Application of Spectrophotometry and Ion Chromatography for Monitoring the Chemical Stability of Dental Ceramics in an Acid Solution

Marko Jakovac[1]
Jasenka Živko-Babić[1]
Lidija Ćurković[2]
Josip Pandurić[1]
Vjekoslav Jerolimov[1]

[1]Department of Prosthodontics
School of Dental Medicine
University of Zagreb
[2]Department of Materials
Faculty of Mechanical Engineering and Naval Architecture
University of Zagreb

Acta Stomat Croat
2002; 93-96

Abstract

The corrosive process of dental alloys is very well known, although little information is available on the corrosion of dental ceramics. The aim of this study was the analysis of the chemical stability of two dental ceramics in an aggressive acid medium. Two samples of feldspathic ceramic fused to Co-Cr and Ni-Cr alloy and a sample of hydrothermal ceramic fused to high-noble gold alloy were deposited in 10^{-3} *mol/L HCl at 50°C during six months. The solutions were analysed after one, two, three and six months. The determination of* Na^+, K^+, Ca^{2+} *and* Mg^{2+} *was performed by ion chromatography (IC), the quantities of the eluted* Si^{4+} *and* Al^{3+} *were determined by spectrophotometric method and the weight loss of each sample was measured by an analytical scale. The changes of the pH values were determined by means of a pH meter.*

The results showed that most ions were eluted after the first three months, while after that period of time elution was significantly lower in each sample. The sample with hydrothermal ceramic showed the most significant elution and the highest weight loss. The pH values changed in each leachate sample, but stabilised after the 3rd month of the investigation. It can be concluded that dental ceramics are not stable in an acid medium.

Key words: *chemical stability, dental ceramics, ion chromatography.*

ORIGINAL SCIENTIFIC PAPER
Received: November 29, 2001

Address for correspondence:

Jasenka Živko-Babić
Department of Prosthodontics
School of Dental Medicine
Gundulićeva 5, 10000 Zagreb
Croatia

Introduction

A prosthetic restoration is a part of orofacial system treatment that must satisfy medicinal, aesthetic and biomechanical conditions. This implies application of metals, ceramic and polymeric materials, individually or combined. The quality of a prosthetic restoration does not depend only on internal factors, i.e. composition of the constituent material and laboratory processing, but also on external factors. These comprise the oral environment and saliva, as an unpredictable and changeable electrolyte with respect to its composition, temperature, pressure, mechanical defects, hard and soft deposits, speed of movement of ions between materials and the environment, and existence of corrosional products in the mouth.

Corrosion in the mouth is a complex occurrence. Beside certain forms of electrochemical corrosion and galvanism, there is also a microbiological and/or physiological corrosion. Beside the well-known corrosion of metals, corrosional degradation can occur also in nonmetals in a moist, alkaline or acid environment. From the chemical point of view dental ceramics are alkalosilicate glass (1-4). They are generally composed of a majority of silica (SiO_2) and commonly contain oxides of Al, Na, K, Ca and colorant oxide. Silicon and aluminium ions have the highest share in the composition of a ceramic material, and they are eluted to the greatest extent (1, 5, 6). In the metal-ceramic system the border surface between the metal and ceramic is the most sensitive to corrosion (7-9). The degradation of dental ceramics in the oral environment generally occurs because of chemical attack (corrosive process), mechanical forces, or a combination of these effects. Based on the European and American standards, dental materials, as all drugs, are nowadays subject to control and testing with respect to their biocompatibility (5, 10). However, all the controls are not a factor of stability of any material in the mouth. Ceramic is referred to as a chemically stable material (3, 11--13). Since it is known that exposure to acids causes damage to the glass surface, the aim of this study was to examine chemical behaviour of feldspatic and hydrothermal ceramic in an acid medium at 50°C and during six months of storage.

Materials and methods

All the examinations were carried out on three metal-ceramic samples (20 x 10 x 2 mm) prepared according to the instructions of the manufacturer at the Laboratory for Fixed Prosthodontics, School of Dental Medicine University of Zagreb.

Sample 1: conventional feldspathic ceramic (IPS Classic, Ivoclar, Schaan, Liechtenstein) on a Co-Cr alloy (Remanium CD, Dentaurum, Phorzheim, Germany)

Sample 2: hydrothermal ceramic (Duceragold, Ducera, Rosbach, Germany) on a high-noble Au-Pt alloy (Degunorm, Ögussa, Vienna, Austria)

Sample 3: conventional feldspathic ceramic (IPS Classic, Ivoclar, Schaan, Liechtenstein) on a Ni-Cr alloy (Wiron 99, Bego, Bremen, Germany).

The samples of metal-ceramics whose size corresponds to a larger metal-ceramic crown were deposited in a HCl solution (Kemika, Zagreb, Croatia), c (HCl) = $1 \cdot 10^{-3}$ mol/L in plastic bottles during six months. All the experiments were conducted at a temperature of 50°C. After one, two, three and six months the solution was separated from the samples by decanting and filtering and analysed.

The quantities of the eluted Na^+, K^+, Ca^{2+} and Mg^{2+} ions were determined using a Metrohm 690 Ion Chromatograph with IC cation column Metrosep Cation 1-2, conductivity detector, and 10 µL injection loop, with Metrohm 687 IC Pump. The mobile phase was 4 mmol/L tartaric acid/1 mmol/L dipicolinic acid dissolved in high purity water. Data acquisition was performed using a Simadzu integrator model C-R5A Chromatopac.

The quantities of eluted Si^{4+} and Al^{3+} ions were determined by a spectrophotometer (UV/VIS Lambda 20, Perkin Elmer, Norwalk, USA).

The initial and final pH of all solutions was recorded by pH meter (MA 5705, Iskra, Ljubljana, Slovenia).

Results

Tables 1 and 2 show the results of elution from the metal-ceramic samples in the examined eluants after the first, second, third and sixth month of storage (Tables 1 and 2). The achieved results indicate dependence of the chemical stability of samples of dental ceramics with respect to the influence of an acid, aggressive medium (10^{-3} mol/L HCl). The stability of the mentioned materials is shown in a cumulative amount of the eluted ions of Na^+ (Figure 1), K^+ (Figure 2), Ca^{2+} (Figure 3), Mg^{2+} (Figure 4), Si^{4+} (Figure 5) and Al^{3+} (Figure 6), in a changed pH value of the eluant (Figure 7) and in a cumulative weight loss of the samples of dental ceramics (Figure 8).

The process of elution of alkaline earth ions (Ca^{2+} and Mg^{2+}) is shown in Figure 3 and 4. In this case the sample 2 (hydrothermal ceramic) loses a considerably greater amount of the mentioned ions than the other two samples of feldspathic ceramic. The difference between sample 1 and sample 3 can also be observed, whereby sample 3 loses a considerably greater amount of Ca^{2+} ions than the sample 1.

Figure 5 shows that the amount of the eluted Si^{4+} ions from hydrothermal ceramic (sample 2) is greater than in the case of conventional feldspathic ceramic (sample 1 and sample 3).

Figure 6 shows even more pronounced deviation in elution of Al^{3+} ions between hydrothermal ceramic (sample 2) and conventional feldspathic ceramic (sample 1 and sample 3).

The starting pH value of the medium in this examination was 2.95. These values increase between the first and second month of the experiment, which is especially striking in the case of hydrothermal ceramic (pH 5.8) (Figure 7).

Figure 8 also confirms the aforementioned results. It shows weight loss of the samples in percentages. It can be observed that the weight loss of hydrothermal ceramic (sample 2) is considerably greater (0.46%) than for the other two samples (with conventional feldspathic ceramic) (0.061%).

Discussion

There have been a number of in vitro studies on the chemical behaviour of restoration materials, especially metals. In this process physiological saline solution or various compositions of artifical saliva are most often used as an electrolyte (14, 15).

For examination of the stability of dental aesthetic materials in a moist medium the majority of authors use distilled water (16-18), with a temperature of 37°C and different periods of storage, from 30 days to one year, measuring weight loss of the samples or testing their flexural strength. The mechanism of dissolution in distilled water represents a catalytic reaction. Dissolution of ions reduces the chemical stability and affects the biocompatibility of materials. However, great differences established between dissolution of ions of certain elements in artificial saliva and in distilled water cast doubt on the clinical importance of examinations in distilled water. This is an indicator that the type of solution, its composition and period of storage influence the solubility of dental materials (5).

On the other hand, change in the strength of a ceramic material in a moist medium should be considered a relative measure of degradation of internal strength in time with respect to increased cracks due to strain, stress and consequential corrosion (14, 17--20). Despite all these insights, behaviour of dental constituent materials in the oral cavity itself is still not completely known.

In this examination elution of Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Si^{4+} and Al^{3+} ions from all three samples can be observed, which was especially pronounced up to the third month of the examination. After the third month the process substantially slowed down, and in the case of Mg^{2+} ions elution came to a standstill. It was a possibility of correspondence between the time of retention of Mg^{2+} and the same of Ba^{2+} in the used method, because the structure of the mentioned ceramics were unknown. Although the mentioned occurrence was present in all the three samples, the sample with hydrothermal ceramic can be singled out, where it was most pronounced. In elution of alkali ions (Na^{+} and K^{+}) a great difference can also be observed in the amount of the mentioned eluted ions between sample 2 and samples 1 and 3. The results indicate that a greater amount of the mentioned ions was eluted from hydrothermal ceramic. It can also be observed that after one month a greater amount of K^{+} ions was eluted from sample 1 in relation to sample 3. At the same time, ion chromatography proved to be a simpler and faster detection method than the traditional AAS method.

In their examination of glass Söderholm et al. proved the importance of the material composition, whereby 24 times more silicon is dissolved from barium glass than from quartz glass. Cumulative dissolution of silicon ions is ten times greater in artificial saliva than in water (16).

Aluminium is more slowly dissolved than silicon and in a considerably greater amount from barium glass (16), which was also shown in these examinations. Beside selective dissolution of alkali ions, Ansauvice also reports on dissolution of structure, considering that alkali metal ions are less stable in the glass phase than in crystalline (1). The stability of glass containing K_2O is half the stability of glass containing Na_2O. This can be explained by the difference in the size of ions, although potassium oxide reduces the solubility of the glass phase.

With regard to the weight loss in all three samples in time, the greatest loss can be seen after the first month and afterwards this value drops, with a somewhat greater weight loss of hydrothermal ceramic in the sixth month of testing, which indicates stabilisation of the chemical reactions after that time.

Natural saliva has a pH value between 6.3 - 6.9, although in the case of certain disorders of the gastrointestinal system it can drop to below 4. Some authors use different pH values of electrolytes: from 1 - 11 (21, 22). It is interesting to follow the changes in the pH values of the eluants whose starting pH value was 2.95. After the first month of the experiment the pH value increased, which is especially pronounced in the sample with hydrothermal ceramic, which had the highest weight loss. This is the sample with the most pronounced elution of all the analysed ions. This mild rise was probably due to the hydrolysis of alkaline and alkaline earth oxides and diffusion of H^+ or H_3O^+ ions from the aqueous solution into the glass and the loss of alkali ions from the glass surface. After the second month of the experiment the pH value reduced to a value slightly higher than the starting value. The pH value later stabilised.

According to Risito et al. alumina ceramic fired onto metal is the most stable (5), which is also shown by our results. They also proved that chemical stability greatly depends on the surface processing, whereby mechanical polishing prevents solubility of hydrothermal ceramic more than glazing of its surface after 16 hours of storage in a 4 % vinegar acid at 87°C. The examination conditions are pursuant to the DIN/ISO standard (2). The same medium, at 80°C for a period of 15 days, was used by Anusavice and Zhang (22), and Milleding et al. conduct testing for 18 hours in the mentioned conditions (23). The selection of the temperature of 80°C refers to the possible temperature maximum in the mouth.

The conditions in which examinations of the samples of dental ceramics were carried out in the present study comprised increased temperature (50°C) and chloride acid medium ($c(HCl) = 10^{-3}$ mol/L), which means that reactions of elution of the examined ions were considerably accelerated and as such rarely present in the oral environment. In the mentioned environment hydrothermal ceramic was found to be the most unstable, which was indicated by elution of a greater amount of ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Si^{4+} and Al^{3+} in relation to the samples with conventional feldspathic ceramic.

These preliminary experiments point to the need for establishing more true conditions for further studies of the chemical stability of dental ceramics, such as artificial saliva and a temperature of 37°C.

Conclusion

1. Dental ceramics are not stable in an acid medium.
2. Most ions were eluted after the first three months.
3. The pH values changed in each leachate sample, but they stabilised after the 3rd month of the investigation.
4. The sample with hydrothermal ceramic showed the most significant elution and the highest weight loss.