Part B: Chemical attack on concrete

B1. General
This Part deals first with sulfate attack and acid attack, these being the principal types of chemical attack that are of concern for concretes placed in the ground in the UK. The aggressive chemical agents responsible commonly occur in both natural ground and land contaminated by activities of man.

Additionally, this Part identifies the more rarely occurring forms of chemical attack, caused by high levels of chemical species such as ammonium and chromium, and organics such as phenols. Generally these agents are found in troublesome concentrations only in contaminated land. With some exception, specific guidance is not given in this Special Digest in respect of protecting concrete from the action of these less commonly destructive agents. Generally the protective principles applied in Part D will be beneficial, for example, specifying a well-compacted concrete, with a low water/cement ratio or providing an appropriate protective coating. Specialist advice should be sought when appropriate.

Finally, this Part explains the action of aggressive carbon dioxide in respect of concrete in contact with flowing water. While not taken into account in a standard ground investigation or general concrete specification, the possible damaging effect of high levels of aggressive carbon dioxide are catered for in Part F in the design of specific precast concrete products such as pipeline systems. The potential for this form of attack should also be taken into account when designing cast-in place structures that carry flowing water, eg culverts.

B2. Principal types of chemical attack on concrete

B2.1 Sulfate attack
The essential agents for sulfate attack are sulfate anions (SO$_4^{2-}$). These are transported to the concrete in various concentrations in water, together with cations, the more common of which are calcium, magnesium and sodium.

Where porous concrete is in contact with saturated ground the water phase is continuous across the ground/concrete interface and sulfate ions will be readily carried into the body of the concrete. Well compacted, dense, low water/cement ratio concrete in such an environment will, however, initially restrict access of the ions to the surface layer.

Migration of sulfate ions from unsaturated ground into the concrete can take place by diffusion provided there is sufficient water to coat the particles of soil, but the rate will be slow and dependent on the sulfate concentration.

The reactions that take place when sulfates enter the concrete matrix are complex and contentious. There is extensive research literature on the topic, including some recent collaborative books and conferences [1-4]. A simple guide is given here in order to understand the basic chemistry and resultant effects. The reactions have been demonstrated to depend on the type of cement, on the availability of reactive carbonate in, for example, the aggregate and groundwater, and on the temperature. Two separate forms of sulfate attack on Portland cement concretes are described here:

- a well-known type (commonly called the 'conventional form of sulfate attack') leading to the formation of ettringite and gypsum;
- a more recently identified type producing thaumasite.

In practice, both can operate together to some extent in field conditions in buried concrete.

Sulfate attack can only be diagnosed when the concrete in question is showing physical signs of degradation such as expansion (with or without notable cracking), surface erosion or softening of the cement paste matrix. The identification of levels of sulfate significantly greater than 4% by weight of cement within the surface of a visually sound concrete does not automatically imply that sulfate attack has taken place; it may only be a warning of potential attack in the future.

B2.1.1 Conventional form of sulfate attack
For sulfate attack to occur leading to the formation of ettringite and gypsum in susceptible concrete the following must be present:

- a source of sulfates, generally from sulfates or sulfides in the ground;
- the presence of mobile groundwater;
- calcium hydroxide and calcium aluminate hydrate in the cement matrix.
In the highly alkaline pore solution (pH>10) provided by the sodium, potassium and calcium hydroxides liberated during the cement hydration reactions, sulfate ions that have penetrated the hardened concrete react with calcium aluminate hydrate to form calcium sulfo-aluminate hydrate (ettringite, \(\text{CaO.Al}_2\text{O}_3.3\text{CaSO}_4.31\text{H}_2\text{O}\)).

The formation of this mineral can be destructively expansive since it has a solid volume greater than the original constituents and it grows as myriad acicular (needle-shaped) crystals that can collectively generate high internal stresses in the concrete.

In sulfate-resisting Portland cement (SRPC), the tricalcium aluminate (C₃A in cement notation) level is kept to a minimum so reducing the extent of this reaction.

Incoming sulfate ions may also react with calcium hydroxide \(\text{Ca(OH)}_2\) to form gypsum (calcium sulfate dihydrate, \(\text{CaSO}_4.2\text{H}_2\text{O}\)). This reaction product also has a greater solid volume than the original constituents and in some cases can contribute to degradation of the concrete. If magnesium ions accompany the sulfates, they may also react with calcium hydroxide, producing brucite (magnesium hydroxide, \(\text{Mg(OH)}_2\)) which because of its low solubility precipitates out of solution, also leading to increase in solid volume. Magnesium ions may also attack calcium silicate hydrates, the principal bonding material in set concrete.

Laboratory tests show that the first effect of the conventional form of sulfate attack is to increase the strength and density of the concrete as the reaction products fill the pore space. When it is filled, further ettringite formation induces expansive internal stresses in the concrete which, if greater than the tensile strength of the concrete, will expansively disrupt the affected region. This cracking together with white crystalline accumulations are the characteristic signs of the conventional form of sulfate attack.

B2.1.2 Thaumasite form of sulfate attack (TSA)

A comprehensive account of this form of sulfate attack has been given in the Report of the Thaumasite Expert Group \(^{[1]}\) and in the proceedings of a special conference \(^{[4]}\) and so only the essentials are mentioned here. Several factors must generally be coincident for TSA to occur in susceptible concrete:

- a source of sulfates, generally from sulfates or sulfides in the ground;
- the presence of mobile groundwater;
- a source of calcium silicate hydrate, mostly derived from cementitious calcium silicate phases present in Portland cements;
- the presence of carbonate, generally in coarse and/or fine concrete aggregates, as bicarbonate in groundwater or as a constituent of the cement;
- low temperatures (since thaumasite formation is most active below 15°C).

The availability of carbonate ions (\(\text{CO}_3^{2-}\)) changes the reaction products when sulfates enter the concrete. Below about 15°C in the presence of water, the reactions between the calcium silicate hydrate, the carbonate and the sulfate ions produces thaumasite (\(\text{CaSiO}_3.\text{CaCO}_3.\text{CaSO}_4.15\text{H}_2\text{O}\)). The calcium silicate hydrates provide the main binding agent in Portland cement, so this form of attack weakens the concrete as well as causing some expansion and, in advanced cases, the cement paste matrix is eventually reduced to a mushy, incohesive mass (as in Figure B1).

Since TSA does not depend on the level of calcium aluminate hydrates, SRPC concretes can be vulnerable to this form of attack. Concretes containing granulated ground blastfurnace slag (ggbs) as part of the cement have good resistance to TSA. Concretes made with other cement types must rely on achieving very low permeability for resistance.

![Figure B1](https://via.placeholder.com/150)

Figure B1 Sample of formerly high quality concrete from highway bridge foundation that has been severely affected by TSA. The outer 50 mm of concrete has been reduced to a mushy...
reaction product rich in thaumasite. White haloes of pure thaumasite can be seen around dolomite aggregate particles.

The effect of temperature variation on the severity of TSA has been explored in accelerated laboratory tests. Concrete specimens, which showed no sulfate attack when immersed in sulfate solutions at a normal laboratory temperatures of around 20°C were progressively more severely affected by TSA when the temperature was lowered below 15°C.

In the field the significance of temperature on the reactions is not so well understood. However, it is likely to be significant since there is a variation within the critical temperature band of 5 to 15°C in near-surface ground. In central and southern England, Meteorological Office data indicate that the seasonal ground temperature variation progressively decreases with depth, converging to a value of about 10 - 12°C. At shallow foundation depths down to 1.2 m below ground level, the typical temperature range is from a minimum of 4°C in March to maximum of 17°C in September. At a depth of 3.0 m, the temperature range is from a minimum of 8°C in April to a maximum of 12°C in October. As in the laboratory, it is likely that the extent of TSA will be increased at the cooler temperatures if the chemical conditions are satisfied. It is relevant to note, however, that minimum ground temperatures below some types of construction will be raised significantly above natural levels due to heat loss from the building, and these sub-structures may, therefore, be less prone to TSA.

B2.2 Acid attack
The acids most commonly encountered by concrete (all found in some natural groundwaters) are carbonic acid, humic acid and sulfuric acid. The first two are only moderately aggressive and will not produce a pH below about 3.5. Sulfuric acid is a highly ionised mineral acid and may result in a pH lower than 2. Other similarly aggressive mineral acids may occasionally be found in ground contaminated by industrial processes.

The primary effect of any type of acid attack on concrete is the dissolution of the cement paste matrix. This weakens the affected concrete, but unlike sulfate attack, the degradation does not involve significant expansion. Neither ettringite nor thaumasite are stable in acid solution so that the reaction product from sulfuric acid attack will be primarily gypsum.

In concrete with siliceous gravel, granite or basalt aggregate, the surface attack will produce an ‘exposed aggregate’ appearance. However, in concrete with limestone (calcium carbonate) aggregates, the aggregate may dissolve at a rate similar to that of the cement paste and leave a smoother surface.

The rate of attack depends more on the rate of water movement over the surface and on the quality of the concrete, than on the type of cement or aggregate:
- Acidic groundwaters that are not mobile appear to have little effect on buried concrete.
- Mildly acidic (pH above 5.5) mobile water will attack concrete significantly, but the rate of attack will be generally slow, particularly if the acids are primarily organic in origin.
- Flowing acidic water may cause rapid deterioration of concrete, therefore high quality concrete is needed.

In the case of humic acid, reaction products formed on the surface of concrete are mainly insoluble and tend to impede further attack.

Several cases of acid attack on concrete in the UK are described by Eglinton (1975) [6]. Occurrence of acidic ground conditions is dealt with in Section C2.2 and assessment of the ground conditions in relation to acidity and mobility of water is included in Section C5.

B3. Other types of chemical attack on concrete
A large number of chemicals have been reported as attacking concrete, albeit most in the longer term and/or at high concentrations. For instance a USA document [7] lists more than 100 potentially destructive inorganic and organic substances. The chance of encountering the vast majority of these in the ground is remote, however, and only the more likely ones are described in this Section or referred to in the Sections on site investigation (Part C).

B3.1 Magnesium ions
Magnesium is a common element in soil and groundwater but is generally only hazardous to concrete when the Mg²⁺ ion is present in high concentrations in association with certain other chemical agents – the key one being sulfate anions. Laboratory studies have found concretes made with some cements are attacked to a greater degree by high concentrations of magnesium sulfate (MgSO₄) than
by equivalent concentrations of sodium sulfate. Because of this effect, recommendations for concrete specification in this and previous Digests have differentiated between low and high magnesium levels when combined with high sulfate concentrations. In practice the high Mg levels will be found in the UK only in ground having industrial residues. Other than the above, magnesium chloride (MgCl₂) is reported [8] to be especially aggressive.

The action of magnesium ions in concrete is complex, but a key mechanism is the replacement of Ca in calcium-silicate-hydrates that form much of the cement paste. This leads to a loss of the binding properties. Formation of brucite (Mg(OH)₂) and Mg-silicate hydrates is an indication of attack.

The determination of magnesium ion content is a routine part of site investigation for brownfield sites and is further discussed in Section C5.1.2.

**B3.2 Ammonium ions**

Ammonium ions (NH₄⁺) will only be a problem to concrete in ground having chemical residues left by man (including in this case agriculture). Ammonium salts are reported [8] to act as cation-exchange compounds, transforming the insoluble calcium in the hardened cement paste into readily soluble calcium salts that are subsequently leached away. During the reaction, ammonia is liberated and escapes as a gas. The removal of both reaction products results in an increase in the porosity of the concrete, leaving it vulnerable to further attack. Ammonium salts are also reported to act as weak acids [8] and neutralise the alkaline hardened cement paste; the removal of the hydroxide ions results in softening and gradual decrease in strength of the concrete.

In addition to the corrosive action of the ammonium ion, some further deterioration may be caused by the action of the associated anions. Ammonium sulfate, (NH₄)₂SO₄, is one of the most aggressive salts to concrete; cases of attack have occurred resulting from spillage of the material around fertiliser stores.

UK guidance is not available on the concentration of ammonium ions that can be tolerated by different types of concrete. However, EN 206-1: 2000 (Table 2) does indicate that a level of NH₄ of 15 to 30 mg/l should be regarded as slightly aggressive, 30 to 60 mg/l as moderately aggressive, and greater than 60 mg/l highly aggressive.

Because of the rarity of chemical attack attributed to ammonium ions, assessment of ammonium concentration is not specifically included in the scheme presented in this document for assessment of ground aggressive to concrete, or for guidance given for specification of chemically resistant concrete. Specialist advice should be sought if the presence of ammonium ions is suspected.

**B3.3 Chloride ions**

Chloride (Cl⁻) is a common anion in soil and groundwater, in most cases being associated with sodium (NaCl is common salt). However, the levels of chloride found in the ground are generally chemically innocuous; indeed, they may be beneficial since there is considerable evidence, from seawater studies, that the presence of chloride generally reduces sulfate attack. This is taken into account for brackish water (12000-17000 mg/l chloride) in Note (e) to Table C2.

No recommendations are given here for concrete exposed to seawater (~18000 mg/l chloride). Reference should be made to BS 6349: Part 1 for maritime structures and BS 8500-1.

While not generally causing chemical attack on concrete, chlorides originating in the ground can lead to degradation of concrete through a physical mechanism involving crystallisation of chloride salts near to the surface of the concrete; this is sometimes called ‘salt weathering’ – see Section B6.

The risk of corrosion of embedded metals in buried concrete in non-aggressive soil is generally lower than in externally exposed concrete. However, high chloride concentrations in the ground will increase the risk of corrosion, since chloride ions may migrate into the concrete and lead to a reduction in passivity at the metal surface. The recommendations for the protection of steel reinforcement given in BS 8500-1 should be followed.

On brownfield sites that have industrial residues, the presence of chloride ions, together with a pH below 5.5, could indicate the existence of hydrochloric acid that may cause acid attack. It will, therefore, be important to determine the amount of chloride in the soil and / or groundwater during site investigation, as described in Section C4. The procedure for taking account of the
measured chloride content in this particular circumstance is given in Section C5.1.2.

Apart from this and the need to identify brackish and sea waters, no account is taken of chloride concentration in the procedure for concrete specification given in Section D.

Specialist advice should be sought if exceptionally high chloride levels are encountered, for example, related to past industrial use of land. Such high concentrations have been reported as chemically affecting hardened concrete. Detrimental mechanisms include the reaction of calcium and magnesium chlorides with calcium aluminate hydrates to form chloroaluminates which may result in low-medium expansion of concrete.

B3.4 Chromium
A potential for attack on concrete from chromium has been reported in the literature. However, in practice this would appear to be limited to concrete in contact with chromite or processing residues.

B3.5 Organic compounds
Phenols are the most commonly encountered troublesome organic group. These are contaminants typically generated as by-products during the manufacture of town gas, tar and coke. The concentrations present are rarely sufficient to attack hardened concrete. However, their presence may well affect the setting of concrete through an inhibition or modification of the hydration of the cement. Where in-situ concrete is placed directly against ground suspected of substantial contamination by phenols, consideration should be given to the use of a barrier, such as polyethylene sheeting, as protection during the setting and hardening period.

It has been reported that where phenol is present in exceptionally high concentrations (eg several thousand mg/l), it has the potential to attack hardened concrete. The phenol is said to react with calcium hydroxide in the cement paste to form calcium phenolate. This crystallises in the pores of the concrete causing deterioration as a result of physical expansion.

Some organic compounds are mildly acidic and affect concrete as described in Section B2.2. In addition to naturally occurring humic acid derived from decay of organic matter, acids may also occasionally be produced by activities of man, for example lactic acid, acetic acid and butyric acids.

B4. Attack from aggressive carbon dioxide
Aggressive carbon dioxide is relevant only to certain situations where water is continually flowing over (or seeping through) the concrete. Diversion pipes or culverts around dams retaining moorland waters containing high concentrations of aggressive carbon dioxide can be subject to erosion, as can poorly compacted concrete, or permeable concrete products (for example some aggregate concrete blocks) used in foundations.

Calcium carbonate (CaCO₃) is practically insoluble in water but calcium bicarbonate (Ca(HCO₃)₂) is soluble. Where carbon dioxide dissolves in water, carbonic acid (H₂CO₃) is formed and this will react with any carbonated cement (or limestone aggregate) to form calcium bicarbonate that goes into solution. This is how swallow holes and caves are formed in limestone. With bicarbonate ions (HCO₃⁻) now in solution, a certain amount of the dissolved carbon dioxide will be needed to stabilise it, so there will be less available to attack further carbonated concrete. It is this remaining available portion of the dissolved carbon dioxide that is referred to as ‘aggressive’. Measures to take account of aggressive carbon dioxide for some uses of specific precast concrete products are incorporated into guidance for specific precast concrete products in Part F. These measures are also relevant to cast-in-situ structures that are in contact with flowing water containing aggressive carbon dioxide (see Note ‘d’ in Table C1).

B5. Attack from pure water
‘Pure’ (soft) water, which contains low concentrations of dissolved ions is aggressive when it flows in quantity over a concrete surface. Concrete surfaces that are carbonated are less prone to this form of attack.

B6. Damage to concrete from crystallisation of salts
In addition to causing chemical attack on concrete, soluble compounds originating in the ground can lead to degradation of concrete through a physical mechanism involving crystallisation of salts, usually sulfates or
chlorides, near to the concrete surface. A classic scenario for this is where concrete of high permeability is partly buried in wet sulfate or chloride-bearing ground and partly exposed to air. Sulfates or chlorides in solution may be drawn through the concrete by capillary suction to evaporate at or close to the free surface. Crystallisation of salts in pores close to the surface of the concrete may generate expansive stresses that disrupt the concrete, while surface salt deposits form a characteristic efflorescence. The process may be aggravated by repeated wetting and drying of the exposed concrete surface; this leads to cyclical salt precipitation and dissolution and fatigue stressing of the concrete fabric.

Additionally, where crystallisation initially occurs at a relatively high temperature producing an anhydrous salt, subsequent wetting may lead to conversion to a hydrous crystalline form of substantially greater volume. A salt particularly implicated in this latter mechanism is sodium sulfate which, subjected to alternate wetting and drying, may alternate between anhydrous thenardite \((\text{Na}_2\text{SO}_4)\) and hydrous mirabilite \((\text{Na}_2\text{SO}_4.10\text{H}_2\text{O})\), with a change in crystalline volume of some 300% and a potentially large cyclical stress change. A comprehensive discussion of the topic is included in *Sulfate attack on concrete* [3].

In the UK, degradation of partly buried concrete due to crystallisation of salts originating from the ground is rarely a problem. For most ground conditions, the measures recommended here to mitigate chemical attack on concrete (and in particular specified free water/cement ratios of 0.5 or less) should also be effective against physical degradation due to crystallisation of likely salts. Further guidance for extreme ground conditions in arid areas is given CIRIA Report C577 [10].

B7. Microbial contribution to chemical attack on concrete

Activity of micro-organisms in the ground can result in changes to the chemical environment that can contribute indirectly to concrete attack. The most widely recognised damage of bacterial origin is the deterioration of concrete in sewers caused by sulfate-reducing bacteria which feed on sulfate in the effluent. Sulfuric acid is produced which attacks the concrete. In contrast, sulfate-oxidising bacteria such as thiobacillus ferroxidans aid in oxidation of pyrite \((\text{FeS}_2)\) in the ground, producing both sulfuric acid and sulfates that subsequently lead to sulfate attack of concrete. The need to take pyrite oxidation into account where pyritic soils will be disturbed by construction is discussed in Section C5.1.3.
References – Part B


British Standards Institution


BS 8500-1: Concrete – Complementary British Standard to BS EN 206-1 – Part 1: Method of specifying and guidance for the specifier