The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete

Principal Investigator

Larry Sutter
Michigan Tech

Co-Principal Investigators

Karl Peterson, Tom Van Dam
Michigan Tech

Doug Hooton
Gustavo Julio-Betancourt
University of Toronto

Background

- Problem Statement
  - Keeping roads safe & passable in winter weather is a primary concern of SHAs
  - Always looking for easier, safe, cost effective means for highway deicing/anti-icing
    - Both accomplished by the use of various brines
    - Chemicals are effective for deicing/anti-icing
  - Chemicals have not been proven to be safe for concrete – may cause premature deterioration

Deicer Scaling - *Deicer chemicals may contribute by chemically interacting with cement paste*

Paste Dissolution/Softening

Chemical attack of concrete - Usually slow process

Corrosion of Reinforcing Steel

Already well documented and understood - Not a focus of this research

Background

- Research Objectives
  - Determine the <u>long term effects on concrete</u> from exposure to concentrated solutions of $MgCl_2$, NaCl, $CaCl_2$, and CMA
  - Identify protective or design strategies that minimize material damage from chemical exposure

Approach

- Characterization of Field Specimens
  - Determine distress mechanisms present in the field
- Phase I Laboratory Experiments
  - Performed on <u>mortar</u> specimens (cement, sand, and water)
  - Identify distress mechanisms
  - Assess the role of mixture properties and deicer types
- Phase II Laboratory Experiments
  - Performed on <u>concrete</u> (cement, sand, aggregate, and water)
  - Confirm distress mechanisms active in concrete
  - Determine the role of deicer concentration, concrete mixture design, and the effectiveness of sealants

Characterization of Field Specimens

- Five Sites Identified by Panel
  - Colorado, State Highway 83, South of Denver near Milepost 57
  - Iowa, eastbound US Highway 34, western end of the Burlington Bridge.
  - Idaho, westbound Interstate Highway 184 west of Boise, near milepost 3
  - Montana, westbound Interstate Highway 90 bridge deck near milepost 117
  - South Dakota, eastbound 26th Street left turn lane
- Two Additional Sites Identified
  - Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange
  - Montana, westbound Interstate Highway 90 bridge deck, near milepost 37.2, Sloway interchange

Phase I - Details

- Expose mortars to deicer solutions at fixed concentrations (less than typical application conc.)
- Monitor Physical Effects
  - Strength Loss
  - Expansion
  - Freeze-Thaw Performance
- Monitor Chemical Effects
  - Petrographic analysis to identify alterations to the mortar

Phase I - Details

- Five different deicer solutions
  - $MgCl_2$ - Magnesium Chloride (15 wt%)
  - $CaCl_2$ - Calcium Chloride (17 wt%)
  - NaCl - Sodium Chloride (23 wt%)
  - Proprietary - Magnesium Based Agricultural Products
  - CMA - Calcium Magnesium Acetate
  - Saturated limewater (control)
- Exposed for various times
- Exposed at different temperatures (40, 72, 135ºF)

Phase II - Details

- Concrete mixtures were made using
  - high quality, partially crushed gravel coarse aggregate
  - natural sand
  - 564 lb/yd^3 Type I/II cement
  - vinsol resin and synthetic AEA
  - *w/c* of 0.45 and 0.55
- Two additional mixtures were prepared,
  - 15 percent replacement of cement with Class F fly ash
  - 35 percent replacement of cement with ground blast furnace slag (GBFS)
- Exposed to same deicers as Phase I

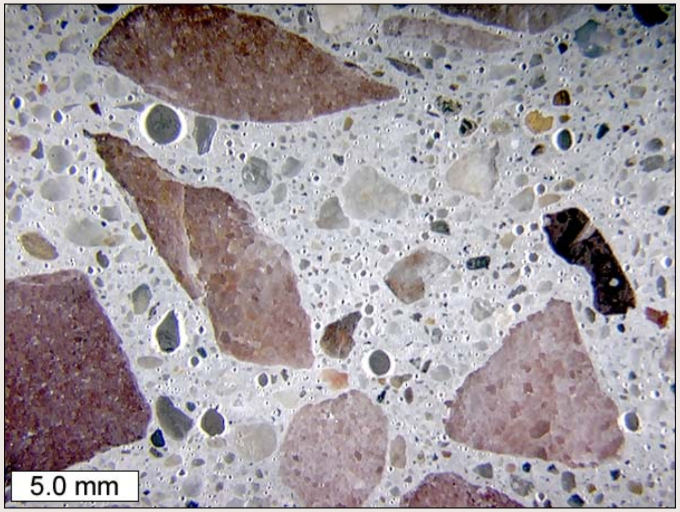
Characterization of Field Specimens

South Dakota EB 26th Street
Left-turn lane onto NB Interstate Highway 29

Sample ID	SD_01	SD_04
Location	at joint	away from joint
Raw data		
Total traverse length (mm)	3625.456	3625.456
Area analyzed (cm^2)	71.0	71.0
Air stops	85	91
Paste stops	396	382
Aggregate stops	907	915
Secondary deposit stops	0	0
Total stops	1388	1388
Number of air intercepts	1577	1420
Number of filled void intercepts	2	0
Results		
Air vol.%	6.1	6.6
Paste vol.%	28.5	27.5
Aggregate vol.%	65.3	65.9
Secondary deposit vol.%	0.0	0.0
Existing average chord length (mm)	0.141	0.167
Existing paste/air ratio	4.7	4.2
Existing air void specific surface (mm^{-1})	28.4	23.9
Existing air void frequency (voids/m)	435	392
Existing spacing factor (mm)	0.158	0.176
Original average chord length (mm)	0.141	0.167
Original paste/air ratio	4.7	4.2
Original air void specific surface (mm^{-1})	28.4	23.9
Original air void frequency (voids/m)	436	392
Original spacing factor (mm)	0.158	0.176

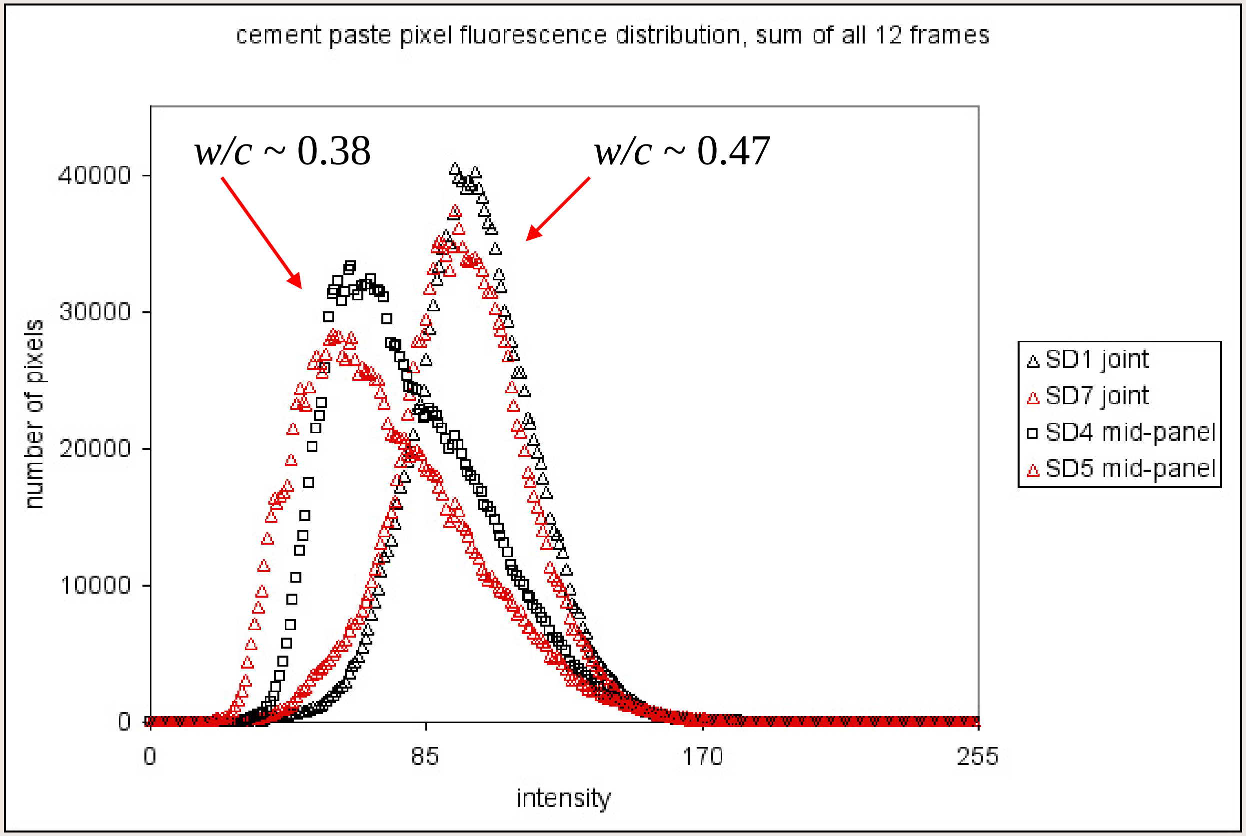
South Dakota EB 26th Street
Left-turn lane onto NB Interstate Highway 29

- Stereomicroscope image of polished surface from core SD_04, magnified here approximately 4x

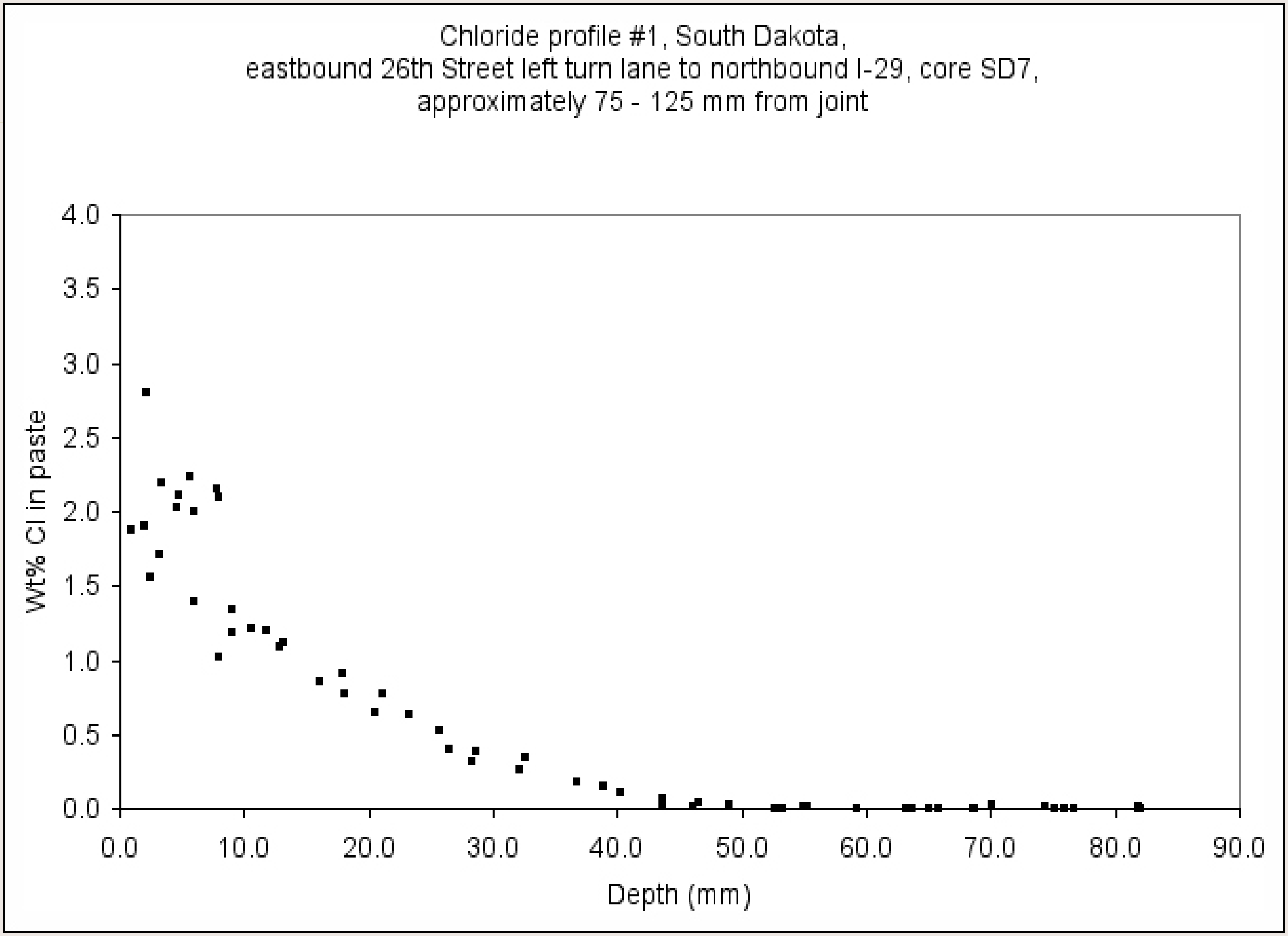


- Stereomicroscope image of polished surface from core SD_04, magnified here approximately 22x.

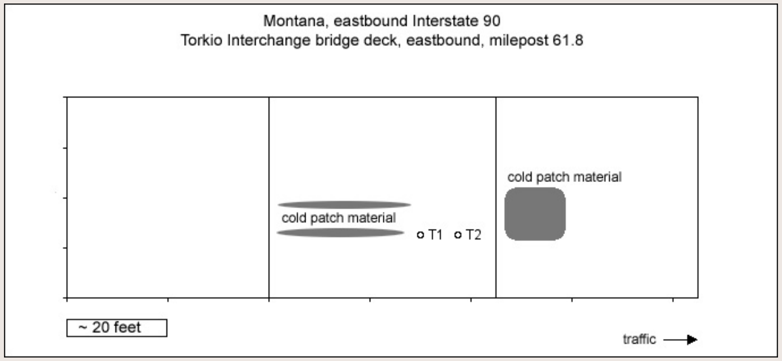
South Dakota EB 26th Street
Left-turn lane onto NB Interstate Highway 29



- Histogram comparing cement paste pixel intensities using all 12 frames as collected from thin sections prepared from cores taken at the joint versus cores taken mid-panel.


Chloride profile #1, South Dakota,
eastbound 26th Street left turn lane to northbound I-29, core SD7,
approximately 75 - 125 mm from joint
Wt% Cl in paste
Depth (mm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0

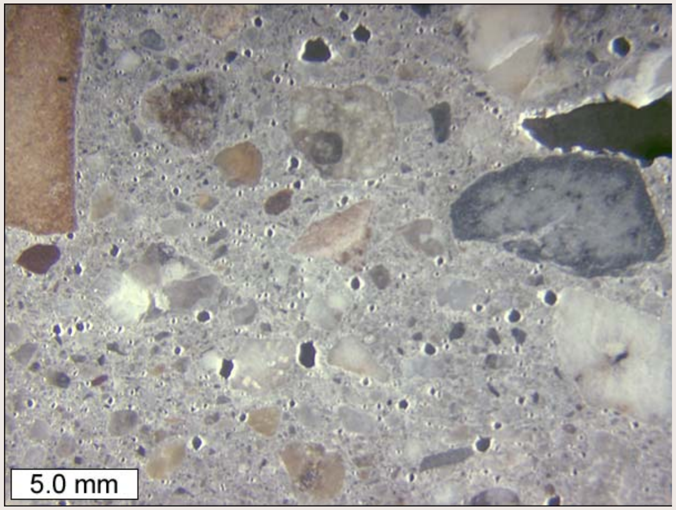
Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange

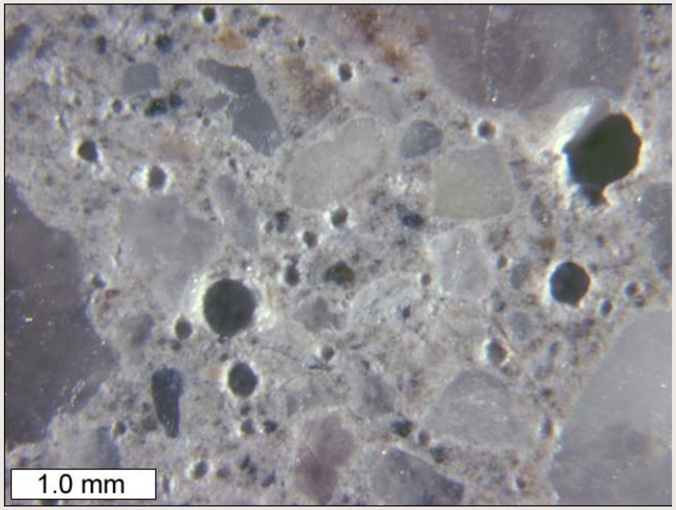


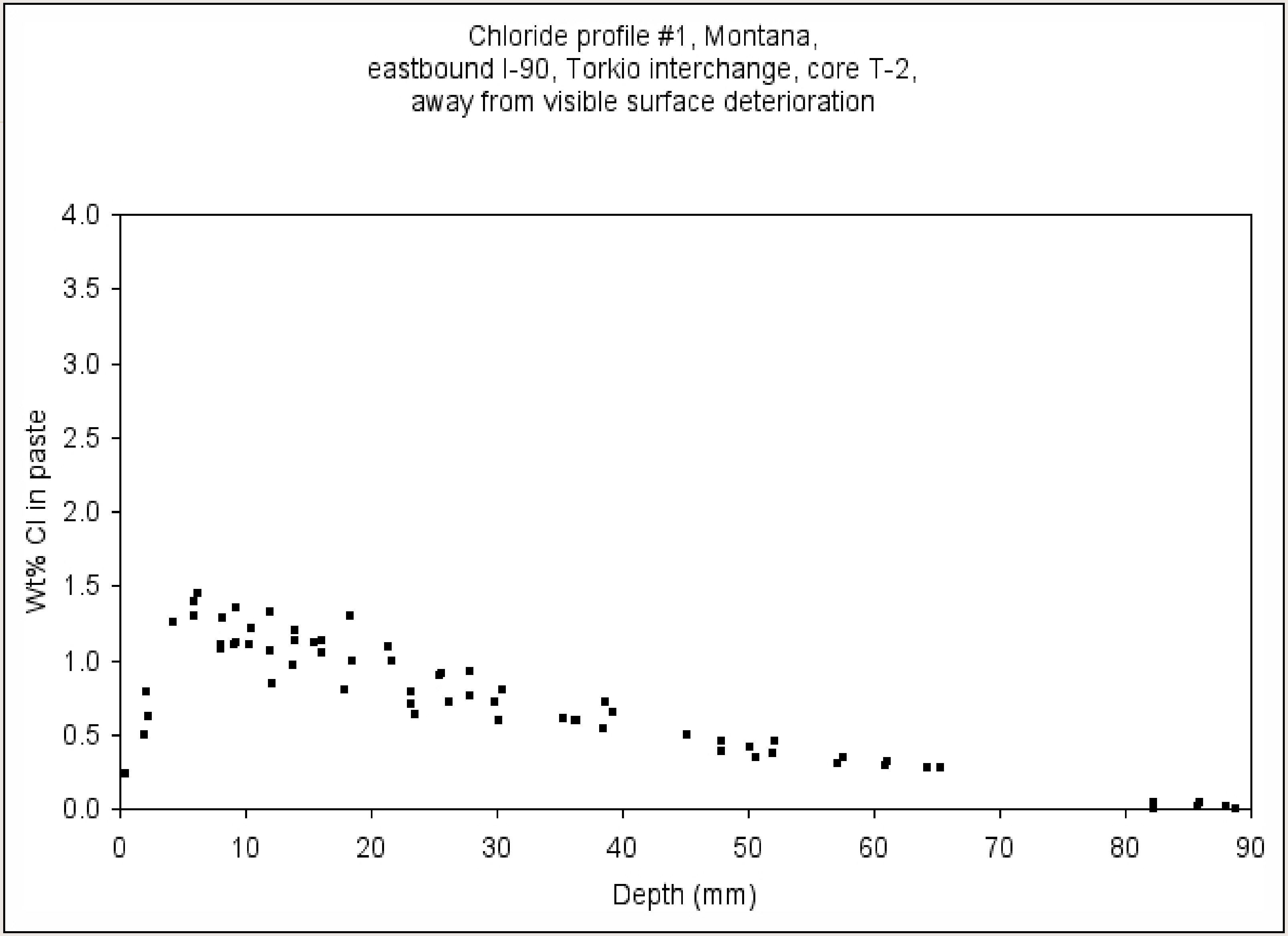
Sample ID	T-2
Location	Area in Good Condition
Raw data	
Total traverse length (mm)	3772.1
Area analyzed (cm^2)	73.9
Air stops	70
Paste stops	413
Aggregate stops	961
Secondary deposit stops	0
Total stops	1444
Number of air intercepts	617
Number of filled void intercepts	0
Results	
Air vol%	4.9
Paste vol%	28.6
Aggregate vol%	66.6
Secondary deposit vol%	0.0
Existing average chord length (mm)	0.370
Existing paste/air ratio	5.9
Existing air void specific surface (mm^{-1})	13.5
Existing air void frequency (voids/m)	164
Existing spacing factor (mm)	0.296
Original average chord length (mm)	0.370
Original paste/air ratio	5.9
Original air void specific surface (mm^{-1})	13.5
Original air void frequency (voids/m)	164
Original spacing factor (mm)	0.296

Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange

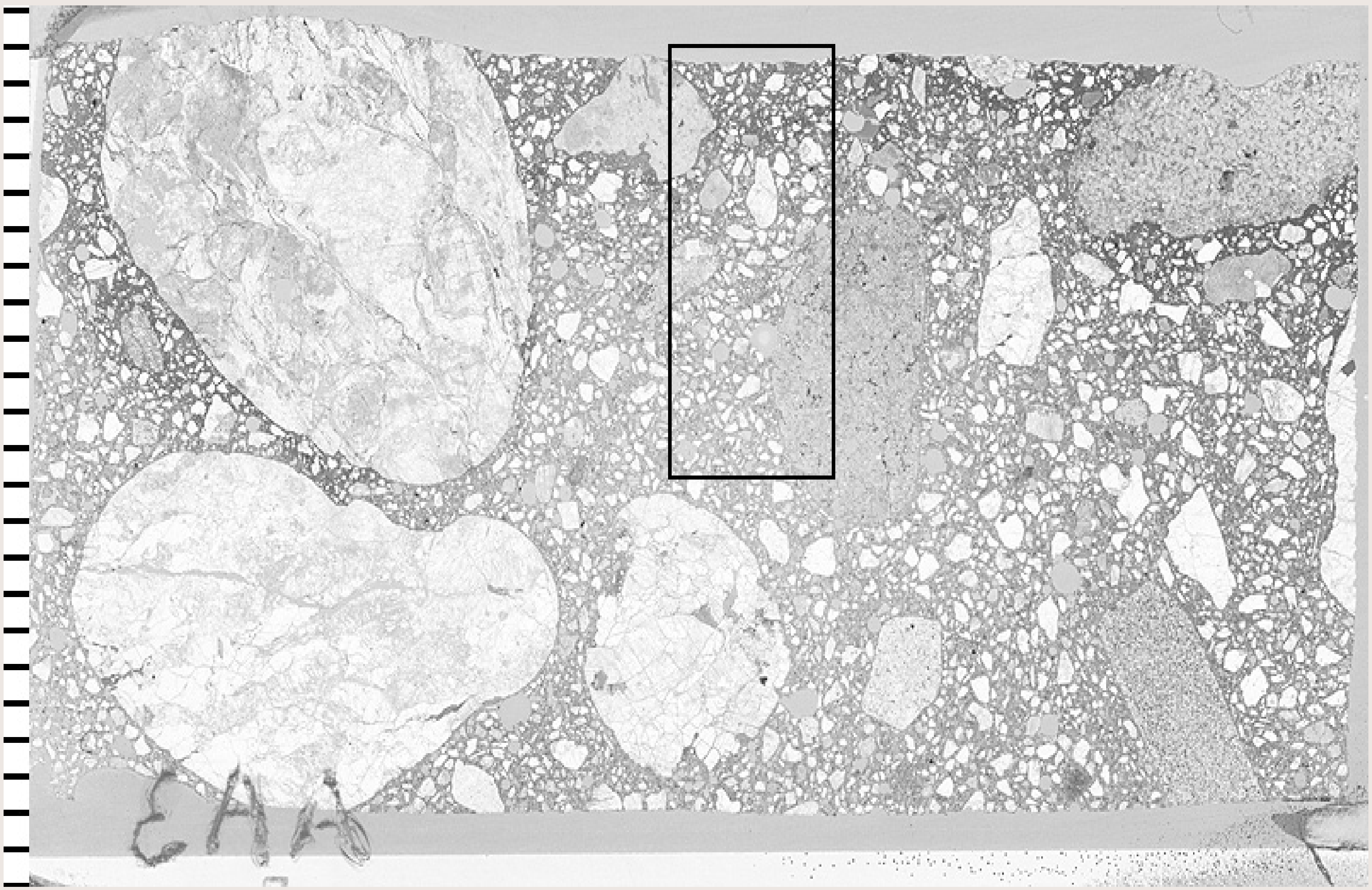
- Stereo microscope images to show air void structure on polished slab from core T-2.






Chloride profile #1, Montana,
eastbound I-90, Torkio interchange, core T-2,
away from visible surface deterioration
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Wt% Cl in paste
0
10
20
30
40
50
60
70
80
90
Depth (mm)

Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange



Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange

X-ray map of Mg

Summary - *Characterization of Field Specimens*

- No site examined showed clear, conclusive evidence of distress that could be linked directly to deicing chemicals
- Common observations included:
  - A reduction in paste density near joints and cracks
  - Higher chloride ingress in those areas with reduced paste density
  - Marginal or inadequate air-void systems
- The Tarkio Bridge (MT) had the strongest resemblance to concrete exposed to deicing solutions in the laboratory:
  - Magnesium enrichment at surface
  - Calcite deposits near crack at depth
- Pronounced efflorescence underneath the Tarkio bridge
- *South Dakota showed significant chloride ingress relative to the age of the pavement*

Phase I Laboratory Results

Cylinders exposed to $MgCl_2$ solution after 84 days of exposure @ 40 ºF. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

Cylinders exposed to $CaCl_2$ solution after 84 days of exposure @ 40 ºF. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

Cylinders exposed to NaCl solution after 84 days of exposure @ 40 ºF. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

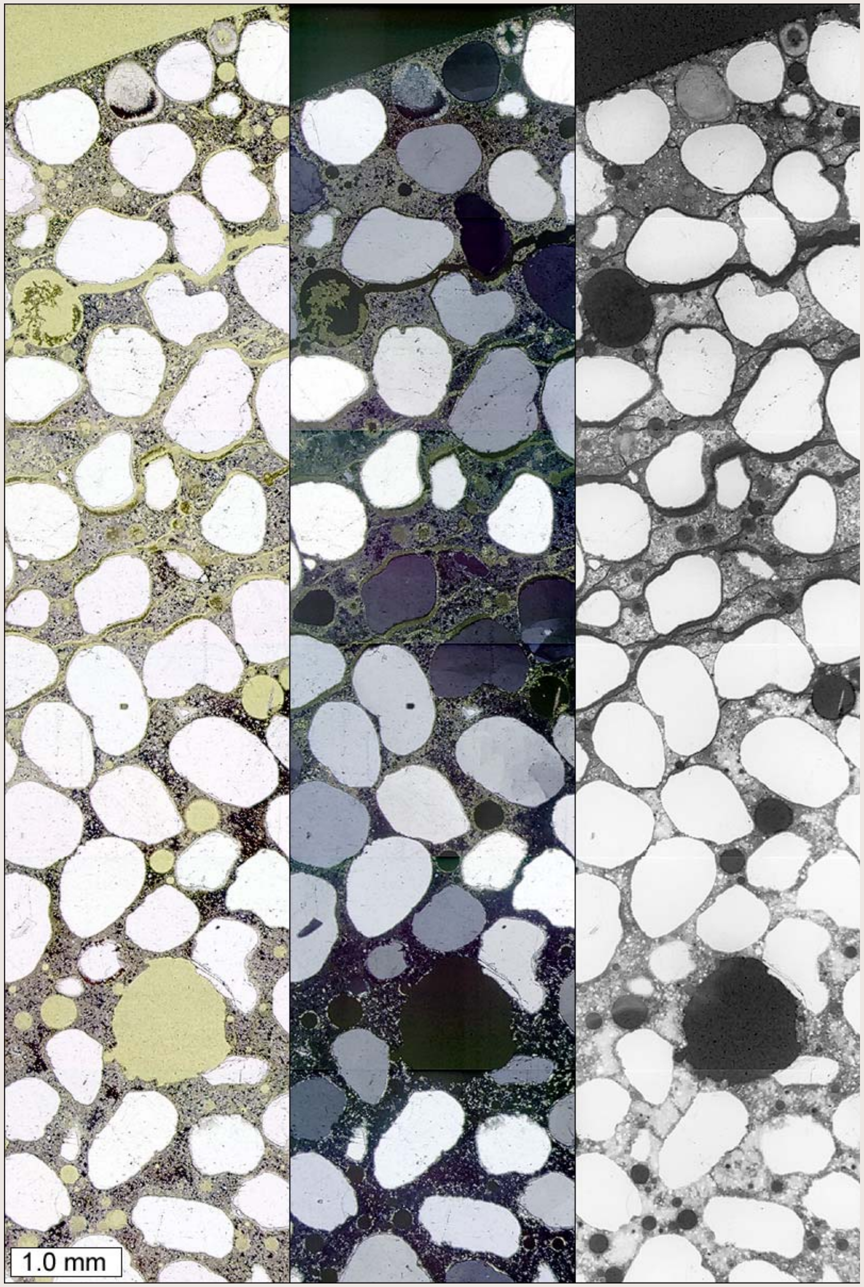
Control cylinders exposed to lime water solution after 84 days of exposure @ 40 ºF. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

Mechanism

- Specimens were held at a constant 40 ºF so no freezing occurred that could result in the damage observed
- Expansion was caused by the formation of calcium oxychloride
- Results from the reaction of calcium hydroxide (*present in the hardened cement paste*) with chloride ions (*provided by the deicer*)

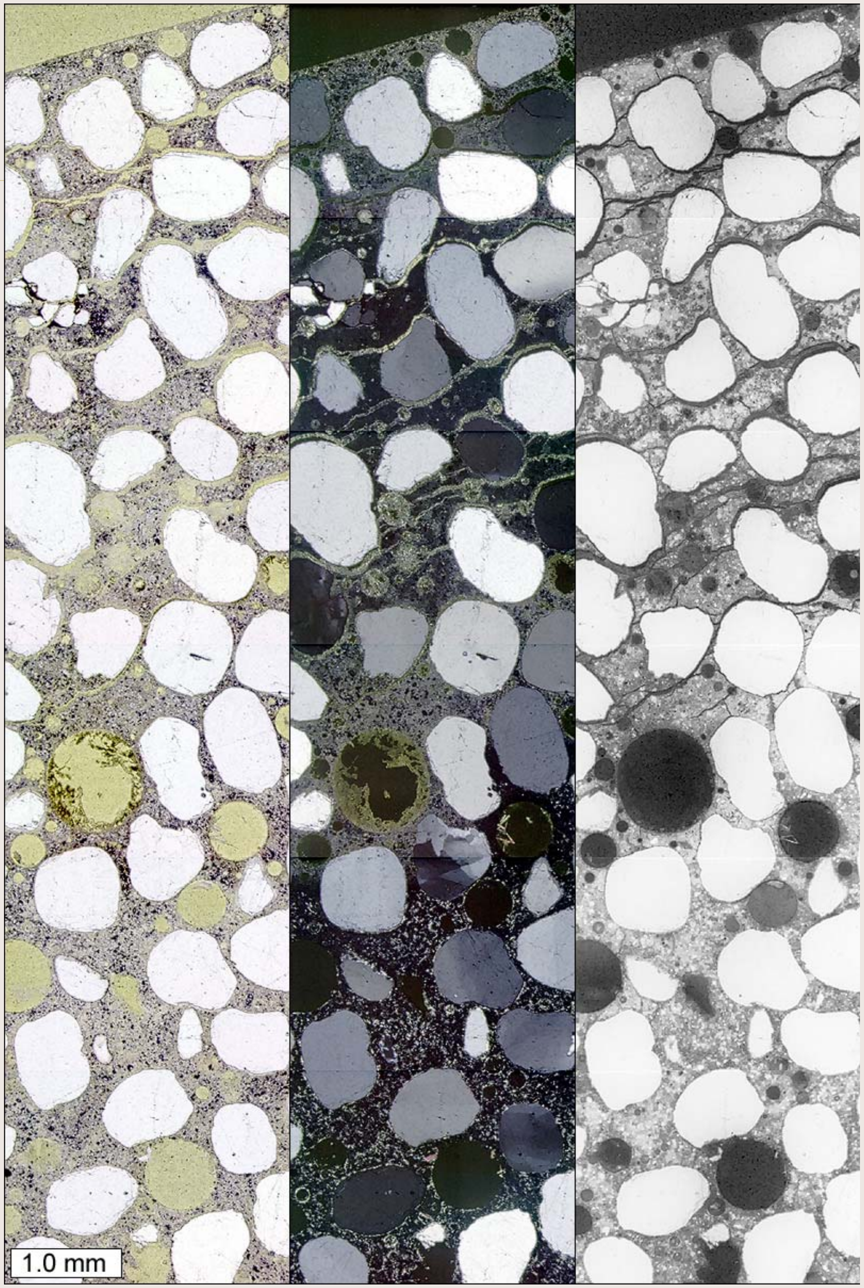
From left to right:
plane polarized light,
cross polarized light, and
epifluorescent mode images of thin section prepared from cylinder immersed in $MgCl_2$ solution.

- Petrographic Analysis
- Thin sections from 0.50 *w/c* specimens
- $MgCl_2$ and $CaCl_2$ show similar alteration
  - Ca(OH)$_2$ depleted region
  - Cracks in-filled with calcium oxychloride



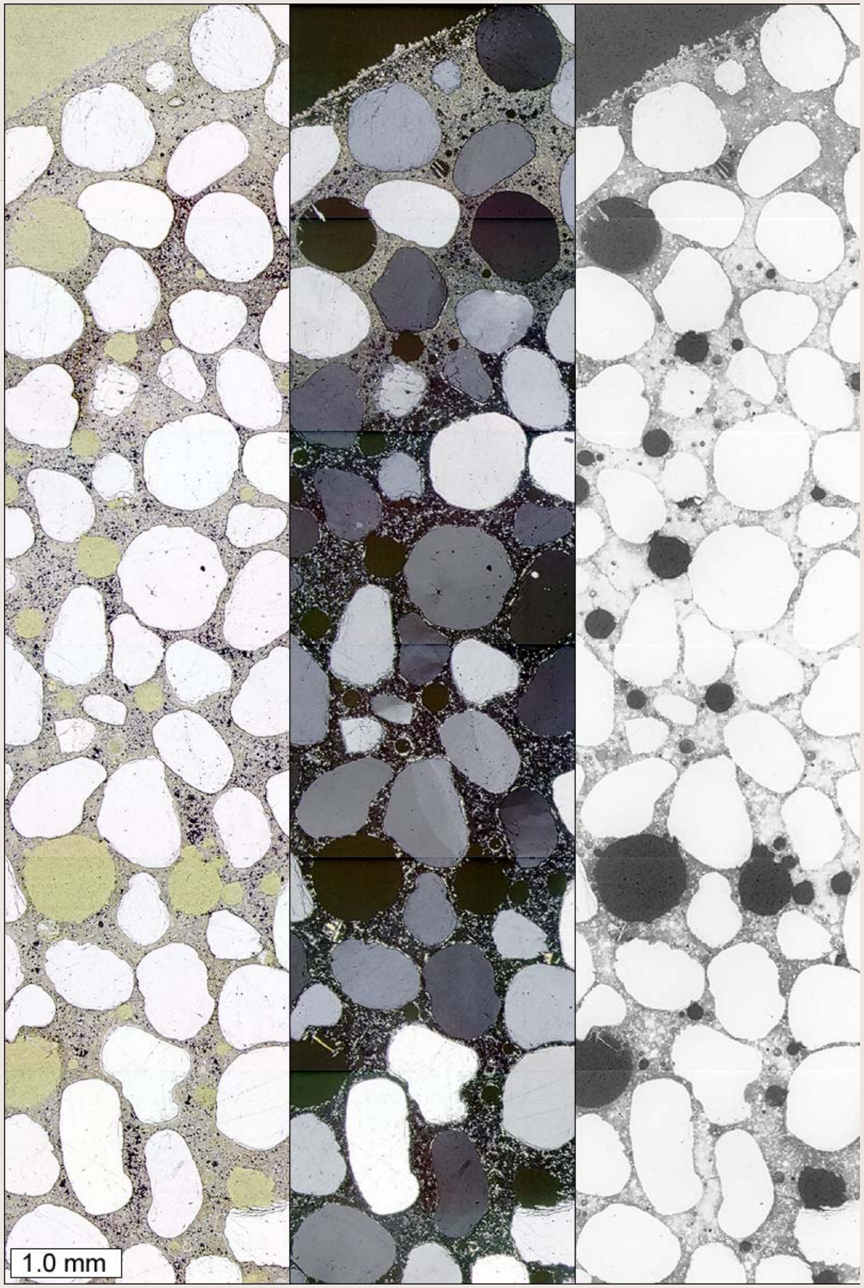
From left to right:
plane polarized light,
cross polarized light, and
epifluorescent mode images of thin section prepared from cylinder immersed in $CaCl_2$ solution.

- Petrographic Analysis
- Thin sections from 0.50 *w/c* specimens
- $MgCl_2$ and $CaCl_2$ show similar alteration
  - $Ca(OH)_2$ depleted region
  - Cracks in-filled with calcium oxychloride



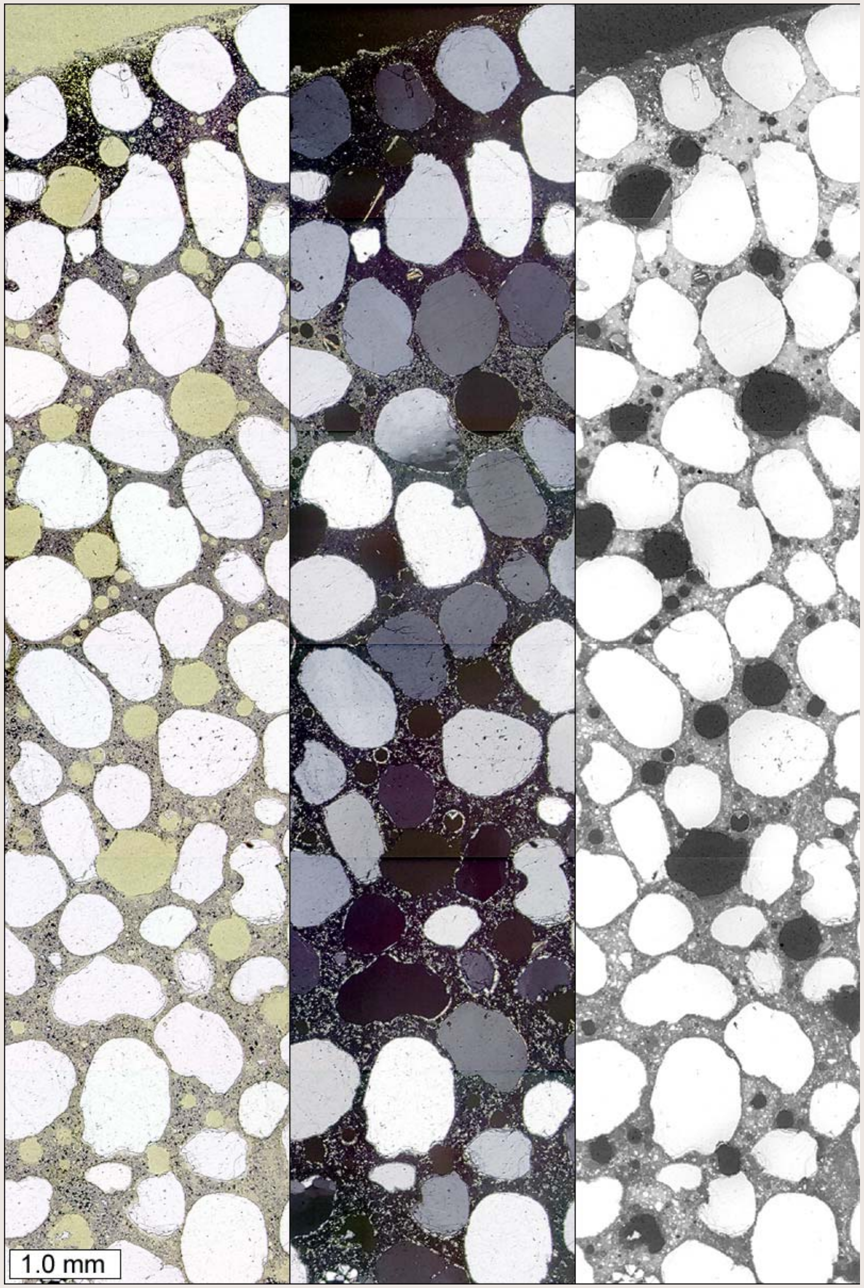
From left to right:
plane polarized light,
cross polarized light, and
epifluorescent mode images of thin section prepared from cylinder immersed in NaCl.

- Petrographic Analysis
- Thin sections from 0.50 *w/c* specimens
- NaCl and lime water controls show no alteration



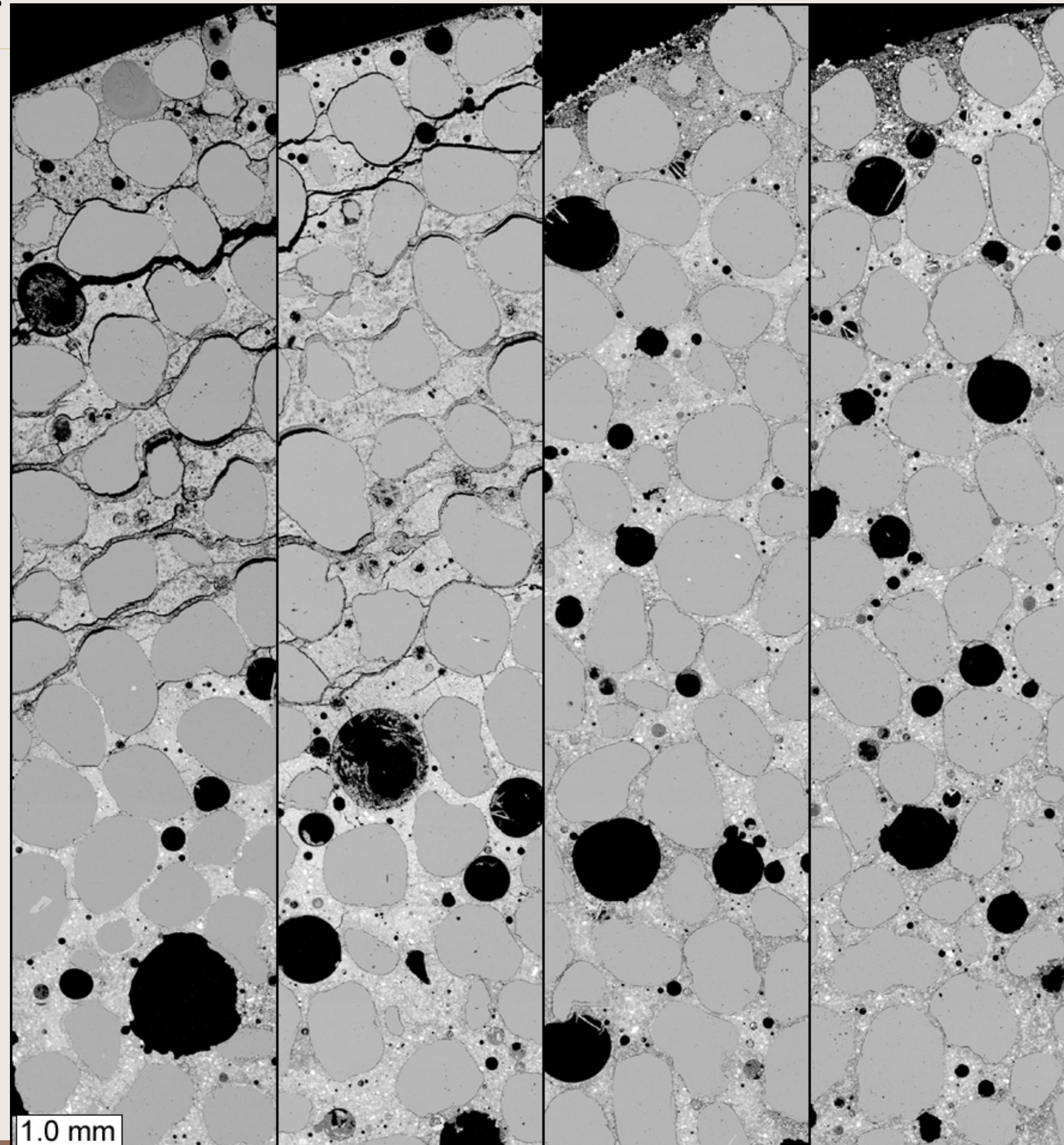
From left to right: plane polarized light, cross polarized light, and epifluorescent mode images of thin section prepared from cylinder immersed in lime water.

- Petrographic Analysis
- Thin sections from 0.50 *w/c* specimens
- NaCl and lime water controls show no alteration

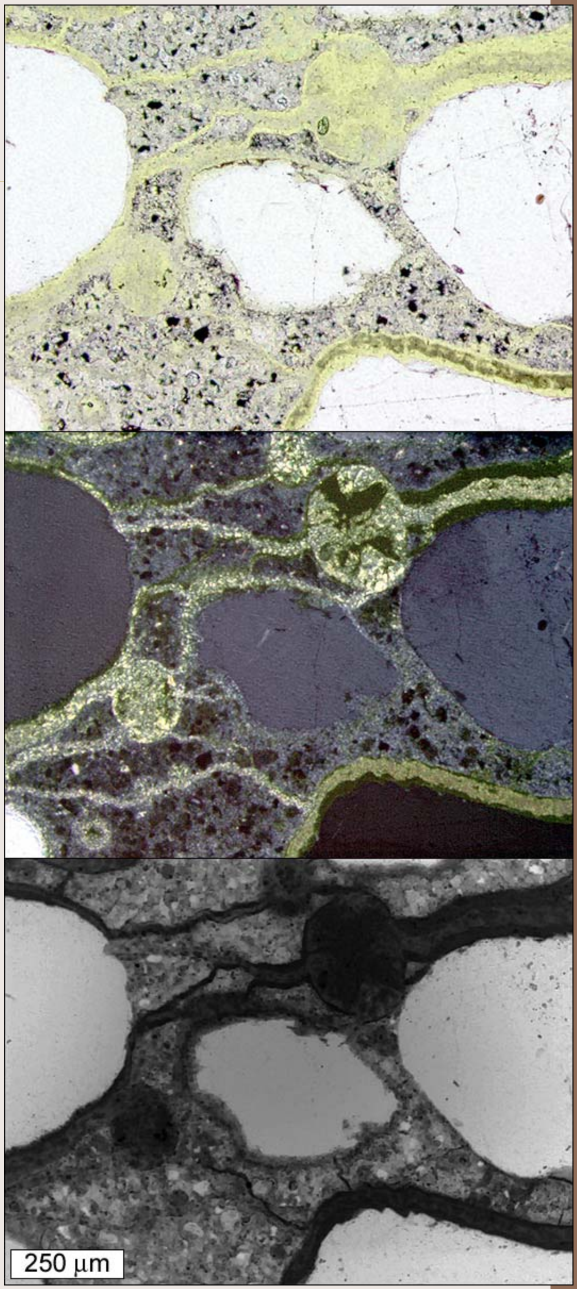


Scanning electron microscope images of thin sections prepared from cylinders immersed in, from left to right, $MgCl_2$, $CaCl_2$, NaCl, and saturated lime solutions.

- SEM Analysis
- Backscattered electron images
  - Parallel cracks
  - $Ca(OH)_2$ and oxychloride deposition in the voids of the $MgCl_2$ and $CaCl_2$ specimens



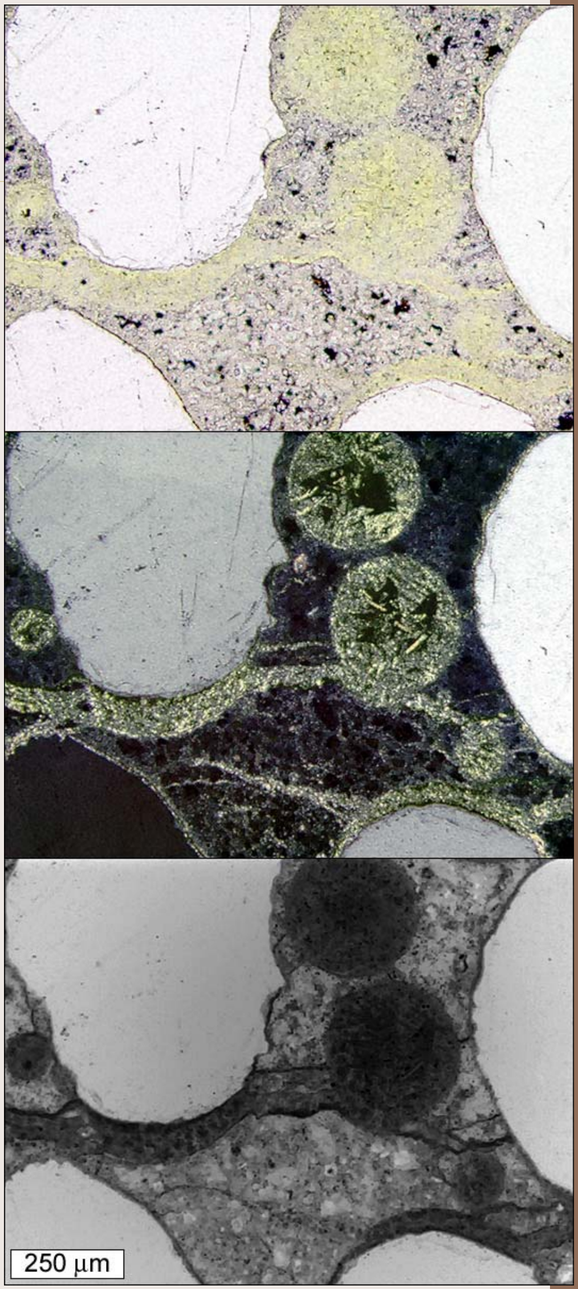
From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.



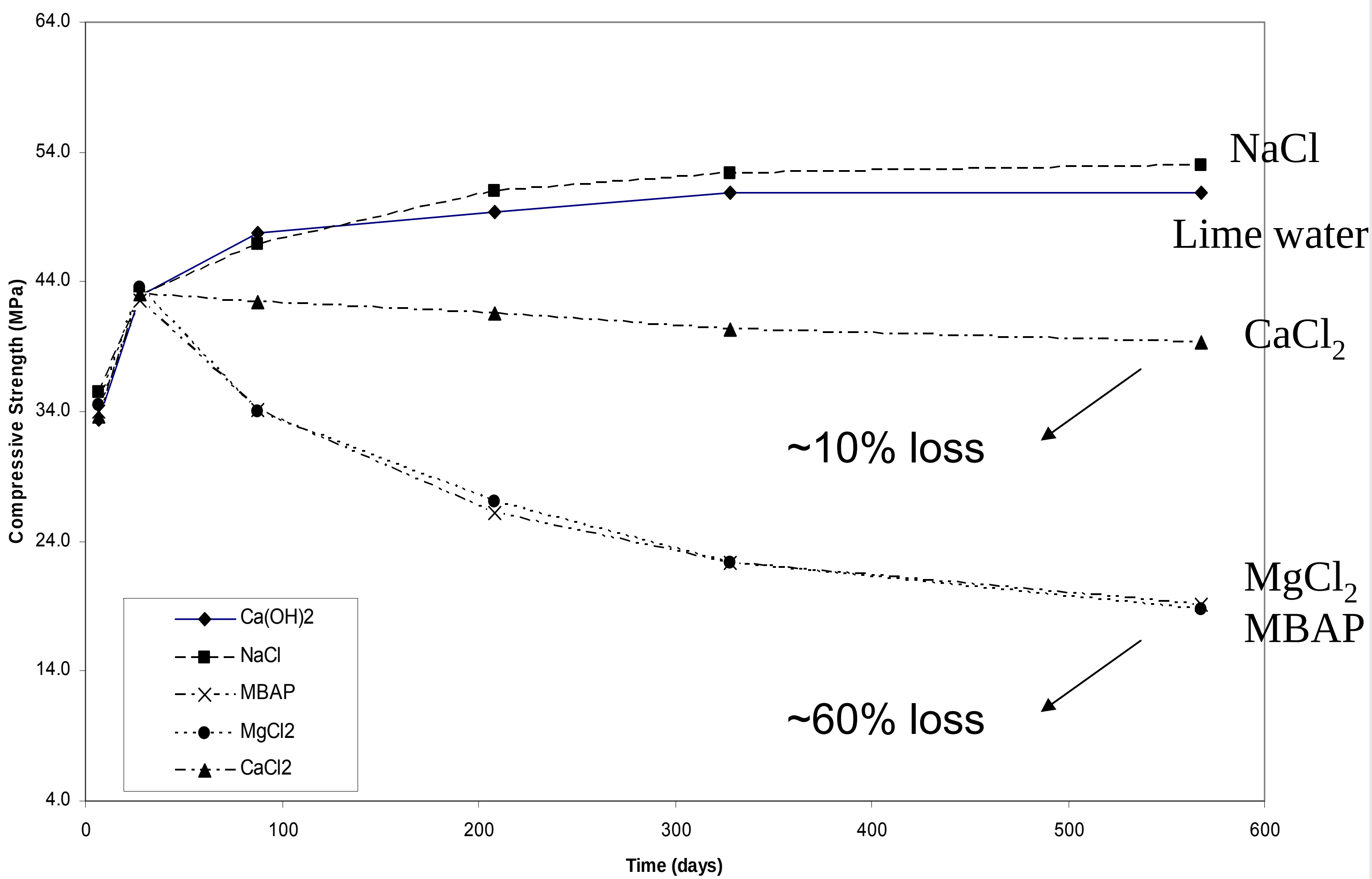
- Petrographic Analysis
  - Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from $MgCl_2$ solution immersed sample

From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.

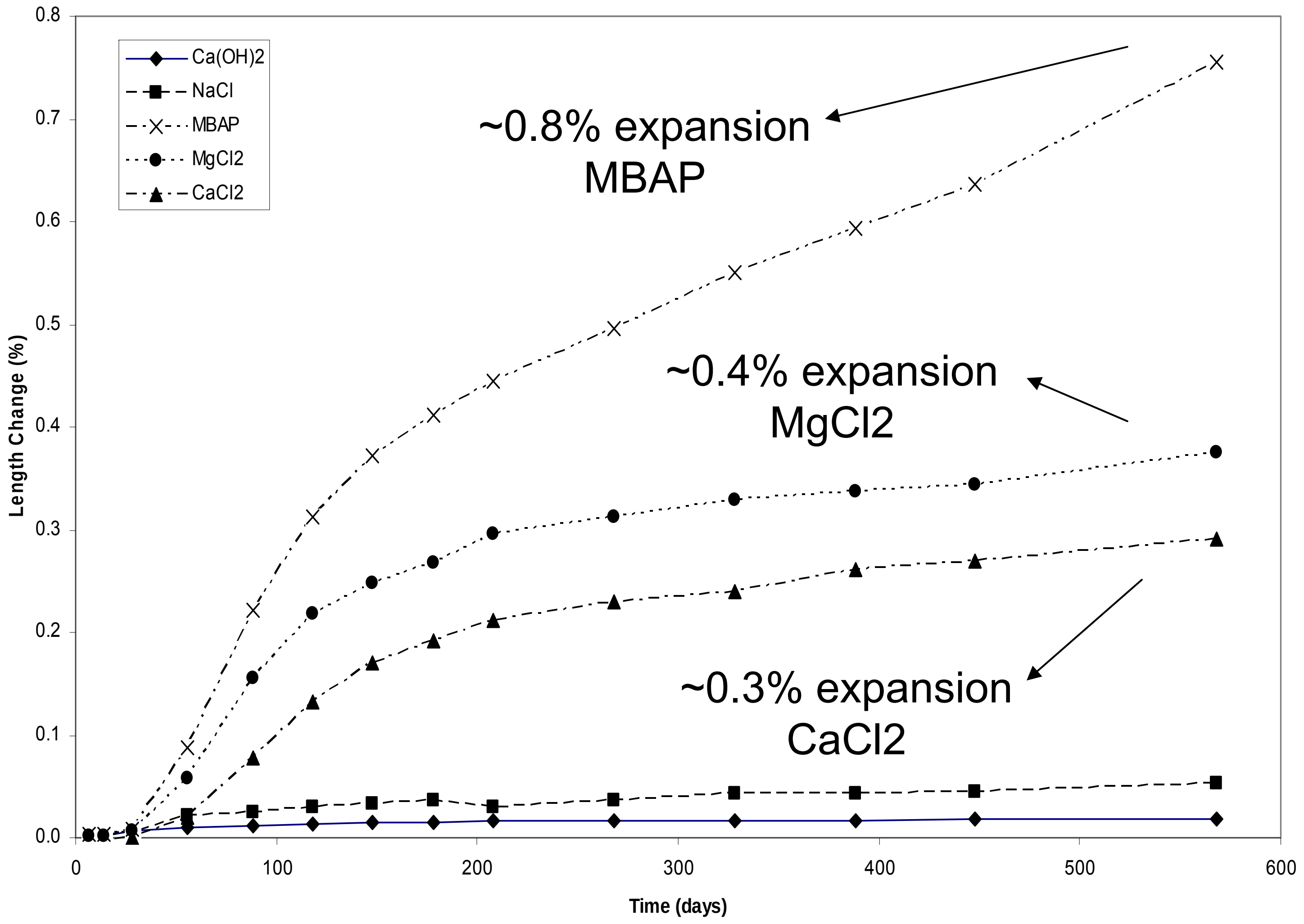
- Petrographic Analysis
  - Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from $CaCl_2$ solution immersed sample



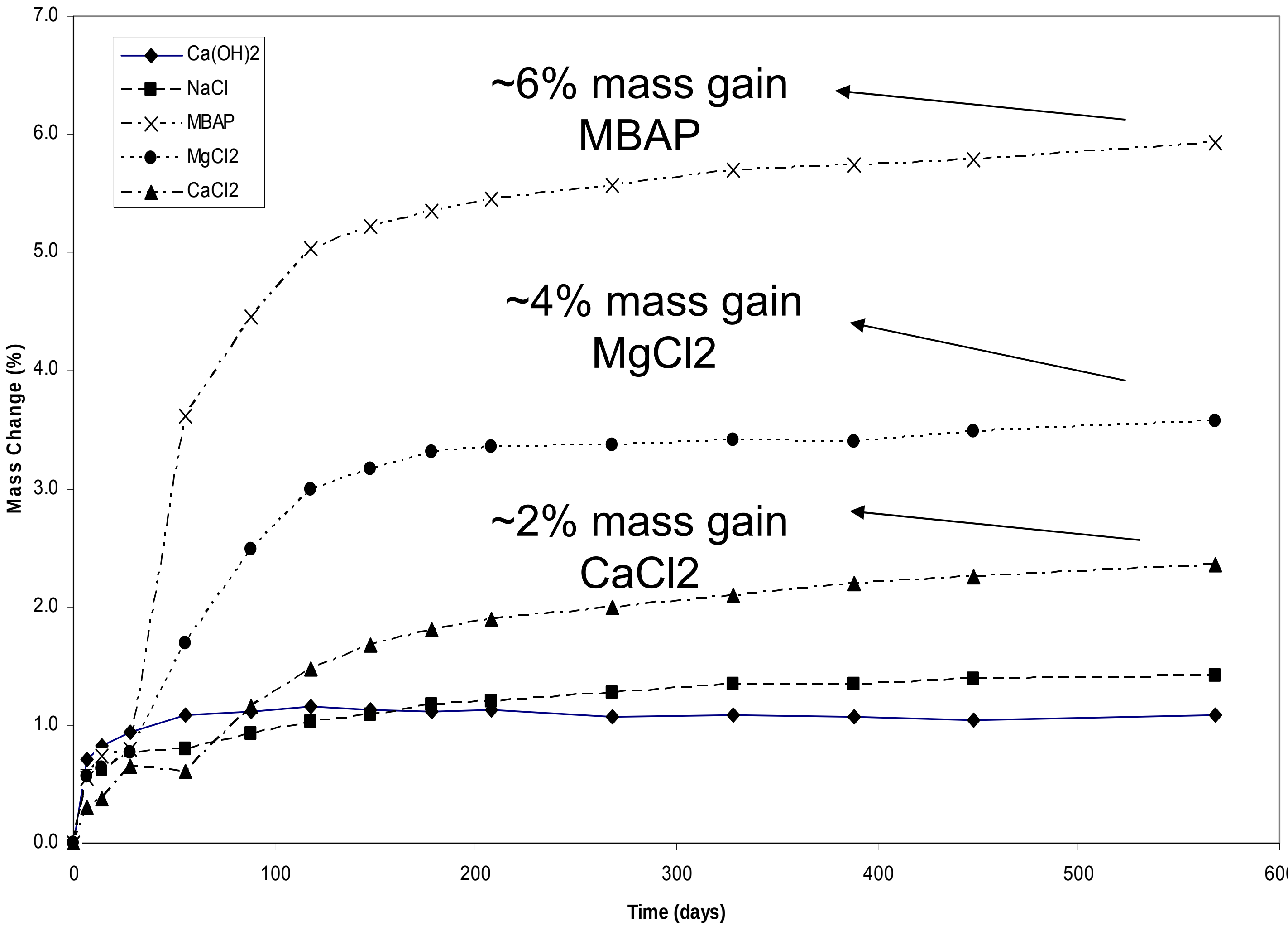
Compressive strength evolution with time of mortar cubes



Length change of mortar bars

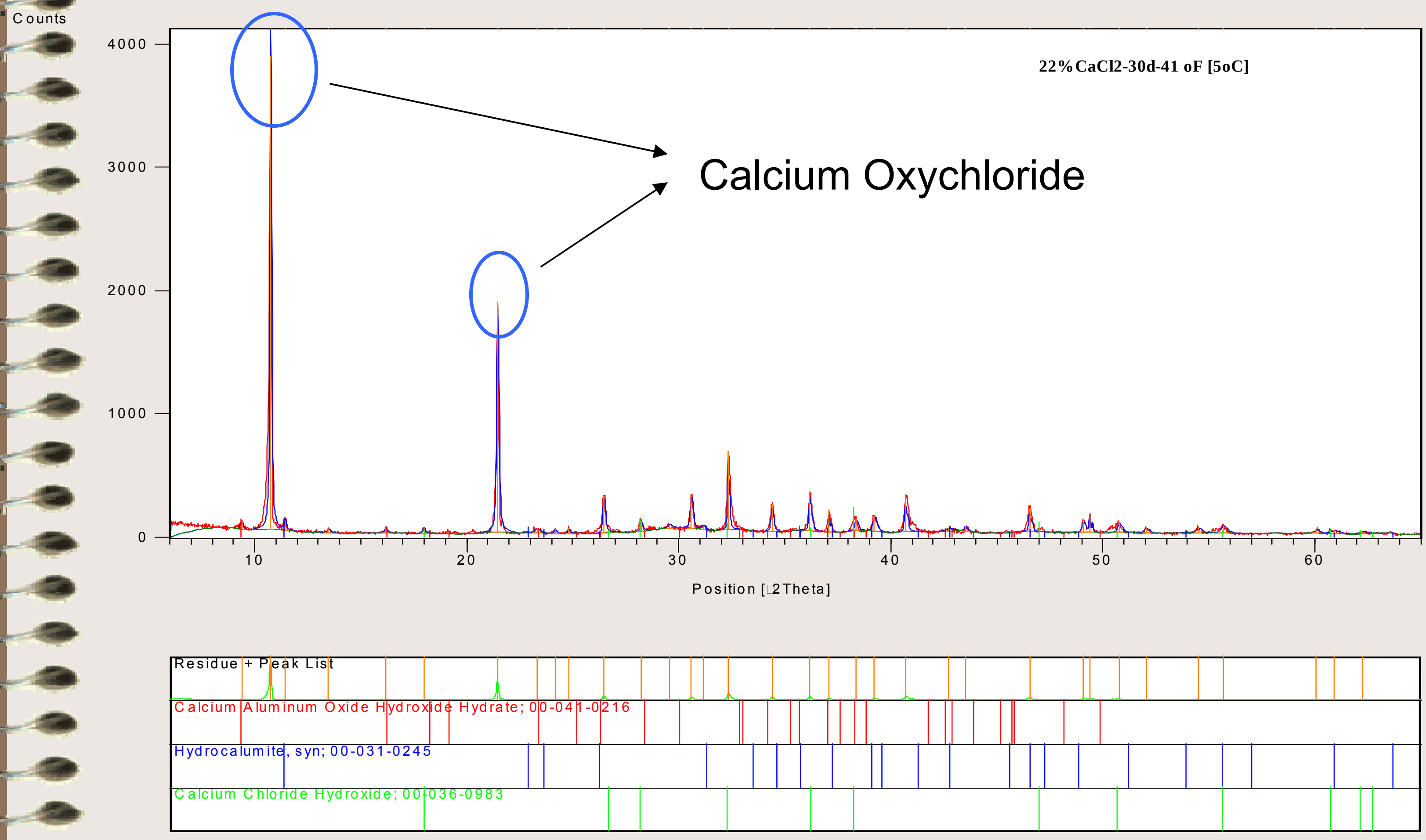


Mass change of mortar bars



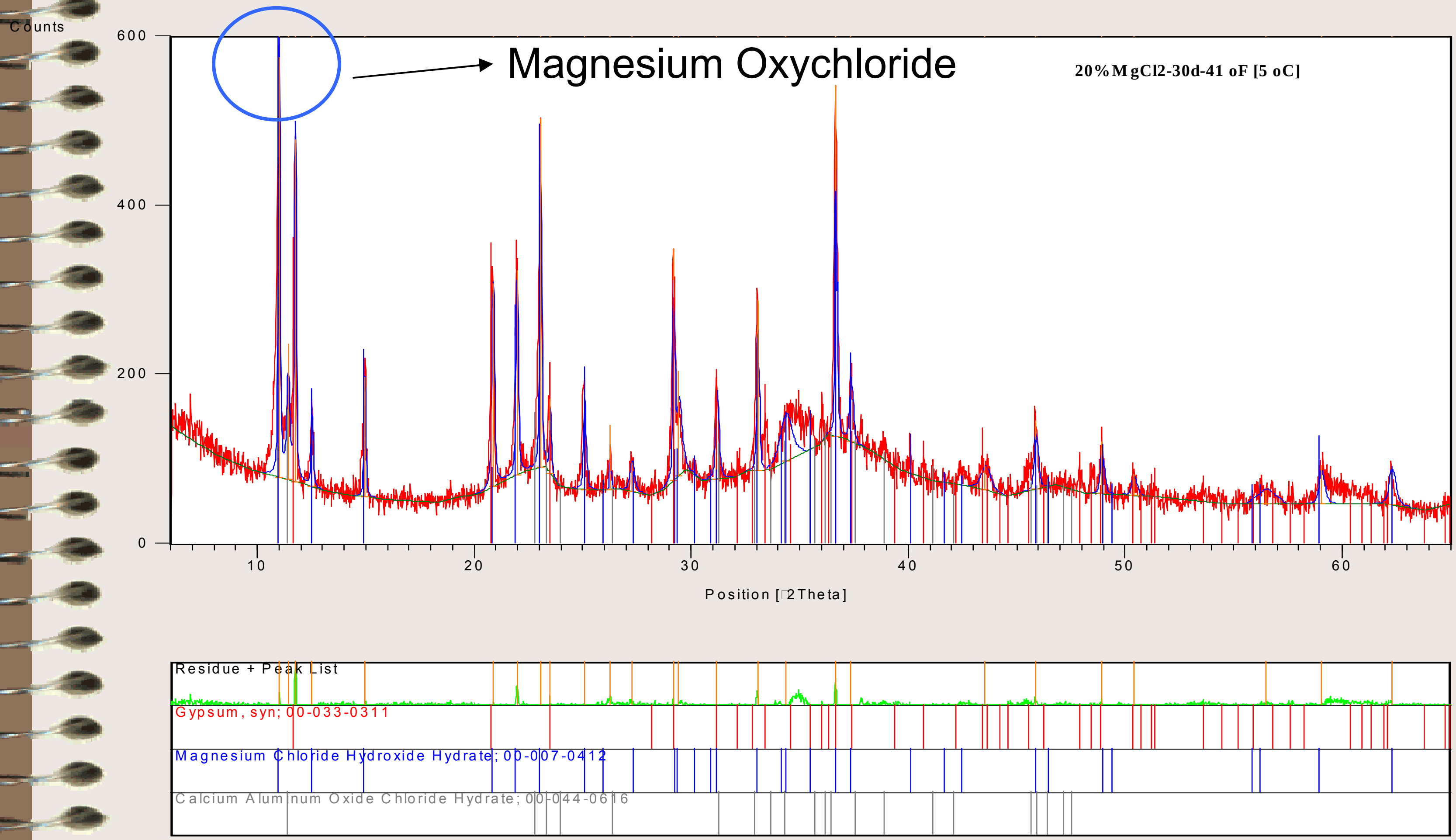
Mortar disc after 150 days of exposure to 28% $CaCl_2$ @5C

X-ray diffractogram for mortars exposed to 22% $CaCl_2$ – 30d @5C



Mortar disc after 150 days of exposure to 20% $MgCl_2$ @5C

X-ray diffractogram for mortars exposed to 20% $MgCl_2$ – 30d @5C

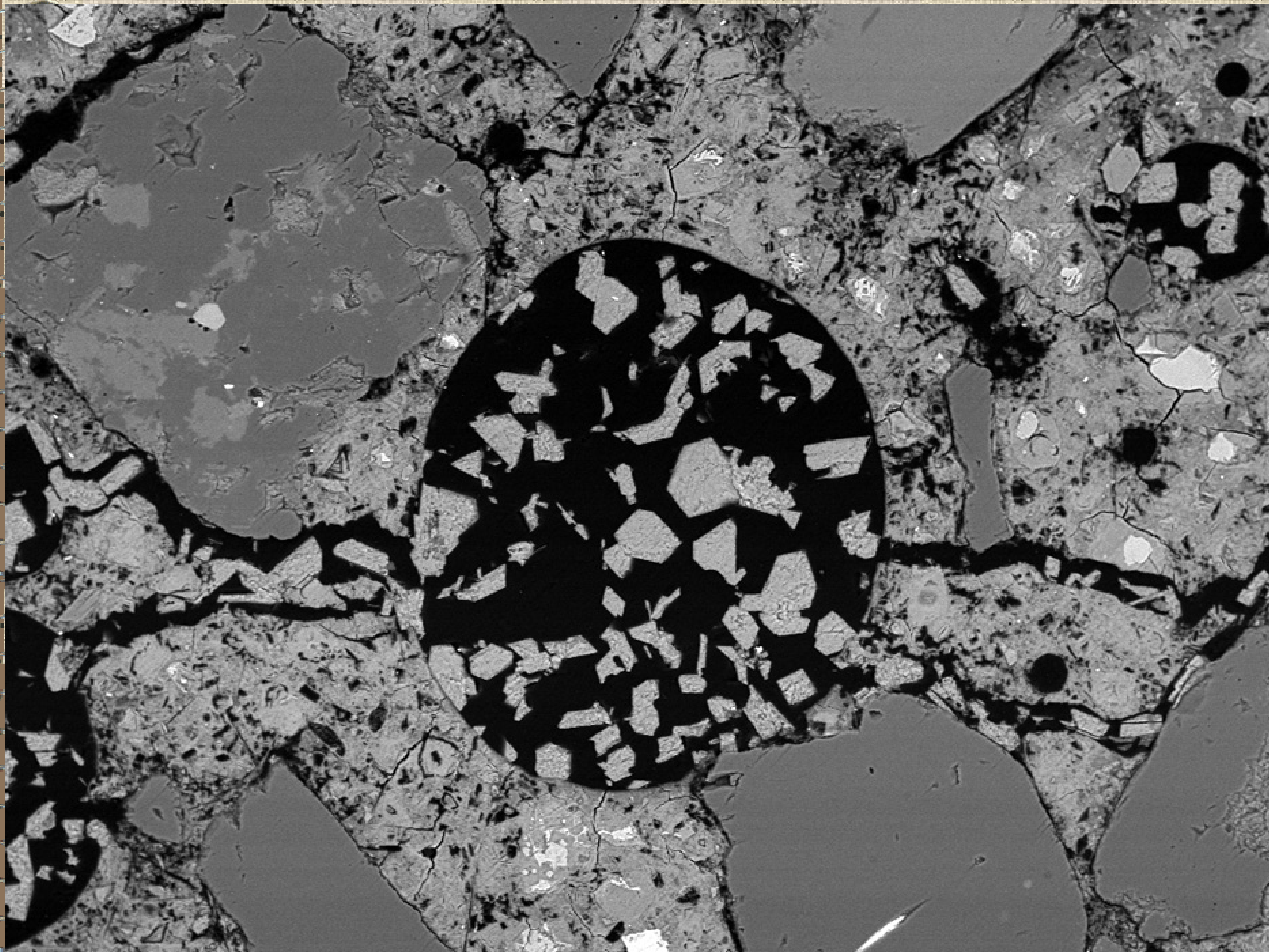


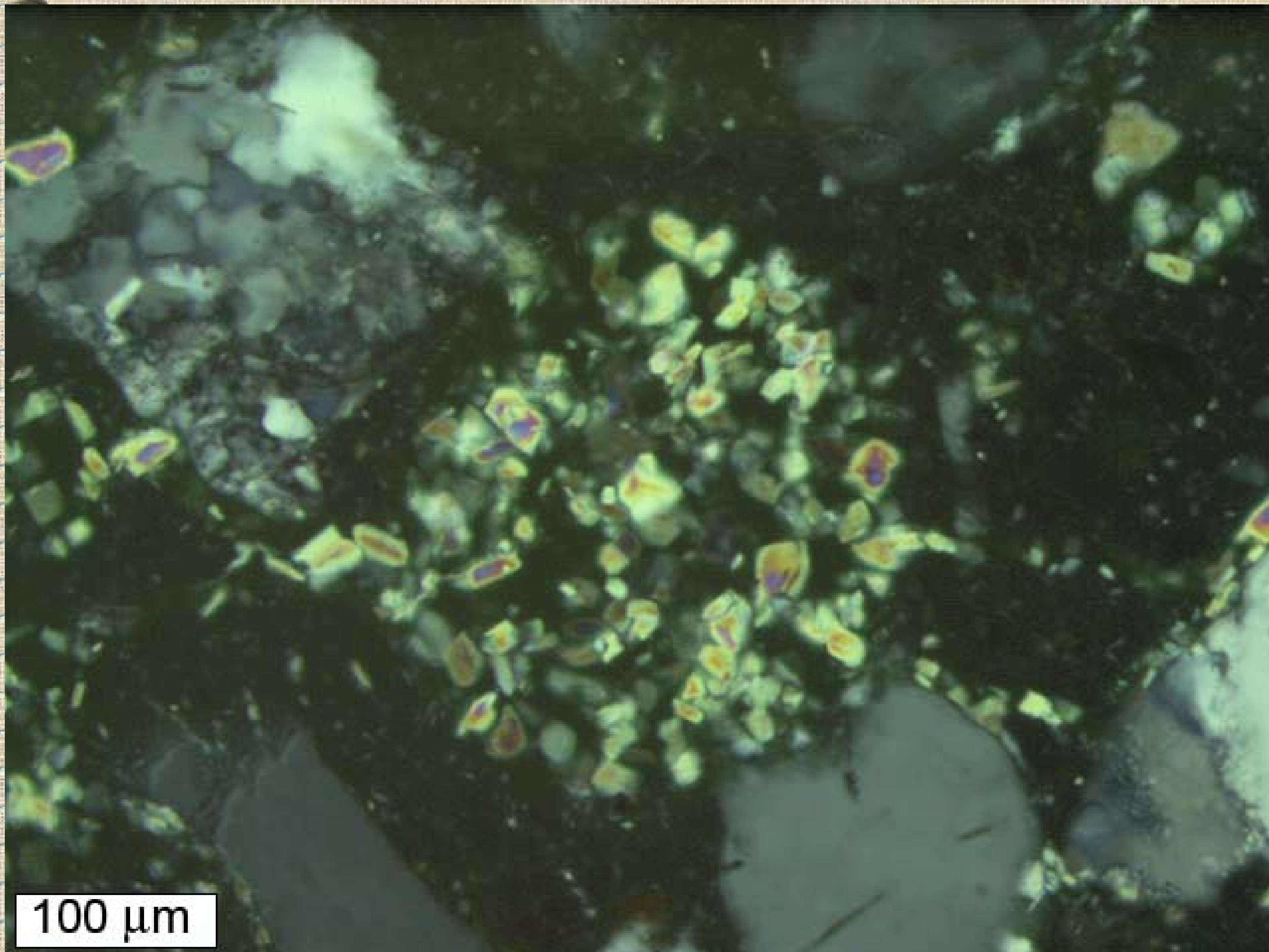
Laboratory Results - Phase II

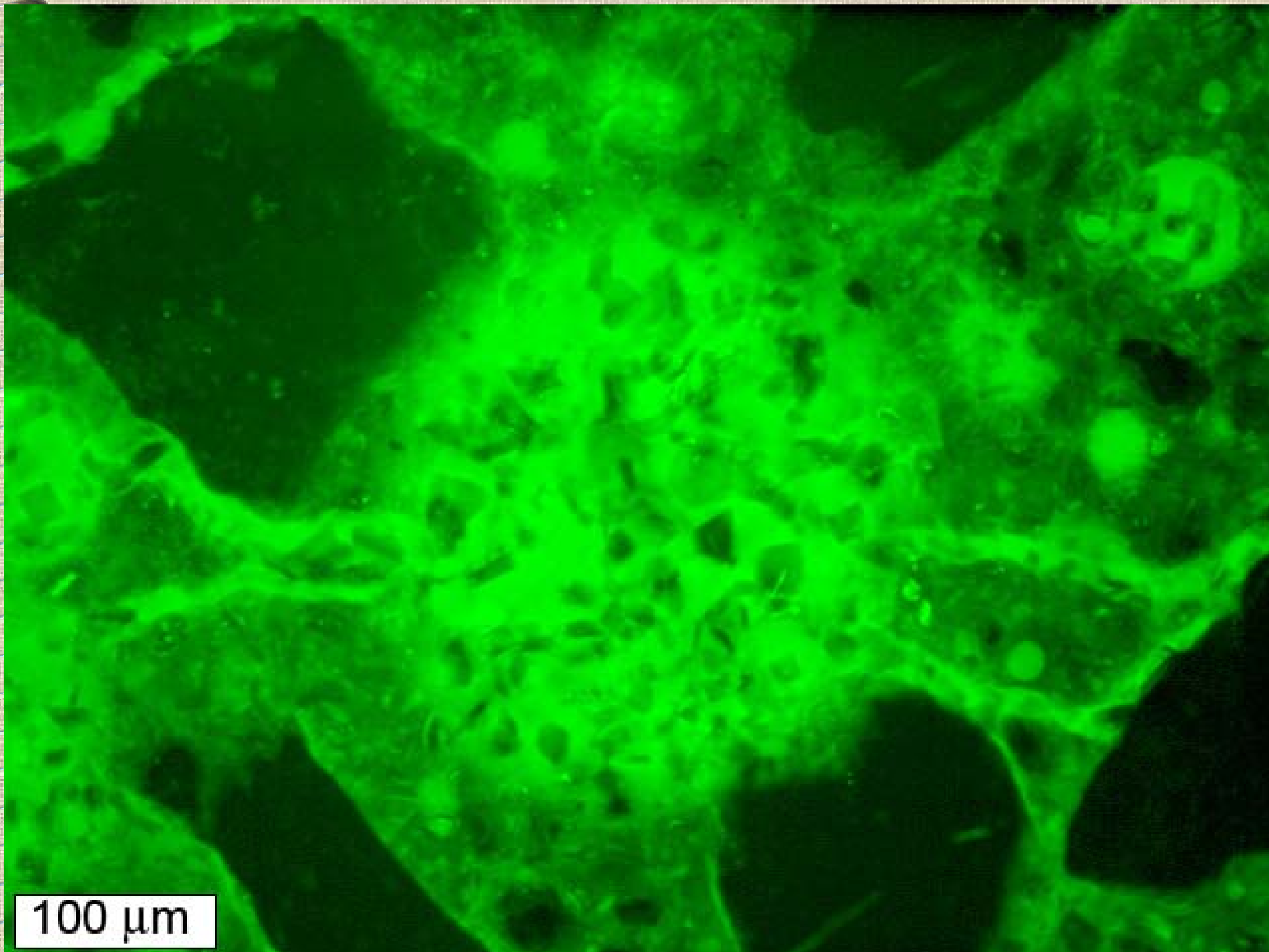
17% $CaCl_2$ – 500 days – 40 deg F

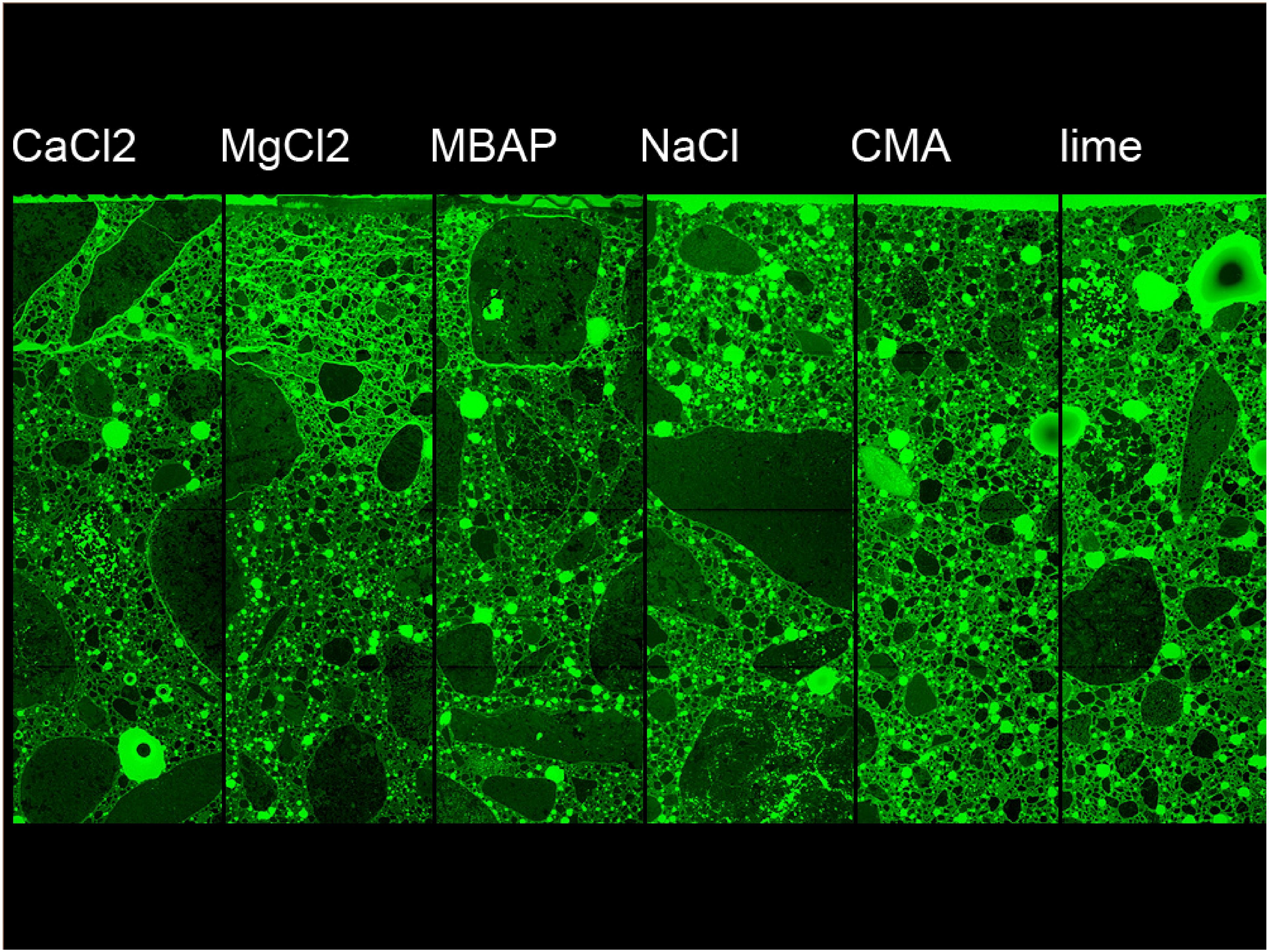
15% $MgCl_2$ – 500 days – 40 deg F

15% $MgCl_2$ MBAP – 500 days – 40 deg F

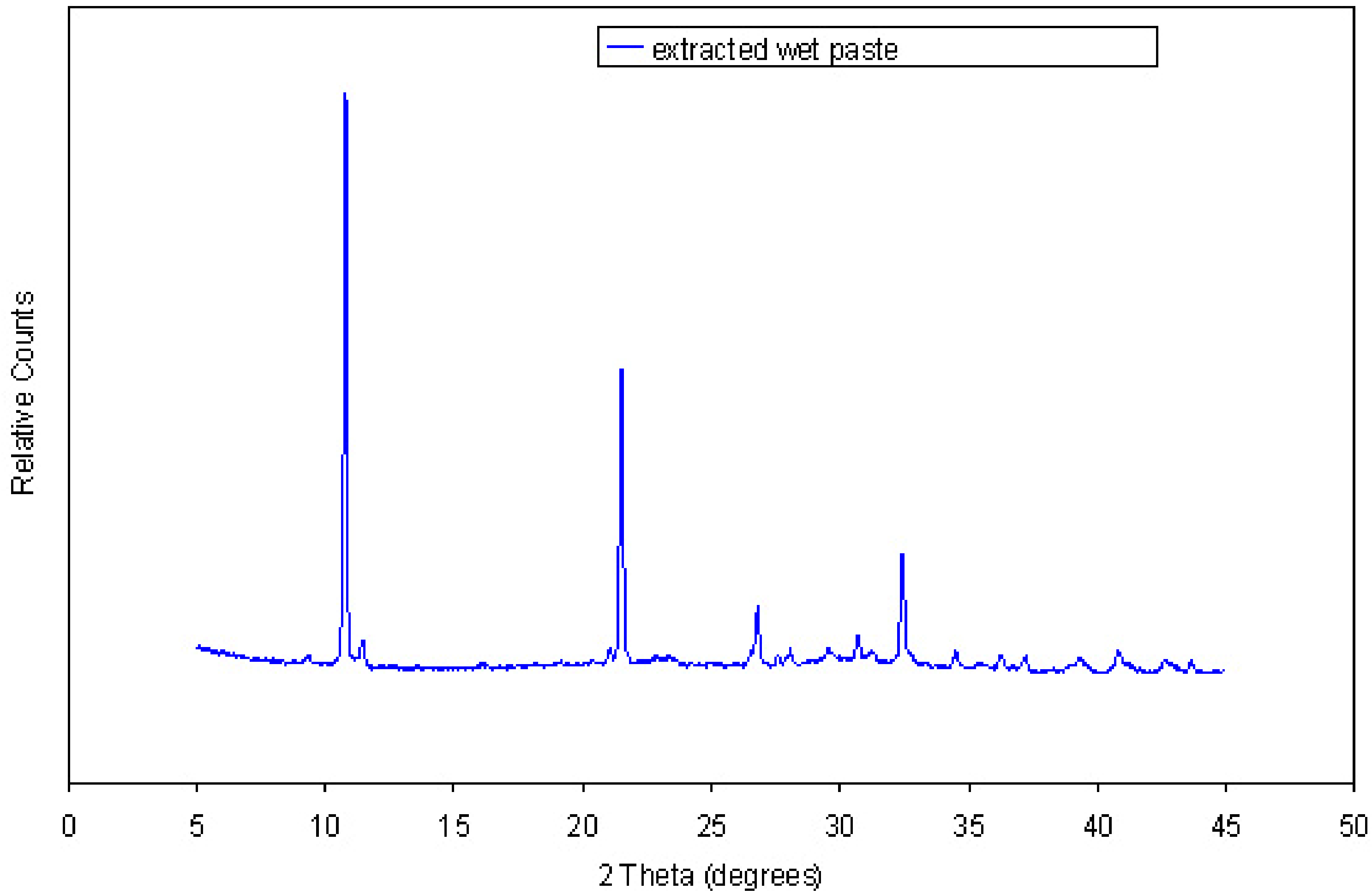


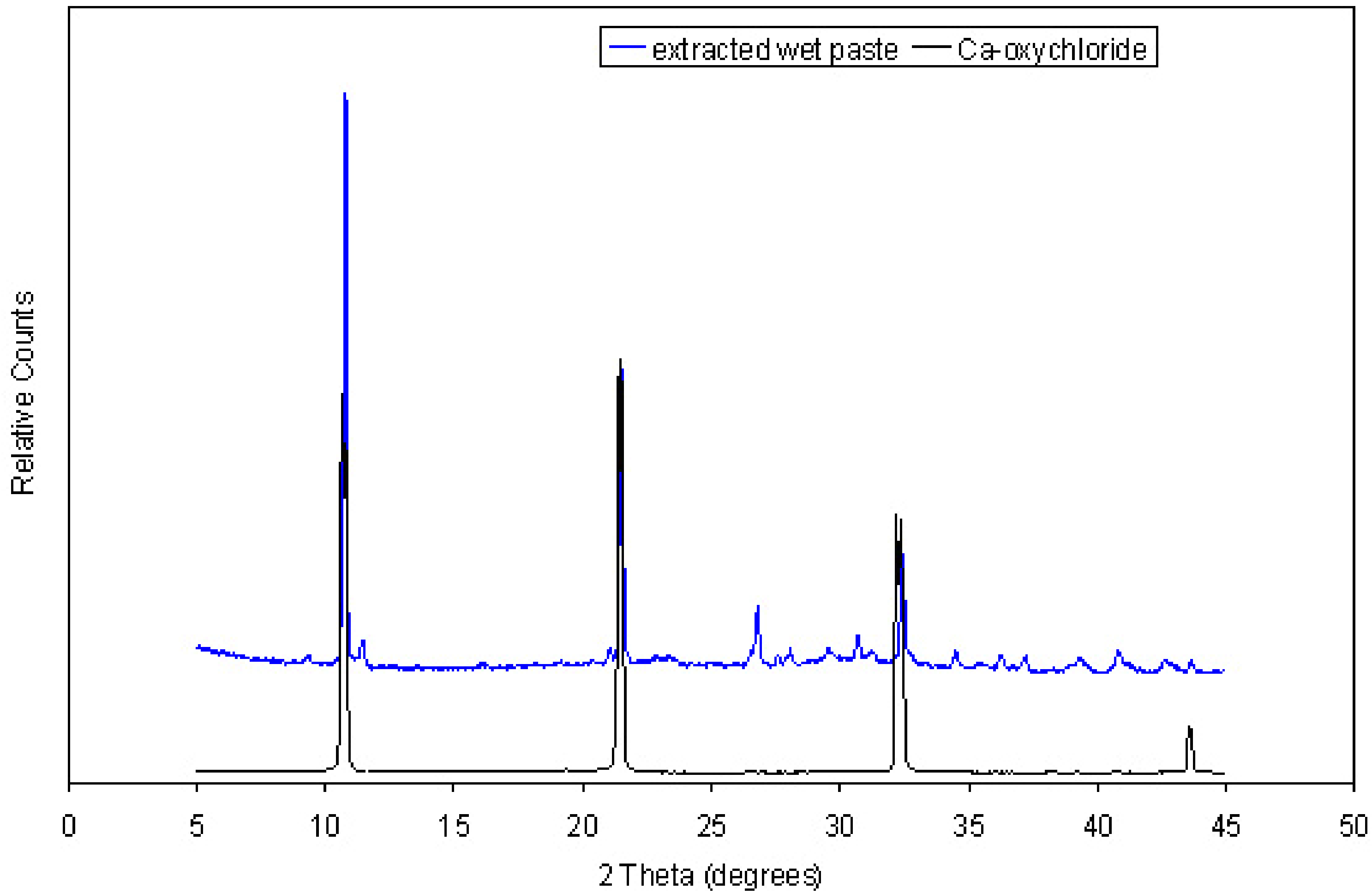

100 μm


100 μm



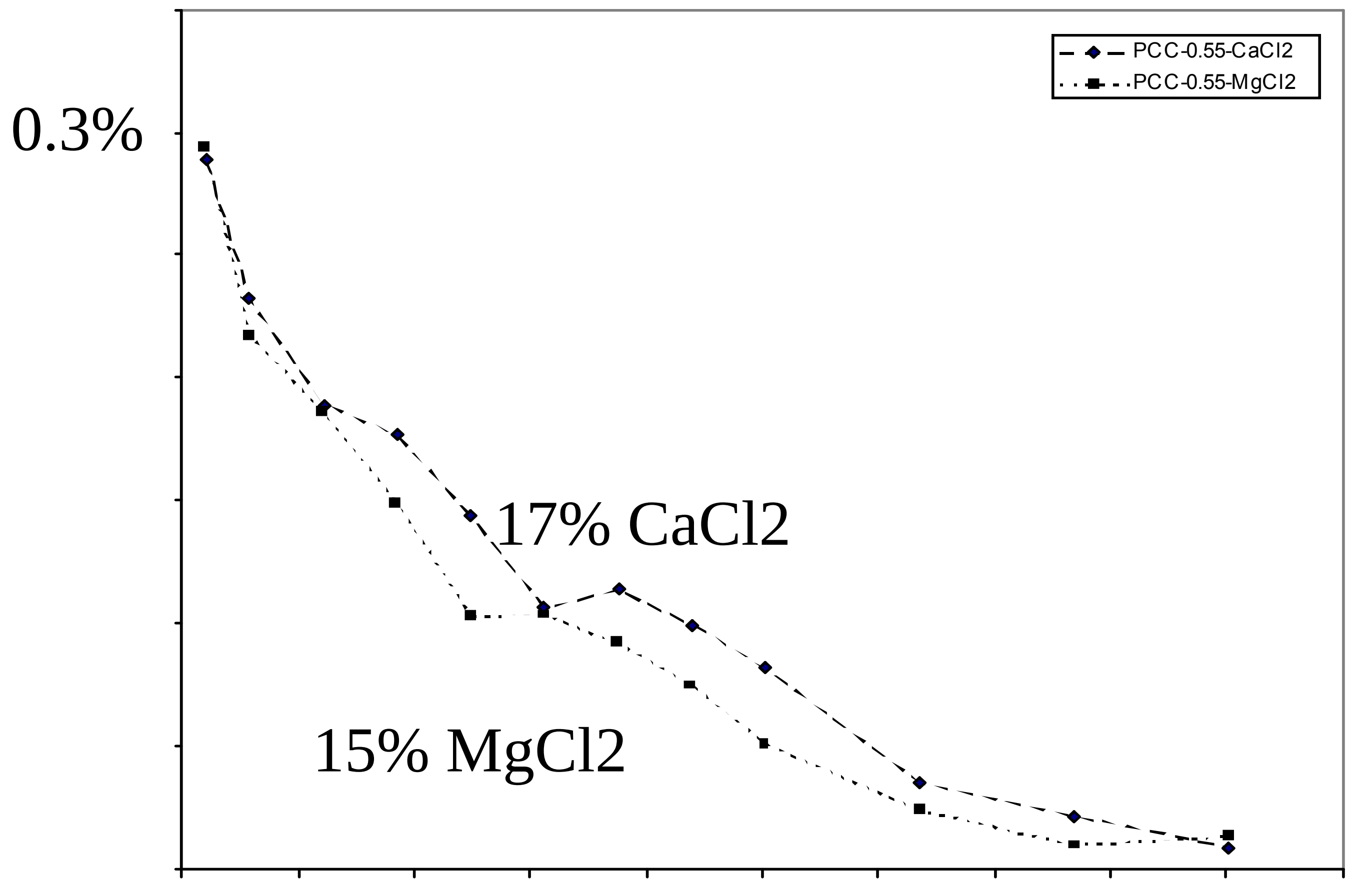
CaCl2
MgCl2
MBAP
NaCl
CMA
lime


extracted wet paste
Relative Counts
0
5
10
15
20
25
30
35
40
45
50
2 Theta (degrees)

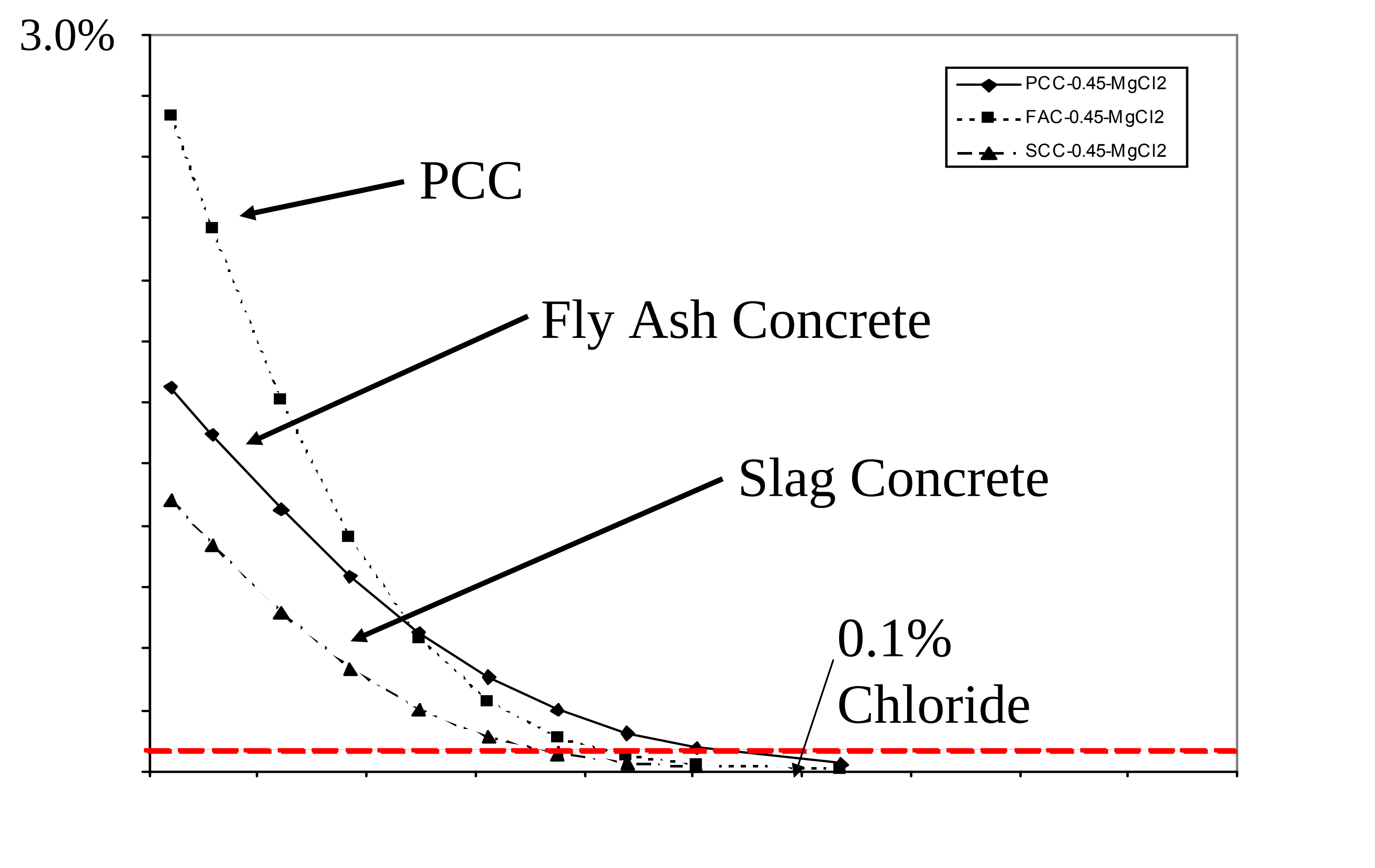


extracted wet paste
Ca-oxychloride
Relative Counts
0
5
10
15
20
25
30
35
40
45
50
2 Theta (degrees)

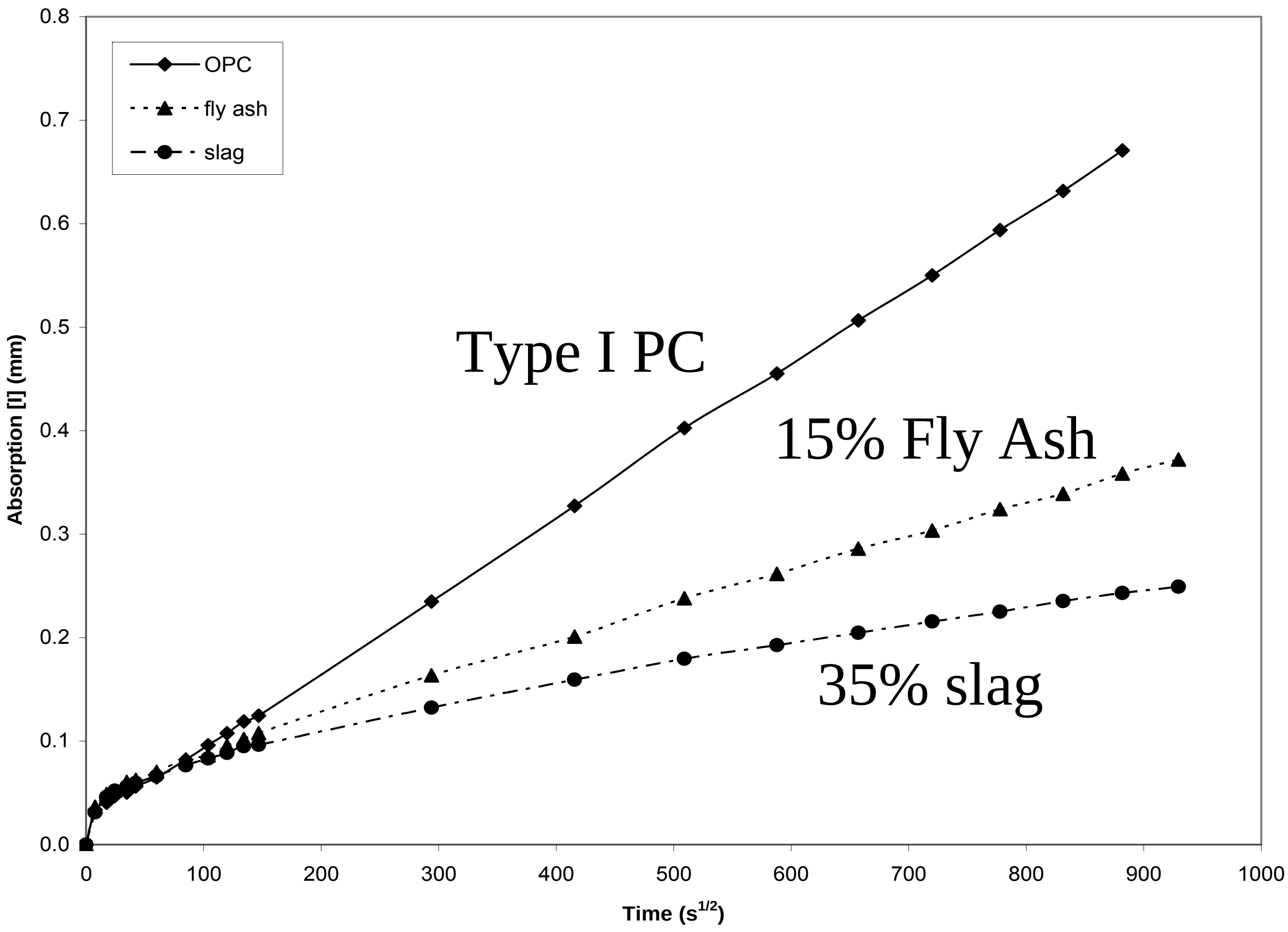
Silane Sealer Profiles



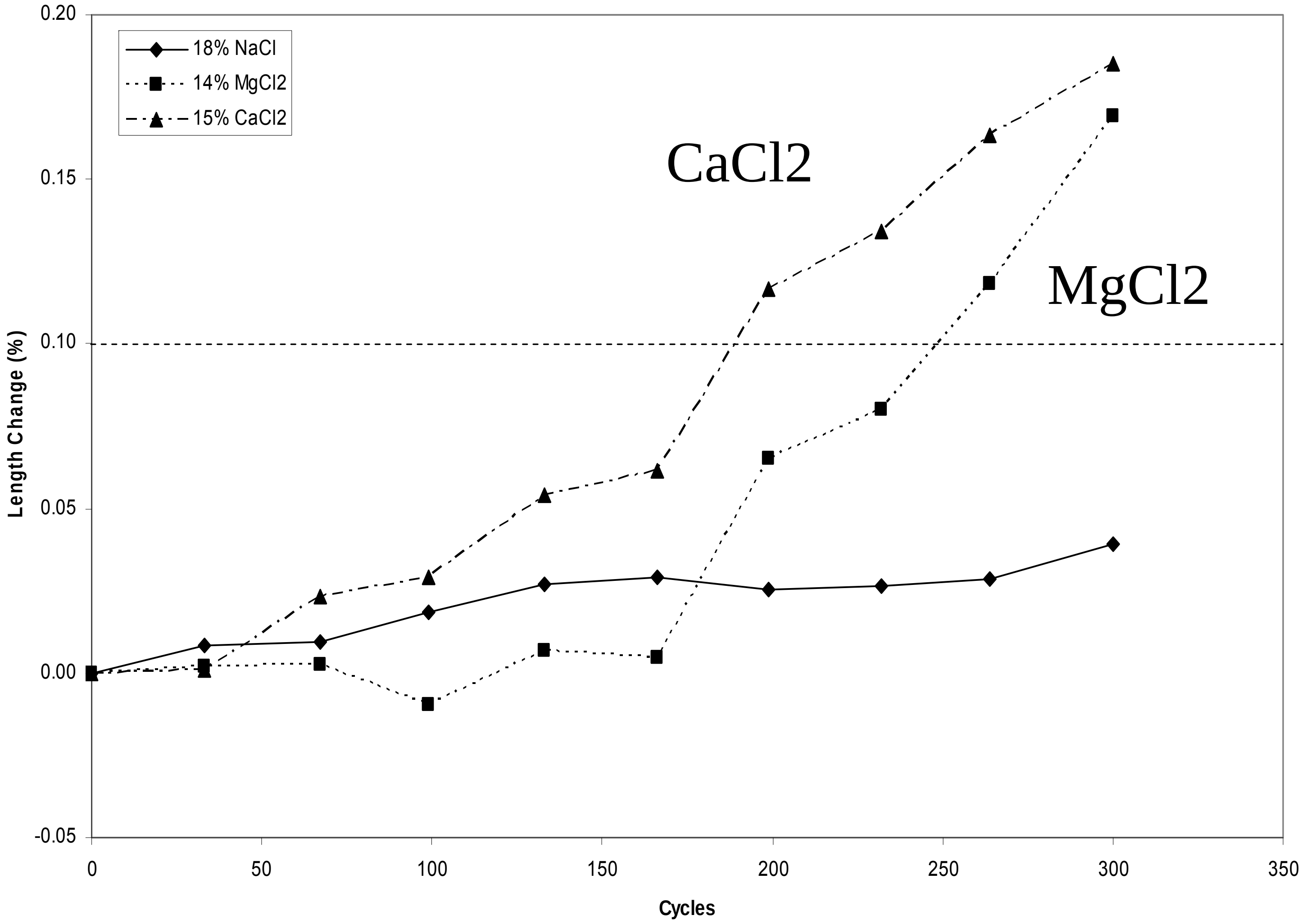
Typical Diffusion Profiles for 0.45 *w/c* Concrete Exposed to 15% $MgCl_2$ - PCC, 15% Fly Ash, 35% GGBFS Mixtures



Sorptivity of 15% $MgCl_2$ into 0.45 *w/c* Concrete Mixtures



Freeze Thaw Testing - Length change of concrete prisms

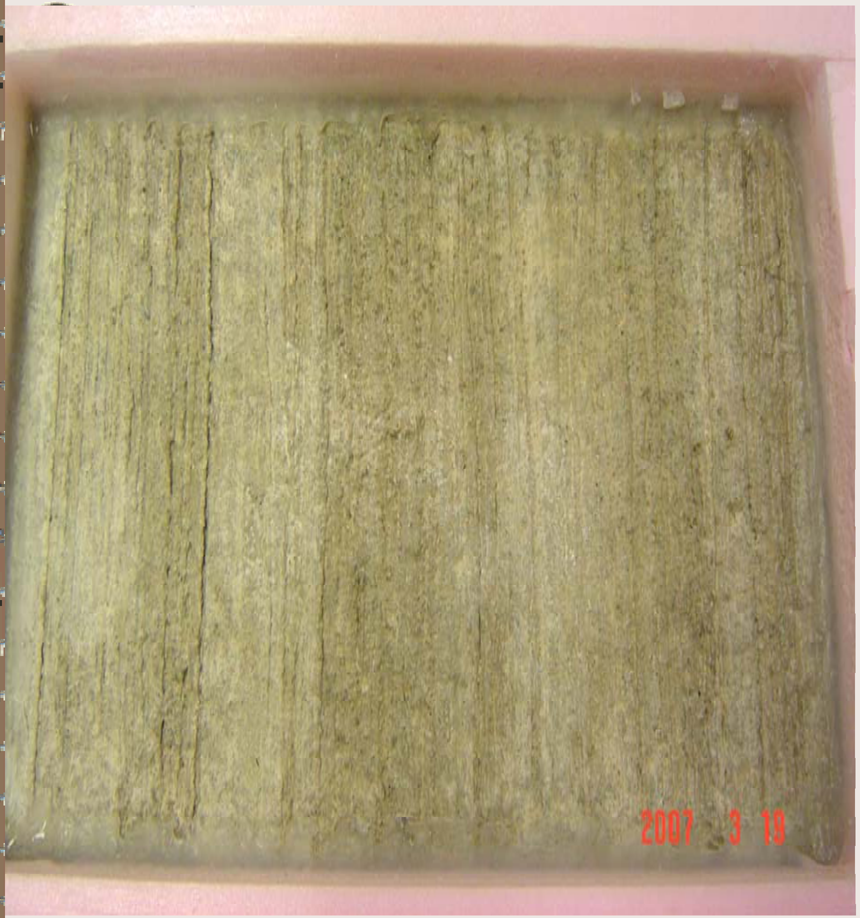


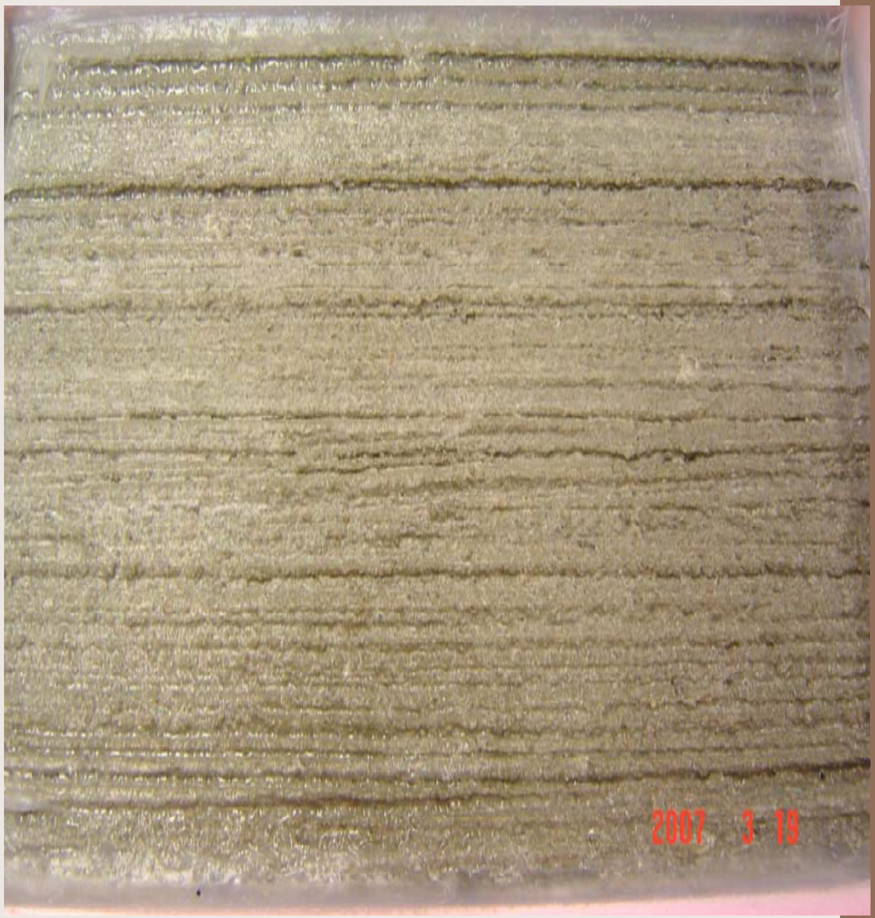
Concrete prisms subjected to 133 cycles of freeze/thaw cycles in 17% $CaCl_2$

Concrete prisms subjected to 133 cycles of freeze/thaw cycles in 15% $MgCl_2$

Concrete slabs at cycle 0

Pre-exposed to high concentration 1 year - scaling test at low concentration





23% NaCl + 3% NaCl

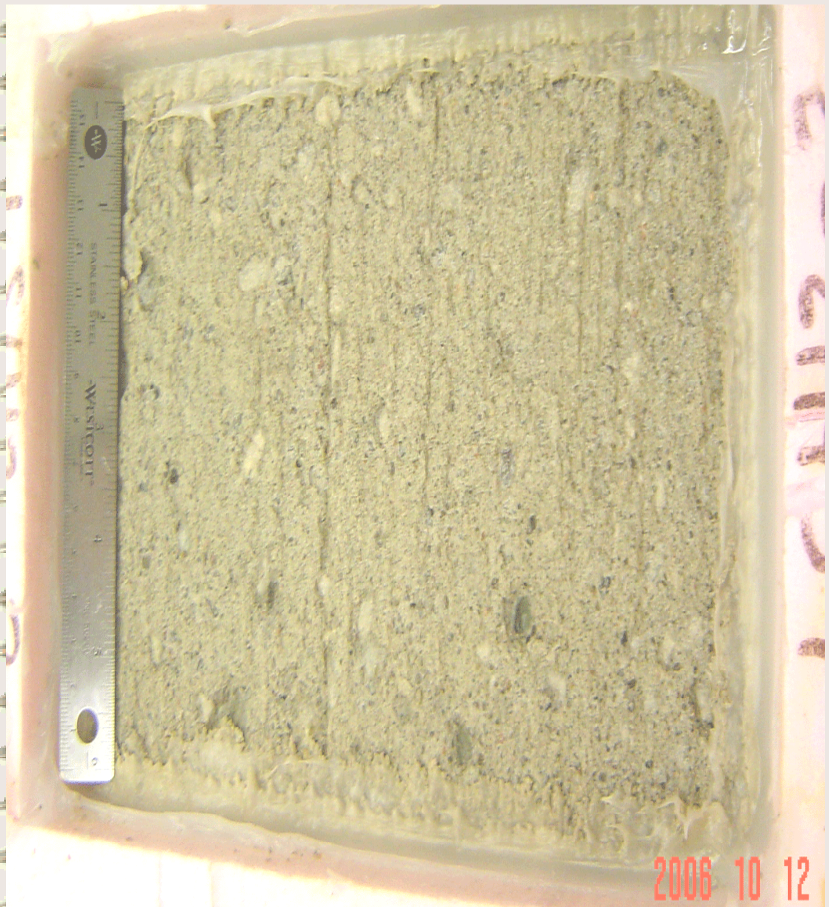
22% $CaCl_2$ + 4% $CaCl_2$

Concrete slabs at cycle 50

23% NaCl + 3% NaCl

22% $CaCl_2$ + 4% $CaCl_2$

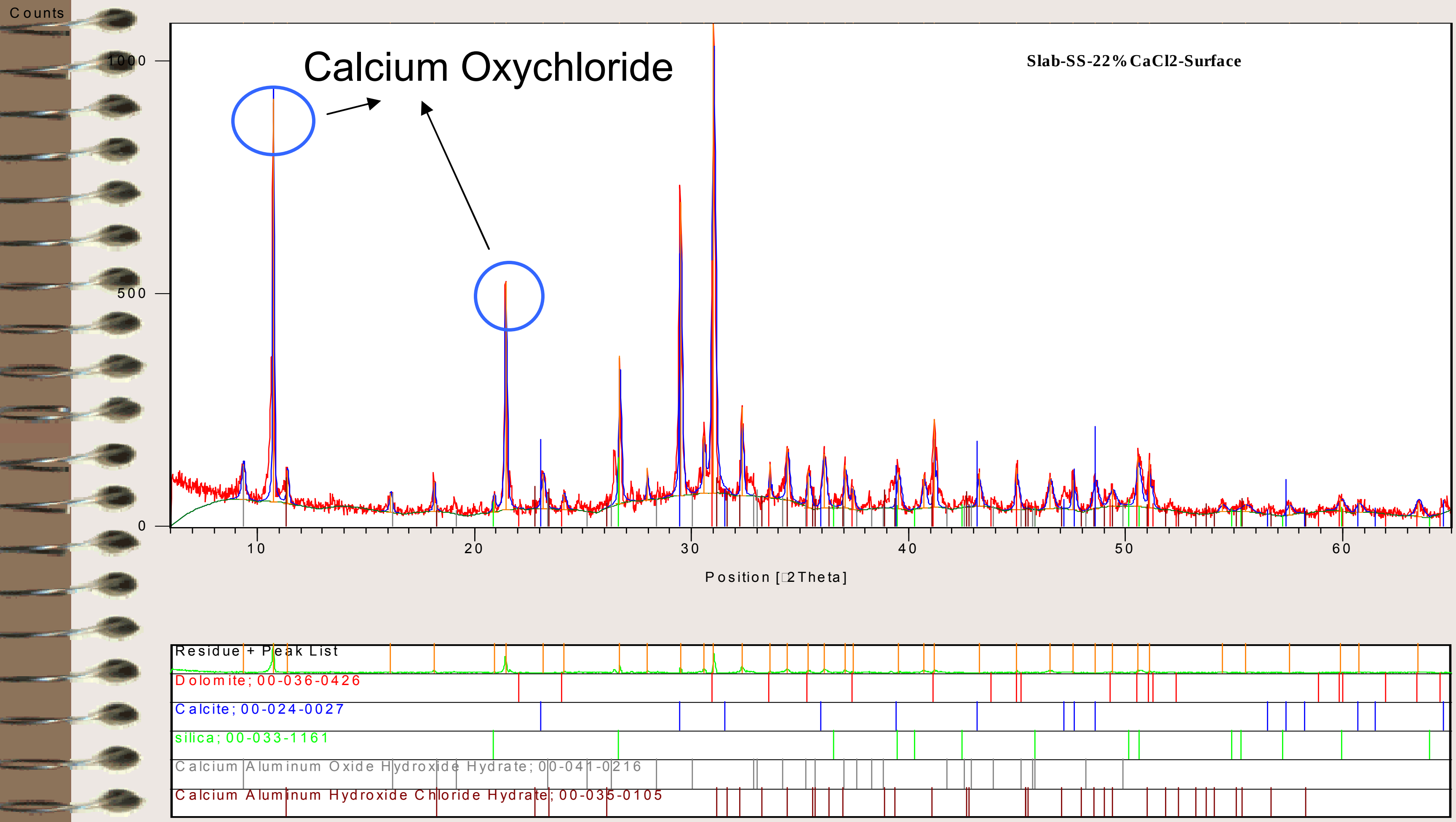
Concrete slabs at cycle 100



23% NaCl + 3% NaCl

22% $CaCl_2$ + 4% $CaCl_2$

X-ray diffractogram for surface of concrete slab exposed to 22% $CaCl_2$ for 1 year



Conclusions

- $MgCl_2$, $CaCl_2$, and proprietary deicers containing $MgCl_2$ cause expansion, cracking, and loss of strength for concrete and mortars exposed at 40 ºF
- NaCl caused no observed distress to concrete, however it is known to be detrimental to reinforcing steel in concrete
- Results for CMA were mixed, in some tests causing degradation but not in others

Conclusions

- Of the deicers tested, $MgCl_2$ caused the highest amount of expansion and strength loss
- $CaCl_2$ caused the most visible damage in the shortest time
- In the tests performed, NaCl caused no observed strength loss or expansion
- Pessimum concentration determined for $MgCl_2$ was 20% and for $CaCl_2$ it was 22%

Conclusions

- $MgCl_2$ and $CaCl_2$ exposed specimens exhibited unacceptable expansion and change in dynamic modulus in freeze-thaw testing
  - Cyclic freeze-thaw exposure exacerbates the damage caused by these deicers
- In all cases, the mechanism of failure is the formation of oxychloride phases by the interaction of the deicer with calcium hydroxide in the hardened cement paste

Conclusions

- Concrete mixtures prepared with ground blast furnace slag or fly ash as a portland cement replacement <u>performed significantly better</u> in tests as compared to concrete prepared with portland cement only
- <u>Silane and siloxane sealants</u> both <u>improved</u> the <u>performance</u> of concrete exposed to deicing chemicals
- Sealants are a good maintenance strategy but need to be reapplied every 3-5 years in order to remain effective

Questions

- How quickly will distress occur in “real-world” applications?
  - Exact concentration of deicers, as applied, varies
    - Concentration varies
    - Application rates
  - Deicers are <u>diluted by weather events</u> (positive)
  - When deicers are applied in an anti-icing strategy, high concentration solutions are presented to the concrete and if the weather doesn’t occur <u>no dilution</u> results (negative)

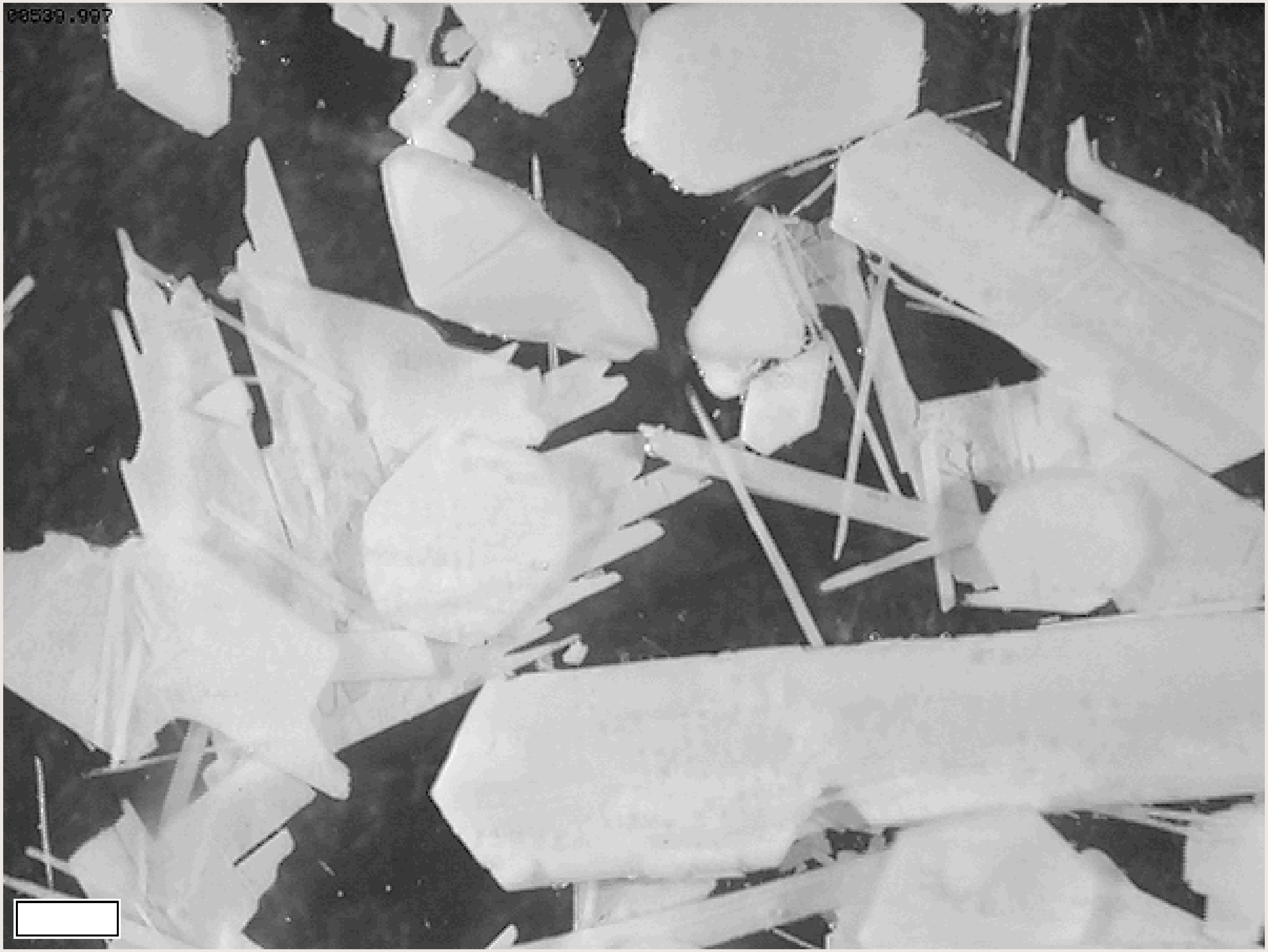
Questions

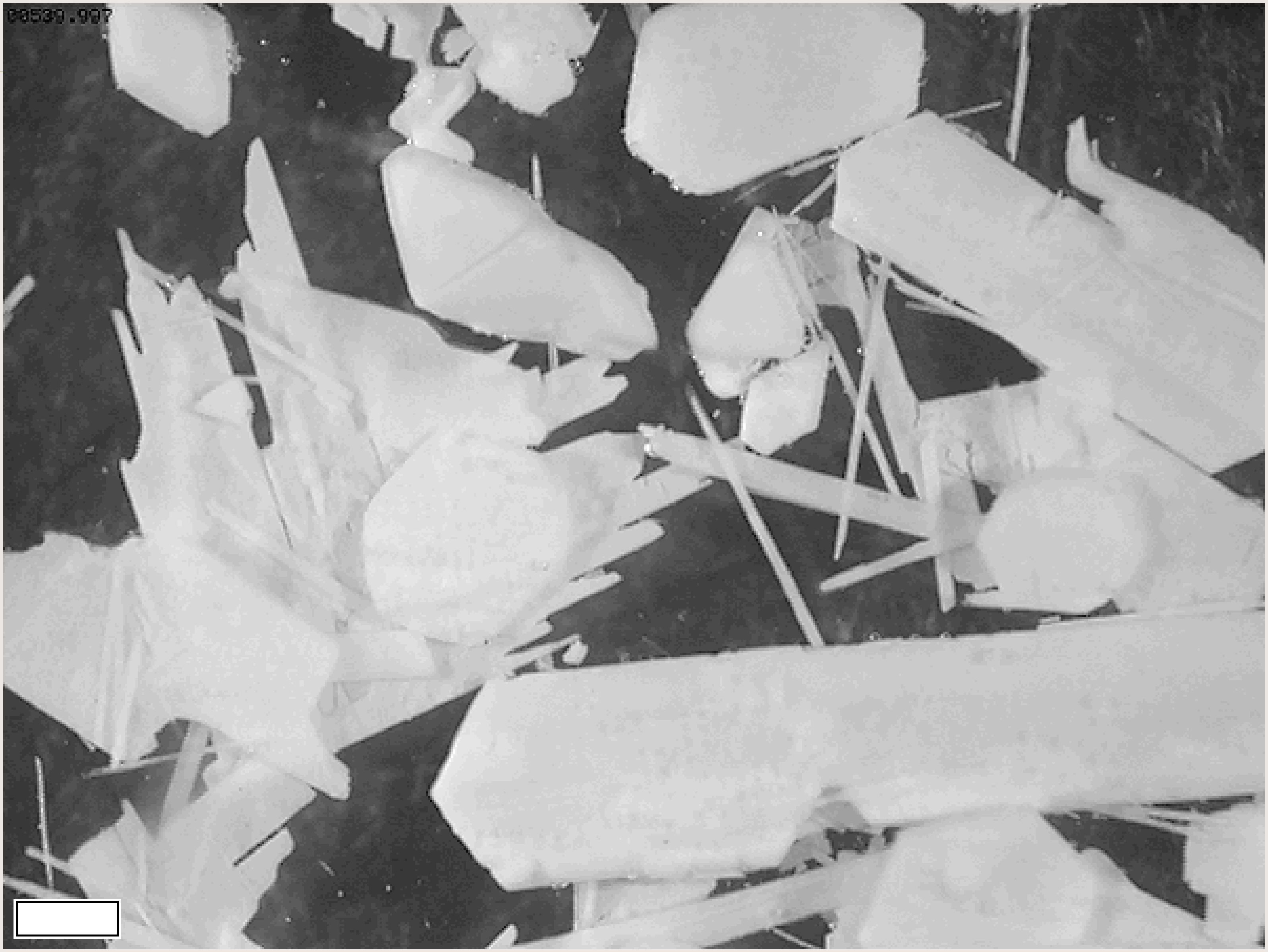
- What is the relationship between field observations and laboratory observations?
  - Field distress, in some cases resembles laboratory distress (positive)
  - Oxychloride phases were not seen in field samples. Why?
    - Oxychloride phases are very unstable and can alter between various states of hydration
    - Oxychloride phases can revert to other phases (e.g. calcite) which <u>ARE</u> seen in field cores

Montana, eastbound Interstate Highway 90 bridge deck, near milepost 61.8, Tarkio interchange

Laboratory tests confirmed that oxychloride phases quickly convert to calcite ($CaC0_3$- or calcium carbonate) when exposed to atmosphere in the presence of water

Calcite Deposits


00539.997


00539.997

Future Work

- Determine life-cycle impact of deicers

Future Work

- Determine life-cycle impact of deicers

Future Work

- Determine life-cycle impact of deicers

Future Work

- Other suggested areas for additional research include:
  - Further testing to determine the effect of different replacement levels of SCMs on the resistance of concrete to deicers
  - A detailed experiment to determine the effects of *w/c* on deicer related distress
  - A study of highway deicer chemical contributions to alkali-silica reaction (ASR)
  - Further testing to better understand field reports of scaling related to use of $MgCl_2$ and $CaCl_2$