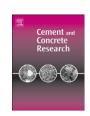
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Toward a better comprehension and modeling of hysteresis cycles in the water sorption-desorption process for cement based materials

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ABSTRACT

The aim of this work is to describe a method based on a simple representation of the pore size distribution, which is able to predict hysteresis phenomena encountered in water sorption–desorption isotherms, particularly for cementitious materials. The hysteresis effect due to network constrictivity is taken into account in order to extend models of transfer in porous media to situations involving wetting–drying cycles. This is not achieved in earlier models and their performance in terms of prediction in such conditions is thus limited. The present modeling is based on an idealized pore size distribution. This has three modes, associated with C–S–H pores, medium capillary pores, and large capillary pores including consideration of cracks. The distribution is assessed from the chemical composition of the cement, the formulation of the material, the degree of hydration, the total water porosity and the intrinsic permeability.

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1. State of the art

The modeling of transfer properties through porous media is a widely studied topic, especially in the field of civil engineering with cementitious materials. Pore network models have been developed to assess the liquid and gas permeability [1–6] and the water diffusivity of such materials [7,8], to simulate mercury intrusion [9] or to study the kinetics of capillary imbibition [10]. The aim of our study is to develop a physical model representing the hydric behavior of the porous space. As in previous work, our model is based on the size distribution of pores and can lead to an estimate of the water content of the material, whatever its humidity history. However the proposed study is not restricted to finding the sorption and desorption isotherms but also predicts the non-linear connecting paths anywhere between them. This non-linearity is due to hysteresis.

Aligizaki [11] describes the different types of hysteresis (de Boer classification [12] and IUPAC classification [13]) and the different theories on the origin of the hysteresis. The author mentions, among others, McBain [14] and Brunauer et al. [15]. Mc Bain explains the hysteresis effect by the presence of ink bottle pores. The wide part is filled at high relative humidity but can only be drained during desorption when the narrow part is at low relative humidity. Brunauer et al. [15] assumed that, for the same pore, capillary condensation and evaporation occurred at different relative humidities. Based on test results of nitrogen adsorption, Aligizaki [11] deduced that the shape of the hysteresis loop obtained on cement pastes was of the B or D type

according to the classification of de Boer or the H3 type according to the IUPAC classification. This reflects the fact that the pores are composed of large capillaries with narrow necks or have flattened shapes (corresponding, for example, to the representation of the C-S-H gel structure in sheets). By performing several cycles of wetting-drying at different levels of relative humidity between 3% and 100% on various cementitious materials, Baroghel Bouny [16,17] infers that hysteresis is present throughout this range of relative humidity. It is significant between 33% RH and 100% RH and the author attributes its origin to the difference between the mechanisms of condensation and evaporation due to the shape of the pores or to the possible presence of different shapes in the liquid-vapor interface. For low RH (RH <33%), a change of microstructure due to the departure of water strongly bound to the C-S-H explains the hysteresis. Other possible causes cited by the author are the presence of "multi-scale ink-bottle pores" or "kinetic effects" which complicate and delay the establishment of balance especially in the median range of RH where moisture transport is slower due to the discontinuity of the liquid phase. Also according to Baroghel Bouny [16], the hysteresis effect is a short-term phenomenon corresponding to a thermodynamically unstable condition and should subside and disappear after a certain period of time depending on the temperature and relative humidity range. This is confirmed by other researchers, e.g. Ishida et al. [18], who suggest a gradual dispersion of water in the ink bottle pores under the effect of temperature. In a recent publication, Poyet [19] uses the heat involved in the exothermic adsorption process to explain the effect of temperature on the first desorption isotherm. An increase in temperature hinders the process, decreasing the number of adsorbed molecules and therefore the water content. Conversely, the desorption process is encouraged. Espinosa and Franke [20] explain hysteresis by the fact that the pores affected by capillary condensation

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