STM JOURNALS

Research & Reviews: A Journal of Dentistry

ISSN: 2230-8008 (Online)
ISSN: 2348-9561 (Print)
Volume 15, Issue 3, 2024
September—December
DOI (Journal): 10.37591/RRJoD

https://journals.stmjournals.com/rrjod/

Research RRJoD

Influence of Acidic Naf-Hf Solution on Dental Minerals

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Abstract

The effect of solutions of sodium fluoride in hydrofluoric acid on the fluoride-dental minerals reaction system was investigated. The fluoride concentration in each fluoride solution was kept at 1.23% as the fluoride concentration in the acidulated phosphate fluoride solution at pH 3. The acidic sodium fluoride-hydrofluoric acid solutions with different contents of sodium fluoride and hydrofluoric acid were prepared. These solutions were added to synthetic powder hydroxyapatite and calcium hydrogen phosphate crystal, respectively, and then precipitated for 10 min at room temperature. Acidulated phosphate fluoride solution (pH 3.0) was used as a control fluoride solution. The results of the analysis showed that the CaF_2 content in the samples treated with acidic NaF-HF solution with relatively low hydrofluoric acid content was almost like that of the samples treated with acidulated phosphate fluoride. However, the CaF_2 content in the samples treated with acidic NaF-HF solution with high hydrofluoric acid content was higher than that of the samples treated with acidulated phosphate fluoride. It was found that the chemical reactivity of hydroxyapatite with fluoride solution was related to the content of hydrofluoric acid and the ionic atmosphere, that is, the higher the content of hydrofluoric acid and lower the ionic concentration, the higher the reactivity.

Keywords: Acidic sodium fluoride-hydrofluoric acid solution (ANHS), CaF_2, hydroxyapatite, fluorapatite, calcium hydrogen phosphate (burshite), chemical reactivity

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Received Date: October 03, 2024
Accepted Date: October 07, 2024
Published Date: October 29, 2024

Citation: Ki-Ho Rim, Mi Yong Kim, Mi Hyang Jong, So Yon Kim, Chol Ho Kim, Byong So Ri. Influence of Acidic Naf-Hf Solution on Solution on Dental Minerals. Research & Reviews: A Journal of Dentistry. 2024; 15(3): 27–37p.

INTRODUCTION

Currently, fluoride therapy is one of the most effective preventive methods in caries prevention. Attempts to prevent dental caries by applying high concentrations of fluoride to teeth have been made since the 1940s, with the development of various fluorides, such as 2% sodium fluoride solution, 8–10% tin fluoride solution, acidulated phosphate fluoride (APF) solution, 38% diammine silver fluoride solution, fluoride varnish, and fluoride-molybdate solution, which have been used as anticarious agents [1–10].

Among them, APF solution have been highly effective and have been studied for many years as a solution with the addition of phosphoric and hydrofluoric acids to enhance the effectiveness of sodium fluoride [11–14]. Since calcium phosphate was lost when enamel reacted with an acidic sodium fluoride solution, phosphoric acid was selected as the acid solution and the pH was lowered [15].

Fischer et al. reported that acidified fluoride increased enamel acid resistance and the effect

increased with lower pH [16]. Reported that the content of hydrofluoric acid was above 50% at pH 3 and 100% at pH 7 was present as fluoride ions [17]. However, it has been reported that this fluoride can cause artificial erosion of the enamel or discoloration of ceramic and resin fillers due to its acidic pH [17–19].

This composition of solution not only has the above disadvantages in clinical practice, but also has been reported that PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ ions, which are generated by the stepwise dissociation of phosphate, can negatively affect the chemical reactivity of fluoride ions, creating an anionic atmosphere with F^- ions [20].

To overcome this disadvantage of APF solutions, we have proposed a new fluoride solution consisting of sodium fluoride and hydrofluoric acid, and have demonstrated its anticarious effect clinically [21]. However, no reports have been published on the chemical reactivity of fluoride solutions consisting of sodium fluoride and hydrofluoric acid.

In this paper, we examined the chemical reactivity of the acidic NaF-HF solution to confirm that this solution is more chemically reactive than the APF solution with the same fluoride ion concentration.

MATERIALS AND METHODS

Materials

The calcium hydrogen phosphate ($CaHPO_4 \cdot 2H_2O$, 98.5%) was purchased from Merck company. Calcium nitrate (Ca $(NO_3)_2$, 99%, Merck company), ammonium hydrogen phosphate($(NH_4)_2HPO_4$, 98%, Merck company), and sodium hydroxide (NaOH, 99%, Merck company) were used to synthesize hydroxyapatite (HA).

The acidic NaF-HF solutions were prepared from sodium fluoride (NaF, 98%, Merck company), hydrofluoric acid (HF, 40%, Merck company), and distilled water.

APF solution was prepared by sodium fluoride, phosphoric acid (H_3PO_4, 85%, Merck company), hydrofluoric acid (HF, 40%, Merck company), and distilled water. The cow incisors were purchased from Songam Myonggi cattle farm, the DPRK.

All experiments were carried out using analytical grade chemicals.

The pH of the solution was measured using a pH meter (Testo 206 pH), the identification of the reaction products was performed using an X-ray diffractometer (D8 ADVANCE) and the determination was carried out using DIFFRAC pusl EVA software.

The surface morphology of the tooth enamel was observed using a scanning electron microscope (Quanta 200).

Methods

Fluoride-HA Reaction

HA synthesis

HA was prepared in powder form under atmospheric conditions through reaction of calcium nitrate with ammonium hydrogen phosphate by using a solution-precipitation method [22, 23].

The main chemical reaction involved in the synthesis of HA powder is well described by the following Equations (1) and/or (2).

$$10Ca^{2+} + 6HPO_4^{2-} + 2OH^- \Rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H^+ \quad (1)$$

$$10Ca^{2+} + 6H2PO_4^- + 2OH^- \Rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12H^+. \quad (2)$$

Calcium nitrate 4-hydrate (36.15 g; 98%, Merck PROLABO) dissolved in water (525 mL) was prepared. Ammonium hydrogen phosphate (12 g) dissolved in water (375 mL) was slowly added to the calcium nitrate solution with vigorous stirring. The solution was brought to pH 11 by adding concentrated sodium hydroxide solution. In consequence, the obtained precipitation was HA [24].

The precipitate was aged overnight at room temperature and was thoroughly centrifuged and washed with deionized water. The processes of centrifuging and washing were carried out three times. The resulting powder was dried in a freeze-drier system (Alpha 1-2 LD, Germany) for 10 h. Finally, the dried powder was calcined in an electrical box furnace at 10008C for 1 h after heating at the rate of 58°C/min in air.

Fluoride solution preparation

The APF solution was prepared as follows according to the method described in Reference [14]. The solution employed contained 1.23 percent fluoride, and 0.1M orthophosphoric acid. It was made in a polyethylene container by dissolving 2.000 g of sodium fluoride in 99.175 mL of 0.1 mol/L orthophosphoric acid and adding dropwise 0.870 mL of 40 percent hydrofluoric acid to make a final fluoride concentration of 1.23 percent. The pH of the solution was approximately 3, like that of stannous fluoride solutions used for topical applications.

Various sodium fluoride-hydrofluoric acid solutions were prepared by varying the contents of sodium fluoride and hydrofluoric acid as follows.

1. 2.000 g of NaF and 0.868 mL (0.330 g F) of 40% hydrofluoric acid were added to distilled water to give a total of 100.0 mL of acidic NaF-HF solution 1(pH 4.08).
2. 1.500 g of NaF and 1.461 mL (0.555 g F) of 40% hydrofluoric acid were added to distilled water to give a total of 100.0 mL of acidic NaF-HF solution 2(pH 3.72).
3. 1.000 g of NaF and 2.053 mL (0.780 g F) of 40% hydrofluoric acid were added to distilled water to give a total of 100.0 mL of acidic NaF-HF solution 3(pH 3.39).

Reaction between high concentrations of fluoride and HA

The above-prepared HA powders were manually milled by an agate mortar. In polyethylene containers, 300 mg of them were suspended in 40 mL of 1.23% acidic NaF-HF solution 1, 2, and 3 and 1.23% APF for 10 min, respectively.

The resulting product was centrifuged, washed, dried, and used as the analytical sample. All experiments were repeated three times.

Meanwhile, in the same way, 300 mg $CaHPO_4$ was also added to 40 mL of 0.123% each fluoride solution for 10 min, and the resulting product was centrifuged, washed, dried, and used as the analytical sample.

The prepared powders were measured by using Bruker AXS D8 ADVANCE X-ray diffraction (XRD) analysis of which 2θ was 0.02°/0.5 s, the scanning region was 20°~80°, had a CuKα1(λ=1.5406Å) controlled at 40 kV and 40 mA. The phase analysis of X-ray diffraction data was conducted by using EVA program, and FindIt program was used for the Rietveld refinement of ICSD (inorganic crystal structure database) database of the crystal structure by using TOPAS 3.0.

Scanning Electron Microscopy (SEM) of Tooth Enamel Surface Exposed to Fluoride Gel

1% subacidic NaF-HF gel containing 1.0 wt% of NaF and 1.447 mL of 40% HF per 100 mL gel (pH 5.67, Pyongyang Pharmaceutics Company, DPRK) and 1.23% APF gel (pH 4.0, A. R. Medicom inc., USA) were used. We have got the upper incisors of cow from Songam Myonggi cattle farm, and it is approved by the Ethics Board of Kaechon City People's Committee, DPRK.

The foreign bodies were removed from the crown of the cow incisors, demineralized with alcohol, and then divided into three specimens. Of these, each fluoride gel was applied for 4 min on the enamel surface of two specimens, respectively. After the remaining fluoride was completely removed by washing in running water, the samples were washed again with deionized water and dried.
The remaining one sample was used as a control.

All three specimens were then etched by immersion in 5M HCl for 10 s. They were washed with deionized water to remove the excess HCl completely and dried to give SEM samples

The samples were subjected to gold deposition (EMITECH K450X, England) and the surface was observed under an accelerating voltage of 10 kV by SEM (Quanta 200, Nederland).

RESULTS

Reaction Between Fluoride Solutions and HA

Qualitative Phase Analysis of Reaction Products

The results of XRD analysis of the samples exposed to each fluoride are shown in Figure 1. As shown in Figure 1, the diffraction lines of HA and CaF_2 were observed in all samples.

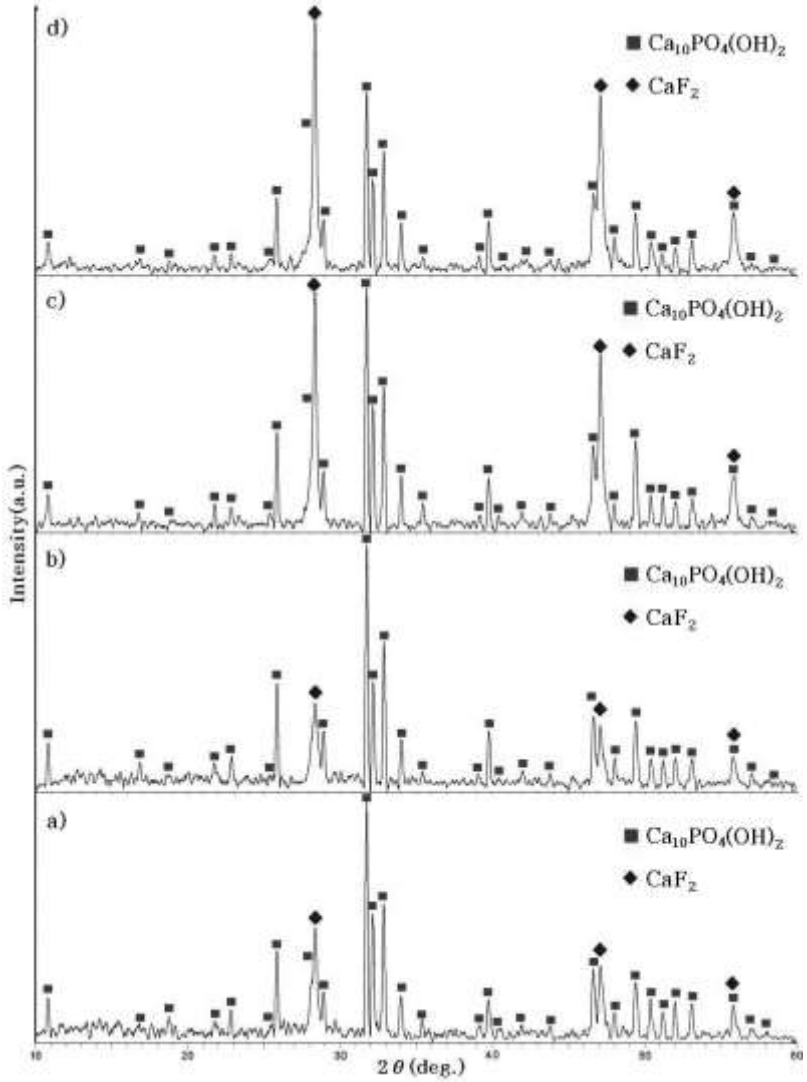

Figure 1. X-ray diffraction patterns of HA are treated with each fluoride solution.
(a: APF, b: NaF-HF 1, c: NaF-HF 2, d: NaF-HF 3).

Quantitative Phase Analysis of Reaction Products

The quantitative phase analysis of CaF_2 calculated by Rietveld XRD patterns is shown in Table 1. As shown in Figure 2 and Table 1, the CaF_2 content of HA treated with each fluoride solution was the highest in NaF-HF 3 and similar in APF and NaF-HF 1.

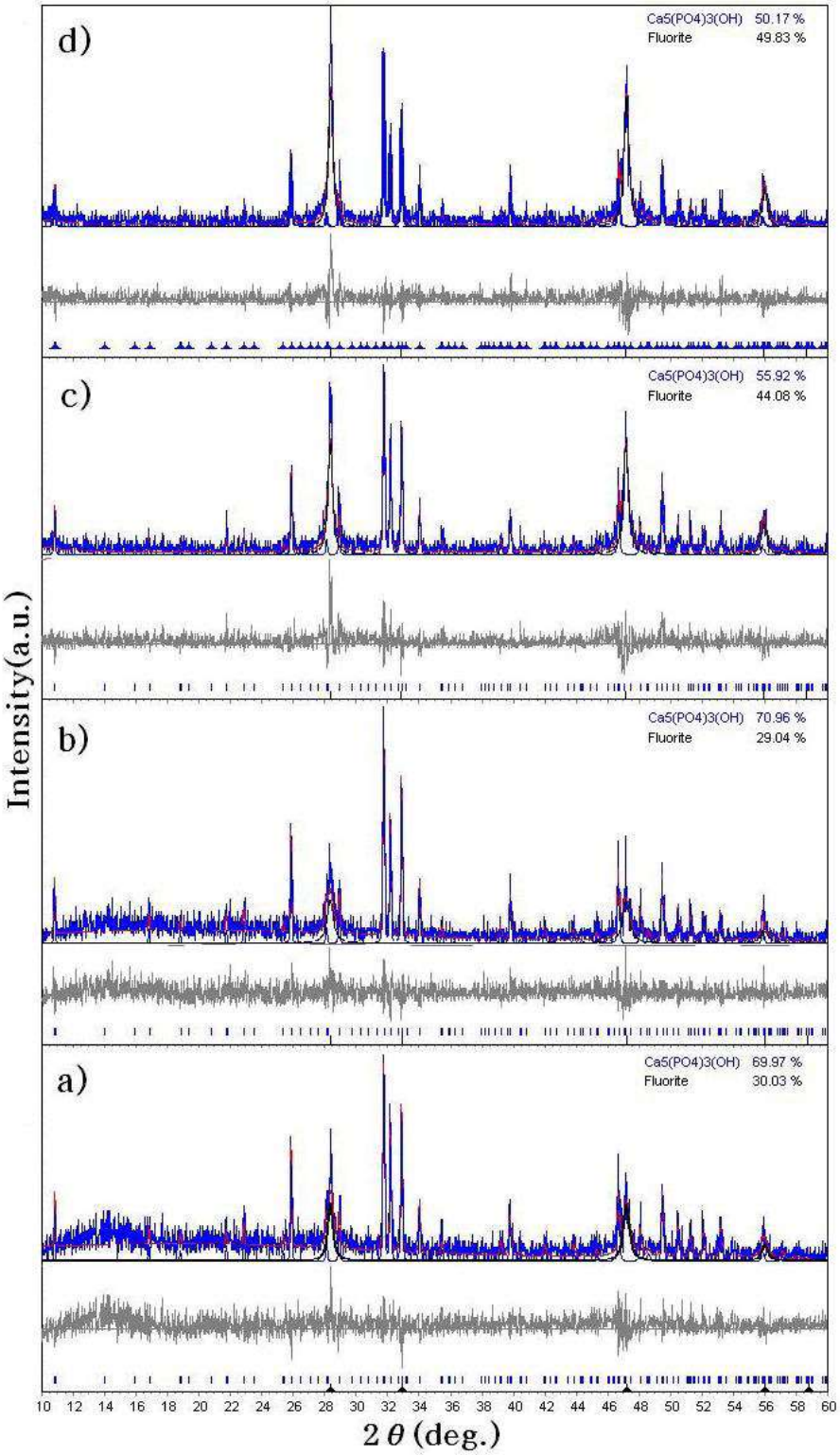

Figure 2. Rietveld XRD patterns showing calcium fluoride content of HA treated with each fluoride solution (a: APF, b: NaF-HF 1, c: NaF-HF 2, d: NaF-HF 3).

Table 1. CaF_2 content (by wt%) of HA is treated with each fluoride solution.

Fluoride	APF	NaF-HF 1	NaF-HF 2	NaF-HF 3
Content %	30.03	29.04	44.05	49.83

Reaction between Fluoride Solutions and $CaHPO_4$•$2H_2O$

Qualitative Phase Analysis of Reaction Products

The XRD results of $CaHPO_4 \cdot 2H_2O$ treated with each fluoride solution are shown in Figure 3. As shown in Figure 3, all samples exhibited $CaHPO_4$, HA, and CaF_2 diffraction lines.

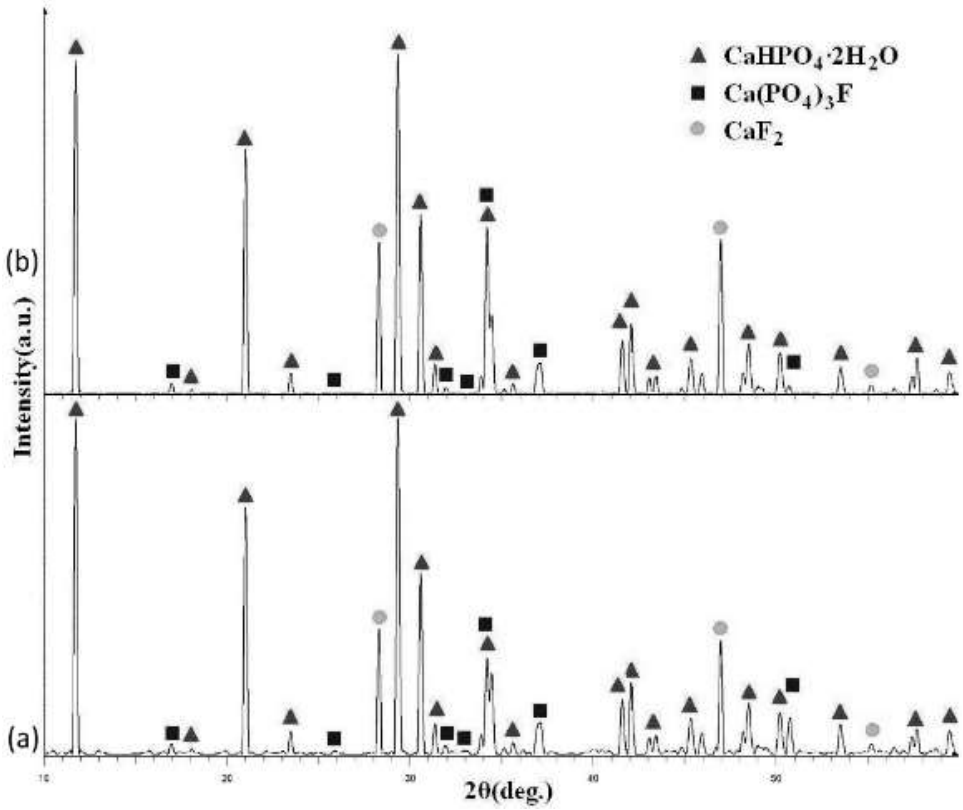

Figure 3. XRD patterns of $CaHPO_4 \cdot 2H_2O$ treated with each fluoride solution (a: APF b: NaF-HF 2).

Quantitative Phase Analysis of Reaction Products

The quantitative phase analysis of HA and CaF_2 calculated by Rietveld XRD patterns is shown in Table 2 and Figure 4. As shown in Table 2 and Figure 4, when $CaHPO_4 \cdot 2H_2O$ was treated with each fluoride solution, the CaF_2 and HA contents in the samples were higher in the NaF-HF2 solution related samples than in the APF treated samples.

Table 2. CaF_2 and HA contents (by wt%) of $CaHPO_4 \cdot 2H_2O$ treated with each fluoride solution.

Fluoride	APF	NaF-HF 2
CaF_2	9.54	15.87
HA	10.19	21.53

SEM of Tooth Enamel Surface Exposed to Acidic Naf-Hf Solution

Figure 5 shows SEM images of the tooth enamel surface treated with fluorides.

As shown in Figure 5a, after acid etching, the convex sides of enamel were exposed and the areas around it was found to be dimple due to the erosion of inorganic material, which was like that of the "honeycomb."

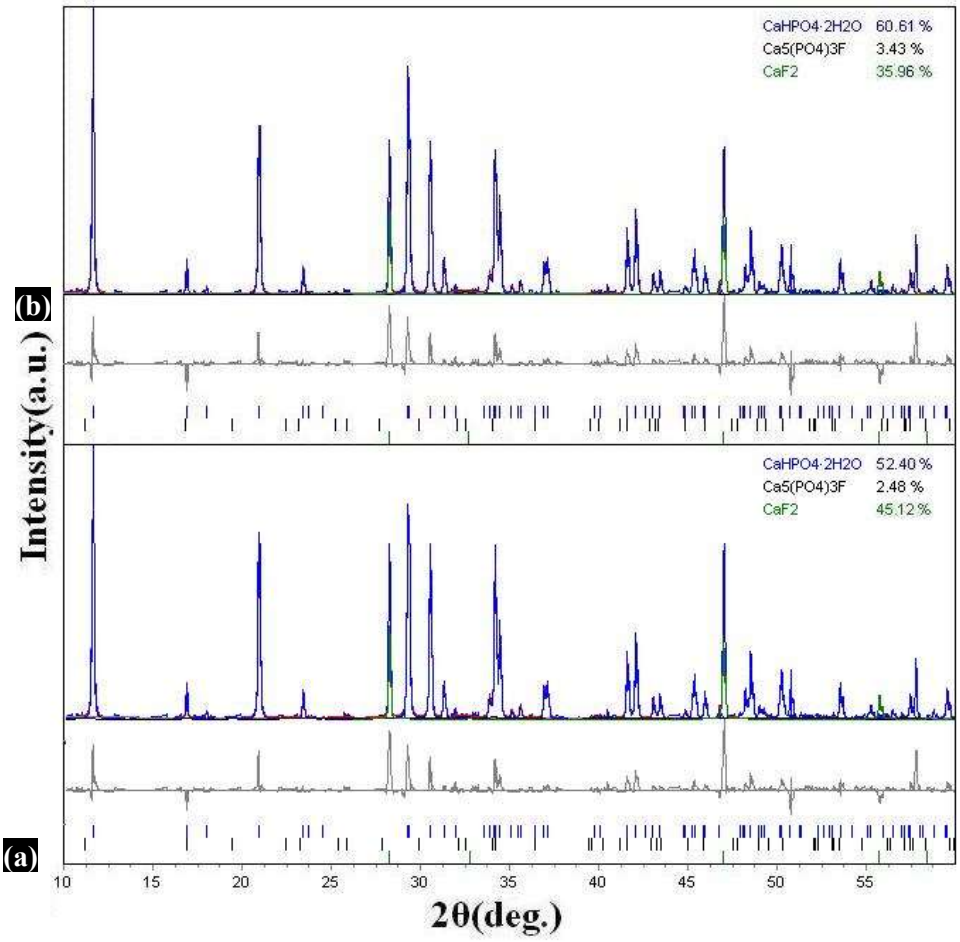

Figure 4. Rietveld XRD patterns $CaHPO_4 \cdot 2H_2O$ treated with each fluoride solution (a: APF b: NaF-HF 2).

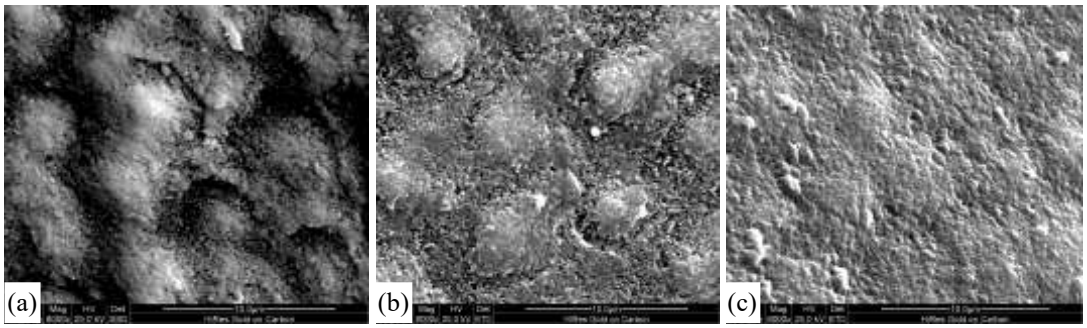

Figure 5. SEM images of enamel surfaces treated with 1.23% APF gel and 1.0% subacidic NaF-HF gel (SEM magnification: 6000×, a: contrast, b: 1.23% APF gel, c: 1.0% subacidic NaF-HF gel).

The erosional phase between the convex sides was obvious and the less eroded convex sides appeared to be frozen with snow on the surface. Thus, different convex surfaces with a dimple depth of about 5 μmwere observed to be continuous or independently present.

The enamel surfaces shown in Figure 5b and 5c were very similar.

In both figures, the eroded dimples were almost absent, and the "honeycomb" phase appeared to be noticeable only in some of Figure 5b; whereas in Figure 5c, a relatively weak erosive phase was seen, and the dimples showing them were traceable.

DISCUSSION

We note that the caustic of APF solution is in solution pH, and we examined whether any changes in chemical reactivity occur when the phosphate solution is not included.

The hydrofluoric acid contained in the fluoride solution causes an acid-based reaction with HA, the main component of dental enamel. The insoluble fluoroapatite formed then gives rise to acid resistance of dental enamel [11, 12] Hence, we believe that the content of hydrofluoric acid will have a great effect on the NaF-HA reaction system.

Therefore, the primary objective of our experiment was to find the composition ratio of sodium fluoride and hydrofluoric acid in NaF-HF solutions with higher chemical reactivity than APF solutions.

The fluoride ion concentration in each fluoride solution was kept at 1.23% as the fluoride concentration in APF solution (pH 3.0).

The acidic NaF-HF solutions were prepared by varying the contents of sodium fluoride and hydrofluoric acid differently. The content of sodium fluoride varied from 2% to 1% and the content of hydrofluoric acid from 0.33% to 0.78%.

The ratio of NaF to HF in the solution that produced more CaF_2 than that in the APF solution was set as the optimum composition ratio when they reacted with the synthetic HA and $CaHPO_4{\cdot}2H_2O$, respectively.

The formula for dental inorganic matter is $Ca_{10}(PO_4)_6(OH)_2$, but the apatite synthesized in aqueous solution under biotemperature conditions can be expressed as three molecules of $Ca_3(PO_4)_2$ and one molecule of $Ca(OH)_2$ in the condensed form $3Ca_3(PO_4)_2Ca(OH)_2$, which is a basic compound.

The reaction of acid with dental inorganic materials is described by chemical equation as follows:

$$3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 2H^+ \rightarrow 10Ca^{2+} + 6PO_4^{3-} + 2H_2O. \quad (3)$$

Thus, dental inorganic matter is dissolved in acid. However, the presence of fluoride in the reaction system is known to cause two different reactions between topically applied fluoride and tooth mineral [12].

When reacting with low concentration of fluoride solution, fluoride replaces hydroxyl groups in HA and forms fluoroapatite

$$3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 2F^- \rightarrow 3Ca_3(PO_4)_2 \cdot CaF_2 + 2OH \quad (4)$$

When reacting with high concentrations of fluoride solution, the calcium fluoride formation reaction is dominant

$$3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + 20F^- \rightarrow 10CaF_2 + 6PO_4^{3-} + 2OH^- \quad (5)$$

According to the experimental data, calcium fluoride was formed in samples treated with high fluoride concentration, and its content increased with increasing the content of hydrofluoric acid in the acidic NaF-HF solution. (Figures 1, and 2; Table 2) This indicates that the chemical reactivity of the fluoride solution is more dependent on the content of hydrofluoric acid than the fluoride concentration in the solution.

From Table 2, the chemical reactivity of both fluoride solutions with composition ratios of 1.5 g of sodium fluoride and 0.56 g of hydrofluoric acid, 1 g of sodium fluoride, and 0.78 g of hydrofluoric acid, respectively, is higher than that of the APF solution.

Caries lesions are inorganic substances called "caries crystals", which are beta-$Ca_3(PO_4)_2$(Whidlokite) and $CaHPO_4 \cdot 2H_2O$(Burshite) [23–25].

Thus, we have chosen $CaHPO_4 \cdot 2H_2O$ as a test sample and examined the chemical reaction products with fluoride solutions.

As can be seen in Table 2, the contents of calcium fluoride and fluorapatite, both of which characterize the chemical reactivity, were higher in the acidic NaF-HF solution 2 treated samples than in the APF treated samples.

The application of the acidic NaF-HF solution 2 to the dissolution product of apatite, $CaHPO_4$ 2H2O, resulted in CaF2 and FA and was highly reactive. Hence, it is expected that NaF-HF solution not only can have a caries progression-inhibiting effect but also has a high effect.

The chemical reactivity of the acidic NaF-HF solution was also observed on SEM images of the samples that were applied to the cow incisors.

As shown in Figure 5, the fluoride-treated tooth surfaces showed little change even after 5 M hydrochloric acid. The degree of surface modification was less in the acidic NaF-HF solution 2 treated samples than in the APF solution.

This indicates that the fast kinetics of the chemical reaction shown in Table 2 was reproduced by SEM on the enamel surface.

This phenomenon is expected to occur because the total fluoride content in the acidic NaF-HF and APF solution is the same, but the content of hydrofluoric acid is about 1.7 times higher in the acidic NaF-HF than in the APF solution.

The reason may also be due to the absence of the effect of the phosphoric acid contained in the APF solution. Phosphoric acid is a weak acid dissociated into $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} in water. These phosphate anions are F^- like anions, which can form an ionic atmosphere, preventing F^- ions from reacting with H^+ cations to form hydrofluoric acid.

However, in the acidic NaF-HF solution, no such ionic atmosphere exists, and the chemical reactivity is expected to increase due to the relatively high concentration of hydrofluoric acid.

The limitations of the study are that the pH of the sodium fluoride-hydrofluoric acid solution is about 4, so that no solution has been proposed to the problem of dental erosion.

We have solved this problem by making a subacidic NaF-HF gel (pH = 5.7). This compositional characteristic has been shown to be anticarious [21].

CONCLUSIONS

The chemical reactivity of HA with fluoride solution depends on the content of hydrofluoric acid and the ionic atmosphere; it is enhanced with higher HF content and lower ion concentration.

Acknowledgments

This study was supported by the Department of Neorgronic Chemistry Research, Faculty of Chemistry, Kim Il Sung University, Democratic People's Republic of Korea and was funded by Pyongyang University of Medical Sciences.

Conflict of Interest
None declared.

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