Pergamon

Cement and Concrete Research, Vol. 28, No. 11, pp. 1537–1544, 1998
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0008-8846/98 $19.00 + .00

PII S0008-8846(98)00139-2

INTERACTION OF ALKALI AND ALKALI EARTH METAL HYDROXIDES WITH MICROSILICA

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(Received September 24, 1997; in final form August 27, 1998)

ABSTRACT

Microsilica is inert to trimethylsilylation unless activated by alkaline conditions. In a sodium hydroxide–microsilica model system that simulates the alkaline conditions present in Portland cement, microsilica can be activated to produce polyorganosiloxanes. A calcium hydroxide–microsilica model system is shown to possess pozzolanic reactivity, and calcium hydroxide reacts with microsilica to form an intermediate C-S-H gel that also can be trimethylsilylated to produce polyorganosiloxanes. © *1998 Elsevier Science Ltd*

Introduction

The interaction of microsilica with Portland cement has been the subject of numerous detailed investigations (1,2). There are three separate effects caused by the addition of microsilica to cement: a pozzolanic reaction, together with active and passive filler effects. These can function both independently and synergistically.

The concentration of calcium hydroxide in pure cement pastes provides a good indication of the extent of hydration achieved (3), although the presence of a pozzolana will result in the consumption of some calcium hydroxide produced by the hydration reaction. Research has shown that pozzolana can absorb large amounts of calcium ions from the cement surface, lowering the calcium ion concentration in the liquid phase and therefore accelerating the dissolution of major components of cement hydration, especially C_3S (3).

Greenberg (4) proposed the following mechanism for the pozzolanic reaction. Calcium hydroxide is chemisorbed onto the microsilica surface due to the high pH of the surrounding solution. This subsequently reacts to form a hydrated layer on the silica surface. Due to pozzolanic activity, the durability of the cement specimens is improved, and voids and pores within the specimen become filled with crystals of calcium-silicate-hydrate, which help bridge the remaining gaps between cement grains. In addition, microsilica will fill any residual holes, such that the resulting specimen is homogenous and dense.

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During the hydration of Portland cement, a large amount of calcium hydroxide is formed together with the major cementitious phase of amorphous calcium-silicate-hydrate. Pozzolans such as microsilica react with calcium hydroxide to form cementitious calcium silicates and aluminate hydrates. The chemical and physical nature of microsilica can help enhance strength and reduce permeability when incorporated into concrete or cement pastes. Microsilica reacts with calcium hydroxide produced during cement hydration to create an increased amount of calcium-silicate-hydrate binder. The content of the weak calcium hydroxide decreases with a corresponding increase in calcium-silicate-hydrate, which provides strength and durability (5).

It is widely accepted that calcium-silicate-hydrate formed by the pozzolanic reaction between microsilica and calcium hydroxide has a smaller Ca:Si ratio than calcium-silicate-hydrate produced during hydration of Portland cement without microsilica. Several researchers (6,7) have investigated this effect and found that the smaller ratio could be attributed to lower basicity, as the microsilica reduces the concentration of potassium and sodium ions in the pore solution.

This paper discusses the observed pozzolanic reaction and the chemical interaction of sodium hydroxide solution with microsilica. The detailed mechanism of the microsilica reaction with ordinary Portland cement system is largely unknown, and attempts to monitor the silicate anion polymerisation reaction proved difficult to characterise unambiguously. The trimethylsilylated silicate anion present may have been derived from ordinary Portland cement or from microsilica due to a pozzolanic reaction (the combination of calcium hydroxide from hydrated cement combining with microsilica to produce a calcium-silicate-hydrate gel, which could be subsequently trimethylsilylated).

The properties of microsilica in isolation from the cement system were studied. Microsilica was trimethylsilylated using the Lentz method (8) and modified Lentz method (9); however no polyorganosiloxanes were produced, suggesting another mechanism was involved. As microsilica would react in the presence of ordinary Portland cement, sodium hydroxide solution was used to simulate the chemical environment present in the cement system. The addition of sodium hydroxide solution to microsilica produced polyorganosiloxanes, which strongly implies that microsilica requires an alkali medium to activate it. Several authors (2,10–12) have reviewed the literature concerning the pozzolanic behaviour of microsilica. A model system was devised to monitor the pozzolanic activity of microsilica as it depletes calcium hydroxide from the hydrating system.

There is considerable literature on the reactions of silica with water under a variety of conditions (13). However, opinions differ as to the nature of silica in dissolved water. It was found (14,15) that when silica reacts in solution and is analysed by photocolourimetric measurements, it reacts in ionic and not colloidal form. Further investigations (16–18) showed that dissolved silica in solution in the monomeric or dimeric state actually does not break down into ions but appears to be in hydrated form.

The work reported here confirms the observations that the solubility of silica increases dramatically above a pH of 10.7, which appears to involve silica depolymerisation, with silicate ions being formed (19). From the measurement of the diffusion rate at a pH above 13.6, the metasilicate ion corresponding to a monomer is stable. Between pH 13.6 and 10.9, the disilicate ion is the main ion present in solution. However, the work reported in this paper shows that even higher molecular weight silicate ions can be produced under controlled conditions.

Experimental

Reaction of Microsilica (MS) with Sodium Hydroxide (NaOH) Solution

Pure dry powdered MS (10.00 g) was weighed and placed in a Pyrex three-necked round-bottomed flask. Sodium hydroxide 2.5 M (50 cm^3) was added and the slurry stirred for predetermined time intervals of 5, 6, and 7 h, respectively. After stirring, the slurry was subsequently trimethylsilylated via the Lentz or modified Lentz method.

For the Lentz method (reagents used in the Lentz methods were used directly without pretreatment), water (40 cm^3), propan-2-ol (100 cm^3), concentrated hydrochloric acid (50 cm^3), and hexamethyldisiloxane (66 cm^3) were added to the slurry, and the reaction mixture stirred and heated under reflux for 6 h at a temperature of 72°C. After cooling, the mixture was separated into a hexamethyldisiloxane layer, a water-propan-2-ol layer, and an interfacial layer by centrifuging the mixture for 20 min at 3000 rpm. The organic layer was isolated and the excess solvent removed by rotary evaporation at 50°C/10 mm Hg to yield a mixture of polyorganosiloxanes. The insoluble products (termed recovered material) were filtered, washed with water, propan-2-ol, and diethyl ether, and dried at 100°C in an oven to constant weight.

In the modified Lentz method, water (20 cm^3), propan-2-ol (50 cm^3), concentrated hydrochloric acid (25 cm^3), and hexamethyldisiloxane (33 cm^3) were added to the reaction mixture, stirred, and heated under reflux at a temperature of 72°C for 1 h. The separation procedures followed those of the Lentz method.

Reaction of Calcium Hydroxide (CH) with Microsilica (MS)

Calcium hydroxide Analar grade (~300 g) plus a 40% addition of MS (~200 g) was incorporated with water to give a water-to-solid ratio (w:s) of 0.88. This paste was mixed for 4 min and transferred to 30-cm^3 plastic beakers, which were agitated to remove air bubbles. The samples were stored for 1 day in a moist atmosphere, demoulded, and subsequently stored at 20°C under saturated lime water until required.

The prepared samples were dried with tissue paper and crushed by pestle and mortar, as they proved too soft to pass through a hammer mill. The resulting powder was passed through a 100-μm sieve. It was felt that the standard Lentz method would be too harsh for the paste; therefore, the modified Lentz method (9) was adopted for this experiment, with the same conditions and separation method as for the MS + NaOH system. Polyorganosiloxanes were analysed by high-performance liquid chromatography using a Waters Associates model 501 chromatograph fitted with seven microstyrogel columns with toluene as the mobile phase. Tert-butylbenzene was used as an internal standard.

Results and Discussion

Microsilica (MS) with Sodium Hydroxide (NaOH) System

Several trimethylsilylation methods have been discussed, although the techniques proposed by Lentz (8,19) were adopted for the MS + NaOH system, despite side reactions that produce

TABLE 1
Polyorganosiloxanes produced from the Lentz (L) and modified Lentz (ML) methods using Elkem 965 microsilica.

	Polymer product (%)					
Microsilica experiment	QM_4	Q_2M_6	Q_xM_8	Q_xM_{10}	$>M_{10}$	% SiO_2†
MS* + NaOH 5 h L	30.73	11.85	27.46	29.96	0	18
MS + NaOH 5 h ML	50.33	17.7	31.97	0	0	5
MS + NaOH 6 h L	33.73	12.71	24.1	29.46	0	11
MS + NaOH 6 h ML	30.25	12.86	32.51	24.38	0	2
MS + NaOH 7 h L	25.39	9.54	21.28	24.83	18.96	15
MS + NaOH 7 h ML	25.12	11.62	28.57	34.69	0	3

* Denotes that all microsilicas also were subjected to the Lentz technique without NaOH and a nonstirring regime. These were generally observed to produce lower percentage yields of polyorganosiloxanes and, therefore, are not fully described in this paper.

† Denotes % SiO_2 in polymer.

higher molecular weight species. The aims of this study were to investigate the trimethylsilylation reaction between MS + NaOH using both the Lentz and modified Lentz methods. Iler (20) confirmed that the hydroxyl ion in sodium hydroxide solution acts as a catalyst at pH above 11. The hydroxyl ions convert silica to silicate ions to produce a sodium silicate that is readily trimethylsilylated (Eq. 1).

$$SiO_2 + 4NaOH \rightarrow Na_4SiO_4 + 2H_2O \quad (1)$$

As the CH + MS produces a calcium-silicate-hydrate gel due to pozzolanic action, microsilica may react with sodium hydroxide solution to produce an intermediate (Eq. 2).

$$SiO_2 \rightarrow \underset{\text{sodium silicate hydrate gel}}{\text{(N-S-H)}} \quad (2)$$

A separate study has shown that by using microsilicas without the addition of sodium hydroxide, no Q_xM_y polyorganosiloxanes were produced via the Lentz method. It was proposed that to investigate polyorganosiloxanes derived from various microsilicas, the addition of sodium hydroxide to simulate the chemical environment present in an ordinary Portland cement system was essential.

Samples of microsilicas of varying silica content were obtained from different manufacturing processes and investigated using the trimethylsilylation technique. For reasons of clarity, only the results for Elkem 965 microsilica analysed using gel permeation chromatography are described in this paper.

Elkem 965 microsilica was chosen because of a relatively high SiO_2 content (94.8%) and intermediate reactivity. After stirring for a fixed period to activate the SiO_2 content present, it was subjected to the standard or modified Lentz trimethylsilylation technique to verify if high molecular weight species were produced and to determine the distribution of the Q_xM_y polyorganosiloxanes formed.

Table 1 shows relative polyorganosiloxane percentage yields and corresponding %SiO_2

content in polymers for the Elkem microsilica series, against reaction method and stirring duration. It was observed that most SiO_2 was found in polymers produced by the standard Lentz method, which may be attributed to harsh reaction conditions and indicates higher molecular weight species are being produced. In comparison, the percentage SiO_2 content in polymers produced by the modified Lentz method was relatively low, which is ascribed to the relatively mild reaction conditions. The standard Lentz method therefore was adopted to investigate the different Q_xM_y polyorganosiloxanes produced by other microsilicas with varying SiO_2 content, although these are not discussed in detail in this paper.

The Lentz method produced Q_xM_y polyorganosiloxanes and tended to produce a wider spread of QM polymers than the modified Lentz, possibly due to longer exposure to alkaline conditions. Activators such as group I and II metal hydroxides accelerate the dissolution of silicon by breaking the silicon-oxygen bonds (21), therefore producing further polymerisation sites to produce higher molecular weight species.

The Lentz method appears to show a decrease in %QM polymers on further exposure to NaOH, which may be ascribed to silicic acids produced by the reaction remaining as soluble polymers. Alternatively, there may be a decrease in lower molecular weight species at the expense of higher ones, because the 7-h standard Lentz specimen was observed to produce $>M_{10}$ species. Similar trends are observed for the modified Lentz technique.

It was postulated that the standard Lentz technique would produce polymers with a high SiO_2 percentage content and a wider spread of QM polymers relative to the modified Lentz technique; this is due to the harsher conditions used and the extended exposure to NaOH solution. The main difference between the Lentz and modified Lentz reactions is the concentration of trimethylsilylating species and hydrochloric acid in contact with the microsilica base slurry. The modified Lentz reaction has a lower concentration of the hydrochloric acid, which produces the silicic acid, and the trimethylsilylating agent hexamethyldisiloxane. The longer the slurry is in contact with the microsilica slurry, the greater the concentration of silicic acids prior to trimethylsilylation. These silicic acids can condense to form larger polymers, which subsequently can be trimethylsilylated. The higher the concentration of hexamethyldisiloxane in the Lentz reaction, the greater the number of silicic acids that will be end capped and have less possibility for internal cross-linking.

The results show that the proportion of silica that has been converted to silicate and trimethylsilylated by the modified Lentz reaction is considerably lower in than the Lentz reaction. The silicic acids are being produced rapidly, and the trend to higher nonsoluble polymers with a very high Q:M ratio appears to increase with time. The yield of SiO_2 present in the polymers tends to decrease with time. There appears to be a less marked trend with the modified Lentz reaction with time. However, the low concentration of acid and trimethylsilylating agent has led to much smaller yields of polymers.

Calcium Hydroxide (CH) with Microsilica (MS) System

This study was undertaken to observe whether microsilica will react with calcium hydroxide and produce a calcium-silicate-hydrate gel. As previously discussed, there has been extensive research on the pozzolanic reactivity of microsilica (22–24).

Table 2 shows the polyorganosiloxane yields against the period of hydration for the CH + 40% MS system, using the modified Lentz technique.

The QM_4 monomer decreases with increased periods of hydration up to day 48; however,

TABLE 2
GPC analysis for the CH + 40% MS model system.

	Polymer group				
Microsilica experiment	QM_4	Q_2M_6	Q_xM_8	Q_xM_{10}	$>M_{10}$
CH + 40% MS Day 1	20	20.75	18.35	17.15	23.8
CH + 40% MS Day 7	16.35	18.95	17.8	16.3	30.45
CH + 40% MS Day 14	14.35	18.85	18.35	17.2	31.25
CH + 40% MS Day 48	14.25	19.65	16.55	12.3	33.05
CH + 40% MS Day 81	54.25	16.85	15.85	6.1	7.2

on day 81, a sudden increase in the QM_4 species at the expense of the other polyorganosiloxane species was noted. This may be attributed to calcium-silicate-hydrate present, which dissociates in water to produce Ca^{2+} and $SiO_4{}^{4-}$ ions; the $SiO_4{}^{4-}$ ions polymerise slowly to produce mainly monomeric species of low molecular weight and small amounts of higher molecular weight species (i.e., Q_xM_{10} and $>M_{10}$).

Similar trends as in the MS + NaOH system are observed for the CH + 40% MS model system. It was anticipated that the standard Lentz method would be too harsh on the paste system as the samples were very soft; therefore the modified Lentz method (9) method was used in this case.

The calcium hydroxide appears to disrupt the microsilica to a greater extent than does sodium hydroxide. In cement, the production of calcium-silicate-hydrate on hydration is a well-documented phenomenon. In these model experiments, the calcium hydroxide appears to catalyse the formation of extended silicate ions even after day 1. In the case of cement, the accepted theory is for the calcium hydroxide to be precipitated out of the solid solution and the silicate ions grow onto the calcium hydroxide lattice. In these model experiments, a similar effect appears to produce higher molecular weight materials in the calcium rather than the sodium case, perhaps due to differences in the solubility of sodium and calcium ions.

It was apparent that pozzolanic reactivity was present, although the results for day 81 imply the retardation of activity, which may be attributed to the consumption of calcium hydroxide within the CH + 40% MS system to produce calcium-silicate-hydrate, which subsequently dissociates and is unable to further polymerise into higher molecular weight species.

These results confirm the hypothesis that pozzolanic activity exists within the system and that a calcium-silicate-hydrate gel also is produced, which can be readily trimethylsilylated to produce low molecular weight polymers and minimum amounts of higher molecular weight species. The restricted amount of higher molecular weight species is possible due to the consumption of calcium hydroxide by the overwhelming presence of microsilica. Only a limited amount of calcium-silicate-hydrate gel is produced and subsequently trimethylsilylated as free calcium hydroxide is removed from the system by combining with microsilica to produce a calcium-silicate-hydrate gel. It can be concluded, therefore, that pozzolanic activity is present and that calcium hydroxide reacts with microsilica to produce a calcium-silicate-hydrate.

Conclusion

Microsilica in isolation does not undergo trimethylsilylation, possibly because hydrochloric acid is unable to remove cations from the microsilica or break the silicate structure. By simulating the alkaline medium present in ordinary Portland cement, it was possible to activate the microsilica to produce polyorganosiloxanes.

It was proposed that sodium hydroxide solution reacts with microsilica to produce a sodium-silicate-hydrate (N-S-H) phase. In a cement environment, calcium hydroxide from the system reacts with microsilica to produce a calcium-silicate-hydrate phase containing a low Ca:Si ratio, which suggests that sodium silicate hydrate (Eq. 3), is similar to calcium-silicate-hydrate (Eq. 4).

$$\text{NaOH} + \text{microsilica} \rightarrow \text{N-S-H} \qquad (3)$$

$$\text{CH} + \text{microsilica} \rightarrow \text{C-S-H} \qquad (4)$$

It is proposed that different sodium-silicate-hydrate phases may exist, which are analogous to calcium-silicate-hydrate gels; therefore, further study and classification of different sodium-silicate-hydrate gels (Eq. 3) are required.

Results from a model system devised to investigate the reactions between calcium hydroxide and microsilica found that pozzolanic reactivity was apparent, together with evidence that calcium hydroxide reacts with microsilica present to form an intermediate calcium-silicate-hydrate gel. This gel subsequently produces polyorganosiloxanes via the modified Lentz trimethylsilylation reaction method.

The pozzolanic activity observed concurred with the results obtained from thermal analysis, which reinforces the idea that calcium hydroxide is consumed by the overwhelming presence of microsilica at a 40% addition level. The reaction of calcium hydroxide and microsilica results in a strong-lime pozzolana calcium-silicate-hydrate gel.

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