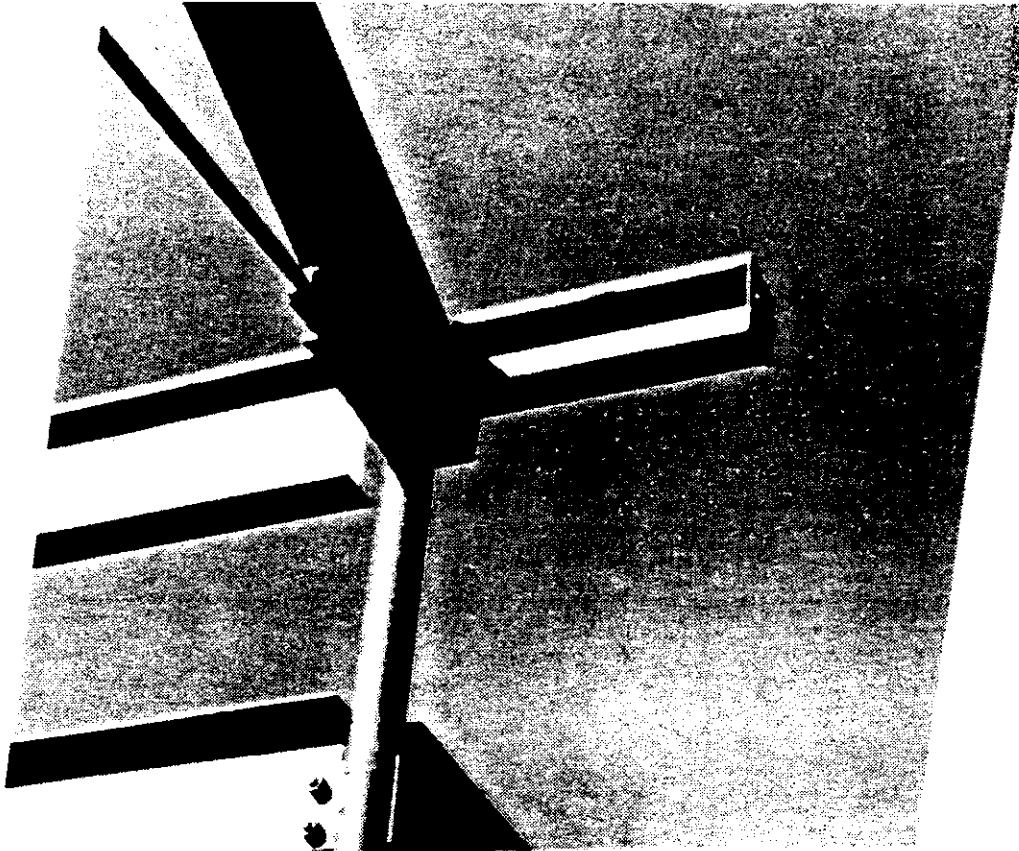


TECHNICAL PUBLICATION NO. 74

**A STUDY OF MARCITE (PLASTER)
DETERIORATION IN SWIMMING POOLS**

Sponsored by the Building Construction Industry Advisory Committee under a grant from the State of Florida Department of Education, the Florida Region VII Council of the National Spa and Pool Institute, the University of Florida, and the National Spa and Pool Institute



Principal Investigator: E. Dow Whitney
Principal Investigator: Brisbane H. Brown, Jr.

M. E. Rinker, Sr., School of Building Construction
and
College of Engineering - Department of Materials Science and Engineering

Executive Summary

Florida enjoys eighteen percent of the world swimming pool market, larger than California and Hawaii combined. Not surprising since a swimming pool is part of the "Florida life style" and is no longer considered a luxury item. However, over the past few years the pool industry has been plagued by a number of problems involving marcite (plaster) coated pools. These problems include all types of blemishes, etching, mottling and discoloration of marcite pool linings. Although these problems have been investigated for several years no single consensus has been developed as to their cause and consequently what preventative measures to take. Mechanisms responsible for the surface deterioration of marcite remained unknown.

Totally baffled and discouraged, the National Spa and Pool Institute Region VII (Florida) Council formed the Plaster/Marcite Committee in 1988 to seek out the problems that were besieging the industry and to come up with a solution. In the Spring of 1989 three research projects were started, funded by the Building Construction Industry Advisory Committee, a research grant committee operating under the Florida Department of Education, the National Spa and Pool Institute and the University of Florida.

The research program involved both mechanistic studies of marcite corrosion under controlled laboratory conditions as well as field diagnostic studies wherein petrographic, scanning electron microscopic (including energy dispersive X-ray spectroscopy) and X-ray diffraction phase analysis of healthy and deteriorated plaster from actual swimming pools were conducted.

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 calcite aggregate in the cement does not appear to be particularly affected by the leaching process.

Water chemistry plays a major role in both leaching and staining of marcite. Aggressive pool water; i.e., water that has not been properly "balanced" chemically from the instant the freshly marcited pool is first filled can wreak havoc on marcite and pool plumbing resulting in etching and staining.

Recommendations are given for proper control of water chemistry as well as mitigating chemical attack by protecting the marcite surface with suitable chemical barrier coatings and the use of additives to the cement to chemically interact with the calcium hydroxide component of the cement paste in order to make it less reactive chemically and thus less susceptible to attack by pool water.

Copies of this report can requested from the Executive Secretary, Building Construction Industry Advisory Committee, Room 101 FAC, School of Building Construction, University of Florida, Gainesville, FL 32611 or by calling (904) 392-5965.

A Study of Marcite (Plaster) Deterioration in Swimming Pools

R 88-14

Grant Managed by:

**Brisbane H. Brown, Jr.
M. E. Rinker, Sr. School of Building Construction**

Research Conducted and Report Prepared by:

**E. Dow Whitney
Department of Materials Science and Engineering**

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1. Background to the Problem

In Florida, swimming pools have almost become a necessity and are no longer a luxury item. They are a source of water storage, a place for family gatherings and entertainment, and the dream of millions of retirees who move to the sunny south to extend their golden years and utilize one of the best exercises known to mankind.

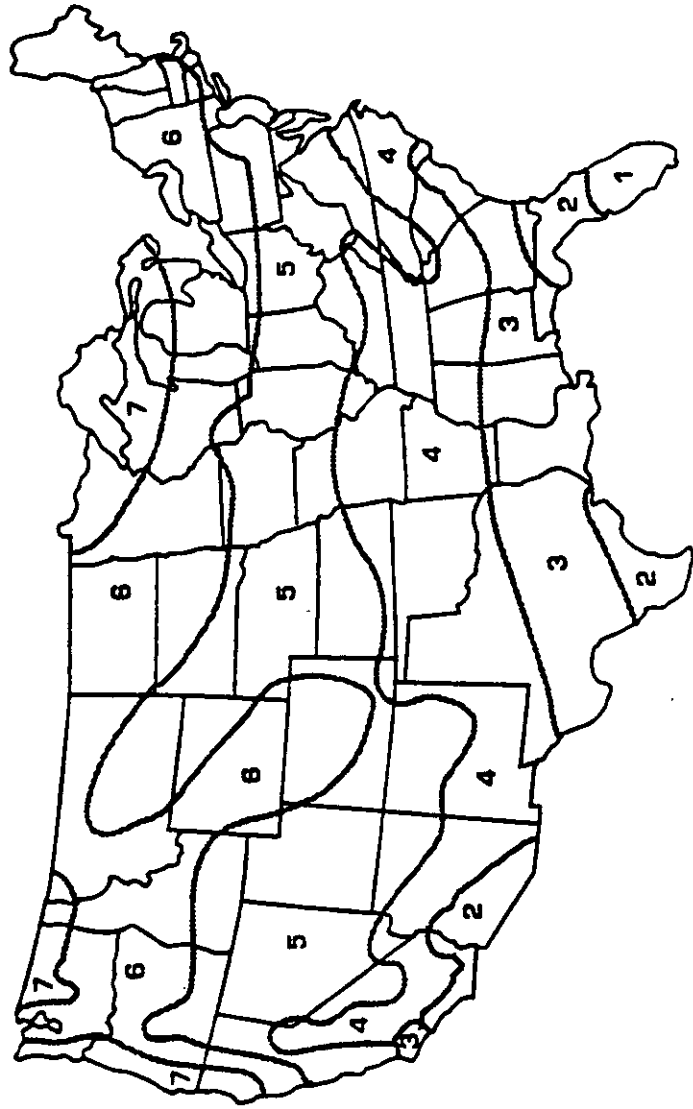
Florida enjoys eighteen percent of the world swimming pool market, larger than California and Hawaii combined. A pool is an affordable item for the retiree with an average income. Concrete technology has allowed swimming pool structure to be long lasting, durable, and a sound investment for the homeowner. With the coming of twenty-first century technology, new filter systems and improved disinfection techniques can assure crystal clear water - water so clear coins can be clearly seen even in deep pools.

However, over the past few years the pool industry has been plagued by a number of problems involving all types of blemishes, etching, mottling and discoloration of plaster pool linings. Most pool contractors feel that these problems did not exist beyond six or seven years ago. Initially, when the problems began, the pool contractor simply recoated the swimming pool and thus satisfied the home owner's complaint. Unfortunately, these complaints compounded and as the pressure increased, many contractors' businesses failed trying to do the "right thing".

The State of Florida has the most stringent licensing laws in the nation. The ultimate goal is to have full certification of all persons in the swimming pool industry from builders to service companies. To date, 30 percent of the pool and spa industry has fulfilled this requirement and the balance are duly registered with the state under the wing of state

SWIMMING SEASON ZONES...

MONTHS WITH AN AVERAGE DAYTIME AMBIENT TEMPERATURE OF 60°F OR HIGHER.



ZONE	SWIMMING SEASON
1	12 MONTHS
2	10-11 MONTHS
3	9-10 MONTHS
4	8-9 MONTHS
5	6-8 MONTHS
6	4-5 MONTHS
7	3-4 MONTHS

Figure 1. Swimming pool season zones. Months with an average daytime ambient temperature of 60° or higher.

legislation. Complaints to the state capital in Tallahassee have led to a number of license revocation, suspensions, and fines. It should be noted that the largest number of complaints relate to the plaster finish - commonly known as "marcite" in Florida.

Marcite (plaster), the interior finish applied to swimming pools, has been under considerable scrutiny in the last few years because of the problems of discoloration, mottling, and etching. Although these problems have been investigated for several years, there is as yet no single consensus as to what exactly is their cause, and consequently what preventive measures to take. To date, the exact nature of the chemical mechanism responsible for the surface deterioration of marcite is still not known.

Totally baffled and discouraged, the National Spa and Pool Institute Region VII (Florida) Council formed the Plaster/Marcite Committee in 1988 to seek out the problems that were besieging the industry and to come up with a solution. In the Spring of 1989 three research projects were started, funded by the Building Construction Industry Advisory Committee (BCIAC), a research grant committee operating under the Florida Department of Education, the National Spa and Pool Institute (NSPI) and the University of Florida. The material to be tested was plaster/marcite, generally composed of a two-to-one mix of marble aggregate to white portland cement or a pre-blend of similar ratio. The problems that needed to be checked were etching, staining and mottling.

Etching at times will occur within a few weeks to years after application of the marcite. Once the problem begins, a yellow, brown, or beige color settles in the damaged area(s). The addition of chelating agents, sequestering agents, vitamin C, etc., will sometimes remove the discoloration. Etching is frequently round in shape, dime sized and starts in the area of the steps and swimouts; as etching increases the damage works

downward and the size of the etch "pit" increases. At other times the spots will be about the diameter of a pencil eraser and all over the marcite surface.

Mottling is a darker appearance on the marcite surface. Sometimes described as having the appearance of clouds of vertical development in the cumulus-type shape. These shadings are more prominent on shady days or at night with the pool light on. These areas can usually be made to disappear simply by draining the swimming pool and letting the sun dry out the spots. Some success has also been achieved by heating the areas with a torch or hair dryer.

Staining is generally caused by minerals in the water that precipitate out of suspension and adhere to the plaster. Usually calcium, copper, iron, manganese and other metallic impurities account for this phenomena.

2. Research Objectives

The purpose of this research effort was to investigate corrosion-related surface deterioration of swimming pool marcite. Marcite deterioration was investigated both from the standpoint of induced textural or compositional defects in the marcite itself and from the standpoint of water chemistry, since it is well known that pure water with low dissolved calcium bicarbonate content (a low temporary hardness) corrodes plaster. As is often the case with soft water, if the water also contains aggressive carbon dioxide this solvent action is increased.

Associated with laboratory studies of marcite corrosion under controlled conditions were field diagnostic studies wherein petrographic, scanning electron microscopic (including energy dispersive X-ray spectroscopy) and X-ray diffraction phase analysis studies of healthy and deteriorated plaster from actual swimming pools were conducted.

It was anticipated that, as a result of this study, information gained on those chemical processes occurring within the plaster-pool water environment scenario that resulting marcite breakdown might serve as the basis for the formulation of badly needed ASTM standards in swimming pool construction.

3. Experimental Procedures

3.1 Instrumentation

Three major analytical instruments were employed in this research, both for field diagnostic studies of pool plaster problems and in controlled laboratory etching and staining mechanism investigations. The analytical techniques were x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy.

The x-ray diffraction units used were a Philips Electronic Instruments APD3720 X-ray diffractometer and a APD3600 X-ray diffractometer. In this technique, X-rays are generated from a target tube and impinged on a sample which is moved through an arc at angles (2Θ) measured with respect to the incident X-rays. The target radiation is scattered by the sample and the X-rays are detected with a scintillation detector. The number of counts, or intensity, versus the degrees 2Θ is recorded on a paper strip chart and/or computer storage. The 2Θ values of the peaks are related to the d-spacings in the crystal lattice of the sample by Bragg's Law ($n\lambda = 2d\sin \Theta$). The intensity is related to the atoms making up the crystal lattice. Compound identification using the JCPDS files of d-spacings and intensities of known compounds is possible. Crystallographic information such as crystal structure, reflections and lattice parameters is also possible. In addition to identification of compounds in crystalline materials, quantitative phase analysis can be conducted.

In scanning electron microscopy a focused electron beam is scanned over the specimen. Backscattered electrons and secondary electrons are produced and detectors measure intensity versus position and display this on a CRT. Magnification is dependent on the size of the area sampled. The techniques can image topographical or microstructural features on polished or rough surfaces, provide qualitative or semiquantitative elemental analysis as well as crystallographic data from single crystals or large grains. The instrument is particularly useful for characterization of microstructures in metal, ceramic, geologic and biological materials, and in studying surface morphology.

In energy dispersive X-ray spectroscopy, high energy electrons excite atoms in a specimen. Atoms can de-excite by emitting an X-ray which has characteristic energy. The X-rays are detected by an Si (Li) detector. The number of counts vs. energy are displayed on a multi-channel analyzer. The technique is particularly useful for elemental identification, qualitative analysis and quantitative analysis. Applications include phase identification and elemental distribution in a material.

3.2 Etching and Staining Mechanistic Studies

An important aspect of this phase of the study was to duplicate typical swimming pool conditions in the laboratory. Several problems for which solutions were found are:

1. Determine a cement specimen surface area to water ratio that was as close as possible to the surface area to water ratio found in a typical swimming pool. Solution to the problem is given in Appendix A.

The radius of the cylinder was found to be equal to 1.27 cm (equivalent to one half inch). The length of the cylinder was 1.5 inches. One inch diameter PVC pipe cut in section was

used as molds for the cement cylinders. Dried cement samples were separated from the PVC mold with a press.

2. Calculation of analogous circulation rates are also given in Appendix A. A flow rate of 1/8 gallon per hour, or 7.88 mL/min was determined. Pumps were chosen which had variable flow rates and had all plastic parts which would be in contact with the leaching solutions. The all plastic pumping mechanism was an important feature because at low pH values metal from the pump could contaminate the solution.
3. A diagram of the apparatus used in performing leaching rate experiments is shown in Figure 2. Cement specimens were suspended in the middle of the leaching solution in order to obtain uniform results. Samples could not rest on the bottom of the container or against the sides. Also, the area over which the string comes into contact with the sample had to be as small as possible so as to minimize the influence of the string upon the etching or staining process. This problem was solved by attaching a small plastic button to the end of a piece of monofilament fishing line. When the cement was placed into the molds the button was pushed into the cement where it became firmly anchored when the cement set. A small hole was drilled into the middle of the container cover and the fishing line was pulled through and tied to a paper clip.
4. The final problem was how to measure the weight loss of the specimen during the leaching process without removing the cement sample from the container which would disturb the etching of the sample. This problem was overcome by obtaining a balance which had provision for weighing from below. The

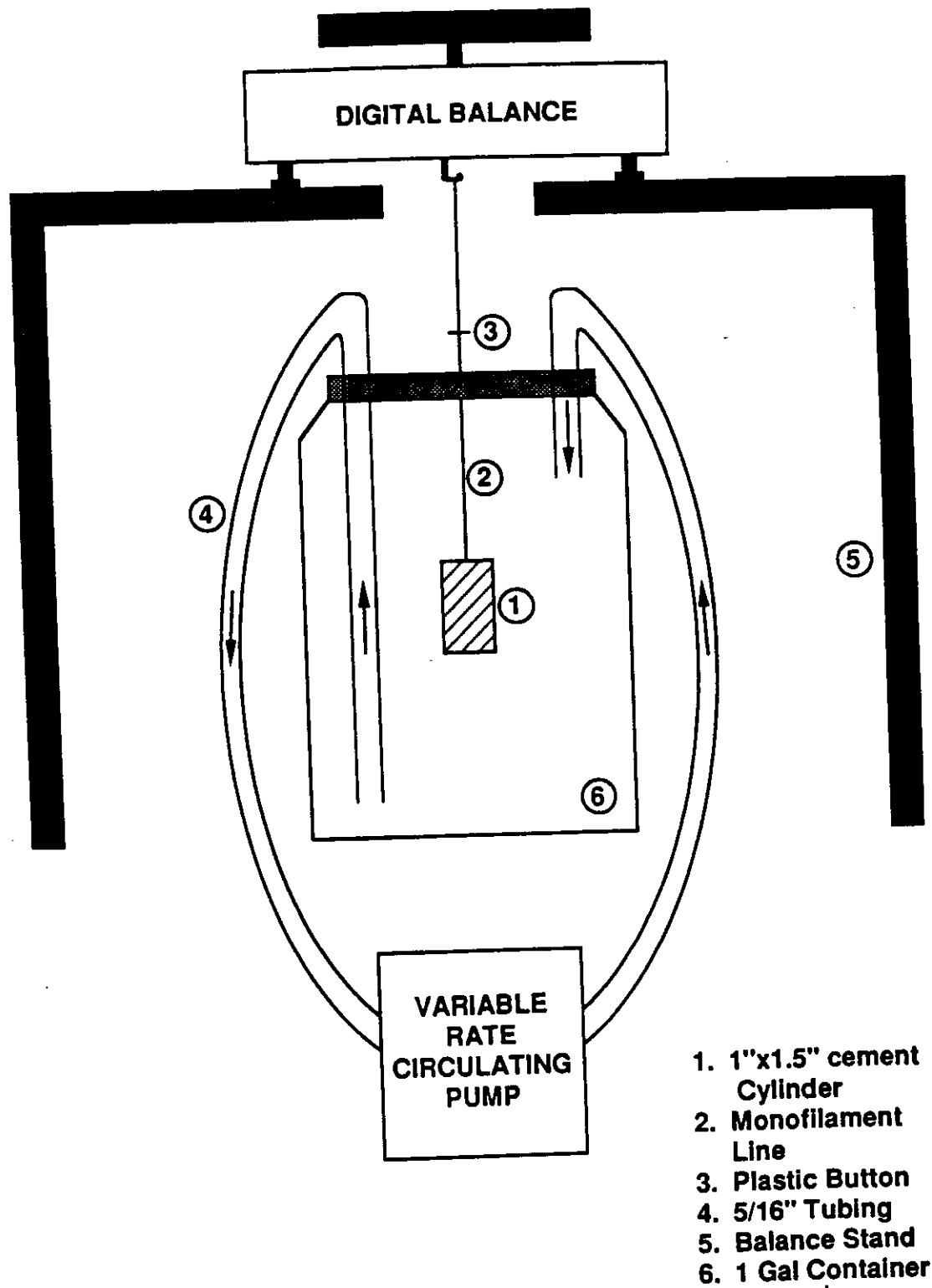


Figure 2. Diagram of apparatus used in performing leaching rate experiments.

balance had a hook on the bottom where a string was attached. Tables were built that supported the balance over the containers so that the string could be attached from the bottom of the balance to the paper clip on top of the container. In this way the mass of the string, paper clip, button and cement sample was recorded. Since only the mass of the cement sample changed as a function of time, a rate of weight loss or leaching rate for any given leaching solution was readily obtained.

Leaching experiments were undertaken for three different water cement ratios (w/c) commonly used in the construction industry and in a pH range of 6.8-7.0. This pH range was chosen because it represents the lower end of the pH range commonly found in pool water. The experimental procedure was as follows:

1. 1" x 1.5" cement cylinders of 0.4 w/c and 0.5 w/c were dried at 100°F for 24 hours and weighed
2. The samples were then placed in the leaching solution (DI H₂O) and allowed to equilibrate.
3. After four days in solution, the pH was adjusted from the 10-10.5 natural pH of the solutions to the 6.8-7.0 pH range for the leaching experiments.
4. At first, pH was very unstable, climbing back toward the natural pH.
5. Daily adjustments were made back to the 6.8-7.0 range stabilized the leaching solutions after five days.
6. After stabilization, the pH was adjusted every 3 to 4 days.

4. Results

4.1 Field Diagnostic Studies of Swimming Pool Problems

Studies of etched and stained plaster obtained from swimming pools was a major part of this research effort. The goal was to determine the differences between healthy plaster and unhealthy plaster in an attempt to identify missing chemical species in etched plaster pits and new species present on the surface of stained plaster.

Analytical methods used to accomplish these tasks were x-ray diffraction and scanning electron microscopy, coupled with energy dispersive spectroscopy.

In this study, X-ray diffraction was used to compare which phases were present (or missing) in unhealthy plaster as opposed to healthy plaster.

With regard to chemical phases which are present in healthy cement, the majority of the material is composed of a matrix which is primarily complex hydrated calcium silicates. These silicates are predominantly amorphous, as opposed to crystalline and are thus difficult to detect with X-ray diffraction. In addition, several crystalline phases form from the hydration reaction (the reaction of calcined cement with water), such as calcium hydroxide (portlandite), magnesium hydroxide and calcium carbonate.

Experimental evidence from X-ray diffraction showed that calcium hydroxide was the predominant phase missing from pits in etched plaster. This is evident from an inspection of Tables 1 through 3 which show the results of X-ray diffraction analyses of etched and non-etched plaster samples taken from swimming pools at various Florida locations. In Appendix B is a listing of some of the more than fifty sources of marcite samples which were received and analyzed as part of the diagnostic studies. These sources included private individuals, condominium associations, hotel/motels, pool contractors and plastering companies, etc. Appendix C is the NSPI Plaster Sample Data Sheet which was requested

Cement Compound (Phase)	Non-Etched	Etched
Calcium Hydroxide Ca(OH)_2	•	◦
Calcium Silicate Hydrate	•	•
Calcium Carbonate CaCO_3	•	•
Silica SiO_2	•	•

- Phase Present
- Phase not present

Table 1. X-ray Diffraction Analysis of Plaster from Pool in Gainesville, Florida

Cement Compound (Phase)	Non-Etched	Etched
Calcium Hydroxide Ca(OH)_2	•	◦
Magnesium Hydroxide Mg(OH)_2	•	•
Ettringite	•	•
Calcium Carbonate CaCO_3	•	•

- Phase Present
- Phase not present

Table 2. X-ray Diffraction Analysis of Plaster from Pool in Sarasota, Florida

Cement Compound (Phase)	Non-Etched	Etched
Calcium Hydroxide Ca(OH)_2	•	◦
Dolomite $\text{CaMg(CO}_3)_2$	•	•
Magnesium Aluminum Hydroxide Silicate	•	•
Calcium Carbonate CaCO_3	•	•
Silica SiO_2	•	•
Calcium Silicate Hydrate	•	•

- Phase Present
- Phase not present

Table 3. X-ray Diffraction Analysis of Plaster from Pool in Lutz, Florida

to be completed and returned with the plaster samples. This information often proved to be very helpful in the diagnosis of specific plaster problems.

Thermodynamic calculations confirmed that portlandite is the most chemically active component of cement. (See Section 5.3.2). Since cement is a basic material, portlandite would be especially susceptible to acidic water. The latter would thus be expected to exacerbate the preferential leaching of portlandite, which in turn results in etching. Experimental evidence showed that portlandite is preferentially leached out of the marcite matrix by aggressive pool water. Since portlandite comprises approximately 25% of portland cement by weight, its absence has deleterious effects upon the structural integrity of pool plaster; i.e., leading to surface degradation and etching.

The other analytical method employed in this phase of the work was scanning electron microscopy (SEM). Marcite was observed up to 15000x on the SEM. Also in conjunction with SEM, energy dispersive spectroscopy (EDS) was performed. While the sample is in the SEM, elemental analysis can be done using this technique. In Figure 3 are shown the results of EDS scans for the elements Ca, Si, Mg and Al while traversing a marcite sample from an existing swimming pool from a non-etched to a spot etched area. The sharp drop in relative concentration of calcium and corresponding relative increase in silicon concentration is evident in going from the non-etched to etched areas.

SEM studies showed that the appearance of the portlandite changes upon etching. Unetched portlandite crystals have smooth, regular faces. Portlandite crystals on etched surfaces are very sparse, as compared to portlandite crystals on unetched surfaces. Contrast in the portlandite morphology in etched and unetched samples lends credence to our conclusions.

In Table 4 are presented data showing relative concentrations of $\text{Ca}(\text{OH})_2$

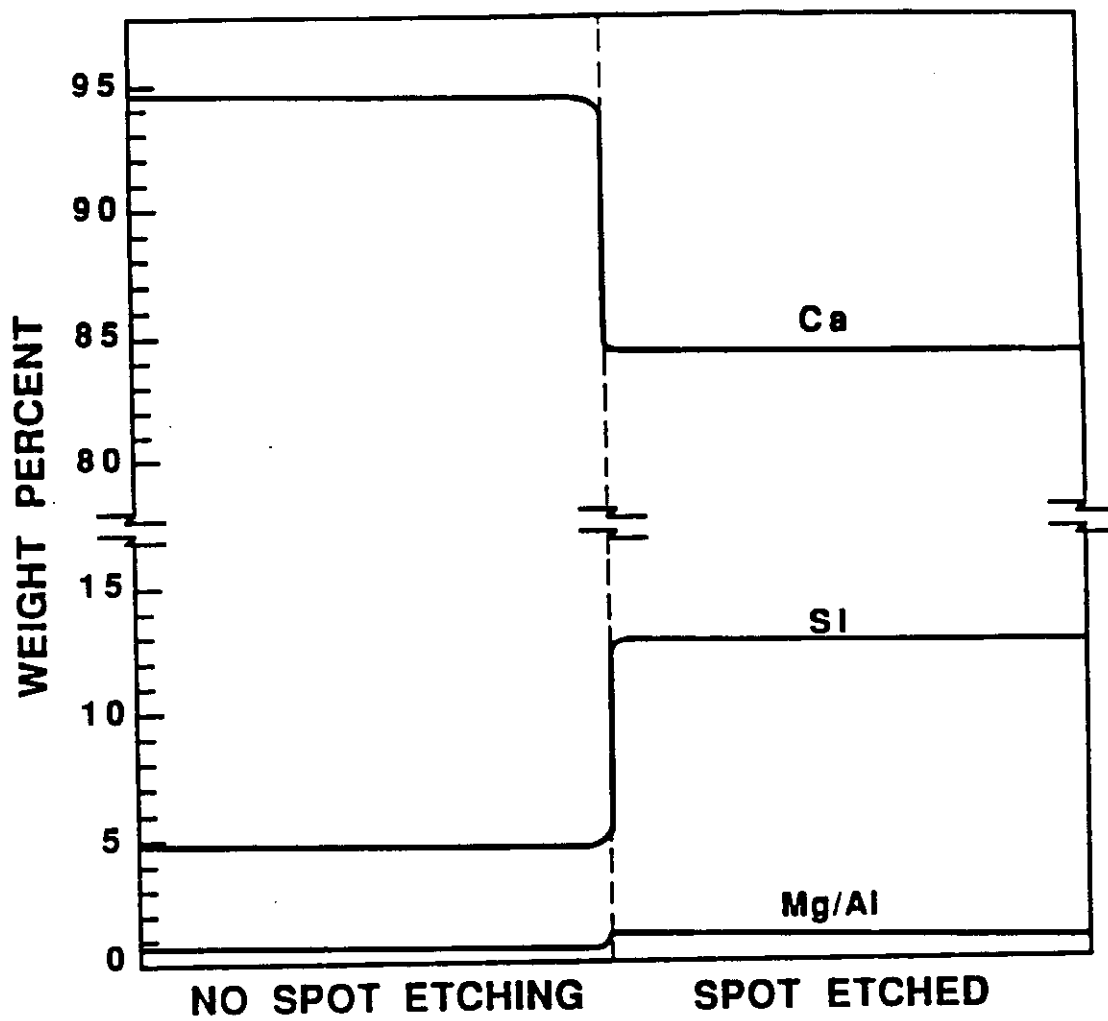


Figure 3. Calcium, silicon, magnesium and aluminum concentration profiles (EDS) in traversing from a non-etched to an etched area in marcite taken from a pool in Gainesville, Florida.

MATERIAL BALANCE
(Normalized to 100)

	TR-1	TR-2	TR-3
Ca(OH)_2	17	21	31
CaCO_3	42	40	12
SiO_2	41	39	57

Table 4. Relative concentrations of Ca(OH)_2 (portlandite) in marcite on a trowelled swimming pool surface.

(portlandite) in marcite on a trowelled swimming pool surface. In swimming pool construction, after the marcite layer is applied to the gunite shell wall the former is trowelled several times (usually three) so as to produce a very smooth surface. According to pool plastering professionals the attainment of a smooth surface involves the bringing of the "cream" or "fat" in the marcite to the surface which is accomplished by trowelling.

Since the trowelling operation is being conducted while chemical hydration reactions are simultaneously taking place in the cement the question was posed, "what effect does trowelling have, if any, on the distribution of developing hydrated phases in the marcite"? In Table 4, TR - 1, TR - 2 and TR - 3 identify samples of marcite removed from trowels during construction of a swimming pool after the first, second and third trowelling, respectively. Phase identification was performed by means of X-ray diffraction.

Although these results are preliminary, they do seem to indicate a preferential concentration of portlandite at the marcite surface as a result of the trowelling operation. Certainly this represents a very dynamic system, both chemically and mechanically, and involves complex morphology and rheology. However, it is interesting to note that the relative increase in phase concentrations with extent of trowelling, i.e., $\text{Ca(OH)}_2 > \text{SiO}_2 > \text{CaCO}_3$, has an inverse relationship with the phase densities, i.e., $\text{CaCO}_3 > \text{SiO}_2 > \text{Ca(OH)}_2$. In light of what will be discussed later in this report with regard to the susceptibility of portlandite to chemical attack by aggressive components in swimming pool water these preliminary observations should be pursued further.

SEM was also instrumental in studies of stained marcite surfaces obtained from the field. Elemental analysis via energy dispersive spectroscopy of stained plaster samples revealed the presence of copper on nearly every sample which was stained blue/green. The origins of the copper staining are either; 1) copper ions form unchelated copper algicides,

or 2) copper ions from corroded bronze or brass plumbing. Once copper ions are in solution in pool water, they combine to form complex compounds on the surface of the plaster. In Figure 4 is shown an EDS scan on a sample of marcite with blue/green staining. In addition to the expected peaks for Ca, Mg, Si and O, a very distinct peak for Cu is noted. Figure 5 is a similar EDS scan on marcite from a swimming pool with distinctive yellow/brown staining. In this case the iron (Fe) peak is predominant.

4.2 Mechanisms of Etching and Staining

In conjunction with field diagnostic studies, laboratory studies were undertaken in an attempt to understand the mechanisms of etching and staining of pool plaster. Experiments were focussed on answering the following questions:

1. What factors do and do not cause etching?
2. What is the mechanism of staining of swimming pool plaster?
3. What can be done to alleviate the problem of etching and staining?

4.2.1 Leaching Experiments

Swimming pool literature suggests that the main causes of leaching are low pH, low calcium hardness and low total alkalinity with high cyanuric acid and high chlorine as possible secondary effects. With these factors in mind a series of leaching experiments were conducted. Deionized (DI) water was used in all experiments which for the purposes of this work is the same as distilled water. DI water is very "soft" as it has no calcium hardness, no alkalinity and a pH of 6.9-7.0. Portland cement samples placed in DI water within a couple of days came to an equilibrium pH of approximately 11.0 with a very high calcium hardness and total alkalinity. Obviously, calcium carbonate had leached out of the

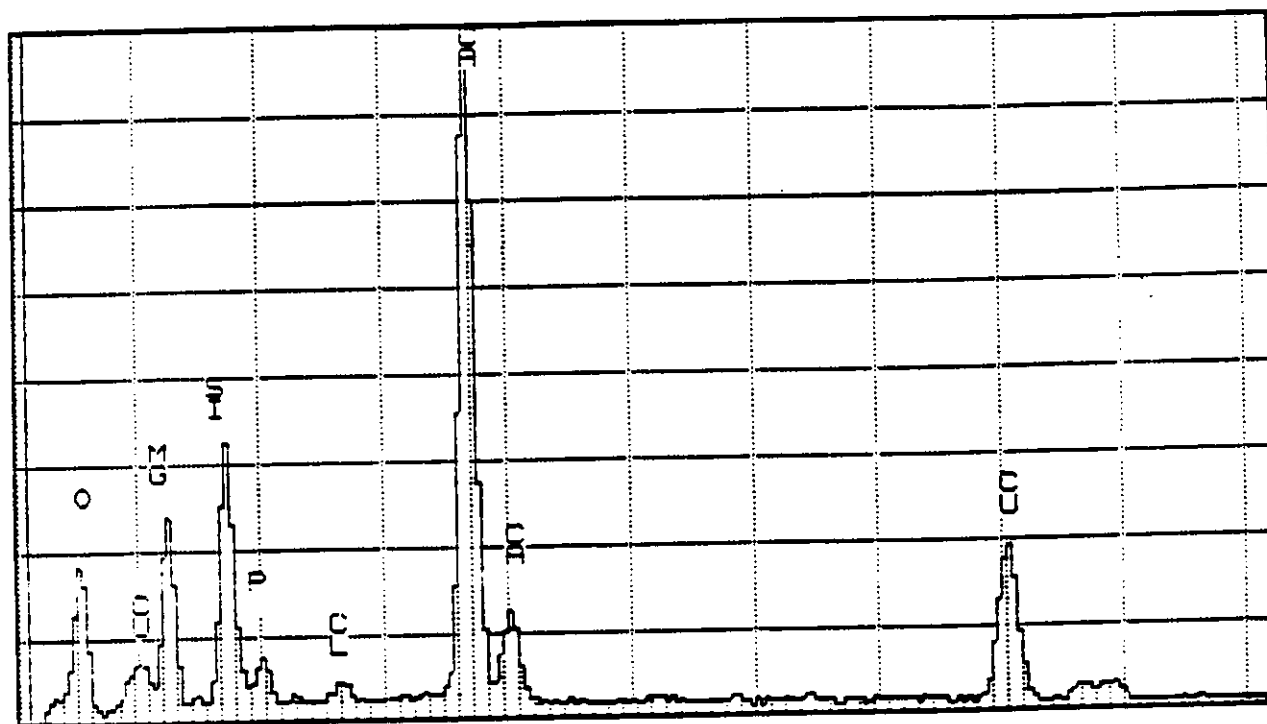


Figure 4. EDS Scan on marcite with blue/green staining.

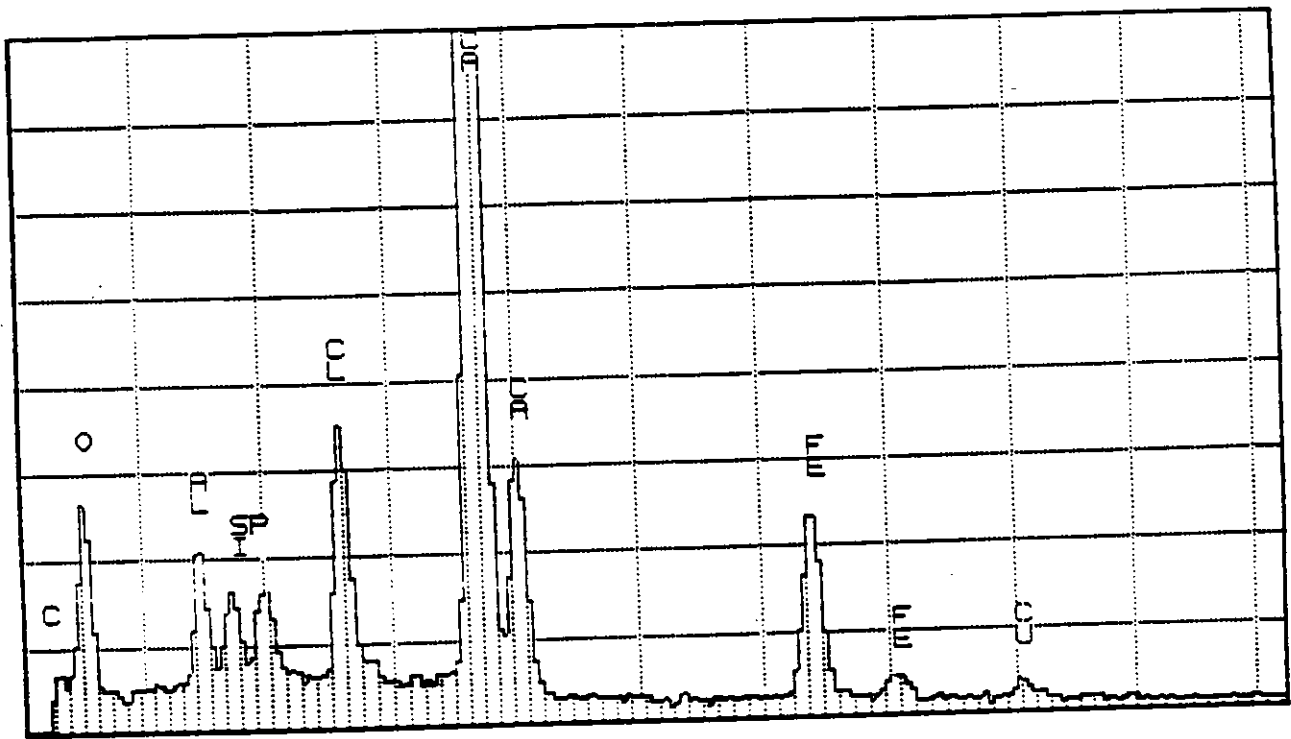


Figure 5. EDS Scan on marcite with yellow/brown staining.

sample which increased both the calcium hardness and alkalinity of the solution and also neutralized the H^+ ions in solution.

A solution of DI water with 500 ppm cyanuric acid was prepared. This amount of cyanuric acid is roughly ten times the normal recommended amount for stabilizing chlorine in a swimming pool. The initial pH of the solution was about 4.0. After the sample was placed in the solution the pH began increasing daily to an equilibrium pH of about 9.0 after a week. Calcium carbonate began precipitating out of solution. Cyanuric acid is a weak acid and even at a concentration of 500 ppm the cement was able to quickly increase the pH and avoid continued leaching. A very slight amount of cement was lost due to leaching, about 0.03 grams out of a 27 gram specimen. In a pool containing 2400 lbs of marcite this amounts to about 2.6 lbs lost. The only conceivable way to attain this high level of cyanuric acid in a pool would be to allow stabilized chlorine to dissolve in non-circulating water. A high local concentration of cyanuric acid would develop which could cause leaching. If solid cyanuric acid granules are permitted to remain in contact with marcite on the bottom of the pool, local pitting will occur.

A solution of DI water and 20 ppm liquid chlorine ($NaOCl$) was prepared. This solution was approximately ten times the normal chlorine concentration in a typical swimming pool. The pH of the solution was about 11.0. When the sample was introduced into the solution, the pH remained almost constant and the sample turned slightly whiter. No leaching occurred.

A solution of DI water and hydrochloric acid was prepared. The portland cement sample was introduced and the pH kept between 4.0 and 4.5 with additions of HCl every two to three days. At the end of the first week the sample had a distinct yellowish tint. It is believed that this yellow stain was caused by HCl coming into contact with iron oxides in

the cement. It has been observed that when cement specimens are brought into contact with dilute HCl a yellowish stain found to be ferric chloride (FeCl_3) formed at the surface for the specimen in contact with the acid. Going deeper into the specimen the yellow stain turned to a dark brown or grey. The later color is due to ferric hydroxide. When the cement comes into contact with HCl the calcium forms soluble "salts" which are leached out of the cement matrix leaving the specimen very etched, porous and brittle. The remaining insoluble salts form what is called the "hydroxide mixture". This mixture largely composed of SiO_2 and ferric hydroxide forms a protective layer on the surface of the undamaged cement.

These observations indicate that yellowish stains found especially in newly filled swimming pools on the bottom of the pool could be caused by a low pH condition. Hydrochloric acid is much denser than water and when poured into a swimming pool will quickly settle to the bottom. pH measurements taken at the top surface of the pool may indicate a normal or even high pH condition while the bottom of the pool is experiencing a low pH condition.

In Figures 6a-c are given the results of the long term leaching experiments of portland cement at three different water/cement ratios. The first measurement of weight loss indicated in Figure 6 occurred after 1056 hours. Weight loss was measured as the change in weight divided by the initial weight.

$$\frac{\Delta W}{W} = \frac{\text{initial weight} - \text{weight measured at time } t}{\text{initial weight}}$$

The initial weights of the samples were recorded between 240 and 288 hours into the experiment. During the "equilibration" period before 240 hours the mass of the samples changing due to tiny air bubbles escaping from the surface porosity and leaching solution

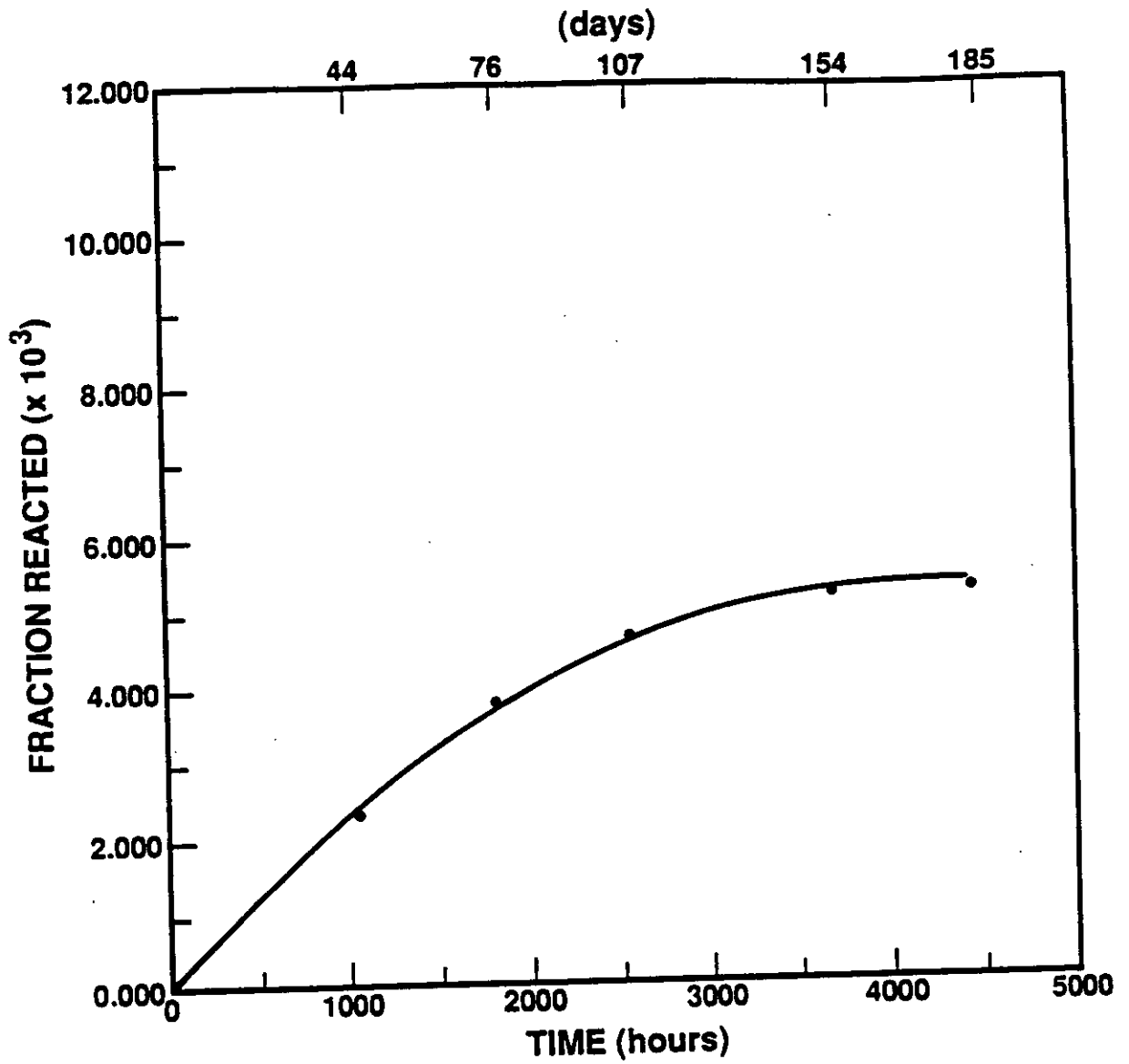


Figure 6a. Long term leaching rates of portland cement in DI water of pH 6.8-7.0.
 Water/cement ratio = 0.40

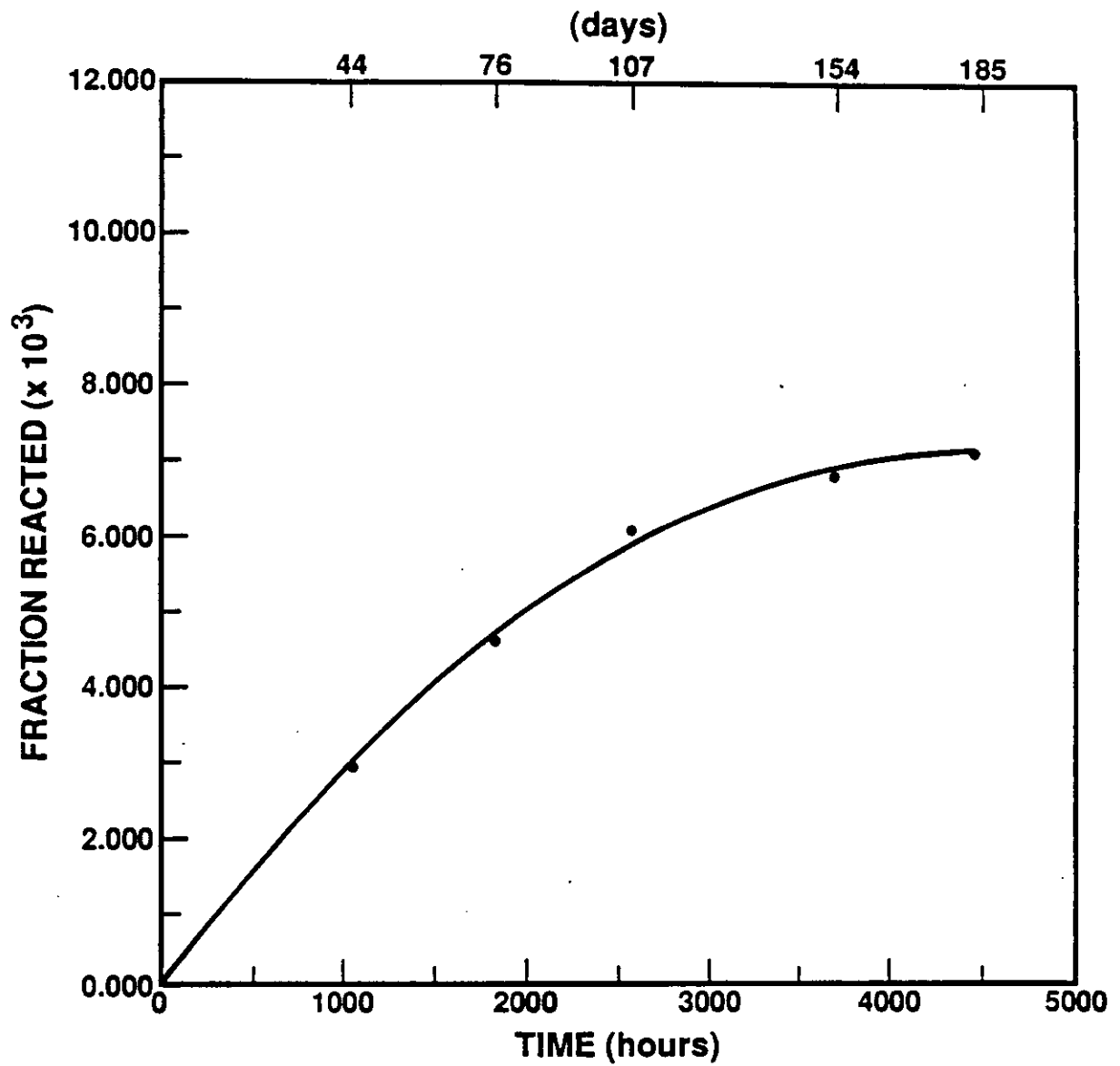


Figure 6b. Long term leaching rates of portland cement in DI water of pH 6.8-7.0.
 Water/cement ratio = 0.45

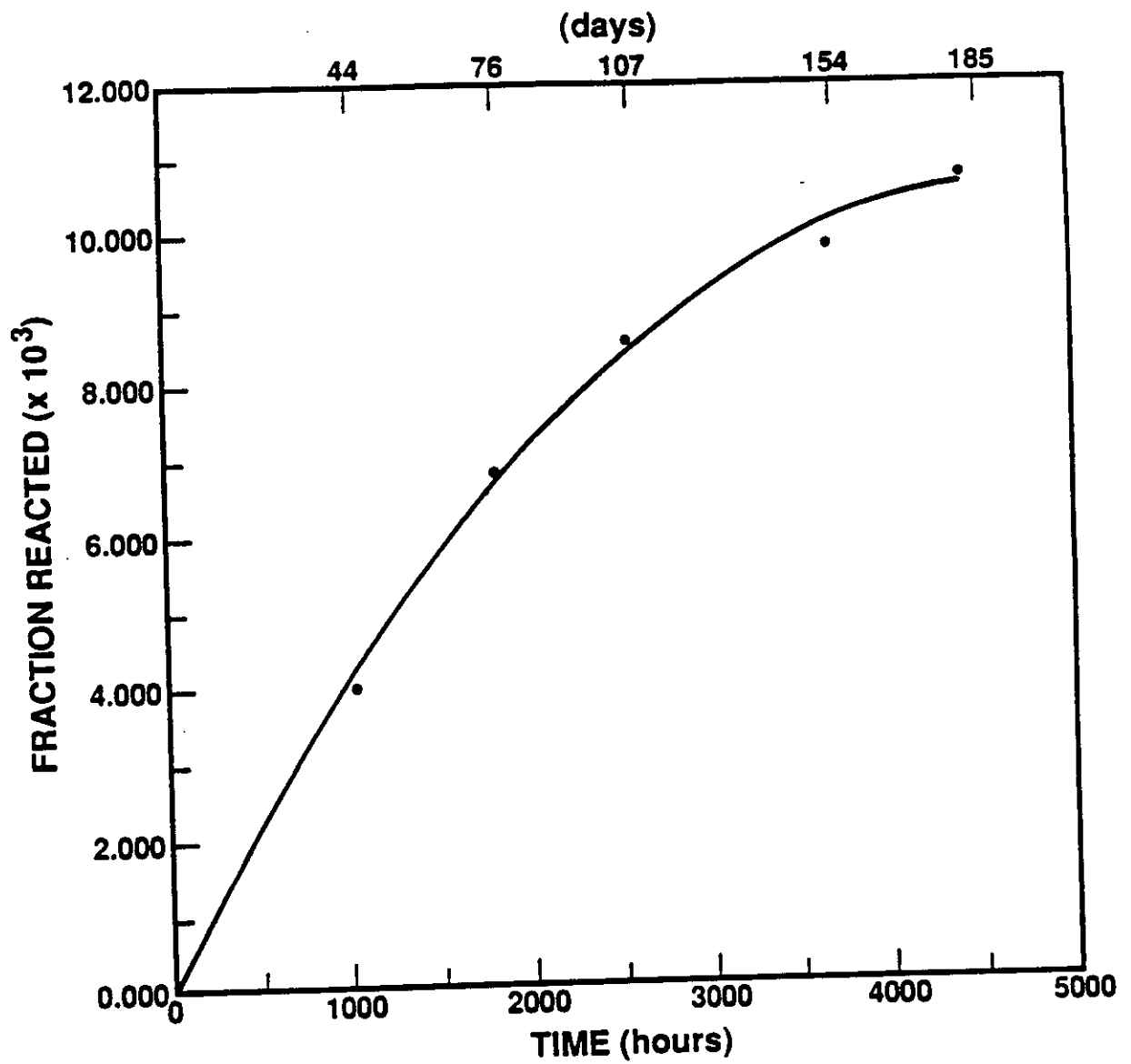


Figure 6c. Long term leaching rates of portland cement in DI water of pH 6.8-7.0.
 Water/cement ratio = 0.50

being absorbed into the samples. The leaching that occurred during this period was accounted for by extrapolating the graph back to zero, as is shown in Figure 6a-c.

4.2.2 Staining

The most common metals in contact with swimming pool water are copper, brass, aluminum and stainless steel. Diagnostic studies showed that of all the samples of pool staining studied as part of this research program, at least eighty percent were various shades of blue, green and aqua. This indicates that these stains were caused by copper. Various combinations of zinc and copper are the following metals: Muntz metal, 40% Zn-Cu; yellow brass, 30% Zn-Cu; and red brass, 15% Zn-Cu. Yellow and red brass are commonly used in manufacturing fittings, impeller blades and pump castings used for swimming pools.

Laboratory experiments consisted of exposing yellow brass, copper, aluminum and stainless steel samples to various corrosive solutions. The solutions were: (1) pure deionized water, (2) DI with HCl added to pH 5.0 and (3) DI water with HCl and 20 ppm chlorine added to pH 5.0.

Since deionized water is extremely "soft" it is very corrosive to all of the metals tested except aluminum and stainless steel. Solutions were prepared and the metal sample and a cement specimen introduced at the same time. Usually signs of corrosion were visible within 24 hours. The usual indication for copper and brass was a slight "greening" of the cement sample that became darker with continued exposure. The iron sample formed a light brown rust colored stain that also became darker with time. The addition of 20 ppm chlorine caused the corrosion rate of the copper and brass samples to increase with a resulting increased rate of cement sample staining. Samples that were introduced into the HCl and 20 ppm chlorine turned much darker than samples in HCl alone. This was

probably due to the strong oxidizing nature of chlorine.

Rapid staining of the samples was indicative that once the metal cations are in solution they quickly attach themselves to the cement surface. The cations lower their free energy state by replacement of themselves with components of the cement surface. Once metal ions are in solution they will rapidly interact with the cement to cause staining. Therefore a drop in pH and an increase in chlorine for only a short time can cause staining in swimming pools, especially when the water hardness is low. This observation is important because in the normal maintenance of swimming pools the chlorine concentration can increase dramatically during the "shocking" process. Also the careless addition of HCl can cause a great drop in pH, especially at the bottom of the pool. The circulating pump picks up water from the drain at the bottom of the pool which is much more acidic than the rest of the pool water. If there are copper components anywhere in the pumping mechanism (and there almost always are) the combined effects of low pH and high chlorine will surely lead to corrosion and within a few hours stains will occur on the plaster surface.

Certainly one way to avoid staining is to remove all sources of copper and iron from contact with pool water. Unfortunately most of the sources of copper are impellers, fittings, gate and ball valves and pump castings, yet all of these parts are readily available in lexan fiberglass or PVC.

The aluminum specimen also showed signs of corrosion but apparently the aluminum cations in solution did not stain the cement. Stainless steels are in general susceptible to corrosion attack by any form of chlorine. Therefore high concentrations of HCl, NaOCl, LiOCl or $\text{Ca}(\text{OCl})_2$ can cause corrosion of stainless steels. At high concentrations of Cl^- the passivating layer responsible for stainless steels corrosion resistance breaks down, and pitting corrosion occurs. Fortunately, the concentration of Cl^- ions in most swimming pools is not

high enough to cause noticeable corrosion of the stainless steels used in ladders, light fixtures, railings, etc. It would appear that at the present time there are not enough problems with stainless steel corrosion to recommend that they be eliminated from swimming pool construction. However, if rust colored stains are noticed around any piece of stainless steel in contact with water, it is indicative that the passivity of the stainless steel has been destroyed and the part in question will continue to rust. The use of steel wool to clean stainless steels is also a big cause of corrosion. Steel wool will scratch the passivating layer on the stainless steel and leave tiny pieces of steel embedded in the stainless steel. These pieces become tiny anodes and will promote corrosion in the stainless steel at an incredibly fast rate. Steel wool should never be used to clean stainless steel in a pool or otherwise.

5. Discussion

5.1 The Corrosive Nature of Soft Water

Water is near to being a universal solvent and it can cause the dissolution of all but the most stable of materials. Very pure water with a low dissolved calcium bicarbonate content, i.e. of a low temporary hardness, will corrode concrete. If, as is often the case with soft waters, the water also contains aggressive carbon dioxide, the solvent action is increased. This action commences by leaching of the "free lime" or calcium oxides. Partial decomposition for the cement binder takes place when all the free lime is removed and thereafter, by successive leachings, practically all the cement can be decomposed. Under normal conditions, provided the concrete is dense, the action is only superficial and does not penetrate far into the mass of the structure. As a result of leaching of the cement matrix from the surface, the concrete will tend to assume a sandy appearance. On the other hand,

pervious concrete is very susceptible to destruction by this action and deterioration to considerable depth can take place. The aggressiveness of a natural acidic soft water is dependent not only on its pH but also on the temporary hardness (bicarbonate content) and the free carbon dioxide content. Water from all common sources contains a variety of dissolved materials. 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 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.

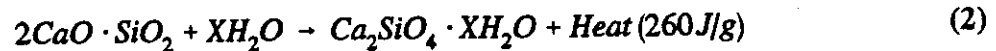
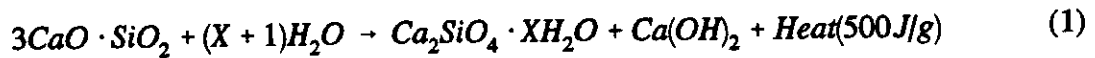
5.2 Portland Cement and Marcite

Marcite is a mixture of limestone (sometimes lime) and white portland cement. 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 desired product.

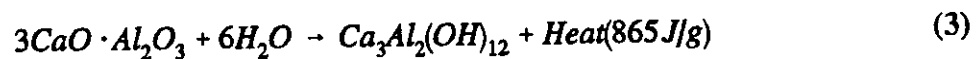
The primary compounds entering into the composition of finished portland cement are: tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$ (54%); dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$ (17%); tricalcium aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (11%) and tetracalcium aluminoferrite, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (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, $CaO \cdot H_2O$, is formed. The hydration of the tricalcium aluminate is as follows:



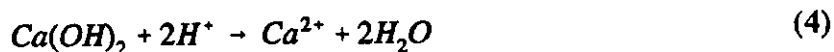
As soon as the cement is mixed with water, a rapid reaction starts. In a few minutes, the gauging water becomes saturated with calcium hydroxide. The di- and tricalcium silicate is hydrated to a gel, releasing calcium hydroxide which slowly crystallizes from the solution. reactions (1) and (3) produce 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.

5.3 Interaction of Swimming Pool Water and Marcite

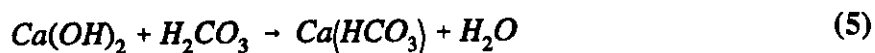
In the process of cement hydration soluble calcium hydroxide is formed. This material is easily dissolved by water that is lime-free and that contains dissolved carbon dioxide. In addition, hydrated cement paste is an alkaline material and therefore pool water

of pH less than 7.0 (acidic conditions) will readily attack a base material such as plaster.

The hydrogen ion will accelerate the leaching of calcium hydroxide:



The nature of the anion that accompanies the hydrogen ion may further aggravate the situation. Carbonic acid can also be very corrosive because of the formation of soluble calcium bicarbonate:

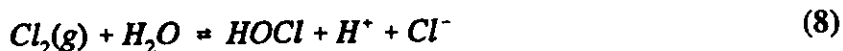


Adding water which has a high pH (basic) to a newly plastered pool which has an alkaline surface can further raise the pH of the water to a sufficient level to convert the bicarbonate ion (HCO_3^-) present in the water to carbonate ions (CO_3^{2-}). This ion then combines with soluble magnesium and calcium 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 plaster 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.

On the other hand, adding water which has a low pH (acidic), as the result of generating the disinfectant, hypochlorous acid ($HOCl$), via the reaction of chlorine gas with water,



can result in chemical attack on the walls of the swimming pool resulting in the selective

solvation or leaching out of mineral constituents from the plaster surface.

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.

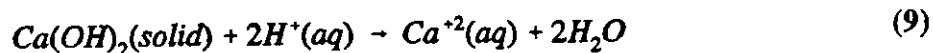
5.3.1 Etching of Marcite

Marcite, composed primarily of white portland cement, is a complex mixture of many different chemical compounds. The major elements in these compounds are calcium, oxygen, hydrogen, silicon and carbon. Results of this study show that a particular calcium compound may be selectively leached, or "dissolved" out of the plaster matrix by aggressive pool water. Calcium compounds are basic by nature, and therefore can be attacked by acids. Thermodynamic calculations (Section 5.3.2) and experimental evidence suggest that the most 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 portland cement, its absence weakens the structure and hastens its disintegration.

5.3.2. Thermodynamics of the Etching Process

In this section are presented the results of applying chemical thermodynamics to show quantitatively the effect of pool water pH on the stability of portlandite, or calcium

hydroxide, Ca(OH)_2 . This was done by calculating the Gibbs free energy change for the chemical reaction isotherm,



The Gibbs free energy change (ΔG) accompanying the reaction depicted above, at constant temperature and pressure, is given by

$$\Delta G_{T,p} = G(\text{products}) - G(\text{reactants}) \quad (10)$$

From chemical thermodynamics it follows that for

$$\Delta G_{T,p} = \Delta G_T^\circ + RT \ln \left(\frac{a_{\text{Ca}^{2+}}}{a_{\text{H}^+}^2} \right)$$

$$\Delta G_{T,p} = \Delta G_T^\circ + 2.3RT [\log a_{\text{Ca}^{2+}} - 2\log a_{\text{H}^+}] \quad (11)$$

Where ΔG_T° is the standard free energy change for equation (9) at a specific temperature (T) expressed on the absolute scale ($^\circ\text{K}$), R is the universal gas constant, p is the pressure, taken as 1 atm and $a_{\text{Ca}^{2+}}$ and a_{H^+} the activities of calcium ions and hydrogen ions in solutions, respectively.

Since, by definition, $\text{pH} = -\log[\text{H}^+]$ and equating molar hydrogen ion concentrations $[\text{H}^+]$ to hydrogen ion activity (a_{H^+}) which is valid for low concentrations of hydrogen ions as found in swimming pools, one can write

$$\Delta G_{T,p} = \Delta G_T^\circ + 2.3RT [\log a_{\text{Ca}^{2+}} + 2\text{pH}] \quad (12)$$

Equation (12) was solved for a variety of pH values. Pressure was taken to be one atmosphere and temperature 25°C (77°F) which is assumed to be "typical" swimming pool water temperature. Finally, the activity of calcium ions in solution ($a_{\text{Ca}^{2+}}$) was taken to

correspond to a calcium ion hardness of 250 ppm (as CaCO_3), a value well within the recommended range for well balanced swimming pool water.

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 value of 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.

In Table 5 are listed the Gibbs free energies of solution of the major constituents found in portland cement and consequently, marcite. These calculations were made following the general chemical thermodynamic guideline enumerated above.

The standard Gibbs free energy of solution, ΔG° , is given by the expression

$$\Delta G^\circ = -RT \ln K_{sp} \quad (13)$$

where R and T have been defined above and K_{sp} is solubility product in pure water for the substance in question. These values are known for $\text{Ca}(\text{OH})_2$ and the two polymorphic forms of CaCO_3 , aragonite and calcite. For the silica (SiO_2) and wollastonite (CaSiO_3) phases, ΔG° was calculated from the expression for the work done by a representative voltaic cell, i.e.,

$$\Delta G^\circ = -nFE^\circ \quad (14)$$

where n represents the number of faradays of electricity possessed in the cell, F represents

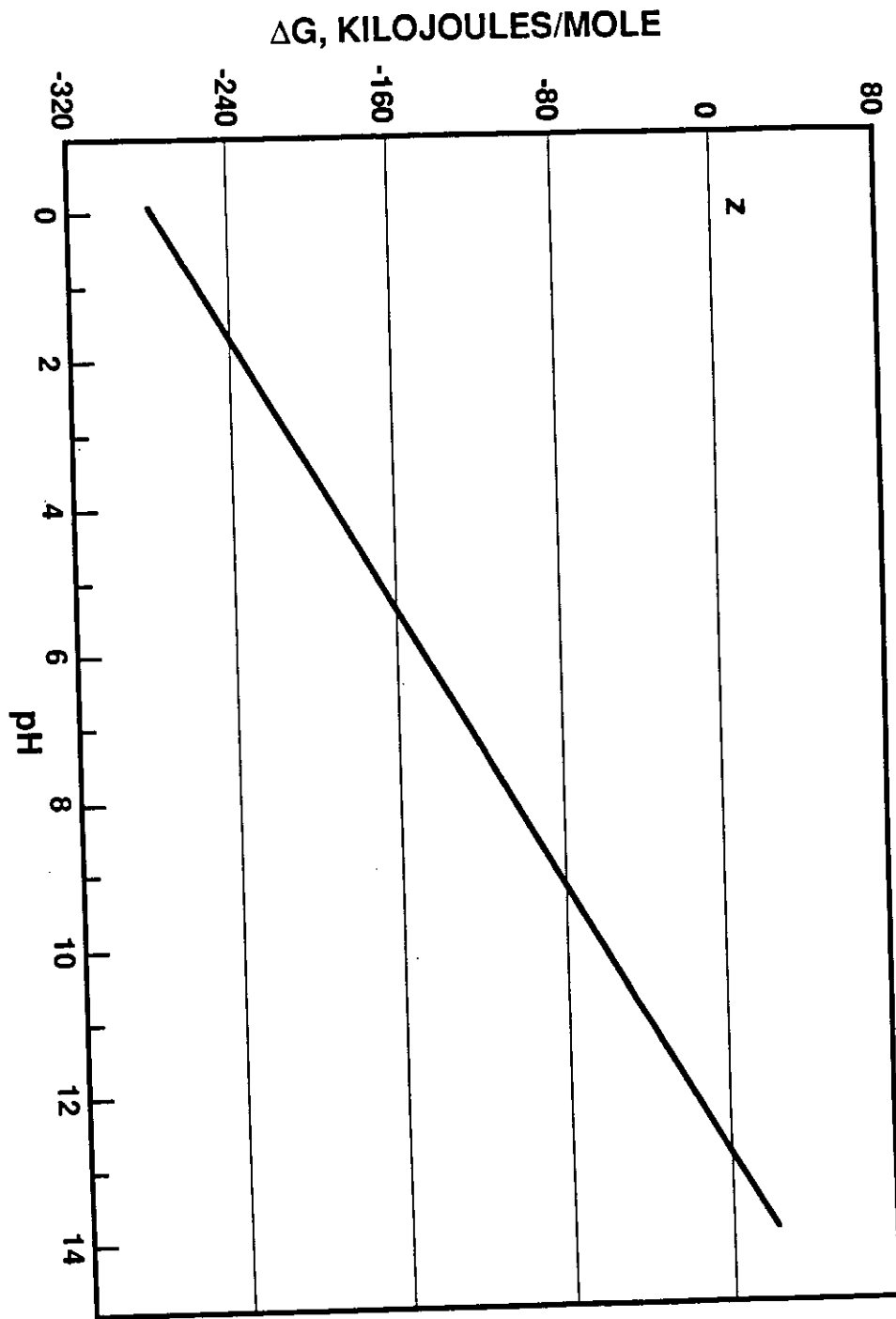


Figure 7. Gibbs free energy change for the reaction of Ca(OH)_2 (portlandite) with hydrogen ions in a solution as a function of pH.

Phase	Gibbs Free Energy of Solution, ΔG^*_{298} (kilojoules/mole)
CaSiO ₃ (wollastonite)	+2881
SiO ₂ (silica)	+949
CaCO ₃ (calcite)	+47.7
CaCO ₃ (aragonite)	+46.3
Ca(OH) ₂ (portlandite)	+29

Table 5. Gibbs free energy of solution of major constituents of marcite

96,500 international coulombs and E° was calculated from standard (oxidation) potentials.

As can be seen from Table 5, the free energy of solution of portlandite is the least positive. Thus chemical thermodynamics predicts that even in pure water of pH 7.0 this constituent of marcite will be the phase most susceptible to dissolution with corresponding pitting and etching of pool walls.

5.4 Staining of Marcite

A major consideration in the maintenance of swimming pools is the prevention of copper staining. Although the occurrence of copper staining has diminished in recent years because of the use of plastics and other materials in place of copper it must still be considered because of the high costs involved in removing the stains. In this section the sources of copper ions in swimming pools, the formation of copper stains and methods of prevention and removal of copper stains will be discussed.

5.4.1 Sources of Copper in Swimming Pool Water

Copper may be introduced into swimming pool water in at least six different ways.

5.4.1.1 Fill Water

One source of copper in swimming pools is from the water used to initially fill the pool or the water used to periodically replace that which is lost by evaporation, splash-out, and filter backwashing. Copper may be present in both the municipal water supply and the water obtained from private wells. Many public water utilities use copper sulfate to limit the growth of aquatic plants in storage reservoirs [1]. Although the amount of copper in municipal water supplies is limited to meet health regulations, the copper concentration

in swimming pools can become high enough to cause staining through repeated refilling of the pools. Water from private wells can contain copper in areas with copper deposits in the earth. Groundwater picks up copper from the earth through the natural processes of erosion and corrosion.

5.4.1.2 Erosion

Copper can enter the swimming pool by erosion of copper materials by circulating pool water. High velocity water can remove small pieces from tubing and other copper containing parts [2]. Erosion is most pronounced in areas with high turbulence such as "ell" and "tee" pipe fittings and pump impellers. These small particles of copper experience aqueous corrosion which eventually leads to copper staining. This source of copper in swimming pool water has been minimized by the use of PVC pipes and plastic parts in circulation pumps in place of copper containing materials [3].

5.4.1.3 Electrolysis

An extremely rare source of copper in swimming pool water is the process of electrolysis. Electrolysis occurs when an electric current carried by a low resistance metal is blocked by a material with a high resistance and the current is forced to leave the metal and be carried through an external path. As the current, or electrons, leave the metal, metal ions with an equal charge are also removed. Copper ions can enter the swimming pool water when an electric current, carried by copper water lines, meets a high resistance plastic or rubber fitting. The electric current is then carried by the flowing water, which in turn picks up copper ions from the pipe. This source of copper ions has been minimized by the use of PVC pipes in place of copper. Where copper pipes are used, they can be

protected from electrolysis by electrically connecting them to a junk pipe or grounding rod which is buried in the ground. The current leaves the system at the junk pipe which is corroded instead of the copper pipes [4]. It is a good idea to always ground pool pumps with brass impellers, with a grounding rod to prevent electrolytic corrosion from occurring.

5.4.1.4 Aqueous Corrosion

A more common source of copper ions is the aqueous corrosion of copper materials in contact with the swimming pool water. The rate of corrosion of copper in swimming pool water is very low and nearly constant in the normal pH range of 7.2 to 7.8 [5]. As shown by the Pourbaix diagram in Figure 8, copper is observed to be stable in this region due to the formation of a passive film which impedes further corrosion. This passive film is stable only over intermediate pH values. At higher or lower pH values an ionic species is stable and corrosion is thermodynamically possible. Experiments have shown that the rate of corrosion of copper increases with decreasing pH over the pH range of 3.0 to 6.5 [6].

The presence of other chemical species can have a substantial effect on the corrosivity of swimming pool water to copper. Figure 9 shows that the presence of chlorine causes a large increase in the corrosion rate of copper in aqueous solutions, even at low concentrations. Another chemical which is often present in swimming pool water and which effects its corrosivity toward copper is ammonia. Ammonia may be introduced into swimming pool water via several mechanisms; one is through bather perspiration. An active swimmer can produce up to two pints of ammonia in one hour [7]. The Pourbaix diagram (Figure 10) indicates that the corrosion of copper becomes thermodynamically favorable in ammonia solutions when the pH exceeds an approximate value of 8.0 [8]. Another factor which effects the aqueous corrosion of copper is the alkalinity, measured as

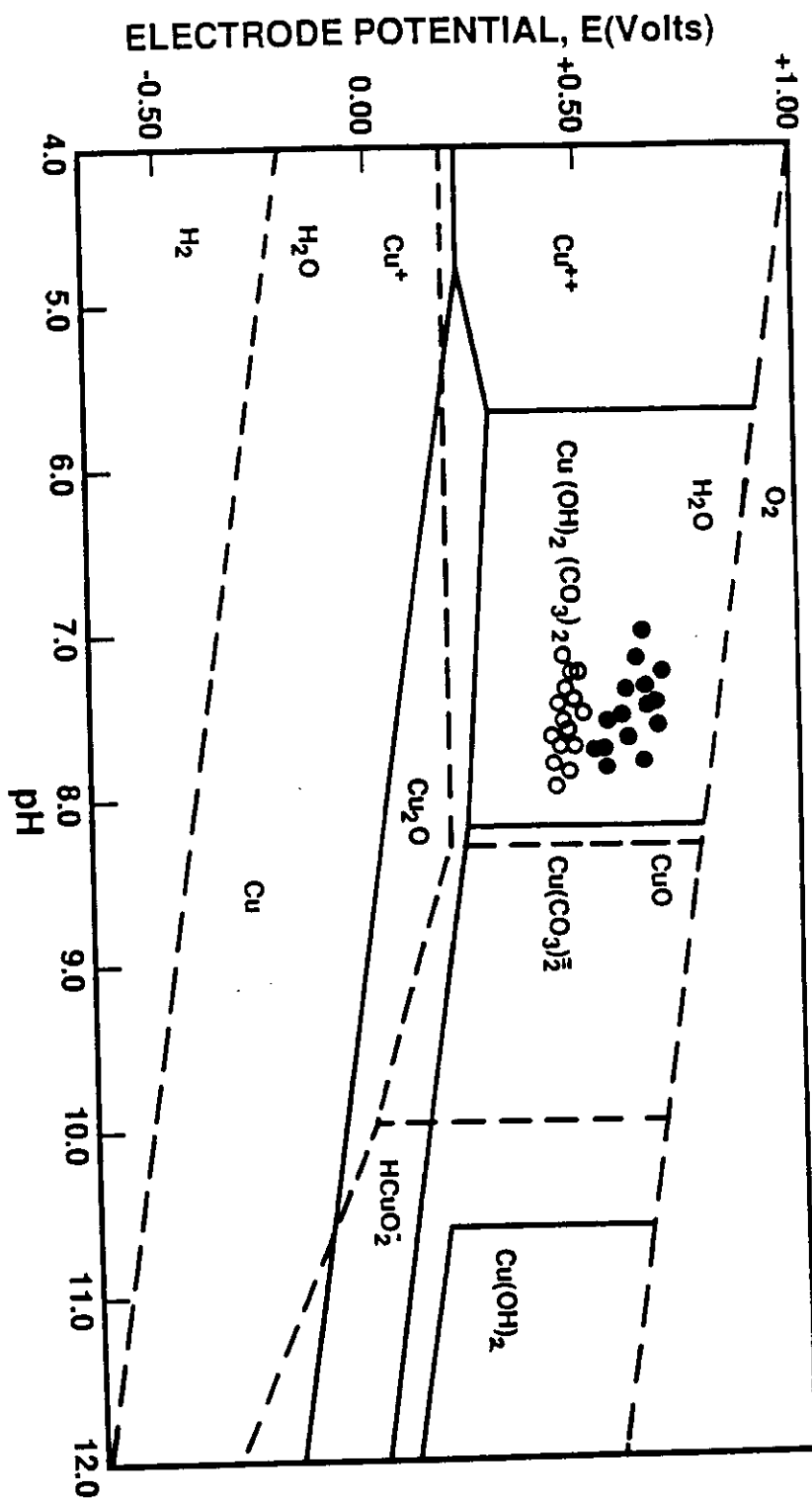


Figure 8. Pourbaix Diagram for 1.6×10^{-5} Cu in the presence of 100 mg/l alkalinity as CaCO_3 . Close circles - aerated; open circles - deaerated.

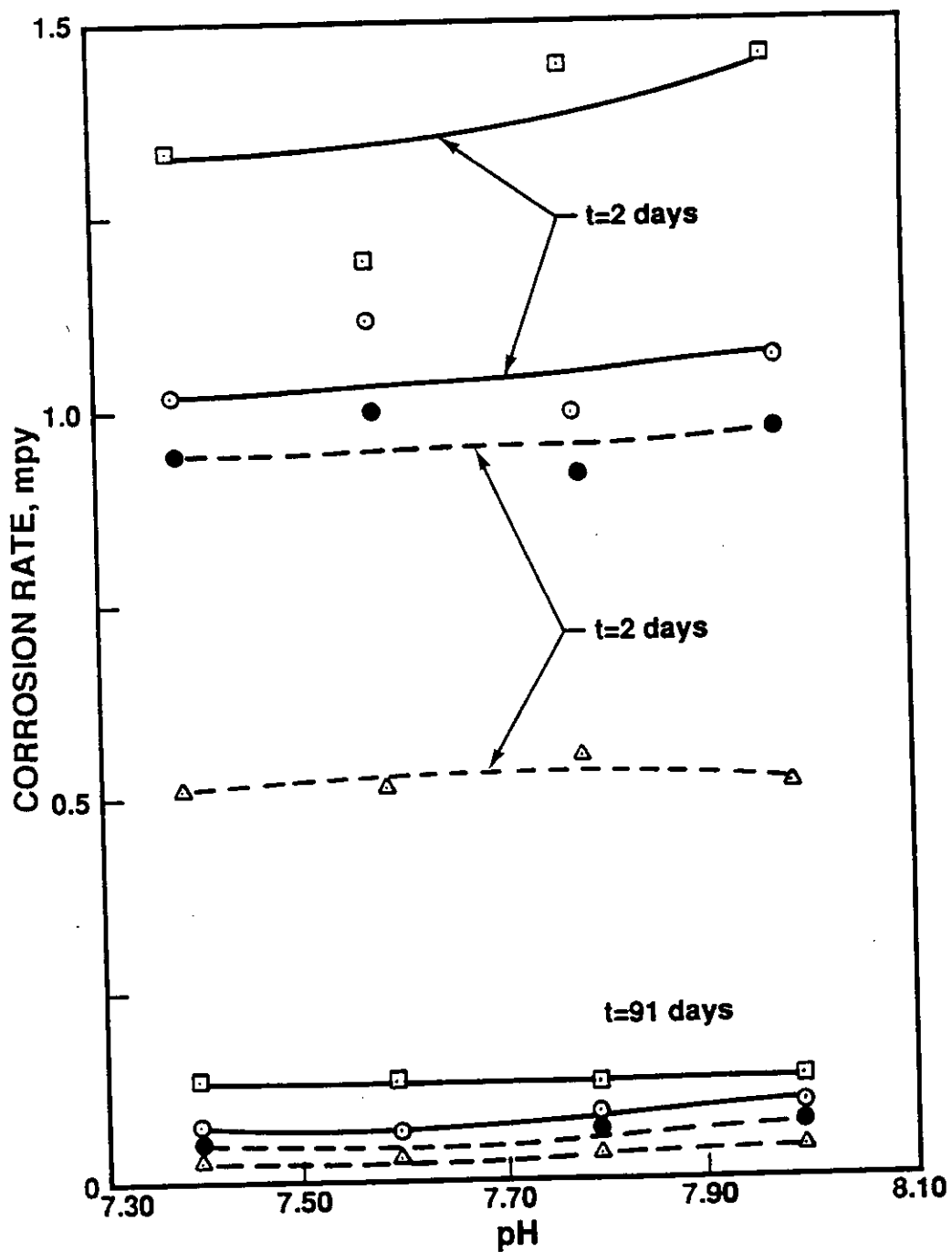


Figure 9. Corrosion rate of copper against pH at two exposure times via weight loss method. Open squares - aerated, chlorine = 1.0 mg/l; open circles - deaerated, chlorine = 1.0 mg/l; closed circles - aerated, no chlorine; open triangles - deaerated, no chlorine.

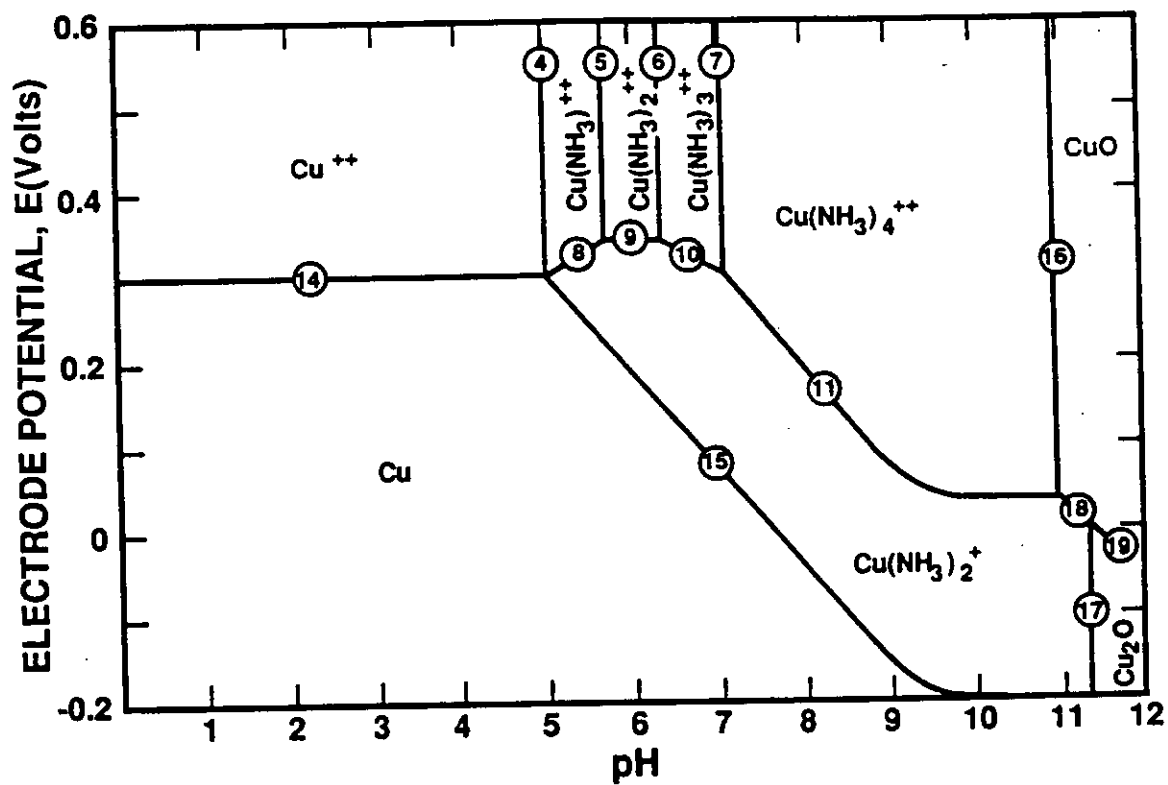


Figure 10. Pourbaix Diagram for H₂O - Cu - NH₃.

calcium carbonate. As Figure 11 shows, increasing alkalinity results in a decreased corrosion rate. This may be attributed to the role of carbonate ions in the formation of the passive films discussed previously.

The most important factor in controlling the corrosion of copper by swimming pool water is the proper maintenance of the pH value. Through the proper use of water test kits and careful attention to instructions for adjusting the pH, copper staining due to corrosion can be prevented. As has already been mentioned, copper staining has become less prevalent since copper pipes have been replaced by PVC, but there are still many sources of copper in the swimming pool system. Copper tubing in heaters, copper fittings, brass and bronze valves, bronze main drain covers, ladders, handrails and other chrome coated fixtures are all possible sources of copper in swimming pool water which can lead to staining [9]. Therefore, it is unwise to ignore the prevention of copper corrosion.

5.4.1.5 Acid Washing

Usually the only method of removing mineral stains, such as copper, iron or manganese, from the pool walls and floor is an acid wash. When the pool surface is acid washed, many of the metal fixtures are covered with acid, and acid enters into the water circulation lines. This acid removes the passive film on copper surfaces and promotes the corrosion of copper. Therefore, during acid washing, a substantial amount of copper is placed in solution. If the pool surface and the circulation lines are not completely cleansed with fresh water, the copper will remain in solution when the pool is refilled. The copper in solution will eventually lead to staining which may be worse than before the acid wash. Great care should be taken to completely flush out and neutralize all of the acid-wash solution [11]. In addition, the attack of marcite by hydrochloric acid as occurs in the acid

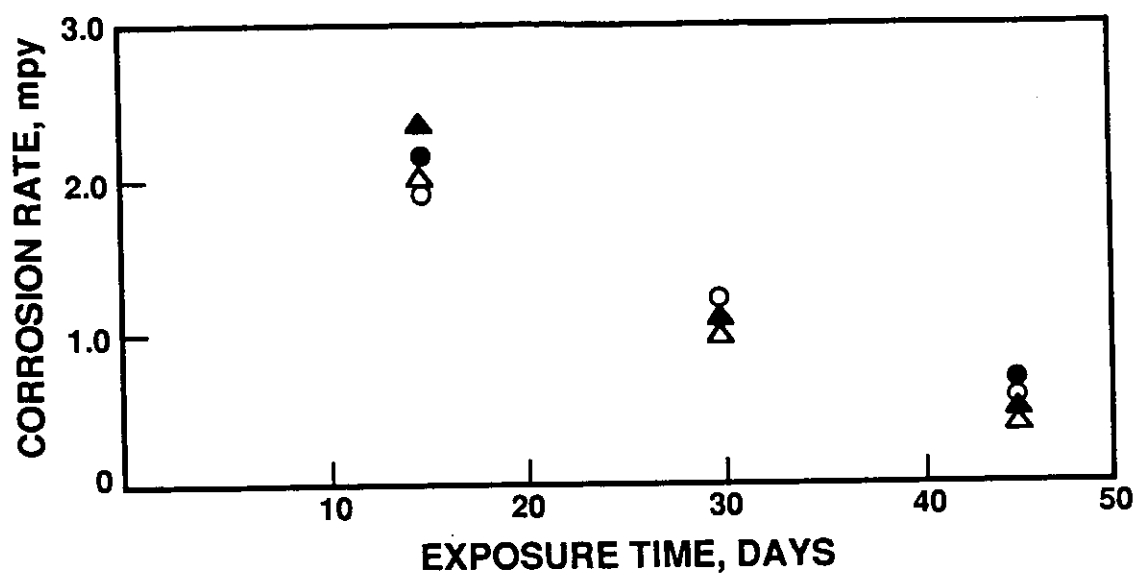


Figure 11. Effect of bicarbonate alkalinity on the rate of corrosion of copper in aerated solutions containing 5 mg/l of chloride and sulfate ions. Closed circles - no alkalinity; open circles - 25 mg/l alkalinity as CaCO₃; closed triangles - 100 mg/l alkalinity as CaCO₃; open triangles - 200 mg/l alkalinity as CaCO₃.

washing of pool walls can yield disastrous results. The attack is physico-chemical. The hydrochloric acid reacts with calcium compounds and forms soluble salts, which are subsequently leached out. Also, there are indications that the hydrochloric acid reacts with other compounds in the plaster to form insoluble salts which have larger volumes (and are less dense) than the material the acid reacted with. This marked increase in volume gives rise to stresses in the matrix which cause it to disintegrate. The appearance of the cement during hydrochloric acid attack changes - yellow stains appear on the surface along with pitting. The yellow stain is due to a compound called ferric chloride, $FeCl_3$, which is found as a result of hydrochloric acid reacting with iron oxides in the cement or in calcium chloride, if the latter has been mixed with the cement as an accelerator.

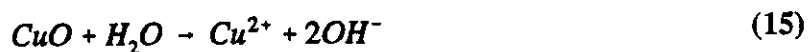
5.4.1.6 Chemical Additions

Copper can also be added to swimming pool water through chemical treatment. There are several commercial formulations which are designed to control the growth of algae, algaecides which contain copper compounds, usually copper sulfate. The effectiveness of these formulations in controlling algae growth is questionable, and they represent a possible source of copper staining [11]. Another source of copper is through the use of copper ionizers as a method of swimming pool water sanitation. These systems have proved to be effective in maintaining a sanitary swimming pool and they should not cause copper staining with proper maintenance and control. However, it is recommended to avoid adding copper to swimming pool water when there are suitable alternatives.

5.4.2 Formation of Copper Stains on Marcite

Copper stains consist of a precipitate of a copper salt. The two most common

precipitates found on swimming pool surfaces are copper (II) oxide, CuO, and copper (II) carbonate, CuCO₃. These two precipitates can be distinguished by the different color stains they produce; a black stain is characteristic of copper (II) oxide, while copper (II) carbonate produces a blue-green stain [12]. The dissolution reactions of these compounds are given by the following equations:



The corresponding expressions for the solubility products are as follows:

$$\text{for CuO: } K_{sp} = [\text{Cu}^{2+}] [\text{OH}^-]^2 = 10^{-20.35} \quad (17)$$

$$\text{for CuCO}_3: K_{sp} = [\text{Cu}^{2+}] [\text{CO}_3^{2-}] = 10^{-9.63} \quad (18)$$

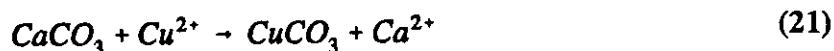
These expressions can be used to give a rough approximation of the copper (II) ion concentration required to produce copper stains. For example, at a pH value of 7.0, a copper (II) oxide precipitate would be in equilibrium with a copper (II) ion concentration of approximately 10⁻⁶ M. More precise calculations are much more complex because the presence of other ionic species disturbs the equilibrium. In the case of copper (II) carbonate precipitation, the concentration of carbonate ions, [CO₃²⁻], is strongly dependent on the pH of the water, as shown by the following reactions:



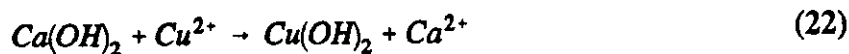
The solubility product expressions provide general guidelines, but more accurate predictions require detailed knowledge of the specific solution in which precipitation takes place.

These copper compounds precipitate on the surface of pool plaster for several different reasons. The surface of swimming pool plaster contains hydrous calcium oxide, which has a high specific surface area which tends to absorb metal ions from solution. The absorbed ions lower the free energy of the solid-liquid interface. This results in a high concentration of copper (II) ions which forms precipitates. Precipitation involves the processes of nucleation and growth. Nucleation can be assisted by occurring on the plaster surface instead of in the bulk solution. Nucleation on a surface (heterogeneous nucleation) produces a lower interfacial energy between the precipitate and the liquid. Growth of the precipitate is assisted by the high concentration of copper (II) ions near the plaster surface.

In addition to the precipitation of copper salts causing staining of marcite, it is possible that staining can result from exchange of copper ions in the pool water with calcium ions from calcium hydroxide and/or calcium carbonate in the marcite. The resulting exchange products are colored. As has been mentioned above, copper (II) carbonate produces a blue-green stain. Copper (II) hydroxide is black. The exchange reactions are:



and



For reaction (21) the Gibbs free energy change is $\Delta G_{298}^\circ = -7.5$ kilojoules/mole, whereas for reaction (22) the Gibbs free energy change is $\Delta G_{298}^\circ = -139.6$ kilojoules/mole.

Thus, whereas chemical thermodynamics predicts that both exchange reactions will take place spontaneously, reaction (22) would be expected to dominate because of the more negative free energy change. This prediction is again in agreement with what has already

been discussed in this report regarding the relative chemical activity of portlandite in marcite pool plaster.

5.4.3 Prevention and Removal of Copper Stains

As mentioned in the section on aqueous corrosion, copper staining can be prevented through careful control of swimming pool water chemistry and by using substitute materials in place of copper where they are available. Once copper ions are present in solution, sequestering agents can be used to prevent copper staining. Sequestering agents form inert chemical complexes with metal ions, which prevents them from precipitating out on the plaster surface [15]. Once copper stains appear on the plaster surface, they are usually removed by an acid wash. In an acid wash, the stains and some of the plaster are leached away by an acid solution.

6. Conclusions and Recommendations

6.1 Maintenance of Water Chemistry

As a result of studies and observations made during the course of this investigation, it is our opinion that the following guidelines set forth the suggested operation parameters for the proper chemical treatment and maintenance of swimming pool waters. Chemical treatment alone will not produce sanitary pool water. A filtration system in proper operational condition is also required to attain sparkling clear water.

	Minimum	Ideal	Maximum
A. Disinfectant Levels			
1. Free chlorine, ppm	1.0	1.0 - 3.0	3.0
2. Combined chlorine, ppm	None	None	0.2
3. Bromine, ppm	2.0	2 - 4	4.0
B. Chemical Values			
1. pH	7.2	7.4 - 7.6	7.8
2. Total alkalinity (buffering), ppm as CaCO ₃ *	60	80 - 140	180
3. Total dissolved solids, ppm	300	1000 - 2000	3000
4. Calcium hardness, ppm as CaCO ₃	150	200 - 400	500 - 1000
5. Heavy metals	None	None	None

*Although reported as ppm CaCO₃, total alkalinity measures the combined influence of bicarbonates, carbonates and hydroxides in pool water; i.e., it would be possible to obtain a positive measurement of ppm "CaCO₃" with no carbonate in the water at all.

6.2 Prevention of Marcite Etching

From this study, the deterioration of marcite has been found to be chemically related and due primarily to leaching of calcium hydroxide (portlandite) from localized areas of pool plaster. Calcium hydroxide is the hydration product that is most readily leached from

concrete.* The leaching is of portlandite from the portland cement paste. Unless the pool water is far out of balance the calcite marble aggregate in the cement is not particularly affected. Acidic pool water (pH less than 7.0) can wreak havoc on marcite and pool plumbing, resulting in etching and staining. Proposed solutions to control the damage aggressive water can produce include; (1) paying careful attention to water chemistry to avoid unbalanced water conditions and (2) providing a chemically inert barrier between the pool water and the marcite surface.

Experimental evidence supports the hypothesis that acidic pool water preferentially leaches the portlandite phase out of the marcite matrix, resulting in etching. The ~~last~~ 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. This option, however, involves the education of pool owners and pool maintenance personnel concerning the importance of *regular* and *thorough* monitoring of pool chemistry. Pool owners must be knowledgeable about the pool chemicals they use as well as pool water chemistry in general.

From knowledge gained on this research program with regard to the swimming pool water - marcite system it is apparent that over time marcite will maintain its pristine and beautiful white surface only if swimming pool water chemistry is continuously and meticulously controlled. This control, i.e., maintaining pool water "balance" must be established from the very beginning and starts when the freshly marcited pool is first filled with water. However, field studies revealed that this is often not the case and that problems

*It should be noted that the temperature of the swimming pool water will also be a factor. Calcium hydroxide is more soluble in cold water than it is in warm water. This may explain observations communicated to us during the course of this investigation by several pool owners in the northern part of the country that extensive pitting and etching were observed in marcited swimming pools in the spring after having been covered over for the winter.

such as marcite pitting etching, mottling, staining and scaling are far too common.

It is our opinion that the "unforgiving" nature of marcite to poor control of water chemistry can be mitigated by protecting the marcite surface with suitable chemical barrier coatings. Suitable coatings would protect the marcite from aggressive water and therefore extend its useful life.

In a recent paper on coating concrete a simplified classification system for concrete exposure conditions is offered [20]. Coatings system recommendations are discussed generically within the context of the exposure classification. The authors of the above-referred paper do not address the problem of marcite deterioration in swimming pools directly. However, based upon their classification of substrates in terms of exposure potential - immersed (canals, pilings, tank linings); atmospheric (walls, low-stress pavement); atmospheric plus mechanical durability (decking, high stress pavement); industrial atmospheric (walls, pavement, floors in splash and spillage environments); and buried (pipelines, foundation slabs), the follow typical coating recommendations can be made as specifically regards marcite exposure conditions in swimming pools.

- High-performance epoxy; one or two coats, 10-12 mils.
- Elastomeric lining, usually polyurethane; 20-40 mils.
- Thermoplastic lining, usually vinyl.
- Polyester, glass filled; 20-60 mils.
- Epoxy, glass filled; 40-200 mils.
- Epoxy with polyurethane topcoat; 6+6 mils.
- Durable epoxy high build; 6-12 mils.
- Polyurethane sealer with polyurethane topcoats; 6-12 mils.
- Silicate or hydrophobic sealer.

- Polyurethane sealer.

Although coated marcite may be initially more expensive, it represents a promising alternative. The concept of coating a cement structure which is continuously immersed in water is not novel. Canals, waste water treatment process structures, tanks and pilings are concrete structures which are routinely coated with either epoxies, polyurethanes, vinyls, or polyesters. The coatings provide protection against reinforcement corrosion, chemical attack, frost damage, mechanical damage, water penetration and salt intrusion. Since selective leaching is involved in marcite deterioration and it is of primarily uncarbonated calcium hydroxide (portland cement hydration product), then precarbonation of the fresh marcite paste may be another method for restricting deterioration. This could be accomplished by initial use of "carbonated" water having a negative Langelier Saturation Index, or by creating a high carbon dioxide atmosphere (e.g. 5 to 7 percent carbon dioxide) and a relative humidity of about 50 percent inside a "tented" pool immediately after the marcite application [21].

Another possibility for eliminating or greatly reducing the leaching of calcium hydroxide from marcite comes from the construction industry [22,23]. The latest additive to strengthen concrete is silica fume. Silica fume, a by-product of silicon alloys and metals production, consists of particles 100 times smaller than portland cement grains. Silica fume improves the strength and durability of conventional concrete by filling voids, making the material extremely dense. It does this in two ways. In conventional concrete, about 25% of the cement paste is calcium hydroxide which does not contribute to concrete strength. Adding silica fume converts nearly all the calcium hydroxide to calcium silicate hydrate, which is the strength ingredient in cement paste. Microphotographs show that the silica fume partially fills the tiny voids between cement grains, and it apparently adds strength in

this way. From the standpoint of plaster chemistry, conversion of calcium hydroxide to calcium silicate hydrate would make the pool plaster much less susceptible to chemical attack.

Copper staining in swimming pools is caused by the precipitation of copper (II) salts on plaster surfaces. These precipitates form from copper (II) ions which enter the swimming pool water through several different methods and common aqueous anions. The most common source of copper ions in solution is the aqueous corrosion of copper containing materials; therefore, the most effective method of preventing copper staining is the careful control of water chemistry. If copper ions enter into solution in the swimming pool, either through corrosion or any other source, a sequestering agent can prevent them from producing stains by blocking their chemical activity. Copper stains can usually be removed from swimming pool plaster by acid washing although this a method of "last resort".

Finally, a word about calcium chloride because of the role this additive can play in the overall integrity of marcite surface. The main benefit of calcium chloride is the acceleration of the hydration reaction of cement, which means it gets harder faster and this saves time and money for the pool contractor. However, care should be exercised when introducing calcium chloride into the cement. Calcium chloride *should not* be introduced into the cement mixture as a solid but only as a solution since the undissolved crystals can attract moisture and can deprive the cement of proper hydration. If the cement is not given the opportunity to hydrate sufficiently, flash setting can occur, which results in cracking. When using calcium chloride as an accelerator, no more than 2% as a solution to the cement should be added.

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Appendix A. Laboratory Simulation of Swimming Pool Parameters

An important aspect of this phase of the study was to duplicate typical swimming pool conditions in the laboratory. To determine a cement specimen surface area to water ratio that was as close as possible to the surface area to water ratio found in a typical swimming pool the following calculations were made.

Consider a swimming pool that is 30' long, 15' wide and an average of 8' deep:

$$\text{volume} = 30' \times 15' \times 8' = 360 \text{ ft}^3$$

$$3600 \text{ ft}^3 \left(\frac{1 \text{ m}^3}{35.314 \text{ ft}^3} \right) = 101.94 \text{ m}^3$$

$$101.94 \text{ m}^3 \left(\frac{100^3 \text{ cm}^3}{1 \text{ m}^3} \right) = 1.0195 \times 10^8 \text{ cm}^3$$

$$1.0194 \times 10^8 \text{ mL} \left(\frac{1 \text{ l}}{1000 \text{ mL}} \right) = 101,940 \text{ liters}$$

$$101,940 \text{ liters} \left(\frac{1 \text{ gal}}{3.7854 \text{ liters}} \right) = 26,929 \text{ gallons}$$

$$\text{surface area of pool} = 2ab + 2ac + bc$$

$$= 2(18)(15) + 2(8)(30) + 15(30)$$

$$= 1170 \text{ ft}^2$$

$$= 1170 \text{ ft}^2 \left(\frac{1 \text{ m}^2}{10.763 \text{ ft}^2} \right) = 108.705 \text{ m}^2$$

$$= 108.705 \text{ m}^2 \left(\frac{10,000 \text{ cm}^2}{\text{m}^2} \right) = 1,087,050 \text{ cm}^2$$

surface area cylinder

$$\begin{aligned}2\pi rl + 2\pi r^2 &= 40.36 \\2\pi(rl + r^2) &= 40.36 \\r(l + r) &= 6.42 \\1.27(l + 1.27) &= 5.05 \\l + 1.27 &= 5.05\end{aligned}$$

$$\begin{aligned}l &= 3.78 \text{ cm} \\&\sim 1.5 \text{ inches}\end{aligned}$$

The radius of the cylinder was set equal to 1.27 cm (equivalent to one half inch). The length of the cylinder was 1.5 inches.

The problem of achieving analogous circulation rates was solved as follows:

The pool industry recommends an eight hour turn over rate. Since one gallon containers were used in these investigations, a flow rate of 1/8 gallon per hour, or

$$\frac{0.125 \text{ gal}}{\text{hr}} \left(\frac{1 \text{ hr}}{60 \text{ min}} \right) \left(\frac{3785 \text{ mL}}{\text{gallon}} \right) = \frac{7.88 \text{ mL}}{\text{min}}$$

had to be achieved.

Appendix B. Sources of Marcite Samples for Diagnostic Studies

Aber Pools/Mr. Marcite	Florida Stucco Corp.
Acapulco Pool	Gardner Pool Plastering
Advanced Pool Design	Gator Pool and Spa Service
Al Jackson Pools	Geo A. Brown and Son
Al Summers	George E. Linnert
Artesian Pools	Gerard Morrissey
Atlantis Condominium	Great Lakes Biochemical Co., Inc.
Atlantis Pools	Guide Corporation
BioLab Inc.	H ₂ O Chemists
Blue Image Pools	Halifax Plantation Pool
Bob Steelman Plaster	Horner Equipment International, Inc.
Bruce Steelman	Imperial Pools
C.F. Pools and Spas	J.J. Tepas
C.L. Industries, Inc.	Jacks Magic
Cascade Pool and Spa, Inc.	Kaplan Pools
Creative Custom Pools, Inc.	Keith Payne Pools
Dadeland Pools	Kelly
Demar Baron Pool Plastering Co., Inc.	Lawden Pools
Eric Herman	Longhammer Pool
Estate Pools	Lotzkar Pool
Estate Pools	Med's Pool Service
Florida Pool Corporation	Ocean Palm Villa

Padgett Pool Plastering

Pensak Pool

Pools by John

Quality Pools

Riverside Cement Company

Rizzo Construction Pool Co., Inc.

Southern Vinyl Waterproofing

Starr-Lite Pools of Highlands County, Inc.

Tonoka Plaster

Town and Country Pools, Inc.

Treasure Coast Pool Service, Inc.

Village Condominium Pool

Village Pools

Wet World

Appendix C. NSPI Plaster Sample Data Sheet

(Please fill out what you can. If you kept a log other than what is listed below, please include a copy with this check list.)

NSPI PLASTER SAMPLE DATA SHEET

1. JOB ADDRESS _____
City & State _____ Zip Code _____
Your Name & Telephone _____ () _____
2. PLASTERING
Plastering Company Name _____
IS THIS AN NSPI ORIGINAL PLASTER SAMPLE? Yes No
 New Pool or Replaster? Commercial or Residential?
3. HOW SOON AFTER PLASTERING WAS THE POOL EQUIPMENT STARTED? (please circle) 1 Day 2 Days 3 Days Other _____
4. HOW MANY DAYS DID IT TAKE TO FILL THE POOL? (please circle) 1 Day 2 Days 3 Days Other _____
5. WHAT WERE THE WEATHER CONDITIONS AT START UP? (Hot, cool, windy, rainy, etc.) _____
6. 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)
C. 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: _____

10. CORRECTIVE/REMOVAL PROCEDURES ATTEMPTED WITH WATER IN POOL

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

11. EMPTY POOL PROCEDURES

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

12. COLOR OF PLASTER

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

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

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

14. NORMAL CHEMICAL ADJUSTMENTS

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

15. CHLORINATION/SANITIZER INTRODUCTION METHOD

- 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) _____
- Ozone
 - Bromine
 - Baquacil
 - Other _____

16. pH CONTROL

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

17. ALGAE CONTROL

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

18. STABILIZER ADDITIONS

- Direct to Pool Granular
- Induced Through Skimmer
- Floater

19. MATERIALS OR PRODUCTS USED (please specify)

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

20. ADMIXTURES

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

21. PRE-FILTRATION WATER CLARIFYING SCHEMES

- Activated Carbon D.E. Cartridge Sequestering Agents Oxidizers None Other_____

22. FILTERING TYPE/CONTAINER

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

23. TIMED CIRCULATION OPERATIONS PER DAY

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

24. PUMP AND STRAINER

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

25. VALVES (EXCEPT WASTE CONTROL)

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

26. PIPING AND MANIFOLDS

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

27. PLUMBING BOTTOM DRAIN LINE

- Plumbed Directly to Pump To Skimmer Closed to Operate Suction Cleaner

28. HEATER

- Fossil Solar Metallic Solar Plastic Electric Resistance Heat Pump

Please provide make and model number _____

29. METALS IN CONTACT WITH WATER

- Skimmer Basket 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 _____

30. GIVE POOL CAPACITY IN GALLONS

- Calculated_____ Owner/Service Co. Estimate_____ Meter Reading_____

31. SURFACE AREA ROUGHNESS COMPARED TO SANDPAPER GRIT

- 400 or Finer 220 120 80 40 Rougher than 40

32. INFORMATION OBTAINED VIA

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

33. WINTERIZING

- Covered Full and Inoperative Completely Empty Anti Freeze in Piping Other_____

Give Length of Swimming Season_____ (specify number of months)

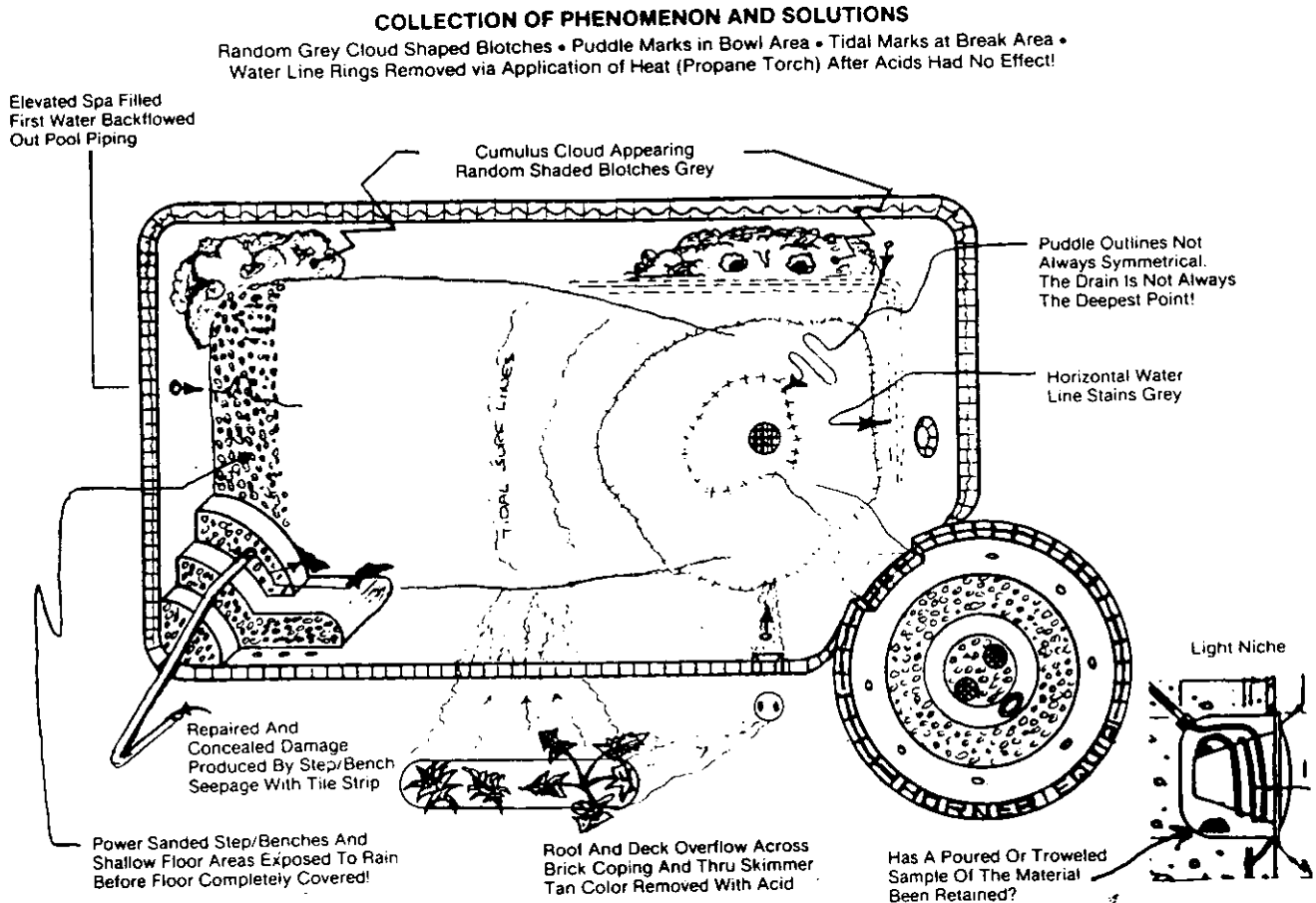
34. ARE THERE TRANSFORMER TYPE OR BURIED UTILITY LINES NEAR THE POOL? Yes No How close? _____

35. RELATIVE SURFACE HARDNESS OF PLASTER

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

36. COLLECTION OF PHENOMENON AND SOLUTIONS

This illustration shows common plaster finish deficiencies along with a brief description of the possible cause. Please indicate on the drawing the locations in the pool where the enclosed samples were taken and circle any characteristics below that are found in the pool. (If you wish you may attach a separate drawing of your pool and indicate the problem(s) found according to this example.)



(Diagram courtesy of Horner Equipment Of Florida)

37. TRANSMIT SAMPLES

Please send an NSPI disk (lid) or 2 x 2 inch sample of plaster deterioration problems (and a 2 x 2 inch sample of non-deteriorated plaster from the same pool, if possible), *in pool water*, along with this form and as much information concerning the history of the pool as you have available, to the address below. If you have questions concerning this data sheet, please contact:

PLASTER RESEARCH PROJECT
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Paul Scheele & Associates
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Crom Corporation
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Gainesville, FL 32602

Construction Engineering Technology
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100 Weldon Blvd.
Sanford, FL 32771-6199

Construction Technology
Valencia Community College
P.O. Box 3028 MC 4-23
Orlando, FL 32802

Construction Technology Dept.
Fl. Agr. & Mech. University
P.O. Box 164
Tallahassee, FL 32307

Construction Management Dept.
Florida Int'l University
V H 230
University Park - Tamiami Trail
Miami, FL 33199

University of North Florida
Div. of Tech. and Voc. Ed.
4567 St. Johns Bluff Road, South
Jacksonville, FL 32216

Building Construction Dept.
University of West Florida
Building 70
Pensacola, FL 32504

Technology
Manatee Junior College
5840 26th Street West
Brandenton, FL 34207

ABC Florida Gulf Coast Chapter
P.O. Box 152107
Tampa, Fl. 33684

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Senior Research Scientist
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