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Keldnaholt, IS-112 Reykjavík

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Icelandic Technology Institute
Keldnaholt, IS-112 Reykjavík

Dr. Guðmundur Guðmundsson
Iceland Cement Ltd.
IS-300 Akranes

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DETERIORATION OF CONCRETE DIAGNOSED BY OPTICAL MICROSCOPY

Niels Thaulow and Ulla Hjorth Jakobsen
G.M. Idorn Consult, RAMBØLL, Bredevej 2, DK-2830 Virum

ABSTRACT

Concrete is normally a very durable material. However, a number of deterioration mechanism may cause premature distress. The principal tool for diagnosing the deterioration mechanism(s) is optical microscopy.

Based on case studies the following types of concrete deterioration are emphazised:

- Alkali Silica Reaction (ASR)
- Sulphate Attack
- Delayed Ettringite Formation (DEF)
- Acid Attack
- Carbonation and Bi-carbonation
- Freeze/thaw

The various mechanisms are mainly diagnosed on the basis of crack pattern, paste texture and secondary mineral phases. It is often found that more than one deterioration mechanism is active, which may accelerate the breakdown of the concrete and challenge the skills of the petrographer.

INTRODUCTION

The present paper is based on (Thaulow and Jakobsen, 1995) extended to cover two more deterioration mechanisms.

It is almost never possible to diagnose the deterioration mechanism based on the visual appearance of the concrete surface. Many people do, however, use the surface crack pattern to make their diagnosis which unfortunately often ends up being incorrect. The surface symptoms caused by different breakdown mechanisms may look alike on the surface of the concrete (e.g. map cracking see Figure 1) but when studied in the microscope the microstructure reveals different crack patterns indicative of the various deterioration mechanisms.

The surface crack pattern does not reveal anything about the number of breakdown mechanisms which may be active at the same time. Furthermore, the surface crack pattern provides no information about the sequence of occurrences of the different mechanisms. It is well known that when concrete is first cracked by one mechanism other breakdown mechanisms may follow (Idorn, 1967).

When diagnosing deterioration mechanisms it is therefore important to conduct a field survey, to examine cores taken from relevant areas (including both sound and damaged areas), and to make use of the information which can be obtained by optical microscopic analysis. It is important to examine a reasonable number of thin sections in order to obtain a good overview of the problem. Unfortunately, for economic reasons the number of thin sections examined is often quite low.

The order in which the deterioration mechanisms occur can under normal circumstances be determined by the use of optical microscopic analysis. The experience of the petrographer is, however, by far the most important factor in assuring a useful outcome of a microscopical investigation.

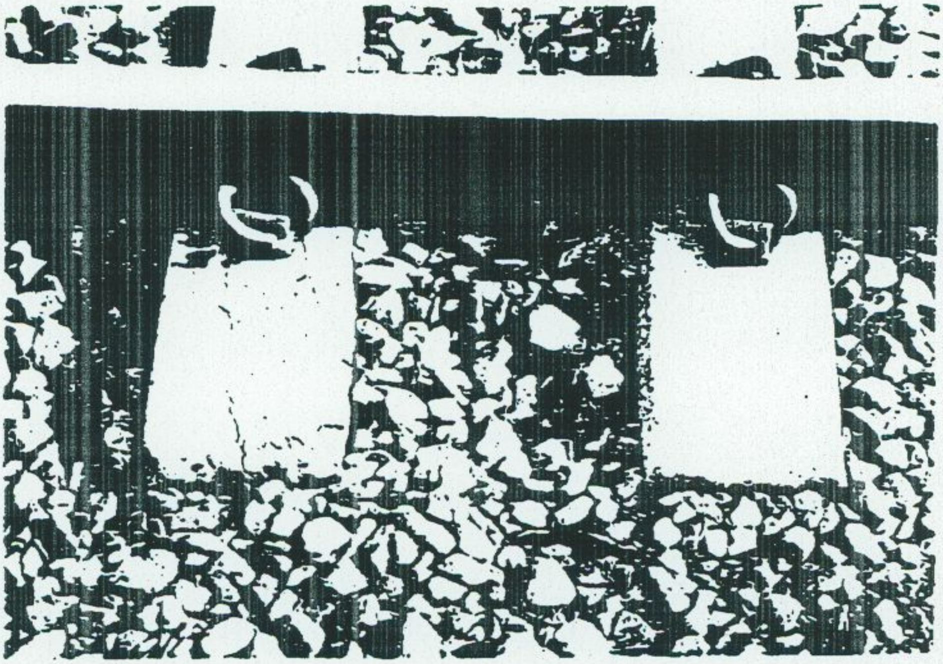

Figure 1 Railroad tie showing map cracks on the surface caused by a combination of alkali silica reaction and delayed ettringite formation.

Sometimes it is possible to date two generations of cracks that intercept each other: if an empty crack crosses a crack filled with material like alkali silica gel or ettringite the empty crack is the younger of the two.

The most important deterioration mechanism is decided on the basis of the relative amount of cracking caused by the different mechanisms.

Alkali silica reaction, ASR and Delayed Ettringite Formation, DEF are often found together in heat cured concrete because high temperatures trigger DEF and accelerate ASR. It should be emphasised, however, that ettringite in cracks and voids is commonly found in ASR affected concrete (Christensen, et al., 1981), where DEF is not present.
This paper describes six types of deterioration mechanisms, their occurrences and their microscopic appearances and differences: alkali silica reaction (ASR), sulphate attack, delayed ettringite formation (DEF), acid attack, carbonation and freeze/thaw.

MICROSCOPIC ANALYSIS

Optical microscopy is performed on fluorescent impregnated thin sections using transmitted polarised light, crossed polarised light and fluorescent light (combination of a blue filter and a yellow blocking filter). A 100 watt halogen light source is used as illumination.

The thin sections are made by vacuum impregnating pieces (35 x 40 mm) of concrete with an epoxy resin containing a fluorescent dye. The impregnated pieces are mounted on slabs of glass and ground and polished to a thickness of 0.020 mm (20 μm). The vacuum impregnation of the samples with epoxy causes all voids and cavities in the samples to be filled with fluorescent epoxy. By transmitting blue light through the thin section in the microscope, the fluorescent epoxy in the various porosities emit yellow light that makes voids, cavities and cracks easy to identify. Aggregates and other less porous phases appear in different shades of green. The fluorescent epoxy also impregnates the capillary pores of the hardened cement paste causing a dense cement paste with low water to cement ratio to appear darker green while a more porous cement paste with a high water to cement ratio appears lighter green. Comparing these green colours to known standards the water to cement ratio (w/c) of the concrete can be estimated with an accuracy of ± 0.02.

Combining information from all 3 types of microscopic illumination usually provides a diagnosis of the concrete distress. While optical microscopy is the primary tool on some occations it is useful to combine optical microscopy with chemical analyses and SEM-EDX analyses (Jakobsen et al., 1997).

ALKALI SILICA REACTION

Mechanism

Alkali silica reaction (ASR) is a chemical reaction that takes place in aggregate particles between the alkaline pore solution of the cement paste and silica in the aggregate particles. Hydroxyl ions penetrate the surface regions of the aggregate and break the silicon-oxygen bonds. Positive sodium, potassium and calcium ions in the pore liquid follow the hydroxyl ions so that electroneutrality is maintained. Water is imbibed into the reaction sites and eventually alkali-calcium silica gel is formed.

The reaction products occupy more space than the original silica so the surface reaction sites are put under pressure. The surface pressure is balanced by tensile stresses in the centre of the aggregate particle and in the ambient cement paste.

At a certain point in time the tensile stresses may exceed the tensile strength and brittle cracks propagate (Svenson, 1991, Thaulow and Andersen, 1988). The cracks radiate from the interior of the aggregate out into the surrounding paste.

The cracks are empty (not gel-filled) when formed. Small or large amounts of gel may subsequently exude into the cracks. Small particles may undergo complete reaction without cracking.

Microscopic appearance

Alkali silica reaction is diagnosed primarily by four main features (Andersen and Thaulow, 1990):

- Presence of alkali silica reactive aggregates
- Crack pattern
- Presence of alkali silica gel in cracks and/or voids
- $Ca(OH)_2$ depleted paste

Alkali silica reaction is primarily diagnosed by the presence of cracks in *reactive aggregates* radiating out into the cement paste. Reactive aggregates contain amorphous or microcrystalline silica, SiO_2. Frequently, alkali silica gel is also observed, however, the amount of gel is not a measure of the extensiveness of the reaction but dependent on the type of reactive aggregate. Aggregates containing reactive silica, such as porous flint (Figure 2a), react rapidly to form alkali silica gel both at the surface and inside the aggregate. More dense polymineralic particles, such as mylonitizised granites (Figure 2b) containing microcrystalline quartz, react more slowly. In such cases only small amounts of gel formation are needed to separate the grain boundaries, leading to expansion and cracking of the aggregate.

The *crack pattern* observed depends on the type of reactive aggregate (Figure 2). Aggregates without preferred orientation of the mineral grains such as porous flint create three-legged cracks with angles of 120° between cracks. In aggregates with oriented minerals such as mylonites cracks are often parallel to the mineral orientation.

Figure 2 Alkali silica reactive aggregates in concrete. (A) cracked porous flint particle with gel in the cracks (arrow). The image is taken in ordinary light. Scale bar measures 330 microns.

In aggregates such as sandstones the cracks may run along grain boundaries. Typically for all types of aggregates the cracks are wide in the centre and narrow toward the rim of the aggregates. Locally the cracks tend to be perpendicular to the surface of the reactive particle (radial cracks).

If a certain number of reactive particles are present in the concrete a continuous crack pattern is present. Usually, the cracks follow the line of least resistance perpendicular to the tensile stresses of the concrete. At the surface of the concrete, cracks perpendicular to the surface are commonly seen. Beneath the surface, a large number of cracks tend to be parallel to the surface. These cracks usually run through the cement paste and reactive aggregates, and in rare cases even sound aggragates may be cracked.

Another diagnostic feature of alkali silica reaction is the presence of *alkali silica gel*. Alkali silica gel is a clear, colourless isotropic material with low refractive index (1.46 - 1.53) and a typical shrinkage crack pattern (Figure 3a) (ASTM C356, 1993). Alkali silica gel may, however, be partly crystalline, showing an orange interference colour in crossed polarised light. This feature is generally only observed in gel that is situated in cracks inside aggregates or in cracks of rather old concrete (Thaulow et al., 1989). Gel may be observed replacing the outer part of e.g. a porous flint particle (Figure 2a), be situated in cracks and/or in air voids. Ettringite in pores and cracks is commonly found in ASR-affected concrete. The trained petrographer can, however, distinguish alkali silica gel from massive ettringite formation (Figure 3b) by the slight birefringence of ettringite. Furthermore, ettringite exhibits a different crack pattern consisting of almost parallel microcracks. The use of a yellow fluorescent epoxy for preparing the thin sections facilitates the distinction between alkali silica gel and ettringite (Thaulow et al., 1996).

In cases of intensive ASR the $Ca(OH)_2$ of the paste can be dissolved leaving a *black and opaline shining paste* when observed in crossed polarised light. Generally, the dark paste areas are found in a narrow zone around reactive aggregates and along gel containing cracks.

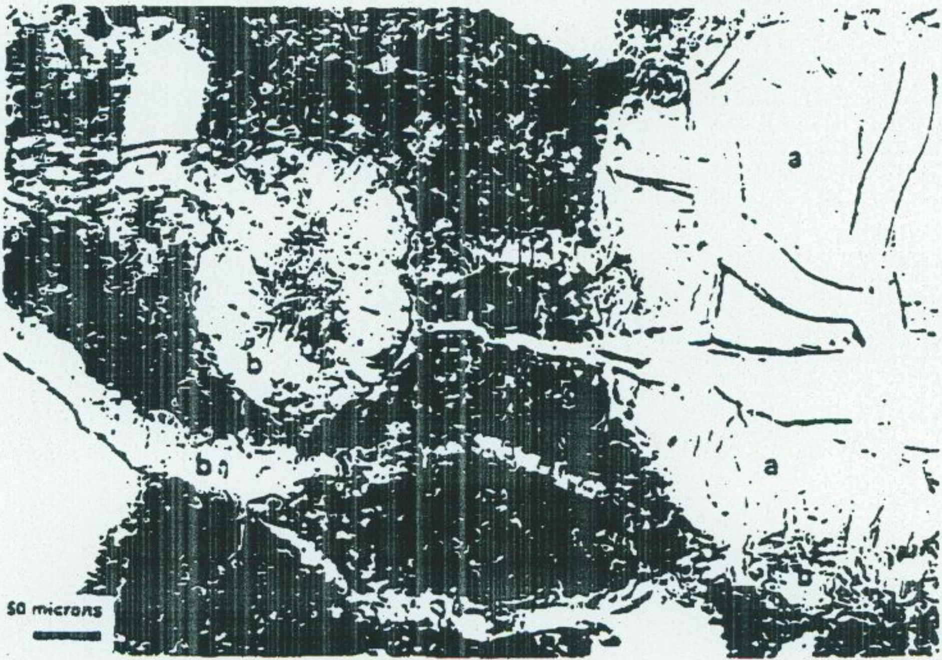

Figure 3 Difference between alkali silica gel (a) and ettringite (b) in voids. The image is taken in ordinary light. Scale bar measures 50 microns.

SULPHATE ATTACK

Mechanism

Sulphate ions may attack components of cement paste. Such attack occur when concrete is in contact with sulphate containing water e.g. sea water, swamp water, ground water or sewage water. The often massive formation of gypsum ($CaSO_4 . 2H_2O$) and of ettringite ($3CaO . Al_2O_3 . 3CaSO_4 . 32H_2O$) formed during the sulphate attack may cause concrete to crack.

The formation of gypsum requires a high concentration of sulphate in the ambient water in contact with the concrete. The formation of ettringite occurs by a transformation of the calcium and aluminium containing components in the cement paste. Formation of sulphate phases takes place through dissolution of the cement paste as the sulphate ions consume calcium ions from calcium hydroxide and from the C-S-H (decalcification).

Microscopic appearance

Sulphate attack is diagnosed primarily by four main features:

- Surface parallel cracks in the cement paste and along aggregate paste interfaces
- Presence of gypsum and/or excessive amounts of ettringite in voids, cracks and paste
- Dissolution and decalcification of cement paste
- External sulphate source

Sulphate attack is diagnosed when the concrete contains surface *parallel cracks* (Figure 4a) filled or partly filled with gypsum. The cracks occur parallel to and near the surface of the concrete. The orientation depends on the possible expansion direction of the concrete. The cracks traverse the cement paste and follow aggregate surfaces.

Gypsum is diagnosed by its texture and birefringence when observed in crossed polarised light. The interference colour is white to grey. Gypsum is typically observed in parallel cracks and in voids near the surface (Figure 4b). Gypsum is not always recognisable in the optical microscope. If gypsum precipitates in the cement paste scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) is useful for positive identification (Jakobsen et al., 1997).

Ettringite is identified as needle shaped crystals with low birefringence. It has to be emphasised that the occurrence of ettringite in voids and cracks is common in every mature water-exposed concrete; ettringite by itself is <u>not</u> a diagnostic feature of sulphate attack (Christensen et al., 1981).

To diagnose sulphate attack, near-surface paste expansion forming surface parallel cracks in the cement paste must be present. Chemical analyses of the sulphate content in the surface and the interior is helpful. Furthermore, in order to distinguish sulphate attack from delayed ettringite formation an *outside sulphate source* must be identified.

Figure 4 Concrete subjected to external sulphate attack. Gypsum appears in surface parallel cracks, in the cement paste and in gypsum filled voids (arrow). The image is taken in ordinary light. Scale bar measures 130 microns.

DELAYED ETTRINGITE FORMATION (DEF)

Mechanism

Delayed Ettringite Formation, DEF is a form of internal sulphate attack. A number of factors such as concrete composition, curing conditions and exposure conditions influence the potential for DEF (Thaulow et al., 1995). The fundamental reaction mechanism is still debated (Johansen et al., 1993b, Lawrence, 1995, Johansen and Thaulow, 1997). DEF is believed to be a result of improper heat curing of the concrete where the normal ettringite formation is suppressed. A large amount of sulphate is bound in the C-S-H and the sulphate concentration in the pore liquid is high for an unusually long period of time in the hardened concrete. Eventually, the sulphate reacts with calcium and aluminium containing phases of the cement paste and the cement paste expands. Due to the paste expansion empty cracks (gaps) are formed around aggregates (Figure 5). The cracks may remain empty or later be partly or totally filled with ettringite (Johansen et al., 1993a).

Microscopic appearance

DEF is diagnosed primarily by four main features:

- Presence of gaps completely surrounding aggregates. Ettringite may be present in the gaps
- Wider gaps around large aggregates than around small aggregates
- Absence of external sulphate source
- High concrete temperature during curing

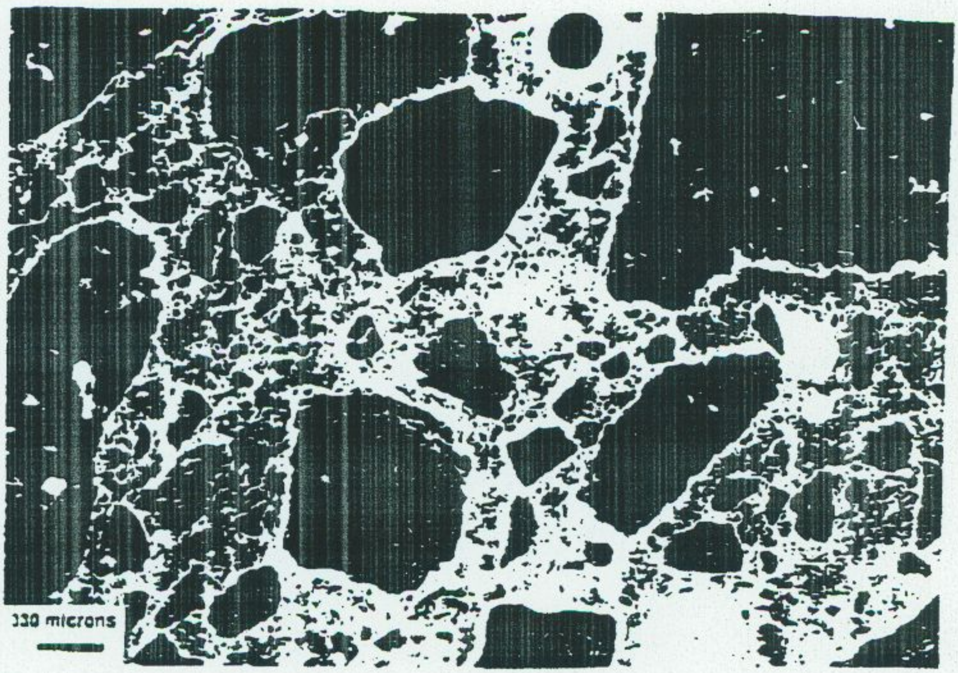

Figure 5 Gaps around aggregate particles in an improperly heat cured railroad tie. The image is taken in fluorescent light. Scale bar measures 330 microns.

In diagnosing DEF, cracks or *gaps* have to be observed around the aggregate particles (Figure 5). The gaps may be empty, partly filled by needle shaped ettringite or filled with a more massive type of ettringite. In contrast to other researchers (Heinz, 1986, Heinz and Ludwig, 1987), we do not believe that the crystal growth of ettringite in the gaps created the gaps (Johansen and Thaulow, 1997).

The *width of the cracks* are directly proportional to the diameter of the aggregates, resulting in wide cracks around coarse aggregates and narrow cracks around fine aggregates (Johansen et al., 1993a). Under ideal circumstances gaps are only seen around the aggregates. However, in field concrete narrow cracks are also observed perpendicular to the aggregate surfaces (Figure 5). Usually aggregate particles are not cracked by DEF. This may, however, occur in limestone aggregates.

DEF is distinguished from external sulphate attack because gypsum is normally not formed in DEF. Furthermore, the paste expansion in DEF is not limited to the surface regions of the concrete. It is useful to know the curing conditions of the concrete, as high internal temperature during curing is a prerequisite for delayed ettringite formation.

It has to be emphasized that freeze/thaw of critically water saturated concrete may result in paste expansion and in gap formation.

ACID ATTACK

Mechanism

Concrete is susceptible to acid attack because of its alkaline nature. The components of the cement paste break down during contact with acids. Most pronounced is the dissolution of calcium hydroxide which occurs according to the following reaction:

$2\ HX + Ca(OH)_2 \rightarrow CaX_2 + 2\ H_2O$ (X is the negative ion of the acid)

The decomposition of the concrete depends on the porosity of the cement paste, on the concentration of the acid, the solubility of the acid calcium salts (CaX_2) and on the fluid transport through the concrete. Insoluble calcium salts may precipitate in the voids and slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids such as phosphoric acid and humic acid are less harmful as their calcium salt, due to their low solubility, inhibit the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulphate attack.

Microscopic appearance

An acid attack is diagnosed primarily by two main features:

- Absence of calcium hydroxide in the cement paste
- Surface dissolution of cement paste exposing aggregates

Acid attack is usually diagnosed when *dissolution of calcium hydroxide* is observed. Dissolution of $Ca(OH)_2$ makes the cement paste totally black and opaline shiny when observed in crossed polarised light (Figure 6).

Dissolution of the calcium hydroxide is observed in the surface of the concrete and around cracks in contact with the surface. The depth of the dissolution depends on the porosity of the concrete (water/cement ratio) and the type of acid.

Generally, cracks are not produced by the acid attack itself, but instead *exposed aggregates* are observed on the surface, due to the disintegration of the cement paste. The cement paste is converted to silica gel with shrinkage cracks.

Chemical analyses may be helpful in identifying which acid is present.

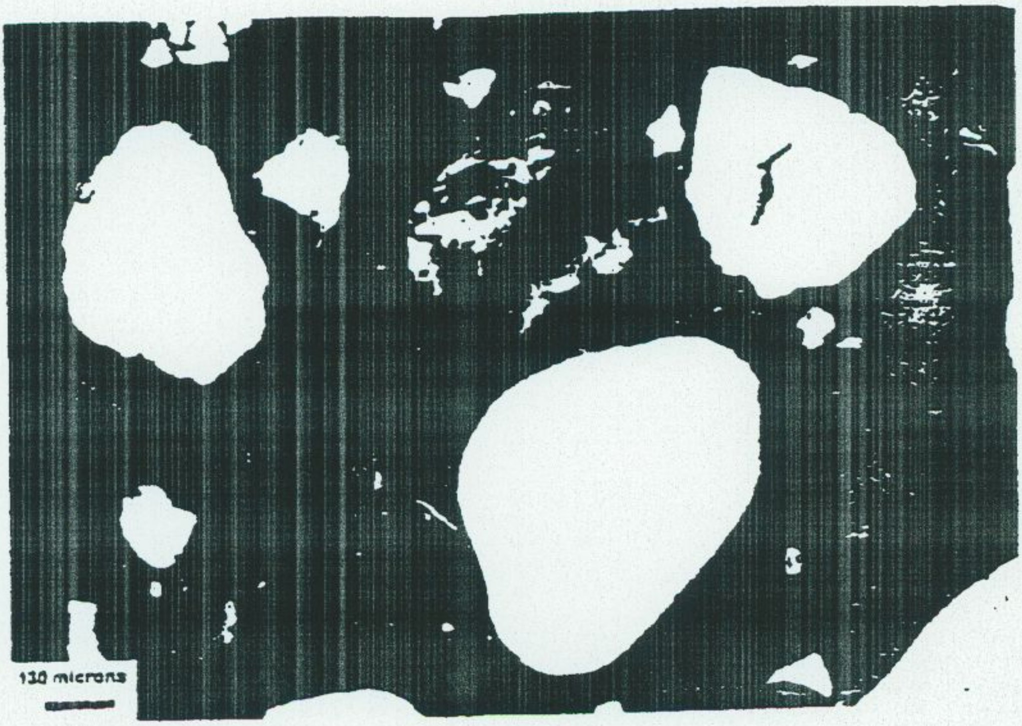

Figure 6 Acid attacked concrete. The paste appears black with an opaline shine when illuminated in crossed polarised light. Scale bar measures 130 microns.

CARBONATION AND BI-CARBONATION

Mechanism

Carbonation may be seen as a special type of acid attack, where the acid is carbon dioxide. All calcium bearing phases of the cement paste are attacked and converted. Low soluble calcium carbonate, $CaCO_3$, is precipitated instead and acts as a good, durable binder in most cases.

The reaction is often given for calcium hydroxide, that is the first phase that reacts and disappear:

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

calcium carbonate is normally found as calcite.

The porosity of the paste is often unchanged or lower in the carbonated zone that is found at the surface of the concrete and along cracks perpendicular to the surface. By comparing the depth of carbonation at the surface with the depth of carbonation at the crack it is often possible to estimate the age of the cracks.

In very porous concrete with high w/c and low content of calcium hydroxide the carbonation may lead to increased porosity and loss of strength.

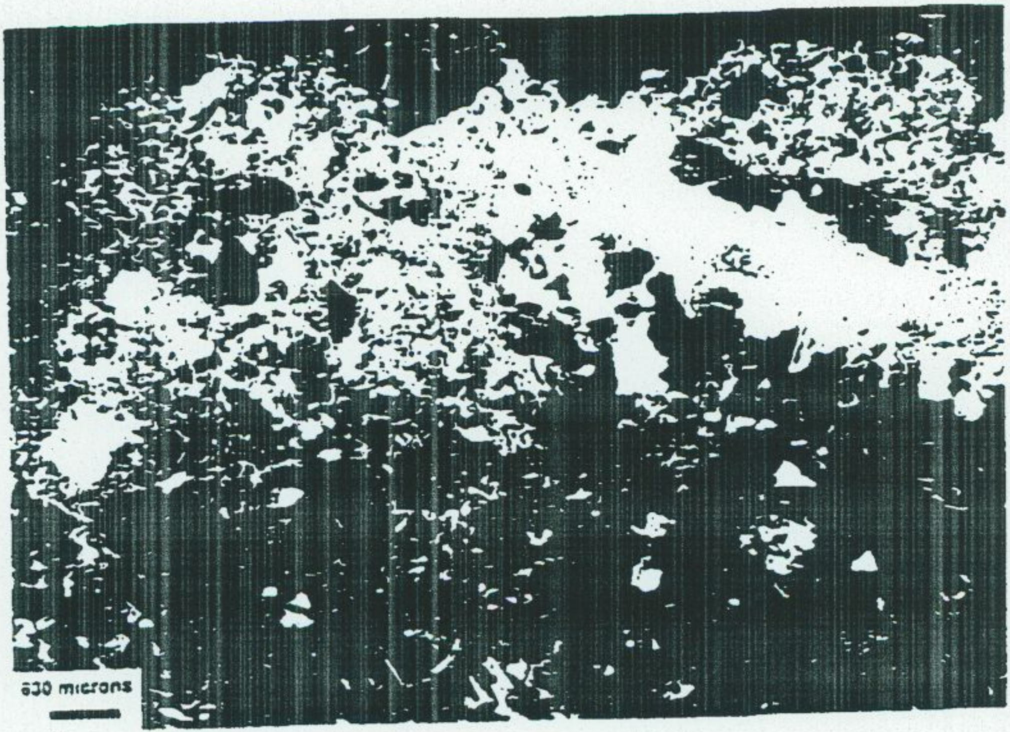

Figure 7 Carbonated concrete. Calcite crystals of high birefringence appear in the surface zone. The image is taken in crossed polarized light. Scale bar measures 630 microns.

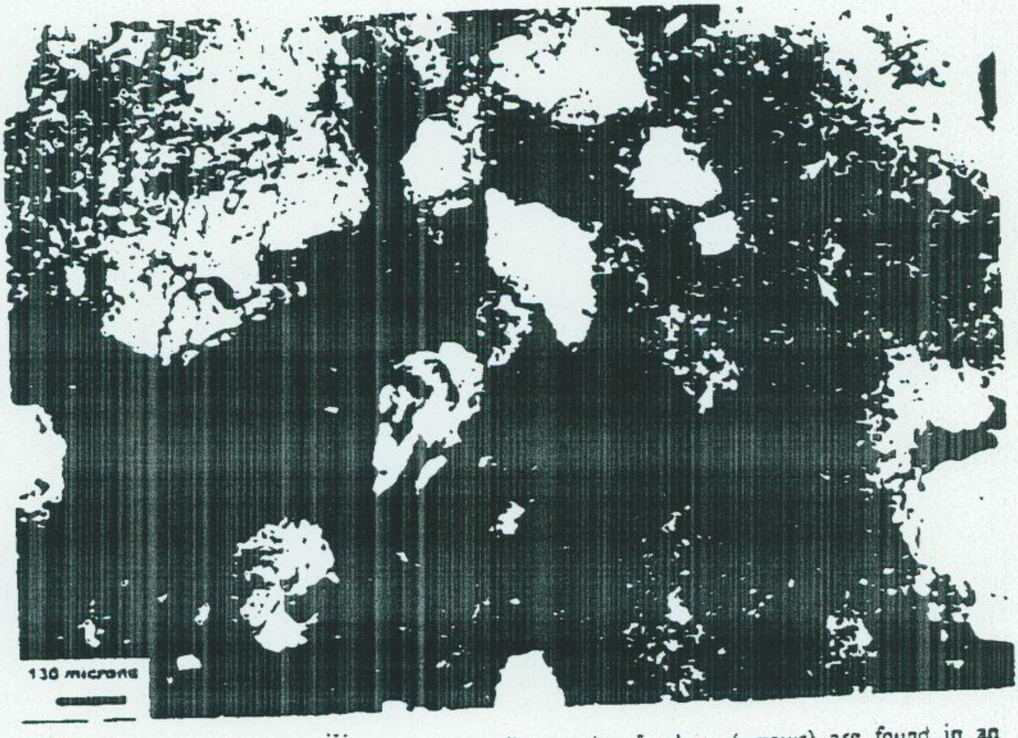

Figure 8 "Bi-carbonation" Large "pop-corn" crystals of calcite (arrows) are found in an isotropic matrix. The image is taken in crossed polarized light. Scale bar measures 130 microns.

FROST ATTACK

Mechanism

Deterioration of concrete exposed to freezing and thawing occurs when the concrete is critically water saturated. The fundamental mechanism of frost damage is related to the volume increase occuring when water freezes to ice. Several mechanisms have been proposed over the years (Laugesen et al., 1996).

- Hydraulic pressure
- Osmotic pressure
- Microscopic ice lens growth
- Thermal incompanbility between matrix and aggregates
- Shock freezing
- Thermal expansion of ice during heating.

None of these mechanism can alone explain all observations. There is no concensus regarding the mechanisms (ACI C201, 1995).

Microscopic appearance

Frost damage is diagnosed primarily by the following features:

- Surface scaling
- Internal cracking due to paste expansion

Surface scaling is the loss of paste and mortar from the surface of the concrete. By the process coarse aggregate particles may be exposed and finally lost. Internal cracking due to paste expansion is typical for frost attack and for sulphate attack and for DEF. It may be difficult to diagnose "pure" frost attack unless the other mechanisms can be excluded based on knowledge obtained from other sources than the thin section.

Freeze thaw damage is often combined with other types of concrete distress. Often it is not diagnosed or misdiagnosed. In Denmark the diagnosis "frost attack" has traditionally been given only after excluding other possible causes such as ASR. This means that the occurrence of frost attack in Denmark may be more common than generally believed. In Norway, on the other hand, there has been a tradition to diagnose frost attack only in many concrete structures. First by the work of (Jensen, 1993) ASR was generally accepted in Norway.

Under ideal conditions frost attack creates gaps around the aggregate (Idorn et al., 1993). See Figure 9.

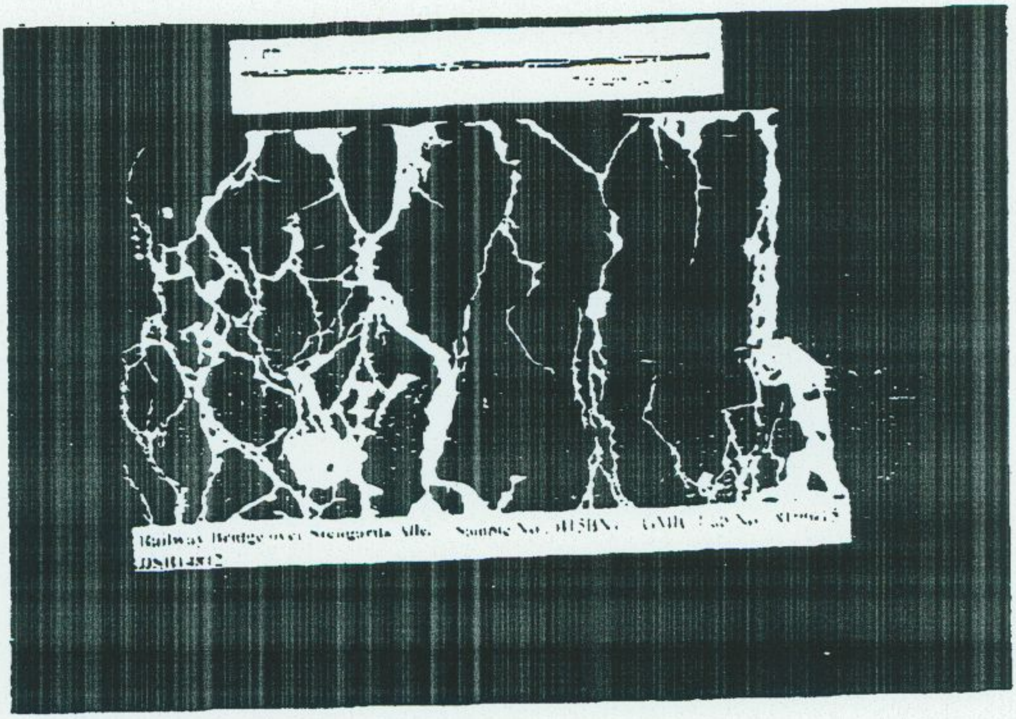

Figure 9 Macro-photo in UV-light of fluorescent impregnated, cut concrete core with frost damage. Scale bar measures 10 cm.

As frost attack normally proceeds from the concrete surface and inwards the paste expansion forms delamination cracks sub-parallel to the surface with a distance of around 10 mm between cracks. Figure 9.

CONCLUSIONS

- With an experienced petrographer at the optical microscope thin section microscopy is the principal tool for diagnosing the different deterioration mechanisms in concrete.
- With optical microscopy it is possible to uniquely discriminate between different deteriorating mechanisms, such as ASR, DEF, sulphate attack, acid attack, carbonation and freeze/thaw.
- Each of the deterioration mechanisms mentioned in this paper can usually be diagnosed by crack pattern, presence and position of various precipitates, types of aggregate and the condition of the cement paste.
- Optical microscopy can usually detect whether several deterioration mechanisms are present at the same time. Furthermore, it is possible to evaluate which was first and what is the main cause of the distress.
- Optical microscopy should always be supplemented by a field inspection and (if possible) examination of production data. Sometimes it is useful to supplement the optical thin section microscopy with SEM-EDS or chemical analyses. However, optical microscopy should always be performed as the first step before other types of microanalyses because optical microscopy provides both insight and overview

REFERENCES

Idorn, G.M. (1967) Durability of Concrete Structures in Denmark. *D.Sc. thesis, Technical University of Denmark*, Copenhagen.

Christensen, P., Chatterji, S., Thaulow, N., Jensen, A.D. and Gudmundsson, H. (1981) Filling up pores and fractures in 'weathered' concrete structures. *Proceeding Third International Conference on Cement Microscopy*, Houston, Texas, pp. 298-306.

Heinz, D. (1986) Schädigende Bildung ettringitähnlicher Phasen in wärmebehandelten Mörteln und Betonen, *Thesis*, RWTH Aachen.

Heinz, D. and Ludwig, U. (1987) Mechanism of Secondary Ettringite Formation in Mortars and Concretes after Heat Treatment, *Massivbau Baustofftechnologie*, University of Karlsruhe, Vol. 6. pp. 33-92.

Thaulow, N. and Andersen, K.T. (1988) New knowledge on alkali-silica reactions (in Danish), *Dansk Beton*, No. 1. pp. 14-19.

Thaulow, N., Holm, J. and Andersen, K.T. (1989) Petrographic Examination and chemical analyses of the Lucinda Jetty Prestressed Concrete Roadway, *Proceedings 8th International Conference on Alkali Aggregate Reaction*, Kyoto.

Andersen, K.T. and Thaulow, N. (1990) The Study of Alkali-Silica Reaction in Concrete by the use of Fluorescent Thin Sections ASTM STP 1061, (eds. Erlin and Stark) *Petrography Applied to Concrete and Concrete Aggregates*, Philadelphia.

Svenson, E. (1991) Eigenstresses generated by diffusion in a spherical particle embedded in an elastic medium, *International Journal Mechanism Science*, Vol. 33, No. 3. pp. 211-223.

Johansen, V., Thaulow, N., Jakobsen, U.H. and Palbøl, L. (1993a) Heat Cured Induced Expansion, *Proceedings 3rd Beijing International Symposium on Cement & Concrete*, Beijing 1993.

Johansen, V., Thaulow, N. and Skalny J. (1993b) Simultaneous presence of alkali silica gel and ettringite in concrete, *Advances in Cement Research*, vol. 5, no. 17, pp- 23-29

Idorn, G.M., Johansen, V. and Thaulow, N., (1993) Assessment of causes of cracking in concrete, *Materials Science of Concrete III, (J. Skalny ed.)*, pp. 91-104

Jensen, V., (1993) Alkali Aggregate Reaction in Southern Norway, *Doctor Technical Thesis, University of Trondheim*

ASTM C-856 (1993) *Standard Practice for Petrographic Examination of Hardened Concrete*, vol. 04.02, pp. 422-434

Lawrence, C.D. (1995) Delayed Ettringite Formation: An Issue ? *Material Science of Concrete IV*, (eds. J. Skalny & S. Mindess), American Ceramic Society, pp. 113-154.

Thaulow, N., Jakobsen, U.H., (1995) The diagnosis of chemical deterioration of concrete by optical microscopy, *MRS Fall meeting, Boston* (in Press)

ACI C201 (1995) Frost attack on concrete, *Draft Report, Chapter 2*

Thaulow, N., Johansen, V. and Jakobsen, U.H. (1996) What Causes Delayed Ettringite Formation ? *MRS Fall meeting, Boston* (in Press)

Laugesen, P., Geiker, M., Pedersen, E.J., Thaulow, N. and Thøgersen, F. (1996) HETEK, Method for test of the frost resistance of high performance concrete, *State of the Art, Danish Road Directorate, Report no. 55*

Thaulow, N., Jakobsen, U.H. and Clark B. (1996) Composition of alkali silica gel and ettringite in concrete railroad ties: SEM and X-Ray diffraction analyses, *Cement and Concrete Research*, vol. 26, no. 2, pp. 306-318

Johansen, V. and Thaulow, N., (1997) Heat curing and late formation of ettringite, *ACI Spring convention, April 1997, Seattle,* (submitted for publication)

Jakobsen ,U.H., Johansen, V. and Thaulow, N. Optical Microscopy - a primary tool in concrete examination!, *19th ICAM Conference, Cincinatti 1997, USA* (in press)

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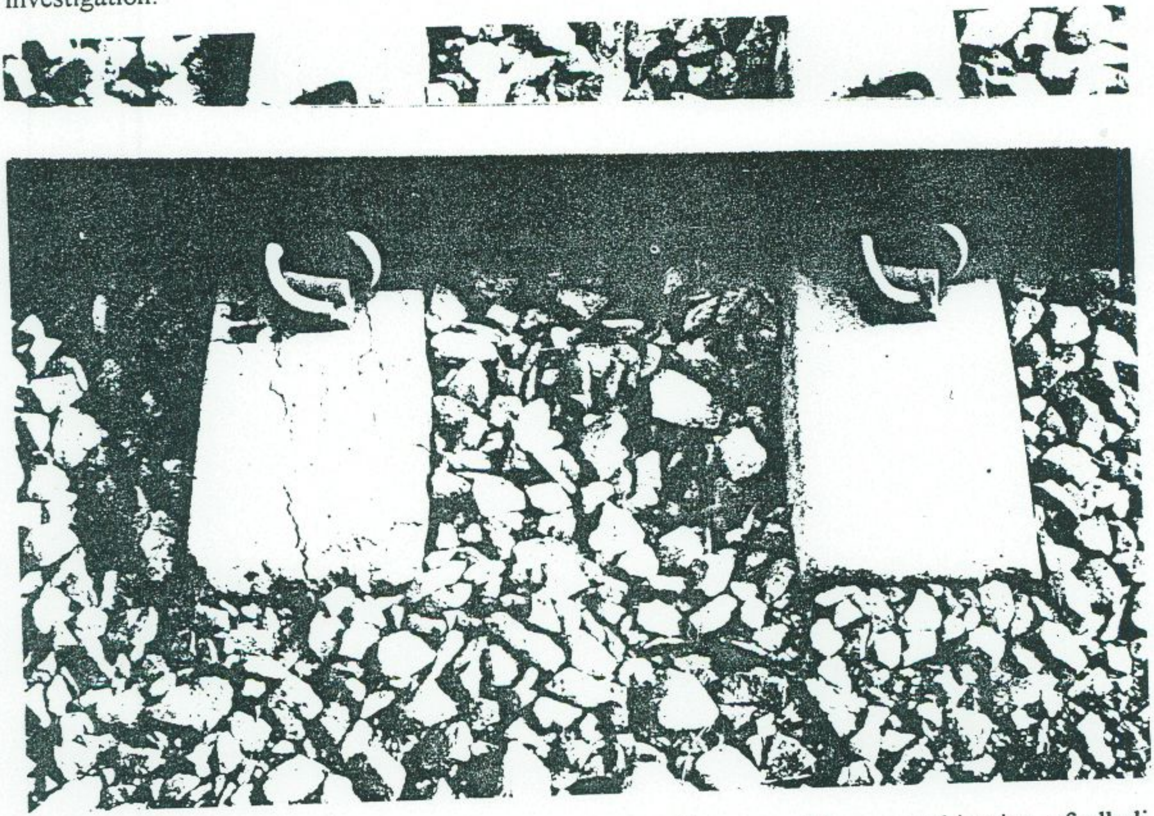

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MICROSCOPIC ANALYSIS

Optical microscopy is performed on fluorescent impregnated thin sections using transmitted polarised light, crossed polarised light and fluorescent light (combination of a blue filter and a yellow blocking filter). A 100 watt halogen light source is used as illumination.

The thin sections are made by vacuum impregnating pieces (35 x 40 mm) of concrete with an epoxy resin containing a fluorescent dye. The impregnated pieces are mounted on slabs of glass and ground and polished to a thickness of 0.020 mm (20 μm). The vacuum impregnation of the samples with epoxy causes all voids and cavities in the samples to be filled with fluorescent epoxy. By transmitting blue light through the thin section in the microscope, the fluorescent epoxy in the various porosities emit yellow light that makes voids, cavities and cracks easy to identify. Aggregates and other less porous phases appear in different shades of green. The fluorescent epoxy also impregnates the capillary pores of the hardened cement paste causing a dense cement paste with low water to cement ratio to appear darker green while a more porous cement paste with a high water to cement ratio appears lighter green. Comparing these green colours to known standards the water to cement ratio (w/c) of the concrete can be estimated with an accuracy of ± 0.02.

Combining information from all 3 types of microscopic illumination usually provides a diagnosis of the concrete distress. While optical microscopy is the primary tool on some occations it is useful to combine optical microscopy with chemical analyses and SEM-EDX analyses (Jakobsen et al., 1997).

ALKALI SILICA REACTION

Mechanism

Alkali silica reaction (ASR) is a chemical reaction that takes place in aggregate particles between the alkaline pore solution of the cement paste and silica in the aggregate particles. Hydroxyl ions penetrate the surface regions of the aggregate and break the silicon-oxygen bonds. Positive sodium, potassium and calcium ions in the pore liquid follow the hydroxyl ions so that electroneutrality is maintained. Water is imbibed into the reaction sites and eventually alkali-calcium silica gel is formed.

The reaction products occupy more space than the original silica so the surface reaction sites are put under pressure. The surface pressure is balanced by tensile stresses in the centre of the aggregate particle and in the ambient cement paste.

At a certain point in time the tensile stresses may exceed the tensile strength and brittle cracks propagate (Svenson, 1991, Thaulow and Andersen, 1988). The cracks radiate from the interior of the aggregate out into the surrounding paste.

The cracks are empty (not gel-filled) when formed. Small or large amounts of gel may subsequently exude into the cracks. Small particles may undergo complete reaction without cracking.

Microscopic appearance

Alkali silica reaction is diagnosed primarily by four main features (Andersen and Thaulow, 1990):

- Presence of alkali silica reactive aggregates
- Crack pattern
- Presence of alkali silica gel in cracks and/or voids
- $Ca(OH)_2$ depleted paste

Alkali silica reaction is primarily diagnosed by the presence of cracks in *reactive aggregates* radiating out into the cement paste. Reactive aggregates contain amorphous or microcrystalline silica, SiO_2. Frequently, alkali silica gel is also observed, however, the amount of gel is not a measure of the extensiveness of the reaction but dependent on the type of reactive aggregate. Aggregates containing reactive silica, such as porous flint (Figure 2a), react rapidly to form alkali silica gel both at the surface and inside the aggregate. More dense polymineralic particles, such as mylonitizised granites (Figure 2b) containing microcrystalline quartz, react more slowly. In such cases only small amounts of gel formation are needed to separate the grain boundaries, leading to expansion and cracking of the aggregate.

The *crack pattern* observed depends on the type of reactive aggregate (Figure 2). Aggregates without preferred orientation of the mineral grains such as porous flint create three-legged cracks with angles of 120° between cracks. In aggregates with oriented minerals such as mylonites cracks are often parallel to the mineral orientation.

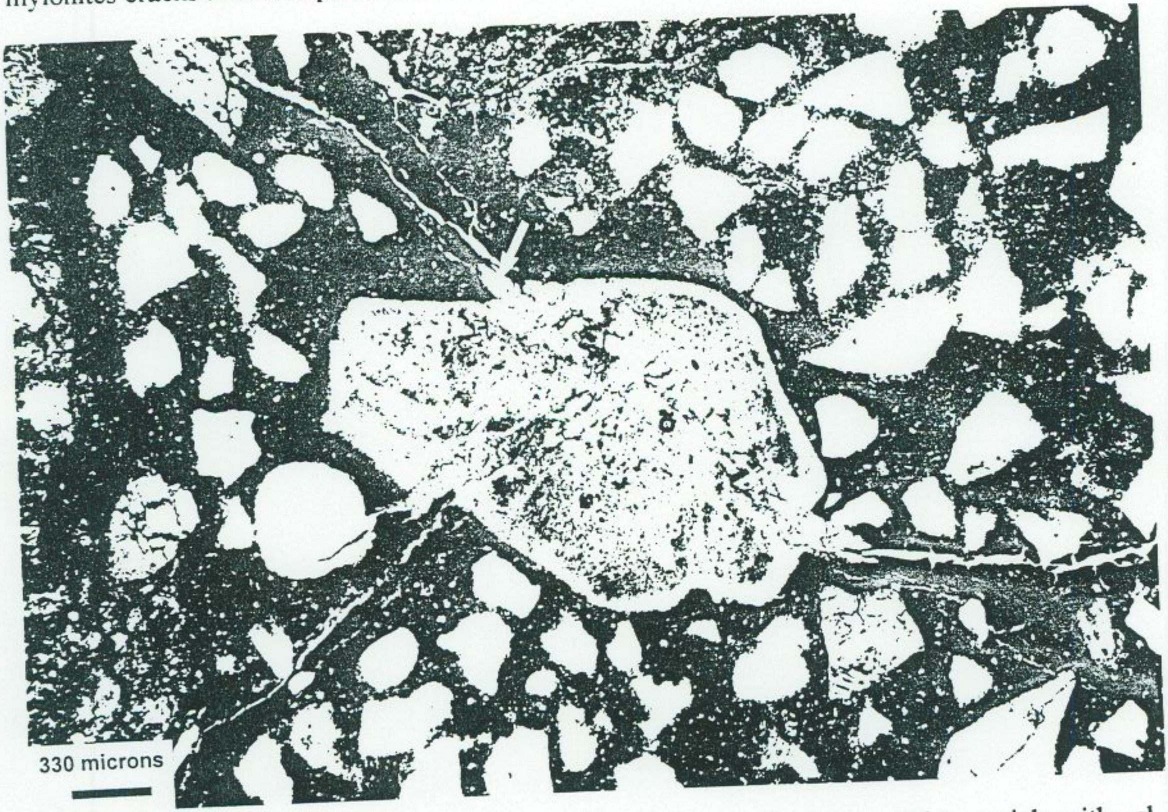

Figure 2 Alkali silica reactive aggregates in concrete. (A) cracked porous flint particle with gel in the cracks (arrow). The image is taken in ordinary light. Scale bar measures 330 microns.

In aggregates such as sandstones the cracks may run along grain boundaries. Typically for all types of aggregates the cracks are wide in the centre and narrow toward the rim of the aggregates. Locally the cracks tend to be perpendicular to the surface of the reactive particle (radial cracks).

If a certain number of reactive particles are present in the concrete a continuous crack pattern is present. Usually, the cracks follow the line of least resistance perpendicular to the tensile stresses of the concrete. At the surface of the concrete, cracks perpendicular to the surface are commonly seen. Beneath the surface, a large number of cracks tend to be parallel to the surface. These cracks usually run through the cement paste and reactive aggregates, and in rare cases even sound aggregates may be cracked.

Another diagnostic feature of alkali silica reaction is the presence of *alkali silica gel*. Alkali silica gel is a clear, colourless isotropic material with low refractive index (1.46 - 1.53) and a typical shrinkage crack pattern (Figure 3a) (ASTM C856, 1993). Alkali silica gel may, however, be partly crystalline, showing an orange interference colour in crossed polarised light. This feature is generally only observed in gel that is situated in cracks inside aggregates or in cracks of rather old concrete (Thaulow et al., 1989). Gel may be observed replacing the outer part of e.g. a porous flint particle (Figure 2a), be situated in cracks and/or in air voids. Ettringite in pores and cracks is commonly found in ASR-affected concrete. The trained petrographer can, however, distinguish alkali silica gel from massive ettringite formation (Figure 3b) by the slight birefringence of ettringite. Furthermore, ettringite exhibits a different crack pattern consisting of almost parallel microcracks. The use of a yellow fluorescent epoxy for preparing the thin sections facilitates the distinction between alkali silica gel and ettringite (Thaulow et al., 1996).

In cases of intensive ASR the $Ca(OH)_2$ of the paste can be dissolved leaving a *black and opaline shining paste* when observed in crossed polarised light. Generally, the dark paste areas are found in a narrow zone around reactive aggregates and along gel containing cracks.

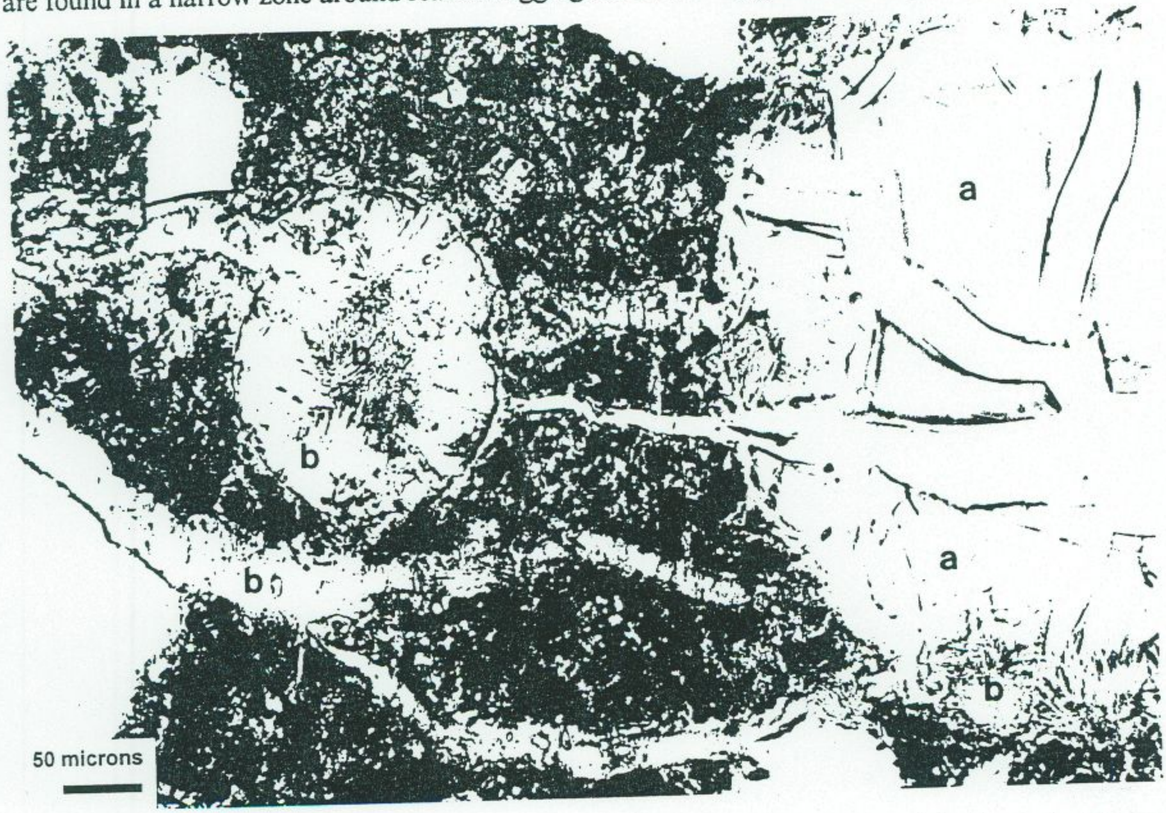

Figure 3 Difference between alkali silica gel (a) and ettringite (b) in voids. The image is taken in ordinary light. Scale bar measures 50 microns.

SULPHATE ATTACK

Mechanism

Sulphate ions may attack components of cement paste. Such attack occur when concrete is in contact with sulphate containing water e.g. sea water, swamp water, ground water or sewage water. The often massive formation of gypsum ($CaSO_4 . 2H_2O$) and of ettringite ($3CaO . Al_2O_3 . 3CaSO_4 . 32H_2O$) formed during the sulphate attack may cause concrete to crack.
The formation of gypsum requires a high concentration of sulphate in the ambient water in contact with the concrete. The formation of ettringite occurs by a transformation of the calcium and aluminium containing components in the cement paste. Formation of sulphate phases takes place through dissolution of the cement paste as the sulphate ions consume calcium ions from calcium hydroxide and from the C-S-H (decalcification).

Microscopic appearance

Sulphate attack is diagnosed primarily by four main features:

- Surface parallel cracks in the cement paste and along aggregate paste interfaces
- Presence of gypsum and/or excessive amounts of ettringite in voids, cracks and paste
- Dissolution and decalcification of cement paste
- External sulphate source

Sulphate attack is diagnosed when the concrete contains surface *parallel cracks* (Figure 4a) filled or partly filled with gypsum. The cracks occur parallel to and near the surface of the concrete. The orientation depends on the possible expansion direction of the concrete. The cracks traverse the cement paste and follow aggregate surfaces.

Gypsum is diagnosed by its texture and birefringence when observed in crossed polarised light. The interference colour is white to grey. Gypsum is typically observed in parallel cracks and in voids near the surface (Figure 4b). Gypsum is not always recognisable in the optical microscope. If gypsum precipitates in the cement paste scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) is useful for positive identification (Jakobsen et al., 1997).

Ettringite is identified as needle shaped crystals with low birefringence. It has to be emphasised that the occurrence of ettringite in voids and cracks is common in every mature water-exposed concrete; ettringite by itself is not a diagnostic feature of sulphate attack (Christensen et al., 1981).

To diagnose sulphate attack, near-surface paste expansion forming surface parallel cracks in the cement paste must be present. Chemical analyses of the sulphate content in the surface and the interior is helpful. Furthermore, in order to distinguish sulphate attack from delayed ettringite formation an *outside sulphate source* must be identified.

Figure 4 Concrete subjected to external sulphate attack. Gypsum appears in surface parallel cracks, in the cement paste and in gypsum filled voids (arrow). The image is taken in ordinary light. Scale bar measures 130 microns.

DELAYED ETTRINGITE FORMATION (DEF)

Mechanism

Delayed Ettringite Formation, DEF is a form of internal sulphate attack. A number of factors such as concrete composition, curing conditions and exposure conditions influence the potential for DEF (Thaulow et al., 1995). The fundamental reaction mechanism is still debated (Johansen et al., 1993b, Lawrence, 1995, Johansen and Thaulow, 1997). DEF is believed to be a result of improper heat curing of the concrete where the normal ettringite formation is suppressed. A large amount of sulphate is bound in the C-S-H and the sulphate concentration in the pore liquid is high for an unusually long period of time in the hardened concrete. Eventually, the sulphate reacts with calcium and aluminium containing phases of the cement paste and the cement paste expands. Due to the paste expansion empty cracks (gaps) are formed around aggregates (Figure 5). The cracks may remain empty or later be partly or totally filled with ettringite (Johansen et al., 1993a).

Microscopic appearance

DEF is diagnosed primarily by four main features:

- Presence of gaps completely surrounding aggregates. Ettringite may be present in the gaps
- Wider gaps around large aggregates than around small aggregates
- Absence of external sulphate source
- High concrete temperature during curing

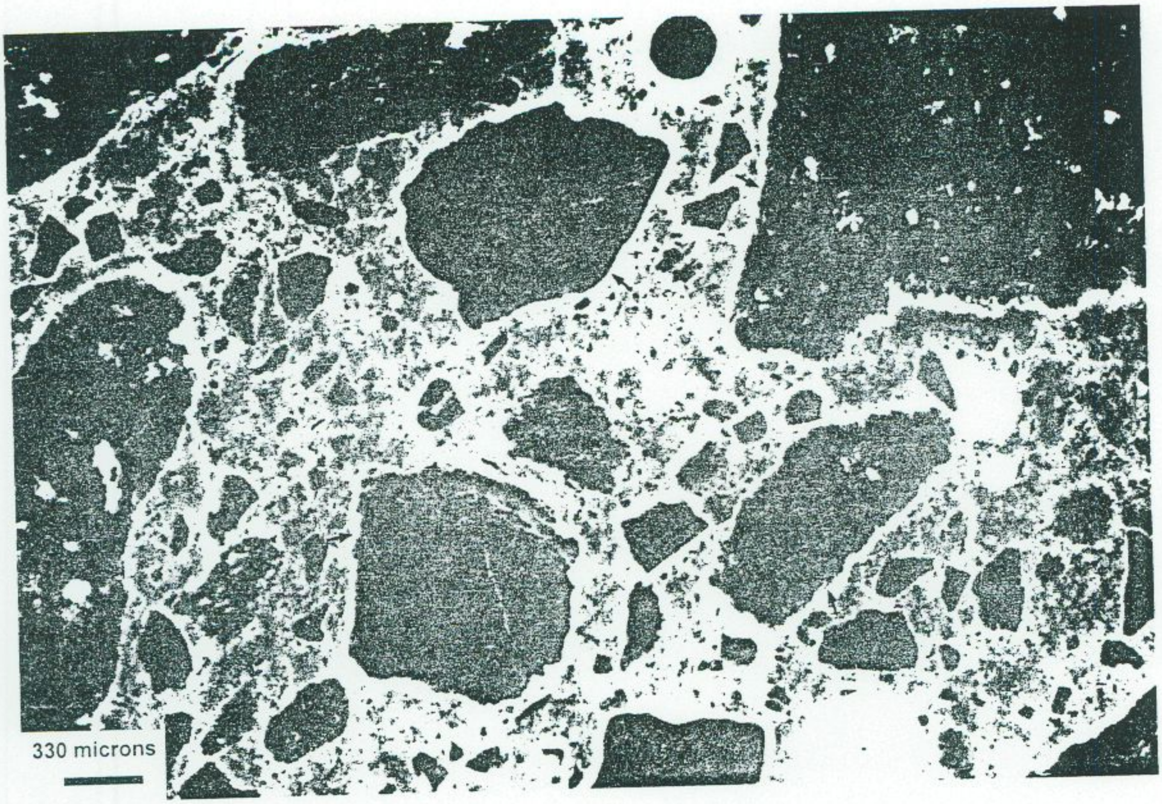

Figure 5 Gaps around aggregate particles in an improperly heat cured railroad tie. The image is taken in fluorescent light. Scale bar measures 330 microns.

In diagnosing DEF, cracks or *gaps* have to be observed around the aggregate particles (Figure 5). The gaps may be empty, partly filled by needle shaped ettringite or filled with a more massive type of ettringite. In contrast to other researchers (Heinz, 1986, Heinz and Ludwig, 1987), we do not believe that the crystal growth of ettringite in the gaps created the gaps (Johansen and Thaulow, 1997).

The *width of the cracks* are directly proportional to the diameter of the aggregates, resulting in wide cracks around coarse aggregates and narrow cracks around fine aggregates (Johansen et al., 1993a). Under ideal circumstances gaps are only seen around the aggregates. However, in field concrete narrow cracks are also observed perpendicular to the aggregate surfaces (Figure 5). Usually aggregate particles are not cracked by DEF. This may, however, occur in limestone aggregates.

DEF is distinguished from external sulphate attack because gypsum is normally not formed in DEF. Furthermore, the paste expansion in DEF is not limited to the surface regions of the concrete. It is useful to know the curing conditions of the concrete, as high internal temperature during curing is a prerequisite for delayed ettringite formation.

It has to be emphazised that freeze/thaw of critically water saturated concrete may result in paste expansion and in gap formation.

ACID ATTACK

Mechanism

Concrete is susceptible to acid attack because of its alkaline nature. The components of the cement paste break down during contact with acids. Most pronounced is the dissolution of calcium hydroxide which occurs according to the following reaction:

$2\ HX + Ca(OH)_2 \rightarrow CaX_2 + 2\ H_2O$ (X is the negative ion of the acid)

The decomposition of the concrete depends on the porosity of the cement paste, on the concentration of the acid, the solubility of the acid calcium salts (CaX_2) and on the fluid transport through the concrete. Insoluble calcium salts may precipitate in the voids and slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids such as phosphoric acid and humic acid are less harmful as their calcium salt, due to their low solubility, inhibit the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulphate attack.

Microscopic appearance

An acid attack is diagnosed primarily by two main features:

- Absence of calcium hydroxide in the cement paste
- Surface dissolution of cement paste exposing aggregates

Acid attack is usually diagnosed when *dissolution of calcium hydroxide* is observed. Dissolution of $Ca(OH)_2$ makes the cement paste totally black and opaline shiny when observed in crossed polarised light (Figure 6).

Dissolution of the calcium hydroxide is observed in the surface of the concrete and around cracks in contact with the surface. The depth of the dissolution depends on the porosity of the concrete (water/cement ratio) and the type of acid.

Generally, cracks are not produced by the acid attack itself, but instead *exposed aggregates* are observed on the surface, due to the disintegration of the cement paste. The cement paste is converted to silica gel with shrinkage cracks.

Chemical analyses may be helpful in identifying which acid is present.

Figure 6 Acid attacked concrete. The paste appears black with an opaline shine when illuminated in crossed polarised light. Scale bar measures 130 microns.

CARBONATION AND BI-CARBONATION

Mechanism

Carbonation may be seen as a special type of acid attack, where the acid is carbon dioxide. All calcium bearing phases of the cement paste are attacked and converted. Low soluble calcium carbonate, $CaCO_3$, is precipitated instead and acts as a good, durable binder in most cases.

The reaction is often given for calcium hydroxide, that is the first phase that reacts and disappear:

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

calcium carbonate is normally found as calcite.

The porosity of the paste is often unchanged or lower in the carbonated zone that is found at the surface of the concrete and along cracks perpendicular to the surface. By comparing the depth of carbonation at the surface with the depth of carbonation at the crack it is often possible to estimate the age of the cracks.

In very porous concrete with high w/c and low content of calcium hydroxide the carbonation may lead to increased porosity and loss of strength.

Figure 7 Carbonated concrete. Calcite crystals of high birefringence appear in the surface zone. The image is taken in crossed polarized light. Scale bar measures 630 microns.

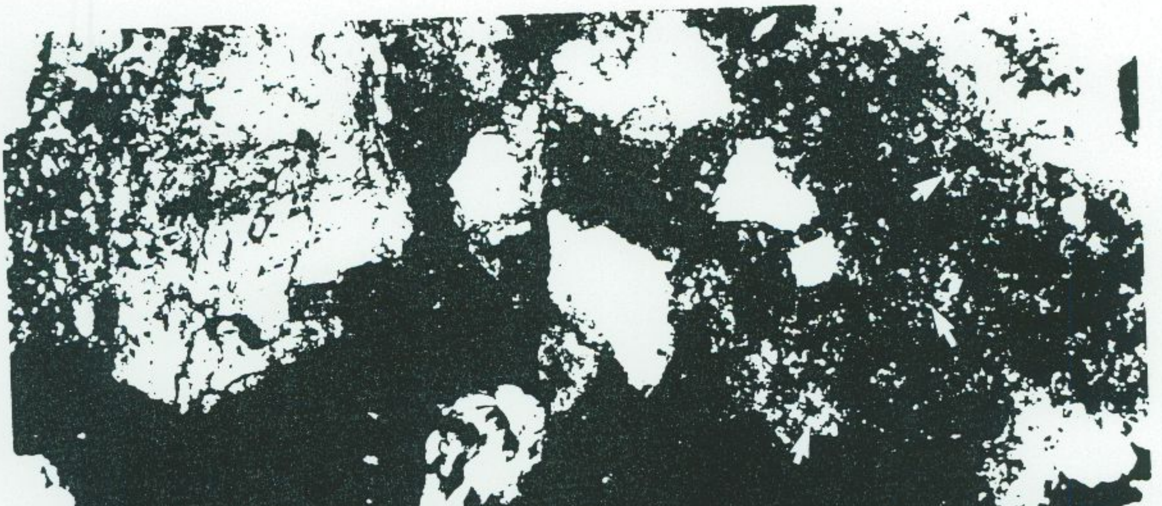

Figure 8 "Bi-carbonation". Large "pop-corn" crystals of calcite (arrows) are found in an isotropic matrix. The image is taken in crossed polarized light. Scale bar measures 130 microns.

FROST ATTACK

Mechanism

Deterioration of concrete exposed to freezing and thawing occurs when the concrete is critically water saturated. The fundamental mechanism of frost damage is related to the volume increase occuring when water freezes to ice. Several mechanisms have been proposed over the years (Laugesen et al., 1996).

- Hydraulic pressure
- Osmotic pressure
- Microscopic ice lens growth
- Thermal incompatibility between matrix and aggregates
- Shock freezing
- Thermal expansion of ice during heating,

None of these mechanism can alone explain all observations. There is no concensus regarding the mechanisms (ACI C201, 1995).

Microscopic appearance

Frost damage is diagnosed primarily by the following features:

- Surface scaling
- Internal cracking due to paste expansion

Surface scaling is the loss of paste and mortar from the surface of the concrete. By the process coarse aggregate particles may be exposed and finally lost. Internal cracking due to paste expansion is typical for frost attack and for sulphate attack and for DEF. It may be difficult to diagnose "pure" frost attack unless the other mechanisms can be excluded based on knowledge obtained from other sources than the thin section.

Freeze thaw damage is often combined with other types of concrete distress. Often it is not diagnosed or misdiagnosed. In Denmark the diagnosis "frost attack" has traditionally been given only after excluding other possible causes such as ASR. This means that the occurrence of frost attack in Denmark may be more common than generally believed. In Norway, on the other hand, there has been a tradition to diagnose frost attack only in many concrete structures. First by the work of (Jensen, 1993) ASR was generally accepted in Norway.

Under ideal conditions frost attack creates gaps around the aggregate (Idorn et al., 1993). See Figure 9.

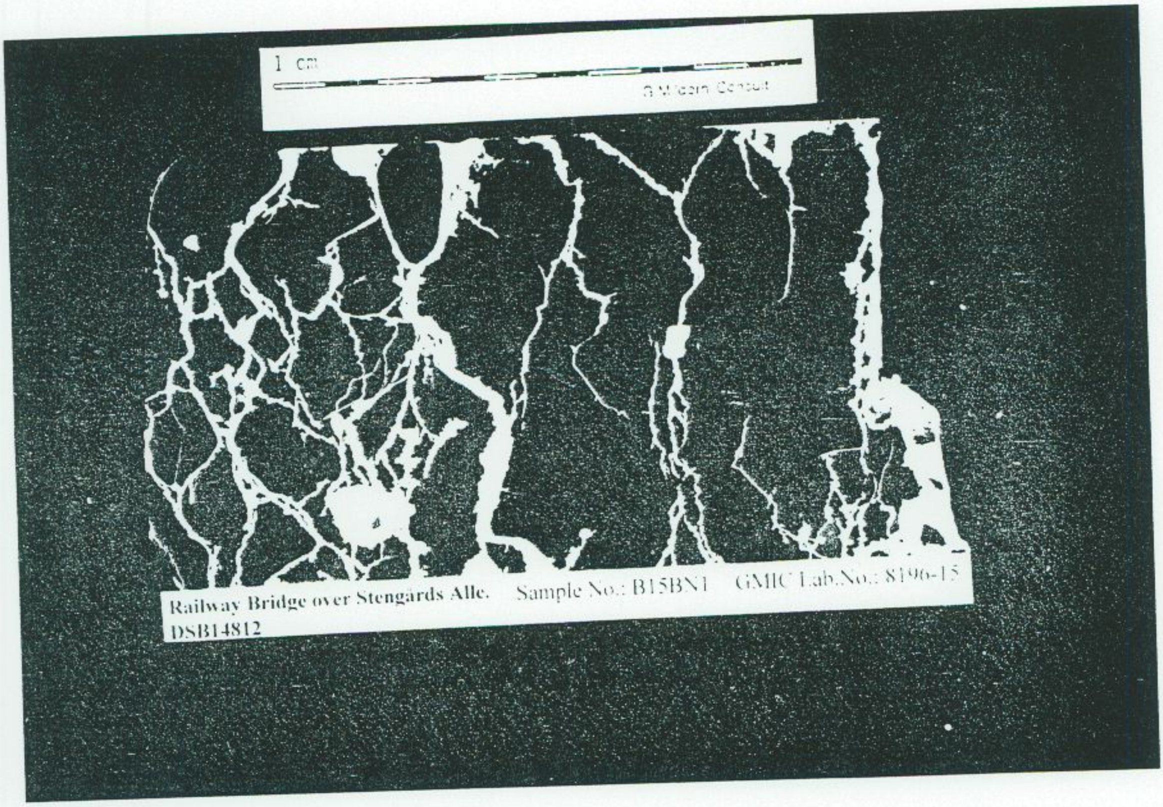

Figure 9 Macro-photo in UV-light of fluorescent impregnated, cut concrete core with frost damage. Scale bar measures 10 cm.

As frost attack normally proceeds from the concrete surface and inwards the paste expansion forms delamination cracks sub-parallel to the surface with a distance of around 10 mm between cracks. Figure 9.

CONCLUSIONS

- With an experienced petrographer at the optical microscope thin section microscopy is the principal tool for diagnosing the different deterioration mechanisms in concrete.
- With optical microscopy it is possible to uniquely discriminate between different deteriorating mechanisms, such as ASR, DEF, sulphate attack, acid attack, carbonation and freeze/thaw.
- Each of the deterioration mechanisms mentioned in this paper can usually be diagnosed by crack pattern, presence and position of various precipitates, types of aggregate and the condition of the cement paste.
- Optical microscopy can usually detect whether several deterioration mechanisms are present at the same time. Furthermore, it is possible to evaluate which was first and what is the main cause of the distress.
- Optical microscopy should always be supplemented by a field inspection and (if possible) examination of production data. Sometimes it is useful to supplement the optical thin section microscopy with SEM-EDS or chemical analyses. However, optical microscopy should always be performed as the first step before other types of microanalyses because optical microscopy provides both insight and overview.

REFERENCES

Idorn, G.M. (1967) Durability of Concrete Structures in Denmark. *D.Sc. thesis, Technical University of Denmark*, Copenhagen.

Christensen, P., Chatterji, S., Thaulow, N., Jensen, A.D. and Gudmundsson, H. (1981) Filling up pores and fractures in weathered concrete structures. *Proceeding Third International Conference on Cement Microscopy*, Houston, Texas, pp. 298-306.

Heinz, D. (1986) Schädigende Bildung ettringitähnlicher Phasen in wärmebehandelten Mörteln und Betonen, *Thesis,* RWTH Aachen.

Heinz, D. and Ludwig, U. (1987) Mechanism of Secondary Ettringite Formation in Mortars and Concretes after Heat Treatment, *Massivbau Baustofftechnologie*, University of Karlsruhe, Vol. 6. pp. 83-92.

Thaulow, N. and Andersen, K.T. (1988) New knowledge on alkali-silica reactions (in Danish), *Dansk Beton*, No. 1. pp. 14-19.

Thaulow, N., Holm, J. and Andersen, K.T. (1989) Petrographic Examination and chemical analyses of the Lucinda Jetty Prestressed Concrete Roadway, *Proceedings 8th International Conference on Alkali Aggregate Reaction*, Kyoto.

Andersen, K.T. and Thaulow, N. (1990) The Study of Alkali-Silica Reaction in Concrete by the use of Fluorescent Thin Sections ASTM STP 1061, (eds. Erlin and Stark) *Petrography Applied to Concrete and Concrete Aggregates*, Philadelphia.

Svenson, E. (1991) Eigenstresses generated by diffusion in a spherical particle embedded in an elastic medium, *International Journal Mechanism Science*, Vol. 33, No. 3. pp. 211-223.

Johansen, V., Thaulow, N., Jakobsen, U.H. and Palbøl, L. (1993a) Heat Cured Induced Expansion, *Proceedings 3rd Beijing International Symposium on Cement & Concrete,* Beijing 1993.

Johansen, V., Thaulow, N. and Skalny J. (1993b) Simultaneous presence of alkali silica gel and ettringite in concrete, *Advances in Cement Research,* vol. 5, no. 17, pp- 23-29

Idorn, G.M., Johansen, V. and Thaulow, N., (1993) Assessment of causes of cracking in concrete, *Materials Science of Concrete III, (J. Skalny ed.),* pp. 91-104

Jensen, V., (1993) Alkali Aggregate Reaction in Southern Norway, *Doctor Technical Thesis, University of Trondheim*

ASTM C-856 (1993) *Standard Practice for Petrographic Examination of Hardened Concrete*, vol. 04.02, pp. 422-434

Lawrence, C.D. (1995) Delayed Ettringite Formation: An Issue ? *Material Science of Concrete IV*, (eds. J. Skalny & S. Mindess), American Ceramic Society, pp. 113-154.

Thaulow, N., Jakobsen, U.H., (1995) The diagnosis of chemical deterioration of concrete by optical microscopy, *MRS Fall meeting, Boston* (in Press)

ACI C201 (1995) Frost attack on concrete, *Draft Report, Chapter 2*

Thaulow, N., Johansen, V. and Jakobsen, U.H. (1996) What Causes Delayed Ettringite Formation ? *MRS Fall meeting, Boston* (in Press)

Laugesen, P., Geiker, M., Pedersen, E.J., Thaulow, N. and Thøgersen, F. (1996) HETEK, Method for test of the frost resistance of high performance concrete, *State of the Art, Danish Road Directorate, Report no. 55*

Thaulow, N., Jakobsen, U.H. and Clark B. (1996) Composition of alkali silica gel and ettringite in concrete railroad ties: SEM and X-Ray diffraction analyses, *Cement and Concrete Research,* vol. 26, no. 2, pp. 306-318

Johansen, V. and Thaulow, N., (1997) Heat curing and late formation of ettringite, *ACI Spring convention, April 1997, Seattle,* (submitted for publication)

Jakobsen ,U.H., Johansen, V. and Thaulow, N. Optical Microscopy - a primary tool in concrete examination!, *19th ICAM Conference, Cincinatti 1997, USA* (in press)