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Nuclear Magnetic Resonance Spectroscopy of Cement in Solid State

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ABSTRACT: *Concrete is the universal material whereupon present day civilisation is assembled, giving long haul strength, impermeability and sturdiness for lodging and foundation. The central compound connections which control the design and execution of concretes have been the subject of extreme exploration for quite a long time, yet the complex, crystallographically scattered nature of the key stages which structure in solidified concretes has brought difficulty up in getting nitty gritty data about nearby construction, response instruments and energy. Strong state atomic attractive reverberation (SS NMR) spectroscopy can resolve key nuclear underlying subtleties inside these materials and has arisen as a critical instrument in portraying concrete construction and properties. This audit gives an exhaustive outline of the utilization of multinuclear SS NMR spectroscopy to comprehend compositionestructureeproperty connections in concretes. This remembers anhydrous and hydrated stages for Portland concrete, calcium aluminate concretes, calcium sulfoaluminate concretes, magnesia-based concretes, antacid actuated and geopolymer concretes and manufactured model frameworks. Progressed and multidimensional tests test 1H, 13C, 17O, 19F, 23Na, 25Mg, 27Al, 29Si, 31P, 33S, 35Cl, 39K and 43Ca cores, to contemplate nuclear construction, stage advancement, nanostructural improvement, response systems and energy. Accordingly, the components controlling the actual properties of concretes would now be able to be settled and perceived at an uncommon and fundamental degree of detail.*

KEYWORDS:Solid-State Nmr ;Spectroscopy; Portland Cement; Calcium Aluminate Cements ;Calcium Sulfoaluminate Cements ;Magnesia-Basedcements;Alkali-Activated Cements

I. INTRODUCTION

Modern society is heavily reliant on cementitious materials in constructing our built environment. Second only to water interms ofcommodityuse[1,2],theworldwideproductionofconcreteex- ceeds10 billionton nesperannum.Themostcommoncementused toproduceconcreteisPortlandcement(PC)[3],acomplexmaterial made up of multiple calcium-rich mineral phases that react with water and harden to provide strength, impermeability and resis- tance to thermal, mechanical and chemical stresses over long timescales[4].TheexcellentphysicalpropertiesofPChaveresulted in its incorporation into virtually all of the modern built environment.

However,PCproductionresultsinlargeassociatedCO_2emissions,approximately0.73e0.99tCO_2/tPC,whichis~8%ofc

urrentglobalanthropologicalCO_2emissionswhenconsideringaPCpro- ductionvolumearound4Gtperannum[5,6].Consequently,low-moments(i.e.non- zerospin)andappliedmagneticfieldsanden- ables determination of the local chemical environments of NMR-active nuclei, regardless of the level of crystallographic order or disorder, and this is essential in its application to the study of ce- ments. In cements, nuclei of interest include ^{1}H, ^{13}C, ^{17}O, ^{19}F, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{33}S, ^{35}Cl, ^{39}K and ^{43}Ca (Table 1). Solid-state (SS) NMR is ideally suited to study both anhydrous and hydrated solid phasesincementitiousmaterials.Itsapplicationtocementsamples ofdifferentagesisinvaluableinresolvingthereactionmechanisms, kinetics and structural evolution that dictate the propertiesandperformanceofcements(andthusalsoconcretesmadeusingthesecements).NMRcanalsobeappliedasapowerfultoolprobingthe dynamics of mobile ions and water within cementitious materials, in particular through the use of ^{1}H NMR relaxometry which pro- vides information about water mobility and pore size distribution [8,9]. These various applications and nuclei will be discussed in detail in the sections whichfollow.

CO_2cementitiousmaterialshaveemergedasattractive,moresustainablealternativestoPC[4].Supplementarycementitiousmate- rials (SCMs) such as coal fly ash (FA), blast furnace slag,calcined clays, finely ground limestone and silica fume are widely used in concrete.ByblendingPCwithSCMs,itispossibletoenhanceand control physical properties, e.g. strength, durability, phaseforma- tion and reaction kinetics, and also to improve sustainability by reducingassociatedCO_2emissionsandvalorisingindustrialwastes [7].PC-freebinderssuchascalciumaluminatecements(CACs)and calcium sulfoaluminate (CSA) cements, magnesia-based cements, alkali-activatedmaterials(AAMs)andgeopolymers,amongothers, have also received significant attention from academia and in- dustry due to the enhanced technical properties and/or sustain- ability that they can provide, when compared with PC[4].

Thecomplexchemicalnatureofcementsystems,whichoften involvecrystallographicallydisorderedphasesandwhichcontinue to evolve as a function of time for many years afterinitialmixing

II. SOLID-STATE NMR SPECTROSCOPY

An NMR experiment involves holding a sample in a magnetic field(denotedB_0)andapplyingpulsesofradiofrequencyradiation to induce precession of the nuclear spin and measuring theelec- tromagnetic response produced as the nuclei relax back to their equilibriumstates.Theelectromagneticsignalismeasuredasafree inductiondecay,whichisthenconvertedtoanNMRspectrumby applying a Fourier transform. The NMR spectrum contains reso- nances characteristic of near-neighbour atomic environments [10,11]. Terms representing the magnetic dipolar interaction, chemicalshieldingandquadrupolarinteractionsbetweenthenu- cleus and its environment are of particular interest in the study of cements.

NMR spectra of solids are broadened (compared to those of liquids) due to dipolar interactions, anisotropy of the chemical shielding and quadrupolar interactions between the intrinsic nu- clear electric quadrupolar moment and the surrounding electric field gradient [10]. This necessitates the application of sample spinning methods to reduce broadening.

Magic angle spinning (MAS) requires spinning a sample at an angleofcos^2(q_{MAS})¼1/3(q_{MAS}z54.74°)withrespecttothestatic magneticfield(B_0)sothatdipolarinteractionsaresuppressed,and both chemical shielding anisotropy and first-order quadrupolar interactions are removed [10,11], narrowing spectral lineshapes. This means that the local chemical environments of spin S ½ nuclei (which do not¼ experience second-order quadrupolar in- teractions) can be represented in terms of the isotropicchemical shift (d_{iso}) in MAS NMR spectra. Quadrupolar nuclei (S > ½) expe- rience additional second-order quadrupolar interactions, so the quadrupolarinteractiontermoftheHamiltonianisnon-zerounder MAS conditions. This limits spectral resolution due to anisotropic broadening of the signals. However, these second-order quad- rupolarinteractionsareinverselyproportionaltothestrengthofB_0 andcanthusbereducedthroughtheuseofhighmagneticfields [10,11]. Owing to the disordered structure of many cementitious phases,significantlinebroadeningoccursatallpracticallyachiev- able MAS rates, and so the spectra for relevant nuclei are often poorlyresolved

.The presence of paramagnetic species within cementitious materials can limit the applicability of SS NMR for their charac- terisation;thesespeciesinfluencetherelaxationandchemicalshift ofnearbynuclearspins,whichcanseverelydampenandshiftthe NMR signal of these nuclei [10]. This is particularly problematic in standard ‘grey’ PC and in ferrite-containingsulfoaluminatecements, which each contain tetracalcium aluminoferrite ($4CaOAl_2O_3Fe_2O_3$,C_4AF),aswellasinbinderscontainingcoalFA (containing Fe_2O_3) [13]. The use of Fe_2O_3-free cement systems for spectroscopicanalysis[14e16]can,therefore,beadvantageous.

Recent advances in this understanding of the chemistry and materials science of cements, in which the application of SSNMR hasplayedapivotalrole,arediscussedinthefollowingsection.

III. TERMINOLOGYUSEDINDEFININGTHELOCALSTRUCTUREOFSILICATES AND ALUMINATES

Si sites are generally identified using notation of the type Q^n(mAl) (represented by Q) is bonded to n other tetrahedral atoms (m of which are Al) via oxygen bridges. Q^n(mAl) Si sites within cemen- titious materials typically resonate in the region from 60 ppm to120 ppm relative to tetramethyl silane, with significant overlap between the broad resonances observable in disordered solid phases, but a more negative chemical shift induced by a higher connectivity (i.e. higher n) (Fig. 1) [11,16e18].Each additional tetrahedral Al atom which replaces an Si neighbouring aQ^n(mAl) silicon site also increases the chemical shift by approximately 5 ppm [11], and this provides an important point ofdifferentiation

betweenQ^n(mAl)sitesasafunctionofnandm,althoughtheeffects of the two parameters cannot always straightforwardly be discriminated without application of multinuclear NMR techniques.

. Bridges betweentwotetrahedralAlsitesaredisfavoured(acrystallographic and thermodynamic observation known as ‘Loewenstein's princi- ple’ [19]). Tetrahedral and octahedral Al sites typically resonate within the regions 80e50 ppm and 20 - 0 ppm, respectively, rela- tive to $Al(H_2O)^{3þ}$(aq), while resonances assigned to five-coordinated Al and highly distorted tetrahedral Al environments have been observed in the region 50e20 ppm, Fig. 2[11,17,20e22].

IV. CHARACTERISATION OF CEMENTITIOUS MATERIALS

1.1. MAS NMR of anhydrous cementitiousmaterials

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1.1.1. Portlandcement

PC primarily comprises the ‘clinker’ phases tricalcium silicate (3CaOSiO$_2$, C_3S, in numerous polymorphs), dicalcium silicate (2CaOSiO$_2$, C_2S; the a and b polymorphs of this composition are preferredincementsduetotheirhydraulicnature,whereasg-C_2S isunreactive),tricalciumaluminate(3CaOAl_2O_3$,$C_3A$)andtetra- calcium aluminoferrite. This assemblage of clinker minerals is producedfromlimestoneandsilicatemineralsinarotarykiln,then rapidly cooled and interground with calcium sulphate to formPC [23]. Among these clinker minerals, tricalcium silicate (or a slightly impure form of this phase, containing Al and/or Mg among other substituents,whichiscommonlydescribedas‘alite’inthecements literature [24]) is the predominant constituent of modern PC, definingitshydraulicnatureandhighearlystrengthdevelopment uponcementhydration.Theexpectedvaluesofd_{obs},$d_{iso}$and$C_Q$for different nuclei in various phases in PC are shown in Table 2 and discussed in the followingtext.

1.1.1.1. Tricalcium silicate (alite, hartrurite). C_3S is known to exist in seven polymorphs: three triclinic, three monoclinic and one trigonal. The alite present in PC crystallises from the melt in a trigonal form and upon rapid cooling, transforms into metastable

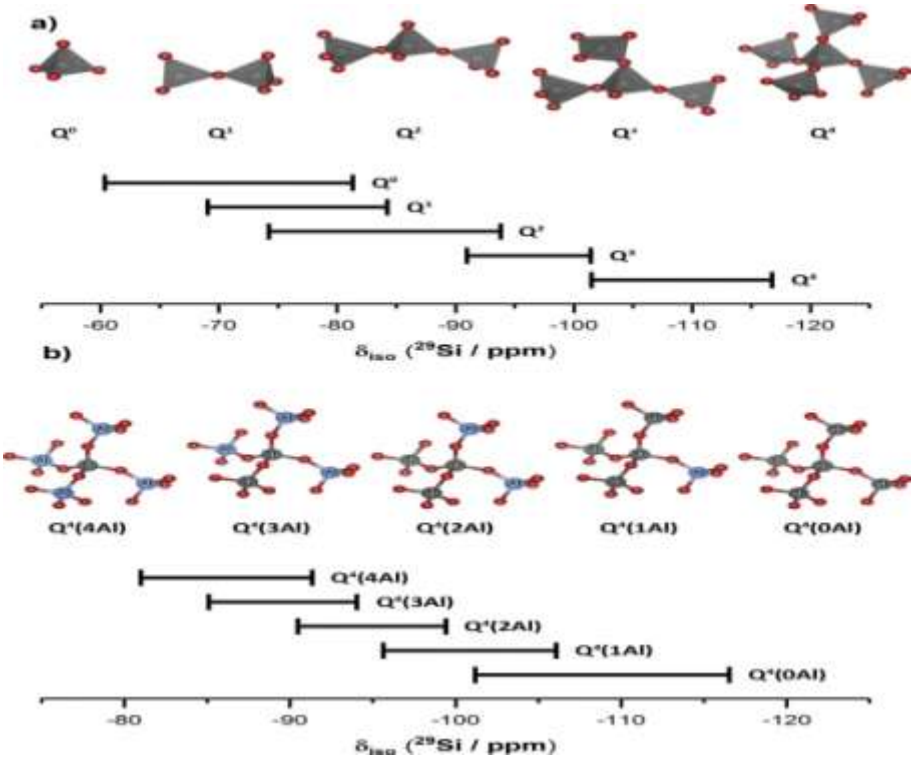

Fig. 1. Typical ranges of ^{29}Si chemical shifts for (a) Q^n and (b) Q^4(mAl) sites in solid silicates [11]. Si, Al and O atoms are represented by grey, blue and red spheres, respectively.

polymorphs, predominantly, the two monoclinic polymorphs M_I and M_{III}[25]. ^{29}Si MAS NMR analysis of the M_I polymorph of alite has shown that Si exists within nine crystallographically distinct sites, approximately within the range from 69 to 75 ppm [26,27], while ^{29}Si MAS NMR spectra of the M_{III} polymorph exhibit overlappingresonancesbetween—66and—78ppmcorresponding to eighteen distinct SiO_4 tetrahedra (Fig. 3)[27,28].

Thecalciumsilicatechainsinalitecanaccommodateanumber
of guest ions which substitute for silicon (e.g. $AlO^{5—}$or $PO^{3—}$for
analysis in 1994 by Skibsted et al. [34] using ^{27}Al MAS NMR [30], then later confirmed unambiguously using ^{27}Al multiple quantum (MQ)MAS NMR.

Reduction of the temperature at which alite forms, whichis desirableforbotheconomicandenvironmentalreasonsincement production, is often achieved by adding ‘mineralising’ additives such as fluoride and phosphate, which substitute into the alite structure.Tranetal.[31]used^{29}Siand^{27}AlMAS,^{19}F-^{29}Sicross
polarisation (CP) MAS and ^{19}F-^{29}Si CP rotational-echo double-

4 4

4 $SiO^{4—}$[30e32]) or oxygen (e.g $F^{—}$for $O^{2—}$[31]). Substitution of $AlO^{5—}$for $SiO^{4—}$in C S chains has been identified crystallographi-
resonance (REDOR) MAS NMR techniques to show that $F^{—}$sub- stitutesfor$O^{2—}$ ionsinthealitephasealone,accordingtoacoupled
4 4 3 4 4

cally since the 1950s [24,33]and was first subjected to NMR
substitutionmechanism$SiO^{4—}$þ$O^{2−}$⁄$AlO^{5−}$þ$F^{—}$[35],witha

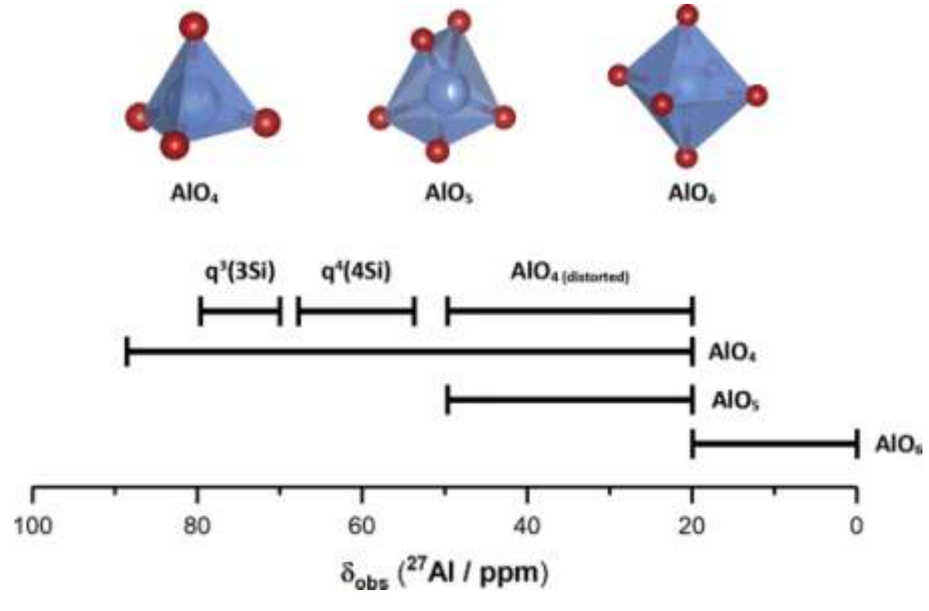

Fig. 2. Typical ranges of ^{27}Al chemical shifts for different aluminium sites in aluminates and aluminosilicates [11]. Al and O atoms are represented by blue and red spheres, respectively.

Table 2

[a] M_I and M_{III} are the monoclinic polymorphs of alite comprising nine and eighteen crystallographically distinct Si sites, respectively.

strong preference for F$^{—}$substitution into interstitial oxygen sites notinvolvedincovalentSi-Obonds.Poulsenetal.[32]showedvia ^{31}P and inversion recovery ^{31}P MAS NMR that PO$^{3—}$ions substitute for SiO$^{4—}$tetrahedra in alite; a substitu^{4}tion level of 1.3 mol. % was identified in the sample studied. ^{4}MASNMRspectroscopytoaseriesofCaF$_2$-modifiedPCscontaining between0.23and0.77wt%fluorine,demonstratingthatincreased fluorine content drives increased fluorine substitution into alitevia adoublesubstitutionmechanismandthatF$^{—}$andAl^{3þ}ionsinalite are likely to be clusteredtogether. $_4$ þ $_4$ þ þ $_{Ca}$

Recently, ^{17}Oe^{29}Si CP heteronuclear correlation (CP-HETCOR)

MAS NMR was used to resolve oxide ion sites bonded to one Si^{4þ}from those bonded to Ca^{2þ}in synthetic tricalcium silicate for the first time [37]. Oxide ion sites bonded to Ca^{2þ}play an important roleinthestructureandreactivityofC$_3$Sbuthaveprovendifficult to resolve. ^{43}Ca MAS NMR analysis of alite was first reported by Moudrakovskietal.[38],withthehigh-field(21.14T)natural abundance^{43}CaMASNMRspectrumofthemonoclinicpolymorph showing a broad, asymmetric resonance consistent with over- lapping^{43}Caresonancesfromthe36non-equivalentsitesforCain this phase and deviations from a perfect lattice (Fig. 4) [28]. This contrasts with the ^{43}Ca MAS NMR spectrum of the triclinic polymorph, which exhibited well-separated ^{43}Ca resonances despite the29non-equivalentsitesforCainthisphase[39],suggestingthat some of these non-equivalent sites are quite similar. This work demonstrates the power of SS ^{43}Ca MAS NMR to resolve polymorphism,whichisvaluableinidentification,characterisationand quantification of metastable polymorphs within cement systems, although the time and instrumentation required to collect high-resolution^{43}Caspectramayprovetobealimitationinapractical sense. Differences in ^{43}Ca MAS NMR spectra have also been exploited for spectroscopic analysis of the CaCO$_3$ polymorphs calcite, aragonite and vaterite [40,41], which are also present in many cementsystems.

1.1.1.2. Dicalcium silicate (belite, larnite). The ^{29}Si and ^{17}O MAS NMR analysis of b-C$_2$S (also known as belite and the dominant polymorph of dicalcium silicate found in PCs) has shown thatSi

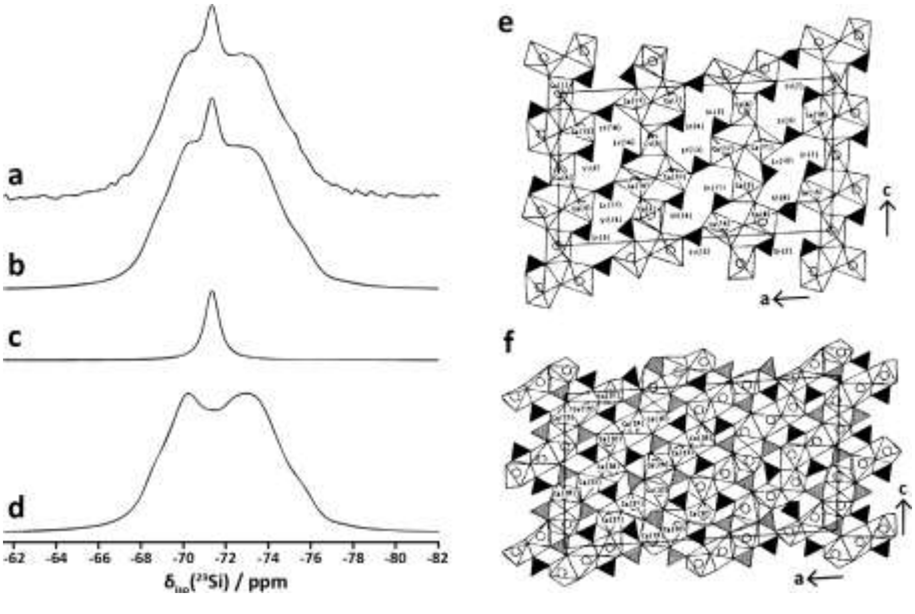

Fig. 3. ^{29}Si MAS NMR spectrum (9.4 T, spinning speed n$_R$¼ 13.0 kHz) of (a) grey PC and (b) its deconvolution, which is composed of the subspectra for belite and alite shown in (c) and(d).AdaptedfromPoulsen etal.[29].Parts(e)and(f)showtwodifferentsections takenthroughthemonoclinicsuperstructureof theM$_{III}$polymorphofalite,vieweddowntheb axis,showingpolyhedralocatedin(e)andabove(f)thea,0,cplane.AdaptedfromNishietal.[28].

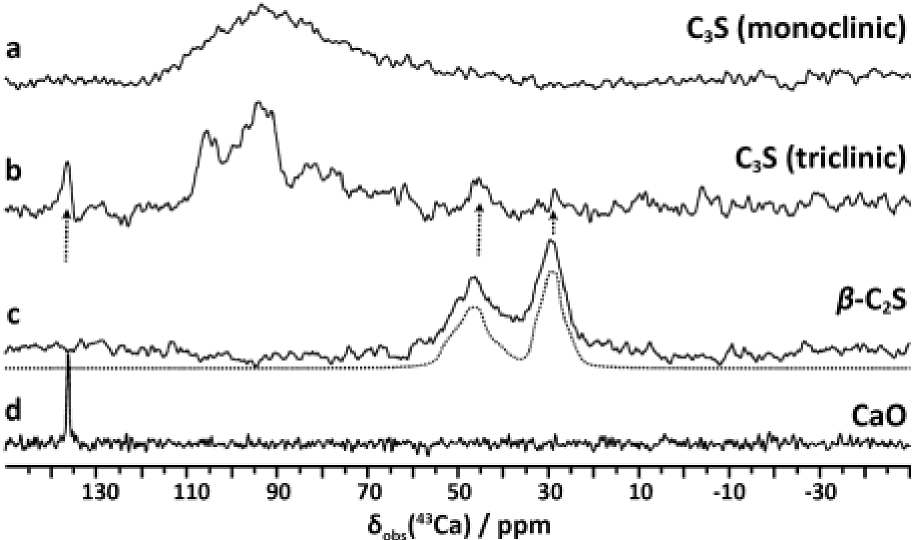

Fig. 4. Natural abundance ^{43}Ca MAS NMR spectra (21.4 T) of (a) monoclinic C_3S, (b) triclinic C_3S, (c) b-C_2S and (d) CaO. The dotted line below spectrum (c), for b-C_2S, shows the spectralsimulationforthesecond-orderquadrupolarinteractions.Theverticalarrowsbelowspectrum(b),fortriclinicC_3S,indicatethepositionsofthesignalsduetoCaOandb-C_2S impurities.AdaptedfromMoudrakovskietal.[38].

exists within a single Q^0 (isolated SiO_4 tetrahedron) environment which exhibits a single ^{29}Si resonance at 71.3 ppm [27,42e44], coordinatedtocalciumviafourSi-O-Calinkages[43].SomePCsalso containtheapolymorphsofC_2S,butthesedonotappeartohave been analysed specifically by high-resolution SS NMR in theavail- able body of literature, so the focus here will be on the bform.

Despitethefactthattherearefourcrystallographicallydistinct oxygensiteswithinb-C_2S[42],asinglebroadresonanceisobserved in the ^{17}O MAS NMR spectrum [43], suggesting that there is some degreeofdisorderinthisphase.Asforthecaseofalite,substitution of $Al^{3þ}$for $Si^{4þ}$in C_2S has been identified crystallographically since the 1950s [45,46]. In 1994, ^{27}Al MAS NMR was used to providethe in C_2S in PC [30], which has significant consequences for the dissolution and hydration reactions of this phase, given the ther- modynamic preference for dissolution of Al from calcium alumi- nosilicates [47]. Skibsted et al. [30]determined quadrupole coupling parameters and the isotropic chemical shift for this unique $Al^{3þ}$guest ion in belite, which exhibited the most deshiel- ded chemical shift (d_{iso}96.1 ppm) yet reported for a tetra-coordinatedAlenvironmentbondedtofouroxygenatoms,further

$SiO^{4—}$tetrahedra for the sample studied) in PCs containing between
4 0.08and0.45wt%P_2O_5,withasimilarcoupledsubstitutioncharge balancing mechanism proposed as described previously foralite, where$Ca^{2þ}$ispartiallyreplacedby$Fe^{3þ}$via$SiO^{4—}$þ2$Ca^{2þ}$⁄
4 $PO^{3—}$þ$Fe^{3þ}$þ¸Ca· 4

The ^{43}Ca MAS NMR spectrum of belite was first reported by Moudrakovski et al. [38], Fig. 4. The high-field (21.14 T) natural abundance^{43}CaMASspectrumexhibitedtwodistinctresonances consistentwiththecrystalstructureofthisphaseandcalculations from density functional theory (DFT) (Table 2). Both sites exhibited extensive asymmetry in Ca-O bondlengths.

1.1.1.3. Tricalcium aluminate. The investigation of C_3A by ^{27}Al MAS andMQMASNMRatmultiplefieldshasshownthatitcontainstwo inequivalent Al tetrahedral sites, which resonate at d_{iso}79.5 ppm and 78.25 ppm, respectively, ar¼anged in six-membered rings of AlO_4 tetrahedra in the cubic (pure) polymorph of C_3A (Fig. 5) [34,49].d_{iso}valueswithin±6ppmofthosedeterminedbySkibsted etal.[49]havealsobeenreportedfortheseAl^{IV}siteswithin$C_3A$by other workers, although with some variability in reported reso- nance positions [50e52]. Four of the six crystallographically non- equivalent calcium sites in C_3A were resolved using high-field (21.1 T) single-pulse 1D^{43}Ca MAS NMR by Moudrakovski et al.[38].

1.1.1.4. Tetracalcium aluminoferrite (brownmillerite). The analysis of

C_4AFbyNMR,andparticularlyby^{27}AlMASNMR,isconstrainedby thenuclear-unpairedelectrondipolarcouplingsbetweenthe^{27}Al nucleus and paramagnetic Fe^{3þ}ions [53e55], which severely broadenthe^{27}AlMASNMRspectraanddampenthesignal[52,55]

, examining $Ca_2Al_xFe_{2-x}O_5$ with x 0.93, 1

and 1.33 (Fig. 6). Increasing Fe content dramatically dampenedand broadenedtheobservedresonances,butdespitethesedifficulties, it was possible to observe that the central transitions showed a dominant resonance for Al^{IV} species at 61 ≤ d$_{obs}$≤ 71 ppm, with increased shielding at higher Fe content, and Al^{VI} species at 0 ≤ d$_{obs}$≤ 20ppm.

Asmentionedinsection2,thepresenceofC_4AFinPCalsohas significant implications for acquisition of ^{29}Si MAS NMR data for C_3S and C_2S phases. A dramatic decrease in the longitudinal relaxation time, T_1, in grey PC has been attributed to the close proximity of these diamagnetic phases to paramagnetic C_4AF [56,57]. However, Poulsen et al. [29] attributed this effectprimarily

toFe^{3þ}ionsincorporatedasguestionswithinCSandCSphases,

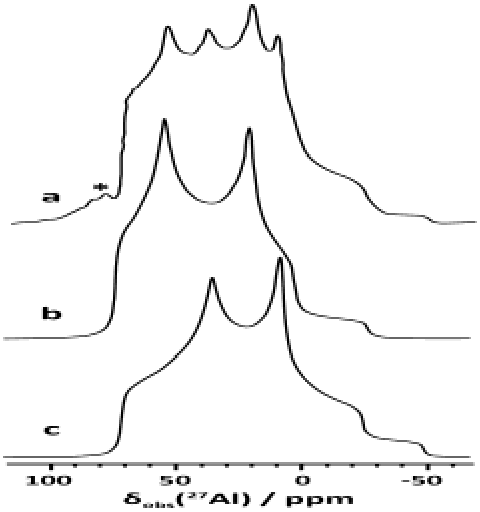

Fig. 5. ^{27}Al MAS NMR spectra (9.4 T, n$_R$¼ 18.0 kHz) of cubic C_3A (3CaOAl_2O_3$): (a)

3 2 showing the resonance from the central transition. Simulations for each of thetw

rather than intermixing with ferrite phases. These effects need to beconsideredcarefullywhenattemptingtoquantifyC_3SandC_2S phases in PC via deconvolution of ^{29}Si MAS NMR spectra as pref- erential incorporation of Fe^{3þ}ions within either of the silicate phases will result in a dampening of the ^{29}Si MAS NMR signal for thatphaseandconsequentlyleadtoincorrectquantification[57]. Further discussion of methods to mitigate this issue is provided insection4.3

AlO_4 sites are shown in (b) and (c). *Resonances from satellite transitions. Adapted from Skibsted et al., 1991[49].

Pake doublet) reflects the dipolar coupling of two ^{1}H nuclei and therefore the internuclear distance between H atoms within the watermoleculesofgypsum[58].Naturalabundance^{43}CaMASNMR (8.6T,n$_R$¼2kHz)hasrevealedasingleCasiteingypsumre dehydrated forms, is interground with PC clinker in small quantities to control the setting rate of the hydrating cement. During PC hydration, C_3A reacts with gypsum to form ettringite (AFt) which is subsequently converted (in part or in full) to monosulfoaluminate (AFm), starting a few hours after initial hydration [23]. In the absence of gypsum, C_3A would hydrate rapidly and setting could occur within minutes (i.e. ‘flash setting’).

The first application of NMR to any of the cement phases discussed in this article was undertaken by Pake, who in 1948 applied ^1H NMR to single crystals and powdered hydrates[74] of gypsum, demonstrating that the splitting observed in the spectrum(the

of gypsum (both natural abundance and enriched with ^{33}S) revealed a single S site in gypsum resonating at d_{iso} 328 ppm (Fig. 7) [59]. However, it was noted that acquisition of natural abundance ^{33}S MAS NMR spectra for PC samples is not practical due to extremely long acquisition times, and consequently, this tech- nique does not appear useful for field samples or those without isotopic enrichment.

1.1.2. Innovation in cements to reduce CO_2 emissions

Commercially produced cements contain a worldwide average of ~20%, but up to 95% in some cases, replacement of PC clinker by

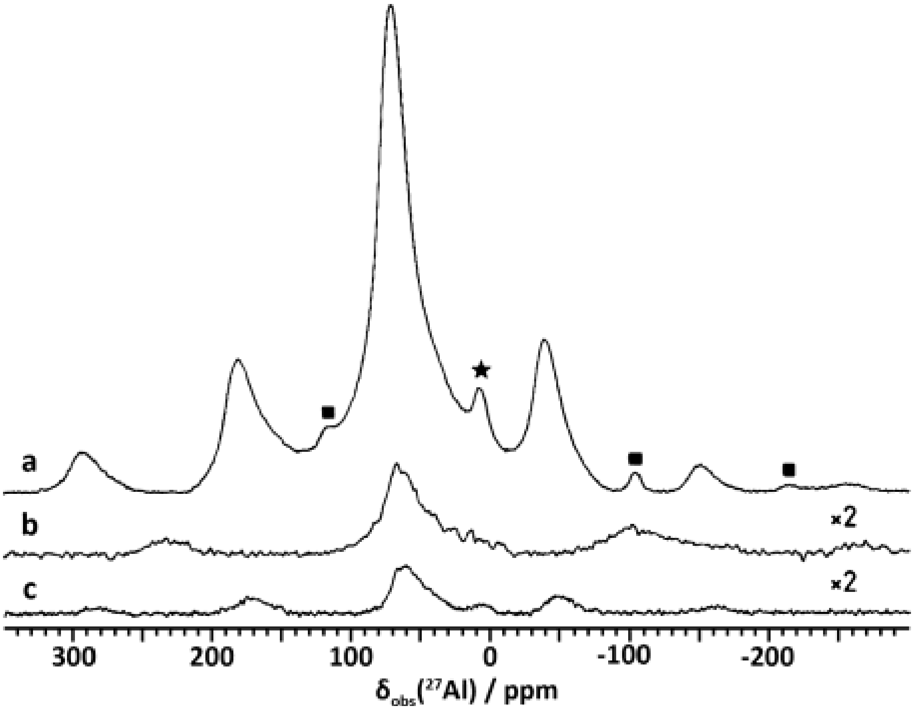

Fig. 6. **^{27}Al MAS NMR spectra** (9.4 T) for the synthetic ferrites (a) $Ca_2Al_{1.33}Fe_{0.67}O_5$, (b) Ca_2AlFeO_5 and (c) $Ca_2Al_{0.93}Fe_{1.07}O_5$, acquired using between 18,000 and 76,000 scans and spinning speeds of 11.6, 17.5 and 11.5 kHz, respectively. The spectra in (b) and (c) are shown on identical intensity scales, which correspond to a vertical expansion by a factor of two relative to the spectrum in (a). The asterisk and squares in (a) indicate the resonance from the central transition and spinning sidebands for the Al^{VI} site. Adapted from Skibsted et al. [55].

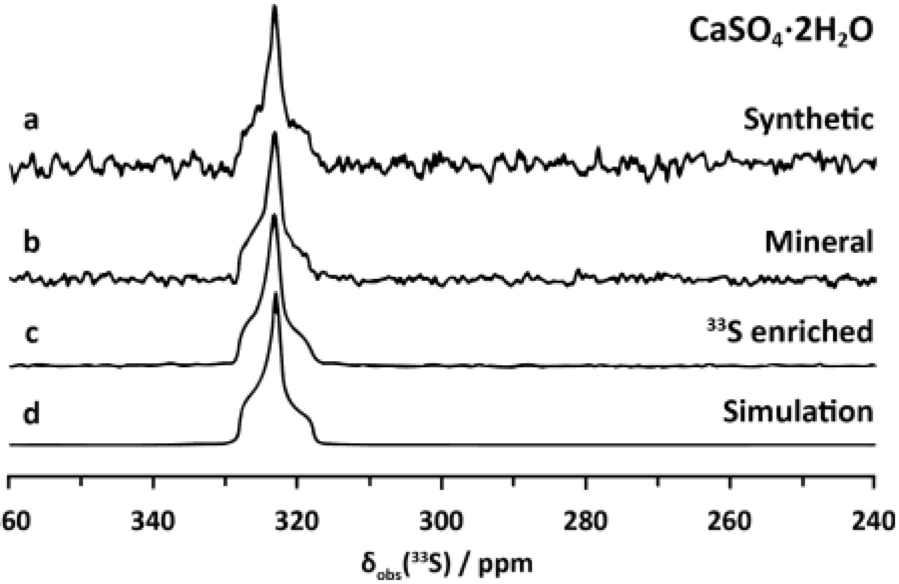

Fig. 7. ^{33}S MAS NMR spectra (19.6 T, n_R¼ 6e8 kHz) of (a) synthetic, (b) mineral and (c) ^{33}S-enriched gypsum ($CaSO_4$\$$2H_2O$) and (d) a second-order quadrupolar model of the central transition adjusted to the experimental data using DMFIT [60] and the NMR parameters reported in Ref. [59]. Adapted from d'Espinose de Lacaillerie et al. [59].

SCMs, while maintaining similar performance to existing cements [61]. The SCMs used are primarily fine limestone, ground granu- lated blast-furnace slags (GGBFSs), coal FAs and silica fume, with recent developments also focussing on ternary blends, e.g.those containingbothcalcinedclaysandgroundlimestone[61].Theuse of non-PC hydraulic clinkers such as CACs, CSA cements, belite- ye'elimite-ferriteclinkersandmagnesia-basedcements,aswellas non-clinkerebased cements such as AAMs, can also offer signifi- cant reductions in CO_2 emissions.

The materials used as SCMs are often crystallographically disordered, compositionally variable and multiphase in nature.SS NMR has consequently been instrumental in characterising the local structure of these materials, which are used both as SCMsin blendswithPCandalsoasprecursorsforalternativecements.The expected d_{obs}, $d_{iso}$and C_Q for different nuclei in the main phases foundincommonSCMsareshowninTable3anddiscussedinthe followingtext.

1.1.2.1. Supplementary cementitiousmaterials

1.1.2.1.1. Limestone. Limestone used as an SCM comprises pri- marilytheCaCO3polymorphscalciteandaragonite,aswellassome dolomite ($CaMg(CO_3)_2$). Calcite and aragonite, as well as the addi- tional $CaCO_3$ polymorph vaterite, are also generated within ce- mentsinserviceasthecalcium-richcementhydratephasesreact withatmosphericCO2inaprocessknownascarbonation[62].^{43}Ca MAS NMR analysis of calcite, aragonite and vaterite [40,41]has revealed substantially different chemical shifts and quadrupolar coupling constants for each polymorph, d_{iso}¼ 21.6, 12.6 and 26 ppm and C_Q1.39, 3.7 and 0.68 MHz for calcite, vaterite and aragonite, respectively. ^{13}C MAS NMR spectra of crystallo- graphically pure calcite and aragonite show single resonancesin each phase at approximately d_{iso}168 ppm and 170 ppm, respectively ¼ [63,64], while crystallographically pure vaterite ex- hibitstwo^{13}CMASNMRresonancesatd_{iso}170ppmand169ppm [65].

1.1.2.1.2. Blast furnace slag. GBFS GGBFS is generated as a sec- ondaryproductofpigironprod¼uctioninablastfurnace;theliquid silicate slag is tapped from the furnace, rapidly cooled by granulationandthengroundtoaparticlesizesimilartothatofPC. It can be blended with PC at replacement ratios as high as 95% under curr¼ent European standards (EN 197-1) [66]and is also aprimary precursor for low-CO_2 cements[4].

GGBFS consists primarily of depolymerised calcium silicate glasses, as well as small amounts of low-crystallinity phases within the melilite group [18,67e70]. The composition of GGBFS is dependentonthecharacteristicsoftheironproducedandoreused, aswellastheoperationaldetailsoftheblastfurnace[69],withCaO, Al_2O_3, SiO_2 and MgO contents typically varying between 35e42 wt %, 7e13 wt %, 34e36 wt % and 6e15 wt % respectively [67e69,71e73]. The Al in the depolymerised silicate glass ischarge balanced mainly by Ca^{2b}cations, with excess calcium cations contributing to the depolymerisation of the aluminosilicate framework [67e69]. As in most glasses, the reactivity of GGBFS is dependentonthelevelofdepolymerisationofthealuminosilicate framework [67,68]. ^{29}Si and ^{27}Al MAS NMR studies of GGBFS were interpretedasindicatingthatsiliconispresentmainlyasadimeric tetrahedral species, and Al is present in tetrahedral coordination [74]. Shimoda et al. [75e78]examined local structures in an amorphous synthetic slag using isotopic enrichment and multi- nuclear MAS and MQMAS NMR, probing ^{27}Al, ^{29}Si, ^{25}Mg, ^{17}O and ^{43}Ca nuclei (Fig. 8), and showed that the amorphous slag frame- work structure can be generally described as a depolymerised chain-like network of SiO_4 tetrahedra branched with AlO_4 tetrahedra,withoxygenatomsoccupyingstructurallyinequivalentsites (dependentontheirbondingnature),andmultisiteoccupancyof Mg and Ca ions. These observations are supported by molecular dynamics simulations [79]. The structure and chemicalcharacteristicsofGGBFSareanalogoustothoseofnumerousothercalcium aluminosilicateglasseswhichhavebeenexaminedindetailusing MAS NMR[80e86].

1.1.2.1.3. Coal FA. Coal FA, a by-product of thermoelectriccoal combustion, comprises primarily Al_2O_3 and SiO_2 within an assemblageofaluminosilicateglassyphases,withsomeadditional minor crystalline constituents, which can include quartz, mullite, ferrite spinels, calcium aluminates and others [87e89]. The characteristicsofcoalFAs(composition,extentofheterogeneityinthe glass and the local structure of each phase within the ash) vary widelybetweensourcesandasafunctionoftimeandaredependentonthetypeofcoalusedandthecombustionprocessthrough which it passes [90e92]. Mineral constituents in coal (mostly sili- cates and aluminosilicates) are melted as the coal is burned, become entrained in the flue gas as small droplets and are then cooledandcollectedasafinepowder,byelectrostaticprecipitators inthechimneystacksofthepowerstation.FAisblendedwithPCat replacementfractionsupto~50%inmanypartsoftheworldasits reactivesilicatefractioncanreactwithcalciumhydroxidethrough

Table 3
Coordination type and expected d_{obs}, $d_{iso}$and C_Q ranges for different nuclei in various supplementary cementitious materials.

Phase	Nucleus	Site	Coordination	d_{obs}(ppm)	d_{iso}(ppm)	C_Q (MHz)	Magneticfield(T)	Reference
Limestone	^{13}C	$CaCO_3$(calcite)	4	168	168	e	8.45,9.4	[63,64]
		$CaCO_3$(aragonite)	4	170	170	e	8.45,9.4	[63,64]
		$CaCO_3$ (vaterite) site1	4	169	169	e	8.45,9.4	[65]
		$CaCO_3$ (vaterite) site2	4	170	170	e	8.45,9.4	[65]
	^{43}Ca	$CaCO_3$(calcite)	6	e	21.6	1.39	8.45,11.75,21.1	[40,41]
		$CaCO_3$(aragonite)	9	e	12.6	3.7	8.45,14.1,18.8	[40,41]
		$CaCO_3$(vaterite)	e	e	— 26	0.68	8.45,11.75,21.1	[40,41]
Blast furnaceslag	^{17}O	Mg-NBO	2	e	55	2.2	16.4	[75]
		(Mg,Ca)-NBO	2	e	66	2.4	16.4	[75]
		Si-O-Al	2	e	68	3.3	16.4	[75]
		(Ca,Mg)-NBO	2	e	81	2.8	16.4	[75]
		(Ca,Mg)-NBO	2	e	92	2.7	16.4	[75]
		Ca-NBO	2	e	120	2.9	16.4	[75]
	^{25}Mg	$(MgO_6)_1$	6	e	17	2.7	16.4	[75]
		$(MgO_6)_2$	6	e	10	4.6	16.4	[75]
	$^{27}Al^a$	Al^{IV}	6	55e68	76	4.3	9.4,14.1, 16.4	[18,20,73,75,199,438]
	$^{29}Si^a$	Q^1	1	—73e—91	—73e—91	e	7.05, 9.4, 14.1, 16.4	[18,20,71,e73,75,199,206,438]
	^{43}Ca	Ca	e	25	e	e	16.4	[75]
Coalflyash	^{27}Al	Al^{IV}	4	40e60	e	e	14.1	[20,88,103e105]
		Al^{VI}	6	10to10	e	e	14.1	[20,88,103e105]
	^{29}Si	Q^4(mAl), m 0-4	4	— 90 to — 120	e	e	14.1	[20,88,103e105]
Metakaolin	^{27}Al	Al^{IV}	4	56e60	e	e	7.05,11.7	[107,110e113]
		Al^V	5	30e40	e	e	7.05,11.7	[107,110e113]
		Al^{VI}	6	0e10	e	e	7.05,11.7	[107,110e113]
	^{29}Si	Q^4(1Al)	4	—103	—103	e	11.7	[110]
Silicafume	^{29}Si	Q^4	4	—110	—110	e	7.1,9.4	[8,119,120]

[a] Thedistributionof ^{27}Al and ^{29}Si MASNMRresonancesforslagtypicallyspansbetween60and80ppm;forclarity,onlytheresonanceinthisdistributionexhibitingthe maximum intensity isprovided.

Table 3 Coordination type and expected d_{obs}, $d_{iso}$and C_Q ranges for different nuclei in various supplementary cementitious materials.

[a]Thedistributionof^{27}Aland^{29}SiMASNMRresonancesforslagtypicallyspansbetween60and80ppm;forclarity,onlytheresonanceinthisdistributionexhibitingthe maximum intensity isprovided.

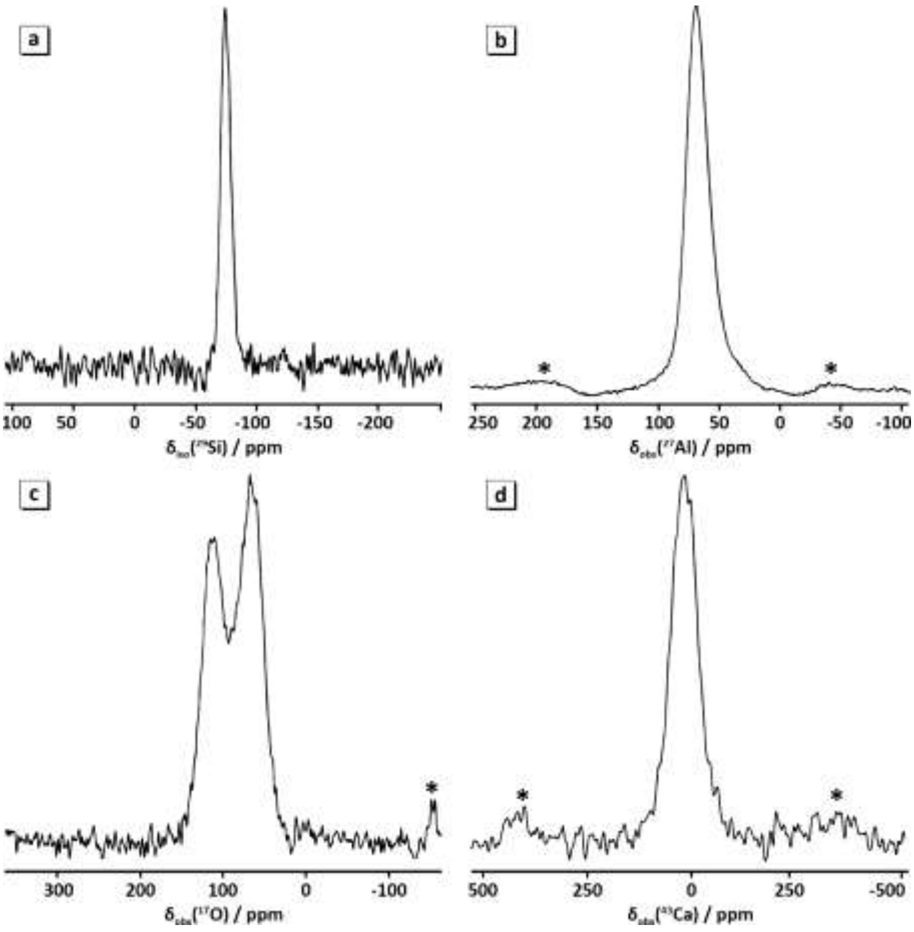

Fig. 8. (a) ^{29}Si, (b) ^{27}Al, (c) ^{17}O and (d) ^{43}Ca MAS NMR spectra (16.4 T, n_R¼ 18 kHz) of synthetic slag enriched in ^{17}O and ^{43}Ca. Adapted from Shimoda et al., 2008 [75]. *Spinning sidebands.

the 'pozzolanic' reaction (Ca(OH)$_2$ reactive silicates ⟶calcium silicate hydrate) to produce desirable binding phases, while reducing b theoverallenvironmentalimpactofthecementandalso valorising this ash which would otherwise be a problematic high- volume waste requiringlandfilling.

Phasesegregationuponcoolingoccursoverthemajorityofthe relevantcompositionalrangeforaluminosilicateglasses,andsoas the molten aluminosilicate materials are quenched rapidly asthe flue gas cools, the various phases formed are finely interspersed within the FA particles. The result is a highly heterogeneous ma- terial,asdifferentFAparticlescoolatdifferentratesandarederived from different mineral matter entrained in the coal [93], resulting in both inter- and intra-particle variation in local phase composi- tion [94]. As a result, FA reactivity when used as an SCM (i.e. blended with PC) or as a precursor for AAM varies significantly between ashes, and between phases within each particular ash [95e102].

ThecrystallinephasespresentinFAoccurinsmallamounts;in thelow-calciumasheswhichareconsideredmostdesirablefor blendingwithPC,thesephases(predominantlyquartz,mulliteand ferritespinels)arerelativelyunreactivewhencomparedtothe aluminosilicate glassy phase. Consequently, knowledge ofthe compositionoftheglassyphaseisimportantforcorrectformula- tion when designing cements containing FA, and SS MAS NMR (usedinconjunctionwithelectronmicroscopy)isakeytechnique thatcanprovidethisinformation,aslongastheashisnottoorich iniron.

^{29}Si and ^{27}Al MAS NMR studies of FA have shown that the vit- reous aluminosilicate phase contains a distribution of Q^4(mAl) Si species, with aluminium mainly present in poorly ordered tetra- hedral coordination, and also revealed the presence of a small amount of Al in octahedral coordination in mullite-like crystallites and glasses (Fig. 9) [20,88,103e105]. The quantity of each Q^4(mAl) Si species, as well as the distribution of Al^{IV} and Al^{VI} sites, is dependentonthelocalphasechemicalcomposition.^{17}OMASNMR studies have shown that alkali and alkali earth metals (mainly Na and K in FA) can act as network modifiers and form non-bridging oxygen sites if present in high enough concentrations in alumino- silicateglasses[106]whichareanalogoustotheglassyphaseinFA.

1.1.2.1.4. Metakaolin. Metakaolin is a layered aluminosilicate material which is used in cements as a pozzolanic additive andis producedbydehydroxylationofkaoliniteclayattemperaturesof 500ee800 °C [107,108]. It is frequently used as an SCM in blends withPC[61,109].^{29}Siand^{27}AlMASNMRstudiesofmetakaolinhave shownthatitconsistsofalternatingbuckledsilicateandaluminate layers [68], with silicon in tetrahedral coordination (Fig. 10a) [110]and aluminium in a distribution of tetrahedral, pentahedral and octahedral coordination (Fig. 10b and c) [107,110e113], with each siteexhibitingasignificantdegreeofasymmetryinthelocalelec- tric field gradient [113]. It has been suggested that metakaolin containsapproximatelyequalamountsoftetrahedral(Al^{IV}),octa- hedral(Al^{VI})andpentahedralAl(Al^{V})[111,114,115];howeverothers havefoundthroughcrystallographicanalysisthatsomeoftheAlis tricoordinated[116].

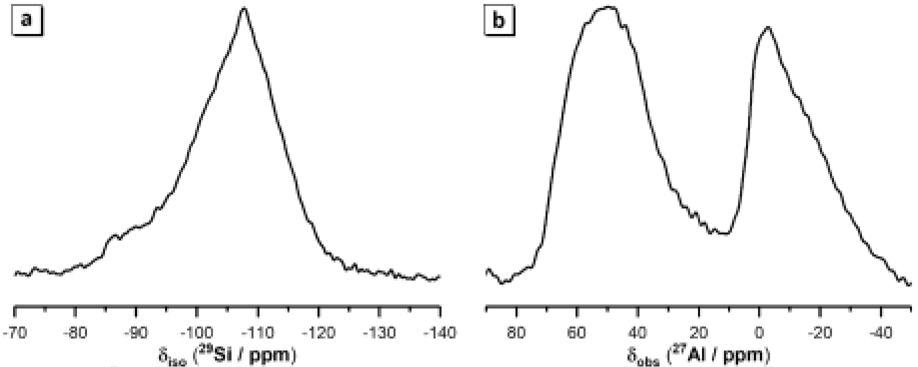

Fig. 9. (a) ^{29}Si and (b) ^{27}Al MAS NMR spectra (14.1 T, n_R¼ 10 kHz) of fly ash. Adapted from Bernal et al. [20]. Note that the spectra are significantly broadened by the presence of iron (5.2 wt% represented as Fe_2O_3 by X-ray fluorescence analysis) in the ash.

1.1.2.1.5. Silica fume. Silica fume is an amorphous form of SiO_2 with extremely small (tens of nm) particle size, produced as a byproductofsemiconductorSimanufacture[118].Itiscommonly blendedwithPCatrelativelylowlevels(upto10wt%)topromote strength development and durability. Published work examining silicafumeviaNMRisfocussedon^{29}SiMASNMRofPC-silicafume blends, which has shown that silica fume comprises a distribution of Si atoms in tetrahedral coordination (Q^4 units), connected by oxygen bridges [8,119,120]. Because silica fume is a pure silica source with a ^{29}Si resonance that is clearly distinct from that of eitherPCoranyofitshydrationproducts,itispossibletoaccurately determine the extent of reaction of silica fume within a blended cement through ^{29}Si MAS NMR; this is much more accurate for silica fume than for any other siliceous SCMs, as the other SCMs haveresonanceswhichatleastpartiallyoverlapthesignaldueto the PC or its reaction products[121].

1.1.2.2. Non-PC hydraulicclinkers

1.1.2.2.1. Calcium aluminate cement. CACs consist primarily of monocalciumaluminate($CaAl_2O_4$,CA),whichtypicallyaccountsfor40e60%wt.%ofcommercialCACs,alongwithsmallerquantitiesof $C_{12}A_7$ and CA_2[23,122]. While considerably more expensive than PC,thesecementsareintendedforuseinapplicationswhererapid hardening is useful and/or when resistance to thermal stresses, chemical(particularlyacid)attackandimpactorabrasionisdesired [122],e.g.refractoryconcretes,cementsandconcretesforeffluent treatment infrastructure, blended cements for marine applications and other demanding service environments. CACs are now restricted from bulk use in structural concrete due to a series of material failures in past decades [123], but this does not limit theiruseinspecialistapplications.Theexpectedd$_{obs}$,d$_{iso}$andC$_Q$for different nuclei in CAC are shown in Table 4 and discussed in the followingtext.

1.1.2.2.1.1. Monocalcium aluminate,CaAl$_2$O$_4$

Monocalciumaluminate,CA,istheprincipalreactivephase whichcontrolstheperformanceofCAC.ThecrystalstructureofCA consists of AlO$_4$ tetrahedra forming six-membered rings in a tridymite-like structure [124]. ^{27}Al MAS NMR isotropic chemical shiftsandquadrupolarcouplingparametersforeachofthesixnon-equivalentAlO$_4$tetrahedrainCAhavebeendeterminedby^{27}Al MASNMRatmultiplefields(7.1,9.4and11.7TinRefs.[50,52]and 18.8 T in Ref. [84]), giving 81.9 ppm ≤ d$_{iso}$≤ 83.8 ppmand

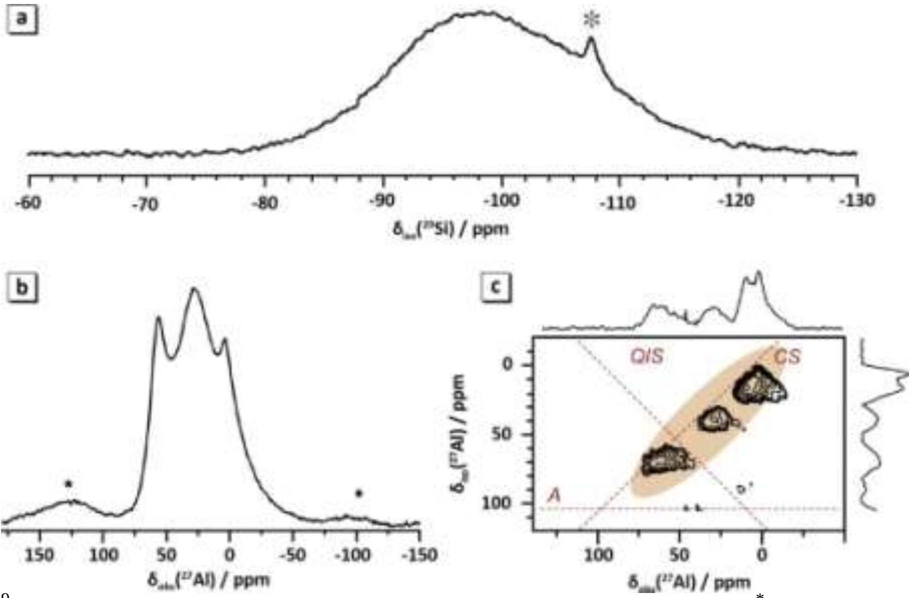

Fig. 10. (a) ^{29}Si MAS NMR (9.4 T, n$_R$6 kHz, adapted from Dai et al. [117]), where *indicates a resonance from ¼ a quartz impurity), (b) ^{27}Al MAS NMR (11.7 T, n$_R$15 kHz, adapted ¼ fromDuxsonetal.[111])and(c)^{27}Altriplequantum(3Q)MASNMR(11.7T,adaptedfromKoberaetal.[113])spectraofmetakaolin.

Table 4 Coordination, expected d$_{obs}$, d$_{iso}$and C$_Q$ for different nuclei in calcium aluminate cements.

Phase	Nucleus	Site	Coordination	d$_{obs}$(ppm)	d$_{iso}$(ppm)	C$_Q$ (MHz)	Magnetic field (T)	Reference
Monocalciumaluminate(CA)	^{27}Al	Al^{IV}	4	e	81.9	2.50	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	83.8	2.60	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	86.2	2.60	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	82.7	3.32	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	81.6	3.37	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	81.2	4.30	7.1, 9.4 and 11.7	[52]
Calciumdialuminate(CA$_2$)	^{27}Al	Al^{IV}	4	e	75.5	6.25	7.1, 9.4 and 11.7	[52]
		Al^{IV}	4	e	69.5	9.55	7.1, 9.4 and 11.7	[52]
Mayenite(C$_{12}$A$_7$)	^{27}Al	Al^{IV}	4	e	85.9	9.7	7.1, 9.4 and	[52]

					11.7	
Al^{IV}	4	e	80.2	3.8	7.1, 9.4 and 11.7	[52]

$\leq$2.5 $\leq$MHz C_Q 4.3 MHz by deconvolution of both the resonance from the central transition and the spinning sidebands. Variations inthegeometryoftheAlO_4tetrahedra(primarilydifferencesinAl- O bond lengths [124]) are primarily reflected in the ^{27}Al MAS NMR quadrupolar parameters rather than in chemical shifts. This work contrasted earlier assertions that the resonance from the central transition could be simulated with a single set of quadrupolarpa- rameters and two isotropic chemical shifts[51].

High-field (18.8 T) ^{17}O MAS NMR of CA has resolved eight res- onancesduetoOatomsinAl^{IV}-O-Al^{IV}linkages[84]withchemical shiftsbetween50and90ppmandC$_Q$valueslessthan2MHz,with the tricluster oxygen site exhibiting the largest C_Q (Fig. 11). This work demonstrated the benefits of utilising high fields which can narrow resonances sufficiently to resolve additional sites; eight of thetwelvecrystallographicallydistinct^{17}OsitesinCAwereableto beresolvedat18.8T[84],whileonlyfiveofthese^{17}Ositescouldbe resolved at 14.1 T[125].

1.1.2.2.1.2. Calcium dialuminate,$CaAl_4O_9$

Calcium dialuminate (CA_2) is found in relatively alumina-rich CAC clinkers that are used as refractory cements and is a slowly reacting cement constituent. Its structure comprises two tetrahe- drally coordinated Al atoms; one AlO_4 tetrahedron contains two tricoordinated oxygen atoms and the other contains a single tri- coordinatedoxygenatom,withtheremainingoxygenseachcon- nected to two Al atoms (Fig. 12) [126,127]. ^{27}Al MAS NMR data collected at multiple fields (7.1 T, n_R¼ 18.0 kHz; 9.4 T, n_R¼ 18.0 kHz and 11.7 T, n_R¼ 15.2 kHz) resolved single resonances for each tetrahedrally coordinated Al atom, with d_{iso}¼ 75.5 ppmand 69.5 ppm [52], and significant C_Q values (6.25 MHz and 9.55 MHz, respectively)duetoelectricfieldgradient(EFG)asymmetrycaused bythenearbytricoordinatedoxygens.EarlierworkbyMülleretal. [51]determinedsimilar$d_{iso}$and$C_Q$valuesforthesiteneighbouring twotricoordinatedoxygenscomparedtothoseobtainedbySkibs- tedetal.[52],butthosefortheAlO_4tetrahedracontainingasingle tricoordinated oxygen atom exhibited larger discrepancies,likely becauseoftheinsufficientresolutionandnotabledistortionofthe centraltransitioncausedbythemuchlowerspinningspeedutilised in those earlyexperiments.

^{17}O MAS NMR (18.8 T) resolved four distinct oxygen sites in CA, resonating between 40 and 72 ppm [84], including a tricluster oxygen atom with three Al^{IV} neighbours (i.e. an O(Al^{IV}) site) resonating at approximately 40.6 ppm and with quadrupolar pa- rameters C_Q¼ 2.5 and h ¼0.4. 3

1.1.2.2.1.3. Dodecacalcium hepta-aluminate (mayenite), $C_{12}A_7$

Mayenite, ($Ca_{12}Al_{14}O_{33}$, $C_{12}A_7$), is generally present as a minor phaseinmorecalcium-richCACclinkers.Ithasalsobeendiscussed in the past as a potential constituent of PC clinkers but is now considered unlikely to form under realistic commercial PC pro- duction conditions [23]. ^{27}Al MAS NMR at high spinning speed (17.8 kHz) resolved two distinct Al^{IV} sites within $C_{12}A_7$, with d_{iso}85.9 and 80.2 ppm, respectively, in close agreement with the known crystal structure [129]and other ^{27}Al MAS NMR in- vestigationsofthisphase[50,51].Differencesbetweenthe$d_{iso}$and,¼quadrupolar parameters (3.8 MHz and 9.7 MHz) of these two Al^{IV} sites arise due to distortions in one of the tetrahedra [50], which result in oxygen mobility [130]. Consequently (althoughmaybe

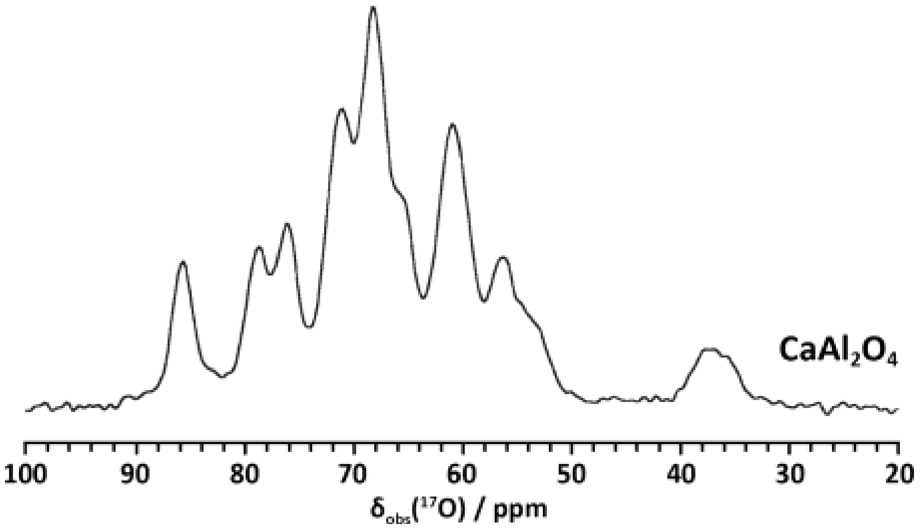

Fig. 11. ^{17}O MAS spectrum of $CaAl_2O_4$ at 18.8 T. Adapted from Stebbins et al. [84].

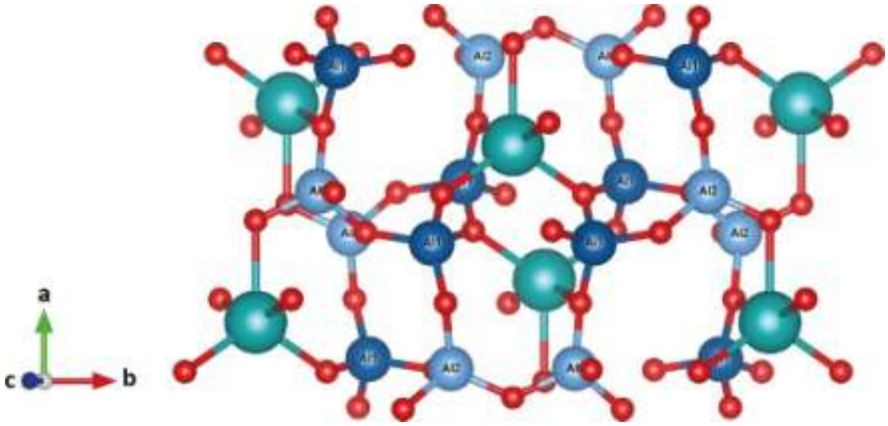

Fig. 12. Illustration of the local environments in the crystal structure of CA_2, based on information obtained from single-crystal diffraction data [127]. The two AlO_4 tetrahedra are denotedbyAl1(containingtwotricoordinatedoxygenatoms)andAl2(containingasingletricoordinatedoxygenatoms). Caatomsarerepresentedbycyanspheres,Alatomsare representedbydarkandlightbluespheres(denotingAl1andAl2,respectively)andOatomsarerepresentedbyredspheres. PreparedusingtheVESTAsoftwarepackage[128].

incidentallyinthecontextofcementchemistry),mayenitehasalso received significant attention as a high-performance oxygen ion conductor[131].

1.1.2.2.2. CSA cements. CSA cements comprise calcium sulfoa-luminate(ye'elimite,$Ca_4(AlO_2)_6SO_4$,$C_4A_3\$$)andotherclinkerpha- ses such as belite, C_4AF, ternesite ($C_5S_2\$$) and/or calcium aluminates and are typically blended with calcium sulphate to regulate the rate of their setting [61,132]. ^{27}Al MAS NMR in- vestigations of commercially produced CSA and synthetic ye'eli- mite showed nearly identical spectra, consisting of a single peak (with maximum intensity at approximately 68 ppm) with two high-field shoulders at approximately 60 and 52 ppm[34,133e135]. Evidence enabling discrimination of two of the eight non-equivalentAlsitespresentinthecrystalstructureofye'elimite (which is an aluminate analogue of the sodalite framework)[136]was identified in this broad peak [133]. Recent work by Skibsted etal.[137]reportedthatthe^{27}AlMASNMRspectralregionforAl^{IV} in ye'elimite (~80 50 ppm) is dominated by overlapping reso- nances from the eight different Al sites. Isotropic projections from^{27}AlMQMASNMRspectraobtainedbythesameauthorsrevealed four distinct resonances with very similar isotropic chemical shifts and quadrupole coupling parameters[34,138].

Ternesite, sometimes also called sulfospurrite, is a common minor constituent in modern CSA cements that is now being un- derstood to have some hydraulic activity but also forms withinPC kilns as an undesirable deposit on the refractory that reduces kiln performance. Ternesite exhibits a single, well-defined ^{29}Si MAS NMR resonance at 73.0 ppm [139], consistent with its crystal structure [140] in which double layers of silicate tetrahedra alter- nate with single layers of sulphate tetrahedra, with calcium 7- coordinated to oxygenatoms.

The application of NMR spectroscopy to the belite and tetra- calcium aluminate phases present in CSA cements has been dis- cussed in detail in sections 4.1.1.2 and 4.1.1.4, respectively.

1.1.2.2.3. Magnesia-based cements. Magnesium silicate hydrate (M-S-H)cementsaretypicallyformedfromasourceofmagnesium andasourceofhighlyreactivesilica,suchassilicafume[141].The magnesiumsourceistypicallylight-burnedMgO,andMg(OH)$_2$can also be used [142]. Although M-S-H was initi¼ally identified as a degradationproductinPCexposedtochemicallyaggressivecon- ditions [141,143], subsequent work has shown that M-S-H gels can also form a cementitious mass to generate high compressive strength [144e148]. These gels will be discussed in detail in section 4.2.6.

The^{25}MgMASNMRspectrumofpolycrystallineMgOexhibitsa single sharp resonance at d$_{iso}$26 ppm [149,150], while the ^{17}O MASNMRspectrumofthiscompoundenrichedwith^{17}Ocontainsa single sharp resonance at 47 ppm [150,151], consistent with octa- hedralMgO$_6$sites¼inthecubiccrystalstructureofthisphase,andin good agreement with first-principles calculations using DFT [152]. The ^{25}Mg MAS NMR spectrum of Mg(OH)$_2$ (brucite) exhibits a typical quadrupolar resonance with d$_{iso}$¼ 14.1 ppm and C$_Q$3.15 MHz [153]. Application of NMR spectroscopy to silica fume has been discussed in detail in section 4.1.2.1.5. Many other magnesia-based cements also exist, including those based onmagnesium carbonates, phosphates and oxysalts (both chloride and sulphate) [141]; MgO is the primary Mg source used in the production of most of thesecements.

4.2. MASNMRofkeycementitiousbindingphases

ThevastmajorityofSSMASNMRinvestigationsofcementitious binding phases, which are often complex, disordered silicates [17,18,20,21,104,154,155], have probed ^{29}Si and ^{27}Al nuclei, yielding information about the coordination states of Al and the connec- tivityofSi(viaoxygenbridgestoSiorAlortonon-bridgingoxygen sites).Thelownaturalabundanceof^{29}Si(4.7%)resultstheneedfor long data acquisition times for non-enriched samples, but the wealth of information obtainable from this technique has meant that it is nonetheless widely used[22].

4.2.1. Calcium silicate hydrategels

Calcium silicate hydrate (C-S-H) is the main product of PC hy- dration. It displays low crystallinity and variable composition and comprises(ingeneralterms)Q^{2}SichainsofvaryinglengthswithQ^1 Si sites at chain termination points, as shown by ^{29}Si MAS NMR [17,54,156,157]. These silicate chains are flanked by an interlayer containingconfinedH$_2$Omolecules,aqueouscationicspecies(Ca^{2þ}and H^{þ}in pure C-S-H, but with scope for substitution, particularly by alkali metals) and a calcium oxide sheet (Fig.13) [158,159]. The silicatechainsarearrangedina‘dreierketten’structure,basedonarepeatingchainunitofthreetetrahedralsites,two‘pairing’andone‘bridging’,wherevacanciesinthebridgingsitesleadtocharacter- istic chain lengths of (3n 1) for integer values of n [160]. The two pairing Si^{IV} units (Q^2(p)) are linked with the calcium oxide sheet [159]. The expected d$_{obs}$, d$_{iso}$and C$_Q$ for different nuclei in C-S-H, aluminium-substituted C-S-H (C-(A)-S-H) and alkali-and

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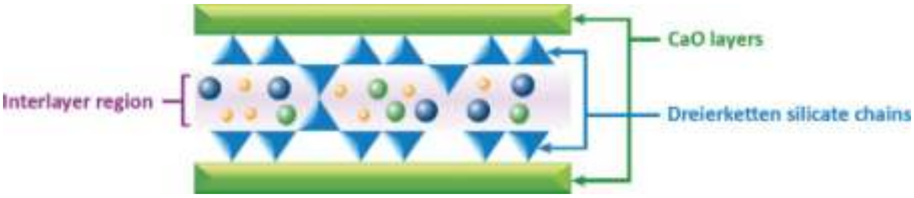

Fig.13. Schematicrepresentationofthestructuralfeaturesofcalcium-silicatehydrate(C-S-H)gels,adaptedfromProvisandBernal[4].TetrahedralSisitesandCaOlayersare shownbybluetrianglesandgreenrectangles,respectively.Circlesdenotevariousinterlayerspecies(waterorcations).

aluminium-substitutedC-S-H(C-(N,K)-A-S-H)areshowninTable5and discussed in the followingtext.

Numerous structural models for C-S-H have been proposed, including those based on jennite [161,162]and tobermorite [159,163], with recent SS NMR work probing both ^{29}Si [164e167]and ^{17}O [168] nuclei indicating strong structural similarity of C-S- H with a distorted tobermorite-like structure. ^{29}Si MAS NMR spectroscopyincombinationwithothertechniqueshasshownthat C-S-H forms a structural series which shows both continuity and diversity, with phase-pure C-S-H exhibiting Ca/Si ratios at least between 0.55 and 2.0 [167,169,170]. Recent work combining dy- namic nuclear polarisationeenhanced (^{29}Si)^{29}Si double quantum coherence(theIncredibleNaturalAbundanceDoubleQuantum Transfer Experiment, INADEQUATE) and (^{1}H)^{29}Si HETCOR MAS NMRanalysisapproaches,withatomisticmodelling,determineda series of atomic level structures for C-S-H based on defective tobermorite with Ca/Si ratios of 1.25e2.0 [170]. These models include a structurally important interlayer calcium site which bridgesQ^{1}silicatespeciesandisassociatedwithstronghydrogen bonding that stabilises the C-S-H, allowing high Ca/Si ratios to be reached in a phase-pureC-S-H.

Despiteexperimentalandanalyticaldifficultiesarisingfromthe lownaturalabundanceandlargequadrupolemomentof^{17}O,MAS NMR spectroscopy probing this nucleus has revealed valuablein- formationregardingtheroleofoxygenspeciesinC-S-Hgels.Cong et al. [43,168] used ^{17}O MAS NMR to study C-S-H in both synthetic gelsandhydratedb-C_2S,identifyingtwonon-bridgingoxygensites (linking a Si atom with two or three Ca^{2þ}ions, Si-<u>O</u>-Ca^{2þ}), a single bridging oxygen site (linking two Si atoms, Si-<u>O</u>-Si), oxygen atoms within surface hydroxyl groups linked with either Ca^{2þ}(Ca-OH) or framework Si atoms (Si-OH) and a single site corresponding to oxygenwithininterlayerH_2Omolecules.Theobservationsofthese ^{17}O MAS NMR resonances (and their relative intensities) support theRichardsonandGroves[159]defect-tobermoritemodelforC-S-H. Both non-bridging and bridging oxygen sites were observed to become less shielded with increasing Ca/Si ratio and decreasing polymerisation,indicatingadecreaseintheaverageSi-<u>O</u>-Sibond angles,consistentwithpreviousobservationsofadecreaseintheb axis of the pseudo-unit cell of C-S-H [167] at a higher Ca/Siratio.

As mentioned previously, natural abundance ^{43}CaMASNMRexperiments face inherent difficulties due to thelownaturalabundance(0.145%),highquadrupolemomentandsmallmagnetogyricratioofthisnucleus,Table1.Consequently,veryfewstudiesprobing ^{43}Ca in C-S-H via MAS NMR have beenperformed.Mou-drakovskietal.[38]used^{43}CaMASNMRtostudyaseriesofC-S-HgelsofdifferingCa/Siratios,aswellasC-S-Hproducedbyhydratingtriclinic C_3S, crystalline 11 Å tobermorite and portlandite(Fig.14).ThecoordinationstateofCa^{2þ}inC-S-Hiscomplexandnotyetfullyresolved, but the work of Richardson [171] indicatestheexpecta-tionthatthemostprobablecoordinationnumbersinplausibleC-S-Hstructuresare6or7dependingonthesitetypeandoccupancy.PairedSiO_4chainsites(Q^{2}(p))andbridgingSiO_4chainsites (Q^{2}(b)) in C-S-H in hydrated PC exhibit overlapping ^{29}SiMASNMRresonances[16,172]andthereforecannotberesolvedindividually

Table 5 Coordination states and expected d_{obs}, $d_{iso}$and C_Q values for different nuclei in C-S-H, C-(A)-S-H and C-(N,K)-(A)-S-H.

Nucleus	Site	Coordination	d_{obs}(ppm)	d_{iso}(ppm)	C_Q (MHz)	Magnetic field (T)	Reference
^1H	Ca-OH	1	1.0	e	e	7.04, 9.4, 11.7	[164,180e182, 310]
	Si-OH	1	4.5	e	e	7.04, 9.4, 11.7	[164,180e182, 310]
	H_2O	1	5.2			7.04, 9.4, 11.7	[164,180e182, 310]
^{17}O	Si-<u>O</u>-Ca	2	e	104e112	2.4	11.74	[43,168]
	Si-<u>O</u>-Si	2	e	60e82	4.5	11.74	[43,168,366]
	Si-<u>O</u>-Al	2		45.5	0.5	14.1	[366]
	Ca-OH	2	e	70	6.5e7.2	11.74	[43,168]
	Si-OH	2	e	4e10	4.4e5.6	11.74	[168]
	Interlayer H_2O	2	e	0	0	11.74	[43,168]
^{23}Na		e	—3	—3.7	1.0	14.10	[14,366]
	Interlayer Na^þ	4	66	e	e	9.4, 17.5	[190,193]
^{27}Al	q^2 charge balanced by interlayer Ca^{2þ}, Na^{þ}or H^{þ}cations						
	q^2 charge balanced by interlayer or surface Al^V or Al^{VI} cations	4	e	74.6	4.5	17.5	[193]
	q^3	4	65	60	4.1	9.4, 11.7, 14.1	[14,20,188,201, 366]
	Interlayer Al^{IV}	5	e	39.9	9.1	7.1, 9.39 and 17.5	[192e194]
^{29}Si	Q^1	4	—80 ±4	—80 ±4	e	7.1,9.4	[17,157]
	Q^{2a}	4	—85 ±4	—85 ±4	e	7.1,9.4	[16,17,172]
	Q^2(1Al)^a	4	—80 ± 4	—80 ± 4	e	9.4, 14.1	[20,21,199]
	Q^2(b)	4	—83.4	—83.4	e	9.4, 11.7, 17.5	[15,172,188,190,193]
	Q^2(p)	4	—85.3	—85.3	e	9.4	[15,172,188,190,193]
	Q^2(p)(1Al)	4	—80.5e—82.0	—80.5e—82.0	e	9.4	[15,172,188,190,193]
	Q^3		—95 ± 4	—95 ± 4	e	7.1, 9.4, 14.1	[20,188,199]
	Q^3(1Al)	4	—90 ± 4	—90 ± 4	e	9.4, 14.1	[20,21,199]
^{43}Ca	Ca-Osheet	6	10e45	e	e	21.14	[38]
	Interlayer Ca^{2þ}	~7	35e85	e	e	21.14	[38]

[a] Q^2 resonances in these studies are not specified as bridging or pairing tetrahedra.

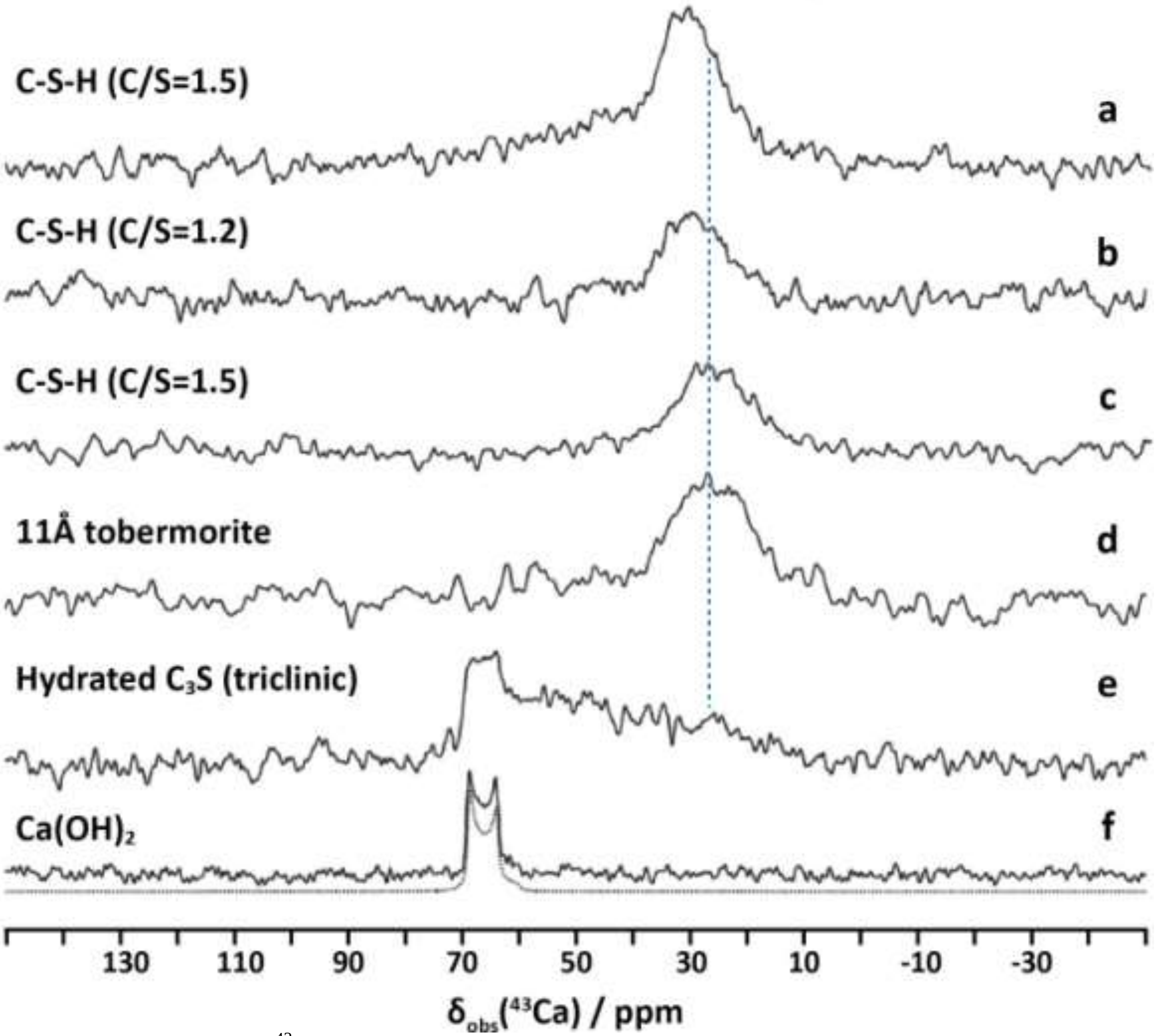

Fig. 14. Natural abundance ^{43}Ca MAS NMR spectra of (a) C-S-H (Ca/Si ¼ 1.5), (b) C-S-H (Ca/Si ¼ 1.2), (c) C-S-H (Ca/Si ¼ 1.2), (d) 11 Å tobermorite, (e) hydrated triclinic C_3S and (f) portlandite ($Ca(OH)_2$). The dotted line below the spectrum of $Ca(OH)_2$ is the simulation for the second-order quadrupolar interactions, and the blue vertical line indicates the centreband position of 11 Å tobermorite. Adapted from Moudrakovski et al. [38].

usingthistechnique;however,thesesitescanoftenberesolvedby their differing ^{29}Si MAS NMR chemical shifts in synthetic C-S-H gels (Fig. 15)[173e177].

^{43}CaMASNMRspectraofthesyntheticC-S-Hgelsshowbroad resonances at approximately 27e31 ppm, very similar tothespectrumof11Åtobermorite[178].AnincreasedCa/Siratioleadstodecreasedshieldingof^{43}Caions(i.e.resonances movetohigher chemicalshift),consistentwithadecreaseinthemeanchainlength (MCL) of the silicate, and also in good agreement with ^{29}Si MAS NMR data[167].

The^{43}CaMASNMRspectrumofhydratedtriclinicC_3Scontainsa

broadresonanceacrossachemicalshiftrangethatincludesthatof the main resonances from C-S-H gels with 0.8 Ca/Si1.5,indicatingthatCSHinhydrated≤cement≤systemsmaycontainvariouslocallydifferentchemicalcompositions[38].Combiningtheseobservationswithanalysisof^{43}CaMASNMRsignalintensityvs.delaytime,Moudrakovskietal.[38] proposedthatCaintheCa-Osheets resonatesat10ppm≤d_{obs}≤45ppmandinterlayer$Ca^{2þ}$ions

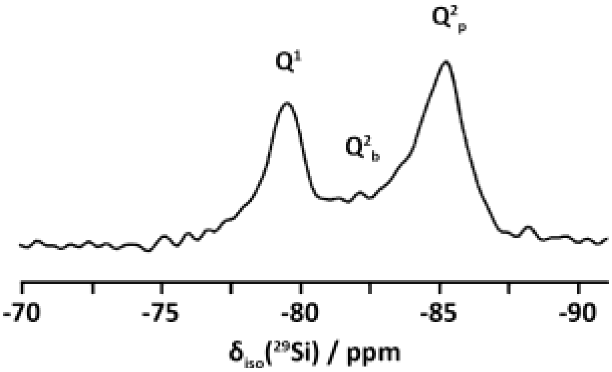

Fig. 15. ^{29}Si MAS NMR spectra of synthetic C-S-H (Ca/Si 1) showing resonances from ¼ pairing(Q^2(p))andbridging(Q^2(b))silicontetrahedra.AdaptedfromLothenbachetal., 2015[177].

tobermorite) may be resolved by differences in chemical shift

resonate at35≤ppm ≤d_{obs} 85 ppm at a field $B_0$of 21.14T.
BowersandKirkpatrick[179]usednaturalabundance^{43}CaMAS
d_{obs}
¼24ppmvs.—9ppm,at21.1T).Byusingthisapproach,itmay

NMRtodemonstratethatdespitebroadspectra,six-coordinateCa (aspresentinjennite)andseven-coordinateCa(aspresentin11Å

be possible to resolve the various locally different chemical com- positions (i.e. those with differing Ca/Si ratios) within C-S-H gels.

Despiteseverelinebroadeningin^{1}HMASNMRspectrawhich resultsfrom^{1}H-^{1}Hdipolarcouplings,thehighsensitivityof^{1}H,and thedevelopmentofmultipulsedecouplingsequenceswhichreduce linebroadening,haveledtotheapplicationofthistechniqueto studyprotonenvironmentsinC-S-H[157].However,theinforma- tionobtainablefrom^{1}HMASNMRspectraofC-S-Hisgenerally limited,duetothedistributionofprotonsacrossmanychemical sitesandthesmallchemicalshiftrange(approximately20ppm) over which ^{1}H in solid phases can resonate [157]. ^{1}H MAS and combined rotation and multiple pulse sequence (CRAMPS) NMR techniqueshavebeenusedtomonitorhydrationofsyntheticC_3S duringtheearlystagesofhydrationandatlongerintervalsupto28 daysofcuring[180e182].Itwasdemonstratedthatitispossibleto resolvearesonancefromprotonsinCa-OHatd_{obs}5.2fromthe overlapping broad resonances of protons in Si-OH andmobile water molecules at d_{obs}0.5e1 ppm ($B_0$7.04 and 9.44 T). Recently,quantitative^{29}SiMASand^{1}H-^{29}SiCPMASNMRexperi- ments have been used to ¼monitor hydration of ^{29}Si-enriched triclinicC_3Sin-situoverthefirst24hofreaction[183].Theseresults were correlated with isothermal calorimetry measurements to identi¼fy the ¼ previously unobserved phenomenon of partial passivationofthesurfaceofC_3Swhichdrivesdecelerationofthe reaction.

4.2.1.1. C-(A)-S-H gels. ^{29}Si MAS NMR has revealed important in- formation regarding incorporation of Al in CeSeH (i.e. forming C- (A)-S-H) in hydrated PC [16,57,167,172,184e186], PCeSCM blends[117,187,188]and2000-yearoldRomanseawaterharbourconcrete [189]. Application of ^{29}Si MAS NMR has allowed observation of resonancesfromQ^1,Q^{2}andQ^2(1Al)siteswhichmakeupthesilicate chainsintheC-(A)-S-Hgel[16,167,172].TheMCLcanbecalculated fromtheintensitiesofQ^n(mAl)resonancesobtainedfrom^{29}SiMAS NMRspectraldeconvolutionsbyusingequation(1),whilethede- greeofAl-Sisubstitutioninthetetrahedralchainscanbeobtained fromtheintensitiesoftheQ^1,Q^{2}andQ^2(1Al)resonances(equation (2)),asdemonstratedbyRichardsonetal.[184,185]andAndersen et al.[186].

region. The role of alkalis in these structures will be discussed further in section 4.2.1.2.

^{27}Al MAS NMR experiments, particularly at high field (B$_0$14.1 T), have proven particularly useful in gaining detailed structuralinformationregardingtheroleofA≤inC-(A)-S-H,inboth synthetic gels and hydrated PC. ^{27}Al MAS NMR experiments at multiplefields(e.g.Fig.16)haveshowninsyntheticgelsandhy- drated PC that the Al^{IV} bridging sites in C-(A)-S-H are charge balanced by interlayer Ca^{2þ}, Na^{þ}or H^{þ}ions (d$_{obs}$¼ 66 ppm, B$_0$¼17.5T)[190,193]orbyinterlayerorsurfaceAl^{V}orAl^{VI}ions
(d$_{iso}$¼ 74.6 ppm, C$_Q$¼ 4.5 MHz) [193]. Al^V sites in theC-(A)-S-H
interlayer can potentially substitute for Ca^{2þ}ions (d$_{iso}$¼ 39.9 ppm, C$_Q$5.1 MHz) [192e194]. From these studies, and others, it was concludedthatAldoesnotentertheCa-Osheet¼northepairing tetrahedral sites in the silicate chains of C-(A)-S-H [22,172,184,190,193,194].

4.2.1.2. C-(N,K)-A-S-H gels. Synthesis of C-(A)-S-H gels in an envi- ronmentcontaininghighalkalimetalconcentrations,suchasinthe
productionofAAMsfromGGBFS[154,160],yieldsaC-(N,K)-A-S- H gel. This is structurally similar to C-S-H, but with Alsubstitution

MCL$_{aluminosilicate}$ ¼

1 2 32
2
1 1 Q 2
2

(1)

Al^{IV}
Si ¼
^{1}Q^{2}ð1AlÞ
Σ Q ^{1}þ Q ^{2}þ Q ^{2}ð1AlÞ Σ (2)

Using^{29}SiMASNMR,Andersenetal.[186]showedthattheAl^{IV}/ Si ratio in C-(A)-S-H in hydrated white PC is dependent on the availabilityofdissolvedAl^{3þ}ions,butindependentofhydration time.Richardsonetal.[190]used^{29}SiMASNMRtodeterminethat AlpreferentiallysubstitutesintoQ^2(b)sitesandthattheMCLof aluminosilicate chains in C-(A)-S-H is dependent on both the availabilityofAl^{3þ}ionsinsolutionandhydrationtime,findingsthat weresubsequentlyconfirmedbyAndersenetal.[184,186].Ithas alsobeensuggestedthatAlmaysubstituteforSiinsmallamounts in pairing sites [188,191,192], although this isthermodynamically disfavouredcomparedtothebridgingsites[191].

Al readily substitutes for Si in the bridging position in alumi- nosilicate chains in C-(A)-S-H up to a ratio of Al/Si 0.1, while at higherAl/Siratios,ka≤toiteand/orstr€atlingitearealsoformed[15]. Analysis by ^{29}Si and ^{27}Al MAS NMR has shown that the Al^{IV}/Si ratio in C-(A)-S-H in hydrated PC can be increased significantly bythe presence of alkali cations (Na^{þ}or K^þ) [16]via a mechanism in which the charge deficit introduced by Al-Si substitution is balancedbyadsorptionorbondingofalkalicationsintheinterlayer

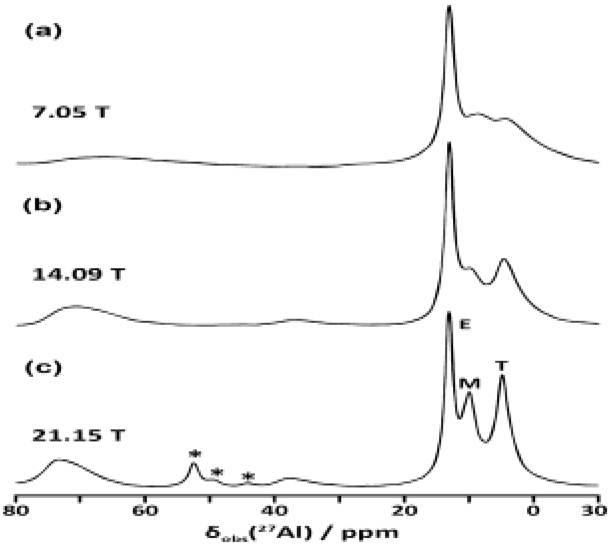

Fig. 16. ^{27}Al MAS NMR spectra of the central transition for white PC hydrated for 12 weeksrecordedat(a)7.05T(n_R¼13.0kHz),(b)14.09T(n_R¼13.0kHz)and(c)21.15T (n_R¼ 9.5 kHz), using ^{1}H decoupling. Spinning sidebands are indicated by *. The resonancesfromthecentraltransitionofettringite,monosulphateandthethirdaluminate hydrate phase (described in section 4.2.8) are indicated by E, M and T, respectively. Adapted from Andersen et al. [172].

inbridgingtetrahedralsitesandintheinterlayerasdiscussedinthe precedingsection,andwithchargebalancingbyalkalications($Na^þ$and $K^þ$) in the gel interlayer, with additional alkalis able to sorb to the gel surfaces [74,154,185,195e197]. The structural characteristics ofthiscomplexgelhavebeenelucidatedlargelybytheapplication of SS NMR; representative spectra of alkali-activated GGBFS are showninFig.17,whileaschematicrepresentationoftheC-(N,K)-A-

$MCL_{crosslinked}$ ¼

Al^{IV}

——

Σ

Σ

$4Q^1þQ^2þQ^2ð1AlÞþQ^3þ2Q^3ð1AlÞ$

$Q^{\ 1}$

$Q^{\ 3}ð1AlÞ$

Σ

(3)

S-HgelstructureisshowninFig.18.AswithC-S-H,theC-(N,K)-A- þ
S-Hgelexhibitsadisorderedstructuresimilartothatofcrosslinked

Si ¼
$\Sigma_{Q}1$
Q^2 $Q^{2}1Al$
(4)
Q^3 2Q1Al
þ ð Þ þ þ ð þ

and/or non-crosslinked, structurally imperfect tobermorite [17,74,195]. As noted previously, there is a strong thermodynamic preference for Al substitution into bridging tetrahedra in the C- (N,K)-A-S-H gel [198].

^{29}Si MAS NMR has provided extensive evidence of thepres- ence of cross-linked (Q^3 and/or Q^3(1Al)) sites within2000-year- oldRomanseawaterharbourconcrete[189],alkali-activatedslag cements [20,188,199]and synthetic analogues[14,15,200e203]. The structure of these C-(N,K)-A-S-H gels was described by Myers et al. [195]as a mixture of cross-linked and non-cross- elinked silicate chains within a defect-tobermorite structure, with crosslinking occurring through partially Al-substituted bridging sites [21,188,193,196]. Using this model and ^{29}Si MAS NMRspectraldeconvolutions,itispossibletocalculatetheMCL and Al^{IV}/Si ratio of the cross-linked C-(N)-A-S-H gel structures usingthefollowingequations(3)and(4)[195].

Crosslinking occurs predominantly in low-Ca C-(N,K)-A-S-H gels,and^{29}Siand^{27}AlMASNMRresultsindicatethattheextentof crosslinking is promoted by increased overall Al content up to a ratioofapproximately1Alper6chainsites[21,204].However,the extentofcrosslinkinghasbeenobservedtodecreaseovertimeas thereactionproceeds,attributedtothelowerAl-bindingcapacity ofcrosslinkedgelcomponents[21].Studyoflaboratorysynthesised gels has shown that the amount of Al which is able to substitute into the C-(N,K)-A-S-H gel appears to be limited toapproximately Al/Si ≤ 0.2, with C-(N,K)-A-S-H gel compositions typically within the range 0.5 <Ca/(Al þ Si) ≤ 1 and 0 <Al/Si ≤ 0.2 [15,192,193,205]. The MCL of the aluminosilicate chains is often 7e10 tetrahedra for C-(N,K)-A-S-H gels produced by sodium silicate or potassium sili- cateactivationofslag[18,206];however,thisdependsontheCa/ (Al þ Si)ratio.

Therearecontlictingreportsregardingthemechanismofalkali uptake and relationship with Al content of the C-(N,K)-A-S-H gel. ^{23}Na MAS NMR analysis has indicated that alkali cations exist in two distinct environments within C-(N,K)-A-S-H gels [164,207,208]; the spectra show a sharp resonance at d_{obs}¼ —7.6 ppm (7.05 T, n_R¼ 10 kHz) [164] attributed to either a

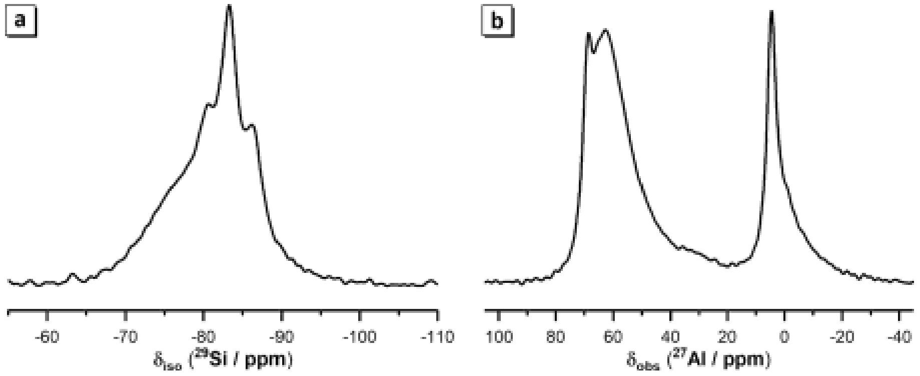

Fig. 17. (a) ^{29}Si MAS NMR spectra (14.1 T, n_R¼ 10 kHz) and (b) ^{27}Al MAS NMR spectra (14.1 T, n_R¼ 10 kHz) of an alkali-activated slag cured for 7 days. Adapted from Bernal et al., 2013[20].

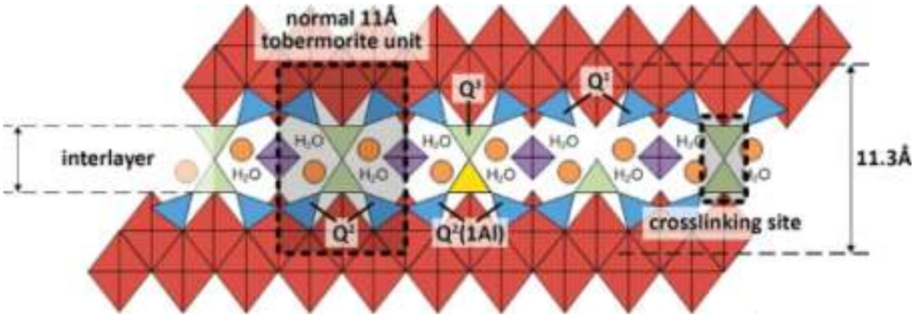

Fig.18.SchematicrepresentationofthestructuralfeaturesofC-(N)-A-S-Hgels,adaptedfromMyersetal.[195].PairedandbridgingSitetrahedraarerepresentedbyblueandgreen triangles,respectively,andintralayercalcium,charge-balancingalkalicationsandinterlayerprotonsand/orcalciumcationsbythereddiamonds,orangecirclesandpurplesquares, respectively.TheyellowtriangleindicatesAlsubstitutingforSiinabridgingtetrahedralsite.

highly symmetric bound alkali site or mobile alkali ions. An addi- tional broad resonance at approximately d_{obs}¼ —3 ppm (14.1 T, n_R10 kHz) [14] to d_{obs}10 ppm (7.05 T, n_R10 kHz) [164]attributed to low-mobility Na within a disordered phase, possibly sorbed to the surface of the nanostructuredgel.

Some observations suggest a direct correlation between Al content and alkali uptake [16,209], supported by an intuitive rationaleofincreasedAlcontentdrivinganincreaseinalkaliuptake tochargebalancetheAlO$^{—}$ $_4$tetrahedra.However,otherobservations suggest an inverse proportionality between Al content and alkali uptake[210]orthatAlcontentdoesnotaffectalkaliuptakeinthe C-(N,K)-A-S-H gel [204,211,212]. Alkali uptake in C-A-S-H gels has been observed to be promoted by lower Ca/Si ratios and higher alkali concentration [213], presumably because lower levels of charge balancing $Ca^{2þ}$increase the requirement for charge balancing by alkali cations. It has been suggested that charge balancing alkali cations in the C-(N,K)-A-S-H gel interlayerinduce additional structural disorder by reducing the periodicity of the interlayerandreducingtheregularityofthestackingofthelayers due to differences in ionic size, indicating that incorporation of alkalis into C-(N,K)-A-S-H has a significant effect on gel nano- structure [13,214]. However, when ^{29}Si MAS NMR was used to investigate compositionesolubilityestructure relationships in syntheticC-(N,K)-A-S-Hgels[204],itappearedthattheC-(N,K)-A- S-H gel structure was actually becoming more (rather than less) crystalline in the presence of alkalis, with both Na and K incorpo- rated into its interlayer space [213]. The additional structural dis- order was observed in C-(N,K)-A-S-H gel systems with lower pH (~13 [214]) than those in which greater ordering was observed (pH >13.5 [204,213]); it is, therefore, likely to be the higher pH of the more alkali-rich systems which drives rearrangement to more crystalline structures, rather than the alkali cations themselves. Elevated temperature also drives increased polymerisation, ordering and phase purity of synthetic C-(A)-S-H gel structures [215].

4.2.1.3. Other guest ions in C-S-H gels (C-S-(X)-H). In addition to $Al^{3þ}$and$Na^{þ}$,otherionicspeciesmaybeincorporatedintotheC-S- H gel structure. Owing to the 100% natural abundance and high magnetogyric ratio of ^{19}F and ^{31}P, SS NMR experiments probing thesenucleihavebeenveryusefulinelucidatingthestructuralsites in which these atoms can exist within the C-S-H gel. ^{19}F MAS NMR has shown that interlayer hydroxyl species may be substituted by F$^{—}$[36,216]. Further analysis of F$^{—}$speciation in C-S-Hby
^{19}F-^{29}Si-^{19}Fforthandback(FB)CPMASNMR(amodifieddoubleCP
MAS NMR experiment which transfers polarisation forth and back between high- and low-g spin nuclei [217]) confirmed the afore- mentionedobservationofF$^{—}$forOH$^{—}$substitutionintheinterlayer, aswellasrevealingasecondFsiteattributedtoF$^{—}$ionsassociated with CaO_6 layers of a jennite-like part of the C-S-H gel[216,217].

4 PO$^{3—}$ions can also be incorporated in the interlayer of C-S-H gels.^{31}PMASNMRanalysisofinterlayerPO$^{3—}$ ionsexhibitsabroad resonance which has the same chemical shift as the PO$^{3—}$ions in alite,somustbeselectivelydetectedusing^{1}H-^{31}PCPMASNMRto enable it to be distinguished from the signal of remnant clinker in an incompletely hydrated paste[32,34].

4.2.1.4. C-S-H e X interactions. SS NMR has also found applications investigating sorption of ions onto cement binding gels[173,218,219]. Static ^{35}Cl NMR experiments and measurement of^{35}Cl spinelattice relaxation time constants (T_1) and spinespin relaxationtimeconstants(T_2)wereusedtostudychloridesorption onto jennite (used as a model C-S-H phase) suspended in lime- saturated NaCl solution [218]. This was intended to simulate hy- dratedPCinserviceinmarineenvironmentsandshowedthat chlorideundergoesrapidexchangebetweensurfaceandbulkso- lution sites and exists predominantly in a hydrated, solution-like chemicalenvironment.

High-resolution ^{29}Si, ^{23}Na and ^{133}Cs MAS NMR was used to study the interaction of sodium and caesium chloride salts with synthetic C-S-H [173]; this work is of particular relevance to the nuclear industry as some caesium isotopes are important fission product radionuclides. This work showed that both $Na^þ$and $Cs^þ$cluster in hydrated C-S-H, while in dry C-S-H $Na^þ$, formed outer- sphere complexes (adsorbed with their hydration sphere) and $Cs^þ$formedinnerspherecomplexes(bounddirectlytothesurface with no intervening watermolecules).

^{1}H,^{13}C,^{27}Aland^{29}SiMASNMRhasbeenusedtoinvestigatethe structureoftheCaCO$_3$polymorphscalcite,aragoniteandvaterite [65,220],aswellasK_2CO_3[220],andtheirformationinhydratedPC (i.e.throughcarbonation)andinteractionwithPChydratephases [221].ThisworkshowedthatcarbonationofhydratedPCoccursin twostages:gradualdecalcificationofC-S-Hbyremovalofcalcium from the interlayer and defect sites until Ca/Si 0.67 is reached (corresponding to ¼ infinite silicate chains in a tobermorite-like structure), followed by further decalcification by removal of cal- cium from the gel layers and formation of a layered or three- dimensional silicate gel. The amount of carbonates formed is directlyproportionaltotheCa/Siratioofthegel.Theapplicationof ^{13}CMASand^{1}H-^{13}CPMASNMRalsoenabledcarbonateanionsin hydrous and anhydrous phases to be distinguished[65,220].

SS MAS NMR has been used to examine the interaction between a variety of organic additives and PC during hydration. Natural abundance ^{43}Ca and ^{13}C MAS NMR was used to examine the interaction between a poly(ethylene-vinyl acetate) (PEVAc) admixture,addedtocementmortarstoimprovefracturetoughness andimpermeability,andhydratedwhitePCoverthefirst3months ofhydration.PEVAchydrolysisoccursimmediatelyasPChydration commences,andinducesminorstructuralchangestothehydrated PC, primarily formation of a small amount of amorphous, low- coordinated calcium sites [222]. This demonstrates that PEVAc admixtures do not induce significant structural changes to hy- dratedwhitePCandarethereforeunlikelytobedetrimentaltothe performance of these cements. Conversely, ^{1}H-^{13}C CP MAS NMR showed that when mixed with 15 wt % poly (vinyl alcohol) and 10 wt % mineral antiblocking agents, PEVAc does not hydrolysein the alkaline solution of hydrating PC and was adsorbed to the surface of the cement binder [223,224]. This is particularly impor- tant in the context of both chemical and physical durability as PEVAc and other similar latex dispersions are commonly used as waterproofing agents and sealants incements.

4.2.2. Alkali aluminosilicate ((N,K)-A-S-H)gels

SS MAS NMR studies of hydrous alkali aluminosilicate in the contextofcementsarerelativelyrecentcomparedtothoseexam- ining C-S-H and related phases in hydrated PC, with the first application probing ^{29}Si speciation in alkali hydroxide/silicate activated metakaolin cements in 1988 [115,225,226]. Since these first experiments, SS MAS NMR analysis probing ^{29}Si and ^{27}Al has playedapivotalroleindeterminingthestructureofalkali-activated aluminosilicatecements,includingthoseknownas‘geopolymers’ [68,227]. The main reaction product of alkali activation of alumi- nosilicateprecursorshasbeenrevealedtobeathree-dimensional hydrous alkali aluminosilicate gel, consisting of highly crosslinked (predominantlyq^4/Q^4)AlO_4^-andSiO_4tetrahedralinkedviabridging oxygen atoms, with a small number of terminal hydroxyl groups forming Q^3 sites. This structure is consistent across alkali alumi- nosilicate gels produced from reagent chemicals [228e231], calcined clays such as metakaolin [104,232e235], and aluminosilicate-rich waste materials such as coalFA

Table 6

Coordination, expected d_{obs}, $d_{iso}$and C_Q for different nuclei in (N,K)-A-S-H.

Nucleus	Site	Coordination	d_{obs}(ppm	d_{iso}(ppm)	C_Q (MHz)	Magnetic field (T)	Reference

			)				
^{17}O	Si-O-Si	2	e	39.0	1.26	14.10	[252,255,371]
	Si-O-Al	2	e	33.0	1.00	14.10	[252,255,371]
	H_2O	2	e	—9.8	0.55	14.10	[252,255,371]
27 ^{23}Na$_4$	ChargebalancingNa^{þ}	6	—3to—5	—1.26 to—2.60	0.70e1.41	11.7,14.10	[112,255]
Al	q	4	58e60	61.0e66.3	1.4e1.9	14.10	[112,255,256]
^{29}Si	Q^4	4	—110 ±6ppm	—110 ±6ppm	e	7.5,9.4, 14.1	[112,236,237,250,251]
	Q^4(1Al)	4	—102 ±5ppm	—102± 5ppm	e	7.5, 9.4, 14.1	[112,236,237,250,251]
	Q^4(2Al)	4	—95 ±4ppm	—95± 4ppm	e	7.5, 9.4, 14.1	[112,236,237,250,251]
	Q^4(3Al)	4	—90 ±4ppm	—90± 4ppm	e	7.5, 9.4, 14.1	[112,236,237,250,251]
	Q^4(4Al)	4	—86 ±4ppm	—86± 4ppm	e	7.5, 9.4, 14.1	[112,236,237,250,251]

[104,105,236e238]. This three-dimensional alkali aluminosilicate gelframeworkisoftendescribedasahighlycrosslinked,disordered pseudo-zeolitic structure [13,239e243], and nanocrystallinezeolite phaseshavebeenobservedaslocalisedregionsoforderingwithin the broadly less-ordered gel framework [239]. The short-range ordering has been observed by ^{29}Si and ^{27}Al MAS NMR spectros- copy [20,112,244,245]together with X-ray and neutron pair dis- tribution function analysis [246e249] to extend to approximately 2e3 nearest neighbour shells. The expected d_{obs}, $d_{iso}$and C_Q for different nuclei in (N,K)-A-S-H gels are shown in Table 6 and dis- cussed in the followingtext.

^{27}Aland^{29}SiMASNMRhaveshownthatAlandSiarepresentin tetrahedral coordination, with Si existing in Q^4(mAl) environments wheremisbetween1and4dependingontheAl/Siratioofthegel, andAlpredominantlyinq^4(4Si)environmentsduetotheenergetic penalty associated with Al-O-Al bonding (Fig. 19) [236,237,250,251]. Reports of the observation of Al^{IV}-O-Al^{IV} bonds withinalkali-activatedmetakaolinhavealsobeenmadeformate- rials with Si/Al close to 1.0 using ^{17}O triple quantum (3Q) MAS NMR [252], despite these bonds being significantly less thermodynami- cally favourable than Al^{IV}-O-Si^{IV} bonds, as entropic effects cause some violation of strict Si-Al ordering [250]. The negative charge associatedwithAlsubstitutionforSiisbalancedbyhydratedalkali cations(Fig.20)andisthoughttobedelocalisedacrossalloxygen atoms,withtheoxygenatomclosesttothechargebalancingalkali cation carrying the majority of this delocalised negative charge [114,252]. The (N,K)-A-S-H gel nanostructure is significantly influ- encedbykineticlimitationsonsilicaandaluminareleasefromsolid precursors if these are used [253,254]and consequently evolves overtimeasthereactionprocessproceeds[237].Schematicrep- resentations of the disordered N-A-S-H gel based on recent struc- tural descriptions are shown in Fig.20.

^{23}Na MAS NMR analysis of metakaolin-derived (N,K)-A-S-H gels (Fig. 21a) [111,257] identified a single disordered Na environment withinthegelattributedtoNa^{þ}inacharge-balancingrole,whose chemicalshift(d_{obs}¼—3.5to—6ppm,B_0¼11.7T)wasindependent oftheSi/Alratio.AqueousNa^{þ}(d_{obs}¼0ppm,B_0¼11.7T)wasalso observedwithintheporesolution,charge-balancingAl$(OH)^{-}_{4(aq)}$species, in samples with Si/Al ≤ 1.40. Charge balancing Na^{þ}sites resonating at a similar frequency (d_{obs}4 ppm, $B_0$14.1 T) have alsobeenobservedinalkalialuminosilicategelsproducedfrom synthetic precursors [228]. ¼These sites ¼resonate at similar fre- quencies to those of hydrated Na^{þ}ions in hydrothermally altered glass [258], providing opportunities to draw structural parallels to betterunderstandthenatureofthecementitiousgels.K^{þ}ionsin alkalialuminosilicategelsbalancethechargedeficitfromAl^{3þ}⇔

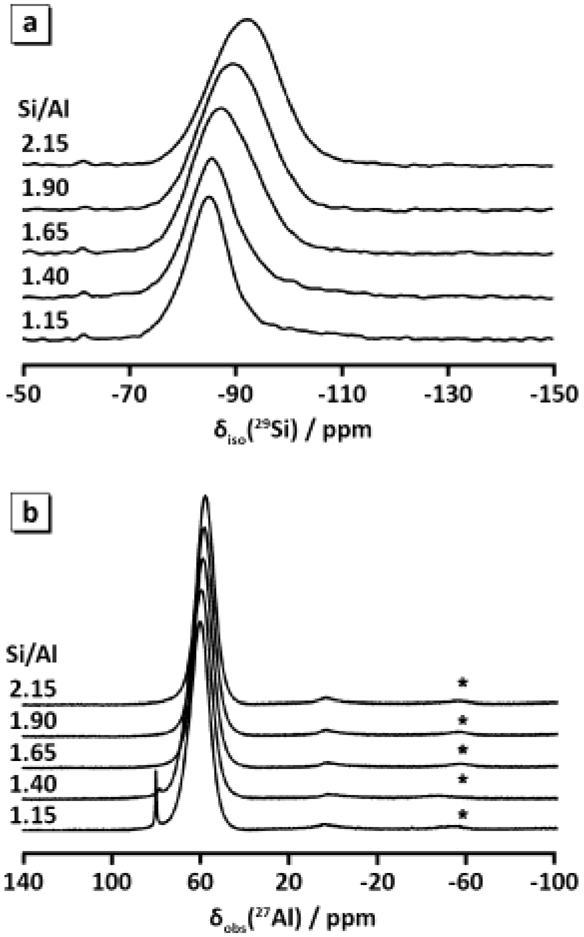

Fig. 19. (a) ^{29}Si MAS NMR spectra (7.05 T, n_R¼ 5 kHz) and (b) ^{27}Al MAS NMR spectra (11.7 T, n_R¼ 15 kHz) of N-A-S-H gels produced by reacting metakaolin with a sodium silicate solution (with Si/Al ratios as marked) and curing for 14 days. Adapted from Duxson et al.[111,112].

Related to this selectivity for larger alkali cations, SS NMR has also been applied to study the interaction of caesium with alkali aluminosilicate gels, to investigate their applicability in nuclear waste immobilisation applications. ^{133}Cs MAS NMR spectra of Cs- doped alkali aluminosilicate gels produced from metakaolin and sodiumsilicateexhibitasinglebroadasymmetricresonanceat approximately d¼ 0 ppm (B ¼ 9.4 T) [261] consistent with that

$Si^{4þ}$substitutionwithinthealuminosilicateframeworkandbehave þ
obs 0

similarlytocharge-balancing$Na^{þ}$ions[259,260](Fig.21b),andthe incorporation of $K^{þ}$ions into the (N,K)-A-S-H gel is preferential compared to $Na^{þ}$ions when both arepresent.
of Cs bound tightly to an aluminosilicate surface (such as that in kaolinite and illite [208,262]), strengthening the appeal of alkali aluminosilicate gels in nuclear waste immobilisation applications.

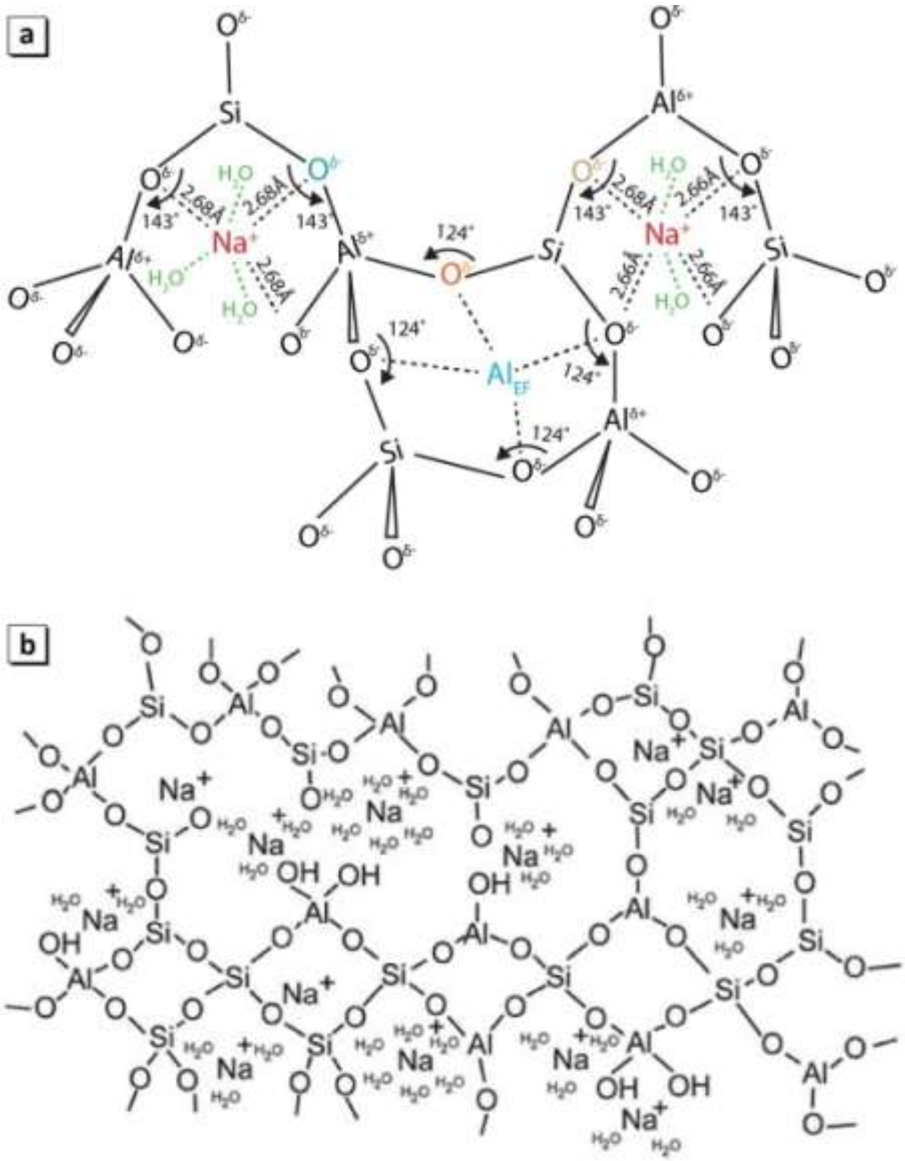

Fig. 20. (a) Schematic representation of a section of N-A-S-H gel adapted from Walkley et al. [255] showing charge-balancing sodium, charge-balancing extra-framework Al (Al_{EF}), bridgingoxygenchargebalancedby$Na^{þ}$andassociatedwiththreeH_2Omolecules,bridgingoxygenchargebalancedbyAl$_{EF}$andbridgingoxygenchargebalancedbyNaþand associatedwithtwoH_2Omoleculesand(b)schematicrepresentationofasectionofN-A-S-HgeladaptedfromRowlesetal.[256].

4.2.3. Multiphase C-(N,K)-A-S-H/(N,K)-A-S-Hgels

Coexistence of C-(N,K)-A-S-H and (N,K)-A-S-H gel frameworks occursinmanycementsystems,includingAAMsbasedonblendsof high-calcium and low-calcium reactive precursors [20,263e265](Fig. 22), and the gels appear to be stable in coexistence [14,20,231,266e268], as long as there is sufficient alkali content [117,266,269e271]. SS NMR has proven particularly useful in determiningthestructureandcompositionofthesecoexistinggel frameworks which are otherwise very difficult to discriminate. Owing to the structural similarity between these two gels, many resonancesintheirSSNMRspectraoverlap;however,thesecanbe distinguished and attributed appropriately with sound chemical reasoningandspectraldeconvolution(discussedinsection4.3).

Using ^{27}Al and ^{29}Si MAS NMR, the growth of an N-A-S-H gel within alkali silicate-PC-dehydroxylated halloysite blends was shown to preferentially consume available Si within the system through rapid reactions involving the initially dissolved silica[270].

^{27}Al and ^{29}Si MAS NMR of AAMs based on GGBFS-metakaolin blends [266], combined with high-resolution X-ray diffractometry [272,273], has also shown significant phase coexistence in these binders, although the dissolution of Ca^{2b}from the GGBFS, and subsequentreactionmechanisms,dependsonbothalkalinityand precursorchemistry.

Structural analysis via ^{29}Si, ^{1}H-^{29}Si CP MAS, ^{27}Al, ^{23}Na and ^{1}H MAS NMR of multiphase C-(N)-A-S-H and N-A-S-H gel frameworks within synthetic AAMs has also revealed strong dependence of reaction kinetics, gel composition and structure on precursor composition [14]. This work demonstrated that increased Cacon- tent of the solid precursor (or blend of precursors) promotes the formationoflow-Al,high-CaC-(N)-A-S-HwithlowerMCL,whereas increased Al content promotes Al inclusion and reduced cross- linking within C-(N)-A-S-H, formation of an additional N-A-S-H gel and increased presence of secondary alumina-rich hydrate phases.

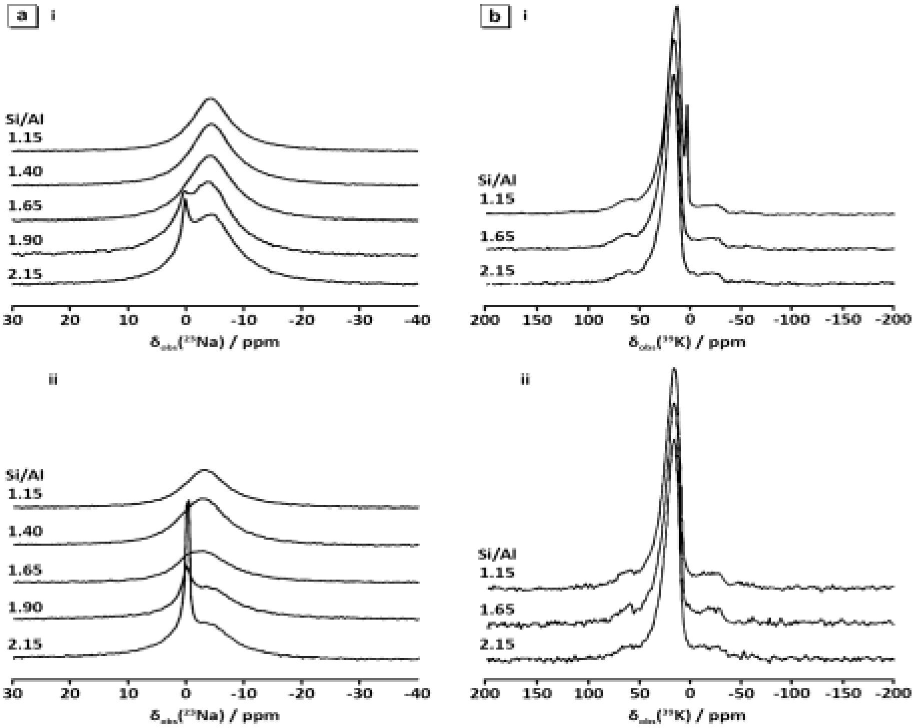

Fig.21.(a)^{23}NaMASNMRspectraof(i)N-A-S-Hand(ii)N-K-A-S-HgelswithSi/Alratiosasmarkedand(b)^{39}KMASNMRspectraof(i)K-A-S-Hand(ii)N-K-A-S-HgelswithSi/Al ratiosasmarked.Allmixed-alkaligelshaveNa:K¼1:1onamolarbasis,andallgelswereproducedbyalkaliactivationofmetakaolin.AdaptedfromDuxsonetal.[111]andDuxson et al.[259].

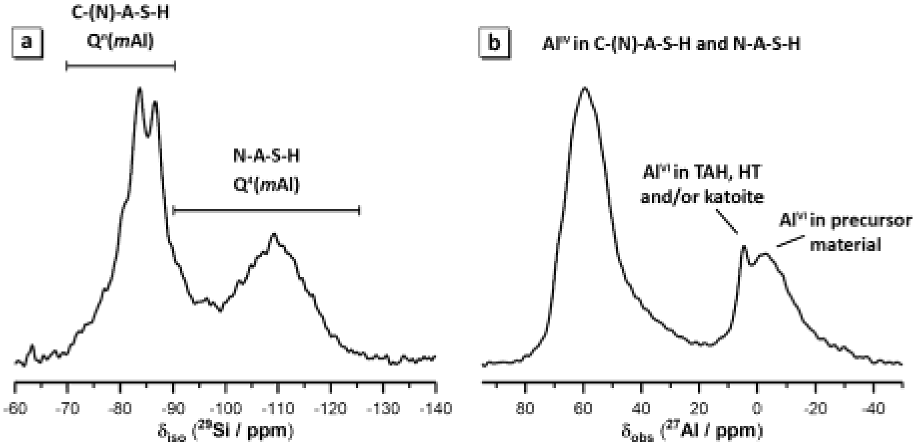

Fig.22.(a)^{29}SiMASNMRspectra(14.1T,n$_R$¼10kHz)and(b)^{27}AlMASNMRspectra(14.1T,n$_R$¼10kHz)ofanalkali-activated50%wt.slag/50%wt.flyashblendcuredfor14days, withcoexistenceofC-(N)-A-S-Hand(N,K)-A-S-Hgels.The^{29}SiMASNMRspectrumshownin(a)exhibitsresonancesduetoQ^n(mAl)(1≤n≤3andm ≤n)speciesinC-(N)-A-S-H andQ^4(mAl)(m≤n)inN-A-S-H,whilethe^{27}AlMASNMRspectrumshownin(b)exhibitsresonancesduetoAl^{IV}speciesinbothC-(N)-A-S-HandN-A-S-H,aswellasAl^{VI}speciesin unreactedprecursormaterialandtheadditionalreactionproductshydrotalcite(HT),thethirdaluminatehydrate(TAH)andkatoite.AdaptedfromBernaletal.[20].

4.2.4. HydratedCACs

CACs comprising primarily CA (with smaller quantities of CA_2 and/or $C_{12}A_7$) hydrate to form mixtures of the microcrystalline metastablephasesCAH_{10}andC_2AH_8,followedbyconversiontothe stablephasesC_3AH_6andamorphousAH_3[122,274].Theexpected d$_{obs}$,d$_{iso}$andC$_Q$for^{27}AlinhydratedCACsareshowninTable7and discussed in the following text; information for other nuclei within these phases is not available in the openliterature.

Skibsted et al. [52] used ^{27}Al MAS NMR to identify overlapping resonancesattributedtooctahedralAlenvironmentsinthestable

Table 7

Coordination, expected d$_{obs}$, d$_{iso}$and C$_Q$ for different nuclei in hydrated calcium aluminate cements.

Nucleus	Site	Coordination	d$_{iso}$(ppm)	C$_Q$ (MHz)	Magnetic field (T)	Reference
^{27}Al	Al inCAH_{10}	6	10.2	2.4	7.1, 9.4 and 11.7	[52]
	Al in C_2AH_8	6	10.3	1.2	7.1, 9.4 and 11.7	[50,276]
	Al in C_3AH_6	6	12.36	0.71	7.1, 9.4 and 11.7	[52]
	Al^{VI} in AH	6	10.4	1.97	7.1, 9.4 and 11.7	[52]
	Al^{IV} in AH	6	11.5	4.45	7.1, 9.4 and 11.7	[52]

C_3AH_6 (d$_{iso}$¼ 12.3 ppm, C$_Q$¼ 0.705 MHz) and amorphous AH_3 (d$_{obs}$¼8ppmatB$_0$¼9.4T)phasesinCAChydratedfor28days;the

isotropicchemicalshiftforC_3AH_6wasdeterminedviasimulationof the spinning sidebands associated with this phase. Analysis of synthetic CAH_{10} at multiple fields exhibited a broad resonance in the octahedral Al region of the ^{27}Al MAS NMR spectrum and allowed determination of d_{iso}¼ 10.2 ppm and
≤1.9 ≤ MHz C_Q 2.6 MHz for this site. These results are consistent withpreviousdataacquiredatlowerfield[275].Subsequentwork
examinedCAChydratephasesusing^{27}AlMAS[50,276]andMQMAS
[276]NMR, enabling determination of d_{iso}¼ 10.3 ppm and
C_Q¼ 1.2 MHz for the octahedral Al site in the metastable C_2AH_8 phase and d_{iso}11.9 ppm and C_Q 4.3 MHz for the ¼amorphous AH_3 p¼hase.
Becauseofthecleardistinctionbetween Alenvironmentsin
hydrated(Al^{VI})andanhydrous(Al^{VI})CAC,thedegreeofhydrationof this cement may be readily determined from ^{27}Al MAS NMR
quantifiedcorrectly;thisisnotalwaysthecaseduetothepresence of ‘NMR invisible’ Al species (see section4.3).
^{27}Al, ^{31}P and ^{1}H-^{31}P CP MAS NMR has also been used to show thatmodificationofCACbyadditionofphosphatepreventstheloss of material performance which is caused by the conversion from themetastablecalciumaluminatehydratestostableC_3AH_6inhy- drated CAC. Instead, phosphate modification yields an apparently stableamorphouscalciumaluminophosphategelcomprisingboth Al^{IV}andAl^{VI}sites[277].Inthesematerials,phosphorusispresentin hydrous environments with varying, but mostly low, degrees of crosslinking.

4.2.5. Hydrated CSAcements

Ye'elimite (C A $) hydrates in the presence of calcium sulphate
4 3
(Fig. 23) [44,50,51]. This, however, relies on the assumption thatall Alresonanceswithinthe^{27}AlMASNMRspectraareobservableand
(C$, added as gypsum or in dehydrated forms) to form ettringite (‘AFt’, Ca Al (SO) (OH) $26H O, see section 4.2.8.2), calcium
6 2 43 12 2

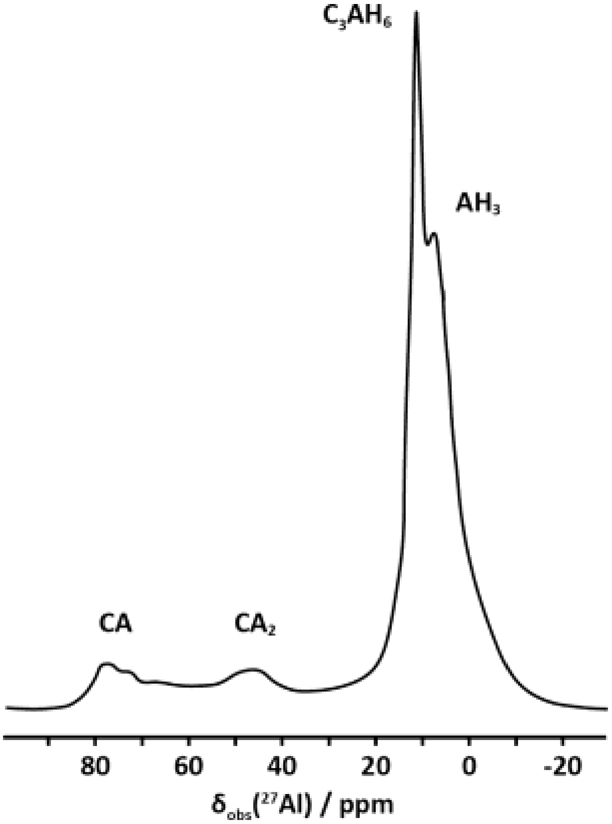

Fig. 23. ^{27}Al MAS NMR spectrum (9.4 T, n ¼ 13.1 kHz) of a calcium aluminate cement

monosulfoaluminate hydrate (‘monosulphate AFm’, $3CaO\$(Al,Fe)_2O_3\$CaSO_4\$nH_2O$, see section 4.2.8.3) and microcrystallinealuminiumhydroxide($Al(OH)_3$),withtheproportionofeach phasedependentonthe$C_4A_3\$/C\$$ratio[278].Thepresenceofbelite along with these phases in a CSA cement, which is common because of the prohibitive cost of Si-free Al sources for cement manufacture,resultsintheformation ofsträtlingite($2CaO\$SiO_2\$Al_2O_3\$8H_2O$;asilica-substitutedAFmphase,seesection 4.2.8.3) and/or C-S-H as additional reaction products. As mentionedinsection4.1.2.2.2,CSAclinkerscanalsocontain$C_5S_2\$$ (ternesite), which hydrates along with alumina-bearing clinker constituentstoformsträtlingite[279,280].MostcommercialCSAcements also contain C_4AF (section 4.1.1.4) as the economically viablealuminasourcesusedincementmanufacturealsocontain significant quantities of Fe; this will typically hydrate (in both CSA and PC cements) more slowly than the hydraulic aluminate phases and yields Fe-substituted forms of many of the same AFm and AFt hydrate phases[281e283].

SSNMRstudiesofhydratedCSA(syntheticandcommercial)and CSA/PCblendshaveshownnarrow^{27}AlMASNMRresonancesfor octahedral Al in ettringite and monosulphate at approximately d_{obs}¼13ppmand10.2ppm(B_0¼14.1T),respectively,aswellasa broad low-intensity resonance at d_{obs}¼ 9 ppm at the same field which is attributed to $Al(OH)_3$[133e135,284,285], consistent with the resonances of pure phases in synthetic samples, section 4.2.4[52,286,287].AswithCAC,thecleardistinctionbetweenAlenvironments in hydrated (Al^{VI}) and anhydrous (Al^{VI}) CSA allows the degreeofhydrationofaluminium-containingphasestobereadily determined from ^{27}Al MAS NMR. This has shown that aluminium- containing phases generally react to form hydrates within 24 h [133e135,284]. Monitoring the degree of hydration in CSA/PC blendsissignificantlymoredifficultduetothepresenceofAl^{IV}sites inC_3AandC-(A)-S-Hphases[133],aswellasthepresenceofFe

Rhydratedfor28days.Thedegreeofhydration,estimatedbyintegrationoftheAl^{IV} Al^{VI} spectral regions, is 86 ± 1%. Adapted from Skibsted et al.[52].

and
which can severely dampen and shift the NMR signal of these nuclei[10];however,itismadepossiblebyspectraldeconvolution using appropriate models and constraints (see section4.3).

4.2.6. Magnesium silicate hydrate (M-S-H)gels

Magnesium silicate hydrate (M-S-H) cements are commonly producedfromMgOandsilicafumeviahydrothermalorambient- temperature processes [288e292], and generally comprise atalc- like or serpentine-like phase [141,293], although there remains somedebatearoundthemostappropriatestructuralmodelforM- S-H. ^{29}Si MAS NMR spectra of M-S-H cements exhibit as many as five distinct ^{29}Si MAS NMR resonances, attributed to Q^1, Q^2, two Q^3 and Q^4 sites [142,146,292,294e298]. The major component of the ^{29}Si MAS NMR spectra is a Q^3 resonance at approximately d_{iso}93 ppm and the Q^1 and Q^2 resonances are typically broad [142,292], indicating the disordered nature of the gel. These envi- ronmentshavebeenattributedtoSisiteswithinadisorderedphase structurally similar to talc ($Mg_3Si_4O_{10}(OH)_2$) [296]and/or serpentine-group minerals (polymorphs of $Mg_3(Si_2O_5)(OH)_4$, such as chrysotile, lizardite and antigorite) [142], with Mg/Si ratios ranging from 0.57 to 1.3[291,293,298].

Alkaline earth aluminosilicate hydrate gel (magnesium alumi- nosilicate hydrate, M-A-S-H) has also been reported [299]. MAS NMR of these materials synthesised from sepiolite ($Mg_4Si_6O_{15}(OH)_2\$6H_2O$) and chrysotile ($Mg_3(Si_2O_5)(OH)_4$) resolved similar Q^{329}Si MAS NMR resonances at 90 ppm, and tetrahedral Mg sites from ^{25}Mg MAS NMR.

4.2.7. Magnesium potassium phosphate cements(MKPC)

Magnesium potassium phosphate cement (MKPC) is aclinker- free acidebase cement which reacts to form struvite-K ($MgKPO_4\$6H_2O$) as a crystalline main strength-giving phase; this phase is structurally analogous to the natural mineral struvite, $NH_4MgPO_4\$6H_2O$, but without requiring the presence of ammo- nium cations for its synthesis [141,300e302]. Application of SS NMR to investigate structural and phase evolution in MKPC is relatively recent, with the most extensive analysis probing ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P and ^{39}K nuclei in MKPC blended with FA and with GGBFS [303]. Struvite-K exhibits a ^{31}P resonance at d_{obs}6.2 ppm [303], which correlates well with the chemical shift of struvite, d_{obs}6.1 ppm [304]. A shoulder on this resonance at d_{obs}4 ppm was observed in MKPC/FA blends (but not MKPC/GGBFS blends)andwassuggestedtoresultfromthepresenceofadisor- dered and/or partially substituted struvite-K phase. The predomi- nant crystalline struvite-K phase exhibits ^{25}Mg and ^{39}K resonances at d_{iso}¼ —1.0 ppm (C_Q¼ 3.8 MHz) and d_{iso}¼ —73.1 ppm (C_Q 2.2 MHz), consistent with previous observations for synthetic versions of this phase [305,306]. An amorphous orthophosphate environmentwasalsoidentified,whichhasnointimateinteraction with hydrogen and no measurable Al interactions[303].

4.2.8. Additional reactionproducts

Manyadditionalreactionproductsarealsoformedalongwith the main silicate gels during hydration of the cements discussed previously and will be discussed in turn in this section. These additional reaction products are often intimately mixed with the dominant silicate gel frameworks [7,231] and can significantly in- fluence the phase evolution and nanostructural development of thesehydratephases.Theexpectedd_{obs},$d_{iso}$and$C_Q$fordifferent nucleiintheadditionalreactionproductsobservedinhydratedPC, CAC,CSAandmagnesia-basedcements,aswellascementsbased onalkalimetaloralkaliearthaluminosilicatechemistry,areshown in Table8.

4.2.8.1. Portlandite.

Portlandite ($CaOH_2$), also called slaked lime, is acommonreactionproductinhydratedPCandisalsopresentasareactionproductorremnantprecursorinpozzolanicorslagbasedbindersactivatedwithlime.Ingeneral,portlanditeformswhentheCa/Siratioissignificantlyhigherthancanbeaccommodatedby C-

S-H or related phases [307]. It consists of layers of octahedrally coordinated Ca bound to oxygen atoms in tetrahedralcoordination [23] with hydrogen occupying a single crystallographic site. It isa keyparticipantinlongertermphaseevolutionofC-(A)-S-Hgelsin blended PC cements via the pozzolanic reaction [308]. High-field natural abundance ^{43}Ca MAS NMR of portlandite [179]and ^{43}Ca MAS NMR of isotopically enriched portlandite at multiplefields [309]have shown a single quadrupolar resonance centred at approximately d$_{obs}$50e60 ppm (7.04, 11.7 and 21.1 T) corre- s¼pondingtoasingleCaenvironmentwhereCaisoctahedrallyco- ordinated by six hydroxyl groups. Correspondingly, ^{1}H MAS NMR spectra of portlandite exhibit a single resonance at d$_{iso}$0.7 ppm from the single Ca-O-H site [180,182,310]. Chloride sorption onto portlanditeinportlanditesuspensionshasbeenstudiedusingstatic ^{35}Cl NMR experiments and measurement¼ of ^{35}Cl spinelattice relaxation time constants (T$_1$) and spinespin relaxation time con- stants (T$_2$) [218]. Chloride on portlandite exists predominantly in a hydrated, solution-like chemical environment and is rapidly exchanged between the surface and bulk solution. Portlandite quantification in hydrated cements by NMR is not usually attempted,asneither^{43}Canor^{17}Onucleiareparticularlystraight- forward to use in such studies, and other techniques such asther- mogravimetry and X-ray diffraction (XRD) can give reliable quantitativeresultsforthisphasemuchfasterandlessexpensively.

4.2.8.2. ‘Aluminate ferrite trisulphate’etype phases. Ettringite is the archetypal ‘aluminate ferrite trisulphate’ (AFt) phase, with a columnarhydrousCSAstructureandaveryhighwatercontent(up to 32 water molecules per formula unit) [311]. Ettringite forms rapidlyintheearlieststagesofhydrationofPC,asC$_3$Areactswith gypsum, or equivalently through hydration of ye'elimite with excess gypsum in CSA cements. Early ^{27}Al MAS NMR experiments (9.4 T) examining ettringite displayed a resonance at d$_{iso}$13 ppm thatappearedcharacteristicofasingleoctahedrallycoordinated AlO$_6$ site [52], which contrasted with the then-proposed crystal structureofettringitewhichcontainedtwodistinctoctahedralAlO$_6$ sites [312]. Recent work using ultraehigh-field (22.3 T) ^{27}Al MAS and MQ¼MAS NMR (Fig. 24) has in fact been able to resolve two distinct octahedrally coordinated AlO$_6$ sites in syntheticettringite [137], consistent with the now well-accepted crystal structure solved by Moore and Taylor [312]. The two AlO$_6$ sites resonate at d$_{iso}$¼ 13.08 and 13.51 ppm and are highly symmetric, displaying verysmallquadrupolarcouplingparametersofC$_Q$0.391MHzand ¼ 0.337 MHz, respectively. The high symmetry and very similar isotropicchemicalshiftsoftheseresonancesareduetoverysmall variations in Al-O bond lengths between sites, consistent with high-resolution powder XRD [313], single-crystal XRD and DFT calculations [311]. As a consequence of the small distinction in isotropic chemical shift values, these resonances remained unre- solved for more than two decades in ^{27}Al MAS NMR spectra ac- quired at lower fields [22,52,57,117,135,186,187,314,315]. This demonstrates the importance of acquiring high-field spectra for quadrupolar nuclei in complex phases, even where crystallinity is high (as in the case of ettringite) and for relatively ‘accessible’ nuclei such as^{27}Al.

Natural abundance ^{43}Ca MAS NMR analysis of ettringite also resolved only a single ^{43}Ca resonance (d$_{obs}$8 ppm) [40] despite the existence of two Ca sites in the crystal structure; this can be attributed to the structu¼ral similarity between the two Ca sites in ettringite and the poor signal-to-noise ratio of the spectrum resultinginpoorlydefinedoverlappingquadrupolarlineshapesfor each site. High-field natural abundance ^{33}S MAS NMR [59]and single-enhanced wideband uniform rate smooth truncation (WURST) and hyperbolic secant (HS) MAS NMR spectroscopy probing ^{33}S [316]identified a single narrow resonance (d$_{iso}$330 ppm, C$_Q$ 0.7 MHz) attributed to the single sulphur site in ettringite, which has a high degree of symmetry as it is within a discrete sulphateanion.

Thaumasite (Ca$_3$Si(OH)$_6$(CO$_3$)(SO$_4$)$12H$_2$O) is a silicate- and carbonate-substituted AFt phase which can form by reaction of sulphate and carbonate ions with cement mine¼rals (i.e. dur¼ing sulphate attack of PC systems) [317]. This similarity has caused difficulty distinguishing thaumasite from ettringite using XRD, infraredspectroscopyorthermogravimetrictechniques.However, thaumasite exhibits a ^{29}Si MAS NMR resonance at d$_{iso}$179.6 ppm [318e320], corresponding to Si in a veryunusual sixfold coordination, meaning that it is readily identifiable by this technique. ^{1}H-^{29}Si CP MAS NMR has been used to identify and quantify thaumasite in PC systems containing carbonate andsul- phate additives and revealed that significant quantities of thau- masite can form in cements with negligible Al content ¼— [320]. WURST and HS MAS NMR spectroscopy probing ^{33}S [316] in thau- masite identified a single narrow resonance (d$_{iso}$¼ 330.9 ppm, C$_Q$ 0.95 MHz), consistent with its crystal structure in which sulphur exists in a single SO^{2-}crystallographic site [321], asin

¼

4

ettringite.

4.2.8.3. ‘Aluminate-ferrite-monosulphate’etypephases.Calcium monosulfoaluminateandsimilarhydrocalumite-likeAFmphasesare observedinmanytypesofcements,includingPC[117,322,323],CSA cements[133e135,284,285]andmanyalkali-activatedslagcements [154,324e326].AFmphasesarelayereddoublehydroxide(LDH)e type structures, with positively charged portlandite-like layers con- tainingone-thirdofAl^{3þ}orFe^{3þ}cationsassubstituentsforCa^{2þ}, balancedbyanionicspecies(commonlySO$^{2—}$,CO$^{2—}$andOH$^{—}$),and
4 3
with significant interlayer H_2O [327e330](Fig. 25). They can be represented by the general formula $[Ca_2(Al,Fe)(OH)_6]$\$X\$xH_2O, where X represents an exchangeable singly charged (e.g. OH$^{—}$) anionorhalfofadoublychargedanion(e.g.SO$^{2—}$,CO$^{2—}$)[322].With
4 3

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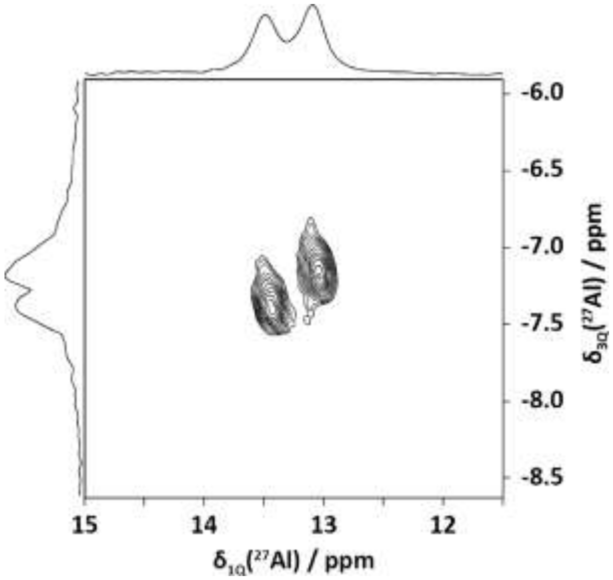

Fig. 24. ^{27}Al MQMAS ¼NMR spectrum (23.3 T, n_R15 kHz, 5 °C sample temperature) of ettringite showing two distinct Al^{IV} sites. Adapted from Skibsted et al.[137].

theexceptionofOH$^{—}$/SO$^{2—}$substitution(upto50mol%)[322],these phasesgenerallydonotformextensivesolidsolutionsbutrathercan coexistasseparatephaseswithcloselyrelatedstructuresbut differing interlayer anions. Consequently, many hydrated cement systemscontainmixturesofdistinctAFmphases.AFmphasesin

hydratedPCtypicallycontaintheanionsSO$^{2—}$(termedmono-aluminosilicateinterlayeranion([(T,$_{4}$)(OH,O)\$0.25HO]$^{-}$,T¼Si ¼ sulphate), CO_3^{2-}(monocarbonate) and/or OH^-(hydrocalumite, C_4AH_{13}) in the interlayer [52,117,322,323,331], while those in alkali- activatedslagsandmetakaolin-richPCblendscommonlycontain interlayerdivalentaluminosilicateanions,$[AlSi(OH)]^{2-}$,formingan AFmstructure,whichisalsogiventhemineralnamestr€atlingite [154,324]. Substitution by multiple anions in ordered positions is also possible, for example, 1:1 hydroxide and carbonate to form hemicarbonateor1:1sulphateandchloridetoformKuzel'ssalt [322]¼. Friedel's salt ($3CaO\$Al_2O_3\$CaCl_2\$10H_2O$) is also observed in hydratedPC,whichhasbeenexposedtoasourceofchloride,e.g. whenservinginmarineenvironmentsorcoldclimateswithroad orAl, ¸ vacancy),aswellastheAl^{VI}inthebrucite-typelayer ($[Ca_2Al(OH)_6\$2H_2O]^{þ}$)thatdefinestheAFmstructure.TheAl^{VI}siteinstr€atlingiteresonatesatasimilarfrequencytoAl^{VI}s itesin monosulphate,andconsequentlystr€atlingiteismoreconclusively identifiedfromitsAl^{IV}resonance,unlessworkingatextremelyhigh fields. The ^{27}Al MAS NMR spectrum of hydrated CSAcollectedatB$_0$22.3 T appears to contain contributions from severalindividualoverlappingAl^{VI}resonances[137],suggestingthatmonosulphate,monocarbonateandstr€atlingitemay beabletoberesolvedin^{27}Al MASorMQMASNMRspectraacquiredatultra-highmagneticfield.The^{29}SiMASNMRspectrumofsyntheticstr€atlingiteexhibitsa

salting.
Thesephaseseachexhibitasingle

^{27}AlMASNMRresonanceat
broad resonance atapproximatelyd$_{obs}$ 86.5 ppm,containing ¼
contributions from resonances resulting from Q^3(3Al), Q^2(2Al),

approximately¼ d$_{obs}$10e12 ppm, depending on field strength [52,117,133], in accordance with their crystal structures containing Al^{VI}[327,332]. Owing to similarities in structure, each of these AFm phasesexhibitsverysimilar^{27}AlMASNMRresonancesatstandard fieldstrengths,andsotheyaremoreoftendistinguishedfromeach other via complementary techniques, e.g. XRD, where their differentbasalspacingscanbeobserved.Themonosulphateand monocarbonate ^{27}Al MAS NMR resonances are severely over- lapping (d$_{obs}$12 ppm), but evidence for more than one peak in this region has been observed by ultraehigh-field ^{27}Al MAS NMR (23.3 T) [137], suggesting that it may be possible to resolve these resonances,andthoseofC_4AH_{13},atultrahighfield.Thesorptionof ¼ chlorideontothemonocarbonateAFmphaseC_4ACH_{11}wasinves- tigated by static ^{35}Cl NMR experiments and measurement of ^{35}Cl spinelattice relaxation time constants (T_1) and spinespin relaxa- tion time constants (T_2) [218], showing that chloride is in rapid exchangebetweenadsorbedsurfacesitesandbulksolutionsitesin each phase and exists predominantly in a hydrated, solution-like chemical environment on the monocarbonate surface. This behaviour is similar to chloride sorption onto portlandite andonto jennite, as discussedpreviously.

Str€atlingite($Ca_4Al_2(OH)_{12}[AlSi(OH)_8]_2\$2H_2O$)isanAFmphase which forms as a hydration product of aluminium-rich cements including PC-metakaolin blends and some non-Portland binders. ^{27}AlMASNMRanalysisofhydratedwhitePC-metakaolinblends [117]andhydratedCSA[137],aswellassyntheticstr€atlingite[333], revealedtworesonancesat¼d$_{obs}$61ppmand11.3ppm(14.1T) attributedtoAl^{IV}andAl^{VI}sites,respectively.Theseresonancesare characteristic ofthecrystalstructureofstr€atlingite[334],which containsAl^{IV}inadouble-tetrahedralenvironmentaspartofthe

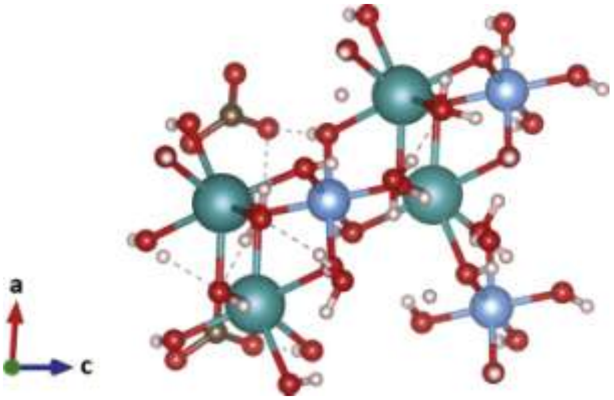

Fig. 25. Illustration of the local environments in the crystal structure of the mono-carbonateAFmphase[$Ca_4Al_2(OH)_{12}$]CO_3\$5H_2Oobtainedfromsingle-crystaldiffraction data[329].Caatomsarerepresentedbycyanspheres,Alatomsarerepresentedbyblue spheres,OatomsarerepresentedbyredspheresandHatomsarerepresentedbylight pinkspheres.PreparedusingtheVESTAsoftwarepackage[128].

Q^2(1Al) and Q^2 sites [333,335], consistent with the crystal structure [334]ofstr€atlingite which containsdoubletetrahedralsilicatering structures. The presence of these resonances is often used to monitor hydration in PC-CSA blends [133].

Asmentionedpreviously,Friedel'ssaltisanAFmphasewithCl^-as its interlayer ion. Variable temperature static ^{35}Cl NMR has shownthatinterlayerCl^-inFriedel'ssaltexhibitsaresonanceat d_{iso}¼ 30 ppm with a quadrupolar coupling constant C_Q 2.22e2.87 MHz, indicating uniaxial symmetry above 0 °C resulting from dynamically averaged interlayer species [336]. Below0°C,the¼Cl^-inthissiteexhibitsreduced(triaxial)symmetry resultingfromarigidcrystalstructure,asindicatedbyaresonance at d_{iso}¼ 26 ppm with a quadrupolar coupling constant C_Q¼ 3.0MHz.

4.2.8.4. Third aluminate hydrate. The ‘third aluminate hydrate’ (TAH)phaseisanamorphousnanoscalealuminatehydratephase which precipitates at the surface of the C-S-Hetype gels formed duringPChydration[172,194,337]andwhichhasalsobeennotedin sodium silicateeactivated GGBFS [18,20,155,324]. TAH is to date onlyidentifiablebyNMR,andconsequently,thetechniqueiskeyto thediscoveryofitsexistence.TAHisdescribedasapoorlyordered $Al(OH)_3$ phase [194,337]which is intimately mixed with other hydrate phases. Stoichiometric arguments and thermodynamic modellingsuggestthatthepresenceofTAHislikelytobelinkedto high concentrations of available Ca and Al [154,338,339], as the opposingchargesonCeSeHandAFmphasesmayproducestrong mutual attractions and physically destroy the AFm crystals [22,340], which would then result in low-crystallinity aluminate (AFm-like) layers being dispersed throughout the CeSeH gel while being undetectable by XRD [22]. This hypothesis is supported by transmission electron microscopy observations [337]. TAH phases exhibit a ^{27}Al MAS NMR resonance at d_{obs}5 ppm (14.1 T) in the spectra of C-S-Hetype gels [172,194,337]and of sodium silicate-eactivatedGGBFS[18,20,155,324].Broadeningofthe^{29}SiMASNMR resonanceattributedtoQ^1Sispeciesinsodiumsilicateeactivated slags [155] is attributed to the presence of Al^{VI}-O-Si linkages be- tween TAH andC-S-H.

4.2.8.5. Hydrotalcite-groupphases.Hydrotalcite($Mg_6Al_2CO_3(OH)_{16}$[CO_3]\$4H_2O),Fig.26)isanMg- ¼ AlLDHmineralwithaprimarylayerof positivelychargedbrucite-likesheets(seesection4.1.2.2.3), comprisingoctahedrallycoordinatedMgboundtooxygenatomsin tetrahedral coordination, with partial replacement of $Mg^{2þ}$by trivalentoctahedrallycoordinatedcations,whichareAlinthecaseof truehydrotalcite[341].TheAlatomsarerandomlydistributedwithin these layers at low concentrations [342] but take on a significantly moreorderedconfigurationatthehigherconcentrationswhichare morecharacteristicofhydrotalcite-groupphasesobservedince- ments[23].AsecondarylayercontainsH_2Omoleculesandanions, mostcommonlycarbonate,CO^{2-},andhydroxyl,OH^-,whichare

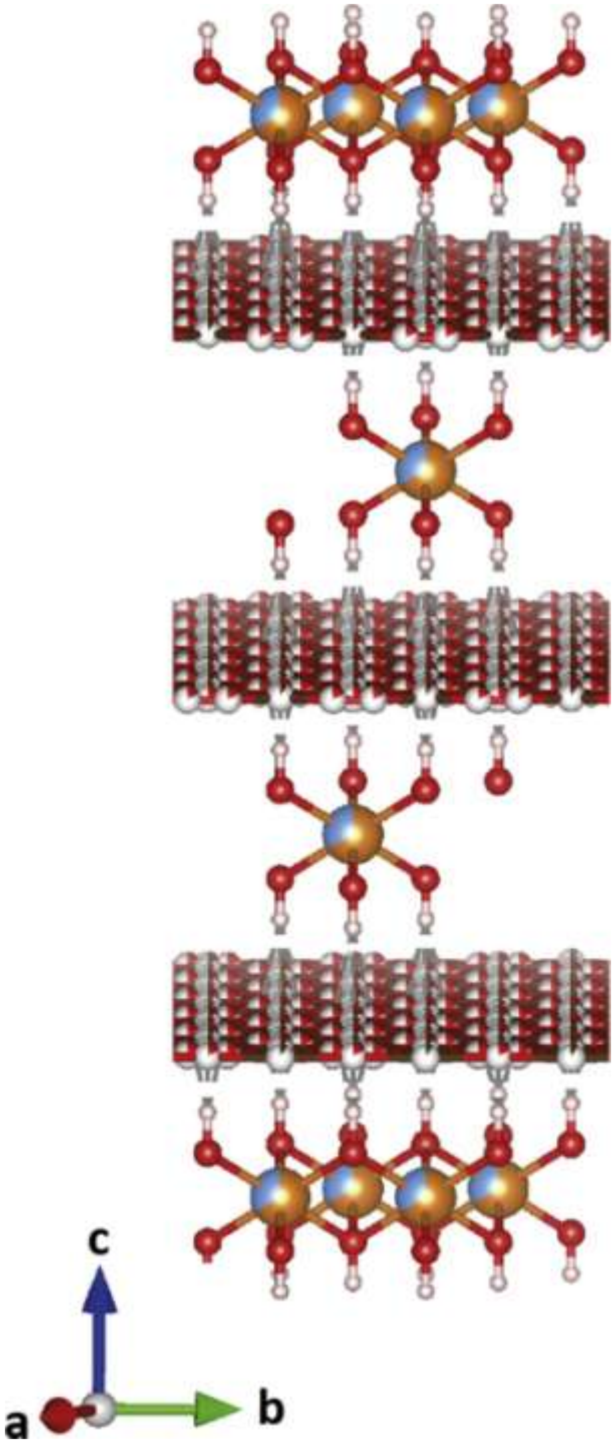

Fig**. 26.** Illustration of the local environments in the crystal structure of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}[CO_3]\$4H_2O$) obtained from single-crystal diffraction data [352]. Mg, Al, C, O and H atoms are represented by orange, blue, red and light pink spheres, respectively. Partial colouring of spheres indicates the average proportion of each respectiveatomoccupyingaspecificsiteinthehydrotalcitecrystalstructure.Prepared using the VESTA software package[128].

intercalatedandchargebalancethenetpositivechargesinducedin the sheets by incorporation of trivalent cations to replace $Mg^{2þ}$[341,343]. More than 40 identified mineral species conform to this generaldescription(butwithdifferentcationandanionsubstituents anddegreesofsubstitution)andarecollectivelydenoted hydrotalcite-supergroupphases.

Quintinite-groupphases,whichareasubsetofthehydrotalcite- supergroup with Mg/Al 2, have been observed on a sub- micrometrescaleinhydratedPC-GG¼BFSblends[99,220,344]andin cementsproducedfrommetallurgicalslagsactivatedwithsodium silicate or sodium hydroxide [71,72,154,190,324,325,345e348], typically occurring when slags with Mg content 5% are used, consistent with predictions from thermodynamic modelling [349]. Thesephasesgenerallycontainhigher Alcontent(Mg/Al¼2)than true hydrotalcite (Mg/Al ¼ 3) [341]. Previous work identified ≤ a phasethatwasdenoted'M_4AH_{13}'andproposedthatitmaybean analogue of the AFm-structured C_4AH_{13}, however, this phase has since been shown to be OH-quintinite ($Mg_4Al_2(OH)_{13}$\$$4H_2O$)) [350,351].

^{27}AlMASNMRspectraofsodiumsilicateeactivatedslagce-

ments exhibit a resonance at d_{obs}9 ppm (9.4 T) attributed to a hydrotalcite-like phase¼containing Al^{VI} sites [325,353], consistent with ^{27}Al MAS NMR analysis of synthetic hydrotalcites [342,353]. Simulation of ^{27}Al MAS NMR spectra of synthetic hydrotalcite- group phases has determined the isotropic chemical shift of this site to be d_{iso}11.8 ppm, attributed to a single Al environment surrounded by Mg atoms in octahedral coordination [354], with broadening of this resonance indicating increased disorder as Al content is decreased. A broad shoulder on this resonance at d_{obs}3 ppm (8.45 T) is observed when the¼ intercalated anion is $CO^{2—}$[354]. High-field (19.6 T) ^{25}Mg MQMAS NMR of these hydrotalcite-group phases resolved a single ^{25}Mg resonance at d_{iso}13.7 ppm assigned to Mg symmetrically surrounded by 3 Mg and 3 Al ions, $Mg(OAl)_3(OMg)_3$[354]. ^{1}H MAS NMR data acquired with high spinning speeds have also been¼used to resolve two distinct hydroxyl resonances in these phases at d_{iso}¼1.3 and 3

5.0ppm,respectively,attributedtoMg_3OHandMg_2AlOHwhichare

observedatMg/Al4and3,respectively[354].Recently,^{17}OMAS ¼and MQMAS¼ NMR resonances attributed to oxygen sites in these two hydroxyl groups were also observed in isotopically enriched synthetic hydrotalcite-group phases [355]. ^{1}H-^{13}C CP MAS NMR of synthetic hydrotalcite revealed a single ^{13}C resonance at d_{iso}170.9 ppm attributed to a single CO_3 site [220]. This work also utilised ^{13}C MAS and ^{1}H-^{13}C CP MAS NMR to resolve carbonate anionsinanhydrous(e.g$CaCO_3$)andhydrousorhydroxylated(e.g. hydrotalciteormonocarbonate)phasesinhydratedPCelimestone¼ blends. The observation of a ^{1}H-^{13}C CP MAS NMR resonance in a hydrated PCelimestone blend exhibiting a chemical shift consis- tent with that of pure hydrotalcite (d_{iso}170.9 ppm) measured on thesameinstrumentshowedexplicitlythathydrotalciteformedin this hydrated cement contained carbonate anions[220].

4.2.8.6. Hydrogarnets. The hydrogarnet series ($Ca_3(Al_xFe_{(1-x)})_2(SiO_4)_y(OH)_{4(3-y)}$; 0 x 1¼and 0 y 3) describes a group of garnet minerals where the $(SiO_4)^{4-}$≤ tetrahedra ≤are ≤partially or completelyreplacedbyhydroxylions.InPChydratedatambient temperatures, the formation of siliceous hydrogarnet is minimal[331,356];however,formationofthesephaseshasbeenobserved in PC hydrated at higher temperatures [357e360] or in the pres- enceofexcessFespecies[357,361],andwater-richmembersofthe grossular - katoite hydrogrossular series ($Ca_3Al_2(SiO_4)_y(OH)_{4(3-y)}$; $0 \leq y \leq 3$) are major hydration products in CACs[52].

Katoite ($Ca_3Al_2(SiO_4)_y(OH)_{4(3-y)}$; 0 y 1.5, often denoted C_3AH_6) exhibits a ^{27}Al MAS NMR ≤resonance≤ with an isotropic chemical shift of d_{iso}¼ 12.4 ppm and a quadrupolar coupling constantC_Q0.6MHz[52,362]duetooctahedralAlsurroundedby six hydroxyl groups in the hydrogarnet structure [51]. Increased substitution of silica into this structure results in a ^{27}¼Al MAS NMR resonance at approximately d_{iso}¼ 4e6 ppm, with thisresonance

shifting towards lower frequencies and exhibiting increased quadrupolar broadening with increasing silica content[50,362].

^{27}AlMASNMRresonancesattributedtokatoitehavebeenobserved

in CACs [50,52]and alkali-activated slags [20,155,197]. ^{29}Si MAS NMR analysis of hydrated CAC attributed a broad resonance at approximately d_{iso}79.9 ppm to Si sites in $[Si(OAl^{VI})_{4-x}]$ $(OCa)_x$ species(classified¼asQ^{0}inthenomenclatureofFig.1astherearenobondstotetrahedralspecies;alloftheAlsubstituentsareoctahe-

dral)andusedspectraldeconvolutiontoquantifythisphaseinthe hydrated CAC[50].

4.3. Spectraldeconvolution

4.3.1. Deconvolutionstrategiesandpitfallsrelatedtospectraof cementitiousmaterials

MathematicaldeconvolutionofMASNMRspectraallowsresolution of individual resonances which contributeto theoverallspectraandcanenablequantificationoftheresonatingspecies[60].Thesimplestcaseinwhichdeconvolutioncanbeperformedisfornon-quadrupolar(spinS ½)nucle¼i;thespectraofwhichcanbedeconvolutedusingaseriesofGaussian,Lorentzianormixed(Voigtor pseudo-Voigt) peaks to simulate individual resonancesusingaleastsquaresfittingmethod[363].Thisisperformedroutinelyinthestudyofanhydrousandhydratedcementsandrelatedphases.The most appropriate lineshape to simulate theindividualres-onances forspinS ½ nuclei depends on the orderinganddy-namics of the material under investigation [364,365];fo¼r orderedandrigidSSsystems,aGaussian(statistical)distributionbestrep-resents the resonance lineshape as interatomicdistancesaregenerallyconstant.Forhighlydynamicsystems(e.g.solutionsorgases),aLorentziandistribution(basedoncollisiontheory)bestrepresents the resonance lineshapeas mobility is high[365].Consequently, resonance lineshapes forspinS ½ nucleiindy-namicSSsystemsmaybebestrepresentedbyVoigtorpseudo-Voigt distributions weighted heavily towards aGaussianprofile.Inreality,dynamicsofsolidsincementitioussystemsareextremelyslow relative to those in solution, and a Gaussian distribution¼ provides a suitable approximation for the resonance lineshapes.

Deconvolutionofthespectraofquadrupolarnuclei(S>½)isalsopossible;however,quadrupolarinteractionsmustbetaken into account when simulating the spectra (Fig. 27). Quadrupolar parameterscanbeestimated[21];however,owingtothelarge variationinNMRparametersacrosssamplesandinstruments,this approach is prone to error must be appropriately justified. It is oftenmoreappropriatetodeterminethequadrupolarparameters directly.

Quadrupolarinteractionscanbedeterminedbyacquiringsingle-pulseMASNMRspectraatmultiplefieldsandsimulatingthe NMRresonancesobservedforthecentraltransitionateachfield withaconsistentsetofNMRparameters(d_{iso},$C_Q$andtheasymmetryparameterh)[30,172];thisisoftenthemostreadilyimplementableapproachifinstrumentsatmultiplefieldsareavailableas itdoesnotrequirecomplexexperimentsorfittingapproaches.

Quadrupolarparameterscanalsobedetermined(alongwith$d_{iso}$and h) at a single field by simulation of manifolds of spinning sidebandsobservedforsatellitetransitionsinMASNMRspectra [367e369],typicallyacrossspectralwidthsontheorderof2MHz. Thismethodcanbecomputationallyexpensiverelativetosimula- tion of single-pulse MAS NMRspectra.

Two-dimensional experiments such as MQMAS NMR techniques[242,255,370]arealsousedtodetermined_{iso},$C_Q$andh,and thus aid in deconvolution of NMR spectra for quadrupolar nuclei. MQMAS achieves high resolution by conversion of symmetricMQ coherence (pQ) to the single quantum (1Q) detectable central transition and plotting pQ and 1Q correlations in two dimensions [371].Consequently,chemicalshiftanisotropyisremovedfromthe MQ dimension, and d_{iso}can readily be determined from the two dimensionalMQMASspectrum.$C_Q$andhcanthenbedetermined by simulating the two-dimensional MQMAS spectrum or the pQdimension of this spectrum using readily available software (e.g. DMFit[60]orQuadfit[372]),informationwhichcaninturnbeused to simulate the single-pulse MAS NMR spectrum. A suitablemodel which incorporates these interactions should be used, e.g. the Czjzek model[373].

When performing any spectral deconvolution, the minimum possiblenumberofconstituentsubpeaksshouldbeusedtoenable an accurate and meaningful interpretation of the spectra [363]. Subpeakwidthsshouldbesetinarationalmanner,consideringthe expecteddisorderwithineachsitetype,andtheirpositionsmustbe consistentwithliteraturedataforspecificsitetypesinpure

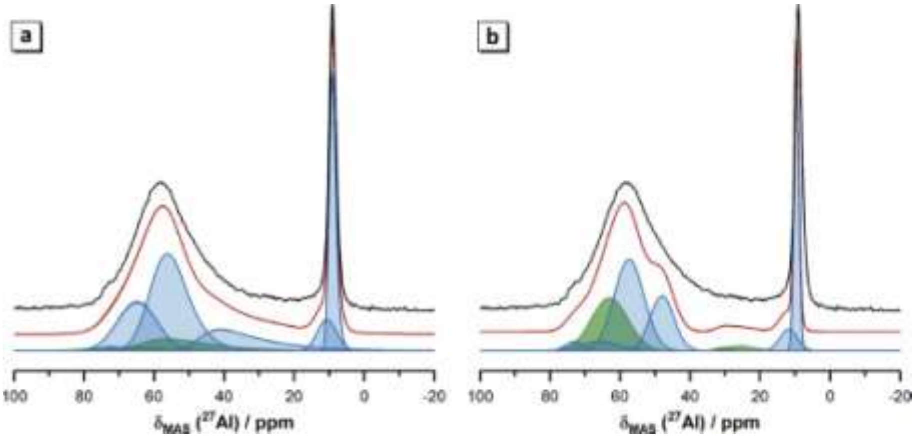

Fig. 27. ^{27}Al (S 5/2) MAS NMR data of a synthetic (calcium, alkali) aluminosilicate gel deconvoluted using (a) the Czjzek isotropic model with quadrupolar parameters determined from ^{27}Al MQMAS NMR data [366]and (b) Gaussian distributions. Deconvoluted resonances (bottom curves) attributed to sites within the precursor are shaded in green, deconvoluted resonances attributed to newly formed sites in the reaction product are marked in blue, the simulated spectrum is marked in red (middle curve) and the ^{27}Al MAS NMR spectrum is marked in black (top curve). The distributions of chemical shifts (as defined by $d_{iso}$and FWHM) are the same in the deconvolutions in both (a) and (b); however, the simulated spectrum in (a) correctly accounts for quadrupolar broadening by using the Czjzek isotropic model, while the simulated spectrum in (b) is deconvoluted incorrectly usingGaussian distributionsanddoes notaccount forquadrupolar broadening.Asaresult,theintensitiesoftheresonancesattributedtoeach newlyformedsitediffer between(a) and(b),andadditionalresonancesmustbeaddedtothedeconvolutionin(b)toprovideasatisfactoryfit.Consequently,any quantificationobtainedfrom(b)isincorrect.Adapted from Walkley et al.,[366].

materials.Therelativedeconvolutedsubpeakintensitiesshouldbe consistent with a mass balance for all elements, the structural constraintsdictatedbydatafromadditionalanalyticaltechniques (e.g.quantitativeXRD)andthosedescribedbyrelevantstructural models,e.g.the'substitutedgeneralmodel'forC-S-Hgels[159],the 'crosslinked substituted tobermorite model' for C-(N)-A-S-Hgels [195]andthethermodynamicsofastatisticaldistributionofSiand Al sites within a Q^4 aluminosilicate network for N-A-S-H products [250].

To provide an accurate representation of binder chemistry, andconsideringthattheconversionofsolidcementitious phasestohydrateproductsisalmostneverfullycompleteina practical cementing binder (even after decades or more), the contributionoftheremnantunreactedprecursortothespectra must be taken into account [13]. This can be achieved either through selective isotopic labelling of the binder [371], by subtraction of a scaled component spectrum for the remnant unreactedprecursorduringdeconvolutionifcongruentdissolution is assumed [18,20,345](Fig. 28) or by using the spectrum of a leached residue (obtained via selective dissolution) to represent a residual precursor component if congruency is uncertain [315,345]. For quantitative analysis, the congruency and kinetics of dissolution and reaction processes involving cementitious precursor materials must be carefully considered and modelled appropriately [14,20]as the underlying assumptionscandramaticallyaffectthefinaldeconvolution.This canbeachievedbyavarietyofmethods,includingthoseused to measure the degree of reaction of SCMs in PCeSCM blends [374].Methodsincludeselectivedissolution[375],scanning electron microscopy [323,376], thermogravimetry [374]and XRD with iterative Rietveld refinement (e.g. the 'partial or no knowncrystalstructure',PONKCS,method[377])approaches.

Inapracticalsense,GGBFSisahighlydepolymerisedglassthat is likely to dissolve close to congruently [325], whereas FA is a much more complex mineral assemblage that dissolves incongruently[101,102].

Quantificationofindividualresonancescanoftenbecomplex, even with seemingly simple spectra of non-quadrupolar nuclei suchas^{29}Si(seethefollowingsection).Quantificationof^{27}Al resonances can be particularly difficult due to the presence of Al species which exhibit resonances so broad that they are often undetectable. ‘NMR invisible’ Al species have been described, largely in older literature, in zeolites, minerals and gels; up to 30% of all Al species in some zeolites could not be observed at 9.4 T [378]. However, these resonances were detectable at high field (18.8 T) [378], highlighting the importance of acquiring SSNMR spectra at the highest field possible if quantification is desired.

4.3.2. Complexities in quantification of tricalcium and dicalcium silicate in PC

The ^{29}Si spin-lattice relaxation time constants (T_1) for belite are approximately 30 times those of alite at the same magnetic field [29], and consequently, it is crucial to ensure that sufficient recycle delays are used during NMR data acquisition to allow for complete relaxation of both alite and belite. This can be achieved via inversion-recovery ^{29}Si spin-lattice relaxation MAS NMR [27,29] (e.g. Fig. 29) or T_1-relaxation-time-filtered ^{29}Si MAS NMR [57]. Deconvolution of such data allows independent quantification, and hence validation, of the relative proportions of alite and belite within PC [27,29]. This work has shown that the determination of alite and belite content in PC using traditional Bogue calculations [379] strongly overestimates the belite content at the expense of alite, consistent with results from XRD and other techniques; the modified Taylor-Bogue calculation [380] provides a much better match to the alite/belite ratio determined by ^{29}Si MAS NMR spectral deconvolution [27].

4.4. DFT computation of NMR spectra and parameters

Isotropic chemical shifts, coupling constants and electric field gradients of molecules can also be predicted ab initio from calculations using DFT [381,382] and used to simulate NMR spectra. Computation of NMR parameters from DFT is widely used to determine the crystal structure and ordering in ceramics, zeolites and other crystalline materials; however, there has been little application of this approach to the phases in cementitious materials. Rejmak et al. [165,166] performed simulations of various C-S-H gel structures based on 14 Å tobermorite and jennite models and calculated the resultant isotropic ^{29}Si chemical shifts. Calculated chemical shifts for Q^2 sites were found to be largely independent of the structural model used, and Q^1 and Q^2 sites each showed a large dispersion of calculated chemical shifts. The calculated ^{29}Si MAS NMR chemical shifts were found to be in good agreement with those of 14 Å tobermorite. This work also showed that terminal silicate sites (Q^1), and paired silicate tetrahedra with an AlO_4 unit within the first coordination sphere (Q^2(1Al)), which exhibit similar isotropic chemical shifts, may be distinguished easily by large differences between their chemical shift anisotropies [166].

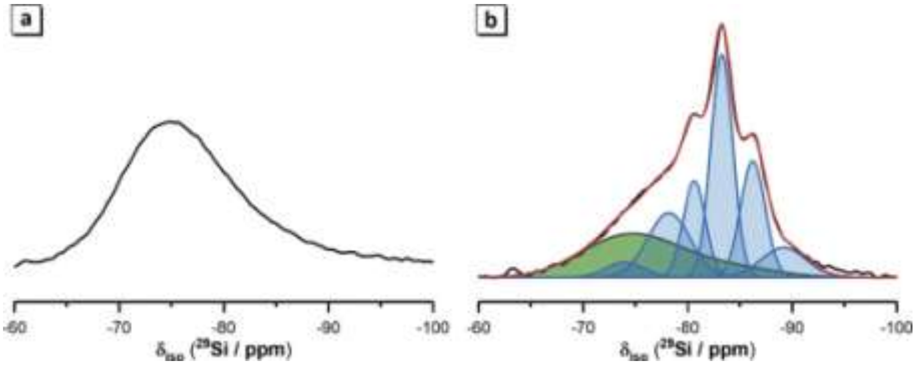

Fig. 28. ^{29}Si MAS NMR spectra (14.1 T, n_R¼ 10 kHz) of (a) an anhydrous slag and (b) a sodium silicateeactivated slag cement (shown in black) with associated deconvolutions (individualresonancesareshowninblueandthesimulatedspectrumisshowninred).Theshadedgreenresonanceisarepre sentationoftheunreactedanhydrousslagcomponent andisbased onthe^{29}Si MASNMRspectrumofthe anhydrousslag,withtheintensityof thisresonancerescaledbyasinglefactorontheassumptionofcongruentdissolution ofslag. Adapted from Bernal et al.[20].

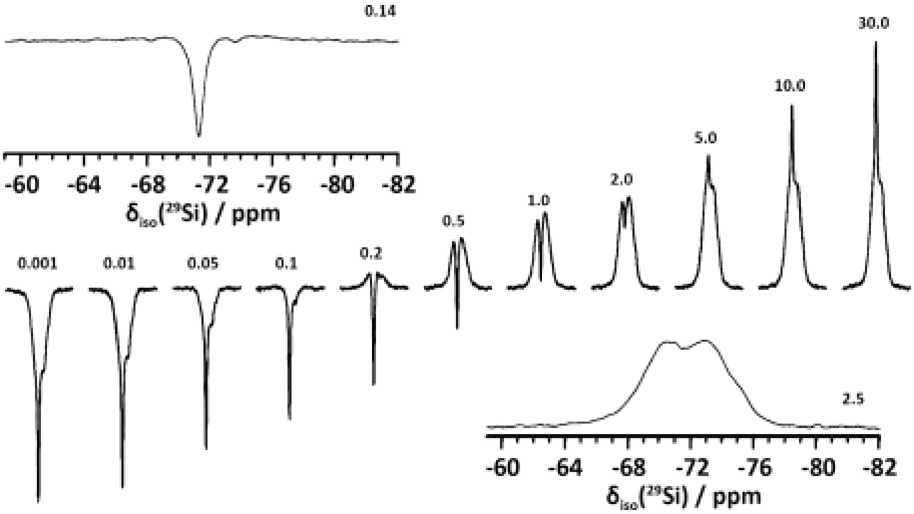

Fig. 29. Inversion-recovery ^{29}Si M¼AS NMR spectra (9.4 T, n_R12.0 kHz) of white PC, illustrating the differences in spinelattice relaxation for alite and belite. The left and right expansionsshowsubspectraofbeliteandaliteobtainedatthezero-crossingsfor^{29}Siinaliteandbelite,respectively.Therecoverytimesinsecondsareindicatedfortheindividual spectra. Adapted from Poulsen et al.[29].

Ab initio prediction of NMR parameters from calculations using DFT is yet to be applied extensively to cementitious materialsand represents an important opportunity for further advancement. In particular, combining DFT predictions with experimental dataac- quired at high field of synthetic model systems will reveal impor- tant new structural insights which may then be used to untangle many remaining questions in more complex, heterogeneous systems.

4.5. ApplicationofadvancedNMRexperimentstocementitious materials

4.5.1. Spin-echo MASNMR

MASNMRspectracontainingbroadresonances,suchasthoseofdisorderedcementitioussystems,canexperienceartefactsand distortionintroducedinthefirstfewmicrosecondsofinstrumentaldeadtimeatthebeginningofthefreeinductiondecay[10]. Spin-echopulsesequences[383]canbeusedtoovercomethisbyrefocussingthespinsystem.Thespinsystemisgivenaninitialnon-selective(90°)pulse,afterwhichthespinsareallowedtoprecess anddephase(duetothevaryingprecessionratesofindividualnuclearmomentswithinthesystem).Applyinga180°pulseaftera timeτflipsthespinsystemandrestoresphasecoherencetotheprecessionatatime2τafterthefirst90°pulse,refocussingthespinsystem[10,383].Asmallnumberofauthorshaveusedspinechopulsesequencesanalysingcementitiousmaterialstoaccuratelyquantifythesitespresentinthesesystems[8,260,299,384].

4.5.2. Cross polarisation MASNMR

CPMASNMRinvolvestransferofmagnetisationfromanucleus with more abundant spins to a nucleus with less abundant spins, allowing acquisition of the NMR spectrum of the less abundant nucleus with a much higher signal-to-noise ratio than would be obtained by MAS NMR [10]. This is achieved by irradiation of the two nuclei at their correct Larmor frequencies in fulfilment of the HartmanneHahn condition [385]. The signal from the less abun- dantnucleusinclosestproximitytothemoreabundantnucleusis preferentially enhanced, and so additional structural information canbegainedbycomparisonofCPMASandMASspectraofthe samesample.^{1}Histhemostcommonhigh-abundancenucleusin cementitious materials, and consequently, this technique canbeparticularly advantageous for probing local environments in cementitious materials where the structural role of water is of interest.

4.5.2.1. ^{1}H-X CP MAS. ^{1}H-^{29}Si CP MAS was used to examine hy- dration of b-C$_2$S and show that the initial hydration products contain monomeric silicate hydrates, the amount of which de- termines the initial hydration rate [386], while ^{31}P MAS and ^{31}P-^{1}H CP MAS NMR were used to demonstrate that the very small quantity of PO$^{3—}$ions involved in the hydration of white PC are accommodated within the interlayer of C-S-H [32,34]. Interlayer PO$^{3—}$ions exhibit a broad ^{31}P resonance with the same chemical shift as that of PO$^{3—}$guest ions in alite, so must be selectively detected using ^{31}P-^{1}H CP MAS techniques. ^{1}H-^{29}Si CP MAS NMR (Fig.30)hasalsobeenusedtoidentifySispeciescloselyassociated $_4$ withwater(i.e.Si-OHlinkages)thatarelikelytoexistaspartofthe C-S-H gel [43,167,185,386e392], C$_4$-(N)-A-S-H gel or AFm phases in alkali-activated slag [154,196], metakaolin [242] and synthetic C- (N)-A-S-H gels [14], while ^{1}H-^{27}Al CP MAS NMR has also been used to identify Al-OH linkages in synthetic analogues of PC hydration products[393]. ^{13}CMASand^{1}H-^{13}CCPMASNMRhavealsobeencombinedto studycarbonationofsyntheticC-S-HandC-A-S-Hgels[221]andto determinetheNMRparametersofinorganiccarbonatesrelevantto cement chemistry [220]. During early studies of TAH, ^{1}H-^{27}Al CP MAS NMR revealed Al(OH)$^{3—}$units closely associated with C-S-H, leadingtotheidentificationoftheTAHasanamorphousaluminate hydroxide or calcium aluminate hydrate produced either as a separatephaseorananostructuredprecipitateonthesurfaceofthe C-S-H gel [194]. ^{1}H-^{29}Si and ^{1}H-^{27}Al CP MAS NMR experiments are also particularly useful for constraining ^{29}Si and ^{27}Al MAS NMR spectral deconvolutions of the C-S-H model system tobermorite and C-A-S-H gels[14,393].

4.5.2.2. X-Y CP MAS. Studies using X-Y CP MAS NMR experiments (thatis,thoseCPexperimentswhichdonotprobeprotons)tostudy cementitiousmaterialsarefewer;however,theyhavestillrevealed new insight into the interactions in these materials. ^{17}O-^{27}Al CP MAS NMR has been used to support a claim that Al atoms within GGBFSareconnectedonlytobridgingoxygenatomsandnotnon- bridgingoxygenatoms[75].^{19}F-^{29}SiCPMASand^{19}F-^{29}SiCPREDOR

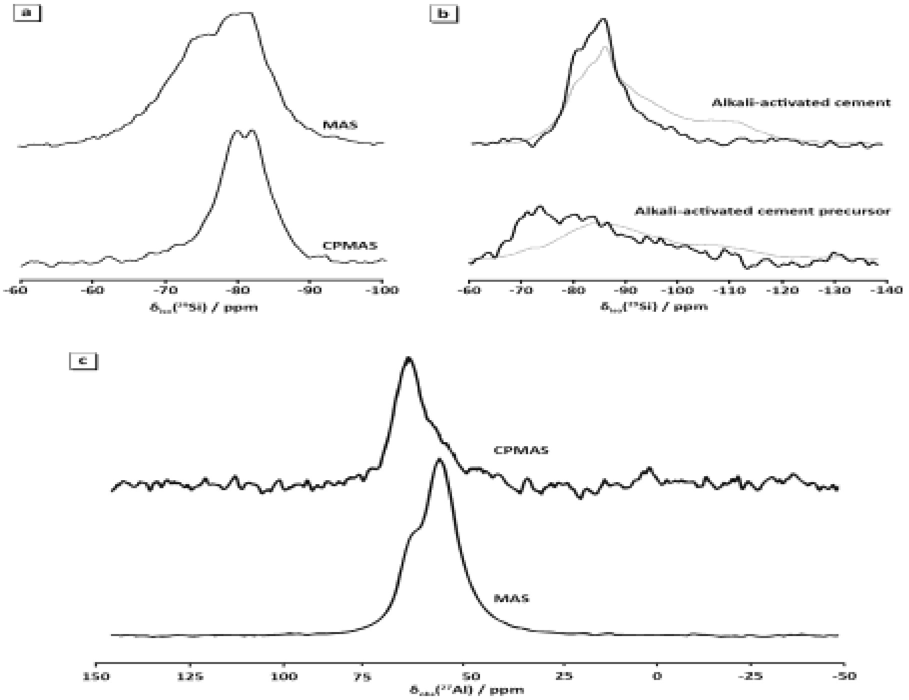

Fig.30.(a)^{1}H^{29}SiCPMASandMASNMRspectraofblastfurnaceslagactivatedwith4MNaOHandcuredfor1day.AdaptedfromWangetal.[154].(b)Single-pulse^{29}Si(grey)and ^{1}H-^{29}SiCP(black)MASNMRspectraofasyntheticcalciumaluminosilicateprecursorandofasyntheticalkali-activatedcementproducedfromit(containingC-(N)-A-S-H),curedfor 3days.Allspectraarenormalisedtoconstanttotalintensity.AdaptedfromWalkleyetal.[14].(c)^{1}H-^{27}AlCP-MASNMRoftobermorite.AdaptedfromHoustonetal.[393].

MASNMRtechniqueshavebeenusedtoshowthatF^{-}substitutes for O^{2-}ions in only the alite phase in white PC, as discussed pre- viously in section 4.1.1.1, aligning with the proposed Si^{4þ}O^{2-} ⁄ Al^{3þ}F^{-}coupled substitution mechanism [35], with ^{19}F-^{29}Si CP REDORMASNMRindicatingastrongpreferenceforF^{-}substitution into interstitial oxygen sites not involved in covalent Si-Obonds.

4.5.3. Multiple quantum MASNMR

Recently,MQMASspectroscopy[394,395],probinghalfinteger quadrupolarnucleiincluding^{17}O,^{23}Na,and^{27}Al,hasbeenusedto obtain high-resolution NMR spectra of synthetic C-S-H [188], CAC [276], AAM [113,242,252,256,276,370,371,396], related reaction products [137,276,354,355,397]and precursors [34,36,75,138]. MQMAS achieves high resolution by conversion of symmetricMQ coherence (pQ) to the single quantum (1Q) detectable central transition, and plotting pQ and 1Q correlations in two dimensions [371]. Consequently, chemical species with similar localstructures andcoordinationenvironments,whichwouldotherwiseresultinoverlapping resonances in one-dimensional MAS NMR spectra, may be resolved.

^{27}Al 3Q MAS NMR has been used to examine symmetry of Al siteswithinsyntheticcalciumaluminatehydratesandtoobtainthe isotropic chemical shift, quadrupolar coupling constant and asymmetry parameter of these sites [276]. ^{27}Al 3QMAS NMR spectraofthesematerialsresolvedadditionalAlsitestothosethat could not be obtained by ^{27}Al MAS NMR alone, including two Al sites within C$_4$AH$_{13}$[276]. ^{27}Al 3Q MAS NMR has also been used to probe Al substitution in C-S-H gels [276,393], identifying two distinct tetrahedral Al sites that were attributed to Al substitution forSiintobothbridgingandnon-bridgingpositions[276],although other studies (as discussed in section 4.2.1.1) have shown that bridging positions are a strongly preferred environment. ^{27}Al 3QMASNMRhasprovidedadditionalinsightintocoordinationand symmetry of Al environments within N-A-S-Hetype gels (Fig. 31a and b), including determination of the isotropic chemical shift (d$_{iso}$), quadrupolar coupling constant (C$_Q$) and asymmetry (h) parameter of the electric field gradient tensor

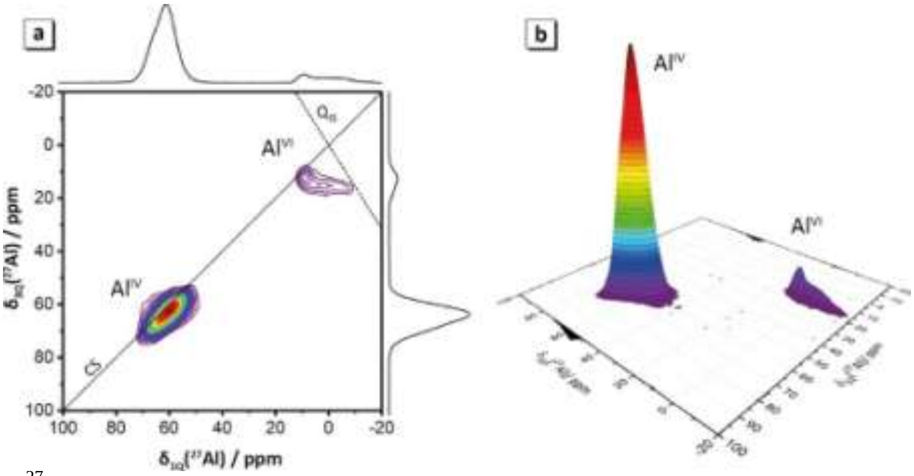

Fig. 31. (a) ^{27}Al MQMAS NMR spectrum (14.1 T, n_R¼ 20 kHz, room temperature) of a synthetic alkali-activated cement containing a N-A-S-H gel (adapted from Walkley et al. [255]) and (b) a three-dimensional representation of the spectrum shown in (a).

[113,242,255,256,370,371,396] and also Al environments in C-A-S- H/N-A-S-H gel blends [396]. Both ^{27}Al 3QMAS NMR [276] and ^{25}Mg 3QMASNMR[354]havealsobeenusedtoresolveindividualAland Mg sites within Mg-containing LDHs, while recent work used ^{27}Al MQMAS NMR to resolve for the first time 8 distinct Al sites in ye'elimite [34,138] and high-field ^{27}Al MQMAS NMR to resolve for the first time two distinct octahedrally coordinated AlO_6 sites in synthetic ettringite [137](see section 4.2.8.2'Aluminate ferrite trisulphate'etype phases). MQMAS NMR, therefore, appears to offersignificantscopeforfutureadvancesintheunderstandingthe atomic structure ofcements.

Processing of MQMAS spectra using standard single-axial isotropic shearing (iso-shearing) in the indirect dimension removes the second-order quadrupolar term and leaves the projectionofthespectraontotheindirectdimensionaxisasapure function of isotropic variables such as the isotropic chemicalshift

(d_{iso})andthequadrupolar-inducedshift(d_{QIS}), allowingchemically

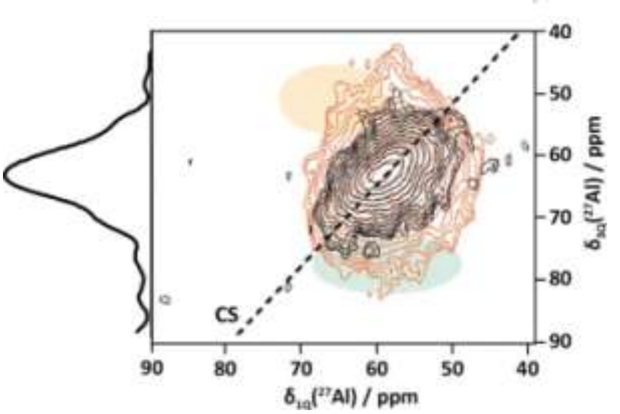

Fig.32.Isosheared^{27}Al{^{1}H}REDOR3Q/MASNMRspectrum(blackcontours)overlaid onanisosheared^{27}AlMQMASNMRspectrum(redcontours)ofasodiumsilicate-

distinct sites to be resolved in the indirect (pQ) dimension [242,371,398,399].Themorerecentlyintroducedmethodofbiaxial Q-shearing [371] in both the indirect and direct dimensions allows orthogonalseparationofd_{iso}fromthequadrupolarparametersd_{QIS}
eactivated metakaolin cement. Adapted from Brus et al. [242]. The main resonance resultspredominantlyfromAlO$_4^-$tetrahedrachargebalancedbyNa^{b}ions,andthe shadedorangeandgreenareasindicateregionswhereAlO$_4^-$tetrahedraconnectedto SiO$_4$tetrahedraviabridginghydroxylgroups(Al^{IV}eOH^{b}eSi^{IV})andAlO$_4^-$tetrahedra chargebalancedbyextra-frameworkAlspeciesareexpectedtoresonate,respectively.

and the quadrupolar coupling constant (C_Q) and is particularly useful for disordered materials which typically give MQMAS spectradisplayingadistributionofchemicalshiftandquadrupolar parameters, that can be difficult to interpret for identification of chemically distinct sites[113,371].

4.5.4. Multiple resonanceexperiments

4.5.4.1. REDOR, TEDOR, TRAPDOR and REAPDOR. REDOR [400e402]and transferred-echo double-resonance (TEDOR) [403e405] are multiple resonance MAS NMR experiments whichexploitheteronucleardipolarcouplinginspin-½nuclei and provide both qualitative and quantitative information about the proximity of the two spins. Transfer of population in double-resonance (TRAPDOR) [406,407] and rotational-echo adiabatic passage double-resonance (REAPDOR) [400,408]experiments extend the principlesofREDORandTEDORtoquadrupolarnuclei.Itshouldbe noted that the X{^{1}H} REDOR and ^{1}H-X CP MAS NMR techniques (where X ^{27}Al or ^{29}Si) provide complementary data; X{^{1}H} REDOR MAS NMR experiments selectively suppress resonances of protonatedspecies,while^{1}H-XCPMASNMRexperimentsenhance thesignalsofspeciesexperiencingdipolarcouplingwithrigid

¼

proton species (i.e. terminal hydroxyl groups, strongly bound H_2O etc.) [242].

Brus et al. [242] applied ^{27}Al{^{1}H} REDOR 3Q MAS NMR (Fig. 32) to identify bridging hydroxyl groups connecting Al^{IV} and Si^{IV} tetrahedrainaseriesofalkali-activatedmetakaolincements,supporting the identification (see section 4.2.2) of charge balancing extra-framework Al species in these systems. ^{29}Si{^{1}H} REDOR 3Q MAS NMR has also been applied to a series of aluminosilicate geopolymers[370]toshowthatthesematerialscontainahetero- geneousdistributionofcharge-balancingNaionsandassociated water molecules, with the Na ions and water molecules preferentially clustered around fully polymerised Q^{4}(4Al) Sispecies.

Recently, Greiser et al. [409] used ^{29}Si{^{27}Al} TRAPDOR NMR, ^{27}Al

{^{29}Si} and ^{27}Al{^{1}H} REDOR NMR experiments to reveal new infor- mation regarding the phase assemblage and nanostructure of cementitious sodium aluminosilicate gels produced via the one- part alkali-activation route using variety of silica sources. This workshowedtheextentofformationofanamorphoussodium

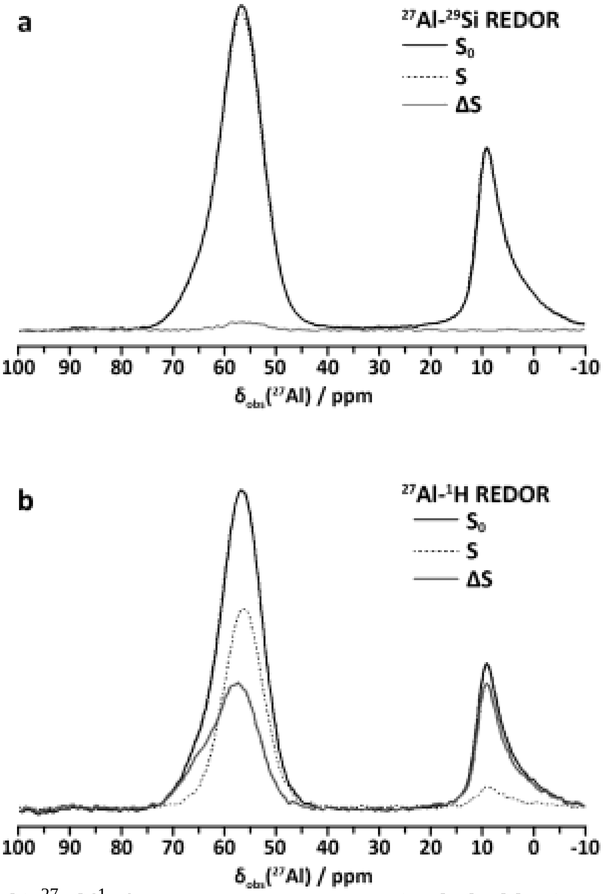

Fig. 33. (a) ^{27}Al{^{29}Si} and (b) ^{27}Al{^{1}H} REDOR NMR spectra (S, dashed line) overlaid with ^{27}Al MAS NMR spectra (S_0, black line) and difference spectra (DS ¼ S_0e S, grey or blue lines) of a cementitious sodium aluminosilicate gel produced via one-part alkali- activation of rice husk ash. Adapted from Greiser et al. [409]. The AlO_6 resonance (d_{obs}¼ 8 ppm) does not show a discernible ^{27}Al—(^{29}Si) REDOR NMR effect and shows a strong ^{27}Al—(^{1}H) REDOR interaction, demonstrating that this resonance is due toAlO_6 within a hydrous alumina gel ($Al(OH)_3$) with little or no Si in proximity.

beenusedtodemonstratetheexistenceofaluminiumephosphorus interactions within phosphate-modified CACs [277], where no other analytical technique was able to provide direct evidence about the existence (or otherwise) of these bonds within the disorderedgelsystemsofinterest.TheuniversalREAPDORcurve [410]which is commonly used to fit REAPDOR NMR data and determineinternucleardistancesis,however,specificallydesigned foranisolatedspinpair(i.e.monodentatestructures)whichlimits itsapplicability(inaquantitativesense)tothepolydentatestruc- tures which comprise mostcements.

4.5.4.2 2D homonuclear correlation MAS NMR spectroscopy. 2D homonuclear correlation MAS NMR spectroscopy (COSY) is a multiple resonance MAS NMR experiment involving transfer of magnetisationbetweentwonucleiofthesameisotopeandisuseful for determining connectivity between different sites when many resonances are present. Double quantum ^{29}Si-^{29}Si COSY experi- ments on synthetic C-S-H isotopically enriched with ^{29}Si has resolvedbothdimeric(Q^1-Q^1)andchainendgroup(Q^1-Q^2)Sisites as well as (Q^3-Q^3) and (Q^3-Q^2) bridging linkages [176], confirming the presence of these sites in C-S-H as discussed in section4.2.1.

4.5.4.3. 2D heteronuclear correlation MAS NMR. 2D HETCOR MAS NMRisamultipleresonanceMASNMRexperimentwhichinvolves transfer of magnetisation between two heteronuclei and isuseful fordeterminingconnectivitybetweendifferentnucleiwhenmany resonances are present. This experiment is similar to the X-Y CP MAS NMR experiment; however, in the X-Y 2D HETCOR experiment, the magnetisation of nucleus Y is allowed to evolve for a (variable) time t_1 prior to being transferred to nucleus X, whose response is measured directly during the detection period t_2[10]. Significantsensitivityenhancementcanbegainedbycombining MQMAS with the HETCOR experiment (HMQC) [411]. Rawal etal.

[57] used ^{1}H-^{29}Si and ^{1}H-^{27}Al HETCOR MAS NMR with different ^{1}H spin-diffusion times to probe correlations between different mo- lecular moieties in hydrated white PC: both short (10 ms, probing strongly coupled species with internuclear distance <1 nm) and long (30 ms for ^{29}Si and 20 ms for ^{27}Al, probing more weakly aluminosilicate gel, coprecipitation of an amorphous hydrous aluminagel(Al(OH)$_3$)andformationofzeoliticphasesaredepen- dent on the silica source, despite very similar Si/Al of the starting reactionmixtures.TheidentificationofamorphousAl(OH)$_3$hasnot beenpreviouslyreportedanddemonstratestheimportanceofus- ing double-resonance NMR techniques to resolve multiple over- lapping ^{27}Al resonances that are often present in single-pulse ^{27}Al MAS NMR spectra (Fig.33).

Tran et al. [396] used a ^{29}Si{^{27}Al} REAPDOR NMR technique to distinguish between Si-<u>O</u>-Al connectivity environments in alkali- activated metakaolin and to identify the number of Al atoms substituted in the second coordination sphere of each probed Si site. The same authors also used ^{29}Si and ^{27}Al MAS, ^{19}F-^{29}Si CP MAS and ^{29}Si{^{19}F} CP REDOR MAS NMR techniques to show that F¯substitutesforO^{2-} ionsinonlythealitephaseinwhitePC,with^{29}Si {^{19}F} CP REDOR MAS NMR indicating a strong preference for F¯substitution into interstitial oxygen sites not involved in covalent Si-Obonds,demonstratingalimitationontheachievabledegreeof fluoridesubstitutionintoalite.^{31}P-^{27}AlREAPDORNMRhasalso coupled species over several nm), Fig. 33. ^{1}H-^{29}Si HETCOR MAS NMR experiments were able to resolve chemically bonded -OH groups,adsorbedwaterandstronglyhydrogenbonded-OHgroups associatedwithQ^1,Q^{2}andQ^2(1Al)Sisites,withchemicallybonded -OHgroupsandadsorbedwaterprimarilyassociatedwithQ^{1}and Q^2(1Al)sites,aswellaswaterstronglyadsorbedtosix-coordinateSi siteswithinathaumasite-likephasethatwasclaimedtobepresent inthehydratedPC[57],althoughtheidentificationofthismineral incementsthathavenotbeensubjectedtochemicaldamageis extremelyuncommon.

ResonancesfromprotonsinH$_2$O,Ca-OHandSi-OHgroupshave also been identified by ^{1}H-^{29}Si HETCOR MAS NMR analysis of synthetic C-S-H [176], with both types of hydroxyl sites correlating with all Si sites in C-S-H and water molecules correlating with Q^1 and both bridging and pairing Q^2 sites. ^{1}H-^{27}Al HETCOR MAS NMR experiments resolved hydroxyl groups chemically bound to Al^{VI} sites within ettringite and TAH and an absence of correlation be- tween ^{1}H species and four-coordinate ^{27}Al^{IV} moieties. Enhanced resolution provided by the ^{1}H-^{29}Si and ^{1}H-^{27}Al HETCOR MAS NMR experiments allowed resolution of ^{29}Si-OH and ^{27}Al-OH bonds which were not resolved in single-pulse MASNMR experiments.

4.5.4.4. Satellite transition spectroscopy. Accurate determinationof d_{iso}, C_Q and h is crucial for an accurate and unambiguous

interpretation of SS MAS NMR spectra. Determination of these parameters from single-pulse MAS NMR spectroscopy observing the central transition (m_S± ½) between nuclear spin states, however, is hindered due to the second-order qu¼adrupolar shift. Satellite transition spectroscopy involves observing the satellite transitions in MAS NMR spectra of quadrupolar nuclei, where re- sidualsecond-orderquadrupolareffectsunderMAS(quadrupolar broadeningandthesecond-orderquadrupolarshift)arereduced relative to the central transition [367]. The dependence of the second-order quadrupolar shift for a particular spin S on the nu- clear spin state transition (m) results in a different net isotropic chemicalshiftforeachm;consequently,bysimulatingallobserved transitions, it is possible to determine the isotropic chemical shift from a single spectrum [367e369]. Jakobsen et al. [412]and Skibsted et al. [368] demonstrated simulation of all transitions in MAS NMR spectra of crystalline powders toaccurately determine C_Q and h for ^{17}O, ^{23}Na and ^{27}Al in systems with large C_Q values (C_Q>2 MHz), as well as applying this method to accurately determinethe^{27}Al$C_Q$valueof1.9MHzforAl^{VI}inhydratedwhitePC [44]. Skibsted et al. [52]also applied this method to a series of calciumaluminatephasesinCACandinPC(Fig.34),determining

^{27}Ald$_{iso}$,C$_Q$andhvaluesanddistributions.Thesewerethenusedto describelinearrelationshipsbetweenC$_Q$andthemeandeviationof bondanglefromidealtetrahedralsymmetry,aswellasbetweenC$_Q$andacalculatedestimateofthegeometricaldependencyof theEFG tensor. This method has also been used to identify the two crys- tallographically distinct octahedrally coordinated Al sites in kaolinite [413], as specified by its crystal structure[414].

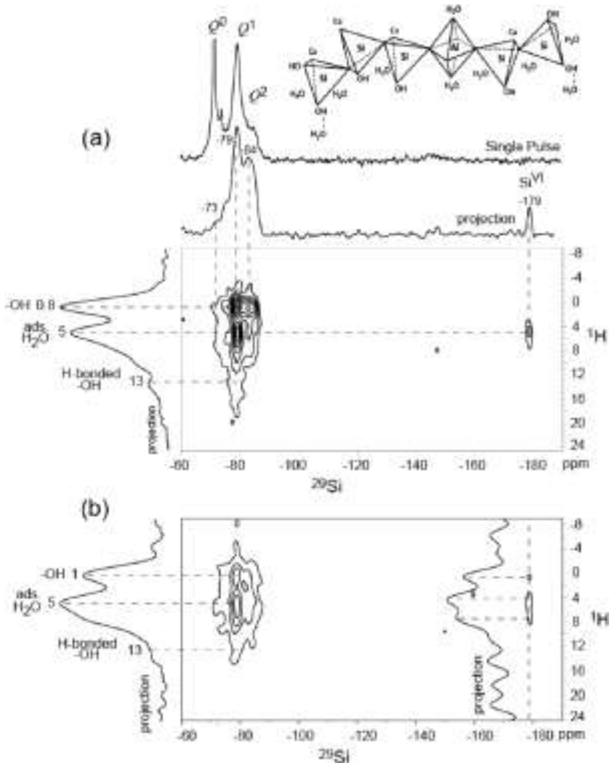

Fig. 34. ^{1}H-^{29}Si HETCOR MAS NMR (11.7 T, n$_R$¼ 6.5 kHz) of white PC with ^{1}H spin- diffusion times of (a) 10 ms and (b) 30 ms. Adapted from Rawal et al. [57].

4.5.5. ^{1}H relaxationNMR

^{1}Histhemostsensitivenucleusincementitiousmaterialswhich maybeprobedusingNMR;however,^{1}H-^{1}Hdipolarcouplingscause severe line broadening which limits the resolution of ^{1}H MAS NMR spectra, which is further compounded by the small chemicalshift range(approximately20ppm)overwhich^{1}Hnucleiinsolidphases resonate. These limitations have impeded the widespread appli- cation of single-pulse MAS NMR experiments probing ^{1}H in cementitiousmaterials.However,^{1}Hrelaxationrates(spinelattice, 1/T_1, and spinespin, 1/T_2) are sensitive to proton mobility in hy- dration products and water in the vicinity of solideliquid interfaces and can therefore provide extensive information regarding porosity, pore size distributions and tortuosity in these cementitiousmaterials.

EarlyworkusedprotonNMRrelaxometrytomonitorhydration of C_3S and PC by measurement of T_1 and T_2 relaxation times [415e421],identifyinganinductionperiod(~3h)[417]aswellas waterinvarioushydratephases[416],mobilewaterinmicropores and water with restricted mobility in a solid gel component [420,421].

Spinespinrelaxationratesaremodulatedbythemotionofthe speciesonwhichthespinsresideandvarybyseveralordersof magnitudeforprotonsinrigid(e.g.solidhydrates)ormobile(e.g. molecular water) species. Rapid measurements of spinespin relaxationratesare,therefore,particularlyattractivetomonitor reactionin-situ[22].Thisapproachhasbeenusedtomonitorhy- drationofwhitePC,andsyntheticC_3SandC_3A[422e424],andled toidentificationoffivecomponentswithdistinctT$_2$valuescorrespondingtocapillaryporewater,solid-likecrystallinewaterand OH$^-$groups(i.e.inportlandite,gypsum,andettringite),mobile water molecules incorporated in CeSeH, water moleculeswith restrictedmobilityintheCeSeHinterlayerandsecondaryhydrationwaterreleasedbythedecompositionofettringite(Fig.35).

Spinespin relaxation times have also been used to observethe retardationofPChydrationinthepresenceofvariousorganicadditives [425]. ^{1}H relaxation rates can also be exploited to link the structureandkineticsattheatomiclevelofcementitiousmaterials to microscale and macroscale engineering properties such as porosity, pore size distributions and tortuosity in hydrated cement pastes, mortars and concretes. Measurement of spinelattice relaxationrateshasbeenusedtodeveloprelaxationmodelsforthe dependencyofT$_1$ontheporesurfacetothevolumeratioandthe presence of nearby paramagnetic ions [426e429], while T$_1$-T$_2$[427,428] and T$_2$-T$_2$[430,431] correlation NMR experiments have been used to identify discrete pores (e.g. large capillary pores or smallergelpores,Fig.36)inhydratedwhitePCandsyntheticC-S-H and measure exchange of water between these locations, by exploitationofthefactthatincreasedporesizeresultsinincreased relaxation times. Variable temperature proton NMR relaxometry experiments have also been used to monitor freezeethaw phenomena in hydrated PC and C-S-H[432,433].

More recently, ^{1}H NMR relaxometry has been used toquantify all the water present, as well as the size and volume of discrete population of pores containing this water, in hydrated white PC both with [8]and without [434,435]silica fume additions. This work showed that addition of silica fume alters the chemical composition of the C-S-H formed, but does not alter the density, and identified four discrete populations of liquid water: water in the C-S-H interlayer in pores approximately 1 nm in diameter, waterintheC-S-Hgelinporesapproximately3nmindiameterand waterinsmall(~10nmindiameter)andlarge(■ 10nmin diameter)capillarypores.Correlationof^{1}HNMRrelaxometrywith results from mercury intrusion porosimetry (MIP) has shown that MIPcanaccuratelydeterminetheporosityofcementpastes[436].

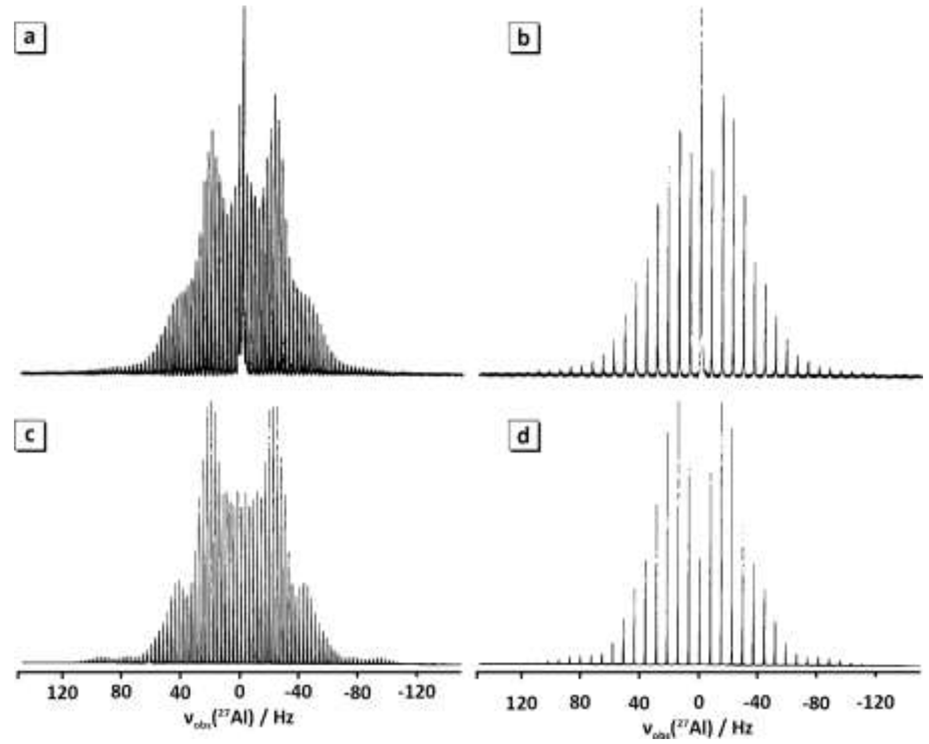

Fig. 35. ^{27}Al MAS NMR spectra of ettringite (C$_6$A\$$_3H_{32}$) recorded at (a) 9.4 T, n_R¼ 6.5 kHz, and (b) 9.4 T, n_R7.5 kHz. Simulations of the satellite transitions in parts (a) and (b) are shownin(c)and(d).AdaptedfromSkibstedetal.[52].

2. Conclusions andperspectives

SS NMR spectroscopy has played a pivotal role understanding the complex compositionestructureeproperty relationships in

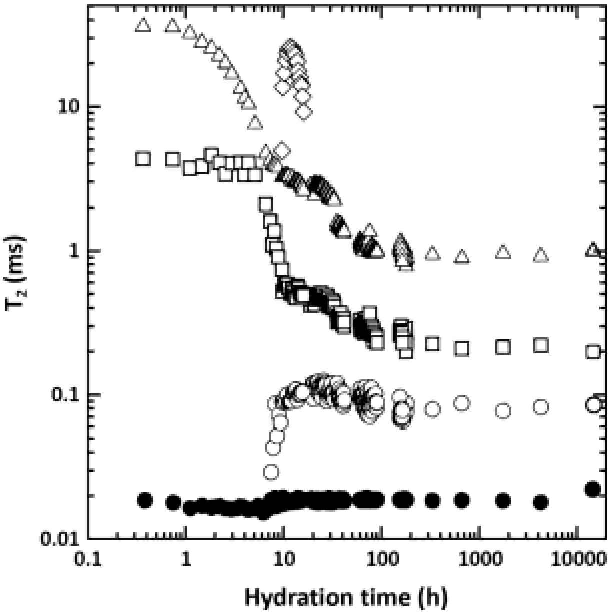

Fig. 36. Proton spinespin relaxation times (T_2) vs. hydration time of white PC hydrated at 20 °C. Proton signals come from water molecules in the pore solution (triangles), crystalline water and OH^-groups (filled circles) in C-S-H and portlandite, more mobile water molecules in the interlayer of C-S-H (squares) and secondary hydration water released by the decomposition of ettringite (diamonds). Adapted from Holly et al. [422].

cementsandrelatedmaterials.Inparticular,SSNMRspectroscopy hasaffordedalevelofinsightintotheiratomicstructure,reaction mechanisms, kinetics of formation and structural evolution which hasbeenpreviouslyunattainableandhasprovidedthebasisforthe currentstateoftheartinunderstanding,modellingandpredicting compositionestructureeproperty relationships, reaction mecha- nism and kinetics in PC, CAC, CSA, magnesia-based, AAM and geopolymer-basedcements.

ApplicationofadvancedMASNMRexperimentsprobing^{1}H,^{13}C, ^{17}O,^{19}F,^{23}Na,^{25}Mg,^{27}Al,^{29}Si,^{31}P,^{33}S,^{35}Cl,^{39}Kand^{43}Canucleihave beenusedtostudytheatomicstructure,phaseevolution,nano-structuraldevelopment,reactionmechanismsandkineticsoccur- ring in these cementitious systems, including multidimensional, multiresonance and in-situ experiments. Single-pulse MASNMR experiments probing ^{27}Al and ^{29}Si nuclei are by far the most routinelyappliedNMRexperimentsusedtostudycementsand have been instrumental in building our current understanding. However,owingtotheextensivestructuralinformationtheseex-perimentshaveprovidedtodate,theirroleincontinuedadvance- ment of the understanding of compositionestructureeproperty relationships in cementitious materials islimited.

Performing NMR experiments at high field ($B_0$20.0 T), probing less commonly investigated nuclei such as ^{17}O and ^{43}Ca in isoto- pically enriched samples and application of less commonly used techniquesincludingCPMAS,MQMASandmultiresonanceexper- iments (e.g. SEDOR, REDOR, TEDOR, REAPDOR and TRAPDOR) presents the best opportunity for elucidation of infor-mationregardingthemechanismswhichcontrolthestructureand physical properties of cementitious materials, that has been pre- viously unattainable. The difficulty in conducting these experi-mentsandinterpretationofthespectraobtained,however,islikely tobethelargestobstacletotheirroutineapplication.Thispresents a key challenge which must be overcome and will requirea concerted,collaborativeeffortfrombooththeSSNMRspectroscopy and cement materials chemistrycommunities.

Conflict of interest
The authors declare no conflict of interest.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtadv.2019.100007.

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