

## **Scale Formation in Deluged Dry Cooling Systems**

**D. R. Pratt**

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SCALE FORMATION IN DELUGED DRY COOLING SYSTEMS

by  
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May 1976

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## 1.0 INTRODUCTION

In the dry cooling concepts under study at Battelle, Pacific Northwest Laboratory, (PNL), waste heat from the power plant condenser is transferred from the intermediate heat transfer fluid to the air by means of an air-cooled heat exchanger (dry tower) utilizing finned tubes. Both water and ammonia are being studied as potential intermediate heat transfer fluids; the feasibility of the use of bare plastic tubes instead of metal finned tubes in the dry tower is also being examined.

During the cooler portions of the year, the cooling tower will operate as a completely dry system. During warm periods, however, preliminary studies at PNL and elsewhere<sup>(1,2)</sup> indicate that deluging portions of the heat exchanger surfaces with water will increase heat rejection capability and significantly reduce the cost of dry cooling. In the deluged dry cooling mode, sensible heating of the air is augmented by heat transfer to the air by evaporation of the deluge water (delugate).

One of the principal uncertainties in the deluge concept is the tendency toward deposition of solids (scaling) from the delugate. Scaling can occur by a) exceeding the solubility limit under continuous flow conditions and b) evaporation of the delugate on the heat exchange surfaces in multiple wet-to-dry cycles. Workers in the USSR studying the concept state that scaling can be avoided by the use of proper water treatment, but the extent of this treatment is not clear.<sup>(2)</sup> Experience in this country has shown that smooth tubes continuously flooded by a massive flow of water will not develop encrustations provided the water

is properly treated and the surface temperature does not exceed about 66°C (150°F).<sup>(3)</sup> Again, however, details concerning proper water treatment are not clear.

On the other hand, a vendor of air-cooled heat exchangers in this country has stated that intentional wetting of extended surfaces in U.S. process plants has been unsuccessful. According to this source, water solids and air-borne dirt create serious fin-side fouling problems which affect both heat transfer and mass air flow.<sup>(4)</sup> This adverse experience has largely been with systems in which water is sprayed on the finned tubes and allowed to completely evaporate; in this case, solids are deposited rapidly in proportion to their concentration in the water and particulate material in the air.<sup>(5)</sup>

Thus the question of deluge water quality is of major importance in evaluating scale formation and its effect on heat transfer in the deluged dry cooling system. Indeed, scaling (fouling) has been described as the major unresolved problem in heat transfer.<sup>(6)</sup> This paper will discuss, in relation to the deluged dry cooling system, the importance of scale prevention, the theory of scale formation and application of this theory to the deluged system, the problems of deluge evaporation, and deluge treatment required to prevent scaling.

## 2.0 THE IMPORTANCE OF CALCIUM CARBONATE SCALE PREVENTION

The importance of preventing the formation of calcium carbonate scale in deluged dry cooling systems can be seen by examining the basic heat transfer equation for heat flow under pure conduction conditions.

The heat flow is controlled by three factors:

- the nature of the conducting surface
- the difference in temperature
- the cross sectional area of the conducting surface.

The heat flow is calculated from the equation: (7)

$$Q = U \times A \times \Delta T,$$

where

$Q$  = Total heat flow (Btu/hr),

$A$  = Area of heat transfer surface ( $\text{ft}^2$ ),

$\Delta T$  = Temperature difference between the two surfaces ( $^{\circ}\text{F}$ ),

$U$  = Heat transfer coefficient (Btu/hr- $\text{ft}^2$ - $^{\circ}\text{F}$ ).

The overall heat transfer coefficient is given by: (7)

$$\frac{1}{U} = R_o + R_i + R_w = R_s$$

where

$R_o$  = Resistance to heat transfer of fluid on the outside of the finned tube;

$R_i$  = Resistance to heat transfer of fluid on the inside of the tube;

$R_w$  = Resistance to heat transfer of the fin;

$R_s$  = Resistance to heat transfer of the scale;

$$= t_s / k_s$$

where

$t_s$  = scale thickness, ft;

$k_s$  = thermal conductivity of scale, Btu/hr-ft<sup>2</sup>-°F/ft.

The thermal conductivity of porous calcium carbonate is about 0.2 Btu/hr-ft<sup>2</sup>-°F/ft, (7) while that of aluminum is about 118 Btu/hr-ft<sup>2</sup>-°F/ft. (8) Thus, small calcium carbonate scale deposits may significantly reduce the cooling efficiency of a deluged system. Table 1 shows the reduction in the overall heat transfer coefficient as a function of calcium carbonate scale thickness for the three dry cooling systems under study. Since fin spacing (except in the plastic system, which has no fins) is  $6.83 \times 10^{-3}$  ft (2.08 mm), scale thickness (on each side of the fin) greater than about  $1.5 \times 10^{-3}$  ft (0.5 mm) will hamper deluge flow and thus further reduce heat transfer.

TABLE 1. Reduction in Heat Transfer Coefficient Resulting From Calcium Carbonate Scale in Deluged DCT Systems.

Thickness, ft	Resistance, R Hr-ft <sup>2</sup> -°F/BTU <sup>s</sup>	Overall Heat Transfer Coefficient, U, BTU/hr-ft <sup>2</sup> -°F		
		Water, Normal System(a)	Ammonia System(b)	Water, Plastic System(c)
0	0	5.01	6.56	15.18
$1.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	5.006	6.555	15.171
$5.0 \times 10^{-5}$	$2.5 \times 10^{-4}$	5.001	6.547	15.125
$1.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	4.995	6.536	15.068
$5.0 \times 10^{-4}$	$2.5 \times 10^{-3}$	4.945	6.452	14.627
$1.0 \times 10^{-3}$	$5.0 \times 10^{-3}$	4.885	6.349	14.111
$5.0 \times 10^{-3}$	$2.5 \times 10^{-2}$	4.450	5.634	11.005

(a) Carbon steel tubes, extruded aluminum fins

(b) Aluminum tubes and fins

(c) Bare plastic tubes

### 3.0 THEORY OF CALCIUM CARBONATE SCALE FORMATION

#### 3.1 SCALING INDEXES

Most water treatment programs designed to control calcium carbonate scale formation in cooling water systems are based on the use of the Langlier Saturation Index.<sup>(9)</sup> This index makes it possible to predict the tendency of a given water at equilibrium to either deposit calcium carbonate scale from solution or to dissolve calcium carbonate with which the water is brought into contact.<sup>(10)</sup> The index takes into

account the water's calcium content, alkalinity, pH, dissolved solids and temperature. Other factors affecting scale formation which the Saturation Index does not account for include rate of heat transfer and concentration of magnesium, sulfate, phosphate and silica. While the index does include a factor for total dissolved solids, it does not distinguish among the various ions in solution; rather, all ions are treated as having the same effect on scaling.<sup>(11)</sup>

For waters in the pH range of 6.5 to 9.5, Langlier's equation for the pH at which the solution is in equilibrium with respect to calcium carbonate is as follows:<sup>(9)</sup>

$$pH_s = (pK_2' - pK_s') + pCa + pAlk$$

where

$pH_s$  = the pH at calcium carbonate saturation;

$pK_2'$  = the negative logarithm of the second dissociation constant for carbonic acid, corrected for the ionic strength and temperature of the solution;

$pK_s'$  = the negative logarithm of the solubility product for calcium carbonate, also corrected for the ionic strength and temperature;

$pCa$  = the negative logarithm of the molal calcium concentration;

$pAlk$  = the negative logarithm of the total alkalinity expressed as equivalents per liter.

The values of  $pH_1$ ,  $pK_2$ , and  $pK_s$  for various temperatures are given in Table 2.<sup>(12-14)</sup> Corrections for ionic strength ( $\mu$ ) are given in Table 3.<sup>(14,15)</sup>

TABLE 2. Equilibrium Values of the Solubility Constant of  $\text{CO}_2$  ( $K_H$ ), the Dissociation Constants of Carbonic Acid ( $K_1$  and  $K_2$ ) and the Solubility Product of Calcium Carbonate ( $K_S$ ) as They Vary With Temperature.

Temperature (C°)	p $K_H$	p $K_1$	p $K_2$	p $K_S$
0	1.11	6.577	10.625	8.023
5	1.19	6.517	10.557	8.087
10	1.27	6.465	10.490	8.150
15	1.32	6.420	10.430	8.215
20	1.41	6.382	10.377	8.280
25	1.47	6.351	10.329	8.342
30	1.53	6.327	10.290	8.395
40	1.64	6.296	10.220	8.515
50	1.72	6.287	10.172	8.625
80	--	(6.315)	(10.122)	8.975

The Saturation Index is defined as the algebraic difference between the actual measured pH of the water ( $\text{pH}_a$ ) and the calculated  $\text{pH}_s$  at calcium carbonate equilibrium:

$$\text{Saturation Index} = \text{pH}_a - \text{pH}_s.$$

The index qualitatively shows the tendency for deposition or solution of calcium carbonate. A positive Saturation Index indicates a tendency to deposit calcium carbonate, while a negative value indicates an undersaturated condition and a tendency to dissolve existing calcium carbonate scale. Waters with a negative Saturation Index do not form a protective scale; common cooling water practice<sup>(11)</sup> is to maintain a slightly positive (~ 1.0) Saturation Index to minimize corrosion.

TABLE 3. Ionic Strength Corrections of the Ionization Constants of Carbonic Acid and the Solubility Product of Calcium Carbonate.

$$pK_1' = pK_1 - \frac{0.5 \sqrt{\mu}}{1 + 1.4 \sqrt{\mu}}$$

$$pK_2' = pK_2 - \frac{2.0 \sqrt{\mu}}{1 + 1.4 \sqrt{\mu}}$$

$$pK_s' = pK_s - \frac{4.0 \sqrt{\mu}}{1 + 3.9 \sqrt{\mu}}$$

The Ionic Strength ( $\mu$ ) can be estimated from

$$\mu = 10^{-5} [4 (TH) - A], \text{ where}$$

TH = Total Hardness in mg/l as  $\text{CaCO}_3$ ;

A = Total Alkalinity in mg/l as  $\text{CaCO}_3$ ;

or, for waters of less than 500 mg/l dissolved solids,

$$\mu = S \times (2.5 \times 10^{-5}), \text{ where}$$

S = Dissolved Solids in mg/l.

Various nomographs have been prepared to simplify the calculation of  $\text{pH}_s$ . A nomograph suitable for this purpose is shown in Figure 1; <sup>(10)</sup> a sample Saturation Index calculation is included therein.

Langlier's Saturation Index was revised by Ryznar <sup>(17)</sup> in an attempt to provide an index which would give quantitative scaling information. His Stability Index is defined by the empirical formula

$$\text{Stability Index} = 2\text{pH}_s - \text{pH}_a.$$

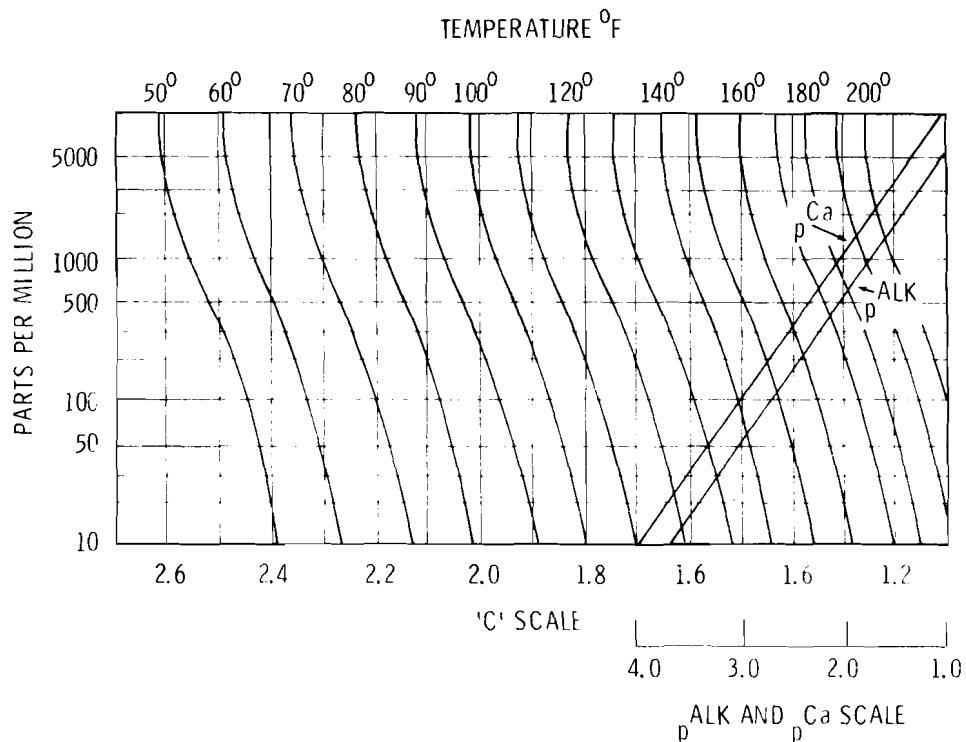


FIGURE 1. Langelier Saturation Index Chart.

To Determine:

pCa: Locate ppm value for Ca as  $\text{CaCO}_3$  on the ppm scale. Proceed horizontally to the left diagonal line down to the pCa scale.

pALK: Locate ppm value for 'M'ALK as  $\text{CaCO}_3$  on the ppm scale. Proceed horizontally to the right diagonal line down to the pALK scale.

Total Solids: Locate ppm value for total solids on the ppm scale. Proceed horizontally to the proper temperature line and down to the 'C' scale.

Example:

Temp. = 140F.	pH = 7.80	pCa = 2.70
Ca Hardness = 200 ppm		pALK = 2.50
M Alkalinity = 160 ppm		C at 140F = 1.56
Total Solids = 400 ppm		Sum = pH = 6.76
		Actual pH = 7.80
		Difference = +1.04
		= Saturation Index

For waters having a Stability Index of 6.0 or less, scaling increases and the tendency to corrosion decreases. When the Stability Index is above 7.0, a protective coating of calcium carbonate scale may not be developed, and corrosion becomes an increasing problem as values increase above 7.5. <sup>(10)</sup>

### 3.2 CRITICAL pH FOR SCALE FORMATION

In Feitler's recent work, <sup>(18)</sup> the theory is postulated that there is a critical pH-- $\text{pH}_c$ --above which scale forms and below which scale does not form. This work points out that the Langlier Saturation Index is based on the solubility of solid calcium carbonate and thus does not adequately predict the point at which precipitation actually occurs in the absence of particles of visible size. Feitler's work has shown that the critical pH,  $\text{pH}_c$ , the pH at which calcium carbonate precipitation actually occurs, is about 1.7 to 2.0 pH units above the saturation pH,  $\text{pH}_s$ . The critical pH of a water can be determined using a scale meter described by Feitler.

Figure 2 shows how the solubility of calcium carbonate varies with temperature and concentrations of calcium and alkalinity. <sup>(19)</sup> The solid line represents a saturated solution, with the area below the curve being unsaturated. The Saturation Index is a means for determining the position of this line, and provides information about the amount of calcium carbonate that will remain in solution in the presence of solid  $\text{CaCO}_3$ . The area above this curve is supersaturated and is divided into two regions. In the metastable region, small unstable nuclei form and dissolve without crystal growth.

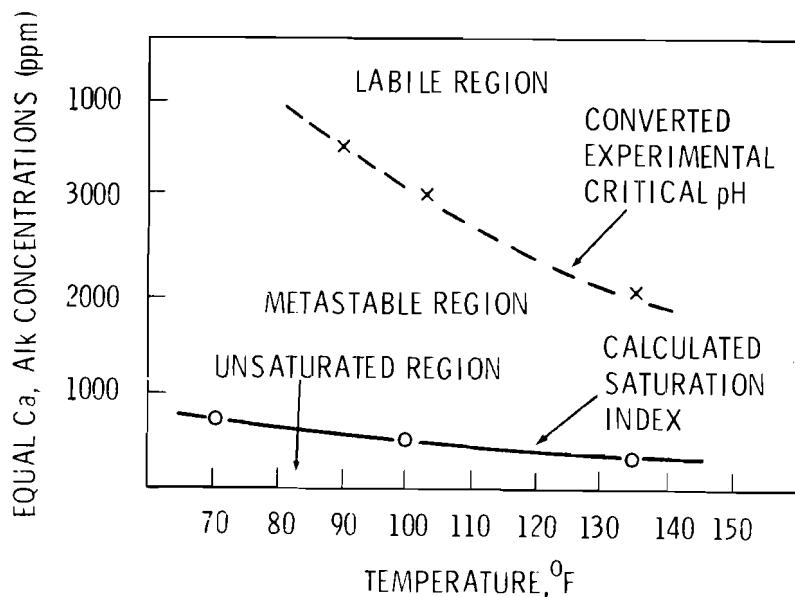


FIGURE 2. Calcium Carbonate Solubility Diagram

In the labile region, nuclei large enough to capture particles form, and crystal growth occurs. The critical pH defines the line separating the metastable and labile regions, and it predicts the amount of dissolved calcium carbonate which must be present for precipitation to take place in the absence of solid  $\text{CaCO}_3$ .<sup>(19)</sup>

The water reuse possibilities predicted by the various scaling indexes are shown in Figure 3.<sup>(11)</sup> The Saturation Index curve is a plot of  $\text{pH}_s$  calculated in the usual way, the Stability Index curve is plotted as  $2\text{pH}_s - 6$ , the Usual Practice curve as  $\text{pH}_s + 1$ , and the Critical pH curve is a plot of experimental data. A temperature of  $49^\circ\text{C}$  ( $120^\circ\text{F}$ ) was used in all cases. Taking the prediction of the Saturation Index at pH 7.5 as one cycle of concentration, the plotted data show the wide variation in water reuse that is predicted by these various indexes.

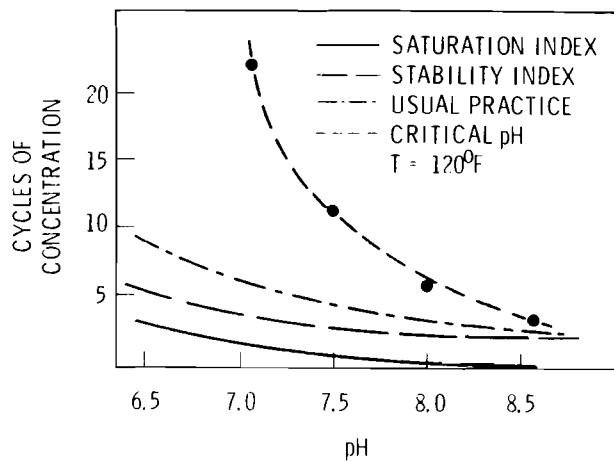


FIGURE 3. Scaling Predictions of Various Indexes.

The data used to generate the critical pH curve are shown in Table 4. From the observed  $\text{pH}_c$  data the free  $\text{CO}_3^{2-}$  concentration was calculated. This made it possible to calculate a critical scaling constant,  $K_{\text{pHc}}$ , the product of the calcium and free carbonate ion concentrations at  $\text{pH}_c$ . The average value of this constant,  $1.8 \times 10^{-7}$ , is 75 times larger than the solubility product ( $K_s$ ) of calcium carbonate as given in Table 1 ( $2.37 \times 10^{-9}$ ) at  $50^\circ\text{C}$ . Since  $K_s$  is the major factor in the Saturation Index, it is apparent that using the  $K_{\text{pHc}}$  value allows the use of much higher calcium/alkalinity values.

TABLE 4. Experimental Values of the Critical pH,  $pH_c$ , and the Critical Scaling Constant,  $K_{pHc}$ , for  $\text{CaCO}_3$ .

Ca (ppm as $\text{CaCO}_3$ )	Alk (ppm as $\text{CaCO}_3$ )	$pH_c$	$(\text{CO}_3^{2-})$	$(\text{Ca}^{++})$	$K_{pHc}$
2000	2000	7.10	$1.02 \times 10^{-5}$	$2 \times 10^{-2}$	$2.04 \times 10^{-7}$
2000	1100	7.38	$1.12 \times 10^{-5}$	$2 \times 10^{-2}$	$2.25 \times 10^{-7}$
1000	1000	7.49	$1.39 \times 10^{-5}$	$10^{-2}$	$1.39 \times 10^{-7}$
500	500	8.00	$2.14 \times 10^{-5}$	$5 \times 10^{-3}$	$1.07 \times 10^{-7}$
300	300	8.64	$6.90 \times 10^{-5}$	$3 \times 10^{-3}$	$2.10 \times 10^{-7}$

It must be emphasized that  $K_s$  and  $K_{pHc}$  are values representing different physical realities. The solubility product,  $K_s$ , defines the amount of calcium and carbonate which remain in solution in the presence of solid  $\text{CaCO}_3$ ; the critical scaling constant,  $K_{pHc}$ , defines the amount of calcium and carbonate which, in the absence of solid  $\text{CaCO}_3$ , must be in solution before scaling can occur.<sup>(11)</sup>

### 3.3 EFFECT OF MAGNESIUM AND SULFATE IONS ON CALCIUM CARBONATE SOLUBILITY

It is known that increasing the concentration of the common ion (in this case either  $\text{Ca}^{++}$  or  $\text{CO}_3^{2-}$ ), which occurs as the cycles of concentration are increased, causes scaling to occur. Increasing the concentration of ions not common to the scale forming compound, however, increases the solubility of that compound. This phenomenon, the salt effect, is taken into account in the Saturation Index in terms of all noncommon ions having an equal effect on solubility.

The fact that all noncommon ions do not have an equal effect on calcium carbonate solubility is pointed out by the work of Akin and Lagerwerff.<sup>(20)</sup> These workers demonstrated that both magnesium and sulfate ions enhance the solubility of calcite relative to its theoretical solubility, with magnesium having the greater effect. A plot showing the relation between the solubility product enhancement factor,  $E$ , and the ratio  $r_{Mg} = [Mg^{++}]/[Ca^{++}]$  is given in Figure 4.<sup>(20)</sup>

Feitler has also shown that magnesium and sulfate ions have an effect on the critical scaling constant,  $K_{pHc}$ , with magnesium having a far greater effect.<sup>(11)</sup> The relationship between  $K_{pHc}$  and concentrations of magnesium and sulfate is shown in Figure 5.<sup>(11)</sup>

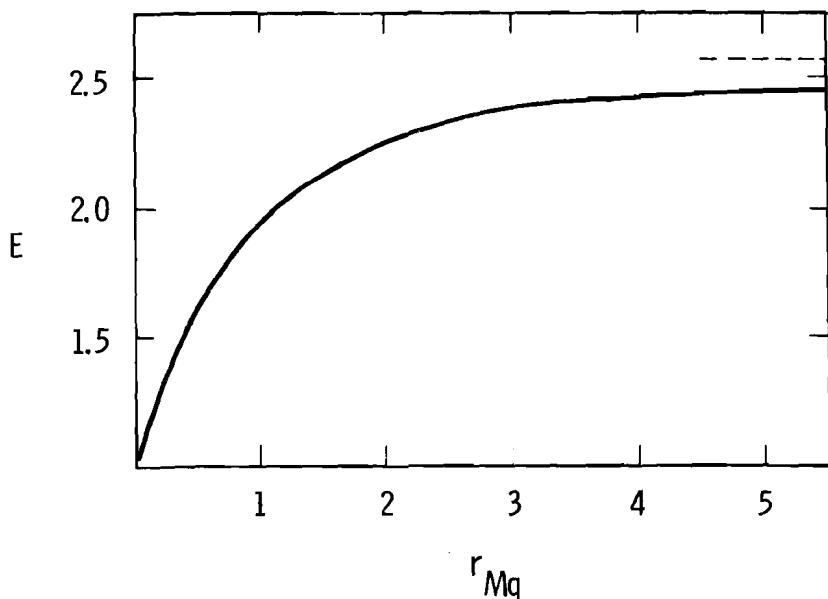


FIGURE 4. Relation Between the Solubility Product Enhancement Factor  $E$ , and the Equilibrium Ratio  $r_{Mg} = [Mg^{2+}]/[Ca^{2+}]$ .

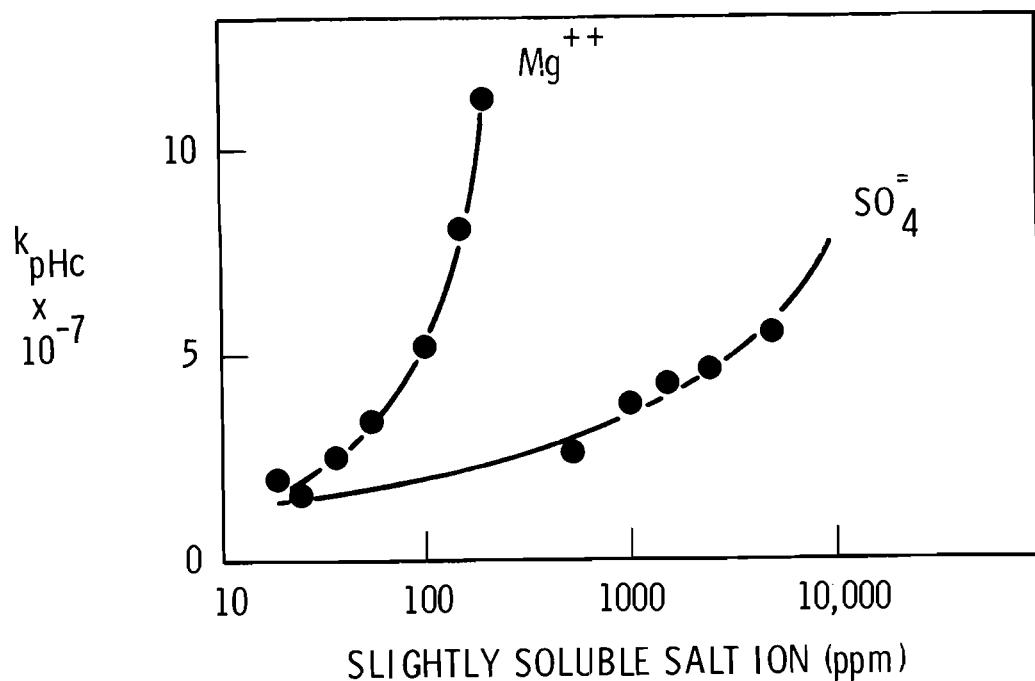


FIGURE 5. Magnesium and Sulfate Ion Effects On the Critical Scaling Constant,  $K_{pHc}$ .

#### 4.0 APPLICABILITY OF SCALING THEORY TO DELUGED DCT SYSTEMS

##### 4.1 "PURE" DELUGATE MAKEUP

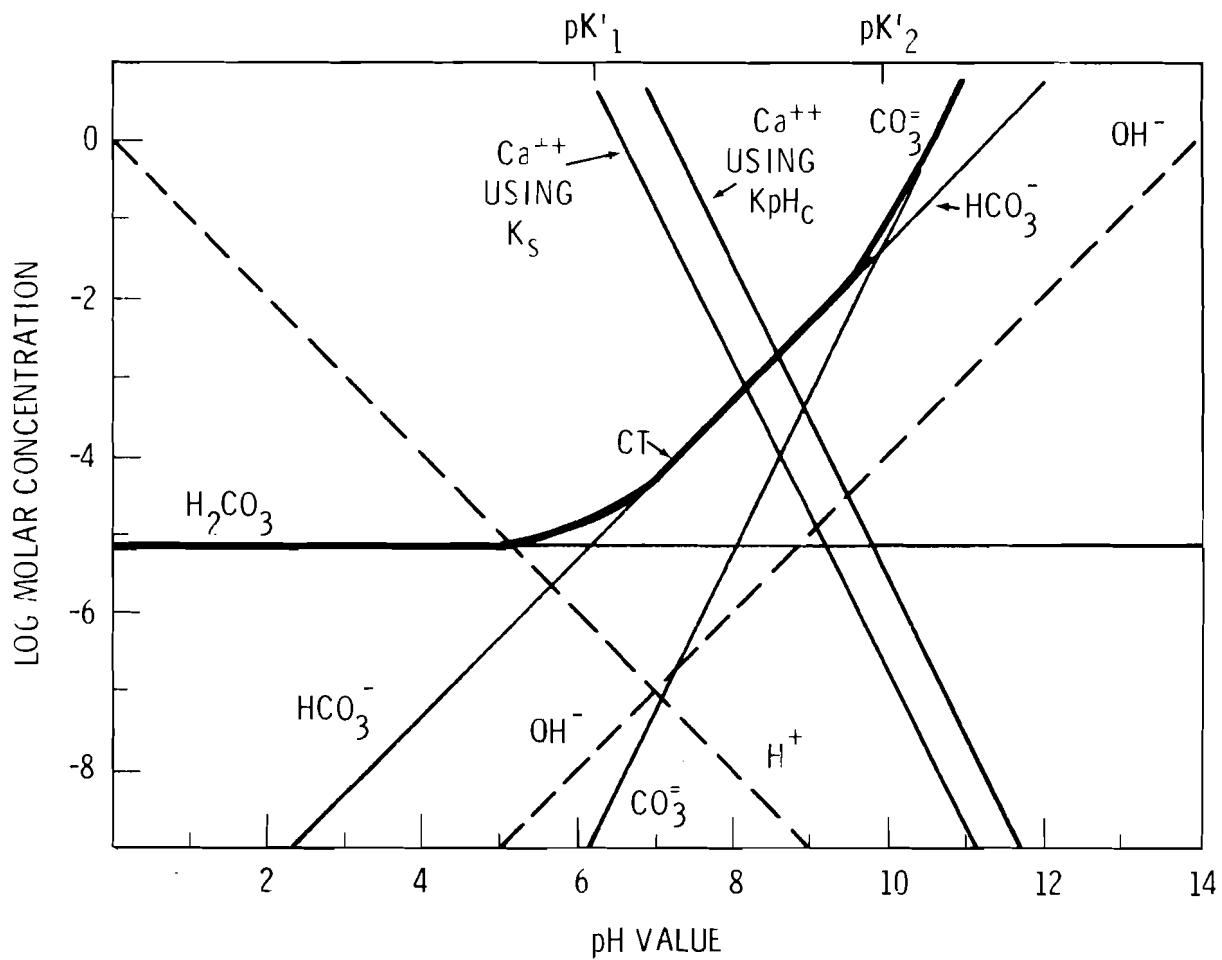
From the above discussion it is apparent that the critical scaling constant  $K_{pHc}$ , should be used to determine that delugate quality which will assure no formation of calcium carbonate scale. The delugate will become scale forming when the product of the calcium ion and free carbonate ion molar concentrations exceeds  $K_{pHc}$ .

Table 5 shows a water, arbitrarily given the designation "pure", that can usually be attained through the use of lime softening, hot process lime soda softening, hot process lime soda softening, reverse osmosis or demineralization, depending on the raw water quality.<sup>(21)</sup> The cost of treating raw water to this quality ranges from \$0.27 to \$0.92 per 1000 gallons, depending on the raw water quality and treatment methodology. Further information on the cost of treating water is given in Appendix A-1.

TABLE 5. "Pure" Water Quality.

Total Hardness	20 - 40 mg/l as $\text{CaCO}_3$
Calcium Hardness	15 - 30 mg/l as $\text{CaCO}_3$
Total Alkalinity	10 - 25 mg/l as $\text{CaCO}_3$
Sulfate	10 - 15 mg/l as $\text{CaCO}_3$
Total Dissolved Solids	50 - 100 mg/l
pH	7.5 - 8.0

For the purpose of the following discussion, it will be assumed that water of the quality described in Table 5 will be used as the original delugate and as delugate makeup water. Figure 6 shows the distribution of solute species, in moles/liter, as a function of pH after the above water in contact with the atmosphere has been allowed to concentrate, as a result of evaporation, to an impurity level 35 times greater than that shown in Table 5 (e.g., 35 cycles of concentration).



**FIGURE 6.** Aqueous Carbonate Equilibrium and Solubility of Calcium Carbonate as a Function of pH in a System Open to the Atmosphere; Ionic Strength = 0.035, Temperature = 40°C.

The set of equations needed to construct this diagram are after Stumm and Morgan<sup>(14)</sup> and are given in Table 6. All calculations are based on a circulating deluge temperature of 40°C (104°F) and an ionic strength of 0.035.

If deluge of this quality is allowed to come to equilibrium, the pH will stabilize at about 8.6, calcium hardness at about 10 mg/l as  $\text{CaCO}_3$ , and total alkalinity at about 90 mg/l as  $\text{CaCO}_3$ . Thus, about 1000 mg of calcium per liter will have precipitated out as calcium carbonate scale. If the water film thickness on the deluged surfaces is 0.25 mm (0.01 inch) thick, the initial  $\text{CaCO}_3$  scale will be about  $1.45 \times 10^{-4}$  mm ( $4.8 \times 10^{-7}$  ft) thick assuming a  $\text{CaCO}_3$  density of 1.75 g/cm<sup>3</sup>. With a deluge makeup rate of 4000 gpm, scale thickness will increase at a rate of about  $4.3 \times 10^{-4}$  mm/day ( $1.9 \times 10^{-6}$  ft/day); the unacceptable level of 0.5 mm ( $1.5 \times 10^{-3}$  ft) of scale will be reached after about 3.2 years of continuous operation.

TABLE 6. The Equilibrium Distribution of Solutes in Delugate Water Open to the Atmosphere, Ionic Strength = 0.035, Temperature = 40°C.

Species:  $\text{Ca}^{++}$ ,  $\text{CO}_2(\text{aq})$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{--}$ ,  $\text{H}^+$ ,  $\text{OH}^-$

Equilibrium Constants:

$$\begin{aligned}
 \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(\text{aq})]} &= K_H = 2.2909 \times 10^{-2} \\
 \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} &= K'_1 = 5.9997 \times 10^{-7} \\
 \frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} &= K'_2 = 1.1926 \times 10^{-10} \\
 \frac{[\text{H}^+][\text{OH}^-]}{} &= K_W = 1.00 \times 10^{-14} \\
 \frac{[\text{Ca}^{++}][\text{CO}_3^{--}]}{} &= K_{\text{pHc}} = 1.8 \times 10^{-7} \\
 \frac{[\text{Ca}^{++}][\text{CO}_3^{--}]}{[\text{CaCO}_3(\text{s})]} &= K_S = 8.273 \times 10^{-9}
 \end{aligned}$$

Concentrations (35 Cycles of Concentration):

$$p_{\text{CO}_2} = 3.1623 \times 10^{-4}$$

$$\begin{aligned}
 C_T &= [\text{Alk}] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{--}] \\
 [\text{Ca}^{++}] &= 1.0 \times 10^{-2}
 \end{aligned}$$

Ionization Fractions:

$$[\text{H}_2\text{CO}_3] = K_H p_{\text{CO}_2}$$

$$[\text{HCO}_3^-] = \frac{K_H p_{\text{CO}_2} K'_1}{[\text{H}^+]}$$

$$[\text{CO}_3^{--}] = \frac{K_H p_{\text{CO}_2} K'_1 K'_2}{[\text{H}^+]^2}$$

$$[\text{Ca}^{++}] = \frac{K_{\text{pHc}} [\text{H}^+]^2}{K_H p_{\text{CO}_2} K'_1 K'_2}$$

From the value of the critical scaling constant,  $K_{pHc} = 1.8 \times 10^{-7}$ , and the expression for the equilibrium concentration of calcium ion,  $[Ca^{++}] = K_{pHc}[H^+]^2 / K_{H^+}K_{CO_2}K_1'K_2'$ , the critical pH at any calcium ion concentration can be calculated. At 35 cycles of concentration,  $[Ca^{++}]$  will be  $1.05 \times 10^{-2}$  moles/liter, and  $pH_c$  is 8.3; delugate at 35 cycles of concentration must be kept at a pH value less than 8.3 if scale formation is to be prevented.

Because of the uncertain conditions in cooling water systems, actual operation should be at some safe factor below this upper limit. A conservative operating pH can be determined by substituting the value of the calcium carbonate solubility product,  $K_s$ , in the above expression and solving for the hydrogen ion concentration; the pH obtained in this way is 7.6. Thus, if water as described in Table 4 is used as delugate and is allowed to concentrate to 35 cycles of concentration, the pH should be maintained in the range of 7.6-7.8 to prevent the formation of calcium carbonate scale. This pH can be maintained by addition of sulfuric acid to the delugate.

The amount of blowdown required to maintain the above delugate quality can be determined from<sup>(10)</sup>

$$\% B = \frac{\% E}{(cycles - 1)}$$

where

$\% B$  = Blowdown expressed as percent of circulation rate;

$\% E$  = Evaporation loss expressed as percent of circulation rate;

cycles = Number of cycles of concentration

Assuming an evaporation rate of 5%, the amount of blowdown required is 0.15%. If the delugate circulation rate if 78,700 gallons per minute, which is the approximate rate for a 1000 MWe plant, the required blowdown rate will be only about 120 gallons per minute.

#### 4.2 OTHER MAKEUP WATER QUALITIES

Table 7 shows other water qualities and the cycles of concentration that can be safely allowed if scaling is to be avoided.

TABLE 7. Use of Various Waters as Delugate as a Function of Water Quality.

Water	"Pure"	Columbia River	Richland City	San Juan River	Sheridan Wyo.
Total Hardness, mg/l as $\text{CaCO}_3$	40	60	95	220	295
Calcium Hardness, mg/l as $\text{CaCO}_3$	30	45	70	165	220
Total Alkalinity, mg/l as $\text{CaCO}_3$	25	60	50	235	420
Total Dissolved Solids, mg/l	100	110	90	390	1550
Allowed Cycles of Concentration	35	22	14	6.0	4.5
Critical pH of Delugate	-----8.3-----				
Operating pH of Delugate	-----7.6-7.8-----				
Percent Blowdown required(a)	0.15	0.24	0.38	1.00	1.45
Blowdown Rate, gpm(b)	120	190	305	790	1125

(a) Assuming 5% evaporation rate

(b) Assuming 1000 MWe plant with delugate circulation rate of 78,700 gpm

#### 5.0 SCALE FORMED BY DELUGATE EVAPORATION

The extended surfaces of the dry cooling tower will be deluged only during warm periods to provide augmented cooling capability. When the dry bulb temperature drops below a specified point, the flow of delugate will be turned off and the tower will operate with the finned tube surfaces dry.

When the deluge flow is turned off, the water remaining on the fin surfaces will evaporate, leaving behind as a scale all of the dissolved impurities it contained. Some of the salt so deposited, such as the compounds of sodium, will redissolve when the fins are again deluged. However, once calcium carbonate scale is formed, the solubility product,  $K_s$ , rather than the critical scaling constant,  $K_{pHc}$ , must be used to determine whether the scale will redissolve.

Assuming that the deluge quality is controlled as shown in Table 7 (pH 7.6-7.8, blowdown rate to ensure maximum calcium concentration of 1000 mg/l as  $\text{CaCO}_3$ ), the product of calcium and free carbonate molar concentrations will be equal to the solubility product of calcium carbonate at this temperature, and the scale will not redissolve. Since solid  $\text{CaCO}_3$  will then be present in the system, the pH must be lowered and maintained at about 7.2 to ensure no further scale formation.

Again assuming a water film thickness of 0.25 mm, (0.01 inch) the thickness of calcium carbonate scale formed on evaporation of the deluge will be about  $1.45 \times 10^{-4}$  mm ( $4.8 \times 10^{-7}$  ft). Assuming that the deluge system is turned off and the water allowed to evaporate 200 times per year, an unacceptable amount of scale (0.5 mm) will build up in 17 years of operation. Thus the major incentive for preventing scale formation by evaporation is reduction in the amount of acid which would have to be added to prevent further deposition. Formation of calcium carbonate scale by evaporation of the deluge can be prevented by deluging the finned surfaces with zero hardness water before turning off the water flow. About 100,000 gallons of zero hardness water will be required for

a five-minute flush. Capital cost of a sodium zeolite system to produce this water will be about  $\$2.5 \times 10^5$ ; operating cost will be about  $\$1.0 \times 10^4$  per year.

## 6.0 DELUGATE TREATMENT FOR SCALE PREVENTION

### 6.1 SIDE-STREAM TREATMENT

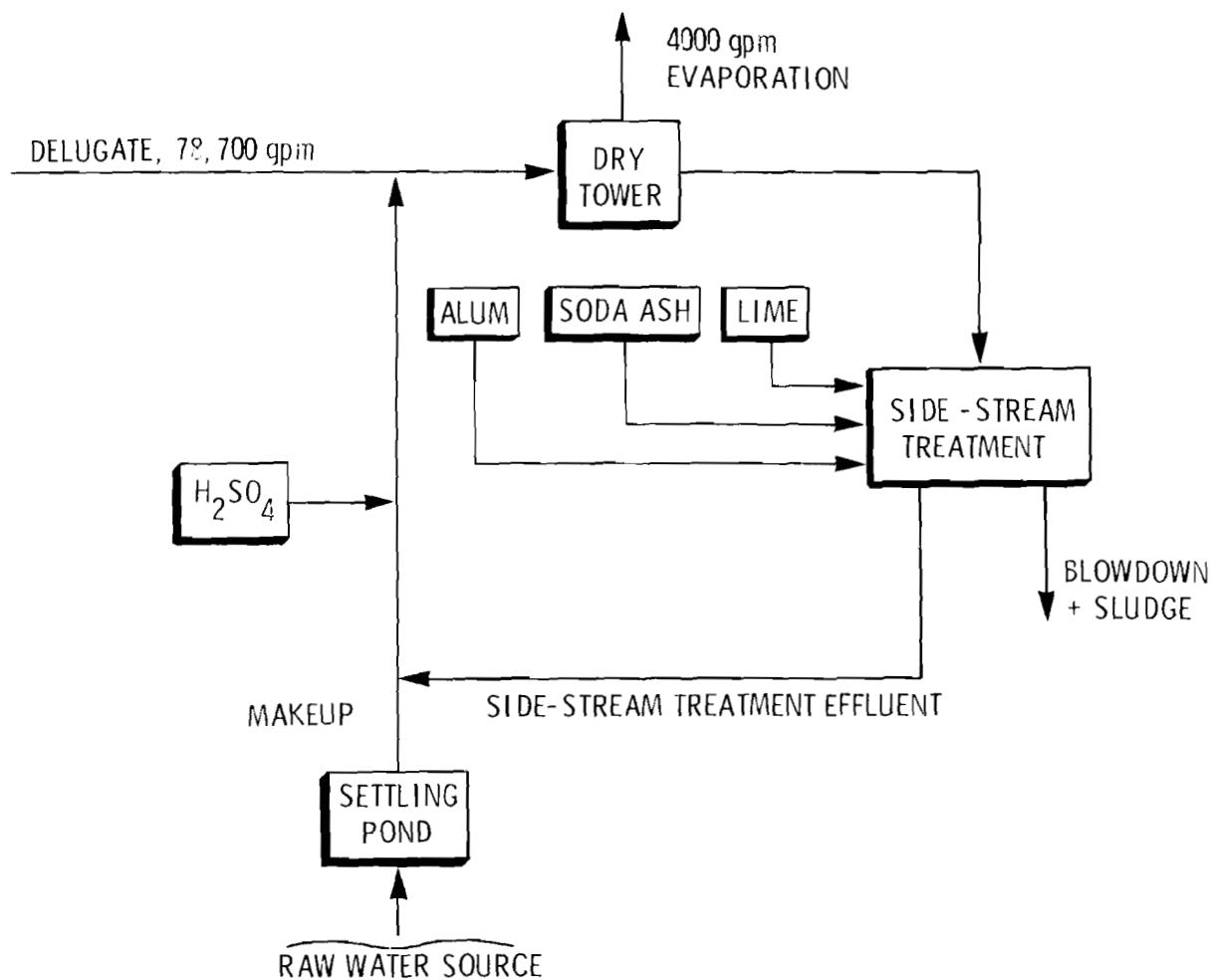
As has been indicated previously, a combination of acid treatment and concentration control is the preferred method for prevention of calcium carbonate scale in deluged DCT systems. Sulfuric acid is generally used in open recirculating water systems because of its low cost.<sup>(10)</sup>

A schematic drawing of the delugate system for a 1000 MWe plant is shown in Figure 7.<sup>(22)</sup> A side-stream taken from the delugate is treated by lime-soda softening. The allowed cycles of concentration, side-stream flow rate, and chemical dose rates will depend on the quality of the makeup water. Typical values are shown in Table 8 for a variety of waters.

Table 9 shows the costs of side-stream and makeup water treatment.<sup>(21,22)</sup> As can be seen, it is considerably less expensive to use the existing raw water supply with pH control and side-stream treatment rather than to attempt to purify the makeup water.

### 6.2 pH CONTROL

The feed rate of 66° Baume sulfuric acid to the makeup water can be calculated from the following formula (assuming a 12-hour



**FIGURE 7.** Treatment of Delugate Water to Prevent Formation of Calcium Carbonate Scale.

day and a maximum allowed delugate alkalinity of 40 mg/l as  $\text{CaCO}_3$ ):

$$\text{gal. H}_2\text{SO}_4/\text{day} = (\Delta C_T) (\text{Makeup Flow, gpm}) (4.12 \times 10^{-4})$$

where  $\Delta C_T = \frac{\text{Alkalinity of Makeup, mg/l as CaCO}_3 - 40}{\text{cycles of concentration}}$

Acid feed rate should be controlled using an automatic pH control system similar to that similar to that shown in Figure 8.<sup>(10)</sup> A typical acid delivery, storage and transfer system is shown in Figure 9.<sup>(10)</sup>

TABLE 8. Approximate Chemical Dosage Rates and Treatment Stream Flow Rates as a Function of Makeup Water Quality.

	<u>"Pure"</u>	<u>Columbia River</u>	<u>Richland City</u>	<u>San Juan River</u>	<u>Sheridan Wyo.</u>
Circulation Rate, gpm		78700			
Evaporation Rate, gpm		4000			
Allowed Cycles of Concentration	35	22	14	6	4.5
Side Stream Flow Rate, gpm	120	190	305	790	1125
Lime Dosage, lb/day	30	50	75	200	280
Soda Ash Dosage, lb/day	260	410	660	1710	2435
Alum Dosage, lb/day	15	25	35	95	135
Blowdown + Sludge Flow Rate, gpm	15	20	35	85	120
Side-Stream Treatment Effluent Flow Rate, gpm	105	170	270	705	1005
Makeup Flow Rate, gpm	4015	4020	4035	4085	4120
Sulfuric Acid Feed Rate, gal/day	40	100	85	400	715

TABLE 9. Approximate Costs of Side-Stream and Makeup Water Treatment.

	"Pure"	Columbia River	Richland City	San Juan River	Sheridan Wyo.
Side-Stream Treatment Costs:					
Capital - $10^4$ Dollars	7.8	10.0	14.0	24.0	30.0
Operating - $10^4$ Dollars/year <sup>(a)</sup>	1.0	1.6	2.5	6.4	9.1
Makeup Treatment Costs:					
Capital - $10^4$ Dollars	66-296	1.3	1.2	3.0	4.2
Operating - $10^4$ Dollars/year <sup>(a)</sup>	14-38	1.1	0.9	4.3	7.7

(a) Assuming operation at 80% capacity.

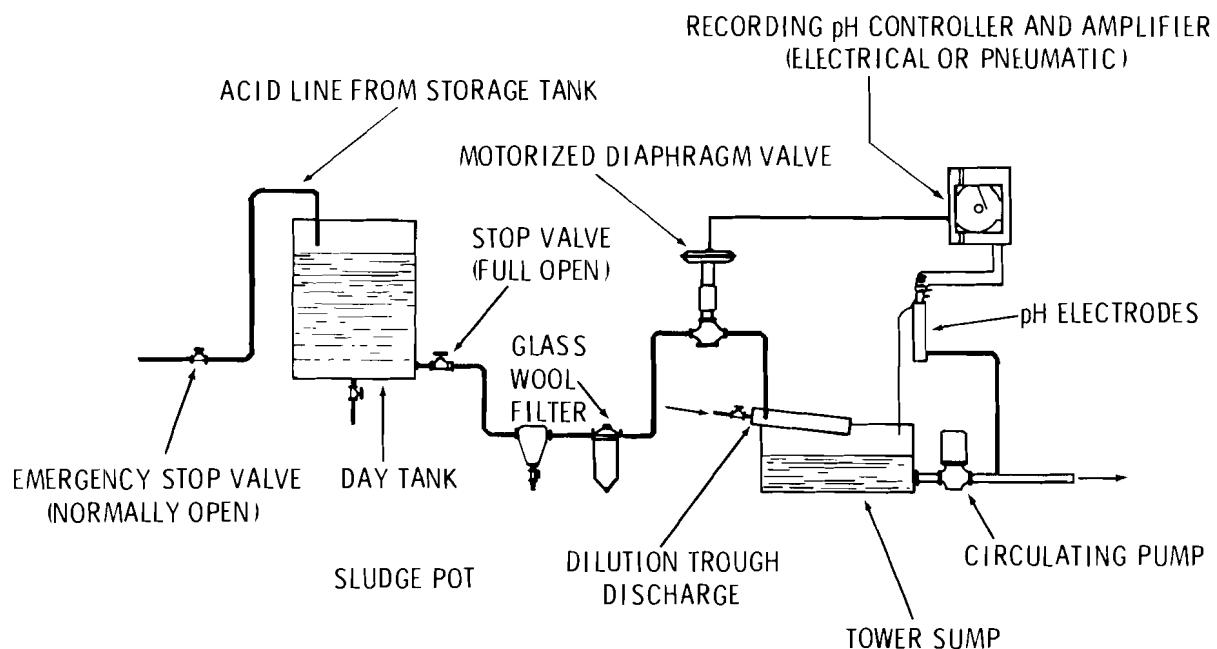


FIGURE 8. System for Automatic Control of Delugate pH.

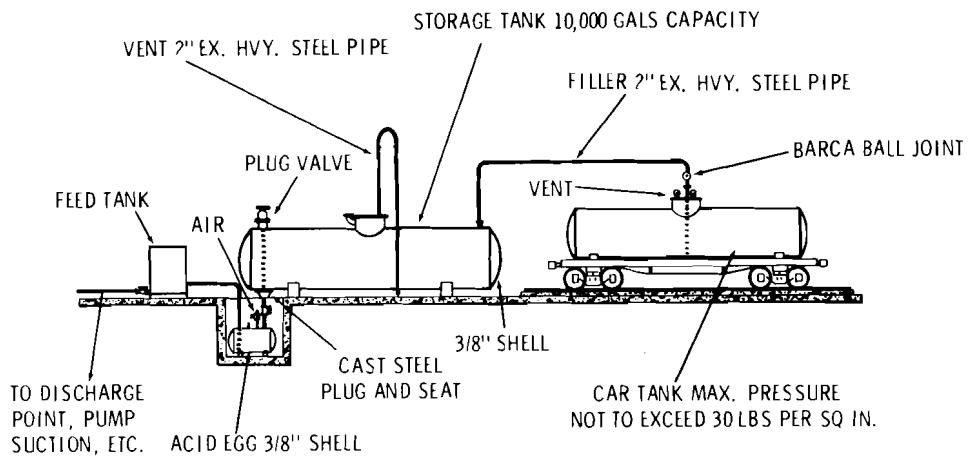


FIGURE 9. Acid Delivery, Storage and Transfer System.

#### 6.2.1 Calcium Sulfate Scale Formation

Of concern with the use of sulfuric acid for pH control is the possibility of calcium sulfate scale formation. A water treatment consulting firm indicates that a good rule of thumb to control calcium sulfate scale is to never allow the product of the concentrations (in mg/l as  $\text{CaCO}_3$ ) of calcium and sulfate ions to exceed 500,000.<sup>(23)</sup> However, Feitler<sup>(11)</sup> has shown that between 5 and 10 times the solubility product concentrations are required before precipitation of calcium sulfate begins. From his data a critical scaling constant of about  $2.5 \times 10^{-3}$  ( $[\text{Ca}^{++}] [\text{SO}_4^{--}]$ ) can be calculated for calcium sulfate.

The concentrations of sulfate in the deluge for the various waters being considered are shown in Table 10. As this table shows, the ion product of calcium and sulfate is less than the critical scaling constant for each of the waters shown; therefore, calcium sulfate scale will not form.

TABLE 10. Buildup of Sulfate Concentration in the Delugate as a Function of Makeup Water Quality.

	<u>"Pure"</u>	<u>Columbia River</u>	<u>Richland City</u>	<u>San Juan River</u>	<u>Sheridan Wyo.</u>
Sulfate in Makeup Water: (a)					
Natural:	15	25	35	175	735
Added:	26	62	53	245	435
Total:	40	87	88	420	1170
Cycles of Concentration:	35	22	14	6	4.5
Sulfate in Delugate: (a)	1400	1915	1230	2520	5265
Calcium in Delugate: (a)	1050	990	980	990	990
$[\text{Ca}^{++}] \times [\text{SO}_4^{--}] \times 10^4$ :	1.5	1.9	1.2	2.5	5.2
Critical Scaling Constant $\times 10^4$ :		-----25-----			

(a) mg/l as  $\text{CaCO}_3$

## 7.0 RESEARCH NEEDS

1 - Not addressed in this paper are the degradation of deluge water quality and fouling of the finned surfaces by air-borne particulate material such as dust, insects, pollen, etc. A systematic study is needed of fouling propensity, cleaning techniques and increased side-stream treatment capacity necessitated by degraded air quality.

2 - Given here is an estimate of the effect of scale on heat transfer and delugate flow. Experimental data is needed to precisely define how much scale can be tolerated and rates of scale deposition as a function of water quality and treatment.

3 - It is recommended herein that zero-hardness water be used to flush the extended surfaces at the end of each deluge cycle. When this water evaporates, a layer of inorganic salts will be deposited on the fin surfaces. Pitting corrosion of the aluminum fins beneath these salt deposits is possible during dry operation. Questions which require laboratory analysis include the following:

- Does pitting beneath the salt deposits occur?
- What is the effect of pitting on the heat transfer performance of the extended surfaces?
- Will flushing with deionized water be required?

4 - An alternate delugate treatment technology is one employing dispersants (such as phosphonates, polyacrylates, etc) to inhibit scale formation. While such materials are widely used as scale inhibitors in wet evaporative towers, their effectiveness in systems allowed to evaporate to dryness is unknown. Dispersants may aid in redissolution of materials deposited by evaporation, and this methodology may prove to be less expensive than control of pH and calcium concentration; laboratory data are required.

5 - Verification of the critical scaling constants, particularly that for calcium sulfate, is required. Accurate determination of these constants is needed as a function of temperature, ionic strength and noncommon ions such as magnesium.

6 - It has been assumed that the alternate wet-dry cycles in the deluge system will control the growth of algae and other biofouling organisms in the system. This assumption requires experimental verification. If biofouling appears to be a problem, control procedures such as the use of chlorine and the use of supplementary biocides must be examined.

7 - The effect of finned-tube design on heat transfer degradation due to scale deposition and corrosion is largely unknown. The least expensive design is one employing aluminum fins wrapped on to carbon steel tubes. Whether this design will be subject to such problems as crevice corrosion, galvanic corrosion, scale formation in the crevice, etc. is an area requiring experimental work. Certainly exposed carbon steel tube ends will be subject to corrosion, and an effective means of protection must be devised.

#### 8.0 SUMMARY AND CONCLUSIONS

Deluging of air-cooled heat exchangers with water during warm periods holds the promise of increasing their heat rejection capability and reducing the cost of dry cooling. One of the principal uncertainties in the use of the deluge concept is the tendency toward deposition of solids from the deluge. Small amounts of calcium carbonate scale may significantly reduce the cooling efficiency of a deluged system by reducing the heat transfer coefficient and interfering with deluge flow. Thus it is important to define deluge water quality in evaluating the formation of scale and its effect on heat transfer in the deluged dry cooling system.

Most water treatment programs designed to control calcium carbonate scale formation in cooling water systems are based on the use of the Langlier Saturation Index. Recent work has shown that the Saturation Index is conservative, and open recirculating cooling systems can be operated at a pH level (the "critical pH") 1.7 to 2.0 pH units above that predicted by the Saturation Index. The presence of magnesium and sulfate ions in the water increases the permissible operating pH even further. Operation at pH levels higher than those derived from the Saturation Index greatly increases the water reuse possibilities of a given raw water supply.

Application of the critical pH concept together with carbonate equilibria in an open aqueous system makes possible the calculation of the concentration of all solute species at any pH. If an arbitrary upper limit of 1000 mg/l as  $\text{CaCO}_3$  for the calcium hardness is chosen, the system must be maintained at a pH level less than 8.3 if formation of calcium carbonate scale is to be prevented. Suggested safe operation is at a pH level somewhat lower than this upper limit, in the range of 7.6-7.8.

When the flow of deluge is turned off, water remaining on the surface will evaporate and deposit as a scale the impurities it contained. Calcium carbonate scale so deposited will not redissolve, since the ion product of calcium and free carbonate species in the deluge will be about equal to the solubility product. If further scale deposition is to be avoided, the deluge operating pH must be reduced to about pH 7.2.

Formation of calcium carbonate scale by evaporation of the delugate can be prevented by deluging the finned surfaces with zero hardness water before turning off the water flow.

The method of choice for the prevention of calcium carbonate scale in deluged DCT systems is a combination of pH control using sulfuric acid and concentration control by the use of side-stream treatment.

Areas requiring experimental data include the effect of air-borne particulates on heat exchanger fouling and degradation of delugate quality, a more precise definition of heat transfer degradation due to sealing and the amount of scale that can be tolerated, the effect of salt deposition on fin corrosion, the use of dispersants to control scale, verification of values of the critical scaling constants, the possibility of biofouling and the effect of finned tube design on scaling and corrosion problems.

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APPENDIX A

COSTS

## APPENDIX A

### COSTS

#### A-1. WATER TREATMENT COSTS

Following are tables which show the cost, in 1975 dollars, of treating raw water of varying quality to various purity levels. Table A-1 shows the capital, operating and total costs (in terms of \$/1000 gal) of a three-mgd treatment plant. Data are given for five raw water types and four treatment levels, which are defined in Tables A-2 and A-3. Information given here is based on data received from J. S. Nordin, Betz Environmental Engineers, Plymouth Meeting, PA.

TABLE A-1. Water Treatment Costs, 3-MGD Treatment Plant  
(1975 Dollars).

Desired Quality, see Table A-2	Raw Water Type see Table A-3	Capitol Cost, \$ x 10 <sup>-5</sup>	Capital Cost,(a) \$/1000 gal	Operating Cost, \$/1000 gal	Total Cost, \$/1000 gal
Potable:	A	4.4	0.104	0.162	0.266
	B	8.6	0.204	0.204	0.408
	C	9.6	0.227	0.240	0.467
	D	10.1	0.239	0.234	0.473
	E	1.7	0.040	0.061	0.101
Pure:	A	4.4	0.104	0.162	0.266
	B	8.6	0.204	0.204	0.408
	C	17.6	0.416	0.352	0.768
	D	10.1	0.239	0.234	0.473
	E	19.9	0.471	0.454	0.925
High Purity:	A	13.4	0.371	0.441	0.758
	B	17.7	0.419	0.461	0.880
	C	17.6	0.416	0.588	1.004
	D	21.1	0.499	0.630	1.129
	E	23.4	0.554	0.652	1.206
Ultra Pure:	A	15.9	0.376	0.496	0.872
	B	20.2	0.478	0.516	0.994
	C	20.1	0.476	0.643	1.119
	D	23.6	0.559	0.704	1.263
	E	23.4	0.554	0.700	1.254

(a) Fixed charge rate = 17.4%,  
Plant capacity factor = 80%,  
Plant Life = 30 years.

TABLE A-2. Typical Raw Water Analyses.

Raw water type A: Surface, medium hardness, low dissolved and suspended solids, low silica.

Raw water type B: Surface, medium hardness, low dissolved solids, high suspended solids, low silica.

Raw water type C: Well water, very hard, high dissolved solids, no suspended solids, high silica.

Raw water type D: Surface water, hard, moderate dissolved solids, high suspended solids, some color, and silica.

Raw water type E: Well water, medium hardness, moderate dissolved solids, no suspended solids, some silica.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Total Hardness, mg/l as $\text{CaCO}_3$	60	50	400	200	100
Calcium hardness, mg/l as $\text{CaCO}_3$	45	30	300	150	75
Sodium, mg/l as $\text{CaCO}_3$	30	20	20	20	600
Alkalinity, mg/l as $\text{CaCO}_3$	60	50	350	150	50
Chloride, mg/l as $\text{CaCO}_3$	20	10	20	20	300
Sulfate, mg/l as $\text{CaCO}_3$	15	10	50	50	350
Silica, mg/l as $\text{CaCO}_3$	2	2	40	8	10
Iron, mg/l	0.1	0.3	0.1	0.3	0.1
Dissolved solids, mg/l	110	100	670	330	660

TABLE A-3. Treatment Levels.

	<u>Potable</u>	<u>Pure</u>	<u>High Purity</u>	<u>Ultra Pure</u>
pH	6.0-9.0	6.5-7.5	6.5-7.5	6.5-7.5
Hardness, mg/liter as $\text{CaCO}_3$	50-150	20-40	2-4	<0.05
Dissolved Solids, mg/liter	100-250	50-100	5-10	<0.05
Iron, mg/liter	<0.3	<0.1	<0.1	<0.01
Silica	10-20	2	<0.1	<0.01

A-2. CHEMICAL, ELECTRICAL AND LABOR COSTS

All operating cost estimates are based on the following costs of water treatment chemicals, electricity and labor:

Lime	-	\$0.017/lb
Soda Ash	-	\$0.03/lb
Alum	-	\$0.20/lb
Sulfuric Acid-		\$0.37/gal (66° Baume)
Labor	-	\$10/wan-hour
Electricity	-	\$0.01/KWH

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