CRITICAL NATIONAL NEED IDEA: A NEW CLASS OF CONSTRUCTION MATERIALS FOR THE NATION'S INFRASTRUCTURE

Submitting Organization: Structures and Materials Testing Laboratory of the University of Wisconsin-Madison

Contributing Organization:

Contact: Prof. Steven M Cramer, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI

Phone: 608-265-2001

Fax: 608-262-6400

Email: cramer@engr.wisc.edu

CRITICAL NATIONAL NEED IDEA:

A NEW CLASS OF CONSTRUCTION MATERIALS FOR THE NATION'S INFRASTRUCTURE

S. Cramer, S. Owen and A. Agosto

The Need

The nation's interstate highway system is now nearly 50,000 miles long and the nation spends approximately \$70B per year on capital outlay and maintenance of state administered roads. The magnitude of the system and the cost are likely beyond the comprehension of the citizenry that must pay for the system to keep it functional. The cost of user delays when portions of highways are closed due to reconstruction or maintenance are largely unmeasured, but even rough estimates would greatly increase the costs beyond simple outlays for capital and maintenance expenditures. In some urban areas such as Los Angeles and Seattle, total reconstruction with highway closure is no longer an option and instead fast repair techniques are conducted on an on-going basis during low traffic volume times.

With high volume, heavily loaded highways and bridges, Portland cement concrete remains the material of choice for construction. There was a time when construction with Portland cement concrete reliably provided long life using relatively simple design rules about the materials employed. Additives were rarely used, high quality aggregates were readily available and obeying simple rules regarding water-to-cement ratio with wet curing provided relatively reliable performance. Now the high use of admixtures, mineral additives such as fly ash, cementitious substitutes such as slag cement, a variety of curing compounds and the use of locally available aggregates that may not be optimal present chemical instabilities leading to an infrastructure product that is less predictable and less reliable. The important concept here is that Portland cement concrete achieves its strength and durability through chemical reactions and there are now more chemical variables to consider in achieving a suitable outcome. Any one of a number of different adverse chemical reactions from anyone of a number of sources often prompted by the presence of water and deicing chemicals can cause premature concrete deterioration. The expense of premature concrete distress is an undocumented cost of construction which further inflates the numbers listed above.

In recognition of the costs and increasing difficulty of complete reconstruction, many states are now experimenting with 50 to 100-year service life concrete. The problem is that they are doing so in an increasing complex chemical environment for cement hydration and are relying on the same rules and tests that guided concrete construction 40 years ago. The failure of anyone component whether it be corrosion of reinforcing steel/dowels, adverse chemical reaction prompted by reactive aggregates or microfines and water intrusion, or incompatible additives makes the likelihood of

hitting these new longevity targets all the more difficult and unlikely. These new longevity standards typically require high performance concrete mix designs but again these are simply enhanced, low water-to-cement ratio mixes that should possess greater strength and durability but have many of the same chemical vulnerabilities as traditional Portland cement concrete.

Two primary limitations of Portland cement concrete exist today in ordinary Portland cement concrete (OPCC) and the typical high performance versions used by the states. The first fundamental limitation is a relatively low tensile strength which primarily exhibits itself as cracks in concrete products. This limitation is addressed by adding reinforcement to the concrete typically in the form of steel fibers, steel bars or steel mesh and/or by controlling the cracking through predetermined crack locations. The second fundamental limitation is that water intrusion into the concrete can cause both physical damage during freezing and thawing and chemical damage by instigating a series of secondary chemical reactions that can cause degradation of the concrete matrix. This type of behavior can cause surface scaling, cracking and crumbling of concrete much earlier than weather and age might be expected to cause similar degradation.

The premise of this paper is that the cost of infrastructure (highways, bridge decks) is unsustainable with current materials. Addressing the challenge of urban infrastructure is one of the engineering grand challenges identified by the National Academy of Engineering (2009). Enhancements to Portland cement concrete that greatly reduce the two fundamental weaknesses - low tensile strength and water permeability - are within reach and implementable but not without focused research and development. Preliminary information suggests that using material science and examining Portland cement concrete from a nanoscale perspective, that the material can be significantly enhanced. The resulting change in concrete properties would transform the performance and expectations of our infrastructure and ultimately result in tremendous cost savings to the public.

The Potential for Alternate Materials

Portland Cement Polymer Concrete (PCPC) provides a promising alternative that builds on the existing concrete industry yet provides an improvement to the product at reasonable cost. These seemingly minor changes would transform how infrastructure is designed and maintained. Portland cement polymer concrete combines the materials of ordinary Portland cement concrete with a polymer or monomer in the wet mix. After the concrete is mixed and molded, the cement hydrates in parallel with polymer curing or monomer polymerization. Common synonyms include polymer cement concrete (PCC), polymer Portland cement concrete (PPCC) or polymer modified concrete (PMC). There are two types of PCPC - pre-polymerized and post-polymerized - which correspond to the use of polymer versus monomer.

Pre-polymerized PCPC contains polymers that are already in a chain polymer structure before they are mixed into the wet mix (El-Hawary 2005). Some examples of polymers used are: epoxy, latex, polystyrene and polypropylene (Popovics 1978). The polymer is mixed into the wet mix and allowed to cure simultaneously with the cement hydration. The material may need to be heated before mixing in order to decrease its viscosity. This process has yielded moderate strength gains in tension and compression but has not shown improvement in the tension-to-compression strength ratios. Such additives are widely available but do not offer transformational changes in the final product.

Post-polymerized PCPC contains monomers that are mixed into the wet mix then polymerized simultaneously with the hydration process. Two common monomers used are styrene and maleic anhydride. While styrene can polymerize on its own to form polystyrene, maleic anhydride cannot and must be polymerized with styrene to create styrene-maleic-anhydride copolymer (Baruah 1996). The monomers must be initiated by a free radical initiator such as benzoyl peroxide or azobisisobutyronitrile (Bevington 1957). After initiation the monomers begin to form polymers or copolymers. In most cases, the polymerization is accelerated by applying heat or radiation light energy to break up the free radical initiators. The monomers then polymerize within the pores of the cement and aggregate. This type of PCPC was attempted several times in the mid 1970's and reported in symposiums of polymer in concrete research put together by the American Concrete Institute (Dikeou 1977). It was tried again in 1980 by S. Hudson Owen, a mechanical engineer in Marshfield, Wisconsin. The fundamental difficulty with this approach is that the monomer is introduced as a hydrophobic resin in an otherwise water-based mixture. The polymerization and dispersion of the monomer combined with simultaneous hydration of the cement paste will not occur naturally and requires special mix control and equipment to be successful. It is a comprehensive solution to this difficulty which has prevented the development and implementation of this superior concrete material.

1970's Polymers in Concrete

In 1971, Gebauer and Coughlin experimented with post-polymerized PCPC using the monomers methylmethacrylate (MMA) and styrene. They cast paste and mortar specimens into 1inch diameter by 2inch high glass vials and used heat or irradiation to polymerize the monomers at 25°C for 28 days. The specimens were then held at 70°C for 8 hours then dried at 105°C for 48 hours after the glass was removed. The mortar had a water to cement ratio of 0.40 and a monomer to cement ratio of 0.20. They conducted several tests including compression tests and absorption tests. They found that the inclusion of MMA yields poorer properties than the control and concluded that the monomer may interfere with the cement hydration process. The inclusion of styrene monomer yielded better results than the control in both compression and absorption. The compressive strength increased 2 to 3ksi from the control 7ksi and the water absorption fell from 7% to about 1.5%. Unfortunately, Gebauer and Coughlin did not conduct any tension or bending tests which could have been used to compile tension-to-compression strength ratios. There was also no information on how the monomers were dispersed into the wet mix. They reported no polymer

matrix, only glossiness while observing the specimens through an electron microscope. Their research does help confirm that styrene monomer post-polymerized PCPC can improve impermeability and compressive strength over OPCC and that styrene monomer tends not to interfere with the cement hydration process.

In 1973, Chen and Jorgensen attempted to produce post-polymerized PCPC using diacetone diacrylamide monomer. This solid monomer was first dissolved in water then mixed with cement and aggregate. The specimens were subjected to heat treatment and moisture curing. The results were poor and the specimens tended to crack and crumble before testing could occur. They concluded that the monomer reacted 'unfavorably' with the hydration of the cement. The remainder of their work focused on pre-polymerized PCPC. This research again showed the sensitivity of cement hydration to certain organic compounds.

In 1974, Morgan, Cook, Chaplin, and Sirivivatnanon conducted a study entirely on post-polymerized PCPC. They used a combination of the following five monomers: acrylonitrile, styrene, methyl methacrylate, vinyl acetate and polyester-styrene. When polymerized, these monomers formed a number of polymers and copolymers. They varied monomer volume, surfactants and polymerization method including irradiation and thermal. Their results showed slight to modest increases in compressive strength for mortars containing up to 10% monomer using styrene and methyl methacrylate. A maximum compressive strength increase of 6.4% was achieved with styrene and 16.3% with methyl methacrylate. Acrylonitrile, vinyl acetate and polyester-styrene trials all yielded strengths less than control and sometimes produced specimens with non-hydrated cement. Some of these specimens emitted monomer odor that indicated polymerization was not complete. This research gave more examples concerning which monomers hinder the hydration of cement and again confirmed that styrene tends not to.

In 1976, Morgan, Cook, Chaplin, and Sirivivatnanon continued on their previous work and focused on paste set time as well as cement hydration effects from monomer inclusion. Three additional monomers were added to the study: isoprene, 2-hydroxy-ethyl methacrylate and butyl methacrylate. They found that acrylonitrile and methyl methacrylate monomers acted as mild set retarders increasing the set time between 125 and 275 minutes. Polyester styrene and 2-hydroxyethyle methacrylate monomers had a large retarding effect delaying set time by more than a day. All other monomers, including styrene, had no significant effect on set time. By measuring the percentage of chemically combined water, they determined that the inclusion of the monomers had a decreasing effect on the amount of hydration. Styrene monomer contributed to a 20% decrease in hydration. This research showed that styrene can partially hinder the hydration of cement even though previous studies have found specimen strengths and set times to be unchanged.

In 1977, the American Concrete Institute under Chairman James T. Dikeou reported on polymers in concrete including post-polymerized PCPC. The report summarized several problems associated with post-polymerized PCPC to date which included: 1) interference with hydration of the Portland cement; 2) chemical reaction between monomer and the cement paste, e.g. hydrolysis; 3) difficulty

in dispersing the organic component through the mix; and 4) poor polymer-aggregate bond. After this report, no other research was found that attempted to create post-polymerized PCPC with styrene or other types of monomer.

1980 Hudson Owen Tests

Building on the work of Steinberg (1968 1969) between 1970 and 1980 S. Hudson Owen, a mechanical engineer, worked privately on developing PCPC. Using a modified custom concrete mixer, he developed a method that successfully produced PCPC with increased performance properties. Lack of funding ended the project and resulted in liquidation of the equipment. However, Mr. Owen documented his work and preliminary investigation has revealed the potential to fully develop PCPC. Although the material was successful in 1980 the mechanisms by which it was successful were not investigated at the time.

Several years ago the information that Owen developed was presented to Dr. Steve Cramer with the request that he evaluate the method of manufacture for PCPC and ascertain its potential to become a transformational technology in the field of material science. Under Dr. Cramer's direction Andrew Agosto wrote an M.S. thesis on applying PCPC to bridge deck design resulting in the conclusions outlined below.

The values in Table 1 are the defined properties for the 1980 PCPC specimens. The strength values in Table 1 are based on compression and split tension cylinder tests conducted in 1980 Mixes that contained 20% Dylark 332 produced the properties in Table 1. Examination of Table 1 reveals a concrete with a tensile strength approximately three to five times higher than expected. The impermeability property was first observed by Mr. Owen in 1980. When water was introduced to the surface of the material it would bead off while water on OPCC would soak in. The 1980 PCPC was sawn into disks and approximately ½ an ounce of water was placed onto one disk and observed overnight. The majority of the water evaporated before soaking in.

PCPC Defined Properties	Value	Based On
Ultimate Tensile Strength	1,500 (psi)	1980 3"x6" Cylinder Tests Run by John
Tension/Compression Ratio	0.30 - 0.50	Herzog at University of Wisconsin- Madison
Compressive Strength	5,000 - 3,000 (psi)	
Water Absorption	Relatively Impermeable	Generally Impermeable by Observation

The properties achieved in Table 1 were preliminary attempts and optimization is possible. While higher compressive strengths are relatively easy to obtain, it is the tensile strength-to-compressive strength ratio and the impermeability which are of special interest.

Work by Agosto

Agosto (2008) further investigated the work by Owen by examining the potential use of the PCPC material for bridge decks. Although he was unable to reproduce the properties observed by Owen because of equipment limitations, he determined that a monomer-water inversion process was necessary to create a semicontinuous polymer matrix and that the timing of the polymerization process and the hydration process were critical to achieving the desired properties. Assuming the properties that Owen achieved could be duplicated, Agosto conducted a preliminary bridge deck design and life cycle cost analysis. His preliminary design showed that with the tensile strength achieved with the PCPC the amount of concrete and steel used for a bridge deck could be reduced by almost 50%. He also found that maintenance costs over a 70 year period would be reduced by nearly 80% compared to a conventional ordinary concrete bridge deck.

<u>Summary</u>

The premise of this paper is that the cost of infrastructure construction and maintenance is unsustainable with current materials. Enhancements to Portland cement concrete to greatly reduce the two fundamental weaknesses - low tensile strength and water permeability - are within reach and implementable, but not without focused research and development. Preliminary investigation into the Owen method for making PCPC with substantially reduced absorption and useable tensile strength indicates that this is a transformational technology that may yield order of magnitude improvements and life expectancy to concrete structures. Substantial research and development work needs to be accomplished to make this technology available for general application. Since a large portion of concrete applications are government controlled structures (roads, bridges, dams) it is logical to request the help of government in developing programs to implement this research. It is requested that the NIST Technology Innovation Program consider this transformational technology for funding and technical support.

References:

- Agosto, A. (2008). *Rethinking Bridge Deck Longevity and Maintenance with Portland Cement Polymer Concrete*, Master of Science Thesis, Department of Civil and Environmental Engineering, University of Wisconsin-Madison, 133 pgs.
- AZoM (2007). Styrene Maleic Anhydride Copolymer. *SMAc. A to Z of Materials*. Retrieved June 27, 2007, from http://www.azom.com/details.asp?ArticleID=889
- Baruah, S. D., & Laskar, N. C. (1996). Styrene-Maleic Anhydride Copolymers: Synthesis Characterization, and Thermal Properties. *Journal of Applied Polymer Science, 60*, 649-656.
- Bevington, J.C. (1957). The Nature of the Initiation Reaction in the Polymerization of Styrene Sensitized by Benzoyl Peroxide. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 239, No. 1218* (pp. 420-432).
- Bosma, M., Vorenkamp, G., Challa, B., & Challa, G. (1988). Influence of the degree of hydrolysis of poly(styrene-alt-maleic anhydride) on miscibility with poly(vinyl acetate). *Polymer, 29, 1694-1698*.
- Bridge LCC (2003) Analyses Interest Rates. *Office of Applied Economics, Building and Fire Research Laboratory, National Institute of Standards and Technology*. Retrieved February 2, 2008, from http://www.bfrl.nist.gov/bridgelcc/analyses.html
- Chen, W., & Jorgensen, E. D. (1973). Stress-Strain Properties of Polymer Modified Cocnrete. *Polymers in Concrete, American Concrete Institute Report, Detroit* (pp. 347-358).
- Civil Engineering (1992) Conference Promotes Polymer Concrete Rehab. ABI/INFORM Global. *Civil Engineering, 62(5),* 21-22.
- Cook, D.J., Morgan, R.P., Chaplin, R.P., & Sirivivatnanon, V. (1976) *Hydration Characteristics of Premix Polymer Cement Materials. Asian Institute of Technology*. Bangkok, Thailand. University of New South Wales, Australia.
- Costantino, R. Henry et al. (2002). Protein Spray Freeze Drying. 2. Effect of Formulation Variables on Particle Size and Stability. *Journal of Pharmaceutical Sciences*, *91(2)*, 388-395.
- Dikeou, J. T. (1977). Polymers in Concrete. *Reported by American Concrete Institute Committee 548, American Concrete Institute 1977*, Detroit, Michigan.
- Ehlen, M. A.(1999) Life-Cycle Costs of Fiber-Reinforced-Polymer Bridge Decks. *Journal of Materials in Civil Engineering*, 11(3), 224-230.
- El-Hawary, M. M., AlKhaleefi, M. A., & Abdel-Fattah, I. H. (2005). On the Mechanical Properties of Polymer Portland Cement Concrete. *Journal of the Chinese Institute of Engineers, 28(1),* 155-159.
- Fleet, L. H., & Gardner, W. H. (1952). *Maleic Anhydride Derivatives; Reactions of the Double Bond*. John Wiley & Sons, New York.
- Gauthier, M.A. et al (2005). Oxygen Inhibition in Dental Resins. Research Reports Biomaterials & Bioengineering. *Journal of Dental Research*, 84(8), 725-729.
- Gebauer, J., & Coughlin, R.W. (1971). Preparation, Properties and Corrosion Resistance of Composites of Cement Mortar and Organic Polymers. *Journal, Cement and Concrete Research, 1(2),* 187-210.
- Grace W.R. (2008) *Grace Construction Products*. Cambridge, Massachusetts. http://www.na.graceconstruction.com/
- Harrisson, S., & Wooley, K. L. (2005). Shell-crosslinked nanostructures from amphiphilic AB and ABA block copolymers of styrene-alt-(maleic anhydride) and styrene: polymerization, assembly and stabilization in one pot. *The Royal Society of Chemistry, Chem. Communication, 26*, 3259-3261.
- Huang, Y., Adams, T., & Pincheira, J. (2004). Analysis of life-cycle maintenance strategies for concrete bridge decks. *Journal of Bridge Engineering ASCE, 9(3),* 250-258.

IES, Inc (2005). Visual Analysis 5.5.22 & Shapebuilder 2.0. *Integrated Engineering Software, Inc*. [CD-ROM].

Morgan, D.R., Cook, D.J., Chaplin, R.P., & Sirivatnanon, V. (1974) *Premix Polymer-Concrete Mortar*. UNICIV Report No. R-132, University of New South Wales, Sydney, Australia. Retreived from University of New Brunswick Libraries.

National Academy of Engineering. (2009). http://www.engineeringchallenges.org/cms/8996/9136.aspx

Ohama, Y. (1995). *Handbook of Polymer-Modifiend Concrete and Mortars, Properties and Process Technology*. New Jersey: Noyes Publications.

- Opeida, I.A. et al (2006). Initiation of Radical-Chain Processes with Mixtures of Benzoyl Peroxide and Azobis(isobutyronitrile). *Russian Journal of Applied Chemistry*, *79*(*5*), 823-826.
- Popovics, S., & Tamas, F. (1978). Investigation on Portland Cement Pastes and Mortars Modified by the Addition of Epoxy. *Polymers in Concrete International Symposium, American Concrete Institute Report*, Detroit, Michigan, 357-363.
- Rezayat Procoat (2005). *Rebar Adding Value to Construction*. Rezayat Protective Coating Company Ltd. http://www.rezayatprocoat.com/rebar.jsp
- Sigma-Aldrich (2008). Sigma-Aldrich Company. St. Louis, Missouri. http://www.sigmaaldrich.com/Area_of_Interest/The_Americas/United_States.html
- Sika Corporation (2003). *Construction Products Division*. Lyndhurst, New Jersey. http://www.sikaconstruction.com
- Sonner, C., Maa, Y-F., & Lee, G. (2000) Process Effects on the Properties of Spray-Freeze-Dried Powders. 3rd World Meeting on Pharmaceutics, Biopharmaceutics & Pharmaceutical Technology, Berlin, Germany.
- Stachurski, Z.H. (2003). Strength and deformation of rigid polymers: structure and topology in amorphous polymers. *Polymer*, *44*, 6059-6066.
- Steinberg, M. et al (1968). Concrete-Polymer Materials. *First Topical Report. U.S. Department of Commerce National Technical Information Service, Brookhaven National Lab BNL50134*, Upton, New York.
- Steinberg, M. et al (1969). Concrete-Polymer Materials. Second Topical Report. U.S. Department of Commerce National Technical Information Service, Brookhaven National Lab BNL50218, Upton, New York.
- Steinberg, M. (1973). Concrete Polymer Materials and its Worldwide Development. *Polymers in Concrete, American Concrete Institute Report*, Detroit, Michigan, 1-9.
- Styrene Polymers to Toys (1985). *Encyclopedia of Polymer Science & Engineering* (Second Edition) (Vol. 16, pp. 1-246). John Wiley & Sons, New York.
- Tasong, W.A., Cripps, J.D., & Lynsdale, C.J. (1998) Aggregate-Cement Chemical Interactions. *Cement and Concrete Research*, 28(7), 1037-1048.