

Overview

This critique deals with a study titled “Plaster Durability in Pool Environments”. The report, published in the *Proceedings of the 27th International Conference on Cement Microscopy*, was written by D. Rothstein of DRP Consulting Inc. in Boulder, Colorado, and D. Kachlakev and N. Pal of California Polytechnic University in San Luis Obispo, California. The report deals specifically with microscopic analysis aspects of phase 1 pool plaster studies conducted at California Polytechnic University on “Etching Deterioration in Plastered Swimming Pools”.

The Rothstein microscopy report is far more scientific than the associated overall phase 1, July 2004 report by Kachlakev and Pal. It explains the systematic nature of the optical microscopy scans, and provides some details on the methodology in the optical and SEM (scanning electron microscopy) examinations and workup of the EDX (energy dispersive x-ray) elemental analysis from the SEM studies. However, the report does have some deficiencies. It suffers from some of the same misunderstandings on pool treatment chemicals. It relies on pool samples from the flawed phase 1 Cal Poly pool study. It adds in irrelevant field samples, for which water chemistry and plaster preparation details are totally unknown. And it surmises trends from a very limited sample collection, some of which were from the field, not the somewhat controlled test pools. Consequently, though the laboratory methods seem sound, conclusions related to the Cal Poly pool studies are limited by the samples provided to DRP Consulting and the problems related to operation of the pools and generation of the samples.

Detailed Discussion

USEFUL CANDOR: The report candidly indicates one of the primary deficiencies in the Phase 1 tank test, namely that the tanks were too small to maintain control of water alkalinity, so the water in all the tanks was unbalanced (scaling). In terms of SA (spot alteration) the Rothstein report also points out that pool water was not closely monitored or recorded, and that “observations from this study ... do not link SA to a specific set of construction practices or water chemistry conditions”. This observation is in stark contrast with the phase 1 report which concluded that “water chemistry is the single, most important parameter influencing the spot-etching deterioration of the plastering surface”.

Some misconceptions on water treatment chemicals and practices present in the phase 1 report were also evident in Rothstein’s related microscopy report. For instance, there is reference to pools sanitized with “trichloride”. The actual sanitizer would more reasonably have been *trichloro-s-triazinetrione*, an active chlorine compound. “Trichloride” is an incomplete name suggestive of a chloride salt of a trivalent metal, for example aluminum trichloride or ferric chloride. Such materials may function well as coagulating agents (water clarifiers), but would lack sanitizing capability.

OPTICAL MICROSCOPY: A useful feature in the Analytical Procedures section is a description of the point count analysis procedure. The microscopic methodology for systematically scanning samples and characterizing loci as intact paste, altered paste or aggregate seems to be a reasonable method for quantifying plaster deterioration. This systematic methodology, however, is limited to the samples provided from the pools. Without a method to prevent bias in collecting core samples from the pools the overall data set could be biased. Also, without a large number of core samples, it is possible that the

microscopic analysis would be done on a sample set that is not representative of the pools involved in the study. If the samples were representative of the respective pools, then it would appear from Table 3 that more plaster deterioration took place in the “aggressive” pool, Pool 3, than in the “balanced” pool, Pool 1. It also appears that addition of 2% calcium chloride to the plaster mix was associated with less plaster deterioration than was omission of the calcium chloride. It also appears the water content of 0.50 in the plaster mix produced more durable plaster than did water content of 0.42. However, it is important to remember that the reliability of these observations hinges on the samples truly being representative of the pool sections they were taken from and on the water chemistry truly being known as balanced or aggressive. Given the lack of water balance data for the pools, and the seeming unfamiliarity of the experimenters with water treatment practices, it is impossible to be sure of the water balance in the various pools.

SEM/EDX ANALYSIS: Scanning electron microscopy can be quite useful in that it not only allows for higher magnification than is possible with optical microscopy, but also the impact of the electron beam on the sample results in production of x-rays. Wavelengths of the x-rays produced allow the analyst to determine what elements are present in the sample, and the intensity of the x-rays is somewhat proportional to the abundance of the given elements. Very light elements cannot be detected in this fashion, as they tend to produce no x-rays or very weak x-ray signals. Even for elements beyond the second row on the periodic table the x-ray intensity is influenced by a number of variables, so the resulting elemental analysis is semi-quantitative at best. Rothstein compensates for three principal causes of variation in signal intensity (atomic number, x-ray absorption by the sample and x-ray fluorescence within the sample) by means of “ZAF correction”, so the resulting elemental analysis, while limited to elements heavier than carbon, allows for least somewhat quantitative comparison between sample locations for the elements it detects.

In view of the above, Table 4 in the paper shows some apparent trends in a field sample:

- Calcium appears to be somewhat depleted at the surface relative to deeper locations, and is especially depleted in a pit in the plaster sample.
- Copper was elevated at the surface and especially in a pit. This is reasonable, as copper was likely not very prevalent in the plaster itself, but may have been in the pool water due to corrosion of pool equipment or use of copper algaecides.
- Sulfur (probably as sulfate) tends to be depleted nearer the surface than at great depth. This is not surprising, as calcium sulfate is more soluble than is calcium carbonate.
- Silicon generally appears to be more abundant near the surface than deep in the plaster.
- Barium seems more abundant near the surface than deep in the sample.
- Chloride levels may be elevated on the pit wall, but otherwise no clear trend is evident.
- Aluminum levels may be somewhat lower on the pit wall than elsewhere, but there is no consistent trend.
- Magnesium and phosphorous show no clear trend.

Interesting as the trends may be, the sample itself is of limited relevance, as it came from the field, a random, marred pool for which no information was available on water balance history or plaster preparation.

The single relevant sample from a test pool came from a badly deteriorated section of plaster (ranking #4, the worst class defined in the report). For this sample the following trends appear:

- Calcium levels seem lower near the surface than deep in the plaster.
- Silicon is relatively depleted in what may be an etched or leached section of the surface, though otherwise no trend is evident.
- Sulfur shows no clear trends, though it may be somewhat higher on average near the surface.
- Chloride seems higher near the surface.
- Aluminum seems lower near the surface.
- Magnesium may be higher near the surface on average.
- Potassium is less abundant near the surface. This is reasonable as the plaster mix may have contained trace levels of potassium. K^+ ions are mobile and could easily be leached from the surface.

While SEM-EDX can be a useful tool, it would be risky to draw conclusions from just a few samples, and even riskier with only a single sample from the test pools. Even between the two samples covered in the report not all the apparent trends are the same. Calcium does seem lower near the surface, especially in altered spots, and chloride seems to be elevated in those same areas, but for the other elements there does not appear to be a consistent trend that applies to both samples. Without many more samples from the pool study, including samples of normal, unblemished plaster, it would be difficult to draw any reliable conclusions about the chemistry associated with spot alteration or the causes thereof.

Similarly, the report is limited to a small set of microscopic/petrographic methods, which in turn limited what could be learned from the few samples studied.

Conclusions

Rothstein recognized that more work would be required to determine “how variations in mix design and construction practices affect the properties of the finished surface in terms of susceptibility to SA [spot alteration]”, and that additional analytical methodologies will be required, along with monitoring, control and recording of pool water chemistry—all of which were absent in the 2004 phase 1 Cal Poly report. The microscopist did not reach any conclusions regarding the cause(s) of spot alteration, opining that “research *may eventually* afford an opportunity to better understand what parameters exert the first-order controls on SA and develop strategies for mitigating this form of deterioration.” This candor did not carry over into the 2004 Cal Poly report on “Etching Deterioration in Plastered Swimming Pools”, which concluded that “water chemistry is the single, most important parameter influencing the spot-etching deterioration of the plastering surface.” The methodology in the microscopic examination, while limited, appears sound; but the number of samples was rather limited and the method of sample selection is not clear (though this was probably outside of Rothstein’s control) and may have been biased. Given the sample selection issues and the water chemistry and plaster preparation uncertainties behind the samples, it would be impossible for the best of microscopic analysis to reach any conclusions about the causes of spot alteration.

The samples provided for petrographic analysis were generated under problematic circumstances, in that the pool water balance parameters (pH, alkalinity, calcium hardness, and temperature) were not controlled, recorded and reported. In addition, plastering variables, such as calcium chloride addition, were confounded with plaster set time, prior to pool filling. Given the limited number of samples,

uncertainties about possible bias in sample selection, and the questionable control in generation of the samples, any conclusions from the report would need to be viewed with caution.