

A NEW MECHANISM OF MINERAL ADMIXTURE SUPPRESSING ALKALI-SILICA REACTION

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Abstract

Taking mineral admixture as partial replacement for Portland cement in concrete is an effective way to control expansion which is due to alkali-silica reaction (ASR); however, the mechanism of the mineral admixture suppressing ASR has not been clearly understood. The focus of this article is not only on the chemical composition and structure of calcium silicate hydrates (C-S-H) gels, but also on alkali adsorption of C-S-H gels, the alkali release of C-S-H gels. It indicates that the enhanced alkali-binding capability of the low CaO/SiO₂ (C/S) molar ratio C-S-H gels can significantly reduce the available alkali for reactive aggregate, resulting in the suppression of ASR. There is further investigation on the relation between the chemical composition and structure of C-S-H gels and its alkali-binding capability in this research. A potential mechanism of mineral admixtures in suppressing ASR put forward from the essential characteristic of materials.

Keywords: alkali, CaO/SiO₂ molar ratio, mechanism, C-S-H gels, ASR

1. INTRODUCTION

The ASR is a most important type of alkali-aggregate reaction (AAR). Excess expansion and cracking may occur in the concrete which is made of alkali-reactive aggregate and high-alkali cement. Researches on this subject have reached an agreement that there are three possible methods to solve this problem, which are: the use of low-alkali cement, the use of non-reactive aggregate, and the addition of certain mineral admixtures or chemical admixture, such as silica fume, fly ash, pozzolana and lithium salts. The use of mineral admixture as partial replacement for Portland cement in concrete has been proved an effective way to control expansion which is due to alkali-silica reaction in field concrete. However, the mechanism of mineral admixture suppressing ASR is still not clearly now.

Some researchers [1-6] have paid more attention on adsorption and dilution of alkali by mineral admixtures, especially indicated acidity of mineral admixture playing an important role in the adsorption of alkali. Meanwhile, they emphasized the action of reduced Ca(OH)₂ content of paste in inhabiting the ASR. However, the effect of hydration products especially that had been changed by the addition of mineral admixture on ASR was ignored. Stade [7] researched the binding of alkali ions into C-S-H gels, which was prepared at 80°C and 150°C, and summarized the amount of alkali hydroxide incorporated increased with decreasing C/S molar ratio of C-S-H gels. Hong et al. [8] drew the same conclusion on C-S-H gel which was synthesized at 20±2°C. Obviously above two viewpoints are arguing. So comparing the alkali absorptivity of mineral admixture with that of C-S-H gels is necessary. To understand the mechanisms of mineral admixture inhibiting ASR, study on the alkali absorptivity of the “real” C-S-H gels in paste is also necessary. In this article, experiments included Na⁺ released from variety compounds of C-S-H gels, chemical analysis, transmission electron microscope (TEM) / energy disperse spectroscopy (EDS) and ²⁹Si MSA NMR on the hydration products.

2. MATERIALS AND METHODS

2.1. Preparation of C-S-H gels

The silica fume was a by-product of the ferroalloy manufacture, the SiO₂ content and K₂O content of silica fume was 96.27 wt% and 0.94 wt% respectively. The C₃S used in experiment was synthesized at 1450°C in the laboratory from a proportional mix of powdered SiO₂ and CaCO₃. The free lime content of C₃S was less than 1.0 wt% examined by method of glycerol-alcohol.

It has been reported that the C₃S might be hydrated completely in ball grinding for two days [9]. C-S-H gels of different C/S molar ratio (0.46< C/S<2.3) were made from the hydration of C₃S

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and silica fume at a water/solid ratio of 10 by the method above mentioned. Based on the results of XRD and loss on ignition of hydrated products at 950°C, it has verified that the single mineral C₃S had mostly hydrated after hydration for two days. However, the C-S-H gel is usually coexisting with Ca(OH)₂, and it is difficult to extract Ca(OH)₂ from hydrated products and avoid destruction of C-S-H gel. So the C/S molar ratio of C-S-H gel is actually the CaO/SiO₂ molar ratio of hydrated products in this article.

2.2. Alkali release and chemical assessment

In a typical alkali release experiment, about 20.0g Portland cement or Portland cement partly replaced by silica fume was weighed; a previously standardized NaOH and KOH solution was added with designed volume to achieve a water/binder ratio of 0.5. A commercial cement with alkali contents of 0.40% (Na₂O_{eq}) was used, produced by JIANGNAN-ONODA. The paste was obtained by adding KOH or NaOH solution to raise the alkali content of the paste to 1.5wt% Na₂O_{eq} of the binder. The paste was sealed into polypropylene bottles and agitated completely. All the test pastes were stored in a moist curing room at 38°C and 100% RH until examination.

Referring the ASTM C311, the hardened cement paste were crushed and sieved at the certain curing ages. The particles passing a 0.315mm sieve were suspended in 50.0ml of distilled water, magnetic stirred for 2h and then filtered. Particles were washed by distilled water for 5 times (experiments showed that the alkali concentration in filtrate was low and steady after washed 5 times). The filtrate was collected. Aluminum, iron, calcium, and magnesium are precipitated from the filtrate by means of ammonium hydroxide and ammonium carbonate. Then Na⁺ and K⁺ in the filtrate was analyzed by flame emission spectroscopy, expressed as Na₂O and K₂O respectively, and Na₂O_{eq} (calculated as Na₂O+0.658·K₂O) was defined as the content of alkali released of hydration products.

2.3. Analysis of alkali released paste

Alkali released powder samples were dispersed with alcohol, carbon coated prior to characterization by TEM at the acceleration voltage of 200kV. Characterization by TEM was done on a JEOL 2010 transmission electron microscope equipped with a VANTAGE DS energy-dispersive detector.

Alkali released powder samples were also tested by ²⁹Si MAS NMR. The high-resolution solid-state NMR spectra were recorded at 79.49 MHz on a Bruker AV-400D spectrometer.

Alkali released sample was preliminary fused by adding sodium carbonate considering the acid-insoluble material by the addition of silica fume. Then according with ASTM C114, chemical composition of sample was examined. However, in the test for content of Na₂O, K₂O in hydrated products, silica is digested in hydrofluoric acid and sulfuric acid, followed by determination of Na₂O, K₂O in the filtrate (see 2.2).

3. RESULTS AND DISCUSSION

3.1. Alkali absorption capacity of C-S-H gels, silica fume and fly ash

In a typical adsorption experiment, about 2.00 g of the C-S-H with different C/S molar ratio, fly ash and silica fume are weighed respectively. A previously standardised NaOH solution in a concentration of 0.300 mol/L [10] was added to achieve a water/solid ratio of 15. The mixture were tightly sealed to prevent CO₂ access and shaken every 24 hours at ambient temperature. The aqueous solution was centrifuged after maintained 14 days to examine the Na⁺ ion concentration in the solution.

The adsorbed amount of alkali can be calculated from the decrease in aqueous NaOH concentration. The adsorbing rate (AR) was defined as:

$$AR = \frac{C_{in} - C_{af}}{C_{in}} \times 100 \quad (1)$$

where:

AR = adsorption, in wt%

C_{in} = initial alkali concentration in solution, mol/L

C_{af} = alkali concentration in solution after adsorbed by C-S-H gels, silica fume and fly ash, mol/L

The AR of variety of C-S-H gels, fly ash and silica fume were shown in Table 1. The AR of fly ash and silica fume were about 8%. The adsorbing Na⁺ capacity of C-S-H gels increased with the decreasing of the C/S molar ratio. When the C/S molar ratio was within the range of 1 to 2, which was the normal range of C/S molar ratio in hardened cement paste, the C-S-H gels adsorbed 12.1-28.3% of Na⁺ in the solution; When the C/S molar ratio was 2.3, there were large quantities of

$\text{Ca}(\text{OH})_2$ in gels, the AR was about 8wt%. This indicated the adsorbing Na^+ capacity of C-S-H gels increased greatly when the C/S ≤ 1.82 , and the maximum of AR reached to 50wt%.

The specific surface area of C-S-H gel is about tenfold compared to cement particles and mineral admixture, so C-S-H gel has a larger specific surface energy to hold the deleterious alkali ions in cement paste.

The results of absorbing alkali capacity identified that C-S-H gels played a key role in the adsorption of alkali in cementitious materials. The absorbing alkali capacity of C-S-H gel is stronger than that of cement paste containing more $\text{Ca}(\text{OH})_2$ and mineral admixture. It is also revealed that the adsorbing alkali capacity of C-S-H gel plays a more important role than that of mineral admixture in cement paste.

3.2. Alkali release

The released alkali amount of different samples was shown in Figure 1. The curve displays the released amount of Na^+ ion or K^+ ion from the hardened cement paste. Figure 1 shows for paste without silica fume (0wt% silica fume, K/Na), that 80% of total alkali is released from hardened cement paste within 7 days of hydration. The amount of released alkali from hardened cement paste has no significant change with the prolongation of curing age. It indicated that some hydration products had affinity for alkali ions. For the paste added with 25wt% silica fume, the amount of released alkali from hardened cement paste decreased continuously with the prolongation of the curing age. The amount of released alkali maintained stably about 40wt% of total alkali content in paste after hydrating for 28 days. For the paste with 40wt% silica fume, the amount of released alkali from hardened cement paste decreased rapidly in the first 28 days, then decreased slowly to 20wt% at the age of 4 months.

The low content of released alkali implies that the paste has a high adsorption affinity for alkali ions. The affinity of hardened cement paste for Na^+ or K^+ is improved by the addition of silica fume. Consequently, solid adsorption affinity rises with the increasing of silica fume content, which leads to the increasing of C-S-H gels in quality and the decreasing of C/S molar ratio.

3.3. Analysis of hydration products

The composition of hydration products which were performed alkali released experiment were examined by TEM and EDS. Relevant HRTEM photomicrographs are presented in Figure 2.

Figure 2a revealed a typical lattice of certain crystals, possibly nanoscale $\text{Ca}(\text{OH})_2$ coexisting with the dehydrated C-S-H gels(as the high vacuum and the incident electron beam of TEM made the C-S-H dehydrate) in the sample without silica fume added. It will contribute a higher value of C/S molar ratio, which is detected by EDS, than the real C/S molar ratio of dehydrated C-S-H. There are a little of nanoscale $\text{Ca}(\text{OH})_2$ and a larger amount of amorphous dehydrated C-S-H gels in hardened cement paste with silica fume (see Figure 2bc). The peak of K is enhanced with the increasing of silica fume (see Figure 2bde).

These results indicated that the addition of silica fume made more content of dehydrated C-S-H gels and obviously enhanced the adsorbing K^+ capacity of cement paste. The mass of C-S-H gels as well as its amorphous structure in nanoscale are important factors that enhanced the amount of alkali reserved in the hydration products.

The alkali released hardened cement paste were also been performed by bulk chemical analysis, K^+ and Na^+ reserved in paste as well as other composites were shown respectively in Table 2. The amount of NaO_{eq} reserved in hydration products increases with the increasing of mass of silica fume. The amount of NaO_{eq} in hydration products without silica fume is 0.21 wt% (as adjusting in NaOH) and 0.16 wt%(as adjusting in KOH) respectively, which are lower than the alkali contents in cement (0.40 wt%). These data indicated that alkali in cement is partly been released. The C/S molar ratio of cement pastes were calculated (the $\text{Ca}(\text{OH})_2$ content in hardened cement paste is subtracted in pure cement paste, whereas $\text{Ca}(\text{OH})_2$ content in paste when added with silica fume is zero).

The average C/S molar ratio decreased with the increasing of mass of silica fume, meanwhile, the amount of alkali (NaO_{eq}) reversed in the hydration products increased with the decreasing of average C/S molar ratio.

The study on the alkali released hydration products proved that, later in the hydration process, the amount of released alkali decreased with increasing mass of silica fume. And the chemical analysis of hydration products suggested that the average value of C/S molar ratio of C-S-H decreased with the increasing of mass of silica fume and furthermore alkali binding in the C-S-H gels with lower C/S molar ratio. So the C/S molar ratio is a key factor to affect the alkali binding capacity of C-S-H gels.

3.4. ^{29}Si MAS NMR

^{29}Si MAS NMR spectra of samples with different mass of silica fume added are presented in Figure 3. From the spectra, the line observed at 65 ppm corresponding to the $\text{Si}[Q^0]$ in the paste. Two lines are also observed at 74 and 78 ppm. They are representatives of $\text{Si}[Q^1]$ and $\text{Si}[Q^2]$ in the C-S-H structure. The structure of the 14 Å tobermorite are considered as the idealized model for the connectivities of $[\text{SiO}_4]$ tetrahedra in the C-S-H phase, the average chain length (CL) of $[\text{SiO}_4]$ tetrahedra for the C-S-H can be estimated [11] from the relative fractions of the different Q-species using the equation as following:

$$\text{CL} = \frac{2(Q^1 + Q^2)}{Q^1} \quad (2)$$

For the sample without silica fume added, the peak of Q^0 is significant, and then with the addition of silica fume, this peak weakened gradually. The Q^2/Q^1 ratio improved with the increasing of mass of silica fume added. Therefore, the CL of $[\text{SiO}_4]$ tetrahedral in C-S-H increases with the increasing of mass of silica fume added at the same curing age and curing condition.

The density of silanol sites, as well as their mean acidities increases with the increasing of CL [12]. The number of bridging tetrahedral increased with the increasing of CL. However, the bridging tetrahedral has two unshared oxygen atoms which lead to a negative charge on the C-S-H structure. In the absence of calcium ions in the interlayer space (low C/S molar ratio), protonation is performed to provide electrical neutrality. So the density of silanol sites increases with the increasing of CL.

The adsorbed alkali of hydration products and the ^{29}Si MAS NMR suggest that, the C/S molar ratio of C-S-H decreases with the increasing of mass of silica fume. At the same time, the average chain length of C-S-H increases with the increasing of mass of silica fume. Thus, the density of silanol sites increases. More KOH or NaOH are needed to provide neutralization. Therefore, the more content of alkalis ions enter into C-S-H gels, the less content of alkalis exist in pore solution of paste, and then the amount of available alkali reduced and ASR was suppressed.

Secondary pozzolanic reaction usually occurs in the later periods of hydration, but the addition of mineral admixture can reduce the early expansion of concrete included high reactivity aggregate, such as silica glasses and opal etc. In high temperature condition, it is can not be explained in this article. Many issues need to be further researched.

4. CONCLUSIONS

The capacity of C-S-H gels to absorbed sodium ions exceeds that of silica fume and fly ash.

The addition of silica fume leads to the increasing of amorphous C-S-H gels in quality, the decreasing of C/S molar ratio and the increasing of density of silanol sites in C-S-H gels. The C/S molar ratio is an important factor for the adsorbed alkali capacity of C-S-H gels. The adsorbed alkali capacity of C-S-H gels increases with the decreasing of C/S molar ratio.

It is suggested that, the reason which enable mineral admixture to suppress the ASR is the more C-S-H produced and lower C/S molar ratio of the C-S-H gels by the addition of mineral admixture. C-S-H gels have high specific surface energy to hold the deleterious alkali in cement paste. The C-S-H gels, even the gels with low C/S molar ratio, can bind more deleterious alkali in cement paste. The alkali concentration in pore solution of paste is reduced, so the ASR is suppressed.

5. REFERENCES

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Table 1 Alkali adsorbed alkali capacity of C-S-H gels and silica fume or fly ash

Sample	C-S-H gel							Silica fume	Fly ash
C/S	2.3	1.82	1.5	1.17	1.94	0.74	0.46		
Initial concentration in solution, mol/L	0.3001								
Na ⁺ concentration in Na ⁺ solution after adsorbed, mol/L	0.2817	0.2637	0.2514	0.2274	0.2151	0.1788	0.1542	0.2757	0.2757
Adsorbed rate */ wt%	6.1	12.1	16.2	24.2	28.3	40.4	48.6	8.1	8.1

*note: the adsorbed rate =the decreased alkali concentration /the initial alkali concentration (Further explanation in text 3.1)

Table 2 Bulk compositions of pastes measured by chemical analysis

Adjusting alkali species	Sample	Chemical composition wt%								C/S		
		LOI	CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	Na ₂ O			
NaOH	0% silica fume	16.84	53.13	1.19	19.14	2.96	4.21	0.05	0.18	97.70	0.21	2.08
	25% silica fume	12.99	42.73	1.58	33.59	2.69	3.83	0.37	0.74	98.52	0.98	1.36
	40% silica fume	12.60	34.33	1.72	42.63	2.14	3.04	0.35	0.90	97.71	1.13	0.86
KOH	0% silica fume	18.33	52.31	1.22	18.23	3.05	4.33	0.14	0.11	97.72	0.16	2.13
	25% silica fume	14.14	41.96	1.56	32.96	2.25	3.20	1.23	0.15	97.45	0.96	1.36
	40% silica fume	13.15	34.05	1.79	42.12	2.05	2.91	1.99	0.15	98.21	1.46	0.87

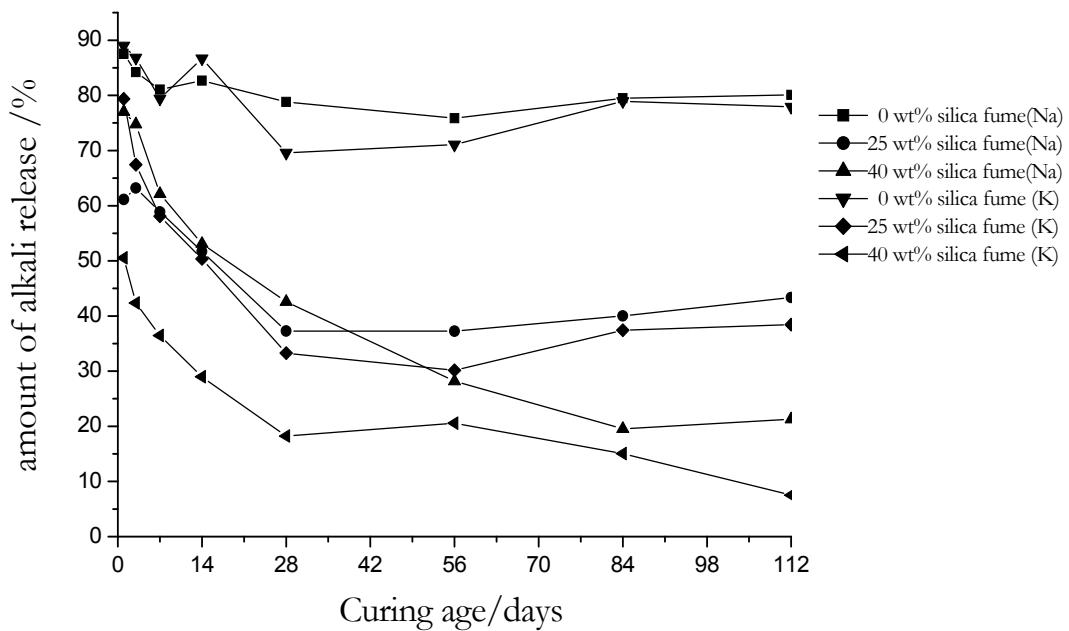
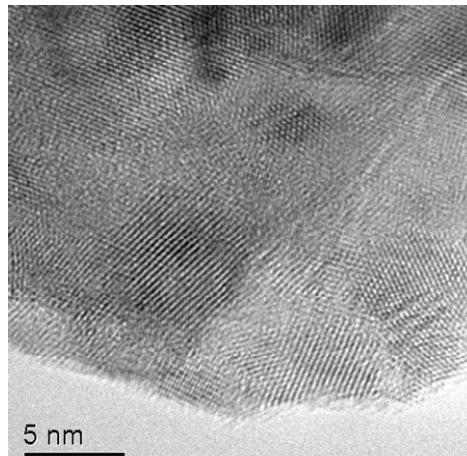
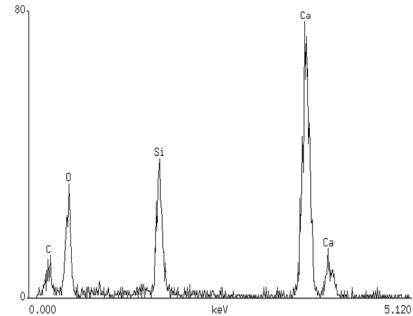


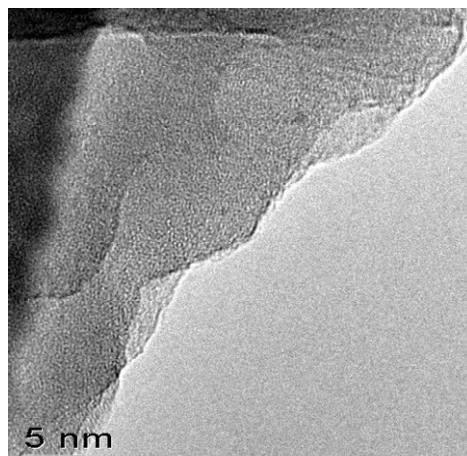
Fig. 1: Alkali release from hydrates with different mass of silica fume



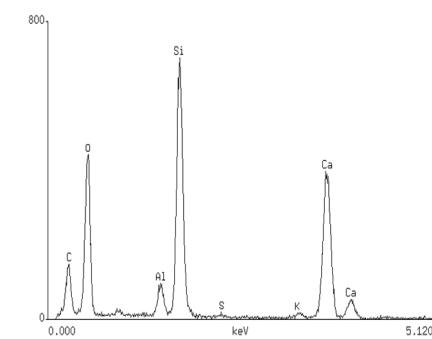
(a) HRTEM image of Portland cement paste



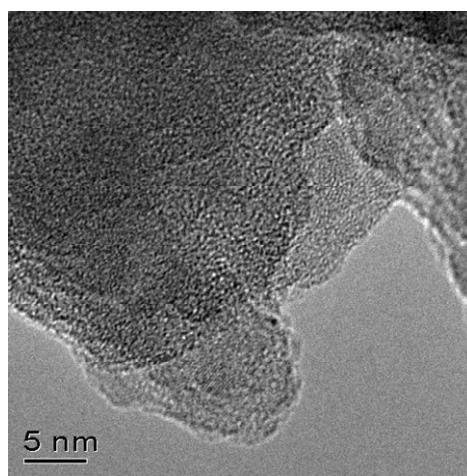
(b) EDS pattern of Portland cement paste in TEM



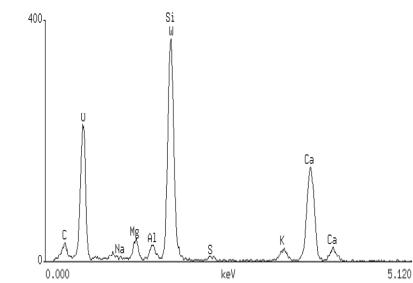
(c) HRTEM image of paste with 25% silica fume



(d) EDS pattern of paste with 25% silica fume in TEM



(e) HRTEM image of paste with 40% silica fume



(f) EDS pattern of paste with 40% silica fume in TEM

Fig.2 HRTEM images and typical EDS patterns of pastes with different amount of silica fume

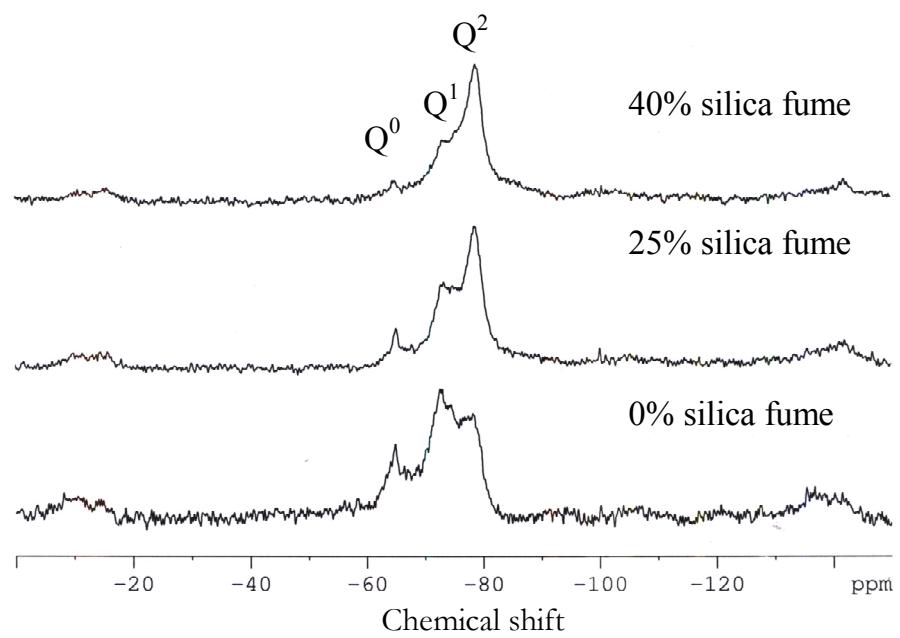


Fig. 3 ^{29}Si MAS NMR spectra of hydrated pastes