Erosion Process of a Glassionomer Cement in Organic Acids

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Received on September 17, 1984

Erosion of a glass ionomer cement in acetic (AA), lactic (LA), citric (CA) and hydrochloric acids (HA) was investigated by means of chemical analysis, SEM observation and infrared (IR) spectroscopy. The larger stability constants of the complex between the acid anions and Al or Ca, or the lower the pH of the acid solutions, the more Al, Ca, Na, Si and F were leached. SEM observation revealed that the cement matrix dissolved out in 0.01 M CA and HA. White precipitates formed in 0.01 M CA and HA after immersion of the cement. They were identified as hydrated silicious gels by IR spectroscopy.

Key Words: Erosion, Glassionomer cements, Organic acids

1. INTRODUCTION

The glass ionomer cement, which was developed by Wilson et al.¹, has been recently in clinical use for luting and filling. Several types of the cement are now commercially available. Durability of the cement in the oral environment is one of the most important properties for evaluation of its clinical usefulness. Nevertheless, there have been only a few in vitro studies on the subject.²-³) Crisp et al.²,³) reported the erosion behavior of the cement in demineralized water and a lactate buffer solution at 37°C. Mesu⁴) examined degradation of the cement in buffer solutions of organic acids such as acetic, lactic and citric acids which may simulate the environment in the mouth. However, further study is required in order to understand the erosion process of the cement. In this study the cement was immersed in the organic acid solutions and leached species were quantitatively analyzed. Moreover, change in surface structures of the cement by the erosion was observed by using SEM. Erosion products were analyzed by means of IR spectroscopy.

2. MATERIALS AND METHODS

Powder and liquid of a glass ionomer cement (Fuji Ionomer Type I*) were mixed in a fixed proportion of 1.4 g/1.0 g for 1 minute at room temperature (18°~26°C). The mixture was poured into a Teflon ring (10 mm in inner diameter and 1 mm high) on a slide glass. Another slide glass was pressed on it after incorporating a known weight of dental floss which was used for suspending the set cement in solution. Three minutes after start of mixing the cement was kept at 37°C and 100% relative humidity. After 57 minutes the set cement was removed from the Teflon mould and was immediately weighed and

* G-C Dental Ind. Co. Ltd., Tokyo, Japan
immersed in a Teflon bottle containing 50 ml of distilled water or acid solutions at 37°C. Acetic, lactic, citric and hydrochloric acids of 0.01 and 0.001 M were used as immersion solutions. After 7 days the cement was taken out from the solution and washed with a small amount of distilled water and dried at 37°C. SEM observation was made for eroded surface and fractured surface of the dry cement. Species leached into the solution were determined by atomic absorption spectroscopy (Na, Ca, Al), spectrophotometry (Si) and an ion selective electrode (F). IR spectra were taken for residues after vaporization of the solutions and precipitates formed in some of the solutions.

3. RESULTS

3.1. Chemical analysis of the solution

Table 1 shows the species leached from the cement in 7 days after immersion. Sodium and fluorine were leached from the cement more than the other species in the water and the 0.001 M acids. The amounts of all the species leached increased in order of water (DW), acetic acid (AA), lactic acid (LA) and citric acid (CA). This trend agreed with that in a zinc phosphate and zinc polycarboxylate cements as previously reported.\(^5,6\) The amounts of the species leached in 0.01 M hydrochloric acid (HA) lay between those in 0.01 M LA and CA. On the other hand, with 0.001 M HA, the order in the amount leached differs in different species. Increase in concentration of each acid by 10 times caused the amount of species leached to increase only by about two to six times, except for Ca and Al. Amount of Ca leached in the 0.001 M acids was much less than that of any other element. However, it extremely increased with an increase in concentration of the acids. Ratio of Al to Ca leached, which are thought to be main constituents of the cement matrix, was much larger in DW and the 0.001 M acids than in the 0.01 M acids.

Table 1 Amounts of species leached in the acids (ppm)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Species</th>
<th>Al</th>
<th>Ca</th>
<th>Na</th>
<th>Si</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td></td>
<td>2.00</td>
<td>0.0139</td>
<td>16.7</td>
<td>2.88</td>
<td>27.1</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.01M</td>
<td>29.4</td>
<td>12.4</td>
<td>60.6</td>
<td>17.7</td>
<td>88.2</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>5.27</td>
<td>0.225</td>
<td>27.3</td>
<td>7.33</td>
<td>39.1</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.01M</td>
<td>59.4</td>
<td>29.3</td>
<td>59.8</td>
<td>26.4</td>
<td>132.8</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>8.17</td>
<td>0.280</td>
<td>33.6</td>
<td>8.31</td>
<td>44.7</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.01M</td>
<td>261</td>
<td>98.4</td>
<td>99.2</td>
<td>81.7</td>
<td>421</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>21.9</td>
<td>0.64</td>
<td>35.6</td>
<td>16.1</td>
<td>66.7</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.01M</td>
<td>121</td>
<td>53.7</td>
<td>74.8</td>
<td>32.8</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>8.41</td>
<td>0.715</td>
<td>32.6</td>
<td>6.82</td>
<td>38.5</td>
</tr>
</tbody>
</table>

3.2. SEM observation

Figure 1 shows a surface and a fractured surface of the cement after drying at 37°C. The surface was smooth, though there were many cracks on it. On the other hand, the fractured surface showed a characteristic structure, in which unreacted glass particles were embedded in a matrix as reported before.\(^7\)
Figure 1  Surface (a) and fractured surface (b) of the set cement.

Figure 2  Eroded surfaces of the cement after immersion in the 0.001 M acids.
Figure 2 shows the surfaces of the cement after immersion in DW and 0.001 M AA, LA, CA and HA at 37°C for 7 days. With DW and 0.001 M AA, LA and HA, many small precipitates, which have not been identified yet, could be seen on the surface of the cement. Unevenness appeared on the surface of the cement after immersion in 0.001 M CA. Although the fractured surfaces of the cement after immersion in those solutions were not shown, they had the same structure as that before immersion shown in Fig. 1–b.

Figure 3 shows the surfaces and the fractured surfaces of the cement after immersion
in 0.001 M AA, LA, CA and HA. With 0.01 M AA and LA, the surfaces seemed to be smoother than that before immersion. However, the cement immersed in 0.01 M CA and HA had very rough surfaces at which unreacted glass particles seemed to be exposed. On the other hand, no changes of fractured surfaces were found after immersion.

3.3. Infrared spectra for the residues and the precipitates

Figure 4 shows infrared (IR) spectra for the residues obtained from the 0.01 M acid solutions. In the spectra except for that of HA, two strong characteristic bands were observed at around 1600 and 1400 cm\(^{-1}\) (shown by \(\uparrow\)). With the spectrum of the residue from HA, only three medium absorption bands were observed around 1630, 1100 and 600 cm\(^{-1}\).

Figure 5 shows IR spectra for the precipitates formed during immersion in 0.01 M CA and HA. Both spectra were identical except for shoulders around 1700 and 1460 cm\(^{-1}\) and a small band at 1400 cm\(^{-1}\) observed in the spectrum for the HA (shown by \(\uparrow\)).

4. DISCUSSION

As shown in Table 1, Na and F were leached more than the other species in DW. These results agreed with those reported by Wilson\(^2\), who showed that the main species released from ASPA cement were Na, Si and F. On the other hand, Na and F leached into DW from 0.1 g of the cement powder, which corresponded to the powder content in a set cement, were 3.84 and 6.29 ppm, respectively and they were less than those from the set cement (Table 1) by four to five times. This finding suggests that Na liberated
Table 2 Formation constants of the acids-Ca or -Al complexes

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formation constants*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$k_1 = 1.12 - 1.14$</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>$k_1 = 0.8 - 1.47$</td>
</tr>
<tr>
<td>Citric acid</td>
<td>$k_1 = 3.15 - 4.9$</td>
</tr>
</tbody>
</table>

* Stepwise constant: The value is given logarithmically.

from cement powder by attack of polyacrylic acid during setting existed as soluble fluorides. The amounts of species leached into the three organic acids increased in the order of AA, LA and CA at the same concentration. Table 2 shows stability constants of the complexes between anions of the organic acids and cations such as Al$^{3+}$ and Ca$^{2+}$ which are the matrix forming elements. The stability constant increases in the order of acetic, lactic and citric acids. The order corresponded to that for the amounts of species leached shown in Table 1. Thus, organic acid which forms more stable complexes with Ca and Al gives the greater solubility of the cement. This tendency was observed in our previous study on zinc phosphate and zinc polycarboxylate cements.

Pulver and Rossington and Eriksson investigated dissolution of silicate cements in several organic acids including the acids used in this study and also concluded that the greatest solubility in citric acid was due to its complex forming ability. With 0.01 M HA, the amounts of species leached lay between those for 0.01 M LA and CA although chlorine ion has no complex forming ability with Al and Ca. Greater solubility in the acid seemed to be due to its higher H$^+$ ion concentration, that is, lower pH (pH=2.28). Eriksson reported that dissolution of silicate cements in organic acids was also influenced by their dissociation constant (pK) and the stronger the acid, the higher was the dissolution. This is also the case for glass ionomer cement. Thus, the degree of erosion of glass ionomer cement in the acid solutions was affected not only by the complexing ability of the acid anion but H$^+$ ion concentration which depends on the dissociation constant. Though it is not clear which factor determines the degree of erosion, H$^+$ ion concentration is the most important factor in acid with lower pH, but as pH rises, complexing ability seems to become important. A further study is now in progress to clarify which of the two processes occurs preferentially.

The ratio of Al to Ca leached from the set cement was large in DW and the 0.001 M acids. However the ratio was not large when 0.1 g of the original glass powder was immersed in those solutions as shown in Table 3. This fact means that Ca was not easily leached once the cement set. As shown in Fig. 1, a surface of the set cement was covered with the cement matrix and the unreacted glass powder was not exposed at the surface. Therefore the Al and Ca leached are derived mainly from the cement matrix at an early stage of erosion. Preferential leaching of Al may be due to greater difference in stability.
between Al-acids complexes and Al polyacrylate in the cement matrix. In fact, complexing ability of Al with the acid anions was higher than that of Ca, as shown in Table 2. With the 0.01 M acids, the ratio of Al to Ca leached was between 2.03 and 2.65. This finding suggests that the glass powder as well as the cement matrix was eroded by the acids. Because the ratio of Al to Ca leached from the original glass powder was between 1.09 and 2.21 in the 0.001 M acids and between 1.70 and 2.45 in the 0.01 M acids. (Table 3)

IR spectra for the residues from 0.01 M AA, LA and CA showed two characteristic bands around 1600 and 1400 cm⁻¹ which was assigned to asymmetric and symmetric stretching vibration of COO⁻ ion.¹⁴ Therefore, those residues mainly consisted of Al, Ca and Na acetates, lactates or citrates. The results of IR analysis for the residue confirm that erosion of the cement in the organic acids proceeded through complex formation. As F and Si were also leached, the residue should contain silicious gel and metal fluorides. The former exhibits a broad strong band around 1100 cm⁻¹¹¹⁵ and the latter, for example Na₃AlF₆ and AlF₃, exhibit around 600 and 670 cm⁻¹, respectively. It was difficult to identify those compounds by IR spectroscopy though several bands were observed around 1100 and 600 cm⁻¹. Because the residues were the mixture of the carboxylate salts of main constituents and those compounds, their absorption bands overlapped one another. On the other hand, IR spectra for the residues from 0.01 M HA showed only three medium bands around 1630, 1100 and 600 cm⁻¹, which seemed to correspond to water (including adsorbed and crystallization water), silicious gel and metal chlorides or fluorides, respectively.

Appearance of the fractured surfaces of the cement immersed in 0.01 M AA and LA was the same as that before immersion. In our previous study on polycarboxylate cements⁶, the fractured surface after immersion in those acids had many pores which were left after dissolution of unreacted ZnO particles. Such pores were not seen for the glass ionomer cement. Original glass powder of the cement did not dissolve fully even in

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### Table 3 Ratio of Al to Ca leached from the set cement and the glass powder in the acids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Al/Ca ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set cement</td>
<td>Glass powder*</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>14.4</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.01M</td>
<td>2.37</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>23.4</td>
<td>1.09</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.01M</td>
<td>2.03</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>29.2</td>
<td>2.21</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.01M</td>
<td>2.65</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>34.2</td>
<td>1.30</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.01M</td>
<td>2.25</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>0.001M</td>
<td>11.8</td>
<td>1.37</td>
</tr>
</tbody>
</table>

* 0.1 g of the glass powder was immersed in the acid solutions for 7 days at 37°C.
concentrated HCl, so insoluble silicious components always remained. Therefore even if some species were leached from the glass powder, such pores as in polycarboxylate cements would not form. With 0.01 M HA and CA, the surface of the cement drastically changed after immersion. Many glass particles were exposed on the surface owing to dissolution of the cement matrix. The cement discs became thin after immersion in those acids, especially in 0.01 M CA. This means that both cement matrix and unreacted glass particles were eroded by the acids.

A white precipitate appeared in 0.01 M HA and CA solutions after immersion of the cement. IR spectra for the precipitate are similar to that for amorphous silica except for a band around 950 cm\(^{-1}\) as shown in Fig. 6. Thermogravimetric analysis of the precipitate showed a weight decrease of 21\% between room temperature and 100\°C and then gradual decrease of 22\% continuing up to 1200\°C. The band disappeared after the heating (Fig. 6 (b)) and the IR spectrum was identical to that for amorphous silica. Soda\(^{16}\) reported that the silanol group (Si-OH) existed on the surface of ground quartz particle from IR analysis and a band assigned to O-H deformation vibration of the silanol group appeared at 950 cm\(^{-1}\). Therefore the band around 950 cm\(^{-1}\) for the precipitate results from the silanol group and may disappear during the heating due to condensation between two of the groups. It was suggested that the precipitates were silicious gels containing water. Figure 7 shows IR spectra for the glass powder and the set cement. With the former spectrum a broad strong band is observed between 1300 and 900 cm\(^{-1}\). This band was assigned to Si-O stretching vibration of the glass\(^{17}\). The glass powder contains network modifying cations such as Na\(^+\) and Ca\(^{2+}\), which result in non bridging oxygen in the glass, and a

![Figure 6 Infrared spectra for (a) the precipitate in 0.01 M CA, (b) after heating up to 1200\°C and (c) amorphous silica.](image)

![Figure 7 Infrared spectra for the cement powder and the set cement.](image)
network forming cation such as Al$^{3+}$. This is the reason why the band is broad. When the cement set the band became slightly sharp and had an absorption maximum at 1070 cm$^{-1}$ and two shoulders around 1160 and 950 cm$^{-1}$. These wave numbers will correspond to those which were assigned to Si-O stretching and Si-OH deformation vibration observed in the spectrum for the precipitate. This suggests that the glass particles released most of their cationic species and accepted protons from polyacrylic acid in the cement liquid during setting. Thus, the glass particles in the set cement had many Si-OH groups on their surfaces, that is, a hydrated silicious gel structure. As the cement matrix were eroded by the citric acid, the glass particles were removed from the cement and migrated into the solution. They would release further cationic species by attack of the citric acid and become a silicious gel. This may be a process of formation of the precipitate in 0.01 M CA. This is also the case for 0.01 M HA. However, with the HA, the precipitate showed a few additional bands in the IR spectrum (Fig. 5), which indicates the existence of other substance. The bands around 1620 and 1400 cm$^{-1}$ can be assigned to asymmetric and symmetric stretching vibration of carboxylate ion. The precipitate may contain polyacrylate ion derived from the cement matrix. This means that polyacrylic salts in the matrix were leached into the acid and precipitated again. The precipitate in 0.01 M CA did not contain the polyacrylic salts nevertheless the matrix was extremely eroded. Therefore the polyacrylic salts in the matrix would dissolve in the citric acid solutions. In the IR spectrum for the residue of the solution, it was difficult to identify the polyacrylic salts because their COO$^{-}$ bands overlapped with those of citrate ion. It is, however, undoubtedly that polyacrylic salts were contained in the residue. Polyacrylic acid combines ionically with Ca$^{2+}$ and Al$^{3+}$ ions to form gels. Especially, Al$^{3+}$ is found to be very effective for the gelation. It was reported that the equivalent ratios of the cations to the acid where gelation begins to occur were 0.87 and 0.20, respectively. Accordingly, even if polyacrylic salts were leached into the solution, they would gel soon and precipitate because large amounts of Al and Ca had been also leached into the solution. This could be the case for the 0.01 M HA solution. With 0.01 M CA solution, as shown in Table 2, Al and Ca form soluble strong complexes with citric acid and the gelation is inhibited. This is a reason why polyacrylic salts were not contained in the precipitates formed in 0.01 M CA. Inhibition of the gelation in citric acid solution was confirmed by the following experiment. A solution containing 250 ppm Al and 6.2 meq/l PAA was titrated with N/10 NaOH and a white precipitate appeared at pH above 2. Though the solution was treated in a similar manner in the presence of 0.01 M CA, no precipitate appeared even at pH of 9.

5. CONCLUSIONS

The amounts of Na and F leached in DW were more than those of any other species. Sodium and fluorine were liberated from the glass powder during setting and would exist as soluble salts in the set cement. This explains the higher elution of those species in DW. The amounts of species leached into the carboxylic acids increased in the order of AA, LA and CA. The larger stability constants of complexes between the acid anions and Ca or Al, the more leached. The amounts leached into 0.01 M HA were between those into 0.01 M LA and CA, though Cl$^{-}$ ion had no complexing ability with those

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EROSION OF A GLASSIONOMER CEMENT

...cations. However, pH of the HA solution was the lowest and the highest H⁺ ion concentration was the cause of such high elution. Thus, the degree of erosion depended largely on the complexing ability of the acid anions and the constituent cations of the cement and/or the pH of the acid solution.

SEM observation of the cement surface after immersion in 0.01 M CA and HA revealed the structure in which the cement matrix dissolved out and the glass particles were exposed on the surface.

A white precipitate formed in 0.01 M CA and HA after immersion of the cement. It was identified as hydrated silicious gel by IR spectroscopy. The precipitate in 0.01 M HA also contained a small amount of polyacrylic salts.

ACKNOWLEDGMENT

This work was supported in part by the grant-in-aid from the ministry of education (No. 59771462) in 1984.

REFERENCES

0.87より大きい合金では AuCu I 型規則格子の微細な
ドメインが粒内に速やかに形成された。この反応により
引き起こされる弾性ひずみ場が時効硬化の原因であっ
た。

タンニン・フッ化物合剤（HY 剤）の配合された
合着用セメントの長期浸水による物性の変化
入江正郎、鈴木一臣、中井宏之
岡山大学歯学部歯科理工学講座

タンニン・フッ化物合剤（HY 剤）の配合されたカル
ボキシレートセメントとリン酸セメントについて長期間
の浸水に伴う物理的性質の変化を検討し、フッ化物の配
合されていない同種セメントと比較した。
圧縮、引張り強さについてみると、カルボキシレート
セメントの場合には HY 剤配合による影響はほとんど
みられないが、リン酸セメントの場合には、強さが明ら
かに増加した。寸法変化、吸水性についてみると、HY
剤の配合されたカルボキシレートセメントの場合、12ケ
月の浸水後では配合されていないものの約2倍の収縮を
示し、吸水率も硬化後の早期からわずかながら増加し
た。一方、リン酸セメントの場合でも、HY 剤配合さ
れたものの吸収も吸水率も逆にわずかながら減少した。

有機酸中におけるグラスアイオノマーセメントの侵食過程
松本茂樹、松本洋子*、山本 喜*、山根正次
九州大学歯学部歯科理工学講座
*九州大学歯学部歯科保存学第二講座

酢酸、乳酸、クエン酸および塩酸中におけるグラスアイ
オノマーセメントの侵食過程を化学分析、SEM 観察
および赤外吸収分析により検討した。
各酸の陰イオンと Al 又は Ca との錯体の安定度定
数が大きい程あるいは、酸溶液の pH が低い程、Al,
Ca, Na, Si および F の溶出量が多くなった。SEM 観
察により、0.01 M クエン酸および塩酸中ではセメント
マトリックスが溶解することが分かった。0.01 M クエン
酸および塩酸中では、セメント浸漬後に白色沈殿が生
成した。その沈殿は、水和ケイ酸質ゲルであることが
IR スペクトルによりわかった。

人エナメル質に対する酸処理法の効果
（酸処理法の臨床応用の改善）
武 谷 道 彦
九州大学歯学部歯科保存第二講座

エナメル質酸処理法に関する研究として、エナメル質
の酸処理面や接着破壊面を SEM を用いて観察した。ま
た、酸処理に伴う Ca の溶出量、中心線平均アラサ、接
着強さの測定を行った。その結果、まず小柱中央部が浴
み、次に小柱端部に著しい量が形成され、酸処理時間が長
くなる程渦は広がり深くなった。接着破壊面には、レジン
とエナメル質の破折が観察された。リン酸はすべての測
定値において大きな値を示した。シトラコン酸とピリビ
ン酸は、Ca の溶出量はリン酸の約半分であったが、そ
れ以外の測定値はリノ酸とはほぼ等しかった。クエン酸は
すべての測定値で最小の値を示した。Ca の溶出量と接
着強さは、酸の濃度が増加するにしたがい一定の値まえ
は増加するが、その後減少した。すべての測定値は、酸
処理時間が長くなる程増加した。シトラコン酸の臨床使
用の可能性が示唆された。