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Characterization of the bioactivity of two commercial composites

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ABSTRACT

The aim of this study was to characterize the ion release, pH changes and apatite formation ability of two potentially bioactive composites Cention N (CN) and Activa (ACT). Ion release and apatite formation was investigated in three different immersion media: Tris buffer pH 7.3 (TB), Artificial Saliva pH 4 (AS4) and Artificial Saliva pH 7 (AS7) in order to mimic the conditions present in the mouth. Fluoride release was followed using an ion selective electrode, whilst all other ions were determined by inductively coupled plasma optical emission spectroscopy. Apatite formation was followed by FTIR and XRD. SEM was used to follow glass degradation and apatite formation on both polished cross-sections and surfaces of the composites.

ACT released very few ions including fluoride upon immersion in TB and AS7, but released more ions including significant quantities of Al in AS4. This would suggest the glasses in ACT are acid degradable fluoro-alumino-silicate glasses similar to the glasses used in glass ionomer cements. There was no evidence of any apatite formation with ACT.

CN released more ions in TB and AS7 than ACT and formed an apatite like phase in AS7. The calcium fluoro-silicate glass in CN was observed to degrade significantly in AS4. CN has bioactive properties that may explain the low incidence of secondary caries found clinically with this composite.

1. Introduction

There is a need to develop a successful alternative to dental amalgam as a result of the Minamata Agreement to phase out amalgams. Existing composite resin restorations generally fail as a result of polymerization contraction, marginal leakage and secondary caries. Good clinical results can be achieved with modern day composite restoratives provided that the dentist isolates the tooth from moisture and saliva, uses a bonding agent and builds the restoration up incrementally to minimize the polymerization contraction [1–3]. However, these procedures are time consuming for the dentist and expensive for the patient. Most general dental practitioners

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hardly use tooth isolation techniques and build up the restoration in relative few increments, resulting in much greater polymerization shrinkage and marginal gaps. The literature indicates that in general practice most composite restorations last only about seven years [3].

Any new alternative to dental amalgams must address the real world situation and accept that any material that sets by a polymerization reaction is going to exhibit a marginal gap and be prone to secondary caries. The solution is to develop composites with reactive fillers that protect the tooth against secondary caries. These are referred to as "bioactive restoratives" discussed recently by Vallitu et al. [4] in a recent editorial in this journal.

Two commercial composite restoratives have recently been launched; CN and ACT. ACT is promoted as a bioactive restorative that forms apatite in the marginal gaps and is claimed to release more fluoride than glass ionomer cements. According to the manufacturer, CN contains three inorganic glasses: a conventional inert barium alumino-silicate glass, an ionomer glass based on a calcium barium alumino-fluoro-silicate and a basic calcium fluoro-silicate glass referred to as an "Alkasite" filler [5]. It is important to note that with ionomer glasses, degradation only occurs as a result of acid hydrolysis of Al-O-Si bonds. As a result, the ionomer glasses do not degrade significantly at pH > 6 and therefore do not release significant fluoride or calcium under these conditions. CN is also claimed to contain ytterbium fluoride.

It is unclear what type of glass the ACT product contains. The paper by Jun et al. [6] on ACT discusses the bioactive glasses (BG) originally developed by Hench and reviewed by Jones [7] in the introduction, which would imply that it contains a BG. A bioactive glass is defined as a glass that dissolves in physiological solution at a neutral pH, releasing calcium and phosphate ions and forms an apatite-like phase. Since the first step involves the ion exchange of Na^+ and Ca^{2+} ions for H^+ ions in solution, the pH rises as it dissolves. However there is no description or details from the manufacturer in the technical brochure on the glass used in this material. In contrast, the paper by Garoushi et al. [8] suggests it contains an ionomer glass in the introduction, but later in the Table describing the ACT states that it contains a bioactive glass. The manufacturer claims ACT to be a bioactive composite and form apatite in the marginal gap of restorations. The manufacturers of ACT also claim this material releases more fluoride than conventional GICs, which is not supported by the results of Garoushi et al. [8].

The purpose of this study is to investigate for the first time the full ion release, pH changes and apatite formation of these two new commercial composites under different conditions of immersion, reflecting the range of conditions that might be experienced *in vivo*. CN has been studied previously [8–11], but the studies have largely focused on curing, shrinkage and marginal leakage [9–11]. It is important to note that marginal leakage and secondary caries are likely to be strongly influenced by ion release, pH changes and precipitation of material such as apatite in the marginal gaps.

Table 1 – Details of the composites studied.

Composite	Batch no.	Manufacturer	Description
Cention N	WT27641	Ivoclar Vivadent Benderestrasse 2 Schaan Lichtenstein	Composite resin containing a mixture of glasses including an alkaline calcium fluorosilicate glass
Activa	170720	Pulpdent Corp 80 Oakland St Watertown MA02472 USA	A composite resin claimed to be bioactive

2. Experimental

2.1. Materials

ACT and CN were obtained from the manufacturers. The details are given in Table 1. CN is presented as a powder, which is hand mixed with the resin by spatulation, whilst ACT comes in two pastes, which are mixed by co-extrusion through a spiral nozzle.

The experimental methods used in this study follow the procedures used by Al-eesa et al. [12–14].

2.2. Preparation of composite disks

The composite disks were produced using Teflon moulds of 10 mm diameter and 1.2 mm thickness. A transparent acetate sheet with a glass slabs was placed below and above the paste filled mould and a 200 gm weight was placed to release any air bubbles and remove excess material. Then the disk was cured using 3 M ESPE Elipar^{TM} light for 40 s.

Disks (132) for each material were produced and divided into 3 equal groups of 66 and each disk was immersed in a 15 mL polypropylene centrifuge tube (Fisher Scientific UK Ltd., Leicestershire, UK) containing 10 mL of one of the following solutions: tris buffer pH = 7.3 (TB), artificial saliva at pH = 7 (AS7) and artificial saliva at pH = 4 (AS4). These three media were chosen because TB has a better maintained pH than de-ionised water; AS7 and AS4 were chosen to mimic remineralising and demineralising enviorments in saliva respectively. At each of the eight time points (0, 6, 24 h, 3, 7, 14, 28, and 42 days), Three disks from each group were removed for analysis at each time point. These disks were removed from their solution, washed and dried for investigation using attenuated total reflectance — fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The solutions after immersion were used for measurement of pH changes using a pH meter (Oakton Instruments pH 11 Portable pH/mV Meter accuracy with ±0.01 of a pH unit), and fluoride measured using an ion selective electrode (ISE) (Orion 9609BNWP with Orion pH/ISE meter 710, Thermo Scientific, Waltham, MA, USA). Ca and

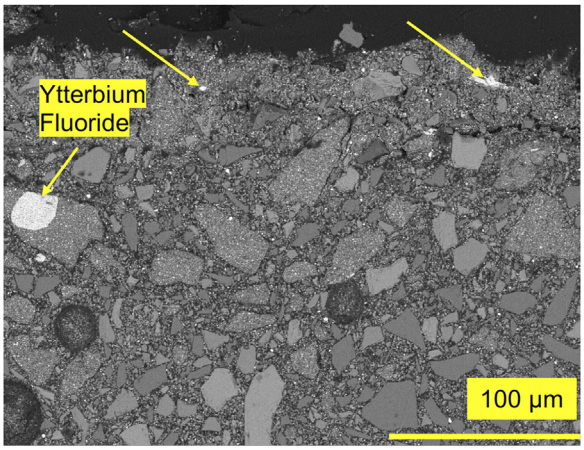

Fig. 1 – Back scattered SEM of CN. The arrows indicate Ytterbium fluoride and three different compositions of glass particles.

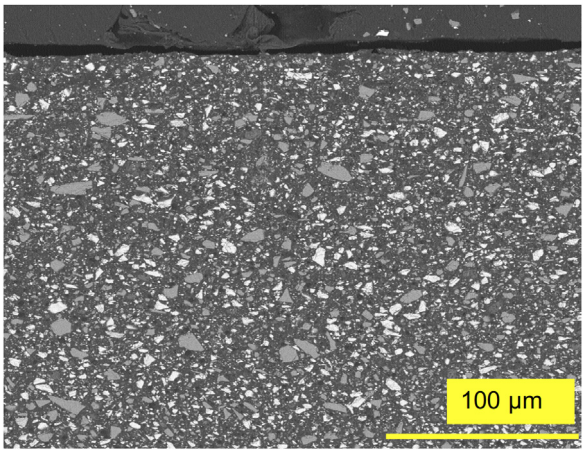

Fig. 2 – Back scattered SEM of ACT with two different glass particle compositions.

PO_4 release were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian Vista-PRO, Varian Ltd., Oxford, UK). The remaining disks were washed using deionised water, dried and re-immersed in one of the three freshly made solutions until the next time point of measurement. Not replenishing the solutions would be expected to decrease the amount of orthophosphate and calcium for forming apatite. Replenishing the solution in part mimics the turnover of saliva in the mouth.

FTIR was carried out in the ATR mode on the intact disks to look for evidence of glass degradation and formation of any calcium phosphate phases on the surface of the disk. SEM was carried out on both surface and cross-sections of the disks. Disks were cut in two, mounted in an acrylic resin and then polished using silicon carbide papers of varying roughness (P600, P1000 and P4000) using a polishing unit (Kemet, Kent 4 Automatic Lapping and Polishing Unit) according to Al-eesa et al. [12]. The samples were carbon coated for SEM.

3. Results

3.1. *Characterization of unimmersed disks*

The initial disks were amorphous with the exception of diffraction peaks for ytterbium trifluoride, which were present in the CN.

Four distinct phases are present in the polished back scattered SEM images of the CN, corresponding to the three glass compositions and ytterbium fluoride (YbF_3), which back scatters very strongly. Fig. 1 shows the back scattered SEM. There are three types of filler particles in addition to YbF_3, two of which are homogenous, but back scatter differently and a third which is granular in appearance. The particle size of the glass particles in CN are relatively coarse with many 20–30 µm particles. The YbF_3 exists as very fine particles <1 µm, but also appears as large particles and clusters. The distribution of both the different glass particles in CN and the YbF_3 is somewhat heterogenous and may well reflect the hand mixing of this material.

Fig. 2 shows the back scattered SEM of ACT. It contains of two types of filler particles that back scatter slightly differently, but both types of particles are much smaller (<10 µm) than in the CN and with a much more even distribution that may reflect the helical mixing delivery system.

3.2. *pH changes upon immersion*

Fig. 3 shows the pH change at each time point for CN and ACT in TB, AS4 and AS7 respectively. The pH in TB increases by 0.35 upon immersion for 6 weeks for CN, and to a lesser extent for ACT. In AS4 the pH also increases by about 0.2 for both ACT and CN at 6 weeks. In contrast, after AS7 immersion, the pH reduces slightly by about 0.1 for both ACT and CN at 6 weeks.

3.3. *Ion release*

Fig. 4 shows the cumulative calcium release for CN and ACT after TB immersion. The CN releases significant amounts of calcium up to 60 ppm and the release is linear with square root time. In contrast ACT releases a total of just over 7 ppm Ca at 6 weeks. There is no significant phosphorus release for both materials. Fig. 5a shows the Ca and P plotted cumulatively after subtracting the initial values for the Ca and P in AS4. It can be seen that there is considerably more Ca release, approximately 240 ppm cumulatively at six weeks from CN, whilst ACT releases 111 ppm Ca into AS4. There is no significant phosphorus release or consumption in AS4 for both composites. The high Ca release in AS4 for CN reflects the fact that the first step in the degradation of the glass is the ion exchange of H^+ ions in solution for Ca^{2+} ions in the glass. The higher the H^+ concentration or the lower the pH, the faster the glass degradation takes place. In the case of ACT, it is probably the acid hydrolysis of Al-O-Si bonds in the ionomer glass that gives rise to the much greater Ca release in AS4 [15,16]. Fig. 5b shows the cumulative P lost against square root time in AS7. There is a decrease in P for the CN of about 40 ppm indicating a loss of P from solution, whilst a slight increase is observed for ACT.

Fig. 6 shows the cumulative Al release for CN and ACT into TB, AS4 and AS7. here is negligible release of Al into TB and

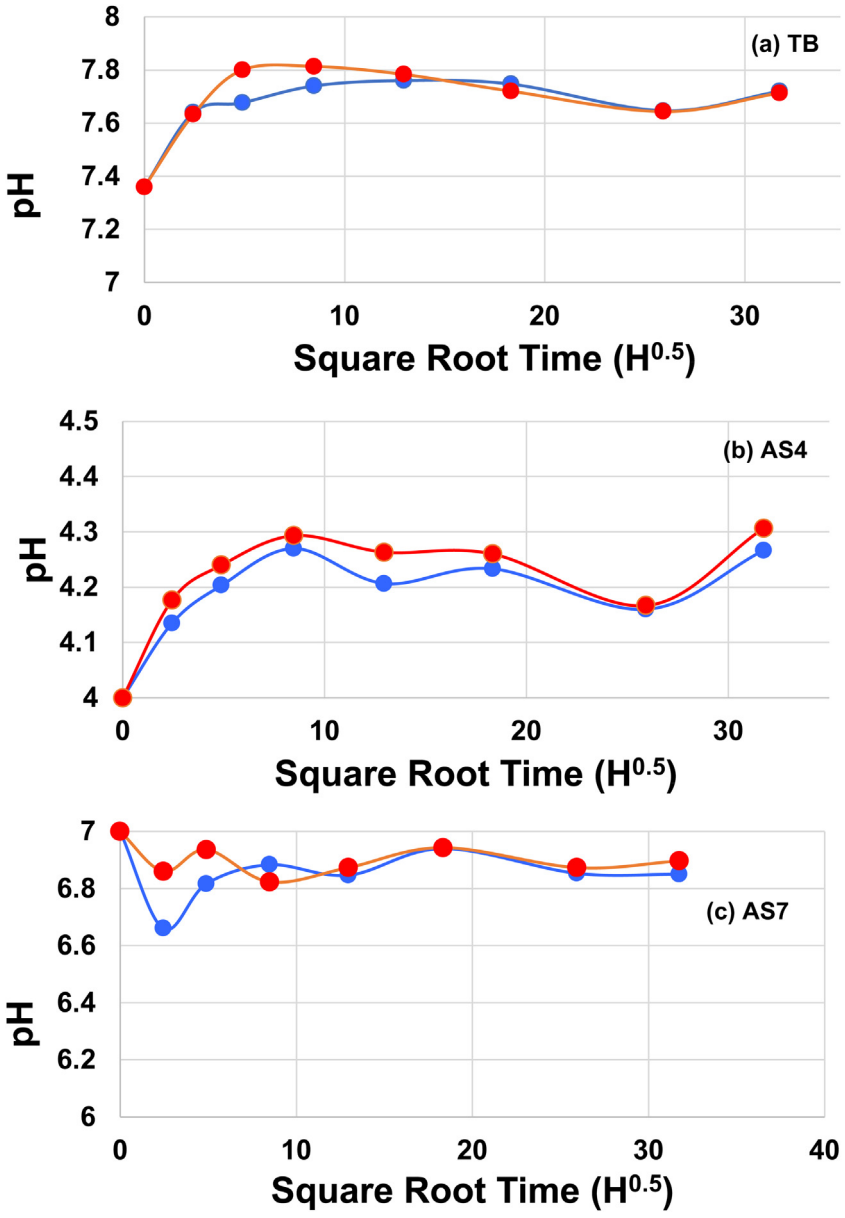

Fig. 3 – (a–c) pH changes of CN (•) and ACT (•) in TB, AS4 and AS7 respectively.

AS7, but significant release in AS4. The Al release occurs as a result of the acid hydrolysis of Al-O-Si bonds that doesn't occur at neutral pH [15,16].

Fig. 7 shows the cumulative Si release into TB for CN and ACT. The release doesn't change dramatically with immersion media. However there is much more Si released from CN than from ACT. This reflects the Si released from the calcium fluorosilicate glass in CN that mirrors the Si release behaviour found for BGs [17,18].

3.4. *Fluoride release*

Fig. 8 shows both CN and ACT composites release fluoride ions after immersion in all the media, but the amount of fluoride released in both cases is relatively low compared to acid-base set glass ionomer cements [18]. In the case of ACT and CN in TB and AS4, the release of fluoride has a square root time dependence suggesting a diffusion controlled release that is also typically found for GICs [19,20]. The CN releases almost twice as much fluoride as the ACT and there is no significant differences in the release of fluoride for ACT in different media. The fluoride release found for ACT is similar to that found by Garoushi et al. [8] though they measured the release into water and used an 8 mm diameter disk compared with a 10 mm disk used here, and eluted into 5 mL as opposed to 10 mL used in the present study. The fluoride release into AS7 for ACT has a square root time dependence, but not, for the CN in AS7. Also, the CN releases less fluoride release in AS7 than in TB that suggesting either a different mechanism of release or possibly some of the released fluoride being consumed to form fluorapatite ($Ca_5(PO_4)_3F$) or calcium fluoride (CaF_2).

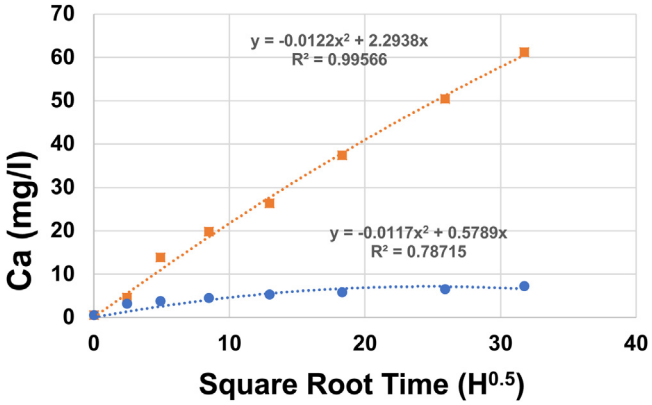

Fig. 4 – Measured cumulative calcium in TB for CN (■) and ACT (●).

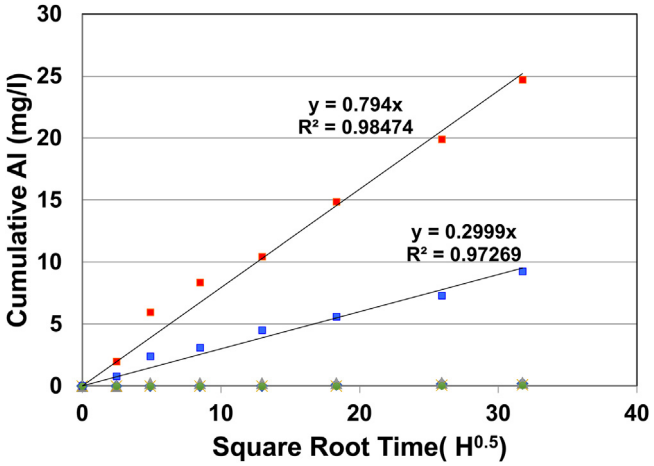

Fig. 6 – Cumulative Al release plotted against square root time. CN AS4 (■); ACT AS4 (■); ACT TB (X); ACT AS7 (●) ;CN TB (◆); CN AS7 (●).

3.5. *ATR-FTIR*

Fig. 9a shows the ATR-FTIR spectrum of CN after immersion in TB. There is a progressive loss in absorbance at 900-960 cm^{-1} corresponding to the loss of non-bridging oxygen (NBO) vibrations [21]. There is no evidence of any vibrations associated with calcium orthophosphate formation at 560 and 600 cm^{-1}. The glasses in CN contain no significant amounts of phos-

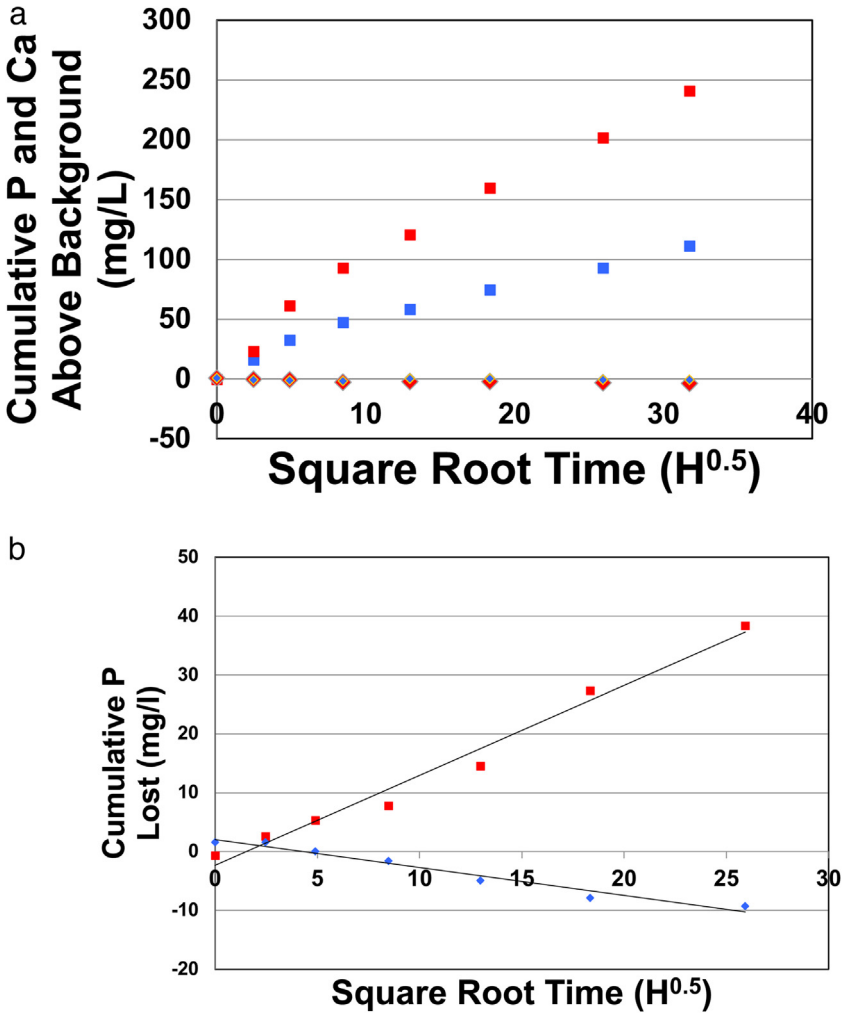

Fig. 5 – (a) Cumulative Ca and P above back ground for CN and ACT in AS4. CN Ca (■) P(◆), ACT Ca (■) P(◆). (b) Cumulative P lost against square root time in AS7. CN (■) ACT (◆).

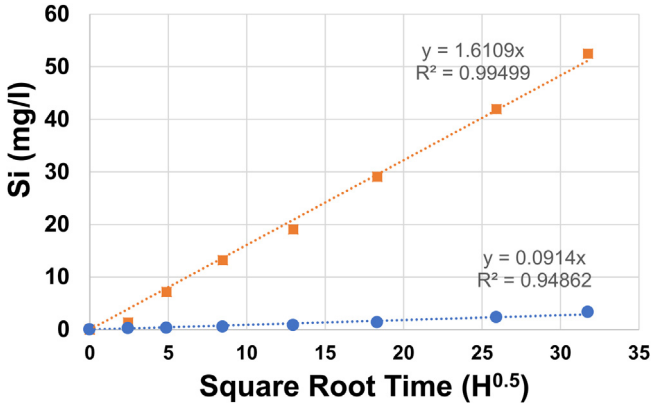

Fig. 7 – Si release into TB. CN(■) ACT (●).

phate and the Tris buffer contains no phosphate, consequently it is not possible to form any calcium orthophosphate phase, including apatite like phases.

Upon immersion in AS4 (Fig. 9b) there are similar changes observed in the FTIR spectra. Again, there is no evidence of any calcium orthophosphate formation despite phosphate being present along with calcium in the immersion solution. Here the pH is probably too low to form an apatite as the pH data indicates the pH did not raise over 4.5 which is where a fluorapatite would start to form.

In AS7 (Fig. 9c) there is again evidence for the loss of NBO vibrations, but there is also evidence for the formation of a calcium orthophosphate with P—O absorbance bands at 568 And 607 cm^{-1} [21–23]. These bands increase in intensity with increasing immersion time. At the same time the band at 1731 cm^{-1}, associated with the carbonyl groups (C=O) of the resin, reduces in intensity. This signal corresponds largely to the UDMA component of the resin. The orthophosphate formed could be either tricalcium phosphate claimed by the manufacturer or an apatite like phase.

The FTIR spectra (Fig. 10) of ACT do not exhibit any significant changes upon immersion. There are some small increases in intensity in the range 1025-1075 cm^{-1} and 1130-1170 cm^{-1} upon immersion in all media. There is no evidence of any split bands at approximately 560 and 600 cm^{-1} for calcium orthophosphate. ACT exhibited an amorphous diffraction pattern both before and after immersion in all media for all times. There was no evidence of any apatite formation after six weeks immersion in AS7 or after immersion in the other immersion media.

Fig. 11 shows the XRD pattern of CN before and after immersion in AS7 for two and six weeks. The CN before immersion shows sharp diffraction lines at 24.63, 26.27, 28.01 and 31.75° two theta corresponding to Ytterbium trifluoride YbF_3 (PDF 34-0102). After immersion, at 2 weeks and 6 weeks, there are new diffraction lines corresponding to an apatite including fluorapatite (PDF 15-876). The diffraction line at ≈25.8° two theta corresponding to the 002 spacing is particularly strong after two weeks immersion and the diffraction lines between 31 and 34° two theta are also present. This would suggest that CN is forming apatite, rather than tricalcium phosphate as claimed by the manufacturer. Though at this stage, it cannot be determined whether the apatite is a hydroxyapatite, a fluorapatite, a mixed fluorohydroxyapatite, or even octacalcium phosphate. Given the release of fluoride based on similar fluoride bioactive glasses, it is expected to be a fluorapatite [24–26]. At six weeks the 002 diffraction is particularly intense and indicates the apatite is forming with the c-axis perpendicular to the surface of the disk. This phenomena has also been observed by Al-eesa et al. [12] with fluoride bioactive glass composites, and highly aligned needle like fluorapatite crystals are also observed by SEM. There was no evidence in the XRD data of calcium fluoride forming upon immersion. Al-eesa et al. [12] have shown using ^{19}F MAS-NMR that the fluoride bioactive glass they studied forms calcium fluorapatite in AS7 and also some CaF_2 in AS4. However in the present case because of the presence of 5–10% of YbF_3 which is paramagnetic, ^{19}F MAS-NMR is not a useful technique here. No significant changes were observed in the XRD patterns upon immersion in Tris Bufffer or AS4.

3.6. SEM of immersed disks

Immersion of CN for six weeks in TB results in a loss of the back scattered intensity in the surface layer of the composite disk up to about 30 μm deep. This occurs primarily from the calcium fluorosilicate glass particles. After immersion in AS4 for six weeks the reacted layer is much more obvious and much more clearly demarcated and about 30–40 μm thick. The reacted layer contains two types of reacted glass particles that may indicate that both the ionomer type glass and the calcium fluorosilicate glass have reacted in the surface layer. The barium boro-alumino-silicate inert glass appears to have been mixed with resin and YbF_3 polymerised, ground up and incorporated back into the composite. It has a speckled appearance which doesn't change upon immersion in AS4. In AS7, CN shows evidence of the reaction of the glass particles at the surface though to a much lesser extent than the samples immersed in AS4. However there is no obvious calcium phosphate layer formed on the surface of the CN despite its detection by XRD and FTIR (Fig. 12). It could be possible that an apatite layer has formed but it is weakly bonded to the surface and easily lost during the grinding and polishing procedure used in sample preparation.

There are no observable changes in the surface of ACT in any of the immersion media when imaged by SEM.

The surface of the Cention disk after immersion in AS7 for six weeks is shown in Fig. 13. Randomly orientated plate like crystals were observed, approximately 1–5 μm across and 0.1–0.3 μm thick.

4. Discussion

Analysis of the CN is complicated by the presence of three different glass compositions in the composite, plus the presence of ytterbium fluoride, howevever the active glass in CN is a calcium fluorosilicate glass, that is compositionally and mechanistically similar in its degradation behaviour to bioactive glasses [1]. This glass, unlike the majority of bioactive glasses, contains no phosphate [5]. This contrasts with the bioactive glasses composites studied in the literature to date that contain phosphate [26–29].

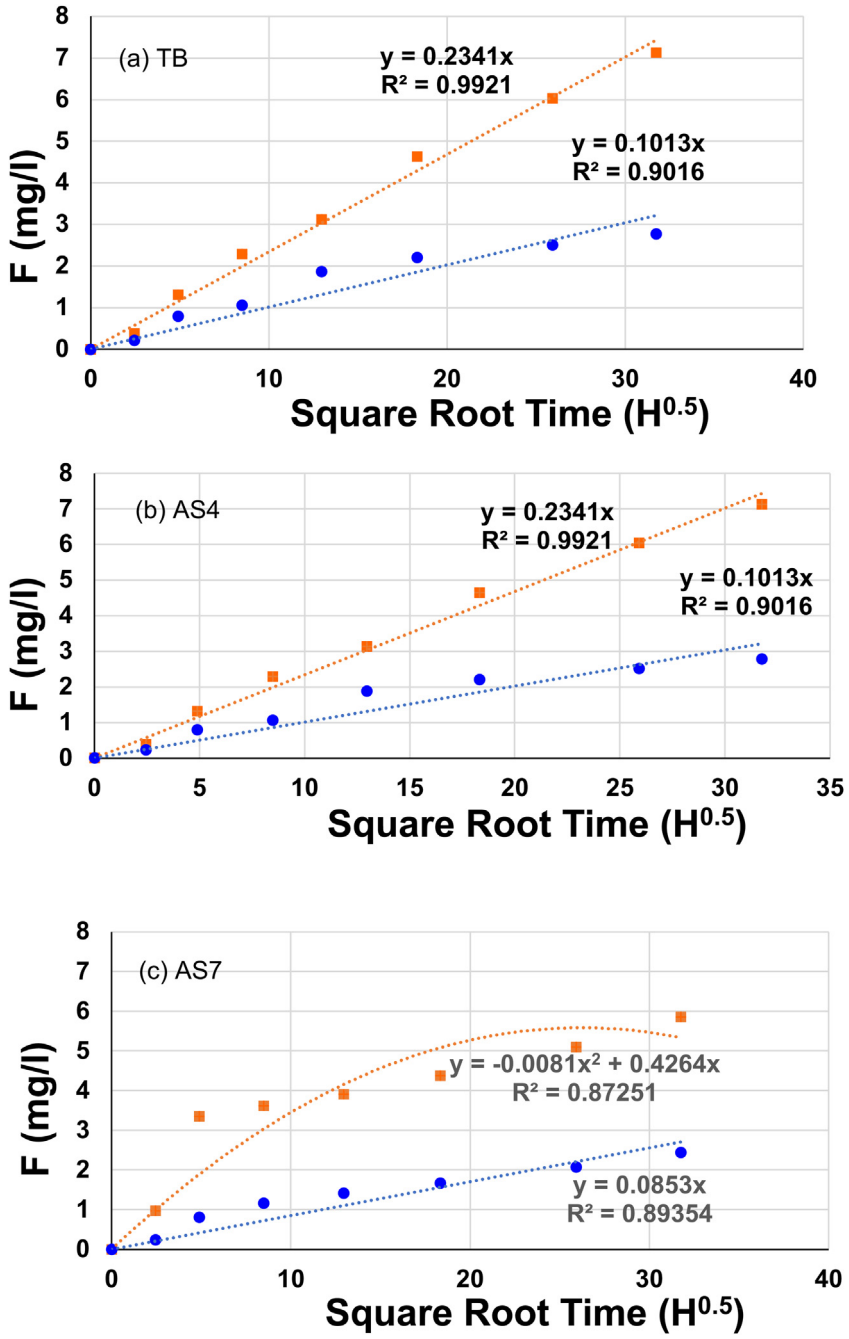

Fig. 8 – Measured cumulative fluoride into TB, AS4 and AS7 for CN (■) and ACT (●).

CN and ACT both increase the pH upon immersion in TB and AS4. In the case of CN, particularly in TB, this is probably due to the ion exchange of Ca^{2+} for H^+ ions in a similar fashion to BG and BG composites [1]. The increase in the pH would also be expected to occur in marginal gaps and would be expected to inhibit the growth of acidophyllic bacteria associated with caries.

Eden [30] and O'Donnell et al. [31] have shown that the amount of apatite formed and the speed of apatite formation increase with the phosphate content of the bioactive glass. Whilst Mneimne et al. [32] have shown that Fluoride containing BGs with high phosphate give faster formation of fluorapatite. Furthermore Mneimne et al. [32] demonstrated fluorite formation is supressed in high phosphate bioactive glasses. There are compositional similiarities between the calcium fluorosilicate glass used in CN and the BG composites studied by Al-eesa et al. [12] recently. It is not possible to compare directly, however, based on the EDAX analysis the calcium fluorosilicate glass in CN, it is thought to be close to example 7 in the patent assigned to Ivoclar [33] (see Table 2 [34,35]). Therefore, the basic active glass in CN is similar to the glass studied by Al-eesa et al., but lacks the P_2O_5 content and the ability to release orthophosphate ions for apatite formation.

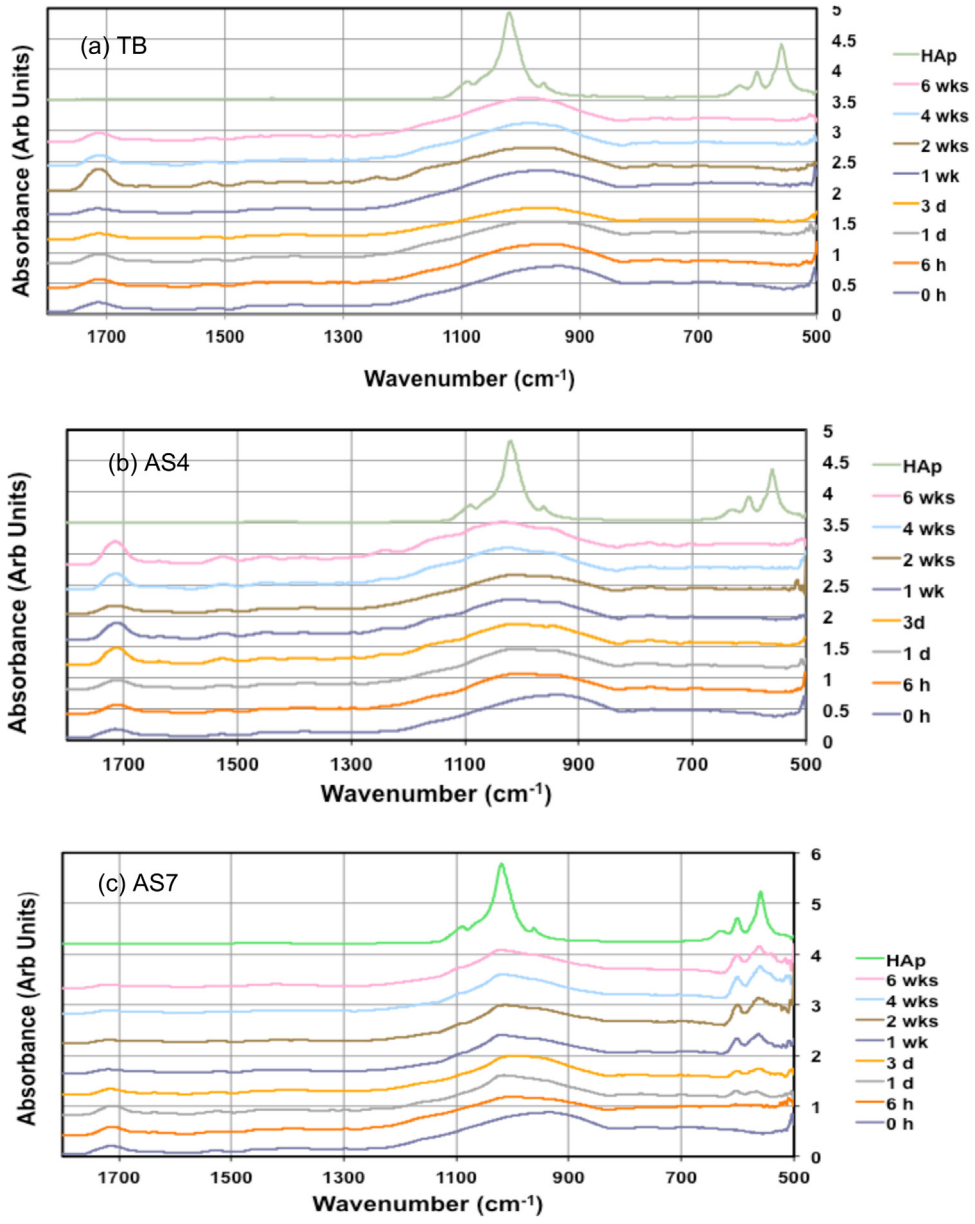

Fig. 9 – ATR-FTIR spectra for CN after immersion in TB, AS4 and AS7 for time periods up to 6 weeks.

Table 2 – Glass composition from EP 0 923 925 A2 [33] compared to that studied by Al-eesa et al. [12–14].

Glass	SiO_2	P_2O_5	CaO	Na_2O	CaF_2	NC	RFI
Example 7	0.48	0.00	0.31	0.08	0.12	2.36	1.53
Al-eesa et al. [12–14]	0.35	0.06	0.43	0.06	0.1	2.19	1.57

RFI is the refractive index calculated according to Duminis et al. [35]. NC is the network connectivity calculated according to Hill and Brauer [34].

Apatite formation by CN is dependant on the availability of orthophosphate from the external media. In the absence of sufficient orthophosphate, it will have a tendency to form CaF_2. CN cannot form apatite in TB since there is no phosphate source. It cannot form apatite in AS4 since the pH is too low to form apatite. However, in AS7 CN shows evidence of apatite from ATR-FTIR and XRD spectral data. This is supported by the observation of a reduction in P and Ca upon immersion in AS7. It is not possible to see clearly the apatite formed in AS7 on the surface of CN in the cross sectional images. This contrasts with the recent study by Al-eesa et al. [12–14] using a phosphate rich fluoride containing bioactive glass, where a relatively thick fluorapatite layer forms up to 20 μm thick. In that study, the apatite crystals are needle like and are highly orientated with the 002 direction perpendicular to the surface. The 002 Bragg diffraction line for apatite formed on CN is also about a factor of two more intense, also indicating some preferential orientation. It is thought that the apatite layer in CN may be possibly removed during the grinding and polishing of the cross sections. To overcome this problem the surface of the disks after six weeks immersion in AS7 were exam-

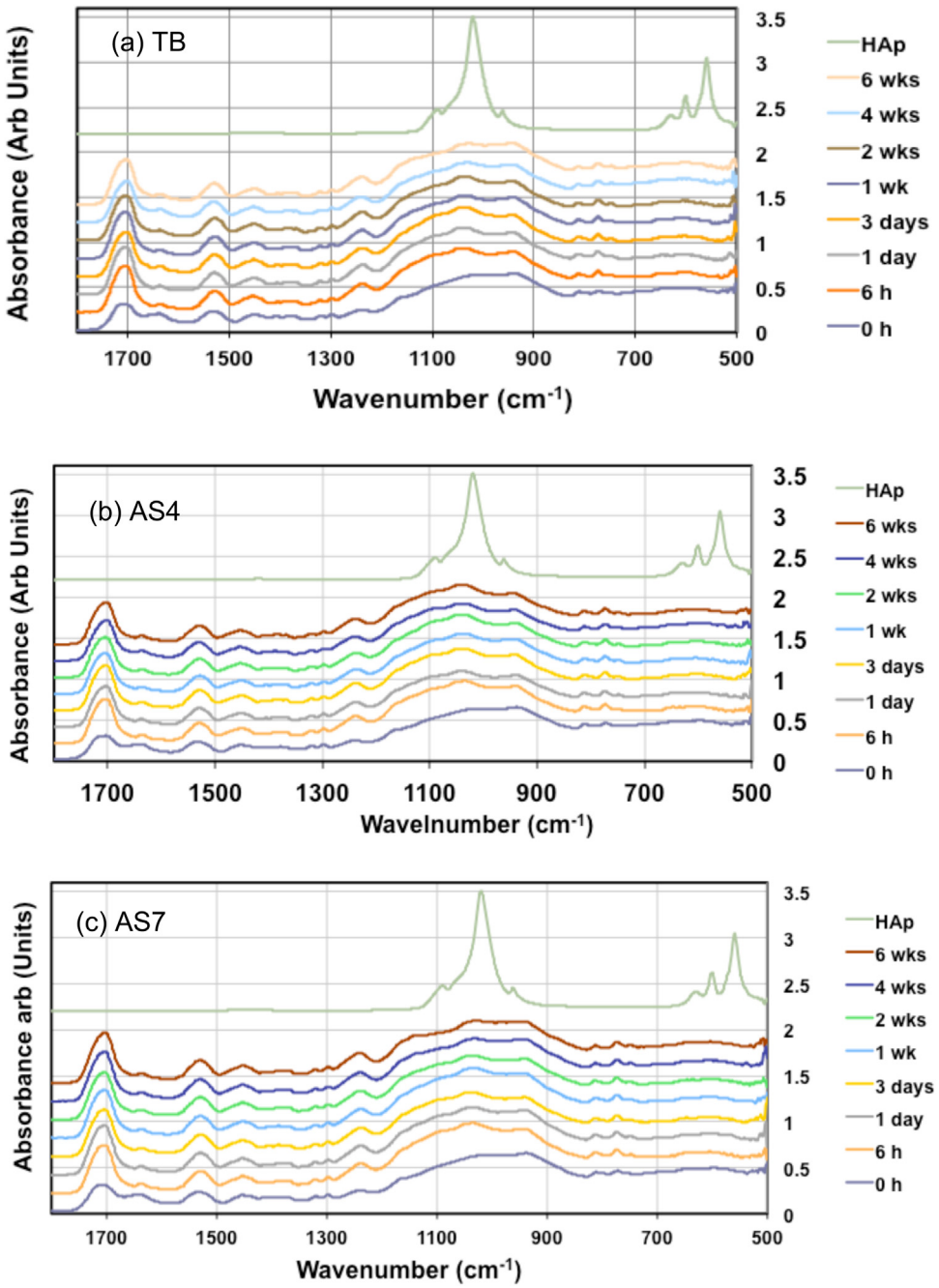

Fig. 10 – ATR-FTIR spectra for ACT after immersion in TB, AS4 and AS7 for time periods up to 6 weeks.

ined. Evidence of crystals with a random orientation and a plate like morphology were found at the surface. This morphology is often indicative of octacalcium phosphate (OCP) or a calcium deficient apatite that has formed via transformation of OCP. Closer examination of the six week FTIR spectrum in Fig. 9c shows a band at 525 cm^{-1} assigned to the P—O bending of a HPO_4^{2-} group that is present in OCP, but is absent in both hydroxyapatite and fluorapatite [37]. OCP, hydroxyapatite and fluorapatite all have almost identical diffraction patterns and very similar FTIR spectra. OCP has a water layer in the crystal structure that corresponds to a large diffraction spacing and a diffraction line a 4.68° two theta that is difficult to detect. The possible presence of OCP and the lack of a needle like geometry typical of fluorapatite is surprising, since even low concentrations of fluoride ions <1 ppm are thought to promote direct apatite formation [38,39]. However CN releases small amounts of fluoride (<1 ppm between 4 weeks and 6 weeks) which is much less than the bioactive glass studied by Al-eesa et al. [14]. The amount of fluoride released by CN may be too low at six weeks to induce the direct formation of apatite. In the CN brochure [8], evidence is presented for a 0.5 μm thick orientated layer of crystals on the surface after immersion in AS for 4 weeks. The crystals have a similar morphology to those observed here but are orientated and are slightly smaller. The

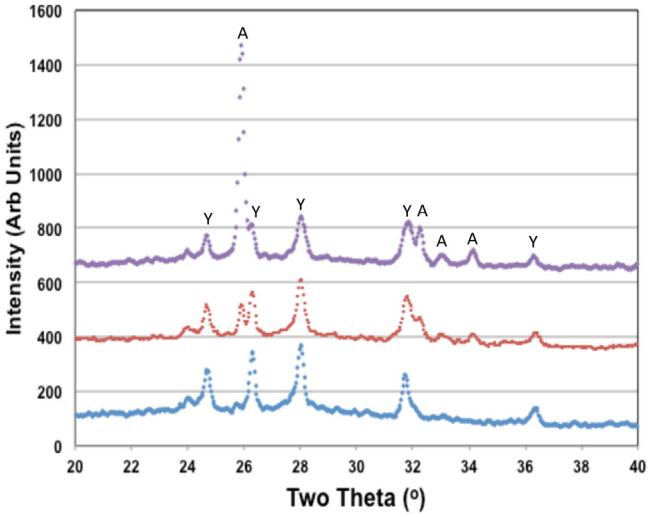

Fig. 11 – XRD patterns of Cention N before immersion (•), after 2 weeks (•) and 6 weeks (•) in AS7. Y = YbF3, A = apatite.

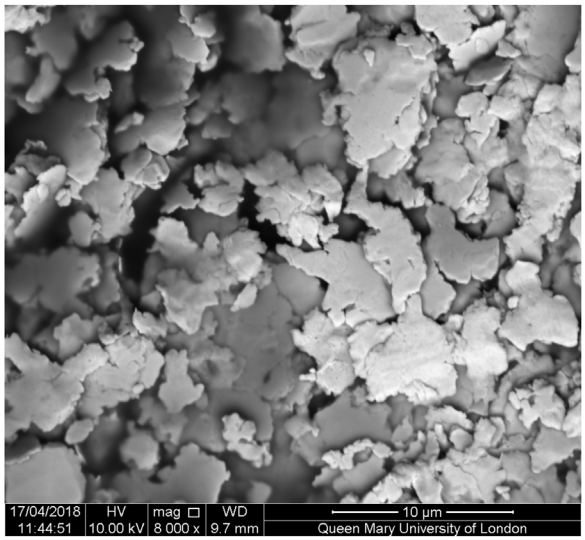

Fig. 13 – Top down surface SEM of CN after 6 weeks immersion in AS7 showing plate like crystal formation.

002 diffraction line at 25.8° two theta for OCP formed from solution saturated in calcium and phosphate by Iijima and Onuma [38] was also observed to be significantly enhanced, also indicating preferred orientation of OCP in the 002 direction.

There was no evidence of the formation of fluorite, CaF_2 formation in any immersion media with CN which might be expected based on the previous studies of Brauer et al. [22]. However CaF_2 has a strong tendency to crystallise as small nanometer sized crystallites that are not easily detected by XRD.

In AS4, there is significant release of Al for both CN and ACT with much more Ca released. This is a result of the acid catalysed hydrolysis of the Al-O-Si bonds in the fluoro-

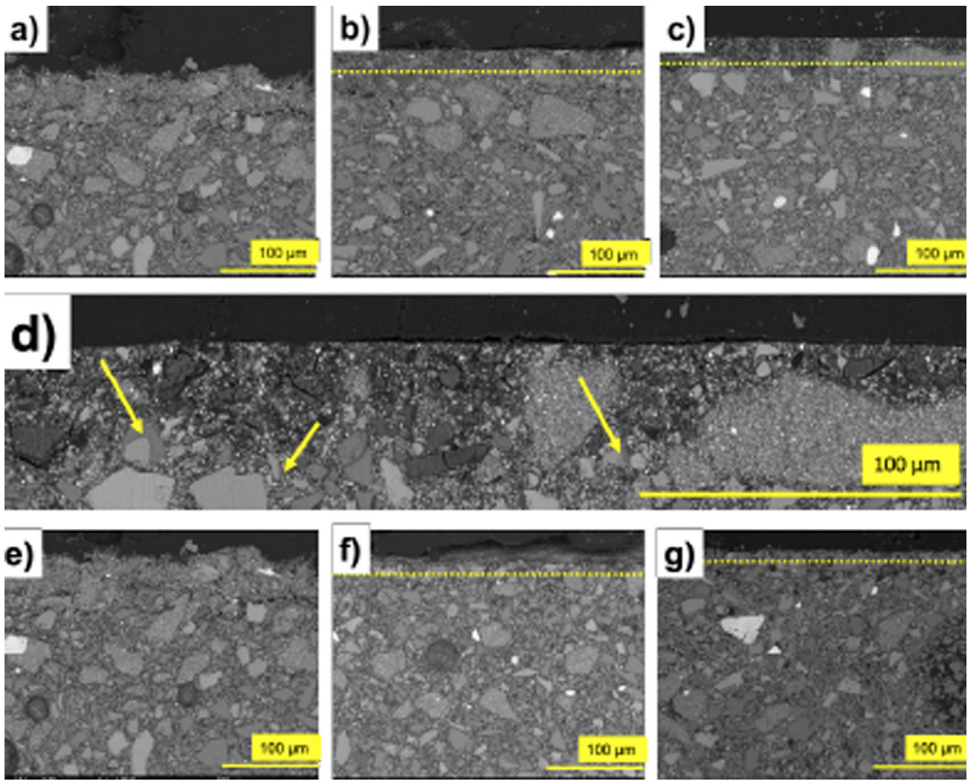

Fig. 12 – SEM Micrographs of CN (a) before Immersion; (b) after immersion in AS4 for 2 weeks; (c) after immersion in AS4 for six weeks; (d) a close-up of the reacted surface layer from Fig. 12c; (e) before immersion; (f) after immersion in AS7 2 weeks; and (g) after immersion in AS7 6 weeks. The dashed line indicates the thickness of the reacted layer in the composite disk.

alumino-silicate ionomer glasses present in both CN and ACT. In the absence of a low pH, CN and ACT release very little Al and in the case of ACT very little Ca indicating that two of the glasses in ACT are probably ionomer type fluoroaluminosilicate glasses, which are not capable of forming apatite and are not bioactive in terms of the definition of being able to form apatite in body like fluids. ACT may be considered to be bioactive in terms of being to able to release fluoride in small quantities, but if this is the basis of the bioactivity, many other dental restorative materials would also be considered to be "bioactive". The higher Al release in AS4 for CN than ACT is surprising given that CN contains relatively little ionomer type glass, but the ionomer type glass in CN may have a higher Al:Si ratio, which would result in more acid hydrolysis [15,16] and more Al release. The difference could also be accounted for by possible surface treatments of the glasses used, for example silylation [36]. The greater reactivity of the ionomer glass in CN is supported by SEM observations of the surfaces after immersion in AS4 that show the presence of only one of the three types of glass particles at the surface in CN, suggesting that both the calcium fluoro-silicate and ionomer type glasses are reacting leaving the unreacted inert glass particles only at the surface.

Reaction of the glass particles of CN, particularly at the exposed surfaces and especially on occlusal surfaces is likely to result in increased wear. It may be advantageous to laminate over the top of exposed surfaces of the CN to reduce wear. For example covering the surface with a conventional composite resin.

The claims of apatite formation with ACT were not substantiated in this study. The evidence presented in the Activa Technical documentation for apatite formation is based on a conference abstact where the authors sputtered coated the samples with gold then determined Ca:P ratios by EDAX to determine apatite formation. Since sputter coating with gold interferes with P determination by EDAX the validity of this is very questionable. If we define "bioactive" as having the capacity to induce apatite formation from physiological solutions ACT is not "Bioactive" within the time period of this study.

5. Conclusions

CN releases Ca^{2+} and F^{-} ions and forms "apatite like" phase upon immersion in AS7 containing orthophosphate. In acidic media (AS4) there is evidence of the calcium fluoro-silicate glass particles undergoing glass degradation at the surface and to a lesser extent in AS7 and TB.

There was no evidence of any apatite like phase formation with the ACT composite in AS7 AS4 or Tris buffer or any significant glass degradation occurring within the experimental time period of six weeks despite the claims by the manufacturer. The fluoride release was significantly less than with a conventional acid base set glass ionomer cement as found by Garoushi et al. [8] despite the claims to the contrary by the manufacturer.

CN is a promising bioactive restorative material that has potential clinical benefits.

In the present study evidence was found for CN forming an apatite like phase, rather than tricalcium phosphate and CaF_2 as suggested in the CN Technical report [6].

Further studies using both ^{19}F and ^{31}P MAS-NMR on a version of CN without the Ytterbium fluoride to avoid the issue with paramagnetic line broading would be useful in distinguishing between the possible phase formed in this composite material.

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