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ESCA STUDY ON THE EARLY C_3S HYDRATION IN NaOH SOLUTION AND PURE WATER

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ABSTRACT

The surface compositions of C_3S samples that had hydrated in NaOH solution and pure water for one to ten minutes were studied by electron spectroscopy for chemical analysis (ESCA). The corresponding liquid phases of early hydrated C_3S were studied by inductively plasma emission (IPE). The results showed that Ca/Si ratios on early hydrated C_3S surfaces were higher than three, and those in NaOH solution were $(Ca+Na)/Si > 3$. A calcium-rich layer formed. The cause of the formation on the calcium-rich layer was analyzed. Accordingly, the calcium-rich layer on the early hydrated C_3S surface must be removed beforehand when CSH composition is studied with ESCA. In order to remove the calcium-rich layer, many technical problems need to be solved. *© 1998 Elsevier Science Ltd*

Introduction

C_3S is the major component in Portland cement, and its early hydration has a decisive influence on the cement setting and hardening process. By means of electron spectroscopy for chemical analysis (ESCA) and scanning electron microscopy (SEM), D. Menetrier and his co-workers (1) studied the hydration of C_3S in its early stages. They also discussed the application of ESCA technique in the studies of surface of C_3S hydration. Their studies provided information on the chemical changes on the surface of early-hydrated C_3S; this information has been widely quoted. However, they did not explain in their papers how the samples were sputtered. Therefore, it is doubtful that their Ca/Si data could stand for the real Ca/Si of CSH.

By means of ESCA and IPE, the authors investigated the surface composition and liquid phase of early-hydrated C_3S samples in NaOH solution and pure water, respectively. It was found that the Ca/Si ratios on early-hydrating C_3S surface were much greater than 3. This result was considerably different from that achieved by D. Menetrier and his co-workers. This phenomenon is analyzed in this paper in order to explore the applicability of the ESCA technique to the studies of the surface of the early-hydrated C_3S.

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Experimental

The Preparation of C_3S

C_3S was prepared by the following procedure. Analytical agents $CaCO_3$ and SiO_2 were mixed according to the molar ratio $CaCO_3$:SiO_2 = 3:1. The mixture was finely ground and rehomogenized. The same batch was burned three times, the first time at 1250°C for 1 h, the second time at 1450°C for 1 h, and the third time for 1 h at 1500°C. The sintered mass was finely ground and rehomogenized after the first two burns. The same batch of C_3S, which was checked by x-ray diffraction (XRD), was used for all hydration experiments. All of C_3S samples had to pass a 0.080-mm sieve. f-CaO of the C_3S was 0.24%.

ESCA Measuring Step

The pellets for ESCA test were prepared according to the introduced method (1). The pellet, 2 mm thick and 12 mm in diameter, was prepared by pressing 400 mg of C_3S powder at 75 KN. Just before being hydrated, the pellets were sintered at 1000°C for 1 h to remove impurities that possibly could have been absorbed on the C_3S surface during preparation.

For hydration, the pellets were submerged in 2 mL of pure water at 15°C or 0.4 N NaOH solution for 1, 5, or 10 min., respectively. During the process the containers were shaken slightly. After the selected periods of time, the samples were withdrawn with a tweezers and then immersed in absolute alcohol so as to extract the water that had been absorbed to break off the hydration. The samples thus obtained were immediately sealed in a nitrogen-filled chamber of the ESCA spectrometer. The nitrogen was pumped with a vacuum air pump until the vacuum degree reached 1×10^{-4} Pa. By this point the remaining water and absorbed alcohol in the sample had evaporated. The samples were then put in the chamber of the ESCA spectrometer.

A Model ESCA LAB MK II x-ray photoelectron spectroscope was used. During the process, the chamber was pumped until the vacuum degree reached 1×10^{-7} Pa. For every sample a low-resolution spectrum was first recorded. Next, a high-resolution spectrum was recorded for high quantitative measurement. The sensitivity factor method was used in the quantitative analysis of the elements. The result data were calculated by $n_{Ca}/n_{Si} = I_{Ca} \cdot F_{Si} / I_{Si} \cdot F_{Ca}$. In the formula, n_{Ca} and n_{Si} represent the atomic number of Ca and Si, respectively. I_{Ca} and I_{Si} represent the photoelectron strength of Ca and Si. F_{Ca} and F_{Si} represent the sensitivity factor of Ca and Si, respectively. In order to set the transmission function value, we measured the Ca/Si ration on the original C_3S surface. The measured results stated that when the transmission function value was -0.5, the Ca/Si ratio of the C_3S surface was 2.93, which approximated 3. Therefore -0.5 was chosen as the transmission function value, during the calculating process.

The surface of the C_3S sample that had been hydrated for 5 min. in pure water was sputtered by Ar beam twice for 1 min. each time. The surface composition was recorded after each sputter. The surface of the sample that had been hydrated for 5 min. in NaOH solution was sputtered once for 1 min. The composition of the sputtered surfaces was also recorded. The results are presented in Table 1.

TABLE 1
The ESCA results of hydrating C_3S samples.

Sample Name		Region	BE(ev)	Stoic	Ca/Si	(Ca + Na)/Si
Original C_3S		Si2p	100.55	1.00	2.93	
		Ca2p	346.50	2.93		
C_3S hydrating in pure water	hydrating 1 min.	Si2p	100.35	1.00	10.07	
		Ca2p	347.00	10.07		
	hydrating 5 min.	Si2p	100.30	1.00	15.54	
		Ca2p	346.60	15.54		
	hydrating 10 min.	Si2p	100.35	1.00	10.38	
		Ca2p	346.50	10.38		
C_3S hydrating in NaOH solution	hydrating 1 min.	Na1s	1071.00	6.48		9.12
		Si2p	100.05	1.00		
		Ca2p	346.00	2.64		
	hydrating 5 min.	Na1s	1072.50	8.63		10.48
		Si2p	98.80	1.00		
		Ca2p	345.65	1.85		
	hydrating 10 min.	Na1s	1070.25	10.19		12.01
		Si2p	99.50	1.00		
		Ca2p	345.55	1.82		
C_3S hydrating in NaOH solution for 5 min.	sputtered 1 min.	Na1s	1071.45	3.76		6.12
		Si2p	101.10	1.00		
		Ca2p	346.60	2.36		
C_3S hydrating in pure water for 5 min.	sputtered 1 min.	Si2p	100.35	1.00	3.87	
		Ca2p	346.10	3.87		
	sputtered another 1 min.	Si2p	100.95	1.00	3.65	
		Ca2p	346.05	3.65		

Liquid Analysis

For each experiment, 2 g of C_3S powder was put into a small bottle with a cover. Then 2 mL of pure water or 0.3 N NaOH solution was poured into the bottle. The bottle was hermetically covered and was shaken on a shaker for a selected time (1, 5, or 10 min.). Immediately after the bottle was taken out of the shaker, the solution was drawn out with a vacuum filler. A Model IPS PLASMA-30 was used. When tested, the air flow rate was 0.4 L/min., and the cooling air (argon) was 14 L/min. The results are presented in Table 2.

Results and Analysis

ESCA measure result shows that the Ca/Si ratio on original C_3S surface is 2.93, which approximated 3. This demonstrated that the sensitivity factor method and the calculating method adopted in this paper were both dependable.

All the Ca/Si ratios on the hydrated C_3S surface are higher than 3. This shows that chemical changes on the C_3S surface must have occurred after contact with water in the first 10 min., causing change on surface composition. This composition, however, cannot be the CSH gel composition, whose $Ca/Si > 3$, simply because this kind of hydrate has not been

TABLE 2
The liquid composition of hydrating C_3S ($N \times 10^{-3}$).

Sample Name		Ca^{2+}	Na^+	Si^{4+}
C_3S hydrating in NaOH solution	hydrating 1 min.	0.95	273	2.85
	hydrating 5 min.	1.75	251	2.42
	hydrating 10 min.	2.05	232	1.42
C_3S hydrating in pure water	hydrating 1 min.	12.8	—	0.00
	hydrating 5 min.	14.0	—	0.00
	hydrating 10 min.	16.4	—	0.00
NaOH solution itself		—	306	—

found up to now. With the electrical double layer theory of Skalny and Young (2), this phenomenon could be explained satisfactorily. First, C_3S dissolved incongruently and left a silica-rich surface layer. The layer absorbed Ca^{2+} and created an electrical double layer in the solution. This layer was brought out after C_3S hydration had stopped due to its electron-attracting function and was left on the C_3S sample surface. After the samples were dried in a vacuum, a calcium-rich layer formed on the C_3S surface. The layer causes the Ca/Si on the C_3S surface to be higher than 3.

The Ca/Si ratios on the surface of hydrated C_3S in NaOH solution were lower than 3. Moreover, Ca/Si ratios decreased from 2.64 to 1.82 with C_3S hydrating time increasing. There was an excess of Na^+ on the C_3S surface composition, and the Na/Si ratio increased from 6.48 to 10.19 as the hydrating time increased. If (Na+Ca)/Si was considered, their values increased from 9.12 to 12.01, which were higher than 3 also. This phenomenon can also be explained by the electrical double layer theory.

The fact that Ca/Si ratios on the dehydrated C_3S surface were lower than 3, and decreased as hydrating time increased, demonstrates that the Ca^{2+} ions that flowed out through capillaries when the samples dried directly in the vacuum were limited, and did not have important influence on the Ca/Si ratios on the hydrated C_3S surface.

The liquid analysis results indicate that when C_3S was hydrated in NaOH solution, the Na^+ concentration in solution decreased greatly, but the dissolved Si^{4+} concentration increased. This proved that Na^+ entered the initial hydrated layer of C_3S. This result conformed with the above results of surface composition tests.

For the C_3S samples hydrated in pure water for 5 min., the Ca/Si ratio decreased gradually as the sample was sputtered by Ar beam. After the sample had been sputtered by Ar for 2 min., however, its surface ratio was still higher than 3, which shows that the calcium-rich layer still existed. How long should the sample be sputtered by Ar beam in order to expose the true layer or hydrated CSH gel? This remains a problem that is very difficult to solve with the techniques that are available.

In the cases of the C_3S samples hydrated in NaOH solution for 5 min., after being sputtered by Ar once for 1 min. their Na/Si ratio decreased from 8.43 to 3.76, and that of Ca/Si increased from 1.85 to 2.36. (Na+Ca)/Si was still higher than 3. Why then did Na atoms decrease so quickly? Because Na atoms could be easily picked off by Ar^+ due to the light quality and weak electric charge of the Na atom. In addition, because the hydrated C_3S sample had been sputtered, the measured surface more closely approached the interior of

C_3S. So the number of Ca and Si atoms correspondingly increased and the Na atoms decreased.

J. F. Young and co-workers (3) studied the relationship between the water content in CSH and the relative humidity. When RH=90%, the CSH formula approaches $C_{1.7}$-S-H_4; when D-dried, that formula approaches $C_{1.7}$-S-$H_{1.2}$. In essence, when the water vapor differential pressure was $1 \sim 10^{-1}$ Pa, CSH would lose 2.8 water molecular. When vacuum degree was 10^{-7} Pa, water vapor differential pressure was much lower than 10^{-8} Pa. Thus, the water in the CSH structure would all but be removed, and the CSH would be decomposed at the condition of the water vapor differential pressure $<10^{-8}$Pa. Therefore, it is doubtful whether the information obtained with ESCA method on CSH was dependable.

The binding energy changed in different samples. The electron binding energy of Ca2p in original C_3S (not hydrated) was 346.50 ev., while that of Si2p was 100.55 ev. water. The energy of Ca2p increased slightly from 346.50 to 347.00 ev, while that of Si2p decreased slightly from 100.48 to 99.94 ev. In the C_3S samples that hydrated in NaOH solution, the binding energy of Ca2p and Si2p both decreased. In the sputtered samples, the Si2p binding energy increased and the Ca2p energy decreased.

Conclusion

As measured by ESCA, the Ca/Si ratios or (Ca+Na)/Si ratios of the surface composition of early-hydrating C_3S samples in pure water and NaOH solution were higher than 3, demonstrating that, in addition to the layer of CSH gel, a calcium-rich layer and sodium-rich layer formed on C_3S surfaces. There are two reasons for the formation of the calcium-rich layer. First, the Ca^{2+} and Na^{+} on the solid-liquid interface were absorbed on the surface of C_3S particles due to the electron attracting function. Second, Ca^{2+}, brought out by the water that had penetrated into the samples and flowed out through capillaries while the vacuum chamber was pumped, gathered on the surface of the C_3S samples. The former reason is more important. In order to obtain the true Ca/Si ratios of CSH of early-hydrating C_3S surface with ESCA, the calcium-rich layer should be removed beforehand.

For hydrating C_3S samples in NaOH solution, Na^{+} instead of Ca^{2+} entered the electrical double layer and the hydrated layer of C_3S.

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