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FRACTAL NATURE OF THE POROUS STRUCTURE OF TRICALCIUM SILICATE DRY GELS

by

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ABSTRACT

A small-angle X-ray experimental study of tricalcium silicate (C_3S) porous gel has been carried out by using synchrotron radiation. The scattering data, obtained under optimized experimental conditions, are in remarkable close agreement with the theoretical predictions from a Menger sponge model of porous fractal structure.

Key-words: Fractals; SAXS; Porous gels.

Porous materials, specially those which exhibit high specific surface areas, are used in many scientific and industrial applications. Silica aerogels are examples of recently discovered very light and porous materials which have interesting properties [1]. These porous solids are prepared by drying a humid gel phase which develops from solutions of organic silica complexes in alcools. Older examples of porous gel phases are the hydration products of tricalcium silicate and, more generally, of common coments (e.g. Portland cement).

Cements contain four phases before hydration. They are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and dicalcium aluminoferrite (C_2AF). Since the structural modifications during hydration and subsequent drying in common cements, are similar to those observed in pure C_3S this single component is generally used as a model for physico-chemical investigations.

The hydration of the starting dry cement, or pure C_3S, is accompanied by an improvement of mechanical properties during the "setting" of the satured paste (C_3S-water mixture). The hydrated and still saturated C_3S exhibits two main phases: a well crystallyzed calcium hydroxide phase (C-H) and a poorly cristallized phase containing hydrates and water (C-S-H), usually considered as a gel, which occupies most of the total volume [2]. Such a gel is very porous, being the pores water filled in the saturated state and empty in the dry state.

When the free water which fils the pores evaporates, the initially saturated system transforms towards a porous material which is called dry gel or aerogel. The drying process maintains

approximately constant the total volume of the system.

The pores in the saturated (humid) tricalcium silicate gels, and also the ones in dry gels, have been classified into three groups: macropores or capilar pores, mesopores or inter-crystallite pores and micropores or intra-crystallite pores [2]. The characteristic average diameters are $\phi \gtrsim 0.1\ \mu$, $10\ \text{Å} \lesssim \phi \lesssim 1000\ \text{Å}$ and $\phi \lesssim 10\ \text{Å}$, respectively.

Small angle X-ray scattering (SAXS) techniques have been often used to investigate porous solids and, particularly, humid and dry C_3S gels. The classical analysis of the SAXS results assumes a porosity which has a tri-modal size distribution corresponding to a model of differenciated macro, meso and micropores. Macropores are too large to contribute to SAXS in the ordinary SAXS angular domain. Mesopores and micropores produce an assymptotic (high angles) experimental SAXS intensity, which is usually well fitted by a modified Porod's law [3]:

$$I(q) = \frac{\rho^2}{\pi} \frac{S}{q^4} + \frac{b}{q^n} \qquad (1)$$

where q is the modulus of the scattering vector, ρ the average electronic density in the matrix, S the surface of the matrix-mesopores interface, b a term associated with density fluctuations related to the intracrystallite micropores and n an integer which depends on the geometry of the micropores or, more generally, on the dimensionality of density fluctuations in the matrix. Parameters n = 2,1 and 0 correspond to one, two and three dimensional fluctuations, respectively. The second term b/q^n in equation 1 accounts for the deviation from the classical Porod's law [4]:

$$I(q) \propto S/q^4 \qquad (2)$$

which holds for simple two density systems.

A more recent approach, which describes the structure of a number of porous systems, is based on the "fractal" model. Bale and Schmidt [5] showed that porous fractals which can be described by a two-electronic density model, also exhibit a positive deviation from the classical $I \propto q^{-4}$ Porod's law. In this systems the deviation of the SAXS intensity from Porod's law reflects on the exponent of q [5]:

$$I(q) \propto \frac{1}{q^{6-D_s}} \qquad (3)$$

D_s being the dimensionality of the porous fractal which has a minimum value $D_s = 2$ for euclidean systems and a maximum $D_s = 3$. For $D_s = 2$ equation 3 exhibits identical dependence on q than classical Porod's law (equation 2).

The fractal nature of porous structures may be due to self-similar (invariant under scale transformation) rugosities of the interphase surfaces or to a porosity having a wide range distribution of pore sizes which satisfy the self-similarity condition. A basic theoretical example of porous fractal is the Menger sponge [6] which has a dimensionality $D_s = 2.73$. To avoid ambiguities in comparing dimensionalities determined from SAXS experiments and those calculated from theoretical models, SAXS intensities should be recorded with a high degree of precision. In earlier SAXS experiments on C_3S, Winslow and Diamond [7] investigated the correspondance between the porosity in dry gels and that in

the parent saturated gels. Recent SAXS experiments [8] permitted to establish the various features which characterise the structural variations in hydrating C_3S. In these precedent works, and in others, the analysis of the scattering intensity was based on the modified Porod's equation 1.

In order to obtain very precise experimental SAXS data, the use of a narrow pin-hole collimation system and a very intense radiation source are required. This avoids errors introduced by mathematical desmearing processes. The suppression of parasitic scattering from air and slits is also necessary in order to minimize substraction errors.

In this work the porous C_3S gel phase, obtained by drying the products of hydration of C_3S, is investigated by SAXS. The analysis of the experimental results is done following classical Porod [3] and Bale and Schmidt [4] fractal approaches.

Microgranulated C_3S powder was mixed with water in a ratio water/solid = 0.5 by weight. The setting of the paste was done by keeping the mixture during 12 hours in a sealed cell and the resulting material dried during 24 hours in a dessicator containing silica gel.

A monochromatic and pin-hole collimated X-ray beam, from the DCI positron storage ring at LURE, Orsay, has been used in the present work. Two parallel silicon crystals produced a monochromatic 8 KeV X-ray beam, collimated by two sets of slits defining a point-like beam cross-section. The double crystal monochromator provided an incident beam which produces a very low level of parasitic scattering at small angles. The beam path was evacuated in order to minimize air scattering. SAXS data have been recorded

by an Elphyse one-dimensional position sensitive X-ray detector.

SAXS data from the C_3S dry gel have been directly plotted in Fig. 1 and 2, without any mathematical desmearing. The parasitic scattering has been kept very low, producing noticeable effects only at high q values. Then, the scattering curves plotted in Fig. 1 and 2 correspond essentially to the measured ones.

In Fig. 1 SAXS intensity is plotted in a $I(q)q^4$ vs. q^2 scale as in previous works. This plot exhibits a linear behaviour in the angular domain corresponding to the outer, assymptotic, part of the scattering curve. The linear fitting is rather poor because the SAXS intensity at high q is subjected to high statistical errors due to the low counting rate. Anyway, the deviation of the experimental scattering data from the classical Porod's law (equation 2) seems established from Fig. 1 since the assymptotic straight line has a clearly positive slope.

The high statistical errors of SAXS intensity in the high q range, generally lead to low precision S and $\underline{b}$ parameters. Another consequence is the possibility of finding reasonably assymptotic linear behavior of Iq^4 as a function of q^n, either for n = 1, 2 and 3. This implies that, from SAXS interpretations based on the classical modified Porod equation, ambiguous conclusions may be inferred.

SAXS intensity has also been plotted in Fig. 2 in a double-logarithmic scale. This plot clearly shows a linear dependence of log I on log q over a wide q domain. The fitting of the experimental points of Fig. 2 to a straight line was done by a least-square method. The resulting slope was $\alpha = 3.26 \pm 0.03$ and the correlation factor R = 0.996. The linear behavior is observed along the whole

analysed q domain ($0.005\ \mathring{A}^{-1} < q < 0.05\ \mathring{A}^{-1}$) over almost four orders of magnitude in scattering intensity.

The plot of Fig. 2 indicates that the experimental SAXS intensity agrees closely with that theoretically predicted for a porous fractal model (equation 3). The slope $\alpha = 3.26$ is associated with a porous fractal structure with a dimensionality $D_s = 2.74$. The minimum and maximum q values for which equation 3 has been proved to be obeyed, indicate that the minimum and maximum characteristic sizes for which the fractality of the structure is verified, are about 20 and 200 $\mathring{A}$, respectively. Measurements for q ranges below $0.005\ \mathring{A}$ and above $0.05\ \mathring{A}$ are required in order to establish the extreme characteristic sizes of fractal behaviour of the studied structure.

The experimental value of the dimensionality $D_s = 2.74 \pm 0.03$ is the same than that of Menger's sponge model. This correspondance indicates that the Menger sponge is a satisfactory model for the fractal structure of C_3S dry gel.

It is clear from the reported results that the classical model of porosity in C_3S gel, based on the existence of differentiated macro, meso and micropores, seems to correspond to a rough approximation. The present experimental results provide a stronger support to a model consisting of a porous fractal structure, having the continuous distribution of pore sizes of Menger's sponge.

Similar dimensionality values may correspond to rather different fractal models. Therefore our conclusion involving the correspondence between the Menger sponge model and the structure of C_3S has been possible because of the high precision of the experimen-

tal data. The use of synchrotron radiation proved to be very useful for this purpose.

The fractal nature of the structure of tricalcium silicate gels implies that the specific interphase area, often used as a technological parameter to characterize the porosity of C_3S and cements, is meaningless as long as the used "yardstick" is not specified. In addition it explains the discrepancies which have been often observed in the reported measurements of surface area of these materials.

FIGURE CAPTIONS

Fig. 1 - Test of validity of the modified Porod law for n = 2 (equation 1). The high statistical errors of experimental data are due to the weakness of the SAXS intensity at high q.

Fig. 2 - Experimental SAXS intensity in log-log scale. The slope α of the solid line corresponds to that of Menger's sponge ($D = 2.73$ and $\alpha = -3.27$). The dashed line indicates the q dependence of SAXS expected from a non fractal porous system ($D = 2$ and $\alpha = -4$).

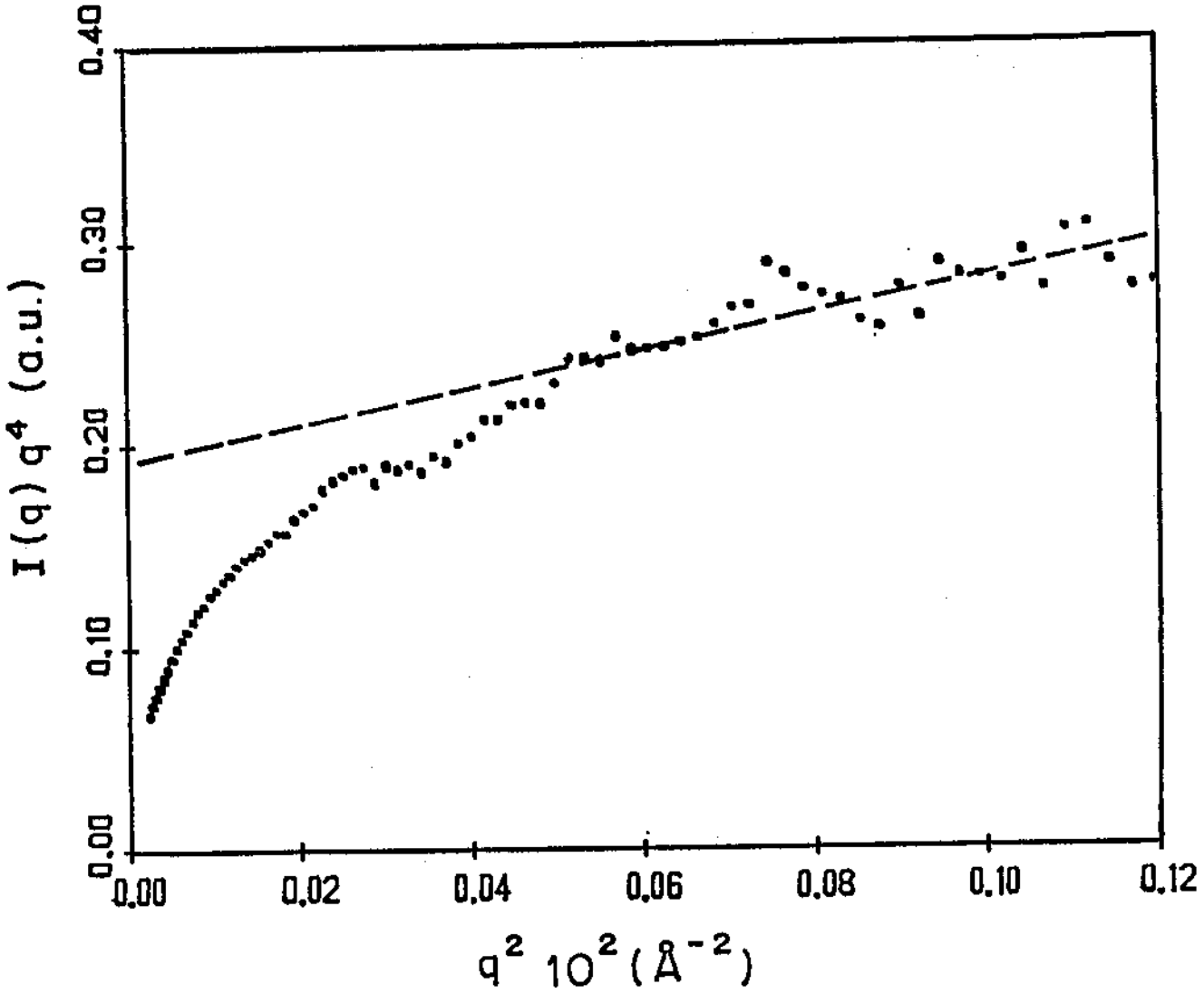

FIG. 1

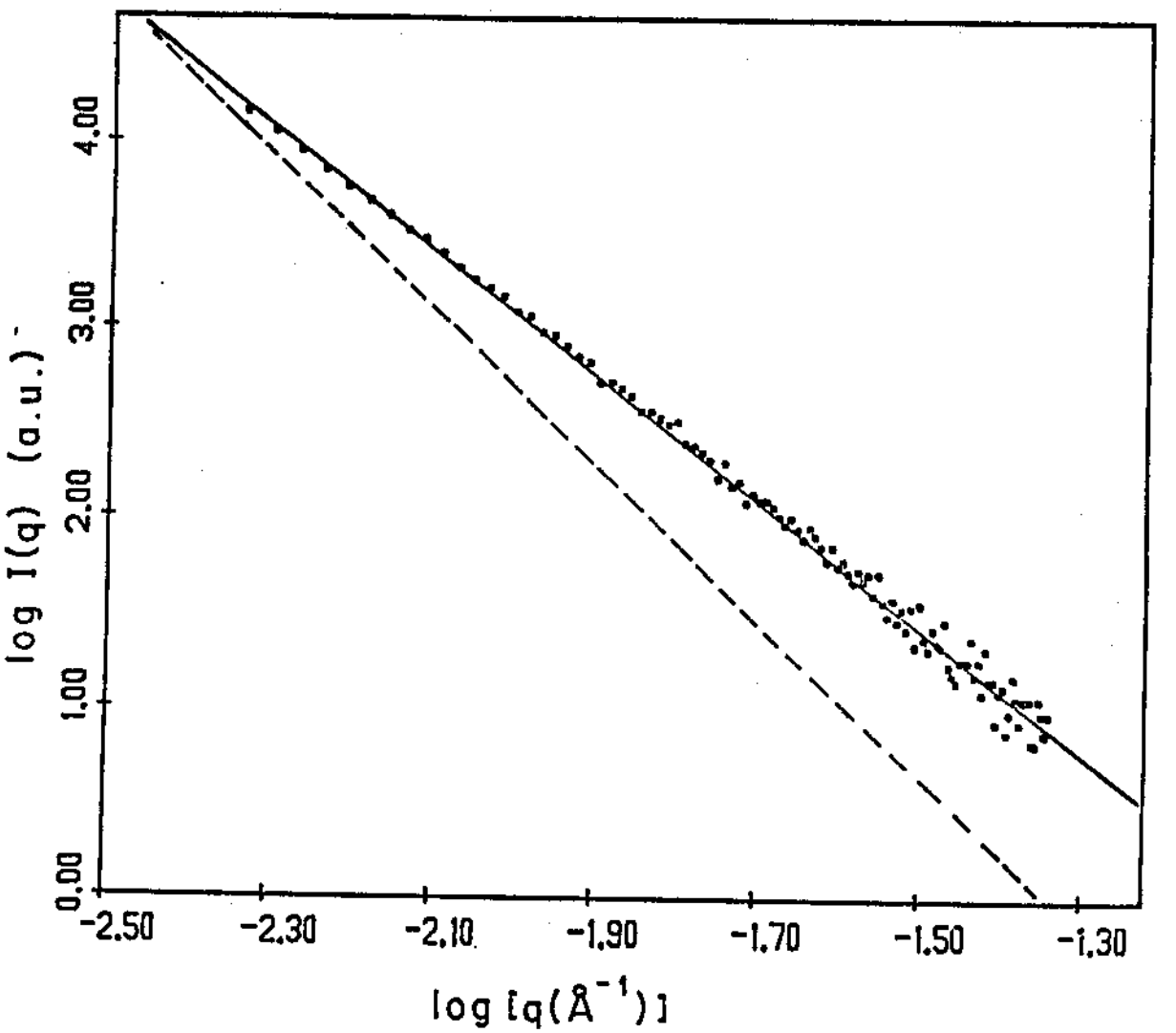

FIG. 2

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