CHAPTER V

SUMMARY

SUMMARY

The work has been devided into following chapters :

Chapter - I	: Introduction
Chapter - II	: Object
Chapter - III	: Experimental
Chapter - IV	: Results and discussions

Chapter - I

Deals with the introductory review of cooling waters and its associated problems. The problematic aspect of corrosion and system of control in cooling water has been discussed in detail.

Chapter - II

Deals with the object of the study. The investigation was aimed to highlight following points:

1. Inhibitor efficiency and its optimum concentration in cooling water.
2. Nature of additives.
3. Effect of surface treatment on inhibitor efficiency.
4. Corrosion study of flowing water at the plant level, which can provide comparative picture of corrosivity, fouling, scaling and pitting with respect to actual cooling waters which have been treated by additives

and makeup water. Thus a system of assessing the effect at the stagnant waters in contrast to flowing waters will too be available.

Chapter III

Deals with experimental part of work. A detailed study of the impact of more prevalent chemical additives in the corrosion inhibition efficiency point of view was performed. The Cooling waters selected from various plants were as follows:

1. Ammonia 2. Urea 3. Ammonium sulphate
4. Caprolactam and 5. Makeup water

The metal selected for the study was mildsteel conforming to IS 1079.

It was aimed to select some of the products which were prescribed as additives to the cooling waters. The experimental investigation were carried out at various concentrations, pH, fraction of time etc. to evaluate their impact on extent of corrosion or general degradation of the metals the waters come in contact with, and assess the corrosion rate and inhibiting efficiency with respect to blank waters. The following additives were selected for study.

1. Benzo triazole
2. Corobit EPA-529
3. Aquacid-105 (H.E.D.P.)
4. Diammonium hydrogen orthophosphate
5. Mixed : Aquacid-105 + Diammonium hydrogen orthophosphate

The experimental conditions kept for the aforesaid study were as follow :

Condition : Stagnant
Temperature : 35 ± 1°C
Material : Mild steel
Duration : 3, 7, 15, 30 days

Apart from the above experiments, the following experiments were also performed:

1. Effect of surface treatment with 2% Benzotriazole
2. Anodic polarisation study to explain the nature of additives
3. Direct study with some flowing plant waters, for their corrosive effect. For this purpose Ammonia and Caprolactam plant waters were selected from three perspectives.
    a) Inlet to cooling tower
    b) Outlet to cooling tower
    c) Makeup water

Chapter IV:

Deals with results and discussion of experimental data.

The results obtained are highly encouraging and thrilling. Much data hither to unobserved have been accumulated from this investigation.

It is proposed to make a thorough assessment of all the comparative results and to evolve a system of evaluation and generalization. In otherwords, the attempt will be to correlate the various factors and generalize conclusions. The study is expected to throw good light, since such detailed studies seem to have not been that elaborately and seriously undertaken in the past. It is also expected to generalize optimum conditions for cooling water additives in respect of the chemical constitutional and physical parameters. The interpretation of the results may lead to the following multidirectional impact.

I. INHIBITORS

(i) Benzotriazole

The metal used generally in heat transfer system is iron, which have incomplete d-orbitals, which can accept and share electrons. The process of chemisorption includes the sharing, or transfer of charge, usually accompanied by a high heat of adsorption. Organic inhibitor such as benzotriazole which have polar group with atom such as Nitrogen having electron pairs available for forming chemisorption bonds. Thus, the inhibitor is the electron donor, and the metal is electron acceptor. Thus in all the five cooling waters positive results of inhibition efficiency is due to formation of film due to complex formation between iron and benzotriazole. The complex formation is confirmed by many workers by X-ray diffraction.

It is observed that with increasing concentration of benzotriazole, the inhibition efficiency increases. It is also supported by existing literature that increased adsorption occurs with higher concentrations of benzotriazole and the existing film may be thicken or unprotected area may be covered. more than 2 % benzotriazole is not required for maximum efficiency.

Benzotriazole with 0.1 % concentration can serve the purpose of tunning the ammonia plant cooling waters least corrosive, with 0.5 % concentration for ammonium sulphate cooling waters and about 2.0 % concentration for other three cooling waters.

The complex film formation activity brings about release of H^+ ions from the benzotriazole moiety resulting into variations in the pH values of cooling waters whose blank pH values were adjusted to be around 7.0.

It is observed benzotriazole addition in cooling water shows fall in pH indicating it is present as an anion.

The equation proposed is as under :

$$C_6H_4N_2NH = C_6H_4N_2N^- + H^+$$

The decrease in pH should show increase in corrosion rate, but corrosion rate decreases even with decrease pH. So the role of benzotriazole as inhibitor can not be the result of changes in pH of aqueous solutions. Hence, its action as an inhibitor must depend entirely on some other mechanism such as film formation.

By anodic polarisation study of benzotriazole we observed benzotriazole has greater inhibition of anodic process.

The other analytical data of the cooling waters do not seem to be effective in modulating the inhibition characteristics of benzotriazole. A comparative evaluation of the inhibition efficiency in reducing corrosion in terms of the concentration of the inhibitor and exposure times is given in Table 79.

In an overall manner, a 2.0 % concentration of benzotriazole seems to be very effective though in specific cases even lesser concentrations can be workable.

Table 79

Comparative Evaluation

Inhibition Efficiency

Cooling waters	Maximum inhibition efficiency % concentration (%) of inhibitor Exposure time in days 3	7	15	30
Ammonia Plant	1.0	0.2	2.0	2.0
Ammonium sulphate plant	0.5	0.5	1.0	1.0
Urea plant	1.0	2.0	2.0	2.0
Caprolactam plant	2.0	2.0	2.0	2.0
Makeup	2.0	2.0	2.0	2.0

(2) Corobit EPA-529

The second inhibitor studied was Corobit EPA-529 with all the five cooling waters. Corobit EPA-529 sold commercially as 'corrosion' and 'scale inhibitor' for open recirculating cooling water systems, is basically a synergestic blend of organophosphonate, zinc and dispersing agent. It is well known for high sequestering value, defloculation property, and crystal distortion property. The overall effective range of pH is found to be from 8.0 to 9.0 in different cooling waters taken for present study.

The maximum efficiency of 100.0 % was achieved with 0.1 % concentration after three days exposure with ammonia plant cooling water. The maximum efficiency is achieved at all the exposure days with ammonia plant, compare to all other plants. The maximum overall efficiency achieved is by 0.1 % concentration in majority of cooling waters is a economically a favourable point.

At more than 0.1 % concentration more organophosphonate is available to react with Ca^{+2} and Mg^{+2} and reduces the hardness of water and increases the corrosion rate. The dispersing agent present in corobit EPA-529 in general manner may work as adsorption type of inhibitor and its effectivity increases in presence of zinc and organophosphonate. At higher concentration of corobit EPA-529 more free dispersant available which work as an anti-precipitant, because a complex forms between calcium ion and carboxyl group. This complex formation reduces the strength of corrosion inhibiting ions and by that way increases the corrosion. so lesser concentration of 0.1 % concentration give better protection.

The anodic polarization study indicate corobit EPA-529 work as a cathodic inhibitor. Due to sequestering ability of phosphonates, the zinc ions present in a complexed form limiting the rate of reaction of zinc with hydroxyl ions. Therefore, useful concentration of zinc retained in solution for longer time and the slow deposition rate of zinc hydroxide allows the formation of a thin hydroxide film at the surface giving desired corrosion resistance.

For at a glance general view, in table 88 is given a comparative evaluation in terms of % inhibition efficiency at the specific concentration of the corobit inhibitor for all the exposure times. It can be easily seen that by and large the most efficient concentration is 0.1 %.

Table 88

Comparative Evaluation

Inhibition Efficiency

Cooling waters	Maximum inhibition Efficiency % concentration (%) of inhibitor Exposure time in days 3	7	15	30
Ammonia plant	0.1	0.2	0.5	0.2
Ammonium sulphate plant	0.1	0.1	0.1	0.1
Urea plant	0.1	0.1	0.2	0.2
Caprolactam	0.1	0.1	0.1	0.1
Makeup	0.1	0.1	0.1	0.1

It may also be noted that while 0.2 % concentration of the corobit inhibitor works better in some exposure times, the margin is still in favour of 0.1 % concentration.

The maximum efficiency achieved differs from cooling water to cooling water and a summary is given in Table 89 for at a glance review.

Table 89

Maximum Efficiency in %

Cooling water plants	Exposure time in days 3	7	15	30
Ammonia	100.0	98.07	99.06	99.64
Ammonia sulphate	70.41	75.47	81.63	88.92
Urea	78.51	81.19	87.10	86.63
Caprolactam	74.24	81.38	83.33	84.78
Makeup	57.04	59.16	66.76	33.07

The maximum efficiency achieved by corobit-EPA-529 is with ammonia plant cooling water system.

(3) Aquacid-105

The third inhibitor taken for study is aquacid-105 with all the five cooling waters. Aquacid-105 is commercially available 'corrosion' and 'scale inhibitor'. Aquacid-105 formulation consist 50 % active matter as 1,hydroxy ethylidene 1,1,diphosphonic acid i.e. organophosphonate. The behaviour of aquacid-105 is found strange from corrosion inhibition point of view.

Aquacid-105 has got better hydrolytic stability, threshold inhibition, sequestering property, defloculation and crystal distortion property. It prevent corrosion by adsorption type of inhibition mechanism i.e. chemisorbed layer on metal surface. But it is observed from the study that aquacid-105 can not be used alone as corrosion inhibitor, because it is found that it has tendency to sequester Ca^{+2}, Mg^{+2}, Fe^{+2}, Fe^{+3} etc. to form the soluble complexes and by that way it increases corrosion rate. It is observed that with increasing concentration from 0.1 to 5 % of aquacid-105 corrosion rate increases in all the cooling waters. Similarly corrosion rate decreases with increases exposure days in all the concentrations of aquacid-105. At prolonged exposure it has tendency to form tight adhesive film on the metal surface which was observed during the study. The pH values, however, show a pattern of increasing sequence as the exposure time increases. One more point of interest is that with lower concentration of aquacid but with higher exposure time, the pH values increases more than those corresponding with higher concentration.

(4) <u>Diammonium hydrogen orthophosphate</u>

The fourth inhibitor taken for study is DAP with all the five cooling waters. Phosphates are found to be very good corrosion inhibitor by forming film on the metal surface. So sometimes phosphates are utilised for prefilmining of various equipments. Now over all efficiency was found excellent with DAP. The 1 % and 2 % give very good protection by forming very tiny film on the metal surfaces. Except urea plant, the inhibition efficiency is found excellent in other four cooling waters. Various scientists have suggested the mechanism of phosphate for corrosion prevention. They are of the opinion that the deposition of cathodic film limits the diffusion of oxygen to metal water interfaces and the precipitation of insoluble ferric compound over anodic sites. With 0.5% concentration efficiency is achieved 90 % and for any process plant with limited concentration to have better efficiency is a positive factor.

From comparative evaluation (Table 102) it can be easily seen that by and large the most efficient concentration are 1 and 2 %.

Table 102

Comparative evaluation inhibition efficiency

Cooling water plants	Maximum inhibition efficiency (%) Concentration % of inhibitor exposure time in days			
	3	7	15	30
Ammonia	1	2	2	2
Ammonium sulphate	1	2	2	1&2

Urea	0.5	2	0.2	0.1
Caprolactam	1	1	1	1&2
Make-up	1	1	2	2

The summary of maximum efficiency achieved is given in table 103 for at a glance review.

Table 103

Maximum efficiency %

Cooling water plants	Exposure time in days			
	3	7	15	30
Ammonia	95.26	96.21	98.92	98.94
Ammonium sulphate	97.91	97.38	94.87	wt.gain
Urea	29.17	57.86	28.33	57.14
Caprolactam	95.19	97.06	96.12	wt.gain
Make-up	96.98	96.31	97.85	98.60

(v) Aquacid + DAP

The fifth inhibitor taken for study is the mixed system of Aquacid-105 + DAP. The behaviour is found strange. It is observed that instead of corrosion inhibitor it works as corrosion accelerator. It is seen that corrosion inhibition was found greater in combination of 0.1 % Aquacid-105 with

DAP compare to the DAP combination with 5 % Aquacid-105. The combination of 0.1 % Aquacid with DAP shows cathodic inhibition but combination of 5 % Aquacid with DAP shows anodic inhibition. On longer exposure time 0.1 Aquacid +DAP mixture give compact film on metal surface. In overall performance 0.1 % Aquacid + 0.5 % DAP give very good efficiency. The comparative evaluation in terms of % inhibition efficiency at the specific concentration of the mixed (aquacid-105 + DAP) for all exposure time is given in below (Table 107).

Table 107

Comparative evaluation

Inhibition efficiency

Cooling water	Maximum inhibition efficiency (%) concentration (%) of inhibitor (Aquacid + DAP) exposure time in days			
	3	7	15	30
Ammonia	N	0.1+0.5	0.1+0.5	0.1+0.5
Ammonium sulphate	N	0.1+0.1	0.1+0.1	0.1+0.5
Urea	0.1+1	N	0.1+0.5	0.1+1
Caprolactam	0.1+0.1	0.1+0.5	0.1+0.5	0.1+0.1
Make-up	N	0.1+0.5	0.1+1	0.1+0.1

N- Negative efficiency

The maximum efficiency achieved differs from cooling water to cooling water and a summary is given in below table for at a glance review.

Table 108

Maximum efficiency in %

Cooling water plants	Exposure time in days 3	7	15	30
Ammonia	N	8.90	30.16	65.65
Ammonium sulphate	N	5.85	32.23	23.21
Urea	36.03	N	76.45	83.47
Caprolactam	7.77	59.77	70.49	85.14
Make-up	N	44.55	47.98	66.40

N- Negative efficiency

From above (Table 108) it is concluded that overall protection by mixed system is higher in caprolactam water compare to other cooling waters.

II. Effect of surface treatment on inhibitor efficiency with 2 % wt/vol Benzotriazole

With a view to explore the inhibitor efficiency of 2 % benzotriazole with rough (treated with IS grit-60) and smooth surface (treated with IS grit-240) of mild steel specimen, The synthetic cooling water was taken and under same experimental conditions cited for inhibitor evaluation with five waters, the experiment conducted. It is observed that at initial stage at 3 days and 7 days exposure the corrosion rate of rough surface was found higher with blank water compare to smooth surface. This is due to rough surface having stresses, scratches etc. favour anodic site formation leads to higher corrosion rate. But at 15 and 30 days there is fall in corrosion rate due to formation of protective layer of corrosion products on the metal surface, which has acted as barrier between water and metal surface.

Regarding inhibitor efficiency it is observed that in both the surfaces inhibitor efficiency increases with increasing in exposure time. While comparing the % inhibitor efficiency at 30 days exposure it is found that smooth surface has higher inhibition efficiency just by 1.26 % compare to rough surface. Hence it is concluded that prolonged exposure of 2% benzotriazole to either rough or smooth surface will not show appreciable change in % inhibitor efficiency.

III Anodic Polarisation study

This study was aimed to decide the inhibition nature of the additives. The polarisation curve of benzotriazole with blank water at concentration of 0.1 % and 2 % shows shift in potential toward anodic direction indicating greater inhibition of anodic process. With increase in concentration shift in pontential toward more anodic side.

The polarisation curve of corobit-EPA-529, at conc. of 0.1% and 5 % with make-up water shows shift in potential toward cathodic direction with respect to blank water indicating greater inhibition of cathodic process. With increasing concentration of corobit EPA-529 more shift in potential toward cathodic direction.

The polarisation curve of aquacid-105 at concentration of 0.1 % shows there is no change in potential either anodic or cathodic direction indicating mixed type of inhibitor. But at concentration of 0.2 % and 5 % there is shift in potential toward anodic direction with respect to blank water. The shift in potential toward anodic direction increases with increasing concentration.

The anodic polarisation curve of diammonium hydrogen orthophosphate with makeup water shows shift in potential toward cathodic direction, indicating greater cathodic inhibition. The increase in concentration from 0.1 % to 2 % more shift toward cathodic direction.

In the anodic polarisation curve of mixed system of aquacid-105 + DAP, at concentration of 0.1 % v/v +0.1 wt/vol, 0.1 v/v + 0.5 % wt/vol, 0.1% v/v + 1 % wt/vol shows shift in potential toward cathodic direction. The cathodic shift increases with increasing concentration of DAP in 0.1 % v/v aquacid-105. While with the system of 5 % v/v aquacid-105 + 1 % DAP the shift in potential is toward anodic direction.

IV Non heat transfer loop

For evaluating water treatment conditions at plant level non heat transfer loop with mild steel coupons was placed in inlet; outlet and makeup water bypass line of ammonia and caprolactam plant cooling water. Average results were computed every month and study is carried out for one full year.

The conclusion made from above study is as follows:

(1) Makeup water of ammonia and caprolactam plant shows positive langlier index for all the samples of 12 months. So it indicate scale foming nature of water hence corrosion rate should fall in negligible corrosion zone but 99 % confidence level of corrosion rate of ammonia plant and caprolactam plant makeup water is 7.91 and 8.07 mpy respectively as shown in (Table 110). But corrosion rate given in the (Table 110) falls under moderate zone.

Table 110

Various parameters of makeup water (99% confidence level)

Makeup water	Hardness / chloride	Alkalinity / Chloride+Sulphate	Corrosion rate mpy
Ammonia plant	3.02	4.01	7.91
Caprolactam plant	3.03	4.15	8.07

The behaviour of higher corrosion rate can be explained as follows:

(1) To make system free from corrosion hardness/chloride ratio of 2.0 and Alkalinity/chloride + sulphate ratio of 5.0 is desired while in make up water of ammonia plant and caprolactam plant hardness/chloride ratio is found 3.02 and 3.03, while alkalinity/chloride + sulphate ratio was found 4.01 and 4.15 respectively.

(2) Langelier positive index will be corrosive if $CaCO_3$ is deposited in non-protective morphology or insufficient carbonate supersaturation to coat the whole system or presence of aggressive ions.

(3) The hidden factor such as organic matter and some kind of algae and slime forming bacteria can have a masking effect on metallic surfaces and promote differential aeration problems, and certain type of bacteria can themselves become involved in the corrosion process causing significant problems.

(4) To keep system free from corrosion the epm (chloride + sulphate/epm (m-alkalinity) ratio of makeup water is 0.1 and pH around 7 and 8 is desired. But in case of makeup water of ammonia plant and caprolactam plant epm (chloride + sulphate)/epm (m-alkanility) was found above 0.5 and pH above 8.0

Regarding corrosion products in supply water Lapidocrocite was found dominant and α-FeOOH and α-Fe_2O_3 existing in small amounts.

The 99% confidence level corrosion rate of makeup water of caprolactam and ammonia plant cooling water with non-heat transfer loop method was found 7.91 and 8.07 respectively after 30 days exposure, but with makeup water in static condition corrosion rate is found 3.75 mpy after 30 days exposure. The higher corrosion rate in non-heat transfer loop is due to velocity. Now the velocity of water disturb the protective film formed and keep the base metal to remain exposed with fresh water enriched with oxygen.

While comparing all the three systems i.e. inlet, outlet and makeup water of ammonia and caprolactam plant, it is observed that in both the cases corrosion rate of inlet system is high compare to outlet and makeup water. The 99% confidence level of corrosion rate is given in below (Table 111).

Table 111

99 % confidence level of corrosion rate in mpy

Plant	Makeup water	Inlet	Outlet
Ammonia plant	7.91	10.59	5.42
Caprolactam plant	8.07	14.01	5.14

The higher corrosion rate in inlet system compare to outlet and makeup water is due to high temperature and process comnamination. The increase in temperature (1) increase the rate of chemical reaction (ii) it lessens the solubility of gases in water (iii) it may effect the solubility of the possible products of corrosion reaction (iv) soften bicarbonate hardness and release CO_2 which accelerates corrosion.

In all the cases i.e. inlet, outlet and makeup water corrosion rate increases with increase in tight scale and corrosion products and loose scales and corrosion products.

In comparision of outlet water of caprolactam plant and ammonia plant with makeup water of both the plants, it is observed that corrosion rate of makeup water is high compared to outlet water, even though makeup water has more positive langelier index compare to outlet water. This can be explained from alkalinity and hardness aspects. Alkalinity of makeup water is high compare to outlet waters and hardness is found less compare to outlet waters. It is well known that hardness imparting corrosion inhibition and alkalinity contribute to corrosion acceleration. This could be due to masking effect rendered by increasing conductivity which subsequently increased the ionic strength.

While comparing outlet water of ammonia plant and caprolactam plant it is observed that corrosion rate of ammonia plant is higher to caprolactam plant. It is clear from (table 112) that hardness of caprolactam plant is high and alkalinity is low compare to ammonia plant. So hardness and alkalinity has direct relation with corrosion.

Table 112

99 % confidence level of cooling water outlet

Plant	Hardness ppm	Alkalinity ppm	Corrosion rate mpy
Ammonia	229.65	65.38	5.42
Caprolactam	397.04	63.75	5.14

It is observed that outlet cooling water of caprolactam plant and ammonia plant shows higher corrosion rate with non heat transfer loop method compare to static condition, this is attributed to the fact that increase in velocity increases the corrosion rate.

Now comparing all the analytical aspect and its relation with corrosivity of water, it can be safely predicted that increasing chloride, sulfate, alkalinity, and dissolve oxygen would accelerate corrosion, where as increase in calcium, buffer capacity, saturation index and exposure time lower the corrosion rate.