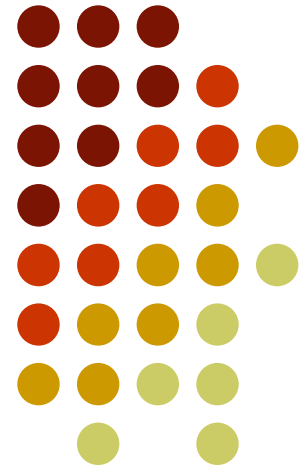


Plain & Reinforced Concrete-1

CE-314

Carbonation of Concrete





SYMBOLS USED IN CEMENT CHEMISTRY

- C = CaO (Calcium)
- S = SiO₂ (Silicate)
- A = Al₂O₃ (Aluminate)
- F = Fe₂O₃ (Ferrite)
- H = H₂O (Water of Hydration, Hydrate)



MAIN COMPOUNDS IN PORTLAND CEMENT

S. No.	Compound	Abbreviation	Typical Percentages
1.	Tricalcium silicate	C_3S	54.1
2.	Dicalcium silicate	C_2S	16.6
3.	Tricalcium aluminate	C_3A	10.8
4.	Tetracalcium aluminoferrite	C_4AF	9.1

C_3S with impurities is known as alite.

C_2S with impurities is known as belite.



- Out of these cement components, C_3A is undesirable. It does not contribute in providing strength.
- The C_3A component of hardened paste can be attacked by sulfates giving calcium sulfoaluminate (called **ettringite**).
- This material expands considerably compared with the volume of the reactants and may cause disintegration of the concrete.
- But C_3A is required in the manufacture of cement as it helps in the combination of lime and silica.



APPROXIMATE COMPOSITION OF PORTLAND CEMENT

Compound	Percentage Content Range	Typical Percentage
CaO	60 - 67	63
SiO ₂	17 - 25	20
Al ₂ O ₃	3 - 8	6
Fe ₂ O ₃	0.5 - 6.0	3
MgO	0.1 - 4.0	1.5
Alkalis (K ₂ O and Na ₂ O)	0.2 - 1.3	1
SO ₃	1 - 3	2
Others		3.5



HYDRATION

- Hydration of C_3S is much quicker than C_2S .
- $2 C_3S + 6H \rightarrow C_3S_2H_3 + 3Ca(OH)_2$
- $C_3S_2H_3$ is named C-S-H compound and is a microcrystalline hydrate.
- $Ca(OH)_2$ is crystalline lime.
- $2 C_2S + 4H \rightarrow C_3S_2H_3 + Ca(OH)_2$
- $C_3A + 6H \rightarrow C_3AH_6$ (Tricalcium aluminate hydrate)
- The above reaction is very quick and may lead to flash set.



SULFATE ATTACK

- Sulfate attack is caused by exposure of hardened concrete to external sources of sodium, calcium or magnesium sulfates usually coming from the ground water.
- These sulfates react with Ca(OH)_2 to produce calcium sulfate (gypsum) and with hydrated C_3A to form ettringite.
- Both of these products have a volume significantly more than the reactants.
- Magnesium sulfate is the most dangerous sulfate as it causes more decomposition of cement products and resulting magnesium silicate has no binding properties.



- When the concrete becomes disintegrated and porous, water takes away the remaining Ca(OH)_2 to the surface by evaporation.
- The Ca(OH)_2 combines with CO_2 to form calcium carbonate.
- This formation of whitish powder on the surface is called ***efflorescence***.
- The leaching of Ca(OH)_2 from the concrete mass further increases the porosity of concrete enhancing the rate of the attack.
- In case of sulfate attack, efflorescence first appears near the edges and corners, which is then followed by cracking and spalling of concrete.
- Crystallization of other salts also causes efflorescence.



PREVENTION

- Gypsum is added to the cement clinker in order to prevent flash set. In the fresh state of concrete, gypsum quickly reacts with C_3A to form ettringite. The corresponding increase in volume is not harmful as the concrete is not in solid state at this stage. Hence, C_3A content for further sulfate attack is reduced.
- Sulfate attack can be reduced by reducing the permeability of concrete.



- A low water cement ratio used with full compaction, either by the use of more cement or by the use of plasticizers, is very beneficial.
- Special types of cements may be used to reduce sulfate attack.
- The concrete may be protected to come in contact with ground water containing sulfate salts. A concentration of sulfur trioxide (SO_3) equal to 1000 ppm is moderately severe while 2000 ppm is very severe. Further, magnesium sulfate is more harmful.



ALKALI-AGGREGATE REACTION

- The active silica present in aggregates may react with the alkaline hydroxides derived from alkalis of cement (Na_2O and K_2O) to produce alkali-silica reaction (ASR).
- This reaction produces alkali-silicate gel that absorbs water and swells exerting internal pressure on the surrounding cement paste.
- This swelling causes expansion, cracking, pop-outs and spalling of the concrete.
- Swelling of the aggregate particles is the most harmful phenomenon.



- Poorly crystallized silica (SiO_2) dissolves and dissociates at high pH (12.5 - 13.5) in alkaline water.
- The soluble dissociated silicic acid reacts in the porewater with the calcium hydroxide (portlandite) present in the cement paste to form an expansive calcium silicate hydrate (CSH).
- The size of silica particles determines the speed of the reaction.
- Fine particles (20 to 30 μm) produce expansion within four to eight weeks, whereas larger particles may take years.
- Generally, this effect is developed after about five years.



- The reactive forms of silica are opal (amorphous), chalcedony (cryptocrystalline fibrous) and tridymite (crystalline).
- Porosity of the aggregate, permeability of the cement paste, the quantity of the alkalis in the cement and the availability of water in the paste affect ASR.
- The reaction is more pronounced in permanently wet conditions and at temperatures greater than 10°C with optimum value at 38°C .



- Mortar-bar test (ASTM C 227 - 90) is the most common test to evaluate the quality of aggregate with respect to ASR.
- Aggregates in crushed fine state of a prescribed grading and cement of equivalent alkali content not less than 0.6 percent are used to make special cement-sand mortar bars.
- The bars are stored over water at 38° C.
- High W/C ratio is used to accelerate the reaction.
- The aggregate is considered harmful if it expands more than 0.05 percent after 3 months or more than 0.1 percent after 6 months.



A low alkali cement, addition of pozzolanic materials and use of at least 30 percent of limestone coarse aggregate is recommended if the use of active aggregates cannot be avoided.



- The conditions required for alkali silica reaction are threefold:
 - (1) Aggregate containing an alkali-reactive constituent (amorphous silica),
 - (2) Sufficient availability of hydroxyl ions (OH^-), and
 - (3) Sufficient moisture, above 75 % relative humidity (RH) within the concrete.
- This phenomenon is sometimes popularly referred to as "concrete cancer".
- This reaction occurs independently of the presence of rebars: massive concrete structures such as dams can be affected.



CARBONATION OF CONCRETE

- Carbonation, or neutralisation, is a chemical reaction between carbon dioxide in the air with calcium hydroxide and hydrated calcium silicate ($C_3S_2H_3$ or CSH compound) in the concrete.
- As a result of this reaction, calcium carbonate ($CaCO_3$) is formed in the concrete.
- The creation of calcium carbonate requires three equally important substances: carbon dioxide (CO_2), calcium phases (Ca), and water (H_2O).



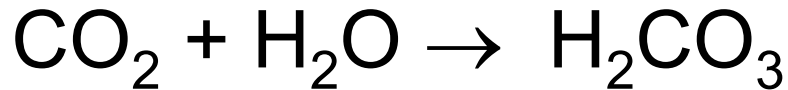
- Carbon dioxide (CO_2) is present in the surrounding air, calcium phases (mainly $\text{Ca}(\text{OH})_2$ and CSH) are present in the concrete, and water (H_2O) is present in the pores of the concrete.
- Cement paste contains 25-50 percentage by weight calcium hydroxide ($\text{Ca}(\text{OH})_2$) along with some potassium hydroxide and sodium hydroxide, which mean that the pH of the fresh cement paste is at least 12.5 to 13.5.
- As a result of carbonation, the pH value of pore water in the hardened cement paste is reduced to around 9.0.
- When all the $\text{Ca}(\text{OH})_2$ has become carbonated, the pH value will reduce up to about 8.3 and up to 7.0 in extreme cases.



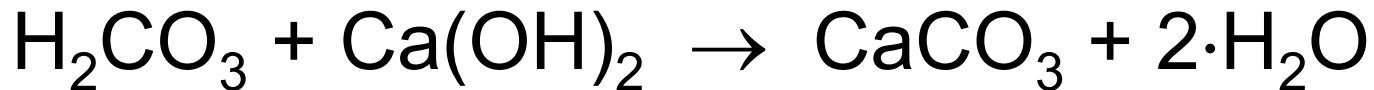
- Carbonic acid is a solution that is formed when atmospheric carbon dioxide dissolves in water (rainwater is essentially carbonic acid).
- When the calcium compounds react with the carbonic acid, the calcium of each of them forms calcium carbonate, the combined water is released as "free water," and the rest of the compounds become silica and alumina gels.
- The exception is the sulfoaluminates, which decompose to form calcium sulfate dihydrate (gypsum) and calcium carboaluminate hydrates.



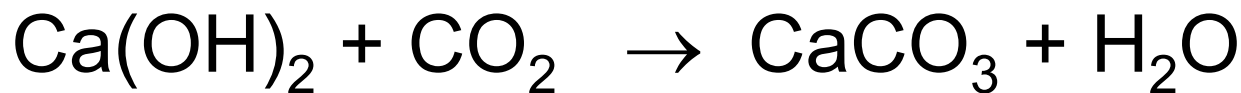
- The first reaction is in the pores where carbon di-oxide (CO_2) from the atmosphere and water (H_2O) react to form carbonic acid (H_2CO_3):



- The carbonic acid then reacts with the calcium phases:



- The above two reactions can be combined in one equation for simplicity as follows:





- Once the Ca(OH)_2 has converted and is missing from the cement paste, hydrated CSH (Calcium Silicate Hydrate - $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) will liberate CaO which will then also carbonate:



- When these reactions take place the pH value will start falling.



- The carbonation process requires the presence of water because CO_2 dissolves in water forming H_2CO_3 .
- If the concrete is too dry ($\text{RH} < 40\%$) CO_2 cannot dissolve and no carbonation occurs.
- If on the other hand it is too wet ($\text{RH} > 90\%$) CO_2 cannot enter the concrete and the concrete will not carbonate.
- Optimal conditions for carbonation occur at a RH of 50% (range 40-90%).
- It is interesting to know that if pore is filled with water the diffusion of CO_2 is very slow.



- Whatever CO_2 is diffused into the concrete, is readily formed into dilute carbonic acid reduces the alkalinity.
- On the other hand if the pores are rather dry, that is at low relative humidity the CO_2 remains in gaseous form and does not react with hydrated cement.
- The moisture penetration from external source is necessary to carbonate the concrete.
- The concentration of CO_2 in rural air may be about 0.03 per cent by volume.
- In large cities the content may go up to 0.3 per cent or exceptionally it may go up to even 1.0 per cent.
- In the tunnel, if not well ventilated the intensity may be much higher.



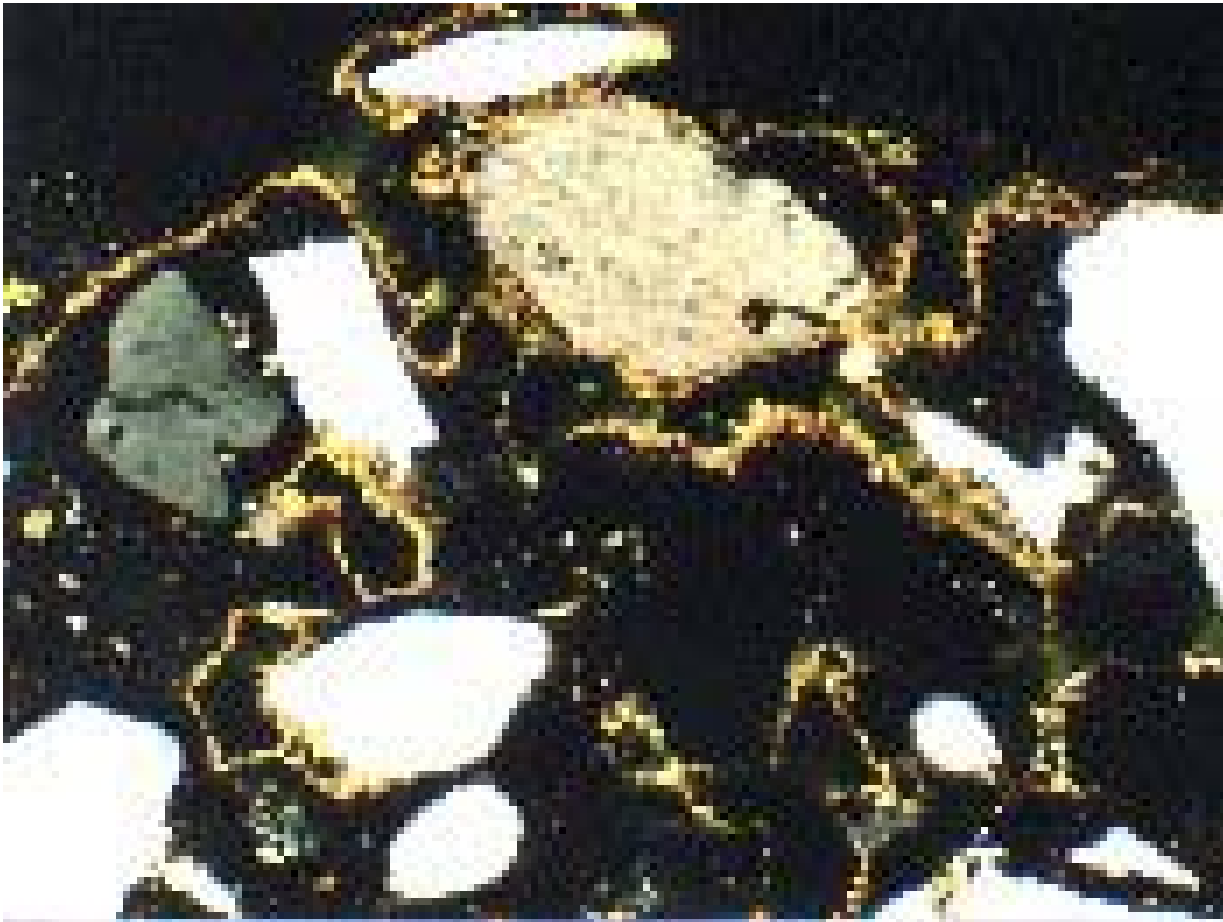
- The carbonation starts at the concrete surface and slowly penetrates inside.
- If the concrete is cracked due to any other reason, CO_2 quickly reaches deep inside and carbonation rate increases.
- This can occur so fast that in minutes the paste at the surface is very thin, but completely, carbonated.
- The water released by the chemical reactions continues both the formation of carbonic acid and the carbonation process.



Fully carbonated paste in the concrete surface. Carbonated paste appears orange-brown in crossed polarized light, Taken from web.



*Carbonated paste along cracks inside a concrete.
The cracks are formed due to alkali silica reaction,
Taken from web, Taken from web.*



Weak carbonation of paste at the rim of large connected voids in zero slump concrete.



Measurement Of Depth Of Carbonation

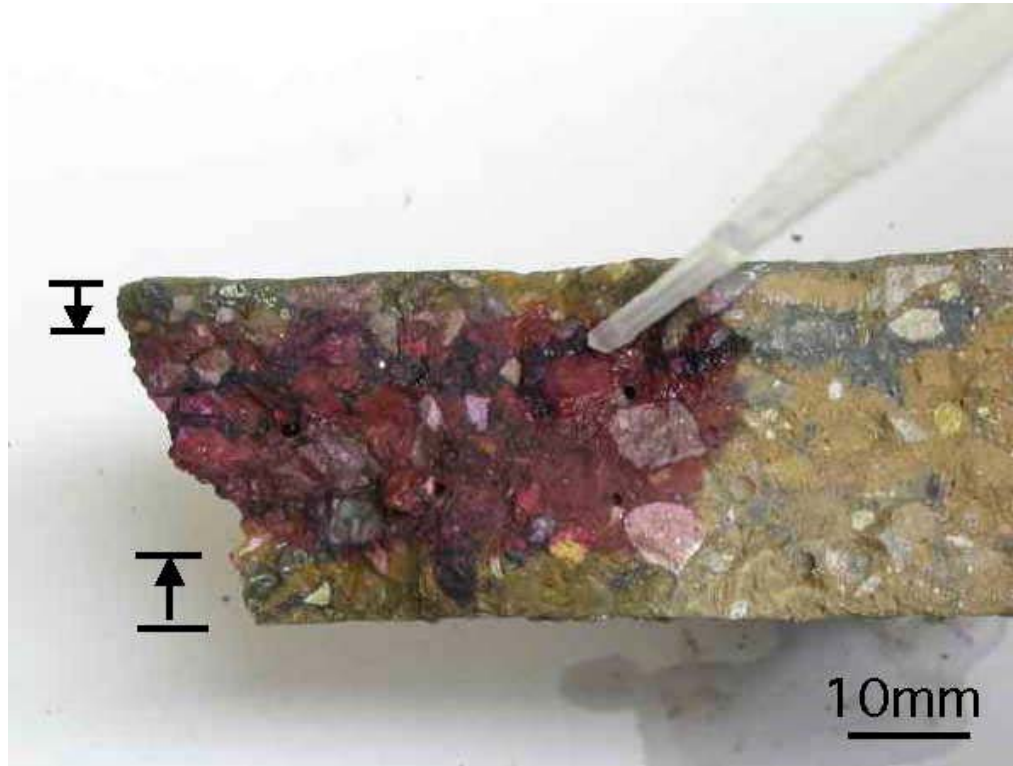
- A common and simple method for establishing the extent of carbonation is to treat the freshly broken surface of concrete with a solution of phenolphthalein in diluted alcohol.
- Phenolphthalein is a white or pale yellow crystalline material.
- For use as an indicator it is dissolved in a suitable solvent such as isopropyl alcohol in a 1% solution.
- If the Ca(OH)_2 is unaffected by CO_2 the color turns out to be pink.



- If the concrete is carbonated it will remain uncolored. It should be noted that the pink color indicates that enough Ca(OH)_2 is present but it may have been carbonated to a lesser extent.
- If the indicator turns purple, the pH is above 8.6.
- Where the solution remains colorless, the pH of the concrete is below 8.6, suggesting significant carbonation.
- A strong, immediate, color change to purple suggests a pH that is rather higher, perhaps pH 9 or 10.



- In confirmation of this, microscopy - either optical microscopy using thin-sections, or scanning electron microscopy using polished sections - shows carbonation effects at greater depths than indicated by phenolphthalein indicator.
- Nevertheless, this test is very useful as a means of making an initial assessment - it is quick, easy and widely used.



Phenolphthalein indicator solution applied to a fresh fracture surface through a concrete slab, Taken from web.



- The indicator has not changed color near the top and bottom surfaces, suggesting that these near-surface regions are carbonated to a depth of at least 4 mm from the top surface and 6 mm from the lower surface.
- Where the indicator has turned purple - the centre of the slab - the pH of the concrete pore fluid remains high (above 8.6, probably nearer 10).



Bi-carbonation

- Occasionally concrete may suffer from the so called bi-carbonation process.
- Bi-carbonation may occur in concrete with very high water to cement ratio due to formation of hydrogen carbonate ions at pH lower than 10.
- Contrary to normal carbonation, bi-carbonation results in an increase in porosity making the concrete soft and friable.
- Bi-carbonation may be recognized by the presence of large "pop-corn" like calcite crystals and the highly porous paste.



"Pop-corn" like calcite crystals present in carbonated paste. The concrete is suffering from bi-carbonation – Taken from web.



Negative Effects Of Carbonation

- Very early carbonation, when concrete is still plastic or semi-plastic (before setting), results in a "carbonation shell" around the cement particles that "seals" the particles and keeps them from hydrating.
- This carbonation results in dusty and weak surfaces and can occur when unvented heaters create high carbon dioxide (and carbon monoxide) environments.



- The carbonation process also causes bound chlorides to be released, which produces a higher concentration of soluble chloride immediately in front of the carbonation zone.
- This may cause chloride attack on steel reinforcement.



- Craze cracking at concrete surfaces is enhanced (particularly at high water-cement ratios) because of the addition of carbonation shrinkage with the normal drying shrinkage.
- The conversion of Ca(OH)_2 into CaCO_3 by the action of CO_2 results in a small shrinkage.
- Since the permeability of concrete is governed by the water/cement ratio and the effectiveness of curing, concrete with a high water/cement ratio and with inadequately curing will be more prone to carbonation.
- The carbonation shrinkage close to 50 % humidity can be as high as the drying shrinkage ($\varepsilon = 0.0009$).



- If the carbonation front reaches embedded steel, the steel can corrode. Good concrete design and construction requires steel to be located deeply enough that the carbonation front will not reach it during a structure's expected lifetime.
- More importantly, it reduces the alkalinity of the concrete which leads to the corrosion of the reinforcing steel.
- The increased volume of the resulting corroded steel results in internal stresses, spalling and delamination, and the ultimate reduction of the structure's capacity.



- Of course, oxygen and moisture are the other components required for corrosion of embedded steel.
- Steel undergoes oxidation or rusting in acidic environments.
- The rusting is prevented in basic environments and the phenomenon is called passivation of steel.
- The steel remains passive for the pH values above 9.5.
- Concrete cover to the reinforcement protects the steel from corrosion by not allowing the carbonation front to reach the reinforcement.



Positive Effects Of Carbonation

- Normal carbonation results in a decrease of the porosity making the carbonated paste stronger.
- Carbonation usually strengthens concrete surfaces, increases wear resistance, modulus of elasticity, surface hardness and resistance to frost and sulfate attack.
- Further, it makes the concrete less permeable.
- As an exception, sometimes carbonation may actually decrease the surface strength in concrete with a very high water-cement ratio because the carbonation can result in segregation of the calcium carbonate and other carbonation products (silica and alumina gels)--a phenomenon known as "bicarbonation."



- A useful result of carbonation is the progressive, but self-limiting, carbonation phenomenon.
- This may allow carbonation to be used to identify the time of cracking (such as cracking caused by earthquakes) by comparing the depth of carbonation cracks to the depth at the surface.
- Estimating the time of cracking from carbonation depth, however, should be left to experts since there are many factors to consider and erroneous opinions may be expected.



Rate of Carbonation

The rate of carbonation depends on the following factors:

1. The level of pore water i.e., relative humidity.
2. Grade of concrete
3. Permeability/porosity of concrete
4. Protection to the concrete
5. Depth of cover
6. Age of concrete



- The highest rate of carbonation occurs at a relative humidity of between 50 and 70 percent.
- The rate of carbonation depth will be slower in case of stronger concrete for the obvious reason that stronger concrete is much denser with lower W/C ratio.
- It again indicates that the permeability of the concrete, particularly that of skin concrete is much less at lower W/C and as such the diffusion of CO₂ does not take place faster, as in the case of more permeable concrete with higher W/C ratio.
- The carbonation process has an ongoing need for carbon dioxide (CO₂) from the atmosphere.



- For carbonation to spread, fresh carbon dioxide from the surface needs to be supplied continuously deeper and deeper into the concrete.
- Low porosity and permeability will decrease the ingress speed of carbon dioxide (CO_2) from the atmosphere, thereby delaying the ingress of the carbonation.
- Depth of cover plays an important role in protecting the steel from carbonation.



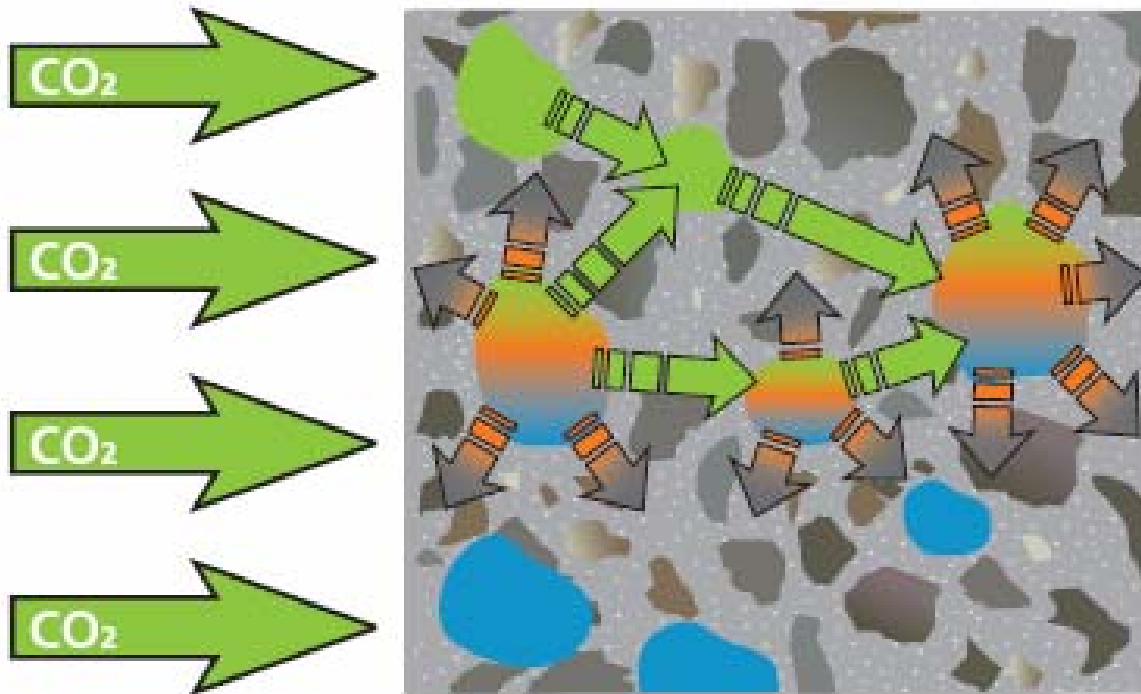
- Within a few hours, or a day or two at most, the surface of fresh concrete will have reacted with CO_2 from the air.
- Gradually, the process penetrates deeper into the concrete at a rate proportional to the square root of time.
- After a year or so it may typically have reached a depth of perhaps 1 mm for dense concrete of low permeability made with a low water/cement ratio, or up to 5 mm or more for more porous and permeable concrete made using a high water/cement ratio.



- Cracks in the concrete allow easy access of carbon dioxide through the concrete cover and greater rate of carbonation is obtained.
- The active coefficient of carbon dioxide diffusion in a concrete crack 0.2 mm wide is about 1000 times higher than in average-quality crack-free concrete.



- The rate of carbonation is mainly influenced by the permeability and the calcium content of the concrete as well as the ambient atmospheric conditions: amount of carbon dioxide, relative humidity, and temperature.
- Concrete carbonates more rapidly in a hot climate than in a moderate climate.



Water
 H_2O

Carbon dioxide
 CO_2

Carbonic acid
 H_2CO_3

Calcium carbonate (carbonation products)
 $CaCO_3$

Taken from web



Concluded