

A GRAVIMETRIC STUDY OF WATER VAPOUR SORPTION ON HYDRATED CEMENT PASTES

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ABSTRACT

To study the pore structure of hardened cement pastes water vapour sorption isotherms are measured in a gravimetric way. The accuracy appeared to be restricted by water vapour effects on the balance (a Cahn 2000 micro balance) and by the employed type of secondary fulcra. It takes several days before the total amount of water vapour is adsorbed or desorbed when the vapour pressure is changed. Therefore a method of extrapolation is employed to calculate the equilibrium amount from the course of the mass change with time.

INTRODUCTION

Concrete is a widely used building material and there is a great interest in improving and controlling the mechanical properties. Some of the mechanical properties of concrete, especially shrinkage and creep, largely depend on the mechanical properties of the hydrated cement paste. The hydrated cement paste is the binding agent between the aggregate particles in the concrete. Hydrated cement paste 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 (ref.1). It has been found that the shrinkage and creep behaviour of concrete using Portland cement differs from that of concrete using Portland blast-furnace cement (ref.2). Therefore researches are being made into the differences in chemical and physical structure between hydrated Portland cement paste and Portland blast-furnace cement paste. The shrinkage and creep of hydrated cement pastes are affected by the presence and the displacement of water in the pores (ref.1). The pore structure of the hydrated cement pastes are analysed by adsorption and desorption measurements with water vapour at 25°C. By using water vapour as adsorbate all pores of importance in shrinkage and creep processes are involved in the measurements.

EXPERIMENTAL SET-UP

The measurement of the amount of water vapour adsorbed by the hydrated cement

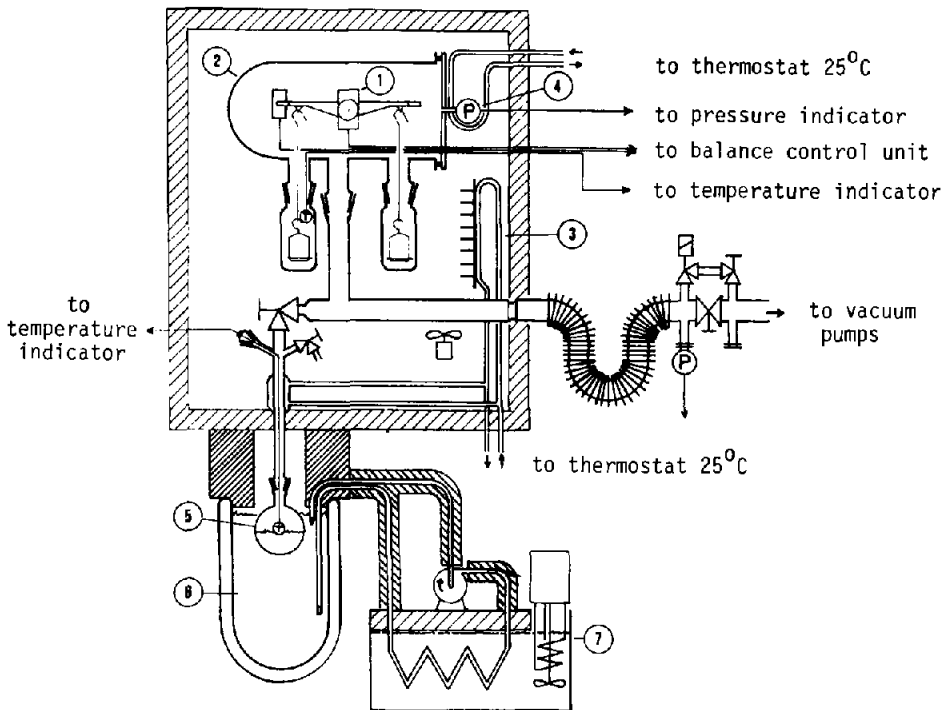


Fig. 1. Schematic drawing of experimental set-up

paste is done by weighing. A Cahn 2000 recording electrobalance (see 1 in Fig. 1) is used for this purpose. The balance is placed in a glass vacuum bottle (see 2 in Fig. 1). The inside of the vacuum bottle and the hangdown tubes for the sample pan and the tare pan are coated with tin oxide. This conductive coating is electrically connected to the balance and grounded to eliminate electrostatic charges and their attendant disturbances. The vacuum bottle and hangdown tubes are mounted in a housing, thermostated at 25°C (see 3 in Fig. 1)

The pressure of the adsorbate is measured with a Druck PDCR 110/W piezo-resistive pressure transducer (see 4 in Fig. 1). The transducer is mounted in the aluminum lid of the vacuum bottle. The pressure of the water vapour is controlled by a "cold finger". For this purpose a small bulb (see 5 in Fig. 1), partially filled with distilled and outgassed water, is connected to the system. The bulb is placed in a thermostated bath (see 6 in Fig. 1). The temperature of the bath is controlled by a programmable thermostat (see 7 in Fig. 1). The thermostated bath can be replaced by a Dewar flask containing a mixture of dry-ice and methanol. At the temperature of -79°C of the mixture the saturation

pressure of water vapour is only 0.07 Pa. At this pressure all the evaporable (not chemically combined) water is removed from the hydrated cement paste.

The vacuum bottle and hangdown tubes are also connected to an oil diffusion vacuum pump and a rotary vane vacuum pump. A set of valves is placed between the pumps and the system to control the pumping speed.

ERRORS IN THE MEASUREMENTS OF THE ADSORBED MASS

In the chosen experimental set-up errors in the measured mass due to thermomolecular flow, convection or electrostatic charges are largely eliminated. Two other sources of error turned out to be of importance in this set-up:

1. Water vapour effects on the balance. There are several reports on mass artifacts using a Cahn-RG balance in water vapour (p. 42 ref.3).
2. Abrupt changes in the measured mass (or shifts of the zero point) after building vibrations. The error originates from the type of secondary fulcrum employed in this Cahn 2000 balance.

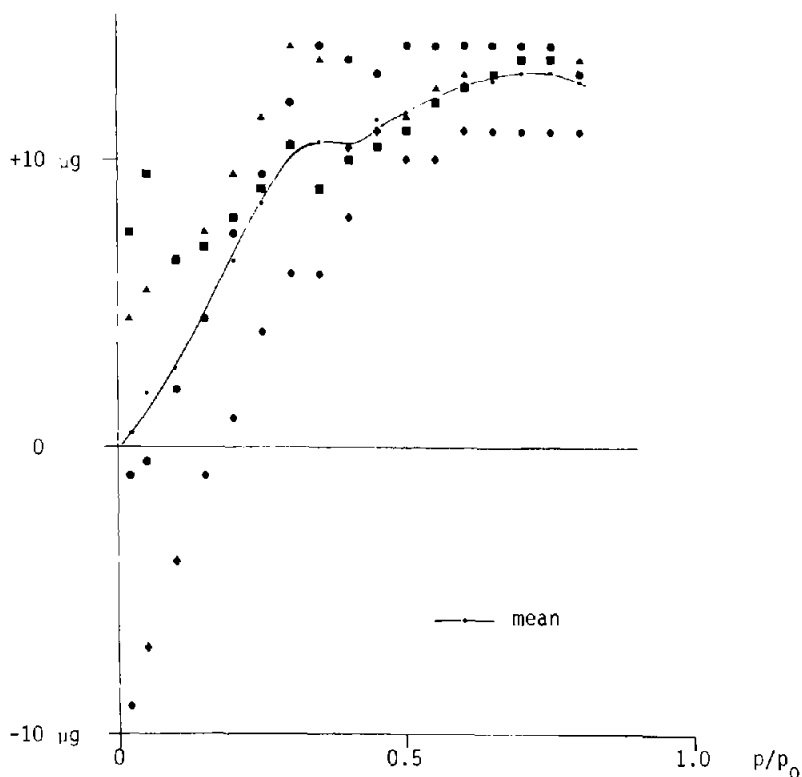


Fig. 2. Pressure dependence of the apparent mass gain for a Cahn 2000 microbalance in water vapour at 25°C, increasing pressure, no load, 4 x.

Water vapour effects

The effect of water vapour on the balance was measured in the set-up described. The balance beam was unloaded and at a temperature of 25°C . The pressure was varied stepwise from 1.6% up to 80% of the saturation pressure at 25°C and reversely. This was done 4 times. The mass artifact measured at the various pressures are plotted in Fig. 2 and Fig. 3. The great spreading of the measured mass artefact in the low pressure range of Fig. 2 is caused by warming up effects. The last measured points of the desorption branch at $p/p_0=1.6\%$ in Fig. 3 were taken as zero point for the mass artefact. From these diagrams it follows that an error of about $15\ \mu\text{g}$ occurs in the mass measurement. Measurements with the balance beam loaded with the suspension wires and the pans (about $85\ \text{mg}$ on each side) showed an mass artefact that might well be $40\ \mu\text{g}$. These measurements were heavily disturbed, so no clear conclusions could be drawn. It is very well possible that this mass artefact is load dependent, like with the Cahn-RG balance (ref.4). More measurements will have to be done to give

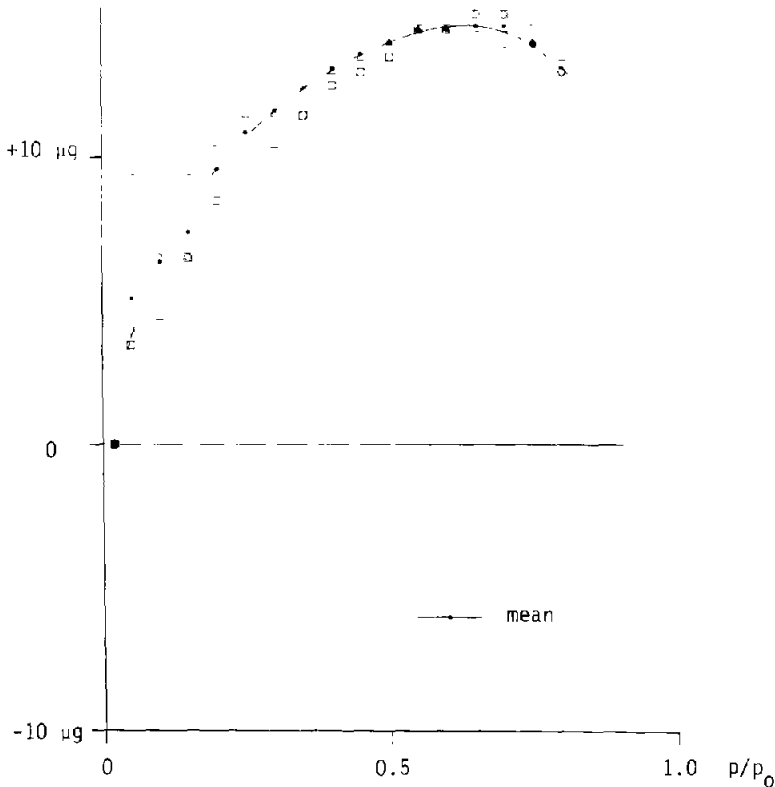


Fig.3. Pressure dependence of the apparent mass gain for a Cahn 2000 micro balance in water vapour at 25°C , decreasing pressure, no load, 4 x.

a decisive answer.

Armlength changes due to vibrations or shocks

In fact the Cahn 2000 microbalance and many other commercially available microbalances are torque measuring instruments. The torque measured can be changed by a change of the mass m , suspended from the balance beam, or by a change Δl of the distance l between the axis of rotation of the beam and the point of impact of the force exerted on the beam by the suspended mass m . The apparent mass change due to such a change of armlength can easily be calculated:

$$\Delta m = \frac{\Delta l}{l} m \quad (1)$$

If the secondary fulcrum consists of a simple round hook, bent in the top end of the suspension wire, hooked on a loop of wire attached to the beam, the distance l can vary easily. During a violent vibration of the beam the hook can lose contact with the loop and the point of impact can be moved (see Fig. 4). The change in armlength Δl can be related to the displacement a of the hook or the angle α , indicated in Fig. 4, the radius r of the hook and the diameter of the wire used for the loop:

$$\Delta l = \frac{d}{2r} a = \frac{d}{2} \sin \alpha = \frac{d}{2} \alpha \quad (2)$$

The angle α is restricted by the coefficient of static friction. For nichrome suspension wires with a diameter of 0.1 mm α can be about 20° in a static situation. In practice however α will be smaller because of the extinguishing vibrations of the beam and the suspended loads.

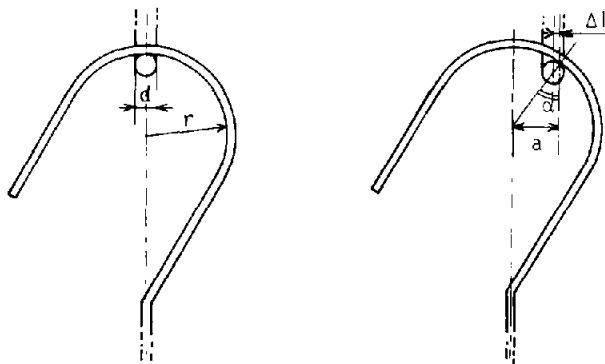


Fig. 4. Armlength change in a secondary fulcrum consisting of a hook on a loop of wire

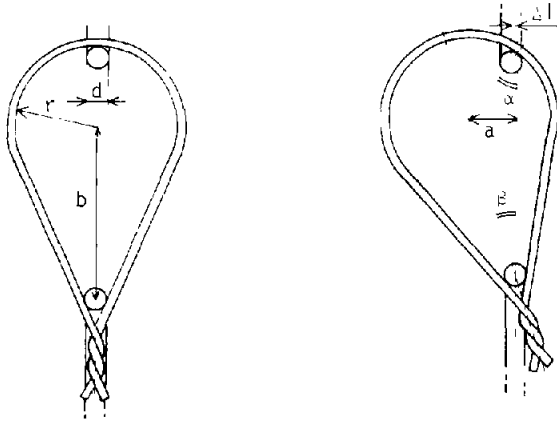


Fig. 5. Armlength change in a secondary fulcrum as used in a Cahn 2000 balance.

On the Cahn 2000 microbalance used for the experiments the suspension wires are suspended from a second loop, hanging on the loop fixed to the beam (see Fig. 5). Now Δl can be related to the dimensions of the second loop, the diameter of the wire of the first loop and the angle β as indicated in Fig. 5:

$$l = \frac{d}{2r} a = \frac{d}{2r} b \sin \beta \approx \frac{d}{2r} b \beta \quad (3)$$

Substituting the actual values $d=0.05$ mm, $r=1.5$ mm and $b=3$ mm and supposing $\beta=3^{\circ}=5.24 \times 10^{-2}$ rad one obtains $\Delta l=2.62$ μm . Using the actual value $l=66$ mm one obtains $\Delta l/l=3.96 \times 10^{-5}$ for the Cahn 2000 microbalance. The changes of armlength are stochastic in nature and they are independent for the left and the right arm of the balance. Using the obtained 3.96×10^{-5} as mean value for $\Delta l/l$ one can calculate with eq. 1 the mean value $\overline{\Delta m}$ of the error in the measured mass difference when the balance is loaded with 500 mg on both sides: $\overline{\Delta m}=\sqrt{2} \times 3.96 \times 10^{-5} \times 500$ mg ≈ 28 μg . Experiments carried out with loads varying from 100 mg on one side up to 600 mg on both sides of the beam showed $\overline{\Delta T}/l \approx 4 \times 10^{-5}$, independent of the load.

From eq. 3 it is clear that the change in armlength can be eliminated for any angle β if $b=0$. This solution is similar to that proposed by Poulis and co-workers for the construction of secondary fulcra with pivot bearings (ref.5). If $b=0$ there will be no force on the second loop to keep it upright. This can be solved by adding a proper counterweight to this loop. (On later versions of the Cahn 2000 microbalance a ribbon suspension is used for the secondary fulcra, thereby eliminating this armlength error.)

CURTAILING THE MEASURING TIME

The adsorption of water vapour in hydrated cement paste involves much time. Using slices 0.5 mm thick, after 5 days no change in mass could be measured. This implies that the measuring of an isotherm at 15 points, both for the adsorption and desorption branch, would involve half a year if waiting for equilibrium. Therefore it was examined whether the equilibrium values can be extrapolated from the course of the mass change with time.

The mass change kinetics were approximated with a first order differential equation:

$$\frac{dm(t)}{dt} = \frac{1}{\tau} (m(t) - m_e) \quad (4)$$

where $m(t)$ is the adsorbed mass at the moment t , m_e is the adsorbed mass in equilibrium going with vapour pressure at the moment t and τ is a time constant. When the pressure is constant after $t=0$ the solution of the differential equation is an exponential function:

$$m(t) = m_e - (m_e - m(0)) e^{-t/\tau} \quad (5)$$

By measuring the mass at three consecutive times t_1 , t_2 and t_3 with equal time intervals Δt one can calculate τ and m_e (see Fig. 6):

$$\tau = \frac{\Delta t}{\ln \frac{m(t_2) - m(t_1)}{m(t_3) - m(t_2)}} \quad (6)$$

With the calculated value for τ and two of the measured masses the mass at any time t can be calculated:

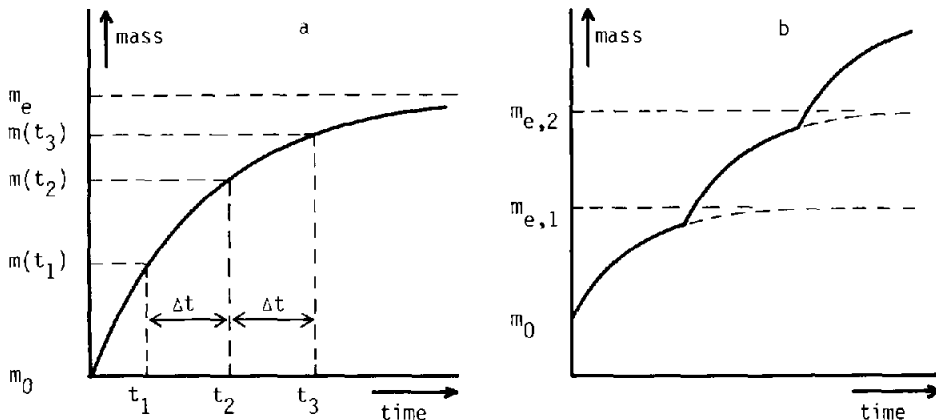


Fig. 6. Mass change versus time curves, a. after a single pressure change
b. after consecutive pressure changes.

$$m(t) = m(t_2) + (m(t_2) - m(t_1)) \frac{e^{-t/\tau} - e^{-t_2/\tau}}{e^{-t_2/\tau} - e^{-t_1/\tau}} \tag{7}$$

m_e is the value of $m(t)$ when t approaches infinity. Combining this with eq. 5, eq. 6 and $t_2 - t_1 = \Delta t$ one obtains:

$$m_e = \frac{m(t_2)^2 - m(t_1)m(t_3)}{2m(t_2) - m(t_1) - m(t_3)} \tag{8}$$

(If $t_2 - t_1 \neq t_3 - t_2$ then τ can be calculated numerically and m_e can be calculated with eq. 7.) Jäntti and co-workers have derived the same formula for calculating the equilibrium mass based on a model for the adsorption kinetics. They applied this method of extrapolation to nitrogen adsorption measurements on active carbon. The equilibration time was 2-3 hours (ref.6). For water vapour adsorption on hydrated cement pastes the equilibration time is about 50 times as long. The long equilibration time will likely be caused by slow penetration of water vapour in small pores then by adsorption kinetics.

The method was employed to calculate the equilibrium masses for an isotherm. The masses measured 2, 6 and 12 hours after a pressure change were used.

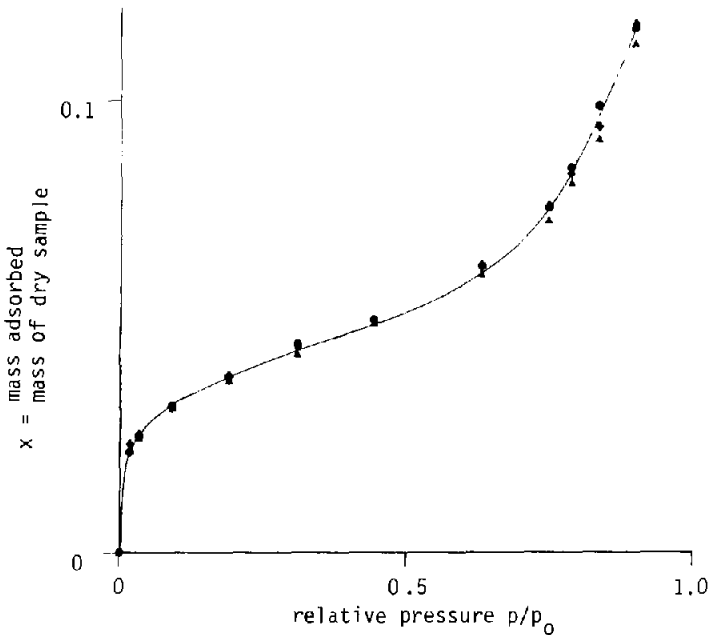


Fig. 7. Adsorption isotherm for water vapour on hydrated cement paste at 25°C. \blacktriangle 6 hours after pressure change, \bullet 18 hours after pressure change, \blacklozenge calculated equilibrium.

The calculated time constant τ varied from 3:10' hour to 15:25' hour. The mean value was 7:30' hour. The equilibrium mass was calculated with the use of this mean time constant $\bar{\tau}$. In Fig. 7 the resulting equilibrium mass and the mass after 6 and after 18 hours are plotted versus pressure. In Fig. 8 the B.E.T.-plots belonging to these isotherms are shown. The resulting B.E.T. specific surface areas are $110 \text{ m}^2/\text{g}$, $112 \text{ m}^2/\text{g}$ and $115 \text{ m}^2/\text{g}$ respectively for the masses measured after 6 hours, the calculated equilibrium masses and the masses measured after 18 hours.

Later experiments showed that the mass change after 18 hours is only about 60 to 85% of the mass change at equilibrium. It was also found that applying eq. 6 to measurements between 24 and 60 hours after a pressure change yields time constants between 25 and 50 hours. The calculated mass changes then differed less than 5% from the real mass change at equilibrium. Besides the method turned out to be very sensitive for errors in the measured masses,

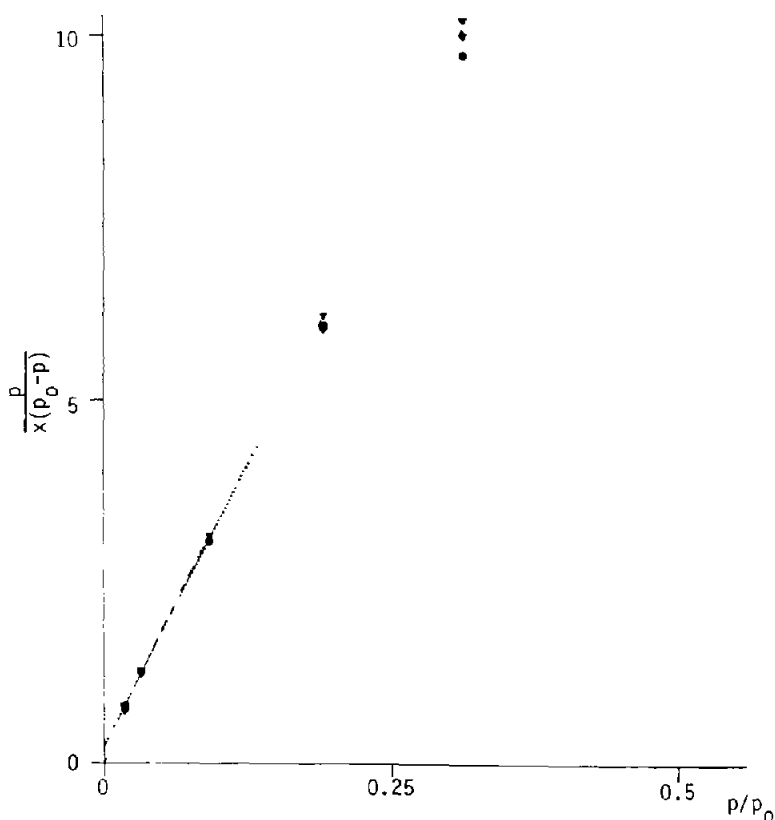


Fig. 8. B.E.T. plots for water vapour on hydrated cement paste.

▼ 6 hours after pressure change, ● 18 hours after pressure change, ◆ calculated equilibrium.

especially when Δt is much smaller than τ . Therefore it was concluded that this extrapolation method cannot reduce the measuring time by more than 60% else the loss of accuracy will be unacceptable. Employing this method for desorption measurements with masses measured 2, 6 and 12 hours after a change of pressure gave very poor results. This is caused by the longer times involved with desorption.

ACKNOWLEDGEMENTS

The authors wish to thank J.A. Poullis and C.H. Massen for their advice and the helpful discussions during the course of this work.

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