By: Dr. Shamshad Ahmad

LECTURE NO. 9

VOLUME OF PRODUCTS OF HYDRATION & MECHANICAL STRENGTH OF CEMENT GEL

Objectives:

- To explain how to determine the volume of following products at different stages of hydration:
  - solid products of hydration,
  - gel water
  - hydrated cement
  - un-hydrated cement
  - capillary pores
  - capillary water
  - empty capillary pores
  - gel/space ratio
- To explain the effect of w/c ratio on the degree of hydration
- To explain the effect of w/c ratio and degree of hydration on capillary segmentation
- To explain mechanical strength of cement gel

VOLUME OF PASTE AT DIFFERENT STAGES OF HYDRATION

- ***Volume of paste at 0% hydration:***

  = absolute volume of dry cement + volume of water added to the mix

- ***Volume of partially hydrated paste:***

  = volume of un-hydrated cement + volume of the solid products of hydration + volume of gel water + volume of capillary water + volume of empty capillary pores

- ***Volume of 100% hydrated paste:***

  = volume of the solid products of hydration + volume of gel water + volume of capillary water + volume of empty capillary pores

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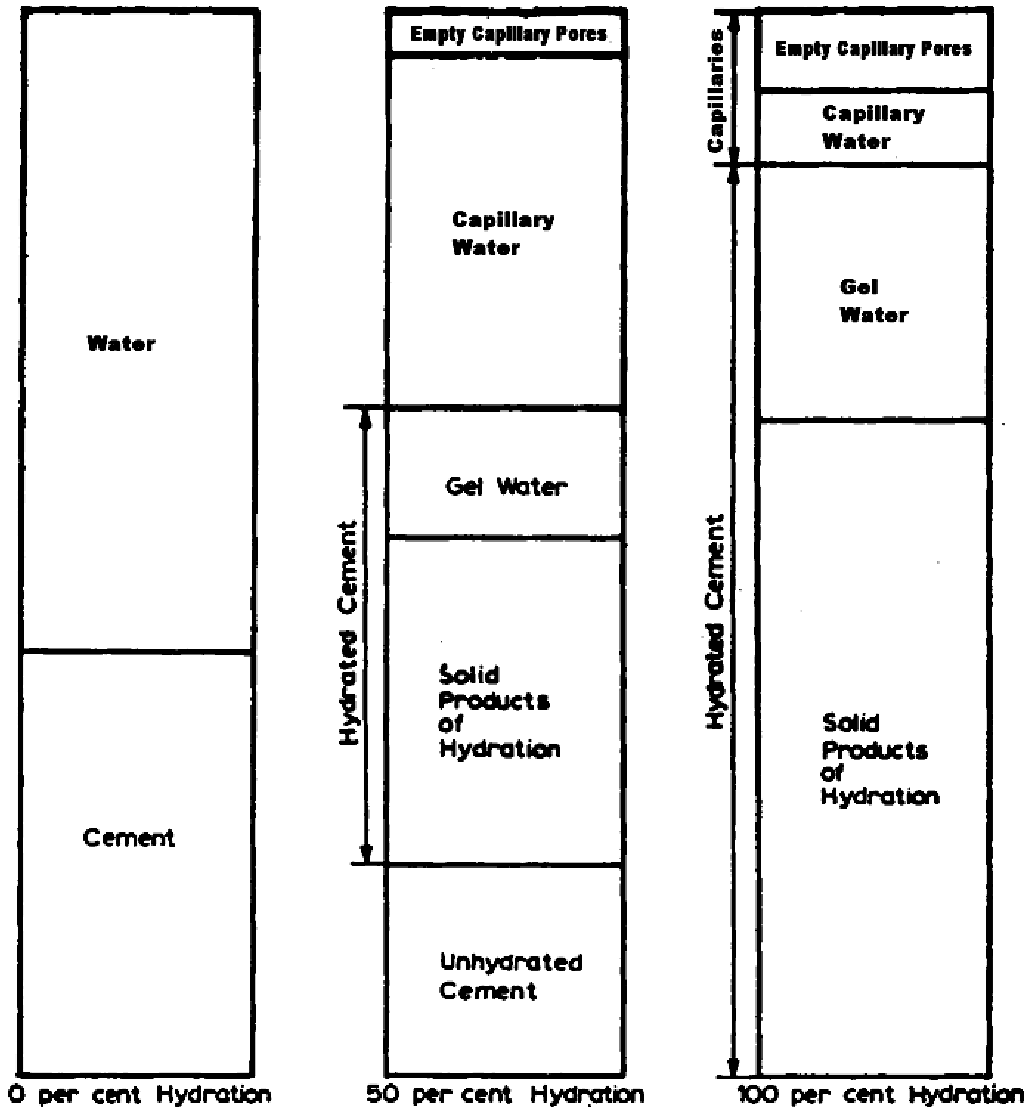
VOLUME OF PASTE AT DIFFERENT STAGES OF HYDRATION



Diagrammatic representation of the volumetric proportions of cement paste at different stages of hydration

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EXPRESSIONS OF THE PARAMETERS USED TO CALCULATE VOLUME OF PASTE AT DIFFERENT STAGES OF HYDRATION

Eq.1

Absolute volume of total dry cement added, V_{tc}

= weight of total dry cement added /specific weight of dry cement (3150 kg/m^{3}or 3.15 g/cm^3 or 3.15 g/ml)

Eq. 2

Absolute volume of dry cement *actually hydrated*, V_{cah}

=weight of dry cement *actually hydrated* /specific weight of dry cement (3150 kg/m^{3}or 3.15 g/cm^3 or 3.15 g/ml)

Eq.3

Volume of total water added, V_{tw}

= volume of combined or non-evaporable water ($V_{n\text{-}ew}$) + volume of gel water (V_{gw}) + volume of capillary water (V_{cw}), if any

Eq.4

Weight of non-evaporable water, $W_{n\text{-}ew}$

=23 % of the mass of dry cement *actually hydrated*

Eq.5

Volume of non-evaporable water, $V_{n\text{-}ew} = \rho_w \times W_{new}$

ρ_w = density of water = 1000 kg/m^3 or 1g/cm^3 or 1 g/ml

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EXPRESSIONS OF THE PARAMETERS USED TO CALCULATE VOLUME OF PASTE AT DIFFERENT STAGES OF HYDRATION

Eq.6

Volume of solid products of hydration, $V_{sp} = V_{cah} + 0.746\, V_{n\text{-}ew}$

Eq.7

Volume of gel water (V_{gw}) may be calculated using the following equation:

$$\frac{V_{gw}}{V_{gw} + V_{sp}} = 0.28\,(\text{i.e. gel porosity})$$

Eq.8

Volume of capillary water, $V_{cw} = V_{tw} - V_{n\text{-}ew} - V_{gw}$

Eq.9

Water/cement ratio of paste (by mass)

= mass of dry cement/mass of total water added

Eq.10

Water/cement ratio of paste (by volume)

= volume of dry cement/volume of total water added

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EXPRESSIONS OF THE PARAMETERS USED TO CALCULATE VOLUME OF PASTE AT DIFFERENT STAGES OF HYDRATION

Eq.11

Volume of hydrated cement, V_{hc} (about $>2\times V_{cah}$) = $V_{sp} + V_{gw}$

Eq.12

Volume of un-hydrated cement, $V_{uc} = V_{tc} - V_{cah}$

Eq.13

Volume of products of hydration per unit of dry cement = V_{hc}/V_{cah}

Eq.14

Volume of capillary pores, V_{cp} (*i.e. decrease in the initial volume of the mixture of cement and water after hydration*)

$= V_{cah} + V_{tw} - V_{hc}$ = volume of empty capillary pores (V_{ecp}) + V_{cw}

Eq.15

Gel/space ratio

$= V_{hc}/(\text{total volume of paste} - V_{uc})$

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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

Example # 1

For complete hydration of 100 g of dry cement, determine the w/c ratio of the mix, volume of products of hydration, and gel space ratio.

Solution:

$$\text{For complete hydration, } V_{tc} = V_{cah} = \frac{100 \text{ g}}{3.15 \text{ g/ml}} = 31.8 \text{ ml}$$

$$\text{Mass of non-evaporable water, } W_{n-ew} = 0.23 \times 100 = 23 \text{ g}$$

$$\therefore \ V_{n-ew} = 23 \text{ ml}$$

$$V_{sp} = V_{cah} + 0.746 V_{n-ew} = 31.8 + 0.746 \times 23 = 48.9 \text{ ml}$$

$$V_{gw} \text{ may be found as:} \frac{V_{gw}}{V_{gw} + 48.9} = 0.28 \ \Rightarrow \ V_{gw} = 19 \text{ ml}$$

$$\text{Assuming that there is no water in capillary pores (i.e., } V_{cw} = 0\text{),}$$

$$V_{tw} = V_{n-ew} + V_{gw} = 23 + 19 = 42 \text{ ml}$$

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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

From previous slide, $V_{cah} = 31.8$ ml; $V_{gw} = 19$ ml; $V_{tw} = 42$ ml

$$\therefore \text{ w/c ratio (by volume)} = \frac{42 \text{ ml}}{31.8 \text{ ml}} = 1.32 \text{ and}$$

$$\text{w/c ratio (by mass)} = \frac{42 \text{ g}}{100 \text{ g}} = 0.42$$

Volume of hydrated cement,

$$V_{hc} = V_{sp} + V_{gw} = 48.9 + 19 = 67.9 \text{ ml}$$

Volume of hydrated cement for 1 ml of dry cement

$$= \frac{V_{hc}}{V_{cah}} = \frac{67.9}{31.8} = 2.13 \text{ ml}$$

$$V_{cp} = (V_{cah} + V_{tw}) - V_{hc} = (31.8 + 42) - 67.9 = 5.9 \text{ ml}$$

$$\text{gel/space ratio } = \frac{67.9}{42 + 31.8} = 0.92 \text{ (by volume)}$$

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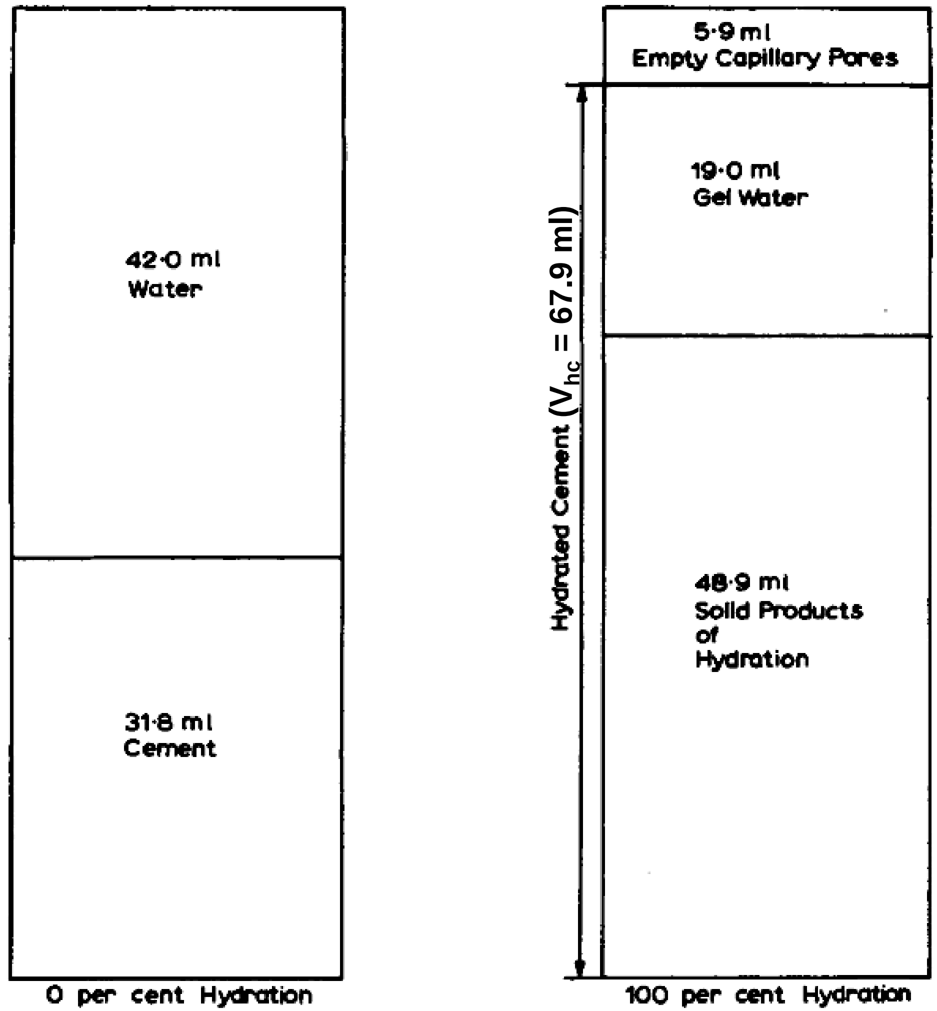
EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS



Diagrammatic representation of volume changes on hydration of cement paste with a water/cement ratio of 0.42

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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

Example # 2

100 g of cement is mixed with water corresponding to a w/c ratio of 0.38 by mass. Determine the volume of hydration products, volume of un-hydrated cement, and gel/space ratio.

Solution:

Let x g of cement (out of 100 g) is hydrated

$$V_{cah} = \frac{x}{3.15} \text{ ml}; \; W_{n-ew} = 0.23x;$$

$$V_{n-ew} = 0.23x \text{ ml}$$

$$\text{w/c} = 0.38 = \frac{W_{tw}}{W_{tc}}$$

$$\Rightarrow W_{tw} = 0.38 \times 100 = 38 \text{ g}$$

$$\therefore \; V_{tw} = 38 \text{ ml}$$

$$V_{sp} = V_{cah} + V_{n-ew}$$

$$= \frac{x}{3.15} + (0.23x) \times 0.746$$

$$= 0.489x \text{ ml}$$

We have:

$$\frac{V_{gw}}{V_{gw} + V_{sp}} = 0.28$$

$$\Rightarrow V_{gw} = 0.28(0.489x + V_{gw})$$

$$\Rightarrow V_{gw} = 0.19x$$

Assuming $V_{cw} = 0$

$$V_{n-ew} + V_{gw} = V_{tw}$$

$$0.23x + 0.19x = 38 \qquad \Rightarrow x = 90.47 \text{ g}$$

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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

$$x = 90.47 \text{ g}$$

$$V_{cah} = \frac{x}{3.15} = \frac{90.47}{3.15} = 28.72 \text{ ml}$$

$$V_{uc} = \frac{W_{tc}}{3.15} - V_{cah} = \frac{100}{3.15} - 28.72 = 3.02 \text{ ml}$$

$$V_{sp} = 0.489x = 0.489 \times 90.47 = 44.23 \text{ ml}$$

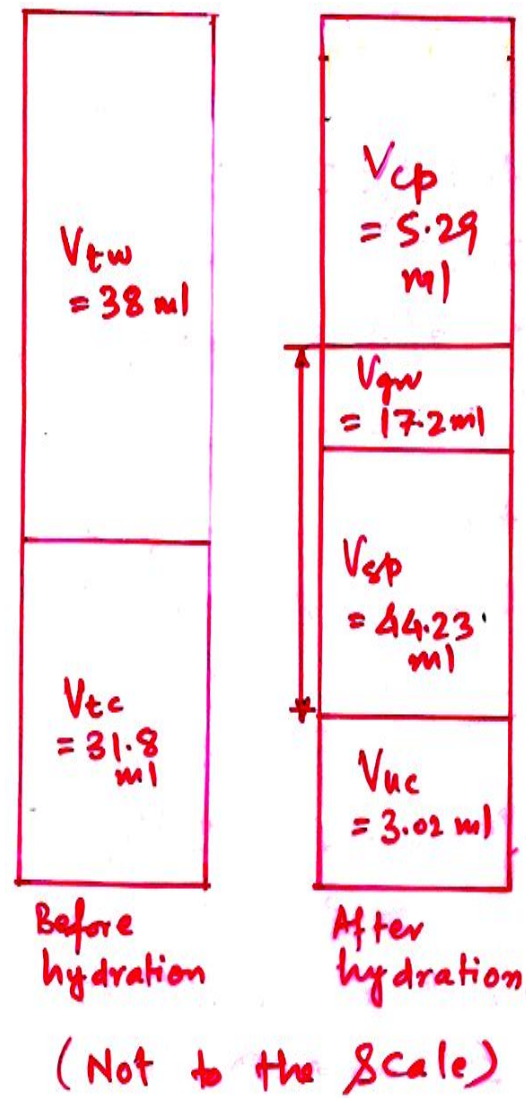
$$V_{gw} = 0.19x = 0.19 \times 90.47 = 17.20 \text{ ml}$$

$$V_{hc} = V_{sp} + V_{gw} = 44.23 + 17.20 = 61.43 \text{ ml}$$

$$V_{cp} = (V_{cah} + V_{tw}) - V_{hc}$$

$$= (28.72 + 38) - 61.43 = 5.29 \text{ ml}$$

$$\text{gel/space ratio} = \frac{V_{hc}}{V - V_{uc}} = \frac{61.43}{(31.8 + 38) - 3.02} = 0.92$$



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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

Example # 3

126 g of cement is mixed with water corresponding to a w/c ratio of 0.475 by mass. Determine the volume of hydration products and gel/space ratio (i) for 50% hydration and (ii) for 100% hydration.

Solution:

(*i*) For 50% Hydration:

$$W_{cah} = \frac{126}{2} = 63 \text{ g}; \; V_{cah} = \frac{63}{3.15} = 20$$

$$W_{n-ew} = 0.23 \times 63 = 14.5 \text{ g}$$

$$\therefore V_{n-ew} = 14.5 \text{ ml}$$

$$V_{sp} = V_{cah} + 0.746 V_{n-ew}$$

$$= 20 + 0.746 \times 14.5 = 30.8 \text{ ml}$$

$$V_{gw} = 0.28(V_{gw} + 30.8)$$

$$\Rightarrow V_{gw} = 11.98 \text{ ml}$$

$$W_{tw} = 126 \times 0.475 = 59.85 \text{ g}$$

$$\therefore V_{tw} = 59.85 \text{ ml}$$

$$V_{cw} = V_{tw} - V_{n-ew} - V_{gw}$$

$$= 59.85 - 14.5 - 11.98 = 33.37 \text{ ml}$$

$$V_{hc} = V_{sp} + V_{gw} = 30.8 + 11.98 = 42.78 \text{ ml}$$

$$V_{uc} = V_{tc} - V_{cah} = \frac{126}{3.15} - 20 = 20 \text{ ml}$$

$$V_{cp} = (V_{cah} + V_{tw}) - V_{hc}$$

$$= (20 + 59.85) - 42.78 = 37.07 \text{ ml}$$

$$V_{ecp} = V_{cp} - V_{cw} = 37.07 - 33.37 = 3.7 \text{ ml}$$

$$\text{gel/space ratio} = \frac{V_{hc}}{V - V_{uc}}$$

$$= \frac{42.78}{(40 + 59.8) - 20} = 0.536$$

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EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS

(ii) For 100% Hydration:

$$W_{cah} = 126 \text{ g}; \; V_{cah} = \frac{126}{3.15} = 40 \text{ ml}$$

$$W_{n-ew} = 0.23 \times 126 = 28.98 \text{ g}$$

$$\therefore V_{n-ew} = 28.98 \text{ ml}$$

$$V_{sp} = V_{cah} + 0.746 V_{n-ew}$$

$$= 40 + 0.746 \times 28.98 = 61.6 \text{ ml}$$

$$V_{gw} = 0.28(V_{gw} + 61.6)$$

$$\Rightarrow V_{gw} = 23.95 \text{ ml}$$

$$W_{tw} = 126 \times 0.475 = 59.85 \text{ g}$$

$$\therefore V_{tw} = 59.85 \text{ ml}$$

$$V_{cw} = V_{tw} - V_{n-ew} - V_{gw}$$

$$= 59.8 - 28.98 - 23.95 = 6.87 \text{ ml}$$

$$V_{hc} = V_{sp} + V_{gw} = 61.6 + 23.95 = 85.55 \text{ ml}$$

$$V_{uc} = V_{tc} - V_{cah} = \frac{126}{3.15} - 40 = 0 \text{ ml}$$

$$V_{cp} = (V_{cah} + V_{tw}) - V_{hc}$$

$$= (40 + 59.85) - 85.55 = 14.25 \text{ ml}$$

$$V_{ecp} = V_{cp} - V_{cw} = 14.25 - 6.87 = 3.7 \text{ ml}$$

$$\text{gel/space ratio} = \frac{V_{hc}}{V - V_{uc}}$$

$$= \frac{85.55}{(40 + 59.8) - 0} = 0.857$$

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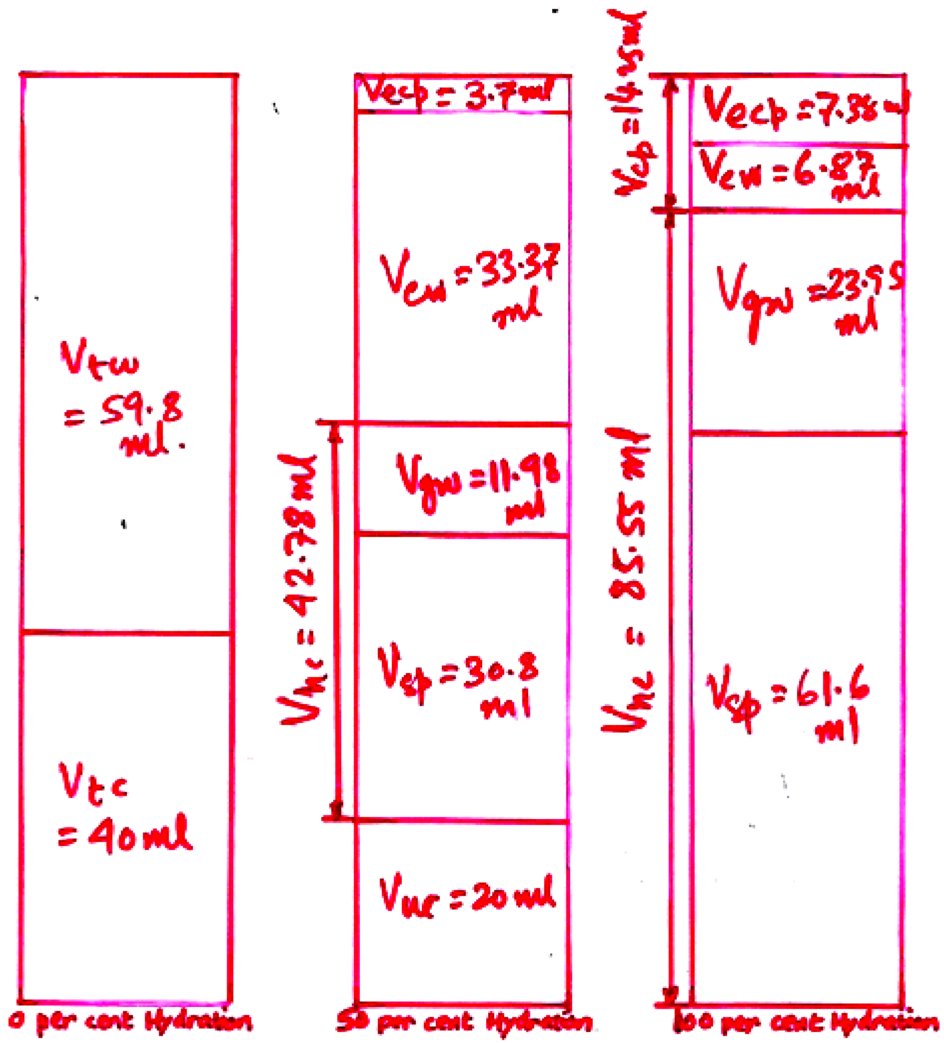
EXAMPLES ON CALCULATION OF VOLUMES OF HYDRATION PRODUCTS AT DIFFERENT STAGES OF HYDRATION AND AT DIFFERENT W/C RATIOS



EFFECT OF w/c RATIO ON DEGREE OF HYDRATION

- **An adequate w/c ratio should be selected for full hydration, because the complete hydration of cement into gel (i.e. solid products of hydration) is possible only when *sufficient water* is available *both for the chemical reactions and for the filling of the gel pores* being formed**
- **Full hydration is possible only when the mixing water is at least twice the non-evaporable water (i.e. minimum w/c ratio for full hydration = $2 \times 0.23W_c/W_c$ = 0.46 say 0.50 by mass)**
- **Gel water, which is firmly held in gel, can not be available for hydration of still un-hydrated cement**
- **Therefore, only the capillary water is used for hydration of still un-hydrated cement**

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EFFECT OF w/c RATIO ON DEGREE OF HYDRATION

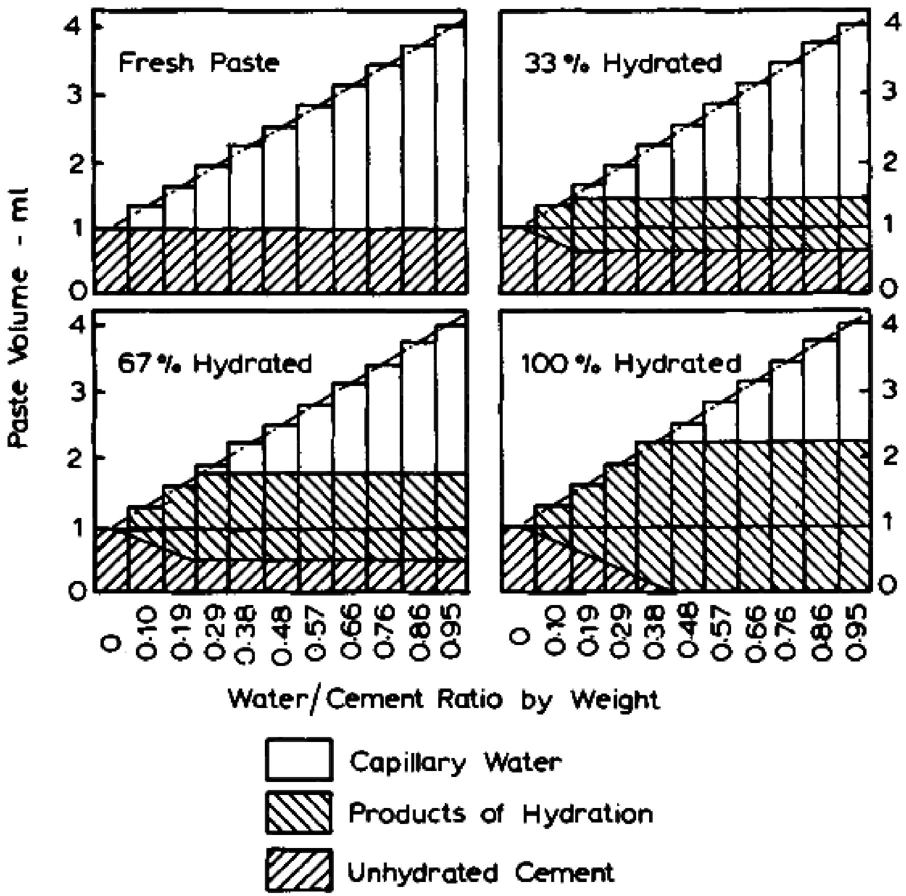
- **For no un-hydrated cement to be left and no capillary pores to be present, w/c ratio should be about 0.38 by mass or 1.2 by volume**

- **No further hydration may take place after a stage when the non-evaporable water has become about 50% of the original water added**

- **If the w/c ratio is higher than about 0.38 by mass, all the cement can hydrate but capillary pores will also be present**

EFFECT OF w/c RATIO ON DEGREE OF HYDRATION

- Following figure shows the relative volumes of un-hydrated cement, products of hydration, and capillaries for mixes with different w/c ratios:



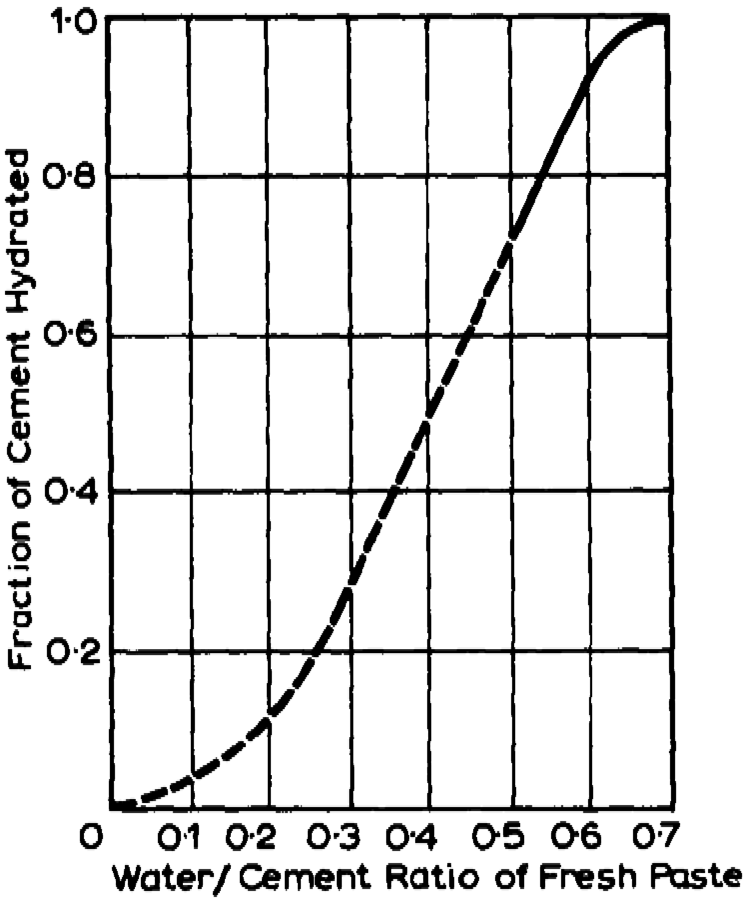
Composition of cement paste at different stages of hydration.[1.10] The percentage indicated applies only to pastes with enough water-filled space to accommodate the products at the degree of hydration indicated

EFFECT OF w/c RATIO AND DEGREE OF HYDRATION ON CAPILLARY SEGMENTATION

- **The capillary porosity of the paste depends both on the w/c ratio of the mix and on the degree of hydration**
- **At w/c ratio greater than 0.38, there will be some volume of capillary pores left even the process of hydration has been completed**
- **These interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste and its vulnerability to cycles of freezing and thawing**
- **However, with the progress of hydration solid content of the paste increases, and in mature and dense pastes, the capillaries can be blocked by gel and segmented. This phenomenon is termed as "*capillary segmentation*"**

EFFECT OF w/c RATIO AND DEGREE OF HYDRATION ON CAPILLARY SEGMENTATION

- **The time required to achieve the state of capillary segmentation (*i.e. time required to achieve a threshold degree of hydration*) depends on the w/c ratio of the paste, as shown in the following figure and table:**



Relation between the water/cement ratio and the degree of hydration at which the capillaries cease to be continuous

Approximate Age Required to Produce Maturity at which Capillaries Become Segmented

Water/cement ratio by weight	*Time required*
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
over 0.70	impossible

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MECHANICAL STRENGTH OF CEMENT GEL

Following are two classical theories which describe hardening or development of strength of cement:

Le Chatelier's theory

According to this theory, the products of hydration of cement contain interlaced elongated crystals with high cohesive and adhesive properties, which give mechanical strength

Michaelis's theory

According to this theory, the crystalline aluminate, sulfoaluminate and calcium hydroxide give the initial strength

and then

the lime-saturated water attacks the silicates and forms a hydrated calcium silicate which forms a gelatinous (i.e. viscous) mass. This mass hardens gradually due to loss of water and gives strength