

# Overview of Delayed Ettringite Formation and Alkali-Silica Reaction

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Delayed ettringite formation (DEF) and alkali-silica reaction (ASR) are complex mechanisms that can significantly diminish the durability and service life of concrete elements. While reduced durability and service life are legitimate concerns, it is also important to recognize that DEF is both relatively rare and commonly misdiagnosed. Likewise, the mere presence of ASR in concrete does not necessarily indicate the end of the useful service life of an element. The purpose of this perspective is to provide an overview on how ASR and DEF are recognized in concrete and show that repairs may be available for arresting or slowing their progression. Articles in future issues of *ASPIRE*<sup>®</sup> will discuss how these mechanisms operate and steps that can be taken beforehand to mitigate ASR and DEF. There is extensive research on ASR and DEF that can provide additional information.<sup>1-4</sup>

## What Are DEF and ASR?

DEF and ASR are chemical reactions that produce secondary deposits within concrete after it hardens and is put into service. In the case of DEF, components in the cement paste react with water

to form secondary deposits that consist of the mineral ettringite, which has the chemical formula  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ . In the case of ASR, reactions occur between aggregate particles and the paste to produce secondary deposits that consist of a gel of indefinite composition that may be expressed as  $(\text{Na}, \text{K}, \text{Ca}) \text{SiO}_3 \cdot x \text{H}_2\text{O}$ .

Note that both ettringite and ASR gel contain water ( $\text{H}_2\text{O}$ ). As such, the infiltration of water into concrete lies at the root of both of these deterioration mechanisms (Fig. 1). The deposits formed by DEF and ASR have a greater volume than the solid phases in the concrete, which results in an internal expansion that causes cracking once the tensile strength of the concrete is exceeded. Minimizing permeability and cracking and keeping the internal relative humidity of the concrete below 70% while it is in service are therefore keys to minimizing deterioration from ASR and DEF.

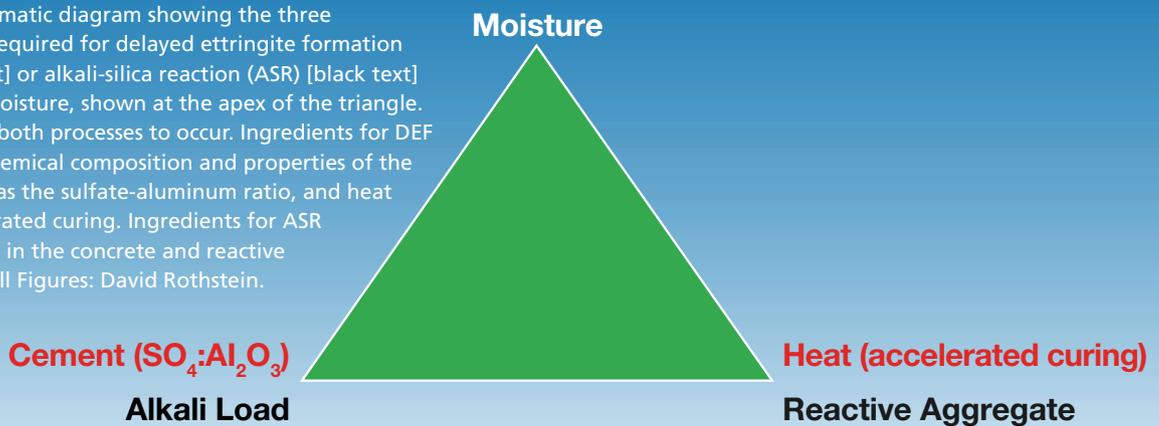
## Diagnosing DEF and ASR

A concrete petrographer can evaluate whether concrete is affected by DEF

or ASR by using various microscopes to examine the internal microstructure of concrete and other cement-based construction materials. Petrographers can document whether there is evidence of internal expansion in the concrete and whether that expansion can be linked to the presence of secondary deposits. Because extensive microcracking is commonly observed in concrete affected by either ASR or DEF, the petrographer must then determine if the secondary deposits associated with the microcracks are ettringite or ASR gel.

Figure 2 shows an example of microcracking in concrete caused by DEF. In many cases, concrete affected by DEF has networks of fine microcracks filled with a material that—even under powerful optical microscopes—appears to be a gel but is actually ettringite. Petrographers may observe microcracks filled with such deposits and assume that ASR is present, unless they use a scanning electron microscope (SEM) to distinguish between ASR gel and ettringite. Most SEMs are equipped with an instrument known as an energy-dispersive x-ray spectrometer (EDS),

Figure 1. Schematic diagram showing the three components required for delayed ettringite formation (DEF) [red text] or alkali-silica reaction (ASR) [black text] to proceed. Moisture, shown at the apex of the triangle, is needed for both processes to occur. Ingredients for DEF include the chemical composition and properties of the cement, such as the sulfate-aluminum ratio, and heat during accelerated curing. Ingredients for ASR include alkalis in the concrete and reactive aggregates. All Figures: David Rothstein.



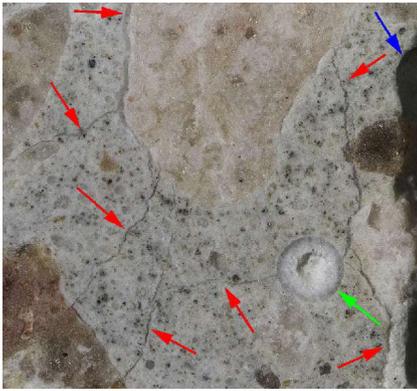


Figure 2. Reflected light photomicrograph of the polished surface of a core from a concrete structure with delayed ettringite formation. Arrows indicate microcracks that are filled with a clear, gel-like material (red), a void filled with ettringite (green), and the outer surface of the core (blue).

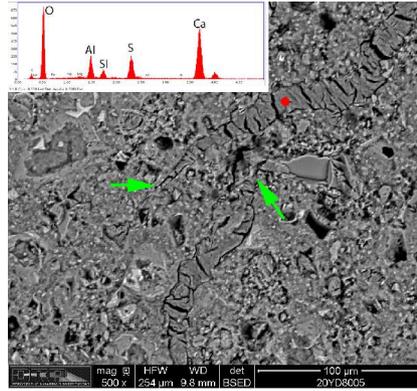


Figure 3. Backscatter electron micrograph at higher magnification showing microcracks (green arrows) from part of the area shown in Fig. 2. The red dot shows the area of the sample that produced the energy-dispersive x-ray spectrometer (EDS) spectrum shown in the upper left. The spectrum indicates the presence of calcium, aluminum, and sulfur, which is consistent with ettringite.

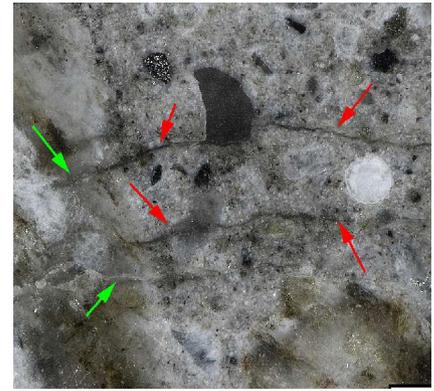


Figure 4. Reflected light photomicrograph of the polished surface of a concrete core with alkali-silica reaction (ASR). Arrows show microcracks with ASR gel within a granitic (and reactive) aggregate particle (green) and microcracks with gel that cut into the paste (red).

which allows determination of the chemical composition of materials that are only microns across. If elements such as calcium, aluminum and sulfur are detected by the EDS, a petrographer knows that the deposit is ettringite (Fig. 3). If the gel deposit contains elements such as sodium, potassium, and silicon, that indicates ASR gel.

Petrographers commonly see deposits of crystalline ettringite in voids, microcracks, and cracks in field concrete that is exposed to moisture. As such, the presence of ettringite alone is not an indicator of DEF or any other form of sulfate attack; it simply indicates that the concrete was exposed to moisture. An experienced petrographer, ideally working with an experienced engineer, is needed to determine whether the concrete is affected by DEF.

Extremely fine-grained, isolated deposits of ettringite in the paste are another feature of DEF. These “nests” of ettringite, which require magnification of about 2000 times to detect, can be identified with a SEM.

Concrete affected by ASR commonly has deposits of both ASR gel and ettringite. However, the patterns of microcracking caused by ASR are often much different from those caused by DEF. With ASR, microcracks can often be traced from the inner portions of reactive aggregate particles into the paste (Fig. 4). In DEF, the microcracks

do not trace to the inner portions of aggregate particles and appear randomly throughout the paste.

Petrographers may use criteria such as whether cracks or microcracks can be linked to DEF or ASR to evaluate the severity of damage. Although not standardized, some methods are available that use petrography to quantify damage from ASR or DEF.<sup>5</sup> When deployed consistently, these methods can be used—along with field-based approaches such as monitoring the widths of cracks—to track the progression of damage over time.

### Implications for In-Service Concrete

Although ASR occurs much more commonly than DEF, it is essential to understand that the presence of ASR gel in concrete does not mean that the concrete is no longer able to serve its intended purpose. ASR is commonly observed in concrete after several years of service, if the concrete is exposed to moisture, with no resulting cracking or even microcracking. A thorough investigation undertaken by experts in both engineering and petrography can determine whether ASR is causing cracking or microcracking that is structurally significant.

Because both DEF and ASR require moisture to progress, reducing the ingress of water is central to minimizing damage from these mechanisms. In

many cases, experienced engineers working in tandem with specialty contractors can determine remediation measures that can greatly prolong the serviceability of an affected concrete element.

### References

1. Portland Cement Association (PCA) Sulfate Task Group. 2001. *Ettringite Formation and the Performance of Concrete*. R&D Serial No. 2166. Skokie, IL: PCA. [http://www2.cement.org/pdf\\_files/is417.pdf](http://www2.cement.org/pdf_files/is417.pdf).
2. Taylor, H.F.W. *Cement Chemistry*. 1997. London, UK: Thomas Telford.
3. Thomas, M.D.A., B. Fournier, and K.J. Folliard. 2013. *Alkali-Aggregate Reactivity (AAR) Facts Book*, HIF-13-019. Washington, DC: Federal Highway Administration. <https://www.fhwa.dot.gov/pavement/concrete/asr/pubs/hif13019.pdf>.
4. Farny, J.A., and B. Kerkhoff. 2007. *Diagnosis and Control of Alkali-Aggregate Reactions in Concrete*, R&D Serial No. 2071b. Skokie, IL: PCA. [http://www2.cement.org/pdf\\_files/is413.pdf](http://www2.cement.org/pdf_files/is413.pdf).
5. Sanchez, L.F.M., B. Fournier, M. Jolin, M.A.B. Bedoya, J. Bastien, and J. Duchesne. 2016. “Use of Damage Rating Index to Quantify Alkali-Silica Reaction Damage in Concrete: Fine versus Coarse Aggregate.” *ACI Materials Journal* 113(4): 395–407.