CONTROL OF CALCIUM SCALE AND CORROSION OF MEDICAL CITY COOLING WATER SYSTEM USING SULFURIC ACID

Najwa S. Majeed
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

ABSTRACT

This research include a method to control heavy calcium carbonate scale forming and corrosion prevention by the deposition of sufficienty thin protective CaCO3 scale using sulfuric acid(H2SO4) and depending on Ryznar stability index controlling method.

Two samples of water were taken from medical city cooling towers (make up water and circulating cooling water).Their characteristics include methyl –orange alkalinility(M-Alk.),Ca+2 hardness,actual pH(pHa)and total dissolved solids(T.D.S)are determined

Experiments were adapted to show the effect of reducing M-Alk.and pHa of circulating water by the addition of H2SO4 acid on Ryznar stability index(RSI)to approach the desired stability index range in which the tendency of circulating water to form heavy scale or corrosion is very little.

Other experiments were adapted to show the relation between calcium concentration with corrosion rate in MPY(millimeter/year)using a suitable corrosion coupon.

INTRODUCTION

Water– formed deposits, commonly referred to as scale ,can be defined as crystalline growth of an adherent layer barrier of insoluble salt or oxide on a heat exchanger surface(1). The rate of formation is a complicated function of many variables including temperature, concentration of scale–forming Species, ph, water quality and hydrodynamic condition(1).The normal solubilities of scales increase with temperature but a few, such as calcium carbonate and calcium sulfate, have the opposite trend(2). Unfortuntely,these scales are commonly found in cooling water systems.Calcium carbonate is perhaps the most common scale found in medical city cooling towers due to the increase of temperature in summer season which lead to an increase in vaporization rate. As vaporization proceeds the dissolved solids (e.g.,the mineral salts content of water increased also(3).

Protective coating in the form of $CaCO_3$ scale develops by regulating and adjusting the pH, Alk and Ca^{+2} ions maintain a slightly supersaturated solution of $CaCO_3$(4,10). By Such control, a thin, impervious and adherent layer can be deposited on the surface requiring protection. Sulfuric acid is the most common acid used for this purpose due to its accessibility,low cost and minimal secondary problems.

$CaCO_3$ is a general inhibitor that covers both anodic and cathodic areas because its precipitation does not depend on the products of electrochemical reactions(4) , although an alkaline film on the cathodic surface is an added factor favoring precipitation of the $CaCO_3$.

Sheppard and Bacon (5) , Faninet .al(11) ,investigated the use of CaCO3 scale for corrosion prevention in cooling tower systems seving steel equipment ,they found that rising temeratures cause the acual pH of the water to drop at the same rate as the $CaCO_3$ saturation pH, scale of uniform thickness,will be deposited.

Extension of the use of $CaCO_3$ scale for prevention of corrosion and the control of excessive scale deposition has been encouraged by Langelier(6). He advanced the idea of calculated saturation index as a mean of predicting the corrosive or scaling behavior of a natural water.

Ryznar(7) developed Langlier method, he refined the Langlier index to allow for a distinction between two waters having the same Langelier index.

Definition and scope

The most important measurements to characterize the impurities in cooling tower water are:

1. Actual pH(pHa): It was defined as the (-ve) logarithm to base 10 of the hydrogen ion activity,expressed in gm-moles/l, it can be measured by pH –meater tools. It was

measured to mconfirm the corrosive and scaling tendency of cooling water.

2. Alkalinity: Commonly expressed as mg/l (ppm) of $CaCO_3$,it was defined as the capacity to neutralize an acid. It can be measured by titration of a sample with a strong acid. Methyl-orange alkalinity (M-Alk) or total alkalinity, is that necessary to cause aclor chang in the methyl-orange indicator (abouth pH=4.3). M-Alk. Has a fairly good correlation with pH of water and was measured to predict the scaling tendency of $CaCO_3$(4).
3. Total hardness and Ca^{+2} hardness: The original definition of hardness included all polyvalent metal ions capable of precipitating soap. The principal contributors to total hardness are Ca^{+2},Mg^{+2},Fe^{+2},it was expressed as mg/l(ppm) as $CaCO_3$. Water containing up to about 50-75mg/l hardness are considered soft,above 200-300 they are very hard, water in the intermediate range are classifies as hard.Calcium hardness referred to calcium ions concentration present in water,it is important to predict the scaling tendency of $CaCO_3$,it can be measured by titration of a sample with EDTA(Ethylene diamine tetra acetic acid)(4).
4. Total dissolved solids (T.D.S):It can be defined as the total concentration of dissolved salts, which have a variety of effects both individually and through interactions. The effects include increased corrosion in addition to scale and deposit formation.It can be expressed as pmm(mg/l) and measured by laboratory meter device.
5. Saturation pH(pHs):It is the pH value corrected according to temperature, M-Alk.,T.D.S and Ca^{+2} hardness used in calculation of Ryznar stability index as shown latter(7).
6. Sulfate ion ($SO4^{-2}$) ppm: Water of high sulfate ion concentration show strong corrosivity(2), it can be measured using spectrophotometer devices.

Many methodshave been proposed to predict the formation of CaCO3. However,they are all based upon the thermodynamic equilibria of carbonic Acid and alkalinity corrected for temperature and dissolved solids (ionic strength). The more commonly used eqation or index is Ryznar stability index (RSI)(7).Ryznar index is defined as:

$$RSI= 2pH_s-pH_a \qquad (1)$$

Where pH_a is the actual pH measured value of water, and pHs is the pH of saturation calculated from the expression:

$$pH_s=A+B-\log(Ca)-\log(M\text{-}Alk.) \qquad (2)$$

Where A,B are constants related to the temperature and dissolved solids content of water respectively and their values are listed in table (A1,&A2)(7) in the appendix A.

The bracketed values are the ionic concentrations expressed in mg/l. The predictive nature of Ryzner index is shown in table 1(7,12).

Table (1)

Ryznar Stability Index	Tendency of Water
4-5	Heavy scale
5-6	Light scale
6-7	Little scale or corrosion
7-7.5	Corrosion significantly
7.5-9	Heavy corrosion
9 and higher	Corrosion intolerable

This index indicate only the tendency for calcium carbonate to deposit ,not the rate or capacity for deposition.

$CaCO_3$ formation can be controlled by the addition of acids or specific chemicals tailored to inhibit its formation or modify the crystal lattice.

Sulfuric acid which is inexpensive is most often used , its addition reduce the water alkalinity sufficiently to create non-scaling condition and produces salts that are more Soluble than $CaCO_3$.

These salts that can reach satuation and must be controlled to prevent precipitation on heat transfer surface(1).

$$Ca(HCO_3)_2 + H_2SO_4 \text{ ----- } CaSO_4 + 2CO_2 + 2H_2O$$

$CaSO_4$ is calcium sulfate, which is more soluble than CaCO3 by at least a factor of 50(9), this phenomena provides the basis for sulfuric acid addition to control $CaCO_3$ in Circulating cooling water systems.

Calcium sulfate shouid not present a scale problem in cooling system using proper blow down procedures(1).

The normal upper limit for calcium and sulfae concentrations in the absence of inhibitor is expressed by (1):

$$[Ca^{+2}]\times[SO4^{-2}] = 500{,}000$$

Where the bracketed values are the ionic concentrations expressed in milligram per liter.

Referring to above upper limit, the sulfate ion concentration must be periodically determind to control the amount added of H_2SO_4 ,where excess of SO_4^{-2} concentration in cooling water show strong corrosively.

Rate of blow down is the quantity of water bleed of cooling tower to prevent concentration from becoming so high , this rate calculated as follows[3]:

$$Blow\ down\ rate = \frac{E}{N.C.-1} \qquad (4)$$

Where: E: Evaporation rate in m3/hr. and equal to R $\Delta T/560$, R: Re-circulating rate of cooling water m3/hr, ΔT : Differences in temperature between the inlet and outlet water of the cooling tower Co, N.C. Number of concentration of salt, calculated from:

$$N.C = \frac{(Ca^{+2}\ hardness\ in\ cooling\ water)}{(Ca^{+2}\ hardness\ in\ make\ up\ water)} \qquad (5)$$

EXPERIMENTAL WORK

1- Measurements: Two samples were taken from medical city site ,the first is from make-up water and the second from re-circulating cooling water and measuring their following charactericit:

a- pHa values:pH values were determind using electric pH meter model 744(Chemic company) calibrated by standard buffer solutions (pH=4 and 7).

b- M-Alkalinity: It was measured using standard titration method, with sulfuric acid.(8)

c- Ca^{+2} hardness (concentration as $CaCO_3$ in ppm): It was measured using standard titration method, with EDTA solution.[8]

d- T.D.S.: Concetrations of total dissolved solids were measured by T.D.S. Meter (PRESTO-TEK CORPORATION)

2-The second step of experimental work included dosing of known concentration and amount of H2 SO4 into a sample of 50 ml, of re-circulating cooling water,and all characteristics of step-1- ,were re-determind and Ryznar stability Index was calculated to predict the tendency of water and the optimum condition of non or little scaling or corrosion were determined.

3-Thethird step included calculation of corrotion rate in Mpy using corrosion rate in Mpy usig corrosion coupon,the expression used to calculate Mpy is:

$$Mpy = \frac{Mpy = Factor\ x\ wt.loss(mg)}{Days\ exposed}$$

RESULTS AND DISCUSSION

Sample Analysis

The following table is the chemical analysis of the make –up and the circulating water of medical site.

Table (2)

	Make-up	Circulating water
Temperature,F°(C°)	104(40)	80(26.6)
Constituents,ppm (Ca^{+2}) calcium hardness,as $CaCO_3$	186	475
Methyl-orange Alkalinity(M-Alk)as $CaCO_3$	150	267
Total solids(T.D.S)	530	900
Actual pH(pHa)	7.82	8.87

Referring to the characteristis of the make –up and circulating water in table (2)and Ryznzr stability-Index tables,the value for the stability-index(RSI)of the make–up water can be calculated in the following mannar:

RSI=2pH-pHa
pHs=A+B-log(Ca^{+2})-log(M-Alk.)

For make-up water, temp.=104° F, A=1.7 from table (A.1), T.D.S=530 ppm, B= 9.869 from table (A.2), Ca^{+2} hard. =186 pmm , log(Ca^{+2})=2.276, M-Alk.= 150 pmm, log(M)=2.15. With the same manner (RSI) for circulating water can be found.

Table (3) summarized the values of A,B,log (Ca^{+2}),log(m) pHs and RSI for these two samples

	Make-up	Circulating water
A	1.7	1.968
B	9.869	9.895
Log(Ca^{+2})	2.276	2.675
Log(m)	2.15	2.4206
pHs	7.143	6.7674
RSI	6.466 (little scale or corrosion)	4.6(scaling)

Referring to **table (1)**, it would be expected that the make-up water would be slightly scale or corrosion causing the circulating water was scale forming. Then the circulating water will deposit scale in heat exchange equipment.

Effect of H_2SO_4 addition

The scale formation could be controlled by the addition of sufficient acid to reduce alkalinity to approach the desired saturation index. Many experiments were adopted to choose and determine the best concentration and dosing amounts of H_2SO_4 acid.It was found that 5wt% of H_2SO_4 and dosing amount shown in table (4) are the suitable values.

Table(4) pHa,M-Alk,Ca^{+2} and T.D.S values versus H_2SO_4 amount

5 wt.% 0.02N H_2SO_4 amounts ml.(ppm)	pHa	M-Alk. ppm	Ca^{+2}hard	T.D.S
Without H_2SO_4	8.87	267	475	900
0.005(0.97)	8.66	225	350	1000
0.008(1.552)	8.48	200	245	1020
0.015(2.97)	8.3	180	200	1200
0.02(3.88)	8.14	168	170	1200
0.03(5.82)	7.99	160	150	1300

Table(5)Values of pHs and RSI

pHa	M.Alk.	pHs	RSI	Tendency
8.87	267	6.7674	4.6	Heavy scale
8.66	225	6.983	5.306	Light scale
8.48	200	7.187	5.894	Tend to light scale
8.3	180	7.428	6.565	Little scale or corr.(optimum required case)
8.14	168	7.554	6.968	Little scale or corr.(optimum required case)
7.99	160	7.738	7.486	Corrosion significant

Values of M-Alkalinity were plotted versus pHa, pHs and RSI in figs.(1),(2),&(3) respectively.

Field application

Three tests of the data of table (4) were applied practically on medical city cooling tower with a total volume (v)=1000m^3. Table (6) shows the results of practical application of the laboratory test of table(4)

Table(6) Application data

5wt% 0.02n h_2so_4		Cooling water specification				Ryzner Variablees		Tendency
Laboratory reading	Field reading	Pha	M-alk	Ca^{+2}	T.d.s.	Phs	Rsi	
0	0	8.83	270	490	1000	6.8	4.63	Heavy scale
0.008ml	160	8.479	200	250	1020	7.178	5.894	Tend to light scale
0.015ml	300l	8.29	179	200	1200	7.43	6.6	Little scale or corrosion(optimum)
0.02ml	400l	8.15	170	169	1200	7.56	6.97	Little scale or corrosion(optimum)

From Fig(3),it was shown that the stability index of 5.894-6.968 in the circulating water would be satisfied and this could be obtained by redusing its methyl orange 168-200 ppm as shown in Fig(1), corresponding to a pHa of 8.14-8.48 and Fig.(2), corresponding to a pHs of 7.187-7.554.

Corrosion Results

Laboratory results of corrosion rate using corrosion coupon technique tabulated in table (7). The MPY the unit of corrosion rate calculated from the equation:

MPY=areafactor*wt.loss/days exposed …..(6)

Where 1 MPY=0.040 mm/y. The area factor for used coupon is 0.83,the days exposed is 30 days, and the wt. loss of coupon determined by a sensitive balance, then MPY calculated using equation (6) as follows:

For wt. loss=68.67 mg
MPY=0.83*68.67/30=1.9

The other values of MPY calculated in the same manner.

Table (7)

Ca^{+2} hardness (ppm)	Wt. Loss (mg)	MPY
475	68.67	1.9
350	90.36	2.5
245	130.12	3.6
200	144.5	4.0
170	148.19	4.1
150	253	7.0

Referring to qualitative classification of corrosion rate(6)shown in table (7) it is obvious from results of table(6) that soft water which are low in calcium is more Corrosive than water of high calcium content,Fig(4)show that increasing incalcium concentration reduces general corrosion and a zone of probable performance was with the condition of Ca^{+2} conc. =170-245 and MPY=3.6-4.1, at these conditions, the uniformity of scale deposition is likely to be produce a protective layer against corrotion.

Table (8) Qualitative Classification(6) for Corrosion Rate

Description	Carbon steel <1-2	Copper Alloys <0.1
Negligible	<1-2	<0.1
Mild	2-5	0.15-0.2
Moderate	5-10	0.2-0.35
Severe	>10	0.5-1

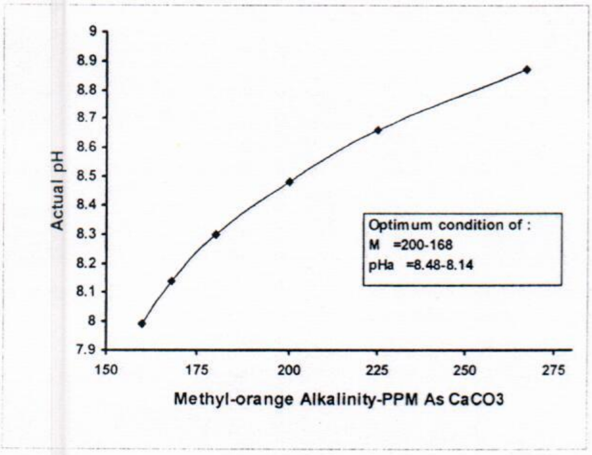

Fig. (1)

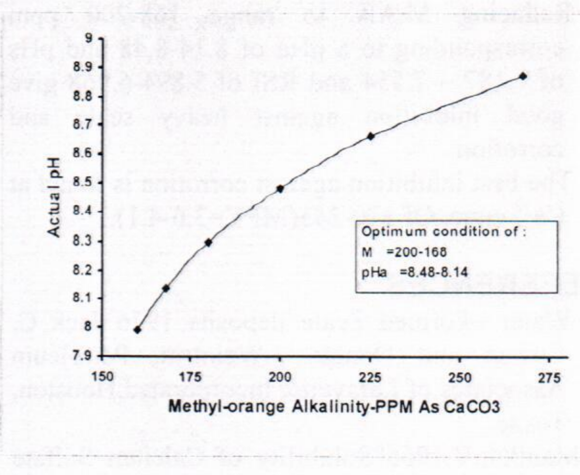

Fig. (2)

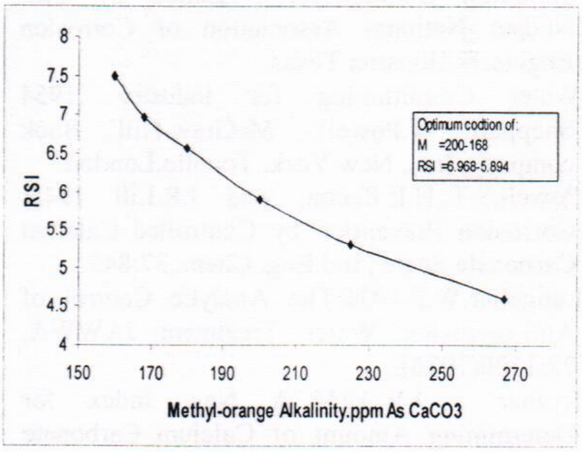

Fig. (3)

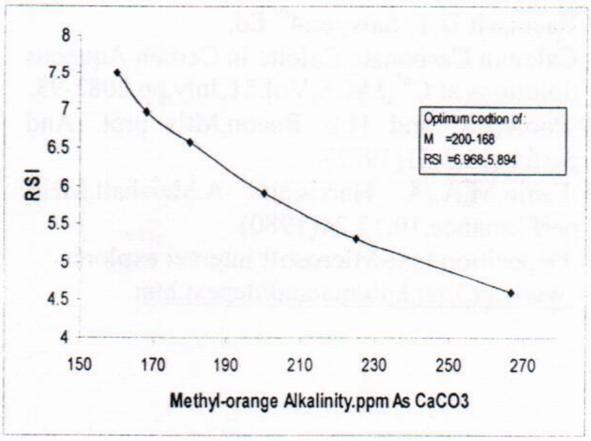

Fig. (4)

CONCLUSIONS

1. Sulphuric acid is the most proper acid used to control heavy $CaCO_3$ scale and to produce a thin and adherent layer of $CaCO_3$ on the surface requiring protection.

2. Reducing M.Alk to range 168-200 ppm corresponding to a pHa of 8.14-8.48 and pHs of 7.187 – 7.554 and RSI of 5.894-6.968 give good inhibition against heavy scale and corrotion.
3. The best inhibition against corrotion is found at Ca^{+2} conc. Of 170-245(MPY=3.6-4.1).

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APPENDIX

Table (A-1) Constant A as a function of water temperature

Water temp.(C^o)	Water temp.(F^o)	Constant A
0	32	2.6
4	39.2	2.5
8	46.4	2.4
12	53.6	2.3
16	60.8	2.2
20	68	2.1
25	77	2
30	86	1.9
40	104	1.7
50	122	1.55
60	140	1.4
70	158	1.25
80	176	1.15

Table(A-2):Constant B as a function of T.D.S (7)

T.D.S (ppm)	Constant B
0	9.7
100	9.77
200	9.83
400	9.86
800	9.89
1000	9.9