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Water invasion, freezing, and thawing in cementitious materials

Marcel Ausloos *, Eric Salmon, Nicolas Vandewalle

S.U.P.R.A.S., Institut de Physique B5, Université de Liège, B4000 Liège, Belgium

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Abstract

A simple model of fluid invasion, freezing, and thawing in a porous medium was developed using an "invasion percolation-like" approach. The fluid freezing process is considered as destroying the internal structure of the porous medium. The evolution of the pore size distribution after several invasionfrostthaw events is investigated numerically. Those results are qualitatively consistent with experimental measurements on fiberreinforced cements.

Keywords: Invasion percolation; Invasion-frost-thaw events; Fiber-reinforced cements; Pore size evolution

The invasion of fluid in porous media is a subject of interest in the statistical physics community [1–4] because percolation and growth phenomena are involved [5–7]. Although these phenomena were studied by the so-called invasion percolation [7] and epidemic model [8], the destructive effects of fluid freezing in the material have been studied less often. Several studies [2,3] showed that the freezing of water in porous media affects the internal porous structure.

The aim of the present paper is to study the aging of porous materials such as fiber reinforced cements with a simple invasion-freezing-thawing model. The kinetics of the invasion and the geometry of aged invasion clusters are investigated and simulation results are presented.

1. Freezing-thawing process simulation

The model is assumed to be as simple as possible to serve as a basis for further developments under more realistic constraints. The model is based on the well-known invasion percolation model [2]. An **L** × **L** square lattice (Fig. 1A) with vertical periodic boundary conditions represents the porous material. Each cell of the square lattice represents a pore. Each pore is connected with its four nearest neighbours. A random number r_i between 0 and 1 is assigned to each pore i. This number r_i represents some measure of the pore size. In the present model each pore is characterised only by *that* number whatever its real size, surface, shape. . . . Although this is a gross approximation, it is necessary to reduce the number of parameters as much as possible to obtain simple "universal" laws.

After invasion (Fig. 1B) from the bottom row up to percolation, i.e., up to any one of the sites first reached on the upper row, the fluid is assumed to freeze at once (Fig. 1C). To simulate some damage due to freezing, the size of each invaded pore is assumed to increase according to Eq. (1):

$$r_i \rightarrow r_i + \varepsilon(1 - r_i) \quad (1)$$

where ε is a random number taken from a flat distribution between 0 and 1. The fluid then is removed completely (by instantaneous drying) such that new fluid invasion can take place. The invasion-freezing-thawing process is repeated a large number **n** of times. The parameter **n** can be associated with a succession of experimental processes to evaluate age on fiber-reinforced cements [9,10]. We investigated **L** × **L** lattices with **L** varying from 10 to 500. Iterations up to **n** = 200 were performed. The following data are a compendium of more than 50 cases.

Fig. 2 presents the normalised distribution of pore sizes $N_{mat}(r)$ in such a virtual porous medium with an initially uniformed size distribution ranging between 0 and 1 with increasing invasion-damage freezing (**n** = 1, 2, 3, 6, 12). Similar data are presented in Fig. 3 starting from a uniform pore size distribution initially between 0 and 0.3. A similar evolution of the pore size distributions as drawn in Fig. 3 was observed for true fiber-reinforced cements [9,10] as shown in Fig. 4. It is seen that the number of big pores grow with **n** and the number of small ones decreases in relative value.

* Corresponding author. Tel.: 32 4 366 37 52; Fax: 32 4 366 29 90; Email: ausloos@gw.unipc.ulg.ac.be.

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0.45	0.99	0.58	0.78	0.12
0.19	0.67	0.81	0.91	0.70
0.84	0.75	0.62	0.98	0.72
0.35	0.53	0.50	0.09	0.36
0.60	0.81	0.77	0.16	0.91

A

0.45	0.99	0.58	0.78	$0.12^{(9)}$
0.19	0.67	0.81	0.91	$0.70^{(8)}$
0.84	0.75	$0.62^{(6)}$	0.98	$0.72^{(7)}$
$0.35^{(2)}$	$0.53^{(5)}$	$0.50^{(4)}$	$0.09^{(1)}$	$0.36^{(3)}$
$0.60^{(0)}$	$0.81^{(0)}$	$0.77^{(0)}$	$0.16^{(0)}$	$0.91^{(0)}$

B

0.45	0.99	0.58	0.78	$0.95^{(9)}$
0.19	0.67	0.81	0.91	$0.90^{(8)}$
0.84	0.75	$0.63^{(6)}$	0.98	$0.76^{(7)}$
$0.84^{(2)}$	$0.67^{(5)}$	$0.65^{(4)}$	$0.54^{(1)}$	$0.4^{(3)}$
$0.65^{(0)}$	$0.90^{(0)}$	$0.78^{(0)}$	$0.16^{(0)}$	$0.99^{(0)}$

C

Fig. 1. Sample of a 5 × 5 square latice before invasion *(A)*, after invasion up to percolation *(B)*, and after freezing and before thawing *(C)*. The number in the "pore" represents some measure of the "size" of the pore. The number on a grey background is related to the invaded and later damaged pore size, and the exponent in parentheses represents the time of invasion.

However, in few cements the smallest pores do not disappear with aging. In contrast, freezing-thawing cycles seem to create new small pores (Fig. 5). Nakamura et al. [9] proposed that freezing slowly ages the pore edges, and some fissures appear with the same magnitude as the smallest pores. During the following invasion these fissures act like new pores [10]. This kind of observation is noticeable in Fig. 3, as is a transient effect over a small number of cycles. Subsequently, the growth of large cracks or pores should follow naturally.

2. Discussion

In this report it is of interest to note a few items that require either some debating approximations or reference to relevant work in the field.

First, this model is a two-dimensional model. Most of the time, observations of fluid invasion in materials are made by three-dimensional measurements, such as Hg, or He, or water invasion, and porosimetry. The bulk measurements are, in fact, used after some hypothesis on the network structure, which is hidden. To "see" the interior of the porous medium, slices can be taken and examined using various microscopes. The rescaling between two-and three-dimensional local porosity distributions [11] and the geometrical reconstructions of porous structures from two-dimensional imaging [12] are intense fields of research that have not yet given a coherent picture that allows treatment of one or the other technique as perfectly complementary. Therefore, from a modelisation point of view, two-dimensional structures often are used, as they are here.

In our previous work, we proposed models for constructing random media networks taking into account internal degrees of freedom and external constraints [13,14]. In principle, this could lead to better definition of the pore structure than that given here by a single number between 0 and 1. Such a generalisation is left for further investigation.

Next we assumed a trivial law of invasion based on capillarity arguments [15]. If a better description is needed, one should take into account the kinetics and the dynamics, such as osmosis and pressure equilibration throughout the medium [16,17], wetting conditions [18], interface pinning [19], and oscillations of the invading front [20]. As is known, pore invasion taking into account pore surface local slope and the angle of contact of the fluid is a major unsolved question of great complexity. Another very challenging point is the liquid-solid (water-ice) phase transition that is implied in the model. The case of such phase transitions in reduced dimensions, the more so in noninteger dimensions, has not been determined even for hard spheres [21]. The case of a complex fluid such as real water, not even considering impurities and chemical reactions, is not within the realm of our present knowledge.

In keeping with the spirit of so-called extremal dynamics in statistical mechanics, we invented the basic rule presented in Section 2 for the change in characterisation of the pore. One could improve upon it, e.g., first by taking into account information from the (P,V,T) phase diagram and then using the Clapeyron equation to obtain a better *estimate* of the relative change in pore size, surface, or volume. However, one question should be what power law to use, i.e., what effective dimensionality to consider, for changing r_i, because the pore obviously is neither a cylinder nor a sphere. Another

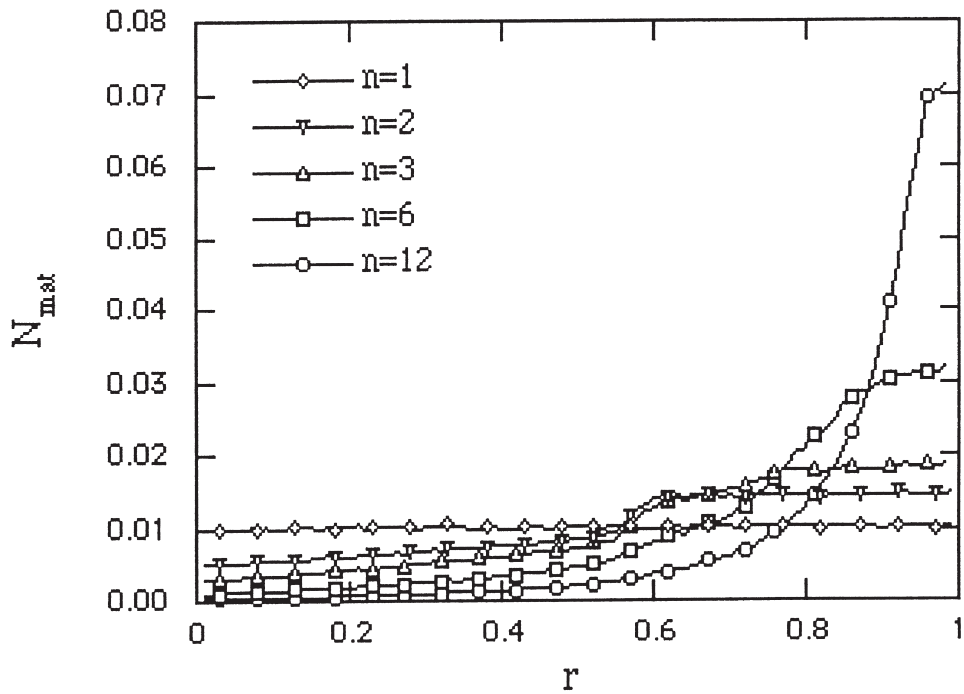

Fig. 2. Normalised distribution of pore size $N_{mat}(r)$ in the material before different invasion damages.

way would be to consider corrrelations between pores such that the characterisation is made in some adequate neighborhood, through a condition on the range available for ε, as we did in (biological) evolution studies [22,23]. Moreover, the reverse process, i.e., drying of wet porous material [24], is an interesting problem in itself. We are aware that sublimation, as here, is not a common process. However, available time scales might favour such a concept.

Concerning the analysis of the fracture processes, other stochastic models are available in which the pore size itself and its distribution are not the relevant parameters; the percolation cluster(s) and the fragment distribution are the key ingredients analyzed [25–27]. There are techniques other than the mercury intrusion method used by Nakamura et al. [10], such as application of ultrasonic wave attenuation for estimating frost action on limestone [28].

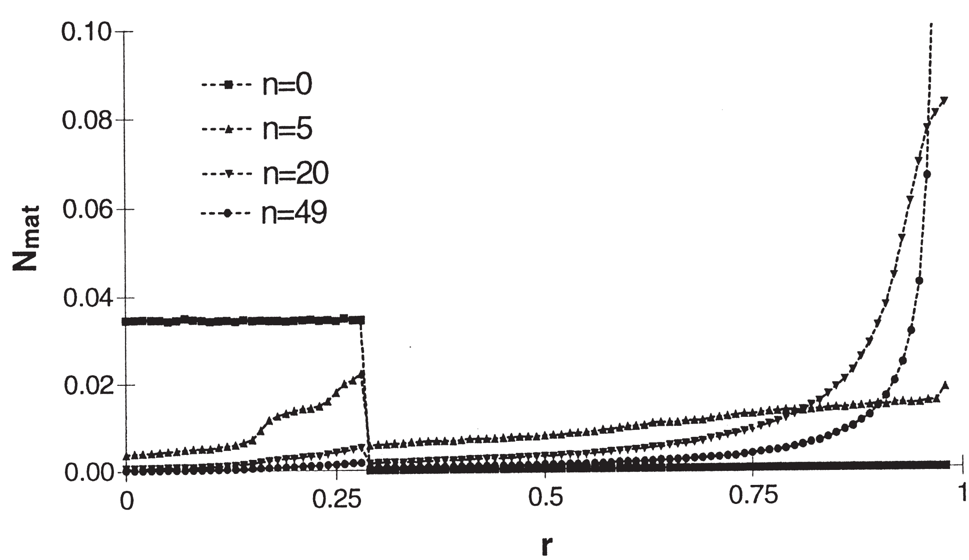

Fig. 3. Normalised distribution of pore size $N_{mat}(r)$ in the nonuniform pore size material after different damages.

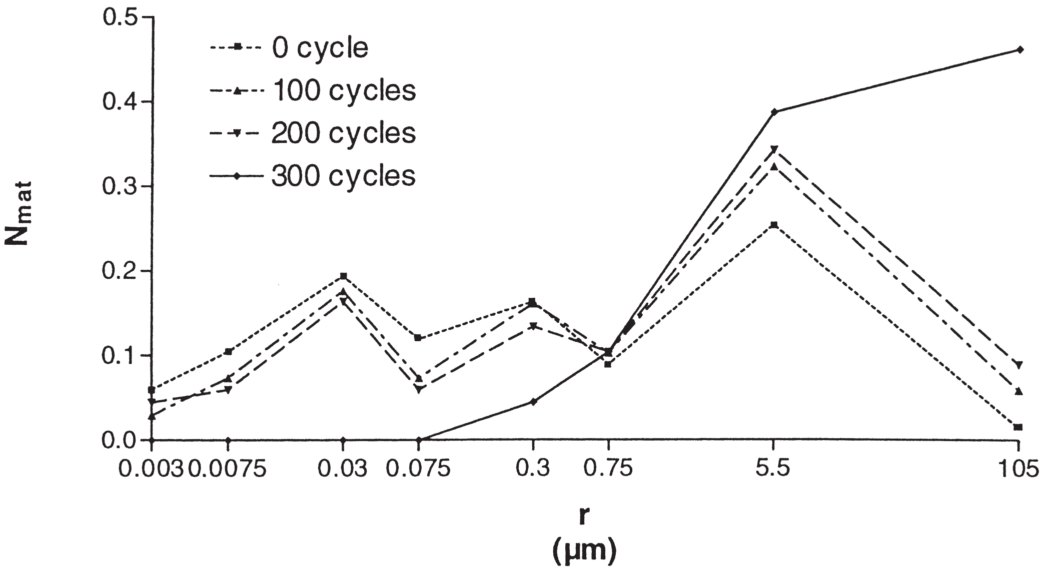

Fig. 4. Evolution of pore size distribution for the F3 sample of fiber-reinforced cement from [10].

3. Conclusions

We investigated a simple model of porous material degradation following several fluid invasion-freezing-thawing cycles. Fluid transport is based on the invasion percolation model. The simulation data show a different behavior with respect to the relative pore size distribution for low and high numbers of cycles. The initial geometry of the porous network is thus a highly dominant factor for damage prediction. Development of the model toward a more realistic model with other constraints is feasible, including three-dimensional studies and better physical approximations. The present model and the fiber-reinforced cements pore size distributions considered were found to follow the same qualitative laws.

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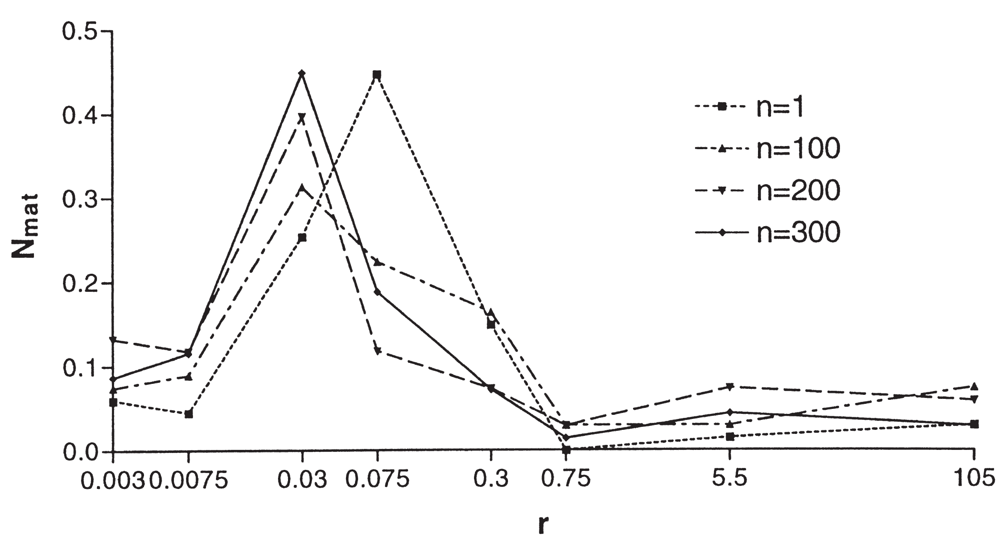

Fig. 5. Evolution of the pore size distribution for the E2 sample of fiber-reinforced cement from [10].

References

[1] A. Bunde, H.J. Herrmann, A. Margolina, H.E. Stanley, Phys Rev Lett 55 (1985) 653.
[2] L. Furuberg, J. Feder, A. Aharony, T. Jössang, Phys Rev Lett 61 (1988) 2117.
[3] M. Sahimi, Flow and Transport in Porous Media and Fractured Rock, VCH, Weinheim, 1995.
[4] M. Sahimi, Rev Mod Phys 65 (1993) 1393.
[5] H.J. Hermann, Phys Rep 136 (1986) 153.
[6] A.L. Barabasi, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, New York, 1995.
[7] D. Stauffer, A. Aharony, Introduction to Percolation Theory, Taylor & Francis, London, 1994.
[8] N. Vandewalle, M. Ausloos, J Phys A. 29 (1996) 309.
[9] M. Nakamura, T. Fukushima, M. Kamitani, J Ceram Soc Japan 100 (1992) 849
[10] M. Nakamura, A Discussion on Frost Action from the Viewpoint of Porosity, Paper contributed at the International Workshop on Mass-Energy and Deterioration of Building Components, Paris, 1995.
[11] B. Virgin, E. Haslund, R. Hilfer, Physica A 232 (1996) 1.
[12] C.P. Fernandes, F.S. Magnani, P.C. Philippi, J.F. Daïan, Phys Rev E 54 (1996) 1734.
[13] M. Ausloos, N. Vandewalle, R. Cloots, Europhys Lett 24 (1993) 629.
[14] N. Vandewalle, M. Ausloos, Phys Rev E 50 (1994) R635.
[15] J. Koplik, J Fluid Mech 119 (1982) 219.
[16] T. Chou, Phys Rev Lett 80 (1998) 85.
[17] D. Quenard, H. Sallee, Mater Struct 25 (1992) 515.
[18] M.J. Blunt, H. Scher, Phys Rev E 52 (1995) 6387.
[19] T. Delker, D.B. Pengra, P.-Z. Wong, Phys Rev Lett 76 (1996) 2902.
[20] D. Quéré, Europhys Lett 39 (1997) 533.
[21] M. Schmidt, H. Löwen, Phys Rev Lett 76 (1996) 4552.
[22] M. Ausloos, N. Vandewalle, Acta Phys Pol B 27 (1996) 737.
[23] M. Ausloos, I. Mroz, A. Pekalski, N. Vandewalle, Physica A 248 (1998) 155.
[24] M. Ilic, I.W. Turner, Appl Math Modelling 10 (1986) 16.
[25] M. Ausloos, J.M. Kowalski, Phys Rev B 45 (1992) 12830.
[26] R. D'hulst, N. Vandewalle, M. Ausloos, Phys Rev E 55 (1997) 12830.
[27] E. Salmon, M. Ausloos, N. Vandewalle, Phys Rev E 55 (1997) R6348.
[28] M. Bellanger, J.M. Rémy, F. Homand, Mater Struct 29 (1996) 552.