Critique of Marcelle Dibrell's July 31, 2015 Article on Cal Poly Phase 2 Report

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Overview

In the July 31, 2015 issue of *Service Industry News* [1] Marcelle Dibrell, Ph.D. provided analysis of a phase 2 report on plaster etching and discoloration experiments by Damian I. Kachlakev and Nirupam Pal of California Polytechnic University.[2] On the whole Dibrell's analysis gives valuable perspective on what the data provided in the phase 2 report really mean, as opposed to what Kachlakev and Pal asserted in the largely unsupported conclusions in the report.

Detailed Discussion

Dibrell starts the analysis by noting that the National Plasterers Council funded study was conducted in four phases, and that analysis of the data would logically start with phase one, but that there had been too many admitted difficulties in controlling pool chemistry for that phase and that the report failed to disclose the data needed to check the conclusions of the report. Marcelle politely passed over the appearance that the Cal Poly team was quite low on the learning curve for dealing with pool water chemistry, test coupon preparation, etc. during that phase of the work.

Dibrell then moves on to analysis of the data provided in the phase two report. The most significant contribution Dibrell makes is the calculation and plotting of calcium carbonate saturation in the test pools and spas, using data provided in Appendix C of the phase two report. Dibrell's plots of LSI versus date for the twelve pools and two spas involved in the study show that the researchers failed to attain the stated objectives: that pool 8 and spa 13 would contain aggressive water, while the other pools and spa would have balanced water. (In fact, Appendix C of the Cal Poly Report shows that the target ranges for most of the water balance parameters listed in Tables 2.1 and 2.2 of the report were not actually maintained on any of the pools or spas.)

Figure 2.7 in the Cal Poly report does provide a plot of LSI versus date for a single pool (pool 4), however this plot shows a suspiciously high percentage of the data points with perfect, LSI = 0.0, balance (>70% of the points) and only a single point <0, whereas Dibrell's plot for the same pool shows considerable variation with some of the points (<20%) within 0.2 units of zero on the plus or minus side, but none exactly zero. From a statistical standpoint, the Dibrell plot looks plausible, whereas the Cal Poly plot looks highly improbable—all the more so considering the wide variation in pH, alkalinity, hardness and cyanuric acid shown for the pools in appendix C and in Figures 2.2 through 2.5.

To provide a spot-check on Dibrell's LSI plots, the data from Appendix C for pools 1 and 5 were independently used to calculate LSI and plots were prepared, as shown in **Figure 1** and **Figure 2**, on the following pages. In general, the agreement with Dibrell's plots is fairly close, apart from an offset of ~0.4 on average in the LSI between the current graphs and Dibrell's, with Dibrell's having the less -scaling LSI.

Some disagreement between Dibrell's calculated LSI values and the ones provided in the current critique is to be expected in view of the following considerations:

1. Detailed temperature data were not provided in the Cal Poly report or appendix, so assumptions had to be made. Since the pools were not heated, it was assumed for the current analysis that the water temperature during the study would approximately equal the average ambient air

temperature for the month. Average monthly temperatures for the 2004 to 2005 timeframe were obtained from an internet database[3] and used in the LSI calculations. Dibrell did not disclose any temperature assumptions, and it is unlikely that she would have used exactly the same temperature assumptions as used in this critique, but the impact on LSI would be minimal (~0.09 LSI difference for a 10°F temperature disagreement).
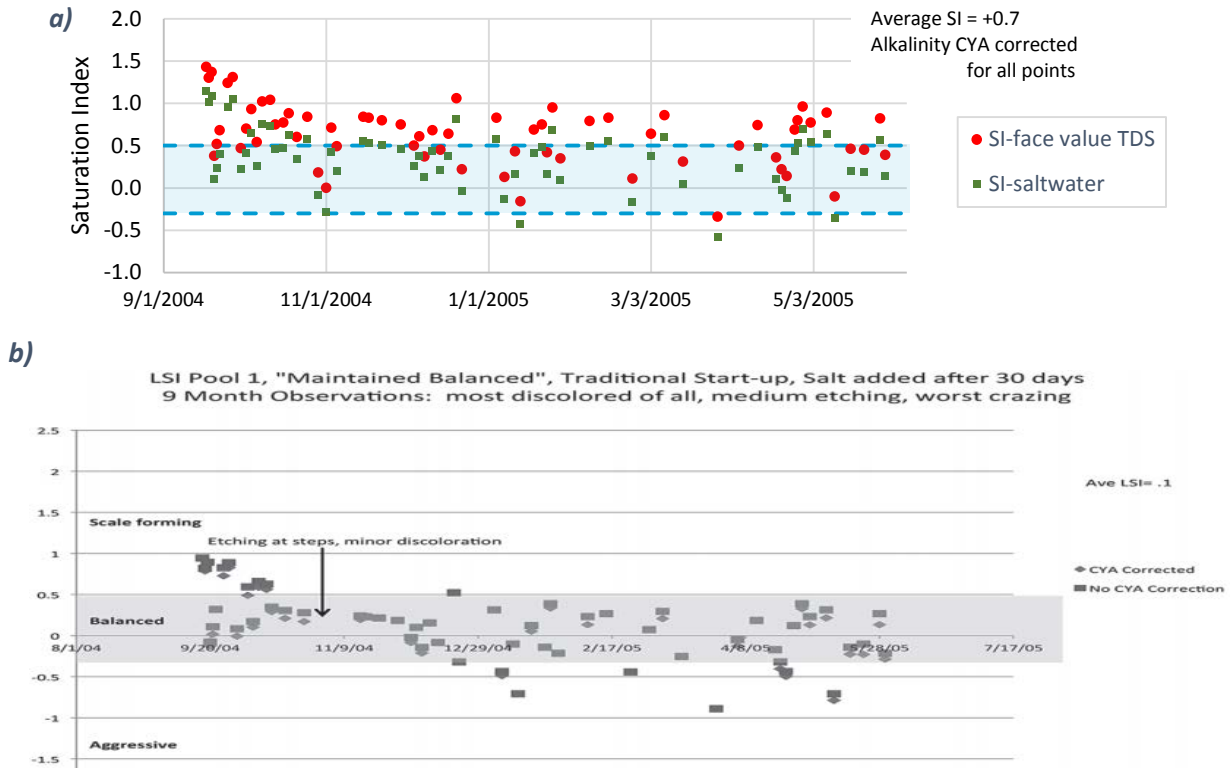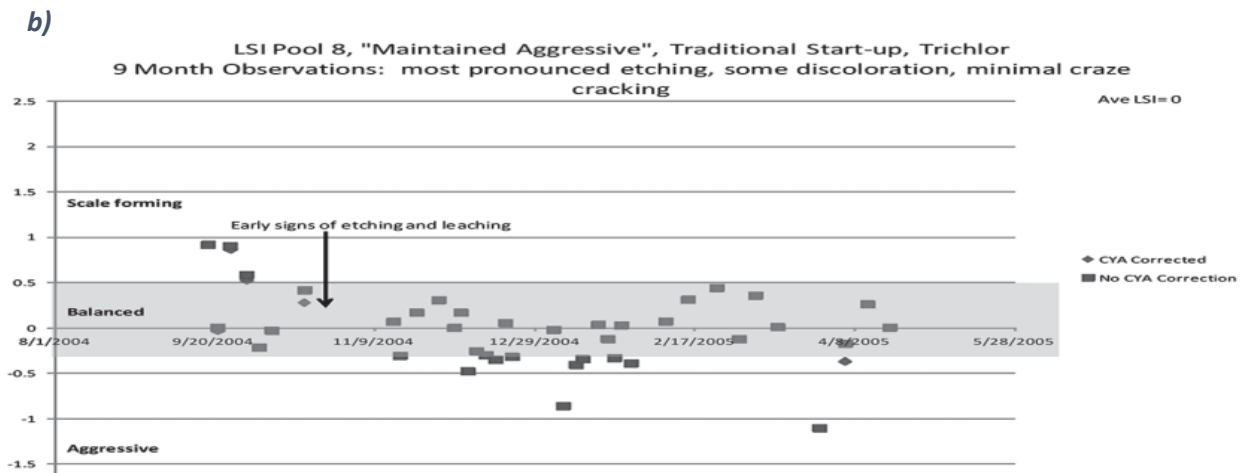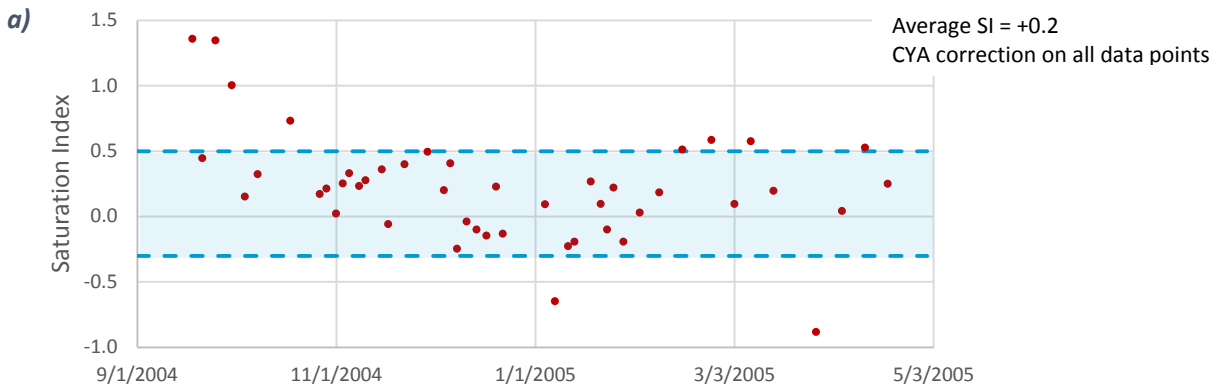

Figure 1. *Saturation Index calculated for pool 1. a) Calculated from reported pH, alkalinity, CYA, and calcium. TDS assumed to be 600 ppm and water temperature assumed to be historic monthly average temperature for San Louis Obispo. Calcium readings in Appendix C assumed to be calcium concentration as ppm Ca. Red circles (•) correspond to LSI calculated taking TDS reported in Appendix C at face value. For the green squares (■), ~3.400 ppm sodium chloride is added into the TDS reported in Appendix C, since pool 1 was allegedly a saltwater pool. b) For comparison, Dibrell's plot of LSI for the same pool. Note the offset in LSI between the two graphs. Dibrell used the same data, but may have assumed different temperatures and TDS. She also appears to have assumed the calcium data in appendix C was meant to read as calcium hardness (as ppm calcium carbonate).*

2. The Cal Poly report provided no data on TDS, except for pool 1. For the present critique, the TDS was averaged for the pool 1 data, and this value of TDS (rounded to 600 ppm) was used in the LSI calculations for pool 8. For pool 1, the reported (or for some dates interpolated) TDS was used to calculate LSI based on face-value TDS (red circles). However, since pool 1 was reportedly a saltwater pool, an extra series (green squares) is plotted in which an allowance was made for 3,400 ppm sodium chloride salt added to the TDS value reported in Appendix C. This was to account for the 3,200 ppm of salt added to the pool (3,600 measured by ASTM method), and evidently not included in the TDS values reported in Appendix C. (It is a bit mystifying that the Cal Poly team would report TDS levels ranging from 400 to 800 for a saltwater pool. Either the salt was never added after all, or an estimated salt contribution to TDS was subtracted from each measured value to provide the numbers for pool 1 in Appendix C. Either way, the record

betrays a lack of care in data reporting.)

In actual practice, it is to be expected that TDS would gradually increase due to evaporation and chemical addition, but occasionally drop when water is drained and replaced to lower CYA, TDS or calcium concentrations. Thus, Dibrell's assumptions on TDS may have been somewhat different, but the impact on LSI would be fairly small, ~0.02 for a for an error of 100 ppm in the TDS. For Dibrell's calculation of LSI, it appears that she took saltwater into account.

3. Dibrell may have used TDS only in a general way, to set a constant in a simplified LSI equation, based on a TDS range, e.g. a constant of -12.1 for a TDS < 1,000, whereas for the present critique the TDS was used to estimate ionic strength (0.000025 × 600 ppm TDS = 0.015 ionic strength), which in turn was used to adjust activity coefficients for calcium and bicarbonate, and thereby calculate the saturation index more precisely. (The method of Wojtowicz[4] was used for the current work.)

4. To correct alkalinity for the cyanuric acid (CYA) contribution, Dibrell may have used a fixed CYA factor of ~0.3, whereas for this critique a pH-dependent CYA factor was used: $(50.043/129.07)/(1+10^{6.88-pH})$. Again, the impact on LSI would be small, generally <0.03 for the current work, given the modest CYA concentrations reported.

a)

b)

Figure 2. *Saturation Index for Pool 8. a) Calculated from reported pH, alkalinity, CYA, and calcium. TDS assumed to be 600 ppm and water temperature assumed to be historic monthly average temperature for San Louis Obispo. b) For comparison,*

5. While the Cal Poly report claims that water analysis tests (pH, alkalinity, hardness, etc.) were conducted and recorded daily, there numerous gaps in the data in Appendix C. To obtain more complete LSI plots, some interpolation could be used to fill in approximations for the missing data. For the present critique, it was assumed that interpolation would be safe enough for cyanuric acid and calcium, which tend to change slowly, and even for alkalinity; however, interpolation of pH was considered too risky, so gaps in the data were left for those days with no pH data. Dibrell may have considered any interpolation risky and simply left out the days with missing calcium or alkalinity data. (Since so few CYA data points per pool were reported, it appears that Dibrell was willing to risk assumptions about it, otherwise her plots would have had far fewer points. For example, for pool 8 only 5 CYA readings were reported.) The interpolated calcium and alkalinity estimates used in the current critique would have little impact on the appearance of the plots apart from the addition of points very close to existing points in the charts.

6. Most of the disagreement between the LSI plots in the current critique and Dibrell's plots for the same pools stems from different interpretation of "Calcium" in the tables in Appendix C. Dibrell clearly interpreted calcium to mean calcium hardness (expressed as ppm calcium carbonate), whereas for the current critique calcium was interpreted as calcium concentration (ppm calcium). The 2.5-fold difference between calcium hardness and calcium concentration (100 formula weight for calcium carbonate/40 atomic weight for calcium = 2.5) would result in a 0.4 offset in the LSI between Dibrell's plots and the ones generated for the current critique, since log (2.5) = 0.4. Dibrell may have been correct in assuming calcium hardness was meant in the headings in Appendix C, as the term calcium hardness is used in "Figure 2.3: Total Calcium Hardness Measurements for Pool 1 Based on Standard Method". However, the assumption that the ambiguous heading "Calcium" in the tables of Appendix C may actually be ppm Ca is consistent with the calculation cited in section 2.3.3. The 20,040 factor in the equation would give results in ppm (or more literally mg/L) calcium, not calcium carbonate, for which the factor should be 50,000. It's not clear that the Cal Poly authors know the difference, so either guess could be valid as to what is meant by Calcium in Appendix C. (The equation in section 2.3.3, apart from the errant use of "acid" where EDTA is meant, comes from EPA method 215.2, which provides separate formulas for calculation of calcium (section 7.1) and calcium hardness (section 7.2).[5]

If the calcium assumption made by Dibrell is true, her plots can be viewed as the more reliable. If not, then the pools are even more scaling than she indicated, and aggressive pool water would be an even less likely explanation for any etching of the pool plaster. It should be noted, however, that the graphs in Dibrell's article show occasional dips into rather aggressive ranges for several of the pools, including "balanced" pools. With a number of gaps of a few days or longer in the data, it is possible that the pools spent enough time in aggressive ranges to account for modest etching or staining. In addition, the rather scaling water present most of the time could result in stained deposits, depending on what metal traces may have been present in the water.

In addition to gaps in the data, there are some unexplained dips in variables that should be relatively stable. For example, Figure 2.3 in the phase 2 report shows calcium hardness dipping about 100 ppm below adjacent readings. There were two such dips (2/24/05 & 3/15/05) shown in the chart, and another on September 26 omitted from Figure 2.3. While such dips are possible in principle, due to draining and replacing of water followed later by calcium addition, however then the CYA (Fig. 2.5) and TDS should have dropped, but they did not. Similar, though less extreme, unexplained swings in alkalinity also occur. These questionable swings may explain some of the data gaps. Perhaps the most extreme outliers were deleted from the data tables; however even the data that are reported may be called into question.

The most critical factor for calculating calcium saturation is pH. To their credit, the Cal Poly team used a pH meter to measure pH, and the meter was calibrated with buffers before taking measurements. However, as pointed out in section 2.3.1, the samples were poured into beakers (of unspecified dimensions, to unspecified depth in the beakers, and probably stirring and open to the atmosphere) before measuring pH. Then a pH reading was taken when "a stable reading was established". There is enough ambiguity in the term stable and the unspecified time period, that it is possible the reading was taken only after significant outgassing of dissolved carbon dioxide, at which point the pH would be more stable. However, this could give artificially high pH readings, calling even the pH data into question.

Given how questionable the Cal Poly data are, and given the numerous, and sometimes sizeable, gaps in the data, it is risky to say that the report *proves* etching was not caused by aggressive water. However, Dibrell is right to point out that the data do not support the Cal Poly conclusion that aggressive water caused etching of the plaster.

Dibrell pointed out an important distinction between spot alteration and general etching. This distinction is less evident in the phase 2 report, though if the photos in Figures 3.2 and 3.3 are meant to show etching, non-uniform spot alteration was most evident. Dibrell's observations regarding Cal Poly's use of the term "etched spots" in connection with "balanced" pools are also appropriate. The occurrence of "spot etching" in pools that—according to the data—were generally either balanced or scaling does call aggressive water into question as a cause. It *appears* that the Cal Poly researchers were predisposed to find aggressive water as the primary cause of spot etching, regardless of what the data showed.

Plaster defects and impurities may provide spots that are particularly susceptible to discoloration, but especially so upon exposure to certain water balance conditions, such as water that is excessively corrosive or scale forming, or swings in pH or water balance. In the observations on spa 13 at the May 21st examination (p. A8), the phase two report notes that etched spots had grown and begun to connect. It appears likely that some plaster locations were more susceptible, but as etching continued, it spread to adjacent regions and became more general.

Conclusions

Dibrell's detailed analysis of water balance for the vessels involved in the test was valuable and telling, but her article could have benefited from a similarly detailed analysis of the correlation, if any, between spot discoloration, cracking, etc. and plaster mix/application variables. Also, her conclusion that aggressive water cannot have caused the reported etching is somewhat dependent on the reliability of the data used to calculate LSI, and as indicated previously, there is reason to question the accuracy of

the Cal Poly data. Dibrell's conclusion that the experiment provided no reasonable explanation for the cause of "spot etching" is a reasonable one, since the reported etching did not correlate with the calculated LSI, and since general etching is not the same as spot alteration.   Also, in connection with her extensive TDS plots, it would have been informative for Dr. Dibrell to point out the uncertainties in the raw data reported by the Cal Poly team: Did the heading "Calcium" really mean calcium concentration, or was it the 2.5× larger calcium hardness? How could a saltwater pool have TDS levels below 800 ppm? Why were there so many sizeable gaps in the data? Perhaps Dr. Dibrell was too polite to point out the glaring deficiencies in the Cal Poly data.

References

1. Marcell Dibrell, "Plasterers Say Standard Is Not Good Enough", *Service Industry News*, **29** (14), 8–18, July 31, 2015.

2. Damian I Kachlakev and Nirupam Pal, "Etching Deterioration of Plastered Swimming Pool Surfaces: The Effects of Water Chemistry, Sanitizers, Start-up Procedures, Calcium Chloride Percentages and other Factors on Surface Deterioration", National Pool Industry Research Center, California Polytechnic State University, San Luis Obispo, California, October, 2005.

3. Weather Underground archives for San Luis Obispo, California, KSBP/San Luis County Airport, for 2004 and 2005.
   https://www.wunderground.com/history/airport/KSBP/2005/8/26/MonthlyHistory.html?req_city=San+Luis+Obispo&req_state=CA&req_statename=&reqdb.zip=93401&reqdb.magic=1&reqdb.wmo=99999

4. John A. Wojtowicz, "A Revised and Updated Saturation Index Equation", *Journal of the Swimming Pool and Spa Industry*, **3** (1), 35–41, 2001.

5. ALS Environmental, Technical Resources, EPA Methods, 215.2 "Calcium Titrimetric (EDTA),
   http://www.caslab.com/EPA-Methods/PDF/EPA-Method-2152.pdf

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