

# Concrete degradation

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**Concrete degradation** may have various causes.

Concrete can be damaged by fire, aggregate expansion, sea water effects, bacterial corrosion, calcium leaching, physical damage and chemical damage (from carbonatation, chlorides, sulfates and distilled water).

This process adversely affects concrete exposed to these damaging stimuli.



Degraded concrete and rusted, exposed rebar on Welland River bridge of the Queen Elizabeth Way in Niagara Falls, Ontario.

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## Aggregate expansion

Various types of aggregate undergo chemical reactions in concrete, leading to damaging expansive phenomena. The most common are those containing reactive silica, that can react (in the presence of water) with the alkalis in concrete ( $K_2O$  and  $Na_2O$ , coming principally from cement). Among the more reactive mineral components of some aggregates are opal, chalcedony, flint and strained quartz. Following the alkali-silica reaction (ASR), an expansive gel forms, that creates extensive cracks and damage on structural members. On the surface of concrete pavements the ASR can cause pop-outs, i.e. the expulsion of small cones (up to 3 cm (1 in) about in diameter) in correspondence of aggregate particles.

When some aggregates containing dolomite are used, a dedolomitization reaction occurs where the magnesium carbonate compound reacts with hydroxyl ions and yields magnesium hydroxide and a carbonate ion. The resulting expansion may cause destruction of the material. Far less common are pop-outs caused by the presence of pyrite, an iron sulfide that generates expansion by forming iron oxide and ettringite. Other reactions and recrystallizations, e.g. hydration of clay minerals in some aggregates, may lead to destructive expansion as well.

## Corrosion of reinforcement bars



Example of flat piece of concrete having dislodged with corroded rebar underneath, Welland River bridge across Queen Elizabeth Way in Niagara Falls, Ontario.

The expansion of the corrosion products (iron oxides) of carbon steel reinforcement

structures may induce mechanical stress that can cause the formation of cracks and disrupt the concrete structure. If the rebars have been poorly installed and are located too close to the concrete surface in contact with the air, spalling can easily occur: flat fragments of concrete are detached from the concrete mass by the rebars corrosion and may fall down.

## Chemical damage

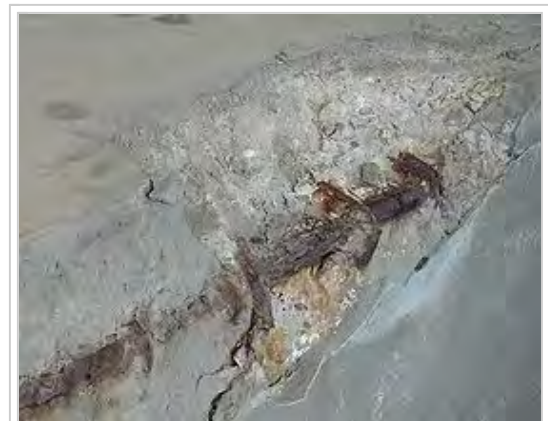
### Carbonatation

Carbon dioxide from air can react with the calcium hydroxide in concrete to form calcium carbonate. This process is called carbonatation, which is essentially the reversal of the chemical process of calcination of lime taking place in a cement kiln. Carbonatation of concrete is a slow and continuous process progressing from the outer surface inward, but slows down with increasing diffusion depth.<sup>[1]</sup>

Carbonatation has two effects: it increases mechanical strength of concrete, but it also decreases alkalinity, which is essential for corrosion prevention of the reinforcement steel.<sup>[1]</sup> Below a pH of 10, the steel's thin layer of surface passivation dissolves and corrosion is promoted. For the latter reason, carbonatation is an unwanted process in concrete chemistry. It can be tested by applying phenolphthalein solution, a pH indicator, over a fresh fracture surface, which indicates non-carbonatated and thus alkaline areas with a violet color.<sup>[2][3]</sup>



Typical crack pattern associated to the alkali-silica reaction affecting a concrete step barrier on a US motorway (photograph, courtesy of the Federal Highway Administration (US Department of Transportation).



Carbonatation-initiated deterioration of concrete at Hippodrome Wellington, Belgium.

## Chlorides

Chlorides, particularly calcium chloride, have been used to shorten the setting time of concrete.<sup>[4]</sup> However, calcium chloride and (to a lesser extent) sodium chloride have been shown to leach calcium hydroxide and cause chemical changes in Portland cement, leading to loss of strength,<sup>[5]</sup> as well as attacking the steel reinforcement present in most concrete. The Queen Elizabeth 10 story hospital in Kota Kinabalu, contained a high percentage of chloride causing early failure.

## Sulfates

Sulfates in solution in contact with concrete can cause chemical changes to the cement, which can cause significant microstructural effects leading to the weakening of the cement binder (chemical sulfate attack). Sulfate solutions can also cause damage to porous cementitious materials through crystallization and recrystallization (salt attack).<sup>[6]</sup> Sulfates and sulfites are ubiquitous in the natural environment and are present from many sources, including gypsum (calcium sulfate) often present as an additive in 'blended' cements which include fly ash and other sources of sulfate. With the notable exception of barium sulfate, most sulfates are slightly to highly soluble in water. These include acid rain where sulfur dioxide in the airshed is dissolved in rainfall to produce sulfurous acid. In lightning storms, the dioxide is oxidised to trioxide making the residual sulfuric acid in rainfall even more highly acidic. Local government infrastructure is most commonly corroded by sulfate arising from the oxidation of sulfide which occurs when bacteria (for example in sewer mains) reduce the ever-present hydrogen sulfide gas to a film of sulfide (S-) or bi-sulfide (HS-) ions. This reaction is reversible, both readily oxidising on exposure to air or oxygenated stormwater, to produce sulfite or sulfate ions and acidic hydrogen ions in the reaction  $\text{HS}^- + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^-$ . The corrosion often present in the crown (top) of concrete sewers is directly attributable to this process - known as crown rot corrosion.<sup>[7]</sup>

## Leaching



Example of secondary efflorescence in parking garage exposed to diluted road salt from vehicles entering the garage during winter.

When water flows through cracks present in concrete, water may dissolve various minerals present in the hardened cement paste or in the aggregates, if the solution is unsaturated with respect to them.

Dissolved ions, such as calcium ( $\text{Ca}^{2+}$ ), are leached out and transported in solution some distance. If the physico-chemical conditions prevailing in the seeping water evolve with distance along the water path and water becomes supersaturated with respect to certain minerals, they can further precipitate, making deposits or efflorescences inside the cracks, or at the concrete outer surface. This process can cause the self-healing of fractures in particular conditions.

### Decalcification

Within set concrete there remains some free "calcium hydroxide" ( $\text{Ca}(\text{OH})_2$ ),<sup>[8]</sup> which can further dissociate to form  $\text{Ca}^{2+}$  and hydroxide ( $\text{OH}^-$ ) ions".<sup>[9]</sup> Any water which finds a seepage path through micro cracks and air voids present in concrete, will readily carry the ( $\text{Ca}(\text{OH})_2$ ) and  $\text{Ca}^{2+}$  (depending on solution pH and chemical reaction at the time) to the underside of the structure where leachate solution contacts the atmosphere.<sup>[10]</sup> Carbon dioxide ( $\text{CO}_2$ ) from the atmosphere readily diffuses into the



Stalactites growing beneath a concrete structure as a result of calcium hydroxide being leached from concrete and deposited as calcium carbonate to create calthemite forms beneath structure

leachate and causes a chemical reaction, which precipitates (deposits) calcium carbonate ( $\text{CaCO}_3$ ) on the outside of the concrete structure. Consisting primarily of  $\text{CaCO}_3$  this secondary deposit derived from concrete is known as "calthemite"<sup>[10]</sup> and can mimic the shapes and forms of cave "speleothems", such as stalactites, stalagmites, flowstone etc.<sup>[11]</sup> Other trace elements such as iron from rusting reinforcing may be transported and deposited by the leachate at the same time as the  $\text{CaCO}_3$ . This may colour the calthemites orange or red.

[12]



Calthemite flowstone stained orange from rusting reinforcing (iron oxide) being deposited along with calcium carbonate

The chemistry involving leaching of calcium hydroxide from concrete can facilitate the growth of calthemites up to  $\approx 200$  times faster than cave speleothems due to the different chemical reactions involved.<sup>[13]</sup> The sight of calthemite is a visual sign that calcium is being leached from the concrete structure and the concrete is gradually degrading.<sup>[10][14]</sup>

In very old concrete where the calcium hydroxide has been leached from the leachate seepage path, the chemistry may revert to that similar to "speleothem" chemistry in limestone cave.<sup>[10][11]</sup> This is where carbon dioxide enriched rain or seepage water forms a weak carbonic acid, which leaches calcium carbonate ( $\text{CaCO}_3$ ) from within the concrete structure and carries it to the underside of the structure.<sup>[15]</sup> When it contacts the atmosphere, carbon dioxide is degasses and calcium carbonate is precipitated to create calthemite deposits,<sup>[10]</sup> which mimic the shapes and forms of speleothems.<sup>[11]</sup> This degassing chemistry is not common in concrete structures as the leachate can often find new paths through the concrete to access free calcium hydroxide and this reverts the chemistry to that previously mentioned where  $\text{CO}_2$  is the reactant.<sup>[10]</sup>

## Sea water

Concrete exposed to seawater is susceptible to its corrosive effects. The effects are more pronounced above the tidal zone than where the concrete is permanently submerged. In the submerged zone, magnesium and hydrogen carbonate ions precipitate a layer of brucite, about 30 micrometers thick, on which a slower deposition of calcium carbonate as aragonite occurs. These layers somewhat protect the concrete from other processes, which include attack by magnesium, chloride and sulfate ions and carbonation. Above the water surface, mechanical damage may occur by erosion by waves themselves or sand and gravel they carry, and by crystallization of salts from water soaking into the concrete pores and then drying up. Pozzolanic cements and cements using more than 60% of slag as aggregate are more resistant to sea water than pure Portland cement. Sea water corrosion contains elements of both chloride and sulfate corrosion.

## Bacterial corrosion

Bacteria themselves do not have noticeable effect on concrete. However, sulfate-reducing bacteria in untreated sewage tend to produce hydrogen sulfide, which is then oxidized by aerobic bacteria present in biofilm on the concrete surface above the water level to sulfuric acid. The sulfuric acid dissolves the carbonates in the cured cement and causes strength loss, as well as producing sulfates which are harmful to concrete. Concrete floors lying on ground that contains pyrite (iron(II) sulfide) are also at risk. Using limestone as the aggregate makes the concrete more resistant to acids, and the sewage may be pretreated by ways increasing pH or oxidizing or precipitating the sulfides in order to inhibit the activity of sulfide utilizing bacteria.

## Physical damage

Damage can occur during the casting and de-shuttering processes. For instance, the corners of beams can be damaged during the removal of shuttering because they are less effectively compacted by means of vibration (improved by using form-vibrators). Other physical damage can be caused by the use of steel shuttering without base plates. The steel shuttering pinches the top surface of a concrete slab due to the weight of the next slab being constructed.

## Thermal damage

Due to its low thermal conductivity, a layer of concrete is frequently used for fireproofing of steel structures. However, concrete itself may be damaged by fire. An example of this was the 1996 Channel fire, where the fire reduced the thickness of concrete in an undersea tunnel connecting France with England. For this reason, common fire testing standards, such as ASTM E119 (<http://www.astm.org/Standards/E119.htm>), do not permit fire testing of cementitious products unless the relative humidity inside the cementitious product is at or below 75%. Otherwise, concrete can be subject to significant spalling.

Up to about 300 °C, the concrete undergoes normal thermal expansion. Above that temperature, shrinkage occurs due to water loss; however, the aggregate continues expanding, which causes internal stresses. Up to about 500 °C, the major structural changes are carbonation and coarsening of pores. At 573 °C, quartz undergoes rapid expansion due to phase transition, and at 900 °C calcite starts shrinking due to decomposition. At 450-550 °C the cement hydrate decomposes, yielding calcium oxide. Calcium carbonate decomposes at about 600 °C. Rehydration of the calcium oxide on cooling of the structure causes expansion, which can cause damage to material which withstood fire without falling apart. Concrete in buildings that experienced a fire and were left standing for several years shows extensive degree of carbonation from carbon dioxide which is reabsorbed.

Concrete exposed to up to 100 °C is normally considered as healthy. The parts of a concrete structure that is exposed to temperatures above approximately 300 °C (dependent of water/cement ratio) will most likely get a pink color. Over approximately 600 °C the concrete will turn light grey, and over approximately 1000 °C it turns yellow-brown.<sup>[16]</sup> One rule of thumb is to consider all pink colored concrete as damaged that should be removed.

Fire will expose the concrete to gases and liquids that can be harmful to the concrete, among other salts and acids that occur when gases produced by a fire come into contact with water.

If concrete is exposed to very high temperatures very rapidly, explosive spalling of the concrete can result. In a very hot, very quick fire the water inside the concrete will boil before it evaporates. The steam inside the concrete exerts expansive pressure and can initiate and forcibly expel a spall.<sup>[17]</sup>

## Radiation damages

Exposure of concrete structures to neutrons and gamma radiations in nuclear power plants and high-flux material testing reactor can induce radiation damages in their concrete structures. Paramagnetic defects and optical centers are easily formed, but very high fluxes are necessary to displace a sufficiently high number of atoms in the crystal lattice of minerals present in concrete before significant mechanical damage is observed.

## Repairs and strengthening

It may be necessary to repair a concrete structure following damage (e.g. due to age, chemical attack, fire,<sup>[18]</sup> impact or reinforcement corrosion). Strengthening may be necessary if the structure is under strength (e.g. due to design or construction errors or because of a change of use).

### Repair techniques

The first step should always be an investigation to determine the cause of the deterioration. The general principles of repair include: arresting and preventing further degradation; treating exposed steel reinforcement; and filling holes left by the removal of spalled or damaged concrete;

Various techniques are available for repairing concrete structures. The selection of the appropriate technique will depend on the cause of the initial damage (e.g. corrosion of the reinforcement, chemical attack, fire) and whether the repair is to be fully load-bearing or simply cosmetic. Repair techniques will not improve the strength or performance of the structure beyond its original (undamaged) condition.

Techniques for arresting and preventing further degradation include: Cathodic protection; Chloride extraction; Re-alkalisation; repair of cracks and surface coatings.

One novel proposal for the repair of cracks is to use bacteria. *BacillaFilla* is a genetically engineered bacteria designed to repair damaged concrete, filling in the cracks, and making them whole again.

Techniques for filling holes left by the removal of spalled or damaged concrete include: mortar repairs; flowing concrete repairs and sprayed concrete repairs.

### Strengthening techniques

Various techniques are available for strengthening concrete structures, to increase the load-carrying capacity or else to improve the in-service performance. These include increasing the concrete cross-section, adding material such as steel plate or fibre composites to enhance the tensile capacity and providing additional prestressing.

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