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Original Article

Effect of excessive trichloroisocyanuric acid in swimming pool water on tooth erosion

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Abstract

The effect of chlorinated water on tooth erosion was studied. Tooth specimens were bathed in a pH cycling system of chlorinated water and artificial saliva under one of the following conditions: I) a 4 hour continuous cycle, and II) a 1 hour/ day cycle for 4 weeks. Each group was divided into four subgroups for testing in chlorinated water with pH of 2, 3, 4 or 5. Enamel loss and percentage of surface microhardness change (%SMC) were measured. After 4 hour, chlorinated water with pH 2, 3, 4 and 5 produced enamel loss of 1.4, 0.4, 0.0 and 0.0 micrometers, and %SMC was reduced by 57.2, 13.7, 2.9 and -0.2% respectively. After 4 weeks, erosion was recorded at 63.3, 1.0, 0.0 and 0.0 micrometers, and %SMC was reduced by 97.2, 52.1, 5.7 and 1.5%, respectively. The study revealed that the pH level of chlorinated water and the duration of exposure are important factors in enamel erosion.

Keywords: swimming pool water, tooth erosion, tooth hardness, trichloroisocyanuric acid

1. Introduction

Dental erosion is defined as a loss of dental hard tissue caused by acids acting on the tooth surface. This may be caused by a variety of factors including food, vomiting, gastroesophageal reflux, diet, medication, environment, or lifestyle (Zero, 1996). A recent study found that acidic swimming pool water is one of the causes of dental enamel erosion (Lussi, 2006). Additionally, several clinical reports have shown that swimming in pools with improperly maintained chlorination can cause enamel erosion (Savad, 1982; Gabai *et al.,* 1988; Geurtsen, 2000; Dawes & Boroditsky, 2008; Jahangiri *et al.,* 2011).

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Although a number of chlorination systems are used for swimming pools, previous clinical case reports focused on two types of chlorination which caused severe and rapid erosion of teeth. First, gas chlorination resulted in the formation of hydrochloric acid in water (Geurtsen, 2000). Second, excessive use of trichloroisocyanuric acid (TCCA) tablets caused cyanuric acid residue in water (Jahangiri *et al.,* 2011). TCCA is widely used as a disinfectant in swimming pools. When TCCA is added to the water, it produces hypochlorous acid (HOCl) and cyanuric acid. Hypochlorous acid is a weak acid which is not harmful to people and acts as a disinfectant. Cyanuric acid stabilizes chlorine in the presence of sunlight and thus extends the chlorine's life. Therefore, if TCCA is added excessively, after the chlorine has been used and degraded the cyanuric acid will still remain and accumulate in the water, causing the pool water to become acidic. When teeth come in contact with pool water while swimming, these

acids will react with the hydroxyapatite of the enamel and initiate the process of erosion.

The standard pH ranges of swimming pool water differ from country to country, for example: pH 6.5–8.5 in Italy, 6.5–8.3 in Germany, 7.2–7.8 in the UK, and 7.2–8.0 in Australia (Tachikawa *et al.,* 2002). The critical pH value for tooth enamel dissolution is 5.5 (Meurman & ten Cate, 1996). Chlorinated water is safe for tooth enamel if it meets accepted standards but if the pH of chlorinated water is less than the critical pH, tooth enamel will tend to dissolve. Several studies have reported pH values of swimming pool water which were lower than recommended levels. Gabai *et al.* (1988) found that the pH levels of 14 pools varied between 3.6 and 7.8. The pH of 60 outdoor swimming pools in South America varied between 4.5 and 9.6 (Martins *et al.,* 1995). About 31% of 139 swimming pools in Thailand were found to have a pH level below 5.5 (Chanduaykit *et al.,* 2005).

Many types of dietary acids have been investigated for their erosive potential; different types and concentrations of acid lead to different erosion rates of enamel (West *et al.,* 2000; Shellis *et al.,* 2010). However, although the association between swimming pools and tooth erosion is well known, few in vitro studies exist regarding the effects of chlorinated water on enamel surfaces. The lack of such information makes it difficult to carry out a tooth erosion risk assessment of low-pH swimming pool water.

In our recent study (Chuenarrom *et al.,* 2010), where enamel specimens were soaked in chlorinated water with pH 3.85 and pH 2.91 for 1 h, we found that enamel loss was 1.4 mm and 7.0 mm, respectively. This result caused us to be quite concerned, as the water was sampled from public swimming pools. However, these results could not accurately indicate the enamel loss due to chlorinated water because teeth were bathed in pool water for 1 h without pH cycling between chlorinated water and saliva. During swimming, remineralization of teeth can occur by continually being bathed in natural saliva, which may reduce the erosive potential of chlorinated water.

The purposes of this study were to evaluate the effects of pH levels of chlorinated (TCCA) water and duration on tooth enamel loss and hardness. This may contribute to an enhanced understanding of the erosive potential of excessive trichloroisocyanuric acid in swimming pool water on enamel surface.

2. Materials and Methods

Eighty human premolar teeth were selected from a collection of teeth which had been extracted as part of routine dental treatment in a local dental clinic. The inclusion criteria for the study was that the teeth have healthy enamel and an absence of cracks. The protocol for collecting the extracted teeth was approved by the human research ethics committee of the Faculty of Dentistry, Prince of Songkla University. The sample size $(n=10)$ for each treatment in this study was calculated from the previous study (Chuenarrom *et al.,* 2010) that after 1 h immersion in pool water with pH 2.91 and 3.75, the mean erosion depth of enamel was 7.0 and 1.4 micrometers with a standard deviation of 1.0 micrometers. A sample size calculation in each group was based on having 80% power of test at α = 0.05.

Each tooth was embedded in a rectangular acrylic resin block; the outer surface of each side of the block was ground flat using a 320-grit silicon carbide paper until the enamel was exposed. This was followed by grinding with 600- and 1200-grit silicon carbide paper under tap water, and polishing with a 1 mm diamond suspension to produce an optically flat area of enamel approximately 2×2 mm². All specimens were evaluated for initial hardness using a Vickers microhardness tester (HM-211, Mitutoyo Corp., Kanagawa, Japan) under a load of 100 g for 15 s. Half of the exposed enamel surface was designated as the reference area and protected with nail varnish, while the other half of the enamel surface was designated as the test area.

Four different samples of chlorinated water with pH 2, 3, 4 and 5 were prepared from a mixture of TCCA tablets and tap water. The pH of the chlorinated water was measured using a pH meter (pH900, Precisa Gravimetrics AG, Dietikon, Switzerland). The artificial saliva used in this study was similar to that described by McKnight-Hanes and Whitford (McKnight-Hanes & Whitford, 1992).

Eighty specimens were divided into two groups. The first group was randomly distributed into four subgroups ($n =$ 10) for testing in chlorinated water at four different pH levels in a pH cycling system for 4 hours. The hardness and erosion depth of specimens were measured every hour to monitor changes of the enamel surface. The second group was distributed similarly to the first group, but subgroups were tested in a pH cycling system for 1 hour per day over a period of 4 weeks. After each cycle, specimens were immersed in artificial saliva and incubated in a 37ºC oven. The hardness and erosion depth of specimens were measured every week.

The automatic pH cycling appliance was constructed to simulate the changes of pH in the mouth while swimming. The system was comprised of demineralization and remineralization (de-min and re-min) solution tanks, a sample container and a timer control box. Each timer was used to control the release of the required volume of solution from the de-min or re-min tank into the sample container; it also controlled the draining of solution from the sample container. The automatic procedure of the appliance began with 50 ml of chlorinated water in the de-min tank being released into the sample container to immerse the specimens for 1 min before draining out from the sample container. Next, 50 ml of artificial saliva in the re-min tank was released into the sample container to immerse enamel specimens for 5 min before draining out. The cycle was conducted until 1 hour was complete; then the nail varnish protecting the reference area was removed. The specimens were washed with tap water and air-dried for 15 min. Changes of the enamel surface were evaluated with a Vickers microhardness tester, a profilometer (SE-2300, Surfcorder, Kosaka Laboratory Ltd., Tokyo, Japan)

and a measuring microscope (MM-400, Nikon Corp., Kanagawa, Japan).

The percentage of surface microhardness change (%SMC) was calculated from the difference between the baseline Vickers microhardness value (W_0) and the microhardness value after testing in a pH cycling system $(HV₁)$: %SMC = $100 \times (HV_0 - HV_1)/HV_0.$

Enamel loss was measured using a contact stylus profilometer with a 5 mm radius stylus tip under a 4 mN load. The stylus traveled perpendicular to the specimen surface with a velocity of 0.5 mm/sec across the reference and tested areas. The differences in height in relation to the reference and tested areas were measured and averaged. A photograph of the enamel was recorded to verify the quantitative results, using a measuring microscope at $500\times$ magnification.

Repeated measures analysis of variance were used to investigate statistically significant differences among different treatment groups over time, followed by a Tukey HSD test in order to determine which groups differed from each other. The level of significance was set at $p<0.05$.

3. Results

The average baseline microhardness value of all specimens in this study was 356.7 ± 22.8 kg/mm². The experiment conducted for 4 hours in a pH cycling system is summarized in Table 1. Enamel softening and loss occurred in chlorinated water with a pH less than 5. However, the profilometer could not detect enamel erosion in chlorinated water with a pH greater than 4, whereas the microhardness test could detect %SMC of enamel which was reduced by 0.9% after 1 h exposure to chlorinated water with pH 4. The microscope image (Figure 1 (a3)) demonstrates the change of the enamel surface exposed to chlorinated water with pH 4.

Table 2 summarizes the results of the 4-week experiment. It shows that chlorinated water with pH 2 and pH 3 caused enamel loss. The greatest erosion occurred in the specimen group exposed to chlorinated water with pH 2 for 4 weeks that microhardness value changed from 346.4 kg/mm² to 9.6 kg/mm² or hardness value reduced by 97.2% (%SMC), and enamel was eroded up to 63.3 mm. The microhardness evaluation revealed that chlorinated water with pH 2, 3 and 4 caused a decrease in enamel hardness. Microhardness data and microscope images (Figure 1 (B)) confirmed that chlorinated water with pH 4 affected the enamel surface, although the profilometer could not detect enamel loss in chlorinated water with pH 4. For pH 5, the results from all measuring methods were consistent: chlorinated water with pH 5 did not cause enamel erosion.

Repeated measures ANOVA revealed significant differences (p<0.05) between treatment groups. Tukey's multiple comparison in Table 1 and 2 showed that enamel erosion depended on the pH level of chlorinated water and contact time.

4. Discussion

TCCA was chosen for this study because it is commonly used in smaller pools (Jahangiri *et al.,* 2011), and in many countries (Tachikawa *et al.,* 2002). After hydrolysis in water, TCCA is converted to HOCL, which has strong microbial activity. The hydrolysis by-product, cyanuric acid, acts as a stabilizer and prevents conversion of HOCL into hypochlorite ion (OCL) owing to sunshine and heat, which

Table 1. The mean (standard deviation) of enamel loss and percentage of surface microhardness for chlorinated water with different pH values in a pH cycling system of 4 h

Measure and pH of chlorinated water	1 h	2 _h	3 _h	4 h
Enamel loss (μm)				
pH2	$1.3(0.2)^{a}$	$1.3(0.4)^{a}$	$1.3(0.3)^{a}$	$1.4(0.6)^{a}$
pH3	0.0(0.0)	$0.2(0.06)^{A}$	$0.3(0.13)^{Bb}$	$0.4(0.12)^{Bb}$
pH4	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
pH ₅	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
$\%$ SMC				
pH2	$52.7(5.3)^{a}$	$56.4(5.9)^{a}$	$55.0(10.8)^{a}$	$57.2(8.9)^{a}$
pH3	2.3(5.4)	$12.8(4.7)^{Ab}$	$13.4(3.6)^{Ab}$	$13.7(2.8)^{Ab}$
pH4	0.9(3.0)	2.5(3.4)	2.0(4.8)	2.9(5.1)
pH ₅	$-0.1(5.1)$	$-1.2(5.6)$	$-0.5(2.9)$	$-0.2(2.6)$

Groups in each row of enamel loss or %SMC with same capital case letters were not different by Tukey's multiple comparison of α < 0.05. Groups in each column of enamel loss or %SMC with same small case letters were not different by Tukey's multiple comparison of α < 0.05.

Table 2. The mean (standard deviation) of enamel loss and percentage of surface microhardness for chlorinated water with different pH values in a pH cycling system of 1 h/d for 4 weeks

Measure and pH of chlorinated water	1 week (1 h/d)	2 weeks (1 h/d)	3 weeks (1 h/d)	4 weeks (1 h/d)
Enamel loss (mm)				
pH2	$6.5(1.5)^{a}$	23.5 $(4.3)^{Aa}$	49.0 $(4.7)^{Ba}$	63.3 $(8.0)^{\text{Ca}}$
pH3	$0.6(0.2)^{A}$	$0.9(0.3)^{AB}$	$1.0(0.4)^{B}$	$1.0(0.2)^{B}$
pH4	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
pH5	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
$\%$ SMC				
pH2	$54.8(11.7)^{a}$	94.3 $(2.8)^{Aa}$	93.5 $(3.5)^{Aa}$	$97.2(0.8)^{Aa}$
pH3	$24.9(11.0)^{b}$	36.6 $(11.0)^{Ab}$	47.2 (9.4) ^{ABb}	52.1 $(7.1)^{Bb}$
pH4	2.7(4.3)	3.2(3.8)	8.4(6.7)	5.7(6.4)
pH ₅	$-0.3(4.5)$	1.5(5.4)	2.5(4.8)	1.5(3.4)

Groups in each row of enamel loss or %SMC with same capital case letters were not different by Tukey's multiple comparison of α < 0.05. Groups in each column of enamel loss or %SMC with same small case letters were not different by Tukey's multiple comparison of α < 0.05.

Figure 1. Microscope images showed changes on the exposed enamel surface, (A) after pH cycling experiments for 1 h, (B) after pH cycling experiments of 1 h/d for 4 weeks (upper half of each image is the reference area, lower half is the tested area).

has low microbial activity. Cyanuric acid also decomposes to hydronium ion (H_3O^+) and cyanurate. High concentration of this H_3O^+ causes a decrease in pH level of pool water. Adding more TCCA in pool water in order to obtain high efficiency of disinfectant, without checking pH and chlorine level, causes a low pH of the water.

The automatic pH cycling appliance used in this study was designed to simulate pH changes in an oral environment while swimming. Enamel specimens were bathed in chlorinated water for 1 min to simulate swimming time for a distance

of 25–50 m; this was followed by 5 min of resting time in artificial saliva. This cycle was assigned from observing general swimming behavior in public pools. The appliance automatically controlled pH changes, simulating the natural conditions. It was designed as a replacement for the method in which specimens were alternately soaked (manually) in de-min and re-min solutions. Although the manual method was simple, the specimens needed to be washed with water before being immersed in the other solutions; otherwise the pH of the solution would change and would not simulate

the effects of chlorinated water and saliva on tooth enamel during swimming. With the automatic pH cycling appliance, when the chlorinated water that had bathed specimens was drained out, specimens were immediately bathed in artificial saliva.

Three measuring instruments were used to detect erosion. A microscope imaging (Figure 1) indicated the first sign of enamel erosion in qualitative measurement. The reference and tested areas of enamel surface in Figure 1A showed clearly as different colors at the first hour in the pH cycling system (except in $pH 5$) which is in accord with the quantitative data from microhardness test (Table 1). However, a profilometer could not detect enamel erosion at the early stage of enamel erosion.

Within the boundaries of the present study, the data in Tables 1 and 2 and Figure 1 indicate that pH 4 is the critical pH of chlorinated water for enamel erosion. In the early stage of erosion, enamel hardness decreased and could be monitored using a microscope or a microhardness tester. If erosion occurred continuously until the %SMC of enamel reduced about 10%, the profilometer could detect enamel loss of about 0.2 mm, and if the %SMC of the enamel reduced by more than 50%, erosion levels higher than 1 mm were detected.

The results indicated that the pH level of chlorinated water, frequency of contact, and duration time affected dental erosion. These parameters could be used to predict enamel erosion over long periods: for example, if chlorinated water with pH 3 eroded enamel by 1 mm after 4 weeks of swimming 1 hour/day, the enamel would erode approximately 12 mm in 1 year. Then in future years, the erosion might tend to be more than 12 mm per year because the softened enamel surface would accelerate enamel loss.

Chlorinated water with pH 2 was also investigated, although it seems very extreme for swimming pool water, because clinical studies of tooth erosion from swimming (Dawes & Boroditsky, 2008; Jahangiri *et al.,* 2011) found that rapid and severe erosion may result from pool water with a pH lower than 3. The present study showed that in a 1-week experiment, chlorinated water with pH 2 eroded enamel at approximately 10 times the rate at pH 3.

A previous study of enamel erosion from chlorinated swimming pools, which assigned conditions without using a pH cycling system, found that the %SMC of enamel decreased by 29% after a tooth was immersed in chlorinated water with pH 3 for 120 min (Kitsahawong *et al.,* 2003). This was similar to the present findings, where %SMC decreased by 37% after contacting chlorinated water with pH 3 for 112 min (or 14 hours in the pH cycling system). Saliva could not remineralize enamel during swimming in chlorinated water with pH 3 or lower because a lesion was formed; hence the chance for additional remineralization was lost. While chlorinated water with pH 4 and pH 5 softened the enamel surface in early weeks, the surface hardness tended to increase after 4 weeks (Table 2).

Dental erosion from chlorinated swimming pool water has been reported in many countries (Geurtsen, 2000; Kitsahawong *et al.,* 2003; Dawes & Boroditsky, 2008). Quality control of swimming pool water is a problem for pool operators because it requires knowledge of chemical control in order to correctly adjust pH levels. The addition of chlorine, regardless of the proper amount, results in residual acid in the water. The pH scale is logarithmic; each whole pH value below 7 is ten times more acidic than the next higher value. Hence, if pH values of pool water are 3 or 4, raising the pH up to 7.0 is very difficult and requires a great deal of alkalinity. The pH and free chlorine levels should be monitored closely.

5. Conclusions

The pH level of swimming pool water is an important factor that influences tooth erosion in swimmers. The frequency and duration of swimming are co-factors affecting faster tooth erosion. The critical pH of chlorinated water on enamel erosion may be lower than pH 5 and it is necessary to do further study for risk assessment of swimmers accurately. The results obtained in this study support previous clinical studies indicating that low pH pool water can cause very rapid and extensive dental erosion.

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