A Theoretical calculation from material to information networks

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Abstract: The problem of the mathematical calculation of the pore size distribution of cement and cement – like materials showing a fractal pore construction is solved by the inversion of the Laplace transform which connects the pore size distribution function to the magnetization relaxation rate function calculated by Nuclear Magnetic Resonance experiments.

Key-words: Laplace transform, pore size, relaxation rate, cement, fractal, NMR.

1. Introduction

The problem of cement hydration is of strategic importance to the world construction technology and economy [1 – 7], [10], [12 – 14]. The possibility of the fractal geometry of the pore structure in cement – like materials, as well as in rocks, and its study by experimental methods is well known for years. The theory of fractals [8], [9], has applications in a diverse spectrum of physical problems (see for example [11] and [16]).

The fractal geometry of the pores of cement has been studied by the use of various techniques and methods [1 – 7], [10], [12] (and references therein).

In this work, some results having been obtained by Nuclear Magnetic Resonance (NMR) experiments are examined. The results are analyzed according to the theory developed in [7] and [10] and the resulting equation is regarded as a linear Fredholm equation of the first kind [12] The solution of the equation requires the inversion of the Laplace transformation of the relaxation rate distribution function [7].

2. DESCRIPTION OF THE EXPERIMENTAL METHOD

Nuclear Magnetic Resonance is a standard method for studying cement hydration. The experiment is described by the fundamental equation for the calculation of the magnetization recovery function:

$$(1):\ \frac{M_0-M}{M_0}=e^{-(\frac{t}{T_{1AV}})^{\alpha}}$$

where M0 is the maximum magnetization of the material when in relaxed condition in a static magnetic field, M is the magnetization measured at a specific time after the material has received the excitation of an exterior high radiofrequency pulse, t is the time after the excitation and T_{1AV} is the average spin – lattice relaxation time measured from the bulk of the sample. Finally, α is a parameter related to the fractal dimension of the cement pore structure, taking values: o.5 ≤ α ≤ 1 [7]. The theoretical model describing cement hydration is based on two fundamental equations:

$$(1):\ \frac{M_0-M}{M_0}=e^{-(\frac{t}{T_{1AV}})^{\alpha}}$$

and

$$(2):\ e^{-(\frac{t}{T_{1AV}})^{\alpha}}=\int_0^{\infty}P(\frac{1}{T_1})e^{-\frac{t}{T_1}}d(\frac{1}{T_1})$$

A third equation connects the pore size distribution with the relaxation rate distribution, permitting the modeling of the pore geometry, once the relaxation rate distribution function $P(\frac{1}{T_1})$ is known.

$$(3):\ g(\xi)d\xi=P(\frac{1}{T_1})d(\frac{1}{T_1})$$

Here, T_1 indicates the relaxation time of a specific pore, in any part of the cement bulk, since T_1 depends primarily by the pore geometry and size. Equation (2)

connects the local values of T_1 to the average value T_{1AV}, referring to the cement sample as a whole, during the experiment.
In the next sextion, the solution of Equation (2) is given. For reasons of convenience, the following substitutions are used:

$$\frac{1}{T_1} = l, \ (\frac{1}{T_{1AV}})^{\alpha} = \lambda,$$

and equation (2) becomes:

$$(4): \int_0^{\infty} Ae^{-lt} P(l) = A_0 e^{-\lambda t^{\alpha}}$$

3. THE INVERSION OF THE LAPLACE TRANSFORMATION IN EQUATION (4).

The equation:

$$(4): \int_0^{\infty} Ae^{-lt} P(l) = A_0 e^{-\lambda t^{\alpha}}$$

is in fact a Laplace transformation of the relaxation rate probability distribution $P(l)$. The result of the transformation is the average magnetization recovery function $A_0 e^{-\lambda t^{\alpha}}$ where A_0 is the magnetization at t = 0, λ is the average relaxation rate raised to the α power. By inverting the transformation, we obtain the equation:

$$(5): \ P(l) = q \int_{c-i\infty}^{c+i\infty} e^{-\lambda t^{\alpha}} e^{lt} dt$$

Where q is a suitable normalization constant.
By the calculation of the integral, the desired probability function will be obtained.
To achieve the calculation, a more suitable path is chosen, such that, united with the straight line $(c-i\infty, c+i\infty)$ it creates a closed contour in the complex numbers plane which contains no singularities. (Fig. 3). The definition of this path is as follows: Taking the origin as center, a circle of radius R tending to infinity is defined. As R goes on to infinity it will include the points $c-i\infty$, $c+i\infty$, as well as $-\infty - i\varepsilon$, $-\infty + i\varepsilon$, where ε tends to zero. The arcs from $c-i\infty$ to $-\infty - i\varepsilon$ and $-\infty + i\varepsilon$ to $c+i\infty$ are included in the new path. A second circle is defined, again having the origin as center but with a radius equal to η, tending to zero. The arc between the two points D = – η - iε and F = - η + iε is excluded and the rest of the circle is included in the new path. Finally, the two straight line intervals, (- ∞ - iε, - η – iε) and (-η + iε, - ∞+ iε) are included to complete the closed contour A – C - D - E - F - H - B - A (Fig. 3), where A = $c-i\infty$, C = $-\infty - i\varepsilon$, D = –η-iε, E = η, F = -η+iε, H = $-\infty + i\varepsilon$, B = $c+i\infty$.
The integral breaks down to the following parts:

I_1 = $\int_A^C e^{lt} e^{-\lambda t^{\alpha}} dt$ which is an integral along the quadrant of a circle of radius R, tending to infinity, starting from A: c - i∞ and ending at C: - ∞ - iε.

I_2 = $\int_C^D e^{lt} e^{-\lambda t^{\alpha}} dt$ which is an integral along a straight line parallel to the negative real semiaxis at a distance - ε, from C: - ∞ - iε to D: – η – iε.

I_3 = $\int_D^E e^{lt} e^{-\lambda t^{\alpha}} dt$ which is an integral along the arc of a circle with a radius η tending to zero, from the point D: –η-iε, through E: η to F: -η+iε.

I_4 = $\int_E^H e^{lt} e^{-\lambda t^{\alpha}} dt$ which is an integral along a straight line parallel to the negative real semiaxis at a distance ε, from F: -η+iε to H: $-\infty + i\varepsilon$

I_5 = $\int_H^B e^{lt} e^{-\lambda t^{\alpha}} dt$ which is an integral along the quadrant of a circle of radius R, tending to infinity, starting from H: $-\infty + i\varepsilon$ to B: $c+i\infty$.

I_1 may be transformed as follows: t = $\mathrm{Re}^{i\theta}$, I_1 = $\int_{-\pi/2}^{-\pi} e^{l\,\mathrm{Re}^{i\theta}} e^{-\lambda R^{\alpha} e^{i\alpha\theta}} dt$ =

$$= \int_{-\pi/2}^{-\pi} \mathrm{Re}^{i\theta} \exp(lRe^{i\theta}) \exp(-\lambda R^{\alpha} e^{i\alpha\theta}) d\theta =$$

$$\int_{-\pi/2}^{-\pi} \exp(lR(\cos(\theta) + i\sin(\theta)) \exp(-\lambda R^{\alpha}(\cos(\alpha\theta) + i\sin(\alpha\theta)) d\theta$$

I_5 may be transformed in a similar manner:

$I_5 =$

$$\int_{-\pi}^{\pi/2} \mathrm{Re}^{i\theta} \exp\{(lR(\cos(\theta) + i\sin(\theta)) - (\lambda R^{\alpha}(\cos(\alpha\theta) + i\sin(\alpha\theta))\} d\theta$$

In both these integrals, the absolute value of the integrand is: $\exp(lR\cos(\theta) - \lambda R^{a}\cos(\alpha\theta))$, where cos(θ) and cos(αθ) are negative quantities and α < 1. Therefore the integrant exponent, dominated by the term: $lR\cos(\theta)$ goes to - ∞ as R goes to ∞ and as a result the integrand goes to zero So the contribution of I_1 and I_5 is zero.

Next, $I_3 =$

$$\int_{-\pi}^{\pi} \mathrm{Re}^{i\theta} \exp\{(lR(\cos(\theta) + i\sin(\theta)) - (\lambda R^{\alpha}(\cos(\alpha\theta) + i\sin(\alpha\theta))\} d\theta$$

, where now R tends to zero. Again the contribution of I_5 is zero.

By reversing signs and integration limits and due to symmetry considerations, the contribution of $I_2 + I_4$ is:

I = $2\int_0^{\infty} e^{lt} e^{-\lambda t^{\alpha}} dt$. This is a real integral, easily calculated by numerical methods.

4. Conclusions

A method has been presented here for the calculation of the pore size distribution of Ordinary Portland Cement and other cementicious material, such as C_3S, which show indications of a fractal pore structure, with fractal dimension substantially larger than 2, reaching 2.7 – 2.8. By calculating the parameters α and T_{1AV} through NMR magnetization recovery experiments, inverting the Laplace transformation equation and calculating the ensuing integral, the relaxation rate distribution $P(\frac{1}{T_1})$ may be calculated. Then , by use of the equation:

$$P(\frac{1}{T_1})d(\frac{1}{T_1}) = g(\xi)d\xi \text{ [5], [6], [7]}$$

the pore size distribution may be calculated.
This result is very useful in the theoretical and experimental studies for the understanding and improvement of the properties of cement and cement – like materials, which is of strategic value for the economy and the development of new materials and technologies.

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