Assessment of the Potential for Phosphate Ion-Concrete Interactions

Dan J. Naus*

Les R. Dole**

Catherine H. Mattus**

***Metals and Ceramics Division**

****Nuclear Science & Technology Division**

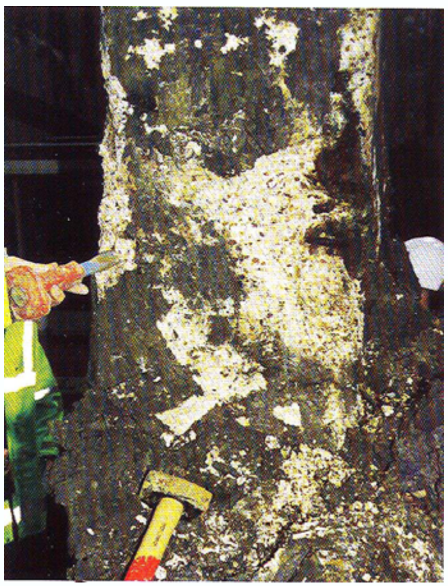
Oak Ridge National Laboratory

Presentation Outline

- **Background**
- **Objective and Approach**
- **Primary Deliverables**
- **Literature Review**
- **Contacts with Researchers**
- **Design of Experiment**
- **12-Month Test Results**
- **Preliminary Conclusions**
- **Primer on Concrete Durability**

- Background

Portland Cement Concretes Located in Soils can be Susceptible to Chemical Attack

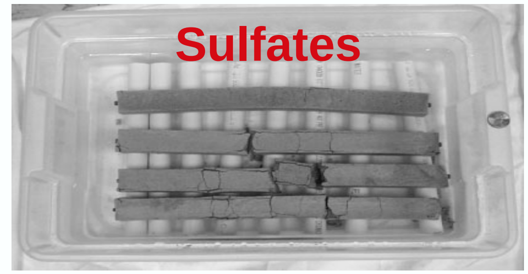


Sulfate attack of 30-year-old bridge sub-structure

- **Sulfate attack - sulfate ions attack C_3A to form ettringite and gypsum that can expand to disrupt concrete**
- **Acid attack - carbonic, humic, and sulfuric acids can cause dissolution the cement paste matrix**
- **Salts**
  - **Magnesium - replace calcium in C-S-H leading to loss of binding properties**
  - **Ammonium - form soluble salts that are leached away**
  - **Chloride ions - surface scaling due to salt crystallization**
- **Organic compounds - react with calcium hydroxide to produce physical expansion**
- **Aggressive CO_2, pure water, salt crystallization, and microbial**

Potential Degradation of RC Structures Due to Chloride and Sulfate Ions has Resulted in Building Codes Establishing Exposure Limits

Corrosion of steel reinforcement in bridge superstructure



TDOT study at Univ. Texas 0.352 molar, 5% $NaSO_4$ soln.

Type of member	Maximum water soluble Cl^- in concrete, % by wt. cement
Prestressed concrete	0.06
RC exposed to chloride in service	0.15
RC that will be dry and protected from moisture	1.00
Other RC construction	0.30

Sulfate Exposure*	Water soluble SO_4 in soil, % by wt.	SO_4 in water, ppm
Negligible	0.00-0.10	0-150
Moderate	0.10-0.20	150-1500
Severe	0.20-2.00	1500-10,000
Very severe	Over 2.00	Over 10,000

*Also Maximum, w/c, minimum strength, and cement type req'ts.

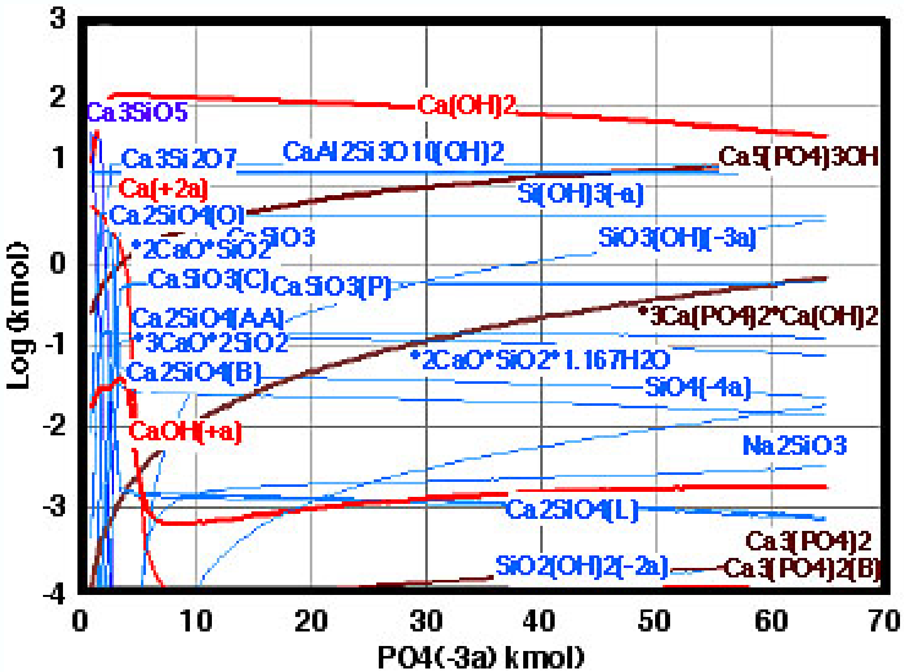
If $Ca(OH)_2$ in Pore Structure were Converted into Apatite (Hydroxyapatite) Due to Presence of Phosphates, Concrete Decrepitation Might be Possible

- **Dr. Powers found that phosphate concentration necessary for apatite formation is relatively low ($P_t = 1.52 \times 10^{-17}$ moles/kg H_2O)**

Phosphate replacement of $Ca(OH)_2$ in OPC [$5Ca(OH)_2 + 3PO_4(-3a) = Ca_5(PO4)_3OH + 9(OH)(-a)$]					
T (˚C)	ΔH (kcal)	ΔS (cal/K)	ΔG (kcal)	K	Log K
0	-7.725	127.84	-42.64	1.33E+34	34.122
20	-7.391	129	-45.21	5.08E+33	33.706
40	-6.563	131.73	-47.81	2.36E+33	33.372
60	-5.497	135.02	-50.48	1.31E+33	33.118
80	-4.271	138.6	-53.22	8.63E+32	32.936
Formula	FM (g.mol)	Conc. (wt, %)	Amt. (mol)	Amt. (g)	Vol (l or ml)
$Ca(OH)_2$	74.095	56.527	5	370.473	165.39
PO4(-3a)	94.971	43.473	3	284.914	0
$Ca_5(PO4)_3OH$	502.32	76.645	1	502.321	159.98
OH(-a)	17.007	23.355	9	153.066	0
Thermodynamic database in Outokumpu's HSC Chemistry V5.11 Code					Volume change = -3.3%

Phases in OPC that Form Under Increasing Exposure to Phosphate

Equilibrium Phases for an OPC that is Inundated with Phosphate Ions

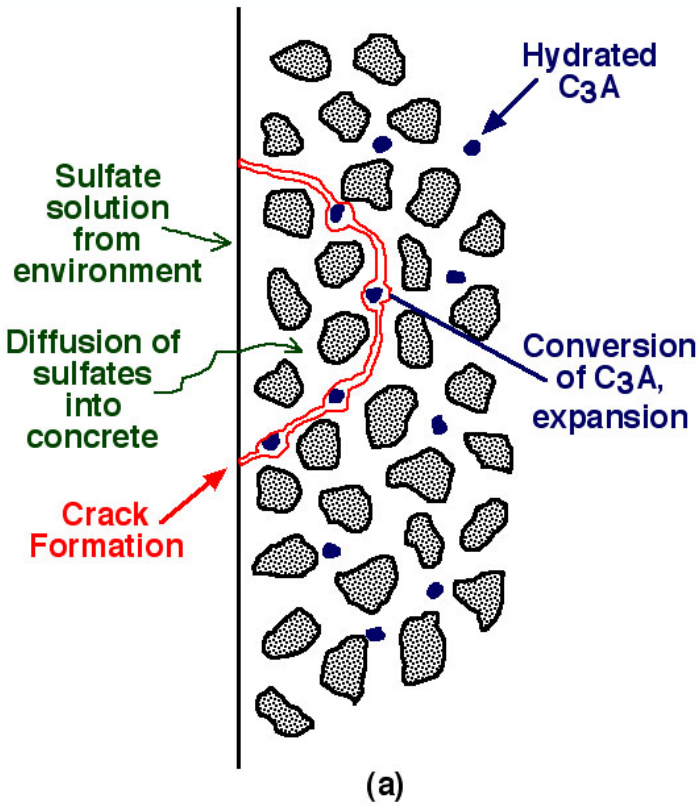


Ca(OH)2 phases, **Aluminosilcate phases**, **Phosphate phases**

In an OPC system the formation of calcium hydroxyapatite is capable of replacing the free calcium (Portlandite) and successfully competes for calcium in aluminosilicate matrices

- Objective and Approach

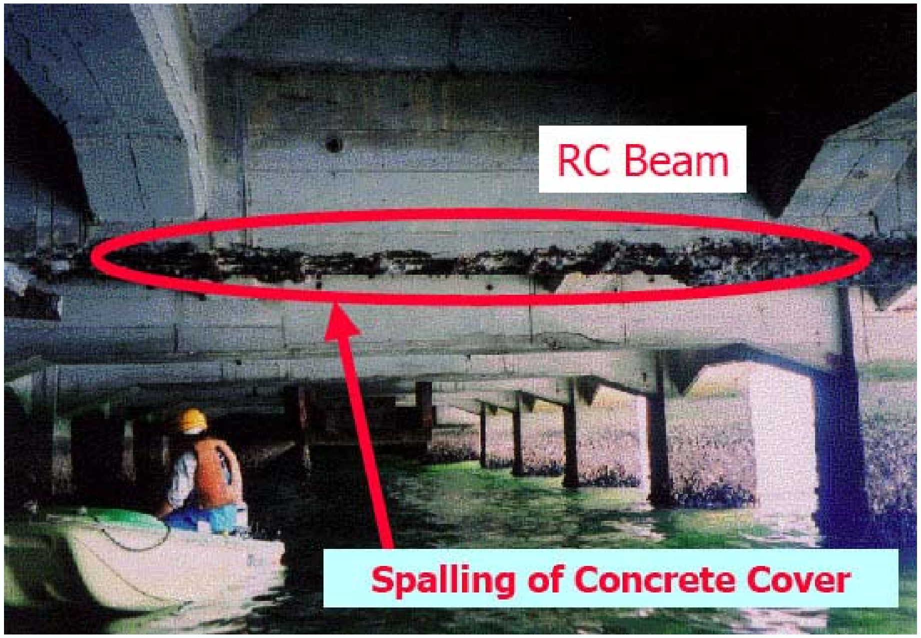
Program Objectives



Mechanism of sulfate attack

- **Understand significant factors that may lead to the establishment of phosphate limits**
- **Provide recommendations (technical basis), as appropriate, on whether a limit on phosphate ion concentration in ground water is required to avoid degradation of concrete structures**
- **Provide recommendations, as appropriate, in the form of Staff guidance on phosphate ion concentration limits**

Approach



Steel reinforcement corrosion

- **Review literature and available industry standards**
- **Contact cognizant concrete research personnel and organizations**
- **Conduct “limited” laboratory study**
- **Obtain and evaluate concrete samples from structures in high phosphate environments**
- **Prepare primer on factors that affect durability of NPP concrete structures**

- Program Deliverables

Primary Products

- **“Interim Report: Assessment of Potential Phosphate Ion-Concrete Interactions” - August 2005**
- **“Laboratory Investigation on Effect of Phosphate Ions on Concrete Materials’ - April 2006**
- **“Primer On Durability of Nuclear Power Plant Concrete Structures - A Review of Pertinent Factors” - June 2006**
- **“Criteria for Assessment of Phosphate Effects on Nuclear Power Plant Concrete Structures” - November 2006**

- Literature Review

Literature Review Did Not Identify Any Pertinent Information Relative to Interactions of Phosphate Ions and Cementitious Materials

- **Navy report identified phosphate compound contained as antioxidant in engine oil as source of aircraft concrete parking apron scaling**
- **Phosphate compounds have been used as set retarders in concrete mixes**
- **Phosphate materials have been used to produce a number of cement-based binders or phosphate-cements**
- **Phosphogypsum, main by-product of phosphate fertilizer industry, has been evaluated as road base material and set retarder in Portland cement**
- **Phosphates in form of phosphoric acid will cause slow disintegration of Portland cement-based materials**
- **Several articles addressing apatite and dental applications**

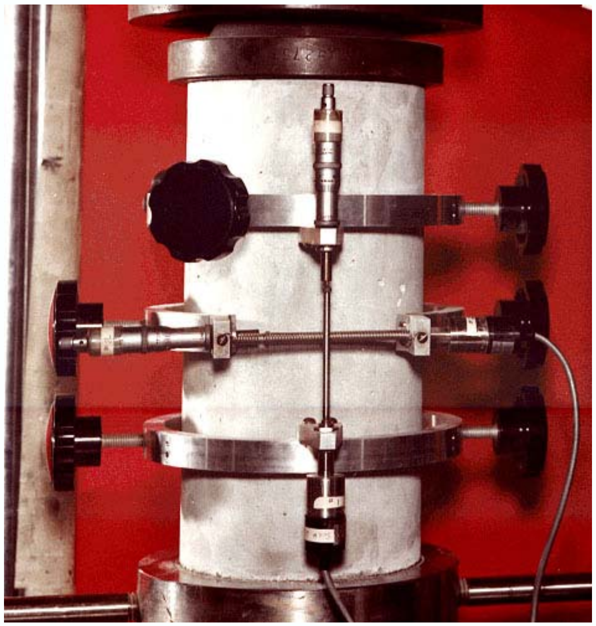
- Contacts with Researchers

Recognized Experts Contacted were Not Aware of Potential Deleterious Phosphate Ion-Cementitious Materials Interactions

Contact	Organization
Dr. Andrew Boyd	University of Florida
Dr. Paul Brown	Penn State University
Dr. Gerard Canisius	Building Research Est. (UK)
Dr. George Hoff	Hoff Consulting LLC
Mr. Charles Ishee	Florida DOT
Mr. Richard Kessler	Florida DOT
Dr. Neil Milestone	University of Sheffield (UK)
Dr. George Sommerville	British Cement Association
Dr. Peter Taylor	CTL Group
Dr. Michael D. A. Thomas	University New Brunswick
-	Florida Inst. Phosphate Res.
-	IMC phosphates

- Design of Experiment

As Literature Review and Contacts with Cognizant Research Personnel Revealed Little Information, A Laboratory Study was Designed and Implemented



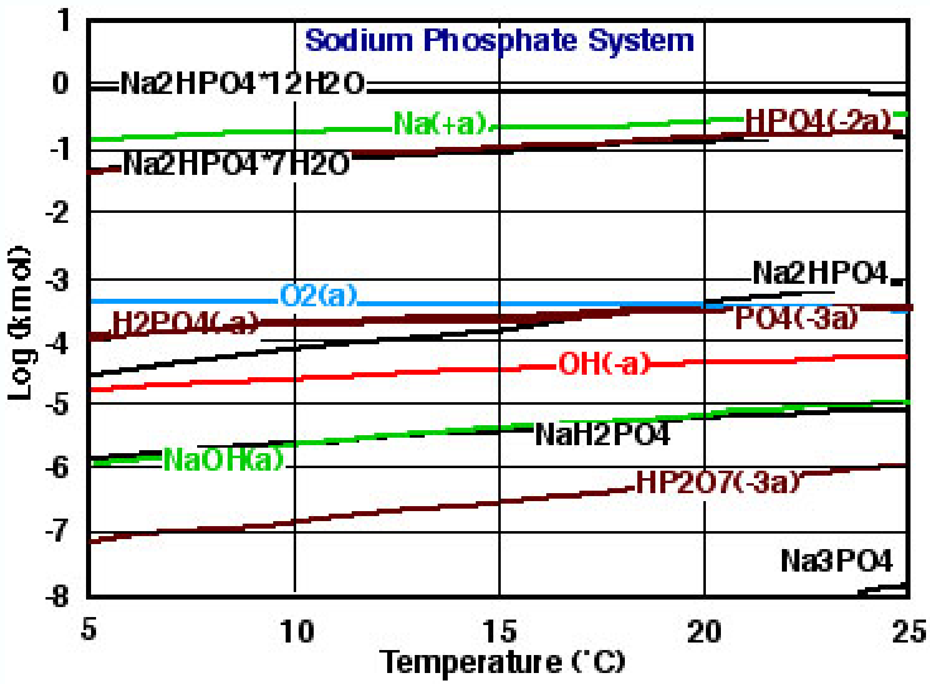
Compression test of Concrete cylinder

- **Thermodynamic calculations investigating phosphate concentrations as controlled by soil minerals**
- **Experimental program**
  - **Cement paste**
  - **Exposure solutions**
  - **Test specimens**
  - **Test procedures**

Study of Phosphate Concentrations as Controlled by Soil Minerals

- **Depending on soil, dominant cations may be calcium with magnesium, and/or sodium - determine phosphate solubilities in soil pore waters**
- **Relative phosphate solubilites calculated as they would be controlled by respective phosphate compounds**
- **Application**
  - **Assist in design of laboratory exposure tests**
  - **Aid in interpretation of field observations of concretes exposed in situ**

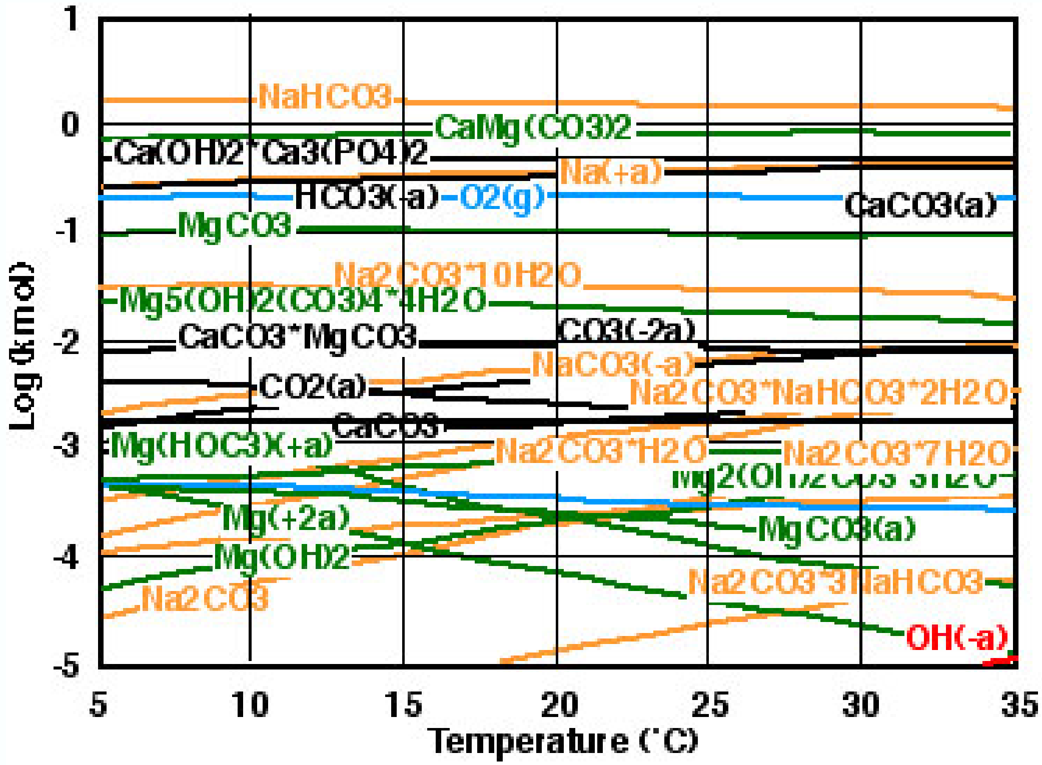
At Equilibrium, Na-, Mg-, and Ca-Rich Systems Saturate Phosphate Aqueous System



System	Molar Range
Na	10^{-1}
Mg	10^{-3}
Ca	10^{-5}

- **One mole of solids placed on one liter water and equilibrium concentrations calculated**
- **Calcium-rich cements and limestone/dolomite aggregates will extract phosphates from nearly all ground waters**
- **Phosphate concentrations maintained with Na_2HPO_4*$12H_20$ or $Mg_3(PO4)_2$**

Cement-Dolomite Aggregate System Exposed to CO_2 in Air or Groundwater



- **Calcium in cement-aggregate system will extract phosphate from sol'n**
- **Calcium hydroxyapatite forms in Na*Mg*Ca systems in presence of CO_2 from air or ground water**

Experimental Program Incorporated Approach Utilized to Investigate Sulfate Resistance of Cementitious Materials

Prism and Cube Test Specimens

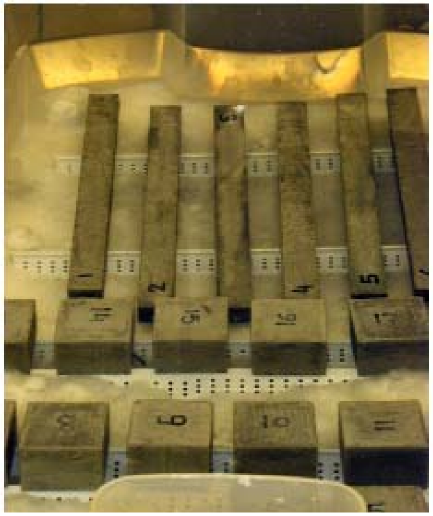
Length Change

Compression Test

Weight Change

Laboratory Investigation

- **Portland cement paste (w/c = 0.4) cubes (2” x 2” x 2”) and prisms (1” x 1” x 11”)**
- **Exposure solutions**
  - **Saturated calcium hydroxide (reference)**
  - **Saturated magnesium phosphate (low-solubility salt)**
  - **Saturated sodium hydrogen phosphate dodecahydrate (high-solubility salt)**
- **Test intervals**
  - **30-days**
  - **3-months**
  - **6-months**
  - **1-year**
- **Examination**
  - **Compressive strength**
  - **Length and weight change**
  - **X-ray diffraction/SEM**



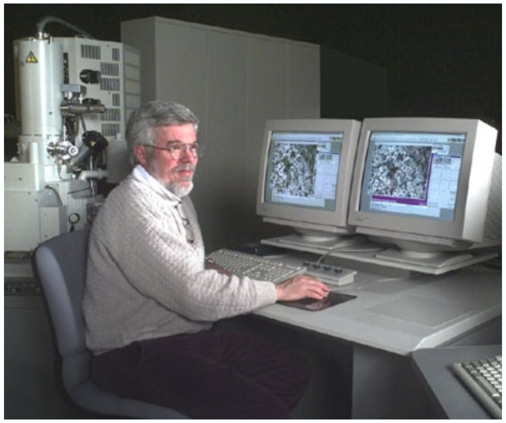
Na_2HPO_4 - 1 Month Exposure

Test Specimens

- 12-Month Test Results

12-Month Test Results Provided in a Letter Report

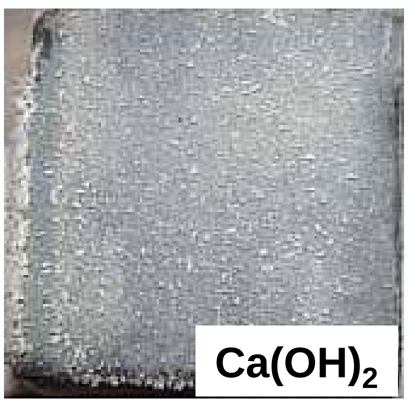
- **Length and weight change**
- **Compressive strength**
- **X-ray diffraction**
- **SEM examination**



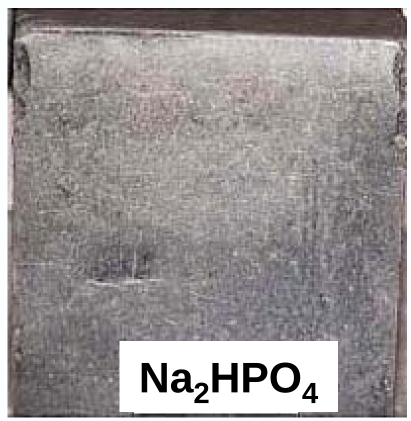
Field Emission Scanning Electron Microscope

Room Temperature X-Ray Diffractometer

Excess Solids of Salts were Poured on Bottom of Containers with Sufficient Water To Cover Specimens



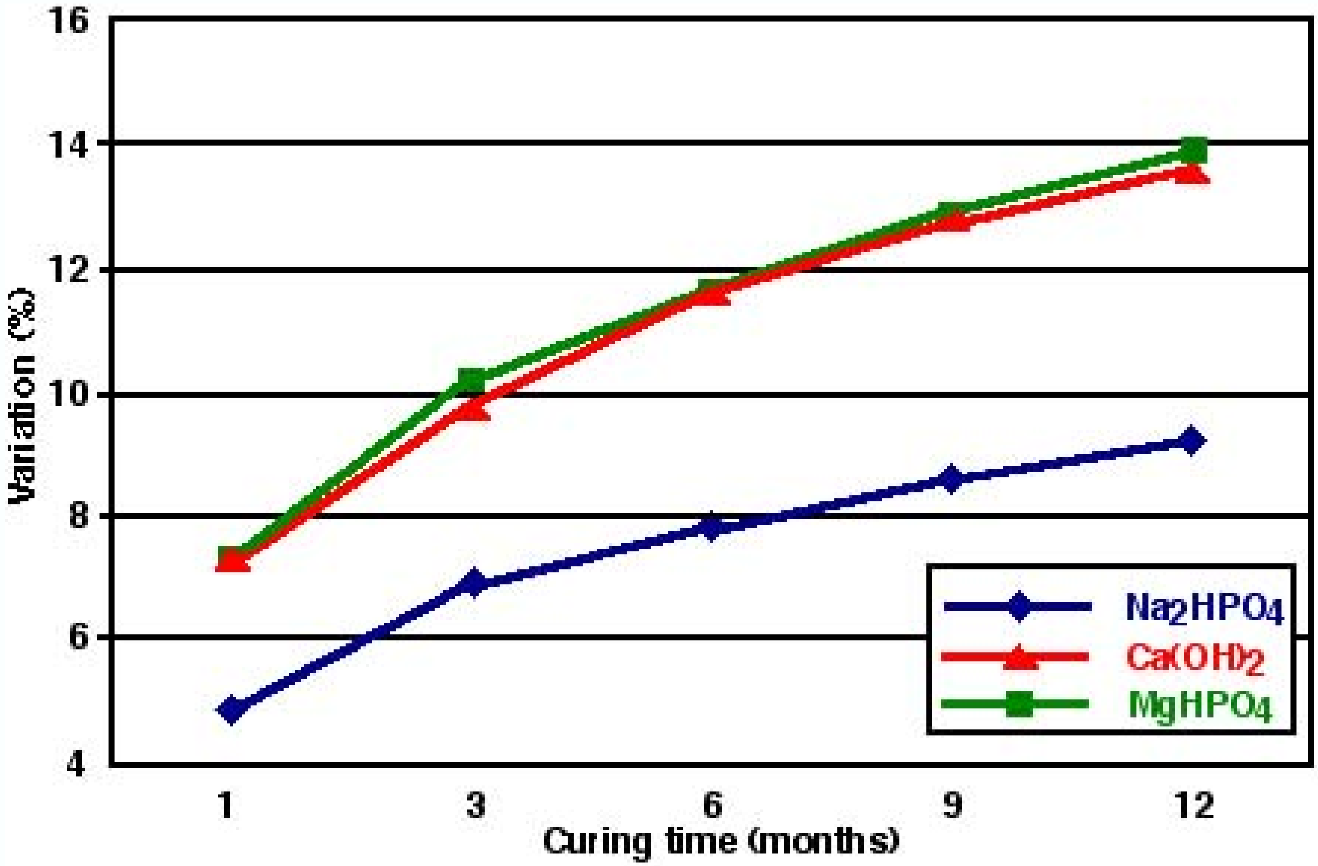
$Ca(OH)_2$



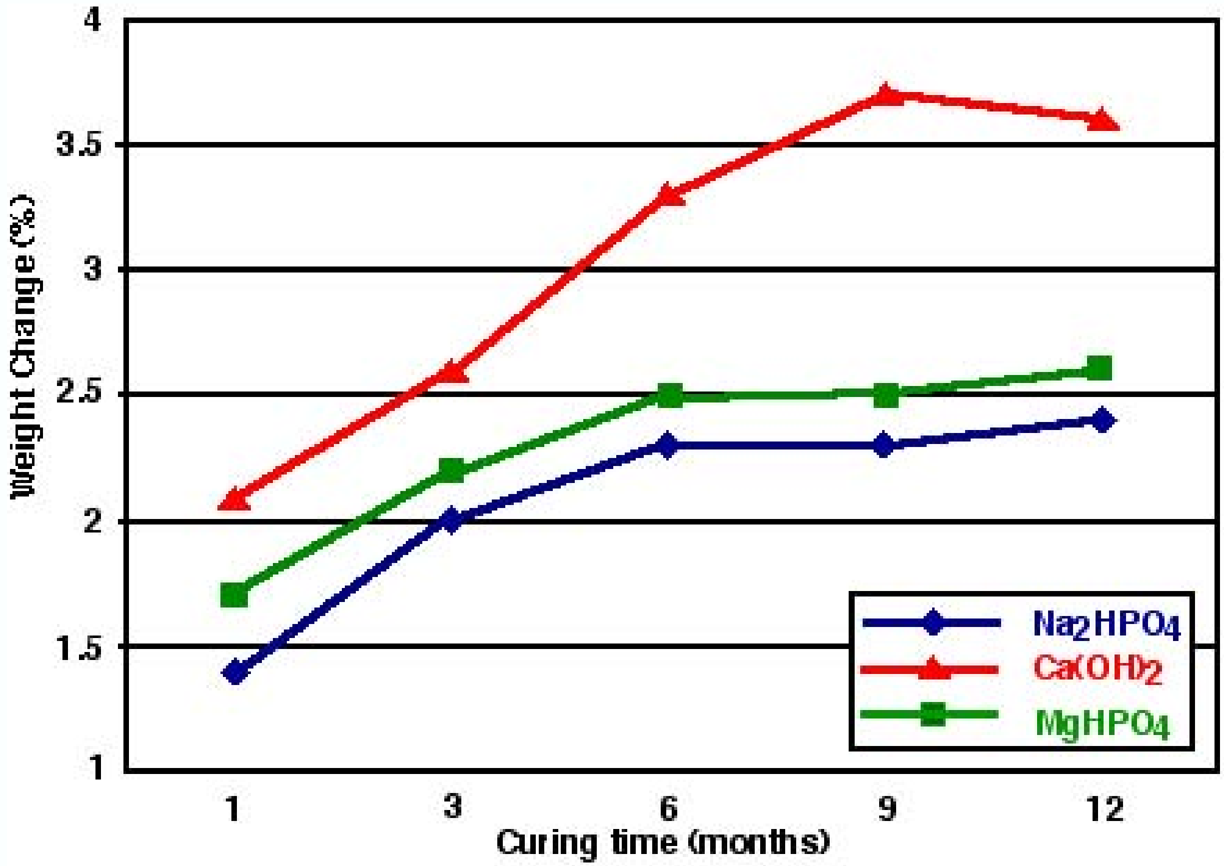
Na_2HPO_4

$MgHPO_4$

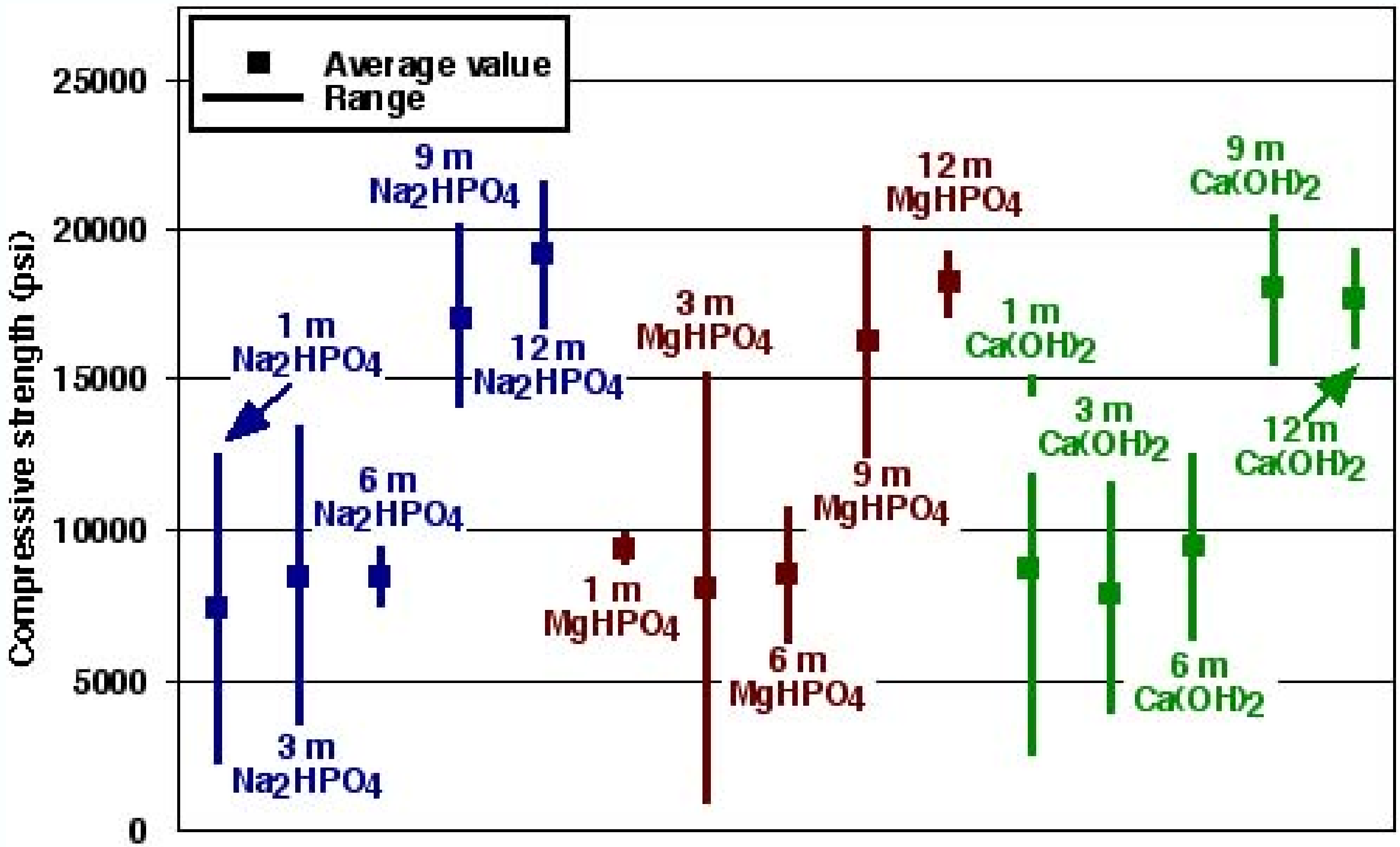
Specimens Cured in Phosphate Solutions did not Exhibit Excessive Length Changes



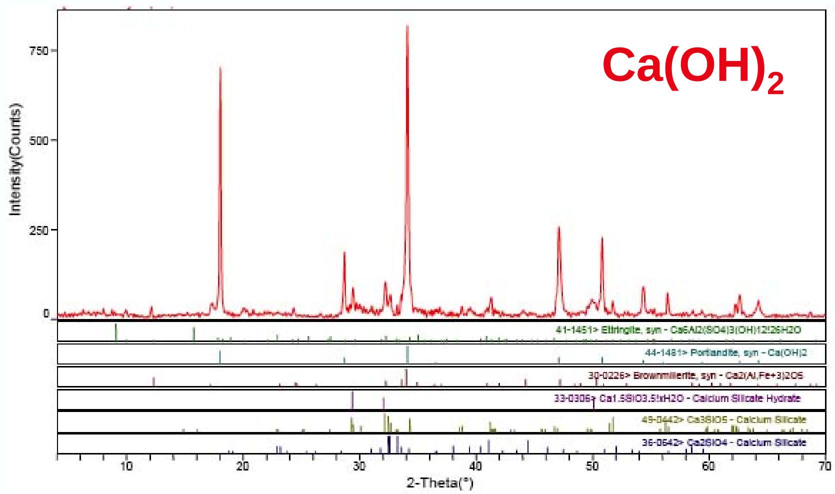
Specimens Cured in Phosphate Solutions did not Exhibit Excessive Weight Changes



Compressive Strength Results were Consistent for Each of the Solutions

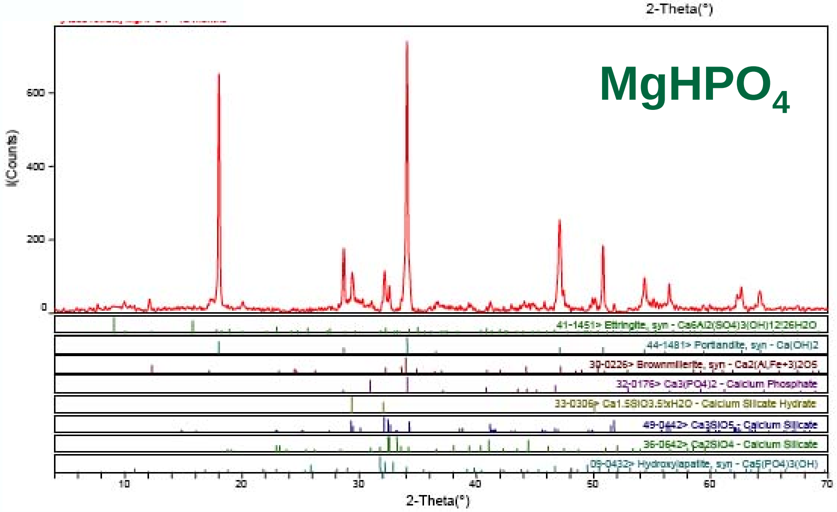


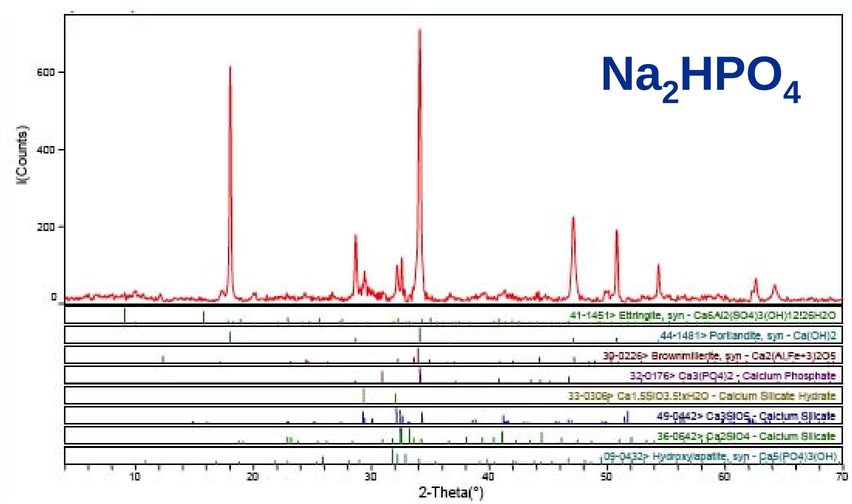
X-Ray Diffraction Spectra Obtained were Very Similar for Each Solution



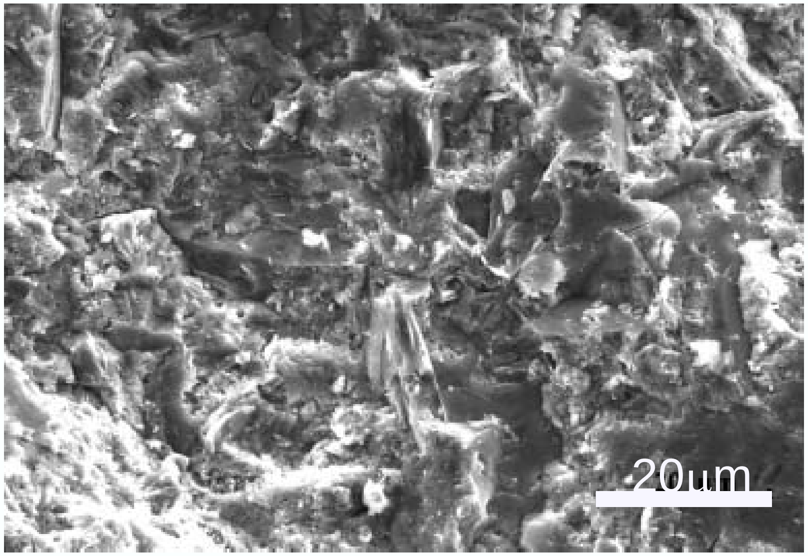
Hydrated Phases Identified

- **Portlandite**
- **C-S-H**
- **Ettringite (?)**
- **No mineral w phosphate**

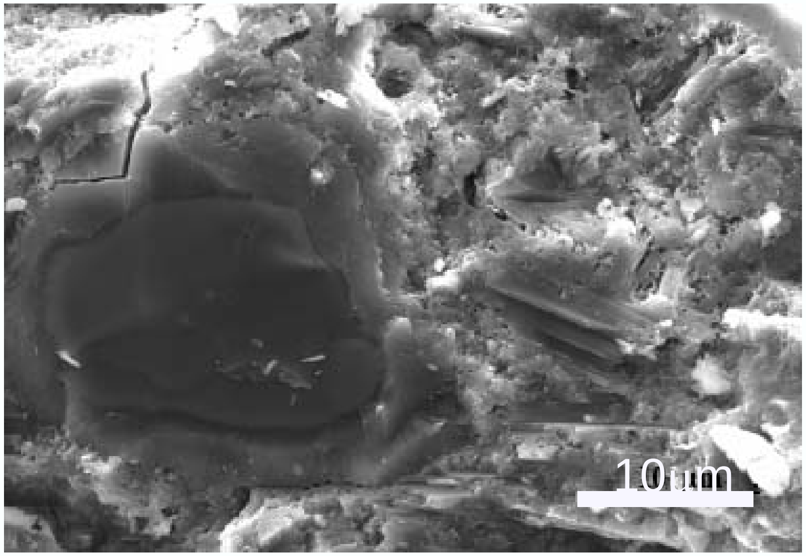




SEM Confirmed Results found by X-Ray Diffraction

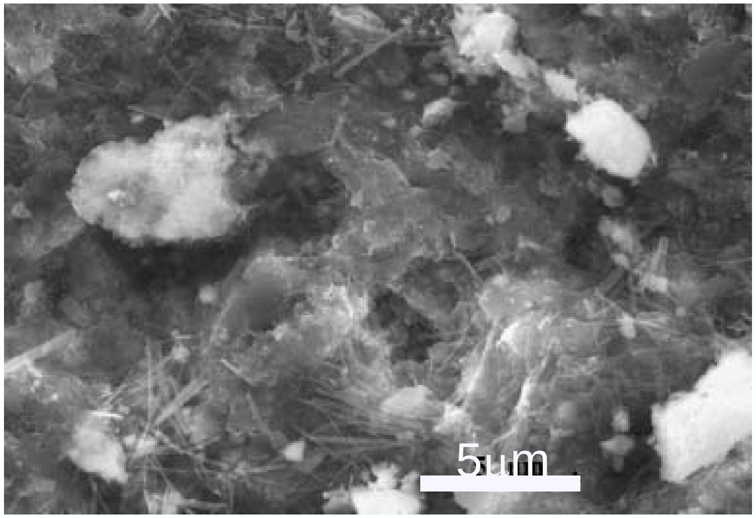


View of Cement Paste: Na_2HPO_4 at 12 months

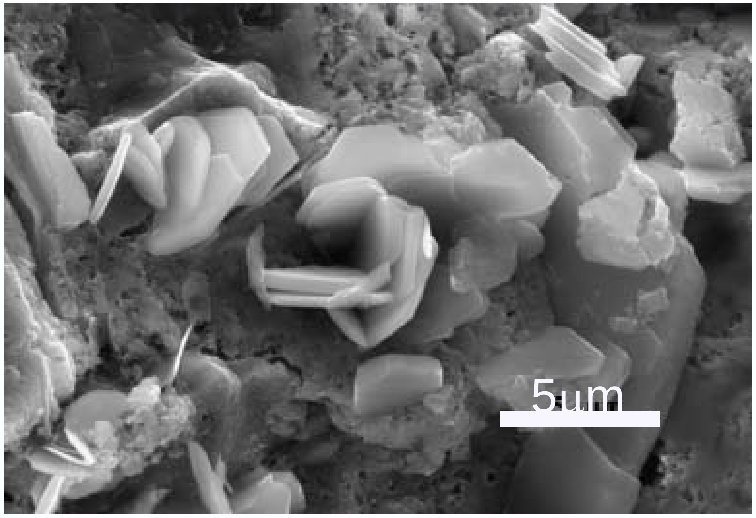


C_3S in Dense Layer of C-S-H $Ca(OH)_2$ and Calcium Sulfo-aluminates Visible in Cement Paste: Na_2HPO_4 at 12 months

SEM Confirmed Results found by X-Ray Diffraction (cont.)



Ettringite in Cement Paste: $MgHPO_4$ at 12 months



Calcium Sulfoaluminates Abundant: $MgHPO_4$ at 12 months

- Preliminary Conclusions

Thermodynamics Supports Potential for Expansive Reactions Involving Phosphate Ions and Cementitious Materials, but to Date Kinetics Does Not

Ettringite Needles (X 2000)

- **Preliminary conclusions**
  - **No harmful interactions of phosphates and cementitious materials unless phosphates are present in form of phosphoric acid**
  - **Phosphates have been incorporated into concrete as set retarders, phosphate cements used for infrastructure repair**
  - **No standards or guidelines pertaining to applications of RC structures in high-phosphate environments**
  - **Contacts with researchers indicate that potential interactions between phosphates and cementitious materials has not been a concern**
  - **Twelve-month laboratory results indicate similar performance of specimens submerged in phosphate solutions and calcium hydroxide**

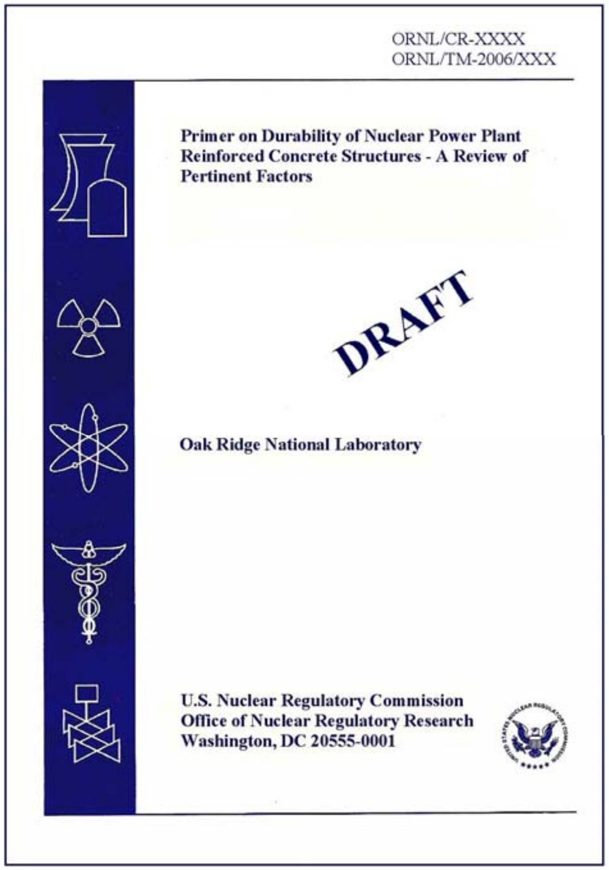
- **Structural Sampling**

Working with FDOT to Obtain Concrete Core Samples from Bridge Substructure in Bartow County

Analyte	Calibration Status	Compound	Concentration (%)	Calculation Method
Al	Calibrated	Al	3.224	Calculate
Si	Calibrated	Si	24.243	Calculate
P	Calibrated	P	18.444	Calculate
S	Calibrated	S	0.547	Calculate
K	Calibrated	K	0.591	Calculate
Ca	Calibrated	Ca	44.552	Calculate
Ti	Calibrated	Ti	0.712	Calculate
Mn	Calibrated	Mn	0.234	Calculate
Fe	Calibrated	Fe	6.653	Calculate
Zn	Calibrated	Zn	0.226	Calculate
Sr	Calibrated	Sr	0.306	Calculate
Y	Calibrated	Y	0.035	Calculate
Zr	Calibrated	Zr	0.093	Calculate
Ba	Calibrated	Ba	0.112	Calculate
U	Calibrated	U	0.028	Calculate

- Primer on Concrete Durability

Report on Durability of Reinforced Concrete has been Prepared


ORNL/CR-XXXX
ORNL/TM-2006/XXX

Primer on Durability of Nuclear Power Plant Reinforced Concrete Structures - A Review of Pertinent Factors

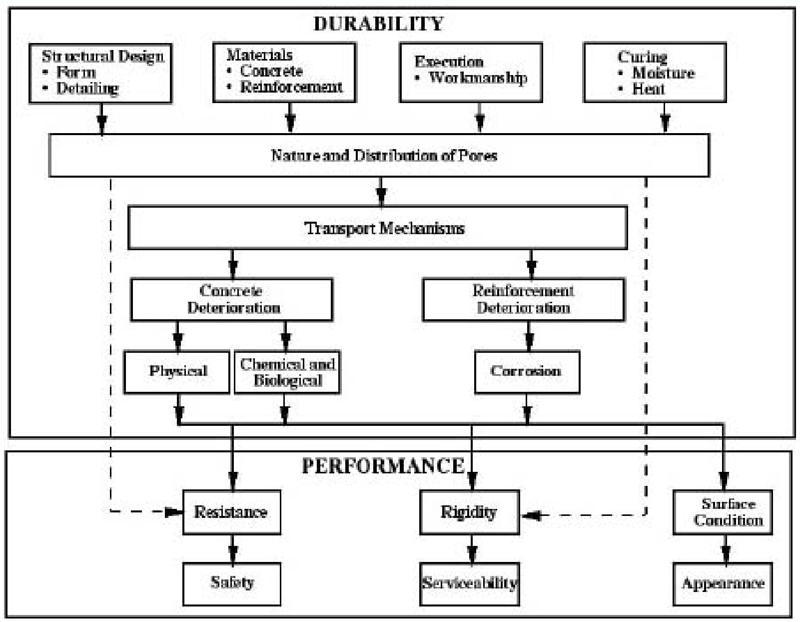
DRAFT

Oak Ridge National Laboratory

U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001

- **Introduction**
- **Historical Perspective on Concrete and Longevity**
- **Materials of Construction**
- **Aging and Durability**
- **Summary and Conclusions**
- **Appendix A: Safety-Related Concrete Structures**
- **Appendix B: Nuclear Power Plant Concrete Structures Operating Experience**
- **Appendix C: Commentary on Cracking and Corrosion**

1. Introduction



Relationship Between Durability and Performance

- **As concrete ages, changes in its properties occur as a result of continuing microstructural changes**
- **Water is single most important factor controlling degradation process**
- **Incidences of degradation will increase with age, primarily due to environmental-related factors**

2. Historical Perspective on Concrete and Longevity

Pantheon
(Built 119-128 A.D.

Colosseum
(Comp. 80 A.D)

- **Cement has been around for 12 million years with oldest concrete about 7600 years old**
- **Ancient structures survived because of careful materials selection and construction, mild climatic conditions, and lack of steel reinforcement**
- **Portland cement invented in 1824**

3. Materials of Construction

Basic Concrete Constituent Materials

- **Concrete**
- **Conventional steel reinforcement**
- **Prestressing steel**
- **Liner plate**

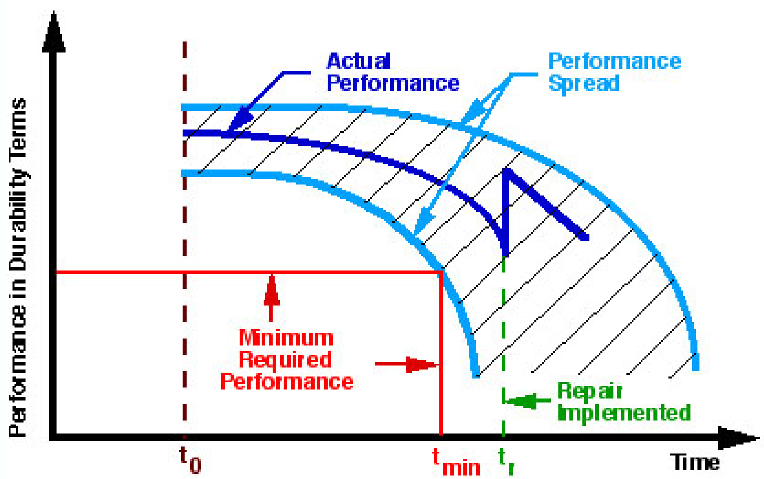
4. Aging and Durability

Mat'l System	Degradation Factor	Primary Manifestation
Concrete	*Physical processes*	
	Cracking	Reduced durability
	Salt crystallization	Cracking/loss material
	Freezing and thawing	Cracking/scaling/disintegration
	Abrasion/erosion/cavitation	Section loss
	Thermal exposure/thermal cycling	Cracking/spalling/strength loss
	Irradiation	Volume change/cracking
	Fatigue/vibration	Cracking
	Settlement	Cracking/spalling/misalignment
	Chemical processes	
	Efflorescence/leaching	Increased porosity
	Sulfate attack/DEF	Volume change/cracking
	Acids/bases	Disintegration/spalling/leaching
	Alkali-aggregate reactions	Disintegration/cracking
	Aggressive water	Disintegration/loss material
	Phosphate	Surface deposits
	Biological attack	Increased porosity/erosion

4. Aging and Durability (cont.)

Mat'l System	Degradation Factor	Primary Manifestation
Mild Steel Reinforcing	Corrosion Elevated temperature Irradiation Fatigue	Concrete spaling/cracking/section loss Decreased strength Reduced ductility Bond loss
Post-Tensioning	Corrosion Elevated temperature Irradiation Fatigue Stress relaxation/End effects	Strength loss/reduced ductility Reduced strength Reduced ductility Concrete cracking Prestress force loss
Liner/Strutural Steel	Corrosion Elevated temperature Irradiation Fatigue	Section loss Reduced strength Reduced ductility Cracking

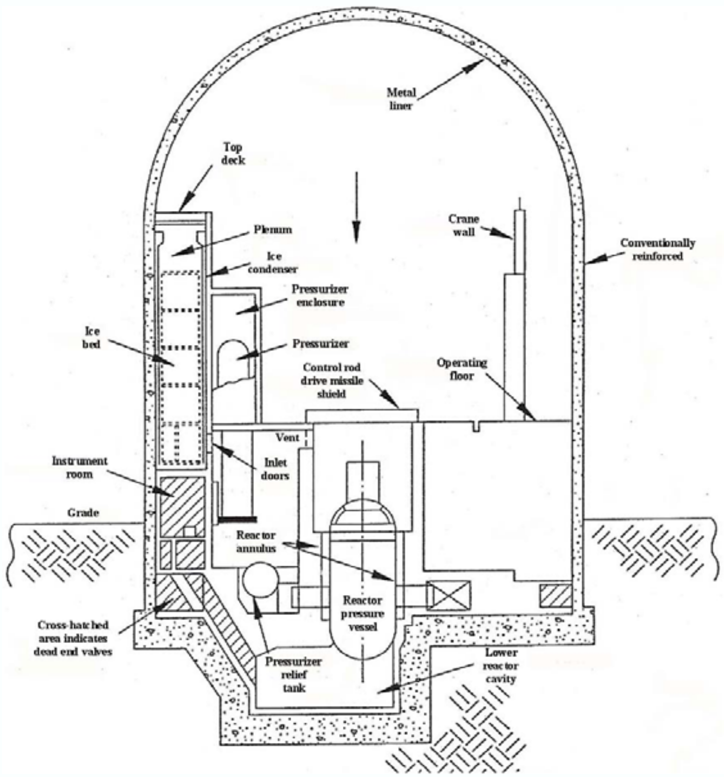
5. Summary and Commentary



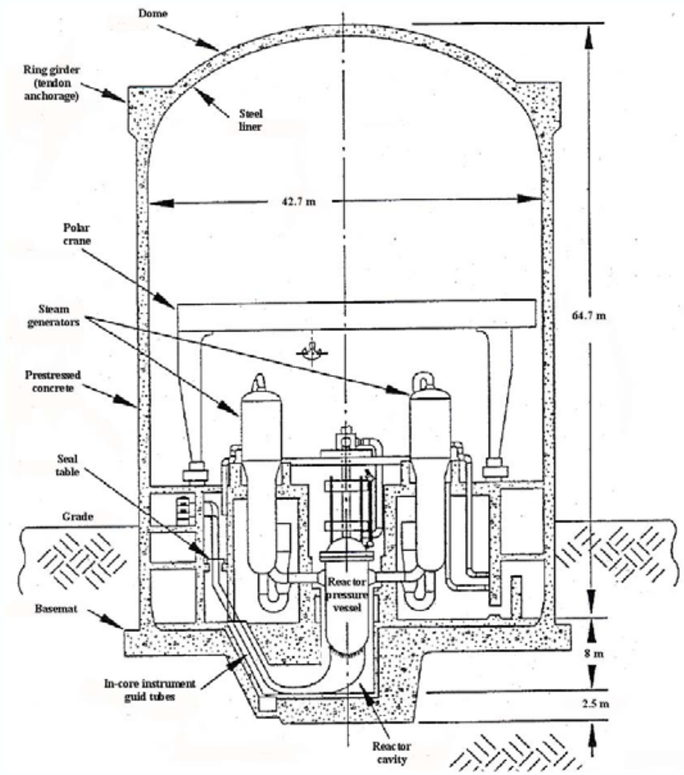
Relationship Between Performance and Service Life

- **Reinforced concrete structures deteriorate due to exposure to environment**
- **Properties of concrete change with age**
- **Water is most important factor controlling concrete degradation**
- **Most prevalent manifestation of concrete degradation is cracking**
- **Most prudent approach for maintaining adequate structural margins as well as extending usable life is through an aging mangement program**

Appendix A: Safety-Related Concrete Structures



PWR Reinforced Concrete with Ice Condenser



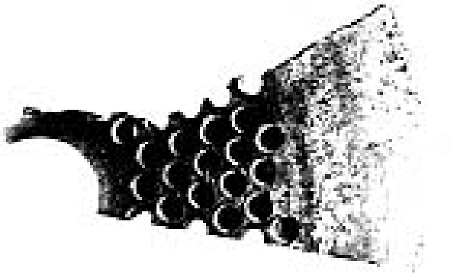
PWR Large Dry Prestressed Concrete

Appendix B: Nuclear Power Plant Concrete Structures Operating Experience

Containment Dome Delamination Repair

Leaching in Tendon Gallery

Water Intake Structure Rebar Corrosion

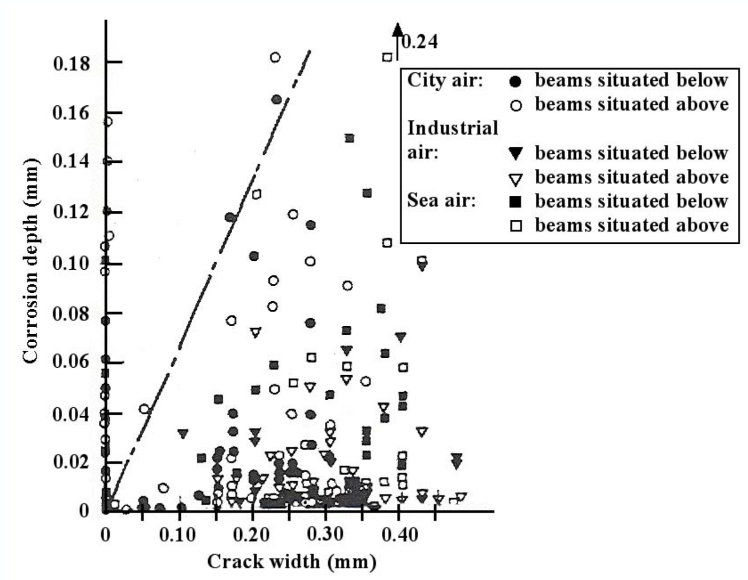


Anchorhead Failure

Concrete Cracking With Grease Leakage

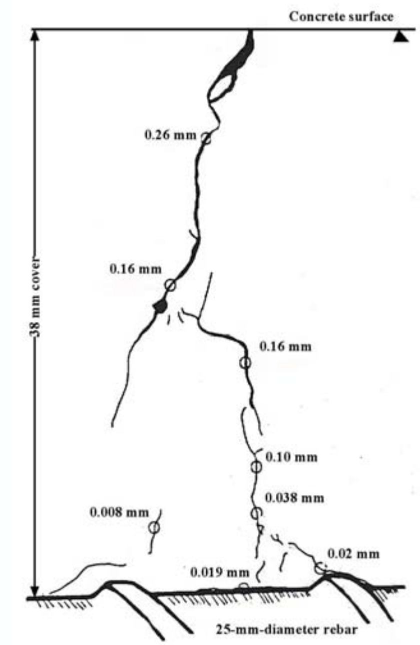
Appendix C: Commentary on Cracking and Corrosion

Crack Characteristics and Corrosion



Corrosion Depth vs Crack Width After 10-Year Exposure

Corrosion Significance And Crack Characteristics



Variation of Crack Width With Depth