Performance deterioration of hardened cement materials due to Freeze-Thaw cycles

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Structural, material and chemical properties should be comprehensively considered on Maintenance system of concrete structure.
The deterioration of concrete under the effect of freeze-thaw cycles has been a problem especially in cold regions.

Anti-freezing agents
Air entraining agents
Purposes of this study

1. Influence of Anti-Freeze Agents on Freeze-Thaw Cycles
   Investigation on hydration products by TG-DTA and XRD

2. Pore structure and permeability change due to Freeze-Thaw Cycles
   Investigation on Pore structure by X-ray CT and Diffusion coefficient

3. Mechanical Performance Deterioration due to Freeze-Thaw Cycles
   Investigation on Tensile Softening Behavior
Experimental Procedure of this study

Mix Proportion and Curing
Cement: Ordinary Portland Cement
W/C: 0.5 (Mortar and Cement Paste)
S/C: 1.0
Curing: 20°C for 28 days
Air entraining agents: 0.4 wt% of cement
Anti-Freezing agents: NaCl, CaCl₂, CH₃COOK and CMA (Calcium Magnesium Acetate)

Preparation of the meso-scale specimens
(Taito Miura and Yasuhiko Sato, 2010)
Experimental Procedure of this study

Temperature History (0, 5, 10, 20, 50, 100 cycles)

A. RILEM CIF/CDF

\[
\begin{align*}
&20^\circ C \\
&-20^\circ C \\
1h &\rightarrow 5h \rightarrow 8h \rightarrow 12h
\end{align*}
\]

B. 1/2 of RILEM CIF/CDF

\[
\begin{align*}
&20^\circ C \\
&-20^\circ C \\
30min &\rightarrow 150min \rightarrow 4h \rightarrow 6h
\end{align*}
\]

C. 1/3 of RILEM CIF/CDF

\[
\begin{align*}
&20^\circ C \\
&-20^\circ C \\
20min &\rightarrow 100min \rightarrow 160min \rightarrow 4h
\end{align*}
\]

D. 1/6 of RILEM CIF/CDF

\[
\begin{align*}
&20^\circ C \\
&-20^\circ C \\
10min &\rightarrow 50min \rightarrow 80min \rightarrow 2h
\end{align*}
\]
Experimental Procedure of this study

Temperature History (0, 5, 10, 20, 50, 100 cycles)

A. RIL

B. 1/2 of RILEM CIF/CDF

C. 1/3 of RILEM CIF/CDF

D. 1/6 of RILEM CIF/CDF

E. Cycles in this study
Progresses and Future Plans of this study

1. Influence of Anti-Freeze Agents on Freeze-Thaw Cycles

Measurement Items

- Ca(OH)$_2$
- Monosulfate, Ettringite, Friedel’s salt
- Total chloride, Soluble Chloride

1. Disappearance of Monosulfate and Formation of Friedel’s salt

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$$

2. Disappearance of Ca(OH)$_2$

$$2\text{NaCl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{NaOH}$$

3. Formation of Friedel’s (isolation of C$_3$A and CaSO$_4$ from Monosulfate)

$$\text{CaCl}_2 + C_3A + 10\text{H}_2\text{O} \rightarrow C_3A \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$$

4. Formation of Ettringite

$$3\text{CaSO}_4 + C_3A + 32\text{H}_2\text{O} \rightarrow C_3A \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$$
1. Influence of Anti-Freeze Agents on Freeze-Thaw Cycles

Chloride ion binding capacity

Modeling of Chloride Ion Movement at the Surface Layer of Hardened Concrete (Maruya, 1998)

Free chloride, Bound chloride, Friedel’s salt, Adsorbed chloride

\[
\begin{align*}
C_{\text{free}} & = C_{\text{tot}} - C_{\text{fixed}} \\
C_{\text{fixed}} & = \alpha \cdot C_{\text{tot}} \\
\alpha & = f(C_{\text{tot}}) \\
C_{\text{Sol}} & = \beta \cdot C_{\text{free}}^n
\end{align*}
\]

In the case of concrete structure in marine and cold environment, it is necessary to know the chloride ion movement and binding capacity at the surface layer of hardened concrete.
2 Pore structure and permeability change due to Freeze-Thaw Cycles

Measurement Items (X-ray CT)
Progresses and Future Plans of this study

Pore structure and permeability change due to Freeze-Thaw Cycles

Measurement Items (Mercury Intrusion Prosimeter)
Progresses and Future Plans of this study

2. Pore structure and permeability change due to Freeze-Thaw Cycles

Measurement Items (Chloride ion Diffusivity)

It is still not clear that pore structure change due to Freeze-Thaw cycles influences on Permeability of Cl⁻.
3 Mechanical Performance Deterioration due to Freeze-Thaw Cycles

Measurement Items (Tensile Softening)
Evaluation of tensile softening behavior of cement-paste and mortar deteriorated by NaCl solution (Taito Miura and Yasuhiko Sato, 2010)

**Bending Test**
Size: $5 \times 30 \times 70$ (mm)

**Tensile Softening**
- $\sigma$: Tensile stress
- $W$: Crack width

\[
\sigma_1 > \sigma_2 \\
W_1 < W_2
\]
Experimental Procedure of this study

3 Mechanical Performance Deterioration due to Freeze-Thaw Cycles

A. RILEM CIF/CDF

B. 1/2 of RILEM CIF/CDF

C. 1/3 of RILEM CIF/CDF

D. 1/6 of RILEM CIF/CDF
Progresses and Future Plans of this study

Strain Behavior during 10 cycles

A. RILEM CIF/CDF
B. 1/2 of RILEM CIF/CDF
C. 1/3 of RILEM CIF/CDF
D. 1/4 of RILEM CIF/CDF
3. Mechanical Performance Deterioration due to Freeze-Thaw Cycles

Tensile Softening Behavior after 10 cycles

- A. RILEM CIF/CDF
- B. 1/2 of RILEM CIF/CDF
- C. 1/3 of RILEM CIF/CDF
- D. 1/4 of RILEM CIF/CDF

Graphs showing the relationship between tensile stress (MPa) and crack width (mm) for different conditions.
1. Influence of Anti-Freeze Agents on Freeze-Thaw Cycles

1-1. Chemical deterioration of hardened cement materials due to anti-freezing agents.
1-2. Influence of Freeze and Thaw cycles on chloride ion movement and binding capacity of hardened cement material

2. Pore structure and permeability change due to Freeze-Thaw Cycles

2-1. Permeability and pore structure change of mortar under Freeze and Thaw cycles with using X-ray CT.
2-2. Influence of anti-freezing agents type on permeability under Freeze and Thaw cycles

3. Mechanical Performance Deterioration due to Freeze-Thaw Cycles

3-1. Tensile Softening Behavior of Mortar under Freeze-Thaw Action with Different Temperature History
3-2. Influence of anti-freezing agents type on Tensile Softening Behavior under Freeze and Thaw cycles
Thank you for your kind attention