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The Influences of NH_4F-HF System on Dental Minerals

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ABSTRACT

Aim: *The influence of NH_4F-HF system on the fluoride-dental minerals reaction system was investigated. Methods: Fluoride solutions with a fluoride concentration of 1.23% each were used: 1.23% NaF-H_3PO_4-HF(APF, pH 2.1), 1.23% NH_4F-HNO_3 (pH 3.6), and 1.23% NH_4F-HF (pH 3.6). Fluoride solutions prepared above were diluted 10 times and used as 0.123% fluoride solutions. 300mg of Hydroxyapatite (HA:$Ca_{10}(PO_4)_6(OH)_2$) was deposited for 20min by adding 40mL of each of 1.23% fluoride solutions. In the same way, 300mg of calcium hydrogen phosphate ($CaHPO_4 \cdot 2H_2O$) was deposited for 20min by adding 40mL of each of 0.123% fluoride solutions. The HA and $CaHPO_4 \cdot 2H_2O$ were added to the different fluoride solutions and deposited. Each reaction was performed 3 times, respectively. Three reaction samples for each fluoride were mixed, filtered, washed, centrifuged and dried as reaction samples. The reaction products were identified and the content of calcium fluoride was determined by X-ray diffraction. Results: The highest CaF_2 content was found in the HA sample treated by 1.23% NH_4F-HF(pH 3.6) solution, while it was almost absent in the sample treated by NaF. In addition, the highest CaF_2 content was found in the calcium hydrogen phosphate sample treated by 0.123% NH_4F-HF(pH 3.6) solution. Conclusion: The chemical reactivity of ammonium fluoride solution increases with increasing added HF content.*

Keywords: Hydroxyapatite, Calcium hydrogen phosphate, Ammonium fluoride, Hydrofluoric acid, Chemical reactivity.

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INTRODUCTION

Local caries prevention methods with fluoride solutions with high concentration have been applied to demonstrate its effectiveness in practice and are widely used in caries prevention and treatment[1-10]. NH_4F-HNO_3 system showed faster reaction rate with tooth minerals under the same fluoride concentration and pH conditions compared to the sodium fluoride and Acidulated phosphate fluoride(APF) solutions[11]. It was reported that the fluoride content of dental enamel was higher when ammonium fluoride solution of pH 5.0 with 100ppm or 900ppm F^- was used as the mouth rinsing solution than that of NaF solution.[12]

The researchers suggested that the fluoride concentration required for caries resistance on the enamel surface should be 1500-2000ppm. They reported that fluoride over 1500 ppm on the enamel surface was present, even when the enamel treated with ammonium fluoride solution of pH 6 or less was washed with potassium hydroxide or immersed in the artificial saliva. They reported that the mechanism of action was to produce more insoluble CaF_2 on the enamel surface[13].

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Acidulated ammonium fluoride was found to be more reactive fluoride than the sodium fluoride or APF solutions. Therefore, suggested that the fluoride concentration could be lower if it was used for caries prevention[14]. It has been reported that the addition of ammonium fluoride to drinking water has a strong caries preventive effect[15,16].

It was reported that the CaF_2 produced in sample treated with the ammonium fluoride solution with nitric acid at pH 4.2-4.4 was difficulter to dissolve after washing with the potassium hydroxide solution and the artificial saliva than in the sample treated with sodium fluoride under identical conditions[17-20].

The preventive effect of dental caries in newly erupted molars was significantly higher in children who had oral rinse with APF and ammonium fluoride solutions with pH 4.4 and 1,000 ppm for 2 years than in sodium fluoride solution[21]. The reseachers reported that the reactivity between NaF-HF system and HA or $CaHPO_4·2H_2O$ is much higer than that between NaF-H_3PO_4-HF and HA or $CaHPO_4·2H_2O$[22].

However, no the influence of NH_4F-HFsystem on dental minerals has been done. Moreover, no research on the effect on $CaHPO_4·2H_2O$, which is known to be a carious crystal has been reported. We investigated the effect of NH_4F solution with hydrofluoric acid and nitric acid on dental minerals.

MATERIALS AND METHODS

2.1. Synthesis of HA: Solution A was made by calcium nitrate tetrahydrate(36.15g: 98%,Merck company) in 525mL of water. Solution B was made by dissolving diammonium hydrogen phosphate(12g: 99%,Merck company) into 375mL of water. Solution B was slowly added to solution A under strong stirring condition. Sodium hydroxide solution(NaOH, 99%, Merck company) was added until the pH of the solution was 11.

The resulting precipitate was HA. It was aged at room temperature overnight, centrifuged thoroughly and washed with deionized water. The centrifuging and washing process was repeated 3 times. The precipitate was finally dried in a freeze-drying system(Alpha1-2 LD, Germany) for 10h. After air-heating the dried powder at rate of 5℃/min, it was heated in the electric oven of 1000℃ for 1h.

2.2. Preparation of fluoride solutions

2.2.1. Preparation of NH_4F-HF solution with 1.23% F^-

1.75g of ammonium fluoride (98%, Merck company)was dissolved in 99.132mL of deionized water, and then 0.868mL of 40% hydrofluoric acid(HF, 40%, Merck company) was added. The pH of resulting solution was 3.6. The solution that diluted above solution 10 times was used as NH_4F-HF solution with 0.123% F^- concentration.(pH3.6) All operations were performed in polyethylene container.

2.2.2. Preparation of APF solution.

APF solution was prepared according to the procedure described in literature[23]. 2g of sodium fluoride(NaF, 98%, Merck company) was dissolved in 99.132mL of 0.1M orthophosphoric acid(H_3PO_4, 85%, Merck company), and then 0.868mL of 40% hydrofluoric acid(0.33g F^-) was added. The resulting solution was used as APF solution at pH 2.1. A 10-fold dilution solution was used as APF solution with 0.123% F^-(pH 2.56). All operations were performed in polyethylene container.

2.2.3. Preparation of NH_4F-HNO_3 solution with 1.23% F^-

2.40g of ammonium fluoride was dissolved in 97.5mL of deionized water, and then 2.5ml of 0.01M HNO_3 solution(Merck company). pH of solution was 3.6, A 10-fold dilution solution was used as NH_4F-HNO_3 solution with 0.123% F^-(pH 4.6).

2.3. Reaction between fluoride solution with 1.23% F^- and HA

300mg of HA was added to 40mL of each of the different fluoride solutions and deposited at room temperature for 20 min. Each reaction was performed 3 times, respectively. Three samples treated with the same fluoride solution were added, filtered, washed, centrifuged, and dried.

2.4. Reaction between fluoride solution with 0.123% F^- and $CaHPO_4 \cdot 2H_2O$

300mg of $CaHPO_4 \cdot 2H_2O$ was added to 40mL of each of the different fluoride solutions and deposited at room temperature for 20 min. Each reaction was performed 3 times, respectively. Three samples treated with the same fluoride solution were added, filtered, washed, centrifuged, and dried.

The powders were measured by X-ray diffraction(XRD) apparatus(D8 ADVANCE, Nederland) with a Bruker AXS D8 ADVANCE powder diffractometer with a CuKa1 characteristic line(λ=1.540 6Å) controlled at 45kV and 40mA in the scanning range of 20° to 80° with a step interval of 0.02°/0.5. The qualitative analysis of the X-ray measurement data was carried out with the EVA program and Rietveld refinements of crystal structures were performed by TOPAS 3.0 programme using the database of ICSD(Inorganic Crystal Structure Database).

2.5. Scanning electron microscopy(SEM) observation of dental enamel surfaces exposed to fluoride solutions.

After removing the foreign bodies from the tooth and degreasing with alcohol, the crown of the tooth was divided into three pieces, and two of them were exposed to the fluoride solution for four minutes. Then, the pieces were washed with running water to remove the remaining fluoride solutions on enamel surfaces, rinsed again with deionized water and dried. The remaining one piece was used as control.

Then all pieces were demineralized in 5mol/L HCl solution for 10s, washed with deionized water to remove the excess HCl completely and dried using the absolute alcohol. The resulting pieces were used as the test sample. The samples were subjected to gold evaporation(EMITECH K450X, England) and the surfaces of the samples were observed under an accelerating voltage of 10kV using the scanning electron microscope(Quanta 200, Nederland).

RESULTS

3.1. Reactions between fluoride solutions with 1.23% F^- and HA

3.1.1. Identification of reaction products

Fig.1 shows the XRD patterns for HA treated with 1.23% F^- As shown in Fig.1, peaks for HA were observed in XRD patterns of the samples treated with fluoride solution. Also, the peaks for CaF_2 were observed in XRD patterns of HA treated with fluoride solution with 1.23% F^-.

3.1.2. The content of CaF_2

The Rietveld refinements for the samples treated with fluoride solution with 1.23% F^- are shown in Fig. 2. Table 1 shows the CaF_2 contents of the HAs treated with the different fluoride solutions.

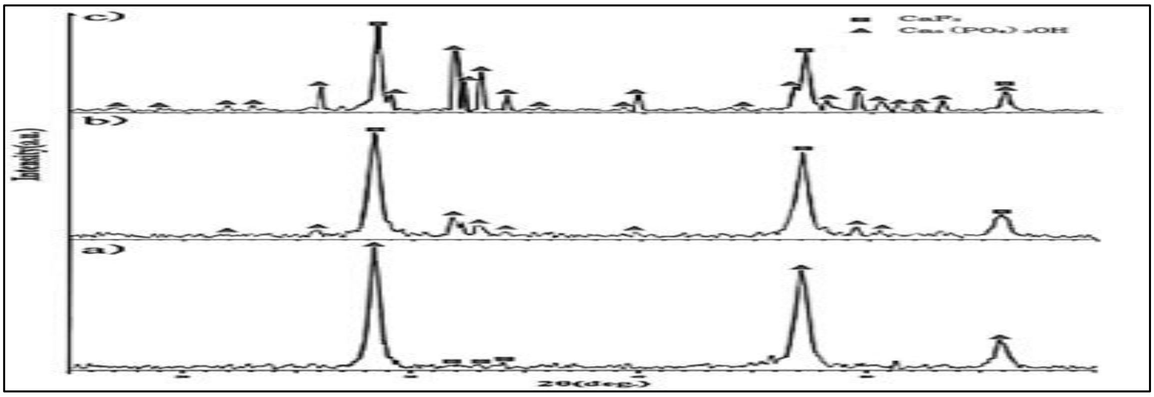

Fig. 1 XRD patterns for HAs treated with different fluoride solutions with 1.23% F- for 10min. *a: NH4F-HF b: NH4F-HNO3 c: APF*

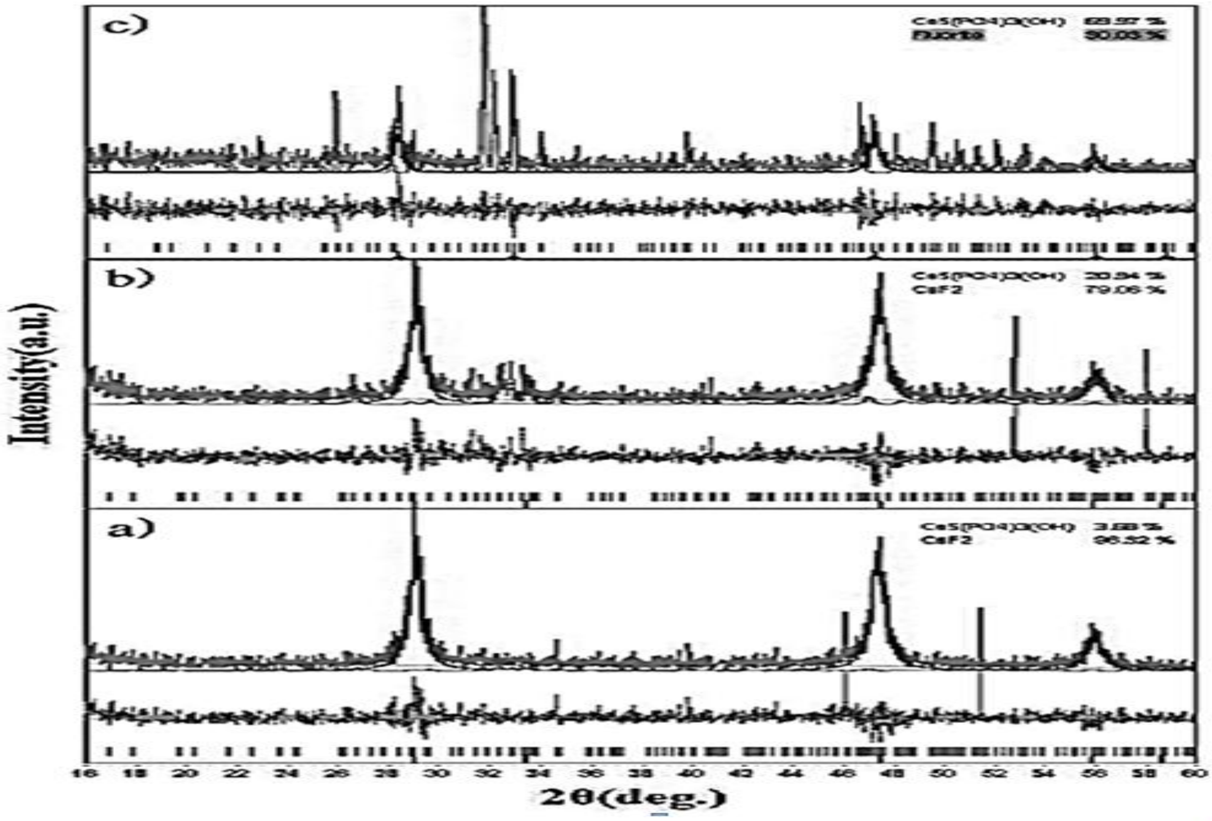

Fig.2 Rietveld refinements for apatite treated with different fluoride solution with 1.23% F- for 10 min a*: NH_4F-HF b: NH_4F-HNO_3 c: APF*

Table 1: CaF2 contents of HAs treated with the different fluoride solutions with 1.23% F- (wt.%).

Fluoride	NH_4F-HF	NH_4F-HNO_3	APF∗	NaF-HF∗
CaF_2 content	96.32	79.06	30.03	44.08
HA content	3.68	20.94	69.97	55.92

As shown in Table 1, after reaction for 20min, the CaF_2 content was 96.32% for HA treated with NH_4F-HF, 79.06% for HA treated with NH_4F-HNO_3, and 30.03% for HA treated with APF, suggesting that the chemical activities of fluorides are different depending on their compositions. CaF_2 content in the HA sample treated by 1.23% NH_4F-HF solution was highest among samples treated by various fluoride solutions. Also, CaF_2 content in the HA sample treated by 1.23% NH_4F-HF solution was higher than that in the HA sample treated by 1.23% NaF-HF solution[22].

3.2. Reactions between fluoride solutions with 0.123% F^- and $CaHPO_4{\cdot}2H_2O$

3.2.1. Identification of reaction products

Fig. 3 shows the XRD patterns for CaHPO4·2H2O treated with fluoride solutions with 0.123% F-. As shown in Fig.3, the peaks for CaHPO4·2H2O, CaF2 and fluoroapatite were observed for both of samples.

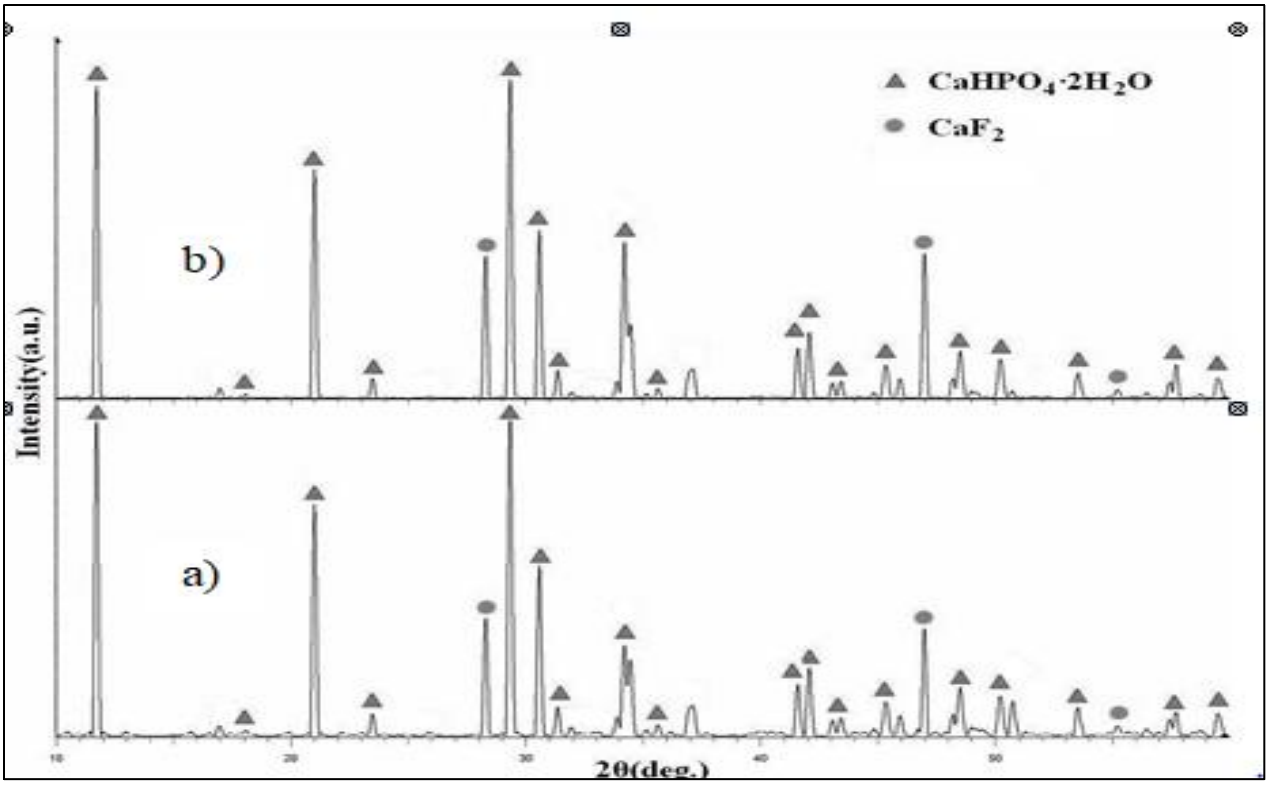

Fig. 3 X-ray diffraction patterns for $CaHPO_4{\cdot}2H_2O$ treated with different fluoride solutions with 0.123% F^-

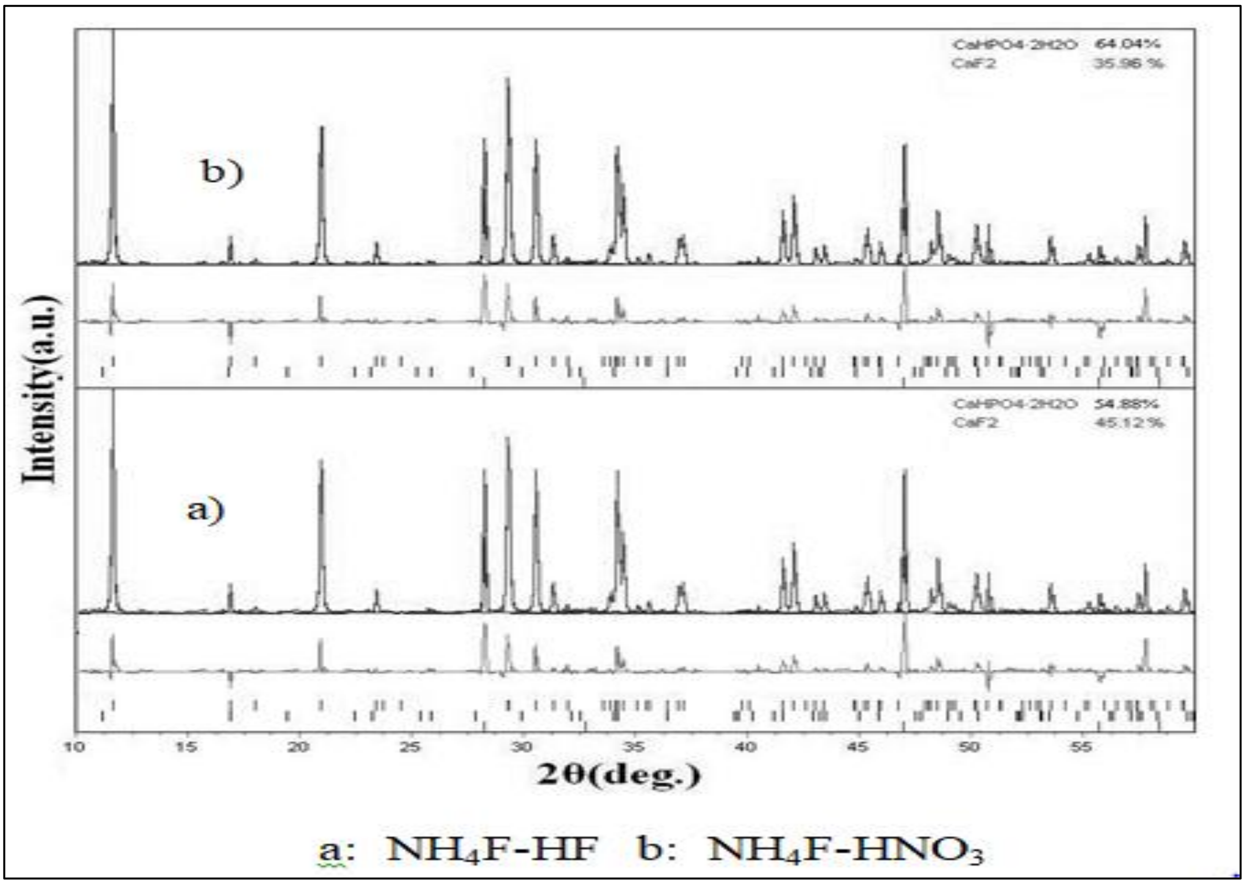

Fig.4 Rietveld refinements for $CaHPO_4 \cdot 2H_2O$ treated with different fluoride solutions with 0.123% F^-

3.2. Reactions between fluoride solutions with 0.123% F^- and $CaHPO_4 \cdot 2H_2O$

3.2.2. CaF_2 content

Table 2 shows the CaF_2 content involved in $CaHPO_4 \cdot 2H_2O$ treated with different fluoride solutions.

As shown in Fig. 4 and Table 2 , the CaF_2 content was the highest at 45.23% in the sample treated with NH_4F-HF and 36.17% and 9.54% in the samples treated with NH_4F-HNO_3 and APF, whereas the FA content was the highest at 10.19% in the sample treated with APF and 3.22% and 2.57% in the samples treated with NH_4F-HNO_3 and NH_4F-HF, respectively.(Fig. 4 and Table 2)

Also, the CaF_2 content involved in $CaHPO_4 \cdot 2H_2O$ treated with NH_4F-HF was higher than that in the $CaHPO_4 \cdot 2H_2O$ treated by NaF-HF solution[22]. (Table 2)

Table. 2 : CaF_2 and FA content involved in $CaHPO_4 \cdot 2H_2O$ treated with different fluoride solutions(wt.%)

Fluoride	NH_4F-HF	NH_4F-HNO_3	APF ∗	NaF-HF ∗
CaF_2 content	45.12	35.96	9.54	15.87
$CaHPO_4 \cdot 2H_2O$ content	54.88	64.04	90.46	84.13

3.3. SEM images of the dental enamel surfaces applied with different fluoride solutions.

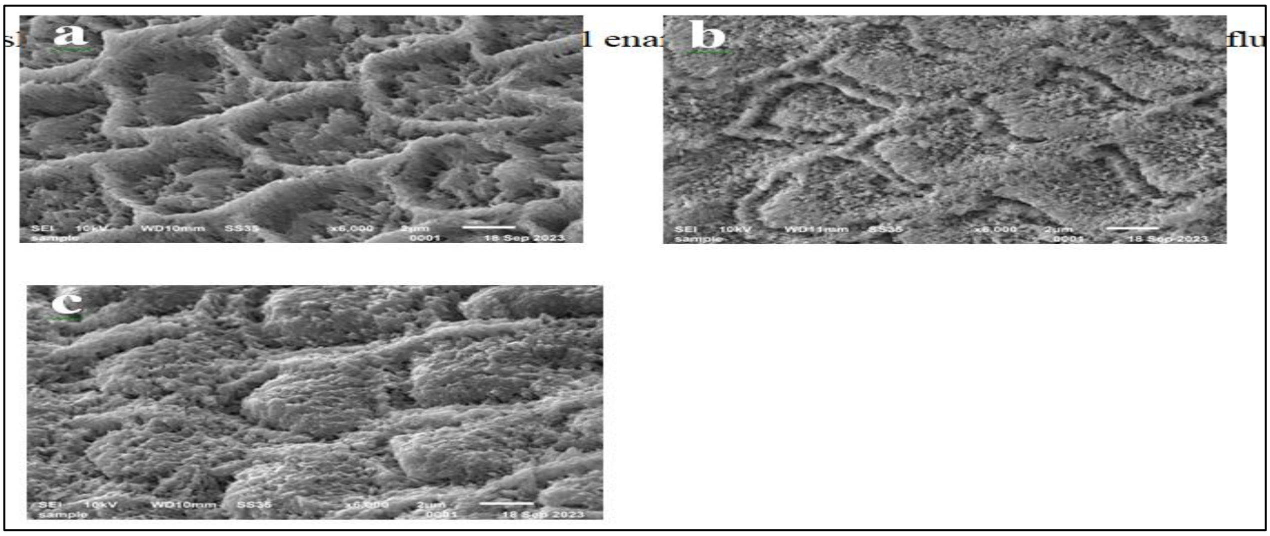

Fig. 5 SEM images of applied with different fluoride solutions a; APF b: nitric acid NH_4F c: hydrofluoric acid NH_4F

As shown in Fig. 4 and Table 2 , the CaF_2 content was the highest at 45.23% in the sample treated with NH_4F-HF and 36.17% and 9.54% in the samples treated with NH_4F-HNO_3 and APF, whereas the FA content was the highest at 10.19% in the sample treated with APF and 3.22% and 2.57% in the samples treated with NH_4F-HNO_3 and NH_4F-HF, respectively.(Fig. 4 and Table 2), Also, the CaF_2 content involved in $CaHPO_4 \cdot 2H_2O$ treated with NH_4F-HF was higher than that in the $CaHPO_4 \cdot 2H_2O$ treated by NaF-HF solution[22]. (Table 2)

DISCUSSION

Inorganic fluorides are either metal fluorides or compounds of fluorine with nonmetallic elements, including hydrogen. Based on this concept of fluoride, we selected NH_4F, the ammonium salt of fluoride, as the test fluoride. Based on our previous work[11], NH_4F-HNO_3 and NH_4F-HF with 1.23% F^- were selected as the test fluoride. We determined the F^- concentration of the fluoride solution as 1.23% in consideration of its clinical application concentration, and evaluated its reactivity by comparing XRD phase analysis data for HA samples treated with differed fluoride solutions with CaF_2 contents involved in the samples obtained by Rietveld refinements. As shown in Table 1, CaF_2 content involved in the sample treated with NH_4F-HF solution was higher than that in the sample treated with NH_4F-HNO_3, APF, and NaF-HF solutions.

The better reactivity in NH_4F-HA reaction system than in APF or NaF-HF reaction system could be due to the different hydrolysis properties of NH_4F and NaF.

NaF is hydrolyzed in aqueous solution producing OH^-, and the solution is slightly basic.

$NaF+H_2O \rightleftarrows HF+NaOH$ (1)

$F^-+H_2O \rightleftarrows HF+OH^-$ (2)

Because OH^- is formed due to the hydrolysis of NaF, the equilibriums for reaction(1), reaction(2), and reaction(3) shift from right to left. Consequently, products are less formed. However, the equilibrium shifts from the left to the right producing CaF_2 because of acidity due to phosphoric acid in APF solution.

On the other hand, NH_4F is also hydrolyzed as follows:

$NH_4F + H_2O \rightleftarrows NH_3 \cdot H_2O + HF$ (3)

The formed $NH_3 \cdot H_2O$ is a weak base($K_b=1.8\times10^{-5}$) and HF is a weak acid($K_a=7.1\times10^{-4}$), so the resulting solution is slightly acidic and the equilibriums for the above reactions shift from the left to the right, favoring the CaF_2 formation reaction. When the acid is added in NH_4F solution, the acidity of solution becomes stronger and the reaction producing CaF_2 occurs better. In conclusion, more CaF_2 is formed in the samples treated with NH_4F-HNO_3 and NH_4F-HF solutions than the sample treated with APF solution.

The better reation in NH_4F-HF solution than NH_4F-HNO_3 solution is thought to be due to the higher content of HF.

According to the literature[24-25], $Ca_3(PO_4)_2$(Whitlockite) is recognized along with HA in carious lesions. In addition to $Ca_3(PO_4)_2$, the presence of $CaHPO_4 \cdot 2H_2O$(calcium hydrogen phosphate, Brushite) or $Ca_3(H_2PO_4)_2$(calcium dihydrogen phosphate) is also theoretically possible.

Since $Ca_3(H_2PO_4)_2$ is readily soluble in saliva, only $Ca_3(PO_4)_2$ or $CaHPO_4 \cdot 2H_2O$ with low solubility can be present in the lesion.

Therefore, only $Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$ are detected in the instrumental examination for the carious lesions, which is probably referred to as the 《carious crystals》.In our opinion, it is more accurate to consider $Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$ as the degradation products of $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ rather than 《caries crystals》.

Therefore, we studied the effect of the different fluoride solutions on $CaHPO_4 \cdot 2H_2O$ present in carious lesions, together with HA, the main component of dental minerals, and established a viewpoint of the caries progression inhibition process.

The different fluoride solutions with 0.123% F^- were applied to $CaHPO_4 \cdot 2H_2O$, and their change states were observed identifying the products using XRD.

When the different fluoride solutions were applied to $CaHPO_4 \cdot 2H_2O$, the producing CaF_2 content was the highest at 45.23% in the sample treated with NH_4F-HF and 36.17% and 9.54% in the samples treated with NH_4F-HNO_3 and APF. Also, the CaF_2 content involved in $CaHPO_4 \cdot 2H_2O$ treated with NH_4F-HF was higher than that in the $CaHPO_4 \cdot 2H_2O$ treated by NaF-HF solution[22].

As explained above, ammonium fluoride is hydrolyzed in solution and the solution becomes slightly acidic, and the majority of fluorine in the solution is present as the form of hydrofluoric acid.

As in the above experiments, the CaF_2 content was higher in the acidic NH_4F-$CaHPO_4 \cdot 2H_2O$ systems than in the acidic APF-$CaHPO_4 \cdot 2H_2O$ system.

As shown in Fig. 1, the corrosion observed in the SEM images of fluoride-treated dental enamels was due to the fact that the majority of the dental minerals were consisted of the basic compound, hydroxyapatite. There was little corrosion on the fluoride-rich dental enamel surface.

The shortcoming of this study is that the pH of ammonium fluoride solutions is set at 3.5, which is slightly strong acidic. The reason for doing so is that the more acidic the fluoride solution, the more the produced HF content. By adding 0.5% HF to NH_4F, fluoride is formed on the surface of dental enamel which can effectively suppress the corrosion of the dental enamel. Since there are reports that fluoride solutions can corrode dental minerals or plastic fillers when they are acidic, this issue is considered to be elucidated.

CONCLUSION

The reaction between NH_4F and HA or $CaHPO_4 \cdot 2H_2O$ takes place better when the ammonium fluoride solution becomes acidic by adding HF than HNO_3.

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