

Does Fluoride Cause Corrosion of Titanium Dental Implants?

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ABSTRACT

Aims: There is very little information known about the effects of fluoride on the corrosion of titanium dental implants. Corrosion of implants can lead to peri-implantitis and eventually implant failure. The aim of this study is to search and analyze the available literature to identify whether fluoride causes corrosion of titanium or Ti-6Al-4V, two materials commonly used to construct dental implants.

Materials and methods: Three online databases were used to search for literature relating to this subject. These included Medline, Cumulative Index to Nursing and Allied Health Literature (CINAHL), and Dentistry and Oral Sciences. A scoping search was initially undertaken to identify potentially relevant literature. The studies were narrowed down by titles and abstract and then full-text review, based on predetermined inclusion/exclusion criteria. Five studies were selected. The relevant information from the studies were extracted using a customized data extraction tool. The data were then analyzed allowing the conclusions to be drawn.

Results: Of the five studies included in this mini-systematic review, all concluded that fluoride does cause corrosion of dental implants, particularly, in the presence of an acidic pH.

Conclusion: Consideration must be given when prescribing topical fluorides for patients with titanium dental implants. Corrosion can occur in the presence of high fluoride levels, particularly if the oral environment is acidic.

Keywords: Acids, Corrosion, Dental implants, Fluoride, Implants, Minisystematic review, Titanium.

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INTRODUCTION

Dental patients have become less accepting of edentulous spaces and are now keener than ever to replace missing teeth, with the restoration of esthetics and function being the main drivers for seeking prosthodontic rehabilitation.¹ Dental implants are commonly used to replace missing teeth.² Titanium has always been the material of choice for dental implants. It was considered due to its lightness and good mechanochemical properties.³ It was found to be the only biomaterial to osseointegrate⁴ and was assumed to have bioactive properties due to the formation of a hydrated oxide layer which could incorporate calcium and phosphorous.⁵ The high stability of titanium is created thanks to the formation of the titanium oxide (TiO₂) layer, which forms on the outer aspect of the implant. The stability of the implant can, however, be compromised if the TiO₂ layer is lost and cannot reform. This then makes titanium as unstable as any other metal.⁶

Corrosion is the deterioration of a metal as a result of an electrochemical attack from the surrounding medium, which can lead to metal ion release.⁷ The metal ions which are released have a detrimental effect on the peri-implant tissues.⁸ Metal ions will cause the activation of inflammatory response cells, cytokines, and pro-inflammatory mediators and will result in an increase in osteoclastic activity. Products from the degradation of dental implants have cytotoxic (cell killing) and genotoxic (damaging to cells genetic material) potential for the tissues surrounding implant.⁹

Fluoride may contribute to the corrosion of dental implants. Fluoride has been used in dental hygiene products for many years. It is predominately used in the prevention of dental caries. Dentists will prescribe higher dosages for those who are at a higher risk of the disease.¹⁰

With the numbers of dental implants being placed increasing, and with the continued drive for the prevention of dental caries through the delivery of topical fluoride, it is important to explore whether corrosion of titanium dental implants can occur in the

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presence of topical fluoride. This mini-systematic review aimed to search the current literature for evidence that fluoride causes corrosion of titanium dental implants.

MATERIALS AND METHODS

This minisystematic review followed multiple-ordered stages to help identify, critically appraise, and analyze the available body of evidence in this area of research. These stages included an extensive literature search, study selection based on predetermined inclusion/exclusion criteria, data extraction, and data analysis. The literature search was conducted using three separate databases. The aim is to identify as many *in vitro* studies as possible addressing this same research question. Data analysis and interpretation were then conducted. All relevant information was extracted from the studies. The results of the studies were then analyzed in depth.

Literature Search

The literature search was conducted using three separate databases on the Elton B Stephens Company (EBSCO) platform. The databases used included Medline, Dentistry and Oral Sciences, and CINAHL.

The search for literature was undertaken using a combination of free text and indexed terms.

Inclusion and Exclusion Criteria

The inclusion and exclusion criteria are included in Table 1 (see Appendix).

Study Selection and Quality Assessment

The identified studies were screened by title and abstract and any irrelevant studies removed. The remaining full texts were screened using the predetermined inclusion and exclusion criteria and only the most suitable studies retained. These studies were then screened for quality using a customized risk of bias (RoB) tool. This had to be created because no suitable RoB tools were identified after searching the literature for previously constructed tools. Its purpose was to provide an effective way to qualitative assess nonrandomized control trials which were then to be used in the systematic review. It would also ensure that the papers retrieved are nonbiased and conducted using a sound methodology. The studies were then grouped as “strong,” “medium,” or “weak” based on the score of the RoB tool. Only studies which were considered as “strong” were included in the review. Altogether, five studies were included in this review.

Data Extraction

Data were collected with the aid of a specifically designed “data extraction form.” This tool streamlined the data extraction process by making it clearer and more concise and made the data extraction process reproducible.

The tool contained the following information:

- Reference—authors name, the title of the paper, and publication details
- Objective of the study
- Materials to be studied
- Intervention
- Analysis
- Outcome

Data Analysis

Narrative analysis of each study was undertaken, and similarities were identified. The conclusions drawn from the included studies were based on the similarities found in each individual study.

RESULTS

A glossary of terms has been included at the end of this report.

Five studies were included in this minisystematic review and the findings from each study were as follows.

Boere et al.¹¹—The authors tested samples of pure titanium electrochemically using a corrosion cell. Three experiments were conducted: experiment I—fluoride added to the test solution of sodium chloride (NaCl) of 9.0 g L⁻¹ immediately; experiment II—fluoride added to the same test solution after at 100 hours; experiment III—fluoride added to the same test solution after 3 weeks. This was conducted at pH 4 using a hydron buffer. The data were collected, and standard electrochemical measurements were obtained. These included corrosion potential (E_{corr}) and polarization resistance (R_p).

Corrosion was identified graphically by a drop-in polarization resistance with an increasing concentration of fluoride and change in E_{corr} from positive (+ve) to negative (-ve).

Experiment I pH 4: sodium fluoride (NaF) was added immediately. There was a limiting value for NaF concentration

whereby concentrations lower than this would not affect E_{corr} or R_p , after this limit was reached, the corrosive process occurred.

Experiment II pH 4: NaF added at 100 hours. The starting value for R_p was higher and the influence of HF was detected with lower concentrations of fluoride. This occurred because the longer that titanium was placed in solution, the thicker the protective oxide layer became (resulting in a higher starting value for R_p). With the continual addition of HF, the oxide layer became depleted resulting in a steep fall in corrosion potential and polarization.

Experiment III pH 4: NaF added after 3 weeks. The trend was similar to experiments I and II.

The data show that even at low concentrations, when NaF is added at a low pH, titanium attack begins.

In the experiments conducted at pH 7, results show that the polarization resistance is relatively stable and consistent. The R_p and E_{corr} are maintained due to a lack of acidic hydrogen ions. The hydrogen ions will bind to the passive oxide layer on the sample surface and begin degrading the surface.

Joska et al.¹²—The authors tested samples of pure titanium in an electrochemical cell. The samples were tested in multiple different test solutions: NaCl (9 g/L)—abbreviation PS-n.a.; NaCl (9 g/L) + 5,000 ppm—abbreviation PS-n.a./5,000; NaCl (9 g/L) + buffer solution (to change pH to 5.8)—abbreviation PS-5.8; NaCl (9 g/L) + 5,000 ppm + buffer solution (to change pH to 5.8)—abbreviation PS-5.8/5,000; NaCl (9 g/L) + buffer solution (to change pH to 4.2)—abbreviation PS-4; NaCl (9 g/L) + 5,000 ppm + buffer solution (to change pH to 4.2)—abbreviation PS-4.2/5,000; model saliva—1.5 g/L KCl, 0.5 g/L NaH₂PO₄·H₂O, 1.5 g/L NaHCO₃, 0.5 g/L KSCN; 0.9 g/L lactic acid—abbreviation MS (control solution).

The data were presented using potentiodynamic (polarization) curves. From this, current density (A/cm²) and corrosion potential (E) were measured. The samples were placed in the test solutions. Current density increased, and corrosion potential became more negative when fluoride was added.

The corrosion potential and the polarization resistance were then measured again the time. The graphs showed that in both PS n.a./5,000 and PS 5.8/5,000, the corrosion potential was negative suggesting that corrosion was occurring. After placement into the model saliva, this began to reverse until the corrosion potential returned positive and the polarization resistance also began to increase which suggested that the passive TiO₂ layer was beginning to reform. In the PS 4.2/5,000 test solution, the corrosion potential did not become positive again suggesting that electrons were still present in titanium. Polarization resistance also stayed very low suggesting no repassivation. The corrosion process did not stop in this test.

The impact on the passive TiO₂ layer was the greatest with an acidic pH. A drop in the polarization resistance with all PS n.a./5,000, PS 5.8/5,000, and PS4.2/5,000 would suggest that the TiO₂ layer is deteriorating.

Surface analysis-impedance spectra-taken for the titanium sample in PS 4.2/5,000 solution. This confirmed the presence of a layer of corrosion products after exposure to the test solution. X-ray photoelectron spectroscopy was run on this and showed layers of titanium, potassium, fluoride, and oxygen elements on the surface of the sample.

These findings conclude that prolonged exposure to fluoride will lead to corrosion of titanium, particularly if the pH is low.

Nakagawa et al.¹³—Samples of commercially pure titanium tested in an electrochemical cell. The data were presented

using polarization curves. From this, the corrosion potential was measured.

The anodic polarization curves were first measured in artificial saliva (NaCl 0.4 g, KCl 0.4 g, CaCl₂·2H₂O 0.795 g, NaH₂PO₄·2H₂O 0.78 g, Na₂S₉·H₂O 0.005 g, NH₂CONH₂ 1.0 g, distilled water 1,000 mL) which would act as a control and 0.1% NaF solution at pHs 7.1 and 4.0.

Similarities were seen in the polarization curves for artificial saliva and 0.1% NaF solution at pH 7.1. This would suggest that no corrosion is occurring. When assessing the polarization curve for 0.1% NaF at pH 4.0, the corrosion potential dropped suggesting an increase in the number of free electrons in the sample. The current density also increased which suggests a change to the surface characteristics of the sample metal. The sample then began to passivate.

The same tests were then re-run with an increased fluoride concentration, this time 0.5% with varying pH levels. The corrosion resistance was lost at 0.1% NaF (452.4 ppm) at pH 4.2 and at 0.5% NaF at pH 5.4.

Limit values were measured from the polarization tests and the immersion tests. They showed that at 100 ppm, corrosion would occur at approximately pH 3, at 1,000 ppm approximately pH 5, and at 10,000 ppm approximately pH 6.5.

Surface Analysis

Analysis of dissolved titanium and fluoride—The concentration of dissolved titanium in solution was measured in µg/cm² and was measured in solutions of 0.05 and 0.1% NaF at varying pHs.

The solutions were tested immediately once anodic polarization tests were conducted after 24 hours in solution. With 0.05% NaF solution at pH 3.5, over 400 µg/cm² was identified in the solution. This increased to approximately 1,750 µg/cm² after 24 hours. At 0.1% NaF, over 1,000 µg/cm² was identified in the solution and this increased to around 2,700 µg/cm² after 24 hours. Dissolution was identified at all pHs measured in both 0.05 and 0.1% solutions.

Milošev et al.¹⁴—Samples of pure titanium and Ti–6Al–4V tested in an electrochemical cell. Data were extracted and polarization curves were plotted allowing corrosion potential, E_{corr} and current density, J_{corr} to be measured. The results are displayed in Table 2 (see Appendix).

In artificial saliva, E_{corr} for both Ti and Ti–6Al–4V were negative in value (more so, for Ti–6Al–4V) but returning to positive. This suggests that samples were passivating and becoming more stable (most likely as a result of an increase in the thickness of the TiO₂ layer). In artificial saliva, Ti was found to be very stable, whereas Ti–6Al–4V was less protected to localized corrosion.

The addition of NaF led to significant changes in the polarization curves. For both Ti and Ti–6Al–4V, the E_{corr} value became significantly more negative indicating that a dissolution process is occurring through a reduction and oxidation-type reaction. Free electrons explain the negative change. The current density is also increased with the addition of fluoride.

These results would indicate that corrosion resistance is reduced by the addition of fluoride.

Immersion tests—Samples were immersed in artificial saliva for 32 days with and without the addition of NaF. The concentration of dissolved titanium ions in solution was measured. The amount of dissolved titanium from the Ti and Ti–6Al–4V samples was similar in artificial saliva. This was 10 µg/L. This value indicates low levels of corrosion. After the addition of NaF, this figure vastly increased to around 45,000 µg/L for Ti–6Al–4V and 68,000 µg/L for Ti. Average values and standard deviations were calculated. This significant increase confirms the corrosion of the samples.

Schiff et al.¹⁵—Samples of titanium and Ti–6Al–4V tested in an electrochemical cell. Polarization curves were plotted, and corrosion potential, polarization resistance, and current density were measured after immersing samples for 24 hours.

The corrosion potential was initially measured in the Fusyama Mayer artificial saliva (KCl (0.4 g/L), NaCl (0.4 g/L), CaCl₂·2H₂O (0.906 g/L), NaH₂PO₄·2H₂O (0.690 g/L), Na₂S₉·H₂O (0.005 g/L), urea (1 g/L); pH of artificial saliva is 5.3). The titanium sample was stabilized at 25 mV/SCE. This suggests repassivation of the metal. This then changed to –80 mV/SCE in the acidified saliva (Fusyama Mayer artificial saliva pH 2.5). This is not significantly different from the artificial saliva and the corrosion potential is only slightly negative suggesting that the passive layer is not degraded. In the fluoridated saliva (Fusyama Mayer artificial saliva with 1,000 ppm fluoride), the potential dropped to –300 mV/SCE. This would indicate that the protective passive layer had been changed and that corrosion was occurring. With the acidified and fluoridated saliva (Fusyama Mayer artificial saliva pH 2.5 with 1,000 ppm fluoride), the potential dropped significantly to –850 mV/SCE. This again shows a significant change to the passive layer leading to corrosion of the metal.

The Ti–6Al–4V also showed a similar pattern. This changed from 0, –50, –370, –800 mV/SCE in the Fusyama Mayer artificial saliva, acidified saliva, fluoridated saliva, and fluoridated acidified saliva, respectively.

The results for both corrosion potential and current density would suggest that corrosion is caused by the presence of fluoride and acidified fluoride solutions.

DISCUSSION

All of the studies which were analyzed showed that fluoride did cause corrosion of titanium and Ti–6Al–4V alloys. The study by Broere et al.¹¹ proved that there was a minimum fluoride concentration needed to cause corrosion at a neutral pH, below which no effects were seen. However, at a low pH, the concentration of fluoride needed to cause corrosion was low and this was due to the effects of hydrogen fluoride on the passive TiO₂ layer found on the metal/alloy surface. The study found that the concentration of fluoride in the mouth is 0.2–1.5 mmol after the use of fluoride-containing toothpaste. After the use of fluoride rinses, the concentration can increase to 1.2–2.9 mmol. When fluoride gels are used, the concentration can be as high as 7 mmol. These concentrations are well beyond what is capable of causing corrosion.

Joska et al.¹² also concluded that fluoride caused corrosion of pure titanium. This was found to be more profound when the pH was more acidic. The study also examined the surface of the titanium after exposure to the test solutions and this showed a clear build-up of corrosion products. It is these corrosion products which will begin to cause peri-implant inflammation and potentially implant failure.

The study by Nakagawa et al.¹³ measured limit values from the polarization tests and the immersion tests and showed that at 100 ppm, corrosion would occur at approximately pH 3, at 1,000 ppm approximately pH 5, and at 10,000 ppm approximately pH 6.5. These findings are very significant as some prescribed toothpastes can have a concentration as high as 5,000 ppm fluoride and topical fluoride varnishes can be as high as 22,600 ppm. The findings are significant, particularly if the pH is reduced such as in high plaque areas.

Milošev et al.¹⁴ also provided conclusive data on the effects of fluoride and the corrosion of pure titanium and Ti–6Al–4V.

Both the electrochemical tests and the visual tests confirmed that corrosion of the samples occurred in the presence of fluoride and with an adjusted pH of 5.3. The pH remained constant throughout the experiments with the only fluoride being adjusted.

The study by Schiff et al.¹⁵ again concluded through electrochemical testing that fluoride has a significant effect on the corrosive properties of pure titanium and Ti-6Al-4V. The effects were more significant in the presence of low pH.

CONCLUSION

The studies have shown that high concentrations of fluoride will indeed cause corrosion of dental implants made from pure titanium or Ti-6Al-4V. The studies also showed that low concentrations of fluoride will cause corrosion in the presence of an acidic pH, a situation which can commonly occur in the mouth. The concentration of fluoride dentifrices must be considered in dental implant patients to ensure that peri-implant tissues are not compromised due to the release of corrosive products from titanium dental implants.

CLINICAL SIGNIFICANCE

The concentrations of fluoride prescription must be considered for patients with dental implants. Prescriptions of a high level of fluoride may have a negative impact on the peri-implant health due to the formation of corrosion products.

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APPENDIX

Table 1: Inclusion and exclusion criteria

Category	Inclusion	Exclusion
Language	English	Non-English
Date of publication	No limit	No limit
Population	<ul style="list-style-type: none"> • Dental implants • Pure titanium • Ti-6Al-4V 	<ul style="list-style-type: none"> • Orthodontic implants • Mini implants • Zirconia implants • Experimental titanium alloys
Intervention	<ul style="list-style-type: none"> • Topical fluoride application • Studies which assess fluoride application at different pH • Studies which examine corrosion in artificial saliva • Studies which examine corrosion in saliva substitute 	<ul style="list-style-type: none"> • Studies which examine the effects of mechanical trauma on corrosion • Studies which artificially change the surface characteristics of the metal prior to testing for corrosion
Study design	<ul style="list-style-type: none"> • <i>In vitro</i> 	<ul style="list-style-type: none"> • <i>In vivo</i>
Other	<ul style="list-style-type: none"> • Full texts available 	<ul style="list-style-type: none"> • Texts without full access or texts with restricted access

Table 2: Results from paper by Milosev et al.

Material	Artificial saliva		Artificial saliva + 0.25% NaF	
	E_{corr}/V	j_{corr}/V	E_{corr}/V	j_{corr}/V
Ti	-0.40	5.0×10^{-8}	-0.62	1.2×10^{-8}
Ti-6Al-4V	-0.54	1.2×10^{-7}	-0.69	4.0×10^{-6}

