New Plaster Start–up Chemistry Using Sodium Bicarbonate

Kim Skinner and J. Que Hales
Pool Chlor
Doug Latta
Aqua Clear

A study was performed that compared the effects of different chemical start–up procedures on the surface of swimming pool plaster. Lab research was performed by simulating traditional start–ups and acid start–ups (both utilizing muriatic acid), and high alkalinity start–ups (using sodium bicarbonate) with plaster coupons, which were subsequently analyzed. Field research was also conducted to confirm consistency with the lab results. Experimental results and conclusions are given.

The study was performed by the authors, and the presentation, along with additional and unique data and hypothesis, was made by John Maziuk of Church & Dwight. The additional information is available by purchasing the audio cassette tape of the presentation (instructions on page 6).

Introduction

The methods of traditional and alternative start–up techniques have been addressed in the trade press over the course of the last several years. Beginning in 1992 Pool & Spa News began a summary of the various methods being used, including the traditional (Herman 1992a; Zielinski 1992), the acid (Herman 1992b), and the sodium bicarbonate (Herman 1992c) technologies. A follow–up article was printed in 1997 (Ericksen 1997) which summarizes the various methods. Hard data, however, has been difficult to come by when attempting to evaluate the merits of the various methods. The sodium bicarbonate method of start–up chemistry is described and documented in this paper.

When first added to water, the components of swimming pool plaster undergo many chemical transformations which convert the cement, aggregate, water, and additives into a solid, cured, and hydrated mass. Typical of concrete products utilizing portland cement, 50 to 80% of the total hydration of the plaster is achieved in 28 days, with the final hydration occurring slowly over years and even decades (Lea 1971). Because of the fact that the plaster is placed in a 100% hydrated environment (i.e., underwater) within hours of the finish–trowelling, the chemistry of that water during those first 28 days is a contributing factor in the ultimate strength, durability, and appearance of the swimming pool surface.

Proceedings of the 2nd Annual Chemistry Symposium
National Spa and Pool Institute - November 1997
Pages 34–41

The Chemical Ramifications of Plaster Curing Under Water

In a plaster–surfaced swimming pool, calcium is typically cured from the plaster surfaces of the pool when the initial start–up chemistry is performed using traditional water chemistry start–up techniques. A result of the chemical phase changes of curing swimming pool plaster and its submersion in water is that calcium is released from the plaster surface. Because of the high pH nature of the plaster, this calcium is typically released in the form of calcium hydroxide. The calcium hydroxide immediately changes the chemistry of the water as it fills the pool, with pH levels reaching in excess of 10.0 when mere inches of water fill the bottom of the pool.

A Note Regarding Influence of pH on Calcium in the Carbonate Continuum

[Please note that there are more detailed reactions taking place, but that simplified versions of these reactions are used for clarity and are consistent with simplifications used in swimming pool chemistry texts. The symbols and equations used represent components of, and changes in the water, but are not meant to be inclusive of every component or change.]

Changes in the pH of pool water affect the bicarbonate (HCO_3^-), carbonate ($CO_3^=$), and hydroxide, or hydroxyl (OH^-) phases of alkalinity. Hydroxide alkalinity begins to be appreciable in water with pH levels in excess of 9; carbonate when pH levels range between 8.3 and 12; bicarbonate at pH levels between 5 and 10. When pH levels drop below the mid–4 levels, bicarbonate alkalinity is converted to carbonic acid and thus is no longer alkalinity. It is important to note that at concentrations typically found in swimming pool water, the hydroxide and bicarbonate forms of calcium are generally soluble in water, where the carbonate form is generally insoluble.

Between each combination of alkaline forms, a buffer level exists. The midpoint buffer level for the carbonic/bicarbonate combination is 6.4 and the midpoint buffer level for the bicarbonate/carbonate combination is 10.2. When the primary alkalinity species is bicarbonate, and little or no dissolved CO_2 is present, the pH will approach the midpoint, which is 8.3. Thus water with a significant hydroxide component tends to have a pH of about 12 or higher, water with a significant carbonate component tends to have a pH of about 10, and water with a significant bicarbonate component tends to have a pH of about 8.0.

When a pool is filled with untreated tap water, the water balance parameters of that fill water create a condition where calcium hydroxide dissolves from the pool plaster surface into the pool water. This dissolution of calcium hydroxide raises the pH of the pool water to levels ranging from as low as the upper 8 pH level to as high as the 11 pH level (depending on the alkalinity of the water) and adds as much as 150 ppm of dissolved calcium to the pool water. This high pH, excess calcium water condition creates the need for a chemical "start–up" process.

The "Traditional" Method of Start–up Chemistry

When performing a traditional start–up, the pool is first filled with untreated tap water. Since the resultant pH of the water generally exceeds 9, once the pool is filled, enough muriatic acid is added to the water to achieve a pH in the 7.2–7.6 level and a total alkalinity level in the 80–120 range. As the acid is added, and the pH of the water is lowered through the carbonate toward the bicarbonate pH range, soluble calcium hydroxide in the pool water undergoes a conversion to calcium carbonate, and forms a white crystalline precipitate commonly referred to as "plaster dust". Settled precipitate in the pool must be brushed regularly in order to prevent its attachment to the plaster, and to allow the filtration system to remove the precipitate from the pool. Unless extreme diligence is exercised, some of the calcium carbonate will scale onto the plaster surface, but since most plaster pools are white, the precipitate is not visible. Calcium removed from the plaster wall when this technique is utilized ends up either being filtered out, left soluble in the water, scaled on the plaster surface, or any combination thereof.

The "Acid" Method of Start–up Chemistry

With the increasing popularity of colored plasters, scaling of calcium carbonate onto the pool wall has become undesirable and even unacceptable to pool owners. As a strategy to prevent this scaling, several alternative start–up methods have been developed. One of the alternative strategies is referred to as the "acid start–up".

When performing an acid start–up, the pool is first filled with untreated tap water. Again, the resultant pH of the water generally exceeds 9. Once the pool is filled, enough muriatic acid is added to the water (commonly around 4 gallons of acid per 10,000 gallons) to achieve a pH in the mid–4 pH level, with a resultant total alkalinity level of 0. This pH level is low enough to solubilize all calcium in the pool water. After about a week, the pH of the pool is gradually raised *up* to the mid–7 pH range, thus avoiding pH levels where calcium becomes insoluble. Calcium removed from the plaster wall when this technique is utilized ends up as soluble calcium bicarbonate in the water.

The "Sodium Bicarbonate" Method of Start–up Chemistry

Another alternative to the traditional start–up is referred to as the high alkalinity, or sodium bicarbonate start–up. When performing a sodium bicarbonate start–up, the pool is filled with tap water which has been **pretreated** with sodium bicarbonate. This pretreatment consists of dissolving about 30 pounds of sodium bicarbonate per 10,000 gallons into a holding tank, and then filling the pool through the holding tank. When this method is employed, the pH of the pool water rarely exceeds 8.3, and the alkalinity level of the pool water is usually in the 300 – 340 ppm range. After the water is stable (usually 4 to 6 days), enough muriatic acid is gradually added to the water until the total alkalinity is eventually lowered to the 80–120 ppm range, whereupon the pH tends to equilibrate to the mid–7 range. This method also avoids pH levels where calcium becomes insoluble.

If any calcium is removed from the plaster wall when this technique is utilized it ends up as soluble calcium bicarbonate in the water.

Lab Experimentation

Coupons of pool plaster were formed using cement, aggregate, calcium chloride, and water. The coupons were labeled, and divided into three basins of water. Chemical start–up procedures were used to mimic a) a traditional start–up, b) an acid start–up, and c) a sodium bicarbonate start–up. After seven days, all coupons were placed into one basin at each location, and the water was kept balanced for a period of two months. At this point, one coupon from each start–up procedure was removed for microscopic surface analysis. The remaining coupons were then subjected to acidic conditions for 48 hours, and then they also were removed for microscopic analysis.

Materials Used:

- The bottoms of six plastic five gallon buckets, approximately 1 inch in depth
- Three plastic containers – 32 gallon size
- Twenty pounds of white portland cement
- Thirty pounds of marble aggregate
- Six ounces of calcium chloride (78% flake type)
- One gallon of muriatic acid
- One gallon of sodium hypochlorite
- Three tablespoons of sodium bicarbonate
- One tablespoon of cyanuric acid (stabilizer)

Six plaster coupons were formed in the bottom of five gallon buckets. The buckets were sawed off so that the coupons formed were about an inch in thickness.

Three plastic containers, each thirty–two (32) gallon size, were used to submerge the plaster coupons in the three different water conditions. The coupons were placed in a vertical position in the container.

To make the plaster coupons, six ounces (3/4 cup) of calcium chloride was added to one gallon of water and mixed. Then twenty pounds of cement and thirty pounds of aggregate were added and mixed together. The plastic buckets (depth of one inch) were then filled with pool plaster and trowelled to a smooth hard finish. All six plaster coupons were then labelled.

To accomplish the desired water conditions, a water analysis of the tap water was performed, including tests for total alkalinity, total hardness, and pH. Results were recorded. Each of the three plastic containers was then filled with thirty gallons of the tap water.

The ratio of thirty gallons of water to 2 coupons of about .75 square feet each (or 1.5 square feet of plaster surface to 30 gallons of water) is analogous to average pool conditions, where the square footage of plaster surface to volume of pool water is roughly 20 gallons of water to 1 square foot of plaster.

To simulate a traditional start–up, two plaster coupons were placed vertically into one of the three plastic containers, which was then filled with tap water. The water was then treated with one teaspoon or 5 milliliters of muriatic acid (equivalent to about .45 gallons in a 10,000 gallon pool) to maintain pH at 7.5.

For the acid start–up, two plaster coupons were placed vertically into a second of the three plastic containers, which was then filled with tap water. The water in the second container was treated with three tablespoons or 45 milliliters of muriatic acid (equivalent to about 4 gallons in a 10,000 gallon pool).

For the sodium bicarbonate start–up, water in the third container was treated with three tablespoons or 42 grams of sodium bicarbonate (equivalent to about 31 pounds in a 10,000 gallon pool, which results in about 220 ppm of added alkalinity). The coupons were then placed vertically into the treated water in the container.

The plaster coupons were then lightly brushed twice daily. After one week with plaster coupons in their respective start–up waters, all coupons were removed and placed vertically into one 32 gallon plastic container with new fresh tap water (30 gallons). Water in this plastic container was treated with one tablespoon or 10 grams of cyanuric acid (equivalent to about 7.34 pounds or 90 ppm in 10,000 gallons), one teaspoon or 5 ml of sodium hypochlorite (equivalent to about .5 gallons or 6 ppm in 10,000 gallons, with an additional dose added after 1 month), and one–half teaspoon of muriatic acid (equivalent to about 1 quart in 10,000 gallons). Additional acid was added occasionally as necessary to maintain a pH of 7.6.

The coupons were then lightly brushed twice a week. After two months, one plaster coupon from each of the three start–up procedures was removed, and labelled "traditional – before acid wash", "acid – before acid wash", and "sodium bicarbonate – before acid wash".

To simulate an acid wash, three tablespoons of muriatic acid was added to the plastic container with the remaining three plaster coupons. After 48 hours, they were removed, and labelled "traditional – after acid wash", "acid – after acid wash", and "sodium bicarbonate – after acid wash".

Results of Lab Testing

After the samples were collected, they were first subjected to microscopic analysis. As shown in photographs 1 through 12, it was consistently noted that the coupons which underwent simulated traditional start–up chemistry had surfaces which were composed primarily of cement, with a moderate amount of aggregate showing through. Coupons which underwent simulated acid start–up chemistry were visually rougher, and more of the surface was exposed aggregate. Coupons which underwent simulated sodium bicarbonate start–up chemistry were visually smoother, and more of the surface was cement. Indeed, the sodium bicarbonate–started coupons were so smooth that the experiment was re–run several times with black plaster to verify that the smooth surface was, in fact, original cement and not a deposition (since a deposition would be white and show against the black background). For those coupons which were acid washed, it was noted that subjecting the coupons to an acid wash did, indeed, clean the coupon surfaces of surface coloration, but no difference was noted relative to how the various types of start–up procedures influenced how well the coupons "stood up" to the acid wash.

When emptying the containers after the initial start–up chemistry was completed, it was noted that there was a consistent absence of calcium scale in the bottoms of the acid and sodium bicarbonate vessels, and a precipitate of calcium in the bottom of the vessel where the traditional method was employed. Since all coupons were consistently brushed, no appreciable scale was evident on the surface of any of the coupons.

Field Observation / Experimentation

After the laboratory experimentation, traditional and sodium bicarbonate start–ups were performed in pools under careful observation. pH meters were suspended in the pools before the water was turned on, and the results were graphed. Probe 1 was located 6" above the main drain, probe #2 was located 3 feet above the main drain, and probe #3 was located 6 feet above the main drain (see Figures 1–4). The probes were connected to a Model 600 Electronic pH recorder and data logger, manufactured by Kruger & Eckels. The Recorder/data logger was custom manufactured specifically for this type of testing by, and after consultation with Gerald Eckels of Kruger & Eckels. The probes were set to sample pH at 30 second intervals and values were directly downloaded into a computer graphing software package designed for the datalogger.

Consistent with what was observed in the lab experimentation, pH levels in traditionally started pools were observed at an average of 9.8 as soon as water came into contact with the first pH probe. The pH remained constant as the pools filled, and changed only after acid was introduced after filling. pH levels in the sodium bicarbonate pools rose only to the 8.1 – 8.3 range (see Graphs 1 and 2). Table 1 contains readings from a sample residence where the new grey plaster pool was started using sodium bicarbonate, but where the spa was filled with untreated tap water. Readings include tap water, the pool when it was 6 inches, 3 feet, and 6 feet full, the pool after it was completely full (day #1) and again the following day (#2), and finally the spa chemistry. In this pool, there was virtually no calcium precipitate in the pool, but there was the normal amount in the spa.

Alkalinity tests were performed in the pools utilizing the phenolphthalein method, which differentiates between hydroxide and carbonate alkalinity on the one hand and bicarbonate alkalinity on the other. These tests indicated that the traditionally started pools contained hydroxide and/or carbonate alkalinity, and that the sodium bicarbonate started pools contained no hydroxide/carbonate alkalinity.

Dosages for the sodium bicarbonate start–up method have been roughly established as follows: the calcium and alkalinity levels of the source water were ascertained and added together. Enough sodium bicarbonate was then added to increase the combina-

	Expressed as ppm	Tap	6"	3'	6'	#1	#2	Spa
pH	pH meter reading	7.5	7.7	8.1	8.1	8.1	8.1	10.2
Total Hardness	$CaCO_3$	88	48	82	84	82	84	56
Total Calcium	$CaCO_3$	66	32	66	66	58	62	32
Total Alkalinity	$CaCO_3$	128	1060	276	254	248	246	106
Total Dissolved Solids	ppm	200	1100	400	350	350	350	225

Table 1 – Chemistry of "Bicarb Start–up" Water in Sample Pool and Spa

tion calcium/alkalinity level to at least 400 ppm, but not exceeding 500 ppm. As a practical average, this required approximately 15 to 30 pounds of sodium bicarbonate per 10,000 gallons. The resultant alkalinity levels were generally in the 320 ppm range.

Results of Field Testing

It was found in the field testing that the resulting plaster surfaces in the pools were consistent with the results achieved with the coupons in the lab. Little or no calcium precipitate or scale was produced, and the plaster and water looked and felt superior to what is achieved via traditional methods. Continued study of the sodium bicarbonate start–up method will include x–ray diffraction and SEM analysis of the various surfaces, softness or permeability tests, microscopic testing for roughness, etc. Research is also ongoing relative to the recommended length of time to wait before filling a pool after the finish trowelling is completed, and the use of small amounts of acid in conjunction with sodium bicarbonate start–ups under certain fill–water conditions to ensure pH levels in the desired range.

Conclusions

It has been observed that a superior finish, the avoidance of calcium precipitate formation, a more maintainable surface, safer application (over acid), and a lower chance of damage to the plaster is achieved via the sodium bicarbonate start–up method.

References

Ericksen, Anne Baye. *"The Start–up Basics"*. Pool & Spa News April 9, 1997 pp. 55–63.

Herman, Eric (a). *"Off on the Right Foot"*. Pool & Spa News January 27, 1992 pp. 66–76.

Herman, Eric (b). *"The Upstart Start–up"*. Pool & Spa News February 10, 1992 pp. 52–58.

Herman, Eric (c). *"Breaking Out the Bicarb"*. Pool & Spa News April 20, 1992 p. 24.

Lea, F. M. *The Chemistry of Cement and Concrete* 3rd Edition Chemical Publishing Company, New York, N.Y. 1971 pp. 241, 243.

Zielinski, Stan. *"Protecting New Plaster Pools"*. Letter to the Editor, Pool & Spa News March 23, 1992 pp. 16–24.

About the Presenter and Authors

John Maziuk Jr. is a chemical engineer employed by Church & Dwight Co., Inc. at their Corporate Research & Development Center in Princeton, NJ as the Group Manager of Product Applications and Development.

Kim Skinner is the co–owner of Pool Chlor, and is based at the Bay Area Pool Chlor office in Livermore, California. A former general manager of Skinner Swim Pool Plastering in the Los Angeles area, he has been with Pool Chlor for the past 24 years.

J. Que Hales has been the manager of the Tucson branch office of Pool Chlor for the past 14 years, and also runs the corporate MIS, publishing, and mailing operations. He is the president of the National Association of Gas Chlorinators, and the editor of the *Journal of the Swimming Pool and Spa Industry.*

Doug Latta is the owner/principal of Aqua Clear Pools Inc. of Chatsworth, California. He is the founding and past president of the National Association of Gas Chlorinators, a member of the board of the Swimming Pool Chemical Manufacturers Association, and the current president of the Swimming Pool Trades and Contractors Association – a California–based safety, education, and support association.

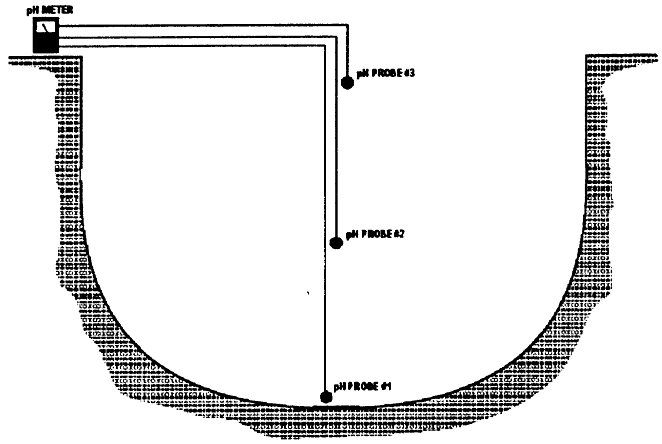


Figure 1 – Cutaway View of Swimming Pool with pH Probes in Place

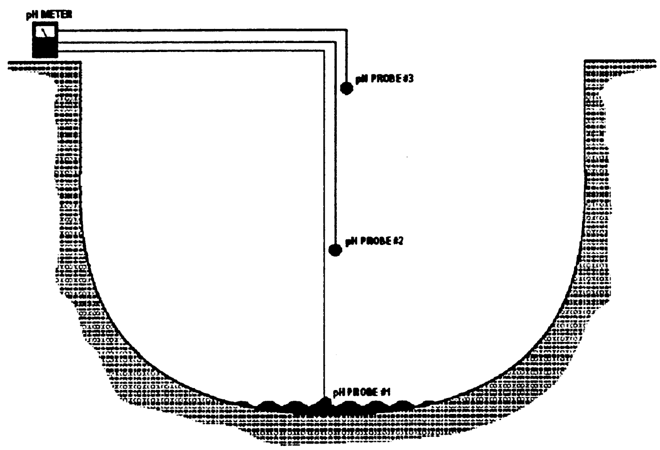


Figure 2 – Cutaway View of Swimming Pool with pH Probes in Place and Water Level at 6 Inches

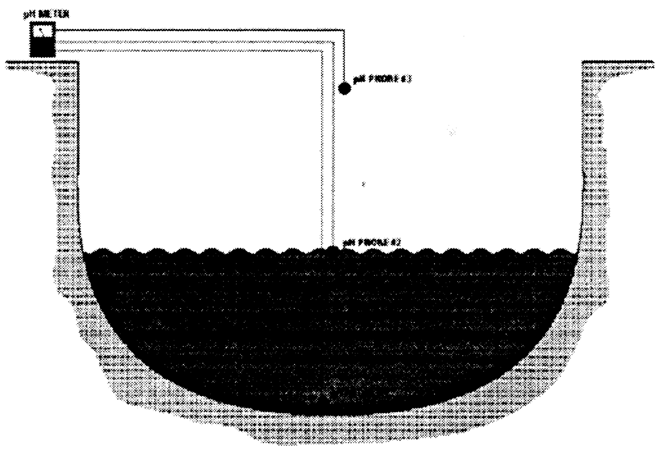


Figure 3 – Cutaway View of Swimming Pool with pH Probes in Place and Water Level at 3 Feet

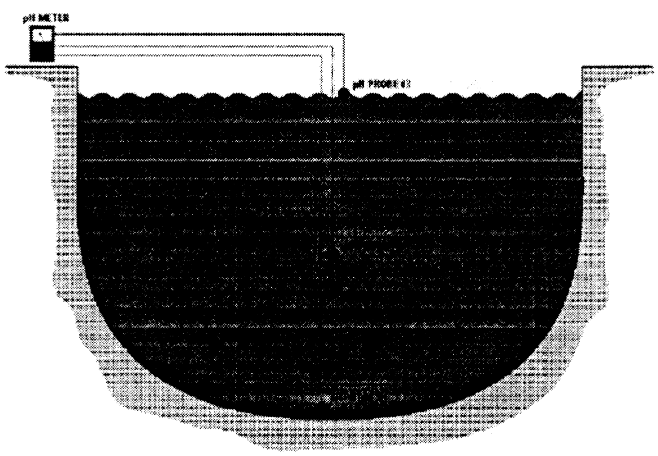
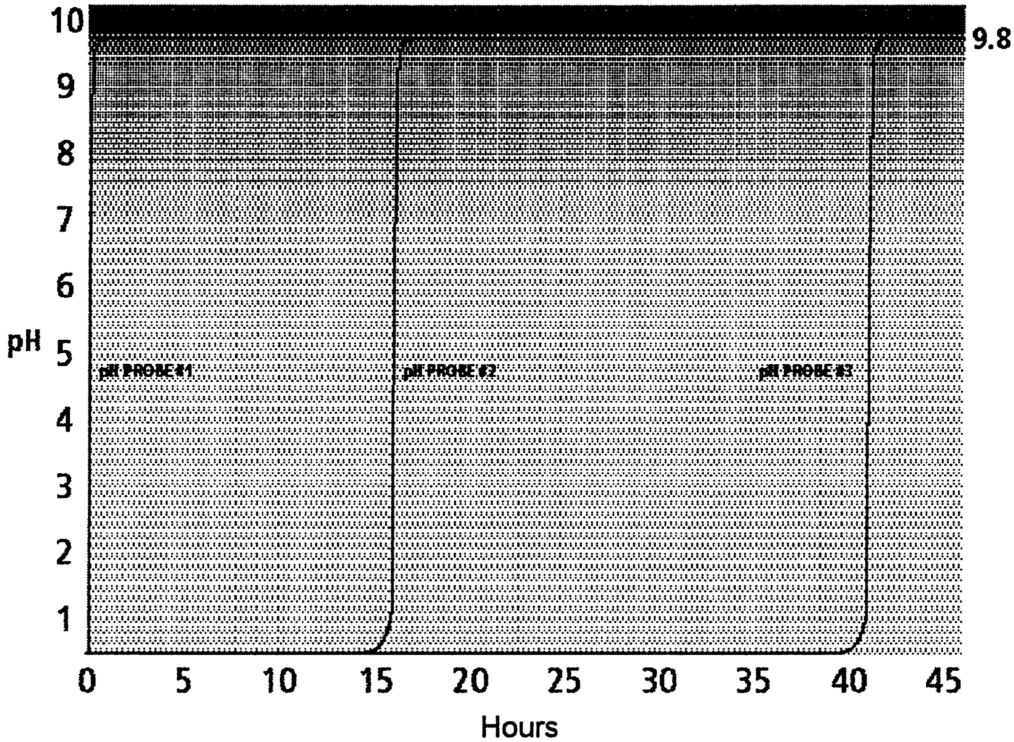
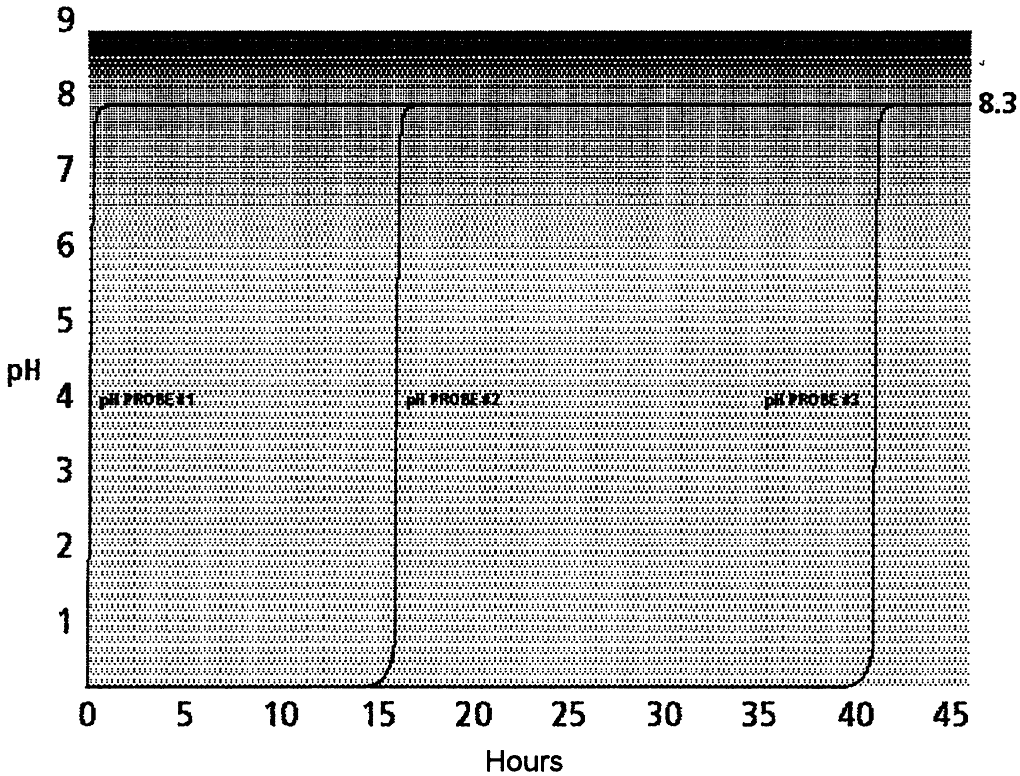


Figure 4 – Cutaway View of Swimming Pool with pH Probes in Place and Water Level at 6 Feet



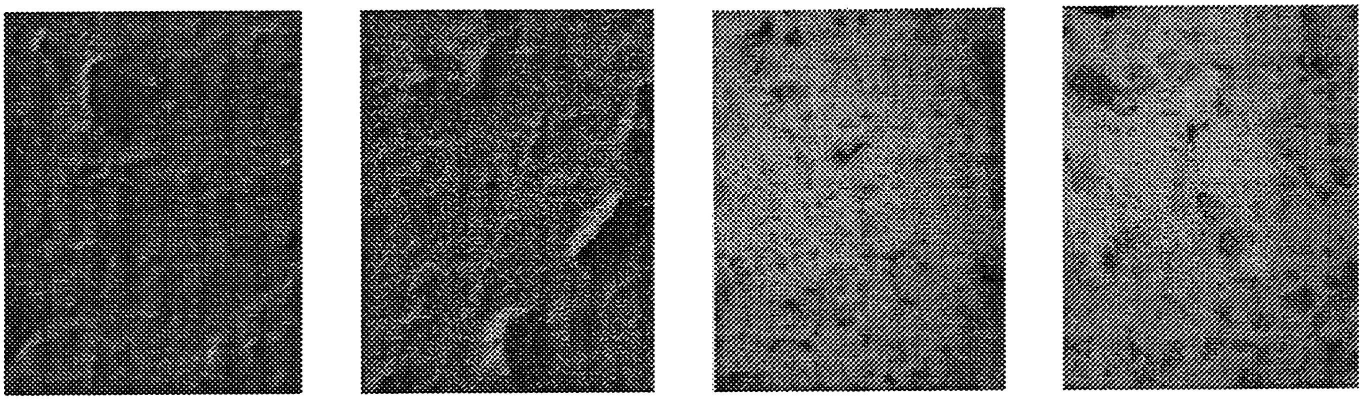
Graph 1 – pH of Plaster Pool During Fill Process (without sodium bicarbonate)

The pH probe/data–logging equipment in this pool registered a transition from no reading (shown as "0") to pH 9.8 as soon as the water came in contact with the probes in each of the three locations.

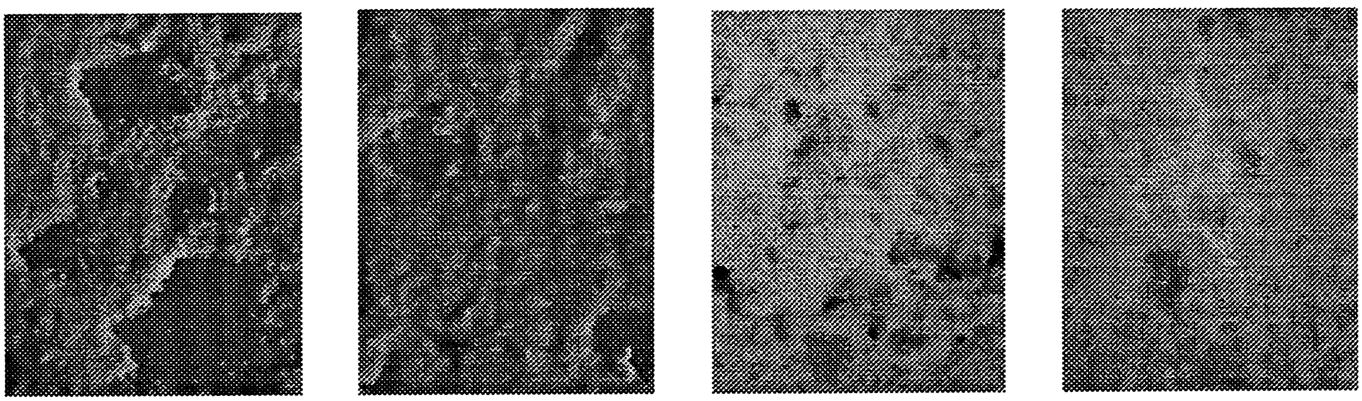


Graph 2 – pH of Plaster Pool During Fill Process (with sodium bicarbonate)

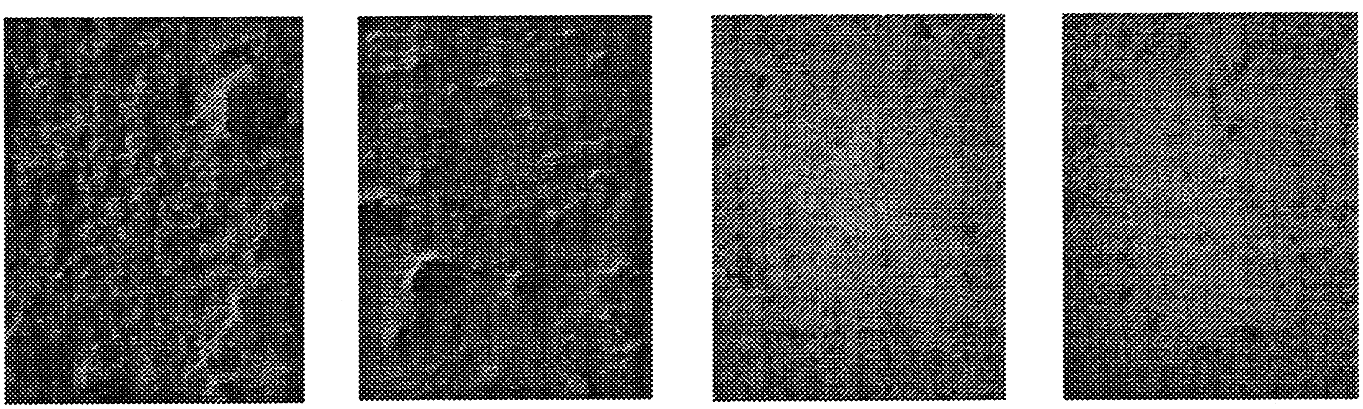
The pH probe/data–logging equipment in this pool registered a transition from no reading (shown as "0") to pH 8.3 as soon as the water came in contact with the probes in each of the three locations.



Photographs 1 through 4 – Traditional
(White Set #1, Black Set, White Set #2 before acid wash, White Set #2 after acid wash)



Photographs 5 through 8 – Acid
(White Set #1, Black Set, White Set #2 before acid wash, White Set #2 after acid wash)



Photographs 9 through 12 – Bicarb
(White Set #1, Black Set, White Set #2 before acid wash, White Set #2 after acid wash)