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Initial hydration of tricalcium silicate as studied by secondary neutrals mass spectrometry

I. Sample preparation and calibration

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Abstract

Secondary neutrals mass spectrometry (SNMS) is a method that enables to establish the chemical composition (stoichiometry) at the surface of solids with an extremely low information depth and thus without interference from deeper regions of the material. The method may be also applied for analyzing the composition of the material as a function of distance from the surface. This is done by gradual material removal from the analyzed surface by sputtering. For these reasons, SNMS is particularly suitable for the study of the hydration of tricalcium silicate (C_3S) in its initial stage. In this first part of the paper, the principle of the method, the sample preparation, and the calibrations for the measurements to be performed are described. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In this series of papers, we present our data found in the study of the hydration of tricalcium silicate (abbreviated C_3S), the main constituent of Portland cement, by secondary neutrals mass spectrometry (SNMS), a method not used in cement research as yet. Due to its extremely low information depth, SNMS is particularly suitable for the study of the hydration process it its initial stage, when the thickness of the layer of the hydrated material covering the nonhydrated substrate is low and the necessity to eliminate the interferences from the latter exists. Also, the method is better suitable for studying materials with low electric conductivity than secondary ions mass spectrometry (SIMS), a method similar to, but not identical with SNMS.

Before applying the method for the study of C_3S hydration, several problems had to be solved and questions answered, notably:

How to produce a suitable target to eliminate the problems arising from the low electrical conductivity of the phases studied.
What is the exact information depth of the method?
Which peaks in the obtained SNMS spectrum to select for determination of the Ca/Si ratio in the material and what is the relationship between the peak intensity ratio and concentration ratio?
What is the rate of material removal in the course of sputtering?

In the first paper of this series, we will deal with these problems, whereas in the second paper we will present experimental data obtained by the use of SNMS on C_3S samples hydrated under different conditions and for different periods.

2. Method and apparatus

In an SNMS analysis, the sample to be investigated is bombarded with ions of a rare gas. These penetrate up to several atomic layers into the surface of the specimen, where they dissipate their energy through collisions with the surrounding atoms. A collision cascade results. Parts of the collision cascade end at the surface and if—as the consequence of it—the atomic particles located there gain enough energy, these will leave the surface. Such particles

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may exist either as positively or negatively charged ions or as neutrals and may be emitted either as single atoms/ions or in combinations of the latter. Parallel to an emission of neutral or ionized particles, an excitation of the atoms of the solid takes also place, resulting in the generation of an electromagnetic radiation, which, however, is disregarded in the SNMS analysis. The theory of the process is discussed in more details in Refs. [1–4]. In the next step, the emitted neutrals are separated from the charged particles and subsequently acquire a charge themselves while passing through plasma. Finally, the particles are divided according to their charge-to-mass ratio using conventional mass spectrometry and counted electronically. A more detailed description of the method may be found in Refs. [3,5–9]. The SNMS method differs from the SIMS procedure mainly by omitting charged particles from the detection process.

The mass spectra obtained in the SNMS analysis provide information on the chemical composition of the surface region of the specimen, notably—in the case of nonhydrated or hydrated C_3S—about the existing Ca/Si ratio. Unfortunately, however, the method cannot be used for a simultaneous determination of the H_2O/SiO_2 ratio in the existing C-S-H phase, mainly due to the absence of suitable peaks, indicating the presence of H_2O, in the produced SNMS spectrum.

In SNMS measurements, most of the particles leaving the surface originate from the upper atomic layer and virtually all of them from a depth not greater than 0.5 nm [7,10]. Thus, the information depth of this method is significantly more favorable than that of ESCA (electron spectroscopy for chemical analysis), a method employed in the past in the analysis of the surface of hydrated binders. As a consequence, the SNMS procedure enables to determine the composition of even very thin layers without interference from deeper regions.

As the ion beam employed in the sputtering process in the SNMS analysis produces a well-defined abrasion of the surface, a compositional depth profile of the sample may be also obtained, which shows the changes in composition of the specimen as a function of the distance from the surface [3,5,7,8].

The analytical work reported within this paper was done with an *I*ons and *N*eutrals *A*nalyzer (model INA 3, Leybold, Koln, Germany). In this apparatus, the plasma adjacent to the sample enables the sputtering, postionization of the neutrals by interaction with the present electrons, and a charge compensation. The employed Kr–plasma had a density of around 5×10^{10} cm^{-3} and a degree of ionization of about 10^{-2}. The energy of electrons exhibited a Maxwell distribution with a medium magnitude of 13 eV.

2.1. Synthesis of the starting materials

In the synthesis of the starting materials, precautions had to be taken to avoid contamination, in particular, alkalis that could impair the SNMS analysis.

C_3S was produced from a stoichiometric blend of high-purity precipitated $CaCO_3$ and precipitated SiO_2. After homogenizing a water suspension of these materials, the blend was first dried at 110 °C and then calcined at 1000 °C. Subsequently, it was burnt at 1600 °C two times for 4 h. The free lime content in the final product was 0.18%.

Dicalcium silicate (C_2S) was produced in an analogous way as with C_3S, yet was burnt at 1600 °C only once. The final product was γ-C_2S combined with smaller amounts of β-C_2S. The content of free lime was 0.12%.

Monocalcium silicate (CS) was produced analogously, yet the burning temperature was only 1450 °C. The final product was α-CS (pseudo-wollastonite) with a free lime content of 0.49%.

2.2. Preparation of the targets

In the preparation of the targets to be studied, appropriate measures had to be taken to avoid a build-up of an electric charge at the surface. As the production of a conductive coating had to be dismissed due to the destructive character of the procedure, the following solution was adopted: The pre-crushed, powdered calcium silicate (fraction 60–90 μm) — in its original state or after being hydrated—was spread over a foil (7×7 mm^2, $h = 0.25$ mm) of metallic indium, using a sieve with an appropriate mesh width. Subsequently, the individual grains were pressed into the metal, using a glass plate. A covering of the surface with the analyzed material of 20–30% was found to be most appropriate. The sample prepared this way was fixed within the apparatus using a sample holder made of high-purity copper.

2.3. SNMS spectrum of nonhydrated C_3S

In Fig. 1, the SNMS spectrum of nonhydrated C_3S is reproduced. The following peaks can be identified:

peaks belonging to krypton, which was used as plasma gas,
peaks belonging to copper, which used for making the sample holder,
peaks belonging to calcium ($m/z = 40$, 44, and 42), silicon ($m/z = 28$ and 29), oxygen ($m/z = 16$), and carbon ($m/z = 12$) were all ionized to the first degree,
a peak belonging to indium was ionized to the second degree ($m/z = 115/2$),
a peak at $m/z = 56$, which most likely belongs to the ion CaO^{+}, but may also belong to Si^{2+} or even to $^{113}In^{2+}$.

Out of these, to estimate the Ca/Si ratio in the material, as well as to determine a depth profile, the peaks belonging to Ca^{+} ($m/z = 40$) and Si^{+} ($m/z = 28$) were selected.

2.4. Variations in peak intensities in the course of measurement

Fig. 2 shows the peak intensities belonging to individual species as a function of sputtering time. The measurement

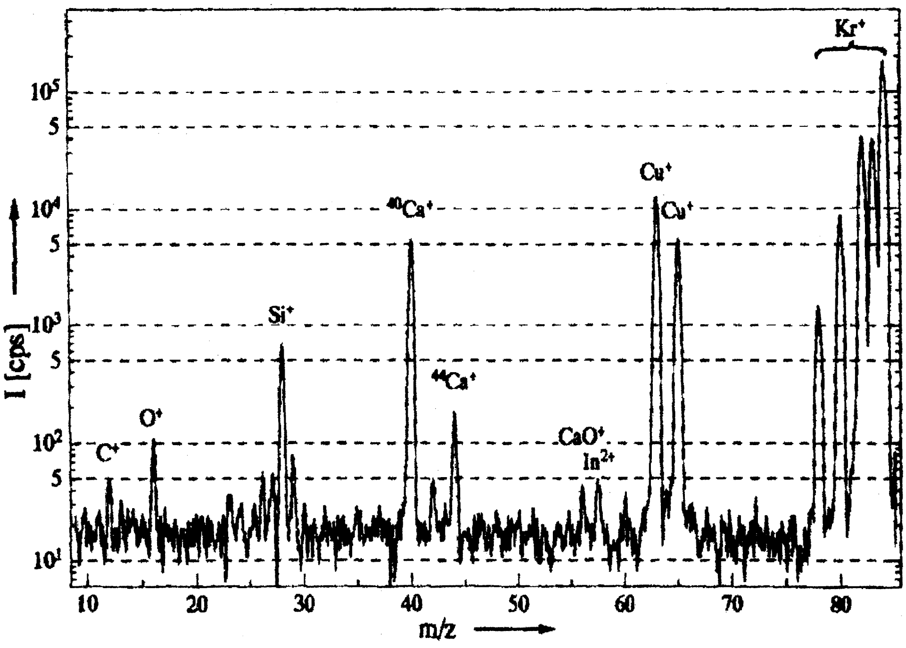

Fig. 1. SNMS spectrum of C_3S.

was performed on a C_3S sample that was allowed to hydrate in a 3% NaCl solution at ambient temperature for 45 min.

The small fluctuations of the intensities of individual signals are the consequence of the statistical nature of the sputtering process and secondary ionization. The relative magnitude of such fluctuations amounted to about ±3–6% for Si and Na and was somewhat lower for Ca and higher for Cl. The occasional greater short-term deviations are due to an insufficient charge compensation of the target.

The anomalies in the intensity of most signals, commonly seen in the first seconds of the experiment, must be attributed to the presence of species adsorbed at the surface, making it necessary to disregard these data.

The figure also reveals a gradual change of the overall intensity of most peaks studied as the measurement progressed:

The moderate increase of the signal belonging to In was probably caused by the rise of the temperature of the target.

The gradual increase of the intensities of signals belonging to Ca and Si was probably due to a rise in the con-

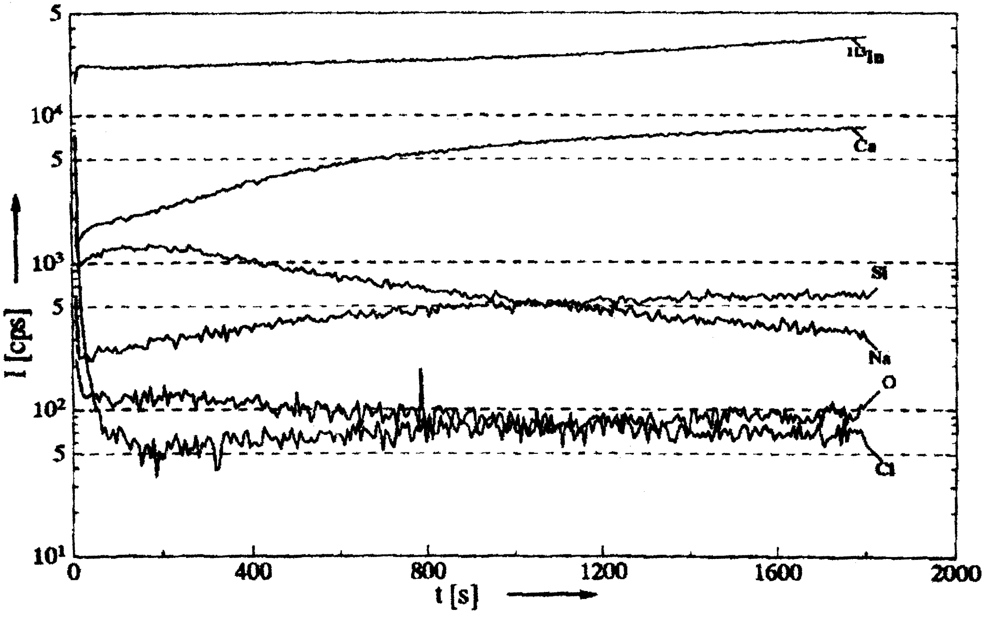

Fig. 2. Intensities of peaks belonging to individual species as a function of sputtering time.

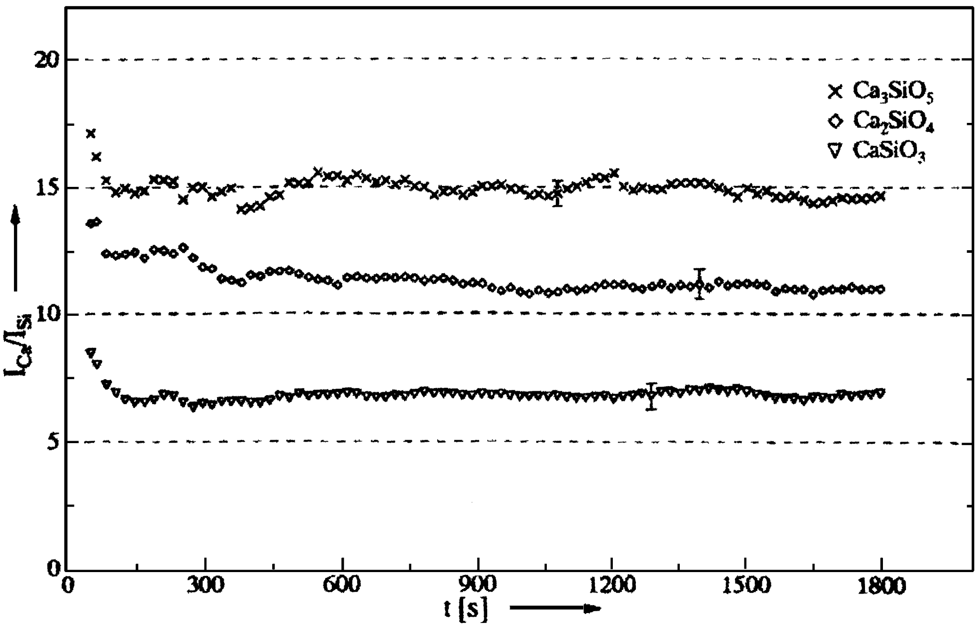

Fig. 3. I_{Ca}/I_{Si} ratios found for CS, C_2S, and C_3S as a function of measuring time.

centration of these species in the present C-S-H phase, resulting from a decrease of the amount of bound water in this phase with increasing distance from the surface. At the same time, however, a parting of bound water from the material due to heating may have also taken place and may have also contributed to the observed changes.

The gradual weakening of the intensities of peaks belonging to Na and Cl indicates a decline of the amount of these species in the present C-S-H phase with increasing distance from the surface.

2.5. Calibration for determination of the Ca/Si ratio

To enable the determination of the Ca/Si atomic ratio in samples of unknown composition, the ratio of the intensities of peaks belonging to Ca and Si (I_{Ca}/I_{Si}) in preparations of CS, C_2S, and C_3S was measured. Fig. 3 shows the I_{Ca}/I_{Si} ratios for these three compounds as a function of time of measurement. The resulting values decreased somewhat within the first seconds of measurement and subsequently stayed virtually constant indefinitely. In establishing the

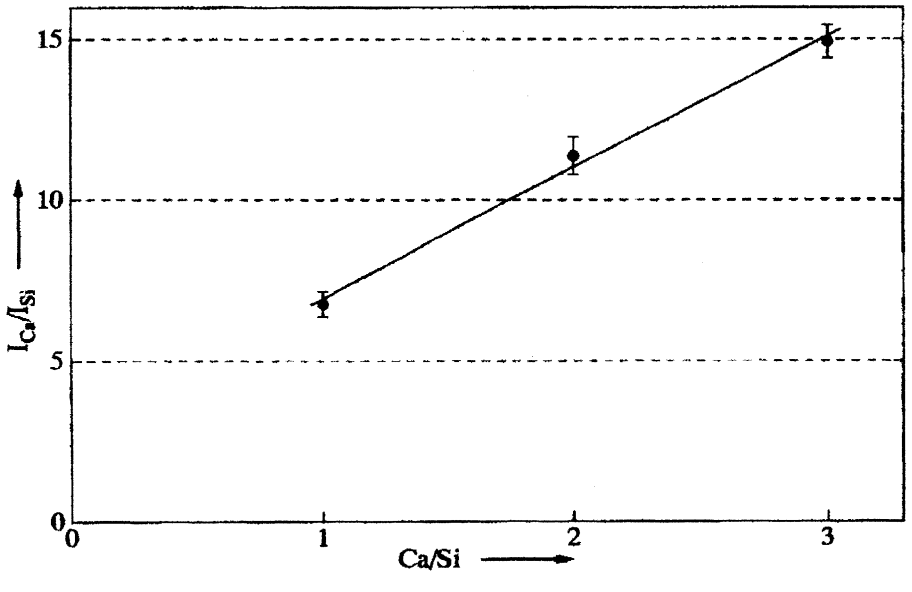

Fig. 4. I_{Ca}/I_{Si} ratio as a function of the atomic Ca/Si ratio.

calibration curve, these initial values were disregarded. Fig. 4 shows the average I_{Ca}/I_{Si} ratios as a function of the Ca/Si atomic ratio in the materials. It may be seen that in the range between Ca/Si = 1.0 and Ca/Si = 3.0, a linearity, not a proportionality, between the Ca/Si concentration ratio and the I_{Ca}/I_{Si} intensity ratio exists, as the pertinent straight line does not pass through the zero point. This phenomenon, commonly called "matrix effect," is caused by differences in the chemistry of the individual samples serving as standards, which in turn affect the energy level of the present electrons and ultimately the amount of the emitted secondary particles.

2.6. Reproducibility

To establish the reproducibility of the measurements, six samples of C_3S were allowed to hydrate for 45 min in a 3% solution of NaCl in water ($w/C_3S = 666$), filtered, and dried. Subsequently, in each the Ca/Si molar ratio was determined twice, using the calibration curve shown in Fig. 4. On the basis of these 12 measurements, a Ca/Si atomic ratio of 2.0 ± 0.15, corresponding to a relative standard deviation of ± 7.5%, was found.

2.7. Calibration for concentration depth profiling

To be able to determine the concentration depth profiles of hydrated C_3S samples, the rate at which the material is removed in the course of sputtering must be known. To establish this parameter, a gravimetric procedure was employed: Powdered C_3S was applied on an indium foil in a way as described above and the fraction of the surface covered with C_3S was determined microscopically by electronic image processing. Subsequently, the sample was sputtered for 7200 s and the resulting loss of mass was measured gravimetrically. In a parallel experiment, the loss of mass of a plain foil due to sputtering was also determined. Based on the obtained results, the rate of C_3S removal due to sputtering (z) was calculated, taking into consideration the density of this material ($d = 3.074$ g cm^{-3}). The following value was found and used in measurements reported in Part II of this series of papers:

$$z = 0.303 \pm 0.080 \text{ nm/s}.$$

It has to be noted, however, that the value found this way represents the average rate of material removal. In a sample consisting of a set of nearly spherical particles, the actual rate of removal at each point of the studied surface will depend also on the degree of deflection of the surface from the vertical plane. Generally, the removal rate increases moderately up to about 60° and declines rather abruptly at even higher angles [8].

In a separate experiment, the evenness of the material removal in the course of sputtering was also tested. To do so, a plain copper surface was sputtered for 170 min and the characteristics of the crater produced in the sputtering process were determined by the aid of a profilometer. It was found that the crater was evenly deep with an average depth of 2930 ± 100 nm, which corresponded to a copper removal rate of 0.29 nm/s.

3. Conclusion

SNMS is a method that allows the measurement of the Ca/Si ratio in hydrated calcium silicates at an extremely low information depth, i.e., less than 0.5 nm. This enables the determination of this parameter in very thin C-S-H layers, including those that form at the C_3S surface after short hydration times, without interference from underlying regions. The method is also well suitable for the determination of the composition within the formed C-S-H region as a function of the distance from the surface. However, to obtain reliable data, an accurate calibration must precede the measurement.

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