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Elucidation of Brown Stains in Wellness Center Pools

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Abstract

The Sentara RMH Wellness Center (Harrisonburg, VA) is experiencing the formation of persistent brown stains on the plaster bottoms and walls of the saltwater swimming pools. Staff has previously removed the stain by scrubbing with muriatic acid. However, even with the re-plastering of the pools, the stain has returned. The goals of this project are to identify the chemical constituents of the stain, the source(s) of the stain and to recommend possible mitigative strategies. The chemical components of the water and stains were evaluated with a variety of methods, including commercial stain identification products, Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) and Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS). The composition of the stain was determined to be a combination of copper and iron. The source of the stain is thought to be corrosion of heaters and associated plumbing. Low pH and calcium hardness are contributors to corrosion, pitting, and stain formation.

Key Words: Stain Identification, Saltwater Pools, Water Chemistry

1. Introduction

1.1. Sentara Rockingham Memorial Hospital (RMH) Wellness Center

The Sentara RMH Wellness Center (Harrisonburg, VA) is a facility dedicated to health maintenance and improvement. The amenities of the wellness center include indoor and outdoor tracks, cardio and strength equipment, educational activities, saunas, and pools. The Wellness Center has three pools: the hot tub, the warm pool (23,000 gal, 90° F), and the fitness pool (104,000 gal, 65° F). All of these pools are heated and chlorinated separately. The hot tub is surfaced with tile, while the warm and fitness pools are surfaced with plaster.

The pools were built in 1997 and filled with tap water from the Harrisonburg City Municipal Potable Water Supply. Disinfection was achieved by the periodic manual addition of sodium hypochlorite. In 2008, the warm and fitness pools were filled with salt (NaCl) water. This was done so that disinfection could be accomplished by an automated electrolysis process that generates hypochlorite from the chloride ions of the salt water.

In 2014, a brown stain became apparent on the plaster pool bottoms and walls (Figure 1). In 2016, the pools were washed and re-plastered. Since 2016, the stain has reappeared and darkened with time. Along with the development of the brown stain erosion and pitting of the plaster has been observed.



Figure 1. The fitness pool at Sentara RMH Wellness Center.

1.2. Water Chemistry

1.2.1. chlorine

In most chlorinated pools, hypochlorous acid (HOCl) is the sanitizing agent¹. In freshwater pools, hypochlorite ions (OCl-) may be introduced as either sodium, lithium, or calcium hypochlorite salts² (1). Freshwater pools may also be chlorinated by purging chlorine gas (Cl₂) in the water to form hypochlorous acid (3). In saltwater pools, chlorine gas may be generated by electrolysis (4) to form OCl- (5), then HOCl (2).

Control of acidity (H⁺) and basicity (OH⁻) is critically important in the disinfection of pools. The concentrations are generally monitored electrochemically and recorded as pH (6). The autoprotolysis reaction of water (7, $K_w = 1.00 \times 10^{-14}$, 25° C) indicates that when [H⁺] = [OH⁻], the value for pH = 7.00. Values for pH>7 have greater concentration of OH⁻ and are basic, while pH<7 are acidic with greater concentration of H⁺. The pH values for pool water must be adequate to form OCl⁻ in the base electrolysis (5) process, but low enough for HOCl formation (2). Thus pools are typically kept near pH 7.4, which is close to the pK_a value for HOCl. Lower pH values would yield proportionally more HOCl, but have a secondary effect of dissolution of metal fixtures and plumbing and the degradation of plaster in the structure of the pool. Feed water supplied to fill pools is typically treated with muriatic acid (31% HCl) to reduce pH or carbonate salts (e.g. NaHCO₃, Na₂CO₃) as needed to raise pH to the target value.

$$NaOCl (aq) \rightarrow Na^{+} (aq) + OCl^{-} (aq)$$
(1)

$$\mathrm{H}^{+}\left(aq\right) + \mathrm{OCl}^{-}\left(aq\right) \leftrightarrow \mathrm{HOCl}\left(aq\right) \tag{2}$$

$$\operatorname{Cl}_{2}(g) + \operatorname{H}_{2}\operatorname{O}(l) \longrightarrow \operatorname{H}^{+}(aq) + \operatorname{HOCl}(aq) + \operatorname{Cl}^{-}(aq)$$
(3)

$$2\text{NaCl}(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2\text{NaOH}(aq)$$
(4)

$$Cl_2(g) + 2NaOH(aq) \longrightarrow H_2O(l) + OCl^{-}(aq) + NaCl(aq)$$
(5)

$$pH = -\log[H^+] = 14.00 - \log[OH^-]$$
(6)

$$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$$
(7)

Electrolysis is the chemical process of employing direct electrical current to drive a nonspontaneous chemical reaction. Aqueous sodium chloride solutions in saltwater pools produce chlorine at the anode in a flow through cell with H_2 produced at the cathode (4). After electrolysis, the chlorine reacts with hydroxide ions to form hypochlorite ions (5), which may then form hypochlorous acid with hydrogen ions (2).

1.2.2. calcium hardness

Calcium hardness is a measurement of the dissolved calcium ions expressed as milligrams of dissolved calcium carbonate per liter. Routine monitoring of calcium hardness is important for pool management because the pool walls and bottom contain calcium carbonate. Though the solubility constant, K_{sp} , of CaCO₃ (8) is low, it is greater than zero, meaning that some will dissolve in water. The recommended range for pool water is between 200-400 mg/L. For the reduction or prevention of pitting and erosion of pool walls and bottom, calcium chloride (CaCl₂) may be added (9) to provide calcium ions that block the dissolution of plaster CaCO₃ (10). However, if there are no calcium ions in the water, the solid calcium carbonate will dissolve until it reaches equilibrium with the calcium ions and carbonate ions.

$$K_{sp} = [Ca^{2+}] [CO_3^{2-}]$$
(8)

$$\operatorname{CaCl}_2(aq) \leftrightarrow \operatorname{Ca}^{2+}(aq) + 2\operatorname{Cl}^{-}(aq)$$
 (9)

$$\operatorname{CaCO}_3(s) \leftrightarrow \operatorname{Ca}^{2+}(aq) + \operatorname{CO}_3^{2-}(aq) \tag{10}$$

1.2.3. pH

The recommended pH range for saltwater pools is between 7.4 and 7.6 for two reasons: to keep the plaster from dissolving and to keep the water safe for swimmers³. If pH is below 7.4, dissolved carbonate ions will react with hydrogen ions in the solution to form bicarbonate ions (11). This removes carbonate ions from the solution and therefore shifts the equilibrium of the calcium carbonate (10) and increases the solubility of the CaCO₃ in the plaster which leads to the degradation of plaster, as mentioned above.

$$H^{+}(aq) + CaCO_{3}(s) \rightarrow HCO_{3}^{-}(aq) + Ca^{2+}(aq)$$

$$\tag{11}$$

1.3. Staining

Brown staining of pool surfaces is commonly caused by organic matter, iron and copper, as explained in the following sections.

1.3.1. organic matter

Organic stains result from algae, dirt or leaves that have settled on the bottom of the pool⁴. Low chlorine levels can contribute to the accumulation of organic matter and vice versa. Chlorine levels will be depleted as hypochlorite oxidizes organic material, whereas organic material will accumulate rapidly if chlorine levels are too low to readily oxidize the incoming matter. Heavy wind or rain can cause organic matter, such as leaves and dirt to accumulate in swimming pools via runoff and displacement.

1.3.2. iron

Iron stains may be the result of iron compounds in pool chemicals, the corrosion pipes, fixtures and heaters. The stains occur when iron (II) ions are oxidized by oxygen in the water to iron (III) ions (12), which then react with hydroxide ions to form iron (III) hydroxide, which eventually precipitates as iron (III) oxide hydrate (13)⁵.

$$4Fe^{2+}(aq) + 4H^{+}(aq) + O_{2}(aq) \rightarrow 4Fe^{3+}(aq) + 2H_{2}O(l)$$
(12)

$$\operatorname{Fe}^{3+}(aq) + \operatorname{3OH}^{-}(aq) \to \operatorname{Fe}(\operatorname{OH})_{3}(s)$$
(13)

1.3.3. copper

Copper stains may originate from algaecides containing copper, corroding pipes and heaters. These stains can occur when aqueous copper (II) ions and hydroxide ions form copper (II) hydroxide ($Cu(OH)_2$) (14), a blue solid. The heating of copper hydroxide will yield the formation of copper (II) oxide (CuO) (15), a black solid.

$$\operatorname{Cu}^{2+}(aq) + 2\operatorname{OH}^{-}(aq) \to \operatorname{Cu}(\operatorname{OH})_{2}(s)$$
(14)

$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(l)$$
(15)

1.4. Onsite Stain Identification

There are a variety of commercially available products for identification of pool stains. These products generally include packets of chemical powders, sponges, wipes or solutions that the manufacturer provides for the user to follow a regimented set of instructions to identify the material in the pool stain. Usually manufacturers will provide limited information about the chemical composition of their products and treat them as "proprietary." One of such supplies is, "Jack's Magic Stain Identification KitTM" (JMSID) (Largo, FL) which is an example of the conventional approach to stain identification.

1.4.1. organic stain

Organic stains can be identified with the application of hypochlorite tablets or crystals to the area. The disappearance of the stain indicates that it was composed of organic material because as the hypochlorite ions are applied to the stain, hypochlorous acid forms, which will break down the stain if its components are organic.

1.4.2. iron stain

Iron stains can be identified with JMSID or with other chelating agents. JMSID can identify iron stains and scale. An iron stain is the precipitation of iron oxide and iron scale if the precipitation of iron oxide and calcium carbonate together such that the iron oxide is embedded in the calcium carbonate. Manually applying Jack's Magic Stain Solution #1 to the stain as instructed will identify the stain as iron if it is removed. Similarly, the application of Stain Solutions 1 & 2 will identify the stain as iron scale if it is removed. The chemical constituents of JMSID were elucidated in a separate project (Table I) to understand the process by which the stains are identified.

Table 1. The identities of each substance included in Jack's Magic Stain Identification Kit.

Stain Solution #	Name of Solution	Chemical Name	Chemical Formula
1	"Iron, Cobalt, and Etching Stuff"	Calcium ascorbate	$Ca(C_6H_7O_6)_2$
2	"Copper and Scale Stuff"	Sulfamic acid	H ₂ NSO ₃ H
3	"O ₂ Safe Shock"	Sodium carbonate	Na ₂ CO ₃

Stain Solution #1 contains ascorbate, which is a chelating agent for iron. Ascorbic acid has two pKa values (4.10; 11.79), one of which is below pH 7. This means that in neutral conditions, ascorbic acid is deprotonated once, giving rise to a negative charge on the oxygen it came from. The negative charge on the oxygen and the partial negative charge on the double-bonded oxygen allow the ascorbate ion to chelate iron (III) ions, which are present in iron (III) oxide (Figure 2).



Figure 2. An ascorbate ion chelates an iron (III) ion.

Stain Solution #2 contains sulfamic acid, which hydrolyzes in water (16) and can form sulfuric acid with the hypochlorous acid in the pool water $(17)^6$. Applying sulfamic acid to the stain will form sulfuric acid, which will reduce the concentration of carbonate ions, shifting the equilibrium of calcium carbonate so that the calcium covering the stain dissolves and the stain is exposed. The ascorbate is to be applied after the sulfamic acid, which will chelate the iron that was blocked by calcium carbonate formation.

$$H_2NSO_3H(aq) + H_2O(l) \rightarrow (NH_4)HSO_4(aq)$$
(16)

$$(NH_4)HSO_4(aq) + HCIO(aq) \rightarrow NH_2CI(g) + H_2SO_4(aq) + H_2O(l)$$
(17)

1.4.3. copper stain

Copper stains can be identified with two tests from JMSID. The first test involves the addition of Stain Solution #2 (sulfamic acid) to the stain. The removal of the stain indicates that copper is present. The addition of sulfamic acid to the pool water produces sulfuric acid, as mentioned above. The sulfuric acid will not only react with the calcium carbonate in the plaster, but also with copper hydroxide (18) and copper oxide (19) to form copper sulfate and water in both cases, thus dissolving the copper. This is a test for copper scale because it removes calcium carbonate and copper stains.

$$H_2SO_4(aq) + Cu(OH)_2(s) \rightarrow CuSO_4(aq) + 2H_2O(l)$$
(18)

$$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$$
⁽¹⁹⁾

An alternate test for copper can also be performed with Stain Solution #3 (sodium carbonate) and the sulfamic acid. The sodium carbonate raises pH and introduces carbonate ions in the water so that when the sulfamic acid is introduced and sulfuric acid is formed, the hydronium ions do not accelerate the dissolution of calcium carbonate, thus only dissolving copper hydroxide and copper oxide. This is a test for copper stains because the hydronium ions that accelerated the dissolution of calcium carbonate in the first test react with the carbonate ions to form bicarbonate (20) before affecting the equilibrium of calcium carbonate.

$$\mathrm{H}^{+}(aq) + \mathrm{CO}_{3}^{2-}(aq) \leftrightarrow \mathrm{HCO}_{3}^{-}(aq) \tag{20}$$

1.5. Laboratory Stain Identification

Stains can be identified with a variety of laboratory methods, including Inductively-Coupled Plasma – Mass Spectrometry (ICP-MS) and Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDS).

1.5.1. inductively-coupled plasma – mass spectrometry (ICP-MS)

Analysis with ICP-MS yields information about the trace elements present in the liquid sample. Essentially, the instrument breaks the components of the sample into atoms and counts the atoms by mass to measure concentrations of trace elements in parts per billion (μ g/L). Samples from the water columns of the wellness center pools could contain elements from the stain, such as iron or copper that could be detected with ICP-MS.

1.5.2. scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS)

Analysis with SEM-EDS provides physical characterization of a solid sample. With SEM-EDS, the solid sample is bombarded with electrons and the patterns of electron movement are monitored and translated into an image⁷. The image provides a visual representation of the surface of the material. While some electrons are reflected off of the sample, others are absorbed. The absorbed electrons may fall into a lower orbital and emit energy. Emitted energy is specific to each element, so the energy that is emitted is measured and the elements in the sample are identified in weight percentages. This provides compositional information about the solid sample.

1.6. Site-Specific Information for Wellness Center Pools

The warm and fitness pools are experiencing staining while the hot tub is not. The stained pools are surfaced with plaster and share a chlorination system. The hot tub is surfaced with ceramic tile and has its own chlorination system. Each pool has its own heating unit.

Since the development of the stain in 2014, several attempts have been made to remove the stain. The surfaces of the pools have been washed with muriatic acid (31% HCl) and ascorbic acid, both of which temporarily removed the stain. Currently, commercial water clarifier and metal treatment chemicals are being manually introduced to the pool water to manage the stain.

In 2016, the pools were washed with muriatic acid and re-plastered, but the stains reformed. In 2017, the pool filters were changed and eliminated as the metal source because the stain continued to darken. In 2018, management plans to clean and re-plaster the pool again.

2. Statement of Goals

Sentara RMH Wellness Center is experiencing a persistent brown stain on the floors and walls of their pools. The goals of this project are to identify the composition of the stain, the source of the stain, and recommend mitigative strategies.

3. Sample Collection

Representative samples were collected from Sentara Wellness Center on two occasions. On the first, water samples were collected for a screening analysis to determine the overall composition of the water (Table 2). On site, temperature and conductivity were measured with a conductivity meter and conductivity readings were later adjusted for conductivity at 25° C. Additional water samples were collected from WC2 and WC3 in glass BOD bottles with no air so that chlorine present in the sample would not dissipate. All samples were stored in high-density polyethylene bottles at 4° C in darkness.

Table 2. Descriptions and justifications of water sample locations in Wellness Center pools.

Sample ID	Location Description
WC1	Taken from the incoming water source, Harrisonburg city tap, to see if metals are entering the pool
WCI	through the incoming water
WC2	Taken from the middle edge of the fitness pool to see if there is a concentration of metals present
WC2	that could be causing the stain
wee	Taken from the middle edge of the warm pool to see if there is a concentration of metals present
WC3	that could be causing the stain
WC4	The stain was agitated with a scrubbing brush in an attempt to suspend the stain in solution and a
	sample of the suspended stain was collected to try to identify the stain

On the second visit, solid samples were collected from the sodium chloride used in the pool, the calcium chloride flakes, and the plaster from the walls and floor of the fitness pool. The sodium chloride and calcium chloride samples were collected to be tested as a potential source of the stain. The plaster was collected for analyses by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS), and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS).

4. Methodology

4.1. Water Analysis

All water samples were analyzed with an Inductively-Coupled Plasma Mass Spectrometer (Agilent Technologies 7800 ICP-MS) to determine the concentrations of various trace elements, including beryllium, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, molybdenum, cadmium, antimony, thallium, lead, thorium, and uranium. Certified standards were used for calibration⁸. Samples were filtered with 0.2 µm syringe filters (Fisher Scientific) before being analyzed with ICP-MS.

Concentrations of certain ions (chloride, nitrate, sulfate, sodium, potassium, magnesium, and calcium) were determined through Ion Chromatography (Dionex 3000 ICS). Samples were filtered with 0.2 µm syringe filters (Fisher Scientific) before being analyzed with IC.

The pH of each sample was measured in the lab with a pH meter. Alkalinity of each sample was determined with a titration using 0.0993 M HCl, titrated until approximately pH 4.0. Alkalinity was calculated in parts per million.

Chlorine concentrations were determined with an iodometric titration⁸. A 0.01015 M solution of sodium thiosulfate was used as the titrant and a starch solution was used as the indicator. Acetic acid was added to the water samples to maintain a low pH (3-4). In the acidic solution, hypochlorite ions interact with iodide and hydrogen ions to form iodine, chloride, and water (21). The resulting solution appears yellow due to the presence of iodine. Starch solution was added as an indicator that changed from dark purple to clear over the progression of the titration. This indicates the transformation of iodine to iodide, which also indicates the transformation of chloride to hypochlorite (21).

$$2\mathrm{H}^{+}(aq) + \mathrm{OCI}^{-}(aq) + 2\mathrm{I}^{-}(aq) \leftrightarrow \mathrm{CI}^{-}(aq) + \mathrm{I}_{2}(aq) + \mathrm{H}_{2}\mathrm{O}(l)$$

$$\tag{21}$$

4.2. Sodium Chloride Analysis

A sample of 1.0 g sodium chloride (Diamond Pure's Splash Ready Salt) was diluted to 100 mL with deionized water, filtered with a 10 µm syringe filter, and analyzed with the ICP-MS for trace elements.

The sodium chloride was also tested for sodium ferrocyanide with colorimetry. Standards of sodium ferrocyanide were prepared with reagent grade sodium chloride to generate a calibration curve. The addition of sulfuric acid and

ferrous sulfate heptahydrate in the presence of sodium ferrocyanide causes the formation of ferrous ferrocyanide, indicated by a blue color change.

4.3. Calcium Chloride Analysis

A sample of 1.0 g calcium chloride (Calcium Chloride Flakes, product of China) was diluted to 100 mL with deionized water, filtered with a10 µm syringe filter, and analyzed with the ICP-MS for trace elements.

The calcium chloride was also tested for sodium ferrocyanide with colorimetry. Sodium ferrocyanide standards were prepared with reagent grade calcium chloride to generate a calibration curve. The addition of sulfuric acid caused calcium sulfate to precipitate and the ferrous sulfate heptahydrate caused the formation of ferrous ferrocyanide, indicated by a blue color change. The prepared standards and calcium chloride sample were filtered with 10 μ m syringe filters before they were tested for absorbance to remove any suspended calcium sulfate that could interfere with absorbance readings.

4.4. Plaster Analysis

A dry sample of 0.392 g plaster (from Wellness Center) was dissolved with trace metal grade nitric acid, diluted to 50 mL with deionized water, filtered with a 0.2 μ m syringe filter (Fisher Scientific), and analyzed with ICP-MS for trace elements.

A large crystal of plaster was prepared for Scanning Electron Microscopy (Zeiss SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) with a coating of gold. The SEM bombards the sample with electrons and the secondary electron detector records the patterns at which the electrons are reflecting off of the sample or being absorbed by the sample and the patterns of electron movement are monitored and translated into an image. The EDS identifies elementspecific x-rays and relates them to the atoms from which they came and displays the percent weight of each element on the monitor.

The four tests with Jack's Magic Stain ID Kit were done on the plaster surface of the fitness pool. Sections of nylon material were filled with 20-25 g of each powder for each of the four tests and tied tightly. The nylon pouches were applied to four different areas of the stain according to the instructions of Jack's Magic. Additionally, chemicals associated with the identities of JMSID Stain Solutions were tested to confirm the identity of JMSID chemicals (Table 1).

5. Results

5.1. Jack's Magic Stain Identification Kit

The JMSID Kit tests showed the presence of copper and iron in the fitness pool stains (Table 3).

Table 3. Jack's Magic Stain Identification Results

Test #	Stain Solutions Used	Test for	Results
1	1	Iron, cobalt and etching	Positive
2	2	Copper scale	Positive
3	3 and 2	Copper	Positive
4	2 and 1	Iron scale	Positive

5.2. Water

The water analyses showed similar results among the pool water samples (WC2, WC3, & WC4) in all relevant parameters (Table 4). The pH of the fitness pool averages at about 6.90 while the pH of the warm pool is 7.24. ICP-MS analysis showed concentrations below detection limits for all trace elements except copper and aluminum (Table 5).

 Table 4. Key Water Chemistry Parameters

Parameter	WC1	WC2	WC3	WC4
рН	8.88	6.88	7.24	6.91
Alkalinity	26.9	74.3	75.2	73.4
Chloride	6.26	2909	2617	2776
Calcium hardness	19	200	292	194
Chlorine	0.63	3.48	3.53	Х

 Table 5. Key Trace Metals in Water Samples

Parameter (ppb)	WC1	WC2	WC3	WC4
27 Al	6.1	4.9	5.6	44.5
57 Fe	0.0	0.2	0.1	0.2
63 Cu	3.2	8.7	3.0	14.0

5.3. Salts

The analyses of the sodium chloride and calcium chloride salts with ICP-MS showed that trace amounts of these metals were below detection limits, or close to zero (Table 6). The bulk analysis of the plaster through ICP-MS shows the presence of iron (17 ppb) and copper (89 ppb) (Table 6).

Parameter (ppb)	Stained Pool Plaster	Calcium Chloride Flakes	Diamond Pure Splash Ready Salt
57 Fe	17	0	0
63 Cu	89	0	0

5.4. Plaster

The surface analysis of plaster with SEM-EDS confirms the presence of iron and copper, however the SEM-EDS shows a different ratio of copper to iron on the surface than in the bulk sample (Table 7). SEM-EDS imaging also shows major differences between plaster (left) and tile (right) surfaces (Figure 3).

Table 7. Elemental Weight Percentages of Key Elements in Plaster Samples

ID	Stained Pool Plaster	Unstained Pool Plaster
% Fe	1.5	0.3
% Cu	1.0	0.0



Figure 3. SEM imaging of a stained plaster sample (left) and an unstained ceramic tile obtained (right) at 10 μm. The unstained ceramic tile was obtained from and area of the building uncontaminated by the stain.

6. Conclusion

From the ICP-MS, SEM-EDS, and JMSID results, the identity of the stain was determined to be copper and iron because each analysis showed the presence of both metals. Additionally, Jack's Magic Stain ID Kit indicated the presence of scale, which is the precipitation of calcium carbonate along with the precipitation of the stain.

The stain develops on plaster surfaces rather than ceramic tile surfaces. One of the reasons for this is because on the plaster surface (Figure 3, left), there is more surface area and more nucleation sites than there are on the tile surface (Figure 3, right). With less sites to anchor to and increased water flow due to the hot tub jets, the stain does not settle on the tiles in the hot tub.

The exact source of the stain could not be determined through the previous tests. However, some sources were eliminated. ICP-MS results showed no trace copper or iron in the sodium chloride or calcium chloride, which eliminates them as the sources of iron and copper. Though the source cannot be determined absolutely, possible sources can be identified and removed. For example, the heaters, pumps, and metal pipes in the room with the chlorination system all show external signs of corrosion. The outer corrosion of the pipes indicates that there could be corrosion on the inside as well. To eliminate these as sources, the pipes, heaters, and pumps should be replaced in combination with well-maintained water chemistry parameters. This would eliminate corroded pipes as a source because maintaining the water chemistry properly would prevent interior corrosion of the pipes.

The cause of the outer corrosion of the pipe and fixtures is due to the fuming of muriatic acid. The muriatic acid is added directly to a reservoir in the same room as the chlorination system. The fumes from the muriatic acid corrode the floors and walls of the room, along with the fixtures of the chlorination system. However, the extent to which the muriatic acid penetrates the fixtures is not known.

The pH of the pool water is lower than the recommended range of 7.4-7.6. The pH is maintained at 7.0 which allows for excess hydronium ions to contribute to the dissolution of iron and copper in the pipes and metal fixtures. Keeping the pH at 7 also contributes to pitting in the plaster. The hydronium ions combine with carbonate ions to form bicarbonate ions, which decreases the concentration of carbonate ions, shifting the equilibrium of calcium carbonate towards the ions, causing the calcium carbonate to dissolve.

The pitting in the plaster is also caused by low calcium hardness levels. In the warm pool, calcium hardness levels are within range, unlike the fitness pool. The calcium levels in the fitness pool are below the recommended range, which means that there are not enough calcium ions dissolved for the calcium carbonate to be at solubility equilibrium, so the dissolution of calcium carbonate occurs.

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