PREDICTING CALCIUM OXALATE SCALE

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ABSTRACT

Calcium oxalate scale is frequently encountered in the sugar refining and paper making processes. This paper outlines a simple index for the prediction of calcium oxalate scale. The development of a more refined index, based upon free ion concentrations, is also discussed.

INTRODUCTION

Most indices for predicting scale are derived from the definition of the solubility product for the scale in question. For example, the commonly used Calcite Saturation Level[1] and classic Langelier Saturation Index[2] for predicting calcium carbonate scale are derived from the relationship:

$$\{Ca\}\ \{CO_3\} = K_{sp} \qquad (1)$$

where {Ca} is the calcium activity;

{CO_3} is the carbonate activity; and

K_{sp} is the solubility product at the temperature evaluated.

The Saturation Level or Ratio is the ratio of the current ion activity product (IAP) to the ion activity product expected at equilibrium:

$$\text{Saturation Level} = \frac{\{Ca\}\ \{CO_3\}}{K_{sp}} = \frac{IAP}{\text{Solubility Product}} \qquad (2)$$

It can be shown that the Langelier Saturation Index is the base ten logarithm of the Saturation Level, when the saturation level is calculated from the total analytical value for calcium, and carbonate is estimated from the total analytical value for alkalinity.

Saturation Levels indicate the driving force for scale formation with respect to equilibrium. If a water has a Saturation Level greater than 1.0, it is supersaturated with the respect to the sclae. If the Saturation Level is 1.0, the water is at equilibrium and would not be expected to form or dissolve scale. Waters with a Saturation Level less than 1.0 are undersaturated and might be expected to dissolve an existing scale.

Logarithmic indices have a similar interpretation. A water with a log index greater than 0.0 would be supersaturated with respect to the scale evaluated, and would have an increasing tendency to form the scale with increases in the index. A water wih a log index of 0.0 would be at equilibrium. Scale would not be expected to form or dissolve. A negative index value would indicate that the water might tend to dissolve an existing scale.

Saturation Levels calculated by commercial computer programs are typically based upon the free ion concentrations (e.g. free calcium and free carbonate). The free ion concentrations are based upon the most likely distribution of species and subtract ‘bound’ ion concentrations from the total analytical values to obtain the free ion concentration.[1]

This paper describes the derivation and development of indices for predicting calcium oxalate scale based upon analytical values, and based upon free ion concentrations using an ion association model. The indices derived in this paper are based upon the solubility product for calcium oxalate:

$$\{Ca\}\ \{C_2O_4\} = K_{sp} \qquad (3)$$

where $\{Ca\}$ is the calcium activity;

$\{C_2O_4\}$ is the oxalate activity; and

K_{sp} is the solubility product for calcium oxalate at the temperature evaluated.

The simple Saturation Level is calculated from the expanded form of equation 3:

$$\text{Saturation Level} = \frac{\alpha Ca(Ca)\ \alpha C_2O_4\ (C_2O_4)}{K_{sp}} \qquad (4)$$

where αCa is the activity coefficient for the calcium ion;

αC_2O_4 is the activity coefficient for the oxalate ion;

(Ca) is the molal calcium concentration;

(C_2O_4) is the molal oxalate concentration; and

K_{sp} is the solubility product for calcium oxalate at the temperature evaluated.

The analytical value for calcium is used calcium concentration. The oxalate ion concentration must be estimated from the analytical value for total oxalic acid. This is done using an alpha distribution.[3] The alpha distribution method calculates the ion fractions for a diprotic acid such as oxalic as follows:

$$[Oxalic_{total}] = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^=] \quad (5)$$

$$\alpha_0 = [H_2C_2O_4]/ [Oxalic_{total}] \quad (6)$$

$$\alpha_1 = [HC_2O_4^-]/ [Oxalic_{total}] \quad (7)$$

$$\alpha_2 = [C_2O_4^=]/ [Oxalic_{total}] \quad (8)$$

$$\alpha_0 = \frac{[H]^2}{[H]^2 + K_1[H] + K_1 K_2} \quad (9)$$

$$\alpha_1 = \frac{K_1 [H]}{[H]^2 + K_1[H] + K_1 K_2} \quad (10)$$

$$\alpha_2 = \frac{K_1 K_2}{[H]^2 + K_1[H] + K_1 K_2} \quad (11)$$

$$[C_2O_4^=] = \alpha_2 [Oxalic_{total}] \quad (12)$$

Figure 3 depicts a full distribution of oxalic acid species at 25 °C, as calculated using the alpha distribution method. Table 2 summarizes the α_2 versus temperature. Note that α_2 approaches a value of 1.0 in alkaline waters, and can be assumed to be 1.0 above a pH of 8.

Activity coefficients for calcium and oxalate are calculated using the extended Debye-Hueckel method in this example. Values for K_1, K_2, and K_{sp} and there variation with temperature were obtained from published values.[4,5]

Calculating the Simple Index

The calculation of the simple saturation level index requires the following information:

1) Analytical values for calcium and total oxalic acid.
2) The pH, TDS, and temperature.
3) The thermodynamic constants for $K_1$and K_2 for oxalic acid
4) The K_{sp} for calcium oxalate.
5) Activity coefficients for calcium, the oxalate ion.

The thermodynamic constants, activity coefficients, and analytical conversion factors reuired have been combined in Table 2 and Table 3 to facilitate index calculation. A modification of equation 4 to account for the values included in the tables yields the following simplified formula:

$$\text{Saturation Level} = \frac{\text{Factor 1 [Ca] [Oxalic acid}_{total}]}{\text{Factor 2}} \quad (13)$$

where [Ca] is the analytical value for calcium in mg/L as Ca;

[Oxalic acid $_{total}$] is the analytical value for oxalate in mg/L as C_2O_4;

Factor 1 is the α_2 value from Table 2;

Factor 2 includes the composite thermodynamic properties and conversion factors from Table 3.

The base ten logarithm of the Saturation Level can be used for interpretation, if desired, in the manner in which the Langelier Saturation Index is evaluated.

Adding Calcium oxalate to An Ion Association Model

For increased applicability in varying waters, calcium oxalate Saturation level should be calculated using an ion association model. Ion association models estimate the free ion concentrations prior to index calculation. They account for ‘common ion effects’ and ‘ion pairing.’ It is recommended that the ion pairs for aqueous CaC_2O_4, $CaHC_2O_4$, MgC_2O_4, and $MgHC_2O_4$ be added to the calculation matrix and used to adjust the free ion concentrations for calcium and oxalate.

Acknowledgement

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References

1. R.J. Ferguson, “Computerized Ion Association Model Profiles Complete Range of Cooling system Parameters,” International Water Conference, paper no. IWC-91-47, (Pittsburgh, PA: Engineer’s Society of Western Pennsylvania, 1991).
2. W.F. Langelier, “The Analytical Control of Ant—Corrosion Water Treatment,” JAWWA, Vol. 28, No. 10, p. 1500-1621, 1936.
3. W. Stumm and J.J. Morgan, Aquatic Chemistry, 2nd Edition, John Wiley and Sons, New York, New York, p. 173-177, 1981.
4. R. Kettler, D. Palmer, D. Wesolowski, J. Solution Chemistry,20,905 (1991).
5. E Konigsberger,L-C Tran-Ho; Curr.Topics Soln.Chem.,2,183 (1997).

Figure 1: Calcium oxalate pK_{sp} vs Temperature

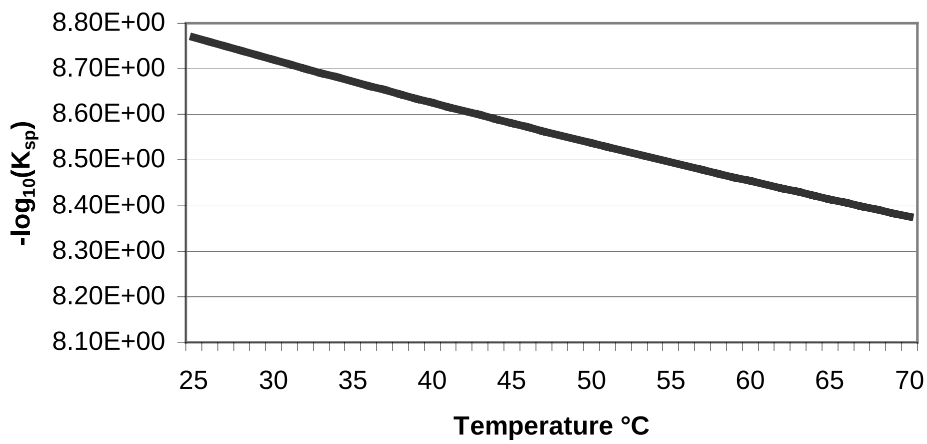

Figure 2: Oxalic acid pK_1 and pK_2 vs Temperature

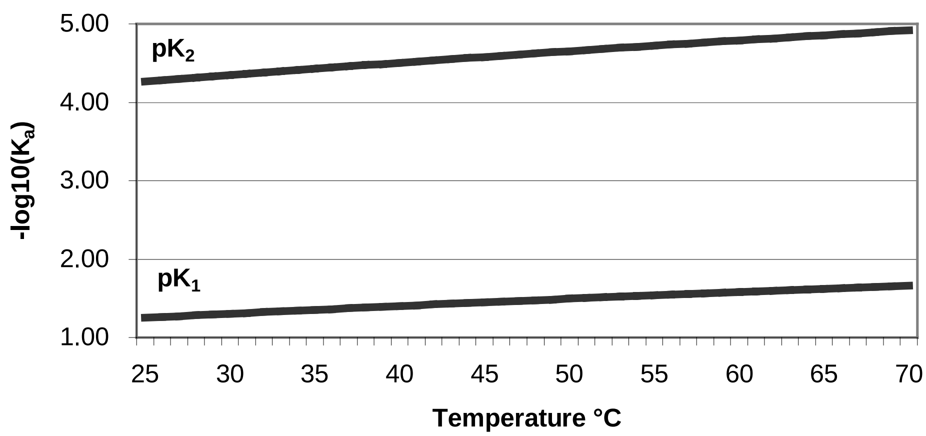

Figure 3: Oxalic acid Distribtion vs pH

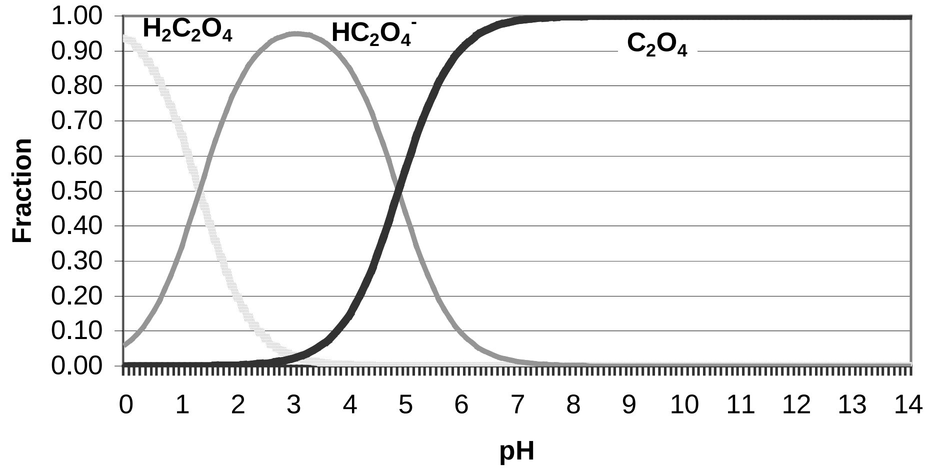

Figure 4: $C_2O_4^=$ Fraction of Total Oxalate vs pH, T

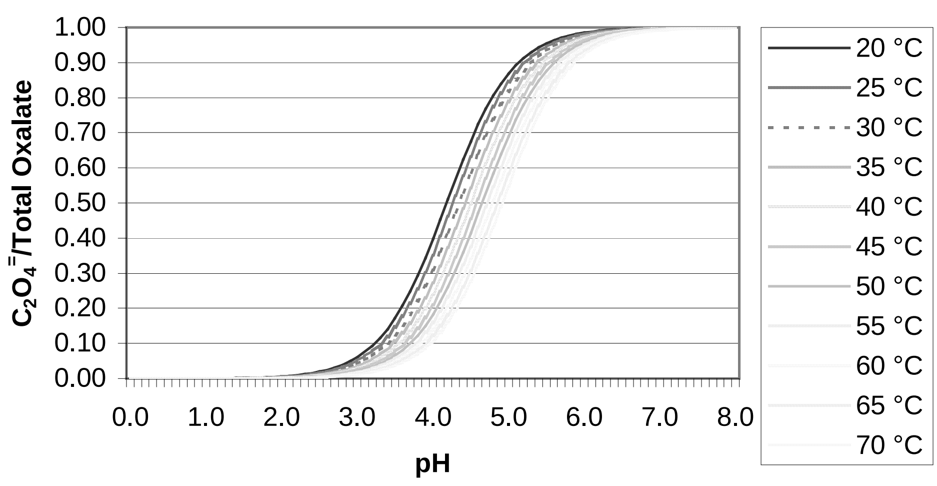

Table 1: Interpreting Indices			
	Saturation Level	Log_{10}(Saturation Level)	Scaling Tendency
Supersaturated	> 1.0	> 0.0	Scale forms
At Equilibrium	1.0	0.0	Neither forms or dissolves
Undersaturated	< 1.0	< 0.0	Will tend to dissolve

Table 2: Oxalate ($C_2O_4^{=}$) Fraction of Total Oxalic Acid Species versus pH and Temperature

pH	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C
1.0	0.00026	0.00019	0.00015	0.00011	0.00009	0.00007	0.00005	0.00004	0.00003	0.00003	0.00002
1.2	0.00052	0.00040	0.00031	0.00024	0.00019	0.00015	0.00012	0.00009	0.00008	0.00006	0.00005
1.4	0.00102	0.00080	0.00063	0.00049	0.00039	0.00031	0.00025	0.00020	0.00016	0.00013	0.00011
1.6	0.00188	0.00149	0.00118	0.00095	0.00076	0.00061	0.00050	0.00040	0.00033	0.00027	0.00022
1.8	0.00332	0.00266	0.00214	0.00173	0.00141	0.00115	0.00094	0.00077	0.00064	0.00053	0.00044
2.0	0.00566	0.00458	0.00372	0.00304	0.00249	0.00205	0.00170	0.00141	0.00117	0.00098	0.00082
2.2	0.00941	0.00766	0.00627	0.00515	0.00426	0.00353	0.00295	0.00246	0.00207	0.00175	0.00148
2.4	0.01534	0.01255	0.01032	0.00853	0.00709	0.00592	0.00496	0.00417	0.00353	0.00299	0.00255
2.6	0.02462	0.02023	0.01671	0.01388	0.01158	0.00970	0.00817	0.00691	0.00586	0.00500	0.00428
2.8	0.03899	0.03219	0.02669	0.02224	0.01862	0.01566	0.01323	0.01123	0.00957	0.00818	0.00703
3.0	0.06094	0.05056	0.04212	0.03524	0.02961	0.02498	0.02117	0.01802	0.01540	0.01321	0.01137
3.2	0.09375	0.07829	0.06559	0.05514	0.04653	0.03941	0.03351	0.02860	0.02451	0.02108	0.01820
3.4	0.14130	0.11908	0.10053	0.08507	0.07217	0.06142	0.05244	0.04492	0.03861	0.03331	0.02883
3.5	0.17179	0.14562	0.12353	0.10496	0.08936	0.07627	0.06529	0.05605	0.04827	0.04171	0.03615
3.6	0.20722	0.17683	0.15086	0.12880	0.11012	0.09432	0.08097	0.06970	0.06016	0.05208	0.04522
3.7	0.24775	0.21302	0.18294	0.15707	0.13494	0.11606	0.09999	0.08633	0.07471	0.06482	0.05639
3.8	0.29323	0.25430	0.22003	0.19015	0.16428	0.14199	0.12284	0.10644	0.09240	0.08038	0.07009
3.9	0.34322	0.30048	0.26220	0.22829	0.19851	0.17254	0.15001	0.13053	0.11373	0.09925	0.08679
4.0	0.39692	0.35108	0.30922	0.27147	0.23781	0.20805	0.18191	0.15907	0.13920	0.12194	0.10697
4.1	0.45320	0.40525	0.36052	0.31942	0.28212	0.24863	0.21882	0.19245	0.16925	0.14892	0.13115
4.2	0.51069	0.46180	0.41520	0.37149	0.33108	0.29418	0.26080	0.23088	0.20423	0.18062	0.15978
4.3	0.56789	0.51934	0.47203	0.42671	0.38398	0.34421	0.30765	0.27436	0.24429	0.21732	0.19325
4.4	0.62332	0.57636	0.52958	0.48381	0.43975	0.39795	0.35881	0.32256	0.28933	0.25909	0.23178
4.5	0.67569	0.63140	0.58635	0.54132	0.49707	0.45425	0.41337	0.37485	0.33892	0.30575	0.27535
4.6	0.72400	0.68322	0.64090	0.59774	0.55446	0.51173	0.47014	0.43021	0.39232	0.35674	0.32364
4.7	0.76759	0.73085	0.69203	0.65168	0.61042	0.56889	0.52768	0.48736	0.44840	0.41118	0.37599
4.8	0.80613	0.77370	0.73885	0.70199	0.66362	0.62426	0.58449	0.54484	0.50582	0.46788	0.43140
4.9	0.83962	0.81147	0.78079	0.74784	0.71296	0.67657	0.63913	0.60114	0.56308	0.52542	0.48857
5.0	0.86826	0.84421	0.81767	0.78876	0.75770	0.72479	0.69039	0.65488	0.61870	0.58228	0.54603
5.1	0.89245	0.87216	0.84953	0.82459	0.79745	0.76829	0.73735	0.70493	0.67136	0.63702	0.60228
5.2	0.91264	0.89572	0.87666	0.85545	0.83212	0.80674	0.77947	0.75049	0.72004	0.68843	0.65596
5.4	0.94304	0.93157	0.91847	0.90366	0.88708	0.86871	0.84853	0.82661	0.80302	0.77789	0.75137
5.6	0.96329	0.95571	0.94697	0.93698	0.92566	0.91294	0.89878	0.88313	0.86598	0.84735	0.82729
5.8	0.97652	0.97159	0.96587	0.95929	0.95177	0.94325	0.93366	0.92294	0.91104	0.89794	0.88361
6.0	0.98506	0.98188	0.97819	0.97392	0.96902	0.96343	0.95709	0.94995	0.94197	0.93309	0.92327
6.2	0.99052	0.98849	0.98613	0.98339	0.98023	0.97661	0.97249	0.96783	0.96258	0.95671	0.95018
6.4	0.99400	0.99271	0.99120	0.98945	0.98743	0.98511	0.98246	0.97946	0.97606	0.97224	0.96798
6.6	0.99620	0.99539	0.99443	0.99332	0.99203	0.99055	0.98886	0.98694	0.98476	0.98231	0.97955
6.8	0.99760	0.99708	0.99648	0.99577	0.99496	0.99402	0.99294	0.99172	0.99033	0.98876	0.98700
7.0	0.99849	0.99816	0.99778	0.99733	0.99681	0.99622	0.99554	0.99476	0.99388	0.99288	0.99176
7.2	0.99904	0.99884	0.99860	0.99831	0.99799	0.99761	0.99718	0.99669	0.99613	0.99550	0.99478
7.4	0.99940	0.99927	0.99911	0.99894	0.99873	0.99849	0.99822	0.99791	0.99755	0.99715	0.99670
8.0	0.99985	0.99982	0.99978	0.99973	0.99968	0.99962	0.99955	0.99947	0.99938	0.99928	0.99917

Use a factor of 1.0 above pH 8.0

Table 3: Composite Factor for Calcium Oxalate Saturation Level versus Temperature, TDS

°C	TDS 25	TDS 100	TDS 250	TDS 500	TDS 1000	TDS 2500	TDS 5000
25	7.5077	9.2268	11.4866	14.3588	18.9716	29.7112	43.3730
26	7.6863	9.4494	11.7679	14.7157	19.4516	30.4837	44.5265
27	7.8679	9.6760	12.0544	15.0793	19.9409	31.2722	45.7049
28	8.0526	9.9066	12.3461	15.4497	20.4397	32.0769	46.9087
29	8.2404	10.1412	12.6430	15.8270	20.9482	32.8980	48.1382
30	8.4314	10.3798	12.9452	16.2113	21.4665	33.7359	49.3939
31	8.6256	10.6226	13.2529	16.6026	21.9946	34.5908	50.6762
32	8.8229	10.8695	13.5659	17.0012	22.5329	35.4629	51.9856
33	9.0235	11.1206	13.8845	17.4069	23.0813	36.3525	53.3226
34	9.2274	11.3760	14.2087	17.8201	23.6401	37.2599	54.6876
35	9.4345	11.6356	14.5385	18.2406	24.2093	38.1854	56.0812
36	9.6450	11.8995	14.8740	18.6687	24.7891	39.1292	57.5037
37	9.8588	12.1678	15.2152	19.1044	25.3797	40.0917	58.9557
38	10.0760	12.4405	15.5622	19.5477	25.9812	41.0730	60.4377
39	10.2966	12.7177	15.9152	19.9989	26.5937	42.0736	61.9501
40	10.5207	12.9993	16.2741	20.4580	27.2174	43.0936	63.4936
41	10.7482	13.2855	16.6390	20.9251	27.8525	44.1335	65.0686
42	10.9792	13.5762	17.0099	21.4002	28.4990	45.1934	66.6756
43	11.2137	13.8716	17.3870	21.8835	29.1572	46.2737	68.3152
44	11.4518	14.1717	17.7704	22.3751	29.8272	47.3748	69.9879
45	11.6935	14.4764	18.1599	22.8751	30.5091	48.4968	71.6943
46	11.9387	14.7859	18.5559	23.3835	31.2031	49.6402	73.4350
47	12.1876	15.1002	18.9582	23.9005	31.9094	50.8053	75.2105
48	12.4402	15.4193	19.3670	24.4262	32.6281	51.9923	77.0214
49	12.6965	15.7433	19.7823	24.9606	33.3594	53.2017	78.8683
50	12.9565	16.0723	20.2043	25.5039	34.1034	54.4337	80.7518
51	13.2202	16.4062	20.6329	26.0562	34.8603	55.6887	82.6725
52	13.4877	16.7451	21.0682	26.6175	35.6304	56.9670	84.6311
53	13.7591	17.0891	21.5104	27.1880	36.4136	58.2691	86.6281
54	14.0342	17.4382	21.9595	27.7678	37.2103	59.5952	88.6642
55	14.3133	17.7924	22.4155	28.3570	38.0206	60.9457	90.7400
56	14.5962	18.1519	22.8785	28.9557	38.8446	62.3209	92.8563
57	14.8830	18.5165	23.3486	29.5639	39.6826	63.7214	95.0137
58	15.1738	18.8865	23.8258	30.1819	40.5347	65.1473	97.2129
59	15.4686	19.2618	24.3103	30.8097	41.4011	66.5992	99.4546
60	15.7674	19.6424	24.8021	31.4475	42.2820	68.0773	101.7394
61	16.0702	20.0285	25.3013	32.0953	43.1775	69.5821	104.0682
62	16.3771	20.4201	25.8079	32.7532	44.0879	71.1141	106.4416
63	16.6880	20.8171	26.3221	33.4214	45.0134	72.6735	108.8604
64	17.0031	21.2197	26.8438	34.1000	45.9540	74.2608	111.3253
65	17.3223	21.6279	27.3732	34.7891	46.9101	75.8765	113.8372
66	17.6457	22.0418	27.9103	35.4888	47.8819	77.5209	116.3969
67	17.9733	22.4614	28.4553	36.1992	48.8694	79.1945	119.0050
68	18.3051	22.8867	29.0082	36.9205	49.8730	80.8977	121.6625
69	18.6412	23.3178	29.5690	37.6527	50.8928	82.6309	124.3702
70	18.9816	23.7547	30.1379	38.3961	51.9291	84.3948	127.1289