

STUDIES OF FRACTAL ASPECTS OF CEMENT

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Small angle neutron scattering can be used to reveal the fractal nature of matter. The problems of fractal aspects of the structure of cement are related to those of fractal aspects of silica aerogels. Natural cement, when mixed with water, transforms after a series of chemical reactions (in a large part) into an amorphous phase called C-S-H. It is believed that the cationic sublattice composed of CaO_6 octahedrons constitutes the C-S-H structural basis, to which the SiO_4 tetrahedral chains are attached. It is a layer structure in which the cation sublattice determines the way of SiO_4 condensation. It is natural to expect that in this way one may obtain a really amorphous substance, since some tetrahedrons may be lacking, which leads to defects. We present here the results of a small angle neutron scattering and X-ray diffraction study of several samples with the pure C-S-H phase for which during the process of chemical synthesis various ratios of molar contents of CaO and SiO_2 were used (various C/S ratios). We obtained a gradual change of fractal characteristics with the change of C/S ratio.

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1. Introduction

The problems of fractal aspects of the structure of cement are related to those of fractal aspects of silica aerogels. The latter were subjected to various studies performed by the small angle neutron scattering (SANS) method, which provides not only the evidence, but also a quantitative description of the fractal structure [1-3]. Those studies analyzed the linear part of the dependence: logarithm of the scattered neutron intensity vs. logarithm of the neutron momentum transfer. The existence of such a linear part can be treated as a proof of a power law character of the substance density correlation function (pseudo Ornstein-Zernicke function) [1-3]:

$$g(r) \sim r^{D-3} \exp(-r/\xi), \quad (1)$$

where ξ is the correlation length and D is the Hausdorff dimension [4] of the

analyzed sample ($0 \leq D \leq 3$). Hence, one obtains a neutron scattering law (Ornstein-Zernicke law) [1, 2, 5]:

$$I(q) \sim q^{-D} \quad \text{or} \quad \log I(q) \sim -D \log q. \quad (2)$$

The Hausdorff dimension D is now a slope coefficient of the linear part of the $\log I$ vs. $\log q$ dependence (if it does exist, of course). If D is smaller than 3, it indicates the fractal behaviour of the sample and D is called the *fractal dimension* [1-4]. In the papers concerning this problem, the fractal dimension $D = 2.4$ was obtained for common silica aerogels. The linear part existed in a large range of momentum transfers Q (from *ca.* 0.005 to 0.100 \AA^{-1}).

There are cases when the dependence logarithm of scattered intensity vs. logarithm of momentum transfer has a slope which if treated in the same way would lead to a dimension larger than 3, which is nonsense. Therefore, Porod has suggested that the slope arises from the surface of the scattering clusters in the sample, and introduced the following density correlation function [5]:

$$g(r) \sim 4\varphi(1-\varphi)r^{2-D_s}, \quad (3)$$

where φ is the volume fraction of scattering clusters in the sample and D_s is the Hausdorff dimension of the cluster's surface ($2 \leq D_s \leq 3$) [2, 3]. It provides the following neutron scattering law [2]:

$$I(q) \sim q^{-(6-D_s)} \quad \text{or} \quad \log I(q) \sim -(6-D_s) \log q. \quad (4)$$

If D_s is greater than 2, it means a fractal behaviour of the cluster's surface and D_s is called the *surface fractal dimension* [2, 3].

An extension of these problems to *natural cement* may be summarized as follows [6, 7]. The natural cement, when mixed with water, transforms after a series of hydration and hydrolysis chemical reactions into a "cement paste". The cement paste is in a majority an amorphous system with only a little amount of crystalline phases. The amorphous phase is called C-S-H. It consists of the

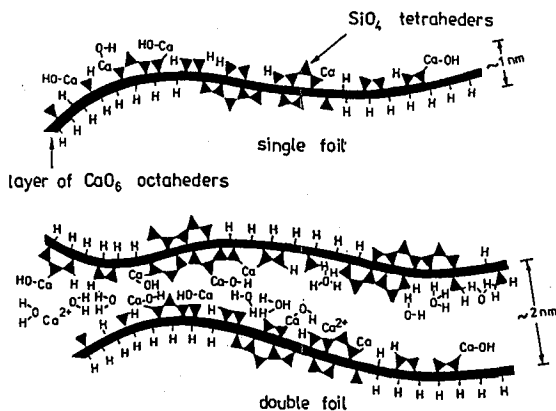


Fig. 1. Schematic picture of the structure of cement (after [7], courtesy of W. Kurdowski).

tri- and di-calcium-silicate compounds with a different Ca/Si (C/S) molar ratios (e.g.: $\text{Ca}_2\text{SiO}_4 \cdot n\text{H}_2\text{O}$, $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot n\text{H}_2\text{O}$, $\text{Ca}_3\text{Si}_3\text{O}_9 \cdot n\text{H}_2\text{O}$, and so on). The C-S-H phase fully determines behaviours of the paste [6]. It is believed that the cationic sublattice, which is composed of the CaO_6 octahedrons, constitutes its structural basis, to which the SiO_4 tetrahedral chains are attached. This is a layer structure in which the cation sublattice determines the way of SiO_4 condensation. It is natural to expect that in this way one may obtain a really amorphous substance, since some tetrahedrons may be lacking, which leads to defects. This rather complicated situation is shown in Fig. 1 [7].

Taking the mentioned cement features into account, in this paper we present results of a X-ray and a SANS study of several samples, consisting of the *pure* C-S-H phase which we treat as a *model* of the real cement paste. Various ratios of molar contents of CaO and SiO_2 were used (various C/S ratios) during the process of chemical synthesis. As it is shown in the following sections, we obtained a gradual change of fractal characteristics with the change of C/S ratios.

2. Samples and their X-ray diffraction testing

To accelerate the C-S-H phase preparation an amorphous SiO_2 was used (the Aerosil product of the Degussa Company). The specific surface of that product was about $200 \text{ m}^2/\text{g}$. The C-S-H phase was obtained from an aqueous suspension

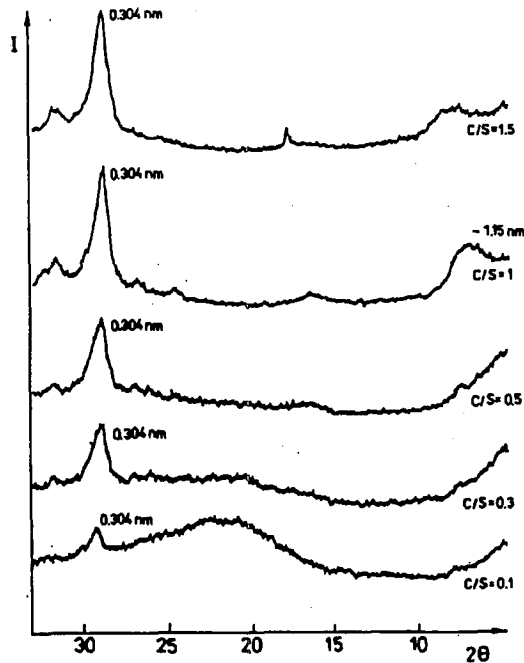


Fig. 2. X-ray diffraction patterns for samples with various C/S ratios. The spectra are shifted along the "I"-axis to clarify the picture.

of SiO_2 and $\text{Ca}(\text{OH})_2$ by shaking in the course of many weeks (for the crystalline SiO_2 this process needs much longer time). Various C/S ratios were obtained by selecting proper molar quantities of the reacting substances. The suspension was carefully protected from the atmospheric CO_2 during the process of shaking. Five samples were prepared in this way — with C/S = 0.1, 0.3, 0.5, 1.0 and 1.5.

The X-ray diffraction patterns (Fig. 2) show clearly that the sample with the lowest C/S ratio (0.1) is amorphous, as evidenced by the broad band in the central part of the pattern. A trace of the broad band can be seen also for C/S = 0.3. Further patterns show an increasing crystallinity. It is evidenced by two reflexes mainly, one at *ca.* 0.3 nm and another at *ca.* 1.1 nm, both characteristic of the tobermorite structure.

Basing on X-ray diffraction patterns solely, we can form the following picture: at C/S = 0.1 an amorphous silica gel, which is a porous substance, will be dominant. Then gradually the C-S-H substance is formed. It is also amorphous but with crystallites resulting from the ordering by attachment of SiO_4 chains to CaO_6 layers as explained in Sec. 1. One has to notice that the X-rays give evidence of the increasing amount of crystallites but the X-rays are not so good as means of detecting the disorder which comes from increasing number of defects due to lack of SiO_4 tetrahedrons. From this point of view the SANS method seems to be complementary to the X-ray diffraction.

3. SANS results

Figure 3 presents the SANS results for the five samples. We believe that the slope is dominated by the surface fractals. If so, one should try to obtain the surface fractal dimension by subtracting 6 from the negative slope (formula (4) in Sec. 1). Figure 4 and Table present the so obtained D_s values for our samples. The surface fractal dimension D_s as obtained from the slope for small C/S is not far from 2, $D_s = 2.2$, which is not very different from what was obtained in [1], where $D_s = 2.0$. Perhaps this means that the walls of the pores are rather smooth. When

TABLE
Surface fractal dimension (D_s) as a function of CaO/SiO₂ ratio.

C/S ratio	D_s
0.1	2.16 ± 0.02
0.3	2.20 ± 0.02
0.5	2.34 ± 0.03
1.0	2.39 ± 0.03
1.5	2.44 ± 0.02

C/S ratio increases the substance becomes gradually C-S-H, containing CaO_6 foils to which the SiO_4 tetrahedrons become attached, the walls of the pores become less and less smooth which should lead to an increase in D_s . And that is what we indeed observe.

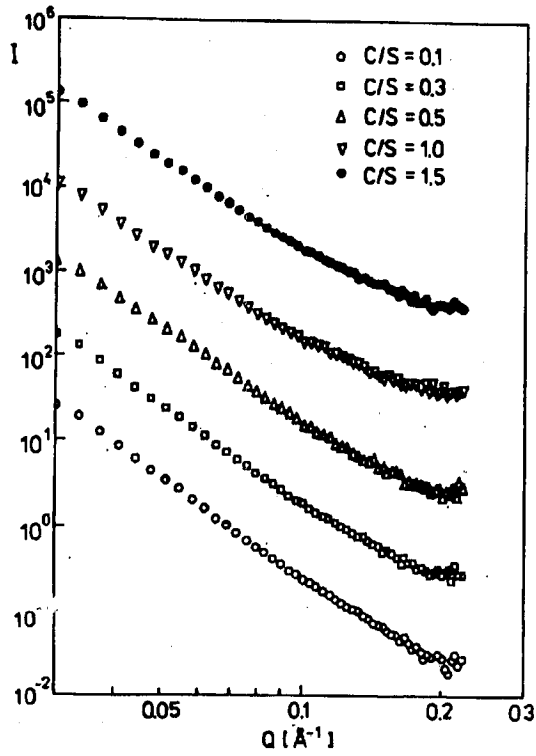


Fig. 3. SANS diffraction patterns for samples with various C/S ratios. The spectra are shifted along the "I"-axis to clarify the picture.

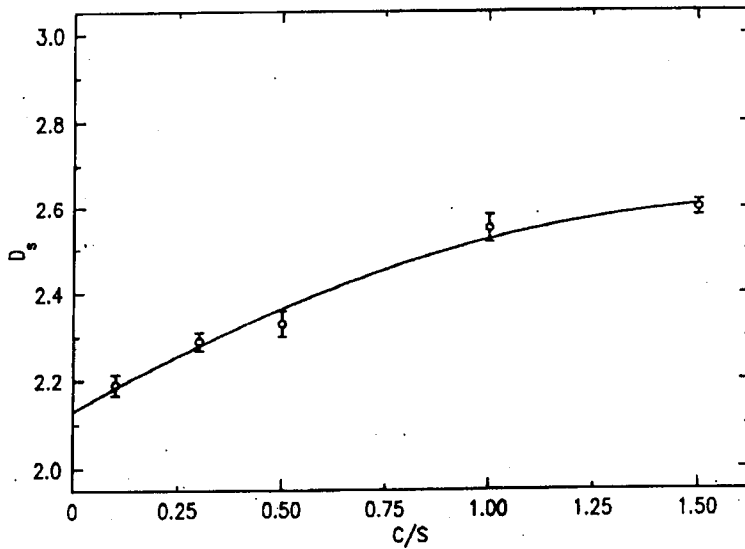


Fig. 4. SANS results for samples with various C/S ratios.

4. Conclusions

Five samples of C-S-H gels were studied, with attention paid to their increasing CaO/SiO₂ molar ratio from 0.1 to 1.5. The X-ray diffraction gave evidence of an amorphous structure at low C/S values and of an increasing crystallinity for the C-S-H phase at higher C/S. The SANS study gave evidence of an increasing fractal character of the surface of the pores which accompanies the process of crystallites formation as evidenced by X-rays. The walls of the pores become surface fractals.

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