NRC Publications Archive Archives des publications du CNRC

Collapse of structure in sepiolite and other layered silicate systems Beaudoin, J. J.; Grattan-Bellew, P. E.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien
DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0008-8846\(80\)90110-6](https://doi.org/10.1016/0008-8846(80)90110-6)

Cement and Concrete Research, 10, May 3, pp. 347-359, 1980-05-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=ac5f65b3-67bc-4fac-af6d-b9410904736a>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=ac5f65b3-67bc-4fac-af6d-b9410904736a>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the
first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la
première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez
pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

7871

Ser
TH1
N21d
no. 899
c. 2

BLDG.

**NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA**

**COLLAPSE OF STRUCTURE
IN SEPIOLITE AND OTHER LAYERED
SILICATE SYSTEMS**

by
J. J. Beaudoin and P. E. Grattan-Bellew

ANALYZED

Reprinted from
CEMENT AND CONCRETE RESEARCH
Vol. 10, No. 3, May 1980
p. 347-359

DBR Paper No. 899
Division of Building Research

This publication is being distributed by the Division of Building Research of the National Research Council of Canada. It should not be reproduced in whole or in part without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division may be obtained by mailing the appropriate remittance (a Bank, Express, or Post Office Money Order, or a cheque, made payable to the Receiver General of Canada, credit NRC) to the National Research Council of Canada, Ottawa, K1A 0R6. Stamps are not acceptable.

A list of all publications of the Division is available and may be obtained from the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa, K1A 0R6.

COLLAPSE OF STRUCTURE IN SEPIOLITE
AND OTHER LAYERED SILICATE SYSTEMS

J.J. Beaudoin and P.E. Grattan-Bellew
Building Materials Section, Division of Building Research
National Research Council of Canada, Ottawa, Canada
K1A 0R6

(Communicated by F.H. Wittmann)
(Received Dec. 31, 1979)

ABSTRACT

Collapse of structure due to removal of water from sepiolite and other layered silicates was studied. Data from three systems - sepiolite, hydrated C_3S , and hydrated portland cement - are presented. Changes in mechanical properties and helium flow characteristics were correlated with collapse processes in sepiolite. Similarities in helium flow characteristics of the three systems are discussed to elucidate the role of decomposition processes in microstructural collapse. The sepiolite system appears to have potential as a model for the study of collapse processes in other cementitious systems.

SOMMAIRE

On étudie l'effondrement de la structure de la sépiolite et d'autres phyllosilicates sous l'effet de l'élimination de l'eau. On présente des données relatives à trois systèmes - sépiolite, C_3S hydraté et ciment Portland hydraté. Dans le cas de la sépiolite, on a établi une corrélation, d'une part entre les modifications des propriétés mécaniques et des caractéristiques d'écoulement de l'hélium, et d'autre part le mécanisme d'effondrement. On examine les caractères communs de l'écoulement d'hélium pour les trois systèmes, afin d'élucider le rôle des processus de décomposition lors de l'effondrement de la microstructure. Il semble qu'on puisse utiliser le système basé sur la sepiolite, comme modèle d'étude des processus d'effondrement dans les autres systèmes contenant un matériau cimentant.

Introduction

The term "collapse of structure" describes a situation where due to the removal of structural water[†] (sometimes referred to as load-bearing water) the silicate layers are displaced relative to one another by deformation processes involving consolidation of hydrates due to folding, buckling, rotation, distortion or other mechanisms.

Volume changes - shrinkage and creep - in hydrated portland cement paste are processes that involve collapse of structure of layered CSH* and the amount of volume change is dependent on the state of collapse of the microstructural units (1). For example, when cement paste is autoclaved under certain conditions a high density, low surface area product - $\alpha\text{C}_2\text{SH}$ - will form. Shrinkage and creep of this material is significantly lower than normally cured portland cement paste as collapse of structure has already taken place during autoclaving.

Few experiments have provided direct evidence of structural collapse in hydrated portland cement (2). X-ray low-angle scattering experiments enabled Winslow (3) to follow changes in surface area of hardened portland cement paste from the wet condition to the dry state; he observed that surface areas decreased from approximately 600 m²/g to 200 m²/g. On rewetting most of the original surface area was regenerated. This provided evidence that the structure had not stabilized on first drying and that water could reenter the layered structure.

Modulus of elasticity measurements on samples of hydrated portland cement increase by as much as 100% when the samples are wet due to increases stiffness of the solid when water is present in interlayer positions (4). On drying there is a continuous decrease in the solid volume of cement paste but the system retains its stiffness except at very low humidity when a large decrease in stiffness occurs accompanied by collapse of the layered structure.

Irreversible shrinkage and creep strains in hydrated portland cement have been attributed, in part, to irreversible structural changes involving translation of the ends of silicate chains into closer proximity with each other (5).

Attempts to relate volume changes occurring in hydrated portland cement with microstructural changes have been mostly qualitative (6). Helium diffusion techniques provided a tool for quantitative assessment of microstructural changes (7). Measurements of solid volume, and helium intake on removal of interlayer water from the hydrated cement system, enabled estimates to be made of the space occupied by water prior to its removal. Changes in the rate of helium intake and in total helium intake as water was removed provided a means of detecting structural collapse (8).

[†] In crystals containing coordinating water, the water molecules play an essential role in maintaining the structure intact.

* Cement chemistry nomenclature is used where C = CaO, S = SiO₂, H = H₂O.

At present, there is no general agreement about the state of water in hydrated portland cement and its role in the collapse process, although the view that interlayer water plays a major role in shrinkage and creep processes in this system is gaining acceptance. It was thought that a systematic study of the removal of water from a well crystalline layered system, wherein water is held in well-defined states, would enable an assessment of the ability of helium diffusion methods to elucidate the role of various types of water in structural collapse processes. Sepiolite ($8 MgO \cdot 12 SiO_2 \cdot n H_2O$) was the layered silicate system chosen for this purpose. Sepiolite, which contains zeolitic water, coordination water and octahedral OH, is a microporous solid having pore space in the form of long, narrow molecular size channels and grooves. Details of folding and collapse processes on removal of coordination water have been studied using X-ray diffraction, thermogravimetric analysis and infra-red spectroscopy (9, 10, 11).

This paper is a report of the results of helium diffusion, length change, modulus of elasticity and microhardness measurements for sepiolite as water is removed in steps from 11% RH condition. Similarities in helium diffusion and other test results of sepiolite, C_3S and hydrated portland cement are discussed with a view to the use of sepiolite as a model for the study of CSH layered systems.

Experimental

Materials

Vallecas sepiolite was used for all sepiolite samples. Details of chemical and physical properties have been published elsewhere (9, 12). X-ray diffractograms revealed all the sepiolite lines expected. The sepiolite sample contained minor amounts of quartz. Samples were prepared by compacting sepiolite powder into discs 3.2 cm in diameter and 1.25 mm thick at pressures up to 680 MPa. All samples were conditioned at 11% RH prior to testing.

Preparation of hydrated C_3S and portland cement pastes referred to in the text has been reported elsewhere (7, 13).

Procedures

Removal of Water from Sepiolite Samples

Sepiolite samples, conditioned to 11% RH, were placed in a vacuum vessel. Water was subsequently removed in increments by pumping or a combination of pumping and heating for various time periods ranging from a few minutes to several hours. Temperatures ranged from 40 to 850°C. At higher temperatures water was removed by placing samples in a furnace. After each increment of water was removed weight changes were recorded in a dry box; samples were then inserted in the helium pycnometer for solid volume and helium intake measurements. Companion samples, subject to the same conditioning, were selected for modulus of elasticity and microhardness measurements.

Helium Comparison Pycnometry and Helium Intake

The apparatus and procedure for solid volume and helium intake measurements are described in detail in other papers (14, 15). Solid volumes are the instantaneous volumes obtained using helium as a displacement fluid.

Molecular size channels or interlayer spaces that cause a delayed flow of helium into the sample, are, in the first instance, regarded as part of the solid.

Length Change

Samples were cut in a rectangular shape approximately 2.5 by 0.6 cm and mounted on a modified Tuckerman gauge extensometer. The details of this method have been described elsewhere (16). The samples, initially conditioned to 11% RH, were placed in vacuum cells where length change resulting from combinations of pumping and heating was monitored.

Modulus of Elasticity

The method used to measure modulus of elasticity of the sepiolite discs has been reported (4). The procedure involves measuring the deflection of the disc specimen when loaded at its centre and supported at three points on the circumference of a circle 2.5 cm in diameter.

Microhardness

A Leitz microhardness testing machine with a Vickers indenter was used for the microhardness measurements. Ten microhardness measurements were made on each disc tested.

Results

Helium Intake versus Time

Selected helium intake versus time curves are plotted in Figure 1. Water was removed from the samples in increments and each curve, in numerical order, is the result obtained at a further increase in weight loss. The weight losses identified with each curve are indicated in Figure 1. There is a progressive increase in the amount of helium intake at 72 hours as weight loss increases to 6.75%. At weight loss 6.75 to 8.60% there is a successive decrease in both the initial rate of helium intake as well as the total helium intake at 72 hours. The total helium intake at weight loss 8.60% has decreased to nearly that shown by curve 1. The total helium intake and the initial rate of helium intake increase to maximum at 12.82% weight loss. There is a subsequent decrease in helium intake to a value less than that obtained for the starting condition at weight loss of 15.36%.

Total Helium Intake versus Weight Loss

The total helium intake after 40 hours, ΔD , is plotted against weight loss in Figure 2. There is an increase in total helium intake to a maximum of 4.26 cc/100 g at a weight loss of 6.75% followed by a decrease in the value of total helium intake to 1.12 cc/100 g at a weight loss of 8.60%. Upon further removal of water there is a rapid increase in total helium intake to a maximum 6.00 cc/100 g at a weight loss of 12.82%; this is followed by a decrease in total helium intake to a minimum of 0.53 cc/100 g at a weight loss of 15.36%.

The Term $(\Delta V - \Delta D)$ versus Weight Loss

The term $(\Delta V - \Delta D)$, (solid volume change, ΔV , - total helium intake, ΔD) is plotted against weight loss in Figure 3. There is a linear dependence

FIG. 1

Helium intake vs time curves for sepiolite which has been dried in stages from 11% RH

Solid Density versus Weight Loss

Solid density versus weight loss data is plotted in Figure 4. As water is removed solid density (taking account of helium intake) increases from 2.36 g/cc to 3.12 g/cc at 6.80% weight loss. In the weight loss region 6.80 to 8.96% there are three moisture contents where there are significant increases in solid density with little change in weight. Solid density increases from 2.81 g/cc at 8.09% weight loss to 3.76 g/cc at 12.82% weight loss. Further removal of water results in a decrease in density to 2.85 g/cc at 15.36% weight loss.

Length Change Data

Length change, $\Delta l/l$, versus weight change on drying from 11% RH condition is plotted in Figure 5.

between the two terms up to a weight loss of approximately 6.80%. The inverse slope of this curve is approximately 1.00.

In the weight loss region 6.80-8.96% there are three occurrences of large changes in $(\Delta V - \Delta D)$ with very small increases in weight loss (this will be discussed later); for the remaining data in this region there is very little change in $(\Delta V - \Delta D)$ with weight loss. For subsequent weight losses up to 12.82% there is a linear dependence in $(\Delta V - \Delta D)$ and weight change; the inverse slope of the curve is approximately 0.39. Further removal of water results in increased values of $(\Delta V - \Delta D)$ up to a weight change of 15.36%. The inverse slope of a line joining the origin and the final data point is approximately 1.15. An interpretation of the meaning of these curves will be given later.

FIG. 2

Total helium intake at 40 h vs weight loss for sepiolite which has been dried from 11% RH

FIG. 3

The term, $\Delta V - \Delta D$, vs weight loss for sepiolite which has been dried from 11% RH

There is an initial length change of approximately 2% at a weight change of approximately 0.5%. In the weight change region 0.50 to 6.75% there is no additional length change. From 6.75 to 7.80% weight change length increases to 3.1% and from weight change 7.80 to 8.06% there is a large increase in length change to 7.60%.

In Figure 6, the term $3 \Delta l/l$ is plotted against solid volume change, ΔV . There is an initial length change with very little solid volume change. Solid volume change then increases up to 20.80% with no length change. Subsequent fluctuations in solid volume change from 20.8% to 12.8% to 20% to 12.4% occur in the weight loss region 6.70% to 8.04%, where there are large increases in helium intake with little weight change (Figure 3); these fluctuations include the large increase in helium intake at 6.80% weight change. On further removal of water from the system - to 7.8% weight loss - the change in solid volume increases to 24.25%; this weight loss is where a second large increase in helium flow with small weight changes occurs (Figure 3). The curve ($3 \Delta l/l$ versus ΔV) in this region is approximately parallel to the line of equality. Further removal of water (only 0.1%) is

FIG. 4

Solid density vs weight loss for sepiolite which has been dried from 11% RH

FIG. 5

Shrinkage vs weight loss for sepiolite which has been dried from 11% RH

accompanied by a large decrease in solid volume change to 15.8%, the plot point lying near the line of equality. Further removal of water (weight change 8.04%) results in increased length change, the curve being close and approximately parallel to the line of equality.

Mechanical Properties

Mechanical property versus weight change curves are plotted in Figure 7.

Microhardness

As water is removed from the samples conditioned at 11% RH microhardness increases from 337 MPa to 490 MPa at 8.13% weight loss. At 11.90% weight loss microhardness decreases to 181 MPa. Further removal of water to 12.82% weight loss results in a microhardness value of 168 MPa. At weight losses of 13.19 and 15.36% microhardness increases to values of 225 and 379 MPa, respectively. The value of 337 MPa is close to the initial value at 11% RH.

Modulus of Elasticity

At weight losses up to 8.13% there is very little change in the initial modulus of elasticity value 7.2×10^3 MPa. As weight loss increases to 11.90 and 12.82% modulus of elasticity decreases to values of 4.03 and 3.09×10^3 MPa. At weight losses of 13.19 and 15.36% modulus of elasticity increases to values of 3.19 and 5.9×10^3 MPa. Mechanical property results will be discussed in more detail later.

Discussion

In order to facilitate discussion of the helium diffusion, length change and mechanical property results obtained for the sepiolite system in this study, a brief description of the molecular structure of sepiolite is necessary. Figure 8 is a schematic representation (after Cerna et al (9)) of the structure of sepiolite projected on the (001) plane. Water is held in various states: zeolitic water is lost at temperatures near 110°C; first water of coordination at each edge Mg is removed at 175°C under vacuum; second water of coordination is removed at higher temperatures from collapsed channels where diffusion

FIG. 6

Shrinkage vs solid volume decrease for sepiolite which has been dried from 11% RH

FIG. 7

Mechanical properties vs weight loss for sepiolite which has been dried from 11% RH: (a) microhardness, (b) modulus of elasticity

problems delay its escape from the crystal (anhydride forms at about 500°C); octahedral hydroxyls react and disappear as water by 780°C.

Following the model of Cerna et al it is suggested that the crystal folds after the removal of the first water of coordination and that the crystal is subsequently distorted during removal of second water of coordination. It is the hydrogen bridges (at points b (Figure 8)) from the waters of coordination to the oxygen of the neighboring silica surfaces which stabilize the structure. Total dehydroxylation and sepiolite anhydride destruction take place by 780°C.

Helium Diffusion Studies

After reaching a maximum total helium intake at 6.75% weight loss there is a decrease to a minimum at 8.60% weight loss (Figure 2). This decrease is attributed to folding (structural collapse) of the sepiolite crystal due to removal of the first coordination water. Further removal of water up to 12.82% is accompanied by a large increase in total helium intake. This is attributed to the removal of the second coordination water from collapsed channels. The folding processes, themselves, may produce trapped space into which helium may subsequently flow. Further weight loss probably involves dehydroxylation especially at the highest temperatures. At 850°C XRD indicates the presence of enstatite; also some of the quartz has reacted with anhydrous sepiolite.

Consider the ($\Delta V - \Delta D$) versus weight loss plot (Figure 3). The inverse slope of the curve up to 6.75% weight loss is approximately 1.00; this represents the density of the water (zeolitic) which has been removed from the molecular sized channels. In the weight loss region 6.75 to 8.60% there are three verticle "spikes" at weight loss positions where helium intake is large and weight change is small. This is attributed to the diffusion of helium into empty discrete space which has opened up during the folding of the crystal. Opening up and filling of discrete space has been observed in other systems (17).

For the remaining plot points in this region there is very little change in ($\Delta V - \Delta D$) with weight loss; structural collapse of the crystal inhibits the flow of helium into the microspace. A similar characteristic is observed in the ($\Delta V - \Delta D$) versus weight loss plot for the hydrated C_3S system in the weight loss region from 5.0 to 7.0% (Figure 9). This was attributed to the collapse of layered silicates in the hydrated C_3S system (13).

In the weight loss region 8.60 to 12.82% the slope of the ($\Delta V - \Delta D$) versus weight loss curve increases; the inverse slope is approximately 0.39. In this region helium intake increases (curves 7, 8, 9, Figure 1) due to removal of the second coordination water from collapsed molecular sized channels and accessibility of microspace trapped during the folding process. In this region, the structure is apparently distorted as sepiolite anhydride is formed.

FIG. 8

End view of the right-hand edge of a model sepiolite fiber (a) water-SiOH bond (b) water-oxygen bond (after Cerna et al (9))

Further removal of water to 15.36% weight loss involves a dehydroxylation process and further collapse of micro-structure. The term $(\Delta V - \Delta D)$ increases to give a plot point $\{-13.36, 15.36\}$; Figure 3). If this point is joined to the origin the inverse slope of the line gives a value of 1.15 g/cc (similar values were obtained for adsorbed water in other systems (18)) for the density of the water removed, indicating that in this dehydroxylated state helium is now able to enter nearly all the space vacated by water.

The solid density versus weight loss curve for hydrated C_3S (Figure 10) reaches a maximum at 5% weight loss and then decreases (due to structural collapse) as weight loss increases to 7%.

Solid density for sepiolite increases steadily to a weight loss of 6.75% (Figure 4). In the weight loss region 6.75 to 8.60%, there are three vertical "spikes" - large increases in solid density resulting from the accessibility of discrete microspace to helium. As weight loss increases to 12.82% solid density increases to a maximum; there is a decrease in solid volume as helium can now enter space created by the removal of secondary coordination water and the accessibility of previously trapped space.

The density of 3.76 observed at 12.8% weight loss is higher than might be expected. A possible explanation for this apparently anomalous density may be that the volume measured by helium diffusion is not a multiple of the volume of the unit cell which is used in the XRD method of calculating density but a smaller volume due to helium penetrating vacant lattice sites. Gunnar Hagg and Ingrid Sucksdorff (19) showed that there is a direct relationship between density and the number of lattice vacancies in pyrrhotite. Ball and Taylor (20) found that under certain conditions $Mg(OH)_2$ dehydrated to a spinel phase in which there are vacant sites in the lattice. $Mg(OH)_2$ forms the core of the structure of sepiolite (Figure 8) and the work of Ball and Taylor (20) suggests that the spinel phase might be expected to form in sepiolite. The presence of silica layers on either side of the $Mg(OH)_2$ core of sepiolite retards the loss of (OH) ions from the structure and can be expected to increase the probability of the formation of the spinel phase rather than periclase the

FIG. 9

The term, $\Delta V - \Delta D$, vs weight loss for C_3S dried from 11% RH

FIG. 10

Solid density vs weight loss for C_3S dried from 11% RH

normal end product of dehydration.

Helium intake versus time curves for the hydrated portland cement system are given in Figure 11. When the curves begin to cross over (Curve 4) microstructural collapse of the layered silicates is initiated. This initiation of structural collapse coincides with the maxima (at 6% weight loss) in the total helium intake versus weight loss curve for hydrated portland cement (Figure 12).

Structural collapse occurring in the three layered systems studied (sepiolite, C_3S , portland cement), due to the removal of water, is indicated by the helium diffusion technique by the following:

- a decrease in the rate and amount of helium intake;
- a decrease in the slope of the $(\Delta V - \Delta D)$ versus weight loss curve;
- a decrease in solid density.

Length Change Measurements

Reference is made to Figures 5 and 6. The initial length change resulting from removal of 0.50% water is probably due to liberation of some water from crystal edges and the removal of zeolitic water from the ends of molecular size channels. There is no further length change on removal of zeolitic water up to 6.75% weight change; this is expected as removal of zeolitic water is not supposed to alter crystal structure.

From 6.75 to 7.8% weight change, length change increases from 2.0 to 3.2%; a further increase in length to 7.6% occurs as weight change increases to 8.1%. These length changes may be correlated to folding of the crystal structure.

In Figure 6, it is shown that the initial length change is accompanied by a small increase in solid volume; this may be due to structural collapse or folding at the ends of channels. The large solid volume change with no length change is due to the removal of zeolitic water. It is probable that helium is entering, instantaneously, some of the space vacated by zeolitic water accounting for decreased solid volume. Folding of the lattice begins at 6.75% weight change and large fluctuations in solid volume change are due to both folding and opening up of discrete pores (9). The length change due to structural collapse appears to occur in two stages: the first stage up to a solid volume change of 24% involves crystal folding and opening up of discrete pores; the second stage appears to be a consolidation process as the net solid volume decrease is reduced, possibly due to channel walls coming into closer proximity; subsequent shrinkage plot points are close to and parallel with the

FIG. 11

Helium intake vs time curves for hydrated portland cement paste dried from 11% RH

FIG. 12

Total helium intake at 40 h vs weight loss for hydrated portland cement paste dried from 11% RH

line of equality. The latter volume changes correspond to changes of weight which total approximately 0,3%.

Mechanical Properties

Microhardness and modulus of elasticity measurements (Figure 7) were useful in elucidating the structural role of the various types of water in the sepiolite crystal.

Where zeolitic water is removed (up to 6.75% weight change) microhardness increases significantly while there is negligible change in modulus of elasticity values. It is apparent that zeolitic water does not contribute to the stiffness of the crystal. However, the presence of zeolitic water may weaken the Si-O-Si bonds, resulting in decreased strength. This form of stress corrosion has been suggested as a possible mechanism for the weakening of hydrated portland cement in presence of moisture (21). As part of the first coordination water is removed (up to 8.10% weight loss), accompanied by folding of the sepiolite crystal, microhardness continues to increase while modulus of elasticity undergoes little change.

It is apparent that most of the first coordination water does not contribute to the stiffness of the crystal which contains undistorted molecular sized channels whose contribution to the compressibility of the material remains the same even though lattice folding has taken place. Increased microhardness may be due to a reduction in the number of potential stress concentration sites in locations where external hydrogen bridging occurred.

Removal of the remaining coordination water causes distortion and weakening of the structure. Second coordination water bridges the corners of collapsed pore walls and apparently contributes significantly to the stiffness and strength of the crystal. At weight losses greater than 12.82% dehydroxylation begins to occur. This is accompanied by increases in both microhardness and modulus of elasticity. Sepiolite anhydride structure is destroyed, the structure consolidates to form enstatite and weakening effects of trapped space due to removal of second coordination water are apparently removed.

Conclusions

Several experimental techniques - helium diffusion, length change, and mechanical property measurements - permitted elucidation of structural changes in sepiolite caused by water removal. The observations support the following conclusions:

1. a) Helium diffusion techniques can be used to detect microstructural instability due to the removal of water from selected layered silicates, such as hydrated portland cement, hydrated C_3S and sepiolite.
- b) Helium diffusion techniques can be used to follow microstructural changes due to drying in the sepiolite system; these changes involve removal of zeolitic water, lattice folding and distortion caused by the removal of coordination water and consolidation due to dehydroxylation.
- c) Length change measurements on sepiolite samples dried from 11% RH permit the delineation of processes involved in the removal of zeolitic water and coordination water.
- d) Removal of zeolitic water from sepiolite has little or no effect on modulus of elasticity values but results in increased microhardness

values. It is apparent that there probably are different mechanisms associated with the removal of zeolitic water that are operative in determining these two properties; this is the case when interlayer water is removed from portland cement and C_3S systems.

- e) Removal of most of the first coordination water from the sepiolite crystal does not significantly affect modulus of elasticity values. Under the same moisture conditions microhardness values increase due, perhaps, to possible removal of stress concentration sites in locations where hydrogen bridging occurred.
 - f) Removal of second coordination water from the sepiolite crystal is destructive resulting in decreases in both modulus of elasticity and microhardness values.
 - g) Dehydroxylation of the crystal consolidates the structure, eliminates trapped space which may act as potential stress concentration sites, and results in significantly increased values of microhardness and modulus of elasticity.
2. The layered mineral sepiolite may be useful as a model for describing collapse of structure processes accompanying water removal in other layered but less crystalline systems.

Acknowledgement

The authors wish to thank J.J. Wood for his fine work in performing the experiments. This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

References

1. R.F. Feldman. Cem. Concr. Res. 2, 521 (1972).
2. R.H. Mills. Proc. Int. Conference on Structure, Solid Mechanics, and Engineering Design in Civil Engineering Materials, Southampton, U.K., Part 1, 751 (1969).
3. D.N. Winslow. Ph.D. Thesis, Department of Civil Engineering, Purdue University, p. 148 (1973).
4. P.J. Sereda, R.F. Feldman and E.G. Swenson. Highway Research Board Special Report No. 90, 58 (1966).
5. R.F. Feldman. Proc. RILEM/IUPAC Int. Symp. On Pore Structure and Properties of Materials, Prague, C101 (1973).
6. T.C. Powers. RILEM Bull., No. 33, 381 (1966).
7. R.F. Feldman. Cem. Concr. Res. 1, 285, (1971).
8. R.F. Feldman. Cem. Concr. Res. 3, 777 (1973).
9. C. Cerna, J.L. Ahlrichs and J.M. Serratosa. Clays and Clay Minerals, 23, 452 (1975).
10. H. Hayashi, R. Otsuka and W. Imai. The Amer. Mineralogist 53, 1613 (1969).
11. H. Nagata, S. Shimoda and T. Sudo. Clays and Clay Minerals, 22, 285 (1974).
12. J.L. Ahlrichs, C. Cerna and J.M. Serratosa. Clays and Clay Minerals 23, 119 (1975).

13. R.F. Feldman. Cem. Concr. Res. 2, 123 (1972).
14. J.J. Beaudoin and R.F. Feldman. Cem. Concr. Res. 8, 223 (1978).
15. R.F. Feldman, Cem. Concr. Res. 4, 1 (1973).
16. R.F. Feldman. Proc. Fifth Int. Symp. Chem. of Cement, Tokyo, Part III, Vol. III, 53 (1968).
17. J.J. Beaudoin and R.F. Feldman. Cem. Concr. Res. 7, 585 (1977).
18. S. Brunauer. The Adsorption of Gases and Vapors, Princeton University Press, Princeton, 420 (1943).
19. G. Hagg and I. Sucksdorff. Zeit. Phys. Chem. B. 22, 444 (1933).
20. M.C. Ball and H.F.W. Taylor. Min. Mag. 32, 754 (1961).
21. R.F. Feldman and P.J. Sereda. Engineering Journal 53, 53 (1970).