Interim Report: Assessment of Potential Phosphate Ion-Concrete Interactions

1.   Introduction

At the 499th Advisory Committee on Reactor Safeguards (ACRS) meeting, the staff presented its review results on the McGuire/Catawba Nuclear Stations License Renewal Applications. During the staff's presentation, one ACRS member asked the staff why a quantitative allowable phosphate limit is not included as part of the staff's acceptance criteria for defining aggressive ground water/soil environments in license renewal application reviews (see Appendix A). The staff's response was that the current criteria for defining aggressive ground water/soil environments are primarily based on American Concrete Institute (ACI) standards and industry experts opinion and believes that the current criteria are reasonable for defining ground water/soil aggressive environment. The staff also committed to take an in-depth review of the issue (ie., if phosphate limits should be a part of the staff's criteria for aggressive ground water/soil environment).

In a letter dated June 24,2003, to NRC Chairman Diaz, the Chairman of the Advisory Committee on Reactor Safeguards (ACRS), Dr. Mario Bonaca made three recommendations. The third recommendation states, "The Generic Aging Lessons Learned Report (GALL) specifies limits for sulfate ion concentrations in below grade water to avoid decrepitation of concrete. The Staff should consider whether similar limits and guidance are needed for phosphate ion concentration." Based on the above ACRS recommendation, NRR User Need, NRR-2004-002, was developed and forwarded to RES for consideration in January 2004.

2.   Objectives of Investigation

The objectives of the proposed work are to (1) understand the significant factors that may lead to the establishment of phosphate limits beyond those currently accepted in industry codes and standards documents (e.g., local soil conditions that may lead to an aggressive environment); (2) provide recommendations (technical basis), as appropriate, on whether a limitation on phosphate ion concentration in groundwater is required to avoid degradation of concrete structures: and (3) provide recommendations, as appropriate, in the form of staff guidance on the establishment of phosphate ion concentration limits.

3.   Approach

The end product of this research will be a document to assist the staff in establishing a position on phosphate ion concentrations in groundwater for use in review of license renewal applications. Literature and available industry standards will be reviewed and a letter report prepared summarizing the state-of-the-art. An assessment of the effects of phosphate ions on concrete materials and structures will be made through contacts with cognizant researchers, lessons learned from non-nuclear facilities subjected to high phosphate ion concentrations, and a review of the literature. Results of this assessment will be provided in a letter report that presents an evaluation of the effects of phosphate ions on concrete materials and structures. A "bench-scale" laboratory study will be conducted to investigate the effect of different phosphate ion concentrations on strength and length change of cubes and prisms fabricated from Portland

cement paste. A report that can serve as a primer on factors that affect the durability of concrete materials and structures in nuclear power plants will be prepared. Finally, a NUREG/CR report will be prepared that incorporates results from the prior letter reports and provides guidance for use in establishing limits on exposure of nuclear power plant concrete structures to high phosphate ion environments. If required, limits such as those currently in effect for sulfates and chlorides will be provided as well as their basis.

Contained in this report are results of a review of pertinent literature, a summary of contacts with recognized experts in the concrete industry, an assessment of the potential for phosphate ion corrosion of ordinary Portland cements, and a status report on the laboratory exposure tests.

4.   Phosphates and Fertilizer Production[*]

The principal commercial deposits of phosphate rock exist in Florida, North Carolina, and Idaho, with lesser amounts in Utah and Montana. The phosphate mineral, as it exists in the ground, is not soluble in water and thus is hard for vegetation to access. After the phosphate is separated from the sand and clay at the beneficiation plant it goes to the processing plant. There it is finely ground to uniform size and reacted with sulfuric acid to create the phosphoric acid which is concentrated through evaporation, reacted with ammonia, and granulated to produce diammonium phosphate (DAP) and monoammonium phosphate (MAP). Granular triple superphosphate (GTSP), a non-nitrogen fertilizer, is produced by adding phosphoric acid to ground phosphate rock.. DAP fertilizer is water-soluble and is available for vegetation to take up through their roots. When sulfuric acid is reacted with phosphate rock to produce phosphoric acid a by-product is produced. This by-product gypsum is called phosphogypsum. There are approximately five tons of phosphogypsum produced for every ton of phosphoric acid product produced. Phosphogypsum, like natural gypsum, is calcium sulfate, but it contains a small amount of radioactivity due to the radium that naturally occurs in Florida phosphate rock.

Production of fertilizer also requires/produces a large volume of process water. This is the water source for the phosphoric acid, gas scrubbing, phosphogypsum slurry for transportation and storage, operation of condensers, as well as other uses in the chemical complex. The process water has a pH of about 1 to 2 and contains a dilute mixture of phosphoric, sulfuric, and fluosilic acids. The process water is saturated with calcium sulfate and contains numerous other ions found in phosphate rock, as well as ammonia from the solid fertilizer-manufacturing process. The process water is treated with lime to raise the pH to about 4.5, remove any solids formed, lime the water to a pH of about 11, again remove solids formed, air strip the water to remove ammonia, and add acid to reduce the pH to about 6.5.

5.   Literature Review Phosphates and Cementitious Materials

A review of the literature was conducted to identify information related to interactions of phosphate ions and cementitious materials, phosphates incorporated into cementitious materials, and utilization of phosphate-related materials in the infrastructure.

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[*] Source: Florida Institute of Phosphate Research, "Phosphate Primer," www.fipr.state.fl.us.

A chemical analysis approach has been utilized to determine the mechanism for concrete scaling on aircraft parking aprons (1). The study was part of a multi-task Navy study on thermal and chemical deterioration of concrete parking aprons used for F/A-18 aircraft maintenance. The Navy has observed that the concrete pavement is damaged either by aircraft chemicals or heat from the Navy F/A-l8 aircraft auxiliary power unit (APU), or a combination of both.

An acid attack hypothesis has been developed which proposes that engine oil, known to contain phosphorus compounds such as antioxidants, produces acidic compounds through oxidation and hydrolysis. The oil containing the acids drips onto the pavement and gradually decomposes the calcium carbonate or the cement paste (e.g., calcium aluminates and silicates) at the surface of the concrete. Heat from the APU accelerates this reaction and thus produces the surface scale. Forensic chemical analysis were used in determining the mechanism of the concrete scaling. Concrete debris from the airfield was extracted with hexane and the hexane was evaporated to leave an organic residue. The organic residue was analyzed by infrared spectroscopy and mass spectrometry. The extract consisted of ethanol, phenol, and other byproducts expected from the decomposition of the organo phosphate compounds used as antioxidants in the engine oil. After the concrete was extracted with hexane, it was analyzed by x-ray fluorescence (XRF) and electron scanning chemical analysis (ESCA). The results indicated that the material contained calcium phosphate. The calcium phosphate came from decomposition of he pavement by phosphoric acid. Thus it was established that he phosphoric acid did originate from the phenyl orthophosphate and traces of red phosphorus used in the engine oil. It is suggested that engineers mitigate the acidic erosion of the concrete either by: (a) replacing the portland cement concrete in the parking apron area with an acid resistant concrete (magnesium phosphate), or (b) recommending Military Specification (MILSPEC) engine oils without the acid-forming additives. The current acid damage to the concrete can also be lessened by periodically cleaning the affected pavement with a suitable alkaline detergent (pH 10 or higher), such as aqueous trisodium phosphate (TSP).

A study was conducted to assess the capacity of sorption of various ions in calcium silicate hydrates (2). Chloride ion, sulfate ion, and phosphate ion were sorbed in synthesized calcium silicate hydrates (C-S-H). The amount of sorbed chloride ion, sulfate ion, and phosphate ion in C-S-H were 172, 54, and 667 mg/g, respectively. In the case of sorption of phosphate ion, the phosphate ion and C-S-H reacted to produce hydroxyapatite. In the leaching test, 15% chloride ion, 18% sulfate ion, and 34% phosphate ion were dissolved from S-C-H sorbing respective cations; while, 65% of fixed chloride ion in Friedel's salt was dissolved in the leaching test. Therefore, the fixing ability of chloride ion in C-S-H is higher than that in Friedel's salt.

Deicing chemicals were mixed with corrosion inhibitors to reduce rebar corrosion in bridge decks (3). The corrosion inhibitors were thought to penetrate into concrete to the depth of the steel reinforcement and form a passive film on the rebar surface. Previously it was found that corrosion-inhibitor-added deicing salts interacted with 3% NaCI-added concrete and produced precipitates through chemical reactions. The amount of precipitates produced was dependent on the type and concentration of corrosion-inhibitor-added deicing salts. In this investigation, the precipitates formed by chemical reactions between concrete and corrosion-inhibitor-added deicing salts were identified by using chemical analysis and X-ray diffraction methods. The distributions of Cl^-, SO_4^{2-}, and PO_4^{3-} in concrete slabs ponded with corrosion-inhibitor-added deicing salts were determined by chemical analyses of powder samples obtained from the slabs.

The major precipitates were calcium and/or magnesium phosphates as major chemical compounds and gypsum as a minor component. High concentrations of phosphate were observed at the top portion of concrete slabs when the deicing chemicals contained phosphate inhibitors. Voids were observed at the interface of aggregate and mortar in the concrete slabs tested with the deicing salts solutions containing corrosion inhibitors.

Small amounts of phosphorus pentoxide (P_2O_5) in the raw materials used for the manufacture of cement, such as can occur in some limestones, can cause problems (4). The content of P_2O_5 in most Portland cements is of the order of 0.2%; however, satisfactory cements can be manufactured from cement clinker containing up to 2.5% P_2O_5 by correct burning and proportioning, but the rate of hardening is slower. This is because the P_2O_5 decomposes C_3S forming a series of solid solutions between C_2S and $3CaO \cdot P_2O_5$. If larger amounts of P_2O_5 are present, free lime forms. If the lime content is reduced so that free CaO is is not formed, sound cements can be burnt from phosphatic raw materials but they develop strength more slowly because of the reduced $C_3S:C_2S$ ratio. It is also noted in this reference that basic phosphate salts, including even ammonium salt, do not appear to have any serious action on concrete, but definite information is not available on acid salts.

Some inorganic salts (e.g., borates, phosphates, and zinc and lead salts) can act as retarders, but are not used commercially (5). Up to 500 ppm can generally be tolerated in mix water without causing significant set retardation. Basic research on the effect of retarders has shown that they slow down the rate of early hydration of C_3S by extending the length of the dormant period (i.e., second stage of hydration). Thus the setting time of Portland cement, as measured by the penetration test, is extended. The extension of the dormant period is proportional to the amount of retarding admixture used, and when a the dosage exceeds a certain critical point, the C_3S hydration will never proceed beyond the dormant stage and the cement will not set.

The retarding action of sodium salts of phosphoric acid has also been noted (6). Sodium salts of phosphoric, boric, oxalic, and hydrofluoric acid are soluble, but the calcium salts are high insoluble and therefore readily form in the vicinity of hydrating cement particles. Once insoluble and dense coatings are formed around cement grains, further hydration slows down considerably. Phosphates are commonly found to be present as ingredients of commercial set-retarding admixtures.

The influence of a phosphonate-based admixture called aminotri (methylene phosphonic acid) (ATMP) on the hydration of C_3A, C_3A and 25 percent gypsum, and C_3S and Type I Portland cements (normal, high-alkali, and low-alkali) was evaluated (7). Isothermal conduction calorimetric investigations of various mixes containing 0.03 to 0.05 percent of phosphonic acid, at water-cement ratios of 0.35 and 1.0, were carried out at times up to 72 hr. The ATMP acted as a super-retarder for all mixes studied. At a dosage of only 0.05, the exothermal effect for one of the high-alkali Type I cements was delayed by about 16 hr. The hydration of C_3A and C_3S was also retarded by about 40 to 45 min and more than 50 hr, respectively, at a dosage of 0.05 percent. In the C_3A and gypsum system, the third peak corresponding to the reaction of C_3A with ettringite was extended by about 8 to 9 hr.

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Phosphates present in the form of phosphoric acid will cause slow disintegration of Portland cement-based materials (8,9). Portland cements are not resistant to attack by acids. The degree of attack increases as the acidity increases; attack occurs a values of pH below about 6.5, a pH less than 4.5 results in severe attack. The rate of attack also depends on the ability of hydrogen ions to be diffused through the cement gel (C-S-H) after $Ca(OH)_2$ has been dissolved and removed by leaching.

Phosphate materials have also been utilized to develop a number of cement-based binders or phosphate cement materials. A phosphate cement-based binder for rapid repair of concrete has been developed by mixing magnesium oxide (MgO) powder with $NH_4H_2PO_4$ powder and borax powder (10). Magnesium phosphate cements are formed by the reaction of MgO with a soluble phosphate, such as ammonium phosphate, either the mono or dibasic salt; or an agricultural fertilizer solution (11). The magnesia cements have very good adhesion to a wide variety of aggregates and substrates as well as good water and freeze-thaw resistance. Phosphate cements have also been prepared by an acid-base reaction between an oxide, such as MgO, and and acid phosphate, such as KH_2PO_4 (12). The resulting product of the reaction is a binder having a pH between 7 and 8. The binder is then mixed with a silica-based material, such as fly ash, blast furnace slag, or vitreous tuff, to produce a phospho-silicate cement. Phosphate-based additions to high-alumina cements have resulted in increased reactivity that in turn produced higher strengths (13). A magnesium phosphate cement having quick set, high early strength, and good durability has been produced from acid-base reaction of magnesia and phosphates (14).

As noted in the previous section, phosphogypsum is produced in significant amounts as a by-product of the phosphate fertilized industry. Its main constituent is calcium sulfate dihydrate. When compacted, the phosphogypsum can be transformed into a solid that has potential application for road building as well as a construction material. Potential applications cited include:[*] a road base that is cheaper and as effective, if not more, as current road base materials; an agricultural soil amendment that would provide much needed sulfur to the soil; a landfill cover to speed the degradation of waste and extend the landfill life; a material to make ceramic roofing tiles; and a material for marine substrate, such as oyster culch. Considerable research on use of phosphogypsum for building materials has been conducted at the University of Miami (15,16).

6.   Contacts with Cognizant Researchers

Several contacts were made with research personnel that are recognized experts in their knowledge of cementitious materials and concrete. A summary of the results of these contacts is provided in Table1.

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[*] Source: Florida Institute of Phosphate Research, "Phosphate Primer," www.fipr.state.fl.us.

Table 1 Contacts with research personnel.

Contact	Organization	Comment
Dr. Andrew Boyd	Assistant Professor Dept. of Civil Engineering University of Florida Gainesville, Florida	Working on program to evaluate residual effects of phosphates in waste. Phosphates may produce a set-retarding effect. Heard that phosphates may increase corrosion potential but unsubstantiated.
Dr. Paul Brown	Professor of Ceramic Science Materials Science & Eng. Penn State University University Park, PA	If phosphate ion intruded the pore structure of concrete two possible outcomes would be expected: (1) in carbonated zone there would be a slow reaction with $CaCO_3$ to form Hap, but will depend on cation associated with phosphate; (2) if phosphate intrudes non-carbnated zonw, HAp would form as $Ca(OH)_2$ is consumed, from a phase equilibria standpoint Hap is compatible with hydrated cement paste. With respect to expansion, because products formed are microcrystalline it is not expected that expansion would be a problem.
Dr. Gerard Canisius	Structures Group Leader Building Research Est. Garston, Watford, UK	A literature search at BRE did not identify any research related to phosphate ions and concrete. Current researchers at BRE are not aware of any research at BRE or elsewhere in UK.
Dr. George Hoff	Hoff Consulting LLC Clinton, MS	Not aware of work addressing phosphates and concrete except that ACI 201,"Durability, notes that concrete can undergo moderate disintegration when subjected to phosphoric acid. Some research has been conducted on systems that rely on hydration or reaction of phosphate compounds because they have rapid strength development and information can be obtained from A.K. Chatterji, "Special and New Cements," *Proc. 9th Int'l Congress on Chemistry of Cements*, pp. 177-212, New Delhi, 1992.
Mr. Charles Ishee	Structural Materials Lab Florida DOT Gainesville, Florida	Thought that phosphate ion contents were determined for soils and water adjacent to transportation structures. Not aware of any problems or if special design procedures were utilized for concrete structures in high phosphate environments but would check. Will pursue possibility of obtaining concrete core samples from structures in high phosphate areas and providing to ORNL.
M. Richard Kessler	State Corrosion Engineer Florida DOT Gainesville, Florida	Not aware of any problems involving phosphates and concrete.
Dr. Neil Milestone	Senior Lecturer Immobilisation Science Lab. University of Sheffield, UK	Not aware of any problems involving phosphates and concrete. Main effect thought to be buildup of products on exterior surface of concrete.
Dr. George Sommerville	Consultant British Cement Association	Unaware of any significant work in UK on phosphates as it has not been identified as a major problem.
Dr. Peter Taylor	Principal Engineer CTL Group Skokie, Illinois	Only information is related to phosphoric acid causing acid attack, notes that ACI 515.1-79 notes that 10 to 85% phosphoric acid causes concrete to disintegrate slowly.
Dr. Michael D. A. Thomas	Prof. of Civil Eng. University of New Brunswick, Fredericton	Not aware of problems
	Florida Institute of Phosphate Research Bartow, Florida	Members unavailable to discuss topic.
	IMC Phosphates Lake Forrest, Illinois	No response.

7.   ORNL Study of Potential for Phosphate Corrosion of Ordinary Portland Cements

7.1   Thermdynamic Study

The thermodynamic database in Outokumpu's HSC Chemistry V5.11 code substantiates the basis for Dr. Power's concerns (Appendix A) that phosphate could replace calcium hydroxide [$Ca(OH)_2$] with calcium hydroxyapatite [$Ca_5(PO4)_3OH$]. In Table 2, these data show a very strong tendency for the formation of calcium hydroxyapatite.

Table 2   Phosphate replacement of CaOH2 in ordinary Portland cements (OPC).

$$5Ca(OH)_2 + 3PO_4(-3a) = Ca_5(PO4)_3OH + 9OH(-a)$$
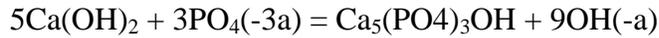
T	deltaH	deltaS	deltaG	K	Log(K)
C	kcal	cal/K	kcal		
0	-7.725	127.84	-42.64	1.33E+34	34.122
10	-7.647	128.11	-43.92	8.03E+33	33.904
20	-7.391	129	-45.21	5.08E+33	33.706
30	-7.016	130.26	-46.5	3.38E+33	33.529
40	-6.563	131.73	-47.81	2.36E+33	33.372
50	-6.054	133.33	-49.14	1.72E+33	33.236
60	-5.497	135.02	-50.48	1.31E+33	33.118
70	-4.901	136.79	-51.84	1.05E+33	33.019
80	-4.271	138.6	-53.22	8.63E+32	32.936
90	-3.612	140.44	-54.61	7.39E+32	32.869

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
$Ca(OH)_2$	74.095	56.527	5	370.473	165.39	ml
$PO_4(-3a)$	94.971	43.473	3	284.914	0	ml
	g/mol	wt-%	mol	g	l or ml	
$Ca_5(PO4)_3OH$	502.32	76.645	1	502.321	159.98	ml
$OH(-a)$	17.007	23.355	9	153.066	0	ml

Volume Change =   -3.3%

The negative deltaG's (<-42 kcal/mole) resulting in very large equilibrium coefficients ($K>10^{33}$) show that this reaction is spontaneous and that the reaction equilibrium goes from left to right as written in Table 2 (calcium hydroxyapatite density of ~3.08 gm/ml). Compared to the conversion of calcium hydroxide to calcite ($CaCO_3$), which naturally occurs in OPC's exposed to air and groundwaters and results in a ~4% volume increase, the formation of phosphates results in a net volume decrease of 3.3% compared to the calcium hydroxide conversion (volume increase ~3.87%).

Since the reaction in Table 2 only describes the reactions of calcium hydroxide and phosphate ions in an isolated system, we looked to see if this strong reaction could compete with the calcium aluminosilicates that are formed in OPC matrices. Figure 1 shows the equilibrium phases for an OPC system that is inundated with phosphate ions.

Figure 1 Phases in OPC that form under increasing exposure to phosphate (calcium hydroxide phases in red, aluminosilicates phases in blue, and phosphate phases in brown).
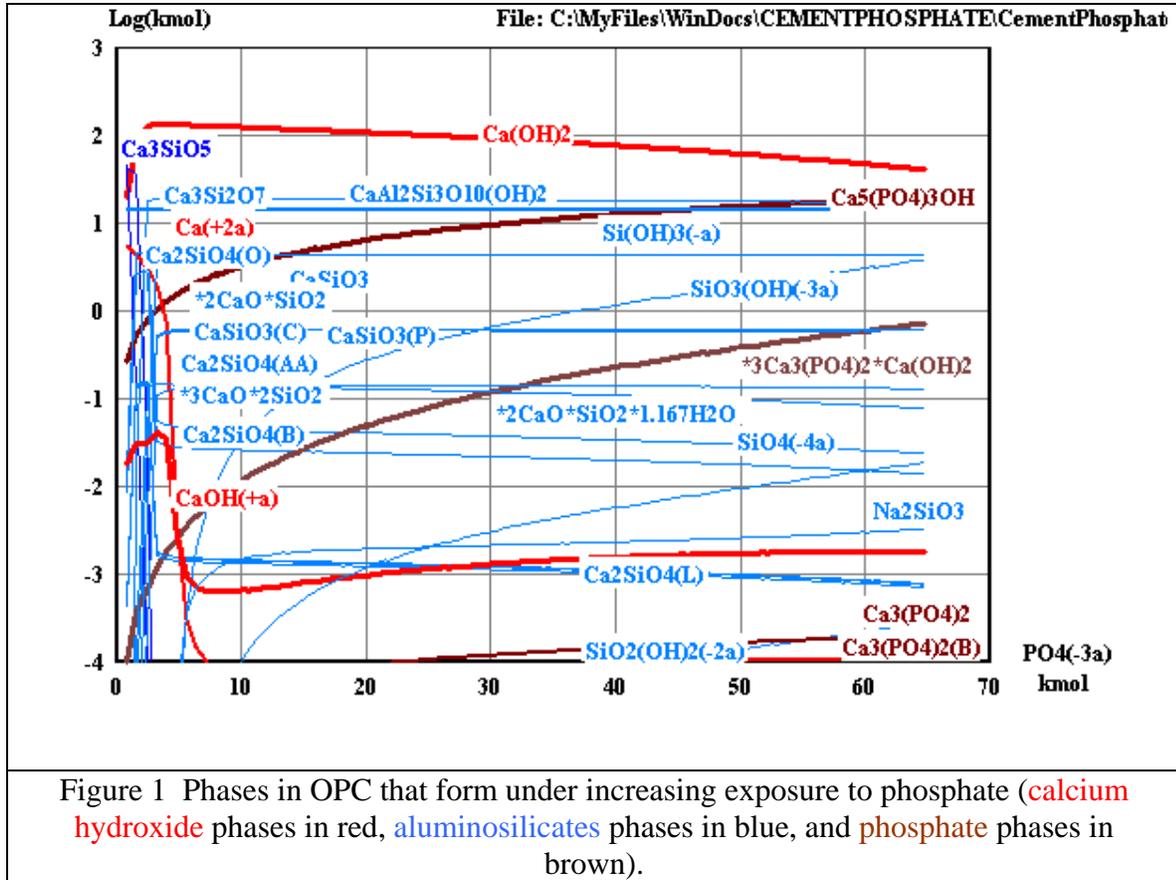
These data show that in an OPC system the formation of calcium hydroxyapatite is still capable of replacing the free calcium hydroxide (Portlandite) and competes successfully for calcium in aluminosilicate matrices.

In a future phase of this work we will examine the effects of excess silica in a pozzolanic formulation with OPC to see if reactive silica will have an effect on the competitive reactions with calcium. The impacts of carbonates in groundwaters, as well as silicates and aluminates, will also be examined.

7.2   Study of Phosphate Concentrations Controlled by Soil Minerals

Depending on its origins in a particular soil system, the dominant cations may be calcium (Ca) with magnesium (Mg), and/or sodium (Na). Therefore these elements will determine the phosphate solubilities in the soil porewaters. Anticipating the design of laboratory exposure tests and the evaluation of field exposure results, we calculated the relative phosphate solubilities as they would be controlled by the respective phosphate compounds.

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Figures 2, 3, and 4 show the sodium, magnesium, and calcium phosphate systems and the saturation aqueous phosphate concentrations, respectively. In these three cases, one mole of solid was placed on one liter of water and the equilibrium concentrations were calculated using Outokumpu HSC V5.11 system free energy minimization code and thermodynamic database. Respectively, the one mole of solids were sodium hydrogen phosphate dodecahydrate ($Na_2HPO_4*12H_2O$), magnesium phosphate ($Mg_3(PO4)_2$), and calcium hydrogen phosphate dihydrate ($CaHPO_4*2H_2O$). These compounds saturated the aqueous systems to the ranges of 10^{-1}, 10^{-3}, and 10^{-5} molar ranges, respectively. This shows that calcium rich cements and limestone/dolomite aggregates will extract phosphate from nearly all common groundwaters.
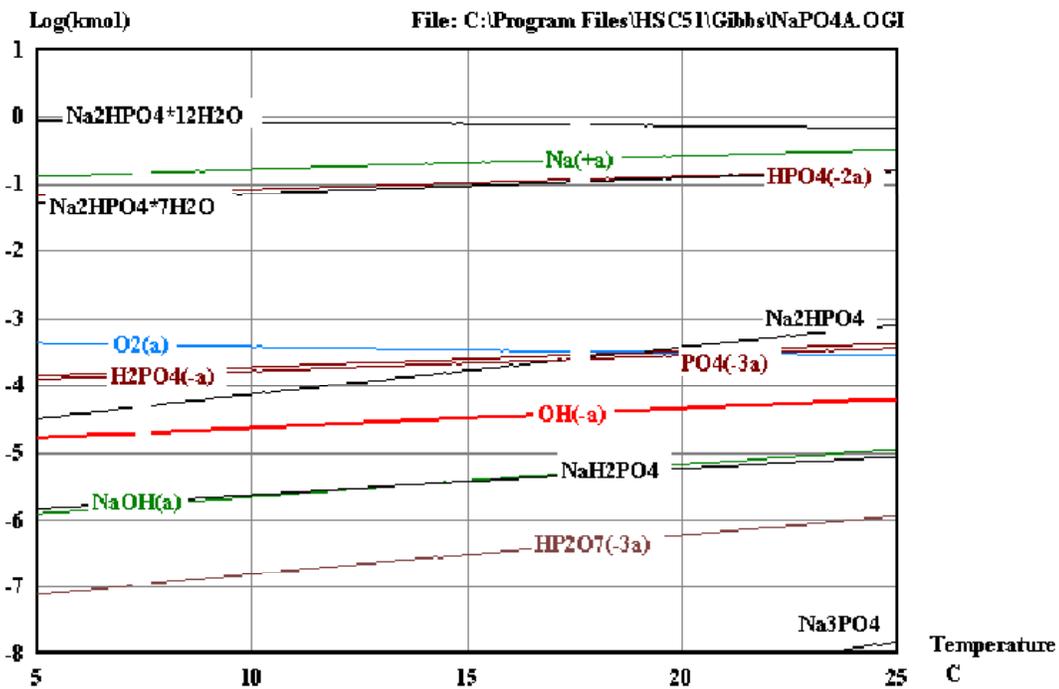
Figure 2. At equilibrium, sodium rich systems saturate the phosphate aqueous system to phosphate concentrations in the 10^{-1} molar range.
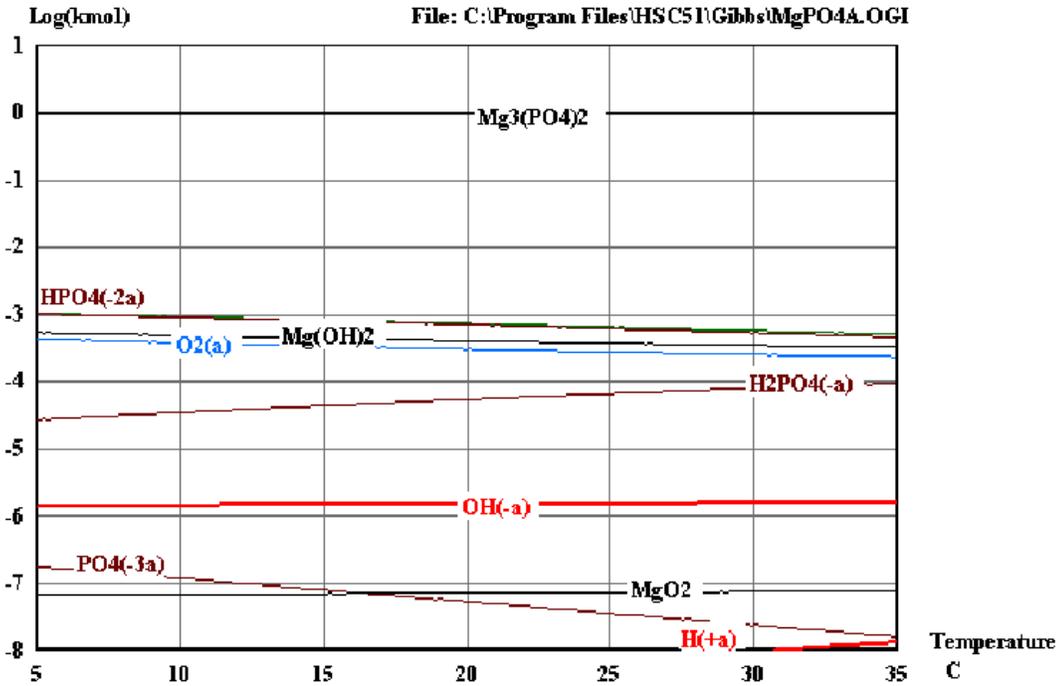
Figure 3. Magnesium rich systems buffer the phosphate solution concentrations in to the 10^{-3} molar range.
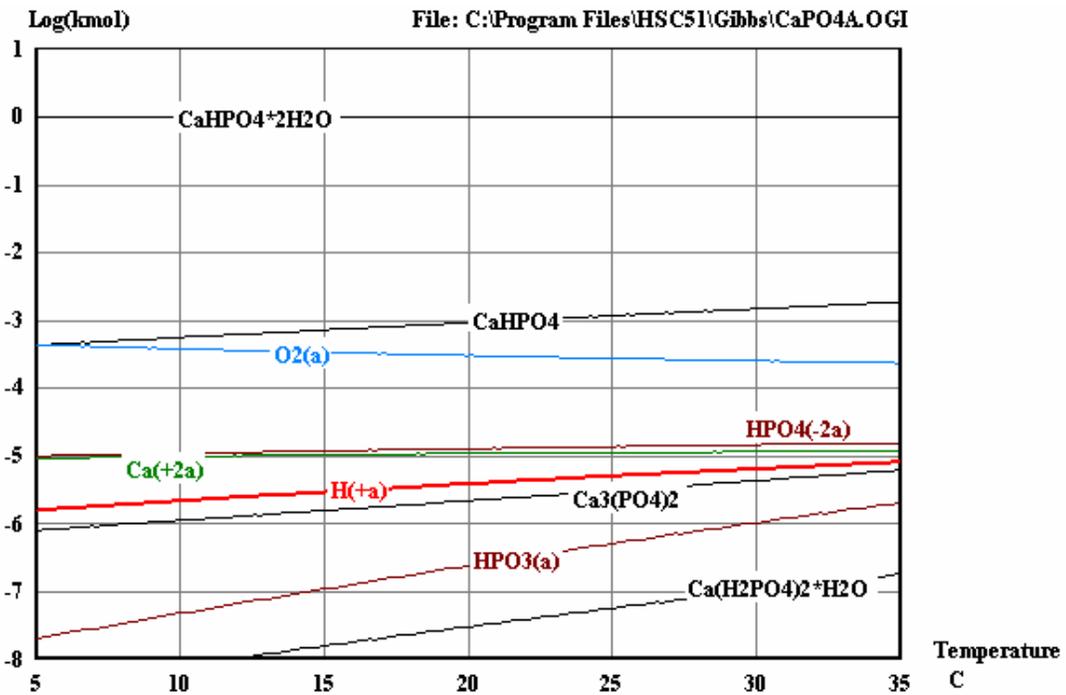
Figure 4. Calcium rich systems like cement and carbonate limestone and dolomite buffer the phosphate concentrations in to the 10^{-5} molar range.

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This shows that during exposure testing of cement, aggregates and concretes, the leachates' phosphate concentrations can be buffered for the duration of the testing by adding excess sodium hydrogen phosphate dodecahydrate ($Na_2HPO_4*12H_2O$) and magnesium phosphate ($Mg_3(PO4)_2$). Therefore, during a static exposure tests a constant phosphate concentration can be maintained with these compounds.

In a cement-dolomite aggregate system exposed to CO_2 in the air or groundwater, Fig. 5, calcium in the cement-aggregate system will extract phosphate from the solution and form calcium hydroxyapatite, as shown to be stable in SiO2*Al2O3*CaO.
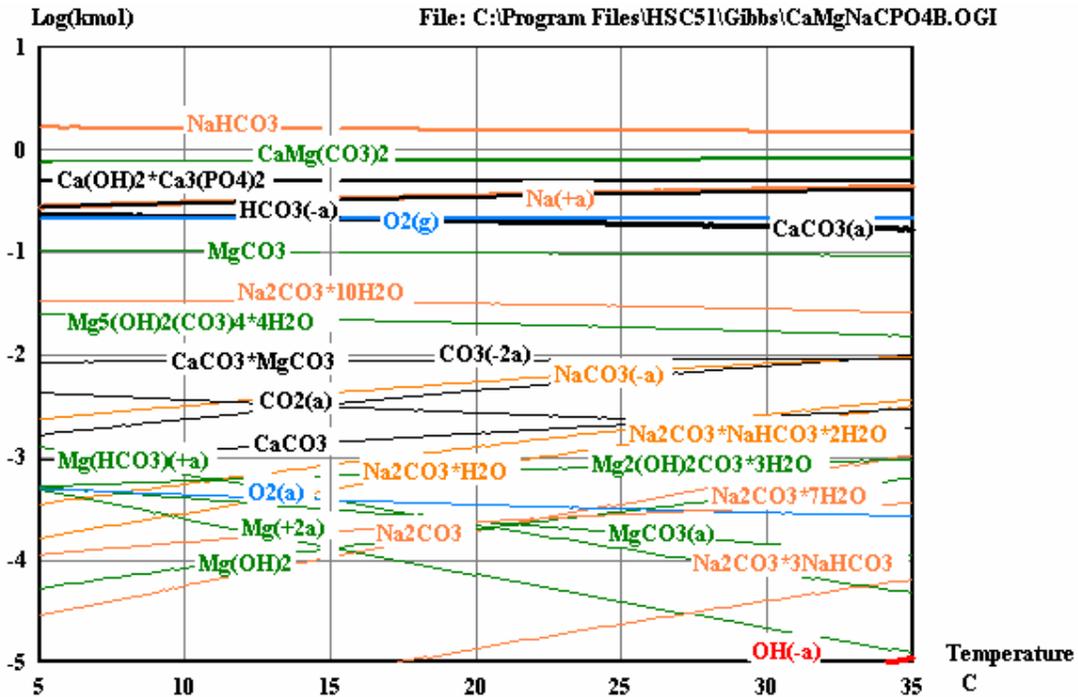
Figure 5. Calcium hydroxyapatite still forms in Na*Mg*Ca systems
in the presence of CO2 from the air or groundwater.

These results were used to design laboratory exposure tests and to interpret field observations of identified concretes that were exposed in situ.

8.   Laboratory Exposure Tests

As results of the literature review and contacts with cognizant concrete research personnel revealed little information concerning the effect of phosphates on cementitious materials, a laboratory study was designed and implemented.

8.1   Experimental Program

An outline of the experimental program developed and being conducted is provided below.

a. Preparation of fresh paste

Type II Portland cement paste having a ratio of water to cement ~ 0.40 was used to fabricate the test articles. This water/cement ratio was selected to generate samples having total porosity representative of that commonly found in current high-strength concrete formulations.   Prismatic length-change (16 specimens) and cube specimens (48 specimens) were fabricated from the mix. One-day after casting, the specimens were removed from their molds and cured under saturated conditions (100% relative humidity) until exposure testing initiated.

b. Exposure solutions

The test specimens were exposed to three test solutions and compared with an unexposed blank. The three solutions represent a control and two concentrations of phosphate ions. The phosphate solutions were selected to provide two concentrations of phosphate ions, both being much higher than normally experienced in service.

1.   A saturated calcium hydroxide solution for control
2.   A saturated low-soluble phosphate salt, magnesium phosphate
        ($MgHPO_4$),
3.   A saturated high-solubility phosphate salt, sodium hydrogen phosphate
        dodecahydrate ($Na_2HPO_4*12H_2O$).

Excess solids of these salts were poured on the bottom of a tray with enough water to cover the cubes and prisms. The aqueous brine solutions become saturated in equilibrium with the excess solids. If the cement extracts phosphate from the brines, this ensures constant concentrations in the exposure brines during the concrete (cement paste) interaction with the brine. The cubes and prisms are suspended above the excess solids by PVC corner braces.

c. Specimens and number of samples per time interval

1.   Compressive strength: triplicate 2-in. cubes for each set of test conditions and
        the blank,
2.   Dimensional change: 1 x 1 x 11-in. prisms with 4 prisms per set of parameter
        tested

d. Time intervals for testing

1.   30-day,
2.   3-months,
3.   6-months, and
4.   1-year.

e. Testing at each time interval

　　1.　　Compressive strength (ASTM C109)
　　2.　　Dimensional change (ASTM C490)
　　3.　　X-Ray Diffraction (XRD)
　　4.　　Scanning Electron Microscopy (SEM) with energy dispersive X-ray (EDX)
　　　　　probes will be applied if XRD measurements indicate the formation of significant
　　　　　new phases or if visual examinations of the exposed specimens show signs of
　　　　　degradation or secondary mineralization.

8.2　　Phosphate-Cement Interactions: One-Month Results

Figure 6 presents the test setup for the exposure testing of the prismatic and cube test articles.

Figure 6 Exposure testing in saturated brines in which PVC corner braces
are used to suspend cubes and prisms above the excess solids (visible).

As noted in Fig. 7, after 1 month exposure the samples placed into the $Ca(OH)_2$ solution exhibit no sign of crystal growth or alteration, as expected.
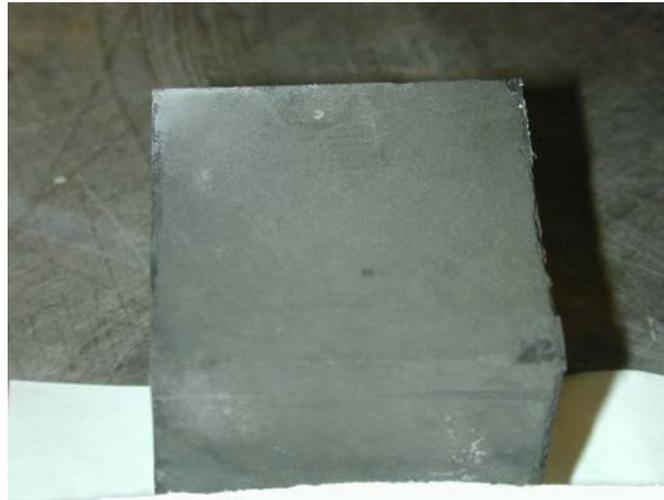
Figure 6 Cube specimen after 1 month in $Ca(OH)_2$

Figures 8 and 9, presents typical cube appearance after 1-month exposure in $MgHPO_4$ and Na_2HPO_4 solutions, respectively. As noted in the figures, the phosphate solutions are beginning to show the formation of small crystals growth on the side of the specimens.
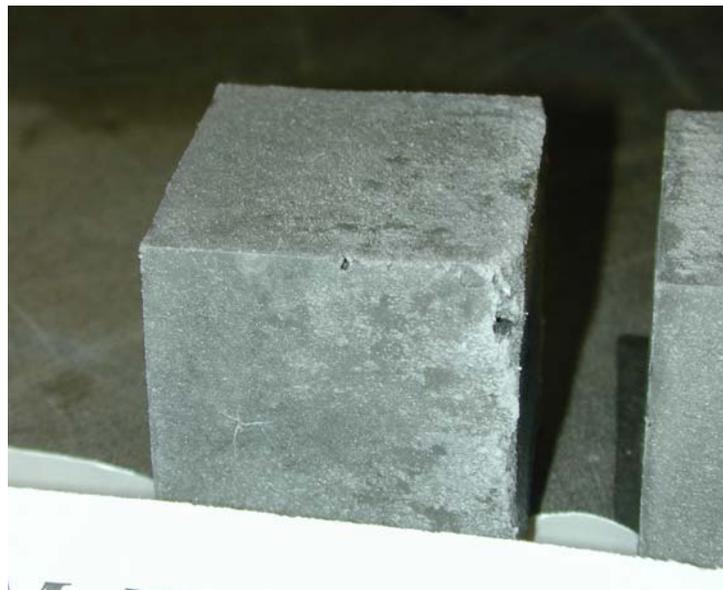
Figure 8 Cube specimen after 1 month in $MgHPO_4$.

Figure 9 Cube specimen after 1 month in Na_2HPO_4.

Weight- and length-change results for specimens after one-month exposure to $Ca(OH)_2$ (reference results) are summarized in Table 3.

Table 3 One-month weight- and length-change results for specimens submerged in $Ca(OH)_2$.

Exposure Time	Change	$Ca(OH)_2$ Sample 1	$Ca(OH)_2$ Sample 2	$Ca(OH)_2$ Sample 3	$Ca(OH)_2$ Sample 4	$Ca(OH)_2$ Sample 5	$Ca(OH)_2$ Sample 6	
1 month	Wt (g)	418.22	412.78	416.26	412.28	422	412.68	
	Δ Wt (g)	6.67	9.79	9.64	8.96	6.23	10.27	
	Δ **Wt** **(%)**	1.6	2.4	2.4	2.2	1.5	2.6	**+2.1%** **average**
	Length	1240	1179	1049	1120	1045	970	
	ΔLength	73	67	74	72	83	74	
	Δ**Length** **(%)**	6.3	6.0	7.6	6.9	8.6	8.3	**+7.3%** **average**

Tables 4 and 5 present weight- and length-change results after one-month exposure to Na_2HPO_4 and $MgHPO_4$ solutions, respectively.

Table 4 One-month weight and length change results for specimens submerged in Na_2HPO_4.

Exposure Time	Change	Na_2HPO_4 Sample 1	Na_2HPO_4 Sample 2	Na_2HPO_4 Sample 3	Na_2HPO_4 Sample 4	Na_2HPO_4 Sample 5	Na_2HPO_4 Sample 6	Na_2HPO_4 Sample 7	
1 month	Wt (g)	400.06	413.45	414.41	400.58	415.36	410.09	420.07	
	Δ Wt (g)	6.62	5.08	4.31	6.17	4.67	6.24	6.67	
	Δ Wt (%)	1.7	1.2	1.1	1.6	1.1	1.5	1.6	**+ 1.4% average**
	length	926	944	1062	1102	1214	1160	1109	
	Δ length	48	50	65	42	55	44	45	
	Δ Length (%)	5.5	5.6	6.5	4.0	4.7	3.9	4.2	**+ 4.9% average**

Table 5 One-month weight and length change results for specimens submerged in $MgHPO_4$.

Exposure Time	Change	$MgHPO_4$ Sample 1	$MgHPO_4$ Sample 2	$MgHPO_4$ Sample 3	$MgHPO_4$ Sample 4	$MgHPO_4$ Sample 5	$MgHPO_4$ Sample 6	$MgHPO_4$ Sample 7	
1 month	Wt (g)	408.18	418.16	416.92	414.58	405.06	408.71	409.68	
	Δ Wt (g)	7.12	4.84	9.03	8.69	4.99	4.72	7.76	
	Δ Wt (%)	1.8	1.2	2.2	2.1	1.2	1.2	1.9	+ 1.7% average
	Length	1107	1158	955	969	1134	1049	1034	
	ΔLength	69	77	70	165	67	81	71	
	ΔLength (%)	6.6	7.1	7.9	*20.5*	6.3	8.4	7.4	+7.3% average (*excluding the outlier*)

After one month of exposure, a few crystals are seen growing on the samples kept in phosphate solutions; however, the change in length of the specimens is not different from that measured for the control specimens $(Ca(OH)_2)$.

8.3   Phosphate-Cement Interactions: Three-Month Results

After three-months exposure the samples kept in the $Ca(OH)_2$ solution show no sign of crystal growth or alteration, as expected.   The surface of the liquid is covered by a hard film of calcium carbonate that protects the samples underneath.

The samples kept in both of the phosphate solutions are beginning to show the formation of small crystal growth on the side of the specimens.   The crystals seen of the samples submerged

in the magnesium phosphate solution appear to be somewhat larger than those observed on the samples submerged in the sodium phosphate solution. Table 6 presents an analysis of the curing solutions.

Table 6 Analysis results for the three curing solutions.

ICP analysis of the curing solutions

Results are in mg/L

	Ca(OH)2 3/01				Ca(OH)2 3/29				Ca(OH)2 06/08/05			
Aluminum	<	0.6	+/-	0.2	<	0.6	+/-	0.2	<	1.2	+/-	0.8
Barium		0.05	+/-	0.00		0.40	+/-	0.01		0.40	+/-	0.04
Calcium		746	+/-	10		715	+/-	22		744	+/-	60
Cadmium		0.03	+/-	0.00		0.03	+/-	0.00	<	0.02	+/-	0.01
Iron	<	0.9	+/-	0.2	<	0.9	+/-	0.5	<	1.8	+/-	1.0
Potassium		1.5	+/-	0.1		78	+/-	2		115	+/-	9
Sodium		5.4	+/-	0.1		28.1	+/-	0.7		40.4	+/-	3.3
Silicon	<	0.3	+/-	0.1	<	0.3	+/-	0.1	<	0.5	+/-	0.3
Strontium		0.41	+/-	0.00		1.62	+/-	0.04		1.7	+/-	0.1

	MgHPO4 3/01				MgHPO4 03/29				MgHPO4 06/08/05			
Aluminum	<	0.6	+/-	0.1	<	0.6	+/-	0.2	<	1.2	+/-	0.2
Barium		0.02	+/-	0.00		0.02	+/-	0.00	<	0.02	+/-	0.00
Calcium		14.8	+/-	0.4		5.2	+/-	0.2	<	2.6	+/-	0.9
Cadmium		0.03	+/-	0.00		0.03	+/-	0.01	<	0.02	+/-	0.01
Iron	<	0.9	+/-	0.7	<	0.9	+/-	0.2	<	1.8	+/-	0.3
Potassium		1.3	+/-	0.2		92	+/-	5		153	+/-	15
Magnesium		67	+/-	2		0.4	+/-	0.1		28.4	+/-	3.7
Sodium		5.7	+/-	0.2		35	+/-	1		62	+/-	7
Silicon		1.7	+/-	0.1		19.3	+/-	1.1		22.3	+/-	2.8
Strontium		0.03	+/-	0.00		0.01	+/-	0.00	<	0.02	+/-	0.00

	Na2HPO4 3/01				Na2HPO4 3/29				Na2HPO4 06/08/05			
Aluminum	<	6.0	+/-	4.5		25	+/-	18	<	1.2	+/-	0.2
Barium		0.18	+/-	0.02		0.14	+/-	0.01	<	0.02	+/-	0.01
Calcium	<	13	+/-	1	<	13	+/-	6	<	2.6	+/-	0.1
Cadmium		0.39	+/-	0.08		0.37	+/-	0.06		0.03	+/-	0.01
Chromium		0.51	+/-	0.11		0.59	+/-	0.01		0.69	+/-	0.04
Potassium		23	+/-	4		129	+/-	5		315	+/-	11
Magnesium		11	+/-	3		16	+/-	6		6.8	+/-	0.2
Sodium		19978	+/-	1160		24131	+/-	819		28235	+/-	999
Silicon	<	2.5	+/-	1.7		3.3	+/-	0.3		5.4	+/-	0.2
Strontium		0.11	+/-	0.01	<	0.10	+/-	0.01	<	0.02	+/-	0.00

Table 7 presents a comparison of one-month and three-month weight- and length-change results for samples submerged in the Ca(OH)$_2$ solution (reference)

Table 7 One- and three-month weight- and length-change results
for specimens submerged in Ca(OH)$_2$.

		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Average Ca(OH)$_2$
1 month	Δ Wt (%)	1.6	2.4	2.4	2.2	1.5	2.6	2.1
	Δ Length (%)	6.3	6.0	7.6	6.9	8.6	8.3	7.3
3 months	Δ Wt (%)	2.1	2.9	2.8	2.8	1.9	3.0	2.6
	Δ Length (%)	8.7	7.7	10.1	9.4	11.7	11.4	9.8

Tables 8 and 9 presents a comparison of one-month and three-month weight- and length-change results for samples submerged in the Na$_2$HPO$_4$ sand MgHPO$_4$ solutions, respectively.

Table 8 One- and three-month weight- and length-change results
for specimens submerged in Na$_2$HPO$_4$.

		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Average Na$_2$HPO$_4$
1 month	Δ Wt (%)	1.7	1.2	1.1	1.6	1.1	1.5	1.6	1.4
	Δ Length (%)	5.5	5.6	6.5	4.0	4.7	3.9	4.2	4.9
3 months	Δ Wt (%)	2.4	1.8	1.5	2.3	1.6	2.2	2.3	2.0
	Δ Length (%)	7.9	7.8	8.1	5.6	7.1	5.9	6.0	6.9

Table 9 One- and three-month weight- and length-change results
for specimens submerged in MgHPO$_4$.

		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Average MgHPO$_4$
1 month	Δ Wt (%)	1.8	1.2	2.2	2.1	1.2	1.2	1.9	1.7
	Δ Length (%)	6.6	7.1	7.9	7.2	6.3	8.4	7.4	7.3
3 months	Δ Wt (%)	2.4	1.7	2.7	2.6	1.8	1.6	2.5	2.2
	Δ Length (%)	9.1	9.4	11.4	10.6	8.9	11.8	10.1	10.2

Figures 10, 11, and 12 present one- and three-month unconfined compressive strength results for specimens submerged in Ca(OH)$_2$ (control), Na$_2$HPO$_4$, and MgHPO$_4$ solutions, respectively.
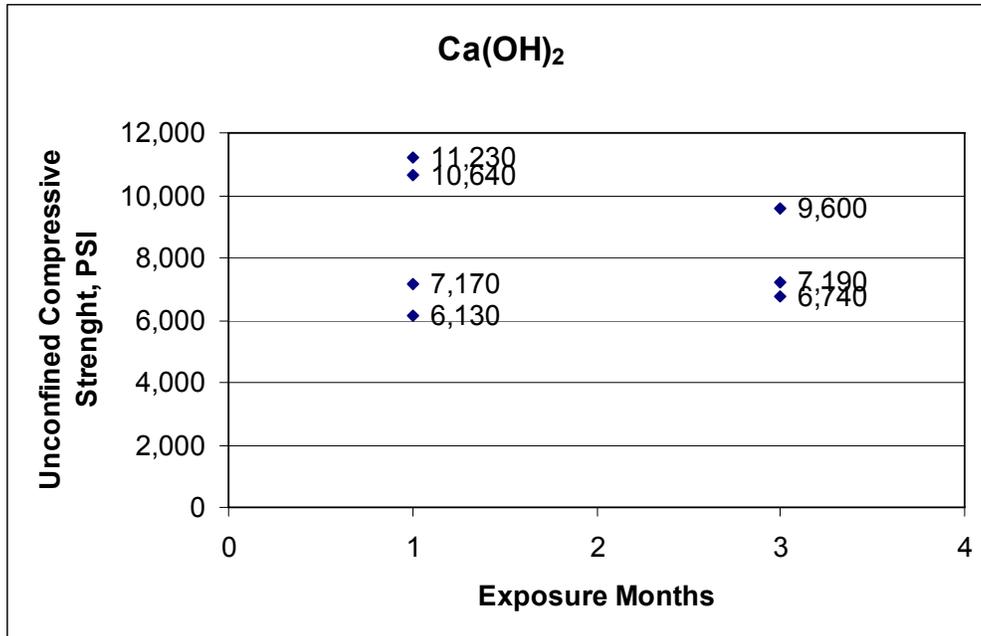
Figure 10 Unconfined compressive strength after one- and
three-month exposure of test specimens in Ca(OH)$_2$.
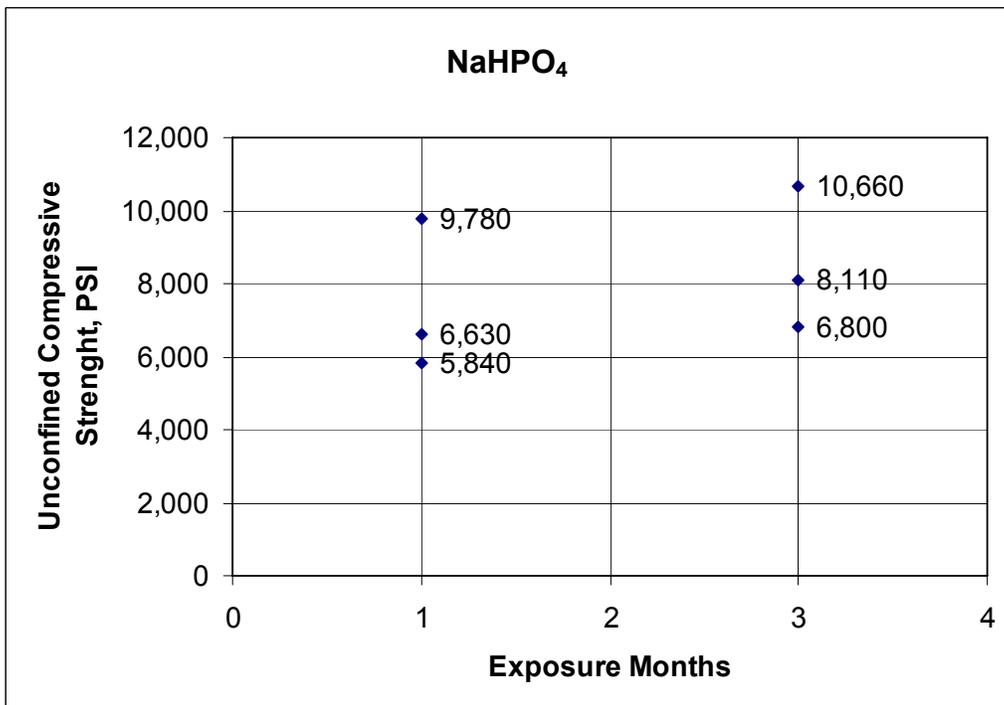
Figure 7 Unconfined compressive strength after one- and
three-month exposure of test specimens in NaHPO$_4$.
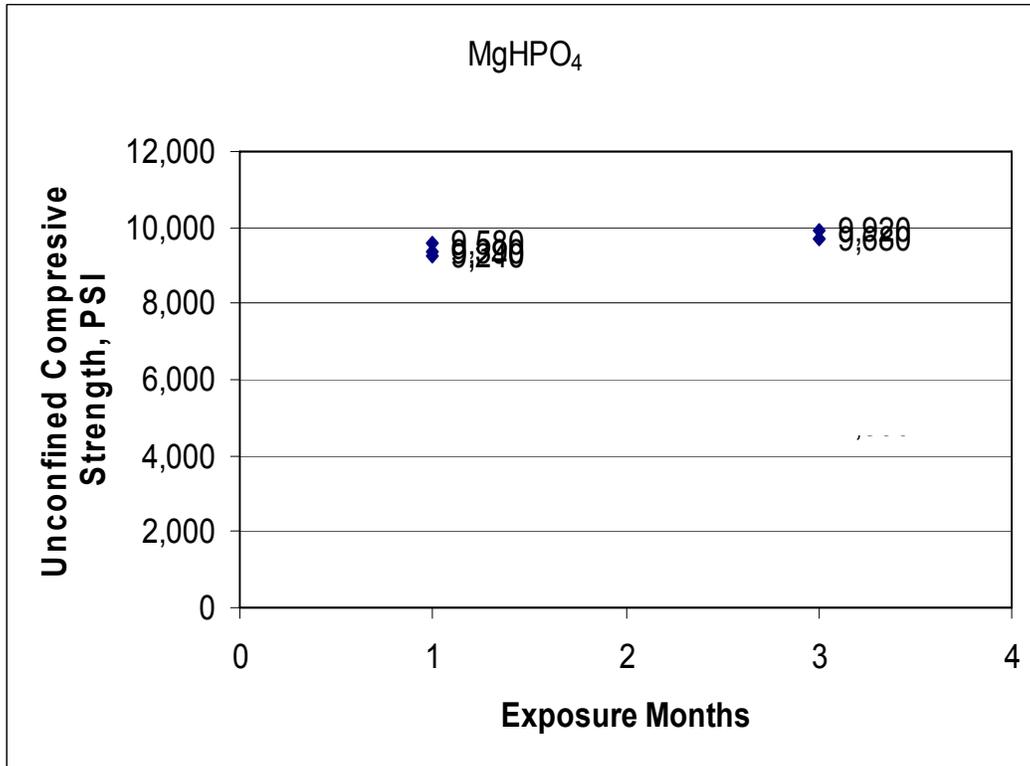
Figure 12 Unconfined compressive strength after one- and
three-month exposure of test specimens in MgHPO$_4$.

After three-months exposures, there does not appear to a significant difference between the unconfined compressive strengths of the specimens submerged in the phosphate solutions and the control specimens (Ca(OH)$_2$).

Pieces of the crushed samples after 3 months of exposure to the three curing solutions were analyzed by s-ray diffraction (XRD) to identify the minerals present.   Spectra were run from the external zone of the sample and from the center of the sample, and then compared to determine if there was an effect of the solutions on the formation of the hydrated phases near the outside border of the specimens. Results presented in Figs. 13, 14, and 15, for the Ca(OH)2, MgHPO4, and Na2HPO4 solutions, respectively, indicate no difference was visible in nature of the phases observed. The minerals identified are these found in a normal neat cement paste. The hydrated phases are Portlandite (Ca(OH)$_2$) and Ettringite (3CaO•Al$_2$O$_3$•3CaSO$_4$•32H$_2$O). Peaks from nonreacted anhydrous constituents of the cement were also identified, tricalcium silicate (3CaO•SiO$_2$), dicalcium silicate (2CaO•SiO$_2$) and, Brownmillerite (4CaO•Al$_2$O$_3$•Fe$_2$O$_3$).
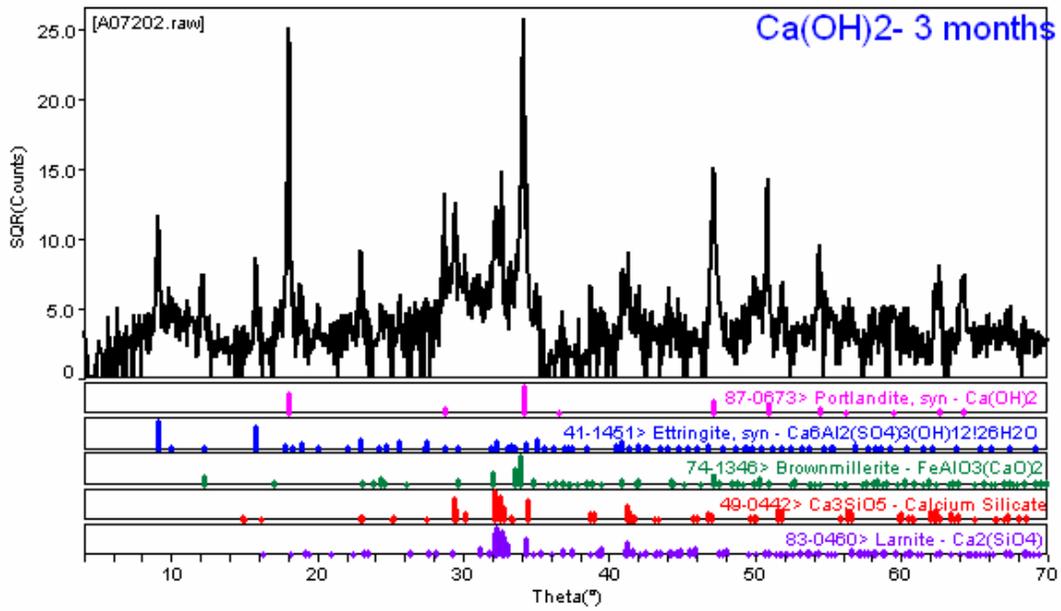
Fig. 13 XRD results after three-months exposure to $Ca(OH)_2$.
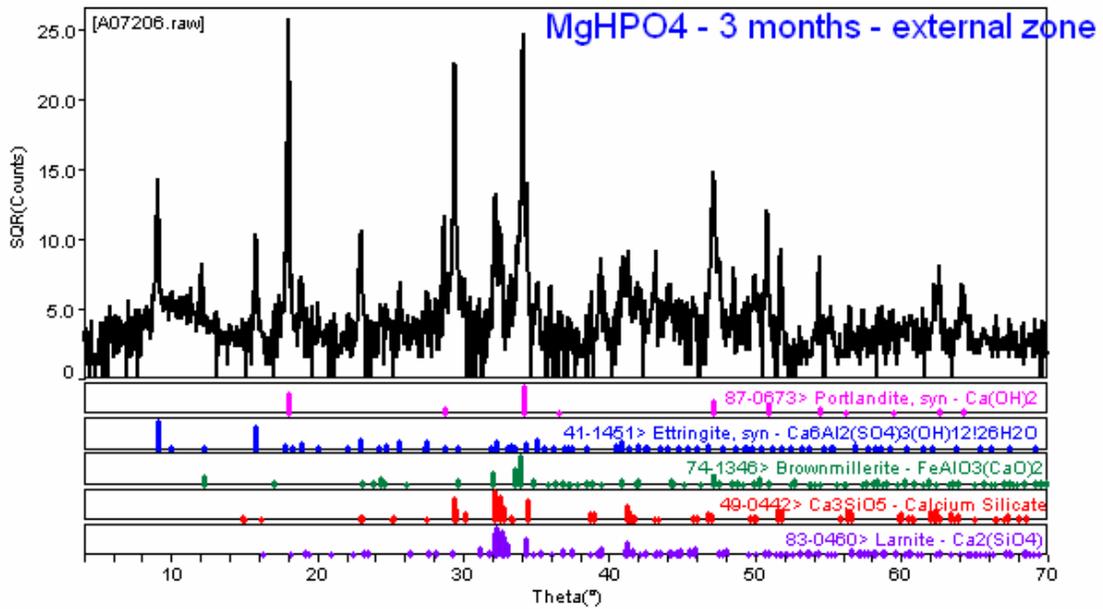
Fig. 14 XRD results after three-months exposure to $MgHPO_4$: external zone.
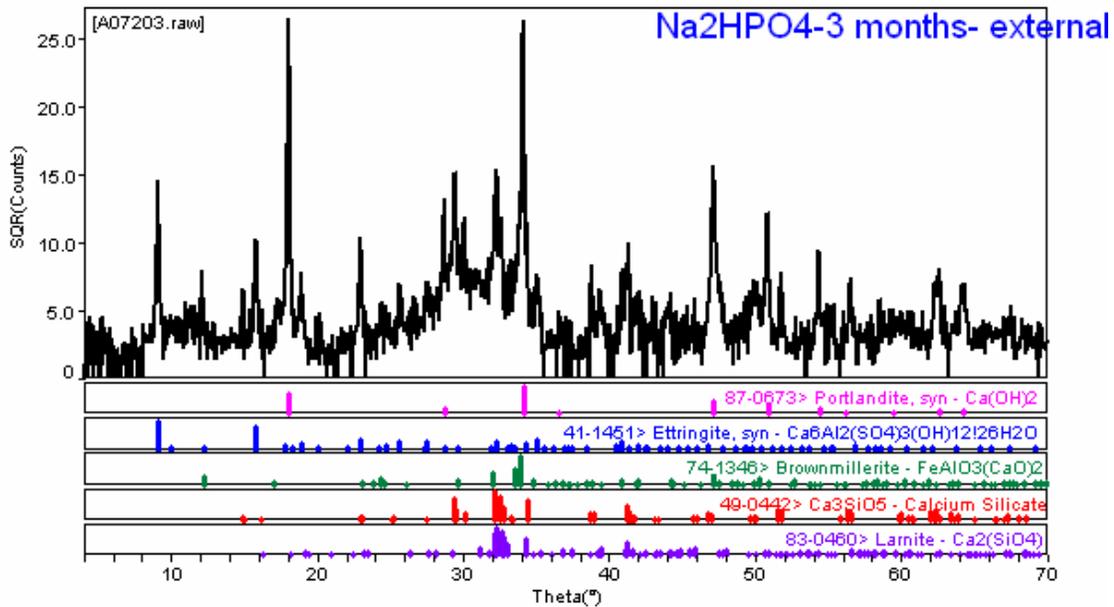
Fig. 15 XRD results after three-months exposure to Na_2HPO_4: external zone.

9.   Conclusions

Although results obtained to date are somewhat preliminary and limited, they tend to indicate no harmful interactions of phosphate and cementitious materials unless the phosphates are present in the form of phosphoric acid. A review of the literature indicates that phosphates have been incorporated into concrete to act as set retarders, phosphate cements have been developed exhibiting quick set and rapid strength gain characteristics for infrastructure repair applications, and phosphogypsum (primary by-product of fertilizer production) has exhibited potential use as a building material. No standards or design guidelines pertaining to applications of reinforced concrete structures to high-phosphate environments have been located. Contacts with several researchers indicate that potential interactions between phosphate ions and cementitious materials has not been a concern so it has not been addressed at their respective research organizations. One potential contact, the Florida Department of Transportation, indicated that they would try to obtain concrete cores from some of their transportation structures sited in high-phosphate environments. If the cores can be obtained and analyzed, this will provide significant insight into the potential for phosphate ion-concrete interactions. Experimental studies obtained over a three-month period indicate similar performance (i.e., compressive strength, weight change, and length change) of specimens submerged in two phosphate solutions (Na_2HPO_4 and $MgHPO_4$) and results from specimens submerged in the control solution ($Ca(OH)_2$). Results after six- and twelve-months exposure will provide a good indication if there are any harmful interactions between phosphate ions and cementitious materials as the phosphate solutions represent concentrations much higher than would normally be found in soils or ground water (accelerated testing).

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