The Alkali Silica Reaction
ASR
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Definitions : AAR, ACR, ASR ?
Chemical reaction in either concrete or mortar between hydroxyl ions (OH) of the alkalies (sodium and potassium) from hydraulic cement (or other sources), and certain siliceous rocks and minerals, such as opal, chert, microcrystalline quartz, and acidic volcanic glass, present in some aggregates. This reaction and the development of the alkali-silica gel reaction product can, under certain circumstances, lead to abnormal expansion and cracking of the concrete.

Starting point
As mentioned in numerous books and publications three conditions are necessary for the alkali-silica reaction to occur:
- presence of reactive silica, coming from the aggregates
- presence of water or moisture, mainly from the pore solution, but also from external water supply during the structure life
- alkali ions, primarily coming from the cement
**Historical note**

- First identification of ASR in California by Stanton in the 40s
- At the very beginning, only poorly crystalline siliceous rocks were considered as reactive (like opal)
- Last 60 years: more and more mineral phases and thus aggregates proved to be reactive
- Cases of ASR have nowadays been identified in nearly every country

**Cracking development**

- Undamaged
- Low expansion 0.04 – 0.06 %
- High expansion > 0.10 %
ASR product responsible for the swelling and the subsequent cracking.
Ettringite
Mixed product (ettringite + low calcium CSH + ASR?)
Amorphous ASR product
Crystalline ASR product

What does ASR product look like?

Transition

Figure 5. Morphology of crystalline ASR product in an air void. Concrete from a bridge.
TEM imaging - Morphology

Accelerated laboratory tests concrete, after 1 month at 60°C in water vapour (SIA standard)

Effect on the mechanical properties

- Drop of compressive strength
- Drop of Young’s Modulus
- Increase of creep

Chemistry of the reaction and its mechanism of expansion
• The incomplete tetrahedras at the surface are charged

In presence of water, ions are adsorbed at the surface

In alkaline solution, the metallic ions adsorb
• Leading to rupture of the silanol bonds

\[ Si-O-Si + 2OH^- + 2Na^+ \rightarrow 2(Si-O-Na) + H_2O \]

• In very well crystallized rocks, this only happens at the surface.
• With amorphous or partially crystallized silica, the alkaline hydroxides can penetrate in the crystal

• Many silanol bonds broken and water penetrating means the structure has a higher volume → EXPANSION
Mechanisms

- Since the 50s, many models about the chemistry of ASR and its expansion have emerged and laid the foundations for understanding these mechanisms (Powers and Steinour, 1955; Dent Glasser and Kataoka, 1981; Wang and Gillot, 1991; Dron and Brivot, 1992, 1993).

- Thermodynamically, the presence of water in this region where adsorption reduces free energy is responsible for the swelling: water is uptaken and trapped in the newly formed product. Since it induces swelling of the product and generates stress in the aggregates, it further leads in most cases to expansion and cracking of the structure.

Open questions

- The role of calcium (must be available for damaging reaction to occur)
- The rheological behaviour of the different products
- The mineral phases dissolution and its link to the products formation and the rate of cracking
- The early stage product formation (composition, structure)
- The cracking mechanism: SWELLING or CRISTALLIZATION pressure?

and more…

Another scheme of the chemistry of the reaction

Rajabipour et al. (2015)
Reactive silica

Reactivity

- Difficulties to assess the reactivity of aggregates, due to the slow nature of the ASR reaction, as well as the aggregates mineral phases complexity and variety.
- Cryptocrystalline or microcrystalline quartz will react more slowly than amorphous silica but can still provoke some deleterious expansion on the long term.

### Reactive mineral phases

<table>
<thead>
<tr>
<th>Reactive substance (mineral)</th>
<th>Chemical composition</th>
<th>Physical character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opal</td>
<td>SiO₂·nH₂O</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>SiO₂</td>
<td>Microcrystalline to cryptocrystalline, commonly fibrous</td>
</tr>
<tr>
<td>Certain forms of quartz</td>
<td>SiO₂</td>
<td>Microcrystalline to cryptocrystalline, cryptocrystalline, but intensely flawed, stained, and/or inclusion, filled</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Tridymite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Rhyolitic, dacitic, latitic, or andesitic glass or cryptocrystalline devitrification products</td>
<td>Silica with lesser proportions of Al₂O₃, Fe₂O₃, alkaline earths, and alkalis</td>
<td>Glass or cryptocrystalline material as the matrix of volcanic rocks or fragments in tuffs</td>
</tr>
<tr>
<td>Synthetic siliceous glass</td>
<td>Silica, with lesser proportions of alkalis, Al₂O₃, and/or other substances</td>
<td>Glass</td>
</tr>
</tbody>
</table>

Thomas et al. (2013)
Swiss case

In Switzerland

- More than 400 structures are affected (Merz et al. 2006)
- 20-30% of Swiss dams are affected
- The mountain formation tends to provide rocks which are vulnerable to ASR, and around 90% of the aggregates were classified as potentially reactive by (Merz & Leemann, 2012).

Sources of alkali

Cement characterization

<table>
<thead>
<tr>
<th>Analysis oxide (XRF)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>20.5 (19 - 21)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6 (4-7)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.5 (2-3)</td>
</tr>
<tr>
<td>CaO</td>
<td>64 (62-65)</td>
</tr>
<tr>
<td>MgO</td>
<td>1.2 (1-4)</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.8 (2.5-3.2)</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.5 (0.3-1)</td>
</tr>
<tr>
<td>NaO</td>
<td>0.2 (0.1-0.5)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1 (1-2)</td>
</tr>
<tr>
<td>CaO free</td>
<td>1 (0.5-1.5)</td>
</tr>
<tr>
<td>resid</td>
<td>0.3 (0.2-0.4)</td>
</tr>
</tbody>
</table>

Molar mass of Na₂O = Na₂O + 62/94 K₂O

Alkalis effect

Thomas et al. (2013)
Thresholds

• Alkali threshold for ASR formation and expansion = 3.0 kg/m$^3$ Na$_2$Oe
• Cement with low alkali content : Na$_2$Oe < ~0.7%

BUT there is evidence nowadays that this approach is not totally reliable

→ Expansion has been found to occur in the field at lower alkali contents than that found necessary to cause expansion in concrete specimens stored over water in the laboratory. The reason for this is that a portion of the alkalis may be lost through leaching under the laboratory conditions.

Test methods

Examples of tests and their characteristics

- **ASTM C 291: Standard Guide for Petrographic Examination of Aggregates for Concrete**
  - **Test Method**: Petrographic examination of aggregates.
  - **Comments**: Useful evaluation to identify many (but not all) potentially reactive components in aggregate. Reliability of examination depends on experience and skill of individual petrographer. Results should not be used exclusively to accept or reject aggregate source – findings best used in conjunction with other laboratory tests (e.g., AASHTO T 303 and/or ASTM C 1293).

  - **Test Method**: Chemical test to assess potential alkali-reactive silica in coarse aggregate.
  - **Comments**: Aggregate test in which crushed aggregate is immersed in 1M NaOH solution for 24 hours – solution is then analyzed for amount of dissolved silica and alkalinity. Poor reliability. Problems with test include: – Other phases present in aggregate may affect dissolution of silica (Bluhol and Fournier 1997). – Test is overly severe, leading aggregates with good field performance to fail the test. – Some reactive phases may be lost during pretreatment processing.
Prevention possibilities

- Avoid reactive aggregates
- Use cement with low alkali content
- Add SCM's
  - calcined clays
  - fly ash

Figure 23. Expansion measured by PC and C40-50 and C60-80 with a sodium hydroxide content of 20% in the concretes of the same strength.

Thomson, A., Embry, R., Frontera, V. et al. 2018

ASR prevention

The role of Al

- Al absorption at the Si surface
- Formation of nodules
- Enhanced alkali binding

Al is not incorporated in the ASR product itself.
Long term

Sometimes, the reaction can arise after 30 to 40 years:

• Cosmetic or structural?
• Replace or repair?

In dams expansion can cause structural problems BEFORE cracking or loss of mechanical performances (no rebars, compression)

Chambon dam, France

Slot Cutting

Diamond wire cutting
Provides stress relief

Chambon dam, France

13 Février 2020 – LC3 Doctoral School - Solène Barbotin

13 November 2021 – LC3 Doctoral School - Solène Barbotin
Conclusions

• ASR will occur with presence of reactive silica, water and alkali.
• It has an impact on structural properties
• It is a long term reaction (can appear after decades)
• Standards exist to assess the reactivity, but can be improved
• Use of SCM’s can mitigate the reaction
• Structures repair is possible but very expensive

• BUT still many open questions due to :
→ great diversity of aggregates and ASR product composition

References

• Scrivener, K., Material Science Lecture, Matériaux de Construction (Bachelor – 3rd Year), Durability : lmc.epfl.ch
• SIA Cahier technique 2042 (2012), Prévention des désordres dus à la reaction alcalis-granulats (RAG) dans les ouvrages en béton, Correctif C1 2012, Correctifs C2 2015

References