

A Critique of the Dow Whitney Report

Que Hales, Doug Latta, and Kim Skinner
onBalance

A study was conducted at the University of Florida which concluded that “deterioration of marcite (including both etching, pitting and staining) is chemically related and is primarily due to leaching of calcium hydroxide (portlandite) from the portland cement paste.” However, a close reading of the draft report itself reveals that no such conclusion can be reached based on the data published. Indeed, critical data, which would be expected to support any conclusions made, are missing from the report.

The study was composed of three major components: research and summarization of pertinent, previously published material; failure analysis of samples acquired from the industry (referred to as “field diagnostic studies”); and a lab study designed to replicate field conditions and cause coupons to exhibit the failure characteristics (referred to as an “etching and staining mechanistic” study).

The study contains numerous incorrect assumptions, which led to a careful analysis of the report. It was discovered that many of the incorrect ideas were plagiarized from material found in an earlier study performed by a Monsanto employee.

Also, the laboratory study utilizing coupons was duplicated by this paper’s authors, and the results are given, which indicate that the conclusions made in the Dow Whitney report about the lab study are unwarranted.

Southeastern and Southwestern United States. In an effort to determine the cause(s) for these phenomena, a study was sponsored by the Building Construction Industry Advisory Committee in Florida, and was funded by the Florida Department of Education, the NSPI Region in Florida, and the University of Florida. This study, released in November of 1990, was called *A Study of Marcite (Plaster) Deterioration in Swimming Pools*. In the pool industry the report is commonly referred to as the Dow Whitney Report, after Dr. E. Dow Whitney, the study’s principal investigator. Unfortunately, all copies extant of the Dow Whitney report are marked “draft”. However, in verbal conversation Dr. Whitney has said that there is no later version of the report, and therefore that the draft version may be referred to as the final report.

Indeed, although many promises were made regarding how the research would be released, including a “traveling roadshow” to educate plasterers and technical articles in trade journals (see Eden 1990), the draft report and a verbal presentation at the 1990 NSPI International Expo in Anaheim were the only releases. The reception to the report by the industry has been primarily cold, since the report seems incomplete and without clear explanations of the causes or solutions to the problems. However, since the report has been used as documentation in litigation, the authors of this paper felt that an in-depth analysis of the Dow Whitney Report is warranted.

Introduction

In the 1980’s, a seemingly widespread outbreak of plaster (aka marcite) spot etching, discoloration, and staining was occurring in pools throughout the

Journal of the Swimming Pool and Spa Industry

Volume 4, Number 2, pages 29–41

Copyright © 2001 by JSPSI

All rights of reproduction in any form reserved.

Sources and Reference Material

As the Dow Whitney Report was carefully studied, sections of the documentation were found that contained incorrect assumptions relative to swimming pool plaster and pool water chemistry. These incorrect assumptions include, but are not limited to, the following two concepts:

- The study claims that the source of the calcium which forms plaster dust in new pools is the hardness of the original fill water (Whitney p. 32). This is incorrect. The actual source of that calcium is the plaster, and specifically calcium hydroxide which is put in solution by filling the pool with water.
- The study claims that about 25% by weight of pool plaster is calcium hydroxide (Whitney p. 33). However, although there is calcium hydroxide in the *interior* of the plaster, after a period of time no calcium hydroxide remains *on the surface* – it is either converted to calcium carbonate or dissolved into the pool water, where it ends up as calcium carbonate precipitate or soluble calcium bicarbonate. The amount of time required to completely form this protective carbonate layer averages ten days to three weeks, and ends around the time plaster dust formation is no longer noticeable.

Since the Dow Whitney Report contained these errors, it was compared to a study done some two decades earlier, which was known to contain similar errors. That study, performed by a Monsanto employee as commissioned by the DeMar Baron Pool Plastering Company, was titled “Swimming Pool Water Treatment Effects on White Cement Surfaces” by Dr. Dwain R. Chapman, dated March 10, 1971. Appendix A is an intralinear comparison of specific text from the two documents.

It was found that sentences, paragraphs, and even an entire page of the Chapman study appear virtually verbatim in the Whitney report. This apparent plagiarism was pointed out to Dr. Whitney in letters sent on 11 December 1999 and on 6 July 2000. The letters were faxed and mailed, and the second mailing was sent requiring a signature. To date there has been no response from these letters.

The Field Diagnostic Research

The “field diagnostic” portion of the Dow Whitney research involved examination of etched plaster samples provided by pool companies. It was termed “a major part of this research effort”. This examination, which was reportedly comprised of x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS), led the researchers to conclude that calcium hydroxide was the material most consistently “missing” from damaged plaster. Unfortunately, although samples were collected and analyzed from 58 listed sources (see Whitney p. 10 and Whitney Appendix B), none

of the SEMs are presented, only summaries of three of the XRDs are presented (Whitney pp. 14–16), and only one summary of an EDS of etched plaster is given (Whitney p. 21). Two additional figures of actual EDS readouts are given (Whitney pages 22–23) but they are listed as depicting blue–green and yellow–brown staining, rather than etching (either of the general, uniform type or of the spot etched type). Additionally, a “Plaster Sample Data Sheet” was reportedly “requested to be completed and returned” with each of the 58 samples, and the provided information was deemed “very helpful in the diagnosis of specific plaster problems”. However, only a blank sample of that form is provided. The survey consisted of some 35 questions, one of which asked what the actual plaster problem was. None of the options is “spot etching”, and no raw data or tabulation of the information from the surveys was included in the published study.

Etching and Staining Mechanistic Studies

In what is termed “an important aspect of this phase of the study”, a lab coupon experiment was conducted to try to determine what the effects on cement paste coupons would be after long-term exposure to mildly aggressive water conditions in a test setup. Other aspects of this phase (i.e., lab research) included looks at iron and copper staining, cyanuric acid effects, high chlorine effects, and the susceptibility of calcium hydroxide to etching at other pH levels than in the experiment, etc.

The conclusion of the study is given at the end of the introduction (Whitney page viii): “From this study it was shown that deterioration of marcite (including both etching, pitting and staining) is chemically related and is primarily due to leaching of calcium hydroxide (portlandite) from the portland cement paste.”

The following is a summary of what is described regarding the lab coupon experiment in the Dow Whitney report:

Section 3.2 – Description of Lab Study (Whitney pages 6 – 9):

- Coupons were formed by filling 1.5” sections of 1” PVC
- The size of the coupons, when submerged in one gallon of water, was calculated to be equivalent to the plaster surface:water ratio of an average pool

- Three water:cement ratios were used: 0.4, 0.45, and 0.5 parts water to 1 part cement (by weight)
- No mention was made of aggregate being used in the coupons, nor was there mention of the use of any admixtures
- A small pump was used to simulate pool circulation
- Coupons were suspended in a gallon of water, and the water was maintained in the 6.8–7.0 pH range for 6 months
- The coupons were regularly weighed in an attempt to document calcium leaching

Figures 6a, 6b, and 6c – Results of Lab Study (Whitney pages 24–26)

Graphs are presented which purport to document what happened in the experiment:

- The x-axis of the graphs (for the 6 month period of the test) are labeled as “TIME (hours)”, and the y-axis are labeled “FRACTION REACTED ($\times 10^3$)”.
- Neither the graphs nor the text of the document contain the actual weights, weight gains, or weight losses of the coupons.
- The graphs seem to show that the reactions were approximately 1/3 complete by 1.5 months, 2/3 complete by 3.5 months, and essentially complete by 6 months. They also seem to show that the water:cement ratio played a role in the amount of weight change.

Conclusion of Lab Results

According to the text of the study,

“Figures 6a–c show that the largest leaching rate occurred at the beginning of the experiment. The 0.4 w/c ratio samples had a lower rate of leaching throughout the experiment and also an undetectable rate of leaching after five months. Since the 0.4 w/c ratio cylinders are denser and have less porosity than the 0.45 w/c and 0.5 w/c cylinders the ability of hydrogen ions to enter the structure and leach out calcium is decreased.

Mathematical modeling, curve fitting, and additional research will be required to determine the diffusion kinetics responsible for leaching rates.” (Whitney page 32)

“Thermodynamic calculations and experimental evidence suggest that the most
The Journal of the Swimming Pool and Spa Industry

chemically active calcium compound in marcite is calcium hydroxide (portlandite), $\text{Ca}(\text{OH})_2$. Thus, when plaster is exposed to acidic water, calcium hydroxide is preferentially leached out of the matrix. Since calcium hydroxide comprises about 25% by weight of the plaster, its absence weakens the structure and hastens its disintegration.” (Whitney page 33)

“Results of the above reaction isotherm calculations are shown in Figure 7. The significance of these results is in the fact that for portlandite in marcite to react spontaneously with hydrogen ions in solution, thus forming soluble calcium salts with resulting pitting and etching of the pool walls, the Gibbs free energy change (ΔG) must be negative. If the value of ΔG is positive, the reaction cannot possibly take place, at least under the conditions specified. As is seen from an inspection of Figure 7, ΔG is negative for all values below 13. This is indicative of the fact that calcium hydroxide is a strong base and will interact with hydrogen ions even when these ions are at the extremely low levels found in water whose pH is above 7.0.” (Whitney pages 34–35)

“Experimental evidence supports the hypothesis that acidic pool water preferentially leaches the portlandite phase out of the marcite matrix, resulting in etching. The least expensive option is to monitor the pool water so as to avoid the occurrence of acidic or other marcite–corrosive conditions such as low water calcium content.” (Whitney page 51)

“...over time marcite will maintain its pristine and beautiful white surface only if swimming pool water chemistry is continuously and meticulously controlled.” (Whitney page 51)

There are, of course, a number of errors and invalid assumptions contained in these statements, as well as valid points that were misunderstood or misinterpreted. They include:

- The key issue of water:cement ratio and its effect on porosity was not further examined, particularly to see if etched spots were more porous than non–etched areas. (Subsequent studies, such as Clark 2000, show porosity to be a key issue.)
- The statement is made that 25% by weight of plaster is calcium hydroxide. However, according to other studies, no hydroxide is actually present on the surface of cured plaster – it carbonates to form a protective layer over the surface. In fact, in non–reinforced concrete applications (including

pool plaster) this carbonation is considered beneficial since it densifies the surface, making it less permeable to water and less susceptible to leaching (Houst 1997). If EDS, XRD, and SEM had been performed on these coupons, as were reportedly performed on the field pieces, this should have been evident.

- The study shows that all water pH levels below 13 are aggressive to plaster, yet levels of 6.8–7.0 (instead of the industry standard 7.2–7.8) are purported by the study to be the final causative agent in the problem.
- The statement is made that “experimental evidence supports the hypothesis that acidic pool water preferentially leaches the portlandite phase out of the marcite matrix, resulting in etching.” However, this simplistic answer does not address the key question: why does it happen in spots?
- The report does not include discussion of the implications of excessive admixture use, e.g., extremely soluble calcium chloride accelerants. The implications of (unfortunately common) finishing practices, such as overtrowelling and surface retempering, are also not represented or discussed in the experiment.
- The study does not address the issue of protective carbonation, or explain how “leaching” (which in other papers involves redistribution of calcium rather than removal...) continues for up to six months, when the protective carbonation layer should have formed after a few weeks.

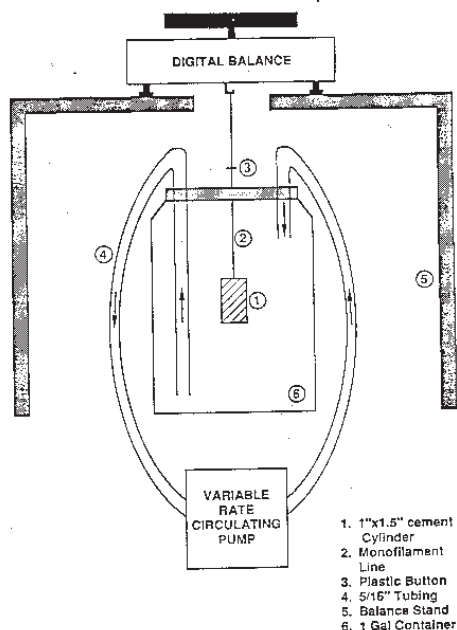
A Re-creation of the Dow Whitney Experiment

In order to see what coupons actually look like when subjected to the “Dow Whitney” conditions, and to document the actual type of etching which results from extended low pH, the Whitney experiment was repeated at the Pool Chlor lab in Tucson Arizona.

Ten coupons were formed of each of the three water:cement ratios, 0.4, 0.45, and 0.5. This means that, for the 0.5 coupons, for instance, 2 pounds of cement was constituted with 1 pound of water. Since the amount of aggregate was not included in the Dow Whitney draft report, in our re-creation two types of coupons were made: some that were just cement–paste coupons (which we suspected the Whitney researchers actually used), and some with a 1:1.5 cement:aggregate ratio—meaning that with the 2 pounds of cement and 1 pound of water, 3 pounds of aggregate was added. The water content for the 0.45 batch was 14.4 ounces, and the water content for the 0.4 batch was 12.8 ounces. No admixtures, such as flow or set modifiers, were added.

The coupons were then allowed to harden overnight, and then they were baked in an oven at 100°F for 24 hours, consistent with the Dow Whitney scenario.

After drying, each of the ten 0.4 w/c samples were suspended in a 10 gallon aquarium filled with 10 gallons of distilled water, and were left to equilibrate for four days (see Figures 1 and 2 for illustrations of the set-ups). The same process was followed with the 0.45 w/c and 0.5 w/c coupons. (The same procedure was also followed with the aggre-



Figures 1 and 2 – Diagram from Dow Whitney Report of Test Set-up and Photograph of Tucson Test Set-up

gate-containing coupons.)

The coupons were then weighed, and the pH of the water in each of the three aquariums was then adjusted to the 6.8–7.0 range. This process of weighing and pH adjusting continued for six months.

It was ascertained by previous experiment that mildly acidwashing a coupon of this size resulted in an average weight loss of 2 grams. Therefore, the digital electronic scale used in the re-creation experiment was an Ohaus Model #SC2020 “Scout”, selected because it is capable of weighing coupons to a hundredth of a gram.

Re-creation results

Over the course of the six months, the coupons each either maintained weight (to the hundredth of a gram) or very slightly increased or decreased in weight (in the range of 0.01 to 0.02 grams). The starting and ending weights are given in Table 1 (for aggregate coupons) and Table 2 (for paste only coupons). The coupons also lost a slight amount of surface, as evidenced by the a translucent appearance on the 0.5 w/c coupons and a clear view of aggregate on the 0.4 w/c coupons (see Figures 3 and 4). There also developed, over the first weeks of the experiment, a film of white powder, assumed to be calcium-based, on the bottom of the aquariums. After six months, when this powder was dissolved and the aquarium water was analyzed, it was found that the calcium level of the water in the aggregate aquariums averaged approximately 300 ppm, and the paste aquariums averaged 220 ppm, as ascertained by an EDTA titration expressing results as CaCO_3 (see Table 3). It can be determined by calculation that if all of the calcium in the sample were CaCO_3 , the weight loss of calcium per coupon would be approximately 1.04 and 0.83 grams respectively. Since the coupons actually maintained, and in some cases even slightly gained weight, it may be that the weight of water incorporated into the cementitious compounds formed exceeds the weight of the calcium lost. However, since this experiment has not been repeated, more experimentation will be needed to see if this result is consistent.

Questions raised by the experiment:

- Did the Dow Whitney experimenters use aggregate in the coupons? It doesn't seem as though they did, which is curious in light of the efforts to make other parameters as “pool-realistic” as possible.
 - Also in this vein, what determinations were
- The Journal of the Swimming Pool and Spa Industry

made to suggest that formed plaster surfaces react in a significantly similar manner as trowelled surfaces? This especially in light of the report's documentation of the changing amount of calcium hydroxide at surface as a result of multiple trowel passes?

- Why do we have no definitive statement on whether the coupons spot etched, since the report includes a definitive definition of spot etching? Where are descriptions or photographs to substantiate the inference that they did?
- What is meant by “percent reacted ($\times 10^3$)” which is the x-axis label in the coupon experiment graphs?
- What would be the “percent reacted ($\times 10^3$)” of coupons in balanced water? In other words, what is the control value, the *expected* amount of calcium loss?
- What is the real significance of a negative Gibbs free energy exchange value? Don't the equations presented predict that *any water with a pH below 13 is, to varying degrees, aggressive to the calcium hydroxide in plaster?*
- Why does the Dow Whitney report repeatedly refer to the pH range of 10–10.5 as the “natural pH” of a water solution exposed to plaster? Isn't it because any water with a pH <13 in a plaster vessel will dissolve calcium hydroxide, thus raising the water's pH, and that the only way to stop this is not pool industry-defined water balance, but rather the maintenance of pH in the pool greater than 13?
- When we performed this experiment (with aggregate-containing or aggregate free coupons), why do the coupons always etch evenly over the entire coupon, and never in a spot pattern?

Critique

In verbal conversation, Dr. Whitney claimed that, when performing this experiment, the coupons always “spot etched”. However, in the report itself, no physical description or photographs of the coupons were given, no weight loss was documented, and no specific statement was given that the coupons either etched (although we suspect they did) or that they spot etched (which we suspect they did not).

Selective Solvation, or Preferential Leaching

An additional point that bears mentioning is

Coupon Number	0.4 C:W		0.45 C:W		0.5 C:W	
	Before	After	Before	After	Before	After
1	26.18	26.48	26.90	27.18	24.72	24.86
2	25.84	26.20	26.49	26.61	24.90	24.68
3	25.51	25.78	27.44	27.61	24.75	25.38
4	25.67	25.80	26.48	26.31	25.14	25.18
5	26.63	26.87	26.45	26.49	25.52	25.37
6	25.38	25.70	28.06	28.32	25.48	25.53
7	26.09	26.28	27.54	27.75	25.85	25.43
8	26.69	26.60	26.05	26.18	25.55	25.36
9	26.03	26.27	25.95	26.08	25.64	25.21
10	26.21	26.40	26.39	26.09	25.32	25.12

Table 1 – Weight (in grams) of Cement Paste With Aggregate at Start and End of Six Month Period

Coupon Number	0.4 C:W		0.45 C:W		0.5 C:W	
	Before	After	Before	After	Before	After
1	21.32	21.78	21.62	21.99	18.90	19.25
2	21.04	21.57	21.05	21.43	19.09	19.44
3	21.00	21.44	21.02	21.35	18.54	18.90
4	21.16	21.75	21.07	21.41	18.93	19.30
5	21.78	22.25	20.82	21.14	18.95	19.30
6	21.64	22.07	21.27	21.61	18.66	18.97
7	21.67	22.14	20.95	21.31	18.24	18.57
8	21.95	22.45	20.74	21.11	18.92	19.28
9	21.28	21.75	21.59	21.94	18.05	18.44
10	21.65	22.11	21.45	21.80	18.94	19.28

Table 2 – Weight (in grams) of Cement Paste Without Aggregate at Start and End of Six Month Period

Coupon Type	0.4 C:W	0.45 C:W	0.5 C:W
With Aggregate	302	294	300
Without Aggregate	224	218	220

Table 3 – Tucson Coupon Test Total Calcium Readings (in ppm as CaCO₃)

the use of the term “preferentially leached” when referring to calcium hydroxide being removed from a plaster surface. As used in the Dow Whitney report, it means that calcium hydroxide is leached preferential to calcium carbonate or any other forms of calcium in

the plaster compound. It is mentioned in the report that “calcium hydroxide comprises about 25% by weight of the plaster”, and it can be assumed that the distribution of this calcium is relatively uniform throughout the surface. No inference is made that

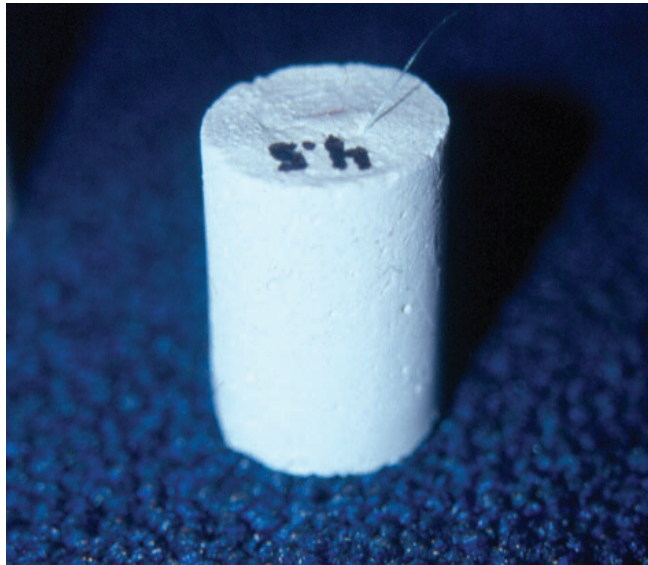


Figure 3 – One of the 0.45 Cement:Water Ratio Coupons from Tucson Test Set-up (Before Six-month submersion)

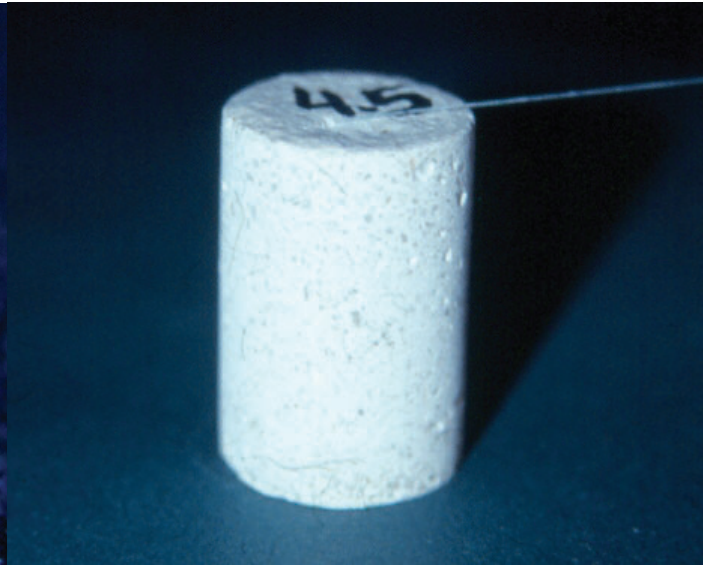


Figure 4 – One of the 0.45 Cement:Water Ratio Coupons from Tucson Test Set-up (After Six-month submersion)

calcium hydroxide is concentrated in round spots of the plaster surface, and that any leaching of calcium hydroxide from the plaster comes only from these spots. Our re-creation of the experiment contradicts Dr. Whitney’s verbal assertion that the coupons etch “preferentially in round spots” – a point that has been used by some in the industry to attempt to explain the spot etching phenomenon.

Prevention

As far as Dr. Whitney’s recommendations to avoid (spot?) etching, he mentions “monitor(ing) the pool water so as to avoid the occurrence of acidic or other marcite-corrosive conditions such as low water calcium content.” (Whitney page 51), and that “...over time marcite will maintain its pristine and beautiful white surface only if swimming pool water chemistry is continuously and meticulously controlled.” However, this conclusion extends beyond the limits of the data: in no way does the experiment demonstrate that balanced water will not cause leaching of calcium hydroxide. And it is well known in the industry that pool surfaces *never* “maintain... pristine and beautiful white surface(s)”. The fact of the matter is that all plaster surfaces in water slowly degrade, and that no regimen exists to prevent this occurrence. The best one can hope for is to constitute plaster, balance start-up water, and subsequently maintain the water and the pool in such a manner as to minimize aggressive tendencies

and to make plaster last as long as it is naturally capable of lasting in a challenging environment.

Conclusion

In attempting to answer industry questions, the Dow Whitney researchers only succeeded in creating more questions. All three phases of the research are problematic – the documentary portion is heavily plagiarized, and contains incorrect information. The field research (failure analysis of pool plaster) is undocumented, and the lab experiment is flawed and undocumented. It is our opinion that the report should no longer be used to support litigation or define causes for spot etching.

References

- Chapman, Dr. Dwain R. “Swimming Pool Water Treatment Effects on White Cement Surfaces.” 1971.
- Clark, Dr. Boyd. “R.J. Lee Group Project # CCH908603.” R.J. Lee Group, May 15, 2000.
- Eden, Cal and Dr. E. Dow Whitney. “Etching, Mottling, and Staining in Plaster coated Concrete Swimming Pools.” *Concrete International*. September 1990. p. 31–32.
- Houst, Y.F. “Microstructural Changes of Hydrated Cement Paste Due To Carbonisation.” in *Mechanisms of Chemical Degradation of*

Cement-based Systems, K.L. Scrivener and J.F. Young, eds. 1997, pp. 90–97.

Whitney, Dr. E. Dow. "A Study of Marcite (Plaster) Deterioration in Swimming Pools." NSPI Technical Publication #74. 1991.

About the Authors

J. Que Hales is the Editor of the *Journal of the Swimming Pool and Spa Industry*. He is currently employed by Pool Chlor, a residential gas chlorine chemical service firm. He has been in the pool industry since 1980, working first as a residential chemical technician, and then as the owner of a small independent cleaning, repair, and retail business. He has managed the Tucson office of Pool Chlor since 1985, and also functions as the Pool Chlor corporate computer systems manager and mailing operations manager. He studied English and Secondary Education at the University of Arizona. He is the co-author of several technical papers which have been reported on in various industry magazines. He has been a member of the Board of Directors of the National Association of Gas Chlorinators (NAGC) since its inception, and is a Past-President of that organization. He is still a board member of the organization's new incarnation – the Swimming Pool Water Treatment Professionals (SPWTP). He also serves on the board of the Southern Arizona Chapter of the National Spa and Pool Institute (SAC-NSPI).

Doug Latta is the owner/principal of Aqua Clear Pools Inc. of Chatsworth, California. He studied at California Lutheran University (BA – Business) and California Coast University (MBA). He is a licensed swimming pool contractor, as well as a general building contractor in the state of California. He is a published author, and is the founding and immediate past president of the NAGC, a member of the board of the Swimming Pool Chemical Manufacturers Association, and the Swimming Pool Trades and Contractors Association, a California-based safety, education, and support association. Doug also serves on the board of the Western Pool and Spa Show and is an active member of SPWTP.

Kim Skinner is the co-owner of Pool Chlor, a chemical service firm with offices throughout the Southwest. He joined Pool Chlor in 1974, after studying chemistry at BYU. Kim has worked in the swimming pool industry for 25 years, and is a former manager of Skinner Swim Pool Plastering, Inc. of Sun Valley, California. He is the co-author of several technical reports on swimming pool water chemistry and plaster phenomena, which have been featured in articles in the trade press. A speaker and panelist at various trade conventions, Kim is also involved with the NSPI, the Chlorine Institute, and the NAGC/SPWTP.

The three coauthors have recently formed on-Balance, a research, educational and consulting firm.

Appendix A – Intralinear Comparison

Swimming Pool Water Treatment Effects on White Cement Surfaces

Dr. Dwain R. Chapman – March 10, 1971

Page 1 / Introduction / 1st sentence:

Water is near to being a universal solvent. Even in its present state it can cause the dissolution of all but the most stable of materials.

Page 1 / Introduction / last sentence of 1st paragraph and entire following paragraph:

The water and whatever else is present in the water will almost always have some effect on the container.

The composition of the container will be the determining factor in the nature and extent of the effects. To determine the effects of swimming pool water, and

A Study of Marcite (Plaster) Deterioration in Swimming Pools

Dr. E. Dow Whitney – November 1, 1990

Page 28 / Section 5.1 / 1st sentence:

Water is near to being a universal solvent and it can cause the dissolution of all but the most stable of materials.

Page 29 / Section 5.1 / last sentence of 1st paragraph and entire following paragraph:

Water and whatever else is present in the water will almost always have some effect on its container.

The composition of the container, in this case the marcite shell of the swimming pool, will be the

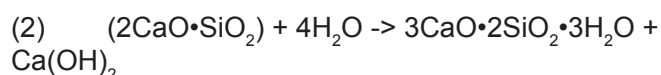
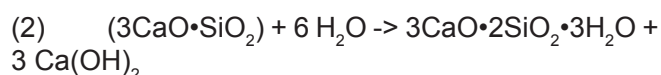
the chemicals used in the water, on white cement it is of importance that we know the composition and properties of the various substituents which are present in the cement.

Pages 1–3 / Introduction / 3rd paragraph of Introduction through end of introduction except for final paragraph:

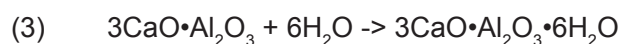
The primary raw material for the manufacture of Portland cement is calcium carbonate or limestone. The limestone is mixed with clay containing silica, aluminum and ferric oxides in the proper proportions and then burned in a rotary kiln at a temperature of about 1450°C (2640°F). A hard “clinker” is formed which is cooled and then ground in a mill. During the grinding about three percent of gypsum is added to help control the setting time of the finished cement.

The primary compounds entering into the composition of finished Portland cement are: Tricalcium silicate, 3 CaO•SiO₂ (54%); Dicalcium silicate, 2 CaO•SiO₂ (17%); Tricalcium aluminate, 3 CaO•Al₂O₃ (11%) and Tetracalcium aluminoferrite, 4 CaO•Al₂O₃•Fe₂O₃ (9%). White Portland cement is richer in alumina but free of ferric and magnesium oxides.

The setting of cement is essentially a hydration reaction to form tricalcium disilicate hydrate, 3CaO•2SiO₂•3H₂O. The hydrate forms a colloidal “mineral glue” which is called “Tobermite”, because it is practically identical with a rare, naturally occurring mineral of that name. The reactions which occur are given below.



In the first reaction about forty percent by weight of calcium hydroxide, Ca(OH)₂, or as it is sometimes called calcium hydrate, CaO•H₂O, is formed. In the second reaction eighteen percent by weight of calcium hydroxide is formed. The hydration of the tricalcium aluminate is as follows:



As soon as the cement is mixed with water, a rapid reaction starts. In a few minutes, the gauging water becomes saturated with calcium hydroxide. The di- and tricalcium silicate is hydrated to a gel, releasing

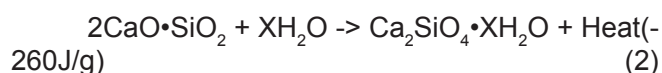
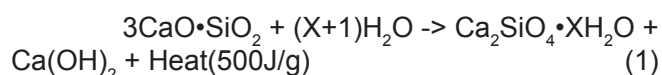
determining factor in the nature and extent of these effects. To determine the effects of swimming pool water and the chemicals used in the water on white cement it is of importance to know the composition and properties of the various substituents which are present in portland cement.

Pages 29–31 / Section 5.2 / the entire page and a half of Section 5.2 except for the first sentence:

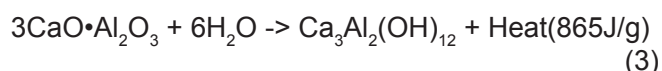
The primary raw material for the manufacture of portland cement is calcium carbonate or limestone and clay containing silica, aluminum and ferric oxides in the proper proportions. The mixture is calcined in a rotary kiln at a temperature of about 1450°C to produce the required product.

The primary compounds entering into the composition of finished portland cement are: tricalcium silicate, 3CaO•SiO₂ (54%); dicalcium silicate, 2CaO•SiO₂ (17%); tricalcium aluminate, 3CaO•Al₂O₃ (11%) and tetracalcium aluminoferrite, 4CaO•Al₂O₃•Fe₂O₃ (9%). White portland cement is richer in alumina and essentially free of ferric and magnesium oxides.

The setting of cement is essentially a hydration reaction to form calcium silicate hydrates. The hydrate forms a colloidal “mineral glue” which is called “tobermite”, because it is practically identical with a rare, naturally occurring mineral of that name. The reactions which occur are given below.



In reaction (1) about forty percent by weight of calcium hydroxide, Ca(OH)₂, or as it is sometimes called calcium hydrate, CaO•H₂O, is formed. The hydration of the tricalcium aluminate is as follows:

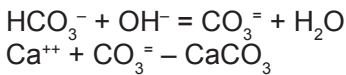


As soon as the cement is mixed with water, a rapid reaction starts. In a few minutes, the gauging water becomes saturated with calcium hydroxide. The di- and tricalcium silicate is hydrated to a gel,

calcium hydroxide which slowly crystallizes from the solution. A microscopic examination of the hardened cement paste shows small amounts of unreacted clinker minerals and crystals of calcium hydroxide. This latter material is a basic or alkaline salt and is of considerable significance in connection with the resistance of cement to attack by aggressive reagents some of which will be discussed later.

Page 4 / Discussion / 1st full paragraph, following two formulas, and first two sentences of following paragraph:

Adding water which has a high pH (basic) to a newly plastered pool which as we have seen has an alkaline surface can further raise the pH of the water to a sufficient level to convert the bicarbonate ion (HCO₃⁻) present in the water to carbonate ions (CO₃⁼). This ion then combines with soluble magnesium and calcium ions in the water to precipitate as insoluble magnesium and calcium carbonate.



This is sometimes referred to as "Plaster Dust", although none of it comes from the cement itself. With water as low as 25 ppm total hardness as much as four pounds of fine chalk dust can be precipitated from the water of a 20,000 gallon pool.

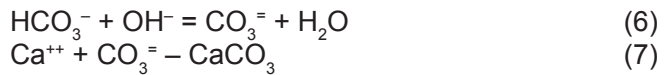
Page 7 / Discussion / 1st full paragraph, second sentence:

It involves a chemical attack on the cement walls of the swimming pool resulting in the selective solvation or leaching out of the cement surface specific minerals.

releasing calcium hydroxide which slowly crystallizes from the solution. reactions (1) and (3) produce rapid setting but low strength in the cement. Reaction (2) is a slower setting reaction but produces higher strength. Microscopic examination of the hardened cement paste shows small amounts of unreacted calcined minerals and crystals of calcium hydroxide. The latter is a basic or alkaline material and is of considerable significance in connection with the resistance of cement to attack by aggressive agents as is discussed below.

Pages 31–32 / Section 5.3 / full paragraph under formula 5, formulas 6 and 7, and first two sentences of following paragraph:

Adding water which has a high pH (basic) to a newly plastered pool which has an alkaline surface can further raise the pH of the water to a sufficient level to convert the bicarbonate ion (HCO₃⁻) present in the water to carbonate ions (CO₃⁼). This ion then combines with soluble magnesium and calcium ions in the water to precipitate insoluble magnesium and calcium carbonates.



This is sometimes referred to as "plaster dust", although none of it comes from the cement itself. With water as low as 25 ppm total hardness as much as four pounds of fine chalk dust can be precipitated from the water of a 20,000 gallon pool.

Pages 32 / Section 5.3 / text following formula (8):

...can result in the chemical attack on the walls of the swimming pool resulting in the selective solvation or leaching out of mineral constituents from the marcite surface.

Appendix B – Survey

NSPI PLASTER SAMPLE DATA SHEET

JOB ADDRESS _____

City & State _____ Zip Code _____

Name & Telephone _____ () _____

PLASTERING

Plastering Company Name _____

IS THIS AN NSPI ORIGINAL PLASTER SAMPLE? Yes No

New Pool or Replaster? Commercial or Residential?

HOW SOON AFTER PLASTERING WAS THE POOL EQUIPMENT STARTED? (please circle) 1 Day 2 Days 3 Days Other _____

HOW MANY DAYS DID IT TAKE TO FILL THE POOL? (please circle) 1 Day 2 Days 3 Days Other _____

WHAT WERE THE WEATHER CONDITIONS AT START UP? (Hot, cool, windy, rainy, etc.) _____

CONDITION / BALANCE OF FILL WATER

A. Did you test the water before you began filling? Yes No

(Please list the measurements for the following, if known:) pH _____ Alkalinity _____ Hardness _____ Dissolved Solids _____

Chlorine _____ Iron _____ Copper _____ Temperature _____ (Specify Fahrenheit or Centigrade)

B. Did you test the water when you finished the start up? Yes No

(Please list the measurements of the following, if known:) pH _____ Alkalinity _____ Hardness _____ Dissolved Solids _____

Chlorine _____ Iron _____ Copper _____ Temperature _____ (Specify Fahrenheit or Centigrade)

Condition / balance of existing pool water. (Please list the measurements of the following, if known:) pH _____ Alkalinity _____

Hardness _____ Dissolved Solids _____ Chlorine _____ Iron _____ Copper _____ Stabilizer _____

Temperature _____ (Specify Fahrenheit or Centigrade)

Type of Calcium Chloride Used: 77% 95% None Other _____

7. PLASTER / START UP

How much "plaster dust" was there when you started the pool up? (please circle) Heavy Medium Light

What method did you use to start up the pool? (please circle appropriate response)

Acid Start Up Light Acid Chlorine Shock Treatment Other (please explain) _____

(raise pH and Alkalinity slowly)

How often was the pool brushed each day? (please circle) Once Twice Three Times Other _____

Was vacuum brush used? Yes No

How long did it take for "plaster dust" to disappear? _____

8. PHENOMENON FIRST APPEARED OR DISCOVERED

Before Completely Full After First Filling Subsequent Fills Overnight Occurrence When First Heated

Within One Month _____ Months After Plaster _____ Years After Plaster Other (Explain): _____

9. APPEARANCE OR CHARACTERISTIC

Spider Web Surface Marks Check Cracks Pimples/Eruptions Drip Marks Under Piping Outlets Discoloration

Grey Blue/Green Pitting Holes Chalking Craters Localized Eroded Rough Areas Barnacles

Localized Rough Buildup Delamination/Pop Offs Roughness on Tile / Light Lens Give Location: _____

CORRECTIVE/REMOVAL PROCEDURES ATTEMPTED WITH WATER IN POOL (10)

- Chlorine Shocking
- Sequestering Agents
- Standing/No Drain Acid Wash
- Drain and Replace Water Immediately Without Acid Washing
- Is Condition Evolving/Worsening? Yes No or Stuck - No Change Since Discovery?
- Pre Acid Wash
- Sanding
- Other repair (specify) _____

EMPTY POOL PROCEDURES (11)

- Chlorine Wash
- Acid Wash
- Power Sanding
- Hydrogen Peroxide Wash
- Application Heat
- Drain and Exposed for Additional Air Drying _____ # Days (please specify)

COLOR OF PLASTER (12)

Was the pool plaster (color) WHITE or TINTED? (If tinted, give color.) _____

DID YOU USE SEQUESTERING AGENTS OR WATER CLARIFIERS? Yes No (13)

If yes, please list which product(s) you used: _____

NORMAL CHEMICAL ADJUSTMENTS (14)

- Daily
- Twice Weekly
- Weekly
- Continuously (feeder)
- Monthly

CHLORINATION/SANITIZER INTRODUCTION METHOD (15)

- Floating/Wandering Trichlor Dispenser
- Tethered Trichlor Dispenser
- Trichlor Dispenser Anchored Deep End
- Trichlor Tablets in Skimmer
- In Line Trichlor Feeder Pressure Type
- Suction Type
- Liquid Chlorine
- Dichlor Granular Broadcast Over Surface
- Calcium Granular Broadcast
- Electrolytic Production Equipment Using Salt Type
- (Specify) _____
- Ion Transfer Copper/Silver
- Gaseous Chlorine Injections
- How Often? (specify) _____
- None
- Bromine
- Baquacif
- Other _____

pH CONTROL (16)

- Muriatic Acid
- Dry Acid
- Soda Ash
- Bicarb
- Other _____

ALGAE CONTROL (17)

- Periodic Shocking Liquid
- Periodic Shocking Granular
- Quaternary Ammonia Algicide
- Elemental Copper Algicide
- Other _____

STABILIZER ADDITIONS (18)

- Direct to Pool Granular
- Induced Through Skimmer
- Floater

MATERIALS OR PRODUCTS USED (please specify) (19)

- A. Factory Blended Material _____
- B. Manufacturer/Vendor of Cement _____
- C. Manufacturer of Aggregate _____

ADMIXTURES (20)

- Troweling Agents
- Liquid
- Flake or
- Granular Calcium Chloride Accelerator
- 77%
- 95%
- Other _____
- Pre Dissolve all Granulars
- Deaerating Inert Ingredients
- Anhydrous
- Retarding Agents
- Additional Cement Added to Factory Blend
- Dusting Dry Cement to Wet Surface
- Calcium Aluminate Cement
- Lime
- Other (specify) _____

FILTRATION WATER CLARIFYING SCHEMES (21)

Activated Carbon D.E. Cartridge Sequestering Agents Oxidizers None Other _____

FILTRATION TYPE/CONTAINER (22)

Non Corrosive (PVC/ABS/Plastic/Other) _____ Metallic D.E. Sand Cartridge Anthracite

FILTER CIRCULATION OPERATIONS PER DAY (23)

No Timer 2 Hours 4 Hours 6 Hours 12 Hours Other (specify) _____

PUMP AND STRAINER (24)

Non Corrosive (PVC/ABS/Plastic/Other) _____ Metallic Bronze Cast Iron

VALVES (EXCEPT WASTE CONTROL) (25)

Non Corrosive (PVC/ABS/Plastic/Other) _____ Metallic Brass Cast Iron

PIPE AND MANIFOLDS (26)

Non Corrosive (PVC/ABS/Plastic/Other) _____ Copper Galvanized Heat Sinks Copper

PLUMBING BOTTOM DRAIN LINE (27)

Plumbed Directly to Pump To Skimmer Closed to Operate Suction Cleaner

HEATER (28)

Fossil Solar Metallic Solar Plastic Electric Resistance Heat Pump

Manufacturer make and model number _____

METALS IN CONTACT WITH WATER (29)

- Ladder Baskets Weights/Handles Return and Hydrotherapy Outlets Chrome Plated Brass Lillypad Gooseneck
- Light Ring Handrails Ladders Bottom Drain Frames and Grate Hydrostatic Plugs
- Thermometer Vacuum Ports Rope Hooks Fountain/Spray Heads Copper Skimmer Tank
- Sacrificial Anode Current Collectors (Zinc Balls) Where located? _____ Electrical Powered Cleaning Robot
- Other _____

ESTIMATED POOL CAPACITY IN GALLONS (30)

Calculated _____ Owner/Service Co. Estimate _____ Meter Reading _____

PLASTER SURFACE AREA ROUGHNESS COMPARED TO SANDPAPER GRIT (31)

400 or Finer 220 120 80 40 Rougher than 40

INFORMATION OBTAINED VIA (32)

Pool Owner Pool Contractor Start Up Personnel Plasterer Service or Retail Advisor

WINTERIZING (33)

Covered Full and Inoperative Completely Empty Anti Freeze in Piping Other _____

Give Length of Swimming Season _____ (specify number of months)

ARE THERE TRANSFORMER TYPE OR BURIED UTILITY LINES NEAR THE POOL? Yes No How close? _____

TEST THE SURFACE HARDNESS OF PLASTER (34)

Easily Scored With Pumice Stone Difficult to Score Some Areas Easily Scored Coin Used Credit Card Edge