DURABILITY of CONCRETE STRUCTURES

Assist. Prof. Dr. Mert Yücel YARDIMCI

This presentation covers the subjects in CEB Durable Concrete Structures Guideline and has been prepared by the graduate students under the supervision of Prof. Dr. Bülent BARADAN in Dokuz Eylül University.

Part - V
DEF - ASR - ACR
&
Biological Attack on Concrete
DEF

(DELAYED ETTRINGITE FORMATION)
What is DEF (Delayed Ettringite Formation)?

Damage (expansion & cracking) of concrete due to the formation of ettringite after the concrete has hardened.

Damage due to DEF was first reported in heat-cured railway ties in Germany in the early 1980’s. (Heinz et al, 1989)
No characteristic properties of visual damages induced by DEF

The study of civil engineering structures shows that not only precast concretes are concerned by DEF

There is a risk for large civil engineering structures

Nevertheless, numerous factors are implicated in the DEF mechanisms.

Those factors can be classified in 3 groups:
Humid Environment

- Wetting and drying cycles
- Tightness problems,

Cement type

- C₃A > 7%
- SO₃ > 2.5%
- Na₂Oₑq > 0.6%

DEF Risk

Temperature

- Massive structure
- High cement quantity
- Exothermic cement
- Concreting in summer
DEF EXPANSION MECHANISMS

\[
\begin{align*}
C_3A & + 3C \, S \, H_2 + 26H \rightarrow C_6A \, S \, 3H_{32} \\
2C_3A & + C_6A \, S \, 3H_{32} + 4H \rightarrow C_4A \, S \, H_{12} \\
C_4A \, S \, H_{12} & + 2C \, S \, H_2 + 16H \rightarrow C_6A \, S \, 3H_{32}
\end{align*}
\]

ettringite

monosulfoaluminate

ETTRINGITE

• Homogenous paste expansion theory

• Crystal growth theory (accumulation of ettringite crystals)

Conversion to monosulfate
Sulfate adsorption by CSH

time

ettringite
Delayed ettringite formation is a form of internal sulfate attack.

PREVENTATION OF ETTRINGITE FORMATION IN EARLY PERIODS OF HYDRATION

CONTINOUS WETTING-DRYING IN OPEN ATMOSPHERE (HEAT)

LATE FORMATION OF ETTRINGITE

$\text{C}_3\text{A}.\text{CaSO}_4.32\text{H}_2\text{O}$

CRACKS
SHANGHAI JINMAO BUILDING

Height: 440 m
Foundation concrete class: C50
Height of foundation: 4 m

40 hours Recorded concrete temperature after casting: 97 °C

Sulfoaluminate based chemical admixture

→ DEF Risk !!!
DEF
(DELAYED ETTRINGITE FORMATION)

PREFABRICATED COLUMNS

TEXAS – prefabricated beam
DEF
(DELAYED ETTRINGITE FORMATION)

BESIDES PREFABRICATION

MASS CONCRETE PRODUCTION ON HOT WEATHERS

IN FIRE

Characteristic
DEF Cracks
Expansion for 502 days: % 0.86

Ettringite formation in void

- 90x
- 330x
- 1000x
- 3000x

%4.5 SO$_3$

5000 cm$^2$/g Blaine
Different forms of Ettringite

DU9-E

%4.5 SO$_3$

5000 cm$^2$/g Blaine
**DEF**

(DELAYED ETTRINGITE FORMATION)

- $\text{C}_3\text{S} + \text{Water} \rightarrow \text{C-S-H} + \text{CH} + \text{Heat}$
- $\text{C}_3\text{A} + \text{Water} + \text{Gypsum} \rightarrow \text{Ettringite} + \text{Heat}$
- $\text{C}_3\text{A} + \text{Water} + \text{Ettringite} \rightarrow \text{Monosulfoaluminate}$

**Micrograph and EDS Spectrum**

- Micrograph showing the formation of ettringite crystals.
- EDS spectrum indicating the presence of Ca, Si, and Al, confirming the composition of ettringite.

**EDS Spectrum Details**

- **Ca**
- **Si**
- **Al**
- **O**
- **Mg**

**Conditions**

- **20kV**
- **X14,000**
- 1μm
- **0656 11 35 SE**
DEF
(DELayed ETTRENGITE FORMATION)
DEF
(DELAYED ETTRENGITE FORMATION)

Cracks & Pores due to DEF

Pores filled with ettrengite formation
Ettringite has - by directed crystal growth - partly filled an air void.

Air void completely filled with ettringite crystals in a damaged pavement concrete.
PREVENTIVE MEASURES AGAINST DEF

- LOW SULFATE BEARING CEMENT
- WATER INSULATION
- PREVENTATION OF MICROCRACK FORMATIONS CAUSED BY OTHER REACTIONS
- CEMENT WITH LOW HEAT OF HYDRATION
- USING POZZOLANIC MINERAL ADMIXTURES (REDUCING SULFATE CONTENT)
- PROPER CURING TEMPERATURES
- USING AIR ENTRAINING AGENTS
THAUMASITE ATTACK (TSA)

Bridge and tunnel structures
Scandinavian countries, England, North America, in particular cold climates

-Sulfate or sulfide source
-Ground CaCO₃ Carbonation or bicarbonates from ground water
- water
- CSH
-Low temperature (<15°C)

Fig. 4. Deterioration in the tunnel drainage channels.
THAUMASITE ATTACK (TSA)

C-S-H + C-S-A-H + CaCO₃

Deterioation of CSH structure
Loss of strength
Mushy like concrete

(CaSiO₃.CaCO₃.CaSO₄.15H₂O)
THAUMASITE FORMATION

Ferenc Puskas Stadium in Budapest (1954)
After World War II, in order to minimise the significant cement deficiency a clinker saving cement mix named Sigma Cement’ was produced to use in construction of stadium in Hungary.

The planned limestone content of the cement amounted to 15%, but contaminated soft limestone was used.

separation of the coarse fraction of the cement clinker is insufficient

The cement produced has low strength and high fineness!

The average temperature in Hungary is about 70% of the year longer than 15 C which is advantageous for thaumasite formation!

Environmental effects, corrosion, also thaumasite formation!!
the strength of the concrete decreased gradually after ten year construction
Specimens were exposed to high concentration of MgSO4 solution

Limestone ratio increases (%0-40)
Limestone increases

C₃A %11.2

C₃A %4.6

20°C Na₂SO₄ (200 g/l) – 1 year

5°C Na₂SO₄ (200 g/l) – 1 year

Limestone increases

C₃A %11.2

C₃A %4.6

20°C MgSO₄ (200 g/l) – 1 year

5°C MgSO₄ (200 g/l) – 1 year
C₃A %4.6

20° C Na₂SO₄ – 1 year

5° C Na₂SO₄ – 1 year

20° C MgSO₄ – 1 year

5° C MgSO₄ – 1 year
C₃A % 11.2

20°C Na₂SO₄ – 1 year

20°C MgSO₄ - 1 year

5°C Na₂SO₄ – 1 year

5°C MgSO₄ – 1 year
Limestone replacement: %40
MgSO₄ solution
(III-M-40)
PREVENTIVE MEASURES AGAINST THAUMASITE FORMATION

FROM THE VIEW POINT OF STRENGTH AND DURABILITY, THE MAXIMUM LIMESTONE INCORPORATION AMOUNT SHOULD NOT EXCEED 10%, ESPECIALLY FOR THE STRUCTURES THAT ARE CONSTRUCTED IN SULFATE BEARING SOILS AT COLD REGIONS.

- LOW C₃A CEMENT
- LOW SULFATE BEARING CEMENT
- REDUCE THE PERMEABILITY of CONCRETE
- MINERAL ADMIXTURES
- WATER PROOFING
ALKALI - SILICA REACTION

ASR
ASR CAN BE EXPLAINED IN A TWO-STEP PROCESS

1. ALKALI + SILICA
2. ASR GEL + WATER

Water and/or alkalis from the environment (e.g. from de-icing salts)

ASR gel; expansion

Diffusion of alkalis (e.g. from cement and admixtures)

Diffusion of water and alkalis into concrete

Crack formation (map cracking and surface parallel cracking)

DETERIORATION OF CONCRETE
ASR REACTIVITY

3 REQUIREMENTS MUST BE MET!

1) HIGH ALKALI OXIDE CONTENT
   \((\text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}) > \%0.6\)

2) REACTIVE SILICA
   (OPAL, TRIDYMITE, CRISTOBALITE, VOLCANIC GLASS, RIYOLITE, ANDESITE & THEIR TUFFS)

3) WATER
   GEL FORMATION (YEARS AFTER)
   (SODIUM + POTASSIUM + CALCIUM SILICATE)

   ↓

   SWELLING

   ↓

   MAP CRACKS
CEMENT

AGGREGATE

MIXING WATER

CHEMICAL AND MINERAL ADMIXTURES

INDUSTRIAL WASTE WATER

DE-ICING SALTS

SEA WATER

ALKALI MIGRATION (WETTING AND DRYING, FREEZING AND THAWING, ELECTRICAL CURRENTS)

\[
\{ (Na_2O)_e = Na_2O + 0.658 K_2O \} \geq 0.6 \%
\]

THE CEMENTS with LESS THAN 0.6% EQUIVALENT \( Na_2O \) are CLASSIFIED LOW ALKALI CEMENT
REACTIVE AGGREGATES

REACTIVITY of an AGGREGATE

COMPOSITION
GEOLOGICAL ORIGIN
TEXTURAL CHARACTERISTICS

REACTIVE FORMS OF SILICA

★ OPAL ★ CHALCEDONY
★ CRISTOBALITE ★ TRIDYMITE
★ CRYPTOCRISTALLINE QUARTZ

REACTIVE MINERALS OCCUR IN

OPALINE or CHALCEDONIC CHERTS
SILICEOUS LIMESTONES
RYHOLITE and RYHOLITIC TUFFS
ANDESITE and ANDESITE TUFFS

UNEXPECTED SOURCES! i.e.: Surface hardeners
GEL FORMATION DUE TO ASR

Gel in air void and cracks.

Ordinary polarized light

Fluorescent light
GEL FORMATION DUE TO ASR

Crystalline ASR gel showing rosette structure

alkali-silica gel
DAMAGES OF ASR

MAP CRACKING
EXPANSION
POP-OUTS
GEL EXTRUDATION
VARIATION IN COLOUR OF CONCRETE
ASR CRACKS
ASR DAMAGE IN BRIDGE ABUTMENTS (İZMİR)
LEAKAGE OF ASR GELS
ASR - EXPERIMENTS

- CHEMICAL AGGREGATE REACTIVITY
- GEOLOGICAL AGGREGATE REACTIVITY
- PHYSICAL & CHEMICAL LENGTH CHANGE of CEMENT MORTARS

TESTS ARE COMPARATIVE NATURE

ONE METHOD MIGHT NOT BE SUFFICIENT
ASR - EXPERIMENTS

25*25*285 mm PRISMATIC MORTAR BARS

ASTM C227 (LONG TERM)

CSA A23.2 -25A  \( \leq \% 0.15 \)

ASTM C1260  \( \leq \% 0.10 \)

ACCELERATED METHODS

LENGTH CHANGE

\( \leq \% 0.05 \) (3 MONTHS)

\( \leq \% 0.10 \) (6 MONTHS)

(14 DAYS; 80°C, NaOH SOLUTION)
AAR-4, ACCELERATED CONCRETE PRISM METHOD

RELATIVE HUMIDITY 100% TEMP. 60°C,
LIMIT EXP. 0.04% at 15 WEEKS

75*75*285 mm
EFFECTIVE MEASURES in CONTROLLING ASR EXPANSION

★ CONTROLLING the AMOUNT of REACTIVE SILICA
★ LIMITING ALKALI CONTENT of CONCRETE
★ CONTROLLING the MOISTURE CONTENT of CONCRETE
★ REDUCING THE PERMEABILITY of CONCRETE
★ USING MINERAL OR CHEMICAL ADMIXTURES
  (Silica Fume, Fly Ash, Zeolite, Salts Of Lithium etc.)

SOME of THESE METHODS MAY BE IMPLEMENTED TOGETHER
REDUCING HYDROXYL CONCENTRATION

WHEN USED AS A PARTIAL REPLACEMENT FOR HIGH ALKALI CEMENT

WHEN USED AS A PARTIAL REPLACEMENT FOR REACTIVE SAND

SILICA FUME

IMPROVED IMPERMEABILITY

REDUCING SOLUBILITY of REACTIVE SILICA

ALKALI DILUTERS

REACTIVE SILICA DILUTERS

RAPID ASR IN A FRESH STATE

PREVENT WATER PENETRATION, ALKALI MIGRATION

SILICA FUME and ASH MAY HAVE VERY POSITIVE EFFECTES IN PREVENTING EXPANSION DUE TO ASR
THE EFFECTIVENESS OF INCORPORATING FLY ASH (CLASS C) AND/OR SILICA FUME IN PREVENTING EXPANSION DUE TO ASR HAS BEEN INVESTIGATED

REACTIVE SAND: FROM AHMETLİ REGİON NEAR İZMİR
CLASS C FLY ASH: FROM SOMA B POWER PLANT
SILICA FUME: PRODUCT of YKS/SKW CONSTRUCTION MATERIALS
HIGH ALKALI CEMENT: PC 42.5 \((\text{Na}_2\text{O})_e = 0.91\% > 0.6\%\)

REACTIVITY of CEMENT-AGGREGATE-MINERAL ADDITIVE COMBINATIONS

25x25x285 mm PRISMATIC MORTAR BARS HAVE BEEN PREPARED

CSA A23.2-25A (ACCELERATED MORTAR BAR TEST)
IMMERSED in 1 M NaOH SOLUTION at 80°C for 14 DAYS & THEIR LENGTHS MEASURED PERIODICALLY.

IF THE EXPANSIONS ARE GREATER THAN 0.15% (at 14 days)

AGGREGATE IS CONSIDERED AS POTENTIALLY REACTIVE!

<table>
<thead>
<tr>
<th>Replacement ratios for Sand</th>
<th>Number of combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Fume</td>
<td>5 - 25 %</td>
</tr>
<tr>
<td>Fly Ash (C type)</td>
<td>5 - 30 %</td>
</tr>
<tr>
<td>Silica Fume + Fly ash</td>
<td>5 - 30 %</td>
</tr>
</tbody>
</table>
AVERAGE VALUES of ALL SPECIMEN INCLUDING CONTROL MIX at 14 DAYS

Mineral admixture ratio (%)

Expansion (%)

Control mix  Silica fume  Fly ash  Silica fume+Fly ash

expansion limit (14 days)
TEST RESULTS INDICATE THAT WHEN SILICA FUME AND/OR FLY ASH ARE USED IN SUFFICIENT AMOUNTS, EXPANSION DUE TO ASR MAY BE DECREASED TO HARMLESS LEVELS.

CLASS C FLY ASH IS NOT EFFECTIVE UNLESS USING HIGH REPLACEMENT LEVELS (ABOVE 25 %).

BELOW 15% OF INCORPORATION OF FLY ASH CAUSED SWELLING. WHEREAS, WHEN EXCEEDING THIS RATIO, THE EXPANSION VALUES DECREASED.

USING 30% FLY ASH AS A SAND REPLACEMENT REVEALED A REDUCTION OF 66% IN COMPARISON WITH THE CONTROL SPECIMENS.
PARTIAL REPLACEMENT OF REACTIVE SAND BY SILICA FUME REDUCED THE EXPANSIONS OF MORTAR BARS IN ALL COMPOSITIONS. (FOR EXAMPLE, INCORPORATING 10% SILICA FUME REDUCED THE EXPANSIONS BY 90% IN COMPARISON WITH THE CONTROL SPECIMENS).

THE DISADVANTAGES OF CLASS C FLY ASH IN TERMS OF CONTROLLING ASR MAY BE COMPENSATED BY INCORPORATING RELATIVELY SMALL QUANTITIES OF SILICA FUME.

FOR EXAMPLE, A COMBINATION OF 10% SILICA FUME WITH 10% FLY ASH SEEMS TO BE A LOGICAL AND FEASIBLE SOLUTION OF THIS PROBLEM.

FURTHER RESEARCH WILL BE PLANNED FOR COMBINATIONS OF FLY ASH AND SILICA FUME WITH DIFFERENT REPLACEMENT RATIOS.
ALKALI – CARBONATE REACTION

ACR
ALKALI – CARBONATE REACTION

Reaction takes place between certain dolomitic limestones and alkali oxides in the pore water of concrete.

\[
\text{MgCO}_3 + \text{CaCO}_3 + \text{sodium or potassium hydroxide} \rightarrow \text{magnesium hydroxide} + \text{calcium carbonate} + \text{sodium or potassium carbonate}
\]

DEDOLOMITIZATION

Cracks
ACR CAN BE EXPLAINED IN A THREE-STEP PROCESS

1. ALKALI + DOLOMITE ➡ MAGNESIUM HIDROXIDE - Mg(OH)$_2$

2. DISSOLUTION OF Mg(OH)$_2$

3. EXPANSION of CLAY

Deterioration of concrete

Water and/or alkalis from the environment (e.g. from de-icing salts)

Diffusion of water and alkalis into concrete

Crack formation (map cracking and surface parallel cracking)

Diffusion of alkalis (e.g. from cement and admixtures)

Mg(OH)$_2$; expansion of clay

Dolomitic Aggregate
ALKALI – CARBONATE REACTION
ALKALI – CARBONATE REACTION

(4) REQUIREMENTS MUST MET SIMULTANEously !!!

(1)
SUFFICIENT ALKALI CONTENT
(PRIMARILY FROM THE CEMENT)

(2)
FINE GRADED DOLOMITIC AGGREGATE

(3)
EXISTANCE of CLAYEY COMPONENTS
in AGGREGATE

(4)
WATER
ALKALI – CARBONATE REACTION

\[
\text{CaMg(CO}_3\text{)}_2 + 2\text{MOH} \rightarrow \text{Mg(OH)}_2 + \text{CaCO}_3 + \text{M}_2\text{CO}_3
\]

M : potassium, sodium or lithium

\[
\text{M}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2\text{MOH} + \text{CaCO}_3
\]

Temperature $\uparrow$  $\leftrightarrow$  Expansion $\uparrow$
EFFECTIVE MEASURES in CONTROLLING ACR EXPENSION

- CONTROLLING the AMOUNT of MAGNESIUM MINERALS
- LIMITING ALKALI CONTENT of CONCRETE
- CONTROLLING the MOISTURE CONTENT of CONCRETE
- REDUCING THE PERMEABILITY of CONCRETE

SOME of THESE METHODS MAY BE IMPLEMENTED TOGETHER
COMBINATION OF ASR AND ACR ATTACKS, at New JERSEY

Dilatation problems due to ACR at Virginia
ALKALi-CARBONATE REACTION (ACR)

MAP CRACKING FORMATIONS DUE TO ACR at Kingston, Ontario
A Test Method For Evaluating ACR with Pittsburgh Aggregate

- 40x40x160 mm Specimens
- Aggregate/Cement = 1
- Water/Cement = 0.32
- 28 Days in 80°C NaOH Solution
- Expansion Limit → 0.1% After 28 Days
Effectiveness of Mineral Additives

**GGBFS**

- 0.249
- 0.149
- 0.136
- 0.123
- 0.113
- 0.092
- 0.000
- 0.050
- 0.100
- 0.150
- 0.200
- 0.250
- 0.300

**Silica Fume**

- 0.403
- 0.290
- 0.249
- 0.133
- 0.092
- 0.000
- 0.050
- 0.100
- 0.150
- 0.200
- 0.250
- 0.300
- 0.350
- 0.400
- 0.450
Scanning Electron Microscopy Investigations of ACR

- SEM Photos Taken From Concrete Specimens Containing Pittsburgh Aggregate (Reference Alkali-Carbonate Reactive Aggregate), After 56 Days in 80°C NaOH Solution

A Void Filled with ACR Product

A General View of the Concrete Specimen

Expansion Cracks
EDS Analysis of ACR

- SEM Photos Taken From Concrete Specimens Containing Pittsburgh Aggregate (Reference Alkali-Carbonate Reactive Aggregate), After 56 Days in 80°C NaOH Solution

A Close Look to an ACR Product

EDS Spectrum of an ACR Product
DELAYED HYDRATION of CaO & MgO
DELAYED HYDRATION of CaO & MgO

HIGH FREE CaO CONTENT
HIGH MgO CONTENT ( > 5%)
CRYSTAL STRUCTURE FORMATION DURING MANUFACTURING

LATE HYDRATION of CaO &/or MgO

LATE FORMATION Ca(OH)$_2$ &/or Mg(OH)$_2$

SWELLING

CRACKS
EFFECTIVE MEASURES in CONTROLLING EXPANSION

★ CONTROLLING the AMOUNT of CaO & MgO
★ CONTROLLING the MOISTURE CONTENT of CONCRETE
★ REDUCING THE PERMEABILITY of CONCRETE

SOME of THESE METHODS MAY BE IMPLEMENTED TOGETHER
DELAYED HYDRATION of CaO
DELAYED HYDRATION of CaO
DELAYED HYDRATION of CaO
BIOLOGICAL ATTACK
BIOLOGICAL ATTACK

BIO-CHEMICAL

BIOLOGICAL, CHEMICAL FORMATIONS

SOME PLANTS & TREE ROOTS

SOME SEA ALGAEAS & MICROORGANISMS

ACID ATTACK

DETERIORATION ON LAYERS CONCRETE SURFACES

PHYSICAL

SWELLING OF GROWING ROOTS IN CAPILLARY PORES

AND / OR

CLOGGING OF PIPES
BIOLOGICAL ATTACK

soybean
SOMETIMES POSITIVE EFFECTS (PREVENTION of $O_2$ INGRESS)
SOMETIMES POSITIVE EFFECTS
(PREVENTION of $O_2$ INGRESS)
EFFLUORESCENCE

LEAKAGE OF CALCIUM COMPOUNDS
(CaCO$_3$, CaSO$_4$)

ACCUMULATION OF SALT
(Usage of sea water)
Efflorescence is a common problem with older concrete surfaces. It is the process in which salt rises to the surface of the concrete, brick, or other surface and crystallizes there, causing decay and crumbling.
EFFLUORESENCE FORMATION ON BRICK WALLS

1. Dissolving of soluble salts in brick by humidity
2. Movement of salt solution in capillary pores
3. Evaporation
4. Salt accumulation 

Salt accumulation 

Effluorecence

R.F.C Column

Brick wall

Soil

Underground water

Saturated concrete

Soil

Underground water