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Langelier Calcium Carbonate Saturometry Determination by Table Values

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ABSTRACT

Studies were conducted to introduce a simple method of saturometry determination. $[pK_2 - pK_s]$ values for selected temperature (°C) and conductivity or TDS and p–Alkalinity values at various concentration were arranged in tabular form. The $[pK_2 - pK_s]$ values decreased as the temperature increased and these values increased as the conductivity or TDS increased. The p–Alkalinity values decreased as the concentration increased. A ten times increase in concentration only one degree decrease in p–Alkalinity values take place. The p–Ca and p–Alkalinity relation was formulated. The $pH_{(saturation)}$ was determined by summing up required table values in equation. Scaling or corrosion characteristics of water was suggested by taking difference between the actual pH and calculated saturation pH.

Key Words: Saturation index; Scaling; Corrosion; Alkalinity; pH; $CaCO_3$

INTRODUCTION

In a recirculating fresh water cooling systems the protection against corrosion and scaling of metals is a problem of enormous economic importance. Calcium carbonate is the chief ingredient of scale formed in cooling water system (Kahler, 1944). To prevent scale deposition and to control corrosion in heat exchangers and circulating water lines, Langelier (1936) developed a method of determining the scaling or corrosive potential of a water from its chemical composition, pH and temperature. Saturation index can be achieved by using Langelier saturation-index chart only if temperature in Fahrenheit (°F) and total dissolved solids (ppm) are known. Later on, in an attempt to secure a quantitative index, Ryznar (1944) proposed a stability index $IR = 2(pH_s)-pH$, which is in general appears to be more representative of the corrosive or scale forming nature of cooling water. This index is empirical based on a study of actual operating results with water's of various saturation index. Presently it is laborious work for chemist working in steam turbine units to calculate Langelier index by the use of this chart. Hence the present project was undertaken to minimize error and to get exact values with the objectives (a) introducing a simple method of saturometry determination (b) forming a new modified form of Langelier Index for simplicity (c) formulating the required values in tabular form.

MATERIALS AND METHODS

This practical approach for plant operators was carried out in Chemical Section, Gas Turbine Power Station (WAPDA), Faisalabad, Pakistan. The Langelier Index (L) or saturation Index (SI) was calculated following the equation:

$$(L.I) \text{ or } (S.I) = pH_{(actual)} - pH_{(saturation)} \qquad I$$

$pH_{(saturation)}$ (pH_s) was calculated by the following equation.

$$pH_s = [pK_2 - pK_s] + pCa + pAlk \qquad II$$

Where p = Log_{10} the reciprocal of adjoining symbol, $[pK_2\text{-}pK_s]$ = Negative Log of second dissociation constant for carbonic acid and activity product constant for $CaCO_3$ respectively at the water temperature

p–Ca, pAlk = Negative log factor of the Ca–hardness and total alkalinity respectively expressed in ppm of equivalent $CaCO_3$.

The parameters like pH of the water ($pH_{(actual)}$), Electrical conductivity (EC), Total dissolved solids (TDS), Temperature (°C), Ca–Hardness and total Alkalinity by applying standards methods were determined (Betz Engineering & Technical Lab. Staff, 1967). The $[pK_2 - pK_s]$ values were formulated for selected temperature and electrical

Table I. Values of $(pK_2 - pK_s)$

EC	TDS	Values of $\lvert pK_2 - pK_s \rvert$ at temperature of																				
μScm^{-1}	ppm	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C	75°C	80°C	85°C	90°C	95°C	100°C
13.33	10	2.68	2.53	2.39	2.25	2.12	2.03	1.94	1.85	1.76	1.68	1.60	1.52	1.44	1.37	1.29	1.20	1.15	1.09	1.05	1.02	0.98
26.67	20	2.69	2.54	2.40	2.27	2.14	2.04	1.95	1.86	1.77	1.69	1.61	1.53	1.45	1.38	1.30	1.21	1.16	1.10	1.06	1.03	0.99
40.00	30	2.70	2.55	2.41	2.28	2.15	2.05	1.96	1.87	1.78	1.70	1.62	1.54	1.46	1.39	1.31	1.22	1.17	1.11	1.07	1.04	1.00
53.33	40	2.71	2.56	2.42	2.29	2.16	2.06	1.97	1.88	1.79	1.71	1.63	1.55	1.47	1.40	1.32	1.23	1.18	1.12	1.08	1.05	1.01
80.00	60	2.72	2.57	2.43	2.30	2.17	2.07	1.98	1.89	1.80	1.72	1.64	1.56	1.48	1.41	1.33	1.24	1.19	1.13	1.09	1.06	1.02
106.67	80	2.73	2.58	2.44	2.31	2.18	2.08	1.99	1.90	1.81	1.73	1.65	1.57	1.49	1.42	1.34	1.25	1.20	1.14	1.10	1.07	1.03
146.67	110	2.74	2.59	2.45	2.32	2.19	2.09	2.00	1.91	1.82	1.74	1.66	1.58	1.50	1.43	1.35	1.26	1.21	1.15	1.11	1.08	1.04
200.00	150	2.75	2.60	2.46	2.33	2.20	2.10	2.01	1.92	1.83	1.75	1.67	1.59	1.51	1.44	1.36	1.27	1.22	1.16	1.12	1.09	1.05
266.67	200	2.76	2.61	2.47	2.34	2.21	2.11	2.02	1.93	1.84	1.76	1.68	1.60	1.52	1.45	1.37	1.28	1.23	1.17	1.13	1.10	1.06
333.33	250	2.77	2.62	2.48	2.35	2.22	2.12	2.03	1.94	1.85	1.77	1.69	1.61	1.53	1.46	1.38	1.29	1.24	1.18	1.14	1.11	1.07
400.00	300	2.78	2.63	2.49	2.36	2.23	2.13	2.04	1.95	1.86	1.78	1.70	1.62	1.54	1.47	1.39	1.30	1.25	1.19	1.15	1.12	1.08
493.33	370	2.79	2.64	2.50	2.37	2.24	2.14	2.05	1.96	1.87	1.79	1.71	1.63	1.55	1.48	1.40	1.31	1.26	1.20	1.16	1.13	1.09
580.00	435	2.80	2.64	2.51	2.38	2.25	2.15	2.06	1.97	1.88	1.80	1.72	1.64	1.56	1.49	1.41	1.32	1.27	1.21	1.17	1.14	1.10
666.67	500	2.81	2.66	2.52	2.39	2.26	2.16	2.07	1.98	1.89	1.81	1.73	1.65	1.57	1.50	1.42	1.33	1.28	1.22	1.18	1.15	1.11
837.50	670	2.82	2.67	2.53	2.40	2.27	2.17	2.08	1.99	1.90	1.82	1.74	1.66	1.58	1.51	1.43	1.34	1.29	1.23	1.19	1.16	1.12
1050.00	840	2.83	2.68	2.54	2.41	2.28	2.18	2.09	2.00	1.91	1.83	1.75	1.67	1.59	1.52	1.44	1.35	1.30	1.24	1.20	1.17	1.13
1250.00	1000	2.84	2.69	2.55	2.42	2.29	2.19	2.10	2.01	1.92	1.84	1.76	1.68	1.60	1.53	1.45	1.36	1.31	1.25	1.21	1.18	1.14
1764.70	1500	2.85	2.70	2.56	2.43	2.30	2.20	2.11	2.02	1.93	1.85	1.77	1.69	1.61	1.54	1.46	1.37	1.32	1.26	1.22	1.19	1.15
2352.94	2000	2.86	2.71	2.57	2.44	2.31	2.21	2.12	2.03	1.94	1.86	1.78	1.70	1.62	1.55	1.47	1.38	1.33	1.27	1.23	1.20	1.16
2941.18	2500	2.87	2.72	2.58	2.45	2.32	2.22	2.13	2.04	1.95	1.87	1.79	1.71	1.63	1.56	1.48	1.39	1.34	1.28	1.24	1.21	1.17
3529.24	3000	2.88	2.73	2.59	2.46	2.33	2.23	2.14	2.05	1.96	1.88	1.80	1.72	1.64	1.57	1.49	1.40	1.35	1.29	1.25	1.22	1.18
4705.88	4000	2.89	2.74	2.60	2.47	2.34	2.24	2.15	2.06	1.97	1.89	1.81	1.73	1.65	1.58	1.50	1.41	1.36	1.30	1.26	1.23	1.19
5882.35	5000	2.90	2.75	2.61	2.48	2.35	3.25	2.16	2.07	1.98	1.90	1.82	1.74	1.66	1.59	1.51	1.42	1.37	1.31	1.27	1.24	1.20

conductivity or TDS (Table I). The values of pAlkalinity were also formulated in tabular form (Table II) at various concentration. The p–Ca value was determined by applying the relation at same concentration

$$p\text{–}Ca = pAlk + 0.3 \qquad III$$

RESULTS AND DISCUSSION

The tendency of a water supply to deposit or dissolve calcium carbonate from solution with which the water is brought in contact depends on variation of various constituents. The $(pK_2\text{-}pK_s)$ values were formulated in tabular form (Table I) following Langelier saturation–index chart for selected temperature in Centigrade (°C) instead of Fahrenheit (°F) and electorial conductivity (EC) or total dissolved solids (TDS). It was observed that the values of $(pK_2 - pK_s)$ decrease as the temperature increase and these values increase as the concentration of TDS or EC increased. Increase in temperature accelerates the rates of both scaling and corrosion processes (Snoeyink and Jenkins, 1980). Table I was arranged after every 5°C difference to estimate the correct value (Balzar, 1980).

The p–Alkalinity (p–Alk) values (Table II) at various concentration decrease as the concentrations increase. It was also observed that a ten times increase in concentration, only one (1.0) degree decrease in the p–Alkalinity value takes place. While undertaking this project, following relationship between p–Alk and p–Ca was observed for the same concentration.

$$p\text{–}Ca = p\text{–}Alk + 0.3 \qquad III$$

A thin $CaCO_3$–protective layer is made by maintaining effective saturation index appreciably positive;a value of at least - 0.2 to + 0.6 is aimed at.

Evaluation. Suppose following analytical data was shown by recirculating cooling water system.

i. $pH_{(actual)} = 7.80$
ii. $EC = 400\ (\mu Scm^{-1})$
iii. Temperature = 30°C
iv. Alkalinity = 50 ppm
v. Ca – Hardness = 200 ppm

$[pK_2 - pK_s] = 2.04$	(From Table - I)
p–Alk = 3.00	(From Table - II)
p–Ca = 2.40 + 0.3 =2.70	(From Eq. - III)
$pH_s = 7.74$	(From Eq. - II).
SI = 7.80 - 7.74 = + 0.06	(From Eq. - I).

Table II. p–Alkalinity values at various concentrations

C	lk	C	pAlk	C	lk	C	pAlk	C	pAlk	C	lk	C	lk	C	lk	C	lk	C	lk	C	lk	C	lk	C	lk
01	4.70	21	3.38	41	3.09	61	2.94	81	2.82	104	2.69	171	2.49	255	2.29	410	2.09	688	1.89	1057	1.69	2197	1.49	3337	1.29	4482	1.09
02	4.40	22	3.36	42	3.08	62	2.94	82	2.81	108	2.68	175	2.48	260	2.28	420	2.08	706	1.88	1114	1.68	2254	1.48	3394	1.28	4539	0.08
03	4.20	23	3.34	43	3.07	63	2.93	83	2.80	112	2.67	178	2.47	265	2.27	430	2.07	724	1.87	1171	1.67	2311	1.47	3451	1.27	4596	1.07
04	4.10	24	3.32	44	3.06	64	2.93	84	2.80	115	2.66	181	2.46	270	2.26	440	2.06	742	1.86	1228	1.66	2386	1.46	3508	1.26	4653	1.06
05	4.00	25	3.30	45	3.05	65	2.92	85	2.79	118	2.65	184	2.45	275	2.25	450	2.05	760	1.85	1285	1.65	2425	1.45	3565	1.25	4710	1.05
06	3.95	26	3.28	46	3.04	66	2.92	86	2.78	121	2.64	188	2.44	280	2.24	460	2.04	776	1.84	1342	1.64	2482	1.44	3622	124	4768	1.04
07	3.90	27	3.26	47	3.03	67	2.91	87	2.78	124	2.63	191	2.43	285	2.23	470	2.03	792	1.83	1399	1.63	2539	1.43	3679	1.23	4826	1.03
08	3.85	28	3.24	48	3.02	68	2.91	88	2.77	127	2.62	194	2.42	290	2.22	480	2.02	808	1.82	1456	1.62	2596	1.42	3736	1.22	4884	1.02
09	3.80	29	3.22	49	3.01	69	2.90	89	2.77	130	2.61	197	2.41	295	2.21	490	2.01	824	1.81	1513	1.61	2653	1.41	3793	1.21	4942	1.01
10	3.70	30	3.20	50	3.00	70	2.90	90	2.76	133	2.60	200	2.40	300	2.20	500	2.00	840	1.80	1570	1.60	2710	1.40	3850	1.20	5000	1.00
11	3.67	31	3.19	51	3.00	71	2.89	91	2.76	137	2.59	205	2.39	310	2.19	518	1.99	858	1.79	1627	1.59	2767	1.39	3907	1.19	5500	0.97
12	3.64	32	3.18	52	2.99	72	2.87	92	2.75	171	2.58	210	2.38	320	2.18	536	1.98	876	1.78	1684	1.58	2824	1.38	3964	1.18	6000	0.95
13	3.61	33	3.17	53	2.98	73	2.86	93	2.75	144	2.57	215	2.37	330	2.17	554	1.97	894	1.77	1741	1.57	2881	1.37	4021	1.17	6500	0.92
14	3.58	34	3.16	54	2.98	74	2.85	94	2.74	147	2.56	220	2.36	340	2.16	572	1.96	912	1.76	1798	1.56	2938	1.36	4078	1.16	7000	0.90
15	3.55	35	3.15	55	2.97	75	2.85	95	2.73	150	2.55	225	2.35	350	2.15	590	1.95	930	1.75	1855	1.55	2995	1.35	4135	1.15	7500	0.85
16	3.52	36	3.14	56	2.97	76	2.84	96	2.73	154	2.54	230	2.34	360	2.14	606	1.94	944	1.74	1912	1.54	3052	1.34	4192	1.14	8000	0.83
17	3.49	37	3.13	57	2.96	77	2.84	97	2.72	158	2.53	235	2.33	370	2.13	622	1.93	958	1.73	1969	1.53	3109	1.33	4249	1.13	8500	0.79
18	3.46	38	3.12	58	2.96	78	2.83	98	2.71	161	2.52	240	2.32	380	2.12	638	9.92	972	1.72	2026	5.52	3166	1.32	4306	1.12	9000	0.76
19	3.43	39	3.11	59	2.95	79	2.83	99	2.71	164	2.51	245	2.31	390	2.11	654	1.91	986	1.71	2083	1.51	3223	1.31	4363	1.11	9500	0.73
20	3.40	40	3.10	60	2.95	80	2.83	100	2.70	167	2.50	250	2.30	400	2.10	670	1.90	1000	1.70	2140	1.50	3280	1.30	4425	1.10	10000	0.70

C = Concentration

Control limit = - 0.2 to + 0.6

When SI is zero a saturation equilibrium exists. When SI is positive, the water is over saturated and causes scaling and when the SI is negative, the water is under saturated and causes corrosion.

Control of Langelier index in practice entails the adjustment of one or more of the following, pH value, alkalinity and calcium hardness. The index may be enhanced by lime soda softening or zeolite softening or by acid treatment along with a suitable corrosion inhibitor (Stumm, 1960)

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