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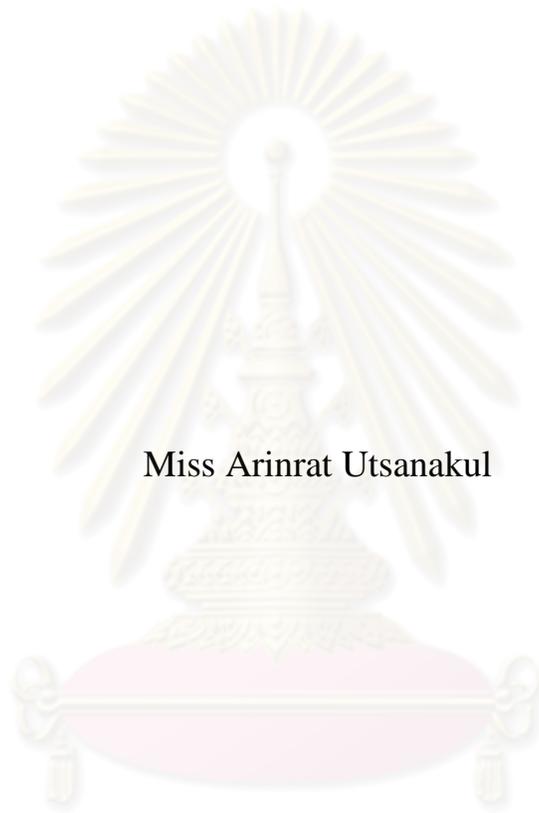
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THE CORROSION RESISTANCE OF POST METAL ALLOYS
COVERED BY TWO CEMENTS



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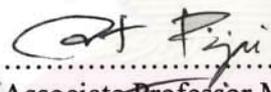
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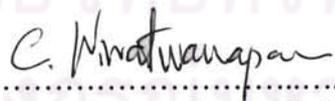
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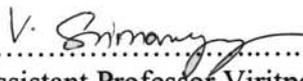

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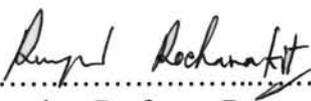
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การศึกษานี้มีวัตถุประสงค์เพื่อประเมินความต้านทานการกัดกร่อนของโลหะผสมทางทันตกรรม 4 ชนิดที่ใช้สำหรับทำเคือยฟัน ได้แก่ โลหะผสมทอง-พลาตาเดียม โลหะผสมเงิน-พลาตาเดียม โลหะผสมนิกเกิล-โครเมียม และโลหะผสมทองแดง-อะลูมิเนียม เมื่อเคลือบด้วยซีเมนต์ 2 ชนิด ด้วยวิธีการทดสอบโดยการแช่ในสารละลายที่เป็นกรด โดยนำโลหะไปขึ้นรูปเป็นชิ้นหล่อที่มีรูปร่างเป็นแผ่นกลมขนาดเส้นผ่านศูนย์กลาง 5.0 มิลลิเมตร หนา 0.8 มิลลิเมตร จำนวนชนิดละ 10 ชิ้นตัวอย่าง จากนั้นแบ่งเป็น 2 กลุ่ม กลุ่มละ 5 ชิ้น เพื่อเคลือบชิ้นตัวอย่างแต่ละชิ้นเพียงด้านเดียวด้วยซิงค์ฟอสเฟตซีเมนต์ (ซิงค์ซีเมนต์อิมพรุฟ) หรือเรซินซีเมนต์ (พานาเวียเอฟสอง) หนา 0.70 มิลลิเมตร หลังจากนั้นนำชิ้นตัวอย่างแต่ละชิ้นแช่ลงในหลอดทดลองซึ่งบรรจุสารละลายผสมของกรดแลคติกและโซเดียมคลอไรด์ปริมาณ 10 มิลลิตร (ค่าความเป็นกรดต่างเท่ากับ 2.25) ในตู้ควบคุมอุณหภูมิ 37 องศาเซลเซียสเป็นระยะเวลา 7 วัน โดยใช้สารละลายที่ไม่มีชิ้นตัวอย่างเป็นกลุ่มควบคุม นำสารละลายไปวิเคราะห์ปริมาณธาตุที่ถูกกัดกร่อนด้วยเครื่องอินคักทีฟลิ คับเปิล พลาสมา ออฟติคอล อิมิชชัน สเปกโทรสโคป โดยรายงานผลจากปริมาณธาตุที่ปล่อยสู่สารละลายในระยะเวลา 7 วันในหน่วยไมโครกรัมต่อตารางเซนติเมตร

ผลการศึกษาพบว่าโลหะผสมทอง-พลาตาเดียมไม่ปล่อยธาตุออกสู่สารละลาย ค่าเฉลี่ยของปริมาณธาตุทั้งหมดที่ปล่อยออกสู่สารละลายในโลหะผสมเงิน-พลาตาเดียม โลหะผสมนิกเกิล-โครเมียม และโลหะผสมทองแดง-อะลูมิเนียมเมื่อเคลือบด้วยซิงค์ซีเมนต์อิมพรุฟเท่ากับ 4.19 ± 2.30 2.31 ± 1.14 และ 185.50 ± 17.83 ไมโครกรัมต่อตารางเซนติเมตรตามลำดับ โลหะผสมเงิน-พลาตาเดียม โลหะผสมนิกเกิล-โครเมียม และโลหะผสมทองแดง-อะลูมิเนียม เมื่อเคลือบด้วยพานาเวียเอฟสองปล่อยปริมาณธาตุออกสู่สารละลายเท่ากับ 3.69 ± 1.51 2.13 ± 0.60 และ 247.31 ± 90.63 ไมโครกรัมต่อตารางเซนติเมตรตามลำดับ การทดสอบทางสถิติโดยใช้การวิเคราะห์ความแปรปรวนแบบสองทางและการเปรียบเทียบชนิดแทมเฮนพบว่า โลหะผสมทองแดง-อะลูมิเนียมปล่อยปริมาณธาตุมากกว่าโลหะชนิดอื่นอย่างมีนัยสำคัญเมื่อเคลือบด้วยซิงค์ซีเมนต์อิมพรุฟและพานาเวียเอฟสอง ในขณะที่ไม่มีความแตกต่างกันอย่างมีนัยสำคัญทางสถิติในโลหะแต่ละชนิดเมื่อเคลือบด้วยซิงค์ซีเมนต์อิมพรุฟและพานาเวียเอฟสอง ปริมาณธาตุที่ปล่อยออกมาสัมพันธ์กับความต้านทานการกัดกร่อน ซึ่งได้รับผลจากชนิดของโลหะผสมแต่ไม่ได้รับผลจากซีเมนต์ 2 ชนิดที่ใช้ในการทดสอบ

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KEYWORDS : CORROSION / ALLOY / CEMENT / ELEMENTAL RELEASE

ARINRAT UTSANAKUL: THE CORROSION RESISTANCE OF POST METAL ALLOYS COVERED BY TWO CEMENTS. ADVISOR: ASST. PROF. PRAROM SALIMEE, Ph.D., CO-ADVISOR: ASSOC. PROF. CHAIRAT WIWATWARRAPAN, 52 pp.

The objective of this study was to evaluate the corrosion resistance of four types of dental alloys: Au-Pd, Ag-Pd, Ni-Cr and Cu-Al alloys covered by two different dental cements using immersion test in acidic solution. The alloys were cast into ten disc-shaped specimens (5.0 mm diameter and 0.8 mm thick). Each alloy was divided into two groups of five according to the types of cement. Each specimen was covered on one side individually by zinc phosphate cement (Zinc Cement Improved) or resin cement (Panavia F 2.0) with 0.70 mm thick. The specimens were immersed in 10 ml lactic acid/NaCl solution (pH = 2.25) and maintained in incubator at 37 °C for 7 days. The solution without specimens was used as a negative control. The released elements from each alloy into the solution were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The elements released after 7 days immersion were reported in $\mu\text{g}/\text{cm}^2$.

The results found that the elements released from Au-Pd were not detected. Mean of the total elemental release of Au-Pd, Ag-Pd, Ni-Cr and Cu-Al alloys covered with Zinc Cement Improved was 4.19 ± 2.30 , 2.31 ± 1.14 and $185.50 \pm 17.83 \mu\text{g}/\text{cm}^2$, respectively. Au-Pd, Ag-Pd, Ni-Cr and Cu-Al alloys covered with Panavia F 2.0 was 3.69 ± 1.51 , 2.13 ± 0.60 and $247.31 \pm 90.63 \mu\text{g}/\text{cm}^2$, respectively. Two-way ANOVA and Tamhane multiple comparisons analysis revealed the total elemental release of Cu-Al alloy was significantly higher than other alloys when covered with Zinc Cement Improved and Panavia F 2.0 ($p < 0.05$). No significant differences were found among each alloy when cemented with Zinc Cement Improved and Panavia F 2.0 ($p > 0.05$). The amount of elemental release was associated with corrosion resistance that was affected by types of dental alloys but not by the two types of tested cement.

Department: Prosthodontics
Field of Study: Prosthodontics
Academic Year: 2010

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Advisor's Signature..... P. Salimee
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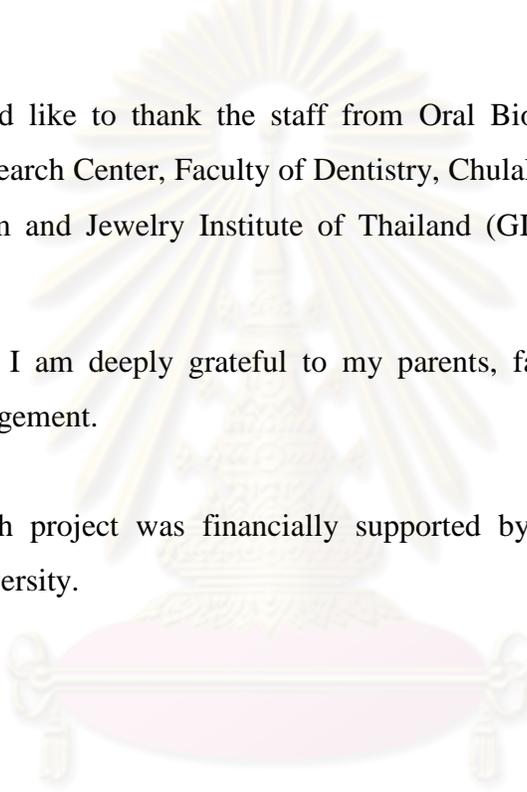
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LIST OF ABBREVIATIONS

| | |
|--------|----------------------|
| °C | degree Celsius |
| µg | microgram |
| µm | micrometer |
| Ag | silver |
| Al | aluminum |
| Au | gold |
| Cd | cadmium |
| Cu | copper |
| Cr | chromium |
| e.g. | exempli gratia |
| et al. | et alii (and others) |
| Fig. | figure |
| Ft | ferrum |
| g | gram |
| GPa | gigapascal |
| In | indium |
| ml | milliliter |
| mm | millimeter |
| Ni | nickel |
| Pt | platinum |
| wt% | weight percentage |
| Zn | zinc |

CHAPTER I

INTRODUCTION

Dental alloys have been used for many years for restorative dentistry that include inlays, onlays, posts, crowns, bridges and framework of removable dentures. In fixed prosthodontics, the mechanical, physical properties and biocompatibility of dental alloys are considered to be important since the restorations are existent in oral cavities for many years. In restoring endodontically treated teeth, the insufficient remaining tooth structure involves the ability of post to retain a restoration [1]. Custom-cast post and cores have been used as a standard treatment for endodontically treated teeth for many years [2]. Although prefabricated posts have been used increasingly, cast posts are still recommended for noncircular root canals and moderate to severe loss of coronal tooth structure [3]. The advantage of well-adapted to root canal shape is that it can obtain more retention than prefabricated post especially when coronal tooth substance is minimal and retention of post to root is critical [4, 5].

Before 1975, type III gold-based alloys were exclusively used for cast restoration [6] since their high corrosion resistance [7] and modulus of elasticity were similar to tooth structure [1, 8]. However, the prices of gold alloys are always continuing to increase. Other alloys have been developed to replace the good properties of gold alloys [6]. Palladium-based alloys became popular during 1980-1990 [6]. These alloys also have a high corrosion resistance [7] but their modulus of elasticity is slightly higher than gold alloys (115-125 GPa). The cost of these alloys is more appropriate than gold alloys however, it still expensive due to the unstable price of palladium [6]. Nickel-based alloys are more economic and are widely used as an alternative. However, their biological and physical properties are of concern due to their high modulus of elasticity, which may cause root fracture in endodontically treated teeth [1]. The modulus of elasticity of nickel-chromium alloys is approximately twice (154-210 GPa) when compared to gold alloy (88 GPa) [9]. Moreover, allergic responses to nickel were reported in some patients [10] and there are reports about palladium allergy in patients who are sensitive to

nickel [11]. Other alternative predominantly base metals are copper-based alloys, such as copper-zinc alloys and copper-aluminum alloys [12]. These alloys have been used for fixed prosthodontics over 25 years without officially clinical reports [13]. These inexpensive alloys are quite popularly substituted for gold alloys in South America, especially in Brazil [10]. Although the modulus of elasticity is comparable to gold alloys, they are reported to corrode more than nickel alloys. Therefore, their applications in clinical use are in doubt, even though the corrosion product of these copper alloys can be removed by brushing [14]. Several studies have reported about corrosive base metal post involved root fracture [15-17], discolored gingival tissue [18] and allergenic responses of oral mucosa closed to dental alloys [10]. Thus, the property of corrosion resistance is an important concern in the clinical use of these alloys.

The International Organization for Standardization (ISO) 10271 describes the protocol for corrosion test methods in dental alloys, including an electrochemical corrosion test, a tarnish test and an immersion test. The electrochemical corrosion test measures the degradation of sample occurring in the electrolyte from the electrochemical reaction and reports in electrochemical values such as current density. For the tarnish test, which usually tests dental alloys containing silver, copper and/or gold, the visible differences such as discoloration and reflectivity after immersion in sodium sulfide hydrate solution are reported. For the immersion test, the samples are immersed in a 0.1 M lactic acid/NaCl solution under the relative motion or minimum relative motion condition between sample and solution. The elements released are analyzed and reported after 7 days [19]. The electrochemical test is convenient since less time consuming and sufficiently sensitive to measure corrosion even in the low rates of noble alloy [7], but the specific elemental release cannot be identified. The immersion test can analyze the specific elemental release in the solution from noble or base metal alloys which when immersed, the released elements can be detected and measured after 7 days [13]. The solution after immersion is measured using either atomic absorption spectrometer (AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES) [20]. Both of them can be used for analyzing the quality and quantity of more than 70 elements. The disadvantage of AAS is that it can analyze only single element at a time [21]. ICP-OES is a multi-element analysis that can measure several elements simultaneously [21]. The data

from these measurements reflect the probability of elements released into the oral environment [22].

The elemental release associated with corrosion resistance of dental alloys [23] may be influenced by many factors, such as alloy composition and microstructure [24], solution composition [25, 26], pH of solution [26, 27] and conditioning times [23, 28-30]. Reduction in pH can also affect elemental release of dental alloys. Wataha et al. reported that reduced pH significantly increased Ni released from nickel-chromium alloy or releasing of Ag and Cu from Au-Pt alloy [26].

Certain dental luting cements, such as zinc phosphate cements used in fixed prosthodontics, present low pH value during initial setting time [31]. The acidity of the cements might affect the elemental release that correlate with the corrosion resistance of dental alloys. Previous studies have examined the elemental release of dental alloys but few studies investigated the immersion test of dental alloys combined with dental cements. Turpin et al. investigated the corrosion behavior of titanium by electrochemical corrosion test and reported that the corrosion susceptibility of titanium covered with zinc phosphate or glass ionomer cements was slightly increased compared to zinc eugenate cement [32]. Demirel, Saygili and Sahmali also found that titanium covered with zinc eugenate and uncovered titanium were higher corrosion resistant than titanium covered with zinc phosphate, glass ionomer, resin-modified glass ionomer and resin cements [33]. Titanium covered with zinc phosphate and glass ionomer cements was more susceptible, which might be caused by fluoride released from glass ionomer cement or the acidic setting of zinc phosphate cement [32, 33].

Nowadays, many types of dental cements are commonly used in fixed prosthodontics. Their pH during cementation might affect the corrosion resistance of the alloys when used to cement the restoration. The corrosion properties of copper alloys which have good elastic modulus when used as a post are very few. The objective of this study was to evaluate the corrosion resistance of dental alloys (gold-palladium alloy: Au-Pd, silver-palladium alloy: Ag-Pd, nickel-chromium alloy: Ni-Cr and copper aluminum alloy: Cu-Al) covered by two different dental cements (zinc phosphate cement: Zinc

Cement Improved and resin cement: Panavia F 2.0) using an immersion test in acidic solution by measuring elemental release using ICP-OES.



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CHAPTER II

LITERATURE REVIEW

Classification system of cast dental alloys

Cast dental alloys are classified into 3 groups: high noble, noble and predominantly base metal alloys, based on the contents of noble elements. High noble alloys consist of noble metal content ≥ 60 wt% that contains at least 40 wt% gold. Noble alloys consist of noble content at least 25 wt%, and predominantly base metal alloys consist of noble content less than 25 wt%. Noble elements include gold, palladium and platinum group except silver [34]. Silver is a precious metal in the commercial market [6]. However, silver is not classified as a noble element in dental material since it can react with air, water and sulfur in an oral environment to form a dark discoloration product (silver sulfide) [9].

Corrosion

An oral cavity is a highly conductive environment which is usually warm and moist with fluctuating temperature and wide variety of pH from foods and drinks. This environment could accelerate a corrosion reaction in dental alloys used in the mouth. Corrosion occurring in oral cavities is usually electrochemical corrosion due to saliva, which is a weak electrolyte. The reaction of oxidation and reduction can occur simultaneously in the distributed site on the surface of dental alloys. The corrosion process is a complicated mechanism [9] and investigation is difficult to measure due to the different conditions among individual patients [35]. The biological reaction of oral tissue might be affected by the elements released from corroded dental alloys, thus the dental alloys should have an appropriate corrosion resistance. The in vitro corrosion test of base metal alloys for fixed prosthodontics recommended that the total amount of

elements released per surface area should not exceed $1,000 \mu\text{g}/\text{cm}^2$. The corrosion resistance of base metal alloys are classified into 3 groups [20].

1. The total amount of elements released in 7 days less than $10 \mu\text{g}/\text{cm}^2$ is classified as an excellent level.
2. The total amount of elements released in 7 days between 10 to $100 \mu\text{g}/\text{cm}^2$ is classified as a good level.
3. The total amount of elements released in 7 days more than $100 \mu\text{g}/\text{cm}^2$ but not exceeding $1,000 \mu\text{g}/\text{cm}^2$ is classified as an acceptable level.

Factors influencing corrosion resistance related to elemental release

There are many factors influencing the corrosion process which affect the elements released from dental alloys.

1. Alloy composition and microstructure

The composition of dental alloys plays an important role in the elemental release [24]. In general, the corrosion resistance of dental alloys decreases with decreasing nobility. Gold and high-gold alloys demonstrate very excellent corrosion resistance [7] that release the least level of some elements such as Cu and Zn, and are more stable than noble or predominantly base metal alloys [29]. Palladium-based alloys also have a high corrosion resistance [7]. Vaidyanathan and Prasad found that corrosion resistance was influenced by palladium content. Those alloys with 20 % Pd or more tend to resist corrosion [36]. Increasing palladium content in palladium-silver alloys provides the improved corrosion resistance [7]. Nickel-chromium alloys with beryllium content released higher elements into the lactic acid/NaCl solution (pH 2.3) due to the selective dissolution of Ni-Be in its eutectic phase that performed as an anode to the Ni-Cr solid solution. In addition, those alloys with lower chromium and molybdenum content showed undesirable corrosion resistance [28]. Huang reported that nickel-chromium alloys contained more than 21 wt% Cr, and provided a higher percentage of Cr_2O_3 and MoO_3 in

the surface oxide layer which resulted in higher corrosion resistance compared to those alloys with 12.4-13.6 wt% Cr [37]. Similar results have been reported by Wylie et al. who found that nickel-chromium alloys containing 25 wt% Cr presented higher corrosion resistance than that containing 12.6 wt% Cr [27]. However, the elements from some high noble alloys with multi-phase microstructure were more easily released compared with other single-phase alloys containing lower overall nobility [24]. In the same component of alloys with single-phase microstructure, a slightly modified composition without altering the microstructure could change corrosion behavior. For example, the release of Ag and Cu was stable when palladium was slightly increased and zinc slightly decreased in high noble alloys (Au-Ag-Cu alloy). The elements released from multi-phase microstructure were more than single-phase microstructure, which could contribute to increase corrosion. Alloy microstructure was a dominant factor affecting the elemental release. The multi-phase microstructure was more critical to elemental release than overall nobility of the dental alloy. Furthermore, Wataha, Craig and Hanks investigated the released elements from dental alloy into cell-culture medium. Elements such as Au, In or Pd did not release at detectable levels. On the other hand, the concentrations of released elements such as Ag, Cd, Cu, Ga, Ni or Zn varied between different alloys. The elemental release was not proportional to the abundance of element in the alloy's component [24].

2. Composition of solution

Different corrosion environments could influence the elements released from the same alloy. The study of Wataha, Nelson and Lockwood reported that the composition of solution significantly affected the elemental release of dental alloys. Although nickel-chromium alloy significantly released Ni into the saline solution (0.85 % sodium chloride in water), several types of dental alloys which contained elements of copper, silver and zinc released more Cu, Ag and Zn into saline with 3% bovine serum albumin solution compared to saline solution and cell-culture medium. The presence of some proteins may alter corrosion behavior resulting in more or less elemental release but the mechanism is not clear [25].

3. The pH of solution

A transient acidic environment could affect elemental release. Reduced pH significantly increased Ni released from nickel-chromium alloy. Condition at pH 1 caused the release of Ni from nickel-chromium alloy with low chromium and absent molybdenum content twice as much compared to pH 4 conditions. The decreasing pH also significantly increased the release of Ag and Cu from Au-Pt alloy. However, the Cu release was significantly increased in a mixture of lactic and sodium chloride solution compared to phosphate-buffered saline at the equivalent condition (pH 1). However, a transient acidic environment could affect the elemental release from nickel-chromium alloys more than high noble or noble alloys [26]. The corrosion resistance measured by electrochemical method in artificial saliva reported that nickel-chromium alloy with higher chromium content (25 wt%) showed higher corrosion resistance. This alloy with lower chromium content (12.6 wt%) was more susceptible to corrode especially at pH 2.5 [27]. The study of Wataha and Malcolm reported that the composition of the alloy surface is important to the release of base metal elements from dental alloy [38]. The reduced pH might alter the surface of the alloys affecting the release of elements [26].

4. Conditioning time

The elements released from alloys were at a high initial rate and the levels of the release continued to increase with time [28-30]. The study of Wataha and Lockwood found that the elemental release into a cell-culture medium was not stopped completely over 10 months [30]. The elements still released but the release rate decreased over time [28-30]. High noble alloy released less elements and was more constant with time, while the noble and predominantly base metal alloys released more elements and tended to increase with time [29].

5. Surface defects [22, 39]

The Fe-Pt alloys with less than 67.2 wt% Pt showed more surface cast defects resulting in a higher amount of Fe released into the lactic acid solution [39].

Effect of elements released from dental alloys

Several studies reported about corrosive base metal post involved root fracture [15-17], discolored gingival tissue [18] and allergenic responses of oral mucosa closed to dental alloys [10]. Petersen reported longitudinal root fracture after restoration with stainless steel post, amalgam core and cast gold crown over twenty years (approximately 21 years). When materials had different electrode potential, a corrosion reaction occurred and corrosion products may change volume in the root canal which causes root fracture [15]. Silness, Gustavsen and Hunsbeth also found a layer of black or brownish-black material covering the rough post surface, root canal wall and the root surface. The fracture surface presented the heaviest discoloration. Energy-dispersive X-ray spectroscopy (EDX) showed those materials were composed of iron and chromium which were the main component of stainless steel post. Those corrosion products migrated and deposited completely or partially completed dentinal tubule adjacent to the post. The root fracture will happen if gradual pressure by increasing corrosion products exceeds the strength of the root. The corrosion process was ongoing, and then diffused to the fractured root surface and periodontal ligament space [16]. The elements composed of metal post could migrate to surrounding hard and soft tissues. Arvidson and Wroblewski reported that a higher amount of copper release was found in an intense blue-green colored dentin-tooth section close to the post. Elements such as Cu, Zn and Ag which were mainly composed in the screw posts were found in discolored gingival adjacent to the extracted tooth. Although the corrosion products had not been seen in radiograph, the post showed a variable degree of tarnish [18]. In 1992 Luu and Walker also reported black corrosion product on the fracture site of longitudinal fractured tooth which have received prefabricated post composed of nickel and chromium (Fig. 1) [17].



Fig. 1 Corroded base metal post in radiograph observed from 1982-1986. The radiographic showed an appearance of corroded post in distal canal and fractured fragment (*Quintessence Int* **23**(6): 389-92) [17].

The elemental release associated with corrosion resistance of dental alloys is correlated with its toxicity [23, 40]. It might be affected by the biological reactions due to the diffusion of elements into the adjacent tissues. Elements such as Ag, Cu, Ni and Zn were determined to have the most tendency to be released [24], resulting in the suspected toxic elements in fibroblast cell culture [29, 40]. Elshahawy, Watanabe and Kramer investigated the cytotoxic effects of metal ions using L-929 mouse fibroblast. The metal ions such as Zn^{2+} , Cu^{1+} , Ni^{2+} , Be^{2+} and Ag^{1+} were highly released and more cytotoxic than Fe^{3+} , Cr^{3+} , Mo^{5+} , Al^{3+} , Pd^{2+} and K^{1+} [40]. However, there are few studies investigating the specific concentration of released elements causing toxicity. The study of Wataha, Hanks and Craig investigated the effects of metal ions on cell metabolism using Balb/c 3T3 fibroblasts and four toxicity parameters: total protein production, 3H -leucine incorporation, 3H -thymidine incorporation and MTT-formazan production. These metal ions of Ag^{1+} , Au^{4+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Pd^{2+} and Zn^{2+} were prepared from Ag_2SO_4 , $HAuCl_4 \cdot 3H_2O$, $CdCl_2$, $CuCl_2$, $NiCl_2 \cdot 6H_2O$, $PdCl_2$ and $ZnCl_2$. The concentrations causing 50% toxicity (TC50 values) exhibit different (wide variety) values when using different toxicity parameters. For example, 3H -thymidine incorporation is the most sensitive to TC50 values for Cd^{2+} (0.05 ppm), Cu^{2+} (2.8 ppm) and Ga^{3+} (4.5 ppm). The potencies of toxic effect might depend on the nature and number of the interaction between the metal ions and the nonspecific binding sites as well as some specific binding sites in the cell. The TCD50 values from four toxicity parameters appeared to be different. The toxic potency of the Cd^{2+} , Ag^{1+} , Zn^{2+} , Cu^{2+} , Ga^{3+} , Ni^{2+} , Au^{4+} , Pd^{2+} , In^{3+} ions based on the lowest concentration of the four parameters assessment was 0.05, 0.63, 1.6, 2.8, 4.5, 10, 17, 32 and more than 50 ppm, respectively. The ppm is a unit based on

mass but μM is a unit based on numbers of atoms that assessed the toxicity of each atom of a metal [41]. In addition, toxic potency did not correlate with the atomic weights (AW). For example, the potency of Au^{4+} (AW = 196) was not similar to Cd^{2+} (AW = 112) or In^{3+} (AW = 114) and Cd^{2+} (AW = 112) also had a different potency [41]. Although many studies have investigated in vitro toxicity of elements released from dental alloy, it is still difficult to compare among these studies because there are many factors affecting the toxicity assessment, such as types of testing methods, types of cell culture systems, types of cell culture medium, exposure time and the amount of used cation salt solutions [40, 41].

Dental luting cements

The ideal properties of dental luting cements include adhesion to tooth structure and restorative materials, optimal strength, insolubility in oral fluids, low film thickness, biocompatibility, anticariogenic properties and easy manipulation [42]. The commercially available dental cements used in fixed prosthodontics are zinc phosphate, polycarboxylate, glass ionomer, resin-modified glass ionomer and resin composite cements [43].

1. Zinc phosphate cement

Zinc phosphate cements are commonly used as a gold standard compared to other dental cements. These cements have a long-term success history in clinical use despite their lack of chemical bonding to either tooth structure or restoration [42]. Zinc phosphate cements remain an optimal cement of choice for cementing cast post, metal or metal-ceramic restoration [42, 43]. The powder of zinc phosphate cement mainly contains zinc oxide (90.2%) and magnesium oxide (8.2%). The liquid is a solution of phosphoric acid [8].

2. Polycarboxylate cement

Polycarboxylate cements contain zinc oxide and magnesium oxide. The liquid is a solution of 32-42% polyacrylic acid, itaconic acid and tartaric acid. The powder combines with 15-18% polyacrylic acid and will be mixed with water [8]. Polycarboxylate cements have the highest solubility [44] and film thickness in water-based cements [8]. The plastic deformation behavior of these cements during loading leads to an undesirable deformation of cement film. This result might affect mechanical retention and then loses its interlocking cemented restoration. Clinical use is limited in long-span and cantilever bridges [45].

3. Glass ionomer cement

The powder of glass ionomer cement is calcium fluoroaluminosilicate glass ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2\text{-Na}_3\text{AlF}_6\text{-ALPO}_4$). The liquid is the solution of polyacrylic acid/itaconic acid copolymer, itaconic acid and tartaric acid in water. Some commercial product, the acid component (polyacrylic acid), is dried and combined with glass powder, thus the liquid may be water or dilute tartaric acid solution [8]. Glass ionomer cement have the chemical bond to tooth structure, fluoride release and sensitivity to moisture [8]. The indication of these cements is similar to zinc phosphate cements [43]. However, patients should limit heavy masticatory stress on cemented restoration until the strength of glass ionomer cements have been fully developed for several days [46].

4. Resin-modified glass ionomer cement

Resin-modified glass ionomer cements are available supplied in both self-cured and light-cured polymerization reaction. These cements can bond to tooth structure, release fluoride similarly to glass ionomer cements and is low soluble in oral fluids. However, these cements are sensitive to moisture and have higher water sorption compared to resin cements [8]. These cements should not be used to lute all ceramic crowns or posts in endodontically treated teeth [42, 43] since the subsequent plasticity and hygroscopic expansion from water sorption after cementation by a hydrophilic nature of polyHEMA might cause a fracture [43]. However, the postcementation expansion effect is still obscured [42].

5. Resin cement

Polymerization is initiated through self-cured, light-cured or dual-cured reaction [43]. Resin cements containing filler content have a good compressive and diametral tensile strength. The filler content does not directly relate to film thickness. The film thickness varies among the manufacturers [47]. These cements are significantly less soluble [48] and have more porosity [49] than glass ionomer, zinc phosphate and polycarboxylate cements, resulting in the protection of interior tooth structure from penetration of oral fluids and bacteria in an oral environment [49]. In addition, their available color shades have made these cements as a cement of choice for esthetic type restorations. However, the proper manipulation requires multiple steps resulting in technical sensitivity [43]. Resin cements are quite popularly used to lute prefabricated and metal post in endodontically treated teeth due to the properties of high tensile strength and well-bonding ability [46]. If endodontic failure occurs later, the metal post that luted with resin cement becomes difficult to remove and becomes a risk to root fracture. Luting with zinc phosphate cements is easier to remove and lowers the risk of root fracture [1]. Zinc phosphate cements remain an optimal cement of choice for luting cast post, metal and metal-ceramic restoration [42, 43].

Effect of dental cements on corrosion resistance of dental alloys

Few studies have investigated the corrosion of dental alloys combined with dental cements. Turpin et al. investigated the corrosion behavior of titanium by electrochemical corrosion test and reported that the corrosion susceptibility of titanium covered with zinc phosphate or glass ionomer cements was slightly increased compared to zinc eugenate cement [32]. Demirel et al. also found that titanium covered with zinc eugenate and uncovered titanium (which has the higher corrosion potential) had a higher corrosion resistance than titanium covered with zinc phosphate, glass ionomer, resin-modified glass ionomer and resin cements. Titanium covered with zinc phosphate and glass ionomer cements was more susceptible to corrode that may induce the ability to depassivate titanium [33]. The results might be caused by fluoride released from glass ionomer

cement or the acidic setting of zinc phosphate cement. Titanium covered with zinc eugenate was more resistant to corrosion since this cement had a neutral setting and no fluoride release [32, 33]. However, the differences of the corrosion potential and the corrosion current density values in each group were small. Therefore, the risk in clinically use may not be expected [33].

Elemental analysis

The elements released from dental alloys were measured using either atomic absorption spectrometer (AAS) or inductively coupled plasma atomic emission spectroscopy (AES) [20]. Both of them have been used for analyzing the quality and quantity of more than 70 elements. Atomic absorption spectrometer is simple, effective and relatively low cost but only single element analysis at a time [21]. ICP-AES or inductively coupled plasma optical emission spectroscopy (ICP-OES) [50] are analytical methods that can measure in a simultaneous multielement analysis [21]. The detection limits of concentration levels (Fig. 2) can monitor below one milligram per liter (ppm) [51]. ICP-OES is the method that was widely used to monitor the interested elements in the samples such as environmental substance and water (drinking water, waste water and groundwater supplies), petroleum products, agricultural and food, geological samples, biological materials and in industrial quality control [21, 51]. This method is high stability, low noise and low background but relatively expensive [21].

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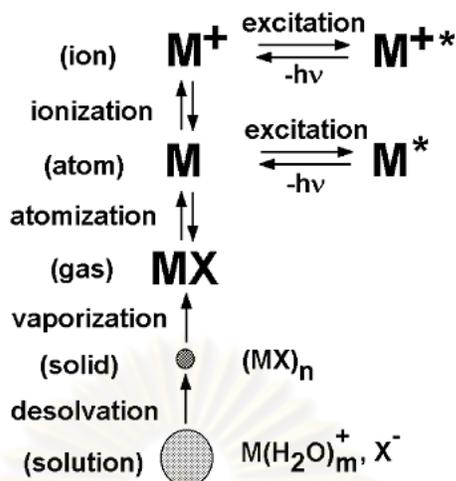


Fig. 4 The process of desolvation, vaporization, atomization, ionization (Boss, C. B and Fredeen, K. J., 1997) [51]

The components of an ICP-OES instrument are shown in Fig. 3. The solution sample flows to a nebulizer that converts the solution into a fine spray of droplets (aerosol). The aerosol is transported into the center of the ICP source where the process of desolvation, vaporization, atomization, ionization occurs (Fig. 4). The external energy supplied by the plasma source excites atoms in ground state to higher energy state (excited state). Then, the atoms in excited state emit energy and turn back to ground state. The emission from each excited atom is characterized by wavelength. A photomultiplier tube (PMT) in spectrometer can detect multiple wavelengths at once, resulting in a simultaneous multielement analysis. The concentration of sample solution is measured using a calibration curve (plots of emission intensity versus standard concentration). Computer systems and software analyze the data and report the type and concentration of interested elements [21, 51].

The purposes of this study

1. To evaluate the corrosion resistance of dental alloys when covered with two different dental cements.
2. To evaluate the concentration of elements released from dental alloys covered with two different dental cements.

3. To evaluate the effect of dental cements on the elements released from dental alloys.

Hypotheses

Hypothesis 1

Null hypothesis: There would be no significant difference in total elements released from dental alloys when covered with different dental cements.

Alternative hypothesis: There would be significant difference in total elements released from dental alloys when covered with different dental cements.

Hypothesis 2

Null hypothesis: There would be no significant difference in total elements released from four types of dental alloys when covered with each type of dental cement.

Alternative hypothesis: There would be significant difference in total elements released from four types of dental alloys when covered with each type of dental cement

Hypothesis 3

Null hypothesis: There would be no significant difference in total elements released from each type of dental alloy when covered with both types of dental cements.

Alternative hypothesis: There would be significant difference in total elements released from each type of dental alloy when covered with both types of dental cements.

Keywords

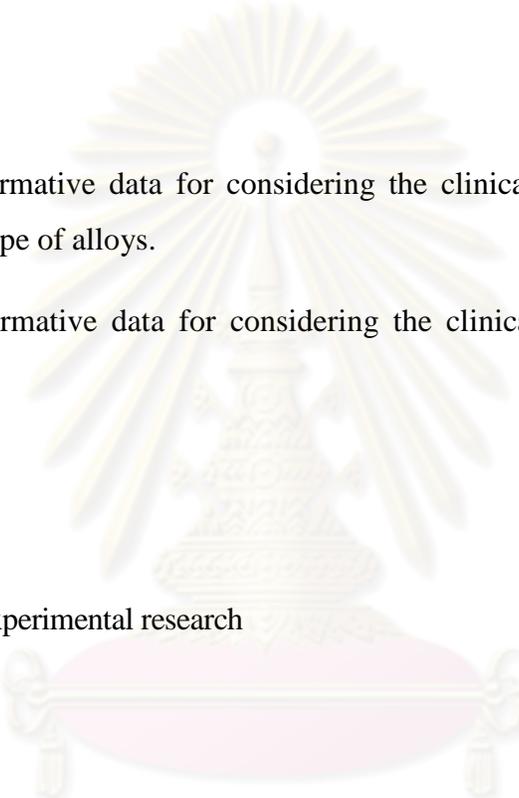
- Corrosion
- Alloy
- Cement
- Elemental release

Proposed benefits

1. To gain informative data for considering the clinical use of appropriate dental cements to type of alloys.
2. To gain informative data for considering the clinical use of dental alloys and cements.

Type of research

Laboratory experimental research



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CHAPTER III

MATERIALS AND METHODS

Materials used in this study

1. High noble alloy: Au-Pd alloy (Jel Burst, Heraeus-Kulzer Inc., USA)
2. Noble alloy: Ag-Pd alloy (Pallag M, Degussa-Huls, Germany)
3. Predominantly base metals: Ni-Cr alloy (4all, Ivoclar Vivadent Inc., USA) and Cu-Al alloy (NPG, Aalba Dent Inc., USA)
4. Zinc phosphate cement (Zinc Cement Improved, S.S. White Group, Gloucester, UK)
5. Resin cement (Panavia F2.0, Kuraray medical, Okayama, Japan)
6. Blue inlay wax (blue inlay casting wax, Kerr, USA)
7. Finishing stone (Shofu Dental Corp., USA)
8. Lactic acid ($C_3H_6O_3$) analytical grade (Ajax Finechem, Auckland, New Zealand)
9. Sodium chloride (NaCl) analytical grade (Carlo Erba Reagent, Milan, Italy)
10. Ethyl alcohol (C_2H_5OH) analytical grade (VWR International Ltd., France)
11. Polyvinyl siloxane impression materials putty type (Reprosil, Dentsply, USA)

Instruments used in this study

1. Inductively coupled plasma optical emission spectroscopy: ICP-OES (Optima 4300DV, Perkin Elmer Inc., USA)
2. Incubator (Contherm 160M, Contherm Scientific Ltd., New Zealand)
3. Light curing unit (Elipar Trilight 3M ESPE, Minnesota, USA)

4. pH meter (GP353, EDT Instruments Ltd., UK)
5. Digital caliper (Mitutoyo, Japan)
6. Digital balance (BP 110S, Sartorius AG, Gottingen, Germany)
7. Test tube screwcap (Pyrex, French)

Specimen preparation

Four types of dental alloys (10 samples of each) used in this study were Au-Pd (Jel Burst, Heraeus-Kulzer Inc., USA), Ag-Pd (Pallig M, Degussa-Huls, Germany), Ni-Cr (4all, Ivoclar Vivadent Inc., USA) and Cu-Al alloys (NPG, Aalba Dent Inc., USA.). These alloys represent high noble, noble and two predominantly base metals classified by the Council on Dental Materials, Instruments, and Equipment [34]. The compositions of these alloys given by the manufacturer are shown in Table I.

Table I Composition of alloys

| Alloy | Au-Pd (Jel Burst) | Ag-Pd (Pallig M) | Ni-Cr (4all) | Cu-Al (NPG) |
|-----------------------|---|--|---|--|
| Composition (wt %) | Au 75.0%, Pd 11.9%, Ag 10.0%, In 1.9%, Sn 1.0%, Re, Ir | Ag 58.5%, Pd 27.4%, Cu 10.5%, Au 2.0%, Zn 1.5%, Ir 0.1% | Ni 61.4%, Cr 25.7%, Mo 11.0%, Si 1.5%, Mn < 1.0%, Al < 1.0%, C < 1.0% | Cu 79.3%, Al 7.8%, Ni 4.3%, Fe 4.0%, Mn 1.6%, Zn 3.0% |

Alloy preparation

Specimens were cast into disc-shaped of 5.0 ± 0.5 mm in diameter and 0.8 ± 0.05 mm in thickness using lost wax technique. A stainless steel mold was used to perform reproducible size and shape of disks. The wax patterns using blue inlay casting wax (Kerr, USA) were cast by lost wax technique according to the manufacturer's instructions. The surface defects (beads or other projections) of the specimens were removed from surface using finishing stone (Shofu Dental Corp.,USA) and wet ground with 600 grit SiC paper separated from each alloy to prevent cross contamination. Surface was blasted with alumina powder (approximately $110 \mu\text{m Al}_2\text{O}_3$). The dimension of each specimen was measured with digital caliper (Mitutoyo, Japan). Finally, the specimens were ultrasonically cleaned in ethanol for 2 minutes then rinsed with distilled water and dried before covering with the dental cements.

Cementation

Ten specimens of each alloy were randomly divided into two groups of five. Each specimen was placed into a silicone mold (Reposil, Dentsply, USA) for controlling the cement thickness at 0.70 ± 0.05 mm [32]. The specimen was covered with two different cements: zinc phosphate cement (Zinc Cement Improved, S.S. White Group, Gloucester, UK) or resin cement (Panavia F 2.0, Kuraray medical, Okayama, Japan) on one side individually (Fig. 5).



Fig. 5 Dental cements used in this study: Zinc Cement Improved (a) Panavia F 2.0 (b)

The cements were mixed according to the manufacturer's instructions. The compositions of these cements given by the manufacturer are shown in Table II except powder of zinc phosphate cement given by Power and Sakaguchi [8]. A microscope slide was located above the cement to produce a flat surface and press the excess cement over the border of the mold. In Zinc Cement Improved ($ZnPO_4$), the setting time was 5½-7 minutes. In Panavia F 2.0 (Panavia), the cement was light cured with a light curing unit (Elipar Trilight 3M ESPE, Minnesota, USA) for 5 seconds around margin and applied OXYGARD II for 3 minutes. Au-Pd and Ag-Pd groups were applied with alloy primer before cementation. After initial setting, the microscope slide was removed. After final setting, the specimen was removed from the mold. Then the excess cement was removed and polished with white stone finishing bur (Shofu Dental Corp., USA).

Solution preparation

This solution was used in standard corrosion testing according to the ISO 10271. Tested solution was a mixture of 0.1 M lactic acid and 0.1 M NaCl solution freshly prepared for experiment by dissolving sodium chloride 5.85 ± 0.005 g and lactic acid 10.0 ± 0.1 g in approximately 300 ml of deionized water, then diluted with water up to $1,000 \pm 10$ ml. The pH of the solution was 2.3 ± 0.1 recorded by pH meter (GP353, EDT Instruments Ltd., UK).

Immersion test

Each specimen was placed in a separate glass container (Pyrex, French) and immersed in 10 ml lactic acid/NaCl solution. All containers were closed tightly to prevent evaporation and maintained in incubator (Contherm 160M, Contherm Scientific Ltd., New Zealand) at $37 \pm 1^\circ C$ for 7 days \pm 1hour. The solution without specimens was used as a negative control. After 7 days, the specimens were removed. The 5 ml of solution in each container were separated for measuring the released elements. The pH of residual solution was recorded by pH meter (GP353, EDT Instruments Ltd., UK).

Table II Composition of dental cements

| Material and composition | Lot No. |
|--|---|
| <p>Zinc Cement Improved (S.S. White Group, Gloucester, UK)</p> <p>Powder: ZnO, MgO, SiO₂, Others</p> <p>Liquid: H₃PO₄ (free acid), H₃PO₄ (combined with Al and Zn), Al, Zn, Water</p> | <p>Powder: 650941</p> <p>Liquid: 300945</p> |
| <p>Panavia F 2.0 (Kuraray, Okayama, Japan)</p> <p>-Panavia F 2.0 paste A: 10-Methacryloyloxydecyl dihydrogen phosphate, Hydrophobic aromatic dimethacrylate, Hydrophobic aliphatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Silanated silica filler, Silanated colloidal silica, dl-Camphorquinone, Catalysts, Initiators, Others</p> <p>-Panavia F 2.0 paste B: Sodium fluoride, Hydrophobic aromatic dimethacrylate, Hydrophobic aliphatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Silanated barium glass filler, Catalysts, Accelerators, Pigments, Others</p> <p>-ED Primer II liquid A: 2-hydroxyethyl methacrylate, 10-Methacryloyloxydecyl dihydrogen phosphate, N-Methacryloyl-5-aminosalicylic acid, Water, Accelerators</p> <p>-ED Primer II liquid B: N-Methacryloyl-5-aminosalicylic acid, Water, Catalysts, Accelerators</p> <p>-OXYGUARD II: Glycerol, Polyethylene glycol, Catalysts, Accelerators, Dyes, Others</p> <p>-Alloy primer: Acetone, 6-(4-Vinylbenzyl-N-propyl)amino-1,3,5-triazine-2,4-dithione, 10-Methacryloyloxydecyl dihydrogen phosphate</p> | <p>51318</p> <p>0377AA</p> |

Elemental analysis

Determined elements were chosen due to their tendency to be released (lability), their toxicity and the main element component. Based on the study of Wataha et al, elements such as Ag, Cu, Ni and Zn were determined to be the most labile elements [24]. In addition, elements such as Cu, Ni, Ag, Cr and Al were also the cytotoxic element to fibroblast cell culture [40]. Au and Pd were non-labile elements [24] but Au was the main component in Au-Pd alloy. The determined elements of these alloys used in this study are shown in Table III. The concentration of the released elements from each alloy were measured using ICP-OES (Optima 4300DV, Perkin Elmer Inc., USA) in units of parts per million (ppm) (Fig. 6) and converted to units of microgram per square centimeter ($\mu\text{g}/\text{cm}^2$) of alloy surface area exposed to the solution. The immersion test resulted per 7 day $\mu\text{g}/\text{cm}^2$. The detection limit and wavelength of determined elements are listed in table IV.

Table III Determined elements of each dental alloy

| Alloys | Au-Pd (Jel Burst) | Ag-Pd (Palliag M) | Ni-Cr (4all) | Cu-Al (NPG) |
|---------------------|----------------------|----------------------|-----------------|----------------|
| Determined elements | Au, Ag | Ag, Cu | Ni, Cr | Cu, Al |



Fig. 6 Inductively coupled plasma optical emission spectroscopy (ICP-OES: Optima 4300DV, Perkin Elmer Inc., USA)

Table IV Detection limit and wavelength of determined elements
(ICP-OES: Optima 4300DV, Perkin Elmer Inc., USA)

| Element | Wavelength (nm) | detection limit (ppm) |
|---------|--------------------|--------------------------|
| Ag | 328.068 | 0.0070 |
| Al | 396.153 | 0.0280 |
| Au | 267.595 | 0.0310 |
| Cu | 327.393 | 0.0097 |
| Cr | 267.716 | 0.0071 |
| Ni | 231.604 | 0.0150 |

Data were analyzed by statistical software (SPSS Statistics version 16.0, SPSS Inc., Illinois, USA). The normal distribution of data was assessed by One-Sample Kolmogorov-Smirnov test. The parametric statistic was analyzed by two-way ANOVA to evaluate the interaction between the effect of dental alloys and dental cements when data was normally distributed. If there were significant differences between groups, the multiple comparisons were analyzed with 95% confidence interval ($\alpha=0.05$). If data was not normally distributed, the non-parametric statistic analyzed by Kruskal-Wallis and Conover-Inman test ($\alpha=0.05$) was performed.

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CHAPTER IV

RESULTS

The elements released from Au-Pd alloy were not detected. Ag-Pd and Ni-Cr alloys did not release detectable levels of Ag and Cr. The mean and standard deviation of the total elemental release are reported in Table V

Table V Mean and standard deviation of total elemental release ($\mu\text{g}/\text{cm}^2$)

| Group | Au | Ag | Cu | Ni | Cr | Al | Total |
|---------------|-----|-----|--------------|-----------|-----|-------------|--------------|
| Au-Pd/ZnPO4 | ND* | ND* | - | - | - | - | ND* |
| Au-Pd/Panavia | ND* | ND* | - | - | - | - | ND* |
| Ag-Pd/ZnPO4 | - | ND* | 4.19±2.30 | - | - | - | 4.19±2.30 |
| Ag-Pd/Panavia | - | ND* | 3.69±1.51 | - | - | - | 3.69±1.51 |
| Ni-Cr/ZnPO4 | - | - | - | 2.31±1.14 | ND* | - | 2.31±1.14 |
| Ni-Cr/Panavia | - | - | - | 2.13±0.60 | ND* | - | 2.13±0.60 |
| Cu-Al/ZnPO4 | - | - | 15.63±16.44 | - | - | 169.88±6.56 | 185.50±17.83 |
| Cu-Al/Panavia | - | - | 193.38±88.51 | - | - | 53.94±13.69 | 247.31±90.63 |

*ND = not detectable

- = not determined

Data were normally distributed assessed by One-Sample Kolmogorov-Smirnov test. Two-way ANOVA revealed that the interaction effect between these variables was not found ($p>0.05$). The dental cements did not affect the total elemental release ($p>0.05$) but the dental alloys had significant effect ($p<0.05$) (Table VI).

Table VI Two-way ANOVA for effects and interactions of cement and alloy

| | Df | Sum of Squares | Mean Square | F | Sig. |
|----------------|----|----------------|-------------|---------|------|
| Cement | 1 | 3113.860 | 3113.860 | 2.187 | .152 |
| Alloy | 2 | 303409.839 | 151704.920 | 106.569 | .000 |
| cement * alloy | 2 | 6438.651 | 3219.326 | 2.261 | .126 |

Robust Tests of Equality of Means revealed significant difference in the dental alloys when covered with each type of dental cement. Tamhane multiple comparisons showed statistically significant difference in Table VII.

Table VII Multiple comparisons of total elemental release in dental alloys covered with each dental cement

| | Au-Pd (Jel Burst) | Ag-Pd (Palliag M) | Ni-Cr (4all) | Cu-Al (NPG) |
|-------------------------|-----------------------------|-----------------------------|------------------------|---------------------------|
| Zinc Cement Improved | ND* | 4.19±2.30 ^a | 2.31±1.14 ^a | 185.50±17.83 ^b |
| Panavia F 2.0 | ND* | 3.69±1.51 ^a | 2.13±0.60 ^a | 247.31±90.63 ^b |

Groups with same letter showed no significant difference ($p>0.05$)

*ND=not detectable

For the total elements released from each alloy when covered with two dental cements, independent sample t-test showed no statistically significant difference (Table VIII).

Table VIII Independent sample t-test in dental alloy covered with two dental cements

| | Au-Pd (Jel Burst) | Ag-Pd (Palliag M) | Ni-Cr (4all) | Cu-Al (NPG) |
|----------------------|-----------------------------|-----------------------------|------------------------|---------------------------|
| Zinc Cement Improved | ND* | 4.19±2.30 ^a | 2.31±1.14 ^a | 185.50±17.83 ^b |
| Panavia F 2.0 | ND* | 3.69±1.51 ^a | 2.13±0.60 ^a | 247.31±90.63 ^b |

Groups with same letter (in column) showed no significant difference ($p>0.05$)

*ND=not detectable

This study revealed that the total elements released from Cu-Al alloy showed a significantly higher amount compared to other group ($p<0.05$) (Table VII). Cu-Al/Panavia released the highest amount of elements but not significantly different from Cu-Al/ZnPO₄ ($p>0.05$). Lowest amount was found in Ni-Cr/Panavia but not significantly different from Ni-Cr/ZnPO₄ ($p>0.05$) (Table VIII).

This study also found that a higher amount of Al released was found in Cu-Al/ZnPO₄ as more Cu released in Cu-Al/Panavia (Table V). Data of the Cu released from Cu-Al/Panavia was not normally distributed. Mann-Whitney test revealed that the Cu released from Cu-Al/Panavia was significantly higher than that from Cu-Al/ZnPO₄ ($p<0.05$). The comparisons of Al release analyzed by independent sample t-test revealed that the Al released from Cu-Al/ZnPO₄ was significantly higher than that from Cu-Al/Panavia ($p<0.05$).

The pH of acidic solution before immersion test was 2.25. The pH values of residual solution after 7 days' immersion are shown in Table IX.

Table IX The range of pH value in the residual solution (min-max)

| | Au-Pd (Jel Burst) | Ag-Pd (Palliag M) | Ni-Cr (4all) | Cu-Al (NPG) |
|----------------------|-----------------------------|-----------------------------|------------------------|-----------------------|
| Zinc Cement Improved | 2.91-3.04 | 2.93-3.06 | 2.91-3.06 | 2.93-3.03 |
| Panavia F 2.0 | 2.13-2.14 | 2.11-2.12 | 2.13-2.15 | 2.13-2.15 |

The specimens in the groups covered with ZnPO₄ presented a more surface area exposed to the solution than Panavia (Fig.7). The non-cemented surfaces of the specimens are shown in Fig. 8.

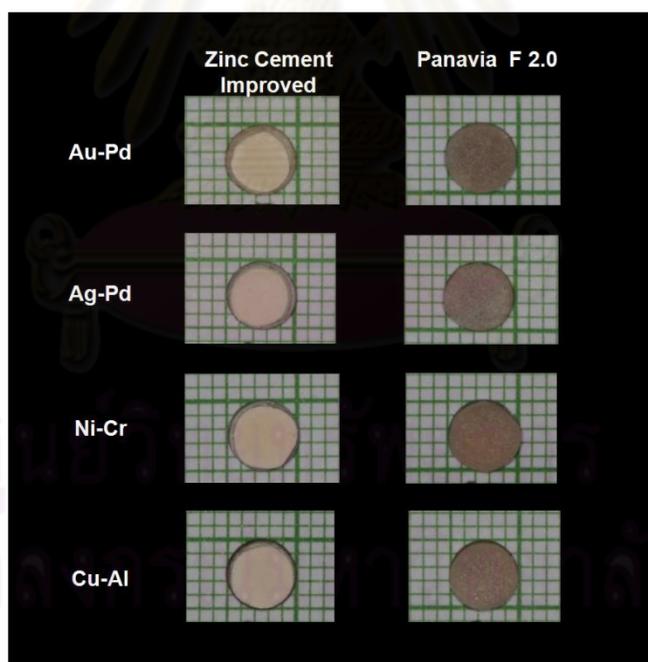


Fig. 7 Alloy groups cemented with different cements after immersion test
Note that Zinc Cement Improved showed solubility around margin of specimens.

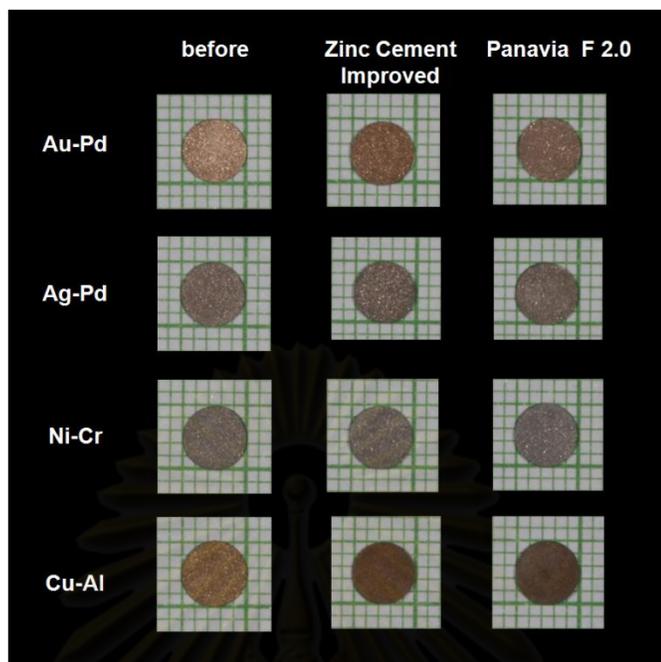


Fig. 8 Alloy groups showed the non-cemented surface before and after immersion test

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CHAPTER IV

DISCUSSION

The results revealed that the interaction effect between dental alloys and dental cements was not found. Thus, the hypothesis that there would be no difference in total elements released from dental alloys when covered with different dental cements was accepted.

The hypothesis that there would be no difference in the total elements released from four types of dental alloys when covered with each type of dental cement was rejected. Cu-Al alloy showed significantly higher amount of total elemental release compared to other alloys when covered with both ZnPO₄ and Panavia, while the elements released from Au-Pd alloy were not detected in this experiment. Although the main component in gold alloy was Au, the release of Au was not proportional to the abundance of element in this alloy [24, 29]. This agreed with the previous studies which reported that high noble alloys did not release detectable levels of Au, Pd and Ag [29, 38] or released below the detection limit. In general, the corrosion resistance of dental alloys decreased with decreasing nobility [7]. The elements released from high noble alloy were more stable than noble and predominantly base metal alloys and did not increase with time [29].

The noble alloy used in this study was Ag-Pd. This present study did not determine Pd since the amount of Pd released from high noble and noble alloys immersed in 0.1 M lactic acid/NaCl solution at pH 1 was so small (less 0.02 $\mu\text{g per cm}^2$) [26]. Previous studies reported the release of Ag and Cu from noble alloys into cell-culture medium [29]. This alloy did not release detectable levels of Ag. However, the detectable of Cu release was found 4.19 and 3.69 $\mu\text{g/cm}^2$ when covered with ZnPO₄ and Panavia, respectively. However, the study of Gil et al. found that the Ag-Pd alloy which contained 46.0 wt% Ag and 30.0 wt% Pd released greater Cu and low level of Ag into the artificial saliva at pH 6.7 [52].

The Ni released from Ni-Cr alloy covered with ZnPO₄ and Panavia was 2.31 and 2.13 $\mu\text{g}/\text{cm}^2$, respectively. Although Ni-Cr alloy has less nobility than Ag-Pd alloy, Ni-Cr alloy released lower total amount of elemental release. The Ni-Cr alloy used in this study contained 25.7 wt% Cr and 11.0 wt% Mo. The improved corrosion resistance might be from the higher amounts of chromium and molybdenum [28] which develop an adequate protective oxide layer [53] that is mainly composed of Cr₂O₃ and MoO₃. The presence of a higher percentage of these surface oxide layers was detected as a film which exhibited a higher resistance of metal ion transfer associated with a higher corrosion property of those alloys [37]. The Ni-Cr alloy with low chromium and absence of molybdenum tended to release Ni greater than the others [23]. In this study, the release of Cr was not detected, which agreed with other reports that the Cr release was very low or below the detectable levels [23, 28].

The greatest amount of elemental release was found in Cu-Al alloy. The total elements released from Cu-Al/ZnPO₄ and Cu-Al/Panavia was 185.50 and 247.31 $\mu\text{g}/\text{cm}^2$, respectively. These findings agreed with the studies of Johansson, Lemons and Hao and al-Hiyasat, Bashabsheh and Darmani that copper-based alloys corroded more than high-gold alloy and Ni-Cr alloys [12, 23]. The greater release might be from the corrosion susceptibility of this alloy [23]. Previous studies reported that the release of Cu was higher than Al [13, 54]. In the study of Eschler et al., the release of Cu and Al were 1,600 and 500 $\mu\text{g}/\text{cm}^2$ [54], but the study of Tibballs and Erimescu found the released Cu and Al was 1,800 and 72 $\mu\text{g}/\text{cm}^2$ [13]. Both studies investigated corrosion using the same commercial Cu-Al alloy (NPG, Aalba Dent inc., USA) with approximately equivalent surface area (10 cm²) to solution volume ratio but the Al release was quite different. In this study, the same commercial alloy was investigated by covering with different dental cements. However, the total amount of Cu and Al release was lower since its lesser surface area (0.32 cm²). The surface area of alloy exposed in the solution in this study was approximately 30 times less than those two studies. In addition, the release of Cu and Al in Cu-Al/ZnPO₄ was 15.63 and 169.88 $\mu\text{g}/\text{cm}^2$, and in Cu-Al/Panavia was 193.38 and 53.94 $\mu\text{g}/\text{cm}^2$, respectively. The Al released from Cu-Al/ZnPO₄ was significantly higher than that from Cu-Al/Panavia and the Cu released from Cu-Al/Panavia was significantly higher than that from Cu-Al/ZnPO₄. The higher amount of Al released from Cu-

Al/ZnPO₄ might be from the aluminum component in this cement. The higher release of Cu in Cu-Al/Panavia compared to Cu-Al/ZnPO₄ might be from the lability to an acidic environment.

The release of Ag and Cu in some alloys was slightly increased in an acidic environment. The reduced pH might alter the composition of the alloy surface that affected the release of elements from dental alloys [26]. In this study, the increased acidic environment resulted from the reduced pH value during the setting of dental cements, especially Panavia F 2.0. The pH value of zinc phosphate cement changed from approximately 2 at two minutes after mixing to 4.89 within 24 hours [31]. The pH value of Panavia F 2.0 was 2.4 as reported by Monticelli et al [55]. An increasing in pH values of solution was found in zinc phosphate cement, which agreed with the study of Yoshida et al. and Nomoto and McCabe [44, 48], but resin cements showed a small decreasing in pH value [48].

The hypothesis that there would be no difference in the total elements released from each type of dental alloy when covered with both types of dental cements was accepted. The comparisons of the elemental release from each alloy when cemented with ZnPO₄ and Panavia were not statistically significant. However, neither Ag-Pd nor Ni-Cr alloys covered with ZnPO₄ tended to release more elements than those covered with Panavia. The result might be from the more solubility of zinc phosphate cement that causes greater surface alloy exposed to the solution. Several studies investigated the solubility among dental cements and found that resin cements (All-Bond C&B, Panavia 21 and Super-Bond C&B) were significantly less soluble than glass ionomer, zinc phosphate and polycarboxylate cements in lactic acid solution at pH 4.0 [48]. The solubility of zinc phosphate cements increased with increasing of immersion time [44, 56]. These cements also more dissolved in decreasing pH value [56]. The opposite result was found in Cu-Al alloy where a higher amount of element was found when covered with Panavia. This finding might imply that Cu-Al alloy is more sensitive to acidic environment compared to other alloys. The pH of initial setting or pH value of tested solution and solubility of dental cements may cause the difference in elemental release of alloys as well. Further studies need to clarify these findings.

The visual examination of the specimens after 7 days' immersion showed that the surface of Cu-Al alloy appeared to be more corroded than other alloys as darkening surfaces were observed. The study of Benatti, Miranda and Muench found that copper-based alloys presented mild to moderate corrosion in the artificial saliva and 0.9% sodium chloride solution after 1 month's immersion. These alloys exhibited more corrosion in sulfide solution, especially after 3 months' period and in the non-self cleaning area which tested in vivo (condition) showed the darkening surface, whereas the Ni-Cr alloy showed little loss of brightness [14]. The study of Johansson et al. reported that the Cu-Al alloys showed tarnish and corrosion more than high-gold alloy and Ni-Cr alloys after 28 days of immersion either in 0.9% sodium chloride solution or artificial saliva [12].

The solubility of dental cement relates to the marginal leakage of the restorations. The oral fluids or electrolytes from oral environment could penetrate to the posts via (1) the permeable cementum and dentin covering the root surface, (2) microleaked coronal restoration and/or (3) fractured site during preparation of post space or cementation, which will initiate the corrosion process [17]. The elements composed of metal post could migrate to surrounding hard and soft tissues. A higher amount of copper release was found in an intense blue-green colored dentin-tooth section closed to the post. Elements such as Cu, Zn and Ag were found in discolored gingival adjacent to the extracted tooth. Although the corrosion products had not been seen in radiograph, the post had a variable degree of tarnish [18]. Silness et al. also found a layer of black or brownish-black material composed of iron and chromium, which were the main components of stainless steel posts, covered on the rough post surface, root canal wall and occasionally on the root surface. These corrosion products migrated and deposited completed or partially completed in dentinal tubule adjacent to the post and then diffused to fractured root surface and periodontal ligament space [16].

The elements released from dental alloys might affect the biological reactions due to the diffusion of elements into the adjacent oral tissues. The amount of released element related with its toxicity [29, 40]. Elements such as Ag, Cu, Ni and Zn were determined to have greatest tendency to be released [24], resulting in suspected toxic elements in

fibroblast cell culture [29, 40]. Elshahawy et al. reported that Cu, Ni and Ag were highly released and were more cytotoxic than Cr and Al [40]. However, there are few studies which investigate the specific concentration of released elements causing the toxicity [41]. The release of Al, Cu and Ni in this study were lower than that the total amount of elements per surface area did not exceed 1,000 μg per cm^2 according to ISO 16744 which classified as an acceptable level of corrosion resistance.

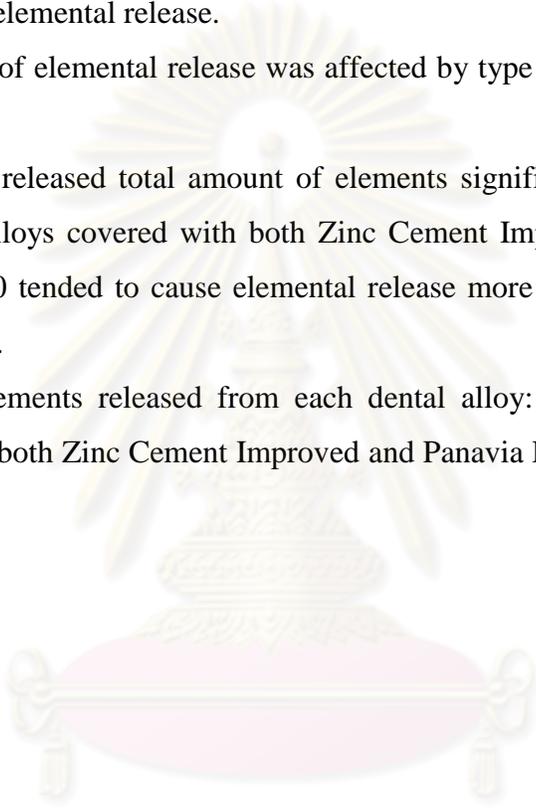
The Cu-Al alloys which has the modulus of elasticity comparable to gold alloys might be an alternative alloys in cast restoration due to cheaper price and good castability. However, these alloys are more susceptibility to corrode. The use of resin cements which are less soluble might help to reduce their corrosion. The result of this study showed no significant difference of corrosion when use these alloys with zinc phosphate cement or Panavia F 2.0. Other kinds of resin cements or glass ionomer cements should be further investigated if it can help to reduce the corrosion of these alloys. Moreover, the corrosion resistance of dental alloys with different composition e.g. Ni-Cr alloy with variety contents of chromium and molybdenum are also significance for investigation.

CHAPTER VI

CONCLUSIONS

Within the limits in this study, the conclusions are:

1. Au-Pd alloys covered with two types of dental luting cements did not release detectable levels of elemental release.
2. The amount of elemental release was affected by type of dental alloys but not by the dental cements.
3. Cu-Al alloy released total amount of elements significantly higher than Au-Pd, Ag-Pd and Ni-Cr alloys covered with both Zinc Cement Improved and Panavia F 2.0. Using Panavia F 2.0 tended to cause elemental release more than using Zinc Improved Cement in this alloy.
4. The total elements released from each dental alloy: Ag-Pd, Ni-Cr and Cu-Al alloys covered with both Zinc Cement Improved and Panavia F 2.0 were not significantly different.



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REFERENCES

- (1) Cheung, W. A review of the management of endodontically treated teeth. Post, core and the final restoration. J Am Dent Assoc. 136 (2005): 611-619.
- (2) Schwartz, R. S. and Robbins, J. W. Post placement and restoration of endodontically treated teeth: a literature review. J Endod. 30 (2004): 289-301.
- (3) Fernandes, A. S.; Shetty, S. and Coutinho, I. Factors determining post selection: a literature review. J Prosthet Dent. 90 (2003): 556-562.
- (4) Zhi-Yue, L. and Yu-Xing, Z. Effects of post-core design and ferrule on fracture resistance of endodontically treated maxillary central incisors. J Prosthet Dent. 89 (2003): 368-373.
- (5) Schmage, P., et al. The fit of tapered posts in root canals luted with zinc phosphate cement: a histological study. Dent Mater. 21 (2005): 787-793.
- (6) Wataha, J. C. Alloys for prosthodontic restorations. J Prosthet Dent. 87 (2002): 351-363.
- (7) Canay, S. and Oktemer, M. In vitro corrosion behavior of 13 prosthodontic alloys. Quintessence Int. 23 (1992): 279-287.
- (8) Power, J. M. and Sakaguchi, R. L. CRAIG'S Restorative Dental Materials. 12nd ed. St.Louis, Missouri: Mosby Elsevier; 2006.
- (9) Annusavice, K. J. Phillips' science of dental materials. 11th ed. St.Louis, Missouri Saunders Elsevier; 2003.
- (10) Leinfelder, K. F. An evaluation of casting alloys used for restorative procedures. J Am Dent Assoc. 128 (1997): 37-45.
- (11) Wataha, J. C. and Hanks, C. T. Biological effects of palladium and risk of using palladium in dental casting alloys. J Oral Rehabil. 23 (1996): 309-320.
- (12) Johansson, B. I.; Lemons, J. E. and Hao, S. Q. Corrosion of dental copper, nickel, and gold alloys in artificial saliva and saline solutions. Dent Mater. 5 (1989): 324-328.
- (13) Tibballs, J. E. and Erimescu, R. Corrosion of dental aluminium bronze in neutral saline and saline lactic acid. Dent Mater. 22 (2006): 793-798.
- (14) Benatti, O. F.; Miranda, W. G., Jr. and Muench, A. In vitro and in vivo corrosion evaluation of nickel-chromium- and copper-aluminum-based alloys. J Prosthet Dent. 84 (2000): 360-363.
- (15) Petersen, K. B. Longitudinal root fracture due to corrosion of an endodontic post. J Can Dent Assoc. 37 (1971): 66-68.
- (16) Silness, J.; Gustavsen, F. and Hunsbeth, J. Distribution of corrosion products in teeth restored with metal crowns retained by stainless steel posts. Acta Odontol Scand. 37 (1979): 317-321.
- (17) Luu, K. Q. and Walker, R. T. Corrosion of a nonprecious metal post: a case report. Quintessence Int. 23 (1992): 389-392.
- (18) Arvidson, K. and Wroblewski, R. Migration of metallic ions from screwposts into dentin and surrounding tissues. Scand J Dent Res. 86 (1978): 200-205.
- (19) ISO 10271. Dental metallic materials-corrosion test methods. 1st ed. 2001.
- (20) ISO 16744. Dentistry- Base metal materials for fixed dental restorations. 1st ed. 2003.
- (21) Skoog, D. A.; West, D. M.; Holler, F. J., et al. Fundamentals of Analytical Chemistry. 8th ed. California: Brooks/Cole Thomson Learning; 2004.
- (22) Ardlin, B. I.; Dahl, J. E. and Tibballs, J. E. Static immersion and irritation tests of dental metal-ceramic alloys. Eur J Oral Sci. 113 (2005): 83-89.

- (23) al-Hiyasat, A. S.; Bashabsheh, O. M. and Darmani, H. Elements released from dental casting alloys and their cytotoxic effects. Int J Prosthodont. 15 (2002): 473-478.
- (24) Wataha, J. C.; Craig, R. G. and Hanks, C. T. The release of elements of dental casting alloys into cell-culture medium. J Dent Res. 70 (1991): 1014-1018.
- (25) Wataha, J. C.; Nelson, S. K. and Lockwood, P. E. Elemental release from dental casting alloys into biological media with and without protein. Dent Mater. 17 (2001): 409-414.
- (26) Wataha, J. C., et al. Effect of pH on element release from dental casting alloys. J Prosthet Dent. 80 (1998): 691-698.
- (27) Wylie, C. M., et al. Corrosion of nickel-based dental casting alloys. Dent Mater. 23 (2007): 714-723.
- (28) Geis-Gerstorfer, J.; Sauer, K. H. and Passler, K. Ion release from Ni-Cr-Mo and Co-Cr-Mo casting alloys. Int J Prosthodont. 4 (1991): 152-158.
- (29) Wataha, J. C.; Malcolm, C. T. and Hanks, C. T. Correlation between cytotoxicity and the elements released by dental casting alloys. Int J Prosthodont. 8 (1995): 9-14.
- (30) Wataha, J. C. and Lockwood, P. E. Release of elements from dental casting alloys into cell-culture medium over 10 months. Dent Mater. 14 (1998): 158-163.
- (31) Charlton, D. G.; Moore, B. K. and Swartz, M. L. Direct surface pH determinations of setting cements. Oper Dent. 16 (1991): 231-238.
- (32) Turpin, Y. L., et al. Corrosion susceptibility of titanium covered by dental cements. Dent Mater. 16 (2000): 57-61.
- (33) Demirel, F.; Saygili, G. and Sahmali, S. Corrosion susceptibility of titanium covered by dental cements. J Oral Rehabil. 30 (2003): 1162-1167.
- (34) The Council on Dental Materials, Instruments, and Equipment. JADA. 109 (1984): 766.
- (35) Geis-Gerstorfer, J. In vitro corrosion measurements of dental alloys. J Dent. 22 (1994): 247-251.
- (36) Vaidyanathan, T. K. and Prasad, A. In vitro corrosion and tarnish analysis of the Ag-Pd binary system. J Dent Res. 60 (1981): 707-715.
- (37) Huang, H. H. Surface characterization of passive film on NiCr-based dental casting alloys. Biomaterials. 24 (2003): 1575-1582.
- (38) Wataha, J. C. and Malcolm, C. T. Effect of alloy surface composition on release of elements from dental casting alloys. J Oral Rehabil. 23 (1996): 583-589.
- (39) Watanabe, I., et al. In vitro corrosion behavior of cast iron-platinum magnetic alloys. Dent Mater. 17 (2001): 217-220.
- (40) Elshahawy, W. M.; Watanabe, I. and Kramer, P. In vitro cytotoxicity evaluation of elemental ions released from different prosthodontic materials. Dent Mater. 25 (2009): 1551-1555.
- (41) Wataha, J. C.; Hanks, C. T. and Craig, R. G. The in vitro effects of metal cations on eukaryotic cell metabolism. J Biomed Mater Res. 25 (1991): 1133-1149.
- (42) Donovan, T. E. and Cho, G. C. Contemporary evaluation of dental cements. Compend Contin Educ Dent. 20 (1999): 197-199, 202-193, 205-198, 210, 212-194, 216-199.
- (43) Diaz-Arnold, A. M.; Vargas, M. A. and Haselton, D. R. Current status of luting agents for fixed prosthodontics. J Prosthet Dent. 81 (1999): 135-141.
- (44) Nomoto, R. and McCabe, J. F. A simple acid erosion test for dental water-based cements. Dent Mater. 17 (2001): 53-59.
- (45) Oilo, G. Luting cements: a review and comparison. Int Dent J. 41 (1991): 81-88.

- (46) Hill, E. E. Dental cements for definitive luting: a review and practical clinical considerations. Dent Clin North Am. 51 (2007): 643-658.
- (47) White, S. N. and Yu, Z. Physical properties of fixed prosthodontic, resin composite luting agents. Int J Prosthodont. 6 (1993): 384-389.
- (48) Yoshida, K.; Tanagawa, M. and Atsuta, M. In-vitro solubility of three types of resin and conventional luting cements. J Oral Rehabil. 25 (1998): 285-291.
- (49) Milutinovic-Nikolic, A. D.; Medic, V. B. and Vukovic, Z. M. Porosity of different dental luting cements. Dent Mater. 23 (2007): 674-678.
- (50) Fifield, F. W. and Haines, P. J. Environmental analytical chemistry. London ; New York: Blackie Academic & Professional; 1995.
- (51) Boss, C. B. and Fredeen, K. J. Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectroscopy. 2nd ed 1997.
- (52) Gil, F. J., et al. In vitro corrosion behaviour and metallic ion release of different prosthodontic alloys. Int Dent J. 49 (1999): 361-367.
- (53) Bumgardner, J. D. and Lucas, L. C. Surface analysis of nickel-chromium dental alloys. Dent Mater. 9 (1993): 252-259.
- (54) Eschler, P. Y.; Luthy, H.; Reclaru, L., et al. Copper-aluminium bronze- a substitute material for gold dental alloy? European Cells and Materials. 5 (2003): 49-50.
- (55) Monticelli, F., et al. Limited decalcification/diffusion of self-adhesive cements into dentin. J Dent Res. 87 (2008): 974-979.
- (56) Eisenburger, M.; Addy, M. and Rossbach, A. Acidic solubility of luting cements. J Dent. 31 (2003): 137-142.



APPENDIX

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APPENDIX

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Appendix

One-Sample Kolmogorov-Smirnov Test

| Cement | Alloy | | Coros |
|---------|--------------------------------|----------------|----------|
| ZnPO4 | Ag-Pd | N | 5 |
| | Normal Parameters ^a | Mean | 4.1860 |
| | | Std. Deviation | 2.30355 |
| | Most Extreme Differences | Absolute | .175 |
| | | Positive | .175 |
| | | Negative | -.127 |
| | Kolmogorov-Smirnov Z | | .391 |
| | Asymp. Sig. (2-tailed) | | .998 |
| Ni-Cr | N | | 5 |
| | Normal Parameters ^a | Mean | 2.3140 |
| | | Std. Deviation | 1.14014 |
| | Most Extreme Differences | Absolute | .268 |
| | | Positive | .225 |
| | | Negative | -.268 |
| | Kolmogorov-Smirnov Z | | .600 |
| | Asymp. Sig. (2-tailed) | | .865 |
| Cu-Al | N | | 5 |
| | Normal Parameters ^a | Mean | 185.5020 |
| | | Std. Deviation | 17.82937 |
| | Most Extreme Differences | Absolute | .311 |
| | | Positive | .311 |
| | | Negative | -.183 |
| | Kolmogorov-Smirnov Z | | .696 |
| | Asymp. Sig. (2-tailed) | | .718 |
| Panavia | Ag-Pd | N | 5 |
| | Normal Parameters ^a | Mean | 3.6900 |
| | | Std. Deviation | 1.50572 |
| | Most Extreme Differences | Absolute | .197 |
| | | Positive | .185 |

| | | | | |
|---------------------------------|--------------------------------|------------------------|--|----------|
| | | Negative | | -.197 |
| | | Kolmogorov-Smirnov Z | | .441 |
| | | Asymp. Sig. (2-tailed) | | .990 |
| Ni-Cr | N | | | 5 |
| | Normal Parameters ^a | Mean | | 2.1260 |
| | | Std. Deviation | | .59994 |
| | Most Extreme Differences | Absolute | | .142 |
| | | Positive | | .128 |
| | | Negative | | -.142 |
| | | Kolmogorov-Smirnov Z | | .319 |
| | | Asymp. Sig. (2-tailed) | | 1.000 |
| Cu-Al | N | | | 5 |
| | Normal Parameters ^a | Mean | | 247.3140 |
| | | Std. Deviation | | 90.63167 |
| | Most Extreme Differences | Absolute | | .278 |
| | | Positive | | .278 |
| | | Negative | | -.230 |
| | | Kolmogorov-Smirnov Z | | .623 |
| | | Asymp. Sig. (2-tailed) | | .833 |
| a. Test distribution is Normal. | | | | |
| | | | | |

Between-Subjects Factors

| | | Value Label | N |
|--------|---|-------------|----|
| Cement | 1 | ZnPO4 | 15 |
| | 2 | Panavia | 15 |
| Alloy | 1 | Ag-Pd | 10 |
| | 2 | Ni-Cr | 10 |
| | 3 | Cu-Al | 10 |

Tests of Between-Subjects Effects

Dependent Variable: coros

| Source | Type III Sum of Squares | Df | Mean Square | F | Sig. |
|-----------------|-------------------------|----|-------------|---------|------|
| Corrected Model | 312962.351 ^a | 5 | 62592.470 | 43.970 | .000 |
| Intercept | 165118.748 | 1 | 165118.748 | 115.992 | .000 |
| Cement | 3113.860 | 1 | 3113.860 | 2.187 | .152 |
| Alloy | 303409.839 | 2 | 151704.920 | 106.569 | .000 |
| cement * alloy | 6438.651 | 2 | 3219.326 | 2.261 | .126 |
| Error | 34164.880 | 24 | 1423.537 | | |
| Total | 512245.978 | 30 | | | |
| Corrected Total | 347127.231 | 29 | | | |

a. R Squared = .902 (Adjusted R Squared = .881)

Descriptives

| Coros | N | Mean | Std. Deviation | Std. Error | 95% Confidence Interval for Mean | | Minimum | Maximum |
|-------|----|----------|----------------|------------|----------------------------------|-------------|---------|---------|
| | | | | | Lower Bound | Upper Bound | | |
| | | | | | Ag-Pd | 5 | | |
| Ni-Cr | 5 | 2.3140 | 1.14014 | .50989 | .8983 | 3.7297 | .94 | 3.44 |
| Cu-Al | 5 | 185.5020 | 17.82937 | 7.97354 | 163.3639 | 207.6401 | 169.38 | 215.63 |
| Total | 15 | 64.0007 | 89.45312 | 23.09670 | 14.4632 | 113.5382 | .94 | 215.63 |

Test of Homogeneity of Variances

Coros

| Levene Statistic | df1 | df2 | Sig. |
|------------------|-----|-----|------|
| 4.152 | 2 | 12 | .043 |

Robust Tests of Equality of Means

| Coros | | | | |
|----------------|------------------------|-----|-------|------|
| | Statistic ^a | df1 | df2 | Sig. |
| Brown-Forsythe | 511.851 | 2 | 4.167 | .000 |

a. Asymptotically F distributed.

Multiple Comparisons

Coros

Tamhane

| (I) alloy | (J) alloy | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|-----------|-----------|--------------------------|------------|------|-------------------------|-------------|
| | | | | | Lower Bound | Upper Bound |
| Ag-Pd | Ni-Cr | 1.87200 | 1.14946 | .398 | -1.9257 | 5.6697 |
| | Cu-Al | -181.31600* | 8.03981 | .000 | -212.4088 | -150.2232 |
| Ni-Cr | Ag-Pd | -1.87200 | 1.14946 | .398 | -5.6697 | 1.9257 |
| | Cu-Al | -183.18800* | 7.98982 | .000 | -214.5237 | -151.8523 |
| Cu-Al | Ag-Pd | 181.31600* | 8.03981 | .000 | 150.2232 | 212.4088 |
| | Ni-Cr | 183.18800* | 7.98982 | .000 | 151.8523 | 214.5237 |

*. The mean difference is significant at the 0.05 level.

Descriptives

| Coros | | | | | | | | |
|-------|----|----------|----------------|------------|----------------------------------|-------------|---------|---------|
| | N | Mean | Std. Deviation | Std. Error | 95% Confidence Interval for Mean | | Minimum | Maximum |
| | | | | | Lower Bound | Upper Bound | | |
| Ag-Pd | 5 | 3.6900 | 1.50572 | .67338 | 1.8204 | 5.5596 | 1.88 | 5.63 |
| Ni-Cr | 5 | 2.1260 | .59994 | .26830 | 1.3811 | 2.8709 | 1.25 | 2.81 |
| Cu-Al | 5 | 247.3140 | 90.63167 | 40.53172 | 134.7799 | 359.8481 | 163.44 | 355.94 |
| Total | 15 | 84.3767 | 128.72655 | 33.23705 | 13.0903 | 155.6631 | 1.25 | 355.94 |

Test of Homogeneity of Variances

Coros

| Levene Statistic | df1 | df2 | Sig. |
|------------------|-----|-----|------|
| 49.272 | 2 | 12 | .000 |

Robust Tests of Equality of Means

Coros

| | Statistic ^a | df1 | df2 | Sig. |
|----------------|------------------------|-----|-------|------|
| Brown-Forsythe | 36.350 | 2 | 4.003 | .003 |

a. Asymptotically F distributed.

Multiple Comparisons

Coros

Tamhane

| (I) alloy | (J) alloy | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|-----------|-----------|--------------------------|------------|------|-------------------------|-------------|
| | | | | | Lower Bound | Upper Bound |
| Ag-Pd | Ni-Cr | 1.56400 | .72486 | .224 | -.9357 | 4.0637 |
| | Cu-Al | -243.62400* | 40.53731 | .012 | -403.3106 | -83.9374 |
| Ni-Cr | Ag-Pd | -1.56400 | .72486 | .224 | -4.0637 | .9357 |
| | Cu-Al | -245.18800* | 40.53260 | .011 | -404.8992 | -85.4768 |
| Cu-Al | Ag-Pd | 243.62400* | 40.53731 | .012 | 83.9374 | 403.3106 |
| | Ni-Cr | 245.18800* | 40.53260 | .011 | 85.4768 | 404.8992 |

*. The mean difference is significant at the 0.05 level.

Independent Samples Test in Ag-Pd alloy

| | | Levene's Test for Equality of Variances | | t-test for Equality of Means | | | | | | |
|-------|-----------------------------|---|------|------------------------------|-------|-----------------|-----------------|-----------------------|---|---------|
| | | F | Sig. | t | df | Sig. (2-tailed) | Mean Difference | Std. Error Difference | 95% Confidence Interval of the Difference | |
| | | | | | | | | | Lower | Upper |
| Coros | Equal variances assumed | .902 | .370 | .403 | 8 | .697 | .49600 | 1.23073 | -2.34208 | 3.33408 |
| | Equal variances not assumed | | | .403 | 6.890 | .699 | .49600 | 1.23073 | -2.42363 | 3.41563 |

Independent Samples Test in Ni-Cr alloy

| | | Levene's Test for Equality of Variances | | t-test for Equality of Means | | | | | | |
|-------|-----------------------------|---|------|------------------------------|-------|-----------------|-----------------|-----------------------|---|---------|
| | | F | Sig. | t | df | Sig. (2-tailed) | Mean Difference | Std. Error Difference | 95% Confidence Interval of the Difference | |
| | | | | | | | | | Lower | Upper |
| Coros | Equal variances assumed | 6.317 | .036 | .326 | 8 | .753 | .18800 | .57617 | -1.14065 | 1.51665 |
| | Equal variances not assumed | | | .326 | 6.057 | .755 | .18800 | .57617 | -1.21861 | 1.59461 |

Independent Samples Test in Cu-Al alloy

| | | Levene's Test for Equality of Variances | | t-test for Equality of Means | | | | | | |
|-------|-----------------------------|---|------|------------------------------|-------|-----------------|-----------------|-----------------------|---|----------|
| | | F | Sig. | T | df | Sig. (2-tailed) | Mean Difference | Std. Error Difference | 95% Confidence Interval of the Difference | |
| | | | | | | | | | Lower | Upper |
| coros | Equal variances assumed | 29.385 | .001 | -1.496 | 8 | .173 | -61.81200 | 41.30856 | -157.06971 | 33.44571 |
| | Equal variances not assumed | | | -1.496 | 4.309 | .204 | -61.81200 | 41.30856 | -173.32977 | 49.70577 |

Descriptives

| | | | Statistic | Std. Error |
|------------|------------|----------------------------------|-----------|------------|
| Cu | Cu/ZnPO4 | Mean | 15.6250 | 7.35206 |
| | | 95% Confidence Interval for Mean | | |
| | | Lower Bound | -4.7876 | |
| | | Upper Bound | 36.0376 | |
| | | 5% Trimmed Mean | 14.7222 | |
| | | Median | 9.0625 | |
| | | Variance | 270.264 | |
| | | Std. Deviation | 16.43970 | |
| | | Minimum | 3.12 | |
| | | Maximum | 44.38 | |
| | | Range | 41.25 | |
| | | Interquartile Range | 22.66 | |
| | | Skewness | 1.986 | .913 |
| | | Kurtosis | 4.181 | 2.000 |
| Cu/Panavia | Cu/Panavia | Mean | 193.3750 | 39.58148 |
| | | 95% Confidence Interval for Mean | | |
| | | Lower Bound | 83.4792 | |
| | | Upper Bound | 303.2708 | |
| | | 5% Trimmed Mean | 192.4826 | |
| | | Median | 168.7500 | |
| | | Variance | 7833.467 | |
| | | Std. Deviation | 88.50687 | |
| | | Minimum | 106.25 | |
| | | Maximum | 296.56 | |
| | | Range | 190.31 | |
| | | Interquartile Range | 174.06 | |
| | | Skewness | .350 | .913 |
| | | Kurtosis | -2.902 | 2.000 |

Tests of Normality

| | Kolmogorov-Smirnov ^a | | | Shapiro-Wilk | | |
|------------|---------------------------------|----|-------|--------------|----|------|
| | Statistic | df | Sig. | Statistic | Df | Sig. |
| Cu/ZnPO4 | .368 | 5 | .026 | .746 | 5 | .027 |
| Cu/Panavia | .226 | 5 | .200* | .864 | 5 | .245 |

a. Lilliefors Significance Correction

*. This is a lower bound of the true significance.

Mann-Whitney

Ranks

| Groups | | N | Mean Rank | Sum of Ranks |
|--------|------------|----|-----------|--------------|
| Cu | Cu/ZnPO4 | 5 | 3.00 | 15.00 |
| | Cu/Panavia | 5 | 8.00 | 40.00 |
| Total | | 10 | | |

Test Statistics^b

| | Cu |
|--------------------------------|-------------------|
| Mann-Whitney U | .000 |
| Wilcoxon W | 15.000 |
| Z | -2.611 |
| Asymp. Sig. (2-tailed) | .009 |
| Exact Sig. [2*(1-tailed Sig.)] | .008 ^a |

a. Not corrected for ties.

b. Grouping Variable: Groups

Descriptives

| Groups | | | Statistic | Std. Error | | |
|---------------------|----------|----------------------------------|-------------------------|----------------------------------|------------------------|------------------------|
| AI | Cu/ZnPO4 | Mean | 169.8750 | 2.93584 | | |
| | | 95% Confidence Interval for Mean | Lower Bound 161.7238 | Upper Bound 178.0262 | | |
| | | 5% Trimmed Mean | 169.9479 | | | |
| | | Median | 171.2500 | | | |
| | | Variance | 43.096 | | | |
| | | Std. Deviation | 6.56473 | | | |
| | | Minimum | 160.31 | | | |
| | | Maximum | 178.12 | | | |
| | | Range | 17.81 | | | |
| | | Interquartile Range | 11.25 | | | |
| | | Skewness | -.459 | .913 | | |
| | | Kurtosis | .789 | 2.000 | | |
| | | Cu/Panavia | Cu/Panavia | Mean | 53.9375 | 6.12101 |
| | | | | 95% Confidence Interval for Mean | Lower Bound 36.9428 | Upper Bound 70.9322 |
| 5% Trimmed Mean | 53.9062 | | | | | |
| Median | 57.1875 | | | | | |
| Variance | 187.334 | | | | | |
| Std. Deviation | 13.68700 | | | | | |
| Minimum | 36.56 | | | | | |
| Maximum | 71.88 | | | | | |
| Range | 35.31 | | | | | |
| Interquartile Range | 25.00 | | | | | |
| Skewness | -.011 | | | .913 | | |
| Kurtosis | -.770 | | | 2.000 | | |

Tests of Normality

| Groups | Kolmogorov-Smirnov ^a | | | Shapiro-Wilk | | |
|-------------|---------------------------------|----|-------|--------------|----|------|
| | Statistic | df | Sig. | Statistic | df | Sig. |
| AI Cu/ZnPO4 | .183 | 5 | .200* | .976 | 5 | .912 |
| Cu/Panavia | .194 | 5 | .200* | .974 | 5 | .900 |

a. Lilliefors Significance Correction

*. This is a lower bound of the true significance.

Independent Samples Test

| | Levene's Test for Equality of Variances | | t-test for Equality of Means | | | | | | |
|-----------------------------|---|------|------------------------------|-------|-----------------|-----------------|-----------------------|---|-----------|
| | F | Sig. | t | df | Sig. (2-tailed) | Mean Difference | Std. Error Difference | 95% Confidence Interval of the Difference | |
| | | | | | | | | Lower | Upper |
| Equal variances assumed | 2.869 | .129 | 17.078 | 8 | .000 | 115.93750 | 6.78866 | 100.28282 | 131.59218 |
| Equal variances not assumed | | | 17.078 | 5.748 | .000 | 115.93750 | 6.78866 | 99.14801 | 132.72699 |

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