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SOLID STATE ^{29}Si AND ^{27}Al NMR AND FTIR STUDY OF CEMENT PASTES CONTAINING INDUSTRIAL WASTES AND ORGANICS

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ABSTRACT

^{29}Si and ^{27}Al NMR and FTIR have been used to study the products of OPC hydration in the presence of a heavy metal containing stabilized waste which is commercially solidified, selected organics and pulverised fuel ash. ^{29}Si NMR unambiguously quantifies the extent of silicate polymerisation, which is severely retarded in mixes containing the stabilized waste. ^{27}Al NMR spectroscopy indicates the presence of both ettringite and monosulfate in a cement containing 2% of the stabilized waste, while only ettringite is detected in the spectra of samples with 19 and 30% additions. Phenol and ethylamine also reduce silicate condensation, although a sample containing both the metal waste and mixed organics showed silicate condensation levels similar to those found in a normal OPC paste. It is difficult to draw firm conclusions from the FTIR results due to band overlap in the region of interest.

Introduction

Cement-based solidification of hazardous wastes in the form of sludges, filtercakes, other residues from waste water treatment systems and contaminated soils, is a widely used technology in the US and is becoming increasingly important in many other parts of the world (1). Either individual waste streams or blended mixed wastes can be solidified, and the waste is generally pretreated in a stabilization process to concentrate the hazardous components into an insoluble residue. Ordinary portland cement (OPC) and a range of other

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pozzolans such as pulverised fuel ash (PFA) have been used to produce solidified materials simply by mixing them into the stabilized waste. The complexity and variability of industrial wastes means that the materials produced are generally poorly characterized. The major requirement is that they retain the hazardous components present in the wastes after subsequent disposal to a landfill, and one of the attractions of using cement as a binding agent is that it is widely used, is relatively cheap and produces materials which are durable under most conditions. This fundamental property relies on the hydration of normal cement producing well defined reaction products. Recent work has demonstrated that when the types of stabilized wastes which are commercially solidified are added to cement, the hydration reactions may be severely retarded (2,3). This is particularly expected to occur at the high ratios of stabilised waste to cement which are used commercially.

In this paper we present Fourier transform infrared (FTIR) and solid state nuclear magnetic resonance (NMR) results as part of our continuing efforts to investigate the effects of real industrial wastes on the main cement phases formed during the solidification process. In particular, the aim of the current work is to gain an increased understanding of factors affecting formation of calcium silicate hydrate (C-S-H), which has a poorly crystalline structure and represents about 60 to 70 vol% of a mature hydrated cement paste.

Vibrational frequencies measured by FTIR can indicate changes in the silicate, sulfate and carbonate phases when hazardous compounds are mixed with the cement paste. In particular, the silicate condensation reaction during cement hydration can be followed by the silicate infrared bands: $\nu_4SiO_4^{4-}$ (out-of-plane Si-O bending); $\nu_3SiO_4^{4-}$ (asymmetric Si-O stretching), and $\nu_2SiO_4^{4-}$ (in-plane Si-O bending). These are typically centered at around 520, 1000 and 450 cm^{-1}, respectively. Some authors have reported FTIR results using cement matrices with individual metal additions (4-7). Lead has been associated with increased silicate condensation, while zinc has been shown to have the opposite effect. Some water-soluble organic species (ethylene glycol, phenol, p-bromophenol and p-chlorophenol) are reported to promote silicate polymerization in solidified samples cured for 56 days (8). Correlations have been suggested between the functional group of the organic compound and the effect on cement hydration (9).

The technique of magic-angle spinning (MAS), in which the sample is rotated rapidly at precisely 54.74° to the direction of the magnetic field, is now routine in recording high-resolution solid state NMR spectra (10). In particular, ^{29}Si MAS NMR spectroscopy has proved to be extremely useful in the structural characterization of silicates (11,12). Spectra are normally interpreted in terms of the different silicon Q^n environments, where n denotes the number of bridging oxygens for each Q (SiO_4) unit. There have been a number of studies using ^{29}Si NMR to investigate the hydration of pure C_3S and β-C_2S phases, and also of typical ordinary Portland cements (13-16). In hydrated cements these show the presence of Q^0 units due to orthosilicate groups, Q^1 units from Si-O-$\underline{Si}O_3$ groups in dimers or terminating polymers, and Q^2 units from Si-O-$\underline{Si}$-O-Si groups in trimers and higher polymers. Under appropriate conditions, ^{29}Si NMR spectra are quantitative which allows the relative concentrations of these groups to be obtained reliably.

^{27}Al MAS NMR spectroscopy is widely used to characterize aluminate phases. Unlike the case of ^{29}Si, ^{27}Al is a quadrupolar nucleus (spin $I={}^5/_2$) which means that ^{27}Al is additionally affected by electric field gradients within the sample due to the quadrupole interaction. This can pose difficulties in spectral interpretation, but 4-coordinate and

6-coordinate aluminium can readily be distinguished (10). Identification of distinct phases containing, say, 4-coordinate aluminium can still be made by ^{27}Al MAS NMR providing that the quadrupole coupling parameters of the ^{27}Al site are known (17,18).

While there have been a number of studies on the effects of model waste compounds on cement hydration, the effect of real industrial stabilized wastes of the types which are commercially treated have not yet been studied in detail by NMR (4,8).

Experimental

The samples in this study were prepared from OPC (ordinary Portland cement, Blue Circle Ltd.), PFA (pulverized fuel ash) and a stabilised filter cake which is commercially produced as an intermediate at a stabilization/solidification plant by blending wastes which originate from a wide range of different industries. The filter cake was oven dried at 105°C for 24 hours and ground to a particle size of less than 150μm prior to forming solidified wastes. The composition of the dried stabilized waste is summarized in Table 1.

TABLE 1
Composition of Metal Waste (concentrations in mg.l^{-1} except total organic carbon, TOC)

Zn	5,770	Total PO_4	152,000
Fe	1,630	Carbonate	81,900
Ca	557	Cl	48,000
Cr	278	Total CN	39,300
Na	132	Soluble SO_3	36,000
Mg	59	NO_3	118
Mn	24	TOC	3.90%
K	18		
Pb, Sr, Al, Ba, Cu, Ni, Ti, Cd		< 10	

In addition the effect of organic species on cement-based solidification was studied using sodium acetate, ethylamine and phenol (all from FSA Laboratory) and tetrachloroethylene (BDH chemicals Ltd.). These particular organic compounds were chosen as they contain a range of different functional groups. Three types of mixtures were prepared:

Type 1 - OPC, deionized water, PFA and stabilised waste at concentrations between 0 and 30 % by weight. The type 1 sample compositions are shown in Table 2. The water-to-solids ratio (w/s) was kept constant except for sample E where more water had to be added to aid mixing.

Type 2 - OPC, water and each organic compound separately with organic concentrations of 0.5, 5 and 10 % (by weight). The w/s ratio was maintained at 0.5.

Type 3 - OPC (18 %), water (44.5 %), PFA (18 %), the stabilised waste (19 %) and the four organic compounds mixed in equal proportions to give a total of 0.5 % by weight. This type of mixture has a composition which was meant to simulate a typical organically contaminated industrial waste.

The samples were mixed by hand for three minutes, and cured in sealed vials for 28 days. After this curing time they were ground using a mortar and pestle to a particle size less than 150 μm.

TABLE 2
Composition of Type 1 samples (wt.%)

Sample	Cement (%)	H_2O (%)	Metal waste (%)	PFA (%)	Water/solids (w/s)
Cement Paste	66.7	33.3	-	-	0.5
A	64.6	33.3	2	-	0.5
B	47.7	33.3	19	-	0.5
C	36.6	33.3	30	-	0.5
D	48.7	33.3	-	18	0.5
E	18.0	45.0	19	18	0.8

Infrared spectra were recorded on a Perkin Elmer 1720 XFT spectrometer in the range 4000-400 cm^{-1} on samples pressed into potassium bromide discs.

Solid-state NMR spectra were recorded on a Bruker MSL-300 spectrometer equipped with a 7.0 T magnet in which the resonance frequencies for ^{29}Si and ^{27}Al are 59.63 and 78.21 MHz respectively. High-power proton decoupling was used for both the ^{29}Si and ^{27}Al spectra, and chemical shifts are quoted relative to external tetramethylsilane (TMS) for ^{29}Si, and relative to 1 M aqueous aluminium nitrate solution for ^{27}Al. Typical acquisition parameters for recording the ^{29}Si spectra were 4-4.5 kHz sample spinning speed, 2.5 μs pulse length and a 3 second repetition time between scans. This was shown to give quantitative spectra, probably because the concentration of paramagnetic species in the cement causes fairly short ^{29}Si spin-lattice relaxation times. The ^{27}Al spectra were recorded using 10 kHz spinning speed, 0.5 μs pulse lengths with a 0.25 s recycle delay between scans. The short pulse length used ($<\pi/12$ flip angle) is necessary to ensure reasonably reliable intensities are obtained when there are sites present that have significantly different quadrupole coupling parameters (19). Due to the demands on spectrometer availability, the NMR spectra were obtained on the samples after various curing times (30-60 days). However, the small additional structural changes occurring during this time period are expected to have only a minor effect on the NMR spectra and the large differences between the observed spectra means that firm conclusions can still be drawn.

Results and Discussion

Figure 1 and Table 3 show the FTIR results for the Type 1 samples. The untreated waste FTIR spectrum shows the expected peaks due to νOH (3450 cm^{-1}) and HOH (1625 cm^{-1}). There is also a characteristic peak at 2108 cm^{-1} arising from the CN stretch reflecting the high cyanide component of the waste, and peaks at 1495, 1408 and 942 cm^{-1}. These latter bands are difficult to assign specifically due to spectral overlap in this region, but probably contain contributions from CO_3^{2-}, PO_4^{3-} and SO_4^{2-} species present in the waste. It is worth noting that in the cement samples containing 19 and 30 % waste (samples B, C and E) the CN stretch at about 2100 cm^{-1} is clearly observed indicating that this component remains essentially unchanged during solidification/stabilization of this waste, although addition of sodium cyanide to cement significantly retards normal hydration reactions (20).

Compared with cement paste prepared without any metal waste, samples B and C show $\nu_3SiO_4^{4-}$ bands shifted to lower frequencies suggesting a lower degree of polymerization of the silicate units in the presence of the stabilised metal waste. Sample A, which contains

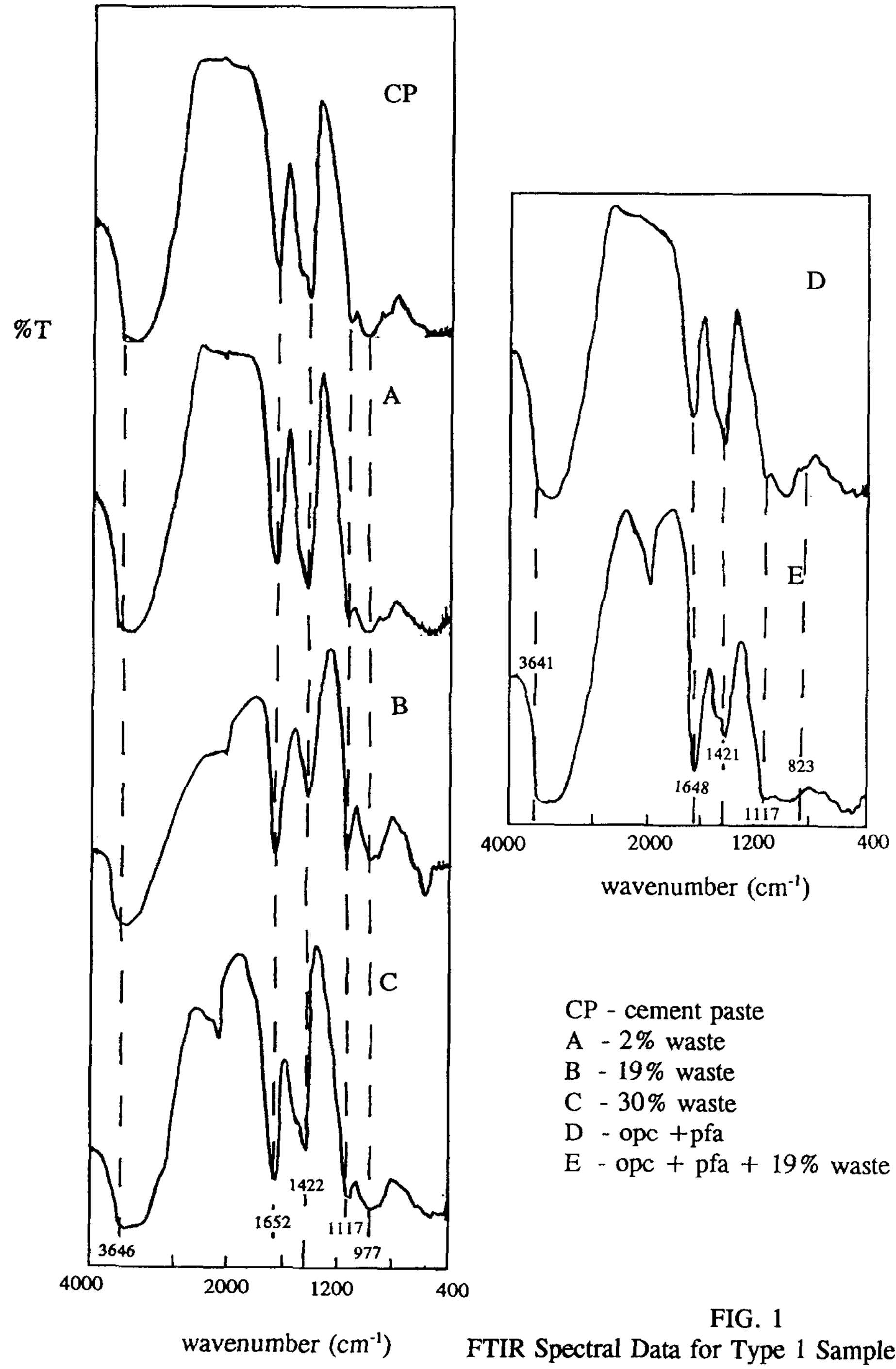

FIG. 1
FTIR Spectral Data for Type 1 Samples at 28 days

TABLE 3
FTIR Spectral Data on Type 1 Samples

	Assignment (cm^{-1})							
Sample	SiO_4^{4-} (ν_3)	SiO_4^{4-} (ν_4)	OH	HOH	SO_4^{2-} (ν_3)	CO_3^{2-} (ν_2)	CO_3^{2-} (ν_3)	OH $Ca(OH)_2$
Cement	930	521	3404	1607	1154	-	1444	-
Cement Paste	969	510	3450	1645	1114	875	1419	3644
A	977	536	3447	1652	1117	873	1422	3646
B	928	526	3425	1642	1118	-	1421	-
C	932	520	3449	1649	1114	-	1420	-
D	989	-	3436	1648	1117	872	1421	3641
E	952	535	3451	1646	1114	-	1421	-

only 2 % of waste, has a $\nu_3SiO_4^{4-}$ band at the same position as normal cement paste within experimental error. The FTIR spectrum on sample D which contains PFA and no waste is quite similar to the cement paste alone. There is a slight shift in the $\nu_3SiO_4^{4-}$ band from 969 to 989 cm^{-1} which may be attributed to the overlap of the $\nu_3SiO_4^{4-}$ band from the cement with a higher frequency band within the PFA. Upon addition of metal waste together with PFA (sample E) the characteristic decrease in vibrational frequency of the $\nu_3SiO_4^{4-}$ band is again observed, indicating that there is a lower degree of silicate condensation in the presence of the stabilised metal waste. Table 3 shows the vibrational frequencies of the other bands. It is, however, difficult to draw firm conclusions from the FTIR results or to quantify the changes occurring due to band overlap in the region of interest. For instance, phosphates form a major part of the metal waste, and these typically give IR frequencies of 1000-1100 cm^{-1}.

^{29}Si MAS NMR spectra of cement paste and cement solidified wastes are shown in Figure 2. In the case of cement paste and sample A, ^{29}Si peaks are observed at -71.2, -78.8 and -84.3 ppm corresponding to Q^0, Q^1 and Q^2 units respectively. The presence of Q^1 and Q^2 units indicates that a considerable degree of silicate condensation has occured, while the Q^0 peak arises principally from unreacted starting material. However, the relative areas under the Q^n peaks are different; the lower proportions of Q^1 and Q^2 peaks for sample A indicate that this sample has a lower degree of polymerization. We can quantify the "degree of silicate condensation" by defining it as:

$$\% \text{ condensation} = 100 \times \sum n\, A(Q^n) / 4 \sum A(Q^n)$$

where $A(Q^n)$ is the area under each Q^n peak which is obtainable by spectral simulation. The % condensation for the cement paste is 23.5 %, while that for sample A is only 16.5 %. Samples B and C on the other hand give ^{29}Si MAS NMR spectra which show only Q^0 units, and no Q^1 or Q^2 units. Hence in the samples containing significant amounts of metal waste the degree of condensation is zero, and no dimers or higher polymers have been formed. The ^{29}Si spectrum of sample D, which contains PFA but no metal waste, shows that silicate condensation has occurred to a similar extent to normal cement paste, indicating that the presence of PFA does not significantly alter the degree of silicate condensation. Sample E, which contains PFA and the same amount of metal waste as sample B, shows that no silicate condensation has occurred. Both samples D and E show an additional broad ^{29}Si resonance around -100 ppm besides the other peaks; this arises from Q^3 and Q^4 silica environments within the PFA.

Thus it is clear that ^{29}Si MAS NMR spectroscopy can easily probe and quantify the extent of hydration reactions in cements, including those containing toxic wastes. The extent of silicate condensation is reduced even when the concentration of the metal waste is only 2 %, while no silicate condensation occurs at higher metal waste concentrations.

In principle ^{29}Si NMR can detect the presence of crystallographically distinct Q^n sites. For instance, seven peaks can be observed (all Q^0) in the spectrum of pure crystalline C_3S between -69 and -75 ppm (21). However, hydrated cements are an inhomogeneous mixture of several largely amorphous phases. This means that the spectral peaks observed are comparatively broad and resolution between distinct Q^0 sites is not normally achieved. A shoulder is, however, observable to the low frequency side of the main Q^0 peak in these cements (at about -73 ppm) which indicates that more than one Q^0 site is indeed present. It should also be pointed out that spinning sidebands were observed in the ^{29}Si MAS NMR spectra (outside the range of the spectra shown in Figure 2). These are peaks separated from the true isotropic resonances by multiples of the spinning speed, and are principally due to the anisotropic coupling between ^{29}Si nuclei and unpaired electrons associated with the paramagnetic components within the sample.

The comparatively small amounts of aluminate present within OPC means that it is not possible to draw any conclusions concerning their state from FTIR. However, ^{27}Al is a fairly sensitive nucleus on which to perform NMR studies, and so can readily be detected. On the other hand, ^{27}Al MAS NMR spectroscopy does have the disadvantage that spectra are difficult to interpret, as ^{27}Al is affected by the quadrupolar interaction; this leads to a field-dependent shift in resonance position and a broadening of the peaks. Tetrahedrally coordinated aluminium is generally observed between 50 and 80 ppm, while octahedrally coordinated aluminium normally resonates between -20 and 20 ppm. The ^{27}Al MAS NMR spectra recorded are also shown in Figure 2. These show that the main aluminium environments in the cements are octahedrally coordinated, and there are only relatively minor amounts of residual tetrahedral aluminium (broad peak around 70 ppm). Hence most of the calcium aluminate phases (principally C_3A) seem to have been hydrated.

There is, however, a distinction between the samples in the ^{27}Al octahedral region. The cement paste and sample A show two distinct environments, one giving a narrow signal at 13.2 ppm, the other a broader signal around 8.5 ppm. The former also has an array of spinning sidebands arising from satellite transitions ($\pm{}^1/_2 \leftrightarrow \pm{}^3/_2$). This peak width and the presence of intense spinning sidebands indicates that this site has relatively small quadrupole coupling parameters. Comparison with the values obtained on pure aluminate hydrate phases (17), indicates that this resonance is almost certainly due to ettringite, $C_6AS_3H_{32}$, which is reported to have an isotropic chemical shift of 13.1 ppm, with quadrupole parameters $e^2qQ/h = 0.36$ MHz and $\eta = 0.19$. The broader peak observed at 8.5 ppm is attributable to the monosulfate phase, C_4ASH_{12}, which is reported to have an isotropic chemical shift of 11.8 ppm with $e^2qQ/h = 1.7$ MHz (17). The higher quadrupole interaction in monosulfate

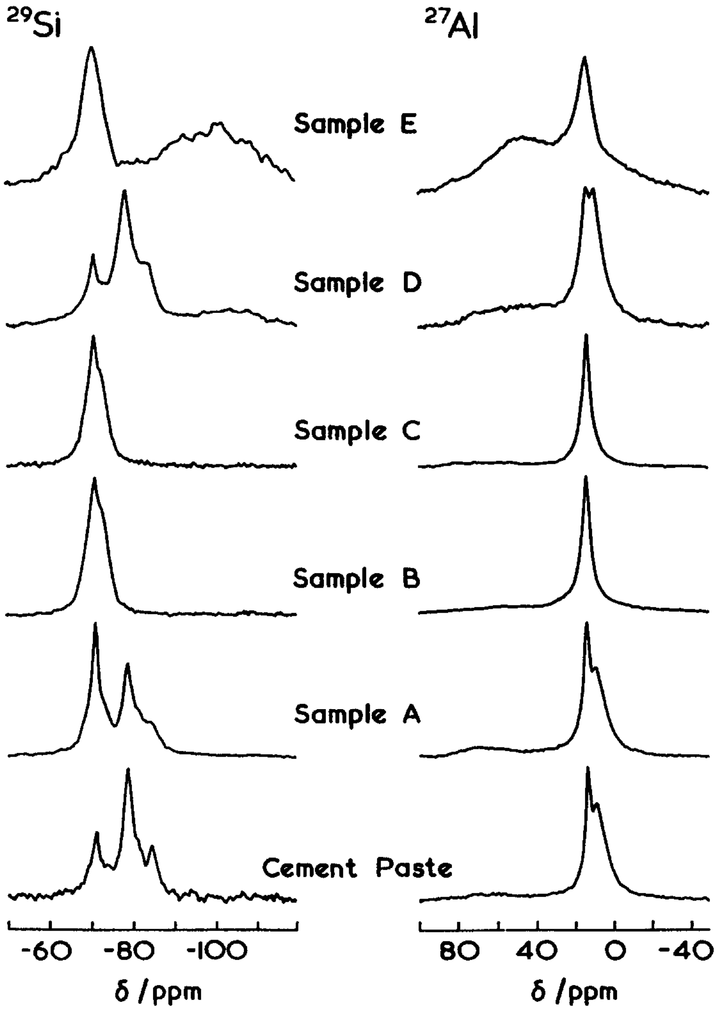

FIG 2
^{29}Si and ^{27}Al MAS NMR analysis of Type 1 samples

causes the shift in resonance position from the isotropic chemical shift to the observed resonance position.

While ^{27}Al NMR spectroscopy detects the presence of both ettringite and monosulfate in sample A, only ettringite is detected in the spectrum of samples B and C. For the samples containing PFA an additional broad peak is observed around 46 ppm, presumably due to an amorphous aluminosilicate glass present within the PFA. The addition of PFA appears to have no effect on the aluminate hydration reactions. Sample E seems to contain ettringite but not monosulfate. Thus the ^{27}Al NMR results show that the metal waste significantly affects the formation of the aluminate hydrate phases in a fashion analogous to that observed for the silicate phases from the ^{29}Si NMR results. Unfortunately one cannot easily quantify the relative amounts of the phases present in ^{27}Al spectra, as the quadrupole interaction means that the peaks are of differing linewidths and may be asymmetric.

FTIR spectra of the samples containing organic compounds (Type 2 samples) are similar to those of cement paste, but in the cases of sodium acetate, tetrachloroethylene and phenol there is an increase in frequency for the $\nu_3SiO_4^{4-}$ band (up to about 1000 cm^{-1}) suggesting a possible increase in silicate polymerization. The FTIR spectra of the sample containing 5 % phenol gave phenol adsorption bands at 1589, 1481 and 1167 cm^{-1}. An additional band at 1275 cm^{-1} in this sample and at 1194 cm^{-1} in the sample doped with 10% sodium acetate could not be assigned.

As stated earlier, it is expected that ^{29}Si NMR will give a more clear cut result on the extent of silicate condensation than FTIR. The ^{29}Si MAS NMR spectra on these compounds all show peaks due to Q^0, Q^1 and Q^2 units at the same positions as normal cement paste. The relative peak areas and the % condensation are summarised in Table 4.

TABLE 4

Summary of ^{29}Si NMR results on cements containing organic compounds.

Sample	A(Q^0)	A(Q^1)	A(Q^2)	% condensation[†]
Cement Paste (CP)	26.1	53.9	20.0	23.5
CP + 0.5% phenol	23.6	53.2	23.2	24.9
CP + 5.0% phenol	57.1	23.4	19.4	15.6
CP + 10.0% phenol	68.5	17.9	13.7	11.3
CP + 0.5% ethylamine	38.4	39.3	22.2	20.9
CP + 5.0% ethylamine	45.1	36.0	18.9	18.5
CP + 10.0% ethylamine	47.1	38.2	14.6	16.9
CP + 0.5% sodium acetate	34.9	45.5	19.9	21.3
CP + 5.0% sodium acetate	34.5	45.2	20.3	21.5
CP + 10.0% sodium acetate	36.8	45.3	17.8	20.2
CP + 0.5% tetrachloroethylene	22.7	55.3	22.0	24.8
CP + 5.0% tetrachloroethylene	34.7	44.7	20.6	21.5

[†] % condensation is defined as $100 \times \sum n\,A(Q^n) \,/\, 4\sum A(Q^n)$

(estimated uncertainty in the values quoted varies with the signal-to-noise ratio of the spectra but is in the range 0.5–1 %)

For the samples containing 0.5 % phenol and 0.5 % tetrachloroethylene there is an apparent small increase in the extent of condensation. However, this is barely greater than the estimated uncertainty in the quoted values, and more work would be needed to confirm whether this is a true effect. In contrast to the FTIR results it is clear that there is a significant reduction in silicate condensation with increasing phenol and ethylamine concentrations, though some condensation still occurs for all the concentrations studied. On the other hand, sodium acetate and tetrachloroethylene have only a minor effect on the formation of C-S-H phases.

For the Type 3 mix, which represents the composition of a typical industrial waste containing some organic contamination, the $\nu_3SiO_4^{4-}$ band is observed at 970 cm^{-1} in the FTIR spectrum, in the same position as cement paste. The ^{29}Si MAS NMR spectrum shows the presence of Q^o, Q^1 and Q^2 units and the presence of PFA, and the degree of condensation is approximately the same as observed for normal cement paste. This is a surprising result, which requires further investigation, as it suggests an apparent accelerating effect of the mixed organics, with the result that the combination of organics and metal waste has little effect on the overall degree of silicate condensation.

Conclusions

FTIR and solid-state ^{29}Si and ^{27}Al NMR spectroscopy have been applied to study the solidification of a real industrial stabilised waste using ordinary portland cement, and to examine the influence of various organic species on the hydration of calcium silicate phases. ^{29}Si NMR is shown to provide an unambiguous quantification of the extent of silicate polymerization within a sample; this is not always possible using FTIR due to the problems associated with band overlap. The results show that silicate condensation is severely retarded in the presence of a metal waste. Phenol and ethylamine are also shown to reduce silicate condensation significantly, while sodium acetate and tetrachloroethylene have only a minor effect. By contrast, a cement sample containing both metal waste and organic species showed a degree of silicate condensation similar to that observed for normal cement paste.

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