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Effects of adding sodium and fluoride ions to glass ionomer on its interactions with sodium fluoride solution

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Abstract

This investigates the effects of the addition of Na and F ions to a glass ionomer cement in which those ions are not inherently present on its interactions with dilute (0.2%) NaF solution. Both the effect of the solution on the cement's surface morphology and the effect of the cement on the solution in terms of take up of Na⁺ and F⁻ and of change in pH are to be investigated. These results are to be compared to previous results obtained with glasses which contained both, one, or neither of the ions as components of their glasses. NaF (1.3% by weight in the mixed cement) was added to the powder components of a glass ionomer based on LG30 glass (which contains Al, Si, Ca, P, and O only). Discs of cement were set in moulds at 37°C for 1 h then stored in water at 37°C for 3 days. Each test disc was then immersed in 10 ml 0.2% NaF solution whereas controls remained immersed in water ($N = 3$ for test and control). Test and control disc surfaces were assessed both qualitatively by electron microscopy and quantitatively by linear profilometry (R_a values). Potentiometry was used to measure solution pH and Na and F concentrations using a pH electrode and suitable ion selective electrodes both before and after cement immersion. The surface of test specimens was subject considerable disruption with the polysalt cement matrix being removed and residual glass particles being disclosed. The controls showed no such disruption. This effect was reflected in a significant difference of R_a . Such an effect was not shown by test and control surfaces of LG30 but a similar effect was to that shown by LG26 (which contains F as a glass component). Solution pH changed by 1 unit which was much more than the change shown by LG30 or LG26 but is similar to that of AH2 and MP4 cements which both contain Na. The Na and F uptake was much lower than for LG30 whereas that of LG26 was higher than LG30. The Na : F ratio was 0.29 : 1 compared to 1.26 : 1 for LG30 (LG26 = 1.01 : 1, AH2 = 1.02 : 1, MP4 = 1.04 : 1). Fluoride addition to a F-free glass ionomer renders it vulnerable to surface disruption by NaF solution showing that fluoride complexes produced in glass dissolution are not necessarily involved in this process. Sodium addition to a Na-free glass ionomer confirms the role of this cement in enhancing pH change in NaF solution. The level of uptake of F⁻ from a NaF solution is much lower than that for the F-free glass ionomer which shows there is no direct relationship between F⁻ uptake and surface disruption. The ratio of Na : F uptake is below 0.3 : 1, but the pH change is similar to cements where the ratio is close to unity which indicates that F⁻/OH⁻ interchange is not a significant mechanism even when anion/cation uptake is not balanced. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

In 1986 Akselsen et al. reported 'total disintegration' of glass ionomer cements (GIC) immersed in 2% neutral sodium fluoride [1]. Although Billington et al. could not reproduce these results, they did report reduced hardness [2]. In addition, they reported changes in solution pH from 6–7 for the 2% NaF solution to 9–10 after 24 h

contact with the cement. Recently, the effect of more dilute alkali metal fluorides on surface structure of glass ionomers has been studied using electron microscopy and surface roughness determined by profilometry. It was shown [3] that cements in which the glass contained fluorine were subject to selective attack on the polyacid matrix between the residual glass particles whereas those containing no fluorine showed little or no attack or surface roughening. A pH change of 1 unit or less was found at the alkali metal fluoride concentration of 900 ppm which contrasted to ~3 pH units change reported for 9000 ppm solution [2]. It was also noted that

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cements containing Na gave rise to larger pH changes than those free from Na (or other alkali metal ion) in the glass.

In 1986 Walls [4] suggested glass-ionomer cement might take up fluoride when exposed to it in appreciable concentrations and subsequently re-release it when the external fluoride level was low (the 'rechargeable reservoir'). Although Forsten *in vitro* [5] and Hatibovic-Kofman and Koch *in vitro* and *in vivo* [6] demonstrated enhanced release for GIC after exposure to fluoride this did not, in fact, demonstrate uptake of F ion followed by re-release. As the GICs these authors used contained intrinsic fluoride, the enhanced release rate might result from faster release of this rather than uptake followed by re-release. In a study by Thevadas et al. [7] the addition of NaF to a fluoride-containing GIC resulted in enhanced release which can be calculated to represent ~3 times the actual quantity of F added as NaF. In 1996 Williams et al. [8] reported that a fluoride-free GIC after immersion in alkali metal fluoride solution released large amounts of fluoride which it must obviously have taken up. It was also shown that the quantity released was far greater than if the water component in the cement was replaced by a solution of the same F concentration as that used for immersion. This study, whilst showing F uptake and re-release was possible, did not demonstrate that this happened with F-containing GICs nor did it determine if all the F uptake of a F-free GIC was available for re-release. Recently, Hadley et al. [9] confirmed that the enhanced release found from F-containing GICs was wholly attributable to uptake with no cement releasing more F than the amount taken up over the period over which enhanced release was detected (97 days or less). Cements in which F was a glass component took up more F ion from solution than to F-free cements and also tended not to release all of the uptaken F ion.

The aim of this study was to examine factors influencing GIC interaction with dilute NaF solution. A GIC which contained neither F nor Na had these elements added by mixing solid NaF into the powder components of the cement. This cement's interaction with dilute NaF solution was compared unmodified LG30 cement (and other GICs which contain F and/or Na as glass components) in respect of effects on:

1. The surface morphology of the cement,
2. The change in pH of the immersing solution,
3. The uptake of Na and F ion from this solution.

2. Materials and methods

The LG30 glass used in the cement formulation is a calcium aluminosilicate glass containing Ca, P, Al, Si, and O. The glasses referred to in comparison data from

previous work are LG26 in which F replaces some O (but all other elements are present in the same molar proportions as LG30); MP4, which has the elements in different proportions to the LG glasses and contains neither F nor P; and AH2 which contains all the elements including Na and F (in different proportions to any of the preceding glasses). The cements contained all ingredients except water in the powder; all were mixed at a powder/water ratio of 7:1 to form cements. The other components of the mixed cement are present in the proportions (by weight); glass 72.3%, polyacid 14.0%, water 12.5%, tartaric acid 1.2% (for unmodified cements). The polyacid used was a homopolymer of acrylic acid with an M_v of ~50 000 g/mol.

In the LG30 + NaF used in this study, the mixed cement contains 1.3% NaF. This level of fluoride addition was calculated to approximate to that released by the dissolution of LG26 glass in neutralising the acid components of that cement. The proportions of the components (apart from water) are reduced proportionately. The cement discs were 1 mm thick and 10 mm diameter and were made using split ring moulds clamped between metal plates protected by cellulose acetate matrices. These were stored for 1 h at 37°C before being removed from the moulds into 10 ml water at 37°C in which they matured for 3 days. Three test discs were each then immersed in 10 ml 0.2% NaF for 24 h; three control discs were each kept in 10 ml water for the same time. Both test and control discs were held at 37°C. All test and control discs were subject to visual examination. Subsequently, a test disc for scanning electron microscopy was desiccated and sputter-coated with gold. For measurement of surface roughness, the two remaining discs were kept at high relative humidity (>90%) to prevent desiccation. The three NaF solutions used for immersion were each split into three aliquots for measurement of Na concentration, F concentration, and pH.

The scanning electron microscope used was a Cambridge Stereoscan 90 operating at 15 kV.

Ion concentration analysis was carried out using a Jenway 3045 Ion Analyser using selective ion electrodes for Na and F. Fluoride measurements were all made using TISAB as decomplexing agent. Further details are given in Hadley et al. [9]. The equipment was calibrated using standards of known sodium and fluoride concentrations and this calibration was checked regularly throughout the series of measurements. Measurement of pH was made also using the Jenway 3045 fitted with a combination pH electrode calibrated against buffers of pH 4.0 and 7.0.

Surface roughness measurement was carried out using a Mitutoyo Surftest (Linear Stylus Profilometer). This device was calibrated using a 3 µm step wedge prior to measurement of test surfaces. A total of 6 measurements were made on different areas of each disc. The cut-off sampling length was 0.8 mm.

3. Results

The electron micrographs in Fig. 1 are presented as a pair comparing water and NaF stored surfaces of LG30 + NaF at a field of view of 50 μm together with similar pairs of micrographs of LG30 and LG26 (at the same final magnification) included for comparison.

Surface roughness results ($N = 6$) are given in the form of a bar chart, Fig. 2. Results from a previous study [3] for LG30, LG26, MP4, and AH2 (before and after immersion in 0.2% NaF for 24 h) are also shown.

The pH value of the immersion solution in contact with LG30 + NaF is shown in a bar chart, Fig. 3, in

comparison with the control NaF solution and solutions after contact with LG30, LG26, MP4 and AH2 (previous study). Additionally, the pH changes relative to that of the control solution are also presented in this figure against the right-hand y-axis.

The uptake of fluoride and sodium, determined as the change in concentration between control NaF solution and NaF solution after contact with GIC, is shown as a bar chart, Fig. 4, with previous results obtained for LG30, LG26, MP4 and AH2 included for comparison. In addition, the molar ratio of Na : F is shown as a separate bar for each cement (readable against the right-hand y-axis).

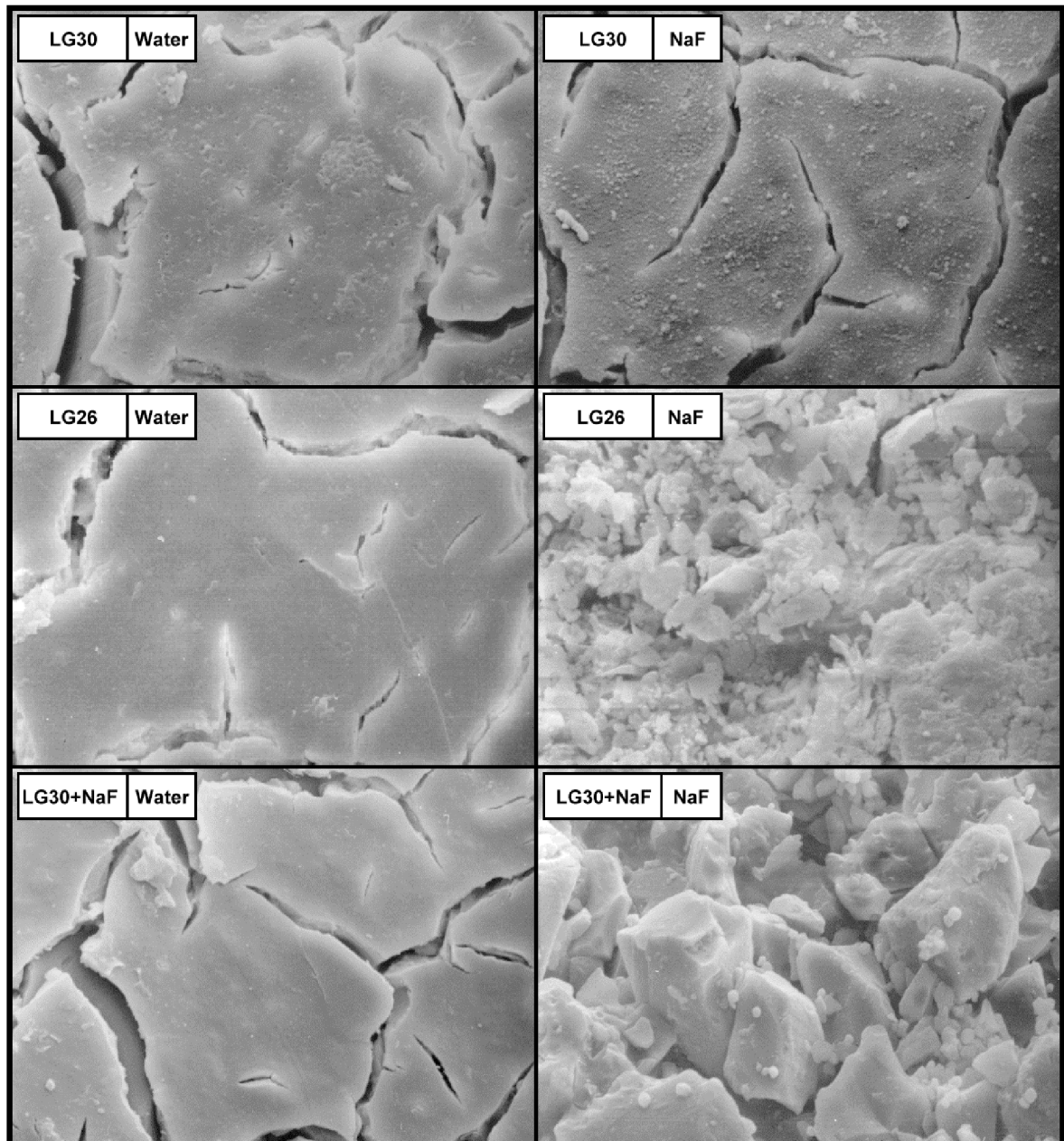


Fig. 1. Scanning electron micrographs of glass ionomer surfaces after immersion in water or 0.2% NaF solution.

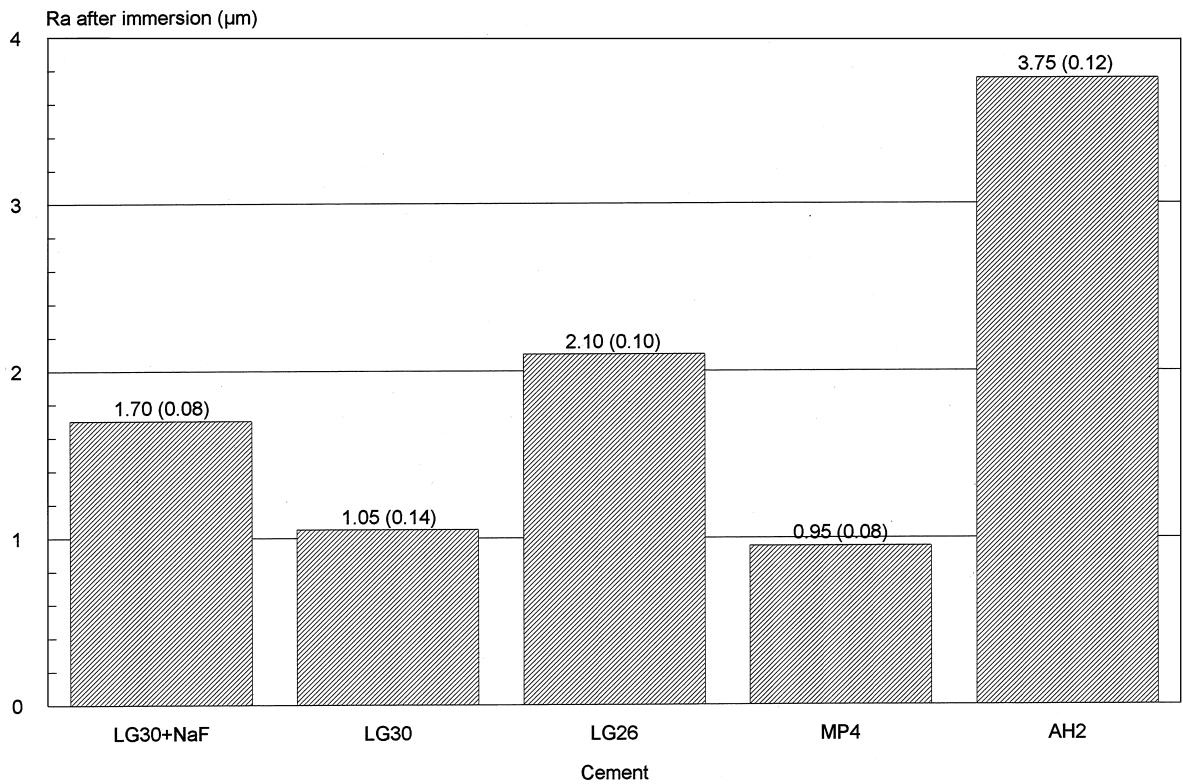


Fig. 2. Surface roughness values (R_a) of glass ionomer surfaces after immersion in 0.2% NaF solution. The figures in parentheses are the standard errors of the means.

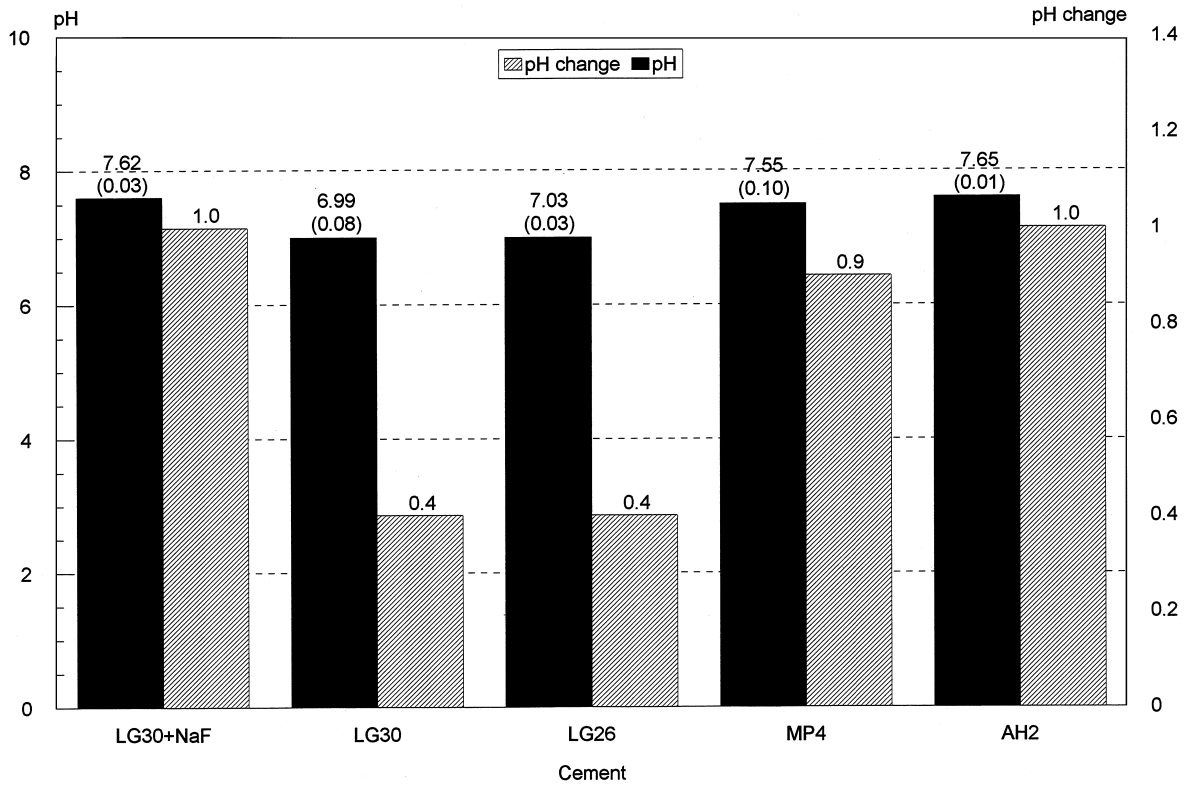


Fig. 3. The pH values of 0.2% NaF solution after contact with glass ionomer for 24 h and pH change compared to initial pH of 6.6 (standard errors in parentheses).

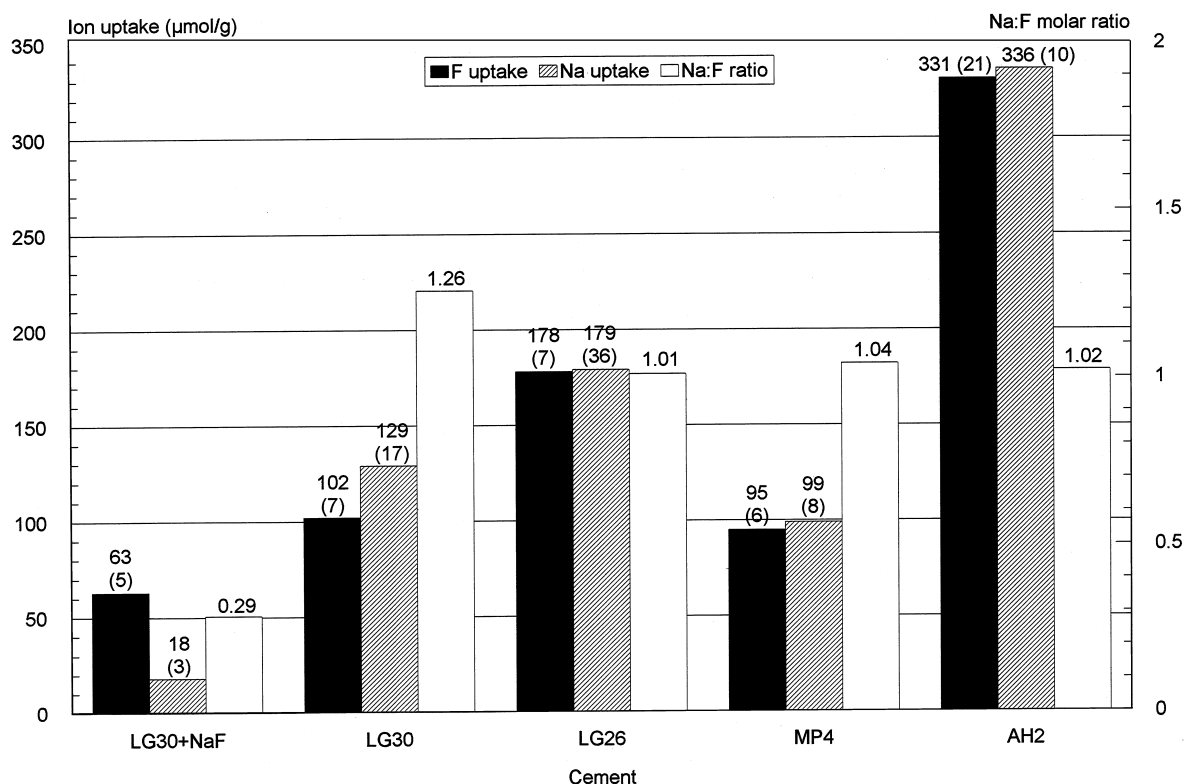


Fig. 4. Uptake of Na^+ and F^- ions by glass ionomers and Na:F ratio of uptaken ions (standard errors in parentheses).

Table 1
Statistical comparisons

Property	Comparison	Probability level
R_a (after NaF immersion)	LG30 + NaF v LG30	$P = < 0.05$
R_a (after NaF immersion)	LG30 + NaF v LG26	$P = > 0.05$
F uptake	LG30 + NaF v LG30	$P = < 0.05$
Na uptake	LG30 + NaF v LG30	$P = < 0.02$
Na:F ratio	LG30 + NaF v LG30	$P = < 0.02$
pH	LG30 + NaF v LG30	$P = < 0.05$
pH	LG30 + NaF v AH2/MP4	$P = > 0.05$

Statistical analysis was carried out using a two-tailed *t*-test on data logarithmically transformed to reduce any possible effects of distribution non-normality. The *P* values obtained are presented in Table 1.

4. Discussion

The addition of NaF to the LG30-based cement makes the cement susceptible to surface attack when immersed in dilute NaF solution. This effect, which is clearly shown in electron micrographs and surface roughness results, shows the cement now behaves like LG26 and quite

unlike LG30 without NaF addition. The level of fluoride addition was calculated to be about that released by the dissolution of LG26 glass in neutralising the acid components of the cement. It should be noted that LG30 takes up a similar level of fluoride when immersed in KF solution to that added in this study and yet does not exhibit surface attack [3,10]. The results found in this study do not enable a full explanation to be provided for the mechanism by which dilute alkali metal fluoride causes disintegration of the polyacid matrix on the GIC surface. For simple GICs, there are two major inter-chain crosslinks postulated in the literature [11] involving either Ca or Al cations. The F ion may act to cause either crosslink to break resulting in the dissolution of matrix. Examination of the literature provides strong indications that the Al-based crosslink is the more crucial to the hydrolytic stability of these cements. Smith reviewed the bonding of alkali earth metal cations with polyacrylic acid and concluded that Ca forms a strongly ionic bond to the carboxyl groups of polyacid which is relatively easily disassociated [12]. Cements based on calcium borosilicate glasses are hydrolytically unstable compared to those based on aluminoborate glasses [13] which are very resistant to water [14]. Wasson and Nicholson [15] examined the infra-red spectra of model cements made from G338 glass and 40% acetic acid in D_2O and found that '... aluminium acetate is identifiable 70 min after

mixing; there is no evidence of calcium acetate however'. Maeda et al. [16] used SIMS to examine a model GIC. They found that, 'In the samples used in this experiment, it was unlikely that Ca^{2+} had almost the same effect as Al^{3+} on the setting process, even though the amounts contained in the glass were as great as the levels of Al^{3+} '. In contrast, they conclude, 'the findings of this experiment indicate that Al plays an essential role in the setting of the matrix ...'. It is therefore necessary to find an explanation of the action of NaF solution on the Al-based crosslinks in the matrix of GICs which contain F from the glass or by addition of NaF powder but not on those where F is absent. Al-based crosslinks are very unlikely, from steric considerations, to have all three ionic valencies satisfied by carboxyl groups so the third valency is likely to be with either F^- (in GICs containing F), SiO_3^{2-} , PO_4^{3-} , or OH^- . In GICs that are based on F-containing glasses or, as in this study, have an F compound added to the cement prior to the start of the setting reaction, the F ion is a very likely candidate to satisfy this valency. It is a small ion and strongly charged; OH^- is not present in appreciable quantities in a setting GIC as studies on internal pH show [17]. In these cements which could have AlF_2^+ reacted with the polyacid such cross-links may be vulnerable to high F^- concentrations and form AlF_2^+ , which would only bond one carboxyl group, or AlF_3 . In either case the one or two carboxyl groups freed could react with the Na of the NaF immersion solution; in both cases the only hydrolytically stable crosslink would be broken.

The size of the effect of LG30 + NaF on the pH of the NaF solution is similar to those shown by AH2 and MP4, which contain Na in the glass, and larger than that of LG30 and LG26 which do not. It should be noted that the solution pH found is very close to neutral (pH 7) when 0.2% NaF solutions are used as contrasted to the pH levels of 9–10 reported by Billington et al. [2] when 2% NaF was employed. Additionally, the extent of pH change does not correlate with the roughness change observed; LG30 and LG26 both exhibit only ~ 0.4 of a pH unit increase yet LG26 exhibits considerable surface roughening which MP4 (with a much greater pH change) does not. Thus, the addition of NaF to LG30 causes the cement produced to act like cements with F-containing glasses in respect of susceptibility to surface attack by NaF solution and like cements with Na-containing glasses in respect of pH changes induced. In uptake LG30 + NaF behaves differently to cements in which the glass contains either F or Na + F. The modified cement takes up much less of Na and F than LG30 whereas LG26 takes up ~ 1.5 times more and AH2, which contains both Na and F in the glass, takes ~ 3 times as much. Not only is the uptake reduced considerably compared to LG30, but also the Na:F ratio is significantly different. For LG30 this is 1.26:1 compared to 0.29:1 for LG30 + NaF. The cements based on

LG26, MP4 and AH2 all have Na:F ratios very close to unity. In respect of uptake, NaF addition does not demonstrate effects similar to those found when Na or F are components of glass.

5. Conclusions

This study shows that the presence of fluoride in a GIC from NaF addition renders the cement vulnerable to surface disruption when immersed in dilute NaF solution. Since this effect is similar to that found where fluoride is intrinsically present (as fluorine in the glass) it can be concluded that it is not necessary to postulate fluoride complexes produced in the dissolution of the glass to account for this vulnerability. Whereas intrinsic fluoride increases F^- uptake compared to F-free GIC, admixed fluoride reduces F^- uptake, from which it can be concluded that there is no causal correlation between amount of F^- uptake and level of surface disruption produced.

The Na added as NaF produces a greater pH change in the NaF immersion solution compared to that produced by Na-free GIC, exactly comparable to GICs with intrinsic Na. This adds confirmation to previous findings that pH is not a causative factor in surface disruption but correlates with presence of Na in the cement.

The level of Na^+ uptake is even more markedly reduced than F^- uptake compared to the GIC without NaF addition. This contrasts with higher Na^+ uptake by GICs where F or Na + F are intrinsically present. Thus, the Na:F uptake ratio differs markedly from unity. This is not observed for the GICs where F or Na + F are intrinsically present. From this it can be concluded that differing levels of F^- and Na^+ uptake do not produce unexpected changes in solution pH i.e. F^-/OH^- interchange is not an important mechanism even when anion and cation uptake balance is not maintained.

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