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APPENDIX A

## MATERIAL BALANCES AND CONCENTRATION RELATIONSHIPS

## IN OPEN RECIRCULATING SYSTEMS

The concentration of dissolved materials in an open recirculating system and the loss of added treatment chemicals from the system are both related to the total volume of the system and the amounts of make-up water, water lost by evaporation, water lost by drift or windage, and water accidentally purged from the system (blowdown or bleedoff). the material balance for the water can be expressed as follows:

$$M = E + B \quad (1)$$

where M = amount of make-up water added

E = amount of water evaporated

B = amount of water lost by drift and blowdown

Since dissolved materials are removed only in the drift and blowdown, these materials become more concentrated in the circulating water. The concentration factor is the ratio of the total water added to the system divided by the total water lost in the drift and blowdown; that is,

$$C = M/B \quad (2)$$

$$\text{or } C = (E + B)/B \quad (3)$$

where C is the concentration factor, commonly called cycles of concentration

Increasing the cycles of concentration decreases the requirement for fresh make-up water. However, it is not practical to operate beyond certain limits on the cycles of concentration, not only because the high concentration of dissolved solids increases scaling tendencies but also because there is a "diminishing returns" effect as the cycles increase. From the previous equations (if  $C = 1$ ),

$$M = EC/(C - 1) \quad (4)$$

Table A-1 which is based on equation (4), shows the amount of make-up water as a function of the amount of water evaporated at various cycles of concentration. From these figures it can be seen, for example, that if the amount of water evaporated were 10 cubic meters (2,700 U.S. gallons) per hour, then the amount of make-up water required at 1.2 cycles would be 60 cubic meters (16,000 U.S. gallons) per hour. Increasing the cycles to 1.5 would reduce the make-up water requirement by 50 percent to only 30 cubic meters (8,000 U.S. gallons), and increasing the cycles to 3.0 would cut the make-up requirement an additional 15 cubic meters (4,000 U.S. gallons). However, if the initial cycles of concentration in this case were 5.0, increasing the cycles to 10.0 would provide only an 11 percent or 1.4 - cubic meter (370 - U.S. gallon) reduction in

Table A-1 Amount of make-up water required at various cycles of concentration

<u>Cycles</u>	<u>Ratio of make-up water to water evaporated</u>
1.1	11.0
1.2	6.0
1.5	3.0
2.0	2.0
3.0	1.5
5.0	1.25
10.0	1.11
15.0	1.07
20.0	1.05

make-up water required per hour.

from the previous relationships another useful equation can be derived that permits estimation of the blowdown rate from the evaporation rate:

$$B = E/(C - 1) \quad (5)$$

APPENDIX B

## STANDARD TEST METHOD FOR CORROSIVITY OF WATER (COUPON TEST)

## 1. Summary of Method

Carefully prepared, weighed metal coupons are installed in contact with flowing cooling water for a measured length of time. After removal from the system, these coupons are examined, cleaned, and reweighed. The corrosivity and fouling characteristics of the water are determined from the difference in weight, the depth and distribution of pits, and the weight and characteristics of the foreign matter on the coupons.

## 2. Interferences

2.1 Deviations in metal composition or surface preparation of the coupons may influence the precision of the results.

2.2 The presence of different metal in close proximity to the coupon, (within 76 mm (3 in )) even if they are insulated from the coupon, constitutes a source of error in the results.

2.4 Results are directly comparable only for the water temperature to which the coupon is exposed.

2.5 Crevices, deposits, or biological growths may affect local corrosivity; results should therefore be interpreted with caution.



### 3. Apparatus

#### 3.1 Coupon Specimens

3.2 Insulating Washer, Screw, and Nut - Use for attaching the coupon to the phenolic rod. The insulating washer has a sleeve that fits into the coupon hole and around the screw.

3.3 Phenolic Rod - Use a 152 mm (6 in ) length of canvas - based 13 mm (0.5 in ) outside diameter phenolic rod attached at one end to a drilled pipe plug, and having a flat surface and a hole at the other end suitable for attachment of the coupon.

3.4 Piping Arrangement, as illustrated in Fig. B-1 for

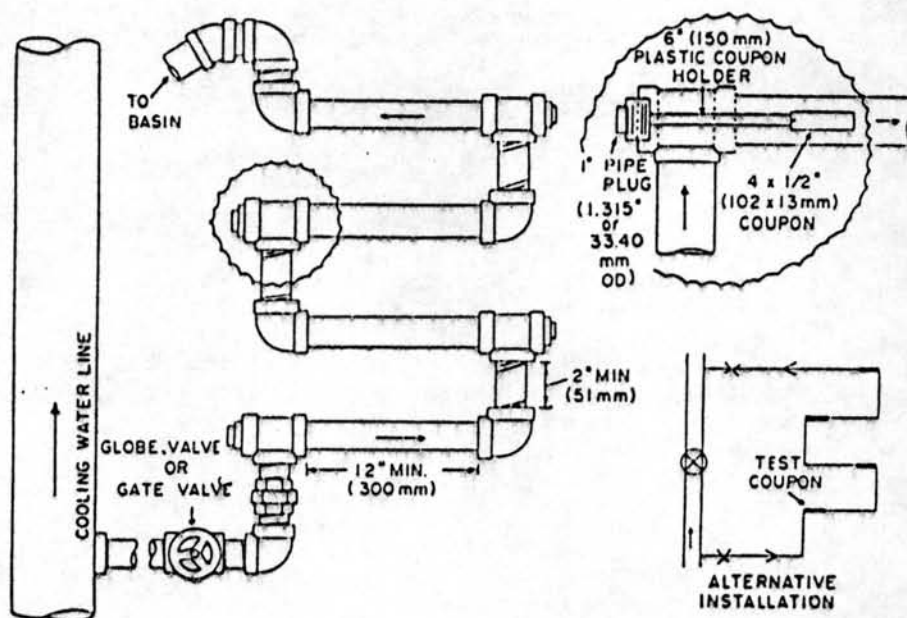


Fig. B-1 Installation of corrosion coupons

installation of coupon specimens. This arrangement has been changed in order that flow passes over the holder end of the specimens first at two locations and over the specimen first at the other two locations. This enables one to determine whether the turbulence provided by the corrosion testers or the elbows influence the results.

#### 4. Procedure

4.1 Weigh the clean, dry specimens on an analytical balance to the nearest 0.1 mg.

4.2 After weighing, store the specimens in a desiccator until ready for use. If storing in a desiccator is inconvenient or impractical, use an alternative method for providing a corrosion-free atmosphere.

4.3 Store ferrous metal coupons in separate envelopes made from vapor phase inhibitor impregnated paper. Store nonferrous metal coupons in sealed plastic envelopes or wrapped in plastic film.

4.4 Attach the coupon to the phenolic rod, using an insulating washer to preclude any contact of coupon with the screw and nut assembly. For added protection, attach the specimen to the holder using a screw and nut of the same metal composition as the coupon.

4.5 Install the holder and coupon assembly in a suitable line or in a bypass piping arrangement as shown in Fig. B-1

4.6 Adjust the rate of flow of water in the test piping to a rate that gives a flow velocity that corresponds to normal flow in those parts of the system under prime consideration. Normally, the flow velocity will be in the range from 0.6 to 1.8 m (2 to 6 ft)/s. Check and readjust the flow as necessary to maintain the desired rate.

4.7 Remove specimens from the system at chosen intervals. Since the corrosion rate will be high initially and then fall to a lower, nearly constant rate, two time series should be chosen.

4.7.1 Use short time intervals for the first time series in order to establish the rate at which passivity occurs. Removal of three or four sets of coupons at 4 to 7-day intervals is recommended.

4.7.2 Use long time intervals for the second time series in order to establish the mean steady-state corrosion rate. Removal of the first coupon after 1 month and remaining coupon at 1 to 3-month intervals is recommended.

4.8 Protect the specimen if cannot be examined, cleaned, and reweighed immediately after removal from the system. Dry

between paper towels. Store the ferrous metal coupons in separate envelopes made from vapor phase inhibitor-impregnated paper or wrap carefully in plastic film. For nonferrous metal coupons, wrap carefully in plastic film. The interim period between removal of specimens and reweighing should be kept to a minimum and in no case should it exceed 1 week.

4.9 Examine the specimen and record either by photograph or by description the appearance of the specimen, paying particular attention to the amount and nature of any adherent deposit. Chemical analysis of the deposit may be performed, but this step is optional.

4.10 For ferrous coupons, use one of the following alternative procedures for cleaning the coupon prior to reweighing.

4.11 For copper to copper alloy coupons use the following procedure for cleaning prior to reweighing. Clean the coupons as well as possible with a plastic knife. Remove oily or greasy deposits by soaking in trichloroethylene. Immerse the coupons in inhibited HCl (1+1.8) for 30 s. Rinse coupons with water, rinse with isopropyl alcohol, and finally, rinse with benzene. Dry coupons between paper towels. Place in a desiccator for 1 hr.

4.12 For aluminum or aluminum alloy coupons, use the following procedure for cleaning prior to reweighing. Clean

the coupons as well as possible with a plastic knife. Remove oily or grease deposits by soaking in trichloroethylene. Immerse the coupons in chromic acid-phosphoric acid solution at room temperature for 30 min. Remove and rinse with water, rinse with isopropyl alcohol, and finally, rinse with benzene. Dry between paper towels. Place in a desiccator for 1 hr.

4.13 subject a weighed blank coupon of the same material to the identical cleaning procedure used for the test specimens and reweigh to determine the blank correction factor to be applied to the coupon weight losses.

4.14 Reweigh each coupon to the nearest 0.1 mg

4.15 If pitting is apparent on the coupon, measure the depth of the pits in a representative area with the dial depth gage. Record the resultant values as pit depths. The number, size, shape, and distribution of the pits shall also be determined and recorded.

4.16 Record the appearance of the cleaned, weighed coupon as "protected", "moderate localized", "moderate pitting", or "severe pitting", by comparing the coupon.

## 5. Calculation

5.1 Calculate the corrosion rate for each coupon as follows

(this equation provides a sufficiently accurate approximation of the actual corrosion rate for most corrosion studies):

$$P = [H(W_1 - W_2)/W_1D] \times 1.825 \times 10^2$$

P = corrosion rate, mmpy,  
 H = original thickness of the coupon, mm,  
 W<sub>1</sub> = original weight of the coupon, mg,  
 W<sub>2</sub> = final weight of the coupon, mg, and  
 D = exposure time, days.

5.2 In certain systems (usually test installations), where all variables are closely controlled, apply the following equations which give more precise corrosion rates. Calculate the corrosion rate for a rectangular coupon as follows:

$$P = 1/[(1/H)+(1/X)+(1/Y)] + [(W_1-W_2)/W_1D] \times 1.825 \times 10^2$$

where:

P = corrosion rate, mmpy,  
 H = original thickness of coupon, mm,  
 X = original length of coupon, mm,  
 Y = original width of coupon, mm,  
 W<sub>1</sub> = original weight of the coupon, mg,  
 W<sub>2</sub> = final weight of the coupon, mg, and  
 D = exposure time, days.

5.3 Express the relationship between corrosion rate in grams per square metre per day ( $\text{g/m}^2 \cdot \text{d}$ ) and penetration in millimetres per year (mmpy) as follows:

$$\text{mmpy} = \frac{\text{g/m}^2 \cdot \text{d}}{d} \times 365$$

where:

$d$  = density of the metal,  $\text{kg/m}^3$ , (for example,  $7860 \text{ kg/m}^3$  mild steel).

APPENDIX C



## CALCULATION OF SATURATION INDEX (LANGELIER)

## AND STABILITY INDEX (RYZNAR)

The Langelier index or calcium carbonate saturation of a cooling water is of value in predicting the scaling or corrosive tendencies of water. The index can be calculated for most cooling waters with reasonable accuracy by use of the data in Table C-1. To compute the index it is necessary

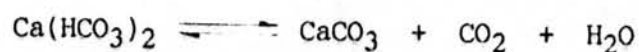
Table C-1 Data for calculation of saturation and stability indexes

Total solids		A	Calcium hardness	C	Total alkalinity	D
p.p.m.			p.p.m. CaCO <sub>3</sub>		p.p.m. CaCO <sub>3</sub>	
50- 350		0.1	10	0.6	10	1.0
400-1100		0.2	12	0.7	12	1.1
			14	0.8	14	1.2
			18	0.9	18	1.3
Temperature		B	23	1.0	23	1.4
°C.	°F.		28	1.1	28	1.5
0	32	2.6	35	1.2	36	1.6
2	36	2.5	44	1.3	45	1.7
7	44	2.4	56	1.4	56	1.8
10	50	2.3	70	1.5	70	1.9
14	58	2.2	88	1.6	88	2.0
18	64	2.1	111	1.7	111	2.1
22	72	2.0	139	1.8	140	2.2
28	82	1.9	175	1.9	177	2.3
32	90	1.8	230	2.0	230	2.4
38	100	1.7	280	2.1	280	2.5
44	112	1.6	350	2.2	360	2.6
51	124	1.5	440	2.3	450	2.7
57	134	1.4	560	2.4	560	2.8
64	148	1.3	700	2.5	700	2.9
72	162	1.2	870	2.6	880	3.0
82	180	1.1	1050	2.7		

to know (1) the total alkalinity, (2) the calcium hardness, (3) the pH, (4) the approximate concentration of total dissolved solids, and (5) the maximum temperature of water.

The principle scale-forming material encountered in cooling water systems is calcium carbonate formed by the decomposition of calcium bicarbonate. This compound not only has an inverse solubility curve, but its solubility at best is much lower in most typical cooling waters than almost all other potential scale-formers that might be present in these waters. Of course, calcium carbonate is soluble in acidic solution, and as the pH of a cooling water is lowered scale generally becomes less of a problem. However, most cooling waters are kept on the alkaline side to reduce corrosion, and thus calcium carbonate scaling remains as a potential problem. Calcium sulfate, calcium phosphate, and other calcium salts as well as occasionally magnesium and barium salts, can also cause scale. Other materials at high concentrations, such as silica or silicates, are possible sources of scale problems, and iron-utilizing bacteria can produce an iron oxide scale.

the decomposition of calcium bicarbonate to calcium carbonate takes place because heating and concentration effects in the cooling water system shift the equilibrium expressed by the equation:



For many years the Langelier calcium carbonate saturation index has been used to predict the scale-forming tendencies of water. This index is based on the relationship:

$$pH_S = pCa + pAlk + C$$

where  $pH_S$  is saturation pH at specified temperature

$pCa$  is log factor of calcium hardness (expressed as ppm  $CaCO_3$ )

$pAlk$  is log factor of total alkalinity (expressed as ppm  $CaCO_3$ )

$C$  is log factor of total solids in ppm at the temperature of the water at the point of scale formation.

To determine the saturation index, obtain values of  $A$ ,  $B$ ,  $C$ , and  $D$  from table C-1, and calculate the saturation pH as follows:

$$pH_S = (9.3 + A + B) - (C + D)$$

Then, using the actual pH of the water, calculate the index:

$$\text{Saturation index} = pH - pH_S$$

If the saturation index is zero, water is in chemical balance. If the index is positive, scaling tendencies are indicated. If the index is negative, corrosive tendencies are indicated.

The Ryznar stability index is a modification of the Langelier saturation index:

$$\text{Stability index} = 2\text{pH}_s - \text{pH}$$

all values of the stability index will be positive, and values above 6.5 indicate a corrosive tendency while values below 6.0 indicate a tendency to form scale, then using the water, calculate the index:

$$\text{Saturation index} = \text{pH} - \text{pH}_s$$

If the saturation index is zero, water is in chemical balance. If the index is positive, scaling tendencies are indicated. If the index is negative, corrosive tendencies are indicated.

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## VITA

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