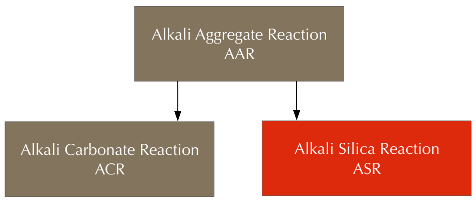
The Alkali Silica Reaction
ASR

Solène Barbotin Albinski

Introduction

Definitions : AAR, ACR, ASR ?

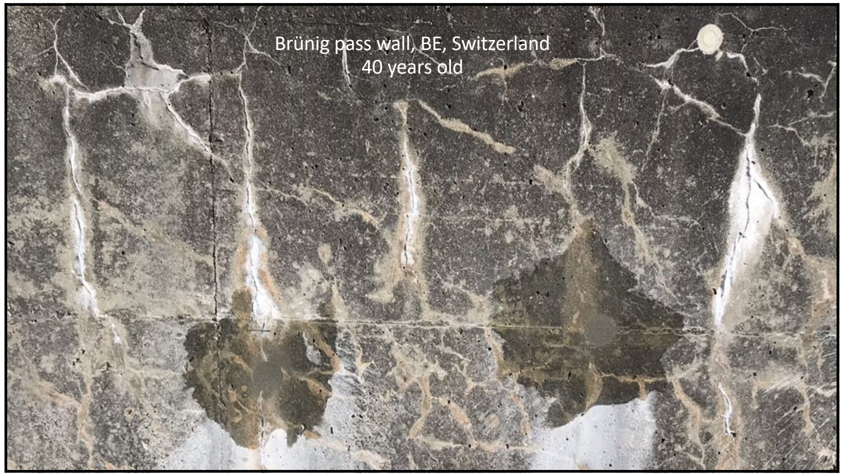
Chemical reaction in either concrete or mortar between hydroxyl ions (OH^-) of the alkalies (sodium and potassium) from hydraulic cement (or other sources), and certain siliceous rocks and minerals, such as opal, chert, microcrystalline quartz, and acidic volcanic glass, present in some aggregates. This 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

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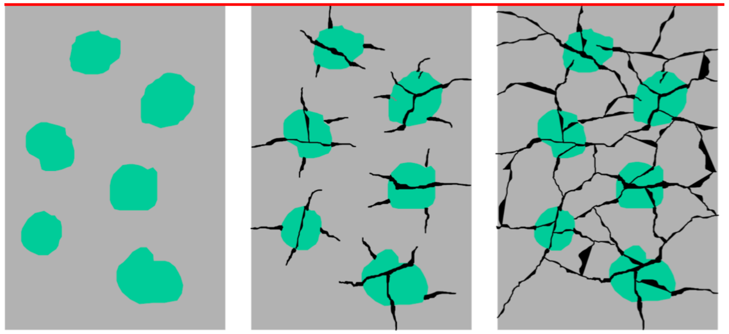
Cracking development



- Undamaged
- Low expansion 0.04 – 0.06 %
- High expansion > 0.10 %

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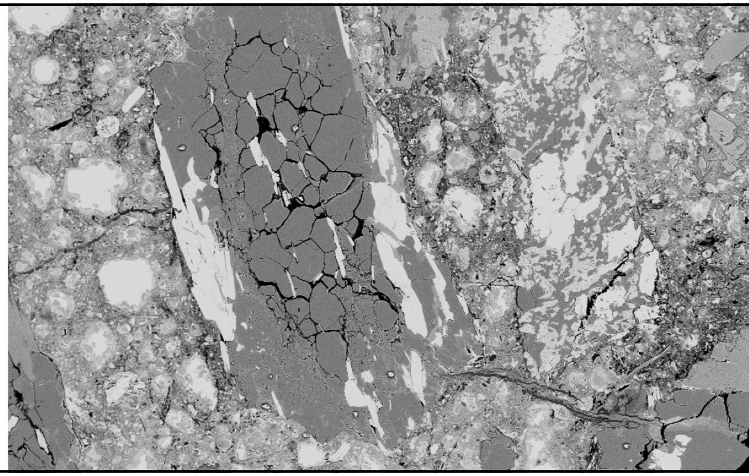

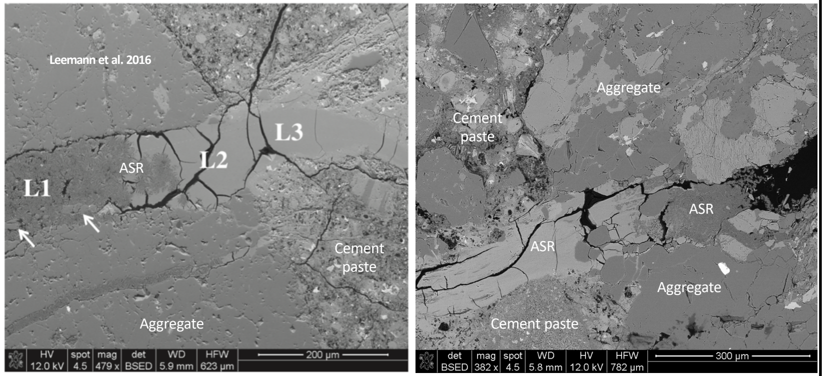

Fig. 4. Vein in concrete CPT-1 with locations L1 (crystalline ASR product) and L2–L3 (amorphous ASR product) indicating the locations, where the Raman spectra shown in Fig. 7B were obtained. The white arrows show quartz fragments embedded in crystalline ASR product. Further to the left of location L1, the vein is empty.

ASR product responsible for the swelling and the subsequent cracking

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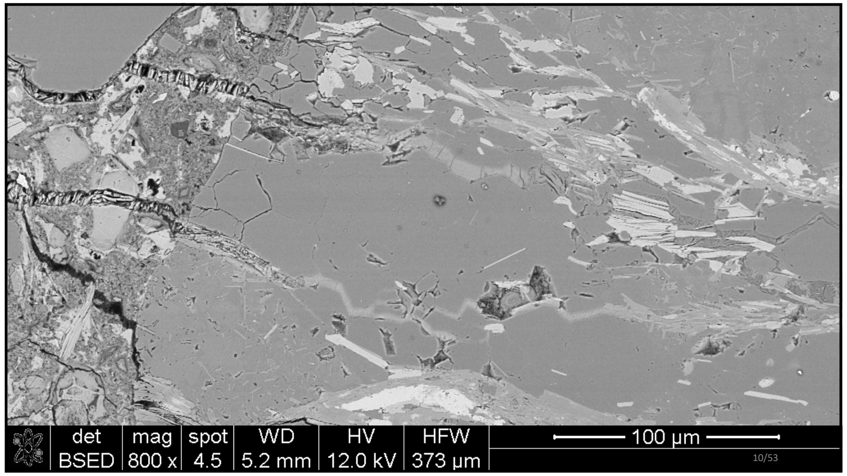
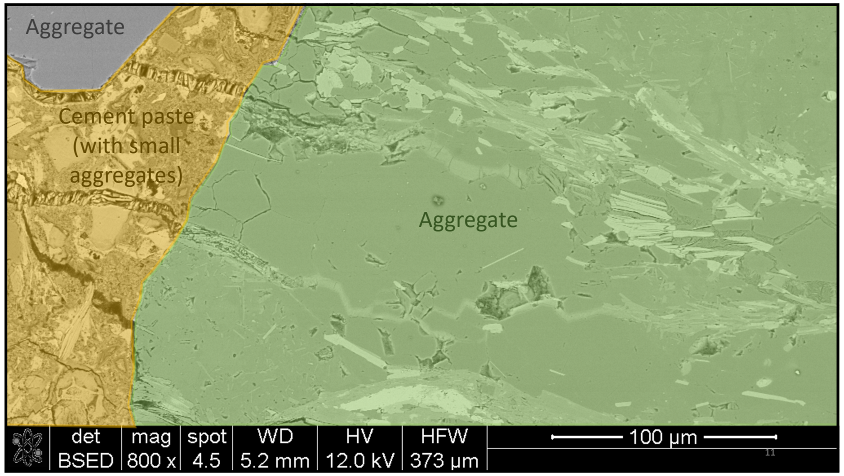
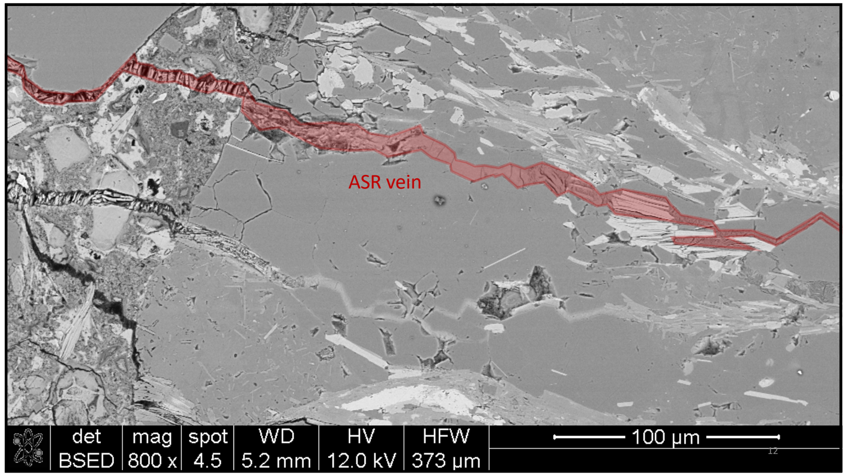
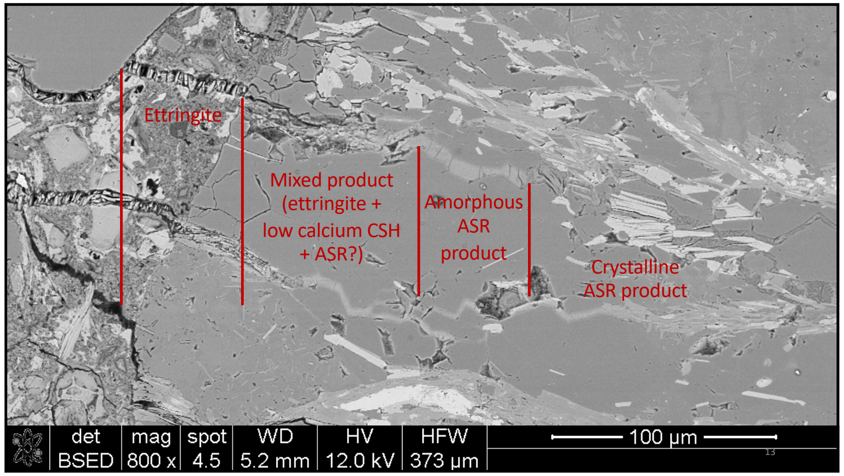
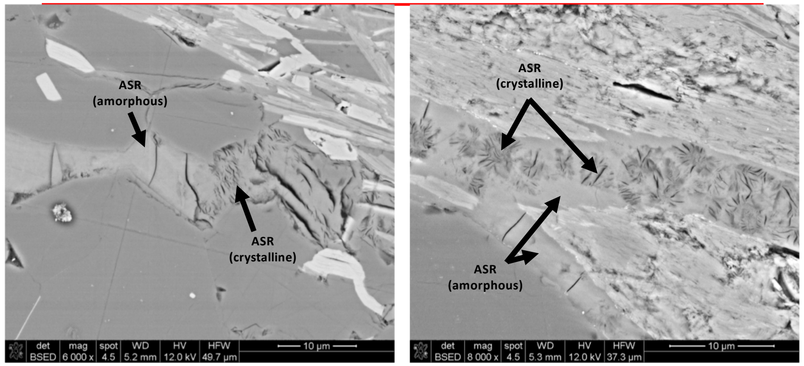






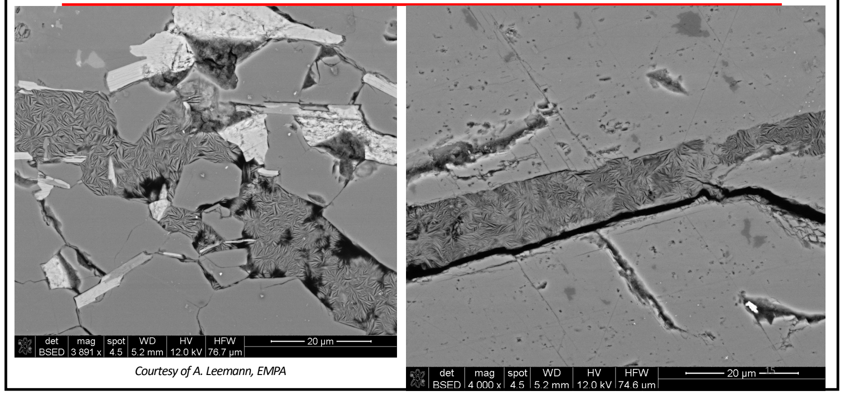


Transition



Pictures : Taken at EMPA with A. Leemann

What does ASR product look like?



Courtesy of A. Leemann, EMPA

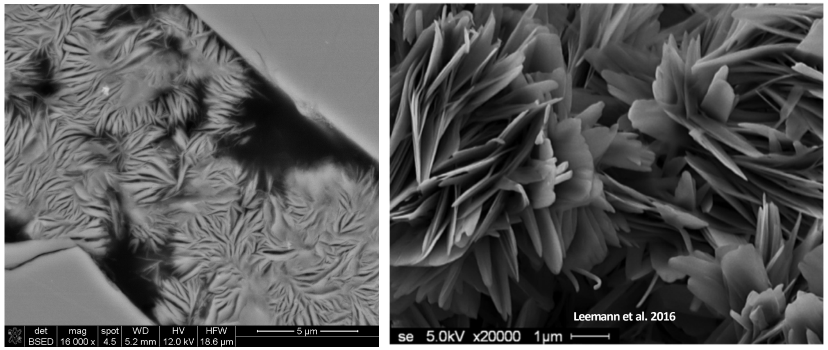
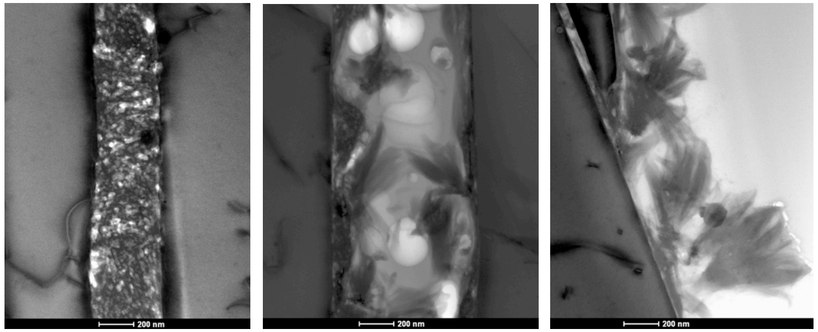


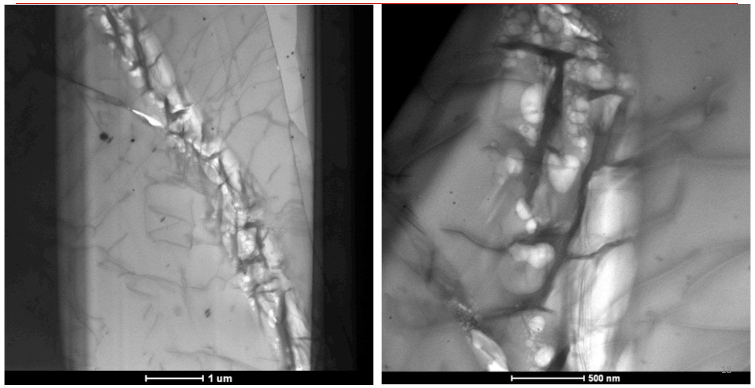
Figure 5. Morphology of crystalline AAR product in an air void. Concrete from a bridge

TEM imaging - Morphology



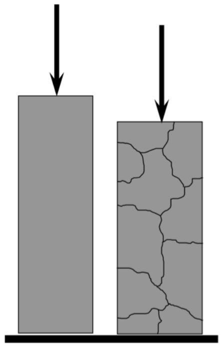
Accelerated laboratory tests concrete, after 1 month at 60°C in water vapour (SIA standard)

TEM imaging - Morphology



Effect on the mechanical properties

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



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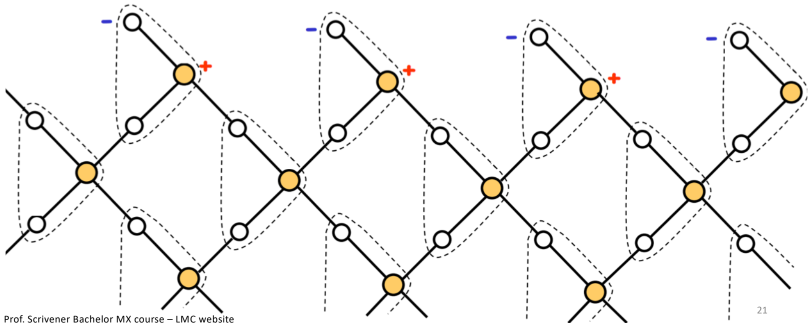
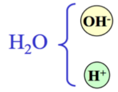
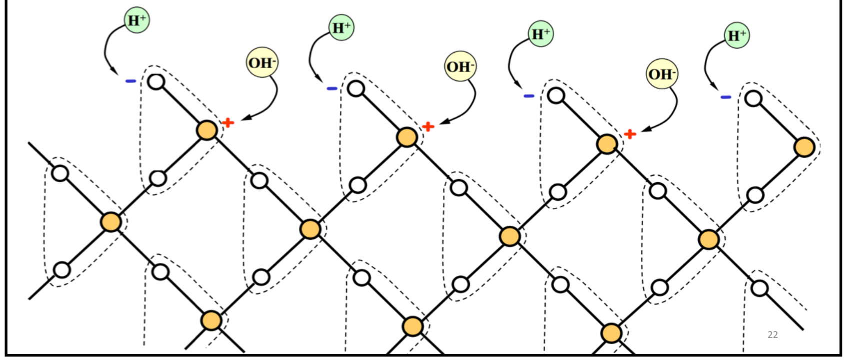
Chemistry of the reaction and its mechanism of expansion

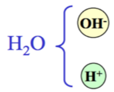
- The incomplete tetrahedras at the surface are charged

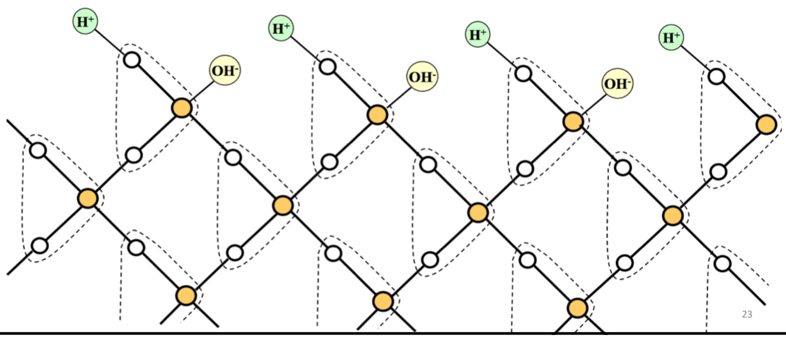




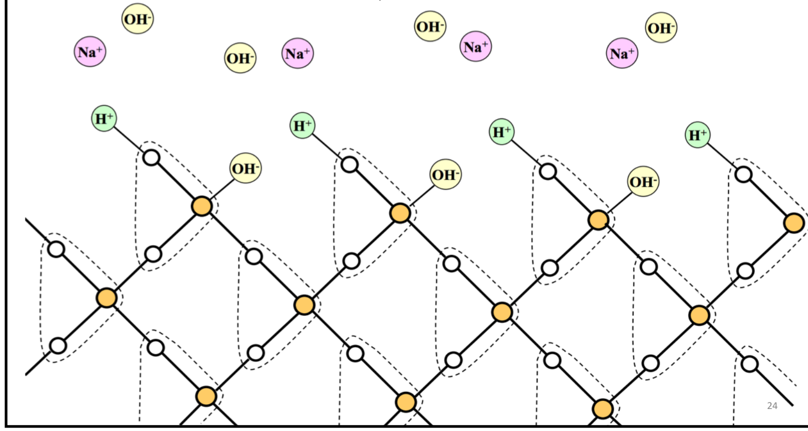
- In presence of water, ions are adsorbed at the surface





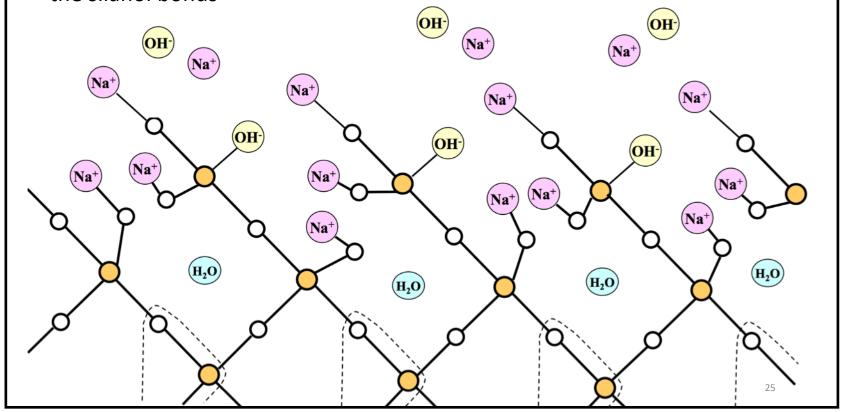


- In alkaline solution, the metallic ions adsorb



- Leading to rupture of the silanol bonds

$$Si\text{-}O\text{-}Si + 2OH^- + 2Na^+ \rightarrow 2(Si\text{-}O\text{-}Na) + H_2O$$



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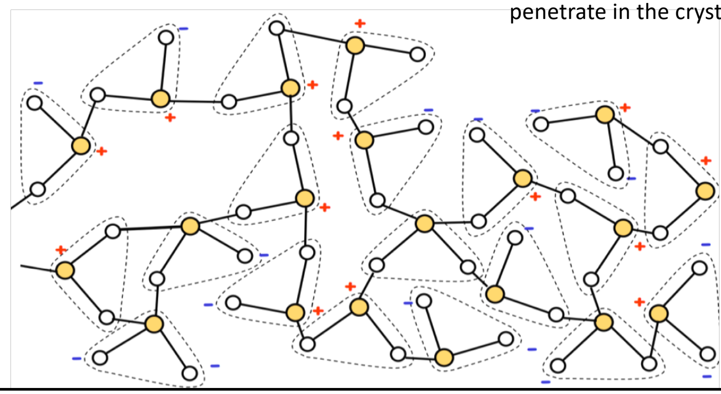
- In very well crystallized rocks, this only happens at the surface.
- With amorphous or partially crystallized silica, the alkaline hydroxides can penetrate in the crystal



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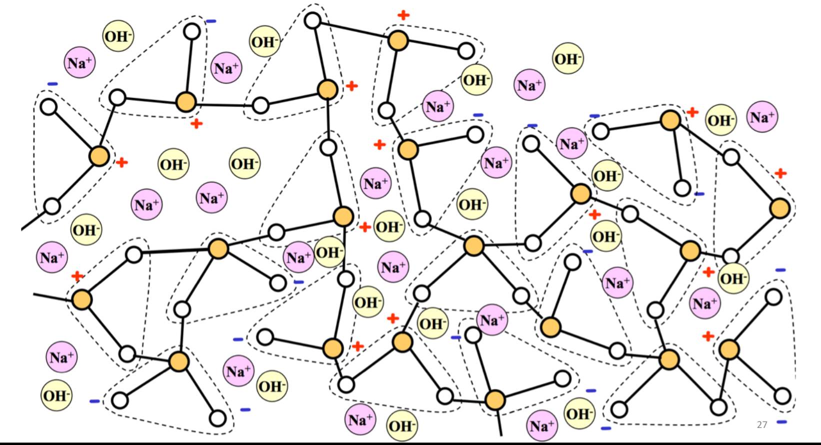

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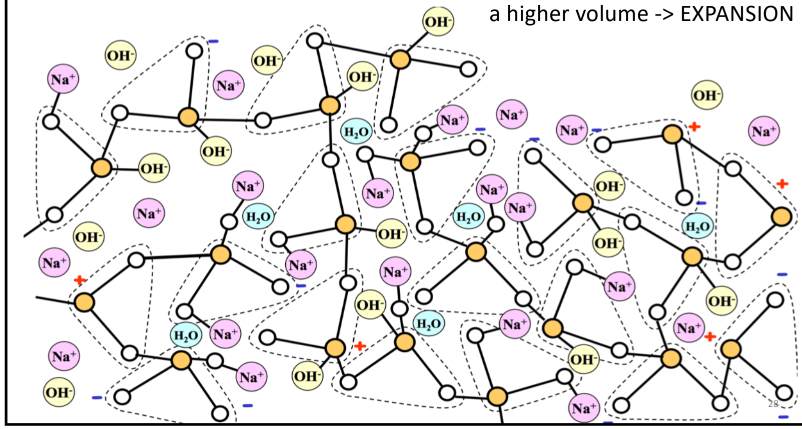
- Many silanol bonds broken and water penetrating means the structure has a higher volume -> EXPANSION



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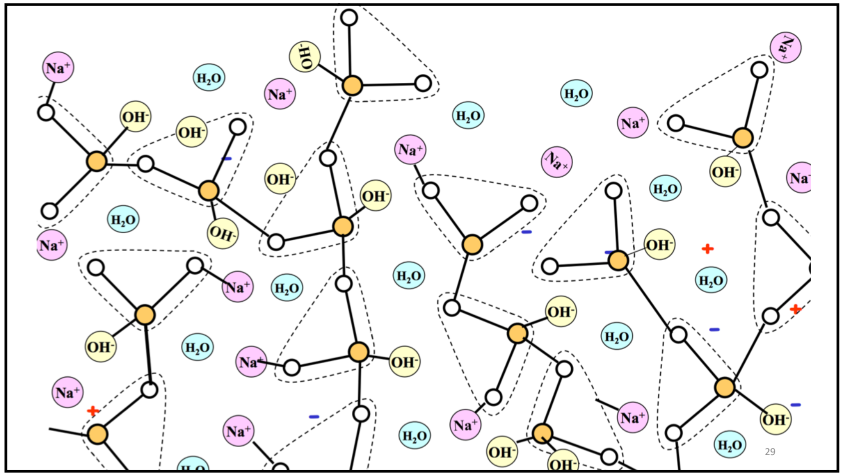
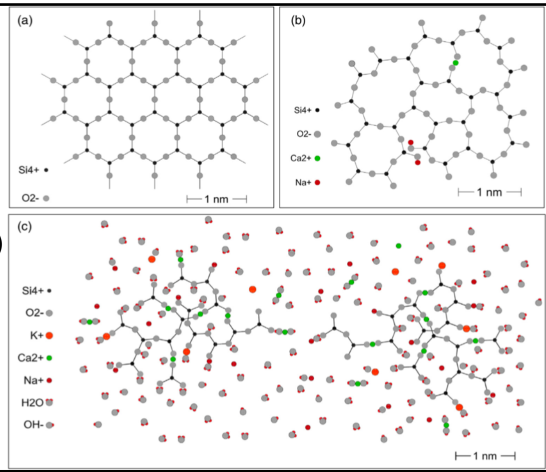


- Another scheme of the chemistry of the reaction

Rajabipour et al. (2015)



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?

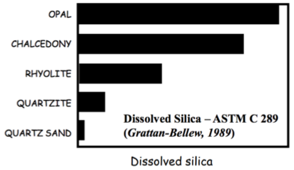
and more…

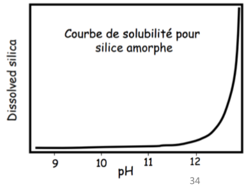
Reactive silica

Reactive mineral phases

Reactive substance (mineral)	Chemical composition	Physical character
Opal	$SiO_2 \cdot nH_2O$	Amorphous
Chalcedony	SiO_2	Microcrystalline to cryptocrystalline; commonly fibrous
Certain forms of quartz	SiO_2	Microcrystalline to cryptocrystalline; crystalline, but intensely fractured, strained, and/or inclusion-filled
Cristobalite	SiO_2	Crystalline
Tridymite	SiO_2	Crystalline
Rhyolitic,dacitic, latitic, or andesite glass or cryptocrystalline devitrification products	Siliceous with lesser proportions of Al_2O_3, Fe_2O_3, alkaline earths and alkalis	Glass or cryptocrystalline material as the matrix of volcanic rocks or fragments in tuffs
Synthetic siliceous glass	Siliceous, with lesser proportions of alkalis, Al_2O_3, and/or other substances	Glass

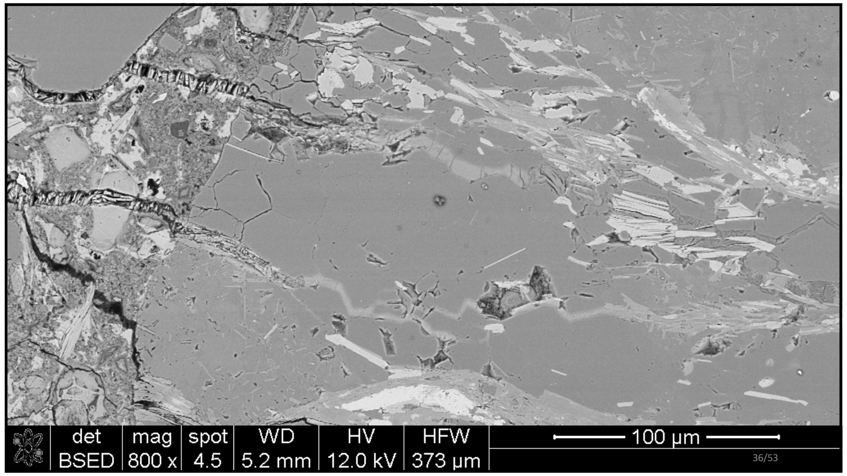
Thomas et al. (2013)





Reactivity

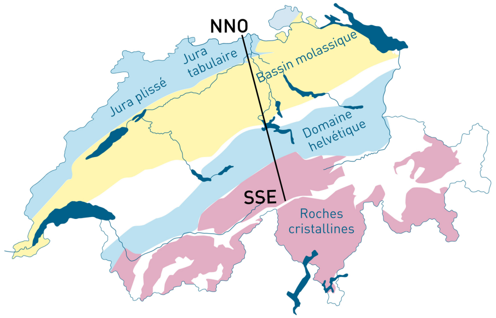
- Difficulties to assess the reactivity of aggregates, due to the slow nature of the ASR reaction, as well as the aggregates mineral phases complexity and variety.
- Cryptocristalline or microcrystalline quartz will react more slowly than amorphous silica but can still provoke some deleterious expansion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



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).



Swiss geology map from Nagra portal

Sources of alkali

Cement characterization

Analyse oxyde (XRF)

SiO_2	20,5	(19 – 21)
Al_2O_3	6	(4-7)
Fe_2O_3	2,5	(2-3)
CaO	64	(62-65)
MgO	1,2	(1-4)
SO_3	2,8	(2,5-3,2)
K_2O	0,5	(0,3-1)
Na_2O	0,2	(0,2-0.5)
PaF(LO)I	1	(1-2)
CaO libre	1	(0,5-1,5)
resid insol	0,3	(0,2-0,4)

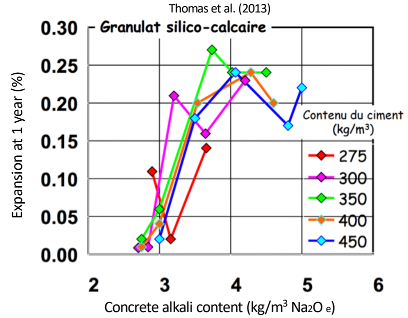
$+Mn_2O_3$, TiO_2, P_2O_5, CO_2

Molar mass of Na_2O

$Na_2O(eq) = Na_2O + 62/94\ K_2O$

Alkalis effect

Thomas et al. (2013)



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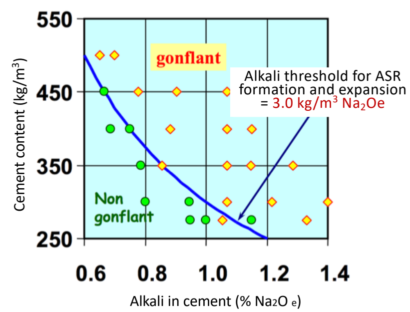


Effect of alkali from concrete (left) and cement (right) on expansion

Thresholds

- Alkali threshold for ASR formation and expansion = 3.0 kg/m^3 Na_2Oe
- Cement with low alkali content : Na_2Oe < ~ 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

History

- Stanton (1940) was the first to developp a test method to assess aggregate reactivity, and he used this technique to also evaluate the use of pozzolans to control ASR-induced expansion.
- Still in use today by some researchers and practitioners, but a wide variety of test methods have been developed and implemented since the time of Stanton's research on ASR.
- Through research and development, as well as trial and error, test methods have evolved over the years, and there has been a general convergence in terms of the tests that are generally used

Thomas et al. (2013)

Examples of tests and their characteristics

Test Method	**Comments**
ASTM C 295: Standard Guide for Petrographic Examination of Aggregates for Concrete	• Useful evaluation to identify many (but not all) potentially reactive components in aggregates. • 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).
ASTM C 289: Standard Test Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method)	• 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 (Bérubé and Fournier 1992). – Test is overly severe, leading aggregates with good field performance to fail the test. – Some reactive phases may be lost during pretest processing.

Thomas et al. (2013)

ASTM C 227: Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)	• Mortar bar test (aggregate/cement = 2.25), intended to study cement -aggregate combinations. • Specimens stored in high-humidity containers at 38°C. • Several reported problems with test, including excessive leaching of alkalis from specimens.
AASHTO T 303 (ASTM C 1260): Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)	• Mortar bar test, originally designed to assess aggregate reactivity. • Bars are soaked in 1N NaOH solution for 14 days. • Accelerated test suitable as screening test, but because of severity of test, it should not be used, by itself, to reject a given aggregate. If aggregate is tested using both AASHTO T 303 and ASTM C 1293, the results of ASTM C 1293 should govern.
ASTM C 1293: Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction	• Concrete prism test, generally regarded as best indicator of field performance, is conducted at high humidity (close to 100%) at 38° C. • Uses high-alkali cement (raised to 1.25% Na_2O_e), with a cement content of 420 kg/m^3. • Developed as aggregate test (using non-reactive fine aggregate to test reactivity of coarse aggregate, and vice-versa). • Test requires one year for completion – this long duration limits its use by many agencies and owners. • Cannot be used to determine the alkali threshold for a given aggregate due to leaching of alkalis from the prisms during the course of the test.

Thomas et al. (2013)

ASR prevention

Prevention possibilities

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

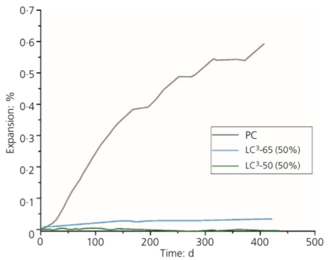


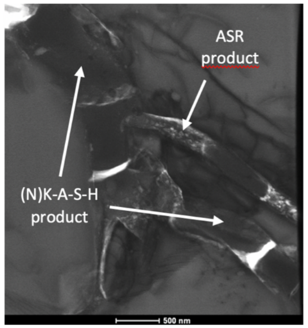
Figure 22. Expansion measured for PC and LC^3-65 and LC^3-50 with a calcined kaolinite content of 50% in the calcined clay

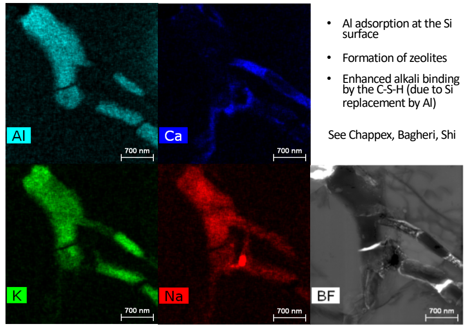
Scrivener K., Avet F., Hanpongpun W. et al 2018

Thomas et al. (2013)

Figure 1.2. The Nant-y-Moch Dam in 2011 – No Symptoms of ASR after 50 Years – Constructed with Reactive Aggregate and 25% Fly Ash

The role of Al





- Al adsorption at the Si surface
- Formation of zeolites
- Enhanced alkali binding by the C-S-H (due to Si replacement by Al)

See Chappex, Bagheri, Shi

Al is not incorporated in the ASR product itself.

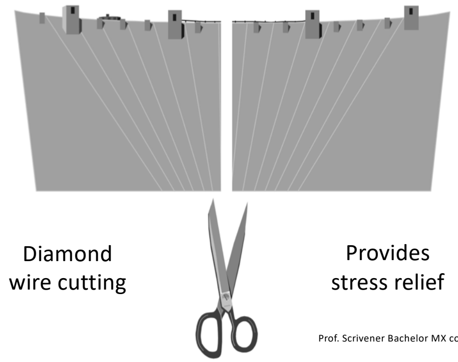
Long term

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)

Slot Cutting



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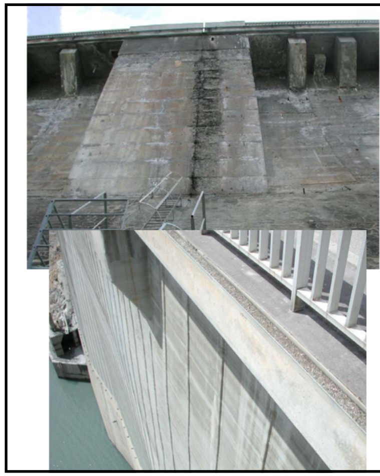
Chambon dam, France

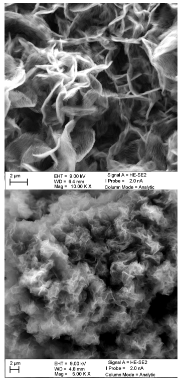


Conclusions

- 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



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