

Commentary on the Alkali-Silica Reaction in Concrete Structures at the Seabrook Nuclear Plant

March 14, 2012

Statement of Purpose

The purpose of this document is to summarize and comment on the analyses of concrete in the Seabrook Nuclear facility with regard to the following:

- establishing the genesis of the alkali silica reaction observed at various locations and in various structures within the complex,
- establishing the extent to which the alkali silica reaction is occurring,
- establishing the likelihood of the occurrence of other deleterious reactions accompanying the alkali silica reaction.

It is a further purpose of this document to pose questions relevant to the analyses that have been previously carried out so the results obtained can be more fully understood. It is also the purpose of this document to suggest further analyses that would serve to define the scope and extent of the alkali silica reaction and related phenomena at the Seabrook facility that are known to adversely affect the durability and performance of reinforced concrete.

The questions posed on p. 3 of ML11178A338 are pertinent to these concerns and the following commentary acknowledges that summary. The questions listed in ML11178A338 are as follows:

- a. *The locations where monitoring or sampling will be conducted, and how these results will be used to address other susceptible locations.*
- b. *The frequency of the monitoring and sampling to establish a trend in degradation of the structure and rate of ASR, and why the provided frequency is adequate.*
- c. *Detailed information about the planned in-situ monitoring or testing and laboratory testing. This should include the test method, frequency, and schedule.*
- d. *How the number of concrete samples taken or planned from each structure will ensure statistical validity.*
- e. *How the length of core samples taken or planned will account for variation of ASR across the wall thickness.*
- f. *How the extent of degradation/corrosion of rebars will be established in the ASR affected areas during the period of extended operation.*
- g. *How the reduction in load carrying capacity in the steel embedments and anchors used to support equipment, piping, conduits, and other commodities will be established in the ASR affected areas during the period of extended operation.*
- h. *How the results of the petrographic examination will be used to determine quantitative damage in concrete and rate of degradation for the period of extended operation.*
- i. *Plans, if any, for relative humidity and temperature measurements of affected concrete areas of the long term.*
- j. *Plans to perform stiffness damage tests to estimate the expansion attained to date in ASR affected concrete.*
- k. *How current and future rate of expansion of concrete will be determined to ensure that bond between the rebar and concrete is effective over the long term.*

- l. *How the results of concrete compressive strength and modulus of elasticity conducted so far will be adjusted to account for future degradation during the period of extended operation.*

Selected documents specific to the issue of the occurrence of the alkali-silica reaction at Seabrook, standard of care documents, and standard test documents:

ACI 349: Evaluation of Existing Nuclear Safety Related Concrete Structures. This guide is various cited in the ML documents reviewed. While it provides a general discussion of ASR, it does not provide any basis for meaningfully establishing the severity of attack, for developing a prediction of the rate of future damage or of providing guidance regarding remediation.

ASTM C 1260: Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method). This test is designed to predict whether aggregate intended for use in concrete is susceptible to ASR. This test is not suitable to evaluate in-place concrete.

ASTM C 1293: Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction. According to the test methodology concrete prisms containing the aggregate to be evaluated are produced. NaOH is added to the mixing water to create a concrete pore solution capable of inducing ASR. This test is not suitable to evaluate in-place concrete.

ASTM C 1567: Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations on Cementitious Materials and Aggregate (Accelerated Mortar-Bar Test). This test is intended to permit assessment of beneficial effects of mineral admixtures, such as fly ash, slag or silica fume, on mitigating ASR. This test is not suitable to evaluate in-place concrete.

Documents reviewed are: ML 103420273, Dec. 14, 2010;
SBK-L-10204, Dec. 17, 2010;
ML 111330689, May 12, 2011;
ML 111360432, May 23, 2011;
ML 11178A338, June 29, 2011;
ML 112241543, Aug. 12, 2011.

Background

Hardened concrete in its simplest form is porous body comprised of the following constituents:

- large aggregate typically having nominal size of ¾ inch or more,
- small, sand sized, aggregate,
- hardened cement paste,
- a pore solution having a high pH.

The cement paste binder forms as the result of a series of chemical reactions of the anhydrous cement powder with the mixing water. The chemical reactions are collectively referred to as hydration. Property development realized as a result of these reactions is commonly regarded as a consequence of a process called curing.

Concrete is typically constituted to contain more water than is needed to support the hydration reactions. This results in concrete being porous. Because the hydration process liberates the sodium and potassium present in the anhydrous cement, the solution filling the pores in a concrete becomes highly basic. Generally this is desirable because, in the absence of chloride, the elevated internal pH of concrete protects embedded steel from corrosion. However, in some instances this highly basic pore solution can react with siliceous aggregate and produce an expansive gel. This reaction is called the alkali silica reaction (ASR). ASR occurs because certain forms of quartz and some silicate minerals dissolve at elevated pH and produce a gelatinous reaction product. The reaction forming this gel is expansive and it produces internal tensile stresses within the concrete. If the tensile capacity of the concrete is exceeded a network of microcracks forms. Unless the concrete is adequately restrained, these processes can result in dimensional instability.

ASR was first recognized in about 1940 in concrete structures in California by Thomas Stanton. ASR can occur in concrete for two reasons. Either the aggregate is inherently susceptible to ASR because it contains constituents that will react with the concrete pore solution or the exposure environment introduces alkali metal ions to the concrete thereby increasing the alkalinity of the pore solution. When ASR occurs as a result of environmental exposure, it is usually associated with the application of deicing salts, such as NaCl, Na acetate or Na formate. However, ASR can also occur as a result of exposure to natural water, such as sea water, having a high Na content.

A variety of strategies have evolved to avoid the occurrence of ASR in new construction. One is to limit the alkali content of the cement used in making concrete. ASTM C-150 establishes a low alkali cement to be one in which the combined contents of Na₂O and K₂O are less than 0.6%. A second strategy to mitigate ASR is to incorporate a source of reactive silica into the concrete mix. This is typically accomplished by the addition of an industrial by-product such as fly ash from coal burning power plants or silica fume from the production of elemental silicon or ferrosilicon alloys. Such a source of silica competes with the reactive silica in the aggregate, produces a non-expansive gel, and, thereby, reduces the pH of the pore solution. A third strategy is to admix a lithium compound with the concrete mix. The incorporation of Li into ASR gel appears to render it non-expansive.

Means to the mitigation of ASR in existing concrete are more limited. Where practical, this can be accomplished by eliminating exposure to water. When this cannot be accomplished, surface application of a Li-based chemical has been reported to be effective. However, the benefit of surface application is limited to the near-surface region of the concrete.

The Origin of ASR at the Seabrook Plant

Based on the review of available documents, the genesis of ASR reaction in several structures at the Seabrook nuclear facility seems not to have been established. Two possibilities exist. The first is that the alkali content originally present in the concrete is sufficient to have manifested ASR in areas where the structures are exposed to a source or sources of moisture. The second is that exposure conditions have allowed sufficient intrusion of salt water to facilitate the occurrence of ASR.

Petrographic analyses have been carried out on cores exacted from various locations and the extent of ASR has been reported to vary from moderate to severe. However, the documents do not provide specificity as to the criteria used to establish the basis to this categorization.

Petrographic analyses have likely been carried out on polished thin sections. If this is so, the physical dimensions of these are nominally 2x2 inches or less. Given that the thicknesses of the concrete walls are 16-18 inches, it would be relevant to have information as to depths within the walls from which the thin sections were obtained. It is important to establish whether ASR is occurring uniformly throughout the wall thickness or whether it is more localized. It would also be relevant to establish the characteristics of the reactive aggregate as a basis for eventually determining whether this aggregate source was used in concrete throughout the complex or whether it was only associated with specific locations in the quarry from which the aggregate was obtained.

SKB-L- 10204 p. 37 states that petrographic analyses were used to establish a reduction in modulus of elasticity of 47%. While scratch tests to evaluate the hardness of cement pasties commonly done as part of a petrographic analysis, these assessments are typically qualitative. It seems inappropriate to assign a specific value to the modulus based on this method. There is benefit in providing further detail as to how this value was obtained.

Observations of accumulated salts on concrete walls

Inspections revealed the accumulation of salts on the interior faces of concrete walls at various locations. This is an indication that significant amounts of moisture have migrated entirely through the walls. It is not unusual to observe this on subterranean walls and the material that has accumulated is often calcium carbonate. This occurs because the migrating water becomes saturated with respect to calcium hydroxide. As the calcium hydroxide solution reaches the concrete surface, it is exposed to atmospheric CO₂ and calcium carbonate precipitates and typically forms an adherent deposit.

If ASR is occurring, it is not uncommon for ASR gel also to extrude out of cracks, undergo a carbonation reaction and form deposits at evaporative fronts on interior surfaces. If the water source contains chloride or sulfate, sodium sulfate or calcium sulfate and sodium chloride deposits can form. These deposits are likely to be friable. There is a diagnostic benefit in sampling the deposits observed at the Seabrook facility and carrying out compositional determinations by X-ray diffraction analysis or by scanning electron microscopy/energy dispersive X-ray analyses.

Establishing whether the deposits contain chloride is of significant importance in establishing the vulnerability of embedded steel to chloride-induced corrosion. The NextEra response on page 26 of SKB-L-10204, comments that risk of damage to concrete due to corrosion of embedded steel is very low. However, this is only true in the absence of carbonation at the level of the steel in the absence of a chloride exposure. Neither of these appears to be the case. SKB-L-10204 reports the observation of heavy corrosion at certain locations. Representative samples of corrosion product should be obtained and analyzed for their chloride contents.

Variability in concrete exposure conditions and effects on durability

While the commentary in the ML reports reviewed is directed towards the walls in certain buildings, there is an absence of commentary directed towards the performance of the concrete floors. Eighty four locations were identified where the extent of spalling exceeded the depth and surface area considered to be above a level of concern. Substantially greater detail should be provided to establish exposure conditions associated with these locations. If the concrete floors in these structures are also undergoing deterioration, commentary on this is appropriate. If they are not, it would be of benefit to establish the anticipated reasons for the absence of ASR.

Two factors may be inducing ASR. Both involve exposure to moisture. First, if the concrete pore solutions typical of Seabrook concrete are inherently capable of inducing ASR then exposure to moisture, regardless of its source, would be adequate to allow ASR to proceed. If a susceptible concrete is in contact with soil, it is not a necessary condition that the porosity of the soil be saturated for moisture to move from it into the pore structure of concrete. Because concrete generally has a finer porosity than soil does and because concrete is hydrophilic, concrete has the capacity of extracting moisture from soil even when the pores in the soil are not water filled. This is sub-saturated flow. The phenomenon of sub-saturated flow may be relevant to Seabrook concrete to the extent that the installation of sumps and drains would not be sufficient to dewater the soil to the point of mitigating ASR. If dewatering is to be promoted as a means to protect concrete from future deterioration by ASR, this should be taken into consideration. Because of this, the dewatering plan cited in SKB-L-10204, pp. 26-27 should be more fully explained to ensure that consideration is being given to this concrete property.

Alternatively, electrolytes in the local natural waters may induce deterioration by at least 3 mechanisms: corrosion of embedded steel, ASR, and sulfate attack

SKB-L-10204, p. 36 cites that below-grade concrete has experienced ground water infiltration. Data available in SKB-L-10204, P. 32 indicates natural water sources in contact with Seabrook concrete have chloride concentrations ranging from 19 to 3900 ppm. Exposure of reinforced concrete to chloride can induce deterioration by two separate mechanisms. Steel imbedded in concrete does not normally corrode because the elevated pH of concrete pore solution facilitates the formation of thin, adherent and protective layers of oxide on the steel surfaces. The phenomenon is called passivation. The presence of chloride ion in the pore solution adjacent to the reinforcing steel reduces the integrity of this passive layer; the process is called de-passivation. This renders the embedded steel susceptible to corrosion regardless of the elevated pH of the concrete pore solution. Exposure conditions should be systematically characterized to establish the probability of corrosion of reinforcing steel that may be accompanying ASR.

While chloride is more potent, sulfate also has the capacity to depassivate embedded steel. The sulfate exposure was reported as 10-100 ppm. While substantially lower than the chloride concentrations, sulfate-containing water having concentrations in this range can be aggressive to concrete. Thus, the analysis of the efflorescing salts on interior concrete surfaces may indicate whether this there a basis for concern regarding sulfate ingress.

A second effect associated with the ingress of sodium chloride is the elevation of the pH of concrete pore solution to a value where ASR can occur. This occurs because certain

cementitious constituents in concrete have a greater capacity to bind chloride than they do to bind sodium. The chemical details are as follows. One of the four major constituents of Portland cement is an impure form of tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$). A portion of this reacts to form a hydrate of composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{OH})_2\cdot 12\text{H}_2\text{O}$. When this hydrate is exposed to chloride, an exchange reaction occurs and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ is formed. This chloride-containing compound is called Friedel's salt. The conversion of calcium aluminate hydrate to Friedel's salt liberates hydroxyl ions to the concrete pore solution. Thus, this reaction can be regarded as converting some of the NaCl that enters a concrete pore solution to NaOH.

The chemical analyses of the ground water reported on page 32 of SKB-L-10204 do not report the cations present or their concentrations. More complete analyses of the ground water chemistry should be carried out. However, it is reasonable to assume that the primary cation is sodium. If it is assumed that NaCl is entering the concrete pore solution and that the Cl is being exchanged for hydroxyl, this provides a mechanism for elevating the pH of the concrete pore solution to a range where ASR could occur.

If ASR at Seabrook is limited to locations where the ground water has high sodium contents, then the extent of ASR will likely be limited to conditions involving exposure to brackish water.

The accumulation of chloride in the Seabrook concrete can be established by petrographic means using scanning electron microscopy. The extent of chloride penetration can be determined by establishing the depth of the front behind which Friedel's salt has formed. Alternatively, bulk chloride determinations could be made. Such analyses would be beneficial in helping to establish the mechanism causing ASR, in providing a basis for correlating deterioration to the exposure condition, and, possibly, providing a basis for modeling exposure-specific deterioration rates.

Accumulation of sulfates could indicate an exposure condition that could produce sulfate attack. While sulfate attack might not be expected to be a deterioration mechanism that would compromise the bulk concrete, it can create friable regions on exterior concrete surfaces which make them unsuitable to accept a waterproofing membrane. This occurs because sulfate attack manifests in two ways. It is expansive and creates a network of microcracks that eventually interconnect and result in concrete spalling. It converts calcium hydroxide to gypsum and causes concrete surfaces to soften.

Physical testing of extracted concrete cores and Windsor probe results

Various physical tests have been carried out on Seabrook concrete. These include the following:

- Establishing the 28 day compressive strengths based on testing companion cylinders of concrete produced at the time of original placement.
- Establishing the compressive strengths of in-place concrete using drilled cores.
- Establishing the splitting tensile strength of in-place concrete using drilled cores.
- Estimating the compressive strength of in-place concrete by using a penetration test.

Each of these methods of testing is generally accepted and the procedures are governed by ASTM standards.

It would be beneficial in evaluating the results of the compressive and tensile tests if more detail regarding the testing procedures were provided. For example the compressive strength of a core can vary depending on its moisture conditioning, depending on its location within the wall of a structure and depending on the length-to-diameter ratio of the core.

Extraction and testing of cores is governed by ASTM C 42: Standard Test Method for Obtaining and Testing Drilled Cores and Sawed Beams of Concrete. The results of core strength testing should be reported as required by Section 7 of this standard.

Physical testing of cores is governed by ASTM C 39: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens. The results of core strength testing should be reported in compliance with Section 9 of this standard.

It is commonly understood that concrete installers pay close attention to the fabrication of companion cylinders. Consequently, the strengths of these may not actually be representative of the strength of the in-place concrete. Typically the strengths of companion cylinders are higher than is the strength typical of the in-place concrete. For this reason, it would be more appropriate to extract control cores from locations where there is no evidence of ASR or other forms of deterioration and then to condition these cores to achieve a moisture condition similar to that of the concrete where ASR is occurring. Doing so may provide a more realistic assessment of any losses in compressive or splitting tensile strengths due to ASR.

Similarly, carrying out Windsor probe determinations in areas where the concrete has not experienced ASR, and is presumably dry, will produce artificially higher apparent strengths merely because dry concrete is more penetration resistant than is moist concrete.

Probe testing is governed by ASTM C 803: Standard Test Method for Penetration Resistance of Hardened Concrete. Table 1 of this standard provides for an assessment of precision of the tests depending on the size of the maximum aggregate. Interpretation of the results of the testing should be consistent with this table and should accord with the reporting requirements cited in Section 10 of this standard.

The ML documents provided did not provide any commentary regarding correlating the strength data with the petrographic results. Nor do they give any indication of how the strength properties varied depending on the location within a wall of the test cylinders. Thus while petrography claims moderate to severe ASR and strength testing indicates substantial reduction, there is benefit in relating the two so presumptive future testing can more fully rely on presently available data to assess the progression of the ASR deterioration reaction.

Summary

Based on the materials available, the following generic areas of uncertainty have been identified:

Whether ASR is inherent to the concrete and is induced merely by exposure to water regardless of its source or whether is ASR being induced because of local ingress of alkalis from the ground water.

Whether other deleterious reactions, especially corrosion of embedded steel and sulfate attack, are accompanying ASR and, if so, the extents of their severities.

Any basis for predicting the rates of corrosion of embedded reinforcement and of ferrous components presently exposed to infiltrating ground water or likely to be exposed in the future.

Lack of quantification of the extent to which ASR is occurring both with respect to the physical locations identified within the structures and with respect to the locations within the thickness of the concrete walls themselves.

Lack of adequate quantification of the extent to which ASR has presently resulted in diminution of mechanical properties as compared to control samples of concrete obtained from non-damaged locations.

Any basis for predicting whether or not ASR will occur at locations not yet identified.

Any basis for predicting the future loss in mechanical properties of concrete at locations where ASR has been identified.

Any basis for establishing the probability of success of a mitigation/remediation strategy.

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Prepared under contract with The Union of Concerned Scientists