The Shrinkage and Bulk Modulus of Cement-Fly Ash Mortar

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ABSTRACT

This paper presents the results of the drying shrinkage of mortars made from ordinary Portland cement and fly ash (ASTM Class F). It is shown that the shrinkage occurs only at a relative humidity (RH) lower than 97%, and the ultimate shrinkage at about 0.02% RH ranged from 700 to 1400 × 10^{-6} m/m. The replacement of cement with fly ash leads to a reduced shrinkage, especially when the comparison is made on the base of moisture loss which is higher for mortar with a higher fly ash content. It is also shown that shrinkage is less for the mortars with a lower water to binder ratio.

It is theoretically shown here that, during drying both the surface energy change in the cement paste and the capillary tension exerted on the wall of the pores effectively induce shrinkage. Based on this, the bulk modulus (E value) of the hardened binder can be estimated by the desorption and shrinkage data.

Keywords: fly ash, drying shrinkage, relative humidity, strength, bulk modulus, surface free energy, capillary tension.

1. INTRODUCTION

Concrete in use is in general exposed to drying conditions, which results in the evaporation of moisture and the drying shrinkage. It was shown previously that, the cement mortar incorporated with more than 30% fly ash as binder tends to lose more moisture compared with the normal Portland cement mortar /1/.

Although drying shrinkage is one of the important properties of concrete which is reported to be responsible for crack formation /2/, there is relatively less information about the shrinkage isotherm of the cement mortar with fly ash.

The published data are generally from the results in one relative humidity condition, typically at 50% RH, tested by the time-dependent method /3, 4/, which reported that the fly ash did not influence the shrinkage significantly. The lower water to binder ratio used in the fly ash concrete is usually considered to be the main reason for this. However, this seems to be the effect of water to binder ratio rather than that of fly ash to shrinkage. Since it is known that drying shrinkage is a function of several factors influencing simultaneously, the single parameter experimental result is not reliable in extending to the general case, especially to other humidity conditions.

In addition, to predict the shrinkage of the mortar, it is important to understand the relation between drying and shrinkage, where several mechanisms have been applied by different researchers. The most important theory is the Gibbs free energy change in the drying surface which was quite successfully applied by Feldman /5/. However, as proposed by Freyssinet /6/, the capillary tension is also not negligible, which has been supported by numerous experimental results /7/. The discontinuity of the shrinkage vs. moisture loss curve shown in Young's review /7/ strongly suggests that shrinkage is better explained by the combination of several different mechanisms. But such a treatment has not been seen so far.

The objectives of this research are:

- to test the shrinkage isotherm of cement mortar with a variation in fly ash content, water to binder ratio and curing condition.

- to analyse the shrinkage isotherm with the desorption isotherm in order to obtain a deeper understanding of the mechanism of shrinkage.

- to analyse the shrinkage based on thermodynamics, especially the combined effect of the changes in Gibbs free energy and capillary tension.

2. EXPERIMENTAL

2.1 Materials

A standard Swedish Portland cement produced by CEMENTA AB, Slite, Sweden was used. It has a Blaine fineness of 365 m^2/kg, and contains (by weight): 64% C_3S, 13% C_2S, 8% C_3A and 9% C_4AF. The fly ash studied was derived from a bituminous coal, which can be classified as a Class F fly ash with a Blaine fineness of 337 m^2/kg and the chemical composition is 48.6% Si_2O, 22% Al_2O_3, 11% Fe_2O_3, 8% CaO, 4% MgO and 2.2% of alkali oxides (as equivalent Na_2O).

2.2 Specimens and tests

The fly ash was added as a replacement for cement ranging from 0 to 60% of the total weight of binder (cement + fly ash). The water-to-binder ratio varies from 0.35 to 0.57. 40 × 40 × 160 mm prisms were cast with a sand-to-binder ratio 2.50 (by weight). On demolding after 1 day, the prisms were placed in different chambers containing water which were then warmed to different temperatures to give a 24 hour warm water (temp. 19° to 75°C) treatment to the prisms, this was followed by water curing at room temperature (19°C). The mix proportioning and the initial curing temperature were arranged according to "Box-Wilson" design /16/ method. The details of these variables are shown in Table I. The specimens for drying and shrinkage test were 2.5 mm thick slices sawn from the prisms water cured for 90 days.

The flexural and compressive strength of the prisms were tested after 3, 7, and 28 days. The water vapour desorption isotherm (the moisture content in the specimen as a function of the ambient RHs at constant temperature) /1/, whereas the shrinkage was determined separately by step-wise drying. The drying was performed in desiccators maintaining a RH 97%, 85%, 76%, 59%, 42%, 33%, 11% by using saturated salt solutions at room temperature (20°C). 10 mm (length) strain gauge produced by Tokyo Sokki Kenkyujo co. Ltd, was glued on the surface of the slice specimen for testing the shrinkage. After reaching the moisture equilibrium, the specimens for desorption isotherm were dried at 105°C, whereas the final drying condition for shrinkage was created by dry silica gel (0.02% RH approx.)

3. RESULTS

The mixtures varied in a wide range of water to binder ratio, thus the consistency of the mixes varied from Flow=25 cm for the mix with W/(C+F)=0.57, to 11.5 cm for that with W/(C+F)=0.36. The specimens were made by the vibrating method to ensure the quality of the dry mixes.

Drying shrinkage of the specimens was measured daily in the first week and once weekly afterwards. In all the RH conditions, the shrinkage occurred mainly during the first week, though the time for reaching the equilibrium state was about 2 months.

The strength of the mortars is shown in Table I together with the mix parameters. The drying shrinkage of the mortar specimens is shown in Figure 1. The desorption isotherms of this set of specimens were published previously /1/, of which the data are rearranged and plotted in Figure 2, to show the relation between moisture loss and shrinkage.

Figure 1 shows that the shrinkage of all the specimens at 97% RH condition was negligible, in spite of that most of them showed a distinct moisture loss at this RH /1/. Further decrease in RH results in significant shrinkage, e.g., at 85% RH an approximate average shrinkage of 150 $\times 10^{-6}$ m/m occurred in these specimens. At 59% RH and 42%, averages of about 300 and 500 $\times 10^{-6}$ m/m shrinkage occurred respectively, which are in the same magnitude as the data reported by Swamy et al. /4/ who tested concrete containing 50% fly ash as binder. Less shrinkage occurred for the mortar with fly ash, but up to this RH the effect is still not obvious, which confirms the results of Gebler and Klieger /3/. The shrinkage close to 0% RH is rather large, ranges from 670 $\times 10^{-6}$ m/m (Mix 4, F/(C+F)=0.48, W/(C+F)=0.40, ini. cured at 30°C) to 1380 $\times 10^{-6}$ m/m (Mix 10, pure cement mortar, W/(C+F)=0.47, ini. cured at 47°C). The latter is to be compared with its high volume fly ash

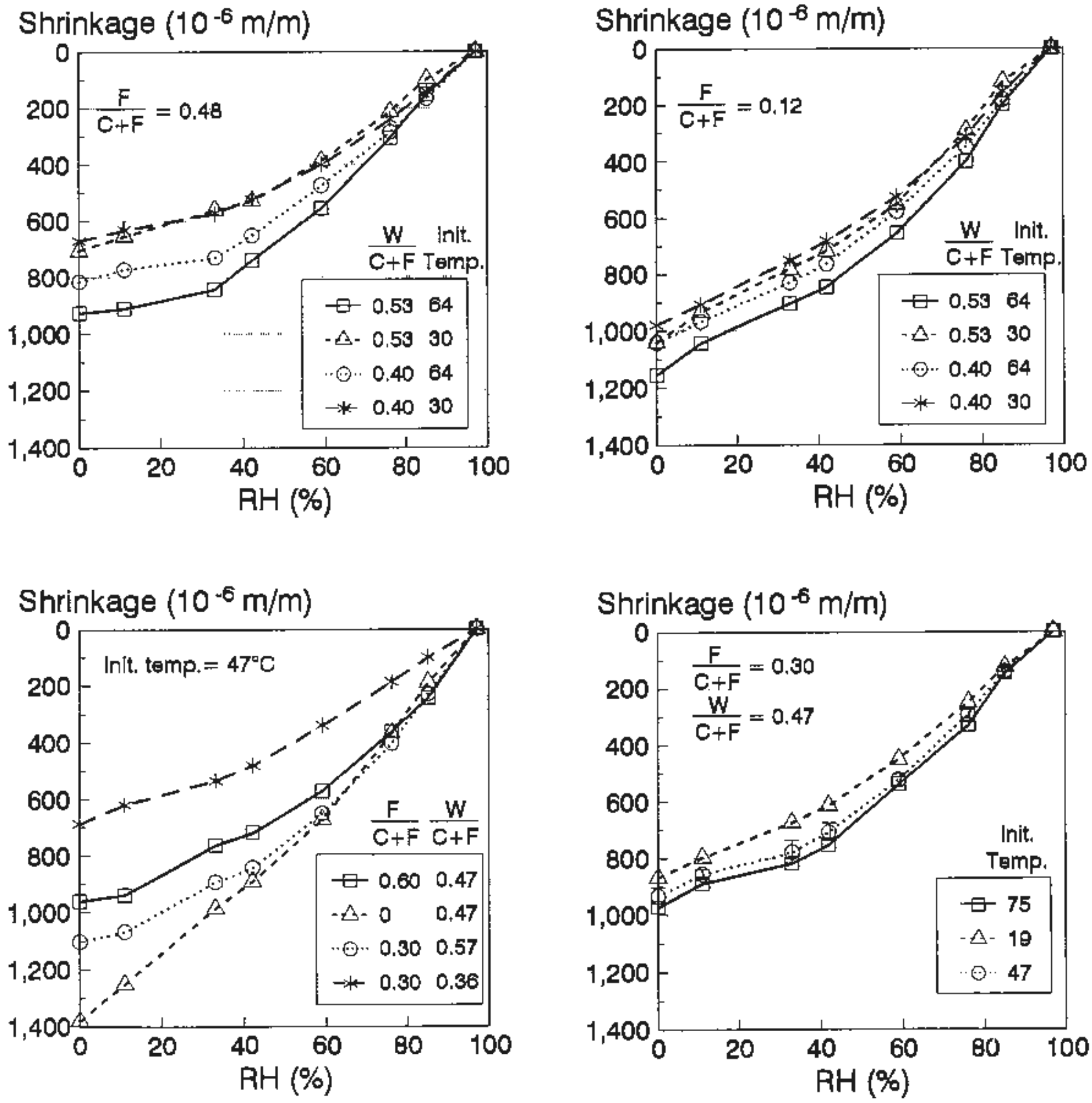

Figure 1. Shrinkage isotherms of cement mortars. The mix parameters are shown in Table I.

counterpart (Mix 9, F/(C+F)=0.60, W/(C+F)=0.47, initially cured at 47°C) which has a final shrinkage of 960 × 10^{-6} m/m. Mortar with a medium fly ash content and water to binder ratio (Mix 15), however, has shown a similar shrinkage compared to the high volume fly ash mix, apparently due to the lower moisture loss in each RH condition /1/. The shrinkage reduces with the decrease in the water to binder ratio. The warm water curing results show that, in the temperature range 19° to 75°C, the mixes initially cured in warmer water developed more shrinkage, especially in the mix with higher content of fly ash (Mix 1 vs. 2, and Mix 3 vs. 4 in Fig.1). However, this effct is less significant compared to the other two.

It was previously shown /1/ that mortar with a high volume of fly ash tends to lose moisture more easily than plain cement mortar.

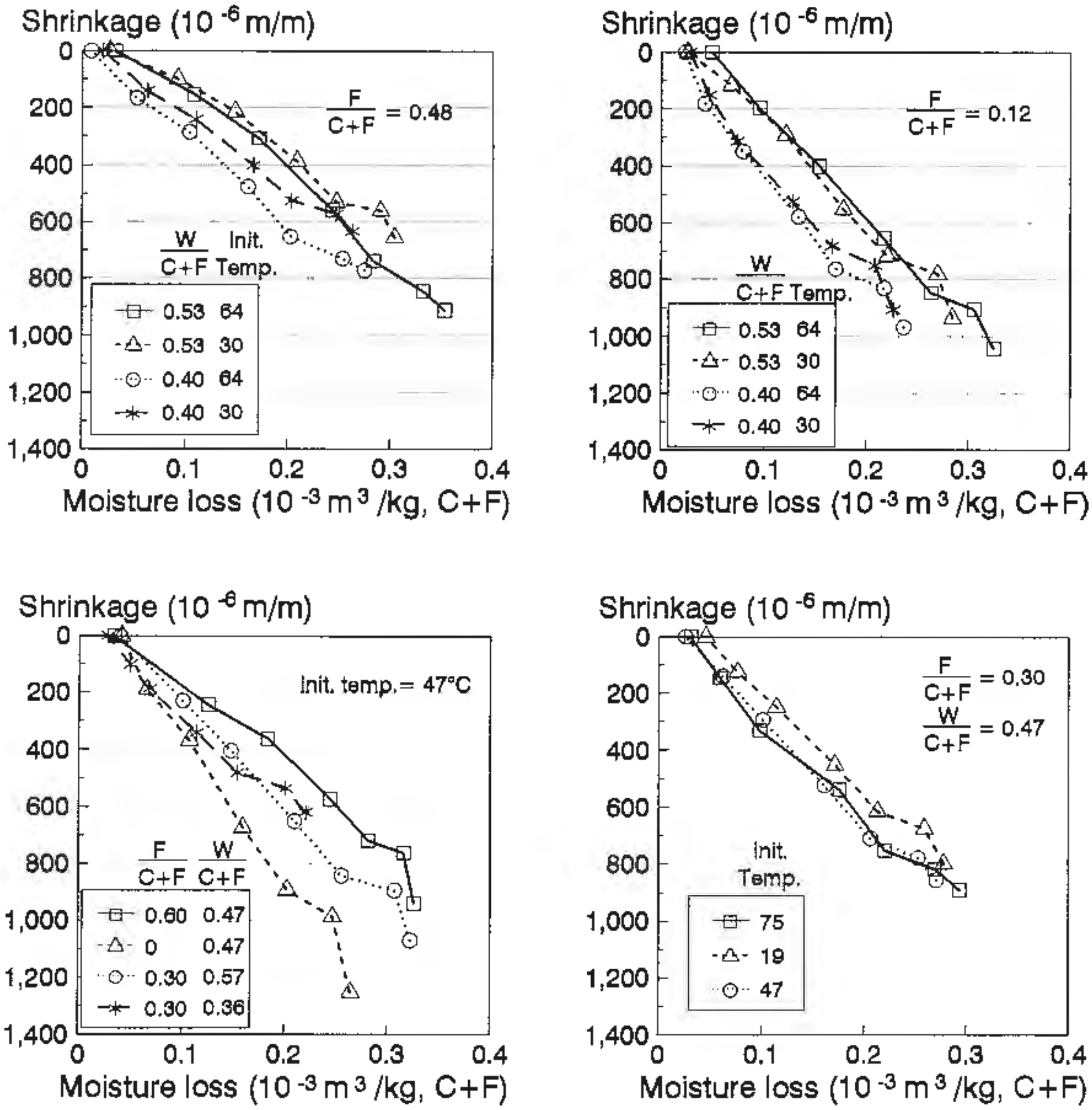

Figure 2. Shrinkage vs. moisture loss in RH range 97% to 11%. Mixes are the same as in Figure 1.

Thus the above results indicate that the fly ash mortar shrinks less in spite of its greater loss of moisture, as is shown in Figure 2 where the shrinkage is plotted against the moisture loss per unit weight of binder. The curve has several discontinuities, noticeably at RH 42% where the slope of the curve becomes lower, and at RH between 33% and 11% where the slope is steeper. With the same amount of moisture loss, the specimens of the lower water to binder ratio show a larger shrinkage. This is in agreement with the results obtained by Roper /8/. When comparing the same moisture loss, the shrinkage appears to decrease significantly with the increase of the fly ash content; and the effect of initial warm water curing becomes even less significant.

The influence of the mix parameters on the properties of the mortars is also demonstrated in the results of strength test (Table I). One needs only to mention that the 28 day compressive strength ranges from 30 MPa for the high volume fly ash mix to 57 MPa for the plain cement mix (at W/(C+F)=0.47). The low volume fly ash mix (F/(C+F)=0.12), with the exception of the mix initially cured at a higher temperature (64°C), also reached this strength. In the range tested, lower water to binder ratio results in a definite higher strength. The initial curing temperature seems to result in a slight decrease in the 28 day strength for mortars with higher water to cement ratio, though the effect is not significant. Figure 3 depicts the dependence of 28 day strength on these factors.

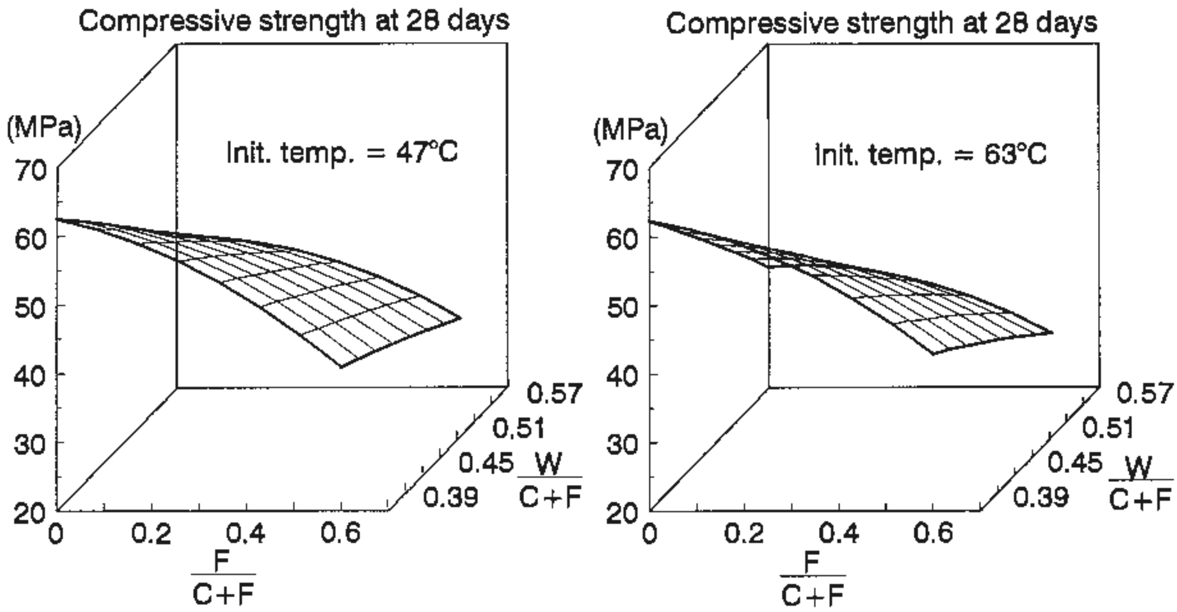

Figure 3. Dependence of the 28-day strength on mix parameters.

4. ANALYSIS

The fact that there is little shrinkage at RH 97%, at which the moisture is lost from the pores of a size larger than 750 Å, confirms the statement made by Mehta /9/, the loss of moisture from large capillary (or macro) pores does not induce shrinkage. Further drying causes water to evaporate from mesopores and micropores (<500 Å, c.f. /10/), in which the change in surface free energy leads to shrinkage /5/. However, the slope of the shrinkage curve becomes less steep when RH is lowered down to 42%. This has been explained by the release of the stress exerted by the surface tension of capillary water which causes some expansion. As stated by Powers, meniscus will disappear due to that the stress in water reaches the breaking point at RH about 40% /11/. It can be seen that as RH decreases from 33% to 11%, the small amount of moisture loss corresponds to a comparatively large shrinkage, which is in full agreement with the results of previous researchers /5, 8/ who explain this as being attributed to the deformation of the hydration products due to the loss of interlayer water.

The dependence of the shrinkage at each RH on the experimental

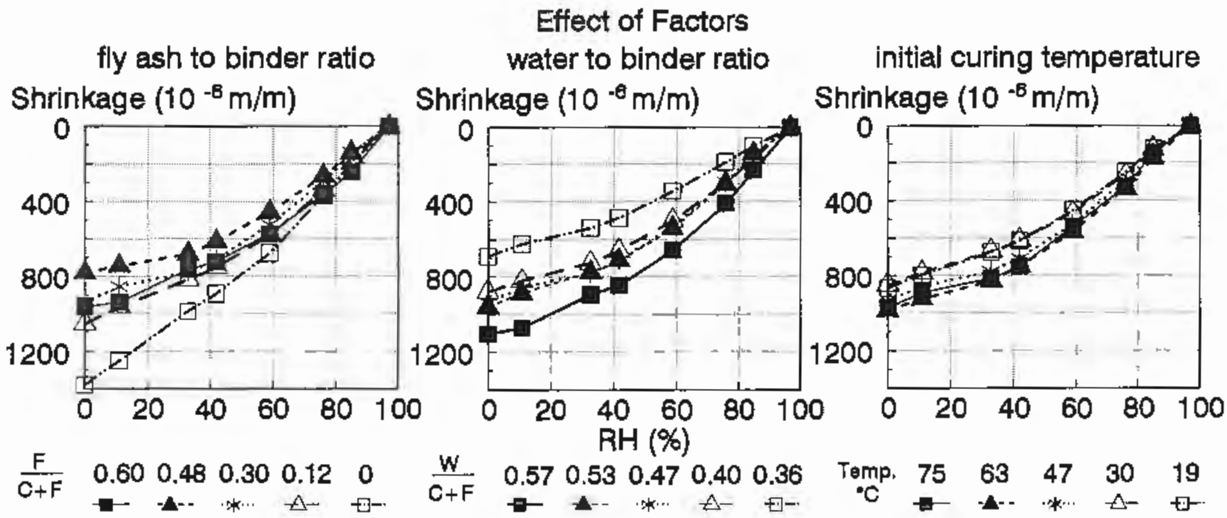

Figure 4. Factorial analysis of the influence of the mix proportion and curing temperature on the shrinkage.

factors is shown more clearly in Figure 4, which is calculated on the base of the orthogonal nature of the Box-Wilson design. It seems that the mortars with a medium-high volume of fly ash, i.e. F/(C+F)=0.48, have the lowest shrinkage which indicates a non-linear effect of fly ash on this property. On the other hand, the shrinkage decreases in the mortars with lower water to binder ratio.

The moisture loss from the hydrated cementitious material is the main cause of the shrinkage, which is strongly suggested by the lower shrinkage which occurred in the mortar with more fly ash which is generally equivalent to only 0.3 of the replaced cement

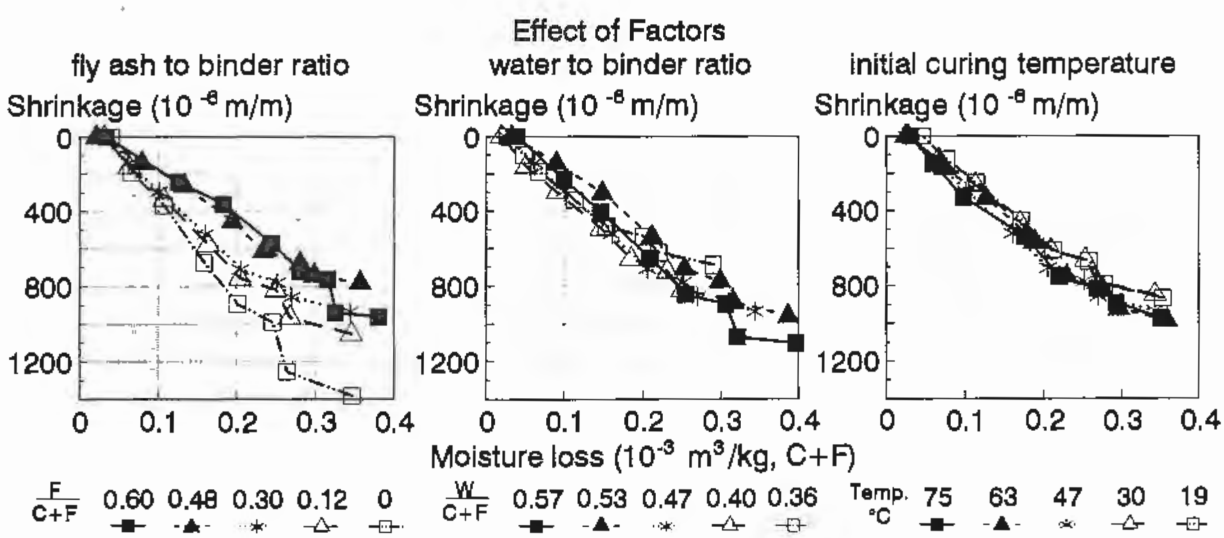

Figure 5. Factorial analysis of the data in Figure 2.

/10/. In addition, the higher curing temperature which enhances fly ash hydration as shown by Huang /12/ leads to, though less significantly, an enhanced shrinkage as is shown in Figure 2 (Mix 13 and 14) also supports this. However, Figure 2 shows that a slightly greater shrinkage is associated with the moisture loss from the mortar with a lower water to binder ratio, although it is well demonstrated that hydration is more advanced for the paste with a higher water to cement ratio /10, 11/. The factorial analysis (Fig.5) of the moisture loss-shrinkage data shows a similar dependence on the mix parameters, except that the effect of the water to binder ratio becomes very small in contrast to a more significant effect of the fly ash content.

Obviously, shrinkage is not only a function of the amount of moisture loss, but also the moisture state and the rigidity of the paste. Thus it is necessary to analyze the results by the mechanisms of drying and shrinkage.

4.1 Theories of free energy change and strain applied to shrinkage

Feldman /5/ stated that the moisture adsorption and desorption accompanied length-change of cement paste can be treated by Gibbs' equation. When vapour pressure changes from P_o to P ($P < P_i$), the free energy of the unit surface of adsorbent changes by

$$\Delta G = RT \int_{Pi}^{P} \Gamma \, d(\ln P) \qquad (1)$$

where Γ is the moles of water adsorbed on the unit area of surface of the adsorbent termed as "surface excess" /13/. For the data in this research Γ can be explicitly expressed as

$$\Gamma = W_e/\rho S_w V_m = V_e/S_w V_m \qquad (2)$$

where W_e is the moisture content in kg/kg of binder, ρ is the density of water in kg/m^3, S_w is the specific surface area in m^2/kg of binder, V_m is the molecular volume of water in m^3/mol, and V_e is the moisture content in m^3/kg of binder.

This change in free energy spontaneously creates a change in surface tension $\Delta\gamma^*$, i.e.,

$$\Delta\gamma^* = \Delta G \qquad (3)$$

$\Delta\gamma^*$ depends on the shrinkage (ϵ), and the bulk modulus (E). The latter is shown to be comparable to Young's modulus of elasticity /11/. This suggests the proportionality of shrinkage induced strain and the stress can be treated in the same way as that in material mechanics. E used later in this discussion mainly has the meaning of a proportionality factor between stress and strain, but not necessarily that of the Young's modulus.

To compress a solid (volume V_o) by exerting the same stress (σ) in all directions, the total energy needed is

$$U = \sigma^2/2E \qquad (4)$$

In three dimensions, the relation between stress and strain (ϵ)

reads /14/

$$\sigma = \frac{3 \cdot \epsilon \cdot E}{1-2\nu} \tag{5}$$

Thus

$$U = \epsilon^2 \frac{9E}{2\ (1-2\nu)^2} V_o \tag{6}$$

where ν is the Poisson ratio. On the other hand, the energy is consumed in decreasing the surface area of this volume, which can be proved to be equal to

$$U = \Delta\gamma^* \cdot \epsilon \cdot 2A_o \tag{7}$$

where A_o is the total area of the volume before pressing. Substitute equation (6) into equation (7) gives

$$\Delta\gamma^* = \epsilon \cdot \frac{9E}{4(1-2\nu)^2} \cdot \frac{V_o}{A_o} \tag{8}$$

This proves Bangham's empirical equation which states the linear relation between surface tension change and strain (c.f. /5/). Combining equations (1-3) with equation (8), we obtain

$$\epsilon = - \frac{4(1-2\nu)^2}{9E} S_o \frac{RT}{V_m} \int_{Po}^{P} \frac{V_e}{S_w} d(\ln P) \tag{9}$$

where $S_o = A_o/V_o$ in m^2/m^3. Obviously, $S_o/S_w = \rho_b$, density of binder in kg/m^3. Equation (9) explains only one part of the shrinkage, as Freyssinet /6/ proposed that the shrinkage is also strongly effected by capillary tension, which was later also stated by Powers. It states that the pressure across the curved meniscus surface (by Laplace - Kelvin equation)

$$\Delta P_w = - \frac{RT}{V_m} \cdot \ln(\frac{P}{P_o}) \tag{10}$$

where V_m is the molecular volume of water in m^3/mol, and P/P_o is the relative pressure ($100 \cdot P/P_o$ = RH), will exert on the adsorbent and thus induce strain. Substituting eq (5) into equation (10) and denote this strain as ϵ_{cap}, we have

$$\epsilon_{cap} = - f \cdot \Phi \cdot \frac{1-2\nu}{3E} \cdot \frac{RT}{V_m} \ln(\frac{P}{P_o}) \tag{11}$$

where Φ is the volumetric porosity of the adsorbent and f is the fraction of the pores with the meniscus built up. It is uncertain, however, how to estimate f. For the sake of simplicity, we assume that f is equal to the moisture fraction that is in equilibrium with the very relative pressure. The total shrinkage is the sum of these two effects: $\epsilon_t = \epsilon + \epsilon_{cap}$, numerically

$$\epsilon_t = \frac{1-2\nu}{3E}\cdot\frac{RT}{V_m}\left\{ \frac{4(1-2\nu)}{3}\int_{P_o}^{P} V_e d(\ln P) + f\cdot\Phi\cdot\ln(\frac{P}{P_o}) \right\} \quad (12)$$

where V_m = 18 x 10 $^{-6}$ m^3/mol. Thus the shrinkage vs. moisture loss curve may have some discontinuities, because capillary tension will be effective only in the RH range where the meniscus exist.

From equation (12), one can deduce that the shrinkage of mortar with a high volume of fly ash is due more to Gibbs free energy change than the capillary tension, because it loses a larger fraction of moisture at high RH /1/. This is also true for mortar with a higher water to binder ratio. On the other hand, mortar with a lower water to binder ratio has a larger fraction of smaller pores, therefore apparently when losing the same amount of moisture it shrinks more. But the more significant effect of fly ash compared to the water to binder ratio (Fig.2, 5) cannot be explained so simply. It has been widely demonstrated that even after a long hydration time the spherical shape of the ash particles still remains /1, SD/, which is due both to the low reactivity of fly ash and the existence of the inert minerals, e.g. mullite and quartz /M/ in the ash particles. It may be that these inert compounds behave as the rigid elements supporting the gel system and therefore the shrinkage is prohibited.

4.2 Bulk modulus from shrinkage data

From equation (12), one important material property, i.e., the bulk modulus of shrinkage (E) can be calculated based on the results of desorption and shrinkage isotherms. Figure 6 shows that the E value so calculated falls in the range of 10 to 40 GPa being higher at high RH. Especially at RH 85% the E value is significantly higher than that at lower RH. This result is in agreement where both the magnitude and trend are concerned with that of Beaudoin and Feldman /15/ who used quite another approach to estimate the E value. This effect can be explained by the incompressibility of water in the capillary, since the otherwise empty pore is certainly more compressible.

Zech and Setzer /17/ treated the dynamic modulus of elasticity (E_d) of a composite material by a statistical model (primarily proposed by Helmuth), and stated that for a two component material

$$E_d = \sum_{k=0}^{n} \frac{nE_1E_2}{k\cdot E_2 + (n-k)E_1} \cdot \frac{n!V_1^{n-k}(1-V_1)^k}{k!(n-k)!} \quad (13)$$

where, E_1 and V_1 are the E modulus and volume fraction of the component 1, and E_2 is the E modulus of the component 2, and n=3 /17/. It may be mentioned in the case of concrete, $n \geq 5$ gives better conformity to the experimental data /18/. It is evident that E_d increases with the increase in moisture saturation for RH $\geq$ ca. 40% /17/.

Some results from the dynamic modulus of elasiticity of the mortar prisms (same mix proportioning as used in this study) conditioned in different RH conditions are shown in Figure 7, which shows a

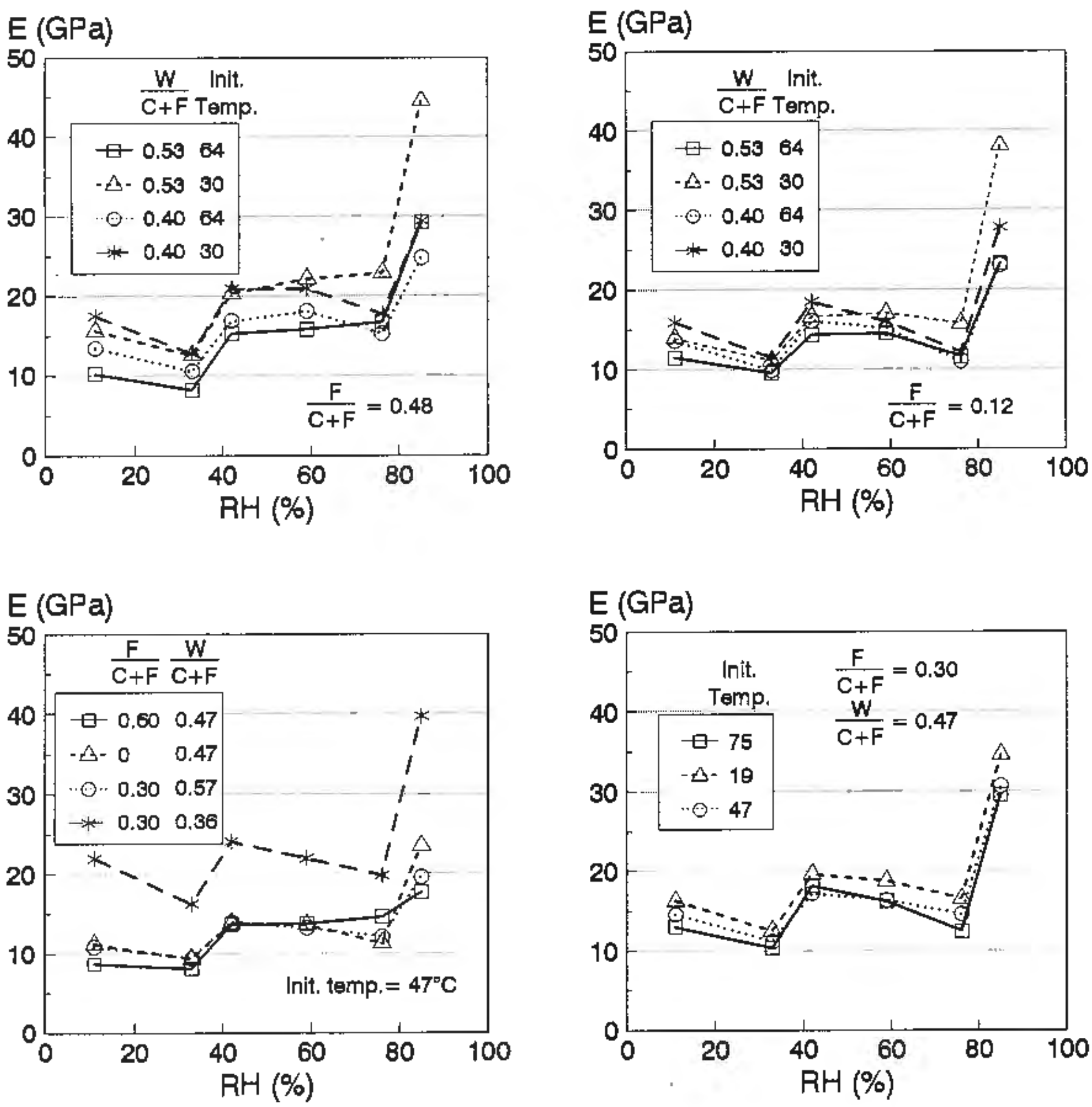

Figure 6. E modulus estimated by equation (12) on the base of the drying and shrinkage results. Mixes are the same as in Figure 1.

higher E_d at higher RH, similar to the case in the E modulus estimated by desorption and shrinkage isotherms.

The E value shown in Figure 6 tends to be slightly higher at 11% RH than at 33% RH, which is not readily explainable. At present, the author feels that this is due to the microcracks which occurred during drying at such a low humidity, which consumed the surface energy and thus compensate the shrinkage.

It is also seen that the E value is higher for mortar with a lower water to binder ratio and initially cured at a lower temperature. The replacement of cement with fly ash leads to a slightly lower E value. These are partly in agreement with the strength results. Besides, it is shown that the 28-day flexural strength of the mortars tested is about 8 to 10 MPa (Table I), while the E modulus in a medium dry condition is about 15 GPa (Fig.6), which results in strain 530 to 670 x 10^{-6} m/m. Observe that this is in full agreement with the shrinkage results. Thus it can be deduced that the tension caused by drying can lead to a stress which is sufficiently high to lead to microstructure failure.

It should be pointed out that the effect of the fly ash and water to binder ratio on shrinkage is not fully consistent with that on strength (c.f. Figure 1 with Figure 3). Thus the bulk modulus dominating shrinkage is not the same as that of the modulus of elasticity, though they fall in the same order of magnitude.

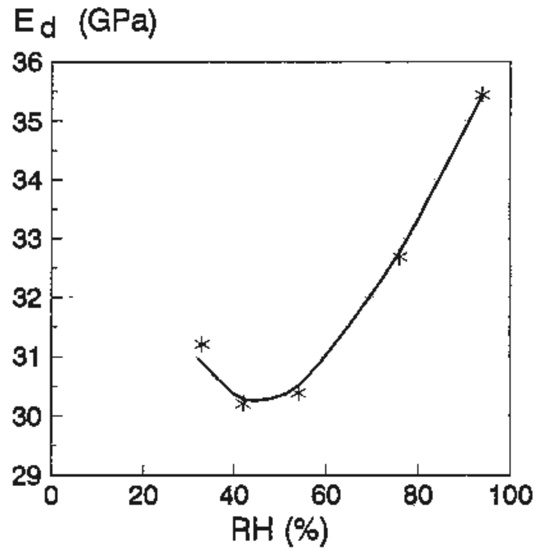

Figure 7. Dynamic modulus of elasticity at different RH.

5. CONCLUSIONS

From the study of drying shrinkage on mortar with different fly ash (Class F) content, water to binder ratio and initial curing temperature, the following conclusions can be drawn.

- The mortar with fly ash has a smaller shrinkage, especially when the amount of moisture loss is considered.

- The increase in water to binder ratio, though leads to higher shrinkage, its influence is mainly due to the higher moisture loss in the mortar.

- The mechanism of shrinkage is theoretically explained by the change in Gibbs free energy and the building-up of capillary tension. The derivation confirms the semi-empirical theory proposed by Bangham, i.e. the shrinkage is proportional to the change in surface tension.

- The bulk modulus of shrinkage calculated on the bases of desorption and shrinkage isotherms is of similar value compared to the Young's modulus of elasticity. It is a function of RH, i.e., being higher at higher RH. The E value is higher for mortar with a lower water to cement ratio, whereas it is slightly lower for mortar with more fly ash. A higher initial curing temperature results in a lower E value, but the effect is not very significant.

6. ACKNOWLEDGEMENTS

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Table I. Mix parameters and strength (MPa)

Mix No	$\frac{F}{C+F}$	$\frac{W}{C+F}$	Temp* (°C)	Flexural			Compressive		
				3d	7d	28d	3d	7d	28d
1	.48	.53	64	5.2	6.4	8.0	24.3	29.5	38.2
2	.48	.53	30	4.4	5.4	7.7	20.6	29.0	41.1
3	.48	.40	64	5.7	6.3	8.5	33.9	35.1	48.4
4	.48	.40	30	5.0	5.9	7.6	27.5	36.3	49.0
5	.12	.53	64	5.9	6.5	7.3	30.5	36.6	39.7
6	.12	.53	30	6.5	7.5	8.5	31.7	40.5	48.0
7	.12	.40	64	6.5	7.4	8.7	42.6	49.9	56.1
8	.12	.40	30	7.6	7.7	8.4	44.7	49.8	56.5
9	.60	.47	47	3.2	4.2	6.4	15.5	18.5	30.1
10	0	.47	47	8.0	8.2	9.0	44.1	46.2	56.5
11	.30	.57	47	4.8	6.2	8.0	26.6	30.7	40.0
12	.30	.36	47	7.1	7.6	10.0	43.9	47.6	52.3
13	.30	.47	75	6.2	7.3	7.6	37.5	41.8	44.7
14	.30	.47	19	6.1	6.7	8.3	27.9	37.8	50.3
15†	.30	.47	47	5.5	6.9	8.5	31.3	37.3	46.8

* 24 hours warm water treatment at 1 day.

† Average of 6 specimens of different batches.