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A GRAVIMETRIC STUDY OF WATER VAPOUR SORPTION ON HARDENED CEMENT PASTES.

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ir. H.H. Willems

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A GRAVIMETRIC STUDY OF WATER VAPOUR SORPTION ON HARDENED CEMENT PASTES.

INTRODUCTION.

I would like to tell you something about my work at the Technical University at Eindhoven in the Netherlands. I am working there at the Department of Architecture, Building and Planning, on a project that deals with the shrinkage and creep behaviour of concrete, in relation to the type of cement that has been used for it.

Mechanical properties of concrete, like shrinkage and creep, largely depend on the mechanical properties of the cementstone which is present between the aggregate.

Cementstone is the product that develops as a result of chemical reactions, when cement and water are mixed. It is a porous material and under normal conditions the pores are more or less filled with water, depending on the relative humidity of the environment.

Shrinkage and creep of cementstone turn out to be affected by the presence and the displacement of water in the pores. Hence my interest in pore structure analysis.

The pore structure and the specific surface area are studied by means of adsorption/desorption isotherms at 25°C. Water vapour has been chosen as adsorbate because in this way all the pores that are of importance in shrinkage and creep processes, are involved in the measurements.

With the developed equipment it is also possible to take up isotherms with other adsorbates, after a few adaptations.
EXPERIMENTAL SET-UP. (See fig. 1)

- The heart of the equipment is a Cahn-2000 recording electrobalance. It is an automatic recording torsion balance. The balance is placed in a glass vacuum bottle. The inside of the vacuum bottle has been supplied with a thin layer of tinoxide, in order to prevent static electric charges. The pans for sample (left) and tare weights (right) are connected to the balance beams by means of extension wires. In the lid which closes the vacuum bottle a piezo-resistive pressure transducer has been mounted. Further the vacuum bottle is connected to a vacuum pump by means of a set of valves; and to a small bulb filled with water. The whole is mounted in a cabinet in which the temperature is held at 25.00 ± 0.05 °C.

- To establish the vapour pressure in the system, the so-called "cold trap" principle is used. In a closed system the vapour pressure will be equal to the saturation vapour pressure at the coldest spot in the system.

- The starting point of an isotherm is established by means of evacuating the system, while maintaining the water bulb at a temperature of -78 °C, by means of a mixture of dry ice and methanol. This is the so-called "P-drying". \( P_{\text{H}_2\text{O}} = 5 \times 10^{-4} \text{ mm Hg or 0.07 Pa} \). Doing so, it is supposed that all the evaporable water is removed.

- When the weight of the sample does not decrease anymore, the valve to the vacuum pump is closed. Hereafter the temperature of the water in the bulb is varied stepwise between -30 °C and +25 °C, by means of a programmable thermostat and a closed circuit in which ethanol circulates.
SOURCES OF ERROR IN THE DETERMINATION OF THE ADSORBED MASS.

- There are a lot of phenomena that may lead to errors in mass-change measurements. Yesterday Dr. Massen has presented a survey of these errors. The experimental set-up has been designed in such a way that most of these errors are greatly reduced.
- In spite of all precautions that were taken, still two sources of error appear to occur in the mass-change measurements with the equipment described before:
  - a) Sorption on parts of the balance.
     During an experiment ad- and desorption will also take place on parts of the balance and the sample pans, because of their relative low temperature (25 °C).
     To study this phenomenon several blank isotherms were taken of the balance, with and without suspension wires and sample pans. The results are shown in fig. 2, 3 and 4.
     From these diagrams it follows that an apparent mass-change of about 30 μg may occur, due to adsorption on parts of the balance, although its construction is practically symmetrical.
  - b) Arm-length changes due to shocks or vibrations.
     As earlier mentioned the sample pans are attached to the balance by means of extension wires. These extension wires hang in pear-shaped eyes, which on their turn hang on wire-bows at the balance beam. (See fig. 5).
     It was found that this construction may cause errors in mass-change experiments. When the balance is exposed to shocks or vibrations, or when a sample or a counterweight is placed on the sample pan, the points were the eyes rest on the wire-bows may shift. This results in an arm-length change and so in an apparent mass-change. (See fig. 6).
AD- AND DESORPTION ON BALANCE, WITH SUSPENSION WIRES AND SAMPLE PANS.

fig. 2.
ADSORPTION ON BALANCE, WITHOUT SUSPENSION WIRES AND SAMPLE PANS.

**Fig. 3.** $p/p_0$
DESORPTION ON BALANCE, WITHOUT SUSPENSION WIRES AND SAMPLE PANS.
With the type of balance used, the measured mass-change is proportional to an exerted momentum of force:

\[ m \propto M_m, \text{ or } m = c M_m, \text{ where} \]

\[ M_m = F \times l, \text{ or } M_m = m \cdot g \cdot l. \]

When the balance is in equilibrium:

\[ M_m = M_1 - M_r \text{ so,} \]

\[ m = c (M_1 - M_r) \]

\[ = c (m_1 \cdot g \cdot l_1 - m_r \cdot g \cdot l_r) \]

\[ = cg (m_1 \cdot l_1 - m_r \cdot l_r) \quad (1) \]

For a symmetrical balance \( m_{\text{measured}} = m_1 - m_r \).

From (1) it follows that \( m_{\text{measured}} = cg (m_1 - m_r) \).

So for a symmetrical balance \( cg \cdot l = l \), or \( cg = \frac{1}{l} \).

\( (2) \)
The change in arm-length and the apparent mass-change can be calculated as follows:

\[ \frac{\Delta l}{h} = \frac{r}{R} \rightarrow \Delta l = h \cdot \frac{r}{R} = \frac{r}{R} \cdot b \cdot \sin \alpha \]

In our case: 
- \( r = 0.05 \) mm.
- \( R = 1.5 \) mm.
- \( b = 3 \) mm.

So for \( \alpha = 5^\circ \):

\[ \Delta l = 8.7 \times 10^{-3} \text{ mm.} \]

When both eyes show an angle of \( 5^\circ \) in the same direction with respect to the vertical axis, this results in an apparent mass-change of:

\[ \Delta m = cg(m_1 \cdot \Delta l_1 - m_r \cdot \Delta l_r) \quad \text{(See 1).} \]

With \( l = 66 \text{ mm} \) and \( m_1 = m_r = 585 \text{ mg} \), the total mass of sample (500 mg) and sample pan (85 mg), it is found that:

\[ \Delta m = \frac{1}{66} \cdot (585 \times 8.7 \times 10^{-3} + 585 \times 8.7 \times 10^{-3}) \]

\[ = 0.154 \text{ mg} \]

\[ = 154 \mu\text{g}. \]
Shock tests which were performed with several mass-sizes, showed that:

\[
\frac{\Delta m}{m_{\text{eff.}}} \leq 4 \times 10^{-5}, \text{ where } m_{\text{eff.}} = \sqrt{m_1^2 + m_r^2}.
\]

With a sample size of 500 mg and 500 mg tare weight this leads to \(\Delta m = 33 \mu g\), which means that in spite of 500 mg sample and tare weights on the sample pans, it appears to be possible for both eyes to shift 1° in the opposite direction, or for one eye to shift 2° more in the same direction of the other eye.

This error can be reduced by:

a. using bigger samples.

b. vibration-free mounting of the balance.

c. changing the construction.
CALCULATION OF THE ULTIMATE MASS-CHANGE VALUES.

Because of the long times involved in the adsorption/desorption experiments, it was examined if the equilibrium values could be calculated from the course of mass-change with time. This has been done by describing the adsorption/desorption process by means of a first order differential equation, and by assuming to be constant over the whole pressure range.

With a first order process, the rate in which a quantity changes is proportional to the difference between its momentary value and the equilibrium value:

\[
\frac{dm}{dt} = \frac{1}{\tau} (m_e - m)
\]

The solution of this equation is:

\[
m_t = m_e + (m_e - m_0) e^{-t/\tau}
\]

if \( t_2 - t_1 = t_3 - t_2 = \Delta t \)

\( \tau \) and \( m_e \) can easily be calculated as follows:

\[
\begin{align*}
\frac{m_2 - m_1}{m_3 - m_2} &= e^{-t_2/\tau} - e^{-t_1/\tau} \\
e^{-t_3/\tau} - e^{-t_2/\tau} &= \frac{1 - e^{-(t_1 - t_2)/\tau}}{e^{(t_3 - t_2)/\tau} - 1} = \frac{\Delta t}{\tau}
\end{align*}
\]

From (3) follows:

\[
\tau = \frac{\Delta t}{\ln \frac{m_2 - m_1}{m_3 - m_2}}
\]

When \( t_3 \) in (3) is replaced by \( t \) one finds that:

\[
m_t = m_2 + (m_2 - m_1) \frac{e^{-(t - t_2)/\tau} - 1}{1 - e^{(t_2 - t_1)/\tau}}
\]
\[ m_e = \lim_{t \to \infty} m_t = m_2 + (m_2 - m_1) \cdot \frac{1}{e^{\Delta t / \tau}} - 1 \] (5)

By substituting (3) in (5) it can be found that:

\[
m_e = \frac{m_2^2 - m_1 \cdot m_3}{2m_2 - m_1 - m_3} \quad (6)
\]

So when the time intervals are chosen equal, \( \tau \) and \( m_e \) can directly be calculated from the course of mass versus time with (4) and (6).

When the intervals are not equal, \( \tau \) and \( m_e \) have to be calculated with (3) and (5). The last has been done in the calculation of the equilibrium values from one preliminary isotherm which is shown in diagram 8. \((t_1, t_2 \text{ and } t_3 \text{ were respectively } 2, 6 \text{ and } 12 \text{ hours}). From diagram 9 it can be derived that the specific surfaces found were respectively 110, 112 and 115 \( m^2/g \) of sample.

Later experiments showed however that the measuring time has to be extended to at least 24 hours, to get a more reliable value for \( \tau \), and so for \( m_e \).

However for the desorption branch this method does not lead to any reproducible results. Further a very big hysteresis loop occurs, which does not close at very low pressures. This means that there have to be many micropores.

The specific surface found is only about 50% of that which is normally found with nitrogen as adsorbate. In literature it has often been reported that the specific surface area appeared to be smaller when measured with water vapour, than when measured with nitrogen. Because of this found contradiction, the BET-method does not seem to be adequate to study micro-
ADSORPTION ISOTHERM CEMENTSTONE.

**ADSORPTION:**
- △ value after 6 hours.
- ○ last measured value.
- ◊ calculated equilibrium value.

**DESORPTION:**
- ○ last measured value.
BET-PLOTS CEMENTSTONE.

\[ \frac{p}{x(p_0 - p)} \]

**ADSORPTION:**
- ▼ value after 6 hours.
- ○ last measured value.
- ◆ calculated equilibrium value.

**DESORPTION:**
- ○ last measured value.

**fig. 9.** $p/p_0$
porous materials. This morning dr. Masters has given a review of other methods, that can be used to study the microporous part of a pore system.

At the end of this presentation I wish to make use of the opportunity to express my thanks to prof. Poulis and dr. Massen of the Department of Physics, who have been a very great help to me in the development of the presented equipment. Because of my background as a chemical engineer, I was not very acquainted with VMT-techniques when I started my investigations.

Further I wish to express my thanks to mr. van der Velden, who did in fact most of the practical work, as the final part of his study for physical engineer.


ir. H.H. Willems.