IAEA
International Atomic Energy Agency

The Abdus Salam International Centre for Theoretical Physics

Joint ICTP-IAEA International School on the Degradation (ageing) modelling of disposed radioactive waste forms and TC Regional Workshop on Approaches to ageing management of waste packages in storage

Lecture: Alkali-silica reaction in cemented waste packages

A case study

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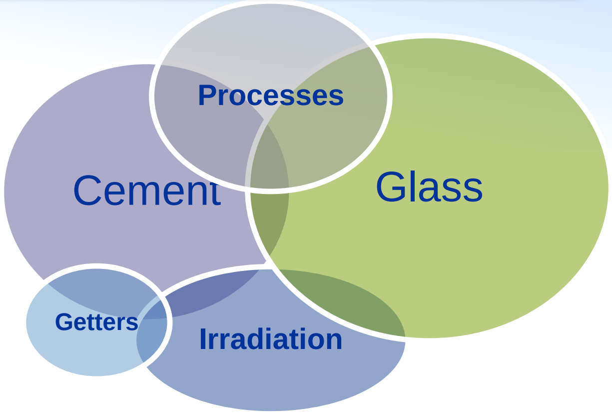
CEA Marcoule

Marcoule Research center



Marcoule research center

Brief Introduction to Contents

1. Short reminder on Alkali silica reaction

    1.1 What is ASR?

    1.2 ASR products

    1.3 Influence on material properties

    1.4 Conditions for ASR development

2. ASR in cemented waste packages – a case study

    2.1 Context

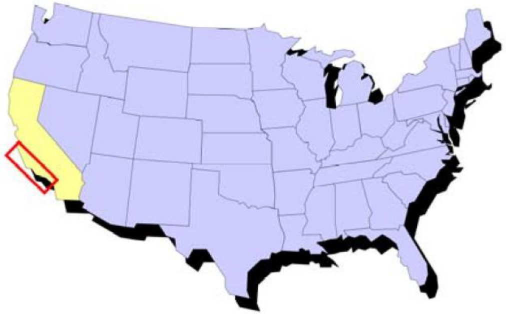
    2.2 Properties of synthetic gel

    2.3 Gel in concrete

1. Short reminder on ASR in concrete

- What is Alkali-Silica reaction (ASR) ?
  - chemical reaction causing cracking and substantial damage in concrete stuctures worldwide,
  - results from non-equilibrium between the minerals present in the aggregates and highly alkaline pore solution of the concrete

- First discovered by Stanton in the late 1930s in the United states, and evidenced in Europe in Denmark by Idorn in 1956



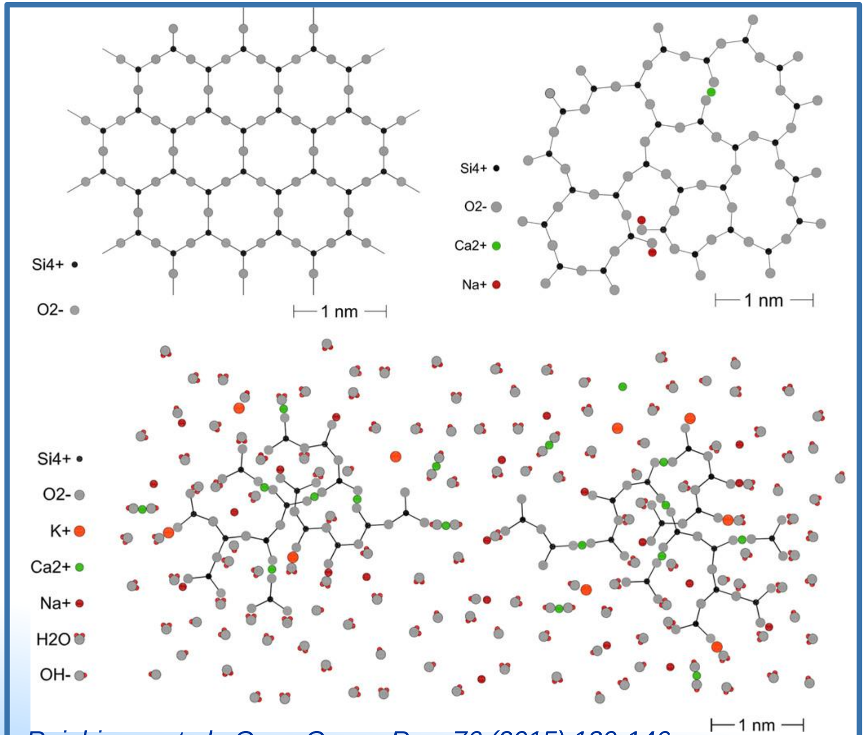
FHWA Workshop, Session 2, Fundamentals of alkali-aggregate reaction

In 2000s

Field cases of ASR in most (if not all) states of USA.

1. Short reminder on ASR in concrete

➢ What are the mechanisms involved in ASR ?



Rajabipour et al., Cem. Concr. Res. 76 (2015) 130-146

❶ Rupture of siloxane bonds through hydroxyl attack

Creation of silanol sites in the siliceous network of the aggregate — Dissolution of silica

$$\equiv Si–O–Si\equiv \xrightarrow{HO^-} \equiv Si–OH \xrightarrow{HO^-} Si(OH)_4$$

❷ Acid / base reactions ⇒ ionization

$$Si(OH)_4 \leftrightarrow (OH)_3\equiv Si–O^- + H^+$$

❸ Neutralization of negative charges on the silica surface

$$\equiv Si–O^- + Na^+_{(aq)} \longrightarrow \equiv Si–O\cdots Na$$

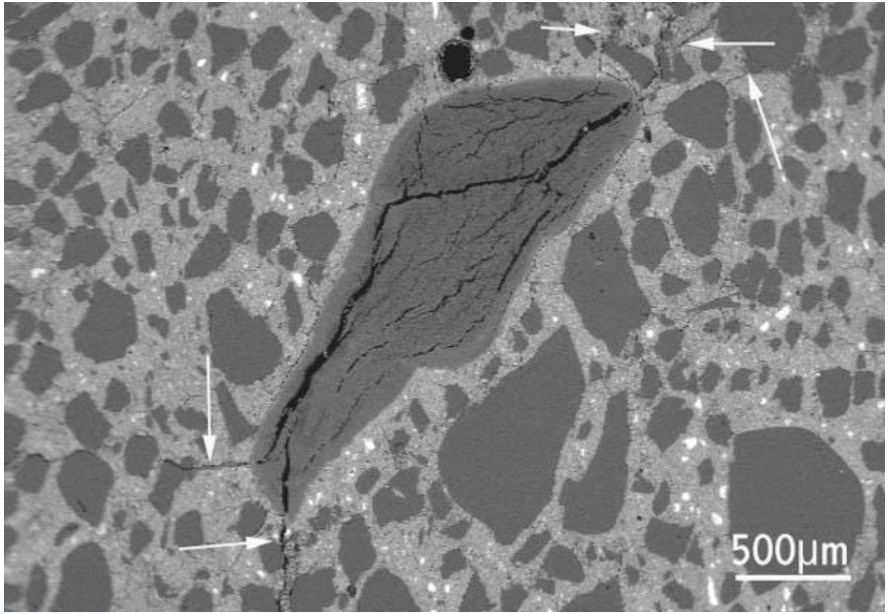
(also involves K^+ & Ca^{2+})

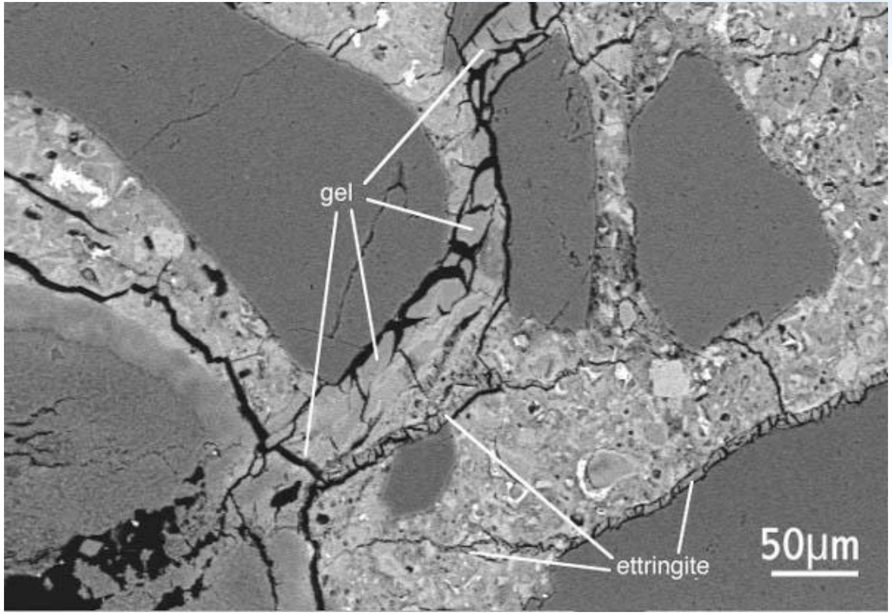
❹ Precipitation / condensation of silicate monomers

$$2\,[(OH)_3\equiv Si–O^-_{(aq)}] + Ca^{2+} \leftrightarrow (OH)_3\equiv Si\text{-}O\cdots Ca\cdots O\text{-}Si\equiv(OH)_3$$

1. Short reminder on ASR in concrete

➢ ASR at the microscale



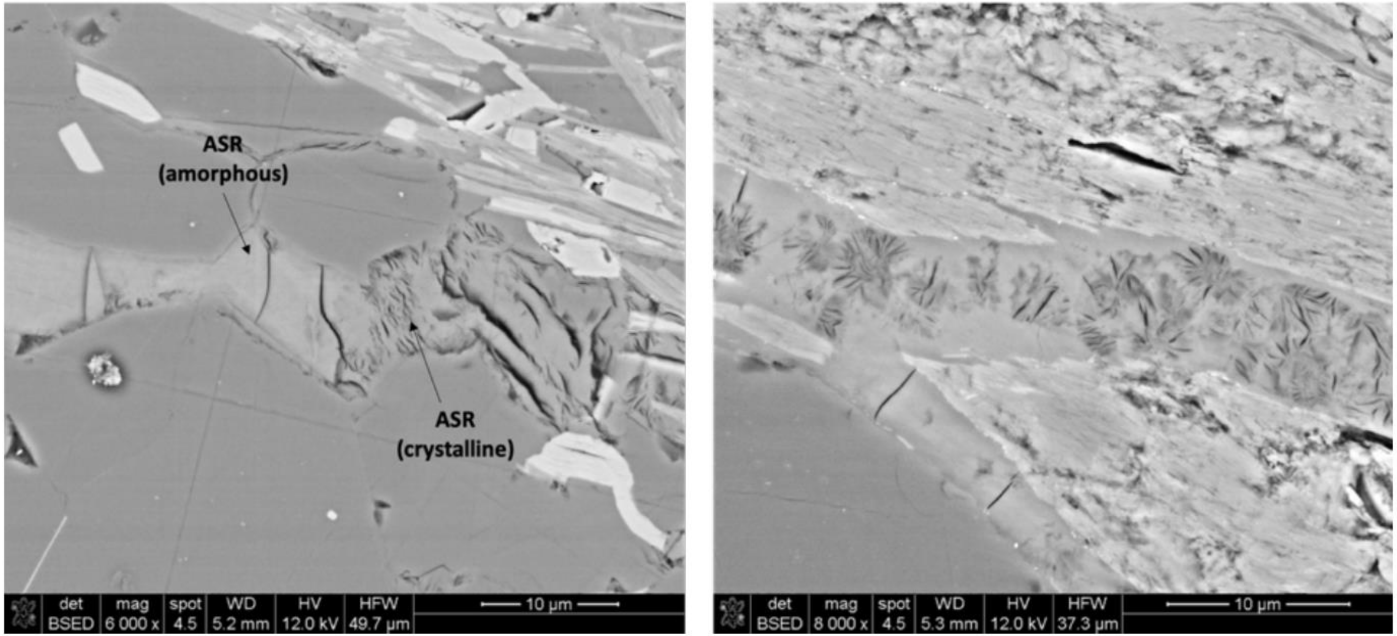


Polished section of concrete, viewed with SEM, showing an aggregate particle with extensive internal cracks due to ASR. The cracks extend from the aggregate into the nearby concrete.

1. Short reminder on ASR in concrete

- What are the products formed ?

S. Albinski, PhD thesis, EPFL (2022)

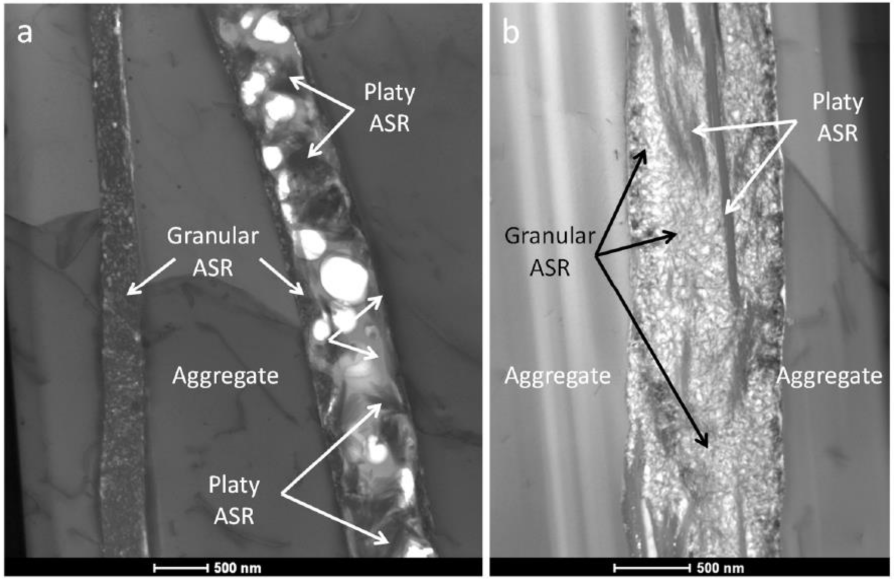


SEM images showing two distinct ASR products morphologies and structures (smooth vs. platy and crystalline)

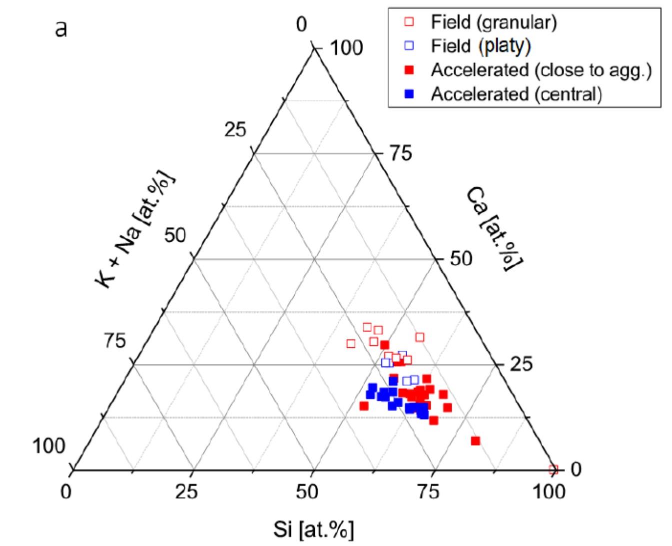
1. Short reminder on ASR in concrete

- What are the products formed ?

Leeman et al., RILEM Technical Letters 6 (2021)



TEM images showing two distinct ASR products morphologies in SiO_2 mineral phase (a) after 4 weeks in accelerated conditions and (b) collected in field concrete

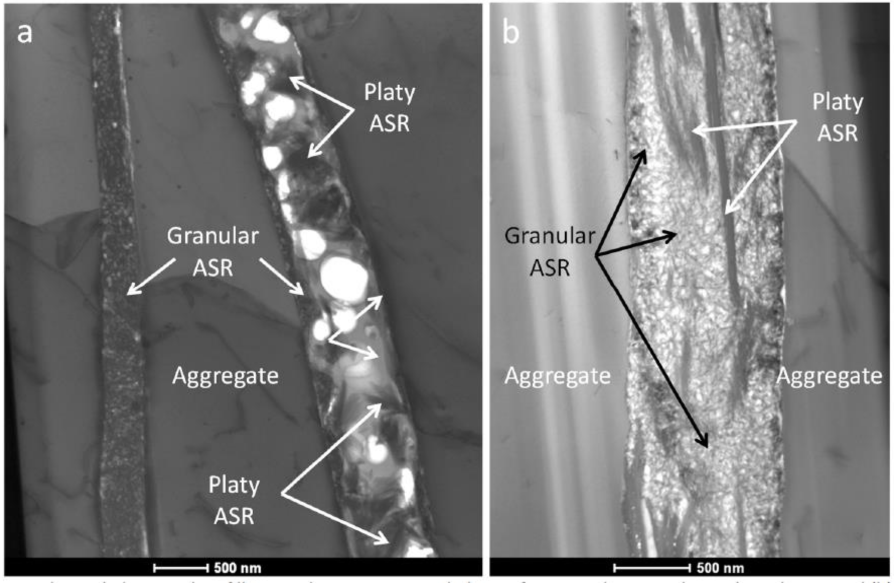


Ca/Si : from 0.3 to 0.5
(K+Na)/Si: from 0.3 to 0.5
K >> Na

1. Short reminder on ASR in concrete

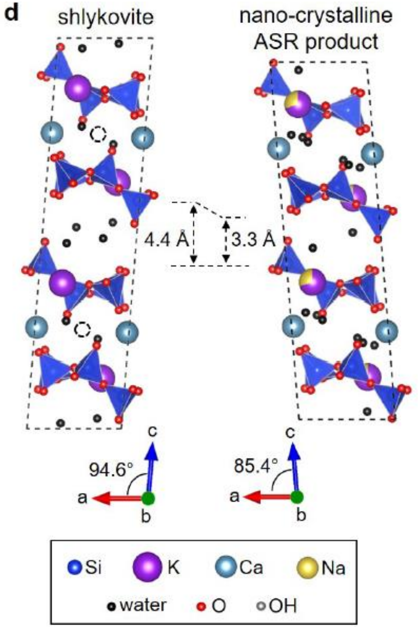
➢ What are the products formed ?

Leeman et al., RILEM Technical Letters 6 (2021)



TEM images showing two distinct ASR products morphologies in SiO_2 mineral phase (a) after 4 weeks in accelerated conditions and (b) collected in field concrete

- Granular product:
  - amorphous
  - Micro XAS spectra similar to C-S-H containing potassium
- Platy product:
  - certain degree of cristallinity,
  - highly resembles shlykovite, a layered silicate mineral ($KCa[Si_4O_9(OH)].3H_2O$)

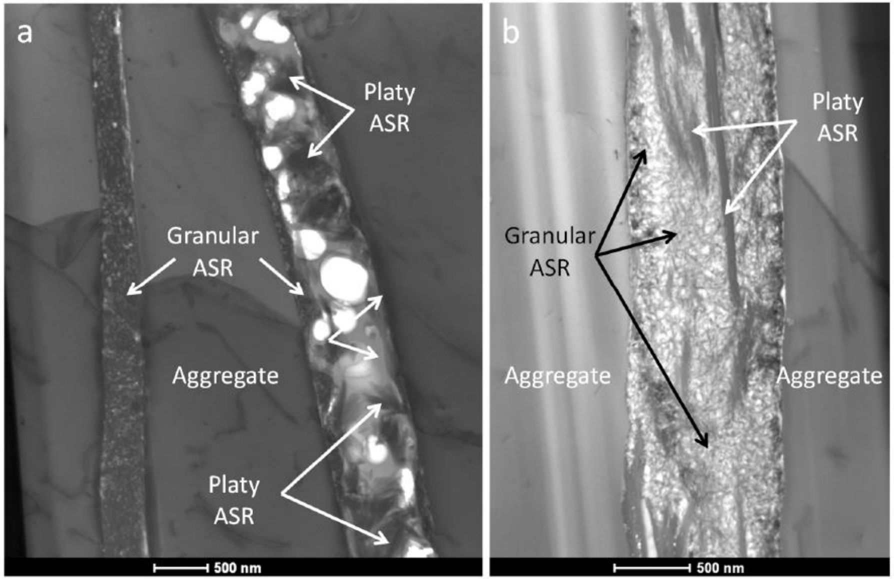


G. Geng et al.,Acta Crystallogr B (2020) 76(4)

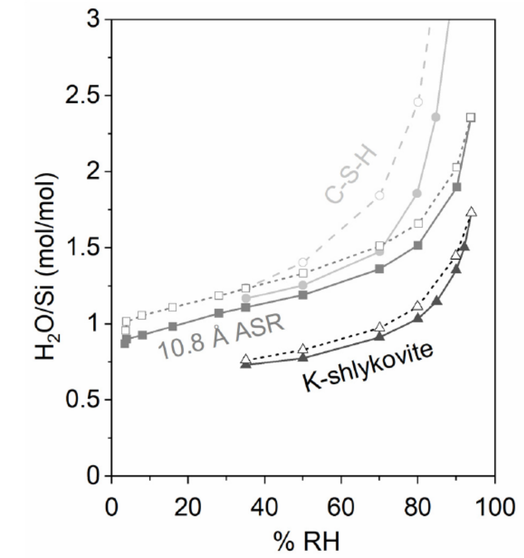
1. Short reminder on ASR in concrete

➢ What are the products formed ?

Leeman et al., RILEM Technical Letters 6 (2021)



TEM images showing two distinct ASR products morphologies in SiO_2 mineral phase (a) after 4 weeks in accelerated conditions and (b) collected in field concrete



Z. Shi et al. Mater Design (2020) 190: 108562

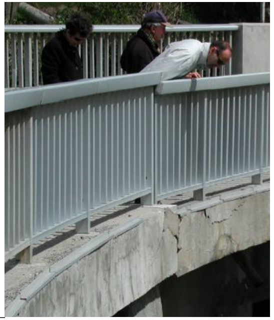
Sorption and desorption (dashed lines) isotherms for synthetic ASR products and C-S-H

Comparable or lower water uptake than C-S-H phase ⇒ swelling of the ASR products cannot be the main mechanism responsible for expansion

1. Short reminder on ASR in concrete

- ASR at the macroscopic scale

A slow process leading to damage after several years or decades

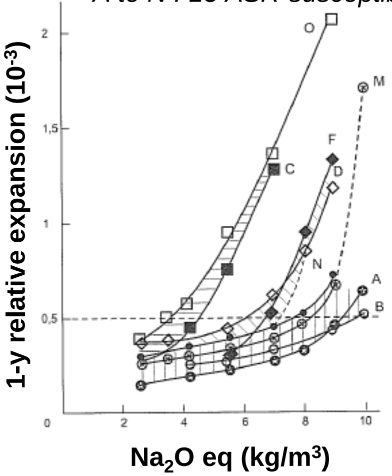


1. Short reminder on ASR in concrete

- Requirements for ASR

M. Berra et al., *Mater. Struct.* 38 (2005) 373-380

A to N : 13 ASR-susceptible aggregates



The critical alkali content depends on the type of aggregate

Typical expansion limit

Silica

Reactive mineral	Physical character
Opal	Amorphous
Chalcedony	Microcrystalline to cryptocrystalline, commonly fibrous
Certain forms on quartz	Microcrystalline to cryptocrystalline; crystalline but intensely fractured, strained, and/or inclusion filled
Cristobalite	Crystalline
Tridymite	Crystalline
Rhyolitic, dacitic, latitic or andesite glass or cryptocrystalline devitrification products	Glass or cryptocrystalline materials such as the matrix of volcanic rocks or fragments in tuffs
Synthetic siliceous glass	Glass

ASR

Alkalies

Water ⇐ Environment

(R.H > 80 – 85 % at 20°C)

1. Short reminder on ASR in concrete

- How to avoid/mitigate ASR ?

Silica

Select non reactive aggregates

- Select constituents with low alkali content
- Beneficial effect of SCMs such as fly ash and metakaolin (Al concentration increased in the pore solution, which slows down the dissolution rate of SiO_2) or silica fume (OH$^-$ concentration decreased)

ASR

Alkalies

Water ⇐ Environment

(R.H > 80 – 85 % at 20°C)

Limit resaturation by water (coating by waterproof organic resin, impregnation with silanes)

1. Short reminder on ASR in concrete

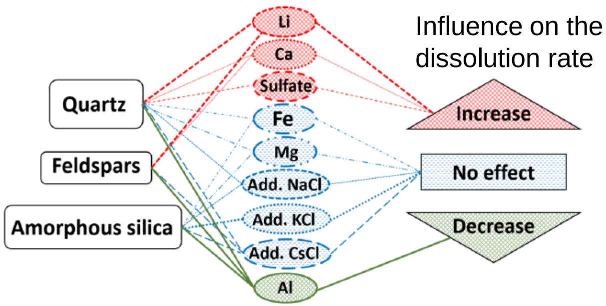
- How to avoid/mitigate ASR ?

+ sealing reinforcement

There is currently no treatment that ensures the definitive repair of a structure affected by ASR: existing processes only extend the lifetime of service.

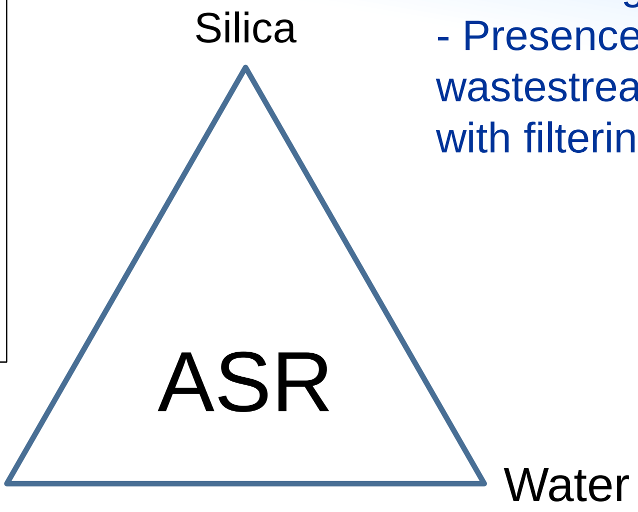
Prevention is better than cure !

2. ASR in cement waste packages – a case study



M. Bagheri et al., Cem Concr Res (2022) 152:106644

- Use of aggregates
- Presence of silica in certain wastestreams (e.g. sludges with filtering media)



High concentrations of alkalies + presence of ions which can influence the dissolution rate of silica: e.g. evaporator concentrates

High w/c ratio to maximize the loading of aqueous waste

<u>Specifities of certain types of cemented waste packages</u>

↳ The conditions for ASR development may be fulfilled

2. ASR in cement waste packages – a case study

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1980 –Doel nuclear power plant, Belgium

Evaporator concentrates (4,50 Bq/g – ^{137}Cs *- LLW) stabilized and solidified in a cementitious matrix

→ Concrete : Portland cement + siliceous aggregates (very limited information on aggregates origin)

Waste pretreatment

Highly borated concentrates

↳ Strong delay of cement hydration ✗

Addition of NaOH

pH set in the range 10-12

↳ Improved workability in the fresh state, decreased setting time

Species	[mmol/kg]	Species	[mmol/kg]
Al	39,9	Mg	30
B	**1133**	Na	2882
Ca	279	Ni	1,2
Cl	133	NO_3^-	13
Cr	1,7	PO_4^{3-}	136
Cu	2,5	Si	225
F	5,2	SO_4^{2-}	127
Fe	45,7	Zn	10,3
Li	8,5		

Evaporator concentrates stored at 80°C

→ Avoid crystallization in the storage tank

Cementation

In-line mixing of waste, cement and aggregates

Casting in 400 L metallic drums → 7500 drums produced

Intermediate storage at Dessel

Doel NPP wikipedia.org


Cemented waste packages– Belgoprocess

2. ASR in cement waste packages – a case study

Formation of a gel-like substance at the surface of some drums

Small contamination (≈ 100 Bq/g_{gel} – ^{137}Cs)

FANC, National report , Belgium, oct. 2014, p. 160.

Are theses packages acceptable for surface disposal ?

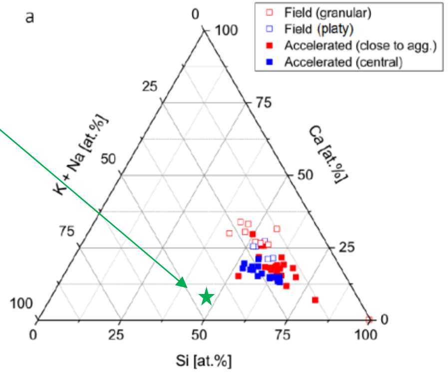
What are the properties of the gel?

How does it affect the quality of the cement matrix ?

How is it formed?

Compared to ASR in conventional concrete structures

- Very **high amount of alkalies** (several tens of kg/m^3 of concrete, instead of a few kg/m^3)
- Peculiar **thermal history**
- **Large volume of gel** exuded in some cases
- **Limited damage** of the cementitious matrix compared to the volume of gel produced
- **Different composition** of the gel
  - Na/Si ≈ 1
  - Ca/Si ≈ 0,001



2. ASR in cement waste packages – a case study

Synthesis protocol

Composition based on gels sampled on the drums surface

Na/Si = 1.02
Ca/Si = 0.001

Species	Conc. [mmol/kg]	Species	Conc. [mmol/kg]	Species	Conc. [mmol/kg]	Species	Conc. [mmol/kg]
Cl	146.9	Al	22.3	**Ca**	**5.7**	Cu	0.0
SO_4^{2-}	48.8	Fe	3.3	**Na**	**5927.4**	Mg	0.8
NO_3^-	6.8	Zn	32.4	**SiO_2**	**5788.6**	Ni	0.0
F	3.3	B	20.1	HO^-	5785.6	Pb	0.2
PO_4^{3-}	7.0	NO_2	1.2	Cr	0.0	**wt.%H_2O**	**41%**

1 Industrial silicate and stock solutions mixing

Concentrated stock solutions

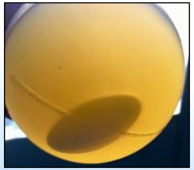
Salt	Conc. [mmol/L]	Salt	Conc. [mmol/L]
$CaCl_2 \cdot 1.5\ H_2O$	2663*	$NaNO_2$	500
$ZnCl_2$	5030*	$Na_2B_4O_7 \cdot 8.3\ H_2O$	109*
$FeCl_3 \cdot 4.8\ H_2O$	1086*	NaCl	4000
$Al_2(SO_4)_3 \cdot 18.2\ H_2O$	994*	Na_2SO_4	1501
NaF	500	$Na_3PO_4 \cdot 10.0\ H_2O$	500*
$NaNO_3$	2000	NaOH	10000

* *Concentrations verified by ICP-AES*

+

Betol 52T (Wöllner GmbH)

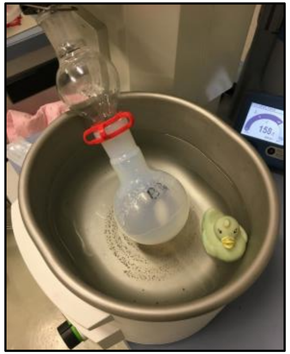
Species	Conc. [mmol/kg]
SiO_2	5177*
Na_2O	2479*



→ Product with 54 wt.% water

2 Evaporation under vacuum

Reduce water content to reach 41 wt.%
T = 55°C // P = 25 mbar



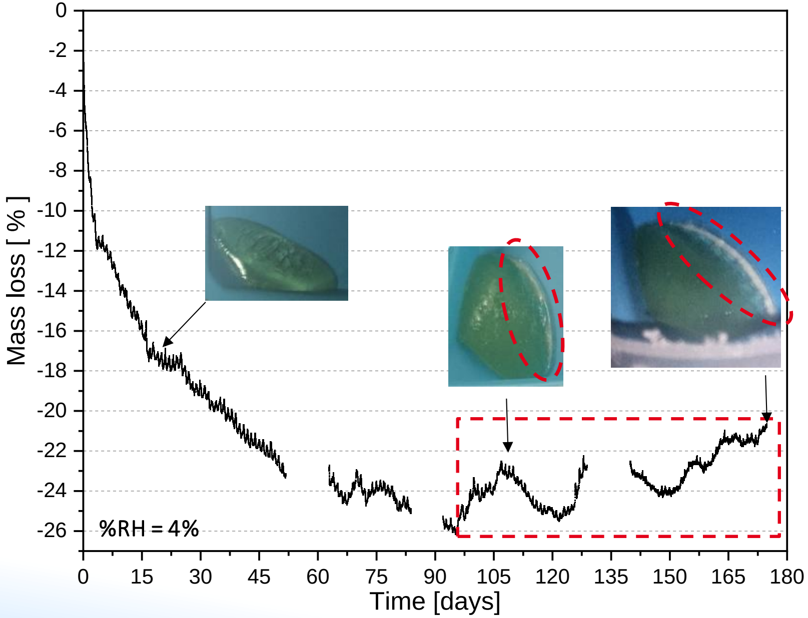
3 Storage under nitrogen

Avoid drying and carbonation

2. ASR in cement waste packages – a case study

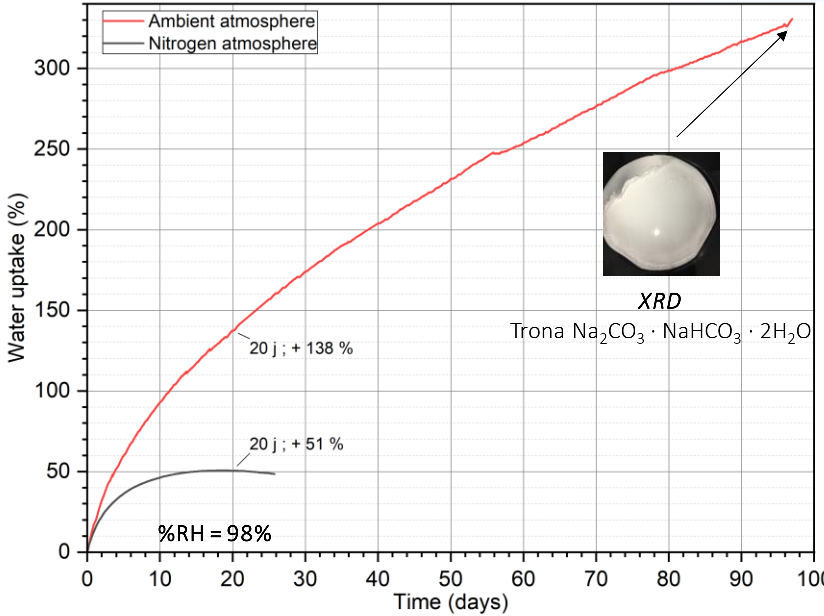
Influence of the environment

Drying



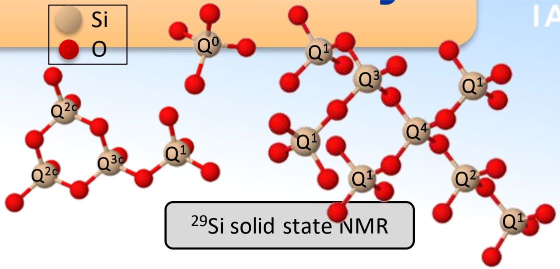
- - 25% mass loss in 90 days
- White solid late formation (carbonation ?)

Water uptake



- Carbonated phase visually observed after 60 days
- With nitrogen : no solid formation, plateau reached after 20 days

2. ASR in cemented waste packages – a case study

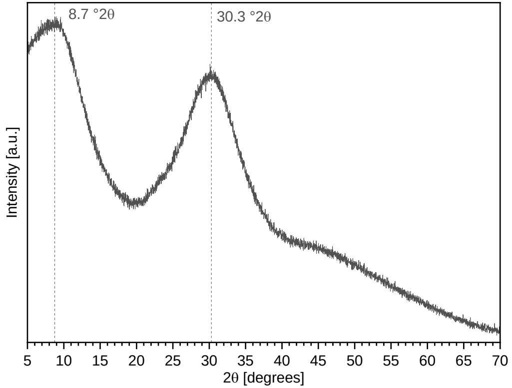


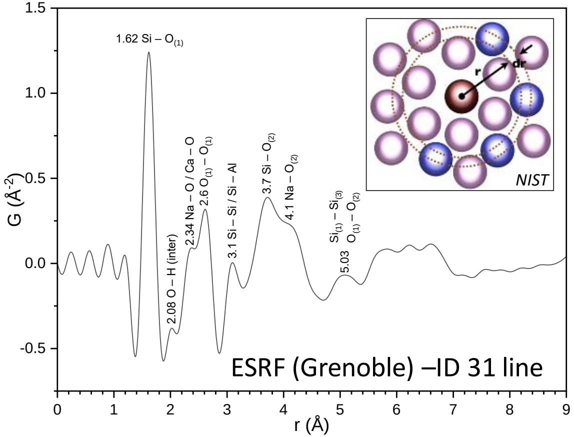
Structural investigation

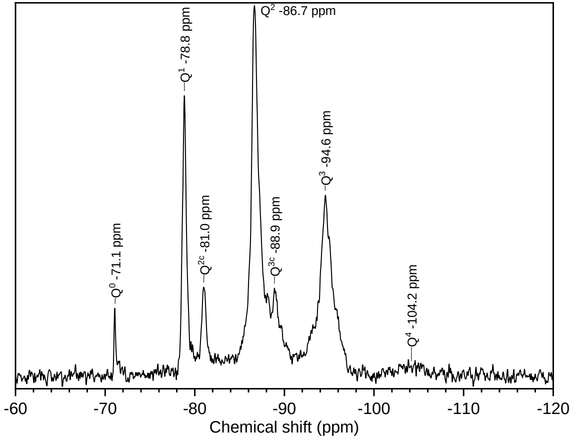
XRD

Pair Distribution Function

^{29}Si solid state NMR







Broad humps
→ Poorly crystalline, amorphous structure

Expected correlations
Correlation up to 7 Å → local order

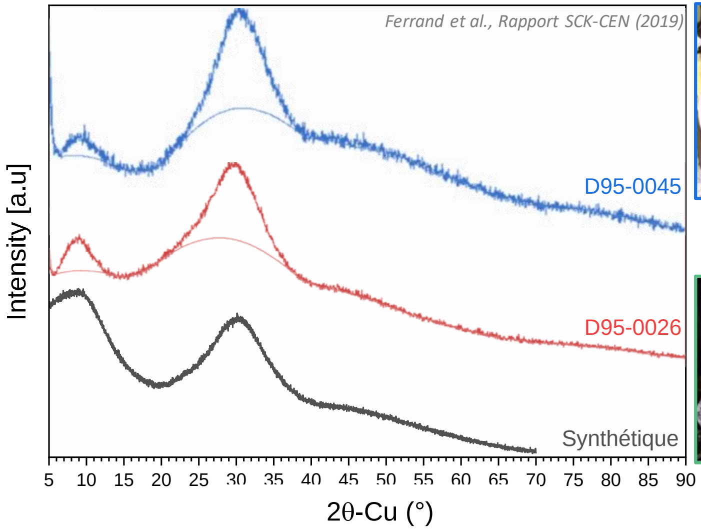
Few fully connected silicon atoms (Q^4)
Mainly Q^1, Q^2 and Q^3 silicon atoms

Population	Q^0	Q^1	Q^{2c}	$\mathbf{Q^2}$	Q^{3c}	$\mathbf{Q^3}$	Q^4
Gel	1.2%	11.3%	3.2%	**40.8%**	5.9%	**36.4%**	1.1%

2. ASR in cemented waste packages – a case study

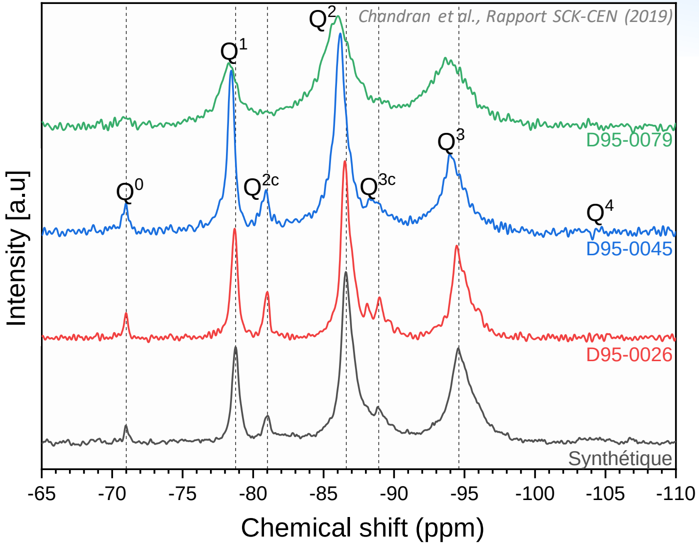
Analysis of gel samples from the surface of real drums produced during the same conditioning campain

X-ray diffraction



Similar XRD patterns

^{29}Si MAS-NMR



Population	Q^0	Q^1	Q^{2c}	Q^2	Q^{3c}	Q^3	Q^4	$\bar{c}$
D95-0079	0,8	15,0	0	**50,3**	0	**33,9**	0	**2,17**
D95-0045	2,3	19,2	4,3	**42,7**	5,5	**26,1**	0	**2,08**
D95-0026	2,0	15,4	4,3	**28,5**	18,8	**31,0**	0	**2,31**
Gel synth.	1,2	11,3	3,2	**40,8**	5,9	**36,4**	1,1	**2,31**

Slight variation of the NMR spectra from one sample to another
Mean connectivity degree of silicates: 2 – 2.3

Synthetic gel = good surrogate of real gel – close to water glass

2. ASR in cemented waste packages – a case study

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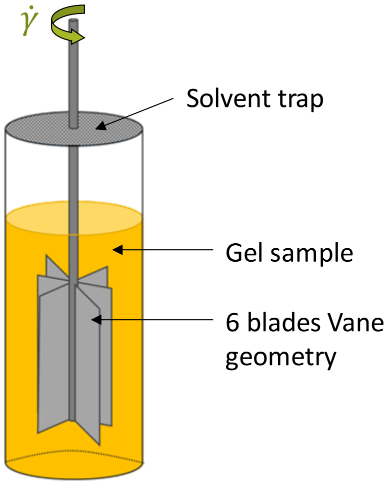
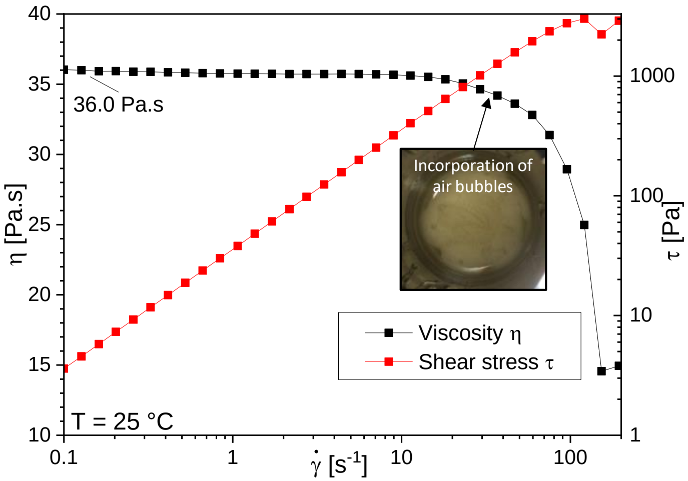
Vane geometry	Shear rate sweep	Influence of temperature

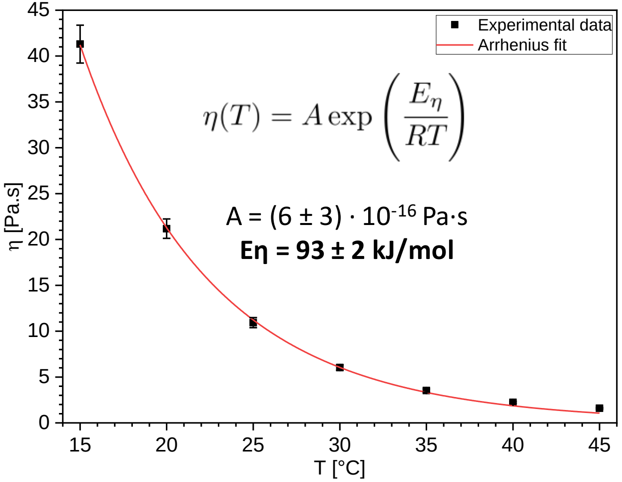


Makes it possible to limit drying during measurement

Synthetic gel with $38\%H_2O$



Synthetic gel with $40\%H_2O$



$\tau(\gamma) = K \cdot \boldsymbol{\gamma} \rightarrow$ Newtonian fluid
Viscosity of the same magnitude order than honey (at 25°C)

Strong decrease of the gel viscosity with temperature

*Yanniotis et al., J Food Eng **72**.4 (2006)*

2. ASR in cemented waste packages – a case study

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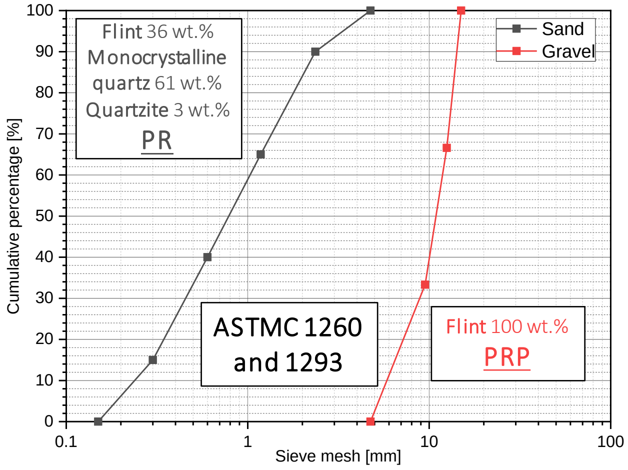
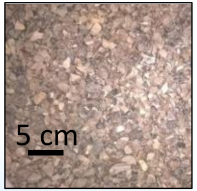
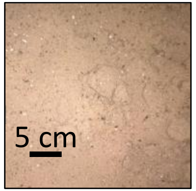
Cement

CEM I 52.5 R SR-3 N/A
(Sulfo 5R – Holcim)

Aggregates







Mixing solutions

Species	Concentration [mmol/kg] C2	C1
NaOH	2476	1825
$NaNO_3$	13	1894
Na_2SO_4	127	–
H_3BO_3	1136	–
Na_2SiO_3	225	–
Na_3PO_4	136	–
NaCl	132	–
$Ca(OH)_2$	279	–

Provide water for cement hydration

C2
Synthetic solution representative of average waste composition

C1
Simplified solution with same Na concentration and pH as C2

C0
Demineralized water

Formulations

Concrete compositon [kg/m$^3_{concrete}$]

	BC2	BC1	BC0
Gravel	1100	1100	1100
Sand	660	660	660
Cement	410	410	410
Concentrate	299	275	213
Aggregate/Cement	4,29	4,29	4,29
Water/Cement	**0,51**	**0,51**	**0,52**

BC2
Mimicks cement waste form
C2 cemented at 80°C

BC1
Study of the influence of the waste composition

BC0
Reference

2. ASR in cemented waste packages – a case study

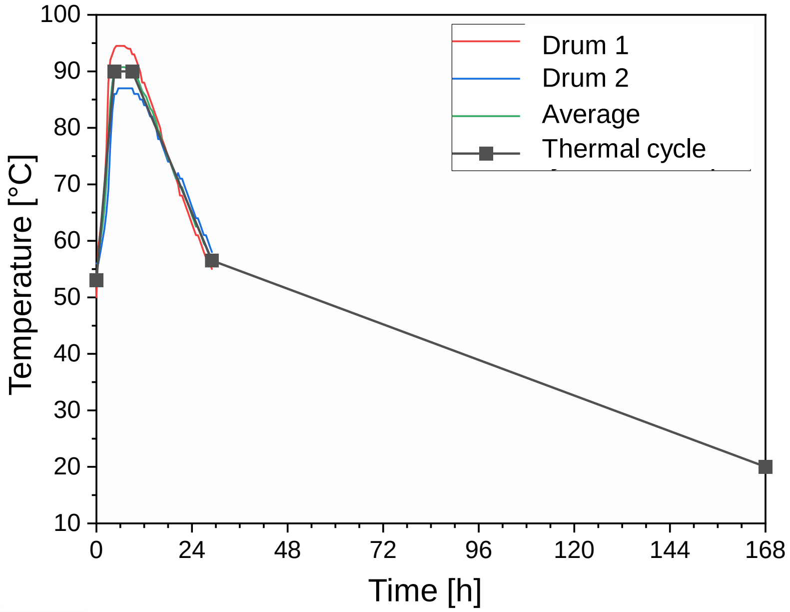
After mixing

ϕ 11 x h 11 cm cylinder specimen

Thermal cycle

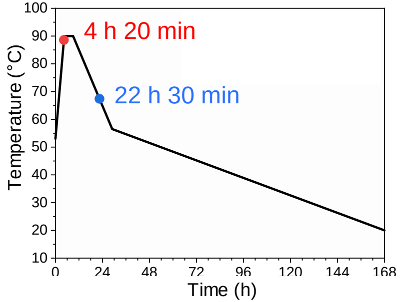
7 d-long thermal cycle

Mimicks the thermal evolution recorded on real drums



2. ASR in cemented waste packages – a case study

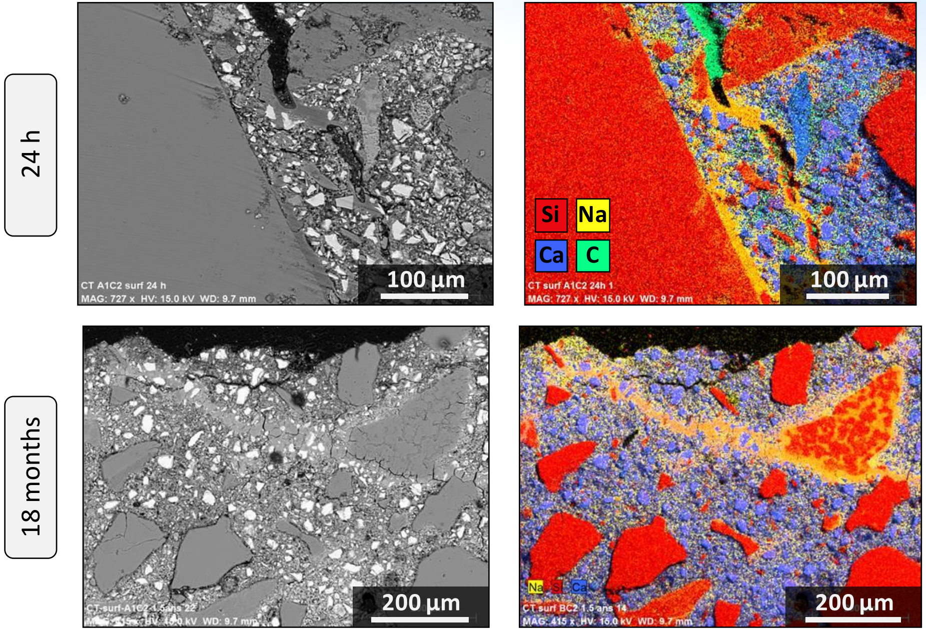
At the macroscopic scale



Gel exudation during isotherm at 90°C

Molar ratio	Gel from concrete plug	Real gel
Na/Si	0,98 ± 0,02	1,02
Ca/Si	0,0028 ± 0,0005	0,001

At the microscopic scale (SEM-EDX)

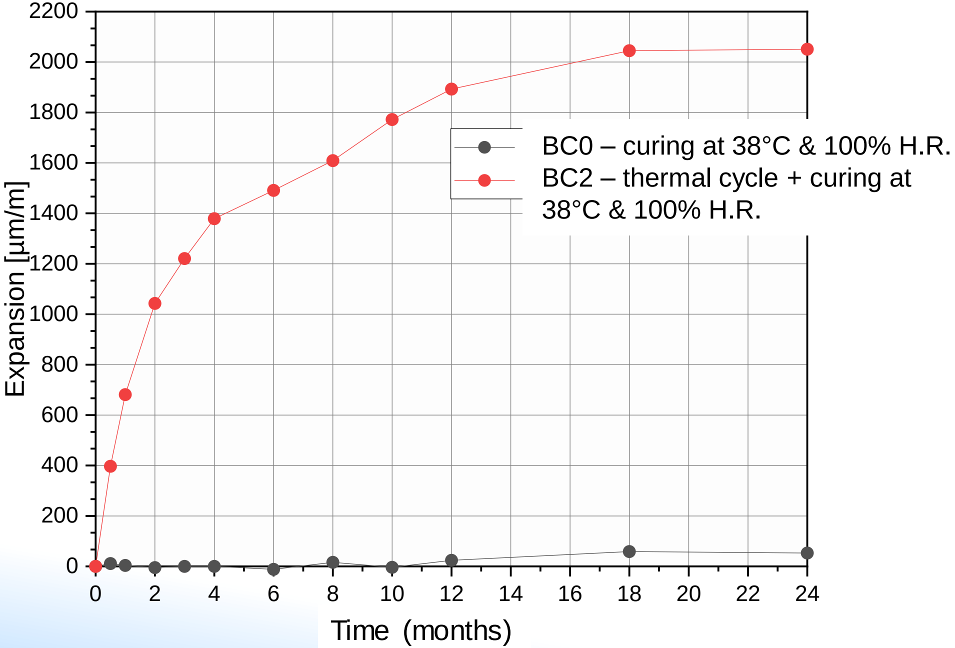


24 h : Gel accumulation in the ITZ and within a nearby micro-crack

18 months : Core attack of some aggregates by alkali hydroxide – presence of cracks filled with gel within the matrix

2. ASR in cemented waste packages – a case study

Volume change

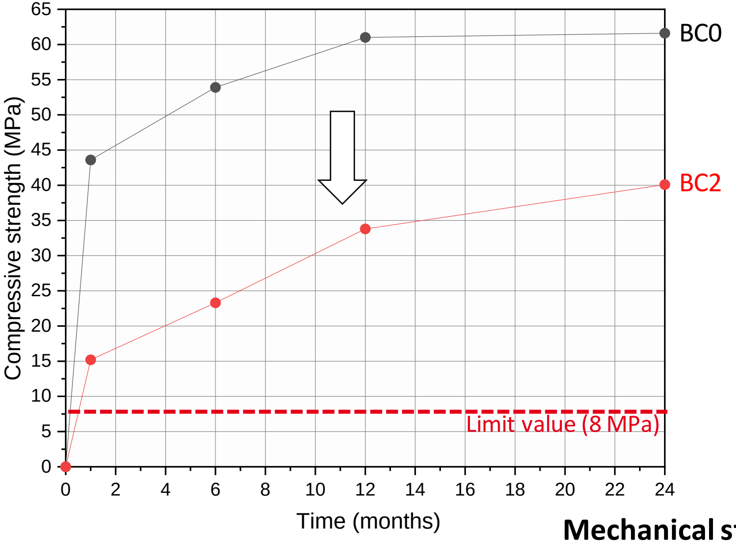


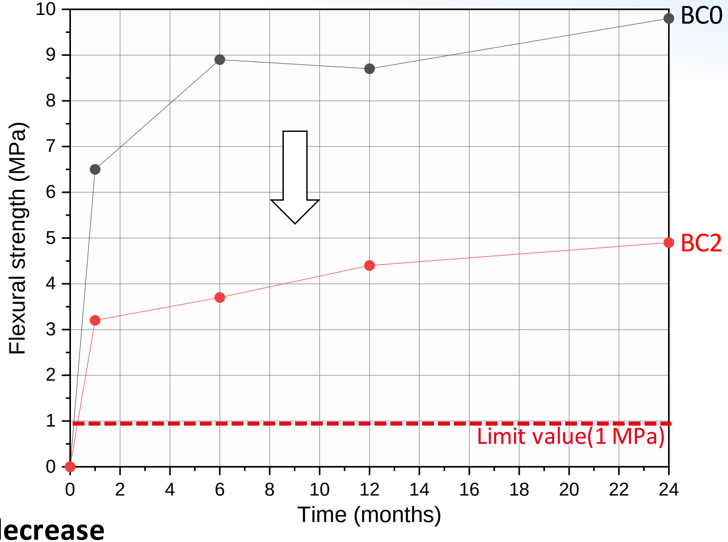
BC0 : Expansion < 60 µm/m at 2 years

BC2 : Significant swelling
Stabilization at ≈ 2050 µm/m at 18 months

2. ASR in cemented waste packages – a case study

Mechanical strength





Mechanical strength decrease

Sun et al.
*NED **241**.10 (2011)*

Incorporation of borated waste

Formation of cracks

Thermal cycle

Knut et al.
*CCR **21**.1 (1991)*

Mechanical strength above the minimum values required by WACs

$R_c > 8$ MPa $R_f > 1$ MPa

2. ASR in cemented waste packages – a case study

Influence of thermal history of concrete

Observations at the macroscopic scale

BC2 specimen cured for 1 week at 20°C & 100% H.R.,
and then at 38°C & 100% H.R.
No thermal cycle

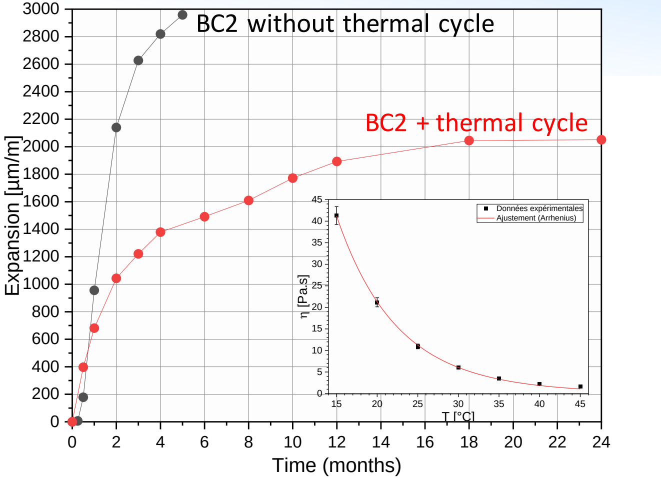
1 week

8 months

No exsudation of gel at early age

Gel exudation delayed by several months
Less gel exuded

Volume change



Reduced expansion when the specimen is submitted to a thermal cycle at early age

Synthetic gels: viscosity decrease when T ↗
η(90°C) ≈ 13,7 mPa·s → easiest exudation → limited swelling

Beneficial influence of the thermal cycle on the expansion of BC2 over 2 y

2. ASR in cemented waste packages – a case study

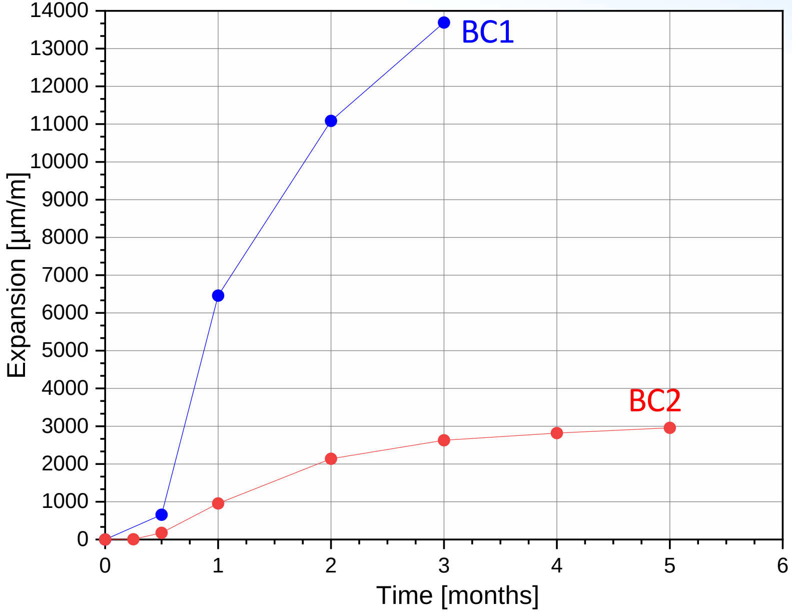
IAEA

Influence of waste composition

Concrete specimens prepared with C1 or C2
No thermal cycle

Species	Concentration [mmol/kg] C2	C1
NaOH	2476	1825
$NaNO_3$	13	1894
Na_2SO_4	127	-
H_3BO_3	1136	-
Na_2SiO_3	225	-
Na_3PO_4	136	-
NaCl	132	-
$Ca(OH)_2$	279	-

Volume change



Huge expansion with concentrate C1

3 months → **BC1** : 13700 µm/m ; **BC2** : 2630 µm/m

2. ASR in cemented waste packages – a case study

Simplified system

Flint aggregate (F.Ag)

XRD (Rietveld) : 98% SiO_2 + 2% $CaCO_3$
Particle size distribution: 0.16 to 0.63 mm

+

Alkaline solution

10 mL/g_{flint}

C2: Concentrate surrogate

Species	Concentration [mmol/kg]	Species	Concentration [mmol/kg]
NaOH	2476	Na_2SiO_3	225
$NaNO_3$	13	Na_3PO_4	136
Na_2SO_4	127	NaCl	132
H_3BO_3	1136	$Ca(OH)_2$	279

or

C1: Simplified solution

Species	Concentration [mmol/kg]
NaOH	1867
$NaNO_3$	1867

Same theoretical pH
Same total sodium content

+

Calcium hydroxide

Mimics the cementitious environment (calcium reservoir)

90°C
4h / 15h / 1 day / 3 days

2 alkaline media studied
CaC1 = C1 + $Ca(OH)_2$
CaC2 = C2 + $Ca(OH)_2$

2. ASR in cemented waste packages – a case study

IAEA

Simplified system

Aggregate

Creation of silanol sites in the siliceous network of the aggregate

≡Si–O–Si≡ (Q^4) $\xrightarrow{HO^-}$ ≡Si–OH (mainly Q^3)

Engelhardt et al. ZAAC ***418****.1 (1975)*

Solution

Dissolution of the aggregate

$\xrightarrow{HO^-}$ Q^0 ($H_2SiO_4^{2-}$)

Precipitation

Formation of precipitates with calcium or other species brought by the concentrate

$\xrightarrow{Ca^{2+}}$ C–S–H

$\xrightarrow{Ca^{2+}, Na^+}$ C–N–S–H

. . .

Bulteel et al. CCR ***32****.8 (2002)*
Garcia-Diaz et al. CCR ***36****.2 (2006)*

Initial state

7% of Q^3 species (not represented)

Alkaline degradation

Alkaline solution + $Ca(OH)_2$
90°C
4h / 15h / 1d / 3d

State 1

Acidic treatment

HCl 1 mol/L
Filtration
Drying at 40°C

State 2

Thermal treatment

≡Si–OH + HO–Si≡

Δ 1000°C

≡Si–O–Si≡ + **H_2O**

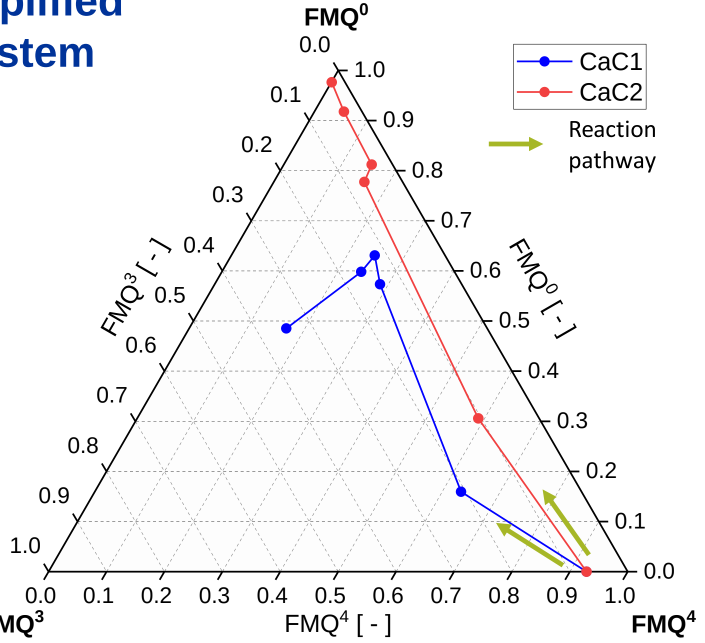
State 3

Sound silica Si–O–Si	Formed precipitates C–S–H ; C–N–S–H ; …
Protonated degraded silica SiOH	Degraded silica SiOH ; SiO···Na ; SiO···Ca···OSi
Residual attack medium $Ca(OH)_2$; Na ; Si (Q^0) ; polyanions	Sound silica + Condensed degraded silica Si–O–Si

2. ASR in cemented waste packages – a case study

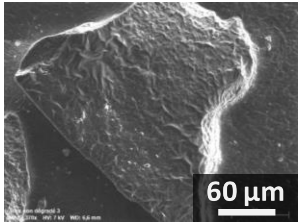
Simplified system

Dissolution of silica

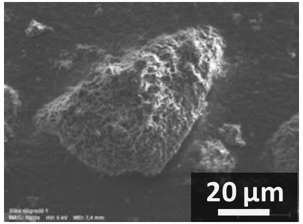


Creation of defects in the silica network

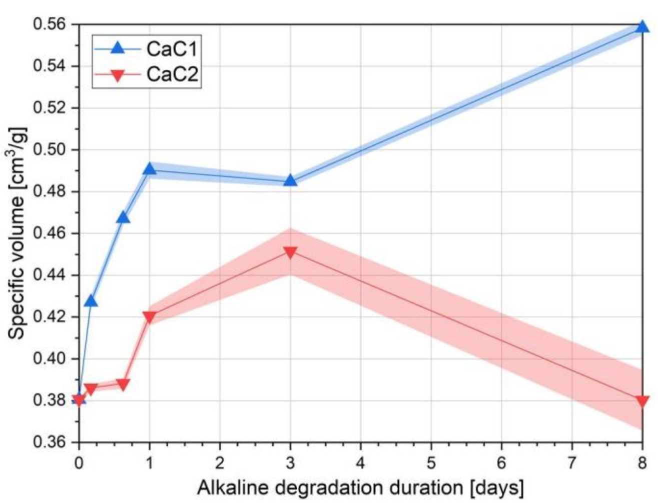
Pristine aggregate



Pristine flint aggregate



Aggregate after a 3-d attack (CaC1)



CaC2
Degradation process driven by dissolution

CaC1
Creation of defects in the silica network
Granular swelling

Conclusion

- ASR may occur in certain types of cemented waste packages
  - Waste with high contents of alkalies (e.g. evaporator concentrates)
  - Siliceous or silica-containing reactive aggregates

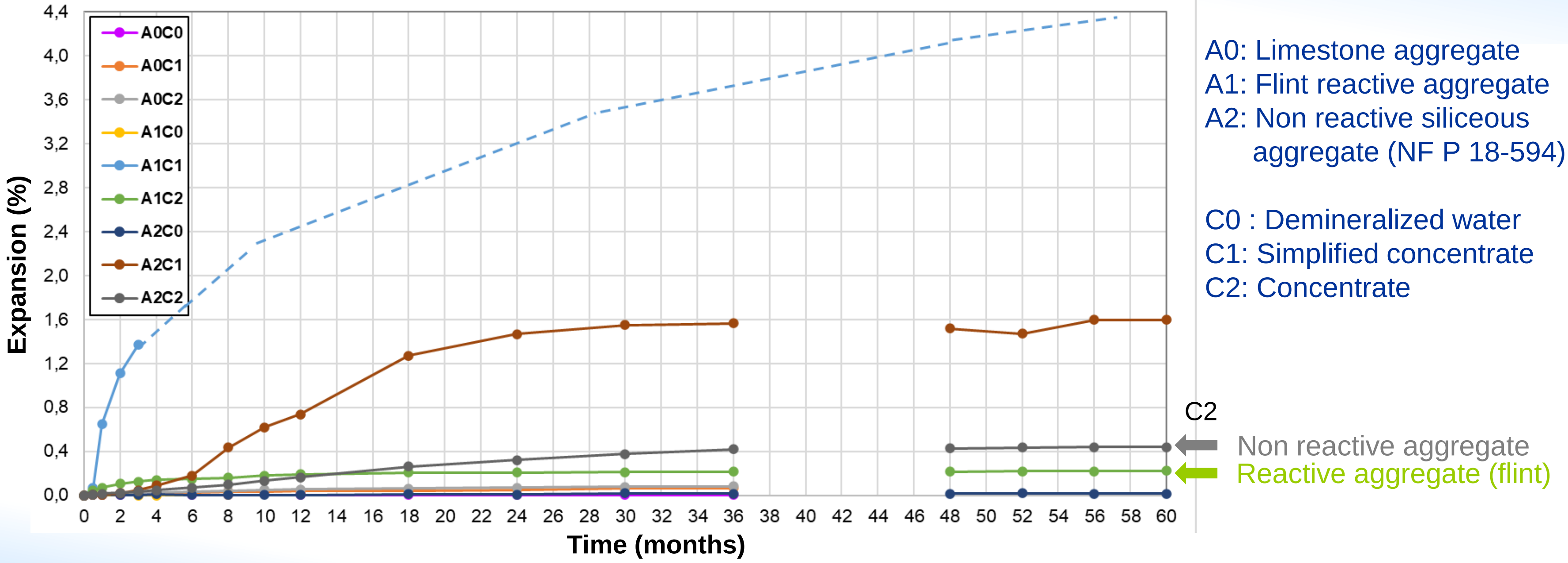
    Solid waste with reactive silica
  - High water content
  - Portland cement
- Specificities of ASR in cemented waste packages, as compared to conventional structural materials :
  - Gel composition (e.g. higher alkali content, smaller calcium content)
  - Gel rheological properties (e.g. reduced viscosity $\Rightarrow$ higher amounts of gel exuded, but limited mechanical damage)
- Properties of ASR products difficult to characterize (drying, carbonation, water uptake…)
- Key factors :
  - Thermal history of waste packages

    Gel formation and exudation accelerated by T increase $\Rightarrow$ reduced strength loss and expansion
  - Waste composition

    Influence on the degradation pathway of aggregates and on granular swelling

Conclusion

Are standardized tests well adapted to assess reactivity of aggregates in alkaline environment ?



A0: Limestone aggregate
A1: Flint reactive aggregate
A2: Non reactive siliceous aggregate (NF P 18-594)

C0 : Demineralized water
C1: Simplified concentrate
C2: Concentrate

⇒ Test reactivity of aggregates under chemical conditions representative of the cement matrix
⇒ Select limestone aggregates (be careful to dolomite !)
⇒ Use blended cement (with FA, MK or slag)

Thank you!