Petrographic Analysis of Concrete Deterioration

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This presentation includes a discussion of the Petrographic Analysis of Concrete Deterioration.

I am a structural engineer that uses the services of a petrographer on a regular basis, and as a result I have found that it is helpful to have a clear understanding of what petrographic analysis is capable of revealing as a part of an investigation of deteriorated concrete. This presentation is therefore based on my experience of working with a number of petrographers over the past 40 years.

In addition, during my career I have been involved with concrete deterioration projects in which the original EOR did not use petrography or other forms of material testing and as a result ended up developing incorrect repairs.

So the real intent of my presentation is to educate structural engineers that are involved with the investigation and repair of deteriorated concrete about the use of petrography to help improve the process.
My understanding of the importance and need for petrographic analysis came through my involvement with renovation projects, so let’s start out today’s discussion by talking about how to deal with deteriorated reinforced concrete.

It is always necessary to first visually assess and measure the extent of damage to the concrete and any observable corrosion activity of the embedded reinforcing.

As a part of the investigation it is also important that concrete core and powder samples be obtained in order to conduct petrographic and other material testing of the concrete. The combination of field observations and petrographic analysis makes it possible to properly determine the cause and therefore the best methods of repair to prevent further deterioration of the concrete and corrosion of the rebar.

In other words, material testing ensures a proper engineering evaluation and approach to the repair of the observed deterioration.

A good example of the importance of material test results and why you should not just rely on visual observations, which can sometimes be miss leading as to the source of deterioration, is a project I was involved with at a large hospital mechanical room. The project involved...

- Leaking Brine Tank – obvious corrosion of rebar in adjacent basement walls – tests indicated carbonation from poorly ventilated boiler room – not chloride contamination.

It is also important for a structural engineer to understand the difference between petrographic analysis and other separate material tests of concrete. As an example, I recently peer reviewed a report of investigation in which the engineer thought a petrographic analysis had been performed when in fact the lab had only performed a chemical analysis of small chunks of concrete that had been provided.
So the process of investigating and developing repairs for a deteriorated concrete structure should involve:

1. On-Site Condition Evaluation Survey
2. Laboratory Petrographic Analysis, and...
3. Determination of Extent of Damage and Remaining Service Life
4. Assessment of Repair Materials and Coatings, and...
5. Assessment of the need for Galvanic or Cathodic Protection Systems
An on-site condition assessment can include a number of different investigative techniques. Most of the investigations that I have conducted have involved these first 5 items listed, which include visual observations, chain dragging (to detect subsurface delaminations), petrographic analysis, carbonation tests and powder samples. For vertical and overhead surfaces tapping the concrete with a small hand held hammer can reveal subsurface delaminations also.

It is not necessary to send separate powder samples for chloride and sulfate content tests because the lab can obtain the same from the cores intended for the petrographic analysis; however, to make this possible the cores normally have to be large enough, or typically at least 4-inches in diameter.

Additional methods of investigation are listed on the next slide.
...and here are additional methods of investigation that can be used as a part of an investigation, and the purpose of each approach. I will provide some additional details on half-cell potential mapping and resistivity later in the presentation.

Concrete compressive strength has not been included in the list because I typically prefer to use a Schmidt or Swiss Impact hammer to obtain qualitative values of the compressive strength of the concrete in the field, which are typically only ±25% as accurate as compression cylinder tests. Therefore, if more accurate concrete compressive results are required, additional concrete core samples should be obtained because it is not practical to use the same core sample for both petrographic analysis and compression tests.
b. Chain Dragging

So back to my list of the top 5 on-site survey techniques: Chain dragging is an inexpensive but very effective method used to locate subsurface delaminations, or voids, which resonate differently than the distinct sound generated by sound concrete. The best results are obtained from slapping the chain against the surface as opposed to simply dragging it across the surface.

This method of evaluating hidden deterioration helps to:

1. Establish accurate quantities for estimating the initial repair costs during the investigation phase, and...

2. Establish the boundaries of the extent of demolition of the deteriorated concrete during the actual repair phase.

GPR (or Ground Penetrating Radar) has also been shown to accurately identify subsurface delaminations by detecting hidden voids in the slab.
Concrete core samples for petrographic analysis should be obtained from areas that exhibit deterioration. It is also recommended that at least one core sample be obtained from what appears to be an undamaged, undeteriorated area of the structure so that a comparison can be made between the damaged and undamaged areas of the concrete. This comparison can be invaluable when it comes to establishing the root cause of the deterioration.

A good example of the importance of this approach involves the need to know whether increased chloride content in a deteriorated area exists when compared to a non-deteriorated area.

For example, if the chloride content is high in both a deteriorated and non-deteriorated area, then chloride based set accelerating admixtures during winter concreting operations when the concrete was originally placed may have been used, particularly if the non-deteriorated area has not been exposed to external sources of chloride like de-icing salts. There are other sources and causes of high chloride content that we will discuss later.

The diameter of a core sample required for petrographic analysis varies to some degree between different labs, but in general cores from 2 inches to 4 inches in diameter are acceptable, even though the ASTM specification for petrographic analysis recommends 6-inch diameter cores.
Phenolphthalein (finel-thowl-ean) is an organic compound that is used as an indicator of the alkalinity of concrete. Phenolphthalein (finel-thowl-ean) turns pink in an alkaline solution but remains colorless in an acidic or neutral solution and can therefore be used to determine the alkalinity of concrete.

As you can see from this slide, the top portion of the core that was exposed to the atmosphere is clear (which indicates a zone of lowered alkalinity of the concrete) while the bottom portion of the core is stained pink, which indicates the presence of alkalinity in the concrete.
Both ASTM C1218 (for water soluble chloride tests) and ASTM C1152 (for acid soluble tests) call for a minimum of 10 gram powder samples. If an adequate number and size of core samples are provided to the lab, then powder samples can be obtained from the cores at the lab. However, it is also possible to obtain samples in the field using a drill. Samples should be taken from different depths from the top or exposed surface of the concrete to provide information on variations in the chloride content based on the distance of the sample from the surface.

I prefer the water soluble test to the acid soluble test for chloride content because it is typically only the “free” or water soluble chlorides that contribute to corrosion. In addition, the published ACI limits on chloride content are based on water not acid soluble content.

The lab results provided for chloride tests are based on a percent of weight of concrete, where as the recommended chloride limits provided by ACI 201 (which we will review on an upcoming slide) are listed as a percent of cement. Therefore, the values based on concrete should be multiplied by a factor of 5 to convert the results to an equivalent percent by weight of cement for comparison to the ACI limits. It should also be noted that there is no correlation between water soluble and acid soluble test results.

The cost of obtaining chloride content test results for individual powder samples varies from lab to lab, but in general the test costs approximately $150 to $200 per sample.
Here is a photo of a concrete core hole, which will be filled in with a high-strength, fast-setting epoxy grout concrete so that the area can continue to be used safely after the sample is obtained. On the right hand side of the same photo a drilled powder sample hole is being filled back up with a durable sealant to fill the small hole for similar reasons.
O.K….jumping back to Item #2 from the list on Slide 3; Petrographic analysis should be conducted by an experienced petrographer. The petrographic evaluation of concrete can determine aggregate type and size, depth of carbonation, air void content, water voids, evidence of excessive water, retempering (which involves adding water and sometimes cement after the mixing is complete) and mode of deterioration. The results of a petrographic analysis can therefore help establish the quality of the concrete and more importantly the best means of repair and protection against further deterioration.
Based upon the site condition assessment and the results of the material testing the extent of damage and remaining service life of the concrete can be established using criteria provided by ACI 365, “Service Life Prediction – State of the Art Report”.

ACI 365 essentially evaluates the time required for the embedded reinforcing to create a delamination and spall based on the concrete cover, chloride ion content, reinforcing size and presence or lack of air-entrainment. This ACI method unfortunately does not include the compounding adverse effects of carbonation.

At the time a spall is created per the calculation, the service life of the member is essentially “over” because repairs will be required for both the spall and the corroded reinforcing to extend the useful service life of the structure.

So from an engineering perspective, the service life of a structure is considered to be over when the extent of deterioration renders the facility inoperable due to impending hazards to public safety, and remediation is required via repair or complete replacement. Therefore, the end of a structure’s service does not mean that it is in a state of eminent collapse but instead implies that the structure can no longer safely function or support minimum loads as required by the building code.
Prior to developing the methods of repair the following questions should also be addressed:

(First) Is the reinforced concrete structurally sound?

Situations that I have encountered in which the structure was not sound have included unsafe conditions that needed to be addressed immediately on the same day as the condition assessment, and structures that had less load carrying capacity than that originally assumed, which resulted in the need to strengthen the structure in addition to making repairs.

(...and Secondly) Does the reinforced concrete require repair or replacement?

I have been involved with a couple of projects in which it was not feasible or technically possible to restore the structure. Both of the projects involved precast, prestressed concrete products. As a result the facilities had to be temporarily shored in order for the owner to buy enough time to construct a new replacement garage. One of these projects was documented in a series of articles in STRUCTURE Magazine beginning in September of 2013. The title of the series of articles was “The Triage, Life Support and Subsequent Euthanasia of an Existing Precast Parking Garage”. The other project was documented in an article in the January 2016 issue of STRUCTURE Magazine and was titled “Precast, Prestressed Thin Slabs in Parking Garage Structures...or...When Thin is NOT a Win-Win”.

For projects that can be repaired, the proper consideration of the materials used for the repair of a deteriorated concrete structure are essential to the success of the renovation of a concrete structure. In addition, protective coatings may also be required to help prevent further corrosion of non-deteriorated areas of the structure.

This slide illustrates a painted epoxy topping that was used at a parking garage; however, deterioration of the concrete still occurred because of problems with the original mix design.
Galvanic and Cathodic protection systems may also be required for some reinforced concrete structures, particularly if the concrete is contaminated with chlorides. An active cathodic protection system provides a sufficient amount of direct electrical current to the reinforcement to slow down or stop the natural corrosion processes from occurring. There are also sacrificial, passive galvanic protection systems available, one of which is illustrated in this slide. The service life of a sacrificial system is approximately 25 years. A properly maintained cathodic system can last as long as 75 years.

A cathodic system is less expensive to install initially than a sacrificial system, however, the greatest disadvantage of a cathodic system is the ongoing costs associated with the operation, periodic monitoring and maintenance of the system. In other words, if a cathodic system is not properly monitored or maintained, it can fail within just a few years after the initial installation. Sacrificial systems on the other hand are essentially maintenance and cost free once they are installed properly, at least until the devices have to be replaced after they have been completely consumed.
So what does Petrography mean, well...

Petrography is a term from geology which means the study of thin sections of rocks. Petrographic analysis is also a valuable tool that can be used to determine the quality of concrete. A qualified petrographic lab will typically use a combination of optical and scanning electron microscopic, or SEM, examination and chemical analysis as a part of the analysis.

This slide illustrates a typical SEM image that has been labeled to indicate the sources and types of deterioration observed.
Here is an example of a polarizing microscope, which is another type of instrument used for petrographic analysis.
This flowchart illustrates the progressive stages of a petrographic investigation with the level of evaluation increasing depending on the amount of detailed information required. We have already discussed the engineers role with the On-Site Investigation.
Standard practice for petrographic examination of concrete is governed by ASTM C856. This specification covers:

1. The qualifications of a petrographer under Section 4.
2. The purposes of the examination under Section 5.
3. The types and use of equipment under Sections 6 and 7.
4. The preparation of samples under Section 8 and 10.
5. The examination of samples under Section 9, and...
6. The preparation of the report under Section 14.

C856 also includes an Appendix on techniques for detecting alkali-silica gel.

It is important for the engineer who is sending samples to the lab to be aware of the information that must be provided for each specimen. The information required for samples is included in Section 8 and includes:

1. The location of where the core was taken.
2. The orientation of the core, in other words was the core taken vertically from either above or below the structure or horizontally through a beam, column or wall.
3. The age of the structure, and...
4. The reasons for and the desired objectives of the examination including the observed symptoms of deterioration or duress of the structure.

It is also important to have a conversation with the petrographer before the actual testing begins. The discussion should begin with a confirmation of the petrographer’s understanding of the purpose of the material testing, which in some cases can lead to recommendations by the lab that less expensive testing, such as chloride powder or carbonation examinations, should be performed first to confirm any suspicions of the likely cause of the deterioration, thereby avoiding the need for a more expensive full blown petrographic analysis.
A qualified petrographic lab can typically provide all of the services listed on this slide, which include:

1. Microscopic examination of cores.
2. Determination of the water/cement ratio and presence of excess water.
3. X-Ray Diffraction analysis of powdered material.
4. Chemical analysis including sulfate and chloride contents and other important chemical ratios.
5. Absorption analysis.
6. ...and, the presence of the potential for reactive aggregate.

Most petrographic labs also can perform a separate air-void analysis under the provisions of ASTM C457.
Most labs also provide thin-section petrography which is also covered in ASTM C856.

Thin-section petrography is typically used to examine mortars, grouts and thin-set cementitious materials when more detailed information is required than what can be achieved via the normal examination of polished sections.

Then-set petrography is also normally combined with energy dispersive spectroscopy (spectroscopy), or SEM/EDS, to enable the detection of distress mechanisms.
A qualified petrographer should also be able to interpret the appearance of the concrete in order to determine if the failure has been caused by a improper mix design or poor workmanship during placement and curing. So in other words, petrographic analysis allows one to look back in time to see what the condition of the concrete was when it was originally mixed and placed.

Some labs employ yellow fluorescent microscopic examination in order to make the determination of the water/cement ratio easier and to help emphasize defects such as micro-cracking and bleeding of the mix water. A reputable lab should have experience in diagnosing all types of deterioration mechanisms that can occur in concrete including; alkali silica reaction, delayed ettringite (et-treng-ite) formation, external sulfate attack, acid attack and carbonation.

Ettringite (et-treng-ite) is the mineral name for Calcium Sulfoaluminate, and is normally found in Portland cement concrete. Sources of calcium sulfate, such as gypsum, are added to Portland cement to prevent flash setting during the early hydration process, improve strength development and reduce drying shrinkage. Sulfate and aluminates are also present in admixtures and other supplementary cementitious materials. The gypsum and sulfate compounds react with the calcium aluminate to form ettringite (et-treng-ite) within the first few hours after adding mixing water. The formation of ettringite (et-treng-ite) in fresh plastic concrete is the mechanism that causes stiffening of the concrete. Therefore, what is referred to as “primary” ettringite (et-treng-ite) is beneficial to concrete.
The cost of obtaining a petrographic analysis of a single concrete core varies considerably between labs, and can range between $1,000 and $1,800. Labs that provide a full range of services, including a service life analysis using proprietary software such as STADIUM marketed by SIMCO Technologies, can charge as much as $2,000 per core.

Thin-section petrography costs approximately $1,200 to $1,300 per sample. Air void analysis, using ASTM C457 costs approximately $450 to $500 per sample.

It is recommended that you always review what type of information will be provided by a lab before you retain their services.

You need to also include the cost of obtaining the cores in the field when estimating the expense of material testing. Typically most concrete coring companies charge a day rate of approximately $1,200 to $1,500 and will obtain as many cores as possible during the allotted time period. A coring crew should also come prepared to provide their own power and water, and high strength grout to patch the holes once the sample is obtained. Lastly, don’t forget to include the cost of shipping to get the samples to the lab unless you are using a local facility.
So let's talk about the types of concrete deterioration that can be identified by petrographic analysis.

Hardened concrete is porous yet its natural alkalinity helps to protect internal steel reinforcement from corrosion. However, the porosity can also contribute to deterioration. For example, gases or liquids can easily penetrate into the pores of the matrix, which can increase the likelihood of rebar corrosion. The reactions between the components of concrete can also be detrimental if they continue for an extended time after the material has hardened.

The next 8 slides will provide examples of concrete deterioration that is **NOT** associated with reinforcing corrosion.
Leaching Corrosion is a type of attack that effects concrete in contact with fresh water and results in the slow elimination of the bond between the cement and aggregate.

I have seen this type of deterioration destroy concrete man-holes that were not adequately waterproofed on the exterior.
Deterioration due to Magnesia or Lime Grains does not occur very frequently. This type of deterioration occurs due to the presence of impurities in the cement or aggregates. The damage typically appears as local aggregate pop-outs as shown in this slide.
Deterioration due to Pyrites (or iron sulphide) in aggregates results in the appearance of rust stains along with the formation of surface "bugholes".
Alkali Silica Reactions, or ASR, occur as a result of a chemical reaction between some types of aggregates which contain reactive silica and the alkalinity of the concrete in the presence of moisture.
Deterioration due to Environmental Exposure includes the waste water treatment process which involves the production of hydrogen sulfide from the bacteria. In an aerobic environment bacteria are also responsible for the production of sulfuric acid, which can also damage concrete.
Deterioration in Sulfate Environments occurs in concrete that is in contact with the ground, ground water or bodies of water that contain sulfates. The resulting chemical reaction typically causes the formation of expansive ettringite (et-treng-ite) crystals.
Delayed Ettringite (et-tren-ite) Formation, or DEF, is typically related to concrete exposed to high levels of heat during the curing process like what is typically used in the prestressed precast concrete industry. During the hydration process, an increase in temperature prevents the formation of primary ettringite (et-tren-ite) but leaves other components available in the concrete that can react over the life of the structure. If the proper conditions are present internal stresses occur within the concrete as the ettringite (et-treng-ite) is formed over the life of the concrete, which can cause cracking.
Deterioration due to Chemical Exposure such as fertilizers containing ammonium nitrates, mineral or organic acids, can also occur. The intensity of the deterioration depends on the concentration and aggressiveness of the chemical as well as the temperature and amount of moisture that is present.
Concrete deterioration caused by reinforcement corrosion is an electrochemical process that requires an anode, a cathode and an electrolyte. For an existing structure, the moist concrete provides the electrolyte and the embedded reinforcement provides the anode and cathode. Water and oxygen must be present for any corrosion to take place and in good quality concrete, the high alkalinity can slow or stop the corrosion process. However, if the concrete alkalinity is lowered (due to carbonization) or if corrosive chemicals (like chlorides) are present the corrosion process will accelerate.

The electrical current that flows between the cathode and anode results in an increase in metallic volume at the anode as iron is oxidized, which precipitates as rust. Rust, as a byproduct of the electrochemical reaction, has a volume three to four times greater than the iron anode from which it originates. As the layer of rust increases due to the ongoing corrosion process, tensile forces generated by the expansion of the rust causes the surrounding concrete to crack, delaminate and ultimately spall and deteriorate. As the surface of the concrete degrades, the corrosion process accelerates as internal areas of the reinforcing that were previously protected by the concrete cover are exposed to additional moisture and deicing salts or other sources of contaminates.
When the chloride content in concrete reaches a critical value, in the presence of moisture, the natural alkalinity of concrete is no longer able to protect the internal reinforcement from the corrosion process. In concrete, an electric field connects zones of chloride to areas where oxygen is reduced so that the corrosion process can take place. The electrical potential value can be measured between these zones by using reference electrodes placed on the concrete surface, which I will illustrate in another slide.

On the next slide I’ll also provide what ranges of chloride content are considered acceptable for different types of concrete products and conditions.

Unlike the previous slide, in which the deterioration occurred on the wearing surface of a parking garage slab where one would expect to find external sources of chlorides, in the form of deicing salts brought in from vehicles, the photo on this slide indicates that the deterioration is occurring on a surface completely protected from exposure to de-icing salts. For this particular project, the culprit that was identified as the source of the corrosion of the prestressing strands was the use of a chloride based set accelerating admixture that had been used in the original production of the precast product. The condition was made worse by the carbonation of the adjacent concrete.
This table was developed by the ACI 201 Committee and recommends limits of water soluble chloride content by weight of cement for different types of concrete products and exposure.

As I mentioned in Slide 9, this table is based on percent by weight of cement while the test results from powder samples are typically based on percent of weight of concrete. As a result a factor of 5 should therefore be applied to the field sample results for proper comparison with the ACI limits.
The accelerated deterioration of undamaged concrete can also sometimes occur after a repair is made if proper measures are not taken to offset the interruption of the Incipient Anode Effect by the repair.

The Incipient Anode Effect results when electrons released by the reinforcing corrosion process flow along the rebar to a point away from the deteriorated area thereby providing cathodic protection of the adjacent non-corroded steel.

If the corrosion cell is removed via a repair, and the surrounding undamaged areas are contaminated with chlorides, accelerated deterioration under and around the repaired area will occur since the natural cathodic protection has been interrupted.

I have seen the premature failure of many repairs occur because of this process, which resulted because the original engineer did not properly investigate the root cause of the deterioration and was therefore unaware of the need to take preventative measures such as the installation of galvanic protection devises around the perimeter of the new repair.
..and here is an illustration of the Incipient Anode Effect
Before we get into a discussion of examples of the types of concrete deterioration that can be established via petrographic analysis, let me first mention a couple of Non-Destructive Evaluation (or NDE) methods that are often used in conjunction with petrographic testing.

First, we have Half-Cell Potential Contour Mapping, which can document active corrosion cells within deteriorated concrete. Half-cell potential corresponds to the equilibrium between the metal corrosion zones and the associated reduction reaction.

To determine the on-site half-cell potential of reinforcement, reference electrodes, as illustrated in this slide, are used to gather measurements. The results of half-cell potential measurements are typical recorded on maps which indicate the equipotential contours of the concrete.

Information obtained from a half-cell potential field investigation can assist with the accurate determination of the nature of duress of the concrete during a laboratory petrographic examination.

This method of NDE is capable of detecting the presence of approximately 90% of any active corrosion, and the primary disadvantage of this method of NDE, other than cost, is that you have to connect to the embedded reinforcing mat.
Here is an example of a half-cell potential contour map. This example from an Interstate bridge indicates that approximately 75% of the area surveyed had readings more negative than -250 mV, which indicates that corrosion is likely occurring over most of the deck.
An Electrical Resistivity Survey measures the potential for corrosion in the concrete to occur and does not involve the need to connect the equipment to the embedded mat of reinforcing bars. This method of NDE is also a better evaluation tool for identifying areas of concrete that have the potential to cause corrosion of the rebar.

This slide illustrates a Resipod which is a 4-point probe used for electrical resistivity surveys of concrete.

This device is capable of:

1. Estimating the likelihood of corrosion.
2. Indicating the rate of corrosion.
3. Providing a correlation to chloride permeability.
4. Determining areas of concrete that require cathodic protection systems (which is what I used this type of NDE method for recently in a parking garage).
5. Identifying areas of wet and dry concrete in the structure.
6. Indicating variations in the water/cement ratios within a concrete structure, and...
7. Identifying areas within a structure that are the most susceptible to chloride penetration.
**Examples of Deterioration that can be Established by Petrographic Analysis**

1. **Acid Attack of Concrete:**

   - Concrete is susceptible to acid attack because of its alkaline nature. The degradation of concrete when attacked by acid depends on the porosity of the concrete, the concentration of the acid, and the solubility of the acid calcium salts.

   - Sulfuric acid is very damaging to concrete as it combines an acid and a sulfate attack. An acid attack is diagnosed primarily by two main features; the absence of calcium hydroxide in the cement paste and the surface degradation of the cement paste which exposes the surface aggregates.

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Let's talk in more detail about examples of concrete deterioration that can be identified by petrographic analysis starting with acid attack.

Concrete is susceptible to acid attack because of its alkaline nature. The extent of damage to concrete when attacked by acid depends on the porosity of the concrete, the concentration of the acid, and the solubility of the acid calcium salts.

The components of hydrated cement paste can breakdown when placed in contact with acids. The most pronounced deterioration is the dissolution of calcium hydroxide. The decomposition of concrete when attacked by acid, as I just mentioned, depends on the porosity of the concrete, and on the concentration of the acid, and the solubility of the acid calcium salts. This is because when insoluble calcium salts migrate into any surface voids the acid attack can be slowed down. Acids such as nitric acid and hydrochloric acid are very aggressive as their calcium salts are readily soluble and therefore easily removed from the attack interface.

Other acids such as phosphoric acid and humic acid are less harmful as their calcium salts, due to their low solubility, inhibit the attack by blocking the pathways of attack at the surface of the concrete. Sulfuric acid is very damaging to concrete as it combines an acid and a sulfate attack.

An acid attack is primarily diagnosed during a petrographic examination by two main features:

1. The absence of calcium hydroxide in the cement paste and...

2. The surface damage of the cement paste which exposes the surface aggregates.
External sulfate attack is a chemical breakdown mechanism in which sulfate ions from an external source attack components of the cement paste. Such an attack can occur when concrete is in contact with sulfate containing water such as seawater, certain types of soil and ground water and sewage water. Often the formation of gypsum and ettringite (et-

Source: The Concrete Producer Online

treng-ite) as a result of the external sulfate attack can cause the concrete to crack and scale. However, both laboratory studies and examinations of field concrete indicate that external sulfate attack is often manifested not by expansion or cracking, but by loss of cohesion and strength.
The microscopic appearance of concrete suffering from external sulfate attack that can be observed during a petrographic examination includes:

A. Parallel surface cracks.

B. The presence of gypsum and ettringite (et-treng-ite).

C. The depletion of calcium hydroxide.

D. The decalcification of calcium silicate hydrates, and on the next slide...
E. Cement Paste Expansion

Sometimes external sulfate attack can also cause the cement paste to expand which results in the formation of gaps around the aggregates. This type of deterioration depends on many factors including the water/cement ratio and the type of cement, exposure time, temperature, the concentration of sulfates and the chemistry of the water.
Concrete suffering from external sulfate attack develops a pronounced mineralogical and chemical zone which can be studied by an optical fluorescence microscope and scanning electron microscope. ASTM C856 also recommends that a chemical analysis be performed to verify that the sulfate content of the concrete has been increased over that which could normally be expected for the particular type of concrete in order to properly diagnose external sulfate attack. The images on this slide provide examples of this type of deterioration.
This slide illustrates gypsum crystals that have formed at a concrete surface placed against sulfate contaminated soils.
This slide shows an example of the typical type of pronounced mineralogical and chemical zone associated with external sulfate attack.
This slide illustrates the formation of magnesium hydroxide in a crack due to external sulfate attack.
3. Delayed Ettringite Formation (DEF)

- DEF is a form of internal sulfate attack.
- DEF occurs as a result of improper heat curing of the concrete in which the normal formation of ettringite is suppressed.

Delayed Ettringite (et-treng-ite) Formation, or DEF, is a form of internal sulfate attack. A number of factors such as concrete composition, curing conditions and exposure conditions influence the potential for DEF.

DEF is believed to occur as a result of improper heat curing of the concrete that suppresses the normal formation of primary ettringite (et-treng-ite). As a result sulfate concentrations in the pores of the matrix are elevated for an unusually long period of time in the hardened concrete. Eventually the sulfate reacts with the calcium and aluminum in the cement paste causing the paste to expand. As a result expansion cracks form around the aggregates. The cracks may remain empty or be filled later with ettringite (et-treng-ite).

DEF is also sometimes referred to as HIDE, or Heat Induced Delayed Expansion, and is also associated with concrete exposed to high heat of hydration that occurs with massive concrete pours such as dams.
DEF is diagnosed via petrographic analysis primarily by the presence of four main features which include:

a. The presence of gaps completely encircling the aggregates.

b. Wider gaps around large aggregate than around small aggregate.

c. The absence of an external sulfate source.

d. ...and documentation of the use of high temperature heat during the curing phase, or mass concrete pours.
The presence of gaps encircling aggregate as a result of DEF is illustrated in this slide.
Alkali Silica Reactions, or ASR, are a chemical reaction which takes place in the aggregate particles between the alkaline solution of the cement paste and the silica in the aggregate particles. ASR reactions occur when hydroxyl ions penetrate the surface regions of the aggregate and break down the silicon-oxygen bonds. Positive sodium, potassium and calcium ions in the pores of the matrix of the concrete follow the hydroxyl ions so that electro neutrality is maintained. Water is absorbed into the reaction sites and eventually alkali-calcium silica gel is formed.
The resulting reaction by-products occupy more space than the original silica so the reaction sites are exposed to internal pressures. Initially the surface pressure is balanced by the tensile capacity of the center of the aggregate particle and the surrounding cement paste. However, when the internal stresses exceed the tensile strength, brittle cracks begin to form and propagate throughout the effected region. The cracks radiate from the interior of the aggregate out into the surrounding paste. The cracks that form are initially empty and not filled with alkali-calcium silica gel. However, small or large amounts of gel may subsequently form in the cracks.
Small aggregate can undergo a complete ASR reaction without cracking. In addition, formation of the alkali silica gel does not always cause expansion of the aggregate. Observation of gel in a concrete sample during the petrographic examination is therefore not a positive indication that the aggregate or concrete will crack.

In addition, because sufficient moisture is needed to promote destructive expansion ASR activity can be significantly reduced by keeping the concrete as dry as possible.

Alkali Silica Reaction is diagnosed via petrographic examination by the presence of four main features which include:

1. The presence of alkali silica reactive aggregates.
2. The nature of the crack pattern.
3. The presence of alkali silica gel in the cracks, and...
4. The presence of calcium hydroxide depleted paste.
Some of the effects of ASR are illustrated in this slide, including a cracked flint aggregate on the left and gel in air voids and cracks on the right.
Here is a slide that illustrates the typical appearance of concrete exposed to ASR deterioration, with the crack pattern representative of the internal expansion forces the concrete is being subjected to as a result of the alkali silica reactions.
Certain dolomitic rocks will cause Alkali-Carbonate Reaction or ACR.

Dedolomitization, or the breaking down of dolomite, is normally associated with expansive ACR. The reaction and subsequent crystallization of brucite can cause considerable internal expansion. The deterioration caused by ACR is very similar to that caused by ASR; however, ACR is very rare because the aggregate that are susceptible to this type of reaction are less commonly used.

Petrographic analysis can be used to determine if ASR or ACR caused the expansive damage.
Carbonation occurs in concrete because the calcium bearing constituents of the concrete react with carbon dioxide and are converted to calcium carbonate. Cement paste contains 25% to 50% (by weight) calcium hydroxide (the Ca(OH)2 noted in this slide), which means that the pH of fresh cement paste is at least 12.5. The pH of fully carbonated cement paste is about 7.

Concrete will become carbonated if the carbon dioxide (CO2), either from the atmosphere, water or other environmental source, enters the concrete according to the formula on this slide.

When calcium hydroxide is removed from the paste, calcium silicate hydrates will liberate the calcium oxide, which will also become carbonated. The rate of carbonation depends on the porosity and moisture content of the concrete and its exposure.
The carbonation process requires the presence of water because carbon dioxide dissolves in water forming carbonic acid. If the concrete is too dry (in other words the moisture content < 40%), the carbon dioxide cannot dissolve and no carbonation will occur. If on the other hand the concrete is too wet (a moisture content >90%), carbon dioxide cannot enter the concrete and the concrete will not become carbonated. Optimal conditions for carbonation occur at a moisture content of approximately 50%.

In general carbonation of exterior exposed concrete structures occurs at a rate of approximately 1-inch every 50-years; however, I have seen accelerated depths of carbonation in poorly ventilated underground parking garages that were not more than 10 years old.
Normal carbonation results in a decrease of the porosity making the carbonated paste stronger. Carbonation is therefore an advantage in non-reinforced concrete. However, it is a disadvantage in reinforced concrete, because as the pH of the carbonated concrete drops to about 9 the natural protection of the internal steel provided by the alkalinity of the concrete is no longer present.

It is also interesting to note that recent studies have shown that the presence of carbonation allows for an increase in chloride penetration. This phenomenon has nothing to do with porosity and everything to do with an increase in free chlorides that are available to begin the corrosion process. This is because carbonation destroys the ability of the hydrated cement to “fix” chlorides, which results in the release of bound chlorides into the concrete. The magnitude of potential for this type of chloride contamination can be determined via acid soluble chloride content tests.

I recently witnessed this condition in an exposed parking garage that was heavily carbonated on the bottom or soffit of the concrete framing, which resulted in corrosion of the internal reinforcing due to the combined lost of alkalinity and release of the bound chlorides in the concrete. Interesting enough, the top surface of the same garage, which was covered with an asphalt topping, had not become carbonized except in areas of the deck where the asphalt topping had been worn away. However, moisture and de-icing salts had still migrated through the asphalt topped areas and become trapped on the deck surface, which resulted in corrosion of the top layer of reinforcing anyway.

Carbonation may be recognized in the field by the presence of a discolored zone in the surface of the concrete. The color may vary from light gray to an orange hue. A light pink hue of concrete, which is indicative of damage due to excessive exposure to heat such as a fire, should not be confused with the orange hue associated with carbonation.

I have never personally observed an orange hue in carbonized concrete, and instead rely on the confirmation of carbonation using phenolphthalein (finel-thow-l-een).

In an optical microscope during a petrographic examination carbonation is recognized by the presence of calcite crystals and the absence of calcium hydroxide, ettringite (et-treng-ite) and unhydrated cement grains.
Occasionally concrete may suffer from a bi-carbonation process. Bi-carbonation may occur in concrete with a very high water/cement ratio due to the formation of hydrogen carbonate ions at a pH lower than 10. Contrary to normal carbonation, bi-carbonation results in an increase in porosity making the concrete soft and friable. Bi-carbonation is recognized during a petrographic analysis by the presence of large "pop-corn" like calcite crystals and highly porous paste.

I have never personally encountered Bi-carbonation of concrete.
Deterioration of concrete from freeze thaw actions may occur when the concrete is saturated, or approximately 90% of its pores are filled with water. When water freezes to ice it occupies approximately 10% more volume than that of water. If there is no space for the expansion to occur in the concrete, freezing may cause internal stresses in the concrete. Damage to concrete from freezing and thawing will start with the first freeze thaw cycle and continue throughout each winter season resulting in repeated deterioration of the concrete surface. Concrete with a high water content and a high water/cement ratio is less frost resistant than concrete with a lower water content.
To protect concrete from freeze-thaw damage, air-entrainment admixtures should be used in the concrete mixture. This type of admixture will create a large number of closely spaced, small air bubbles in the hardened concrete. The air bubbles provide relief to the internal pressure within the concrete caused by the formation of ice by providing many small voids for the freezing water to expand into.

A minimum of 4% to 5% air by volume is needed in a well-distributed pattern with a distance between each void of not less than 0.25 mm in the concrete in order for air-entrainment to be effective in preventing freeze-thaw damage. Typically, I specify 6% air entrainment in concrete mixes intended for exterior exposure.

In the absence of air-entraining admixtures, concrete normally exhibits entrapped air of only approximately 3%, which is insufficient to resist freeze-thaw action.
The deterioration of concrete by freeze thaw actions may be difficult to diagnose via petrographic examination because other types of deterioration such as ASR and carbonation often go hand in hand with the effects of freeze thaw damage. Often it may also be difficult to determine what caused the initial damage, however, if all other mechanisms can be excluded, the typical signs of freeze thaw deterioration include:

a. Spalling and scaling of the surface.

b. Large surface delaminations.

c. Exposed aggregates.

d. Parallel surface cracking, which is sometimes referred to as “D” or Disintegration cracking by highway pavement engineers, and...

e. Gaps around the aggregates.
This slide provides an example of severe freeze-thaw damage.

The image provided on Slide 12 that we looked at earlier is an example of the worse freeze-thaw damage I have ever seen. For that project ice lenses had formed throughout the concrete and the damaged concrete had been converted into a pile of dust and loose aggregates.
This slide provides another example of freeze-thaw damage, which includes parallel surface cracks.
This slide provides an additional example of freeze-thaw crack damage.
This slide provides an example of “D” or Disintegration cracking due to freeze-thaw action in concrete pavement.
Concrete performs very well at normal temperatures; however when exposed to fire or unusually high temperatures concrete can lose strength and stiffness.

The effects and extent of fire damage of concrete can often be determined visually in the field as illustrated in this slide; however, Petrographic analysis can assist in a more accurate determination of the actual extent of damage and need for repair.
This last slide summarizes the most appropriate petrographic methods of determining the types of concrete deterioration discussed in this presentation and the likely quality of the results of the analysis.