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STUDY ON THE POROSITY IN THIN FILMS OF ZINC PHOSPHATE CEMENT*

by

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INTRODUCTION

When a freshly prepared mix of zinc phosphate cement is compressed between two glass plates, many porosities can often be observed in the cement film. If a certain volume of air is enclosed in the cement film between a seated cast restoration and the cavity wall, the thinner the cement film, the greater will be the area where the cast restoration and the cavity wall will not be connected with cement. Such a porous cement film will probably reduce the retention of the cast restoration.

Only few reports have been published concerning the presence of porosity in cement films. *Neukomm* (1953) reported that no correlation could be found between porosity of the cement film and grain size of the powders used, and he deduced that porosity might be influenced by chemical properties of powder and liquid or by technic used for mixing.

In the following study, four factors which may influence upon the degree of porosity were investigated, viz. consistency of the cement mix, mixing time, brand of cement, and exposure of cement powder to carbon dioxide.

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MATERIAL AND METHODS

Cement A, one of the representative products sold on the Danish market was used throughout this study.

Production of test specimens

Thin films of zinc phosphate cement were prepared between two glass plates with optically flat surfaces. The thickness of both glass plates was 5 mm, the diameter was 25 mm of the lower and 5 mm of the upper plate. Cement mixes prepared under various conditions were placed between the two glass plates and compressed under a 2 kg load by using the equipment shown in Figure 1. Normally the load was applied 30 seconds after finishing of the mix and was released after further 15 seconds. The thickness of each film was measured on the dial gauge of the equipment. The scale of the dial gauge had divisions of one micron and zero-reading could be made within ± 1 micron. The compressing time was fixed according to the results from initial experiments which will be described in the following section.

Determination of compressing time

In order to observe any possible influence of compressing time upon size and number of porosities, cement mixes placed between the two glass plates were compressed by using the special equipment shown in Figure 2 which made it possible to observe the porosity directly under the measuring microscope when applying and releasing the compressing load. Relatively thin mixes (liquid/powder ratio 1: 2) were used throughout this initial study.

When the compressing load was released relatively early i.e. not later than four minutes after start of mixing, no change was observed in number and size of porosities (Fig. 3). However, when the cement mix was compressed for a minimum of five minutes, not only the size of pores already existing was increased but many new voids appeared immediately after releasing the load. This increase in porosity was reversible and the original state was restored within a few seconds. This phenomenon could be observed also after compressing times of fifteen minutes, but the speed of the process was reduced by time (Fig. 4). Com-

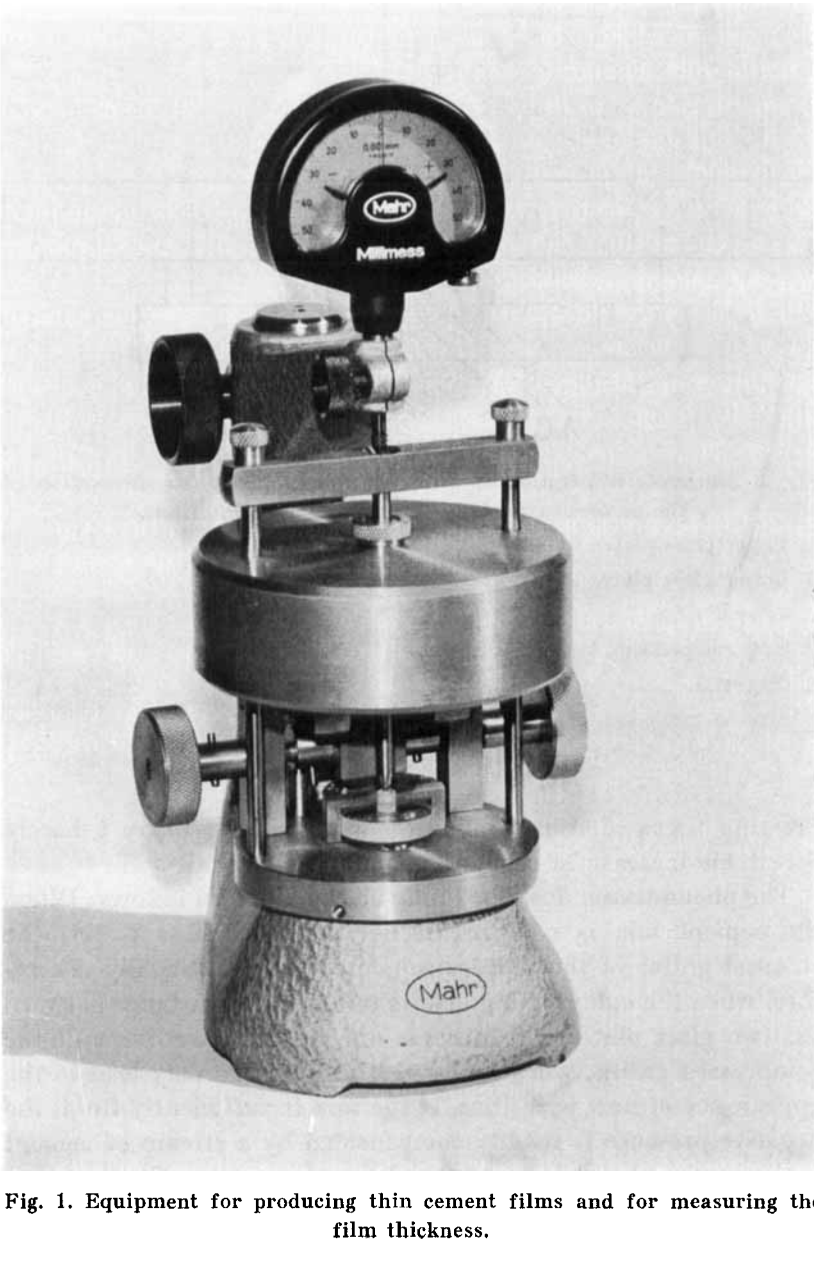

Fig. 1. Equipment for producing thin cement films and for measuring the film thickness.

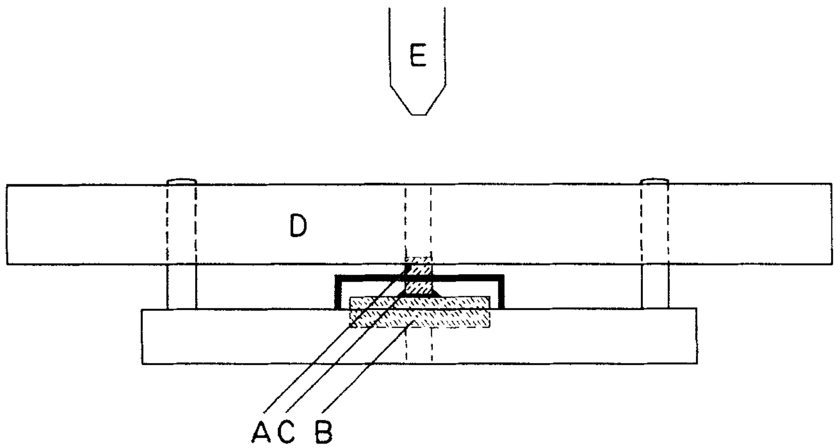

Fig. 2. Schematic illustration of compressing equipment for observation of the process of porosity formation in cement films.

A. Upper glass plate,

B. Lower glass plate,

C. Cement film,

D. 2 kg compressing load,

E. Objective.

pressing times of twenty minutes or more would give a barely detectable increase in size and number of porosities.

The phenomenon described may be explained as follows: When the cement mix is compressed between two glass plates, the coarsest grains of the powder are compressed elastically. Therefore, when the compressing load is released, the distance between the two glass plates will increase due to elastic recovery of the compressed grains, whereby a negative pressure may lead to the appearance of new porosities. If the mix is sufficiently fluid, the negative pressure is readily compensated by a stream of cement from the peripheral excess around the glass plates. On the other hand, if the compressing load is released at a later time when the viscosity of the mix has become considerably higher, many porosities originating in the occurrence of the negative pressure will not readily disappear and some of them are left in the ce-

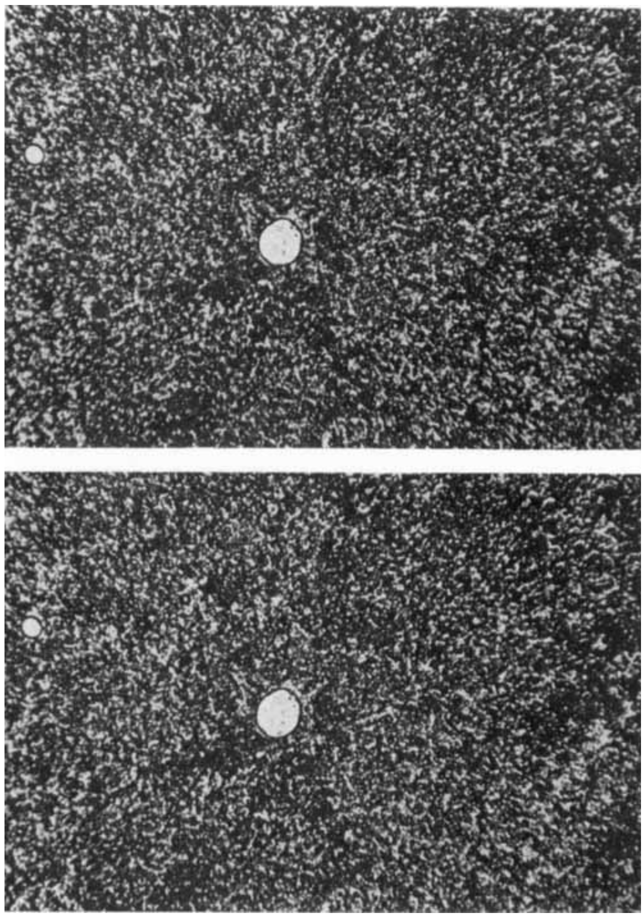

Fig. 3. Photomicrograph of cement film. Compressing time 3 minutes.
Upper 4¾ minutes after start of mixing
Lower 5¼ minutes after start of mixing
Magnification 90 ×.

ment film together with initially present porosities. When the compressing load is released more than twenty minutes after start of mixing, only a slight increase in size of porosity was observed.

To avoid an influence of the phenomena described upon the experimental results, a compressing time of only fifteen seconds was fixed for the following experiments.

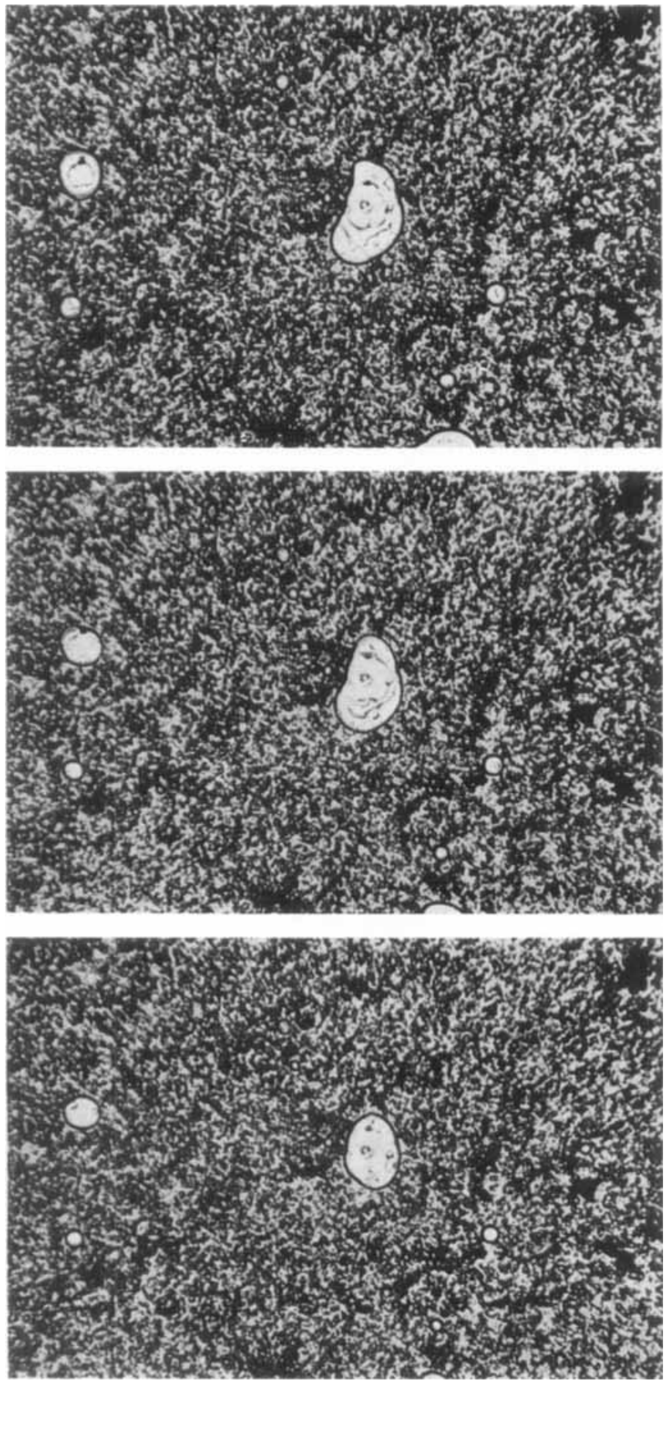

Fig. 4.

Counting and measuring the porosities

The porosities were measured under a travelling microscope with an accuracy of two thousandth of a millimeter. Only a section of the cement film as illustrated in Figure 5 with an area

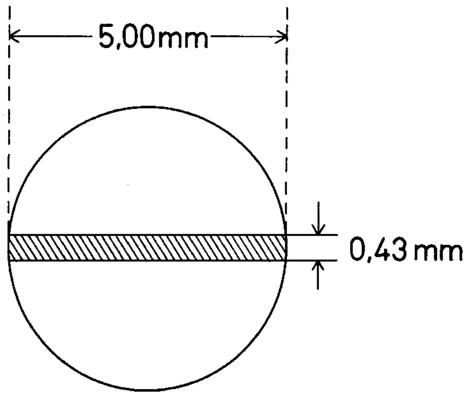

Fig. 5. The hatched part of the cement film was investigated for counting and measuring.

of 2.14 mm^2 was investigated. The majority of porosities were circular in shape; therefore their diameters were measured in only one direction and in calculating their areas they were treated as geometrical circles.

RESULTS AND DISCUSSION

1) Effect of consistency of mixed cement

The porosity in cement films of mixes of various consistency is shown in Table I. The proportion of 0.3 is almost identical with the A. D. A. standard consistency. As can be seen in the table, the porosity will increase with amount of powder incorporated in the liquid. This increase in porosity may be due to difficulty in elimination of enclosed air in the cement mix with

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Fig. 4. Photomicrograph of cement film. Compressing time 15 minutes.
Upper 17 minutes after start of mixing
Middle 18 minutes after start of mixing
Lower 20 minutes after start of mixing
Magnification 90 ×.

Table I

Influence of consistency of mixed cement on the amount of porosity

Gram powder per 0.1 ml liquid	Number of specimens	Total number of porosities	Diameter of porosities μ		Porosity (%)	Average film thickness μ
			Average	Maximum		
0.2	10	35	21	40	0.07 (0.03)	14.2
0.3	10	155	24	80	0.48 (0.06)	16.1
0.4	10	214	22	70	0.51 (0.09)	21.9

Standard deviations are in parentheses

higher viscosity. However, no statistically significant difference exists between medium mix (liquid/powder ratio 1: 3) and thick mix (liquid/powder ratio 1: 4).

2) Effect of mixing time

Three different mixing times, 30 seconds, 60 seconds, 90 seconds were studied in this experimental series; the liquid/powder ratio was 1: 3. The results are shown in Table II. The porosity is greatly increased by prolongation of mixing time; highly significant difference is found between each group. The result is probably due to a more intensive inclusion of atmospheric air by prolonged mixing time.

Table II

Influence of mixing time on the amount of porosity

Mixing time (sec.)	Number of specimens	Total number of porosities	Diameter of porosities μ		Porosity (%)	Average film thickness μ
			Average	Maximum		
30	5	112	21	60	0.49 (0.10)	15.6
60	10	409	20	70	0.76 (0.03)	17.6
90	10	539	22	110	1.31 (0.20)	18.3

Standard deviations are in parentheses

3) Effect of different brands of cement

Four different brands of cement available on the Danish market were tested. Standard consistency of each cement was determined according to the A. D. A. Specification No. 8, and used in this experiment. As can be seen in Table III, Cement D shows the lowest porosity value of the four brands. The porosity of Cement A is about two times as high as that of Cement D, while Cement B and C have porosity values three times as high as Cement D.

4) Effect of exposure of cement powder to carbon dioxide

With the purpose of studying the effect of a possible reaction between cement powder and atmospheric carbon dioxide, the following experiment was made.

Cement powder A was kept for one week in a glass container saturated with carbon dioxide and water vapour at room temperature. This cement powder was mixed with liquid and measurement of porosity carried out in the usual way. Two different proportions of mix of both exposed and unexposed cement were studied for comparison. The results are shown in Table IV.

When powder exposed to carbon dioxide was brought in contact with the cement liquid, innumerable bubbles appeared in the mix. The majority of these bubbles, however, disappeared during mixing.

Table III

Influence of different brands of cement on the amount of porosity

Brand of cement	Number of specimens	Total number of porosities	Diameter of porosities μ		Porosity (%)	Average film thickness μ
			Average	Maximum		
Cement A	10	96	23	60	0.24 (0.03)	15.7
Cement B	10	166	21	80	0.38 (0.08)	16.8
Cement C	10	163	22	70	0.39 (0.06)	13.6
Cement D	10	46	22	60	0.12 (0.05)	34.3

Standard deviations are in parentheses

Table IV

Influence of exposure of powder to carbon dioxide on the amount of porosity

Gram powder per 0.1 ml liquid	Number of specimens	Total number of porosities	Diameter of porosities μ		Porosity (%)	Average film thickness μ
			Ave-rage	Maxi-mum		
0.3 Exposed	10	188	23	100	0.48 (0.17)	16.3
0.3 Unexposed	10	178	24	70	0.47 (0.09)	16.9
0.4 Exposed	10	284	23	80	0.75 (0.12)	19.7
0.4 Unexposed	10	210	22	70	0.51 (0.14)	19.7

Standard deviations are in parentheses

As can be seen in the table, the porosity of cement made of exposed powder is only increased in mixes appreciable more viscous than the standard consistency mix. No significant difference was observed between exposed and unexposed powder in liquid/powder ratio 1: 3, i.e. mixes only slightly more viscous than the standard consistency mix.

SUMMARY

In this study, various factors with possible influence upon the porosity of thin films of zinc phosphate cement were investigated and the following results were obtained (Tables 1—4).

Increasing liquid powder ratio within certain limits and prolongation of mixing time caused a moderate increase of porosity in the film. Different brands of cement show small differences in porosity and the effect of long-time exposure of cement powder to saturated carbon dioxide is only very slight.

The porosity in all preparations was less than 1.6 per cent. This porosity has probably so little influence on the mechanical properties of the cement that it is negligible from a clinical point of view.

RÉSUMÉ

ETUDE SUR LA POROSITÉ DE MINCES PELLICULES DE CIMENT AU PHOSPATE DE ZINC

Dans cette étude, divers facteurs pouvant avoir une influence sur la porosité de minces pellicules de ciment au phosphate de zinc ont été examinés, et les résultats suivants ont été obtenus (tableau 1—4).

L'augmentation du rapport liquide-poudre dans une certaine limite et la prolongation de la durée du mélange provoquaient une augmentation modérée de la porosité des pellicules. Différentes marques de ciment présentent de petites différences en ce qui concerne la porosité, et l'action de l'exposition prolongée de la poudre du ciment au gaz carbonique à saturation est seulement très faible.

La porosité était dans toutes les préparations inférieure à 1,6 p. 100. Cette porosité a probablement si peu d'influence sur les propriétés mécaniques du ciment qu'elle est négligeable du point de vue clinique.

ZUSAMMENFASSUNG

STUDIEN ÜBER DIE POROSITÄT IN ZINKPHOSPHATZEMENT

Der Zweck der vorliegenden Arbeit ist, den Einfluss verschiedener Faktoren auf die Porosität dünner Schichten Zinkphosphatzement zu untersuchen.

Die Ergebnisse sind aus Tabelle 1—4 ersichtlich. Eine Erhöhung des Mischverhältnisses zwischen Flüssigkeit und Pulver verursacht innerhalb gewisser Grenzen eine moderate Erhöhung der Porosität; die gleiche Wirkung hat eine Verlängerung der Ausrührzeit. Verschiedene Fabrikate von Zement weisen kleine Unterschiede in der Porosität auf, und der Effekt langwierigen Kontaktes zwischen Zementpulver und reinem Kohlendioxyd ist sehr gering.

Die Porosität aller Präparate betrug weniger als 1,6 %. Diese Porosität hat kaum irgendeinen wesentlichen Einfluss auf die technologischen Eigenschaften des Zementfilmes.

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