

Measurement of sorption isotherm of porous materials influenced by salt

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Abstract

This paper compiles the past data of the sorption isotherm of Autoclaved Aerated Concrete (AAC) laden with salts ($MgCl_2$ and $NaCl$) and some new experimental data for AAC that contains Na_2SO_4 . The results are related to the type of salt, the salt concentration and the mass of salt that is considered to be crystallised. Finally the existing mathematical model that uses the sorption isotherm for pure water and the salt content in the material is applied to predict the sorption isotherm of AAC laden with Na_2SO_4 . It is shown that even salts like Na_2SO_4 , whose equilibrium relative humidity is 94%, significantly alter the sorption isotherm when a large amount of salt is crystallised in the material and this to an extent depends on the amount as well as the type of salt.

Keywords: moisture, water retention curve, absorption, desorption, salt crystal

1 Introduction

The relation between the water content of a porous material and the relative humidity of the surrounding air in a condition that no exchange of moisture between the material and the air occurs, i.e. sorption isotherm, can be different when the material contains salts. This is because the vapour pressure of a salt solution is lower than that of pure water and because crystallising salts can alter the pore structure of the material.

Water sorption isotherm of porous materials in presence of salts has been measured by Bresler [1], Tanimoto et al. [2], Harimoto et al. [3], Hashikata et al. [4], Abuku et al. [5], etc. and modelled by Bresler [1], Brocken et al. [6], Rucker et al.[7], Abuku et al. [5, 8], etc. Most work was focused on porous materials containing salt solution at low concentration or saturated without salt crystals in the material. Recently, Abuku et al. [5] extended the existing models to a model for a material that contains undissolved salts (salt crystals).

This paper compiles the past data of the sorption isotherm of Autoclaved Aerated Concrete (AAC), commonly called ALC (Autoclaved Light-weight Concrete) in Japan, laden with two different types of salt ($MgCl_2$ and $NaCl$) and some new experimental data for AAC that contains sodium sulphate (Na_2SO_4). Here, AAC was not selected for its susceptibility to salt damage but for academic reasons chosen as model material to study the sorption isotherm of a salt-laden porous material. However, the methodology proposed here is considered to be similarly applicable to other porous materials. In the new measurement, we observe both absorption and successive desorption processes. The results are discussed with respect to the type of the salt and the salt content that is considered to be crystallised. Finally the existing model that uses the sorption isotherm for pure water and the salt content in the material is applied to predict the sorption isotherm of a salt-laden material.

2 Parameters and sorption isotherm model

This section briefly describes some important parameters required to understand the measurement data in the following section and the existing model developed in Abuku et al. [5], which predicts the sorption isotherm of a salt-laden porous material on the basis of the sorption isotherm of the same salt free material, the salt concentration and the amount of undissolved (crystallised) salts.

2.1 Definition of parameters

The moisture content w_w is given by:

$$w_w = \frac{m - m_0 - m_s}{m_0} \quad (1)$$

with m the mass of the material (kg), m_0 the dry mass of the material (kg), m_s the mass of salt in the material (kg).

The salt solution content w_{sw} is given by:

$$w_{sw} = \frac{m - m_0}{m_0} \quad (2)$$

The salt concentration C based on the solvent (water) is given by:

$$C = \frac{m_s}{m - m_0 - m_s} \leq C_{sat} \quad (3)$$

with C_{sat} the saturated salt concentration (kg/kg).

The content of salt crystals w_c is given by:

$$w_c = \frac{m_c}{m_0} \quad (4)$$

Here m_c can be calculated by:

$$m_c = m_s - w_w m_0 C_{sat} \quad (5)$$

2.2 Sorption Isotherm Model

The relative humidity φ' of a material that contains a salt solution with a concentration C is given by:

$$\varphi' = \varphi(1 - x_s) \quad (6)$$

where x_s is the molar fraction (-) and φ is the relative humidity (-) that the material would have when containing pure water of the same volume as the salt solution φ is related to the chemical potential μ_0 of water in the material that depends on the volume of the solution:

$$\varphi = e^{\frac{\mu_0}{TR_v}} \quad (7)$$

with T the temperature (K) and R_v , the gas constant (J/kgK) of water vapour (4.616×10^2). Based on data for pure water, the relation between μ_0 and the water content w_w can generally be obtained as:

$$\mu_0 = \sum_{i=1}^n c_{i,1} \exp(c_{i,2} w_w) \quad (8)$$

with $c_{i,1}$ and $c_{i,2}$ constants. For a material that contains a salt solution, Eq.(8) is replaced by:

$$\mu_0 = \sum_{i=1}^n c_{i,1} \exp\left(c_{i,2} \frac{\rho_w}{\rho_{sw}} w_{sw}\right) \quad (9)$$

with ρ_w the density of water (kg/m^3), ρ_{sw} the density of a salt solution (kg/m^3), and w_{sw} the salt solution content (kg/kg).

When the salt concentration C reaches the saturated salt concentration C_{sat} and salt crystals are deposited, the relative humidity ϕ' predicted with the existing model (Eq. (6)) can thus be modified to the relative humidity ϕ'_{mod} by:

$$\phi'_{mod} = \left(1 - k_c \frac{w_c}{w_{sw}}\right) \phi' \quad (10)$$

where $k_c w_c / w_{sw}$ represents the degree of the influence of salt crystallisation.

3 Experiment

3.1 General

Some new measurements were conducted at a constant temperature of 23 °C. Equilibrium moisture content of AAC in absorption and successive desorption processes is measured in a manner similar to [5]. The porosity Φ_0 and density ρ_0 of the material are respectively $0.786 \text{ m}^3/\text{m}^3$ and 494 kg/m^3 [9].

In the measurement, the following six steps are taken:

- (1) 21 specimens of approximately $10 \times 10 \times 10 \text{ mm}^3$ are dried at 95 °C in an oven. The mass of each dry specimen m_0 is measured at a temperature of 23 °C and a relative humidity of 30 %.
- (2) Three desiccators that contain respectively pure water and Na_2SO_4 solution at a concentration $C_i = 0.0038 \text{ kg/kg}$ or $C_i = 0.0501 \text{ kg/kg}$, are prepared. Seven, eight and six specimens are dipped into respectively pure water, salt solution of $C_i = 0.0038 \text{ kg/kg}$ and a salt solution of $C_i = 0.0501 \text{ kg/kg}$. The air in the specimens is then evacuated by means of a vacuum pump.

- (3) All specimens are kept in the desiccators for more than one week, during which the air in the specimens is continuously evacuated. So all the specimens are considered to have been completely dried.
- (4) The specimens are stored in a large desiccator with a constant relative humidity of 11% that is controlled with saturated LiCl solution. The weight m of the specimens is measured every a few days.
- (5) When a constant weight is reached, the saturated salt water in the desiccator is changed successively from LiCl (11% RH), MgCl_2 (33% RH), NaCl (75% RH), to KCl (84% RH). At each relative humidity level, step (4) is repeated.
- (6) The salt-laden specimen are finally dried at 95 °C. The mass of each dry specimen is then measured to determine the sum of m_0 and m_s , which allows to determine the value of m_s by calculating $m_0 + m_s$ minus m_0 .

Given m , m_0 , and m_s , the moisture content w_w is obtained according to Eq. (1), the salt concentration C by Eq. (3), and the value of w_c by Eqs. (4) and (5).

It should be noted that it is assumed that all parameters are uniform in the specimen. To check whether the surface of the specimen is not blocked by salt crystals, AAC specimens are examined with an optical microscope at a dry condition (RH ~ 30%). However salt crystals were not found at the surface of the specimens. Only when a specimen that was initially saturated with a saturated salt solution and dried, salt crystals were observed at the surface of the specimen. In case parameters are not uniform in the specimen or pores at the surface zone are blocked by salt crystals, the measurement procedure presented in this section and the model may no longer be valid.

3.2 Results

The equilibrium moisture content at different conditions of relative humidity for specimens laden with Na_2SO_4 , related to salt free ones, in absorption and desorption mode is presented in Figure 1. The plotted values are obtained by averaging the data for the 7, 8 and 6 specimens. In the case of salt-laden specimens, the salt concentration during absorption and desorption processes is considered to be equal to the saturated salt concentration C_{sat} , so only the content of undissolved (crystallised) salt w_c calculated using Eqs. (4) and (5) is displayed in Figure 2(a) for the salt solution with the lower C_i and in Figure 2(b) for that with the higher C_i .

Although the equilibrium relative humidity of a Na_2SO_4 solution is 94 % at 23 °C, and hence no significant vapour pressure depression can be expected, the results show that the relative humidity values which are considered to give the same equilibrium moisture content can be very

different when the material contains salt crystals. This can be attributed to the influence of undissolved (crystallised) salts that are considered to change the pore structure.

The moisture content differences between the absorption and desorption processes for pure water and salt solution of the lower C_i are larger than in case of the higher C_i .

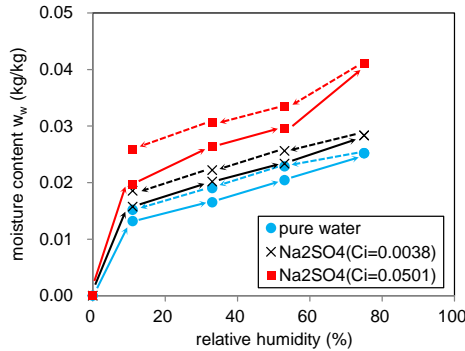


Figure 1: The measured sorption isotherm in absorption (solid line) and desorption (dashed line) processes of an autoclaved aerated concrete specimen laden with Na_2SO_4 solutions at two different concentrations

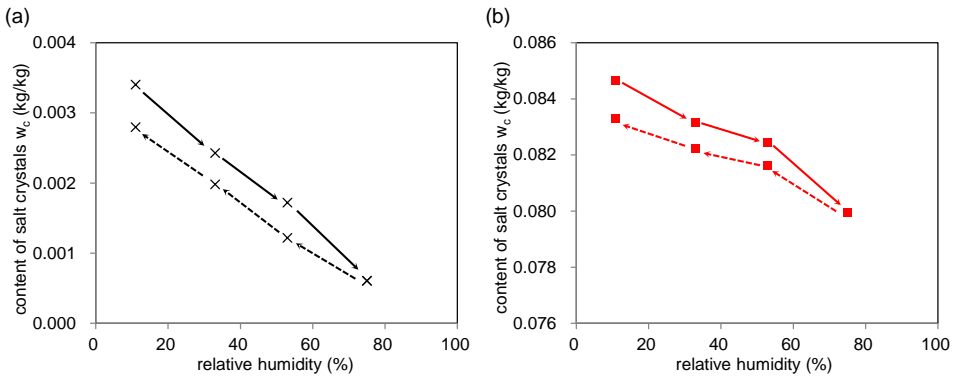


Figure 2: The measured content of salt crystals in absorption (solid line) and desorption (dashed line) processes

4 Discussion

The measurement data for absorption process were modelled using the equations described in section 2.2.

First, the data for pure water are fitted using Eqs. (7) and (8) with $n = 3$, $c_{1,1} = 1 \times 10^7$, $c_{1,2} = -210$, $c_{2,1} = 4 \times 10^4$, $c_{2,2} = -20$, $c_{3,1} = -3.75 \times 10^{-12}$, and $c_{3,2} = 0$. A good agreement is obtained between the measured data and the calculated ones as given in Figure 3. The values of n , $c_{i,1}$ and $c_{i,2}$ obtained here are used below as well.

Abuku et al. [5] found that k_c in Eq. (10) for AAC that contains NaCl and MgCl₂ under the conditions of the study can be obtained by:

$$k_c = c_{k,1} \exp\left(c_{k,2} \frac{m_s}{m_0}\right) \quad (11)$$

with $c_{k,1} = 0.0853$ and $c_{k,2} = 0.0495$. Using this same equation, we also determined $c_{k,1}$ and $c_{k,2}$ to be respectively 0.1229 and 0.0209 for AAC that contains Na₂SO₄. The values of $\ln(k_c)$ given by $c_{k,1} = 0.0853$ and $c_{k,2} = 0.0495$ are compared to those experimentally obtained in Figure 4, showing the dependency of k_c on the type of salt. This dependency becomes larger with increasing ratio m_s/m_0 .

Figure 5 compares the measured and predicted relations between the water content and relative humidity, which confirms that using the model presented in section 2.2 and the model for k_c in this section allows to predict the sorption isotherm of salt-laden AAC given the type and amount of salt in the material. Note that the relative humidity predicted by only Eqs. (7) and (9) and the one by Eq. (6) as well as Eqs. (7) and (9) are also included in Figure 5. By comparing the predicted results, it can be noticed that the influence of salt crystals on the sorption isotherm can become much larger than that of the vapour pressure depression.

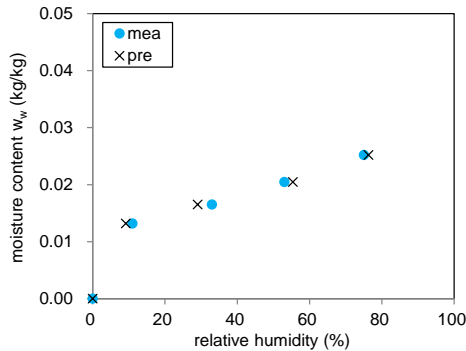


Figure 3: The measured and predicted relation between the water content and relative humidity for pure water

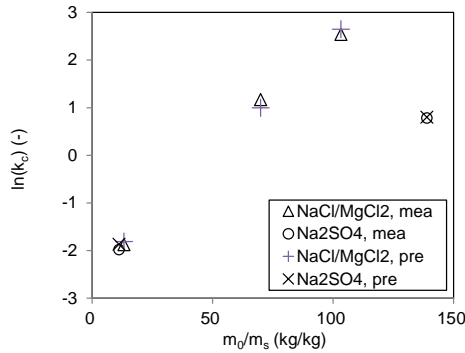


Figure 4: The measured and predicted $\ln(k_e)$ for NaCl/MgCl₂ and Na₂SO₄

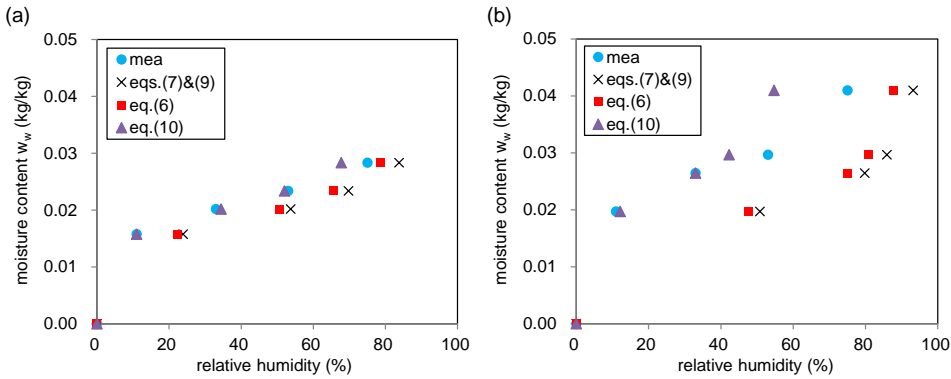


Figure 5: The measured and predicted relation between the water content and relative humidity for salt solution at (a) $C_i = 0.0038$ kg/kg and (b) $C_i = 0.0501$ kg/kg.

5 Conclusions

In this paper, we conducted some new experiments to measure the sorption isotherm of Autoclaved Aerated Concrete (AAC), commonly called ALC (Autoclaved Light-weight Concrete) in Japan, that contains sodium sulphate (Na₂SO₄). The measured data were compared to those obtained for different types of salt (MgCl₂ and NaCl). The compiled data were discussed in relation to the type of material and salt and the salt content that is considered to be crystallised. The mathematical model that uses the sorption isotherm for pure water and the salt content in the material to predict the sorption isotherm of a salt-laden material is validated. A good agreement was obtained also for AAC laden with Na₂SO₄. Moreover, by compiling and comparing the past and present data, it is shown that the degree of the influence of salt crystals is

dependent on the type of salt and the ratio of the salt mass to the mass of the dry material at least for AAC that contains MgCl_2 , NaCl and Na_2SO_4 .

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