

1. INTRODUCTION

Modelling of moisture transport in cementitious materials is one main part to evaluate the durability of cement-based structures. Water vapour sorption isotherms (WVSIs) are one of main properties that are used in modelling to describe equilibrium between liquid and vapour phases [1]. In the literature, numerous of researches have been done on modelling of drying a material [2, 3]. In these models, the desorption isotherm is usually used. Nevertheless, in natural conditions, concrete structures are exposed to the cyclic changing humidity conditions, such as weathering drying-wetting and marine conditions. Modelling in such conditions, both main sorption isotherms, even some scanning curves, are needed. The common approach to get both main sorption isotherms is to fit the measured curves using a relevant equation.

Commonly, two experimental methods are used, static method and dynamic method. Static method uses the saturated salt solution to control a constant RH in a small space, and then waits until the mass of the specimen gets stabilization. This procedure may need long time due to the low moisture transport in a cementitious material. Dynamic method (such as dynamic vapour sorption, DVS) uses tiny samples, but the equipment is expensive to buy and to run. In those experiments, 5% or 10% RH interval is generally used. Thus, for each isotherm, more than ten points have to be measured which leads to a low sufficient measurement. In the other words, regardless which method, it needs long time and a lot of money to carry out measurements.

The more interesting question is that: could we measure the fewer points to get the entire curve by using a curve-fitting equation? Of course, the more measured data can represent the materials properties better. But from the measurement point of view, it is worth finding a method which can use the fewer experimental data to predict both main sorption isotherms. In the literature, there is lack of researches trying to estimate how many experimental data required for modelling.

This attempt raises questions, such as how many points, how to decide them, *etc.* In this paper, we will determine the number of experimental data, find the positions of those points and use statistical criteria to verify that the selected points can represent other measured data to fit the entire curve.

2. COLLECTION OF EXPERIMENTAL DATA AND STATISTICAL CRITERIA

2.1 Experimental data

As mentioned above, WVSIs can be measured by different methods. The saturated salt solution method is a traditional one [1], which controls a certain relative humidity (RH) by a saturated salt solution (see Table 1). The mass of specimen decreases (during desorption) or increases (during adsorption) until a mass stabilized state reaches, which is so-called equilibrium. Another commonly-used method in recent years is DVS [4, 5]. The advantage of this kind of instruments is that one desorption and adsorption loop can be measured in one month or less, more rapidly than the saturated salt solution method, which consumes months and even years. Nevertheless, tiny specimens used in a DVS cannot contain aggregates. Measurements probably observe the sorption behaviour only for the paste in concrete or mortar, rather than the global sorption behaviour of the material. For instance, the influence of paste-aggregate interracial transition zone (ITZ) on the sorption is neglected in this method. Hence, in a DVS measurement, a real equilibrium is probably not reached at each RH step. Another risk is that the tiny specimen can be carbonated quickly during the preparation.

Table 1: RH fixed by salt solutions used in [1, 6].

Salt	Cerium fluoride	Lithium Chloride	Potassium Acetate	Magnesium Chloride	Potassium Carbonate	Magnesium nitrate	Sodium Bromide	Potassium iodide	Ammonium sulfate	Strontium nitrate	Potassium sulfate
RH (100%±1)	3	12	22	33	44	53	63	71	80	90	97

As a result, we just collected WVSIs measured by the saturated salt solution method. Experimental data are gathered in Table 2. All materials from literature [1] are made from the same OPC cement (CEM I 52.5, according to the EN 197-1 European standard). The material in the last row in Table 2 uses another type of cement (R42.5 according to GB/T 4131-1997 Chinese standard). They include ordinary and highperformance hardened cement pastes and concretes.

Specimens used for measurements in [1] are thin slices for concretes (2 or 3 mm thickness with mass between 20 and 100 g) and crushed materials for cement pastes (with mass around 8 g). Measurements started from the desorption isotherm at RH = 100%, decreasing step-by-step to RH = 3%, considered as the dry reference state. Then RH increased to 100% step-by-step to obtain the adsorption isotherm. The equilibrium state for each RH step is defined as that the mass change is less than 0.001 g after one month. The value of water content for each RH step of the sorption isotherm is the mean value of at least three specimens.

Table 2: Collected data of WVSIs measured by the saturated salt solution method [1, 7].

NO.	Name	Materials	Binders	Cement (binder) content ^a	Gravel content	Sand content	Literature
1	B	Concrete	OPC	0.45	2.875	1.688	[1]
2	BH	Concrete	OPC + SF ^b	0.27(0.24)	3.377	2.108	[1]
3	BO	Concrete	OPC	0.43	3.005	1.549	[1]
4	C	Paste	OPC	0.45			[1]
5	CH	Paste	OPC + SF	0.20(0.18)			[1]
6	CO	Paste	OPC	0.35			[1]
7	CN	Paste	OPC	0.45			[1]
8	CP	Paste	OPC	0.60			[1]
9	BN-S	Concrete	OPC	0.50	2.88	1.68	[7]

a. It considers cement content as 1.

b. SF represent silica fume.

2.2 Statistical criteria

A nonlinear least squared optimization procedure has been used to optimize all parameters in the model during the fitting of sorption isotherms. This procedure aims to minimize the sum of squared error (SSE):

$$SSE = \sum_{i=1}^n [S_i^{pr} - S_i^{ms}]^2 \quad (1)$$

where S is the degree of moisture saturation. S_i^{pr} and S_i^{ms} are predicted and measured values, respectively. n is the number of available data.

Two kinds of statistical criteria have been used to evaluate the accuracy of modelling results in the literature [8, 9]: the coefficient of determination (R^2) and the differential

residual-based ($S_i^{pr} - S_i^{ms}$) error metrics. R^2 is defined as the ratio between the dispersion predicted by the model and the total dispersion of the measured data [8].

$$R^2 = \frac{\left(\sum_{i=1}^n S_i^{pr} S_i^{ms} (i) - \frac{\sum_{i=1}^n S_i^{pr} \cdot \sum_{i=1}^n S_i^{ms}}{n} \right)^2}{\left(\sum_{i=1}^n (S_i^{ms})^2 - \frac{(\sum_{i=1}^n S_i^{ms})^2}{n} \right) \left(\sum_{i=1}^n (S_i^{pr})^2 - \frac{(\sum_{i=1}^n S_i^{pr})^2}{n} \right)} \quad (2)$$

The value of R^2 must be between 0 and 1. The differential residual-based statistical criteria commonly-used in the literature are the root of mean square error (RMSE), normalized mean error (NME), mean multiplicative error (MME), *etc.* RMSE is calculated based on SSE, which has been used to as a criterion in the least squared procedure, so here we don't used it again. In this study, we found that NME yielded the same results with MME. The only difference of these two criteria is that NME is in the range of $[0, \infty]$, but MME is in the range of $[1, \infty]$. Thus, we choose MME as the second criterion, which will combine with R^2 and give a new criterion (see Figs. 3 and 4). A function for MME is expressed as [10]:

$$\text{MME} = \exp \left[\frac{\sum_{i=1}^n |\ln(S_i^{pr} / S_i^{ms})|}{n} \right] \quad (3)$$

Note that the absolute value is used in above equation. It can avoid the cancellation of positive and negative residuals. If the value of MME is close to 1, it indicates a better prediction.

Through above description, we know that for a high accuracy fitting, both values of R^2 and MME should be close to 1 (R^2 from a low value and MME form a high value). Hence, these two criteria can be plotted in the same figure. One only needs to compare the distance between R^2 and MME to assess models. If these two values are closer, it implies a better fitting result.

3. DETERMINATION OF NUMBER OF POINTS

Previous studies [11] have shown that three-parameter models can provide a better fitting result than two-parameter models. Two wide-used three-parameter models are proposed by van Genuchten [12] and Fredlund and Xing [13]. Van Genuthen's model (VG3) was firstly introduced to describe the soil-water characteristic curves:

$$S = \left[1 + \left(\frac{P_c}{a} \right)^n \right]^{-m} \quad (4)$$

Fredlund and Xing [1994] improved above model and gave a logarithmic equation (FX):

$$S = \left[\ln \left[e + \left(\frac{P_c}{a} \right)^n \right] \right]^{-m} \quad (5)$$

where a (Pa), m and n are three parameters. e is the Euler's constant. P_c is the capillary pressure, which can be transformed from RH by using Kelvin's equation.

The better performance of three-parameter models indicates if one wants to know both sorption isotherms, at least three points on each isotherm have to be measured (six points

overall). In fact, an alternative method can be employed to reduce number of parameters (and points). Here, we introduce the *first simplification* in this paper, which is written as:

$$a_w = a_d = a \quad (6)$$

where a_w and a_d are the parameter a for the desorption and adsorption isotherms, respectively. In this paper, we let $a = a_d$. Calculated results show this simplification does not reduce the fitting accuracy so much (see two statistical criteria compared in Figs.3 and 4).

Hence, the number of measured points is able to be reduced to five, three on the desorption and two on the adsorption isotherms. Thus, we introduce the *second simplification* in this paper based on the assumption of “five points are enough to calculate both sorption isotherms”.

4. DETERMINATION OF POSITIONS OF THOSE POINTS

A simple way has been used to determine the positions of those points. Firstly, a model (Eq. 4 or 5) is used to fit all collected materials based on the first simplified method, and then calculate the mean residual (MR) of all materials for each RH.

$$MR = \frac{1}{N} \sum_{i=1}^N |S_i^{pr} - S_i^{ms}| \quad (7)$$

where N is the number of materials which have been fitted by this model. The MR results calculated from FX and VG3 models for each RH are given in Table 3.

Then, we can choose the points with the minimum values of MR as the positions that we will use to determine the entire desorption or adsorption isotherm.

Table 3: The mean residual of all materials for each RH.

RH (100%)	Mean residual (FX)		Mean residual (VG3)	
	Desorption	Adsorption	Desorption	Adsorption
12	5.77E-03	6.51E-03	2.85E-02	6.55E-03
22	4.21E-03	1.44E-02	4.11E-03	1.54E-02
33	2.99E-02	1.55E-02	3.21E-02	1.51E-02
44	1.05E-02	2.80E-03	1.29E-02	3.78E-03
53	2.39E-02	7.17E-03	2.39E-02	7.15E-03
63	1.44E-02	1.88E-02	1.49E-02	1.84E-02
71	3.88E-03	1.79E-02	9.98E-03	1.74E-02
80	1.16E-02	4.56E-03	1.11E-02	4.80E-03
90	2.07E-02	7.21E-03	2.54E-02	6.94E-03
97	3.20E-02	2.29E-02	3.17E-02	2.16E-02

4.1 Points on desorption isotherm

MR results from FX model show that three points on the desorption isotherm are at RH=22, 44 and 71%, which correspond to the low, medium and high RH range. However, the minimum values of MR from VG3 are at RH=22, 71 and 80%, which gives two points in the high RH range. The MR value at RH=44% is 1.29E-02 that is no significant different from at RH=80% (MR=1.11E-02). So, to get the same positions for two models, we choose three points on the desorption isotherm are at RH = 22, 44 and 71%.

4.2 Points on adsorption isotherm

Results for the points on the adsorption isotherm from FX and VG3 models reveal high consistency. Two points are at RH=44 and 80%.

In previous study of Feng and Fredlund's model[14] (improved by Pham *et al.*, [8]), we know that if the desorption isotherm is known, we just need two points on adsorption isotherm to predict the entire curve. These two points can be fixed at RH=63 and 90%. Note that in this method, the main isotherm is fitted by Feng and Fredlund's model[14], which is a two-parameter model. It has been shown the prediction of this kind of models is not good as three-parameter models. So, FX or VG3 model will be used to replace Feng and Fredlund's model and we will check the relevance of using two points at RH=63 and 90% for the prediction of adsorption isotherms.

5. RESULTS AND DISCUSSION

5.1 Results

Results for several selected examples (BO, BN-S, CO, CH and B) are shown in Figs. 1 and 2. The suggested five points are highlighted in figures. Results just from FX models are given here because VG3 provides the similar fitting results. We can clearly see that two versions of simplified methods provide the identical shapes of predicted isotherms to the original experimental data for BO, BN-S, CO and B.

However, it seems that the second simplification does not work well on CH (see Fig. 1). It is mainly due to the shape of measured desorption isotherm. For CH, this curve remains at high water content in the range of RH>63%, but when RH<63%, it drops more rapidly than other materials. The shape of this measured curve indicates that CH has more small pores (C-S-H pores), which play a main role in retaining water and controlling moisture transport in the material. This property also can be observed in the adsorption isotherm of CH, which increases consistently from low RH to high RH unlike other materials whose adsorption isotherms increase gently at the beginning but rapidly in high RH range. For instance, results for BO and CO in Fig. 1 clearly show this trend.

Note that the original fitting methods can yield an unreal fitting result, which is that the desorption isotherm can cross the adsorption isotherm at the low RH range, as illustrated in Fig. 2. One advantage of these two simplifications is that they can avoid this unreal phenomenon (see enlarged figure in Fig. 2).

The new criterion for the original model, the first simplification and the second simplification are given in Fig. 3 (FX) and Fig. 4 (VG3). It is clear that for desorption isotherm, the distance between the mean values of MME (\times) and R^2 (+) are nearly same for those three versions of models. That is, these two simplifications have the equivalent prediction accuracy to the original method. But for CH, both FX and VG3 models show the poor performance (see the highlighted diamonds in Figs. 3 and 4).

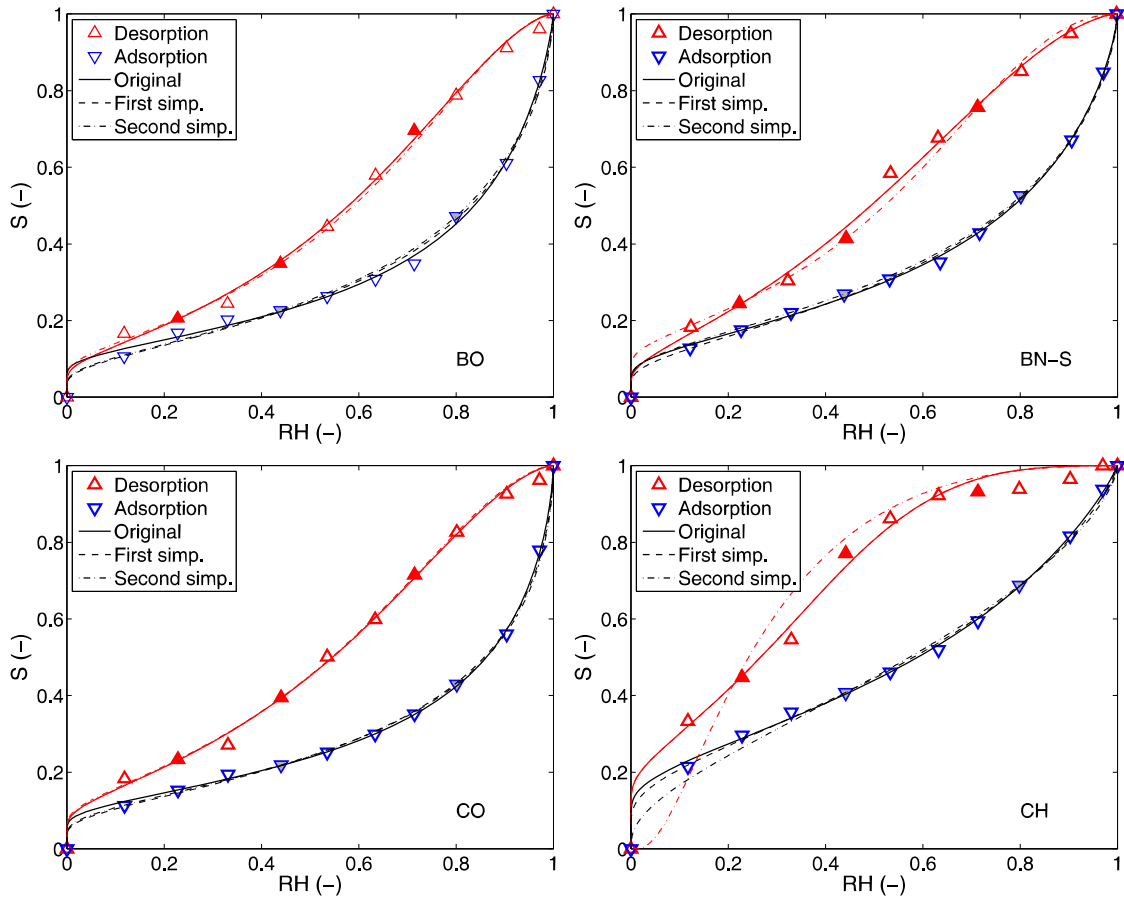


Fig. 1. Comparison of results calculated by three versions of FX model. Points chosen to solve equations are highlighted (solid symbols).

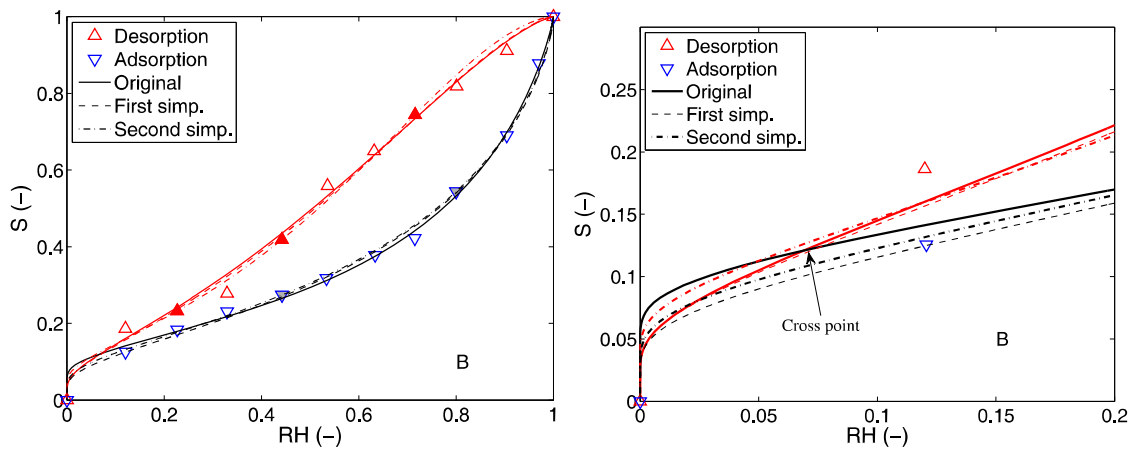


Fig. 2. Sorption isotherms calculated by three versions of FX model for B. Enlarged figure in the low RH range is shown in the right-hand figure.

In contrast, the difference of these three versions of models is clearer in the comparison of prediction results of adsorption isotherms. The distance between mean MME and mean R^2 increases from the original method to the second simplification. Even so, the mean value of MME calculated by the second simplification is around 1.05, which is equal to the MME value in the prediction of desorption isotherm. Thus, the slight difference between the original

method and the second simplification is acceptable. In particular, it proves that the fitting of an adsorption isotherm is usually better than the fitting of a desorption isotherm.

The last column in adsorption figures in Figs. 3 and 4 is calculated by the improved Feng and Fredlund’s model[11, 13]. Obviously, this model does not provide a good prediction. Especially, the value of MME for C can reach as high as 1.29. We can conclude that two points which previously was suggested for Feng and Fredlund’s model[13] cannot be used for FX or VG3 models.

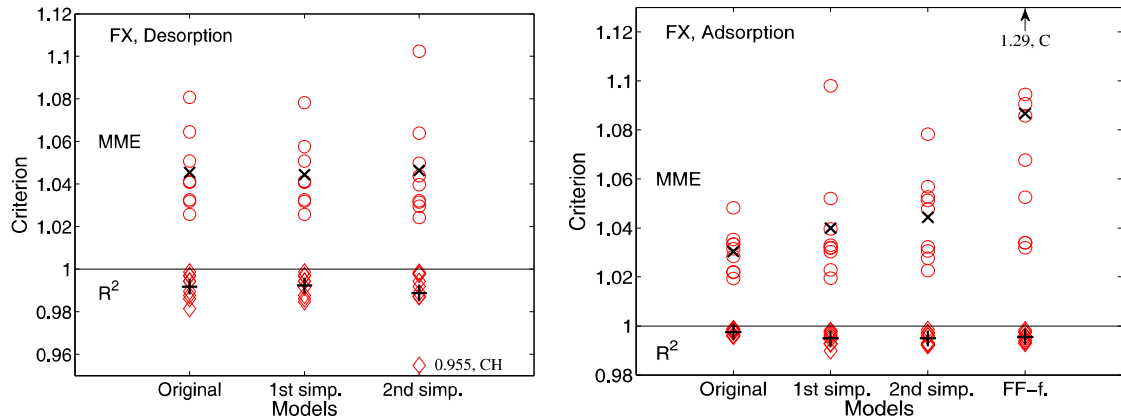


Fig.3. Comparison of R^2 and MME calculated by FX model. Each diamond (\diamond) or circle (\circ) for R^2 or MME stands for one material. “+” is the mean value of R^2 and “x” is the mean value of MME.

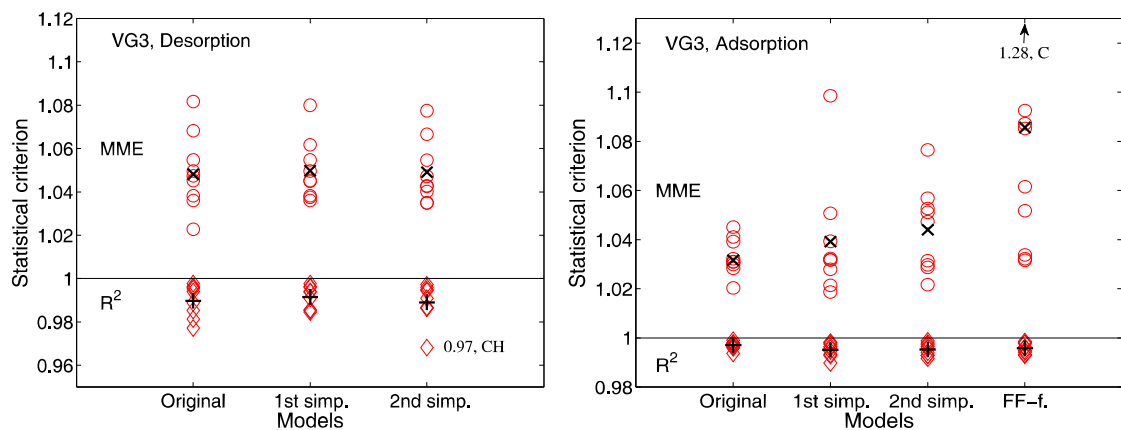


Fig. 4. Comparison of R^2 and MME calculated by VG3 model. Each diamond (\diamond) or circle (\circ) for R^2 or MME stands for one material. “+” is the mean value of R^2 and “x” is the mean value of MME.

5.2 Discussion

5.2.1 The new criterion

The new criterion illustrated in Figs. 3 and 4 is more intuitive than using MMR and R^2 separately. The main problem is that MME may dominate the new criterion because MME has a wider range than R^2 . However, a careful observation on Figs. 3 and 4, we are able to find that only when R^2 is close to 1, MME becomes a dominant criterion. Actually, if values of R^2 for all studied materials are high enough (such as >0.99 , see the figures for adsorption

in Figs. 3 and 4), R^2 reduces to be a less important criterion. Naturally, it requires that MME has to show differences to assess studied models.

5.2.2 Mathematical problems

One can note that for CH, the predicted desorption isotherm actually does not pass three points (RH=22, 44 and 71%) that we have suggested. That is because equations (FX or VG3) cannot be solved using these three points. This is a mathematical problem which is due to non-linear forms of FX and VG3 models. It leads to an issue that in this kind of equations three parameters don't mean that using three points can solve equations for some special cases.

In the case of CH, a "solving equations" procedure becomes a "fitting" procedure. In fact, for the fitting of experimental data, more data can yield a better fitting result.

5.2.3 Comments on the number of points

In the second simplification, we assumed that three points on the desorption isotherm and two points on the adsorption isotherm are enough to solve equations and determine parameters. Results reveal that this assumption is valid for most materials, except CH, which may imply the need to add more points for this kind of material.

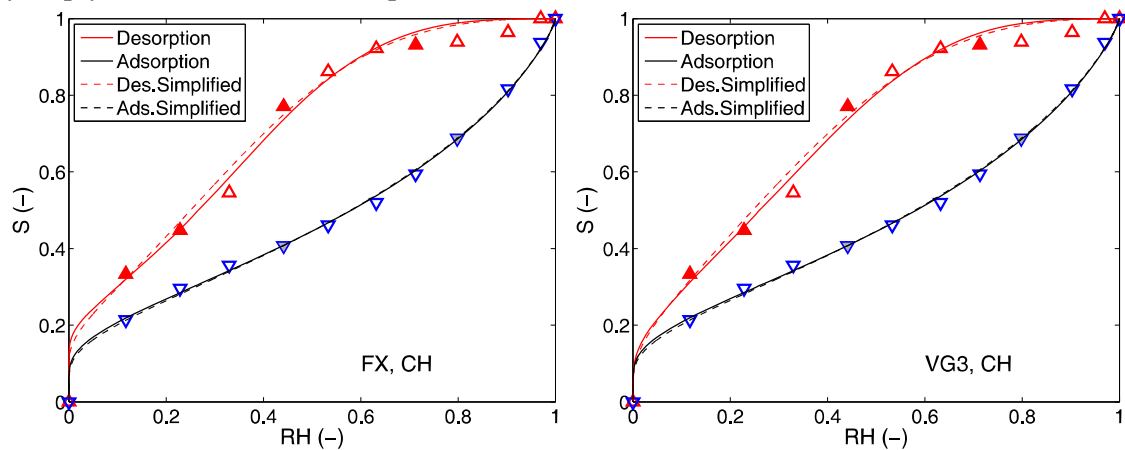


Fig. 5. Results calculated by FX and VG3 models for CH in the case of adding one more point.

As the analysis in previous section (see 5.1), CH has more C-S-H pores, which corresponds to the low RH. Accordingly, water content in the low RH appears to be more important for moisture transport. Thus, we can add one more measured point at low water content. Here, we choose the point at RH=12% and results calculated by FX and VG3 models are shown in Fig. 5.

Obviously, the calculated curves (either for desorption or adsorption) show extremely high agreements with the original method. Adding one more point can improve the prediction accuracy significantly. In the other words, it needs four points to predict the desorption curve for CH, one high performance material.

Hence, the number of points can increase according to the moisture property of materials. However, reducing the number is not acceptable, which can bring unstable parameters.

5.2.4 Comments on the positions of points

Three points on the desorption isotherm means that this curve can be considered as three parts: low RH range (representative RH=22%), medium RH range (representative RH=44% [1]) and high RH range (representative RH=71%). In the low RH range, moisture transport is dominated by C-S-H pores, while in the high RH range it is controlled by capillary pores [15]. The medium range has the mixed influence from both C-S-H and capillary pores. Owing to

different methods to measure WVSIs, those positions may be changed, but these three parts of a desorption isotherm should be always remained.

Note that points at RH=44% are used in both desorption and adsorption predictions. This is a special point that has been pointed out in the literature [1]. The author has found that almost all of studied materials have the same shape of desorption isotherms when RH<44%. It roughly can be considered as the threshold value between C-S-H and capillary pores. This proves our simplifications in an alternative way.

6. CONCLUDING REMARKS AND SUGGESTIONS

In this study, we have proposed a method which uses the fewest experimental data to predict both desorption and adsorption isotherms. Several points in this study need to be remarked:

- Even though FX and VG3 models use different forms of equations, they both can provide quite similar prediction results.
- The first simplification not only can reduce the number of parameters, but also shows high fitting accuracy. So it can be used in further research.
- New criterion has been proposed by combining two traditional criteria, R^2 and MME. It provides an easy way to assess studied models.
- For the OPC cementations materials, suggested five points (three on desorption isotherm and two on adsorption isotherm) are enough to predict both desorption and adsorption isotherms. For special materials (*e.g.*, CH), adding one or more points can improve the fitting accuracy.
- The positions of those points have been verified by collected data and given at RH=22, 44 and 71% for a desorption isotherm and at RH=44 and 80% for an adsorption isotherm. One more point on the desorption curve for CH can be chosen at RH=12%. Results show that only using those chosen points to predict sorption isotherms can give the same fitting accuracy with using original models.
- The number of points can increase based on the property of the material, but it cannot be reduced. In this paper, one point is added in the low RH for CH because CH has more C-S-H pores. If one has a material mainly contains capillary pores, perhaps one or more points are needed in the high RH range, *e.g.*, at RH=80%.

Due to the limited experimental data, the positions of suggested points need to be validated in the future. The research results in this paper are useful for determination of sorption isotherms using an experimental method.

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