

## **MEASURING WATER SORPTION ISOTHERM OF MORTAR CONTAINING CHLORIDE**

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### **Abstract**

The water sorption isotherm of materials is of great importance to predict their durability. Many different methods are used in the literature to measure this water sorption isotherm. Chloride present in concrete elements/structures e.g. in marine exposure, can change the water sorption of the material. In this paper, the water sorption isotherm of a standard mortar with and without chloride is measured with a hygroscopic method. The chloride penetration into the sample is obtained by the vacuum saturation method. Subsequently the sample is placed in a glass vessel and dried. By injecting a known amount of water into the vessel, the water evaporates and is partly adsorbed by the sample until an equilibrium state is reached. With the known amount of the injected water into the vessel, the humidity inside the vessel and the volume of the vessel, one point of the adsorption isotherm is determined. For measuring the next point, more water is injected into the vessel. More points are measured in the same manner until the sample is saturated and with this the adsorption isotherm is completed. Afterwards, the measurement of the desorption isotherm starts with blowing dry air with a known flow, humidity and duration into the vessel. After reaching equilibrium, the first point of the desorption curve is measured. The next point is measured by blowing more dry air into the vessel. This continues until the sample is completely dry and with it the desorption isotherm is also completed.

### **1 INTRODUCTION**

A sorption isotherm describes the relation between the moisture content in the examined material and the relative humidity of the surrounding environment at equilibrium and constant temperature. Since the sorption isotherm depends upon the history of drying and wetting of a sample, the sorption isotherm contains two curves, one for adsorption and one for desorption. The purpose of this paper is to examine the effect of chloride in mortar on the sorption of water in the material, since the presence of chloride affects the sorption of water. The sorption of water in materials has received a lot of attention in the literature: several methods for obtaining a sorption isotherm are known. The simplest method is by weighing the sample: this can be done manually by a quartz spring [1] or by a balance [2]. Another method for acquiring the sorption isotherm of a material is by means of the manometric measuring

technique, as described by Broom [3]. Van der Zanden and Goossens [4] describe a method for obtaining the sorption isotherm of water in paint films. This method will be applied in the present study on reference mortar sample and mortar sample containing chloride.

## 2 EXPERIMENT

### 2.1 Test set-up

A glass vessel with a glass cover is used to measure the sorption isotherm, as shown in Figure 1. The use of rubber rings can disturb the measurements in this set-up, because rubber can absorb or release water [5], and therefore, a Teflon foil ring is placed between the glass vessel and the cover to prevent leakage in and out of the system. The glass vessel contains a humidity sensor and a temperature sensor, which are connected to a data logger. A glass plate is placed in the vessel to capture the added drops of water. The glass vessel is also provided with an inlet and outlet for blowing dry air into the vessel and allowing the air escape from the vessel. An additional opening in the glass cover is used to inject water to the vessel. Furthermore, the glass vessel is placed in a room with a constant temperature and humidity.

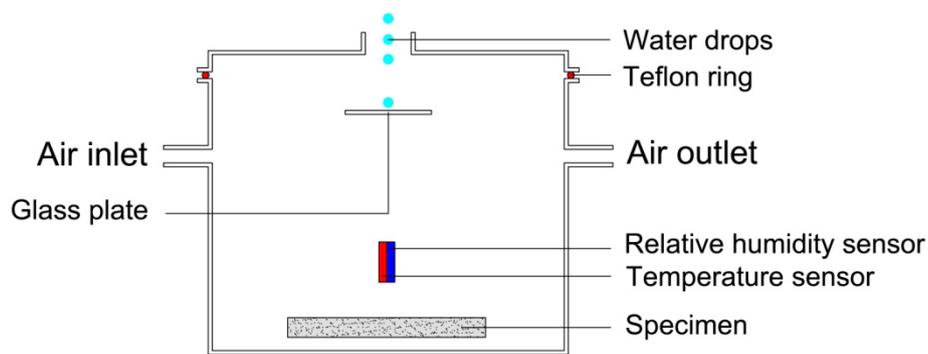


Figure 1: Cross section of the test set-up to measure sorption isotherm of mortar with a hygroscopic method.

### 2.2 Method

The measurement of the adsorption isotherm starts with placing the mortar sample inside the glass vessel and blowing dry air through the vessel for a certain time in order to dry the sample. The air inlet and outlet are then closed. At this point, it is assumed that the sample is completely dry. This assumption is not entirely true, since it is seen from initial equilibrium that the sample contained a small amount of water. However, this amount is very small, as it causes only little change in the relative humidity at the start.

After initial equilibrium a known amount of water is injected on the glass plate in the vessel using a device with which water can be dosed accurately. The injection opening in the glass cover is closed also with a Teflon plug. The injected water evaporates, which increases the humidity inside the vessel. Consequently, the water content of the sample increases as the sample adsorbs water from the air. After certain time, equilibrium is reached in the vessel. Figure 2 gives a characteristic chart of the humidity in the vessel as a function of time. The chart can be divided into three phases. The first phase is an increase of relative humidity as a result of evaporation of the injected water. The second phase is a decrease of relative

humidity resulting from the adsorption of water by the sample. The final phase is the equilibrium state between the relative humidity inside the vessel and the water in the sample.

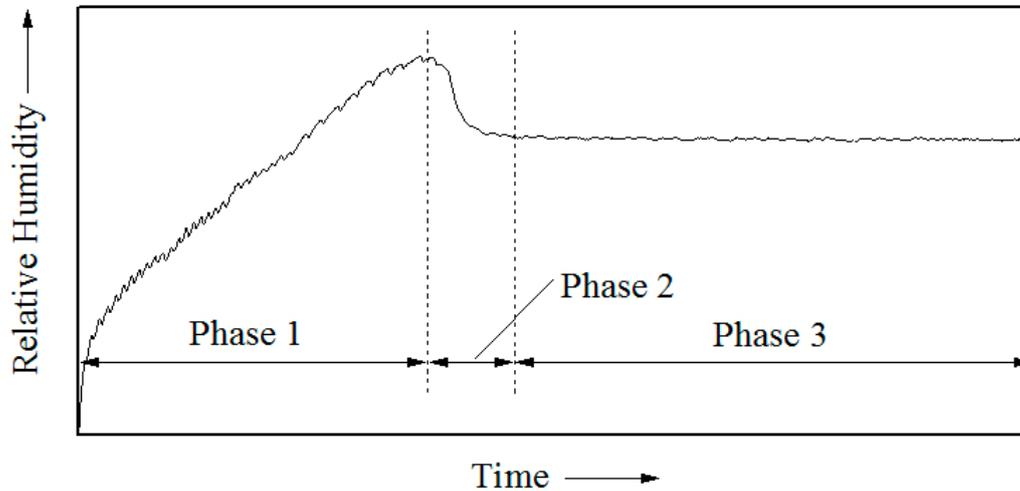


Figure 2: A characteristic chart of the relative humidity in the vessel as a function of time at 21°C (adsorption isotherm).

The total amount of water in the vessel is equal to the known cumulative amount of injected water. The amount of water in the air in the vessel is obtained by calculation from the measurement of equilibrium relative humidity (phase 3). The rest of the total amount of water is adsorbed by the sample. By calculating the amount of water in the sample at certain relative humidity, a single point of the adsorption isotherm is determined.

The measurement of the desorption isotherm starts after reaching an equilibrium relative humidity of approximately 90% in the vessel. One point of the desorption isotherm is calculated by blowing dry air with a known flow and known duration into the vessel. Also in this case, after certain time, equilibrium is reached in the vessel. Figure 3 gives a characteristic chart of the humidity in the vessel as a function of time. This chart can also be divided into three phases; the first phase is the decrease of relative humidity which results from blowing dry air in the vessel. The second phase is the increase of relative humidity resulting from the release of water by the sample. The final phase is the equilibrium state between the water in the air of the vessel and the water in the sample.

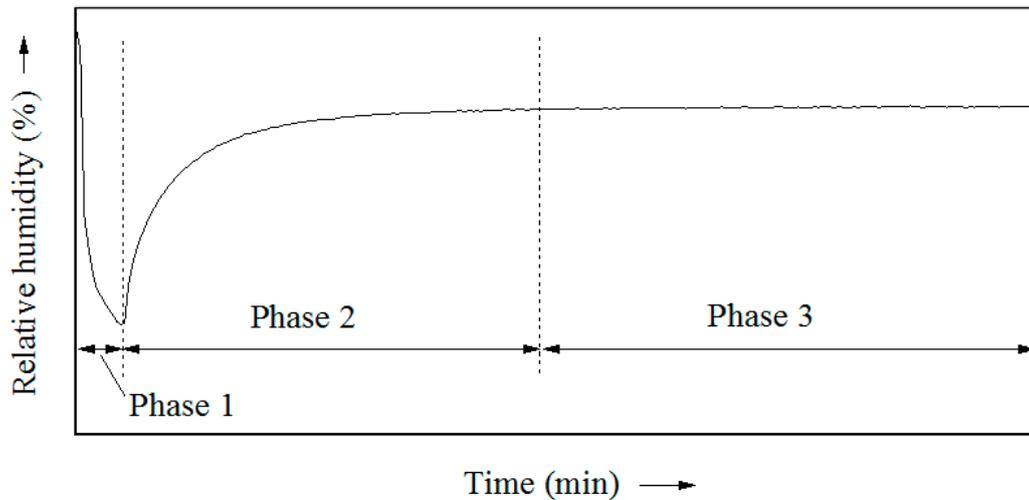


Figure 3: A characteristic chart of the relative humidity in the vessel as a function of time at 21°C (desorption isotherm).

### 3 SAMPLE PREPARATION

In this experiment, mortar samples are examined with a water cement ratio of 0.5 and cement type CEM I 42.5 N. The composition and properties of the mortar are shown in Table 1. The samples are cast in PVC tubes with a diameter of 100 mm. After one day, the mortar is demoulded and cured in water for additional 27 days. Samples of 10 mm thickness are cut from the mortar cylinder and provided with a chloride mass percentage of 2.0%.

Table 1: Composition and properties of the samples

Materials	Mortar	
	Volume [m <sup>3</sup> ]	Mass [kg/m <sup>3</sup> ]
CEM I 42,5N	159.47	502.18
Sand	568.51	1506.54
Water	251.09	251.09
w/c	0.5	
Porosity [%]	17.0	

Chloride is added to the sample by means of the vacuum saturation method, in which four samples are first placed in a vessel and air is removed from the samples by applying vacuum pressure of about 20 mbar for 3 hours. After the air is removed, a sodium chloride solution is poured into the vessel under vacuum. Subsequently, after 45 hours in the solution, the samples are removed from the vessel. One sample is used to determine the sorption isotherm and the other three are used to examine the chloride concentration by titration. Figure 4 shows the chloride concentration profiles measured by titration. It can be seen that the total chloride concentration is approximately 1.0% throughout the samples.

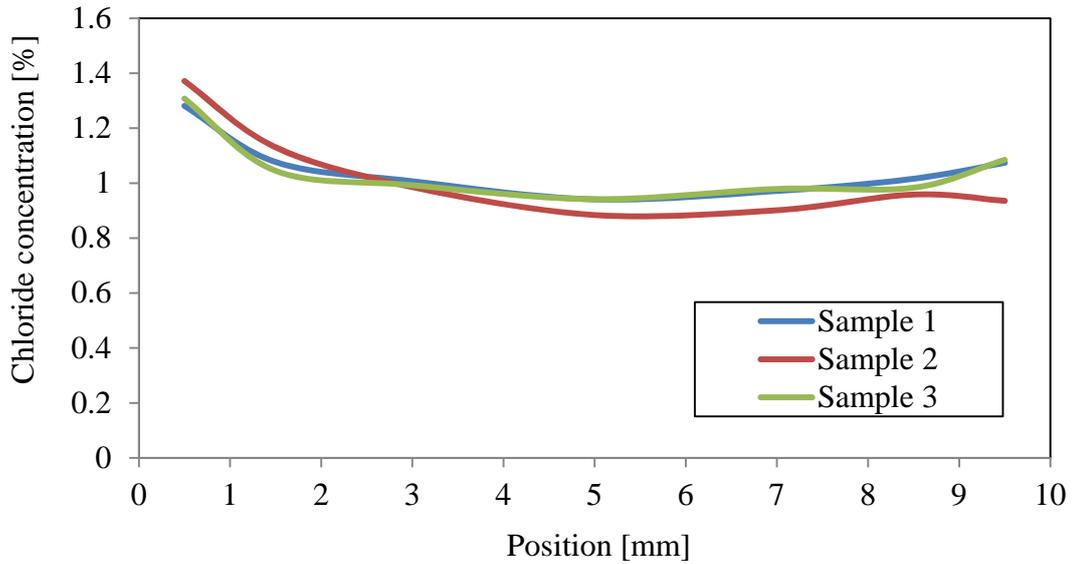


Figure 4: Chloride concentration profiles of mortar measured by titration.

#### 4 RESULTS

For computing the adsorption isotherm, the water content in the sample is determined for various relative humidities inside the vessel as:

$$m_{sample} = m_{total} - m_{air}, \quad (1)$$

where  $m_{total}$  is the total amount of added water,  $m_{sample}$  the water content in the sample and  $m_{air}$  the water content of the air inside the vessel.

With the water content in the air,  $C$ , and the water content in saturated air,  $C_{sat}$ , computed with Antoine's law and the ideal gas law as:

$$C_{sat} = \frac{M}{R \cdot T} \cdot e^{\left( \frac{23.19695 - \frac{3816.44}{-46.13+T}}{T} \right)}, \quad (2)$$

where  $M$  is the molar mass of water,  $R$  the gas constant and  $T$  the temperature in Kelvin. The relative humidity,  $H$ , can be re expressed as:

$$H = \frac{C}{C_{sat}} \cdot 100. \quad (3)$$

With Eqs. (2) and (3) the amount of water in the air becomes:

$$m_{air} = \frac{H \cdot V \cdot M}{R \cdot T \cdot 100} \cdot e^{\left( \frac{23.19695 - \frac{3816.44}{-46.13+T}}{T} \right)}, \quad (4)$$

where  $V$  ( $m^3$ ) is the volume of the vessel.

By dividing the water content in the sample by the volume of the sample, the water content,  $w$ , in the sample at a certain relative humidity is obtained.

To obtain the desorption curve, dry air with known relative humidity is blown in the vessel and air containing water leaves the vessel during a certain period of time. Points on the curve are determined by calculating the amount of water loss during this period. The mass of water leaving the vessel during the drying period is calculated using a mass balance as:

$$m_{out} = \int_0^{\tau} \varphi_v (C_{out} - C_{in}) dt, \quad (5)$$

where  $\varphi_v$  is the volumetric flow of the dry air and  $C$  the water content in the air, with the subscript indicating whether the water content corresponds to the air entering or leaving the vessel.

With Eq. (3), Eq. (5),  $m_{out}$  can be rewritten as:

$$m_{out} = \frac{C_{sat} \varphi_v}{100} \int_0^{\tau} (H_{out} - H_{in}) dt. \quad (6)$$

It is assumed that the dry air entering the vessel mixes well with the air in the vessel before leaving, meaning that the relative humidity of the air leaving the vessel is equal to the relative humidity of the air in the vessel, which is measured every minute. With this assumption and the relative humidity of the air at equilibrium, the water content in the sample can be determined, which follows from a mass balance.

The adsorption isotherm for a sample with no chlorides and a sample with chlorides are determined as shown in Figure 5.

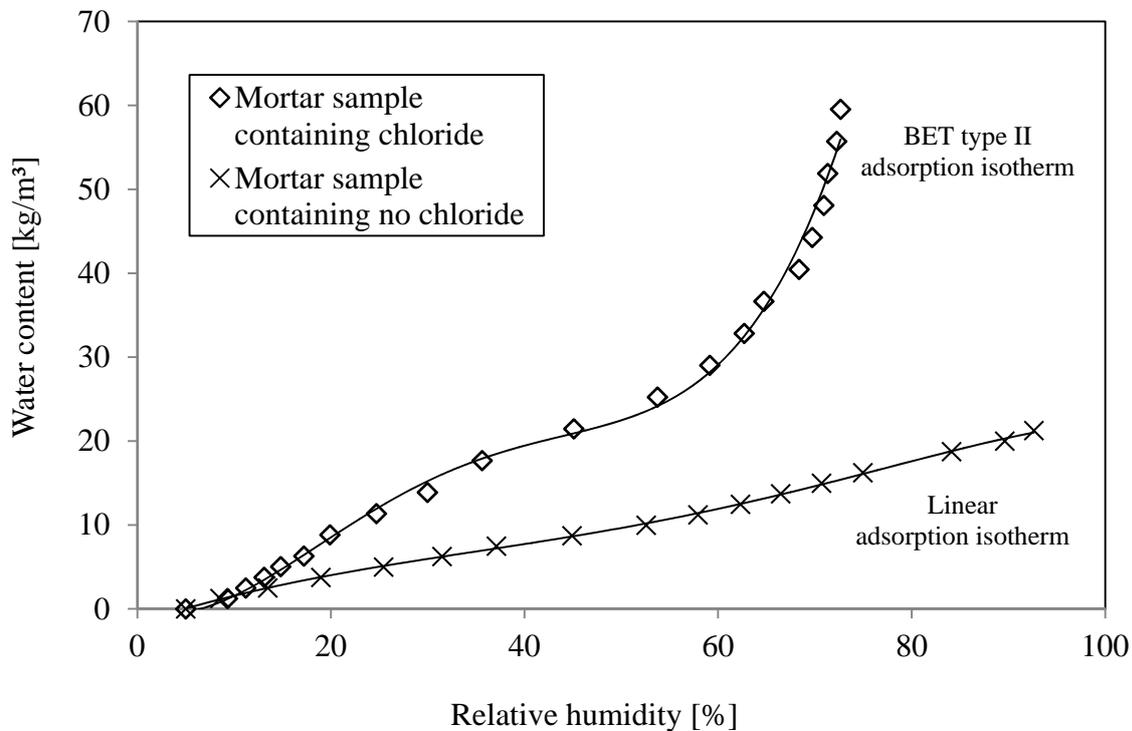


Figure 5: The adsorption isotherm of a mortar sample with and without chloride.

The equilibrium at the start is reached at 5% relative humidity, which is defined as zero in the curves. The adsorption curve of the sample without chloride consists of 16 points, which are obtained by adding 0.1 ml water to the vessel 15 times and 0.2 ml water once. The adsorption curve of the sample with chloride consists of 19 points, which are obtained by adding 0.1 ml water to the vessel 5 times, 0.2 ml 3 times and 0.3 ml 12 times. Equilibrium state is reached approximately in 3 days after adding water.

From the results obtained thus far, it is however seen that the sorption of the sample containing chloride is significantly larger than the sorption of a sample containing no chloride. The difference between the curves can be explained by the presence of chloride, which seems that it absorbs a large amount of water. In fact, the chloride in mortar changes the type of adsorption isotherm from Linear to BET type II adsorption isotherm.

## 5 CONCLUSIONS AND DISCUSSION

The durability of a concrete structure is largely governed by deterioration of the steel rebars as a consequence of corrosion, initiated by the presence of chloride. Also, crystallization of salt present in the pores can damage the material. It is therefore very important to accurately describe water and salt transport in cementitious materials. An important water transport property is the sorption of a porous material. The hygral state of a porous material as a consequence of sorption is described with the sorption isotherm. In this work, the adsorption isotherm of mortar is measured with a hygroscopic method. With this technique, the adsorption isotherm of any porous construction material can be measured. The amount of measured points can easily be adjusted, by increasing or decreasing the amount of added water. For example, by adding 0.05 ml of water instead of 0.1 ml, which is used in this work, twice as much measured points can be obtained. With this technique the desorption isotherm can be measured also.

The linear sorption isotherm for mortar containing no chloride, which is measured in this work, is in good agreement with those found in the literature. Tada and Watanabe [6] have predicted a linear sorption isotherm for a mortar containing no chloride. This was in agreement with experimental data, although the experiment showed larger sorption. Estimated data were, however, in better agreement with experimental data obtained by Daian [7]. In this study, a linear adsorption isotherm is found for a mortar sample containing no chloride.

The effect of the presence of chloride in mortar on the sorption of a sample is also regarded in this study. Mortar samples with chloride content are prepared with vacuum saturation. Sodium chloride solution is used to provide the samples with chloride. A homogeneously distributed chloride concentration throughout the sample is obtained by first drying the sample completely before saturating with sodium chloride solution. From the results obtained thus far it is seen that the sorption of the sample containing chloride is significantly larger than the sorption of the sample containing no chloride. Besides larger sorption as a consequence of the presence of sodium chloride, the sorption curve also transforms from a linear curve to a BET Type II curve [8-9]. Since the BET-model is based on the multilayer adsorption on a solid, the presence of chloride can influence the adsorption mechanism. Some

chloride can be bound to the surface of the pore walls, which in turn can alter the way and quantity at which water is adsorbed on the surface on the pore walls. The larger sorption of a sample containing sodium chloride is also seen in the study of Koniarczyk and Wojciechowski [10], where a higher salt concentration led to more water adsorption in mortar. The larger sorption of a sandstone sample containing salt is also found by Franzen and Mirwald [11]. The increased sorption at high relative humidities can also be explained with the results from the study by Rijniens [12]. In this study, it is found that NaCl tends to adsorb a large amount of water at a high relative humidity.

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