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Kinetics of fluoride ion release from dental restorative glass ionomer cements: the influence of ultrasound, radiant heat and glass composition

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Abstract To compare the effect of ultrasonic setting with self curing on fluoride release from conventional and experimental dental glass ionomer cements. To compare hand mixed and capsule mixing and the effect of replacing some of the reactive glass with zirconia. In a novel material which advocated using radiant heat to cure it, to compare the effect of this with ultrasound. To evaluate the effect of ultrasound on a glass ionomer with fluoride in the water but not in the glass. 10 samples of each cement were ultrasonically set for 55 s; 10 controls self cured for 6 min. Each was placed in 10 ml of deionised water which was changed at 1, 3, 7, 14, 21, 28 days. The solution fluoride content was measured using a selective ion electrode. All ultrasound samples released more fluoride than the controls. Release patterns were similar; after a few days, cumulative fluoride was linear with respect to $t^{1/2}$. Slope and intercept of linear regression plots increased with ultrasound. With radiant heat the cement released less fluoride than controls. The effect of ultrasound on cement with F in water increased only slope not intercept. Zirconia addition enhances fluoride release although the cement fluorine content is reduced. Comparison of capsule and hand mixing showed no consistent effect on fluoride release. Ultrasound enhances fluoride release from GICs. As heat has an opposite effect the heat from ultrasound is not its only action. The lesser effect on cement with fluoride only in the water indicates that of ultrasound enhances fluoride release from glass.

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1 Introduction

Glass ionomer cements (GICs) were first developed in the 1960s by Wilson [1]. They are currently used as one of the alternatives to amalgam restoratives as a tooth coloured restorative cement, as they are aesthetically better than metal restorations and they bond directly to tooth tissue. They may also be used as a dental luting cement having several advantages compared to zinc phosphate cements which had been used for crown cementation previously. They have low setting exotherm and therefore they will not cause thermal damage to the pulp tissue. They also can release fluoride, which provides anticarcinogenic effects. They have good biocompatibility and chemically bond to enamel and dentine. These properties make glass ionomer cements used quite extensively in dental applications [2].

Early water/saliva contamination leading to a softened or disrupted matrix on the cement surface is a distinct problem [2]. The soft surface reduces the wear properties of the cement when in the mouth. In addition to improvements to the GICs, studies are being carried out into methods set acceleration to address this problem.

The methods that have been investigated are the application of ultrasound and heat to accelerate the setting [3–6]. This has been investigated using an ultrasonic scalar device. The results of these studies indicate that application of ultrasonic to GICs accelerates the rate of set of these cements. They showed improvements in the physical properties of the GIC. An increased rate of set as indicated by hardness of a GIC Fuji IX (FIX) was observed using a nano indentation technique [3]. A further study carried out

by Kleverlaan et al. [4] showed an increase in the hardness properties and compressive strength of FIX Fast and Ketac Molar (KM) cements. However they suggested that for this improvement in the mechanical properties was 'The setting of GICs may partially be explained by the heat effect.'

Both studies suggest that the ultrasonic vibration directly enhances the setting reaction of the GIC. The vibration enhances intimate contact of the glass particles with the polyacid solution thus accelerating the reaction. The compaction of the particles leads to enhanced mechanical properties and has the potential for void reduction. Due to the acceleration of the setting times for GICs, this makes the cements less susceptible to water uptake, therefore reducing the development of a softened matrix on exposure to water.

More recently, Rushe and Towler [7] demonstrated the influence of ultrasound on the fluoride release of commercial and experimental glass ionomer luting cements.

This study is designed to investigate the effect of ultrasonic setting (UC) on fluoride release from a range of commercial GICs by comparing that from standard set (SC) samples of the same GICs. A further aim of this study is to compare the fluoride release from capsulated and hand mixed version of the same GICs. Additionally the fluoride release of a glass ionomer containing zirconia as a reinforcing and radiopacifying filler will be compared with the product in a zirconia-free version.

The manufacturers of another commercial Glass Carbomer (GC) product advocate the use of the radiant heat (RC) from a commercial dental curing light to produce the accelerated set created by ultrasound and the effects of the two types of radiation on fluoride release will be compared.

Ultrasound may influence the fluoride release as a result of changes in the glass polyacid reaction or diffusion rate of fluoride through the cement. To investigate this, a GIC with a fluoride free glass with NaF added to the water component will be studied for the effect of ultrasound on fluoride release rate. Cumulative release will be studied over a period of 28 days to enable both initial "burst" and "steady state" release to be evaluated.

Analysis of the elemental composition of all the glasses used in the GICs in the study was carried out by an external laboratory.

2 Materials and methods

There were two conventional GICs used GC FIX (GC Dental, Japan) and KM [3M Espe, Germany] glass compositions shown in Table 1. These were in capsules (CM) and as powder and liquid form for hand mixing (HM). An fluoride free experimental glass LG30 (Limerick University), composition shown in Tables 2, 3. Additionally a commercial GIC Amalgomer (AM, Advanced Healthcare Ltd, UK) which consists of AH2 glass powder and polyacrylicacid homopolymer was available in capsules, powder water presentation for HM and with 19.7% zirconia ceramic particles as radiopacifying secondary ceramic filler particles (AMC). GC (Glass Carbomer, Holland) was available in capsule form only. It contains fluorapatite as a secondary filler and the reactive glass has been treated with dialkyl siloxanes described in European Patent 20040748628. The experimental glass ionomer was made from fluoride free experimental glass LG30 (Limerick University) mixed with polyacrylic acid powder provided by Advanced Healthcare molecular weight 50 kD. Samples were mixed with either water or 2% NaF solution. Details of the glass compositions (analysis by Ceram Research) are given in Table 1.

10 specimens of each cement were prepared for each setting process. All sample preparation was carried out at room temperature. HM was performed using a spatula and paper mixing pad. After activation the capsule was placed in a rotating mixer, Rotomix for 10 s as per manufacturer's instructions. The mixed capsule was then loaded into the gun. A polyethylene mould of dimensions 3 mm diameter and 2 mm thick (Fig. 1) was placed on a sheet of acetate and the mixed cement was injected into the mould, then covered with acetate sheet. The acetate sheets were used to obtain a flat surface area of each specimen, therefore

Table 1 Weight percentage composition of GIC glasses

Element	Si	Al	Ca	Na	F	P	Sr	La
FIX	13.7	17.9	0	1.0	10.2	2.2	19.9	0
KM	12.4	15.0	10.1	1.7	13.3	2.0	0	17.6
LG30	14.6	18.1	13.9	0.05	0.04	6.4	<0.01	<0.01
AH2	18.7	15.8	7.1	5.5	12.9	1.6	0	0
GC	20.0	14.1	2.1	1.9	9.0	2.5	13.6	0

Table 2 Slope (m) and the intercept (C) for the fluoride release of GC over 28 days

Material	m	C	R^2
GC/SC	0.129	0.064	0.998
GC/US	0.345	0.101	0.997
GC/RH	0.102	0.036	0.993

Table 3 Effect of setting methods on slope (m) and intercept (C) of GC

	Effect of US vs. SC	Effect of HC vs. SC
On m	×2.67	×0.79
On C	×1.58	×0.56

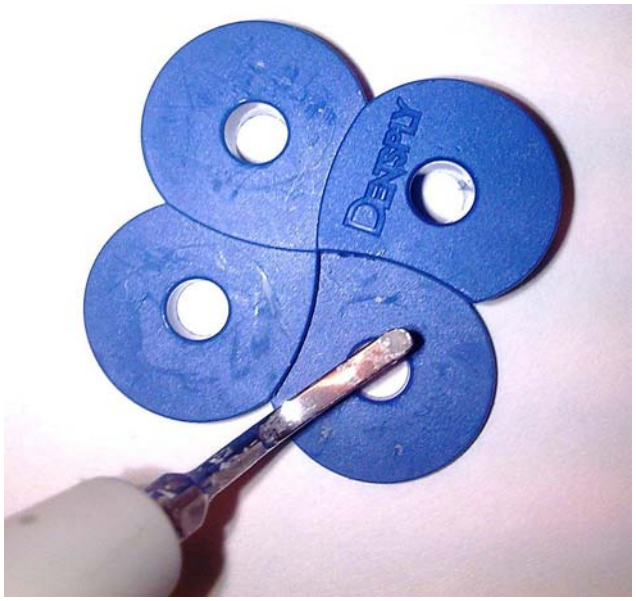

Fig. 1 Application of ultrasound to cement

Fig. 2 Tip of ultrasonic scaler

ensuring that the dimensions remained the same. The specimens were then left for 6 min to SC.

A further set of 10 specimens were prepared and set using a ultrasonic hand piece with a flat tip scaler (Fig. 2), the ultrasound was applied to the cement that was employed using EMS Piezon Master 400 Dental Scaler operating at a maximum frequency of 45 kHz that was set on the maximum power setting. The flat tip of the scaler was moved continuously on the surface in a uniform manner over the acetate sheet where the ultrasonic waves penetrated through into the cement for 55 s as optimized previously [8]. A near uniform US field is found at least to a depth of 4 mm [9].

All samples were placed in 15 ml centrifuge tubes and left to equilibrate for 24 h, before adding 10 ml of deionised water and storing them in an incubator at 37°C. The deionised water was changed at intervals of 1, 3, 7, 14, 21, 28 days. The solutions were then tested for fluoride content using an Orion Ionplus Fluoride Electrode.

3 Results

The plots of the cumulative fluoride release versus $t^{1/2}$ the commercial GICs all show a very strong positive correlation with correlation with $t^{1/2}$. The GC results are shown in Fig. 1 demonstrating the effects of UC and RC compared to SC. The results for capsulated FIX are shown in Fig. 2 showing the results for a conventional GIC with similar fluoride content glass with novel GC. The results in Fig. 3 show the effect of ultrasound on LG30 both with and without NaF addition. In all cases the cumulative fluoride release results show very strong correlations with $t^{1/2}$. Therefore the values of R^2, m, and C for the equations $[F] = m\, t^{1/2} + C$ are shown in Tables 2–13. Together with the effects of various changes in m and C produced by the various changes in experimental variables (type of cure regime, method of mixing, and effect ceramic filler addition) below the relevant tables (Figs. 4, 5).

4 Discussion

Results for all restorative commercial GICs show ultrasound to enhance F-release. This is in line with Rusche and Towler's findings [7] for luting GICs. In both studies the release rate is linear with respect to $t^{1/2}$ indicating a diffusion controlled mechanism. In no instance is there any indication that the UC enhancement falls off with time. In this study good linearity is observed up to 28 days and in Rushe and Towler's case 90 days. In this study their results re-plotted against $t^{1/2}$ show that both m and C of the best fit equation: $[F] = m\, t^{1/2} + C$ are increased for the commercial luting cements Ketac Cem and Fuji I. Our study of the equivalent restoratives KM and FIX show the same effect but m and C are generally increased much more in this study. Their increases for m were $\times 1.4$ for Fuji I and $\times 1.22$ for Ketac Cem and $\times 2.2$ and 2.0 for C. The lesser effect may reflect either the lower glass content of the luting cements or the longer duration of ultrasonic irradiation in this study. This was selected as optimal from a study in the conversion of carboxylic acid groups to carboxylate salt groups using ATR-FTIR [8]. The increase in both m and C suggests that more fluoride is available for release rather than increased diffusion as the major effect. Rushe and Towler discussed possible causes of enhanced fluoride release and suggest the most likely explanation is enhanced reaction due to greater glass surface area available for reaction. They cite reduction in mean particle size due to cavitation [10]. Their general conclusion is in line with our findings for m and C and those of Talal et al. [8] on carboxylate conversion. Further evidence of this is provided by the results on LG30 + NaF. The average effect of UC on m in this study is to increase it by 159% ($\times 2.59$) and

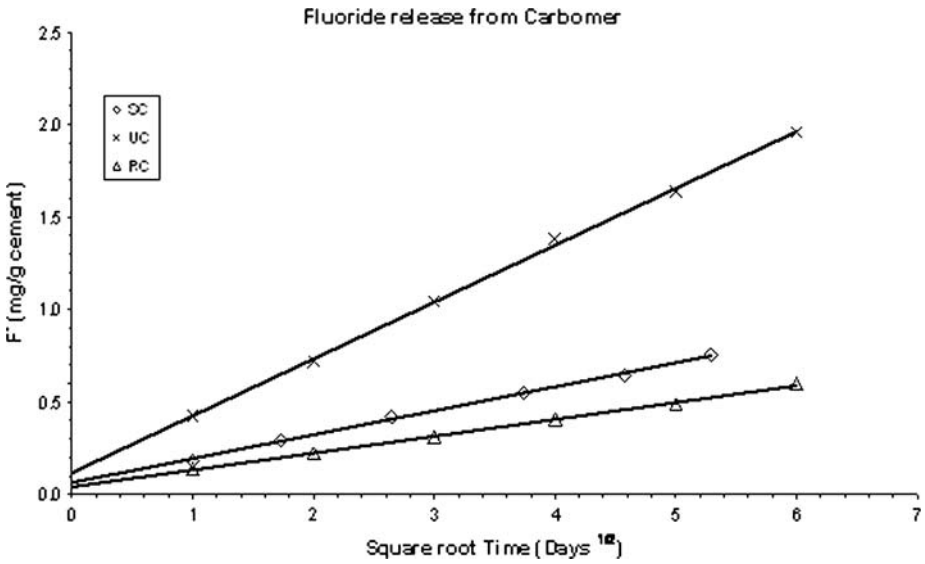

Fig. 3 Fluoride release from Glass Carbomer

Table 4 Slope (m) and the intercept (C) for the fluoride release of both FIX and KM over 28 days

Material	M	C	R^2
KMHMSC	0.0593	0.112	0.926
KMHMUC	0.122	0.427	0.889
KMCMSC	0.110	0.093	0.969
KMCMUC	0.195	0.266	0.961
FIXHMSC	0.057	0.202	0.948
FIXHMUC	0.139	0.281	0.965
FIXCMSC	0.083	0.112	0.976
FIXCMUC	0.316	0.428	0.973

Table 5 Effect of UC versus SC on m and C of KM and FIX

	Material	HM	CM
On m	KM	×2.06	×1.77
	FIX	×2.44	×3.81
On C	KM	×3.81	×2.86
	FIX	×1.39	×1.52

Table 6 Effect of hand mix versus cap mix on m and C of KM and FIX

	Material	SC	UC
On m	KM	×1.85	×1.66
	FIX	×1.46	×2.27
On C	KM	×0.83	×0.63
	FIX	×0.55	×1.52

Table 7 Slope (m) and the intercept (C) for fluoride release of both HM and CM Amalgomer and Amalgomer CR over 28 days

Material	m	C	R^2
AMHMSC	0.161	0.080	0.998
AMHMUC	0.343	0.238	0.991
AMCMSC	0.125	0.076	0.999
AMCMUC	0.378	0.291	0.972
AMCCMSC	0.183	0.549	0.893
AMCMUC	0.510	0.895	0.961

Table 8 Effect of US versus SC on AM HM and CM

	AM/HM	AM/CM	AMCR/CM
On m	×2.13	×3.02	×2.79
On C	×2.98	×3.83	×1.08

Table 9 Effect of CM versus HM of AM

	SC	UC
On m	×0.78	×1.10
On C	×0.95	×1.22

Table 10 Effect of ceramic addition, AMCCM versus AMCM

	SC	UC
On m	×1.46	×1.35
On C	×7.22	×3.08

C by 167% (×2.67) compared to SC for all commercial materials in this study (see Tables 2–10). The Rushe and Towler values [7] increase 30 and 111%, respectively. In contrast, for LG30 + NaF m increases by only 33% and C decrease by 2%. (see Table 5). It therefore seems likely that UC has a small effect on diffusion from the cement

Table 11 Effect of US on LG30 with and without NaF (in the water)

Material	M	C	R^2
LG30SC	0.212	0.812	0.908
LG30UC	0.812	−0.0701	0.962
LG30 + NaFSC	3.294	4.578	0.976
LG30 + NaFUC	4.373	4.492	0.991

The results here are in microg F as contrasted to other tables in mgF

Table 12 Effect of US versus SC on LG30 and LG30 + NaF

	LG30	LG30 + NaF
On m	×3.83	×1.33
On C	× ~0.00	× 0.98

Table 13 Effect of NaF addition

	SC	UC
On m	×15.54	×5.39
On C	×5.6	"v. large"

matrix into the surrounding water and a larger effect on fluoride ion release into the matrix from the glass. Additional evidence in support of this hypothesis is provided by the results from the LG30 controls. Although, the formulation is designed to be fluoride free impurity levels of fluoride were found on analysis by Williams et al. [11] (as shown in Table 1). The increase in m produced by UC is much higher than that produced by UC on the formulation with NaF. (The effect of UC on C did not change.) It therefore seems that most effect of UC is on fluoride ion release from glass into the polyacid matrix although release may be into the depleted layer around glass particles from which release occurs more easily into water than from the non-acid-treated particles [12, 13].

The effect of capsule mixing on fluoride release is very variable. Two of the three materials show increased m for capsule mixed SC compared to hand mixed, whereas for UC all three show increases. All three comparisons show reduced values of C for SC whereas two of them show increases for UC (see Tables 4–10).The effect of method of mixing on F-release has not been subjected to much study, only a poster presentation at BSDR 2005 dealt with effect of porosity on fluoride release and uptake [14] and Verbeek et al. [15] showed considerable increase in both short and longer term release for capsule mixing but for only one material.

Looking at the interaction between method of mixing and effect of UC for FIX and Amalgomer the UC effect is enhanced for both m and C. For KM it is reduced slightly for m but by 24% for C. In a previous study Jones et al. [16] have indicated higher levels of porosity in FIX than in KM. This may therefore suggest that porosity reduction may be a factor influencing the difference observed.

The results for glass GC when self cured are very similar to the other GICs tested in this study. The siloxane incorporation into the material referred to in the manufacturer's patent does not produce any marked difference in the type of [F] v $t^{1/2}$ plot produced. The level of enhancement by UC of m and C is also similar. The interesting feature of this product is the manufacturer's advocacy of the use of a dental curing light with appreciable radiant heat output to accelerate the set. Using the curing light recommended for their specified duration produced reductions in m and C compared to SC. These results are the only ones comparing

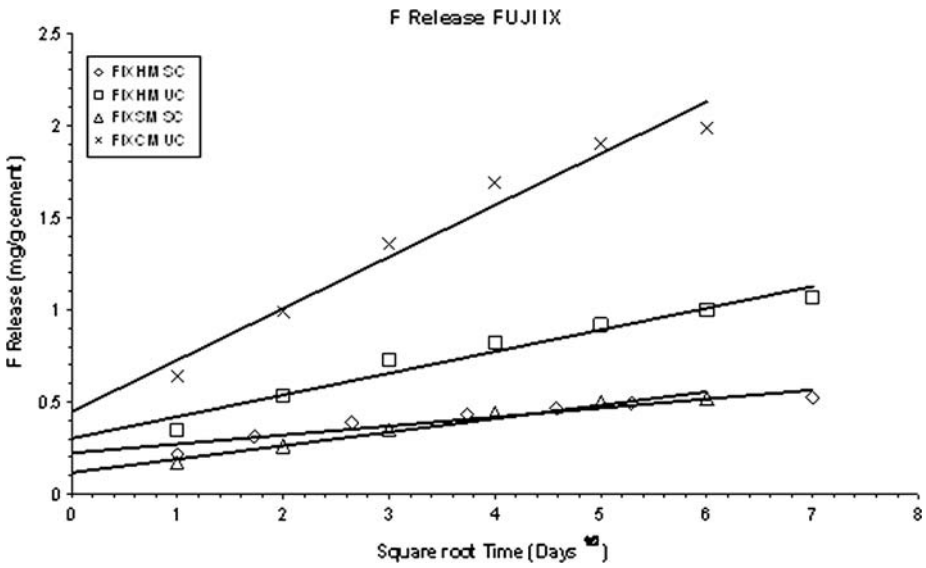

Fig. 4 Fluoride release from capsule and hand mixed Fuji IX

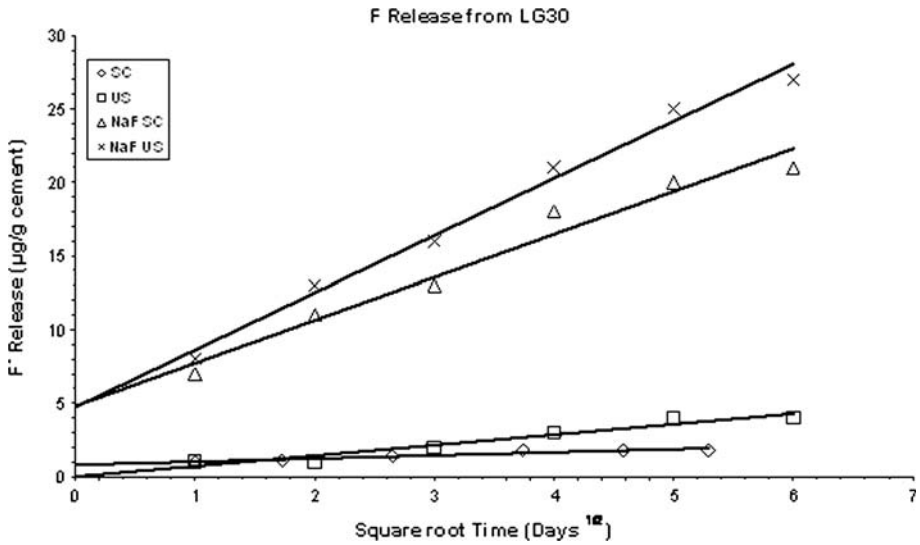

Fig. 5 Fluoride release from LG30 cement with water or 2% NaF solution

the effect of heat and ultrasound on F-release. The effects on compressive strength are reportedly similar on other GICs, i.e. both produce enhancement compared to SC [4]. Examining the conversion of the ratio of carboxylic acid to carboxylate peaks (as described in Talal et al. [8]) shows 187% increase for UC compared 157% for RH after 10 min. After 60 min they are similar UC 187%, RH 195% and SC is 192%. Though not a direct comparison Rushe and Towler [7] showed UC enhanced fluoride release whereas Woolford and Grieve [17] showed reducing levels with increasing duration of infrared radiation. This comparison therefore provides direct evidence that UC produces effects other than those arising from the heat that is generated in its application to GIC.

The results of Amalgomer and Amalgomer CR provide the direct comparison between a GIC and a similar material with a secondary filler 19.7% ZrO. Although the secondary filler is fluoride free and replaces an appreciable proportion of the fluoride containing glass the effect on fluoride release is higher both for SC and UC. Particularly surprising is the relative effects on m and C (see Table 10). The larger effect is on C suggests that the initial "wash out" is greater. Previous studies with GICs having secondary fillers have been of GICs having very large weight percentages of silver or silver tin alloy [18] and showed reduced fluoride release. GC contains fluorapatite as secondary filler but no material without this present was available for a comparison to be made.

Since the composition of all the commercial GIC glasses had been determined (Table 1) it was possible to evaluate the effects of Na and F content on the fluoride release both as m giving a measure of diffusion controlled continuing release and C as a measure of initial "burst" or "washout" behaviour. NOTE this was not a primary objective of this study and the effects would be confounded by other factors such as method of mixing, presence or absence of secondary filler, and different polyacids. The fluoride contents also had a more limited range (9.0–13.3%) as contrasted to (1.0–5.3%) for Na. (The results for LG30 were excluded since it had a negligible F content and would therefore have had effectively no fluoride release thus skewing the statistics.) Table 14 shows the correlation coefficients (in the form of R^2) from linear regression analysis. All values of R were positive but only the effects on m and C of Na for SC samples were statistically significant. The correlations were always weaker for UC than for SC. The absence of positive link between fluoride content (in the range used in commercial dental GICs) and fluoride release has been reported previously [19]. The correlation for C and Na was particularly strong. This is in line with findings with glasses where only the Na content of the glass was varied [20]. Although values of m and C were not determined in that study, the initial release over 64 h increased much more than the subsequent cumulative release from 64 h to 12 weeks. The release relative to the Na-free glass rose from 15% for 0.3% Na to 130% for 1.2% Na for initial release as contrasted with −12% to +39% for subsequent cumulative release.

Further work should include evaluation of the other elements released from the GICs SC, UC, and RC.

Table 14 Effect of F and Na content of glass on F-release (values of R^2 from linear correlations with m and C)

Cure type	Element	M	C
SC	Na	0.66 ($P = 0.05$)	0.88 ($P = 0.01$)
UC	Na	0.53 ($P > 0.05$)	0.12 ($P > 0.05$)
SC	F	0.07 ($P > 0.05$)	0.24 ($P > 0.05$)
UC	F	0.001 ($P > 0.05$)	0.14 ($P > 0.05$)

Evaluation of effect on fluoride ion uptake of these three setting conditions and effect of setting conditions on the susceptibility of GIC to disruption (roughening) by neutral fluoride solution.

5 Conclusions

Ultrasound accelerated setting enhances fluoride release from GICs. Heat accelerated setting has an opposite effect. This confirms that heat generated by UC is not its only effect where the fluoride content of the GIC is present in the water of the GIC rather than in the glass the effect of UC is much less indicating that UC acts on F-containing GICs to enhance fluoride release from the glass component. The effect of HM compared to capsule mixing on fluoride release is not in a consistent direction. The presence of an inert Zirconia secondary filler enhances fluoride release although the fluoride content is reduced. The Na content of the glass enhances initial fluoride release more than subsequent release rate.

References

1. Wilson AD. Developments in glass ionomer cements. Int J Prosthodont. 1989;5:438–46.
2. Davidson CL, Mjőr IA. Advances in glass ionomer cements. Chicago: Quintessence Pub Co; 1999.
3. Towler MR, Bushby AJ, Billington RW, Hill RG. A preliminary comparison of the mechanical properties of chemically cured and ultrasonically cured glass ionomer cements, using nano-indentation techniques. Biomaterials. 2001;11:1401–6.
4. Kleverlaan CJ, van Duinen, Feilzer AJ. Mechanical properties of glass ionomer cements affected by curing methods. Dent Mater. 2004;1:45–50.
5. Algera TJ, Kleverlaan CJ, Prahal-Andersen B, Feilzer AJ. The influence of accelerating the setting rate by ultrasound of heat on the bond strength of glass ionomers used as orthodontic bracket cements. Eur J Orthodont. 2005;26:1–5.
6. Brune D. Heat treatment of glass ionomer, silicate zinc phosphate and zinc polycarboxylate cements. Scand J Dent Res. 1982;90:409–12.
7. Rushe N, Towler MR. The influence of ultrasonic setting on fluoride release from glass polyalkenoate cements. J Mater Sci. 2006;41:5775–7.
8. Talal A, Tanner KE, Billington RW, Pearson GJ. Effect of ultrasound on the setting characteristics of glass ionomer cements studied by Fourier Transform Infra Red Spectroscopy. J Mater Sci: Mater Med. 2009;20:405–11.
9. Harle J, Parsons NS, Mayia F, Pearson GJ. The effect of ultrasound fields on the curing of glass ionomer cements. Barcelona: ESB; 2002.
10. Towler MR, Crowley CM, Hill RG. Investigation into the ultrasonic setting of glass ionomer cements Part I postulated modalities. J Mater Sci Lett. 2003;22:539.
11. Williams JA, Briggs E, Billington RW, Pearson GJ. The effect of adding fluoride compounds to a fluoride free glass ionomer cement on subsequent fluoride and sodium release. Biomaterials. 2003;24:1301–8.
12. Williams JA, Billington RW, Pearson GJ. The glass ionomer cement: the source of soluble fluoride. Biomaterials. 2002;23:2191–200.
13. Luo J, Billington RW, Pearson GJ. Kinetics of fluoride release from the glass components of glass ionomers. J Dent. 2009;37:445–501.
14. Yan ZQ, Sidhu SK, Nomoto R, Mccabe JF. Effects of porosity on the fluoride release and recharging of glass ionomers. BSDR. 2005 (abstract no:0039). Available at: http://iadr.confex.com/iadr/bsdr05/techprogram/abstract_66046.htm.
15. Verbeeck RM, De Moor RJ, San Even DF, Martens LC. The short term fluoride release of hand mixed vs. capsulated systems of restorative glass ionomer cements. J Dent. 1993;3:577–81.
16. Jones CS, Pearson GJ, Billington RW. Effects of viscosity in capsulated glass-ionomer cements. J Dent Res. 1997;76(5):432.
17. Woolford MJ, Grieve AR. Release of fluoride from glass polyalkenoate ionomer cement subjected to radiant heat. J Dent. 1995;4:227–33.
18. El Mallak BF, Sarkar NK. Fluoride release from glass ionomer cements in de-ionized water and artificial saliva. Dent Mater. 1990;6:118–22.
19. Meryon SD, Smith AJ. A comparison of the fluoride release from three glass ionomer cements and a polycarboxylate cement. Int Endod J. 1984;17:16–24.
20. Hill RG, De Barra E, Griffin S, Henn G, et al. Fluoride release from glass polyalykenoate (ionomer) cements. Key Eng Mater. 1995;99–100:315–22.