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Volume change on first drying of hydrated Portland cement with and without admixtures

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**VOLUME CHANGE ON FIRST DRYING OF
HYDRATED PORTLAND CEMENT WITH
AND WITHOUT ADMIXTURES**

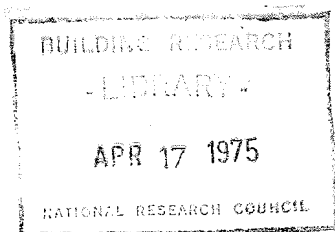
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R. F. Feldman and E. G. Swenson

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VOLUME CHANGE
ON FIRST DRYING OF HYDRATED PORTLAND CEMENT
WITH AND WITHOUT ADMIXTURES

R. F. Feldman and E. G. Swenson
Research Officers, Division of Building Research,
National Research Council of Canada
OTTAWA

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ABSTRACT

The effect of admixtures of several types on the volume change characteristics of portland cement pastes is reported. Samples were cut in the form of wafers and dried step by step through several humidities down to 40 per cent; other samples were dried to the d-dried state. Large first drying shrinkages were obtained with extra dosages of calcium lignosulphonate, hydroxy carboxylic acids, and triethanolamine. Below 40 per cent RH all samples showed similar behavior with further drying or rewetting. It is suggested that the effect of admixture is mainly one of degree of dispersion in terms of alignment of sheets and displacement of ends of sheets.

On examine l'effet de plusieurs genres d'adjuvants sur les caractéristiques de changement de volume des pâtes de ciment portland. Des échantillons taillés sous forme de gaufrettes sont séchés graduellement à des taux d'humidité diminuant jusqu'à 40 pour cent; d'autres échantillons sont séchés à l'état "d-dried". Des doses supplémentaires de lignosulfonate de calcium, d'acides hydroxycarboxyliques et de triéthanolamine produisent un premier retrait au séchage considérable. Au-dessous de 40 pour cent d'humidité relative tous les échantillons ont un comportement semblable lorsque le séchage se poursuit ou qu'il y a réhumidification. Les auteurs suggèrent que l'effet d'adjuvants en est surtout un degré de dispersion en termes d'alignement des feuilles et de déplacement du bout des feuilles.

Volume change or drying shrinkage is one of the least understood problems of concrete technology. Research continues to provide information of value in this area, but it has done little to increase basic knowledge. Some admixtures are known to increase drying shrinkage and creep when present in certain quantities (1 - 6), a fact that sometimes appears to be a further complication. It may well, however, help clarify the over-all drying shrinkage mechanism. The present paper presents the results of studies of drying shrinkage as a function of relative humidity, rate of drying, type of cement, water to cement ratio and admixture content; and draws conclusions with regard to the underlying reasons for shrinkage.

Experimental

Apparatus

A high vacuum apparatus consisting of three special cells, each capable of containing three samples, permitted study of nine samples at a time. The cells were equipped with optical windows to allow measurement of length change by means of optical extensometers on which the samples were mounted (7). Water vapor pressure was controlled by a water source at controlled temperature and was further measured by a gauge.

Materials

Samples were cut in thin wafers 1.2 mm thick, 1 cm wide, and 3 cm long from two Type I cements of total alkali 0.8 and 1.3 per cent. Samples were made at water-cement ratios* of 0.5 and 0.8 and cured for over a year; a number of them contained admixtures. In general, two doses of admixture were prepared, N referring to the recommended dosage and some multiple of it that might correspond to dosages for certain field situations (Table 1). The actual values are given in Appendix A. Admixtures included: two from the set-retarding water-reducing class, i. e. calcium lignosulphonate and a salt of a hydroxy carboxylic acid; two from the air-entraining class, i. e. salt of a sulphonated hydrocarbon and a neutralized vinsol resin; a commercial silicone; and a commercial triethanolamine. The calcium lignosulphonate preparation consisted of 0.4 per cent sugars and 4 per cent reducing bodies.

* Referred to as w/c

TABLE I. SHRINKAGE DATA

Admixture		Shrinkage %			Σ
Type	W/C	RH 100 \rightarrow 40	RH 15 \rightarrow 0	1 RR	M ² /GM
Standard	0.5	0.30 Slow	0.83	0.05	52
Standard	0.8	0.44 Slow	0.94	0.16	63
Silicone N	0.5	0.35 Slow	0.85	0.09	48
Silicone N	0.8	0.46 Slow	0.88	0.18	60
Silicone 2N	0.5	0.33 Slow	0.84		48
Silicone 2N	0.8	0.36 Slow	0.81		65
Vinsol Resin N	0.5	0.30 Slow	0.83	0.07	46
Vinsol Resin N	0.8	0.40 Slow	0.92	0.12	61
Vinsol Resin 4N	0.5	0.33 Slow			44
Vinsol Resin 4N	0.8	0.44 Slow			51
Vinsol Resin 4N	0.8	0.52 Fast			
Lignosulphonate N	0.5	0.34 Slow	0.82	0.07	52
Lignosulphonate N	0.8	0.50 Slow	0.93	0.16	67
Lignosulphonate 3N	0.5	0.64 Slow	0.80		56
Lignosulphonate 3N	0.8	0.94 Slow	0.92	0.60	70
Lignosulphonate 2N*	0.8	0.42 Fast	1.07		47
Lignosulphonate 3N*	0.8	0.46 Fast	1.05		54
Lignosulphonate 4N*	0.8	0.54 Fast	0.93		56
Lignosulphonate 3N	0.8	0.95 Fast			
Lignosulphonate 3N	0.8	0.87 Fast			
Lignosulphonate N	0.8	0.49 Fast			
Standard*	0.8	0.32 Fast			48
H-Carboxylic Acid N	0.5	0.33 Fast	0.86		63
H-Carboxylic Acid N	0.8	0.54 Fast	0.99		
H-Carboxylic Acid 2N	0.5	0.46 Fast	0.85		58
H-Carboxylic Acid 2N	0.8	0.61 Slow			62
H-Carboxylic Acid 2N	0.8	0.72 Fast			79
S-Hydrocarbon N	0.5	0.33 Fast			
S-Hydrocarbon N	0.8	0.47 Slow			51
S-Hydrocarbon 4N	0.5	0.31 Fast	0.83		45
S-Hydrocarbon 4N	0.8	0.47 Slow			65
Triethanolamine N	0.5	0.65 Fast			78
Triethanolamine N	0.8	0.59 Fast			75
Triethanolamine 2.5N	0.5	0.71 Fast	0.92		75
Triethanolamine 2.5N	0.8	0.80 Fast	0.93		91

* Higher Alkali Cement

Procedures

- (a) **Drying.** Two methods of drying were used; one, referred to as slow, involved exposing samples to 11 different humidities from 100 to 15 per cent RH for a total period of six months. The second, referred to as fast, was performed by exposing the samples directly to 40 per cent RH.* With fast drying for as little as four days shrinkage values were similar to those obtained by slow drying.
- (b) **Surface Area Measurements.** The samples were conditioned to 11 per cent RH for approximately one week, evacuated for several hours, and finally dried at 110°C for 3 hours. The surface area was obtained by means of nitrogen adsorption measurements, using Numinco apparatus.
- (c) **Other Measurements.** Samples conditioned to 15 per cent RH were dried by heating to 100°C for about 8 hours under vacuum. Shrinkage during drying was measured, as was length change on some samples during rewetting from 15 per cent to 100 per cent RH and partial second drying.

Results

Typical shrinkage curves for samples dried step by step by the slow method are presented in Figure 1. They include results for an admixture-free sample and for samples containing admixtures. Shrinkage on drying from 100 to 40 per cent RH is least for the admixture-free sample. (Between 40 and 15 per cent RH the shrinkage rate is relatively low.) The curve for the admixture-free sample prepared at a water-cement ratio of 0.5 is presented in Figure 2. On rewetting from 15 per cent RH at approximately one month per point the curve is not totally reversible. After exposure for eight months the length remains 0.05 per cent below the initial value. Second drying to 15 per cent shows a decrease in length relative to this point on first drying, and drying to 0 per cent RH produces a further shrinkage of 0.83 per cent. Results obtained for a normal dosage of a commercial silicone admixture at a water-cement ratio of 0.5 are shown in Figure 3. First drying shrinkage of 0.35 per cent is slightly more than for the standard, 0.30 per cent, and irreversible shrinkage is 0.09 per cent. Results for the vinsol resin at normal dosage are presented

* Relative humidity

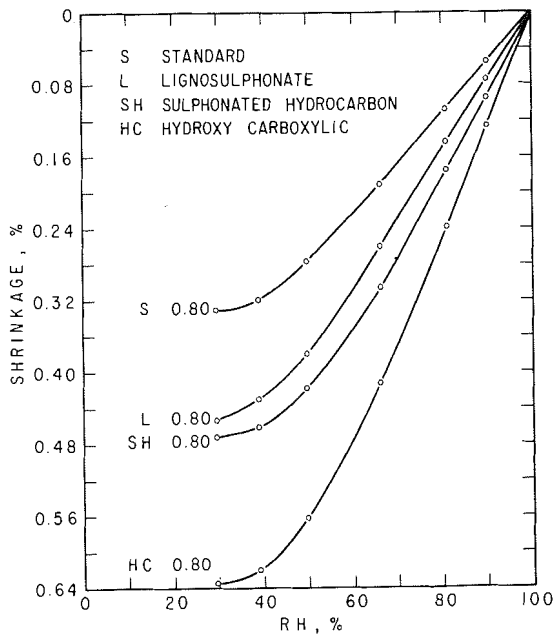


FIG. 1
Drying shrinkage versus
relative humidity, different
admixtures

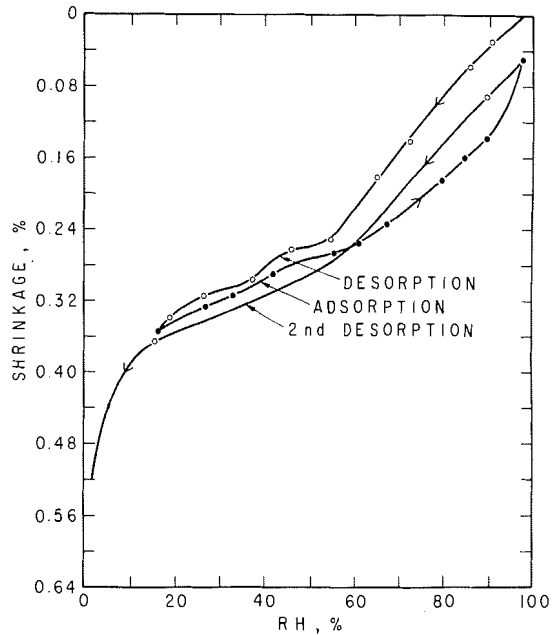


FIG. 2
Length change versus
relative humidity, cement
w/c 0.500, standard

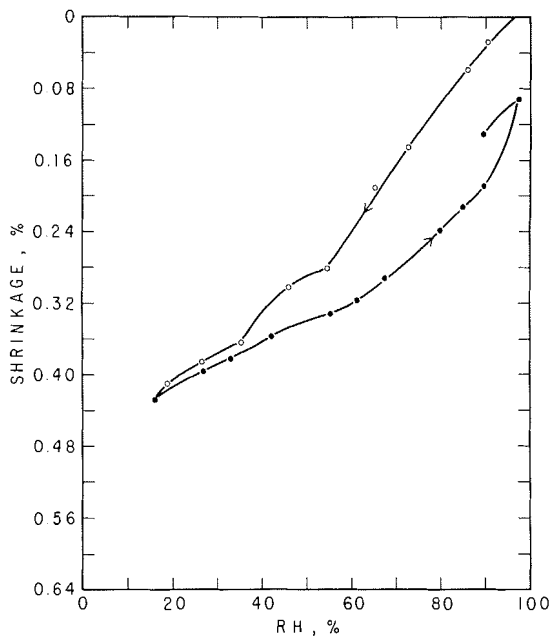


FIG. 3
Length change versus
relative humidity, cement
w/c 0.488, silicone

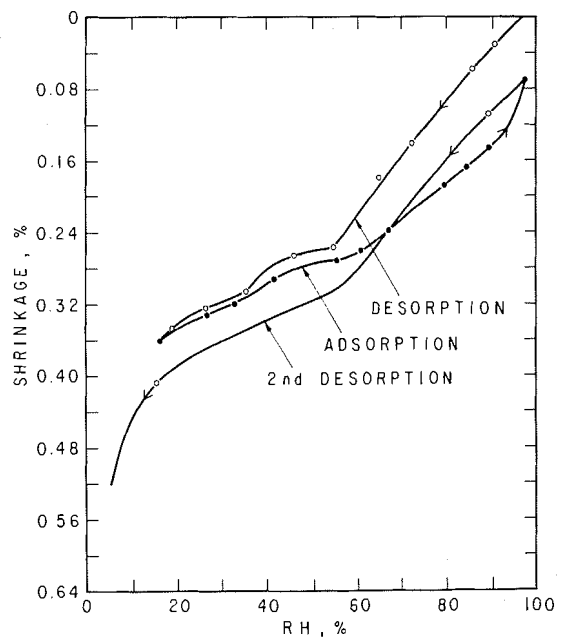


FIG. 4
Length change versus
relative humidity, cement
w/c 0.487, vinsol resin

in Figure 4. These are similar to previous values, 0.07 per cent irreversible shrinkage, and a larger decrease in length at 15 per cent on second drying relative to first drying. A shrinkage of 0.83 per cent on drying from 15 to 0 per cent RH is again recorded.

Results for the admixture-free samples and for those with three times normal dosage of calcium lignosulphonate mix prepared at a water-cement ratio of 0.8 are shown on Figure 5. Shrinkage on drying for the

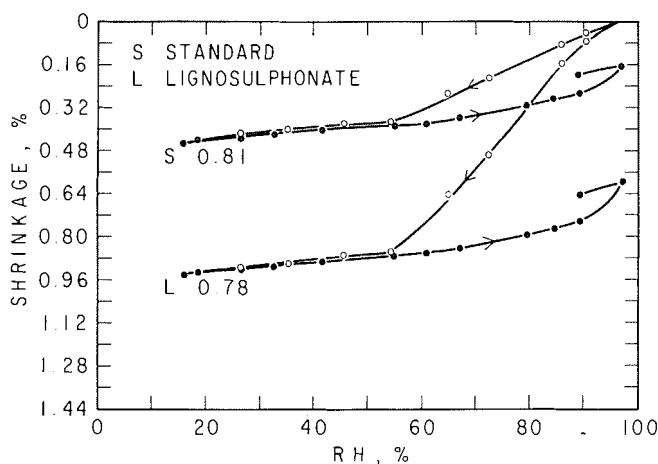


FIG. 5
Shrinkage and expansion
versus relative humidity

100 to 40 per cent RH range is 0.44 per cent for the standard and 0.94 for the calcium lignosulphonate sample. Residual shrinkages after rewetting are 0.16 and 0.60 per cent, respectively. Shrinkages for the same samples following drying from 15 to 0 are similar: 0.94 and 0.92 per cent, respectively.

All samples are listed in Table 1, with admixture content, water-cement ratio and various measured shrinkages. The average shrinkage on drying from 100 to 40 per cent RH for a water-cement ratio of 0.5 is 0.33 per cent (not including the higher than normal dosages and the triethanolamine samples). On the same basis, the average for the 0.8 water-cement ratio samples is 0.47 per cent. This increased shrinkage with increased water-cement ratio has been reported previously (8). As may be observed, three times the normal dosage of calcium lignosulphonate increases shrinkage to 0.64 and 0.94 per cent for the 0.5 and 0.8 water-cement ratios, respectively. For samples made from the higher alkali cement, however, such increase is not observed even at four times the normal dosage of admixture.

Little or no shrinkage increase was observed with any of the vinsol resin or sulphonated hydrocarbon air-entraining agents, although four times the normal dosage was used. Samples containing hydroxy carboxylic acid showed an increase to 0.54 per cent over the average of 0.47 per cent for water-cement ratio of 0.8 at a normal dosage and 0.61 per cent for twice the normal dosage. A shrinkage of 0.72 per cent was recorded at the fast rate of drying. (In another instance, 0.8 w/c, four times normal dosage of vinsol resin showed an increase to 0.52 per cent from 0.44 per cent for fast versus slow drying). At a water-cement ratio of 0.5 shrinkage increased from 0.33 to 0.46 per cent with twice normal dosage of hydroxy carboxylic acid.

Samples containing triethanolamine showed increased shrinkage at normal and 2.5 times normal dosage, 0.65 and 0.71 per cent, respectively, at w/c ratios of 0.5 and 0.59 per cent, and 0.80 per cent at a w/c ratio of 0.8.

Drying samples from 15 to 0 per cent RH resulted in a significant variation in shrinkage with w/c only; the average for a w/c ratio of 0.5 was 0.84 per cent and for one of 0.8, 0.94 per cent. This is independent of the effect of admixture and any shrinkage that occurred on first drying from 100 to 40 per cent RH. For example, with the sample containing three times normal dosage of calcium lignosulphonate prepared at w/c ratio of 0.8, where a first drying shrinkage of 0.94 per cent was recorded on drying from 100 to 40 per cent RH, the shrinkage on drying from 15 to 0 per cent RH was 0.92 per cent. This indicates that differences existing in the samples due to admixture do not persist once they have dried to 40 per cent RH. Figure 5 confirms this; after first drying to 53 per cent RH, the curves are similar for drying shrinkage below 53 per cent down to 15 per cent, and for rewetting. Thus irreversible shrinkage of 0.60 per cent was obtained for the calcium lignosulphonate sample.

Included in Table 1 is the surface area of each sample obtained by nitrogen adsorption: samples were conditioned first to 11 per cent RH and then by means of drying procedures described in the experimental section.

Figure 6 presents the plot of shrinkage from 100 to 50 per cent RH versus surface area, tending to indicate that the greater the surface area the larger the shrinkage.

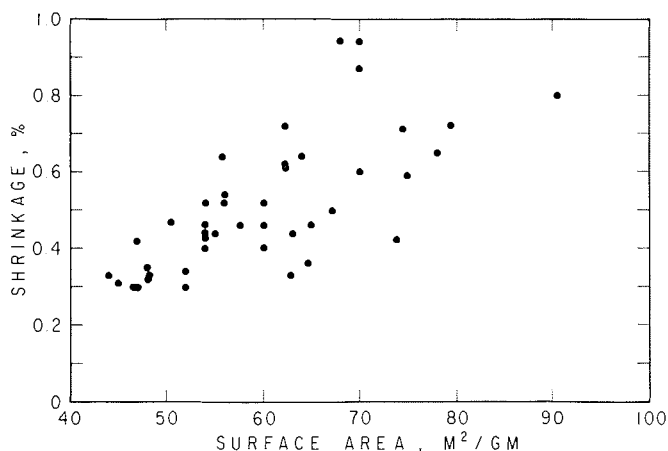


FIG. 6
Shrinkage versus surface
area for several admixtures

Discussion

Most of the results indicate that very large differences in shrinkage behavior of cement paste samples can be obtained on first drying to 40 per cent RH with the addition of certain amounts of different admixtures. Behavior subsequent to first drying is similar, indicating that the difference in drying shrinkage is not associated so much with a property of the morphology or chemical composition of the material as with its degree of dispersion. This concept has been discussed more specifically in a paper related to creep (9), where it is suggested that certain "creep sites" exist. When individual sheets condense into layered material, layering is incomplete, leaving gaps or open ends between sheets which come together on drying. The admixtures, it is thought, enhance this situation. Helium flow analysis on the 0.8 w/c sample of high dosage of calcium lignosulphonate indicates that there is no difference between this sample and samples without admixture after drying to 11 per cent RH.

The surface area studies show a rough correlation with first drying shrinkage; but the dispersed state exists before drying, and drying causes a coming together of sheets and thus a decrease in surface area. Measurement of surface area by nitrogen adsorption requires drying, so

that the measurement represents residual surface area and not initial surface area. It is expected that the greater the shrinkage the greater the reduction in area; that there would be better correlation if the area could be measured in the wet state. Nevertheless, samples that produced very high shrinkage had significantly higher surface areas.

Recent work by Morgan (4, 5), who obtained high creep rates with calcium lignosulphonate and triethanolamine additions, has confirmed some of these considerations.

Conclusions

1. Large first drying shrinkages may be obtained with extra dosages of calcium lignosulphonate, hydroxy - carboxylic acids or triethanolamine (even normal dosage for the latter).
2. On first drying, large shrinkage occurs down to 40 per cent RH; beyond this, all the samples indicate similar behavior, as in the following case:
 - drying from 40 to 15 per cent RH,
 - rewetting to 100 per cent RH,
 - helium flow and density measurements from 11 to 0 per cent RH,
 - drying from 15 to 0 per cent RH for all samples of the same water-cement ratio, regardless of admixture content.

The fact that these results can be obtained by mere drying to 40 per cent RH suggests that the effect of admixture is mainly one of degree of dispersion in terms of the alignment of sheets and displacement of ends of sheets. This concept has been discussed previously in terms of creep. Recent work has clearly shown increased creep through the use of admixtures of calcium lignosulphonate and triethanolamine.

3. Higher alkali cement reduces the effect of admixture on shrinkage, but probably also reduces the effect of admixture on the property for which it was intended (retardation of set).
4. There is indication of a relation between surface area determined by nitrogen adsorption and first drying shrinkage.

5. Shrinkage determined by means of step by step drying over a period of six months is not dissimilar to that determined over a period of four days on exposure to 40 per cent RH.
6. Rewetting for eight months at close to 100 per cent RH produced very slow re-expansion but irreversible shrinkage was the net result.

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Appendix A

Normal Dosages for Various Admixtures

Triethanolamine	0.2 per cent
Sulphonated hydrocarbon	0.0005 ml/gm
Vinsol resin	0.00069 ml/gm
Hydroxy carboxylic acid	0.0021 ml/gm
Lignosol	0.25 per cent
Silicone	0.10 per cent