

Overview

The study, sometimes referred to as the phase 1 study, appears to use rather robust full-factorial experimental design, and draws some strong conclusions on water chemistry being the principal cause of plaster etching, while addition of calcium chloride appears to make plaster more resistant to etching. However, upon closer examination a number of deficiencies appear in the execution of the study: not all relevant variables were taken into account—leading to an unbalanced experimental design with confounded variables; the control variables were routinely out of control; once deficiencies were detected, the authors improvised on the fly and continued rather than restarting the experiment with the problems corrected so as to ensure more reliable data; and there was a clear lack of familiarity with the chemistry of water treatment, or chemistry in general. In addition, the presence of multiple uncorrected errors in the report makes it evident that the report was never peer reviewed. Given the number of deficiencies in the execution of the experiments and evaluation of the results, it is difficult to have any confidence in the data generated or the conclusions drawn. The following sections of this critique present some details on the principal deficiencies noted above.

Control Variables Out of Control, Water Testing

A primary purpose of the work, finally spelled out on the 24th page of the report, was to understand the conditions and mechanisms that lead to spot “etching”. Since pool water chemistry is among the suspected causes, one would expect that every precaution would be taken to control key water balance parameters in the pools and tanks. Table 2-2 indicates the target ranges for pH, free chlorine (FC), total alkalinity and calcium hardness in the tanks, with only pH control being attempted in tank 5. While it is asserted on page 17 that the water chemistry was kept as close as possible to that indicated in Table 2-2, it seems that “as close as possible” was not very close at all. It becomes apparent from the graphs below (adapted from Chapter 5 of the report) that these target ranges are better characterized as a wish list than actual control ranges, as all of the tracked variables were out of control, being outside the control ranges as often as not.

In Table 2-2 (p. 18) and on page 42 it is indicated that the objective was to maintain the pH at 7.2 to 7.4; however, as shown in Figure 1, below, the pH was typically above this range, and often below it, but rarely inside the target range in any of the tanks. Commonly the pH was more than a full unit outside the “control” range. What’s worse is that the pH in tanks 3 and 4, the “aggressive” water tanks, was typically higher than in tanks 1 and 2, which were designated as balanced. Such lack of pH control is especially problematic since pH is the most sensitive determinant of calcium carbonate saturation. (For either carbonate alkalinity or calcium hardness to have an impact equivalent to the pH being a unit outside the target range, the alkalinity or hardness would have to be outside their respective control ranges by a factor of 10!)

As shown in Figure 2 on the next page, total alkalinity was also out of range more often than it was in range. The alkalinity for the “aggressive” tanks, 3 & 4, was often above the control range, while for the “balanced water” tanks (1 & 2), alkalinity swung above and below the target range.

Similarly Figure 3 shows that calcium hardness was also often outside the designated control ranges for the respective tanks.

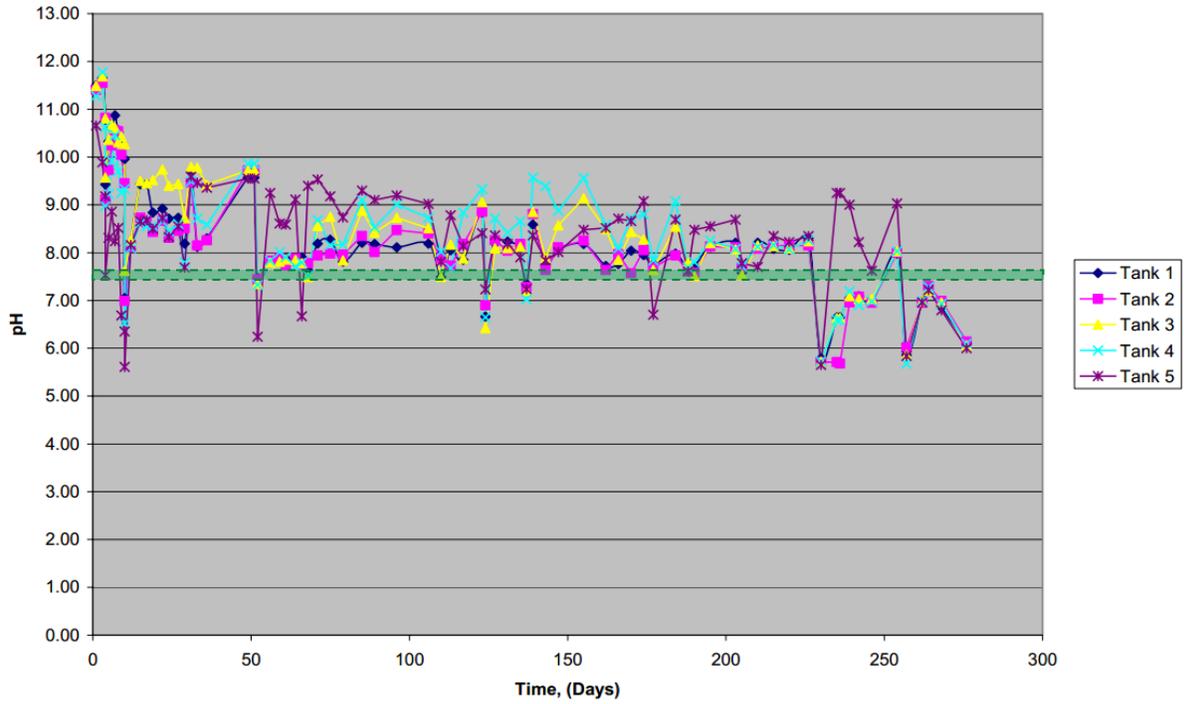


Figure 1. Plot of tank pH from Figure 5.3 in Cal Poly report. The transparent green band denotes the target pH range of 7.4 to 7.6.

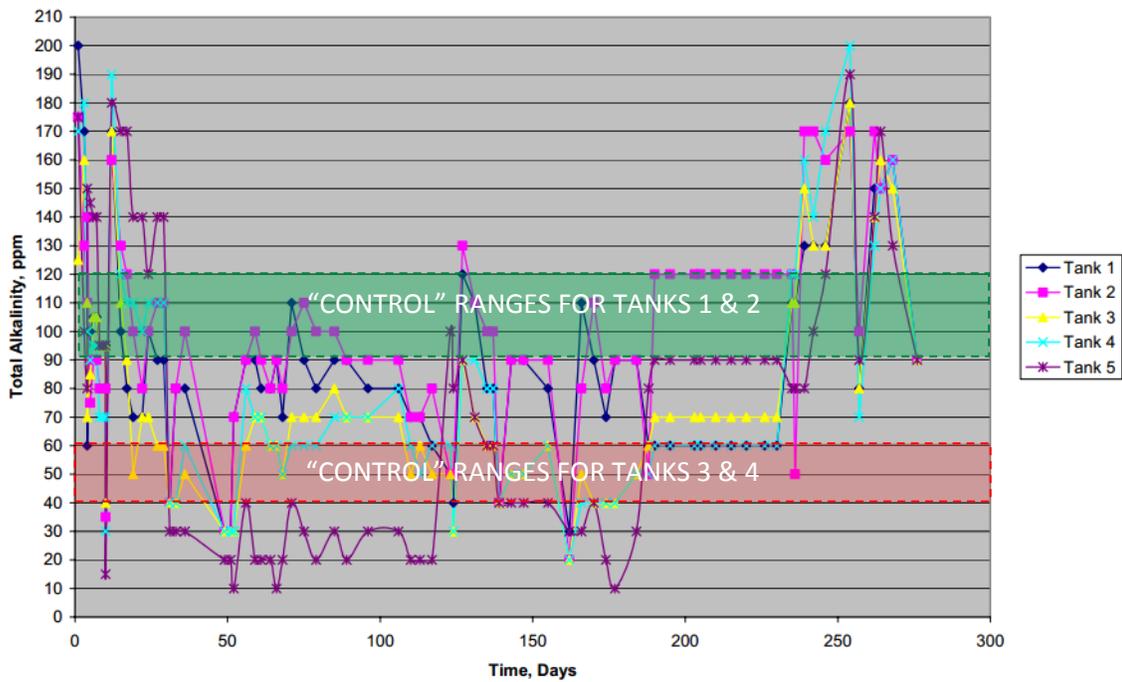


Figure 2. Alkalinity plot for tanks from Figure 5.6 in Cal Poly study. The intended control ranges are indicated by the red and green transparent bands.

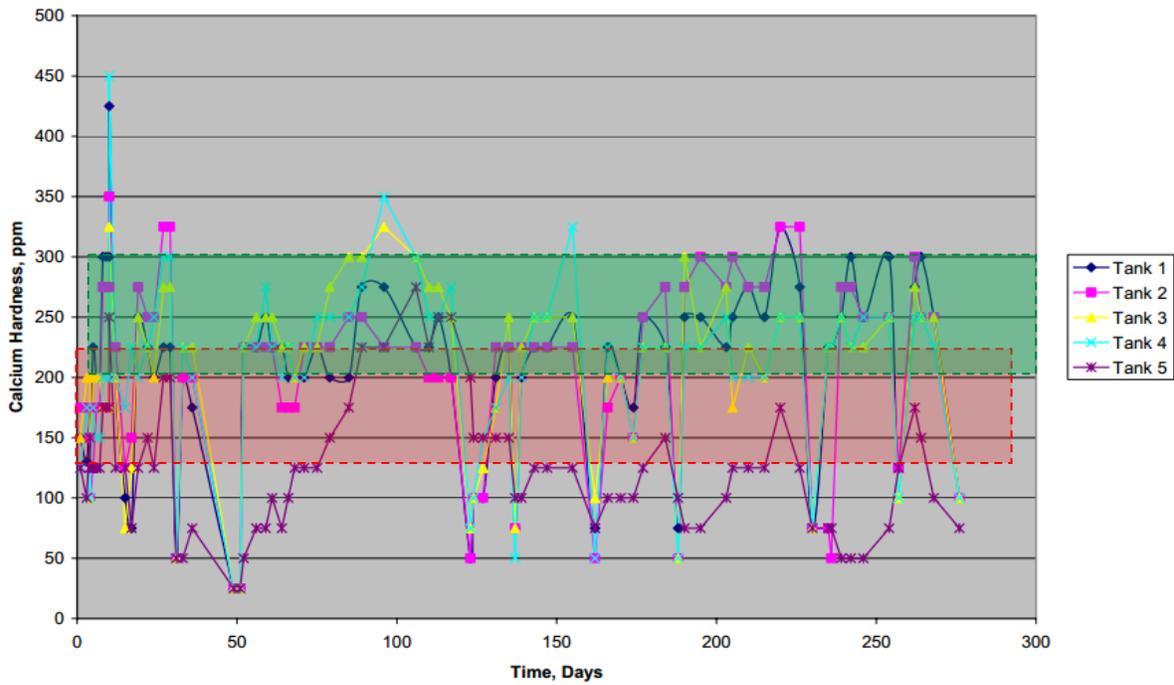


Figure 3. Calcium hardness plot for tanks in Cal Poly study. From Figure 5.7 in Cal Poly report.

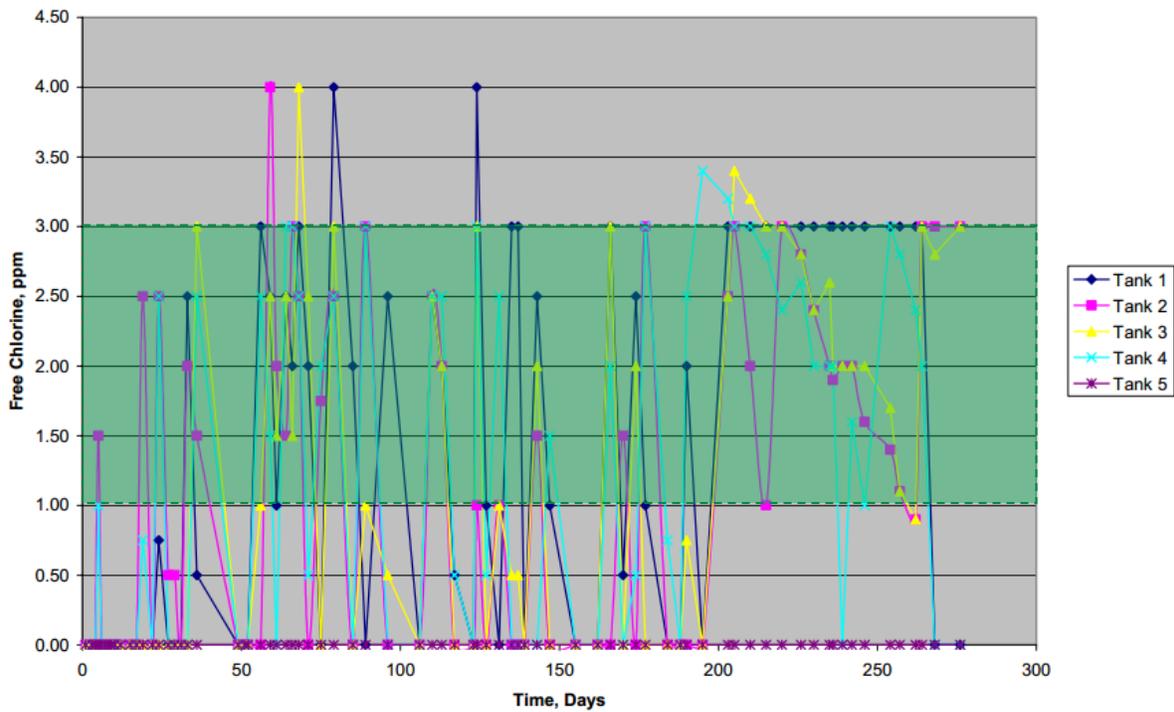


Figure 4. Free chlorine in tanks, from Figure 5.4 in Cal Poly report. The green band denotes the target range for tanks 1-4.

As a final out of control water chemistry influence, Figure 4 shows that while the target free chlorine range was 1 to 3 mg/L, the measured free chlorine level was often zero, introducing the possibility of biofilm gaining a foothold on the plaster, an opportunity for unplanned corrosive influences.

With very limited water circulation in the tanks and no use of chemical controllers for either pH or free chlorine, it is no wonder that those parameters were typically out of control.

In contrast to the tanks, the Cal Poly report gives no indication of how well the free chlorine, pH alkalinity and hardness were controlled in the pools, but one has to suspect that they were similarly out of control. Absent any knowledge or control of critical water balance parameters in the pools, it is impossible to draw any reliable conclusions regarding the impact of water balance on the pool plaster in these studies.

Control Variables Questionable, Plaster Variables

Even the plastering variables may not have been well controlled. Some care was seemingly exercised in controlling water to cement ratio, calcium chloride added, use of supplementary water and number of trowel passes during the plaster mixing and application. However, subsequent handling of the samples may have introduced enough damage and cross contamination to compromise the benefit of the initial control. Prior to storage and shipping the samples were cut, introducing the chance for cracking and other damage. The gunite base layers were then coated with *Thoroseal*[®] cement sealant, by dipping the cut samples, taking care not to contaminate the plaster layer. (p.22) The samples were then sealed in zip-lock bags (6 per bag) and shipped to the test laboratory.

Prior to testing, the samples were piled into tanks of pH 9-10 tap water overnight. (Fig. 1.11) This created an opportunity for cross-contamination between samples and the poorly coated gunite.

For testing, multiple specimens (representing 16 different combinations of the four plastering variables) were placed in each of five tanks (Figs. 1.11, 2.1), with different tanks being used for different water chemistry (bleach versus trichlor, and balanced versus aggressive, with a fifth tank having neither disinfectant nor any attempt at water balance). There was a needless attempt to match the water volume/water depth ratio in the tanks with that in the pools. A more sensible ratio to match would be water volume/plaster area; though maintaining water balance would have been more feasible with a larger volume of water in the tanks than such a fixed ratio would allow for. Control of the water chemistry was further complicated by slow circulation, limited to just one turnover per day. Consequently, added acid and disinfectant may not have been distributed evenly and rapidly enough to ensure comparable exposure among all of the specimens. Thus, specimen placement could have been quite critical, introducing an uncontrolled and untracked variable.

At least some samples were wrapped in wet towels and stored for 120 days before analysis. (p. 65) Reactions and contamination may have taken place during those months of wet storage.

Five weeks after the start of exposure testing with simulated pool water, it became apparent to the experimenters that the *Thoroseal* coatings were too porous and/or alkaline to protect the test water from contamination by alkali in the gunite or in the *Thoroseal* coatings. The Portland cement-based *Thoroseal* sealant was then replaced, or supplemented, with epoxy coating. By that time, however, the exterior plaster surfaces had all been well exposed to each other and to gunite during storage, shipping, rinsing and the initial five weeks of water testing. Instead of starting over with fresh, uncontaminated

samples, the experimenters proceeded with further testing of the compromised samples. The reluctance to scrap contaminated specimens and re-start the experiment calls the findings of the entire project into question.

One important plaster variable glossed over in the phase 1 report is the time between plaster application and filling with (or immersion in) water. While the plaster specimens appear to have had plenty of time to set before immersion in tanks of water, it is not clear that the pools were given adequate cure time before filling, or whether the cure time allowed for all four pools was the same. (The coupons used in the tank studies took some time to process—having to be cut, coated with *Thoroseal*, packaged and sent to the lab—prior to immersion in the tanks.)

It is apparent that different sections of the pools were associated with different settings for the plaster variables (added calcium chloride and supplemental water), and that these sections were applied sequentially.¹ The sections involving plaster with added calcium chloride were applied during early morning hours, when air temperatures were lower, relative humidity higher, and premature drying (before adequate setting and hydration) would have been less likely. The sections without added calcium chloride were applied between 10:30 AM and 2:30 PM, when ambient temperature would have been higher, relative humidity lower and premature drying more likely. The associated microscopy report by Rothstein *et al.* notes the risk of premature drying of pool plaster, due to its richness and the thin layers in which it is typically applied.

Lack of control for the setting-time variable could easily bias the experiment, making it impossible to get a fair assessment of the impact of added calcium chloride. The sections with added calcium chloride had more time to for the plaster to set before the pools were filled. The accelerating effects of calcium chloride may have magnified the impact of a longer setting time. While it is important to keep plaster moist while it is setting, premature exposure to massive amounts of phase water (particularly water that is low in alkalinity and calcium hardness) could result in dissolution of solids from the delicate, uncured plaster. The resultant chemical changes, voids or weakened/reduced density regions could contribute to later appearance of etching or spot alteration.

Table 6-3 and a comparison of Figure 6.10 with Figure 6.11 in the report shows worse deterioration in the pools than in the cast test coupons, which were allowed far more time for the plaster to set. This difference between the coupons and the pools may demonstrate the relevance of plaster cure time before massive exposure to phase water.

The longer cure time for the coupons may also explain the findings on page 76 that in the pools, calcium chloride addition seemed to reduce the appearance of “spot etching”, whereas “this conclusion is not supported by the by the laboratory samples”. The long plaster cure time for the coupons would make any time differences between the various samples relatively inconsequential. In contrast, the pools being filled with water soon after the last sections were plastered, had so little time for the plaster to set that the cure-time differences were significant. Thus, calcium chloride *appeared* to make more stable plaster in the pools, but clearly did not in the coupons.

¹ D. Rothstein, D. Kachlakev and N. Pal, “Plaster Durability in Pool Environments”, 27th International Conference on Cement Microscopy, Table 2. This microscopy report covers samples from the phase 1 California Polytechnic State University study on “Etching Deterioration in Plastered Swimming Pools”.

Unless all four pools were filled simultaneously and at the same rate, a time bias may also have favored different water chemistries (“balanced” vs. “aggressive” or bleach vs. trichlor).

Questionable Understanding of Relevant Chemical Issues

For a study that involves a lot of water chemistry and plaster chemistry, one would expect knowledgeable chemists to be involved, or at least consulted; however, there are enough errors related to chemistry in the report to make it questionable that the report was even reviewed by a chemist. A few examples follow:

- The chlorine-based disinfectants are ambiguously referred to as “cleaning solutions”. (See, *e.g.* p. 22, last paragraph; p. 73 last paragraph.) This suggests a possible confusion of oxidative disinfectants with surfactant based cleansers.
- The chlorinating agent *trichloro-s-triazinetriene*, is frequently referred to as “trichloride”. Seemingly the authors have no appreciation of the difference between a chloride salt and an active chlorine compound, in which the chlorine is in a formal +1 oxidation state.
- In discussing chemical control, on page 42 the authors claim that free chlorine cannot exist at high pH, above 9.0. They try to support this absurd assertion by use of Figure 5-5 (copied from A. T. Palin’s “Chemistry and Control of Modern Chlorination”), which merely indicates how the relative concentrations of elemental chlorine (Cl_2), hypochlorous acid ($HOCl$), and hypochlorite anion (OCl^-) change with pH. In so doing, the authors betray a lack of understanding that free chlorine includes all three of these forms of active chlorine and that even the hypochlorous acid fraction does not drop fully to zero as pH rises above 9. Note that the value: $[HOCl]/([HOCl]+[OCl^-]) = 1/(1+10^{pH-pK_a})$ approaches zero as an asymptote but never reaches it even at very high pH. The authors have confused the term *free chlorine* (an oxidizing form of chlorine with disinfecting properties) with elemental chlorine, *i.e.* chlorine gas (Cl_2). This would also indicate of a lack of familiarity with recreational water treatment and chemistry.
- The authors then proceed to blame the Taylor test kit for failing to adequately distinguish between free and combined chlorine. Since combined chlorine could hardly have been an issue in this case, and since DPD test kits can make an adequate distinction between free and combined chlorine, it is doubtful that the authors understood the tests they were performing or even the meaning of the term “combined chlorine”. (The paper does not actually give a catalog number or any other precise designation for the test kits used.)
- On page 19 the authors attribute high pH in the test water to leaching of calcium from the *Thoroseal*[®] coating that had been applied to the exposed surfaces of the gunite base layers. Calcium ions would not themselves contribute alkalinity, but could in fact reduce alkalinity via precipitation of calcium carbonate. Leaching of calcium hydroxide (more specifically the hydroxide, not the calcium) would be a reasonable explanation for rising alkalinity in the test water.
- On page 43 the authors speculate that high hypochlorous acid concentrations could cause plaster etching. This seems most unlikely since hypochlorous acid is an extremely weak acid ($pK = 7.5$), and since pH was (allegedly) controlled, and the plaster is not oxidizable.
- While not an error *per se*, it is a distraction that chemical formulae in the paper are all shortened to the arcane CCN (Cement Chemistry Notation) abbreviations. Thus, for example, tricalcium silicate becomes C_3S rather than the conventional Ca_3SiO_5 or the equivalent

$3\text{CaO}\cdot\text{SiO}_2$. (To most chemists the formula C_3S would suggest three carbon atoms bound to a sulfur atom, whereas neither carbon nor sulfur is actually involved). The use of CCN is especially problematic since it is used without introduction, needlessly obscuring the discussion of the chemical transformation taking place as cement cures. To add to the confusion, even CCN is misused in referring to gypsum or calcium sulfate dihydrate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), which the authors call calcium sulfate dehydrate on p. 31. The CCN designation they use is CSH_2 , whereas to designate sulfate (as opposed to silicate) in CCN a bar would be required over the S: $\text{C}\bar{\text{S}}\text{H}_2$.

Failure to Cite Authoritative Studies, Containing Empirical Evidence

A further concern is the weak support given for a number of underlying assumptions in the paper. Instead of citing peer-reviewed research to establish a point, the authors frequently preface a working hypothesis with expressions such as the following:

“It is a well know [*sic.*] fact that...”: pp. 36, 60

“it is believed that...”: pp. 36, 37

“It is a consensus among plasterers and researchers that...”: p. 38

Reliance on such terminology in place of suitable scientific citations is suggestive of intellectual laziness at best, and use of false assumptions at worst.

Miscellaneous Misconceptions

There are other seeming misconceptions or misstatements that are of minor significance, but when taken with multiple uncorrected typographical errors and poor syntax they indicate a high level of carelessness in composing the report:

- On page 40 the authors state that “humidity is directly proportional to the water loss from the tanks.” Do the authors really think that enough water was lost from the tanks to have any significant impact on the ambient humidity? Or did they really mean to say that water loss from the tanks was *inversely* related to the ambient humidity.
- On page 36 they seem to equate physical hardness, as measured by the Mohs scale, with resistance to etching. Chemical inertness or low water solubility would seem to be at least as important as physical hardness in resisting etching. So, while hardness may be an important factor in etching, it is hardly the only factor, or even the most significant.

Questionable Findings

It is unlikely that any etching or spot alteration could be reliably correlated with control variables, given how out of control those variables actually were. Nevertheless, the authors concluded that “the water chemistry is the single, most important parameter influencing the spot-etching deterioration of the plastering surface.” This finding is at odds with the little data actually provided in the report. To illustrate this, consider the following graph of the LSI (Langelier Saturation Index) versus time for the five tanks (Figure 5).

The LSI was estimated using the pH, alkalinity, calcium hardness (Figures 1-3 in this critique) and the temperature in Figure 5.1 of the phase 1 report. Since no data were provided for TDS (total dissolved solids) or ionic strength, a value of 600 ppm TDS was assumed. In addition, each point in the Figure 5, below, is based on a rough average of 10-days-worth of data for each input parameter (pH, alkalinity, calcium hardness, and temperature). Given the crowding of points early in the study, a precise daily

estimation of the parameters from the graphs provided would not be more beneficial than a several-day average.

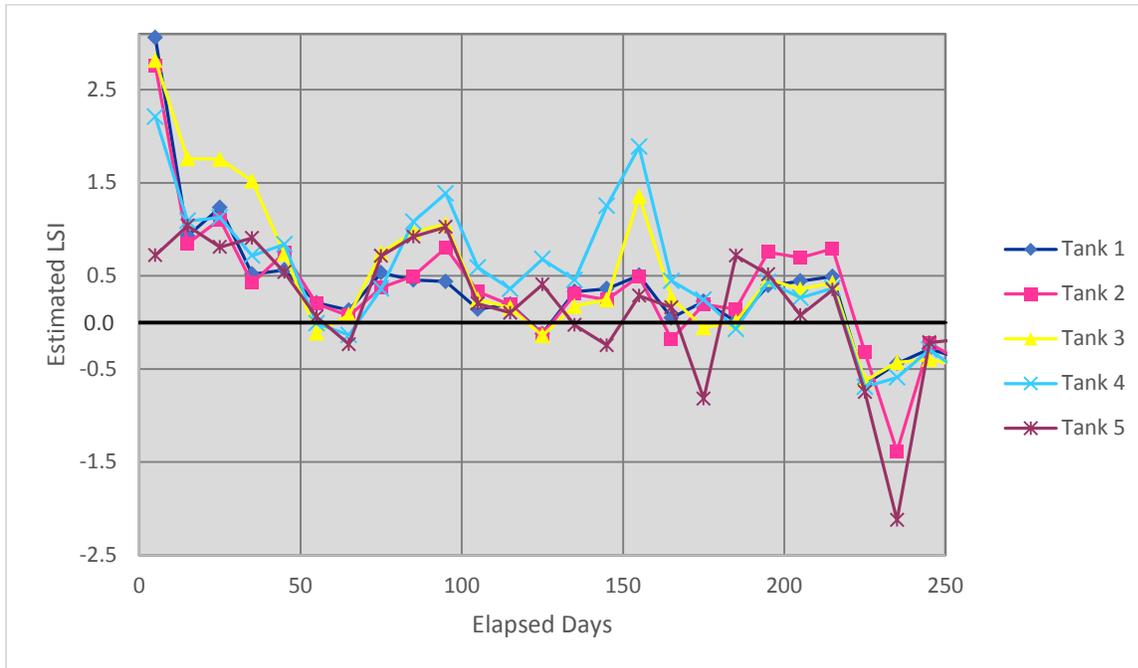


Figure 5. Estimated LSI for the 5 tanks used. Note that tanks 1 and 3 were treated with trichlor. This could have resulted in cyanuric acid accumulation and a resultant downshift in the LSI of 0.1 to 0.2, relative to the plots shown.

It should also be noted that no data were provided on the concentration of cyanuric acid in the tanks. Therefore, the LSI plotted does not take into account the contribution of cyanuric acid to total alkalinity, and the LSI plotted is based on the total alkalinity. Since tanks 1 and 3 were treated with trichlor (*trichloro-s-triazinetriene*), it is possible that CYA (cyanuric acid) may have sometimes accumulated to as high as a 50 ppm concentration in these tanks, depending on the frequency of water replacement relative to the rate of trichlor addition. Taking a 50 ppm CYA concentration into account would shift the affected LSI downward by ~0.1–0.2. Nevertheless, Figure 5 gives a reasonable picture of the relative LSI values for the five tanks.

Table 1 provides the time-average LSI for the each of the five tanks. Table 2 summarizes the semiquantitative surface deterioration results reported in Figures 5.13 through 5.35 of the phase 1 report. In case some of the apparent zero values in the bar charts of the cited figures were actually intended to be blank rather than zero, the mean and median for the five tanks were also calculated omitting all zero values. The trends remain the same whether zero values are included or not. Tank 5 provided the least surface deterioration; tank 3 had the worst deterioration; tanks 1, 2 and 4 were intermediate.

Table 1. Time-average LSI for the five tanks in the Cal Poly phase 1 study.

Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
0.2–0.3*	0.3	0.2–0.4*	0.4	0.1

*The low end of the range for tanks 1 & 3 allows for a continuous CYA concentration of 50 ppm throughout the study.

Table 2. Semiquantitative "etching deterioration score from Figures 5.13 to 5.35 in the phase 1 report.

	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
Average (mean)	2.8	2.5	3.8	2.6	0.2
Mean of non-zero values	3.5	2.5	5.6	2.6	1.0
Median	2.5	2.8	4.3	2.8	0
Median of non-zero values	2.5	2.8	6.0	2.8	1

Figure 5 and Tables 1 and 2 provide some telling information:

- The LSI varied over a wide range in each of the tanks. In general, the tanks were rather scaling during the early weeks and aggressive in the final weeks, regardless of tank number.
- While tanks 1 & 2 were designated as "Balanced" and Tanks 3 & 4 were dubbed "Aggressive" (Table 2-2, phase 1 report), in fact all five tanks appear to be balanced in terms of the time-weighted average LSI.
- Moreover, based on the time-weighted average LSI, tanks 3 & 4 appear to have been *less*, not more, aggressive than tanks 1 & 2.
- Tank 5 appears to have been the most aggressive of the tanks, but the samples in it had the least surface deterioration.
- Tanks 3 & 4, which had the highest time-average LSI (least aggressive), were rated as giving the most severe surface deterioration.
- Plaster samples in tanks 1 and 3, which were treated with trichlor, tended to have worse surface deterioration than samples in the bleach-disinfected tanks (tanks 2 & 4). This is the sole finding that was pointed out in the phase 1 study and not contradicted by the data-based analysis provided in this critique.

The fact that the semiquantitative analysis showed the most extensive "etching" in the tanks with the more aggressive *target* chemistry (phase 1 report, Table 2-2), but the less aggressive *measured* values, suggests a possibility that the researchers only saw what they expected to see, or were encouraged to find. The reported data belie any finding that water balance was responsible for surface deterioration. Of the chemical parameters reported, only the choice of sanitizer appears to have had any bearing on surface deterioration in the tank samples.

Also, careless confounding of variables and a lack of balance in the design of the study led to unreliable conclusion. For example, as noted previously, the plaster set time before pool filling was confounded with the plaster variables: added calcium chloride and supplemental water. Since significantly longer setting time was allowed for plaster sections with calcium chloride added than for sections without, and in sections with supplemental water than in those without, it is impossible to separate the impact of calcium chloride and supplemental water from the impact of plaster cure time. Conclusions drawn from the pool samples related to plaster variables are particularly unreliable.

Conclusions

While it is apparent that the study was a major undertaking, there are many problems with design study imbalance, flawed sample preparation, failure to control of critical variables, and apparent lack of understanding of chemical principles relevant to water balance and sample preparation. These deficits call nearly all of the results and conclusions into question. In particular:

- No data are provided to support the implicit assumption that spot alteration is a form of etching or that it is caused primarily by water chemistry.
- Failure to track or control water balance makes the designation of some pools or tanks as “balanced” and others as “aggressive” meaningless, regardless of any initial water balance targets. Any conclusions based on those designations are as unsupported as the designations themselves.