

A pHs Equation for Calcium Carbonate Scale Prediction in Cooling Water Systems

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(Received 16th March 2006, revised 23rd July 2007)

Summary: Cooling water systems contain a large number of potential scale and scale causing constituents and calcium carbonate is the chief ingredient of scale formed. Scale forming and/ or corrosive tendencies of water can be predicted qualitatively by using the saturation indices. Studies were conducted to introduce a pHs for simplicity. Some of the industrially used empirical indices for predicting CaCO₃ scaling potential are reviewed and their shortcomings are discussed. The theoretically calculated results for pHs equation have been compared and validated with experimental values and with other commonly and industrially used indices. The results showed that pHs equation is a better predictive approach. This equation is a measure of the scaling potential and provides a conservative measure. It is also important to point out that saturation pH (pH_s) value calculated in the present study has shown the same result *i.e.* pH_s = 7.68 as predicted by the literature. Increase in temperature accelerates the rates of both scaling and corrosion processes thus the values of [pK_{a2}- pK_{sp}] are inversely proportional to temperature and are directly proportional to the concentration of TDS. Moreover, it was investigated that the pAlkalinity decreases as the concentration of bicarbonate increases.

Introduction

Scaling problem in a recirculating heating or cooling water system can be recognised by one or more of the following symptoms: reduction in heat transfer rate; reduction in water flow; partial or complete blockage of pipelines, condenser tubes, or other openings *etc.* Even a small buildup of scale on a heat exchange surface reduces water flow. Scale formation is an industrial problem, encountered with water containing ions of the sparingly soluble salts that can readily precipitate on heat transfer surfaces in evaporative concentration operations. Scale formation, hindering the heat transfer process, increases specific energy consumption and operating costs and causes frequent shut down of the evaporator for cleaning [1].

Cooling water systems contain a large number of potentials scale and deposit-causing constituents. These include soluble ions (such as calcium, magnesium, soluble silica, zinc and iron salts) that precipitate as insoluble deposits when they encounter changes in water temperature, pH, concentration or incompatible additives. Examples of deposits are calcium carbonate, calcium phosphate, silica, iron hydroxides, sulfides, calcium sulfate, magnesium salts, zinc phosphate and zinc hydroxide.

Out of these deposits calcium carbonate causes a serious harm to cooling water circulating tubes.

Scale forming and/ or corrosive tendencies of water can be predicted qualitatively by using the saturation indices or simply by Balanced Water Calculation. Langelier [2] developed a method of determining the scaling or corrosive potential of water from its chemical composition.

$$\text{Langelier Saturation Index (LSI)} = \text{pH} - \text{pH}_s \dots (1)$$

where

pH = measured pH in steam water sample

pH_s = saturation pH for calcium carbonate

Later on Ryznar [3] proposed Stability Index (RSI) with the following expression:

$$\text{Ryznar Stability Index (RSI)} = 2 \text{pH}_s - \text{pH} \dots (2)$$

Puckorius (Practical) Scaling Index (PSI) was suggested by Puckorius [4], he used an equilibrium pH rather than the actual system pH to account for the buffering effects:

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Puckorius (Practical) Scaling Index (PSI) = 2 pH_{eq} - pHs.....(3)

where pH_{eq} = 1.465 x log₁₀ [M.Alkalinity] + 4.54.

There are also other indices in the literature which consider the calcium carbonate solubility [5-7]. Presently it is laborious work for power station chemist to calculate saturation index which account for all the aforesaid parameters. Hence the present project was undertaken to minimize error and to get the exact value by introducing a pHs equation for simplicity

Results and Discussion

Collected samples from re-circulating cooling water system were analyzed and results were reported as:

Water Analysis

Following results were obtained after analysis of re-circulating cooling water samples. Results reported are average of three replications.
pH (actual) = 8.2, Temperature = 30 °C, TDS = 500 ppm, Ca- Hardness = 150 ppm as CaCO₃, M. Alkalinity = 100 ppm as CaCO₃. (M: Methyl orange)

Calculation of pHs by Applying Eq. (4)

pHs = (9.3 + A + B) - (C + D).....(4)

A = (Log₁₀ [TDS] - 1) / 10 = 0.17

B = { - 13.12 Log₁₀ (°C + 273) } + 34.55 = 1.99

C = Log₁₀ [Ca⁺² as CaCO₃] - 0.4 = 1.78
D = Log₁₀ [M.Alkalinity as CaCO₃] = 2.0
pHs = (9.3 + 0.17 + 1.99) - (1.78 + 2.0) = 7.68

Calculation of pHs by Applying Eq. (5)

pHs = [pK_{a2} - pK_{sp}] + pCa + pAlk(5)
[pK_{a2} - pK_{sp}] (From Table 1) = 2.13
pAlk (From Table- 2) = 2.70
pCa (From Table- 2 and Eq. 6) = 2.85
pHs = 2.13 + 2.85 + 2.70 = 7.68

Calculation of Saturation Indices:

Langelier Saturation Index (LSI) = pH - pHs.....(1)
= 8.2 - 7.68

= 0.52 (Slightly scale forming and Corrosive)

Ryznar Stability Index (RSI) = 2 pHs - pH.....(2)
= 2(7.68) - 8.2
= 7.16 (Corrosion Significant)

Puckorius Scaling Index (PSI) = 2 (pHeq)* - pHs (3)
= 2 (7.47) - 7.68
= 7.26 (Corrosion Significant)

where

*pHeq = 1.465 x log₁₀ [M.Alkalinity] + 4.54 = 7.47

The goal of this work was to introduce a pHs equation for calcium carbonate scale prediction in cooling water system. It is important to point out that saturation pH (pHs) value calculated by applying the Eq. (4) and (5) have shown the same result *i.e.* pHs = 7.68. Saturation pH (pHs) value calculated by applying the Eq. (5) is the outcome of the present study, which was obtained directly (Table- 1 and 2 and Eq. (6)). The results of the present study (Eq. (5))

Table-1: Values of [pK_{a2}-pK_{sp}] at various concentrations of TDS, EC and Temperature.

EC μ S/cm ¹	TDS ppm	[pK _{a2} -pK _{sp}] values at various Temperature (°C) range										
		0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°
13.33	10	2.74	2.45	2.18	2.00	1.82	1.66	1.50	1.35	1.21	1.11	1.04
40.00	30	2.76	2.47	2.20	2.02	1.84	1.68	1.52	1.37	1.23	1.13	1.06
80.00	60	2.78	2.49	2.22	2.04	1.86	1.70	1.54	1.39	1.25	1.15	1.08
146.67	110	2.80	2.51	2.24	2.06	1.88	1.72	1.56	1.41	1.27	1.17	1.10
200.00	150	2.81	2.52	2.25	2.07	1.89	1.73	1.57	1.42	1.28	1.18	1.11
266.67	200	2.82	2.53	2.26	2.08	1.90	1.74	1.58	1.43	1.29	1.19	1.12
333.33	250	2.83	2.54	2.27	2.09	1.91	1.75	1.59	1.44	1.30	1.20	1.13
400.00	300	2.84	2.55	2.28	2.10	1.92	1.76	1.60	1.45	1.31	1.21	1.14
666.67	500	2.86	2.57	2.30	2.12	1.94	1.78	1.62	1.47	1.33	1.23	1.16
1250.0	1000	2.90	2.61	2.34	2.16	1.98	1.82	1.66	1.51	1.37	1.27	1.20
2352.9	2000	2.92	2.63	2.36	2.18	2.00	1.84	1.68	1.53	1.39	1.29	1.22
3529.2	3000	2.94	2.65	2.38	2.20	2.02	1.86	1.70	1.55	1.41	1.31	1.24
4705.9	4000	2.95	2.66	2.40	2.21	2.03	1.87	1.71	1.56	1.42	1.32	1.25

Table-2: pAlkalinity at various bicarbonate concentrations.

Conc.	pAlk	Conc.	pAlk	Conc.	pAlk	Conc.	pAlk	Conc.	pAlk
01	4.70	02	4.40	03	4.20	04	4.10	05	4.00
10	3.70	20	3.40	30	3.20	40	3.10	50	3.00
100	2.70	200	2.40	300	2.20	400	2.10	500	2.00
1000	1.70	2000	1.40	3000	1.20	4000	1.10	5000	1.00
10000	0.70	20000	0.40	32000	0.20	40000	0.10	50000	0.00

Conc. = M. Alkalinity concentration in ppm.
 pAlk = Negative logarithm of M. Alkalinity concentration.

are in accord with those reported earlier [8-10] which had shown exactly the same result *i.e.* pHs = 7.68 (Eq. 4). Regarding interpretation of results of the same water analysis Langelier Saturation Index (LSI) has shown slightly scale forming and corrosive indication, while Ryznar Stability Index (RSI) and Puckorius (Practical) Scaling Index (PSI) both predicted significant corrosion. Studying the same water sample at 10 °C following value of LSI, RSI

and PSI were obtained:

LSI= 0.07 (Balanced but pitting corrosion possible)
 RSI = 8.06 (Heavy Corrosion)
 PSI = 6.81 (Little Scale or Corrosion)

It is apparent from the above results that the temperature at which the calculation is made has considerable impact on the results. The water chemistry at 30 °C is slightly scale forming and corrosive (LSI) or significantly corrosive (both RSI & PSI), but if the water is exposed to lower temperature (10 °C), it would predict balance (LSI), or heavy corrosion (RSI) or, little scale or corrosion (PSI). These interpretations are in accord with Marangoy and Savvides [11], who reported that increase in temperature accelerates the rates of both scaling and corrosion processes. From the present study it was also observed that the values of [pK_{a2} - pK_{sp}] are inversely proportional to temperature and are directly proportional to the concentration of TDS (Table-1). Furthermore it was found that the pAlkalinity (Table-2) at various concentration decreases as the concentration of bicarbonate increases. It was also observed that a ten times increase in concentration results in only one (1.0) degree decrease in the pAlkalinity value. These findings are in close agreement to the earlier reported results [12]. It was concluded that saturation pH (pHs) value calculated by applying the proposed method is realistic and found exact as declared by previous literature and could be used in industrial applications.

Experimental

This research work was done in Chemical Section, Gas Turbine Power Station (WAPDA), in collaboration with the Department of Chemistry, University of Agriculture, Faisalabad, Pakistan. Water samples were collected from re circulating cooling water system of the WAPDA power station. The parameters like pH, electrical conductivity (EC), or total dissolved solids (TDS), temperature (°C), Ca-Hardness (ppm) and total alkalinity (ppm) were determined by applying the standard methods [13]. Calculation of the saturation pH (pHs) can be done using the chart representing numerical relationship found in various references [14,15] or through the use of the following relationship [8].

$$pHs = (9.3 + A + B) - (C + D) \dots \dots \dots (4)$$

Where

A = (Log₁₀ [TDS] - 1) / 10
 B = {- 13.12 Log₁₀ (°C + 273)} + 34.55
 C = Log₁₀ [Ca⁺² as CaCO₃] - 0.4
 D = Log₁₀ [M. Alkalinity as CaCO₃]

In the present study saturation pH (pHs) was calculated by the following equation.

$$pHs = [p K_{a2} - p K_{sp}] + p Ca + p Alk \dots \dots \dots (5)$$

pK_{a2}= Negative logarithm of the equilibrium constant for the dissociation of bicarbonates.

pK_{sp} = Negative logarithm of solubility product constant for the dissociation of calcium carbonate.

pCa= Negative logarithm of calcium concentration

pAlk = Negative logarithm of bicarbonate concentration.

For the determination of saturation pH (pHs) the values of [pK_{a2} - pK_{sp}] were tabulated for some selected temperature range at various concentrations of TDS (ppm) and electrical conductivity EC (μScm⁻¹) presented in Table-1. The values for pAlkalinity were also tabulated (Table-2) for simplicity at various bicarbonate concentration. The pCa value was determined by applying the relationship at the same concentration as determined by [9].

Table-3: Interpretation of the Saturation Indices.

Indices	Values	Indication
Langelier	2.0	Scale forming but non corrosive
Saturation	0.5	Slightly scale forming and Corrosive
Index (LSI)	0.02	Balanced but pitting corrosion possible
	-0.5	Slightly corrosive but non-scale forming
	-2.0	Serious corrosion
Ryznar	4.0-5.0	Heavy Scale
Stability Index	5.0-6.0	Light Scale
(RSI)	6.0-7.0	Little Scale or corrosion
	7.0-7.5	Corrosion Significant
	7.5-9.0	Heavy Corrosion
	> 9.0	Corrosion intolerable
Puckorius	4.5-5.5	Heavy and Serious Scale
(Practical)	5.5-6.5	Light Scale Prediction
Scaling	6.5-7.5	Little Scale or Corrosion
Index (PSI)	7.5-8.0	Corrosion Significant
	8.0-9.0	Heavy and Serious Corrosion
	> 9.0	Corrosion intolerable

$$pCa = pAlk + 0.3 \dots \dots \dots (6)$$

Saturation pH (pHs) was determined by applying the Equations (4) and (5) and the values obtained were incorporated in Equation (1), (2) and (3) to obtain saturation index (S.I) value. The (S.I) value obtained was interpreted (Table- 3) to make a decision whether there is a prediction of scaling or corrosion [15].

References

1. H. Glade and J. Ulrich, *Chem. Eng. Tech.*, **36**, 277 (2003).

2. W. F. Langelier, *J. Am. Water Works Assoc.*, **28**, 1500 (1936).
3. W. J. Ryznar, *J. Am. Water Works Assoc.*, **36**, 472 (1944).
4. P. R. Puckorius and J. M. Brooke, *Corrosion*, **47**, 280 (1991).
5. H. A. Stiff and L.E. Davis, *Pet. Trans.*, **195**, 213 (1952).
6. T. E. Larson and R. V. Skold, *Illinois State Water Survey*, C-71, 43 (1958).
7. J. E. Oddo and M. B. Tomson, *Corrosion*, **34**, 102 (1992).
8. W. Byrne, In *Reverse Osmosis: A Practical Guide for Industrial Users*, Tall Oaks Publishing Inc., Littleton Co., 111 (1995).
9. K. M. Zia, M. Iqbal, H. Nawaz and G. Samin, *Int. J. Agric. Biol.*, **1**, 353 (1999).
10. R. Sheikholeslami and H. W. K. Ong, *Desalination*, **157**, 217 (2003).
11. V. S. Marangoy and K. Savvides, *Desalination*, **138**, 251 (2001).
12. R. Sheikholeslami, *Water Sci. Technol.*, **49**, 201 (2004).
13. V. A. Prisyazhniuk, *Appl. Therm. Eng.*, **27**, 1637 (2007).
14. V. A. Prisyazhniuk, *Energ. Explo. Exploit.*, **23**, 277 (2005).
15. A. D. Althouse, C. H. Turnquist and A. F. Bracciano, In *Modern Refrigeration and Air Conditioning*, Goodheart-Wilcox Publisher, 74 (2003).