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# Modelling of water vapour sorption hysteresis of cement-based materials based on pore size distribution

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## ABSTRACT

The purpose of this paper is to develop a model for predicting water vapour sorption hysteresis of cement-based materials. The sorption hysteresis was modelled based on the pore size distribution (PSD) and the pore network. The PSD of gel and capillary pores was predicted from the adsorption isotherm. The results indicated that the distribution had two peaks at 3.8 nm and 11 nm of the pore diameters, referring to gel and small capillary pores, respectively. The predicted ratio of gel water to evaporable interlayer water was not a constant, but decreased with an increasing hydration degree. When RH was below 0.25, the predicted sorption hysteresis was solely influenced by the hysteresis of water in interlayer spaces and minor hydrates. The hysteresis in gel pores, small and large capillary pores influenced the shape of desorption isotherms within the RH ranges of 0.25–0.85, 0.35–0.98 and 0.4–1, respectively.

## 1. Introduction

Water vapour sorption isotherm (WVSI) of cement-based materials is the relationship between relative humidity (RH) and equilibrium water content under an isothermal condition, and it is an important material characteristic in predicting the moisture transport in the materials [1]. The sorption isotherm can be divided into desorption isotherm, adsorption isotherm and scanning curves as shown in Fig. 1. At a low RH, the adsorption and desorption of water in calcium silicate hydrate ($(CaO)_x(SiO_2)(H_2O)_y$, C-S-H) interlayer spaces play an important role in the shape of the sorption isotherm. When the RH is increased, water filling in gel and capillary pores starts to dominate. The desorption isotherm (from the highest to the lowest RH) always stays above the adsorption isotherm (from the lowest to the highest RH), which is known as water vapour sorption hysteresis. Hysteresis of the sorption isotherm has an impact on the durability issues of concrete structures, such as moisture and ion transport [2,3]. The scanning curves are between the adsorption and desorption isotherms. They reveal the relationship between RH and water content when the cement-based material is not dried from the highest RH or it is not wetted from the lowest RH. The determination of the scanning curves is an essential task for calculating water content in the concrete subjected to cyclic atmospheric conditions.

There are several reasons for the sorption hysteresis including pore-blocking mechanism [4–6], the difference of the liquid-vapour interface curvatures [7], and the variation of liquid-solid contact angle [8]. For cement-based materials, the hysteresis between the adsorption and desorption isotherms is relatively small within a low RH range (Fig. 1). The hysteresis within this range is mainly related to the collapse and resaturation of C-S-H interlayer spaces. The hysteresis becomes larger at a higher RH range, where pore-blocking mechanism (also known as ink-bottle effects) in gel and capillary pores is considered as the major mechanism for the hysteresis.

Baroghel-Bouny [9] conducted a series of experiments for the WVSIs of cement pastes and concretes by using a saturated solution method. According to the results of the multi-cycles of desorption-adsorption isotherms, the second adsorption isotherm almost overlaid with the first one, while the second desorption curve was shifted upwards below 0.44 RH. The results also indicated that the presence of aggregates did not influence the isotherm of the hardened paste phase. However, it is well known that the inclusion of aggregates produces interfacial transition zone (ITZ), which is more porous than the bulk cement paste [10,11]. The seemingly contrary results can be explained by the fact that the microstructure of bulk cement paste was modified after

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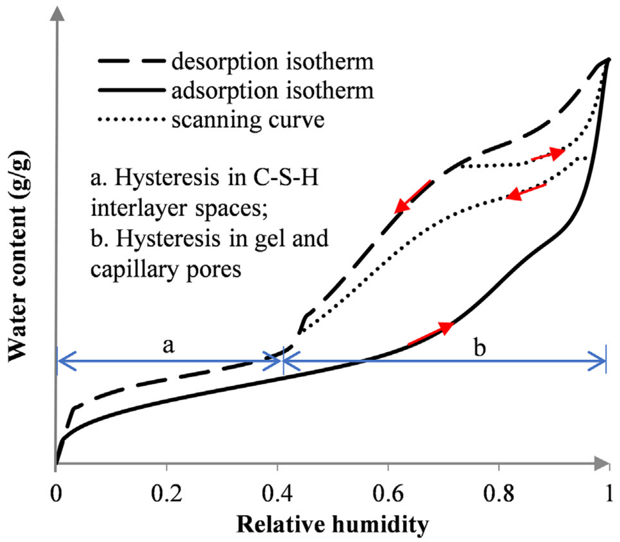

**Fig. 1.** Water vapour sorption hysteresis of cement-based materials.

aggregates were embedded in the concrete. The water-cement ratio of the bulk cement paste was lower than the designed water-cement ratio, because the ITZ had a higher water-cement ratio and the total amount of water used in the concrete was conserved. Consequently, the bulk paste was less porous than the pure cement paste with the same mix and hydration time. This could counteract the effect of the ITZ on the sorption isotherm of the hardened paste phase. Another possible factor was that the pore size range influencing the isotherm shape was much smaller than the typical pores in the ITZ [9].

The modelling for water vapour sorption isotherms of cement-based materials has been developed by many researchers. Xi et al. [12] used the Brunauer-Skalny-Bodor (BSB) model for predicting the adsorption isotherm, and the parameters in the model were empirically correlated to the properties of the cement-based materials. The BSB model is a three-parameter Brunauer-Emmett-Teller (BET) model, in which each parameter has a physical meaning. This model was also applied to represent the first desorption isotherm of concrete [13]. The water vapour sorption hysteresis could be modelled by a domain approach [14]. The water content was obtained by integration of a distribution function within the domain, which was composed of a group of pores in the cement-based materials. Recently a physically-based model for the WVSI was established based on the microstructure that developed with hydration [4]. Besides, by fitting the shapes of experimental isotherms, empirical models for the hysteresis between the adsorption and desorption isotherms were also proposed [15,16].

The pore connectivity of the cement-based material is an essential factor for predicting the water vapour sorption hysteresis. Espinosa and Franke [7] used the size ratio of the bulk pore to the connected smaller pore as a parameter to model the ink-bottle effect. During desorption, the critical RH, at which the entrapped water in the bulk pore starts to evaporate, is influenced by the size of the connected pore in the model. Actually, the fraction of the entrapped water depends on the probability of the intersection of larger to smaller pores. This probability was modelled in terms of the ratio of their pore volumes [17]. Alternatively, the connectivity of smaller pores to large pores was assumed to be proportional to the pore lengths [18]. The pore length was calculated based on different sectional shapes of C-S-H pores and capillary pores. Moreover, Pinson et al. [19] developed a chain model consisting of various sizes of pores to represent the pore network of cement paste.

In this paper, the water vapour sorption hysteresis of the cement-based materials was modelled based on their pore size distributions (PSDs) and pore networks. The water in the C-S-H interlayer spaces and gel/capillary pores was considered separately. The PSD was obtained from the adsorption isotherm based on an assumption of cylindrical pores with layers of attached water. The chain model developed by Pinson et al. [19] was applied to represent the pore networks. The determination for the scanning curve under an arbitrary RH history was proposed, which is a new development based on Pinson et al.'s work [19]. In addition to that, the difference of liquid-gas interfaces between the adsorption and desorption processes was considered, because this can have an impact on the scanning curves. This paper combined all the key points from the existing relevant work to develop a more comprehensive and better model for the sorption hysteresis. The contribution of each pore component to the sorption hysteresis was analysed by using the developed model.

## 2. Classification of water in cementitious materials

In general, cement-based materials have pores in a large range of sizes [8] and various shapes. One of the main hydration products of Portland cement, amorphous C-S-H, has an internal sheet-like structure [20]. The interlayer water is held between the C-S-H interlayers with the spacing of around 1.1 nm and it is strongly bound to the surface of the C-S-H layer [21]. The thickness of the interlayer water is in the range of a few diameters of water molecule. The gel pores exist between C-S-H gel particles with widths about 1–10 nm. The capillary pores are the initially water-filled spaces with widths between 2.5 nm and 10 μm and they are of irregular shapes [22]. Surface tension forces are generated on the interface between the menisci of water and the walls of the pores.

### 2.1. *Evaporable water from C-S-H interlayer spaces and crystalline hydration phases*

Simulation and experiments at the molecular scale both indicated that during desorption the loss of the bound water in the interlayer spaces is negligible at RHs larger than 0.15–0.3 [6,23,24]. After drying at lower RHs, the interlayer water is removed and the spacing between C-S-H layers is reduced. When the cement-based material re-absorbs the moisture from the dried state, water molecules are inserted into the C-S-H layers and the interlayer space swells gradually. The water loss and regain in the space between the adjacent C-S-H sheets is essential for modelling of sorption hysteresis of cement-based materials at low RHs. Based on Feldman's experimental results, it is shown that between 0.1 and 0.3 RH the difference of evaporable water content in the interlayer spaces between adsorption and desorption isotherms is almost constant [25]. Moreover, the remove and delayed recapture of water within crystalline hydration phases also results in the hysteresis [26].

Saturated interlayer water content is dependent on the C-S-H amount and the aggregated layer number of C-S-H. As the hydration degree increases, loose C-S-H is transformed to dense C-S-H and the number ratio of the C-S-H layer to the interlayer of water asymptotically decreases to 1 [27]. The evaporable water in the crystalline hydration is related to the activation energy of de/rehydration for minor aluminate and ferrite phases. Due to the complexity of the C-S-H microstructure and the minor phases, it is currently difficult to determine the evaporable water content in the interlayer and minor hydration phases theoretically.

### 2.2. *Water in gel and capillary pores*

The water in the pores consists of adsorbed layers on the pore wall and condensed water formed by capillary condensation. Due to Van der Waal's forces, the pore walls capture the water vapour molecules in the pores to form the attached layers. The thickness of the adsorbed layer $t_a$ (m) can be calculated by [28].

$$t_a = t_0 \ln\left(\frac{-E_{ad} \bullet C^{1/3}}{RT \ln h}\right) \tag{1}$$