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HELIUM FLOW CHARACTERISTICS OF REWETTED SPECIMENS OF DRIED HYDRATED PORTLAND CEMENT PASTE

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(Communicated by F. H. Wittmann)

ABSTRACT

In an effort to determine how and when water re-enters interlayer spaces the helium flow technique is applied to the dried hydrated portland cement system during re-exposure to water vapour. Two sets of samples at four water-cement ratios were exposed consecutively, to 11, 32, 42, 66, 84 and 100 per cent RH. After each exposure they were reconditioned to 11 per cent RH before measurements were made. Measurements were also taken following second drying.

Results show that water re-enters the interlayer structure after exposure to the lowest humidity. Measurements following second drying show that rewetting regenerates the process that occurred on first drying.

Afin de déterminer quand et comment l'eau pénètre de nouveau les espaces intercouches, on applique la méthode de flux d'hélium au système de ciment portland hydraté séché pendant que celui-ci est exposé de nouveau à la vapeur d'eau. On expose, l'un après l'autre, deux séries d'échantillons comportant quatre rapports eau/ciment à une humidité relative de 11, 32, 42, 66, 84, et 100 pour cent. Après chaque exposition, les échantillons sont reconditionnés à une humidité relative de 11 pour cent avant d'être mesurés. Des mesures sont prises également après le deuxième séchage.

Les résultats montrent que l'eau pénètre de nouveau la structure intercouche après exposition à l'humidité la plus faible. Les mesures prises après le second séchage montrent que le remouillage rétablit le processus qui se produit lors du premier séchage.

Introduction

A new experimental technique has recently been devised (1) whereby changes in solid and pores resulting from the removal of interlayer and physically adsorbed water can be followed. This is the helium flow technique. It has been applied (2) to hydrated portland cement and tricalcium silicate pastes as water was removed from the 11 per cent RH to the d-dry state. This work showed that small spaces in the systems are not narrow-necked, fixed-dimension pores but interlayer spaces that partially collapse when water is removed. Details regarding the sequence of collapse were obtained from these experiments.

It is the purpose of the present work to apply the helium flow technique to the dried hydrated portland cement system during rewetting to determine how and when water re-enters the interlayer spaces.

Experimental

Material

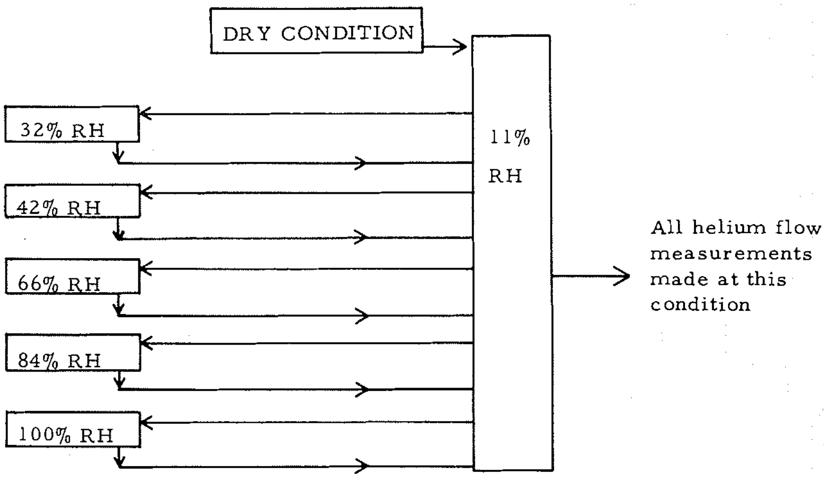
Type I portland cement was paste-hydrated for 2.5 years at water cement ratios of 0.4, 0.6, 0.8 and 1.0 in cylinders 3.2 cm in diameter. Discs 1.25 mm thick were cut and used as samples for helium flow measurements.

Two sets of samples were used at the four water-cement ratios, the total weight being about 15 gm for one set and 35 gm (for higher accuracy) for the other. One set was dried in steps to the previously determined (by conventional techniques) equivalent of the d-dried state (3) (8 to 9 per cent weight loss based on the dried state); the second set was dried, again in steps, to well beyond this condition (about 12 per cent weight loss). At each step of drying helium flow rate and solid volume were measured using the helium pycnometer as a function of weight loss (1).

General Procedure

The same samples were also used in the present work. They were exposed, consecutively, to 11, 32, 42, 66 per cent RH for periods of 30 to 40 days and to 84 and 100 per cent RH for 50 to 75 days. Following exposure at each humidity the samples were re-exposed to 11 per cent RH, usually for 35 to 65 days, when helium flow measurements were made. The conditioning sequence is illustrated in schema. After exposure to 100 per cent RH and conditioning at 11 per cent RH, the samples were dried again, this time in about four steps. The first series of samples was maintained at 11 per cent RH for 10 months, with periodic weighings for the 0.4 and 0.6 W/C, and for about 5 months for the 0.6 and 0.8 ratio pastes before second drying.

Extra precautions were taken to avoid carbonation of the cement. Exposure to different humidities took place in vacuum desiccators containing stirred salt solutions. The desiccators themselves were stored in airtight boxes containing NaOH to absorb any CO_2 that might be present. Levels of CO_2 in all samples, both before and after the experiments, were 2 per cent by weight.



SCHEMA

Results

Sorption Isotherms

Results for the first series of samples are presented in Tables I and II. The time at each condition and the weight change from the dried state are presented for each relative humidity condition. In this

TABLE I

W/C Ratio: 0.6					W/C Ratio: 0.4			
Reading No.	Time	Final Wt, gm	% Change from Dry	Condition	Reading No.	Time	Final Wt, gm	% Change from Dry
	2.5 yr			Hydration		2.5 yr		
1	117 days	16.2645	12.33	11% RH	1	56 days	18.6848	12.14
	40 days	14.4790	-	Incremental drying beyond d-dry		49 days	16.6627	-
				11%		4 days	17.2807	3.71
2	41 days	15.2587	5.39	11%	2	45 days	17.4416	4.68
	20 days	Estimate	-	42%		15 days	Estimate	-
3	9 days	15.5570	7.45	11%	3	29 days	17.7717	6.66
	26 days	Estimate	-	66%		27 days	Estimate	-
4	9 days	15.9138	9.91	11%	4	10 days	18.1393	8.86
	36 days	Estimate	-	84%		28 days	Estimate	-
5	28 days	16.2676	12.35	11%	5	11 days	18.6064	11.67
	27 days	16.2431	12.18	11%	-	-	-	-
	2 days	-	-	100%	-	-	-	-
6	4 hours	20.6531	35.74	Immersed in sat. $Ca(OH)_2$ solution	6	5 days	20.9562 (damp dry)	25.77
7	43 days	16.2636	12.33	11%	7	22 days	18.5148	11.12
8	14 days	16.2508	12.24	11%	8	9 days	18.5253	11.18
9	176 days	16.2215	12.03	11%	9	17 days	18.5120	11.10
10	26 days	16.2200	12.02	11%	10	7 days	18.5030	11.07
11				11%	11	22 days	18.4826	10.95
12				11%	12	234 days	18.4567	10.79

TABLE II

W/C Ratio: 0.8					W/C Ratio: 1.0			
Reading No.	Time	Final Wt (gm)	% Change from Dry	Condition	Reading No.	Time	Final Wt (gm)	% Change from Dry
	2.5 yr			Hydration		2.5 yr		
1	162 days	13.3225	8.88	11% RH	1	202 days	13.1860	8.86
	31 days	12.2365	-	Incremental drying to d-dry.		22 days	12.1132	-
2	38 days	12.8266	4.82	11%	2	70 days	12.6701	4.60
	-	-	-	32%		14 days		
	-	-	-	11%	3	82 days	12.7417	5.19
	35 days			42%		16 days		
3	32 days	13.0282	6.47	11%	4	33 days	12.8016	5.68
	87 days			66%		30 days		
4	24 days	13.2640	8.40	11%	5	35 days	13.1052	8.19
	29 days			84%		32 days		
5	56 days	13.4133	9.62	11%	6	37 days	13.3630	10.32
	8 days	-	-	100%		8 days	-	-
6	4 days	19.0001	55.27	Immersed in sat. $Ca(OH)_2$ solution	7	5 hr	20.9043 (damp dry)	72.57
	-	-	-	32%	8	70 days	13.2828	9.66
7	35 days	13.3585	9.17	11%	9	40 days	13.1815	8.82
8	51 days	13.3485	9.09	11%	-	-	-	-
9	80 days	13.3393	9.02	11%	-	-	-	-

series only the weights at 11 per cent RH, after exposure to the various conditions and following return to the 11 per cent condition, were recorded. For the 0.4 W/C ratio paste, first drying at 11 per cent RH was continued for 56 days; a level of 12.14 per cent above the subsequently obtained dry state (beyond d-dry) was reached. On rewetting at 11 per cent RH for 49 days, 4.68 per cent weight was regained. After each exposure to higher humidities, more weight was retained after each drying at 11 per cent RH. Following immersion in saturated $Ca(OH)_2$ solution, in which the sample lost some weight due possibly to leaching (compare readings Nos. 5 and 7), the sample was maintained at 11 per cent RH for a total of 311 days. During this time readings Nos. 7 to 12 were obtained. Very slight weight loss was recorded, and this resulted in a major hysteresis between rewetting, 4.68 per cent water content and second drying to 10.79 per cent. A similar result was obtained for the 0.6 W/C ratio paste; first drying at 11 per cent RH (12.33 per cent moisture above dry state) was continued for 117 days before final drying commenced. The sample weight at 11 per cent RH increased after each exposure to higher humidities and subsequent return to 11 per cent RH. Finally, after exposure to 100 per cent RH and conditioning for 259 days at 11 per cent RH, the sample weight was 12.02 per cent above that at the dry level, indicating that the sample had almost completely regained all the water lost at the first-dry position. Readings at intermediate points show that weight loss had ceased. The reading after first re-exposure at 11 per cent RH for 41 days was 5.39 per cent, resulting in a large hysteresis. Results for the samples prepared at W/C ratios of 0.8 and 1.0 are presented in Table II. These samples were only dried to the equivalent of d-dry. The results are essentially the same as for the other samples. Features that differ are (a) the smaller hysteresis, since not as much water was removed, and (b) slightly more water retained at the final 11 per cent RH position than at the initial 11 per cent RH position before final drying.

Figure 1 (A, B, C) shows the complete history of drying and wetting, including times at each condition, for the second series of samples of 0.4, 0.6 and 0.8 W/C, respectively. Pastes with 0.4 and 0.6 W/C ratio were

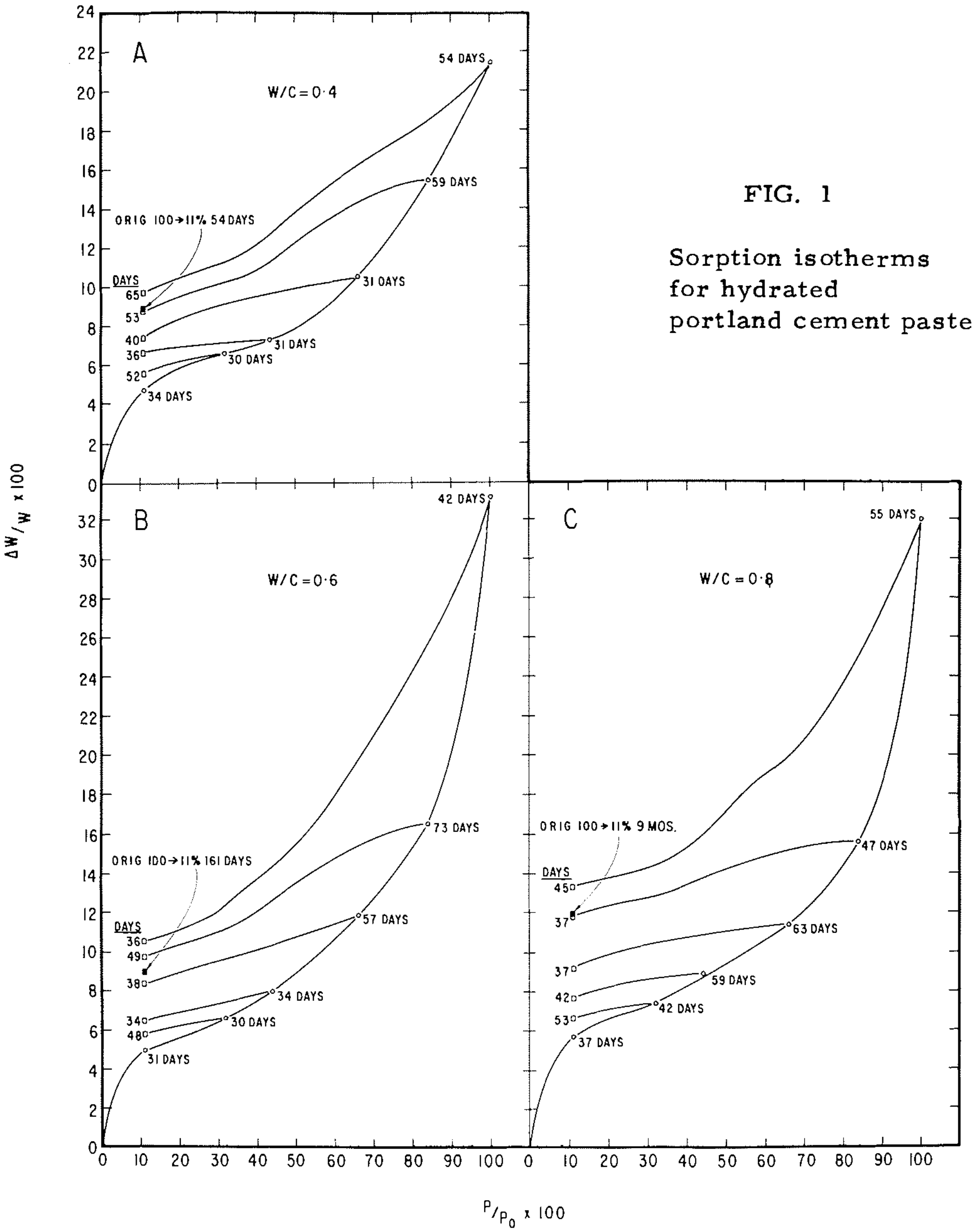


FIG. 1

Sorption isotherms for hydrated portland cement paste

taken to the equivalent of the d-dry state; that with 0.8 W/C was dried further. Consequently, the latter sorbed more on rewetting to 11 per cent RH than the other two. Comparison of series I and II at the same W/C ratios shows that samples dried the most regained the most weight. The amount re-sorbed was 4.75, 4.96 and 5.69 per cent at W/C ratios of 0.4, 0.6 and 0.8, respectively; the amount removed was 8.88, 9.04 and 11.88 per cent, respectively. At each W/C ratio in the second series more water was retained on the samples after exposure to 100 per cent RH and final drying to 11 per cent RH than at 11 per cent RH on first drying. This, in fact, was true after exposure at 84 per cent RH for the 0.6 W/C ratio specimens. The latter fact, as well as the magnitude of the effect and length of time during which the samples were hydrated, 2.5 years, eliminates the possibility that the excess is due to reaction of unhydrated material.

It is clear from the points at 11 per cent RH that sorption is largely irreversible, as has been shown previously (3). The lines joining the points on the sorption curve and the subsequent 11 per cent RH are the "scanning curves." The length of time at each point shows clearly that the scanning curves are not the result of a non-equilibrium situation.

Helium Inflow in Rewetted Samples

Figure 2 (A, B, C) shows helium inflow versus time for 0.6 W/C ratio dried beyond d-dry, 0.6 W/C ratio d-dried, and 0.8 W/C ratio d-dried. Each of the figures gives the flow curve for the final position of first drying and curves for the samples exposed to various humidities and redried to 11 per cent RH.

The following are the main features of these rewetting curves:

1. Helium flow into the samples increases after they are equilibrated with 11 per cent RH. A Type II curve is formed. (Curves of various types have been discussed previously (1).)

2. On exposure to higher relative humidities and redrying to 11 per cent RH, there is a further increase in helium flow rate and total inflow after 40 hr.

3. Helium flow rates continue to increase with relative humidity up to 100 per cent RH, although they level off later, leading to a decrease in total inflow in relation to previous curves. This yields a Type I curve, but helium inflow is greater than the value for the original first dried condition at 11 per cent RH.

4. Helium flow into the samples on drying and rewetting is not a simple function of moisture content. Plots of helium inflow at 40 hr versus weight

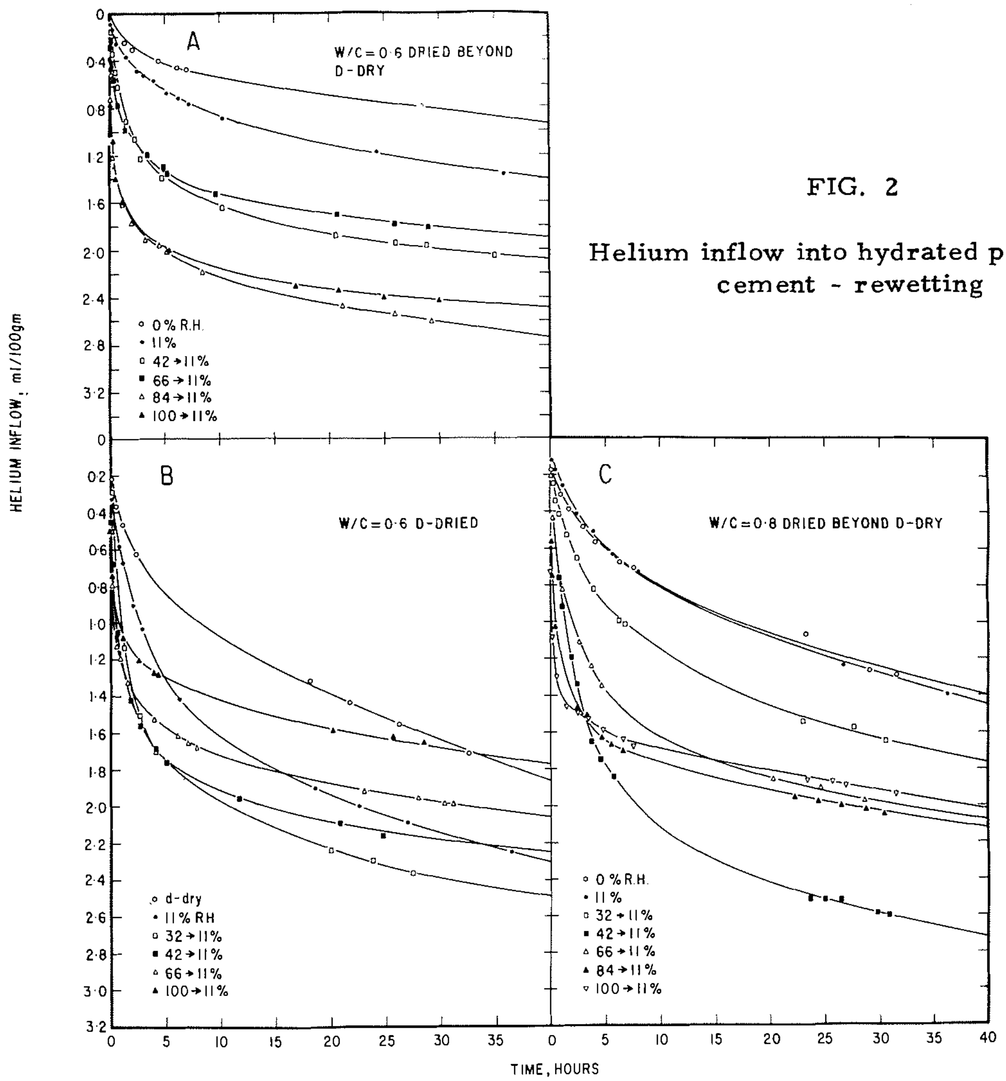


FIG. 2

Helium inflow into hydrated portland cement - rewetting

change (Figures 3 and 4) show different paths between the drying and rewetting processes. First drying, rewetting, and second drying are shown on these plots. (Drying curves are explained in Reference 1.)

In all cases, a maximum is obtained on rewetting, probably due to two opposing effects, one of reopening layers and creating space, the other of filling this space with H_2O molecules and thus preventing an equal amount of helium from entering. As each point is equilibrated at 11 per cent RH, each condition is the same with regard to externally adsorbed water, that is, approximately one monolayer.

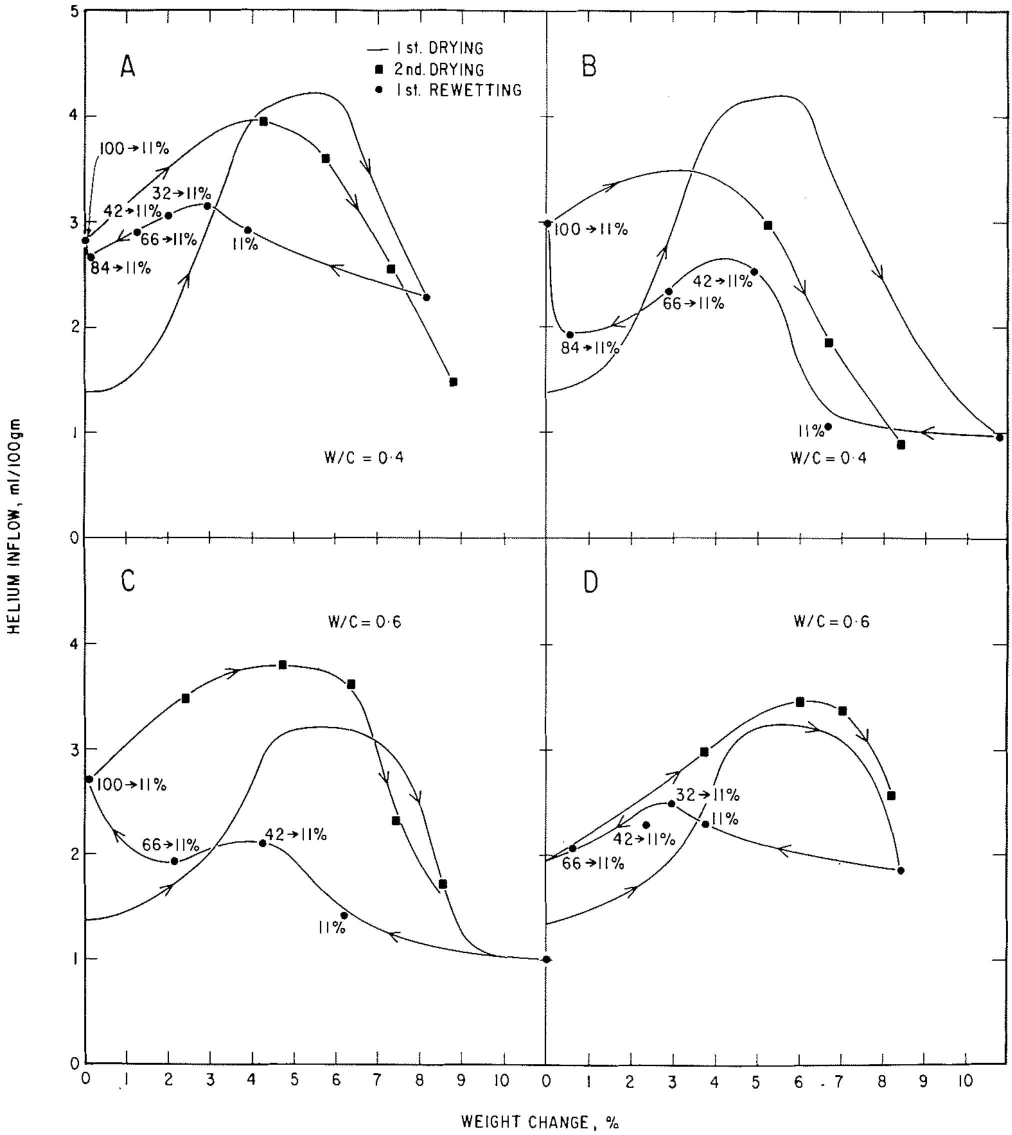


FIG. 3

Helium inflow at 40 hours vs weight change

The rewetting curves for the two levels of drying are not the same. The first point at 11 per cent RH for the sample dried beyond d-dry does not have as much increase in helium inflow as that d-dried only, although more water was sorbed on the former sample. The fact that sorption on the sample was accompanied by a large increase in density (4) showed that the water entered the interlayer structure but that its opening action to allow a greater inflow of helium together with rehydration water molecules was not so large. For

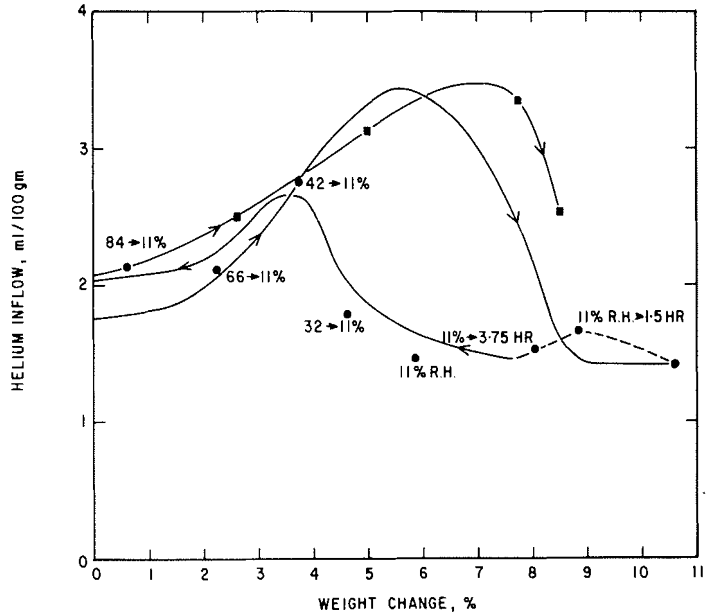


FIG. 4

Helium inflow vs weight change, W/C = 0.8

the 0.6 W/C ratio paste dried beyond d-dry the inflow increase was quite large.

In some instances it may be observed that exposure at 84 per cent RH produced increased helium inflow after a reduction from the maximum, which occurred at 32 per cent RH for the d-dried and at 42 per cent RH for samples dried beyond this point. This fact seems to be associated with the increased solid volume obtained during the behaviour just described (4, 5).

Second Drying

The helium inflow versus time behaviour for second drying is similar qualitatively to that of first drying. This is shown on Figure 5 for the 0.6 W/C paste, second series. It is evident that type I, II, and III curves are also produced for second drying. Total inflow after 40 hr versus weight change curves are included for second drying on Figures 3 and 4, where it may be seen that all essential features of first-drying are reproduced, especially the abrupt collapse after a certain weight loss (1). This confirms the hypothesis that water re-enters the interlayer spaces and re-expands the layer structure. It is evident, however, from the large irreversible contractions

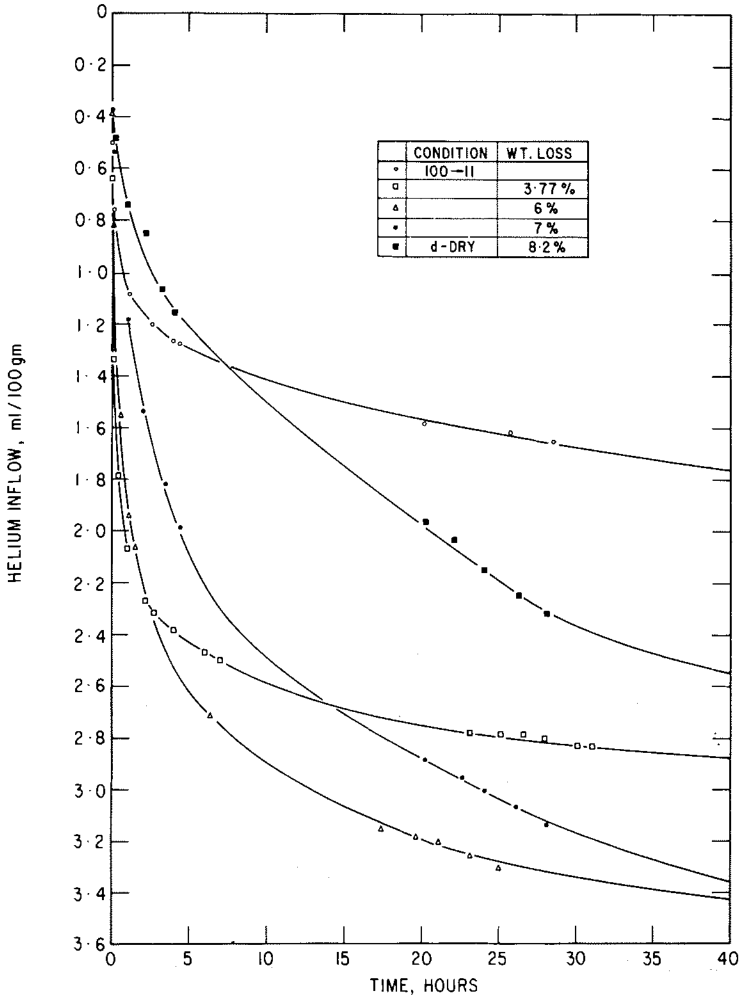


FIG. 5
Helium inflow for 0.6 W/C hydrated cement paste - 2nd drying

observed (5) that other phenomena besides re-entry and re-exit of interlayer water take place on rewetting and second drying.

Discussion

Previous studies (1, 2) utilizing this technique have shown that the spaces responsible for helium flow are interlayer spaces and that they exclude nitrogen but allow penetration by water. The present work now shows by the increased helium inflow after exposure of d-dried samples and samples dried beyond 11 per cent RH that interlayer water partially re-enters at this humidity, and re-enters fully by 100 per cent RH.

The total inflow after 40 hr versus weight change curve for drying and wetting shows, as did length change measurements, that there is a hysteresis in the exit and entry of interlayer water. This was predicted and described by a previous model of hydrated portland cement (3). Second drying characteristics are similar to those of first drying despite changes occurring in the paste in terms of length change and surface area due to drying and wetting cycles (5), but this is ascribed to further aggregation of sheets and formation of layers (5).

Conclusion

1. Irreversibility of sorption and validity of scanning curves are again confirmed.
2. Water re-enters interlayer positions after exposure to humidities as low as 11 per cent RH.
3. The helium inflow results for rewetting are different from those for removal of water, as was expected from the model of hydrated portland cement for dehydration and rehydration of interlayer water.
4. Helium flow curves on second drying are qualitatively similar to those of first drying. Rewetting regenerates helium inflow and in some cases larger values are recorded than for first drying.

Acknowledgment

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