated steel fasteners with AA-2024, galvanic compatibility tests and alternate immersion cycle tests have been found useful, because these tests accelerate the corrosion process and obtain the results in a short period of time. The other advantage of these tests is the condition used in operation can be reproduced.

When zinc-coated bolts and aluminum alloy plate are immersed in an ele-

ctrolyte, and elctrically connected, a galvanic current is produced. Hence by measuring the galvanic current as a function of time and calculating the weight change of aluminum alloy electrode, the galvanic compatibility of aluminum alloy with zinc-coated steel fasteners can be assessed. Zinc coating protects aluminum alloy for the most of the exposure period. When the zinc coating corrodes, it will eventually expose the underlying steel metal surface which leads to the galvanic corrosion of aluminum alloy. The results obtained from the galvanic experiment reveal the same.

By measuring the weight loss of the exposure period, the exact corrosion damage occured to aluminum alloy can be calculated. The corrosion test on the bolted assembly of aluminum alloy and fastener is also performed. Alternate immersion cycle test is chosen for this purpose. The results obtained by alternate immersion tests are in parallel with the results obtained from the galvanic experiment. To substantiate the above results from the above experiments, a simple test is conducted, in which the electrolyte is allowed to drip on the galvanized sheet and the same solution then made to fall on the aluminum alloy plate. The weight loss results indicate that aluminum alloy is corroded by ferrous ions which are dissolved from the galvanized steel sheet.

A model is proposed for the corrosion mechanism of the aluminum alloy with zinc coated steel fasteners. Furthermore, some suggestions have been made for the future work to minimize the galvanic corrosion of the fastened assembly.

2. BACKGROUND:

Although the corrosion phenomenon is well understood by aircraft manufacturers and operators, most current aircraft types continue to exhibit many of of the fundamental corrosion defects shown by earlier designs [1]. For many years, the aircraft industry has confronted varied corrosion problems, largely due to the trend toward lighter and higher strength alloys which present increa-

sed corrosion susceptiblity because of their inherent qualities [2].

Aircraft corrosion problems are of three kinds:

1) wet and moist corrosion of unprotected metal,

2) wet and moist corrosion of protected metal subsequent to protective coating failure,

3) corrosion caused by human factors. The corrosion rates of the aircraft are influenced by weather conditions, atmospheric pollu-

tants and the nature of the metal [3].

During operation, the wing stucture of the aircraft which is partly made of AA 2024-T3, is subjected to in-flight mechanical stress and also influenced by ambient conditions such as, atmospheric humidity, sometimes associated with salinity with posssible stagnation of moisture inside cavities not airtight toward the exterior. These ambient conditions are conducive to corosion phenomena, which starts either from external surfaces or from internal ones

subject to moisture stagnation or to other local negative factors, may then rapidly propagate themselves to other areas of the structures [4].

Environmental effects both in air and on the ground are very important factors in determining the ability of aircraft structure to withstand corrosion damage. In a dry weather, corrosion damage is low, however, if the same aircraft is exposed to a wet and saline climate, the corrosion damage is comparatively higher than the previous situation. During the service, moisture condenses and airborne salts tend to accumulate on skin, crevices and in structural enclosed areas such as flap cavities and undercarriage bays [5].

Corrosion of fasteners and adjacent material has long been a problem and its forms are well documented. Seizing and galling make fastener removal difficult and costly. A 1969 survey shows that airlines are spending 50-100 man-hours per airplane overhaul and 14-20 per maintenance check in drilling out "frozen screws". A joint that is completely sealed and protected against moisture seldom gives problems [6].

Most aircraft are protected with a finish coating which, of course, extends over the fastener patterns on the outside skin. If this coating could be kept intact, the countersink areas of the skins in which the fasteners are installed would not be exposed to corrosive media, hence there is no corrosion damage. This of course, is not the case. Most aircraft finish coatings tend to crack around the fastener heads and thus expose countersink areas to moisture and other corrosive media [7].

A common cause for aicraft corrosion is when the paint is deteriorated or plating and protective finishes are damaged and base metal is vulnerable to corrosion. Most common forms of corrosion are electrolytic in nature and once corrosion starts and affects the internal structure of thematerial it can continue even through the surface. It is an unfortunate fact that aircraft materials which require a high strength/ density ratio are generally all susceptible to corrosion

In general the higher the strength the higher the susceptibility to attack.

The most common forms of corrosion which are encountered by aircraft are: [1], [8], [9], [10], [11], [12], [13] :

1. Pitting corrosion:

When corrosion is localized in well-defined areas and such areas are relatively small as compared with the whole surface, they are defined as pits. Their size, depth and number vary tremendously. For pitting corrosion to occur an electrolyte must be present. Oxygen must also be present to initiate the pitting corrosion [12]. Pitting corrosion is observed on wing and fuselage skin, air intakes, and air intake ducts.

2. Intergranular corrosion:

Intergranular or Intercrystalline attack is selective corrosion of the grain boundaries or closely adjacent material without appreciable attack on the grains or crystals themselves. The mechanism probably involves a difference in potential between the grain boundaries and the grain. In alloys such as aluminum-copper, the precipitates such as (CuAl₂and Al_x Cu_x Mg) are cathodic to

the depleted solid solution [13]. This type of corrosion is encountered in wing and fuselage skin parts of the aircraft.

3. Exfoliation corrosion:

Exfoliation, also called layer corrosion or lamellar corrosion, is a type of selective subsurface attack that proceeds along multiple narrow paths parallel to the surface of the metal. The attack is usually along the grain boundaries, but it has also been seen along striations of insoluble constituents that have strung out in parallel planes in the direction of working. Exfoliation is characterized by leafing, or alternate layers of thin, relatively uncorroded metal and thick layers of corrosion product that are more bulky than the metal from which they came [13].

4. Galvanic corrosion

Two dissimilar metals immersed in the same electrolyte will usually differ in potential. If they are brought into contact, current will flow from the less noble or more active metal through the solution into the more noble or less active metal. The amount of corrosion of less noble metal above its normal rate is called galvanic corrosion. For each environment, a galvanic series can be constructed in which metals are arranged in order of their corrosion potential, with the most active metals at the top, and the most inactive metals at the bottom. This type of corrosion is observed in the vertical stabilizer at the tail section and cadmium coated steel jaw bolts under the main wings which results in damage of aluminum alloy parts [10].

5. Stress corrosion:

This type of corrosion occurs in alloys which are susceptible to cracking when under tensile stress and exposed to corrosive environment. The failure may involve an electrochemical mechanism, attack by a molten phase, hydro gen embrittlement, or some other factor [11]. The stress corrosion cracking failures of aluminum alloys are always intergranular [13]. When stressed in the

longitudinal or short transverse directions, stress corrosion cracking occurs when stresses in the order of yield stress are present [12]. This type of corrosion is seen at the tailwing which is connected to the fuselage and stablizer part and fastener assembled areas in the wing part of the aircraft [10].

6. Filiform corrosion:

This is a special case of crevice corrosion that may occur on an aluminum surface under an organic coating. It takes the form of randomly distributed threadlike filaments, and the growth of these filaments probably involves a differential aeration cell. The corrosion products formed raise a bulge in the surface coating, much like molehills in the lawn [13]. This type of corrosion is observed underpaint schemes usually adjacent to fastener heads [14].

7. Microbiological corrosion:

Micro organisms which live and breed in water contained in jet fuel can cause serious corrosion of metal surfaces in integral tanks. The micro-organisms form dark colored slimy sludge in the fuel tanks and can deteriorate fuel tank sealant, protective treatments and corrode tank pipes and wing structure [14].

To achieve the most efficient aircraft structure, it is necessary to use many different metals which are usually in electric contact. Thus there are more chances of having galvanic or electrolytic corrosion, for instance corrosion of aluminum alloy in contact with copper rivets. While it is possible to overcome galvanic corrosion by theoretical approach, it is not possible in practice. The components which are joined by means of fasteners are highly susceptible to corrosion in the area of joint, if materials having a diferent potential are joined to be electrically conductive [15].

For choosing a proper coating for an aircraft fastener application two important factors are considered,

1) corrosion characteristics of the coating material

2) galvanic compatibility with aluminum alloy [16]. Cadmium and zinc coatings are used as the coating material on steel bolts for fastener purpose. The plating catholically protects the steel bolts and prevents galvanic corrosion at contacts with aluminum alloys. When fasteners are exposed to marine atmosphere the corrosion resistance of cadmium coated bolts is better than the zinc coated bolts, and the galvanic compatibility of cadmium coated bolts with AA 7075-T6 is better than the zinc coated ones.

However, cadmium coated bolts tend to suffer from two major draw-backs: cadmium ion is toxic, the body accumulating the metal from very low dose rates [17]; and cadmium can embrittle high strength steels [18] and titanium alloys [19]. The results obtained from the marine atmosphere conflict with the results obtained from the laboratory, hence to formulate a rapid screening test for galvanic compatibility, the currents generated and weight loss which occur in galvanic cells between the bolts and the aluminum alloy electrode are measured [16]. The other test which is employed is alternate immersion cycle experiment. This method was adopted by Standard Pressed Steel Co., in order to screen fastener materials and coatings for their resistance to corrosion and subsequent stress corrosion of loaded bolts. The advantage of the laboratory tests is that the conditions used can be reproduced precisely and the tests could be accelerated, but their relevance must be established by parallel natural environmental tests [20].

Monel fasteners [23] are used with AA-2024 in the wing structure of the aircraft. The purpose of zinc coating is to anodically protect aluminum alloy from corrosion. On exposure to serious environmental conditions, zinc coating corrodes and expose the cathodic steel surface to aluminum alloy. Hence the corrosion of aluminum alloy is accelerated. In C-130 type aircraft [21], high strength aluminum alloys such as 7178-T6 contain appreciable amount of elements other than aluminum. As a result, they develop anode and cathode areas when in contact with an electrolyte. Corrosion usually originates in countersink areas of the fastener holes and first attacks the end grains. The grain boundaries being anodic to the grains, are converted to corrosion products. These products occupy a greater volume than the original metal and exert tremendous pressure with subsequent expansion within the corroded area. The corrosion then follows a laminar pattern along the grain boundary and destroys the structural integrity of the metal.

There is an evidence to substantiate the galvanic corrosion between aluminum and galvanized steel. Overhead electrical power transmission conductors used in Great Britain constructed from aluminum wires centrally reinforced by galvanized steel strands, in a few regions are found to suffer from internal corrosion, which is associated with the presence of chloride ion [22]. The internal corrosion manifests itself localized attack on the galvanized steel strands. The attack is accelerated after the initial deterioration has started. Initially, as the galvanized steel zinc layer is anodic to aluminum, no significant corrosion on the current carrying strands occurs. However when the underlying iron-containing layers are exposed, corrosion of aluminum commences, as it is then anodic to the steel.

3. EXPERIMENTAL SECTION:

3.1 AA-2024 product classification:

AA-2024 is a mill product, and it is in the form of a sheet. The temper classification number is T-3. These alloys are solution heat treated, cold worked, and naturally aged to a substantially stable condition and it also to applies to products that are cold worked to improve strength after solution heat treatment, or in which the effect of cold work in flattening is recognized in mechanical property limits [23].

3.1.1 Composition of AA-2024:

The composition of AA-2024 is given in table 1. [24].

3.1.2 Physical & Mechanical properties of AA-2024 depending on its thickness is given in table 2.

3.1.3 Sampling procedure:

Mill finish flat AA-2024 was sheared to 5cm \times 1.5cm, with long edge parallel to the rolling direction. Specimens were taken from a bulk sample so that they were representative of material that was tested.

3.1.4 Grain orientation:

The grain structure tends to be equiaxial in the longitudinal direction along the sample surface.

Element	Atomic Conc. (%)		
Silicon	0.5		
Iron	0.5		
Copper	3.8-4.9		
Manganese	0.3-0.9		
Magnesium	1.2-1.8		
Chromium	0.1		
Zinc	0.25		
Others Each	0.05		
Others Total	0.15		
Aluminum	90.9-93.2		

 Table 1 - Chemical Composition of AA-2024

 Table 2 - Physical and Mechanical Properties of AA-2024

Density	Specific	Modulus	Modulus		Min	imum Me	chanical I	Prop	erties	s (Ksi)	Endurance	Brinell
	Gravity	Elasticity	Rigidity		Ter	nsion	Compr.	Sh	ear	Bea	ring	Limit	500 Kg
$(\frac{lb}{in^3})$		(psi)	(psi)	F _m	F _{ty}	Elong %	F _{cy}	F _{su}	F _{sy}	F _{bru}	Fbry	(Ksi)	10 mm
0.1	2.77	10×10 ⁶	4.0×10 ⁶	64	42	12-15	40	40	24	124	76	20	120

3.1.5 Location of samples:

Short transverse specimens were taken from the sheet 2 1/2 plate thickness away from a side of a plate (The side of the plate is defined as the edge parallel to the rolling direction).

3.2 Alternate Immersion Test:

3.2.1 Summary of the test:

Alternate immersion test is an accelerated corrosion test to predict the performance of a given material and is a representative of certain natural conditions. This test involved 1 hour cycle, inclusive of a 10 minute period in aqueous solution of different cocentration of sodium chloride followed by a 50 minute period out of the solution, during which samples were allowed to dry. The above cycle was repeated for 7 days i.e., 168 hours.

3.2.2 Apparatus:

3.2.2.a Cycling mechanism:

There were various methods available to achieve the cycling mechanism. In this experiment, the following technique was adopted: The samples were plaaced in a movable rack, it was periodically lowered to and lifted from the beakers containing solution, by means of timer controlled motor as shown in fig.1.

3.2.2 b Rate of immersion:

The rate of immersion and removal of the samples from the solution should be as rapid as possible. It was about 15 seconds in this experiment. Fig.1. Experimental set-up for alternate immersion cyclic test



3.2.3 Specimens:

3.2.3 a Preparation:

The sheared edges of the samples were refinished by wet grinding prior to testing. Since the sheared edge of the samples were subjected to cold working and might possibly fracture the edges, they were polished. Mill scale on the as-received surface should be removed by polishing. All the surface of the samples including the edges, was surface finished with 240, 320, 400 and 600 size grit paper. Then they were further surface finished with 1, 0.3 and 0.05 micron size iron-free aluminum oxide abrasive powder in the lapping wheels. Care must be taken to avoid excessive heating during surface preparation because this might include undesirable residual stresses and in some cases it might cause metallurgical or chemical changes on the surface.

The edge of the samples were polished in the same way as the faces were. Prior to weighing and measuring, the samples were de-greased with organic solvent such as acetone, then the dimensions were measured to the accuracy of 0.01 mm., rinsed with acetone, and weighed to the accuracy of 0.1 mg. After degreasing the samples were handled with gloves till they were exposed to the solution. Prior to exposure of the samples to the test solution, samples were rinsed with test solution.

3.2.3.b Identification of samples:

Samples were identified by means of notches made around the edges of the specimen as shown in fig.2. The notches were made in such a way that they follow binary code. A reference notch was made either in the lower or upper corner of the specimen. The value of the upper corner notch was zero, whereas the value of lower corner notch was fifteen. The upper or lower edge notches were assigned the following values based on their respective position





the following method was used in identifying value of notches.

The value of the first upper edge notch closest to the upper corner notch was: $2^0 = 1$.

The value of the second upper edge notch closest to the upper corner notch

was: $2^1 = 2$.

The value of the third upper edge notch closest to the upper corner notch was: $2^2 = 4$.

The value of the fourth upper edge notch closest to the upper corner notch

was: $2^3 = 8$.

The reference point for the upper or lower notch was with respect to the hole which is made on the top, to hang the samples.

Similar approach was used to figure out the value of a notch which was made on the lower edge of the sample. Hence with this approach thirty samples were identified without any ambiguity.

3.2.3.c Number of replicate samples:

The best practice was to use one sample for each container. Considering the space constraint, experimental design and number of samples tested, it was appropriate to use as many as three samples in each beaker. The two replicate samples which were tested in the same way would give more accurate results about corrosion rate. It was taken care that the samples tested belong to the same batch and the specimen support prevents the specimen from touching each other. 3.2.3.d Size and area of the samples:

The samples were of rectangular shape and the sample size is 5.0×1.5 cm. A hole is made on the sample and the diameter is 3.0 mm. The total surface area exposed to the sample is given by the following equation,

$$A = 2 (lw + wt + lt - \pi r_1^2) + 2\pi r_1 t = 2 (lw + wt + lt) - 2\pi r_1 (r_1 - t)$$

In case of sample having two holes for fasteners and one hole for hanging it, the total surface area exposed to the solution would be,

A = 2 (lw + wt + lt)
$$-2\pi r_1^2 - 4\pi r_2^2 + 2\pi r_1 t + 4\pi r_2 t$$

= 2 (lw + wt + lt) $-2\pi (r_1^2 + 2r_2^2) + 2\pi t (r_1 + 2r_2)$

where,

I - length of the sample,

w - width of the sample,

t - thickness of the sample,

r,- radius of the hole to hang the sample,

 r_2 - radius of the hole to clamp the fasteners.

3.2.3.e Mounting of the samples:

The support device and container should not be affected by or cause any contamination of the solution. The method of supporting should be designed to insulate the specimens from touching each other physically or electrically.

The shape and size of the specimen supports and holders should be such that:

1. They avoid, as much as possible, any interference of free contact of the specimen with the salt solution.

2. They don't obstruct air flow over the specimen, thereby retarding the drying rate.

3. Drainage from one sample does not directly contact any other sample.

3.2.4 Test Solution:

3.2.4.a Volume of the test solution:

The volume of the test solution should be large enough to avoid any appeciable change in its corrosivity during the test by means of accumulation of corrosion products that might affect further corrosion. The volume of solution/specimen area was 28 ml./ cm².

3.2.4.b Aeration of solution:

The solutions which were employed in this test were not de-aerated and the test simulates the actual service condition in which the material would be exposed.

3.2.4.c Temperature of the solution:

The temperature of the solution was around 23 +/- 1.

3.2.4.d Evaporation loss of the solution:

The average evaporation loss was 1 - 1.5% of total volume of solution. The loss was taken care by means of adding distilled water NOT the salt solution, everyday. The simple way of doing this was to refill the solution to a liquid line and refill to that line everyday.

3.2.4.e Air circulation:

It is an important factor, because it affects both the rate at which the samples dry and the evaporation loss of water from the solution. Forced air blast was avoided because of the difficulty in maintaining uniform drying of the samples. Stagnant air condition was also avoided.

3.2.4 f Test duration:

The duration of the test was based on the inherent resistance to corrosion of the alloy, configuration of the test specimen and the nature of the test solution. In general, the duration of the test should be as long as possible, commensurate with the resistance of the material under the test. The minimum duration of the test in hours was approximately 50 divided by the expected corrosion rate in millimeters per year. The duration of the test was 168 hours. 3.2.4.g Cleaning of the samples after experiment:

The following solution was employed in cleaning the corroded samples:

Chromic acid: 20 grams

Phosphoric acid: 50 milliliters

Water: 1000 milliliters

Temperature of the solution: 80 ° C

The samples were placed in the solution for about 5 minutes and then washed with conc. nitric acid for about a minute. Then they were rinsed with distilled water to remove the loose coating on the sample surface. Then they were weighed to the accuracy of 0.1 mg.

3.3 Potentiostatic Anodic Polarization Measurement: [26]

3.3.1 Apparatus:

The test cell was constructed of following items:

- 1) Working electrode
- 2) two auxiliary electrodes
- 3) reference electrode with a salt bridge connection.

A suitable cell is shown in fig. 3, a round bottom flask has been modified by the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes and thermometer. The salt bridge separates the bulk solut-



Fig. 3. Corrosion cell for potentiostat experiment [25]

ion from the saturated calomel electrode.

Potentiostat:

A potentiostat that will remain as electrode potential within 1mV of a preset value over a wide range of applied currents should be used. For the type and size of standard specimen supplied, the potentiostat should have a potential range from -0.6V to 1.6V and an anodic current output range from 1.0 to $10^5 \,\mu$ A.

3.3.2 Anodic polarization circuit:

A schematic anodic polarization wiring diagram is illustrated in fig. 4. The working electrode was a thin strip which was cut from the AA-2024 plate. The auxillary electrodes were two high-density graphite rods. At the end of every run, the rod was scrubbed with 400 size grit paper. The reference electrode was a saturated electrode calomel electrode.

3.3.3. Experimental prceedure:

The temperature of the solution was maintained around 30° C. The oxygen level in the solution was reduced by means of bubbling nitrogen gas for 30 minutes. The working electrode was prepared 1 hr before the experiment. The samples were wet ground 240- grit SiC paperand wet polished with 600 - grit SiC paper until previous coarse scratches were removed.

The dimensions of the sample were measured to the nearest 0.01 mm. Then they are degreased. The sample was mounted with the help of a rubber gasket. Then sample was transferred to the corrosion cell and the salt bridge probe was adjusted so that it was 2 mm or 2 times the dip diameter.

The open-circuit specimen potential was recorded after 55 min imersion. Start the potential scan 1 hour after specimen immersion. The potential step of 50 mV was used every 5 min., the current value was recorded at the end of each 5 minute period. These steps were were repeated until a potential



Fig. 4. Anodic polarization wiring diagram [26]

•

+1.6 V SCE was reached.

Then using the data obtained from the experiment, a plot was made. The plots obtained from this experiment is given in the results section.

3.4 Galvanic Experiment:

A galvanic current was generated when dissimilar metals immersed in an electrolyte are electrically connected. The measurements of current generated and weight loss occur in galvanic cells between zinc coated steel electrode and aluminum alloy electrode was shown to be a useful and very rapid screening test for galvanic compatibility.

To assess the compatibility of the zinc coated bolts with AA-2024, galvanized steel plate was kept at a fixed distance (about 40 mm) from AA-2024 2024 in aqueous chloride solution, electrical connections were made through the galvanized steel electrode and AA-2024 electrode to a multimeter. The voltage generated was continuously recorded for every 8 hours till 48 hours period and the weight change of AA-2024 electrode was then determined.

3.5 Dripping Electrolyte / Water Experiment:

This was a very simple and efficient method to ascertain the compatibility of zinc coated steel fasteners with AA-2024. In this experiment the electrolyte or distilled water was made to fall on the galvanized steel sheet, and then eventually drips on AA-2024 plate. The flow-rate of the electrolyte was regulated by means of a glass stopper. At the end of the experiment aluminum alloy plate was cleaned by chemical means, accurately weighed and the corrosion rate was determined. (Experimental set-up for the experiment is shown in fig.5)



Fig. 5. Schematic diagram for dripping electrolyte experiment

4. Results & Discussions:

4.1 Alternate Immersion Experiment:

The corrosion rate is calculated from the following equation:

The average corrosion rate (in mpy) = $(K \times W) / (A \times T \times D)$

where,

K - a constant, 8.76 x 10⁶ in millimeters per year unit,

T - time of exposure in hours to the nearest 0.01 h,

A - area in cm^2 to the nearest 0.01 cm^2 ,

W - mass loss in grams,

D - density in g/ cm^3 (2.77)

The results from the alternate immersion experiment are listed in Table 3 & Table 4. By observing the Table 3., it is evident that zinc ions are not responsible for corrosion of aluminum alloy. The effect of zinc ions is well understood by considering the following equation:

Corrosion rate in mpy, at a given concentration of sodium chloride solution

Reduction factor =

Corrosion rate in mpy, at a given concentration of sodium chloride solution

The reduction factor is large at higher concentration of sodium chloride solution, i.e., zinc ions are helpful in reducing the corrosion rate. This effect is not observed at lower concentration of chloride solutions, because of the presence of chloride ions surpass the inhibition effect.

Table 3. Results of weight loss experiment from the alternate

Solution	Additive to the Solution	Weight Loss Area	Corrosion Rate
		$(\frac{mg}{cm^2})$, (mpy)
1 N	none	2.605	19.31
	0.2% ZnCl ₂	0.730	5.416
INACI	0.5% ZnCl ₂	0.841	6.24
01N	none	1.788	13.25
NaCl	0.1% ZnCl ₂	0.539	3.996
Naci	0.5% ZnCl ₂	0.791	5.871
	none	0.799	5.923
· 0.01 N	0.1% ZnCl ₂	0.524	3.891
	0.2% ZnCl ₂	0.819	6.075
NaCi	0.5% ZnCl ₂	0.854	6.329
	Zn metal	0.700	5.190
0.001 N	none	0.253	1.880
NaCl	0.5% ZnCl ₂	0.873	6.480
	none	0.083	0.61
Distilled	6.6% ZnCl ₂	1.377	10.21
Water	0.66% ZnCl ₂	0.840	6.230
	0.066% ZnCl ₂	0.797	5.71

% of ZnCl ₂ in the Chloride Solution	Concentration of Chloride Solution	Reduction Factor
0.1	0.1 N	3.317
	0.01 N	1.522
0.2	1 N	3.5659
	0.01 N	0.975
0.5	1 N	3.095
	0.1 N	2.258
	0.01 N	0.9358
	0.001 N	0.2901

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Fig. 6. Effect of concentration of NaCl with/without ZnCl₂ on corrosion

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of AA-2024





By observing the scanning electron micrographs, it is easy to judge the extent of damage occurred to the samples. The pitting is extensive at higher concentration of chloride solution without zinc chloride. The pitting damage is comparatively very less for a sample maintained in same concentration of sodium chloride solution with zinc chloride in it. This could be easily understood by observing fig 7 to fig 11.

The results of alternate immersion test conducted on assemblies of zinc coated bolts fastened into aluminum alloy plate are listed in table 5. The results indicate that as the zinc coating is slowly removed, vigorous corrosion of aluminum alloy results. As it can be seen in the fig. 12 & 13, the region under zinc coated steel bolt is protected, but the area around the bolt is subjected to galvanic corrosion. The corrosion damage sustained by the fastened assembly of zinc coated bolts on aluminum alloy is more at higher concentration of sodium chloride.

4.2 Galvanic experiment:

The results from the galvanic experiment is listed in table 6. As observed from fig.14, the voltage changes with respect to time. At the initial periods, when the alloy is cell anode and galvanized steel sheet is cathode, the value of the voltage is -0.5233V. After 48 hours the voltage reading was -0.498V. The value of the voltage tend to drop and attains a plateau after some time. As the voltage tend to drop, aluminum alloy electrode tends to be more anodic, Whereas the results from the lower concentration indicate that, there is a drop of potential difference, but it is not as steep as it is in the case of higher concentration.



Fig. 7. Optical micrograph of an uncorroded sample of AA-2024 etched

with Keller's reagent (450 X)

Fig. 8. Scanning electron micrograph of AA-2024 maintained in 0.1N

NaCl without $ZnCl_2$ (250 ^X)

Fig. 9. Scanning Electron micrograph of AA-2024 maintained in 0.1 N

NaCl with 0.1% ZnCl $_{\rm 2}$ (250 $^{\rm X}$)





Fig. 10. Scanning electron micrograph of AA-2024 maintained in 0.01 N

NaCl without $ZnCl_2$ (250 ^X)

Fig. 11. Scanning electron micrograph of AA-2024 maintained in 0.01N

NaCl without ZnCl_2 (250 ^X)





Fig. 12. Optical micrograph of a corroded sample of AA-2024 fastened

with zinc coated steel fasteners kept in 0.01N NaCl ($250 \times$)

Fig. 13. Optical micrograph of a corroded sample of AA-2024 fastened with zinc coated steel fasteners kept in 0.001 N NaCl (250 ^X)





Fig. 14. Time-Voltage plot of galvanic experiment of AA-2024 and galvanized steel sheet maintained at various concentrations of sodium chloride



Table 5. Results of alternate immersion test of AA-2024 fastened with zinc-coated steel fasteners

Solution conc.	Weight loss/ Area (mg/cm ²)	Corrosion Rate (mpy)
0.01 N NaCl	0.8675	6.21
0.001 N NaCl	0.686	4.915

Table 6. Results of weight loss of AA-2024 from galvanic experiment

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Solution Concentration	Weight loss/Area (mg/cm ²)
0.01 N NaCl	7.3
0.001 N NaCl	4.8

The weight loss results indicate the same. There is a considerable amount of weight loss at aluminum alloy electrode at higher concentration of chloride solution than in the case of lower concentration.

4.3 Dripping electrolyte :

The results from the experiment reflect the same as those of alternate immersion and galvanic experiment. By observing the corroded sample, it is evident that, as the zinc coating is slowly removed, ferrous ions come into contact with aluminum alloy electrode resulting in serious corrosion of aluminum alloy (fig. 16). The experiment conducted with distilled water explains that, after the subsequent removal of zinc ions from the galvanized sheet, ferrous ions are dissolved in water and they cause extensive damage to the aluminum alloy. The weight loss calculations indicate that, a substantial portion of aluminum is removed by ferrous ions. The weight loss is directly proportional to the concentration of the solution employed for the experiment. By observing the table. 7, it is evident that, the corrosion rate increases rapidly with the conccentration of the solution.

4.4 Potentiostat experiment:

The experiment is conducted to evaluate, whether zinc ions are responsible for corrosion of aluminum alloy or not. The results indicate that, zinc ions are not responsible for corrosion. By observing fig. 17, it is observed that the polarization curve for the solution without zinc chloride is more steep comparebed to the solution with zinc chloride in it. The solution without zinc chloride is more corrosive than a solution without zinc chloride.

The slope of the polarization curve is quite same for both solutions during the initial part of the experiment., at current density value of 140 mA/cm², the



Fig. 15. Optical micrograph of the corroded AA-2024 from dripping

distilled water experiment (250^X)

Table7. Results of weight loss of AA-2024 from dripping electrolye/distilled water experiment

Solution cocentration	Weight loss (mg/cm ²)
0.01 N NaCl	7.1069
0.001N NaCl	3. 847
NIL	1. 275

Fig. 16.Anodic polarization curve of AA-2024 with/ without ZnCl₂

maintained at 0.1N NaCl



tendency of the curves changes. The curve for the solution without zinc chloride becomes more active, which means that zinc ions are helpful in protecting the aluminum alloy.

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5. Conclusions:

1) The results from the alternate, galvanic and dripping electrolyte experiment reveals the fact that zinc coating catholically protects aluminum alloy for the most of the exposure period. With some of the coating partially or completely consumed, exposing steel layer to aluminum alloy, which leads to the corrosion of the latter.

2) The extent of damage incurred by the aluminum alloy varies with concentration of the electrolyte. The higher the concentration, higher the corrosion rate of aluminum alloy.

3) The results of dripping water indicates clearly that, the water which falls from the galvanized plate is not corrosive during the initial period, that indicates that zinc ions are protective to aluminum alloy. After, the coating is consumed ferrous ions are exposed, and initiate galvanic corrosion.

4) Zinc coating is found to have good corrosion resistance property, and the application of the coating is limited by the environment conditions. By observing the advantages and disadvantages of zinc coating, one has to make a proper choice of coating material depending upon the application. Since cadmium coatings of sufficient thickness are rarely produced (becuse they are expensive), galvanized coatings are preferred to cadmium coatings in indutrial application.

5) The corrosion problem encountered by A-10 aircrafts, is similar to the galvanic corrosion of zinc-coated bolts and AA-2024.

6) The galvanic corrosion of AA-2024 fastened with zinc-coated bolts could be minimized by using a proper coating to aluminum alloy surface.

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