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ORIGINAL ARTICLE

On inhibition of dental erosion

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Abstract

Objective. To examine the erosion-inhibiting effect of different concentrations of hydrofluoric acid. ***Materials and methods.*** Thirty-six human molars were individually treated with 10 ml of 0.1 M citric acid for 30 min (Etch 1), acid was collected and stored until analysis. The teeth were randomly divided into six groups and then individually treated with 10 ml of one of six dilutions (from 0.1–1%) of hydrofluoric acid. The teeth were then again treated with citric acid (Etch 2). The individual acid samples from Etch 1 and 2 were analyzed for calcium by flame atomic absorption spectroscopy and difference in calcium loss was calculated. ***Results.*** The highest erosion inhibiting effect was obtained in groups with the highest concentrations of hydrofluoric acid, where the pH was lowest, below pKa of 3.17, thus the hydrofluoric acids being mainly in an undissociated state. ***Discussion.*** Diluted hydrofluoric acid is present in aqueous solution of SnF_2 and TiF_4 (which are known to inhibit dental erosion): $SnF_2 + 3H_2O = Sn(OH)_2 + 2HF + H_2O$ and $TiF_4 + 5H_2O = Ti(OH)_4 + 4HF + H_2O$. It is also known that pure, diluted hydrofluoric acid can inhibit dental erosion. Teeth treated with hydrofluoric acid are covered by a layer of CaF_2-like mineral. This mineral is acid resistant at $pH < 3$, because it was formed at this pH. ***Conclusion.*** The erosion-inhibiting effect is due to formation of an acid resistant mineral, initiated by tooth enamel treatment with hydrofluoric acid. Hydrofluoric acid is different in having fluoride as a conjugated base, which provides this acid with unique properties.

Key Words: *acid-resistant mineral, CaF2-like mineral, hydrofluoric acid, SnF2, TiF4*

Introduction

Stannous fluoride toothpaste has been on the market for a long time and the erosion inhibiting effect of SnF_2 is well established [1–5]. Titanium fluoride, TiF_4, can also inhibit dental erosion but is a purely experimental solution, which has still not reached the market [6–9]. Stannous tin and in particular titanium, being a transition metal, have high affinity for oxygen, which is a strong ligand for both metals. Fluoride is a less strong ligand. When stannous fluoride or titanium fluoride are exposed to water, the metals take up OH^- from water selectively and thereby produce an acidic aqueous environment, due to the relative increase in number of H^+ ions. This causes an immediate fall of the pH from 7 to 3 by tin (II) and to 1.5–2.0 by titanium, when clinically relevant concentrations of the metal fluorides are used. At the same time the fluoride originally bound in the metal fluorides is displaced from tin and titanium by the OH^- of water, as the oxide ion is the stronger ligand. The fluorides ions react with the protons of the aqueous environments, thereby forming a dilute hydrofluoric acid according to the reactions shown below:

$$SnF_2 + 3H_2O > Sn(OH)_2 + 2HF + H_2O$$

$$TiF_4 + 5H_2O > Ti(OH)_4 + 4HF + H_2O$$

$$HF + H_2O$$

It is remarkable that the erosion-inhibiting metal fluorides form diluted hydrofluoric acid when exposed to water. This is further supported by an interesting recent paper reporting that highly diluted hydrofluoric acid alone can inhibit dental erosion in clinical experiments [4]. In this case the hydrofluoric acid contained no metal ions, as the diluted hydrofluoric acid is acidic in itself and also provides fluoride ions. The metal ions obviously play a role in inducing an acidic aqueous environment, as shown above. It

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Table I. Reduction in solubility of human teeth ($n = 36$) treated with six different concentrations of hydrofluoric acid.

						Reduction		
pH	Group	HF cons %	F− cons M	1. Etch ppm Ca	2. Etch ppm Ca	%	± SE	Significantly different from: Group
3.22	A	0.1	0.05	138.23	69.88	47.64	4.32	All
3.20	B	0.2	0.10	228.22	23.21	89.89	0.87	A, E, F
3.17*	C	0.3	0.15	173.18	13.61	92.20	0.63	A
3.08	D	0.5	0.25	147.63	7.79	94.68	0.67	A
2.97	E	0.7	0.35	180.27	7.52	95.67	0.62	A, B
2.91	F	1.0	0.50	156.22	5.46	96.32	0.54	A, B

*3.17 = pKa of HF.

was previously believed that the metal ions played an important role in the erosion-inhibiting mechanism of the metal fluorides as they are retained on enamel surfaces. However, the observation that diluted hydrofluoric acid by itself, without metal ions, can still inhibit erosion, indicated that the role of the metals may be less important than previously thought.

The aim of the present study was to examine the erosion-inhibiting effect on 36 extracted human molars after their pre-treatments with six different concentrations of hydrofluoric acid, ranging from 0.1–1.0%, each concentration tested with six teeth. Furthermore, to measure pH of the six concentrations and to examine how the erosion-inhibition potential of these six concentrations relate to their pH.

Additionally, the aim was to identify undissociated [HF] and dissociated $[H^+][F^-]$hydrofluoric acid among the six different concentrations of hydrofluoric acids based on their individual pH levels and pKa of hydrofluoric acid (pH 3.17), and to approach the mechanism of action of the erosion-inhibiting effect by low concentrations of hydrofluoric acid.

Materials and methods

Extracted intact molars ($n = 36$) were obtained from the Department of Propedeutics Dental Faculty, University of Oslo. The teeth were thoroughly cleaned with pumice and stored in a humid atmosphere at 4°C, prior to use. The teeth were then cut at the collum and the crowns rinsed in tap water. When air-dried the cut cervical surfaces were covered by an acid-resistant nail varnish. The specimens were randomly separated into six groups ($n = 6$) and all teeth individually pre-treated in 0.1 M citric acid (10 ml, 30 min), representing Etch 1. The acid was collected and stored until analysis. The six different groups were then randomly designated to one of the following categories of treatment with hydrofluoric acid ranging from: A = 0.1%, B = 0.2%, C = 0.3%, D = 0.5%, E = 0.7% and F = 1.0%. Each tooth sample within each group was then individually exposed to 10 ml of the respective diluted solutions for 10 min and then rinsed in deionized water and dried. At this stage the HF treated samples were again exposed to 0.1 M citric acid for 30 min (Etch 2) as explained. The calcium release into the citric acid during Etch 1 and Etch 2 was determined for all individual samples using flame atomic absorption (Atomic Absorption Spectrometer, Model 3300 Perkin Elmer Analytical Instruments, Shelton, CA). Measurements were performed using an air-acetylene flame. Prior to analysis, $LaCl_3$ to a final concentration of 0.5% was added to each standard and sample to prevent chemical and ionization interference.

The amount of calcium released during Etch 1 was used as a measure of the 'normal' enamel dissolution in acid of each individual tooth and compared with the result of the very same tooth analyzed after the HF treatment (Etch 2). The pH of the original dilutions of Groups A–E, containing from 0.1–1.0% of hydrofluoric acids, had been previously recorded, using an Orion 4-Star Plus pH meter (Thermo Electron Corporation, Marietta, OH, USA).

The equation: $[F]\,[HF]\,10^{pH \div pKa}$ was used to identify the ratio of dissociated and undissociated hydrofluoric acid at different pH, by an alternative method.

Statistical analysis

The analysis of the data was performed using Sigma Plot® version 11 (Systat Software Inc, San José, CA). The raw data passed the Kolmogorov–Smirnov normality test. Mean values were calculated for each Etch for every group. Differences between Etch 1 and Etch 2 were analysed by paired *t*-test and differences were considered significant at the value of $p < 0.001$. Percent reductions in calcium solubility after treatment with hydrofluoric acid were also calculated from values of Etch 1 compared with Etch 2. Differences in percent reductions between groups were analysed using one-way ANOVA, with LSD multiple comparison test. Differences were considered significant at the value of $p < 0.05$ and shown in Table I.

Table II. Ratio of dissociated/un-dissociated hydrofluoric acid related to pH according to the Equation.

$(F^{-})/(HF) = 10^{pH \div pKa}$

pH	pKa	pH÷pKa	$10^{pH \div pKa}$	Ratio $(F^{-})/(HF)$
4.17		+1	10^{1}	10/1
3.17	3.17	0	10^{0}	1/1
2.17		−1	10^{-1}	1/10
1.17		−2	10^{-2}	1/100

Results

The results in Table I showed that the higher concentrations of hydrofluoric acid (Groups D, E and F) exhibited a superior erosion-inhibiting effect. It is also seen that the higher concentrations of hydrofluoric acids have the lowest pH levels. Group A represented the lowest concentration of hydrofluoric acid (0.1 %) and had at the same time significantly less effect on erosion inhibition than all the other concentrations. Notably, Group A exhibited a large and unique standard error (Table I). Group B, which contains a 0.05 M higher concentration of F^{-} and a 0.02 units difference in pH, compared with Group A, showed a considerable increase in erosion-inhibition (42.25%). The difference between Groups B and C, also 0.05 M in concentration of F^{-} and 0.03 in pH, only showed a slight (2.31%) difference in erosion inhibiting effect. The erosion inhibiting effects recorded by the high concentrations of HF (Groups D, E and F) were found to be 94%, 95% and 96%, respectively.

Table II shows the pH levels which were chosen to give simple logarithmic exponent values, to easily demonstrate the relationship between pH and the ratio of dissociated and undissociated hydrofluoric acids. The results showed that the undissociated molecules are found mainly below pKa (pH 3.17), whereas dissociated molecules are found mainly above that pH value.

Discussion

A focus on pH of the different solutions of hydrofluoric acid, as shown in Table I (Groups A–E), seems to be of significance, as this makes Table I almost self-explanatory. Group C represented the pKa of hydrofluoric acid (pH 3.17). By definition (Table II) the hydrofluoric acid solution contains equal amounts of dissociated and undissociated molecules at this pH. Correspondingly the solutions in groups D, E and F all had pH below pKa and were, thus, mainly in the form of undissociated [HF] hydrofluoric acid. Well above 90% reduction for all groups C–F, the erosion inhibiting effect seemed to increase evenly with increasing concentration and decreasing pH.

Regarding groups B and A, both exerting pH of the solutions slightly above pKa, it is interestingly noted that, while the inhibiting effect observed in group B was reduced evenly in correspondence with the lowering of hydrofluoric acid concentration and increase of pH as compared to the groups C–F, the effect was dramatically reduced in group A. One would have expected the difference in erosion inhibiting effect between groups B and A to be ~ 4.6% and not the surprisingly large 42.25% based on the difference in pH between these groups, respectively, and pKa. There is, thus, reason to assume that the effect relates to the properties of the undissociated [HF] molecules. It may be suggested that the reason for the fairly good effect in group B and relatively poor effect in group A, despite pH above pKa in both, could be that the concentration of hydrofluoric acid in group B (0.2% HF) was still high enough to provide a sufficient layer of erosion resistant [HF] molecules on the HF-treated teeth, while on the other hand the concentration in group A (0.1%) was not. It does not seem likely that the difference in effect between groups B and A is due to differences in pH, as this is very slight. It was furthermore observed (Table I) that the Standard Error of group A was extremely high compared with the other groups, which may indicate that the erosion inhibiting effect appeared close to being lost at this low concentration.

It appears that the 0.2% hydrofluoric acid solution (group B) represents the lowest concentration with a reliable anti-erosion effect. It is interesting to note that a recent clinical pilot experiment with hydrofluoric acid [4] used a concentration of 0.2%, indicating that the present *in vitro* experiments may have some clinical relevance.

Correspondingly, the small, undissociated molecule [HF] can penetrate human skin, whereas the charged, dissociated molecule [H+][F−] is unable to do so (but should indeed still be treated with respect). This implicates that undissociated molecules are very effective erosion-inhibitors, but at the same time may represent a health-hazard at high concentrations and at low pH. It takes undissociated [HF] to penetrate human skin, but it is the presence of F^{-} in the body fluids that may be fatal to the patient. F^{-} has high affinity for calcium and reacts with the essential Ca ions in the body fluids by forming CaF_2. However, the frequent and extensive use of the stannous fluoride-containing toothpaste (Crest, P&G) during the 1960s indicates that small volumes of SnF_2 with a pH ~ 3 may be safe. This toothpaste, which is available both in Europe and the US, can be used at the present time and can thus be used for inhibition of dental erosion. Clinical use of 0.2% aqueous solution of hydrofluoric acid for topical application, which has been used in short-term clinical trials [4,9], would need further clinical testing before general use can be recommended.

Table II shows that all concentrations of hydrofluoric acid contain both undissociated and dissociated species of molecules, the ratio being pH-dependent. At Log exponent 0, pKa (3.17), the ratio was 1/1 (i.e. equal amounts of dissociated and undissociated molecules). At pH 2.17, the Log exponent was −1 and the ratio 1/10, of which one part is dissociated and 10 parts mainly undissociated, whereas a log exponent of −2 gave a ratio of 1/100, involving one part dissociated and 100 parts undissociated molecules.

Undissociated [HF] molecules at pH 3 or lower are known to be small and uncharged, due to the electrostatic attraction between the proton and the F^-. It is known that undissociated [HF] molecules can cause deposition of acid-resistant calcium fluoride-like minerals if exposed to enamel. These molecules are split under such conditions, and the released H^+ atoms cause disintegration of tooth mineral, whereas its companion F^- atoms at the same time tend to repair this destruction by formation of CaF_2, as F^- has higher affinity for calcium than for a proton. As the undissociated molecules of hydrofluoric acid always provide equal numbers of H^+ and F^- atoms, this situation often leads to an equilibrium of reactions, as indicated above. Hydrofluoric acid is the only acid which has fluoride as its conjugated base, a fact which presumably causes the reactions described above. When dental enamel is exposed to undissociated hydrofluoric acid at pH 3 or below, the enamel starts to disintegrate, due to the low pH of the released protons. The reaction mentioned above is described in more detail in the following:

The first sequence of events involves reduction of phosphate molecules that are integrated parts of the solid enamel minerals to di-hydrogenphosphates (H_2PO_4) by the protons, to become a soluble phosphate species which is subsequently lost from the enamel surface [10]. The calcium sites on the enamel surface which were involved in the binding of the newly lost phosphate are thereby exposed and F^- from the same split molecules react with these calcium groups to form acid-resistant calcium fluoride-like minerals. The calcium groups are integrated parts of the solid mineral, whereas the F^- is supplied from the split molecules. Those calcium fluoride-like groups are acid-resistant because they were all formed at low pH [11]. This reaction seals the slightly damaged enamel surface and arrests further disintegration. The calcium fluoride-like structures are thus able to resist possible future erosion challenges at pH 3, as mentioned above. This reaction is shown by the formula below.

$$\mathrm{Ca_5(PO_4)_3(OH) + 11HF > 3(H_2PO_4)\uparrow}$$
$$\mathrm{+ H_2O + 5Ca > 5CaF_2 + H_2O}$$

Dental enamel contains proteins which represent 5–6% by volume [12], but contribute very little by weight. One class of proteins present in dental enamel is enamelins, which glue the enamel rods and also serve an important role during tooth development. These protein sites probably represent places where the protons can reach the dental enamel in depth, a phenomenon which can be observed when suitable morphological, technical methods are used [13].

Formation of fluorapatite was in the past thought to account for all aspects of the caries preventive effect of fluoride [14]. However, fluoridated toothpaste has been shown to be responsible for the marked improvement in dental health as experienced during the last 50 years in the industrialized world [15], and this effect is obviously local and not systemic, since it is evident also on erupted teeth. Thus, the caries inhibiting effect is dependent on the formation of calcium fluoride [16–18] and not by fluorapatite [10]. Reconsiderations concerning this important research field moves forward irrespective of concepts from the past (see Fejerskov [19]). Ögaard et al. [20] showed that even shark enamel, which contains almost pure fluorapatite, was demineralized in a human caries model. Ögaard [21] examined the properties of KOH soluble and KOH stable fluoride. Saxegaard and Rölla [22] examined fluoride acquisition on and in human enamel during topical fluoride treatment. Calcium fluoride-like minerals can thus form also at ‘ordinary’ pH levels if established caries preventive methods are used, including fluoride toothpastes, as discussed above. However capable of providing caries prevention, calcium fluoride formed under such conditions cannot cause inhibition of dental erosion, as it has not been formed at low pH [11]. The use of acidic solutions of sodium fluoride [23] has been shown to give a good caries preventive effect by adding hydrochloric- or phosphoric acid, but it is still unable to prevent or reduce dental erosion since undissociated hydrofluoric acid [HF] cannot be formed in acidified solutions of sodium fluoride, as shown by Hals et al. [24]. They reported that a solution of titanium fluoride (TiF_4) was able to protect root surfaces exposed to acid at pH 1, whereas APF (acid phosphofluoride, containing NaF) at the same pH was unable to do so. Larsen and Richards [25] concluded that fluoride is unable to reduce dental erosion from soft drinks.

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