Carbonation & Chloride Penetration of Concrete Structures

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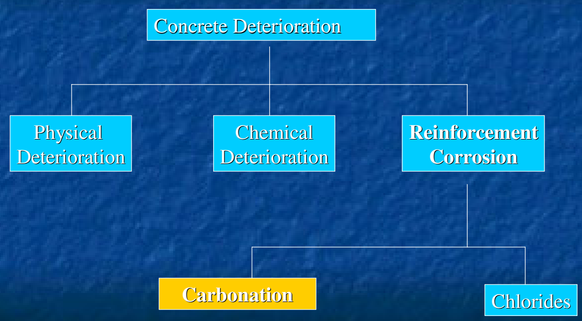
Durable concrete must have the ability to withstand the potentially deteriorative conditions to which it can reasonably be expected to be exposed.

Definition of Concrete Durability

- *Resistance to physical and chemical deterioration of concrete resulting from*
  - *Interaction with environment - external*
  - *Interaction between constituents - internal*
- *Protection of embedded steel from corrosion processes*

Durability



Mechanism of Carbonation

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

involves a physiochemical reaction between atmospheric carbon dioxide and the calcium hydroxide generated in cement hydration. The precipitation of calcium carbonate as shown in the following equation reduces the pH level of concrete.

Mechanism of Carbonation

- *Step 1* $H_2O+CO_2 = HCO_3^- + H^+$
  $HCO_3^- = CO_3^{2-} + H^+$
- *Step 2* $Ca(OH)_2 + 2H^+ + CO_3^{2-}$
  $= CaCO_3 + 2H_2O$
- *This neutralisation reaction penetrates gradually into the concrete surface.*
- *Penetration Rate =* $k \times time^{1/2}$

➢Change in Ph

The atmospheric carbon dio ide diffuses into the hardened concrete through pores and when carbonation reaction takes place, the alkalinity of the concrete reduces from 10 to below 9

Factors affecting carbonation

- *Humidity - ideally 50 70%*
  - *lower, not enough water*
  - *higher water inhibits CO_2 diffusion*
- *Temperature - worse in hot environments*
- *Concentration of CO_2 gas in atmosphere*
  - *Normally 0 03% but increasing annually*
  - *Higher in cities, due to motor vehicles and fossil fuel burning*

Testing Method

The measurement of carbonation depth using the phenolphthalein solution was carried out by spraying the indicator on the split surface of the concrete cylinder The solution became a ***pink color*** *in the carbonated concrete and can be differentiated from the uncarbonated concrete, giving a distinct boundary marking the carbonation front A carbonation depth upto an accuracy of 0 5 mm can be identified with the naked eye*

Samples sprayed with phenolphthalein solution

➢Mechanism- phenolphthalein solution method

The colourless acid/base indicator (phenolphthalein solution) monitoring the carbonation depth is by capturing the depth at which the pH is about 9

It indicates the boundary at which the carbonated front meets with the uncarbonated concrete, where concrete is alkaline

➢Limitation

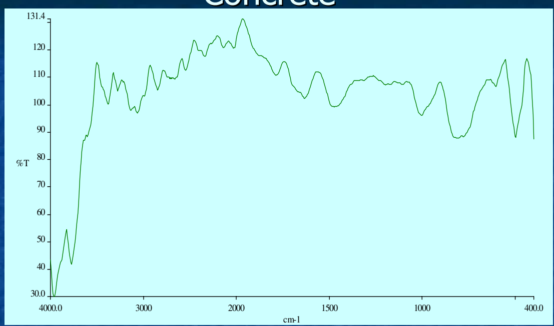
There e ists a partially carbonated zone where the pH value is not easily detected using phenolphthalein indicator Past evidence has shown that carbon dio ide could react at the depths greater than those indicated by phenolphthalein indicator

FTIR – Innovative Approach

FT-IR spectroscopy is a powerful tool for determining the structure of the functional groups that build up the molecules When the IR light passes through the sample, each functional group resonates in its characteristic absorption frequencies in the infrared region of the electromagnetic spectrum

Equipment FT-IR

Concrete

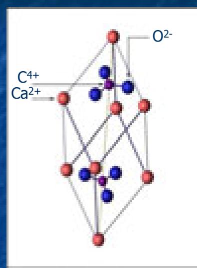


Carbonation

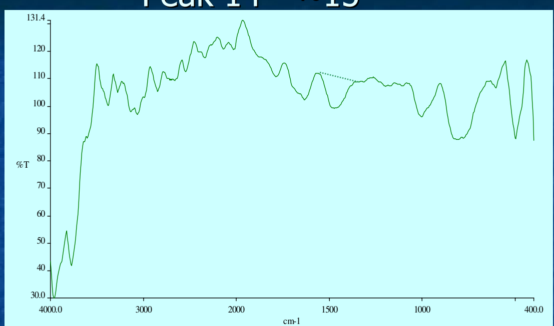
Carbonation - transformation of the C–O bonds of CO_2 to the formation of C–O bonds in the $CaCO_3$.

The three C–O bonds in the inorganic carbonate of the $CaCO_3$ are arranged in a trigonal planar pattern.

The characteristic peak of the C–O functional group in the wave number range of 1410–1510 cm^{-1} was used to identify carbonation in a complex concrete composite.



Peak 14 ~15



IR spectrum analysis

- *produces a scientific measurement of carbonation depth*
- *providing a convenient tool for cross-e amination*
- *overcoming the deficiency of results from conventional analytical methods*

- *cannot give a continuous line representing the carbonation front*

Test program

- *To study the effects of initial curing on the depth of carbonation*
- *Three mi A, B and C with w/c ratios of 38, 6 and 5*

Mix proportion per cubic meter of concrete

	Mix A	Mix B	Mix C
w/c Ratio	0.38	0.46	0.54
OPC (kg)	450	450	450
20 mm granite aggregate (kg)	665	655	645
10 mm granite aggregate (kg)	530	515	510
Rock fines (kg)	535	525	515
Superplasticizer (ml)	2400	0	0

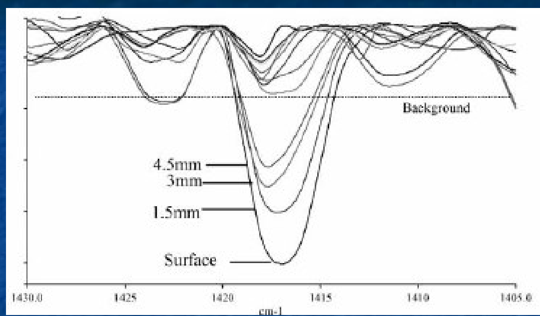
Test method

For each grade:

- *8 numbers of 1 mm cubes and*
- *8 units of 1 Φ×2 mm high cylinders*
- *stored in water at 27±3°C*
- *after 28 days, the cylinders were coated with epo y resin to ensure that the carbon dio ide could only diffuse into the concrete from two ends of the sample*
- *The specimens were transferred to an enclosed chamber to accelerate the carbonation process The concentration of carbon dio ide in the chamber was kept at 2% and was monitored weekly with a portable infrared carbon dio ide analyzer*

Powder samples were taken from the cylinder at depths of , 1 5, 3 , 5, 6 , 8 , 1 , 12 , 1 , 17 , 2 , and 3 mm measured from the surface The IR spectrum of each powder sample was mi ed with KBr in the proportion of 1 : 1 to facilitate quantitative measurement of carbonation depth

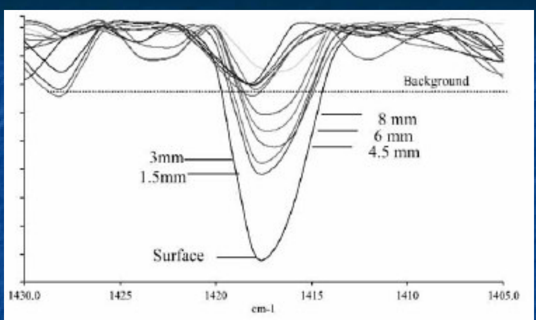
30 day carbonation age



Carbonation depth determined using FT IR

(air cured concrete, w/c 5)

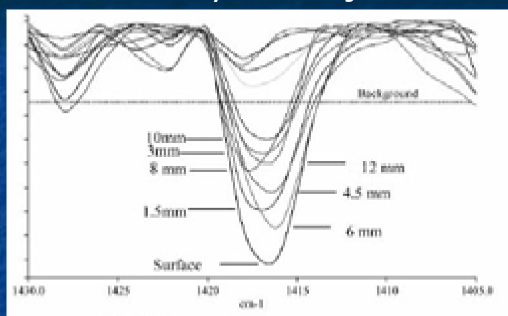
60 day carbonation age



Carbonation depth determined using FT IR

(air cured concrete, w/c 5)

90 day carbonation age



Carbonation depth determined using FT IR

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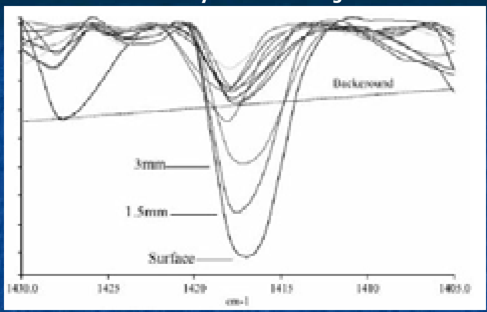
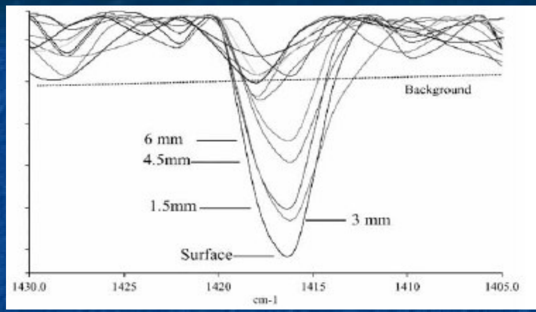


Carbonation depth determined using FT IR

(water cured concrete, w/c 5)

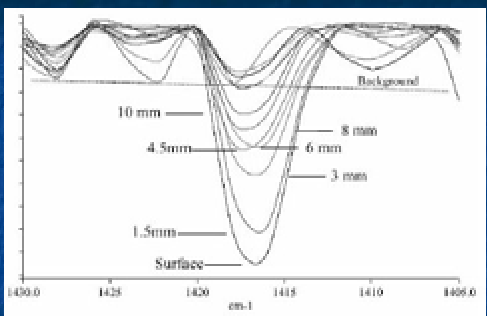
60 day carbonation age



Carbonation depth determined using FT IR

(water cured concrete, w/c 5)

90 day carbonation age



Carbonation depth determined using FT IR

(water cured concrete, w/c 5)

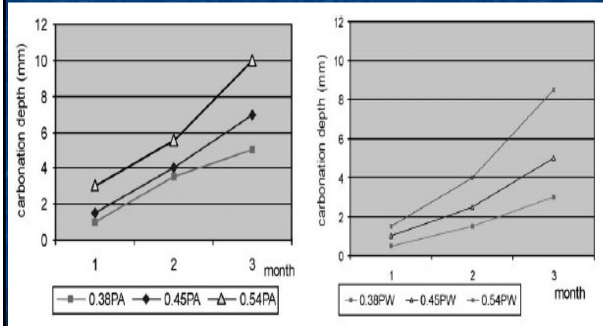
Comparison Phenolphthalein/FTIR (water)

Mix (w/c)	Curing type	Strength (MPa)	Carbonation depth (mm) Phenolphthalein P Infrared spectrum (I) Age (month) 1	2	3	Carbonation rate after constant 3 months P (I)	% increase
A (0.38)	water	78	0.5 (1)	1.5 (3)	3 (4.5)	6.0 (9.1)	49.2
B (0.46)	Water	63	1 (1.5)	2.5 (4.5)	5 (6)	10.0 (12.1)	21
C (0.54)	water	54	1.5 (3)	4 (6)	8.5 (10)	17.1 (20.1)	17.5

Comparison Phenolphthalein/FTIR (air)

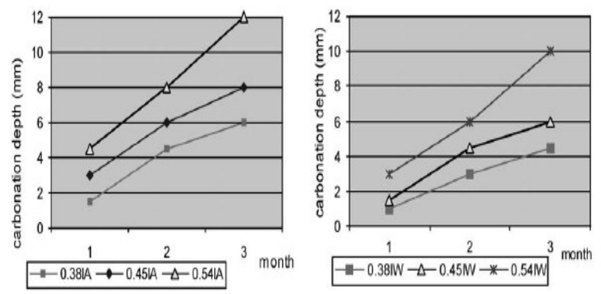
Mix (w/c)	Curing type	Strength (MPa)	Carbonation depth (mm) Phenolphthalein P Infrared spectrum (I) Age (month) 1	2	3	Carbonation rate after constant 3 months P (I)	% increase
A (0.38)	Air	66	1 (1.5)	3.5 (4.5)	5 (6)	10 (12.1)	21
B (0.46)	Air	44	1.5 (3)	4 (6)	7 (8)	14.0 (16.1)	14.2
C (0.54)	Air	35	3 (4.5)	5.5 (8)	10 (12)	20.1 (24.2)	20.4

Carbonation depth increased with time [phenolphthalein solution]



(a) : Air-cured concrete (b) : Water-cured concrete

Carbonation depth increased with time
[FT-IR Spectrum]



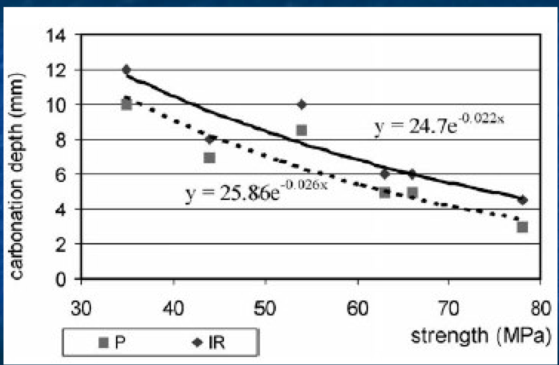
(c) : Air-cured concrete (d) : Water-cured concrete

Comparison of carbonation rate constant K

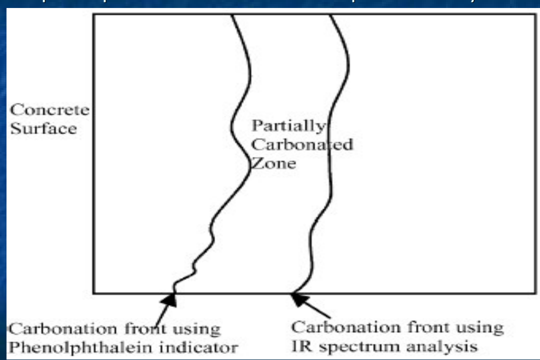
Type	References	Concrete strength (MPa)	Classification (A=accelerated N=normal)	Concrete condition	Carbonation rate constant K (mm year$^{-0.5}$)
High strength	This finding	35—66	A	Air cured	10—20.1 (phenolphthalein)
		54—78	A	28 days water cured then air cured	6—17.1 (phenolphthalein)
Medium strength	Roy	26.5 & 27	A	7 days water cured	11.9 and 10.8
	Balayssac	25—40	N	28 days water cured	7.3 to 2.9
Low strength	Roy	18.5 & 20.5	A	7 days water cured	16.9 and 15.5
	Roy	19.0	N	19 years R.C. Building	5.05

[1] Roy SK Poh KB Northwood DO Durability of concrete accelerated carbonation and weathering studies Building and Environment 1999;34:597 606
[2] Roy SK Northwood DO Poh KB E!ect of plastering on the carbonation of a 19 year old reinforced concrete building Construction and Building Materials 1996;10(4):267 72
[3] Balayssac JP Detriche ChH Grandet J E!ect of curing upon carbonation of concrete Construction and Building Materials 1995;9(2):91 5

Differences (9 days Carbonation depth)



Schematic model of carbonation front using phenolphthalein indicator and IR spectrum analysis



Carbonation depth by way of an IR spectroscopic test can be determined by observing the occurrence of C O characteristic peaks relative to the background noise at wave number 1 15 IR spectrometry gives more consistent results with lower variations in measurement than a phenolphthalein solution The carbonation rate constant found by IR spectrum analysis was 23 9% higher than that obtained using the phenolphthalein indicator

- *Our findings suggested that FT IR spectrum analysis provides a useful tool for providing early warnings of carbonation in structural surveys*
- *Compared with carbonation test using Phenolphthalein indicator, using FT IR analysis is more accurate*

Concrete & Steel Corrosion

Carbonation

Chlorides

Others than sea water e. g. de-icing salts

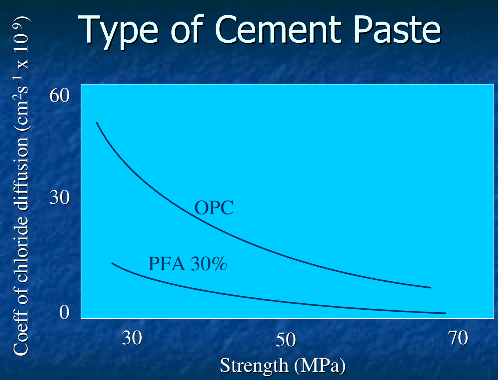
Sea water

Factors affecting chloride attack

- *Concentration of chlorides* - *corrosion will not occur below a threshold level (somewhere between 1 and %)*
- *Humidity, alternate wetting and drying*
- *Temperature* - *worse in hot climates*
- *Concrete permeability and chloride binding capacity, cement content and type*
- *PFA and SF will help resist chloride ingress*

Tests of Chloride ions diffusion

Type of Cement Paste

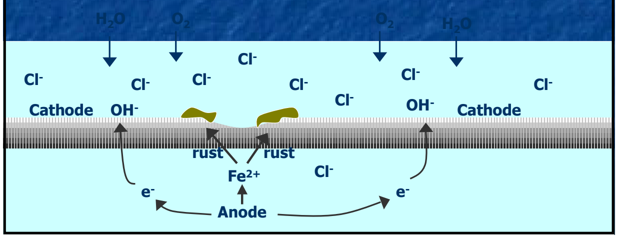


Mechanism of chloride-induced corrosion

- Anode Reaction
  $Fe - 2e \rightarrow Fe^{2+}$
- Cathode Reaction
  $2H_2O + O_2 + \ e \rightarrow \ OH$

$Fe^{2+} + 2Cl \rightarrow FeCl_2$

$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$

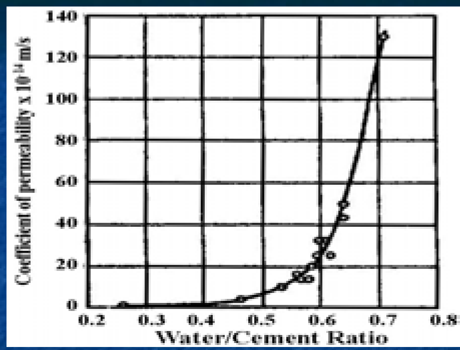


Sources of Chlorides

- *Contact with sea water*
- *From de-icing salts*
- *From beach or sea dredged aggregates*
- *From accelerators (chloride based admi tures now prohibited)*

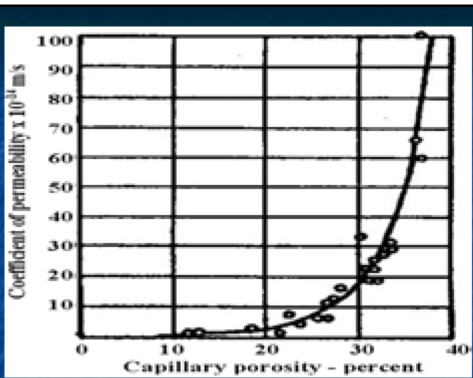
Factors affecting chloride attack

- *Concentration of chlorides* - *corrosion will not occur below a threshold level (somewhere between 1 and %)*
- *Humidity, alternate wetting and drying*
- *Temperature* - *worse in hot climates*
- *Concrete permeability and chloride binding capacity, cement content and type*
  - *PFA and SF will help resist chloride ingress*



Relation between permeability and water/cement ratio for cement pastes

Ref : Neville A M , Properties of Concrete (3rd ed), 1981



Relation between permeability and capillary porosity of cement paste

Ref : Neville A M , Properties of Concrete (3rd ed), 1981

Test program

Mix Proportions of Normal Weight Concrete kg/m³

	Max. 20mm aggregate			Max. 10mm aggregate		
Design Mix	M1	M2	M3	M4	M5	M6
W/C Ratio	0.38	0.46	0.54	0.38	0.46	0.54
Cement Content (kg)	450	450	450	510	510	510
Water Content (kg)	171	207	243	195	235	275
20mm agg. (kg)	667	653	642	--	--	--
10mm agg. (kg)	528.5	517.4	509.2	1117	1089	1062
Crush Rock (kg)	533.6	522.5	514.1	513	500	488
Admixture (cm³)	2400	--	--	1200	--	--

6 days ponding test

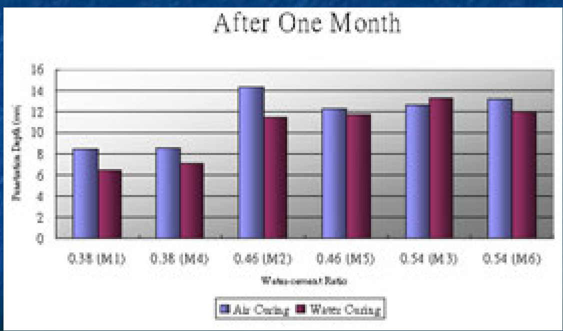
- *The specimens after 28 days were cut into two parts*
- *The vertical surface of concrete cylinder was sealed by epo y to avoid the diffusion of chloride ion through this surface*
- *Test cylinders were soaked in the salt solution for one month and two months*
- *At each month, specimens were taken out from the salt solution and dried for 2 hours at room temperature and humidity The surface of the specimens were cleaned by cloth to remove the salt crystal*
- *Potentiometric Titration Test and $AgNO_3$ Solution Spray Test were taken to determine the chloride content at different depth and the ma imum depth of penetration*

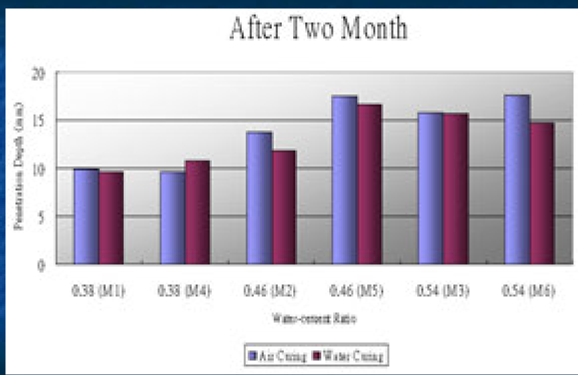
Surface Chloride level (By Potentiometric Titration test)

Chloride content in 0 – 5 mm from top of surface			
w/c	Mix and Curing condition	Chloride content (%)	
		1 month	2 months
0.38	$M1_{air}$	1.599	2.512
	$M1_{water}$	1.488	1.507
0.46	$M2_{air}$	1.935	1.638
	$M2_{water}$	1.396	1.377
0.54	$M3_{air}$	2.605	1.861
	$M3_{water}$	1.824	1.693

Chloride content in 0 – 5 mm from top of surface			
w/c	Mix and Curing condition	Chloride content (%)	
		1 month	2 months
0.38	$M4_{air}$	1.892	2.657
	$M4_{water}$	1.402	1.548
0.46	$M5_{air}$	1.548	1.369
	$M5_{water}$	1.484	1.402
0.54	$M6_{air}$	1.843	2.135
	$M6_{water}$	1.499	1.891

By $AgNO_3$ Solution Spray Test





Depth of Chloride Penetration of M1, M2 and M3 under Air Curing after 2 Months

Depth of Chloride Penetration of M , M5 and M6 under Air Curing after 2 Months

Depth of Chloride Penetration of M2 under Air Curing and Water Curing after 2 Months

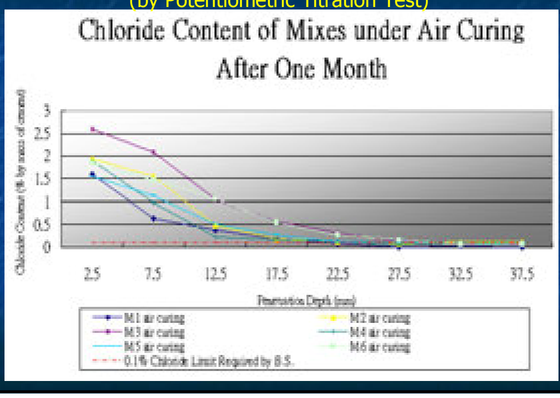
Comparison of Depth of Chloride Penetration Between M1 and M under Air Curing after 1 Months

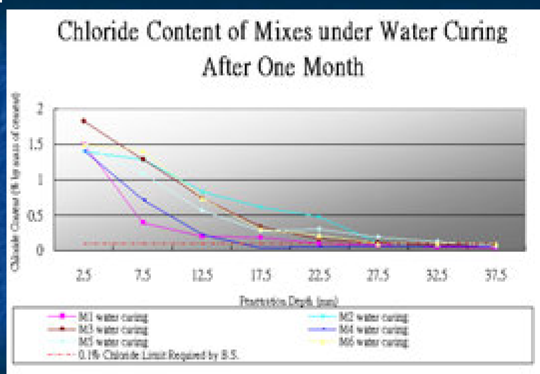
Depth of Chloride Penetration of M3 under Air Curing after 1 and 2 Months Immersion

Chloride ingress profiles (by Potentiometric Titration Test)

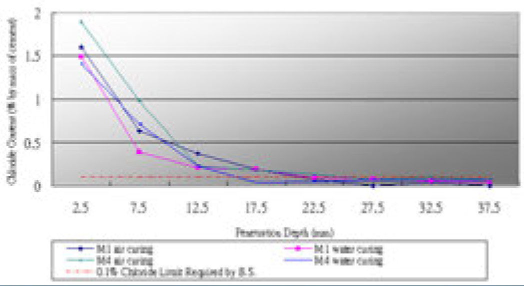
The 2 month chloride ingress profiles are shown by following figures The limit of chloride content of concrete is 1% by mass of cement A horizontal red line is drawn in each figure to indicate the depth of penetration at 1% limit

Chloride ingress profiles
(by Potentiometric Titration Test)

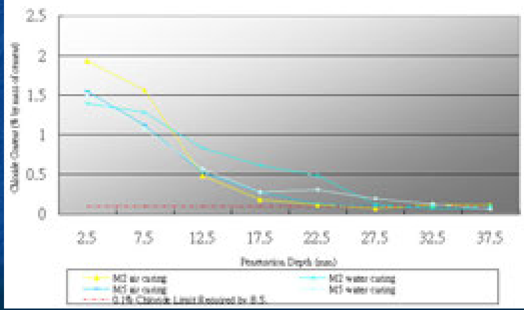




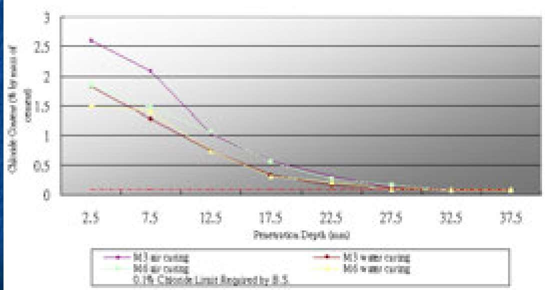
Chloride Content of M1 and M4 (0.38 w/c) After One Month



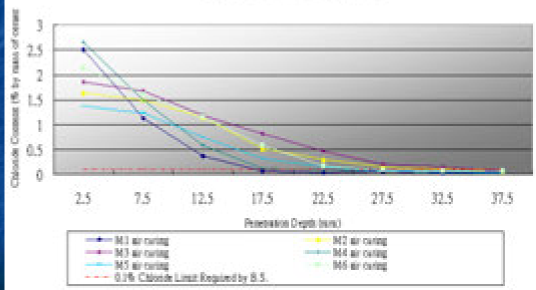
Chloride Content of M2 and M5 (0.46 w/c) After One Month



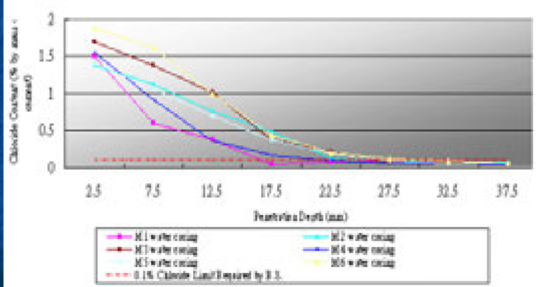
Chloride Content of M3 and M6 (0.54 w/c) After One Month



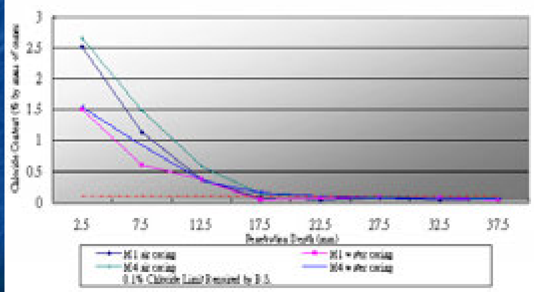
Chloride Content of Mixes under Air Curing After Two Months

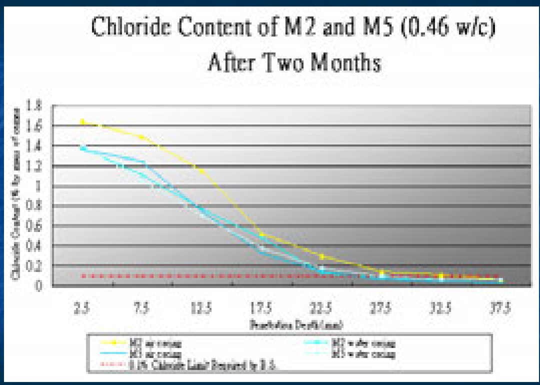


Chloride Content of Mixes under Water Curing After Two Months



Chloride Content of M1 and M4 (0.38 w/c) After Two Months





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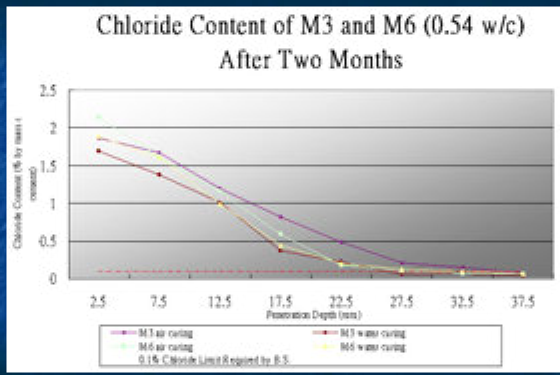

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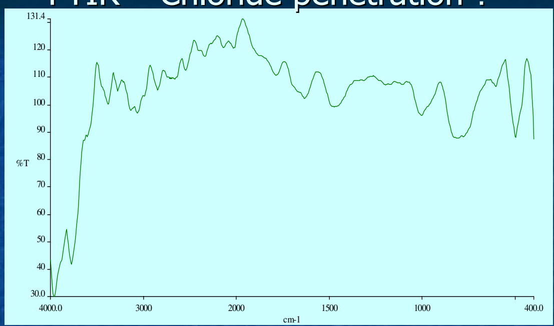
FTIR – Chloride penetration ?



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Thank You!

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