Calcium Nodules

Kim Skinner and J. Que Hales
Pool Chlor

A study was performed that examined the chemical basis behind the formation of calcium nodules on swimming pool and spa plaster. A chemical model was developed which was consistent with both the chemical rationale and with actual nodule samples collected from swimming pools. A laboratory study was designed and successfully conducted to artificially "grow" nodules on plaster coupons.

The Technical Manual of the National Plasterer's Council (NPC) shows pictures of calcium growths on pool plaster (inside front cover and inside right centerfold of the February 1994 revision). These growths are referred to in the Tech Manual as "calcium spores/nodules," and have commonly come to be referred to in the swimming pool industry as "nodules". The captions to the illustrations in the Tech Manual associate the nodules with bond failure cracks (inside front cover) and voids in the material (inside right centerfold) but a detailed explanation of the cause for this particular phenomenon is lacking. The authors of this paper felt that it would be useful, as part of the ongoing research in this area, to publish our opinions on nodules. We hope that, through the process of determining what is "common ground" and what is variance of opinion, constructive research and interaction will be promoted.

In this paper, we will explain, to the best of our knowledge, the reason for the appearance of such nodules, including the chemistry involved. We will then describe research we have performed and our observations on the results of various experiments. Finally, we will list a few opinions regarding nodules that are currently being discussed in the industry, and our opinions regarding them.

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The Chemistry

In order to understand the reason for nodule formation we must first mention a few (layman's level) concepts relative to the curing of plaster, and to the chemistry of aqueous solutions.

Plaster: As plaster cures in water there is a natural process of calcium hydroxide release. This phenomenon is especially prevalent during the first 1 to 2 weeks of a new plaster pool. The process may then continue for years, but at a drastically slower rate. As the calcium hydroxide comes in contact with bicarbonates in the pool water it is converted into calcium carbonate and calcium bicarbonate. In a new plaster pool, the "plaster dust" is a result of the carbonate portion of this reaction. The distribution of the carbonate and bicarbonate forms is influenced by pH, temperature, level of saturation, etc.

Alkalinity: In the pool water there is alkalinity. There are primarily three types: bicarbonate (HCO_3^-), carbonate ($CO_3^=$), and hydroxide (OH^-), also known as hydroxyl. The "carrier" for the alkalinity may be calcium, magnesium, sodium, potassium, etc. Alkalinity may be in the hydroxide state at pH ranges exceeding 9.0, carbonate alkalinity can exist in pH ranges from 8.3 to 10.0, and bicarbonate alkalinity exists in ranges from around 4.6 to 9.0.

With the pH range of pool water normally maintained from 7.2 to 8.2, bicarbonate alkalinity will generally be the only significant type present. While it may be possible to have a very small percentage of carbonate alkalinity exist at these pHs, it begins to be more prevalent at pHs above 8.3. This is due to the fact that dissolved CO_2 in water reacts with carbonate and hydroxide alkalinity, and converts them to bicarbonate.

The Plaster

Occasionally there is a cavity in pool plaster. Cavities may be caused by delamination (separation between the plaster and the substrate, or separation between layers of plaster,) excessive cracking in the plaster, or even by dissolving pockets of insufficiently mixed components of the plaster. If these cavities remain dry and unexposed to pool water, no nodule will form, and the cavity may go undetected indefinitely. In such a case the cavity is referred to as a "void" and is not considered a plaster defect by the NPC: in other words it is not a condition warranting repair, in and of itself. It only becomes a defect if the separated plaster actually "pops off" of the plaster wall, exposing the substrate or under–layer of plaster to open view. If, however, no pop-off occurs, but there is an avenue (pinhole, crack, etc.) which allows the cavity to fill with pool water, then a number of further reactions may occur.

First, as calcium hydroxide continues to bleed from the plaster, it also bleeds from the inner plaster face in the void into the water in that cavity. If the water supply (flow through the crack) is sufficient to rinse the resulting calcium hydroxide into the pool water, no calcium nodule will form. But if the crack is sufficiently small as to only allow water to *slowly* exchange between the void and the pool, this water becomes trapped and experiences local chemical conditions separate from the rest of the pool. The void water becomes more and more saturated, building up its calcium content and increasing its pH. As this happens a (very mild) pressure is also created in the cavity. This pressure eventually pushes high pH, calcium hydroxide–enriched water out the crack or hole until it comes in contact with the pool water. Once this enriched solution reacts with the pool water (regardless of the water balance, as long as carbonate is present) its pH drops and it takes on carbonate. This reaction may then form insoluble calcium carbonate, which may in turn build up a "slag pile" around the exit point of the void, forming a nodule with a continually building exterior and a hollow fissure up the middle. This process continues as long as there is sufficient water and calcium hydroxide release in the void to create the necessary reactants and pressure.

The forming nodule is generally white, unless it traps metals or minerals in its solid form, thus giving it a grey or brown color. The nodules are also generally circular, unless they are influenced during formation by a crack in the plaster (with a resultant long, skinny nodule following the crack or crazing pattern) or by gravity if the nodule forms at the right speed on a vertical surface (giving the nodule a "dripping" shape.)

Due to the need for a rich, soluble calcium source in order to form a nodule, the location of a nodule is necessarily restricted to the immediate egress area around a void. The idea that each nodule must have a "point of attachment" has been discussed in the industry, and the term has been coined and used to describe a scenario where the actual *source* of the calcium is supposed to be dissolved calcium from the pool water. The authors therefore feel that "point of attachment" is an inappropriate term, and that terms such as "calcium supply point" or "point of calcium hydroxide egress" or even "void opening" would be more appropriate. It may also be noted that nodules can be formed in locations other than plaster swimming pools. Indeed, nodules have been found on bridges, dams, and even on non-cement surfaces. However, it is the authors' opinion that in each case where pools or spas are involved (a 100% hydrated environment, as opposed to an atmosphere environment) a scenario similar to the above will be found, i.e.: a soluble calcium salt reservoir or source coming in contact with carbonated water and forming a calcium carbonate node.

An Experiment

In order to demonstrate the principles of nodule formation, nodules were grown in the lab under controlled conditions. Pool plaster was mixed by combining 1 part Federal White Cement with 1½ parts of Georgia Marble's "Pool Mix" brand aggregate. Enough tap water was added to make it workable, and the plaster was troweled into 3½" petri dishes. Before the plaster was completely set up, a strait pin was inserted into most of the coupons. After setting, the pin was removed, and the joint between the plastic dish and the coupon was sealed with silicon sealant. The dishes were then left to sit and cure in trays of water (submersion water). When placed in the water, the air behind the coupons bubbled out the egress, or pinhole, and water filled the void (void water) between the dish and the coupon. After approximately 2 weeks, small nodules began to form on approximately one quarter of the holes. They grew for about a week, starting out barely visible, and growing to a final size of approximately 3 millimeters (ml) across and 2 ml tall. None of the coupons without pinholes formed nodules. The pinholes in some of the coupons without nodules remained open, but others have become plugged (below plaster surface) by a white solid substance.

The test was then repeated, with similar results.

Next, the test was repeated, but the coupons were put in three varying types of water. Some were put in tap water as before, some were put in distilled water with sodium bicarbonate added, and some were put in tap water with calcium carbonate added. Again, the size and number of nodules, and the amount of time necessary to form them was similar to the first and second tests.

Note that up to this point there was no added calcium chloride or other admixtures in the plaster, and there was no chemical balancing of the water in the trays, other than the addition of sodium bicarbonate or calcium carbonate as described above.

In the last set of tests, both calcium chloride and calcium hydroxide was added to the plaster mix. The amount of calcium chloride added was the equivalent of adding 10 gallons of liquid calcium chloride to a 400 by 600 pound batch of mix, and the amount of calcium hydroxide added was the equivalent of adding 12 pounds to a 400 by 600 pound mix. These components were added in order to increase the soluble calcium salt content of the coupons. This time half of the coupons formed nodules, and the nodules formed over a single night. The nodules were of a comparable size. Again, none of the coupons without pinholes developed nodules.

Conclusions

We have drawn the following conclusions from these tests, and present them as facts:

1. Nodules will indeed form under the conditions formulated above.
2. These conditions are analogous to conditions in a swimming pool.
3. Nodules will form without the addition of any admixtures.
4. The addition of soluble calcium salts (such as calcium chloride or calcium hydroxide) will increase both the speed of nodule formation, and the likelihood of nodule formation.
5. Even by abusing the coupons (i.e.: the addition of vastly greater than normal amounts of calcium chloride and calcium hydroxide) no nodules could be formed without the right conditions – a void filled with water and an egress to the water outside the void.
6. Nodules form with the same frequency, at the same rate of speed, and to the same size even if no calcium is present in the initial submersion water.

Hypothesis

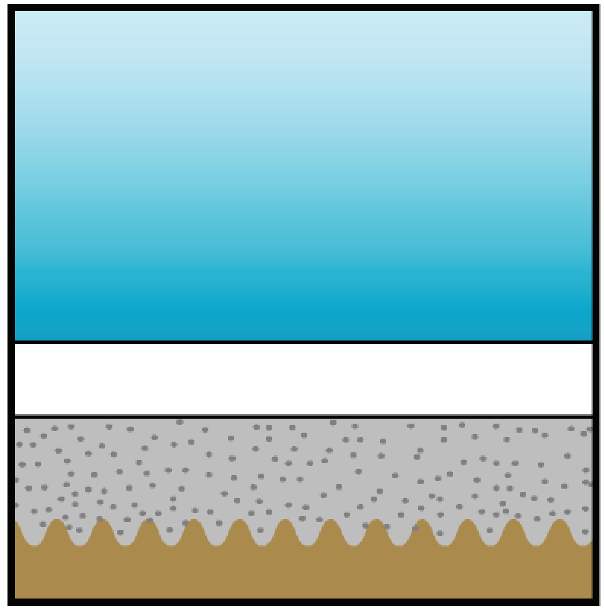
We have drawn the following opinions based on the experience drawn from performing the tests, and present them as hypotheses:

1. The rate of flow of the high pH, calcium hydroxide–enriched solution out of the egress hole is a major factor in whether or not a nodule will form. If the rate of flow is just right, calcium hydroxide converts to calcium carbonate right at the egress hole, forming a nodule. If the rate of flow is too great, the calcium solution dissolves into the submersion water, leaving the hole open (and forming, depending on other factors, either calcium carbonate or calcium bicarbonate.) If the rate of flow is insufficient, the calcium hydroxide may form a carbonate or bicarbonate solid in the hole, thus plugging the egress of additional solution.
2. This rate of flow appears to be influenced by the size of the egress hole, which varied in our tests, despite our attempts to keep them uniform.
3. It appears that the flow rate is also influenced by the pH and calcium hydroxide content of the void water. These levels should be a direct function of the surface area of the plaster exposed in the void. Theoretically, larger nodules could be formed by increasing the size of the coupons. The ratio of water to plaster surface in the void is presumed to be another factor in the size of nodules formed.

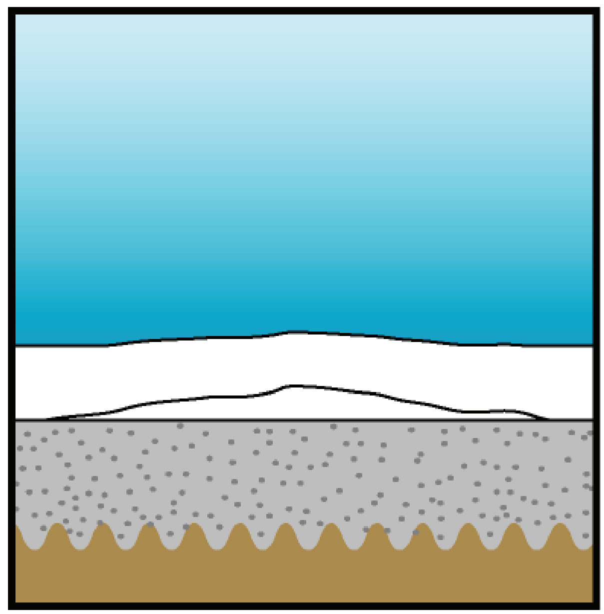
Other industry opinions:

1. It has been argued that there can be another type of nodule, not associated with cavities in the plaster. This is referred to by some as the "aggressively leached" type of nodule. We have for some time, and especially over the past 6 months, made a practice of inspecting a large number of pools drained for replastering, and of cutting out any unusual specimens, including calcium nodules. Every nodule we have found has been associated with either a void, or a check crack of significant capacity and character to isolate water and contain the reactions described above. As a result of our theories, our testing, the findings of the tests, and the lack of a physical demonstration of this type of nodule, we are of the opinion that this theory is erroneous.
2. There is a desire on the part of some (such as Jon Dongell of Precision Pool Plastering) to standardize the terminology used in the pool industry with the terminology used in the cement industry, in order to better gain from their research, and to be in a better position to share with them what we find in pools. We share this

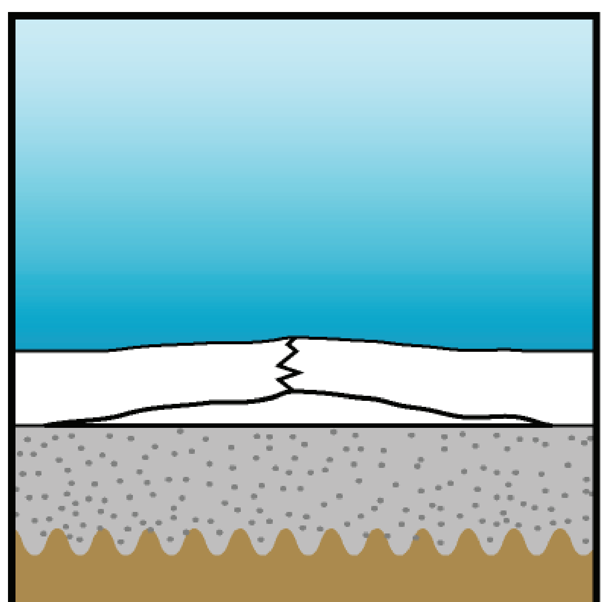
1. Under normal conditions, plaster is bonded to the gunite substrate. Calcium hydroxide bleed-off from the plaster surface dilutes into the pool water and is converted to soluble calcium bicarbonate. Continuous "rinsing" of the hydroxide bleed-off by the circulating pool water, as well as normal pool maintenance (such as brushing), prevents a buildup of high pH material on the plaster surface.



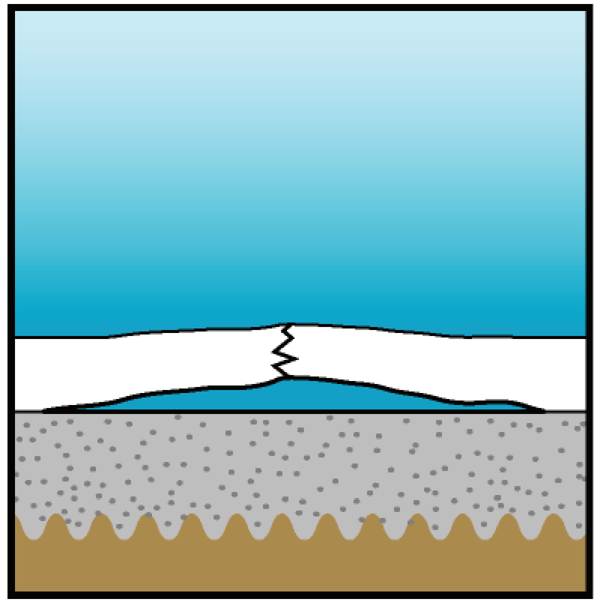
2. Sometimes, an air cavity can be formed between the gunite and the plaster. This is referred to as "delamination" and the cavity is referred to as a "void." As long as the void is not connected to the surface of the plaster, the fact that the void even exists may not be known. Unless the plaster completely separates from the surrounding plaster, creating what is referred to as a "pop–off," this is not considered by the plaster industry as a defect.



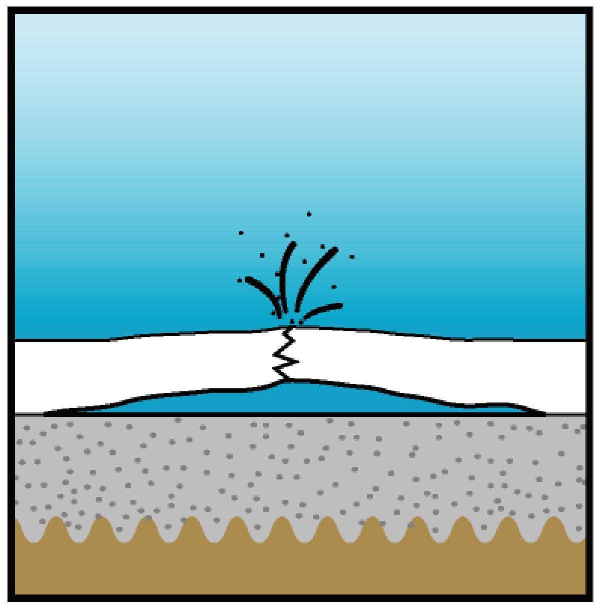
3. In some cases, however, the void is connected to the surface by a small pinhole or hairline crack.



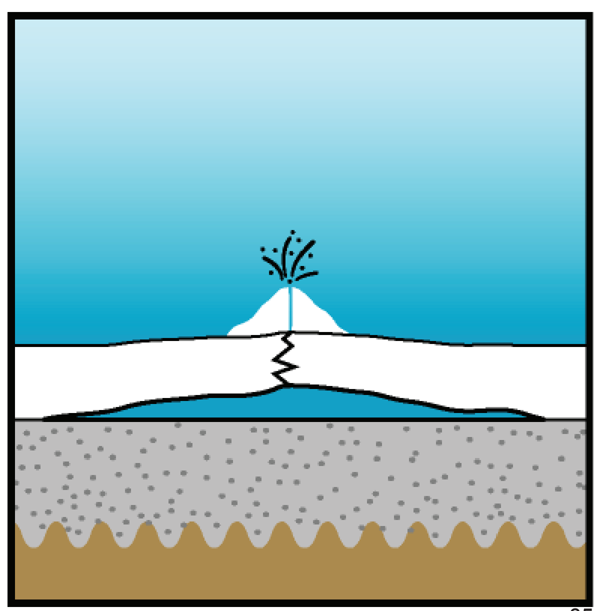
4. Gradually, water from the pool penetrates the void via the hole or crack, and creates a localized chemistry environment completely separate from the water balance in the pool. As calcium hydroxide bleeds into the void water it creates a calcium–rich, high pH solution like a little "calcium/pH factory" beneath the plaster surface. The pinhole or crack is not of sufficient size to create a rinsing effect like that going on at the plaster surface.



5. Interior pressure generated by the "calcium/pH factory" pushes a "plume" of high pH, calcium hydroxide–rich water out the "smokestack" or crack/perforation in the plaster.



6. As the plume solution comes in contact with the pool water at the plaster surface (which, if balanced, is bicarbonate-rich because of the alkalinity and balanced pH) the material is converted to the carbonate form, and builds up a "slag pile" of calcium carbonate around the exit point. This point has been referred to as a "point of attachment" but could more properly be referred to as a "point of hydroxide egress" or "calcium supply point."



desire, as long as the terms adopted accurately describe phenomena common to both industries. Dongell mentions, as an example, adopting the term "efflorescence" rather than the term "nodule". If it can be shown that the efflorescence observed and referred to in cement literature is the same as the nodules we are discussing, i.e. the same causative factors, chemical reactions, and resultant conditions as pool nodules, then we would favor adopting the term. However, we do not favor adopting the term until the determination is made as to whether they are the same phenomenon. Premature adopting of the term could result in misdirection should it turn out that the two are separate phenomena.

About the Authors

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 past president of the National Association of Gas Chlorinators, and the editor of the *Journal of the Swimming Pool and Spa Industry*.