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VARIATIONS OF THE ANIONS POLYMERIZATION DEGREE OF CaO-SiO_2-P_2O_5-H_2O CBC MATERIALS DURING HYDRATION

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ABSTRACT

Changes in the polymeric distribution of anions during the hydration process of the CBC developed from CaO-SiO_2-P_2O_5-H_2O system were studied by IR and NMR (^{29}Si, ^{31}P) measurements. It was revealed that the absorption band of -OH in OHAp moved close to that of the standard OHAp mineral; for the sample hydrated at 365 days, there was 77.28% of the silicate appearing as SiO_2, and a little polymerized phosphate $[P_2O_7]^{4-}$ was also found in the same sample. © *1997 Elsevier Science Ltd*

Introduction

Chemically-Based Ceramics (CBC) was first coined by Roy [1], which is a family of materials in which the consolidation step of the ceramic powder is achieved by the formation of new bonds between the solid phase by a chemical reaction at low temperatures, and not by thermal diffusion or heating as done in almost all traditional ceramics. Hu et al. [2-5] have successively synthesized CBC materials in the CaO-SiO_2-P_2O_5-H_2O system. They found that this was a new kind of inorganic cementitious materials with high early splitting tensile strength. They have characterized the hydration process by XRD and EPMA measurements, but the changes in the degree of the anion polymerization during hydration was not examined. It is known that changes of $[SiO_4]^{4-}$ polymerization degree behave regularly during the hydration of Portland cement. Then how about the polymerization of $[SiO_4]^{4-}$ and $[PO_4]^{3-}$ anions during hydration of this new cementitious materials? A series of work has been done on the CaO-SiO_2-$P_2O_5H_2O$ system [6]. The present work was undertaken to investigate the variations of the polymeric distribution of $[SiO_4]^{4-}$ and $[PO_4]^{3-}$ anions during the hydration process in the system of CaO-SiO_2-$P_2O_5H_2O$.

Experimental

Synthesis of Samples. $Ca(NO_3)_2\cdot 4H_2O$, H_3PO_4 and silica sol were used as the starting materials. After trials of 20 different formula, a typical composition with $CaO:SiO_2:P_2O_5$ = 58.1:12.4:29.5 was chosen, based on its highest splitting tensile strength of paste among all

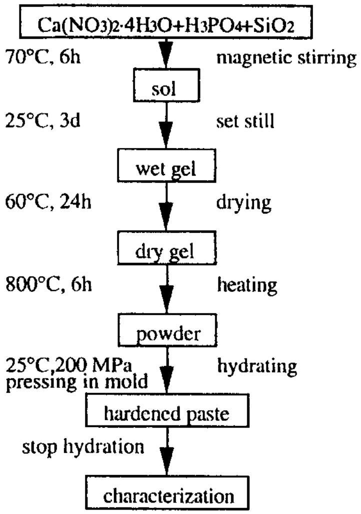

FIG. 1.

Sol-gel procedure of sample preparation of $CaO:SiO_2:P_2O_5$ system.

trials. The CBC were synthesized by sol-gel method. The calcined powder, which had been previously ground to pass through a 45µm sieve, underwent a cold pressing at 280 MPa with 0.18 w/s ratio to obtain cylinders with diameter 12.7 mm, height 5 ~ 8 mm. The compacts were hydrated in 20°C water bath to certain age followed by drying at 70°C for 2h. The sol-gel procedure is illustrated in Fig.1.

Measurement. The variation of the polymerization degree are revealed by infrared (IR) and nuclear magnetic resonance (^{29}Si, ^{31}P-NMR) techniques. The testing conditions for NMR are listed in Table 1. IR—Infrared Spectrophotometers used was a Perkin-Elmer. The sample preparation method followed the KBr disc method. XRD—were performed on a Automated x-ray diffractometer (CuKα radiation, λ = 1.540598Å) interfaced with a microVAX computer. SEM-EDX—An International Scientific Instruments KY-1000B Scanning Electron Microscope (SEM) with a TN-series II Energy Dispersive X-ray analyzer (EDX).

TABLE 1

Conditions for the ^{29}Si, ^{31}P-NMR Measurement

Nucleus	^{29}Si	^{31}P
Field strength of projection (kHz)	44	69
Projection angle(°)	30	30
Repeat time(s)	5	15
Standard compound	TMS	85wt% H_3PO_4
Reference	Q8M8	85wt% H_3PO_4
Chemical shifts to reference(ppm)	-12.35	0

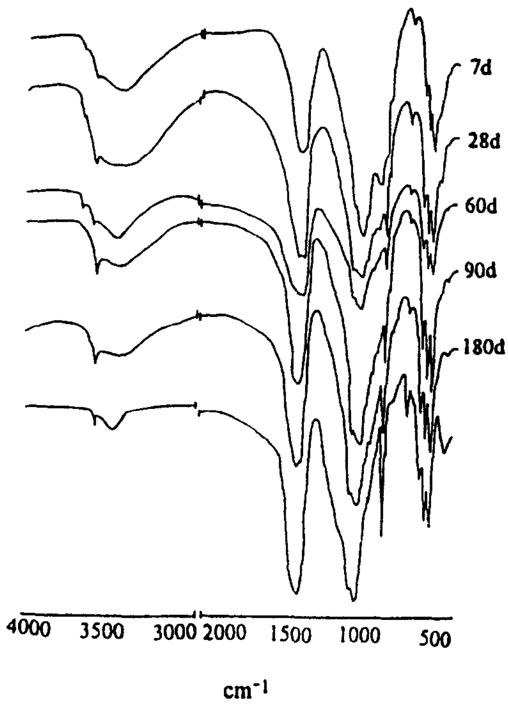

FIG. 2.
FT-IR spectra of the hydrated samples.

Results and Discussion

The IR Spectra of Sample. IR spectra of the samples hydrated for different periods are shown in Fig. 2. The major absorption bands for early hydration samples were similar. Table 2 shows assigned compounds or anions corresponding to observed absorption bands. It can be seen that: (1) the adsorption bands assigned to OHAp, H_2O and CO_3^{2-} appear in all samples, and the 870 cm^{-1} band assigned to CO_3^{2-} becomes stronger as the hydration progresses, which means that the amount of CO_3^{2-} is increasing; (2) 3640 cm^{-1} band appear in the sample hydrated from 7 days to 60 days, indicating the presence of $Ca(OH)_2$, however, for 90 days to 365 days samples, this band disappears, indicating that $Ca(OH)_2$ changed into $CaCO_3$; (3) 990 cm^{-1} band corresponding to β-C_2S appear in samples hydrated from 7 days to 90 days, but for 180 days sample, this band disappears with a new band at 1000 cm^{-1} appearing, and for 365 days sample, both of these bands disappear, meanwhile the wide-band at 1020–1050 cm^{-1} gets wider with increasing hydration time. This implies that the degree of polymerization of $[SiO_4]^{4-}$ increases as the hydration process progresses; (4) the characteristic absorption bands of amorphous SiO_2 at 980 cm-1 and 800–820 cm^{-1} appear in 180 days sample; (5) the stretching vibration bands of -OH in OHAp moves to 3550 cm^{-1} when hydrated to 90 days, and to even lower wave number when hydrated to 180 days and 365 days, closer to that of the standard OHAp mineral (3540 cm^{-1}). However, there is no more exact information about Ca_3PO_4 from IR spectra avialable.

The NMR Spectra of Sample. Fig. 3 shows the ^{31}P-NMR spectra of samples hydrated for different periods. It can be seen that these spectra are almost identical for samples hydrated

TABLE 2

Analysis of the IR Spectra of the Hydrated Samples

Absorption bands (cm^{-1})	7d	28d	60d	90d	180d	365d	The assigned materials or anions**
3640	+*	+	+	-	-	-	$Ca(OH)_2$
3540-3560	3560	3560	3560	3550	3545	3545	OHAp
3400	+	+	+	+	+	+	H_2O
1410-1450	+	+	+	+	+	+	CO_3^{2-}
1070-1090	+	+	+	+	+	+	SiO_2, OHAp, C_3P
1020-1030	+	+	+	+	+	+	SiO_2, OHAp, C-S-H
1000	-	-	-	-	+	-	C-S-H
990	+	+	+	+	-	-	β-C_2S
980	-	-	-	-	+	+	SiO_2,
950	+	+	+	+	+	+	SiO_2, OHAp, β-C_2S
910-920	+	+	+	+	+	+	SiO_2, β-C_2S
870	+	+	+	+	+	+	CO_3^{2-}
840	+	+	+	+	+	+	CO_3^{2-}, β-C_2S
800-820	-	-	-	-	+	+	SiO_2
710	+	+	+	+	+	+	CO_3^{2-},
620	+	+	+	+	+	+	OHAp
590	+	+	+	+	+	+	OHAp
560	+	+	+	+	+	+	OHAp
450-470	+	+	+	+	+	+	SiO_2, OHAp, β-C_2S

* + means having this absorption band, - not having this band.

** there are more than one kind of materials or anions listed in the last column, which means the adsorpton bands of these materials or anions overlap.

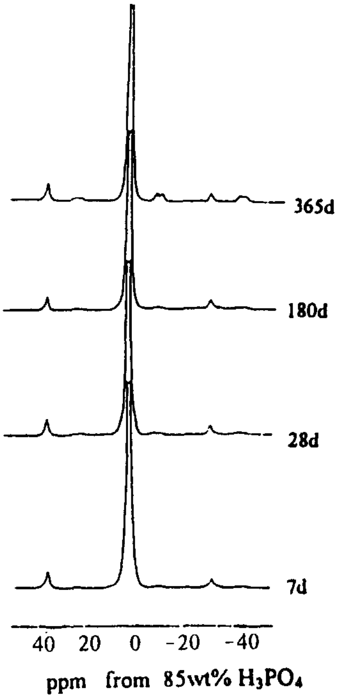

FIG. 3.
^{31}P NMR spectra of the hydrated samples.

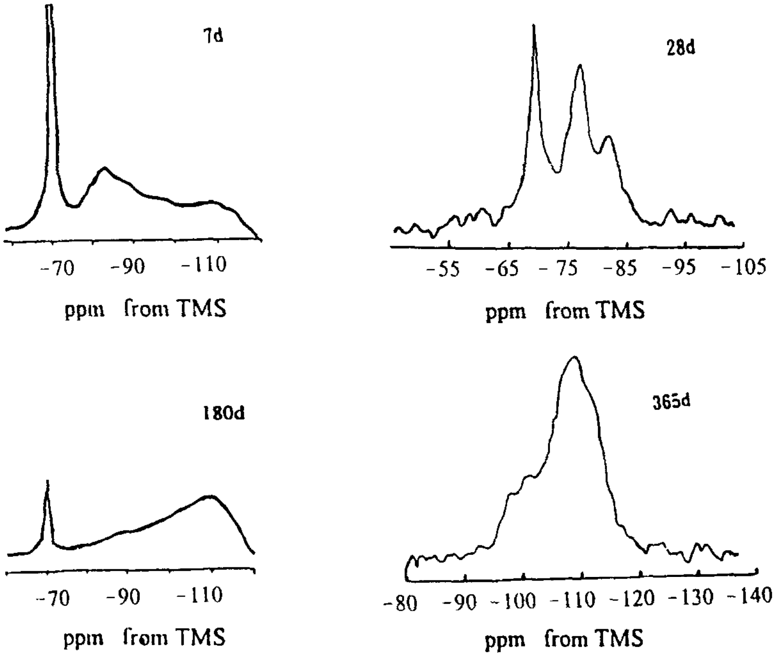

FIG. 4.
^{29}Si—NMR spectra of the hydrated sample.

for less than 180 days, all comprising a very sharp peak at 3.4 ppm corresponding to an isolated $[PO_4]^{3-}$, and a very weak wide-peak at -6.7 ~ -8.0 ppm corresponded to $[P_2O_7]^{4-}$; however, for 365 days sample the latter peak becomes stronger. ^{29}Si-NMR spectra for samples hydrated for different periods are shown in Fig. 4. The ratio of $(Q^1 + Q^2 + Q^3 + Q^4)$ intensity to Q^0 intensity increased with hydration. For 365 days sample, Q^0 had been very weak, but Q^3 and Q^4, especially Q^4 became stronger. The curve fitting method was used to analyze the ^{29}Si NMR spectra of 28 days and 365 days samples. From Fig. 5, the spectrum of 28 days sample is composed of nine peaks at -67.0, -68.9, -70.5, -72.6 and -75.5, -78.4, -81.6 and -83.5, -86.6 ppm. corresponding to Q^0, Q^1 and Q^2 respectively, and the -81.6 ppm peak being divided equally between Q^1 and Q^2; the spectrum of 365 days sample is composed of eight peaks at -97.1, -98.7, -101.3, -104.7 and -108.9, -112.0, -114.5, -117.0 ppm, corresponding to Q^3 and Q^4 respectively, the -104.7 ppm peak being divided equally between Q^3 and Q^4.

The relative intensities (Ii) of the peaks are indicated by their respective areas. The values of Ii and the calculated results are listed in Table 3. It can be seen that there is only 38.29% of isolated $[SiO_4]^{4-}$ group remaining in the 28d sample, implying that β-C_2S in the CBC is very reactive. For 365 days sample, there is 77.28% of the silicate existing in Q^4 form. According to references, there are only Q^1 and Q^2 when β-C_2S is hydrated for 100 days [7]; even when C_3S is hydrated for 420 days, there are also only Q_1 and Q_2 [8] for its ^{29}Si-NMR spectrum. This phenomenon indicates that this new cementitious material is unique in the hydration mechanism and in the structure of the hydration product.

According to the theoretical calculation, if the C_2S contained in the sample hydrated for 365 days is carbonated completely, it will produce 13.93 wt% of CO_2. But the DTA-TG

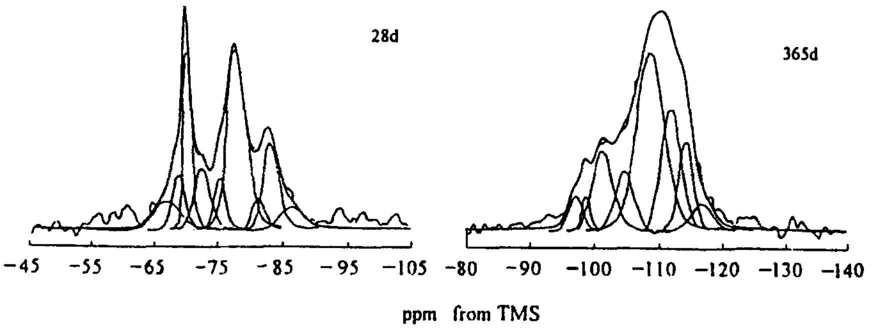

FIG. 5.
^{29}Si—NMR spectra of the 28 days and 365 days samples plotted by curve fitting—observed curve—fitting curve—calculated adsorption peak.

results [6] show that there is only 6.3 wt% of CO_2 existing in the sample, implying that the carbonation of sample is one reason for the appearance of SiO_2.

From the results of XRD and SEM-EDAX[6], it was reported that there were two kinds of new calcium-phosphate-hydrates forming in the samples hydrated at 365 days, with the compositions close to $7CaO{\cdot}3P_2O_5{\cdot}xH_2O$ (abbreviated as $C_7P_3H_x$) and $6CaO{\cdot}P_2O_5{\cdot}yH_2O$ (abbreviated as C_6PH_y). From our compositional analysis of SEM-EDAX, it is found that phosphates and silicates formed solid solution, specially in the case of OHAp -$[SiO_4]^{4-}$ solution.

As the hydration progresses, the amounts of Si^{4+} ions in the OHAp structure are decreased, which means that the Si^{4+} ions have undergone reverse diffusion, causing the accumulation of SiO_2. So that it might be an important reason for the existence of SiO_2. Another reason is probable the reactions between OHAp or β-C_3P and C_2S or C-S-H to produce $C_7P_3H_x$ and C_6PH_y. At the same time, these reactions also produce SiO_2 causing the collapse of the structure of C-S-H. More detailed analysis will be reported later on.

Conclusions

From this study following conclusions may be drawn:

- Results show the absorption band of -OH in OHAp of the hydrated samples is shifted closer to that in the standard OHAp.
- The amorphous SiO_2 appears in the hydration samples at later age, and there is 77.28% of the silicate existing in this form for sample hydrated at 365 days.

TABLE 3

Results Calculated by Curve Fitting

	Q^0		Q^1		Q^2		Q^3		Q^4	
	I_0	%	I_1	%	I_2	%	I_3	%	I_4	%
28 days	99.20	38.29	107.5	41.48	52.41	20.23	0	0	0	0
365 days	0	0	0	0	0	0	10.18	22.72	34.62	77.28

- Under the experimental conditions of this study, it is suggested that a little $[P_2O_7]^{4-}$ appears in the 365 days sample.

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