Title: A Long Term Study on the Setting Reaction of Glass Ionomer Cements by ^{27}Al MAS-NMR spectroscopy

Norhazlin Zainuddin[1,2], Natalia Karpukhina[1,2], Robert G. Hill[1*]

and Robert V. Law[2],

[1]*Department of Materials, Imperial College, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK*
[2]*Department of Chemistry, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK*

Short title: Setting reaction of cements by MAS-NMR

Corresponding Author:

1) Robert G Hill, Department of Materials, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK. Phone: +2075946783 Fax: +2075946757 . Email : r.hill@imperial.ac.uk

Abstract

Objectives. The main objective is the characterization of the setting reaction in glass ionomer cements (GICs) based on experimental glasses using the ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy in order to understand the crosslinking process during the setting reaction.

Methods. Three types of GICs which are based on fluoro-alumino-silicate glasses (LG125, ART10, and LG26Sr) were studied using ^{27}Al MAS-NMR to monitor the setting reaction of the cements.

Results. The result showed clearly the formation of six coordinate, aluminium Al(VI), that crosslink the carboxyl groups in the PAA. The deconvolution study was performed to quantify the amount of each Al species in the cements. The finding showed that composition of original glass has a substantial effect on the setting behavior of the cements.

Significance. Our data demonstrate that the setting reaction of GICs can be followed by ^{27}Al MAS-NMR spectroscopy discovering the conversion of Al(IV) to Al(VI). Considerable amount of the five coordinate aluminium, Al(V), species was found in the cements aged up to one year. The presence of phosphorus has a strong influence on the setting reaction. The formation of Al-O-P species was postulated to be present in the cement.

Keywords

Glass polyalkenoate cement, Glass ionomer cement, ^{27}Al MAS-NMR spectroscopy, Dental materials, Biomaterials

Introduction

GICs which are also known as glass polyalkenoate cements (GPCs), were first reported by Wilson and Kent in late 60s [1]. The major application of these cements is for dental restoration. They are used as adhesives, as fissure sealants and as tooth filling materials. These cements have excellent translucency and the ability to chemically bond to the mineral phase of dental tissues. Over the last ten years they have also been developed for medical applications [2] and are now commercially available as a bone cement and as a pre-set cancellous bone substitute. They are the adhesive of choice for cementing cochlear implants [3].

GICs are formed by the acid-base reaction of an ion leachable fluoro-alumino-silicate glass with an aqueous solution of poly(acrylic acid) (PAA). The presence of fluoride in the glass composition is clinically beneficial, because this fluoride ion is released and readily exchanged for the hydroxyl ion of hydroxyapatite imparting resistance to caries [4].

Although the setting reactions in the GICs have been extensively studied, the setting process is not yet fully understood. There is considerable debate and controversy over various aspects of the setting reaction, including whether the setting reaction continues with time and how both the silica gel phase and polysalt phase affect the long term mechanical properties [5-7].

Various techniques such as pH studies [8], ^{13}C MAS-NMR [9], Fourier transform infra red spectroscopy (FTIR) [10] and Raman [11] spectroscopy have been used to characterize the setting reaction of the cements. However, FTIR [10] spectroscopy is only suitable for semi-quantitative analysis, since the loss of the carbonyl group absorption band from a carboxylic acid (-COOH) during the neutralization can be masked by the asymmetric COO$^-$ salt band. Another problem with the FTIR is the overlap of the absorption bands of the polycarboxylic acid with the strong absorption bands of water. It is also known that the baseline can often hinder the reproducibility of the FTIR spectrum. In contrast, Raman [11] and ^{13}C NMR [9] spectroscopies only concentrate on the neutralization of COOH group in the polycarboxylic acid during the setting process.

Recently, MAS-NMR spectroscopy has been used to study the structure of the glasses used to form GICs [12] and the setting reaction of the GICs [13]. The advantages of this technique are it can probe the structure of the amorphous glasses and give information on the local environment of selected species and their next nearest neighbors. Studies by Matsuya et al. and Pires et al. [7, 13] have shown that the Al switches its coordination number from four, Al(IV), in the glass to six coordinate, Al(VI), in the cement matrix.

Previous studies have largely been based on commercially available cements, where the composition and any pre-treatments (e.g. acid washing) of the glass and the formulation of the cement are not known. In the present study we use

experimental glasses of known composition previously synthesised in our laboratory and has been characterized by MAS-NMR [14]. Knowing the glass composition and the proportions of glass and polyacid enables acid-base calculations to be performed.

The main aim of the present paper is to characterise the setting reaction in GICs based on experimental glasses using the ^{27}Al MAS-NMR spectroscopy in order to understand the crosslinking process during the setting reaction.

Materials and Methods

Preparation of glasses

Three types of glasses with strontium substituting the calcium were chosen for this study. The glasses were selected from a large number of glasses that had already been characterised extensively by MAS-NMR previously [14]. The compositions of the glasses are given in Table 1. The glasses were prepared by melting the reagents in a platinum crucible at high temperature for 2 hours. The synthesis of the glasses has been described previously [14].

Table 1.

Synthesis of glass ionomer cements

GICs were synthesised by thoroughly mixing the glass powder with PAA and water. The weight ratio of glass powder to PAA powder was normalized to the LG26Sr glass to account for the differences in atomic weight of Sr and Ca and the basicity of the glass in the case of the ART10 glass. The ratios of glass to PAA used were respectively 1.86, 2.00 and 1.41 for LG125, LG26Sr and ART10. The powder to distilled water ratio was fixed at 3:1. To terminate the setting reaction for cement aging times less than 1 hour, these were quenched into liquid nitrogen and then dehydrated with ethanol after they had been mixed. For cements aging times greater than a 1 hour they were placed at $37^{o}C$ and

were immersed and stored in water prior to termination of the reaction by the above method. This was done to prevent dehydration at longer aging times.

MAS-NMR measurements

The sample powders were packed in 4 mm zirconia rotor and sealed with a Kel-F end cap. ^{27}Al MAS-NMR spectroscopy measurements were conducted at a resonance frequency of 156.3 MHz using a higher magnetic field (14.1 T) on a Bruker FT-NMR 600. The delay time was 1.0s and spinning rate of 10 kHz. The spectra were referenced to the octahedral site of yttrium aluminium garnet (YAG).

The deconvolution of the overlapped peaks was conducted using Bruker 1D WIN-NMR software. This was carried out using Gaussian peaks and the fitting error for the peak areas was ±15%.

Results

Figure 1a shows the ^{27}Al MAS-NMR spectra for the cements based on ART10 with low phosphorus content at various ageing times together with the original glass. The original glass has a peak at 58.9 ppm assigned to Al(IV) and a shoulder at 45.6 ppm. The Al(IV) site is a tetrahedral coordinated aluminium and the shoulder is assigned to pentahedral aluminium – both in the glass network [15]. There is also a small peak at 2 ppm which is from Al(VI). The cement spectra all show peaks corresponding to Al(IV) at 54-56 ppm and a peak at -2 ppm with increasing intensity which is the Al(VI) site. From the deconvolution, a shoulder between these two peaks is assigned to Al(V) at around 30-34 ppm.

Figure 1(a, b, c).

The original glass and the cements spectra of the LG125 which are based on a mixed Ca/Sr glass and LG26Sr (Sr replacing Ca completely) are shown in Figure 1b and Figure 1c. The composition of the base glasses are given in Table 1. They show trends similar to the ART10 cement, where there are two significant peaks at 50-55 ppm and 2-4 ppm, due to Al(IV) and Al(VI) sites, and a shoulder at ca. 30 ppm. The Al(IV) peaks are found in the glass and in the cement at a slightly lower chemical shift due to the higher phosphate content of the glass and the increased prevalence of Al-O-P bonds. There is also a small

peak at 13-16 ppm presents for all cements which we assign as unidentified new species.

Figure 2(a, b).

A deconvolution study was carried out to fit the peak areas from the MAS-NMR spectrum, as well as to estimate the line width and integrate the peak areas in order to quantify the proportion of each type of Al species present. In this fitting process it must be noted that Al has a 5/2 spin number as it posses an electric quadrupole moment. This means that MAS is only effective for eliminating the first order term, but not the second order quadrupolar contribution, resulting in a quadrupolar line broadening effect. This manifests itself as an asymmetric "tail" on the peaks which can lead to difficulties for exact quantification of peak areas. To simplify the fitting in the present work it was done without taking into account the second order quadrupole line broadening.

For all glasses and cements, the shoulder between the Al(IV) and Al(VI) is assigned to Al(V) site and it remains in the cement even after 1 year ageing time. The integration of each peak is directly proportional to the amount of that specific Al species in the cement, hence, we can follow the conversion of the Al(IV) to Al(VI) during the setting process. Figure 2a and 2b show the examples of the deconvolution of spectra for LG125 glass and LG125 cement with ageing time 1 year.

Discussion

The formation of GIC involves the acid-base reaction of PAA and the glass particle, and ions locked up in the glass network, primarily Al, Ca and F are released [16]. It is thought that the dissolution process [17] of the aluminosilicate glasses involves two processes. Firstly, the ion exchange of these ions (Ca and Sr ions) with protons from PAA. Secondly, these ions along with Al and F ions are also released from the glass dissolution process. Both migrate to the aqueous phase of the cement and the cations ionically crosslink with the carboxyl groups of the PAA. In the glass structure, Al ions exist in predominantly four coordination state to accommodate the tetrahedral silicate network of the glass. However, during the formation of GICs and the release of Al from the glass into the aqueous phase, the coordination number for Al ions increases to six, where six ligands must be attached to the Al^{3+} cation [21]. The MAS-NMR spectroscopy can probe the coordination of an atom and hence, can be used to follow the conversion of Al(IV) to Al(VI) during the setting process.

The chemical shifts obtained from the peak fitting are constant, with the exception of the ART10 glass which shows a significant shift towards zero ppm in the chemical shift of the Al(IV) species particularly during the earliest stages of cement formation. In the glass network the Al^{3+} species can be locally charge compensated by P^{5+} species which mitigates the need for the Al to require a local charge balancing ion (e.g. Gp I or Gp II cation). This makes the Si-O-Al-O-P moiety far less susceptible to acid hydrolysis. This is because there is little or

no possibility for ion exchange of the charge balancing cations with a proton followed by subsequent acid hydrolysis of the Si-O-Al bond [18].

All the cements spectra (Figure 1a, 1b, 1c) show clearly the conversion of Al(IV) to Al(VI) as the setting reaction proceeds. The intensity of A(IV) peak decreases with setting time and the Al(VI) peak becomes more pronounced. From the deconvolution study, the amount of Al(IV) for ART10 declined from 56% to 26%, and for LG125 and LG26Sr it decreased from 50% to 24% and 48% to 26%, respectively. The amount of Al(V) species for ART10, LG125 and LG26Sr cements decreased respectively from 21% to 10%, from 50% to 24% and from 34% to 18%. The reduction in the proportion of Al(V) with time closely follows the reduction in the proportion of Al(IV) which indicates that the intensity of the Al(V) peak is partially due to residual quadrupolar line broadening of the Al(IV) site.

The previous studies [13, 19] showed that the Al(V) peak disappeared after a certain ageing time, but from our data this species is still present in all the cements after 1 year. The reason why the Al(V) remains in the cements may be due to the presence of the relatively high phosphate content of these glass. Also the absolute amount of Al(V) may be overestimated due to the contribution from the quadrupolar line broadening arising from the Al(IV) sites as mentioned above. In addition, most of previous studies [13, 19] have been carried out using lower magnetic field strengths of 4.7 T and 9.4 T, which exacerbates the quadrupolar line broadening, resulting in even more poorly resolved spectra and

a greater asymmetric tail from the Al(IV) peak where the peak of Al(V) might be expected. Whereas, our studies are carried out at higher field (14.1 T) which greatly mitigates the quadrupolar broadening effect. Our observations of high coordinated aluminium species in original glasses are in good agreement with the study by Stebbins et al [20]. They reported that the Al(V) and Al(VI) species still exist in the aluminosilicate glasses as measured at higher magnetic field.

The setting reaction can be followed from the deconvolution of the spectra and determining the ratio of Al(VI) to Al(IV). Since we assume that there are overlapping resonances of Al(V) and quadrupolar effect from Al(IV), we also calculate the ratio of Al(VI): Al(IV)+Al(V). Figure 3 shows a graph of Al(VI) : Al(IV)+Al(V) against log time. The setting of ART10 and LG26Sr cements continue up to 1 year. However, for LG125 cements, which are based on mixed Ca/Sr glass, the setting reaction in term of the conversion of Al(IV) to Al(VI) is completed after 1 day. The difference in the setting process of these cements results from the differences in the glass compositions that we used in this experiment. Thus, a composition of the glass has strong influence on the setting behavior in the cement formation.

Figure 3

Furthermore, we have also calculated the ratio of Al(VI) to Al(IV) from the glass composition that we used in the cement formation. By assuming a simple acid

base reaction between the glass and the PAA with no preferential release of Al^{3+} relative to Ca^{2+} and complete neutralization. For the simplification of the acid-base calculation, it was assumed that there was no five- or six-coordinated Al present in the glass. From the calculation, the ratio of Al(VI) to Al(IV) is 1.59 for all three glasses.

Comparing the results of Al(VI) to Al(IV) ratio from the deconvolution and the calculated ratio of the glasses, we found that the ratio of 1.59 from the glasses matches closely with the ratio of Al(VI): Al(IV)+Al(V). The ratio of Al(VI) to Al(IV)+Al(V) reaches a maximum of about 1.56 for the ART10 cement, and gives 1.12 for LG125 and 1.14 for LG26Sr. This suggests that the intensity assigned as the Al(V) signal is not arisen solely from the residual quadrupolar line broadening of the Al(IV) site but should be attributed to the real intensity of the Al(V) site.

In addition, because the ratio of Al(VI): Al(IV)+Al(V) is lower than the calculated ratio in LG125 and LG26Sr cements, we suggest that the reaction does not go to completion or the Ca^{2+}/Sr^{2+} cations are released preferentially compared to Al^{3+}. This is thought to be due to high phosphorus content in LG125 and LG26Sr creates more stable Al-O-P bonds in the glass. In contrast to the these phosphate rich glasses, the lower phosphate containing glass ART10 would more readily dissolve and tend to favor the release of Al relative to Ca.

It is important to note that the formation of Al(VI) may not correlate exactly with the ionic crosslinking of the cement matrix. Whilst six coordinate Al^{3+} cations are present in the cement matrix it is possible that the types of ligands attached to the Al(VI) change with time. For example the fraction of COO^- ligands attached to it may progressively increase with time. Therefore, we may be able to see changes in the mechanical properties of the cements in the long term although the setting reaction in terms of Al(VI) sites does not change or increase after certain period.

The unknown species at 13-16 ppm which is present at highest concentration at the 2 minutes cements (ART10 and LG26Sr glasses based) and then decreases with time maybe an Al(V) reaction intermediate. This will be a subject of further study in a future.

The obtained results showed that the setting reaction of the cements depends on the glass composition. However, more information on other nuclei such as ^{19}F, ^{29}Si, ^{31}P and ^{13}C using the MAS-NMR in the cements is needed to fully understand the setting reactions. The present study is now being extended to other nuclei present in the cements in order to understand the whole setting process. In addition higher field MAS-NMR spectra would be advantageous to mitigate any contribution to quadrupolar line broadening. Further studies at higher magnetic field (18.8 T) are underway.

Conclusions

^{27}Al MAS-NMR spectra of the GICs showed two peaks of Al(IV) and Al(VI) and a shoulder between these peaks is an Al(V) species. The setting reaction can be followed by deconvolution of the ^{27}Al MAS-NMR spectra. The proportion of Al(VI) increases with setting time which means the formation of octahedral Al ions which crosslink the carboxyl groups of PAA increases. This study also found that a glass composition has a particular influence on the setting reaction: each original glass composition influences different setting behaviour in the forming cement. The role of phosphorus is also important to the setting reaction since Al-O-P bonds present in the glass alter the rate of glass dissolution and ion release. The high phosphate content of glass is thought to be the reason why the Al(V) species still exists in 1 year cement. Further study is required on the nuclei present in the cement by using the MAS-NMR to understand the structural role of each atom in the setting reaction.

Acknowledgements

References

1. Wilson A.D., McLean J., Glass-Ionomer Cement. Quintessence Publishing Co., 1988.

2. Jonck L.M., Grobbelaar C.J., Strating H., The biocompatibility of glass-ionomer cement in joint replacement: Bulk testing. Clinical Materials, 1989; 4: 85-107.

3. Geyer G., Helms J., Ionomer-based bone substitute in otologic surgery. European Archives of Oto-Rhino-Laryngology, 1993; 250: 253-256.

4. Forss H., Prevention of enamel demineralization adjacent to glass ionomer filling materials. Scandinavian journal of dental research, 1990; 98: 173-178.

5. Williams J.A., Billington R.W., Changes in compressive strength of glass ionomer restorative materials with respect to time periods of 24 h to 4 months. Journal of Oral Rehabilitation, 1991; 18: 163-168.

6. Crisp S., Pringuer M.A., Wardlewo.D, Wilson A.D., Reactions in Glass Ionomer Cements .2. Infrared Spectroscopic Study. Journal of Dental Research, 1974; 53: 1414-1419.

7. Matsuya S., Maeda T., Ohta M., IR and NMR analyses of hardening and maturation of glass-ionomer cement. Journal of Dental Research, 1996; 75:1920-1927.

8. Wasson E.A., Nicholson J.W., Change in Ph During Setting of Polyelectrolyte Dental Cements. Journal of Dentistry, 1993; 21: 122-126.

9. Prosser H.J., Richards C.P., Wilson A.D., NMR-Spectroscopy of Dental Materials .2. The Role of Tartaric Acid in Glass-Ionomer Cements. Journal of Biomedical Materials Research, 1982; 16: 431-445.

10. Nicholson J.W., Brookman P.J., Lacy O.M., Wilson A.D., Fourier transform infrared spectroscopic study of the role of tartaric acid in glass-ionomer dental cements. J Dent Res, 1988; 67:1451-1454.

11. Young A.M., Sherpa A., Pearson G., Schottlander B., Waters D.N., Use of Raman spectroscopy in the characterisation of the acid-base reaction in glass-ionomer cements. Biomaterials, 2000; 21: 1971-1979.

12. Stamboulis A., Law R.V., Hill R.G., Characterisation of commercial ionomer glasses using magic angle nuclear magnetic resonance (MAS-NMR). Biomaterials, 2004; 25: 3907-3913.

13. Pires R., Nunes T.G., Abrahams I., Hawkes G.E., Morais C.M., Fernandez C., Stray-field imaging and multinuclear magnetic resonance spectroscopy studies on the setting of a commercial glass-ionomer cement. Journal of Materials Science-Materials in Medicine, 2004; 15: 201-208.

14. Hill R.G., Stamboulis A., Law R.V., Characterisation of fluorine containing glasses by F-19, Al-27, Si-29 and P-31 MAS-NMR spectroscopy. Journal of Dentistry, 2006; 34: 525-532.

15. MacKenzie K.J.D., Smith M.E., Multinuclear solid-state NMR of inorganic materials. Pergamon, 2002.

16. Nicholson J.W., Chemistry of glass-ionomer cements: a review. Biomaterials, 1998; 19: 485-494.

17. Oelkers E.H., Schott J., Devidal J.-L., The effect of aluminum, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. Geochimica et Cosmochimica Acta, 1994; 58: 2011-2024.

18. Griffin S.G., Hill R.G., Influence of glass composition on the properties of glass polyalkenoate cements. Part II: influence of phosphate content. Biomaterials, 2000; 21: 399-403.

19. Stamboulis A., Matsuya S., Hill R.G. *et al.*, MAS-NMR spectroscopy studies in the setting reaction of glass ionomer cements. Journal of Dentistry, 2006; 34: 574-581.

20. Stebbins J.F., Kroeker S., Lee S.K., Kiczenski T.J., Quantification of five- and six-coordinated aluminum ions in aluminosilicate and fluoride-containing glasses by high-field, high-resolution Al-27 NMR. Journal of Non-Crystalline Solids, 2000; 275: 1-6.

21. Criscenti, L. J., Brantley, S. L., Mueller, K. T., Tsomaia, N., Kubicki, J. D. Theoretical and 27Al CPMAS NMR investigation of aluminum coordination changes during aluminosilicate dissolution. Geochimica et Cosmochimica Acta, 2005; 69: 2205–2220.

List of Table

Table 1.

The composition of all glasses studied in mole %.

List of Figure

Figure 1(a, b, c).
Caption. ^{27}Al MAS-NMR spectra of GICs based on a) ART10, b) LG125 and c) LG26Sr at different ageing time. Peak at around 50 ppm is Al(IV) and 0 ppm is Al(VI). The intensity of Al(VI) peak increases with setting reaction.

Figure 2 (a,b).
Caption. Experimental and simulated ^{27}Al MAS-NMR spectra of a) LG125 cement at 1 year ageing time and b) LG125 glass. Peak at ca. 50 ppm is assigned as Al(IV) and -2 ppm is Al(VI). The shoulder between these peak at around 30 ppm is assigned as Al(V) and/or line broadening quadrupolar effect of Al(IV)
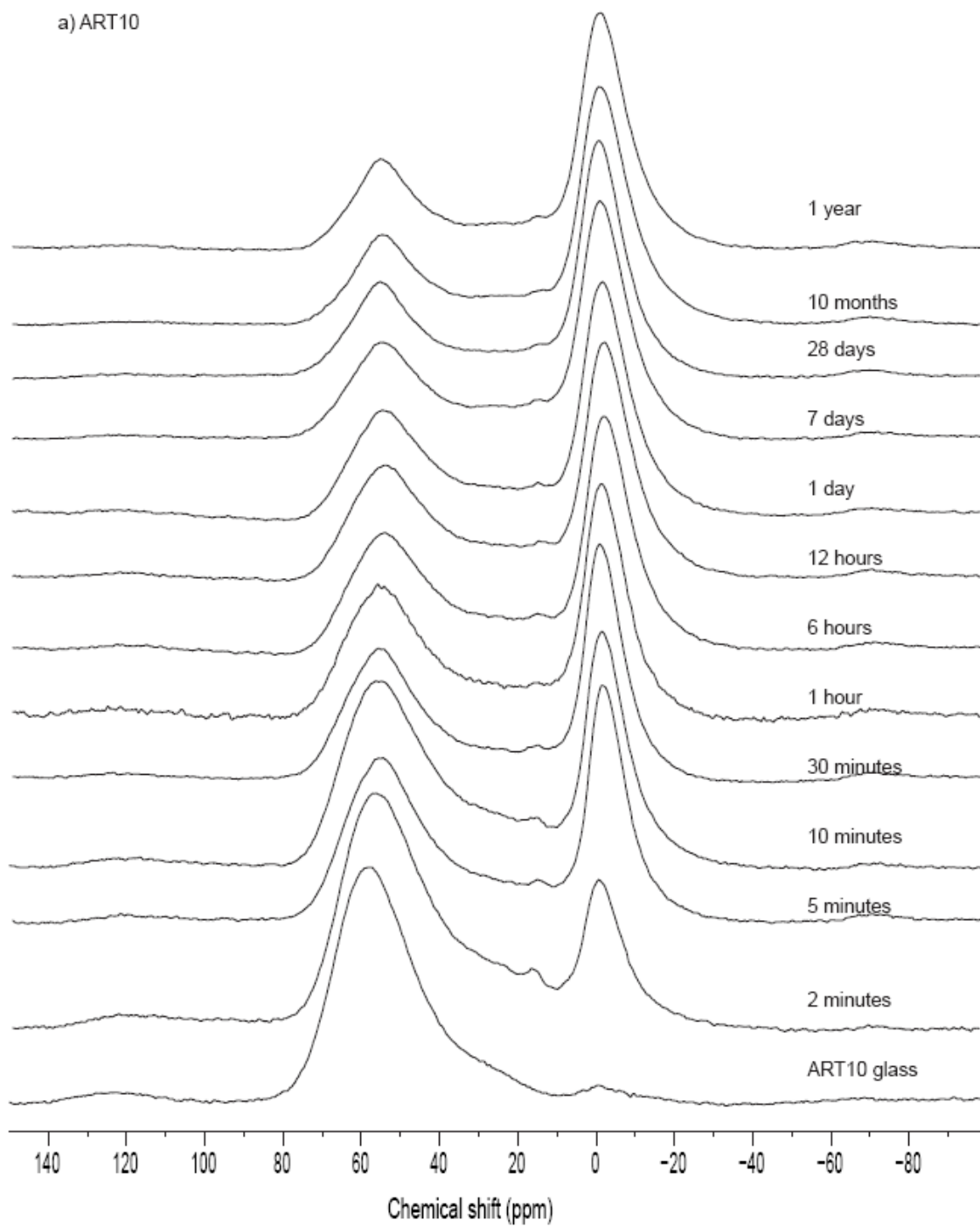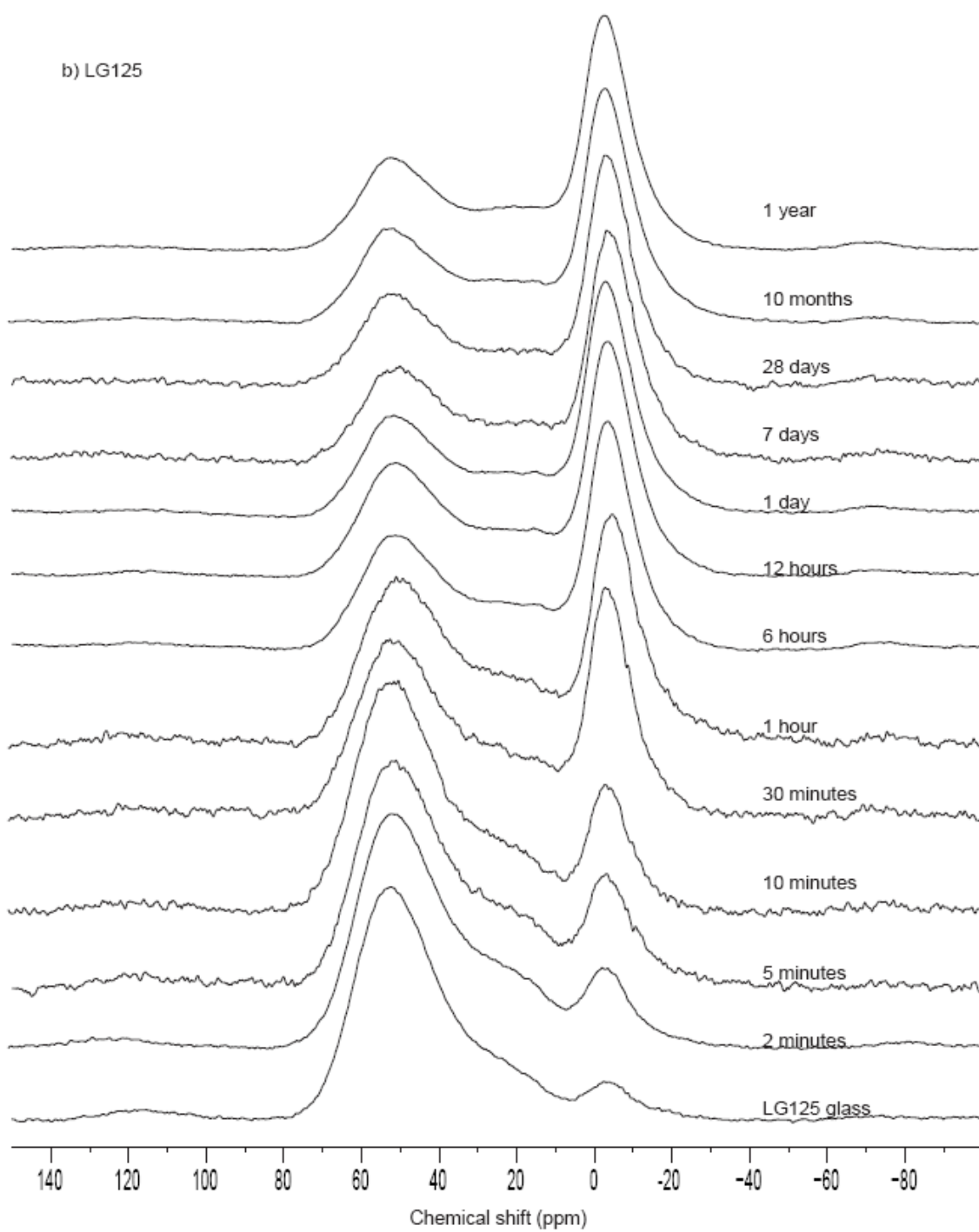
Figure 3.
Caption. Ratio of Al(VI):Al(IV)+Al(V) plotted against log time for (◊) LG26Sr, (■) LG125 and (∆) ART10 cements. The setting reaction for ART10 and LG26Sr continues up to 1 year, whereas for LG125 completes after 1 day. Lines are guide to the eye.
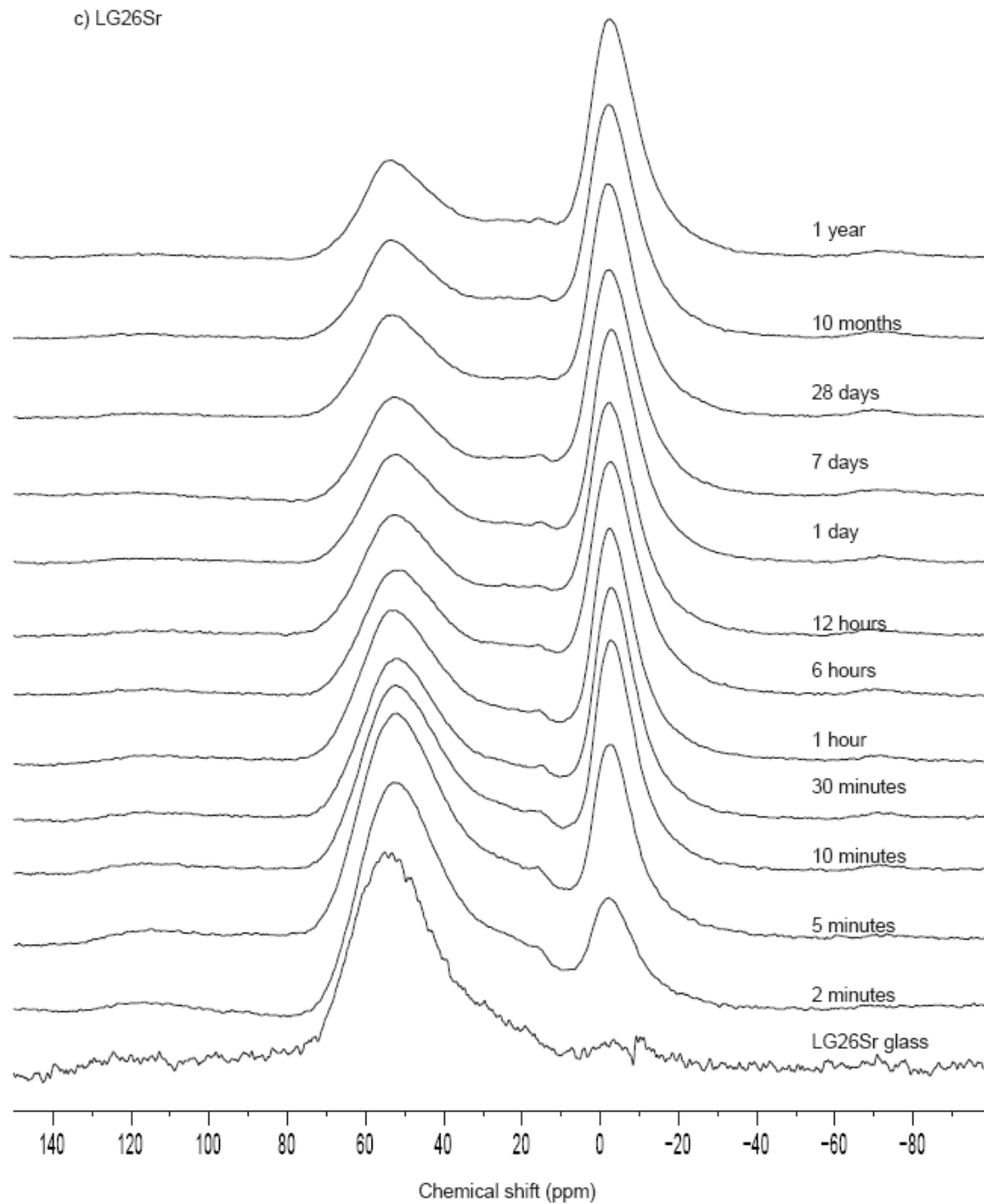
Table 1

Glass (mole %)	SiO_2	Al_2O_3	P_2O_5	CaF_2	SrO	SrF_2
LG125	32.1	21.4	10.7	14.3	21.4	-
LG26Sr	32.1	21.4	10.7	-	21.4	14.3
ART10	34.0	22.6	5.7	-	22.6	15.1

a) ART10

1 year

10 months

28 days

7 days

1 day

12 hours

6 hours

1 hour

30 minutes

10 minutes

5 minutes

2 minutes

ART10 glass

140   120   100   80   60   40   20   0   -20   -40   -60   -80

Chemical shift (ppm)

b) LG125

1 year

10 months

28 days

7 days

1 day

12 hours

6 hours

1 hour

30 minutes

10 minutes

5 minutes

2 minutes

LG125 glass

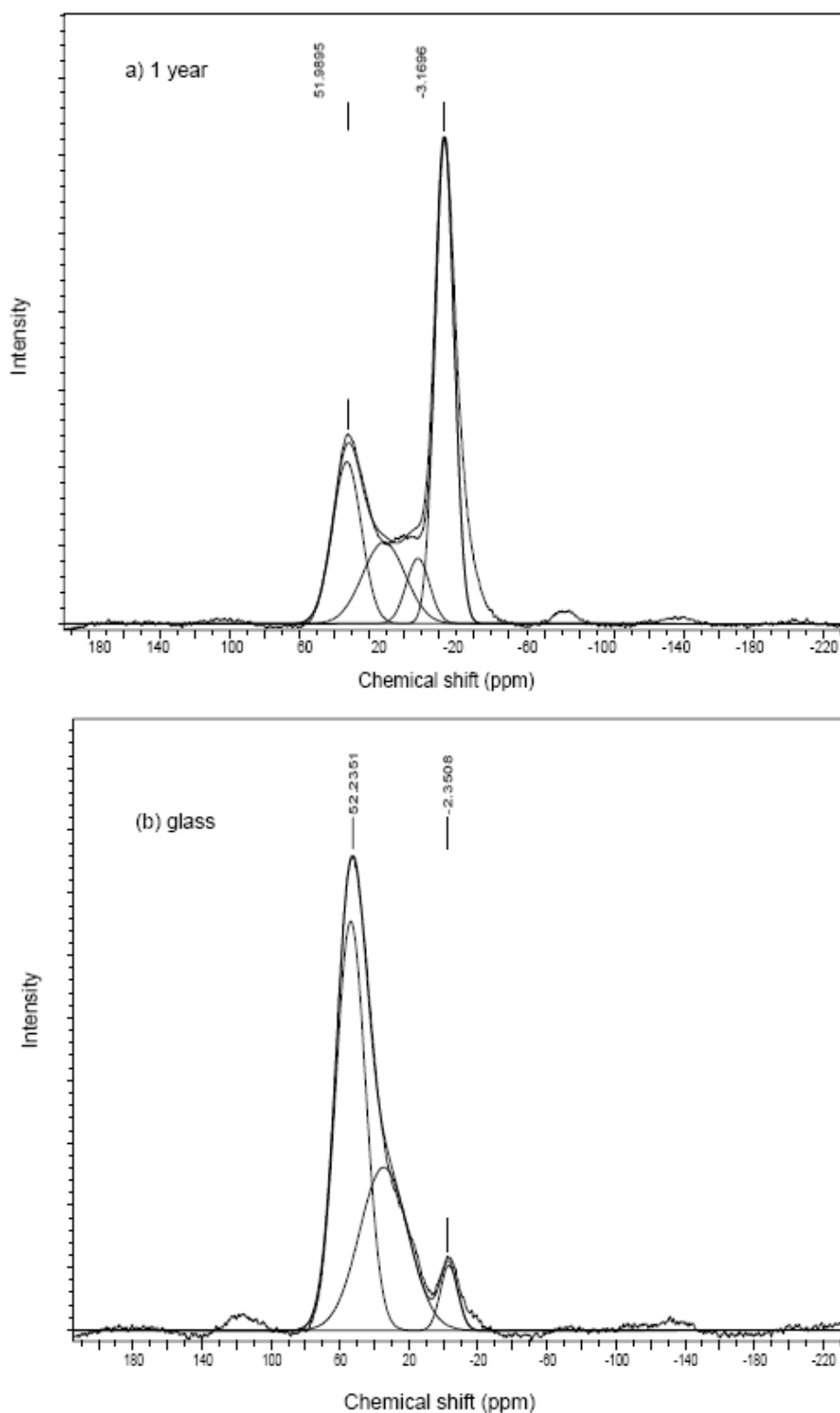140   120   100   80   60   40   20   0   -20   -40   -60   -80

Chemical shift (ppm)

Figure 1 (a, b, c). ^{27}Al MAS-NMR spectra of GICs based on a) ART10, b) LG125 and c) LG26Sr at different ageing time. Peak at around 50 ppm is Al(IV) and 0 ppm is Al(VI). The intensity of Al(VI) peak increases with setting reaction.

Figure 2 (a, b). Experimental and simulated ^{27}Al MAS-NMR spectra of a) LG125 cement at 1 year ageing time and b) LG125 glass. Peak at ca. 50 ppm is assigned as Al(IV) and -2 ppm is Al(VI). The shoulder between these peak at around 30 ppm is assigned as Al(V) and/or line broadening quadrupolar effect of Al(IV).
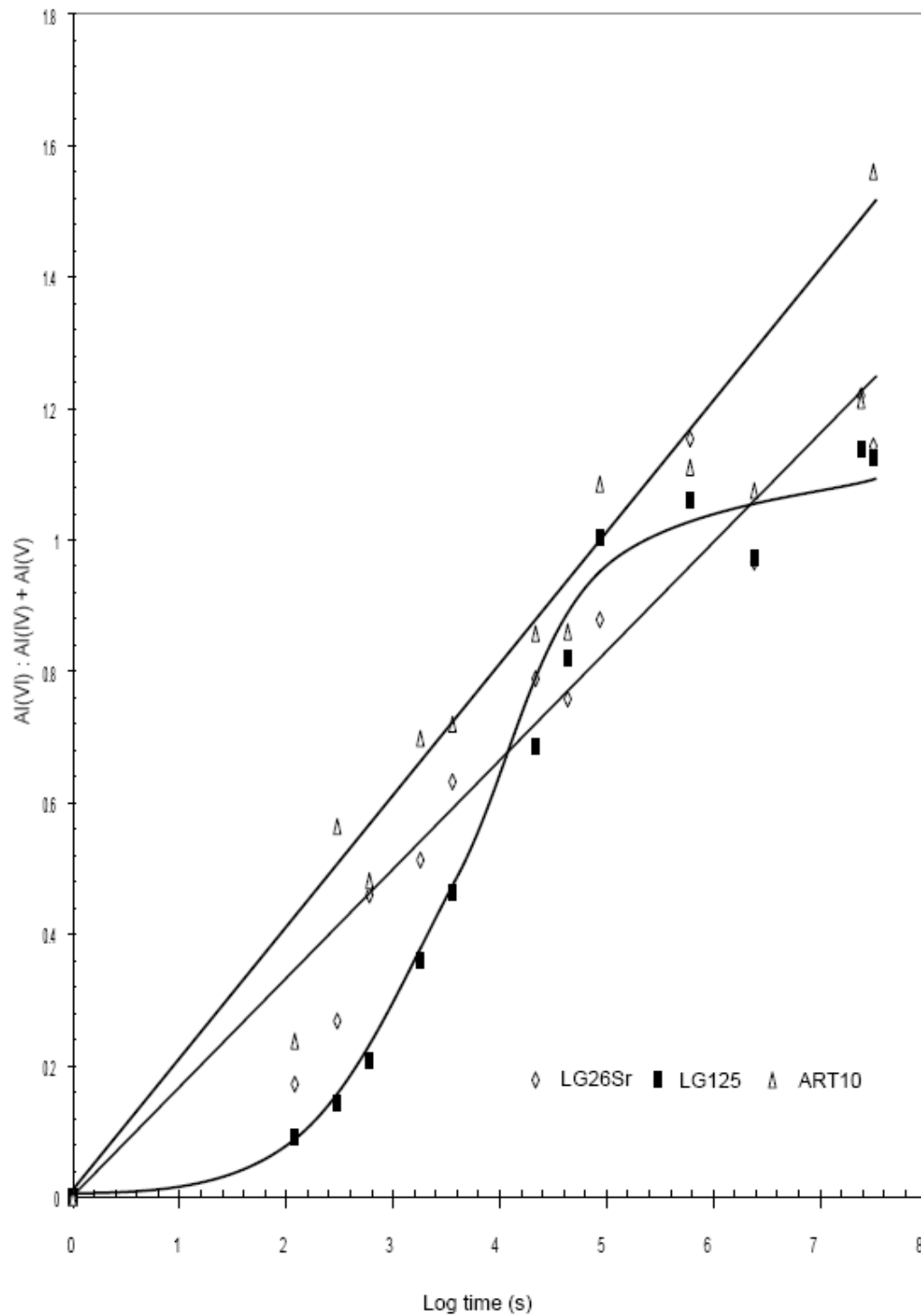
Figure 3. Ratio of Al(VI):Al(IV)+Al(V) plotted against log time for (◊) LG26Sr, (■) LG125 and (Δ) ART10 cements. The setting reaction for ART10 and LG26Sr continues up to 1 year, whereas for LG125 completes after 1 day. Lines are guide to the eye.