
Fractal Structure of C–S–H and Tobermorite Phases

J.A. JANIK^a, W. KURDOWSKI^b, R. PODSIADŁY^c

AND J. SAMSETH^d

^aH. Niewodniczański Institute of Nuclear Physics
Radzikowskiego 152, 31-342 Kraków, Poland

^bMining Academy, Mickiewicza 30, 30-059 Kraków, Poland

^cM. Smoluchowski Institute of Physics, Jagiellonian University
Reymonta 4, 30-059 Kraków, Poland

^dInstitutt for energiteknikk, 2007 Kjeller, Norway

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The C–S–H I phase is the main component of the cement paste, which is a near-amorphous, highly porous gel. Due to high porosity of the sample in this phase we can observe a fractal nature of the volume pores distribution, similar to that observed for silica aerogels. The C–S–H I phase is thermodynamically unstable and crystallize to a tobermorite phase, forming crystal aggregates on the surface of the amorphous paste. The mixture of these two phases, formed in this way, have irregular volume and surface structures, both of which may exhibit the fractal nature. To study the fractal nature of the matter the small angle neutron scattering method is frequently used. We present here the results of small angle neutron scattering studies supported by the X-ray diffraction and scanning electron microscope observations of several samples with the common molar C/S ratio equal to 1. Some of the samples were autoclaved during various time periods to accelerate transformation of the C–S–H I phase to tobermorite. We observed the fractal properties of the volume structure of all samples under study. Moreover, we observed also the fractal behaviors of the surfaces of the samples which were autoclaved.

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1. Introduction

The C–S–H I phase is the main component of the cement paste. Although it is a subject of intensive studies, a complete understanding of some phenomena is still lacking. It is principally due to inhomogeneities existing in the structure of C–S–H I phase and changes of its chemical composition. It is well known that C–S–H I phase is thermodynamically unstable and presents a tendency to crystallization [1]. It transforms to tobermorite but this process is very slow, probably due to difficulties in nucleation. The elevated temperatures accelerate the transformation and high pressure seems to be even more efficient [1]. In the majority of cases the product of transformation presents a mixture of C–S–H I and tobermorite [2]. The C–S–H I phase is a near-amorphous gel with a great specific surface exceeding $150 \text{ m}^2/\text{g}$. It is composed of a few elementary layers forming wrinkled foils whose thickness amounts to several nanometers. This phase is highly porous.

Tobermorite has a layer structure and when well crystallized it forms the plates of hexagonal shape whose size is of the order of several micrometers and their thickness amounts to 20 nm [2].

The mixture of these two phases shows up as an irregular volume structure with a highly porous surface [2]. In recent years a suggestion has been made concerning the fractal character of these materials [3–6]. This paper aims to provide a further support of this hypothesis.

2. Preparation of samples and their characteristic properties

The C–S–H I phase was obtained by long-lasting shaking of the water suspension of $\text{Ca}(\text{OH})_2$ and amorphous SiO_2 . A commercially available material Aerosil (Degussa Co.) was applied as silica. The molar ratio of CaO to SiO_2 was equal to 1 ($C/S=1$). The shaking process lasted 2 months, at temperature of $20 \pm 2^\circ\text{C}$, and at complete isolation from atmospheric CO_2 . Final samples did not contain free $\text{Ca}(\text{OH})_2$ which was confirmed by a disappearance of characteristic lines in the X-ray diffractogram which showed only the characteristic reflections for the C–S–H I phase (Fig. 1). For the C–S–H I phase the most characteristic lines are those at about 1.42, 0.30, 0.28, and 0.18 nm. The characteristic basal reflection is at 1.42 nm. This corresponds to the thickness of the elementary layer of a strongly disturbed C–S–H I phase. The remaining three lines at 0.30, 0.28, and 0.18 nm correspond to shorter distances between layers in the disturbed layer structure of the C–S–H I phase.

The C–S–H I with the low C/S molar ratio were chosen because it transforms in hydrothermal treatment in relatively pure tobermorite [2]. It is due to the fact that C–S–H I is closely related to 1.4 nm tobermorite [7]. The C–S–H I C/S ratio equal to 1 is lower than in Portland cement, but it is very close to that in fly ash cement [8].

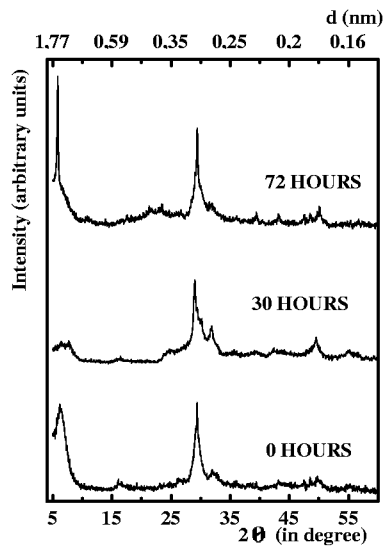


Fig. 1. The diffractograms obtained for the initial sample C-S-H I phase (labeled as 0 HOURS) and the samples which were autoclaved during 30 and 72 hours (labeled as 30 HOURS and 72 HOURS, respectively). The diffractograms are shifted along the intensity axis to clarify the picture. The description of the picture is in the main text.

The C-S-H I phase obtained in this way, was then subjected to an autoclaving process at the temperature of 150°C in the saturated water vapor. This treatment lasted from 10 to 72 hours. As it is seen in Fig. 1, the content of tobermorite increases with the time of autoclaving. In the sample which was autoclaved 30 hours two small reflections appear at *ca.* 1.40 nm and 1.14 nm, instead of the 1.4 nm line of the C-S-H I phase. These two lines correspond to two modifications of tobermorite, the so-called 1.4 and 1.14 ones [1]. Apart from these two characteristic lines also further peaks of 1.4 tobermorite appear at *ca.* 0.281 and 0.297 nm. In the sample which was autoclaved 72 hours the intensity of the 1.4 nm line increases considerably. It is connected with the increasing content of the tobermorite phase in the sample. However, an enhanced and wide background observed between 5° and 10° of 2θ , and between 25° and 30° of 2θ in the diffractograms proves that the amorphous C-S-H I phase is still present.

This conclusion seems to be supported by the scanning electron microscope (SEM) observations. As it is shown in Fig. 2, an initial sample presents a typical amorphous C-S-H I phase. The sample which was autoclaved 30 hours presents only a partial transformation of the C-S-H I phase to tobermorite and the sample treated in autoclave during 72 hours has a distinct predominant content of the latter phase.

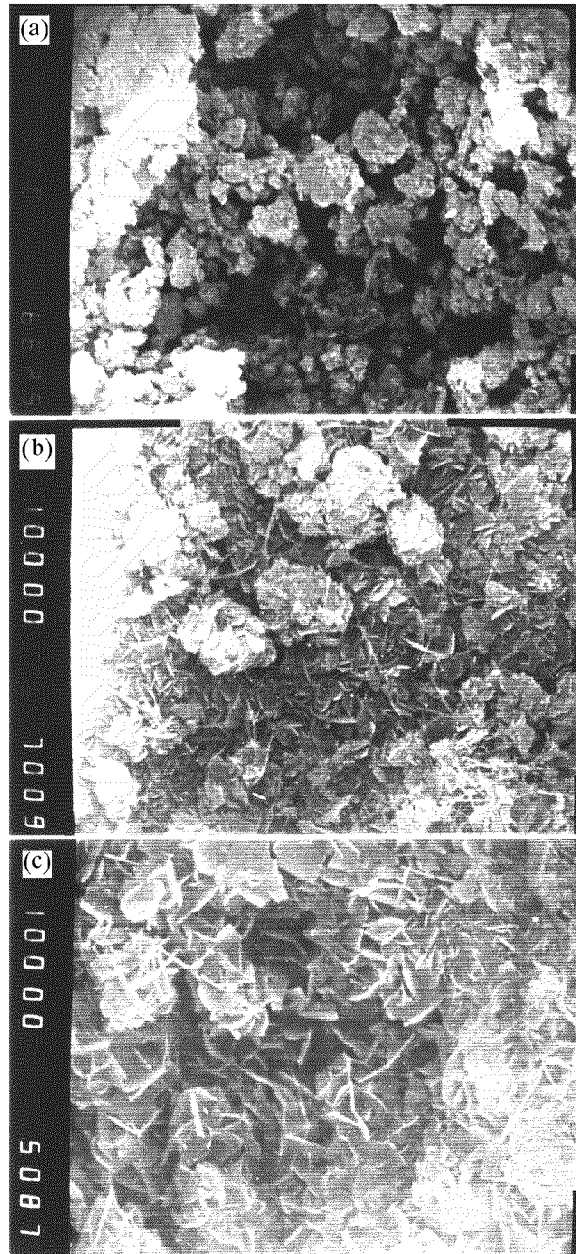


Fig. 2. Scanning electron microscope pictures: (a) pure C-S-H I phase; (b) partial transformation of the C-S-H I phase into the tobermorite phase (autoclaving time 30 hours); (c) advanced transformation of the C-S-H I phase into the tobermorite phase (autoclaving time 72 hours).

3. General information concerning studies of fractal aspects of materials via the small angle neutron scattering

On the basis of information contained in the introduction, we may suspect that our materials under study will exhibit fractal properties, like, for instance, the porous silica aerogels [4, 5]. A characteristic property of such fractal structures is a self-similarity of pores distribution in a wide range of observation scales [4, 6]. For such materials the scaling is described by a universal exponent. Its value is *ca.* 2.4 [4, 5]. This exponent is known as the volume fractal dimension — D_V (Hausdorff dimension) [4, 5, 9, 10]. Not only pores in a bulk material but also a porous structure of its surface may exhibit self-similarity, i.e. fractal behavior. In such cases a surface fractal dimension — D_S is introduced [9, 10].

The so-called Menger sponge (Fig. 3) may serve as an example. This is an ideal (mathematical) fractal for which there is an unlimited self-similarity range. The bulk of Menger sponge forms a volume fractal with the volume fractal dimension $D_V = 2.73$, whereas each of its 6 faces forms a surface fractal (the so-called Sierpiński carpet) with the surface fractal dimension $D_S = 1.89$ [9, 10]. Real (non-ideal) fractal materials have always a limited scaling range [4-6]. The distribution of pores for real materials is of course irregular.

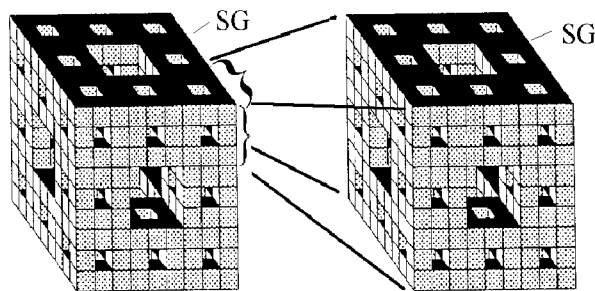


Fig. 3. Self-similarity of the Menger sponge. Any, arbitrarily chosen, smaller part of the Menger sponge (for example, the one in brackets in the picture) looks similar to the whole sponge (in other words: the object, and its smaller part enlarged to the same scale, like in the figure, are indistinguishable). One face of the sponge is shadowed and labeled by SG letters to show the Sierpiński gasket, which is also self-similar. Both Menger sponge and Sierpiński gasket are fractals and their Hausdorff dimensions are 2.73 and 1.89, respectively [9, 10]. The Menger sponge is the volume fractal because its external edges (envelope) form 3-dimensional object (a cube), and the Sierpiński gasket is the surface fractal because its external edges form a 2-dimensional object (a square).

The small angle neutron scattering (SANS) method is one of the methods of studies of fractal properties [3, 4]. The intensity of scattered neutrons vs. neutron momentum transfer obeys (for fractals) the following scattering law [4, 5]:

$$I(q) \propto q^{-D}.$$

In the double log scale this gives

$$\ln I(q) = -D \ln q + \text{const.}$$

If $D < 3$, exponent D may be interpreted as D_V [4, 5]. In some cases, however, it may happen that $D > 3$. For such cases Porod [4, 5, 11] has suggested a different form of the neutron scattering law

$$I(q) \propto q^{-(6-D)}$$

and, consequently

$$\ln I(q) = -(6 - D) \ln q + \text{const.},$$

where D is now the Hausdorff dimension of a surface fractal — D_S [4, 5].

4. Results of SANS measurements

Small angle neutron scattering measurements were carried out in the Risø National Laboratory in Denmark. The incident neutron wavelength varied from 0.3 to 1.4 nm. The sample-detector distance varied from 1 to 6 m. Background and empty sample-holder corrections were made. Data were normalized in relation to H₂O. They were integrated radially.

Figure 4 presents SANS spectra for the initial sample (C-S-H I phase), and for two samples which were autoclaved during 30 and 72 hours. The spectra are presented in the double log scale. Straight lines were fitted to the spectra for evaluating the slopes. When their tangents were smaller than 3, they were interpreted as D_V . When the tangents were larger than 3, they were interpreted as connected with the surface fractal. D_S was then calculated from the following formula:

$$|\tan \alpha| = 6 - D_S.$$

The final results are collected in the Table. The following remarks have to be made:

1. The amorphous sample (C-S-H I phase) shows volume fractal properties only. $D_V \approx 2.4$. This value is similar to that characteristic of silica aerogels [4, 5].
2. The samples which were autoclaved at 150°C in the saturated water vapor show two regions characteristic for fractal properties: at small momentum transfers (corresponding to large values of correlation lengths) these properties may be interpreted as volume fractals with $D_V \approx 2.4$. At large momentum transfers we observe surface fractals with D_S which do not differ significantly from $D_S = 2.6$; it is from the value obtained by us in an earlier paper [3] for the C-S-H I phase, having molar C/S ratio equal to 1.

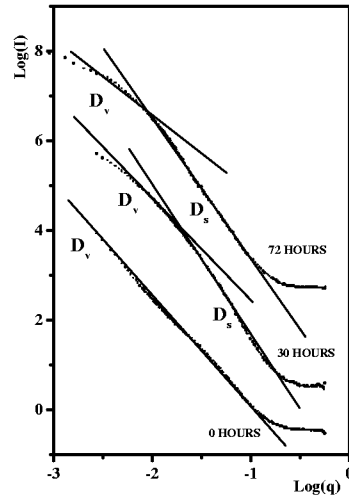


Fig. 4. The small angle scattering spectra obtained for the initial sample C-S-H I phase (labeled as 0 HOURS) and the samples which were autoclaved during 30 and 72 hours (labeled as 30 HOURS and 72 HOURS, respectively). The lines in the picture represent results of the straight line fitting procedure. The fitted lines are labeled by the symbols D_V and D_S which denote volume and surface fractal ranges on the spectra, respectively. The numeric results of fitting are collected in the Table. The spectra are shifted along the intensity axis to clarify the picture.

TABLE

The results of the straight line fitting procedure. D_V stands for the volume fractal dimension and D_S for the surface one. The values of standard deviations are also included in the Table (labeled as \pm).

Autoclaving time [hours]	D_V	D_S
0	2.37 ± 0.12	None
30	2.51 ± 0.23	2.75 ± 0.15
72	2.32 ± 0.22	2.60 ± 0.19

The C-S-H I phase may be treated as the model of the real cement materials, and therefore, it is the subject of many experiments. The very interesting feature of different systems contained silica components (both real and model) is the universality of their fractal behavior (qualitative and quantitative) observed by different experimental methods. Niklasson [12], for example, performed BET (Brunauer, Emmett, Teller) adsorption experiment for the C-S-H I phase and

for an ordinary Portland cement. He observed fractal behaviors of those materials. The fractal dimensions of the samples were between 2.2 and 2.55 which are very similar to the values obtained in this work. Winslow et al. [13], Kriechbaum et al. [14], and Beddoe with Lang [15] performed the small angle X-ray scattering and BET experiments for hydrated Portland cement pastes. They observed two kinds of fractal behaviors (surface and volume) with fractal dimensions very similar to those obtained in our experiments. However, the samples under study in the above-mentioned papers are different than the materials we used, but the fact of the similarity of the chemical composition and strong similarity of the physical behavior (qualitative and quantitative) may show certain general universality of the inner structure of cement materials.

5. Conclusions

The evidence of fractal properties of C-S-H I phase was obtained by using the small angle neutron scattering. The volume fractal dimension value of *ca.* 2.4 was obtained for all samples studied.

The samples with an increasing content of tobermorite showed two regions of fractal properties: one corresponded to the volume fractals with $D_V \approx 2.4$ and one corresponded to the surface fractals with $D_S \approx 2.6$.

This interpretation agrees qualitatively with the microscopic observations: the volume fractals are connected with gel pores characteristic of the C-S-H I phase. These gel pores survive partially after autoclaving, i.e. some quantity of C-S-H I gel remains in the sample. The surface fractals are connected with randomly distributed polycrystalline aggregates, formed of tobermorite crystals.

The results presented in this work are in good qualitative and quantitative agreement with the results obtained by other authors for very similar systems but using different experimental methods. It may suggest the existence of the certain general universality of the inner structure of cement materials.

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