Determining the Appropriate Amount of Time to Isolate Portland Cement Concrete from Receiving Waters

Requested by
Margaret Lawrence, Environmental Division

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Executive Summary

Background

In bridge construction, footings and columns made of portland cement concrete (PCC) are often constructed by pouring PCC into forms set into the stream bed and allowing it to cure. Under some circumstances, contact with the uncured PCC may cause a significant increase in the pH of the surrounding waterway, negatively affecting aquatic life. As PCC cures, the potential for increasing pH in surrounding waters declines.

A solution's pH is a measure of how acidic or basic it is, with a pH of 7 representing a neutral solution. Acids have a pH below 7, while bases have a pH above 7. Formally, pH measures the hydrogen ion activity of a solution. For most basic solutions, however, a simpler but accurate way to determine pH is by measuring the concentration of hydroxyl (OH^-) ions in the solution. Additionally, pH is a logarithmic scale, so a one-point increase in pH reflects a tenfold increase in hydroxyl concentration.

Caltrans is currently required by the California Department of Fish and Wildlife (CDFW) to isolate via an impermeable barrier any PCC formed in flowing water for a minimum of 30 days as a project requirement in the state Fish and Game Code Section 1600 Streambed Alteration Agreements. (Section 1602(a) of the code prohibits "the deposit or disposal of debris, waste or other material containing crumbled, flaked or ground pavement where it may pass into any river, stream or lake.") Caltrans pours PCC concrete into a water-tight form, so there is no contact between PCC and flowing water until the form is removed.

Extended isolation from adjacent water of structural concrete construction or repair projects may add contractor time and cost to projects. Caltrans wishes to protect water quality while also undertaking concrete construction projects as cost-effectively as possible. To help balance these needs, Caltrans is interested in learning about research on the effects of freshly poured concrete on the pH of adjacent waters and how long after pouring the pH could remain significantly increased.

This Preliminary Investigation is based on a limited review of available literature and guidelines of selected agencies, and interviews with academic and industry experts.

Summary of Findings

Research

Effects of Leaching from Fresh Concrete (see page 5)

We were only able to identify four literature citations directly related to measuring the effects of fresh concrete on pH levels in water. All four citations are based on laboratory research conducted by investigators at RMIT University in Melbourne, Australia. In publications from 2009 to 2013, the authors describe laboratory research on the release of hydroxyl ions from freshly cast concrete exposed to water. The research shows a decline in pH to neutral levels within a few days of exposure.

CTC & Associates spoke with RMIT's Sujeeva Setunge, one of the investigators involved in the research. She cautioned that while her research and that of her colleagues is unique in its scope, the research is in its early stages and has been limited so far to laboratory testing of concrete specimens. The group's research simulating stream flow has been limited to relatively short periods of exposure. She offered to discuss the group's findings and outstanding research questions with Caltrans.

Effects of Concrete Grout on Water pH (see page 8)

This section describes two research projects by state agencies in Maryland and Virginia. While not directly related to construction of concrete footings or columns, the projects may be of interest to Caltrans, as concrete grout (a mixture of water and cement) contains the components of PCC that are likely to affect water pH.

In the Maryland project, repairs to steel culverts using concrete grout were shown to spike water pH above the state regulatory limit of 8.5. However, laboratory and field testing suggested that spikes in pH are most significant within the first few hours, and highly localized.

The Virginia study examined the use of concrete grout to repair bridge piers damaged by scour. The study found that turbidity curtains were effective at protecting the waterway from elevated pH levels. Made of permeable fabric, turbidity curtains are installed around a construction site no more than 1 meter beyond the perimeter of the placement of concrete grout. They span the entire height of the waterway, from the stream bed to the surface. The permeable curtain allows the high-pH water inside to slowly "bleed out" into the waterway at large. This results in a detectible but minor increase in the pH of the waterway. In some cases the "bleeding out" process took up to 30 hours, but the pH in the waterway never increased beyond Virginia's regulatory limit of 9.0.

The study also found that in-stream pH values could be kept below 9.0 through the use of a combination of site-specific placement techniques and an anti-washout admixture.

Mitigation Methods (see page 10)

The studies we reviewed mentioned a few mitigation methods aimed at reducing the impact of exposing waterways to early-age concrete (including concrete grout). The approaches used in these studies include:

- Isolating the curing concrete using dewatering approaches such as cofferdams.
- Conducting repairs involving concrete grout behind a permeable-fabric turbidity curtain, allowing water with an elevated pH level to slowly bleed out into the surrounding waters.
- Adding an antiwashout admixture to concrete grout.
- Using a waterborne acrylic-based emulsion barrier to prevent leaching from the concrete. However, researchers concluded that the barrier appeared to contain ammonia, which is harmful to wildlife.
- Carbon dioxide sparging (bubbling carbon dioxide through the water to help lower pH levels).

Variables Affecting Impact of Concrete on Water pH (see page 10)

Several of the studies cited in this Preliminary Investigation examined how different variables affect the extent to which the pH of a waterway is impacted by exposure to early-age concrete. In those studies, the following factors were found to play a role:

- Flow rate of the waterway. Several studies found this to be the most significant factor.
- Amount of concrete. The studies used several parameters to quantify this, including total concrete surface area, total concrete volume, and several ratios.
- Cement type. Mixtures made with pulverized fly ash and ground-granulated blast-furnace slag were tested, along with ordinary portland cement mixtures.
- Geometry of the concrete specimen.

Agency Policies

We identified two agencies with policies related to PCC and pH.

- At the Department of Fish and Wildlife in Washington State, the Habitat Conservation Plan acknowledges that “structures constructed in aquatic settings can adversely impact the pH of surrounding water via contact between water and uncured concrete.” The plan requires that concrete be cured before it comes into contact with an adjacent water body, although it does not define “cured.” A representative of the department said that the state would defer to manufacturer specifications for the specific concrete.
- The British Columbia Ministry of Environment requires cast-in-place concrete to remain isolated from water inside sealed formed structures until cured, defined as in “approximately 48-72 hours.”

Expert Consultation

The experts that we interviewed from industry associations and Transportation Research Board committees were not concerned about the impact of poured concrete on aquatic pH, pointing to the fairly rapid curing process, after which high-pH water would be unlikely to diffuse from the concrete into surrounding water.

Gaps in Findings

While we found some evidence that structural concrete only affects the pH of surrounding water for a relatively short time after casting, we found only limited research that directly studied this, particularly under field conditions.

Next Steps

Potential next steps for Caltrans include:

- Request documentation from the California Department of Fish and Wildlife for the scientific basis for isolating structural PCC from surrounding waters for 30 days.
- Conduct a 50-state survey of state DOTs asking for details about any policies at their agencies or state environmental agencies related to isolation of structural concrete in streams to prevent high pH.
- Follow up with the researchers and agency representatives cited below to further discuss their findings and policies.
- Initiate a field research project to measure the effects over time of poured concrete footings and columns on the pH of adjacent waters.

Detailed Findings

Research

Effects of Leaching from Fresh Concrete

"**Leaching of Alkali from Concrete in Contact with Waterways,"** S. Setunge, N. Nguyen, B. Alexander and L. Dutton, *Water, Air & Soil Pollution: Focus*, Vol. 9, pages 381-391, December 2009.
Citation at
http://www.researchgate.net/publication/225808681_Leaching_of_Alkali_from_Concrete_in_Contact_with_Waterways

Abstract:

> Concrete is usually the preferred material for construction of structures in contact with water during their service life. Early age exposure to water is beneficial for curing of concrete structures. However, the pollution of water from freshly cast concrete in contact with water has not been investigated in detail. A significant increase in the alkalinity has recently been observed in a stream in contact with freshly installed concrete culverts. High alkalinity has caused distress to fresh water fish in the stream. A preliminary laboratory study was commenced to explore the effect of leaching of alkali into water from freshly placed concrete. Freshly cast concrete specimens were exposed to fresh water, covering a range of conditions observed in the field such as volume of concrete/volume of water, age of exposure and cement content. Analysis of the results indicated that early age contact with fresh concrete can lead to an increase in the pH levels of water up to 11, similar to the levels of pH observed in pore water inside freshly cast concrete. It was noted that until an age of 4 days from casting of concrete, the age of exposure does not significantly affect the changes in the peak pH levels of water. Continuous monitoring of water in contact with concrete also indicated that the pH levels diminish with time, which is attributed to the possible reaction of calcium hydroxide with atmospheric carbon. The paper will present the experimental study, the results, analysis and outcomes as well as planning of a more comprehensive study to observe possible ways of reducing the leaching of alkali from freshly placed concrete.

Leaching of Alkali from Freshly Cast Concrete in Contact with Water, Robert Adamson, Master of Engineering thesis, RMIT University, Melbourne, Australia, August 2011.
Citation at http://researchbank.rmit.edu.au/view/rmit:160070
Full report at http://researchbank.rmit.edu.au/eserv/rmit:160070/Adamson.pdf

Abstract:

> There has been very little work done on the effect of leaching of alkali from concrete in to water which can cause environmental pollution. After a recent construction of culverts, a road authority in Australia observed that the pH of water had increased causing adverse effects on wildlife. Work presented in this thesis therefore was aimed at understanding the leaching of alkali from concrete in contact with waterways and also understanding what would be an effective barrier to minimise the pollution of water.

Preliminary experiments conducted on stagnant water indicated that the pH of water can rise to values as high as 11.5 after exposure of concrete to water. A literature review showed that though there had been some experiments using a supply of recycled water and more using stagnant water, there had been little to no research on the effects of concrete on a constant supply of flowing water. Eight major variables were identified as contributing to the pH change in water when in contact with concrete and five were short listed for the experimental study.

In order to optimise the laboratory work, the theory of Design of Experiments (DOE) was adopted to plan a series of experiments and analyse the effect of major variables. Five parameters: surface area to volume ratio of concrete, flow rate, the exposure to air, presence of pozzolanic additives in concrete and the age of concrete at exposure were varied in the investigation. Custom-designed testing equipment was built in the laboratory for observing the change in pH of flowing water when exposed to freshly cast concrete at various ages. Thirty four experiments were conducted using the testing apparatus and the results were analysed.

Experimental results indicated that the change of pH of water vs time follows a parabolic curve with peak pH being reached within 20 to 180 minutes from exposure depending on the variables selected. Major variables affecting peak pH were identified as the surface area to volume ratio of concrete and the flow rate. The major variable affecting the time to reach peak pH from initial exposure was observed to be the flow rate. Two models were derived using the theory of Design of Experiments (DOE) to predict the peak pH and the time to reach peak. Whilst the relationship for peak pH had a poor correlation with the results of the validation tests, the relationship for time to reach peak pH appeared to be sound. Poor correlation of the peak pH, flow rate and surface area to volume ratio relationship was attributed to the fact that the major variable appears to be the total surface area of the specimen and not the surface area to volume ratio as initially hypothesised.

Experiments conducted on a number of potential barriers identified that a water borne acrylic based emulsion was most effective in reducing the leaching of alkali from concrete. However, it has been concluded that this barrier requires further investigation since it appears to contain ammonia which in itself is harmful to wildlife.

"Effect of Leaching on pH of Surrounding Water," David W. Law and Jane Evans, *ACI Materials Journal*, pages 291-296, May-June 2013.
Citation at http://trid.trb.org/view/2013/C/1251807

Abstract:

When concrete structures—such as pier supports—are placed in water, they can have a detrimental effect on the surrounding environment by causing the pH to rise. This rise in pH can harm and kill animal and plant life. The concentration of hydroxyl ions leached from concrete can be affected by a number of factors, including cement type, shape of structure, ratio of surface area and volume, and the flow of the water. This paper presents the results of a research project that investigated three mixtures: 100% ordinary portland cement (OPC), 30% pulverized fly ash (PVA), and 65% ground-granulated blast-furnace slag (GGBS). Tests were conducted in both stagnant and flowing water using a range of specimen geometries and sizes. The results showed that

the mixture, volume/surface area, and geometry of the specimen can affect both the rate of leaching and the cumulative number of moles of hydroxyl ions leached.

"Effect of Leaching from Freshly Cast Concrete on pH," D. Law, S. Setunge, R. Adamson and L. Dutton, *Magazine of Concrete Research,* Vol. 65, No. 15, pages 889-897, 2013.
Citation at http://researchbank.rmit.edu.au/view/rmit:21439

Abstract:

> The pollution of water through release of hydroxyl ions from freshly cast concrete exposed to water can have a detrimental effect on aquatic life by causing a rise in pH. The concentration of hydroxyl ions leached from concrete can be affected by a number of factors. A detailed study has been undertaken to ascertain the effect of parameters such as flow rate, age of concrete after exposure, air quality, cement type, surface area and the volume of concrete. This paper presents the results of the experimental programme and a predictive model for change of pH of water after exposure to freshly cast concrete. Analysis of the results showed that the flow rate was the most significant factor in both the peak pH observed and the time to the peak pH. The volume of the sample was also identified as being a significant factor in the peak pH.

The paper notes that the study's goal was "to investigate the impact of leaching on the pH in slow-flowing streams, simulating the conditions reported in the Queensland event." (See page 890.) The Queensland road authority in Australia observed toxic effects on aquatic species downstream after construction of concrete culverts.

The researchers tested 16 specimens at 1 and 4 days after casting to investigate the impact of delaying the exposure of the curing concrete to flowing water. They observed a slightly higher peak pH in the samples that were exposed earlier, but the difference between the two groups was not significant.

During the 24-hour test period, the water showed a rapid increase in pH when the concrete specimens were initially immersed followed by a gradual decrease back to the initial pH.

Regarding the study's findings, the paper states (see page 896): "The practical implications of the results are that care should be taken when casting concrete structures in water where the volume of water and rate of flow are relatively low, such as in culverts and small streams. In these situations a rise in pH may occur, which could impact on the aquatic flora and fauna. Factors that may assist in reducing the pH rise are reducing the total volume of concrete and delaying the exposure to the water. These results, and previous research, have also indicated that factors such as the surface area/volume ratio, the use of replacement materials such as FA and the geometry of the structure may also have an impact on the pH rise. Further research is required before more definitive guidance can be given on these factors."

Effects of Concrete Grout on Water pH

Identification of Techniques to Meet pH Standard During In-stream Construction, James G. Hunter Jr., Dong Hee Kang and Mark M. Bundy, Maryland State Highway Administration, March 2014.
http://www.roads.maryland.gov/OPR_Research/MD-14-SP109B4D_pH-Standard_Report.pdf
This study investigated techniques for reducing the spike in the pH of water traveling through culverts, which are typically made of galvanized steel but repaired by paving the bottom with concrete grout. Repairs can spike water pH above the state regulatory limit of 8.5. The study's laboratory and field testing suggested that spikes in pH are most significant within the first few hours, and highly localized. However, if the length of time the water was in contact with uncured concrete was extended—due to the culvert length, a slow flow of water through the culvert, or ponding in the culvert—the spike in pH also lasted for a longer time. The longest pH spike observed in the field downstream of a culvert lasted 28 hours.

In a phone conversation, researcher James Hunter said the research project reflected Maryland's concern related to the grouting of culvert inverts. Hunter said he wasn't certain how the results of this project would apply to concrete poured underwater in structural applications. He noted that those applications would have significantly more concrete, which would tend to increase the impact on water pH, but also larger volumes of water, which would reduce the potential effect on pH. He agreed that the ratio of surface area of concrete to volume of water is likely an important factor that would apply in structural applications.

Hunter noted that field measurements do not necessarily reflect laboratory results because of additional components of river water.

The flow-through test used in this study evaluated the effects of several methods of mitigating pH impacts, including sediment bags and carbon dioxide sparging. Hunter said that sediment bags are not feasible for structural concrete applications, but that carbon dioxide sparging may provide some impact to reduce pH spikes.

Minimizing the Impact on Water Quality of Placing Grout Underwater to Repair Bridge Scour Damage, G. Michael Fitch, Virginia Transportation Research Council, June 2003.
http://www.virginiadot.org/vtrc/main/online_reports/pdf/03-r16.pdf
This project was a response to environmental permits that the Virginia Department of Transportation had to acquire for bridge rehabilitation projects involving underwater placement of tremie concrete. Due to the effect of concrete on water quality—including incidents of fish kills and high pH levels—the Virginia Department of Environmental Quality had requested that nearly all in-stream scour repairs be conducted in a dry environment with the bridge piers protected by cofferdams until the concrete sets.

The project included field monitoring at 31 sites. Several water quality measures were monitored at several locations downstream from these repairs, but pH was the only one that was significantly affected.

- 11 sites were repaired using tremie concrete, which was placed under the waterline and behind a geotextile fabric, which was placed behind riprap.
    - Five of the sites did not use a turbidity curtain to control sediment. These sites typically experienced increases in pH, and pH exceeded the Virginia state standard of 9.0 at two sites. The greatest pH increases were observed within 10

meters of the concrete pour area, but pH decreased only slightly from those levels at downstream locations. The pH spikes lasted between 1.5 and 4.6 hours.

    - At the six sites where a turbidity curtain was used, the pH rose significantly within the curtain, but outside the curtain the pH never exceeded the 9.0 limit. Since the turbidity curtains were not watertight, they allowed the high-pH water inside them to slowly "bleed off" into the main part of the waterway. This "bleeding off" process took more than 30 hours in some instances until the water inside the curtain had the same pH as the water outside of it. The process contributed to a slightly elevated pH in the waterway outside of the curtain while it occurred, but not beyond regulatory limits.

- 20 sites were repaired using grout bags. However, due to unusually dry weather, work at several of these sites was done in the dry and did not produce water quality data.
    - Only two of the sites where work was done underwater did not use turbidity curtains. At one, the pH climbed to over 11 quickly and did not decline for 5.5 hours; at this site, stream flow had stopped due to dry weather so the high-pH water had pooled. At the second, efforts were made to prevent concrete from entering the stream's flow by diverting water around the area where grout bags were being replaced.
    - Twelve sites did use turbidity curtains. Impacts on water pH were similar to those for tremie concrete placement: high pH within the curtain and slightly elevated, but generally legal, pH levels outside of the curtain.
    - At one site, an anti-washout admixture was used in conjunction with grout bags. This admixture was successful at keeping water pH below the 9.0 limit. Details on the admixture were not provided in the report.

The report includes an assessment of the various factors that affect concrete placement's impact on water pH. These include:

- **Stream flow**: A high stream flow will tend to reduce the impact on pH.
- **Grout pumping rate:** In most cases, sites with high pH values had grout pumping rates in excess of 13 cubic yards per hour, even though some of these sites had only small amounts of grout placed.
- **Presence of turbidity curtains:** Turbidity curtains were effective at isolating high-pH water within the curtain and releasing it into the stream slowly, so its impact on the waterway's pH as a whole was minimized. Researchers did find that fish could be trapped and killed inside the turbidity curtain. Once they realized this, they made an effort to install each curtain as close as possible to the bridge abutment and then drag it outward to its final location to avoid trapping fish inside. Turbidity curtains were also more successful if the bottom of the stream was smooth. Containment was less successful if the bottom had large rocks, riprap or brush.

A flowchart on page 20 of the report provides guidance for decision-making based on the stream flow and feasibility of various concrete placement options.

Design and Control of Concrete Mixtures, EB001, 15th Edition, Steven H. Kosmatka and Michelle L. Wilson, Portland Cement Association, 2011.
http://members.cement.org/EBiz55/ProductCatalog/Product.aspx?ID=245
This book is a guide to concrete applications, methods, and materials published and updated by the Portland Cement Association for more than 85 years. Chapter 11 on durability addresses some of the physical characteristics of concrete that are relevant to how diffusion can cause concrete to affect the pH of water.

Capillary pores in concrete can contain a high-pH solution of hydroxides from the cement paste in water. This solution can, in theory, diffuse into surrounding water to affect its pH. However, diffusivity (the ability of dissolved ions to move through concrete) and permeability (the ability of fluid to migrate through concrete) decreases as the water in the initial mix reacts with the cement to form a solid matrix. The decrease in diffusivity is particularly large when the concrete has cured enough that the pores in the concrete become discontinuous (typically at 30% porosity). As shown in Table 11-1 on page 196 the length of time this takes varies depending on the water-to-cement ratio of the mix. At a 0.5 water-to-cement ratio, pores become discontinuous after about 14 days. Less water in the mix reduces the amount of time necessary for pores to become discontinuous, while more water increases it. See Appendix A of this Preliminary Investigation for an excerpt of this guidebook that includes Table 11-1.

Mitigation Methods

The studies we reviewed mentioned a few mitigation methods aimed at reducing the impact of exposing waterways to early-age concrete (including concrete grout). The approaches used in these studies include:

- Isolating the curing concrete using dewatering approaches such as cofferdams.
- Conducting repairs involving concrete grout behind a permeable-fabric turbidity curtain, allowing water with an elevated pH level to slowly bleed out into the surrounding waters.
- Adding an antiwashout admixture to concrete grout. Researchers also placed the grout in grout bags designed to prevent washout of cement paste and fines.
- Using a waterborne acrylic-based emulsion barrier to prevent leaching from the concrete. However, researchers concluded that the barrier appeared to contain ammonia, which is harmful to wildlife.
- Carbon dioxide sparging (bubbling carbon dioxide through the water to help lower pH levels).

Variables Affecting Impact of Concrete on Water pH

Several of the studies cited in this Preliminary Investigation examined how different variables affect the extent to which the pH of a waterway is impacted by exposure to early-age concrete. In those studies, the following factors were found to play a role:

- **Flow rate:** Several studies found that the flow rate of the waterway had the most significant impact on how much the waterway's pH was affected. The studies assessed peak pH level, time to reach peak pH, and overall impact.
- **Amount of concrete:** The studies used several parameters to quantify this, including total concrete surface area, total concrete volume, ratio of concrete surface area to

concrete volume, ratio of concrete surface area to water volume, and ratio of concrete volume to water volume.

- **Cement type:** Mixtures made with pulverized fly ash and ground-granulated blast-furnace slag were tested, along with ordinary portland cement mixtures.
- **Geometry of the concrete specimen.**

The studies also examined other variables, including:

- Age of concrete at exposure.
- Concrete exposure to air.
- Grout pumping rate.

Agency Policies

We conducted a brief Internet search for state policies related to this issue and found only two that addressed concrete curing in forms underwater, detailed below.

British Columbia

Instream Works, British Columbia Ministry of Environment
http://www.env.gov.bc.ca/wld/instreamworks/index.htm
This website offers best management practices for projects that involve work in or around a stream. In particular, the General Best Practices (http://www.env.gov.bc.ca/wld/instreamworks/generalBMPs.htm) list includes several related to concrete works. BMPs related to concrete curing include:

- **GBP37** states that "cast in place concrete must remain isolated from water inside sealed formed structures until cured (approximately 48-72 hours), as concrete leachate is highly toxic to fish and other aquatic life."
- **GBP41** requires that concrete works in streams "monitor pH frequently in the watercourse immediately downstream of the isolated worksite until the works are completed. Emergency measures should be implemented if downstream pH has changed more than 1.0 pH unit, measured to an accuracy of +/- 0.2 pH units from the background level, or is below 6.0 or above 9.0 pH units."
- **GBP43** requires that concrete works in streams "isolate and hold any water that contacts uncured or partly cured concrete until the pH is between 6.5 and 8.0 pH units and the turbidity is less than 25 nephelometric turbidity units (NTU), measured to an accuracy of +/- 2 NTU."

Washington

Compiled White Papers for Hydraulic Project Approval Habitat Conservation Plan, Washington Department of Fish and Wildlife, March 2009.
http://wdfw.wa.gov/publications/00803/

> **Contact:** Randi Thurston, project manager, hydraulic project approval, Habitat Conservation Plans, Washington Department of Fish and Wildlife, 360-902-2602, Randi.Thurston@dfw.wa.gov.

Section 7.6.3 of the Habitat Conservation Plan acknowledges that "Structures constructed in aquatic settings can adversely impact the pH of surrounding water via contact between water and uncured concrete." The plan requires that concrete be cured before it comes into contact with an adjacent water body, although it does not define "cured." In an email, Thurston said that the state would defer to manufacturer specifications for the specific concrete.

According to the plan, fresh and salt water typically ranges from a pH of 6.5 to 8.5, which is also the Washington standard for fresh water. Citing the 1999 U.S. Department of Energy study *pH-Neutral Concrete for Attached Microalgae and Enhanced Carbon Dioxide Fixation—Phase I*, the plan states that curing concrete surfaces can have pH as high as 13 during the three to six months it takes for concrete to cure underwater. However, the potential for impact of the surrounding water is most significant during construction, "when concrete wash-off and slurries come into concrete with water."

Expert Consultation

We consulted with several experts on portland cement concrete. None were aware of any research that directly evaluated how long concrete placed underwater would affect the pH of that water. In the absence of directly related research, several of the experts that we interviewed discussed the properties of concrete and its likely impact on aquatic pH. These interviews are summarized below.

National Ready Mixed Concrete Association

Contact: Colin Lobo, Senior Vice President of Engineering, National Ready Mixed Concrete Association, 240-485-1160, clobo@nrmca.org.

In an email, Lobo said he was not aware of any research regarding the length of time that concrete needs to be isolated from flowing water to avoid impacting its pH, or whether concrete does impact water pH. He did observe that underwater concrete construction is common, and he also said that factors such as the volume and surface area of concrete exposed to water, volume of water, flow rate of water, and age when curing is initiated would all affect concrete's impact on the pH of water in contact with concrete.

Transportation Research Board

Contact: G.P. Jayaprakash, TRB Senior Program Officer—Soils, Geology and Foundations and staff representative for the TRB Standing Committee on Foundations of Bridges and Other Structures, 203-334-2952, gjayaprakash@nas.edu.

Jayaprakash forwarded a request for information to the members of the TRB Standing Committee on Foundations of Bridges and Other Structures. Those who responded did not identify any committee activities or regulations related to the isolation of concrete from flowing water, and informally suggested they did not believe the impact of concrete on water pH was a significant concern.

Contacts

CTC contacted the individuals below to gather information for this investigation.

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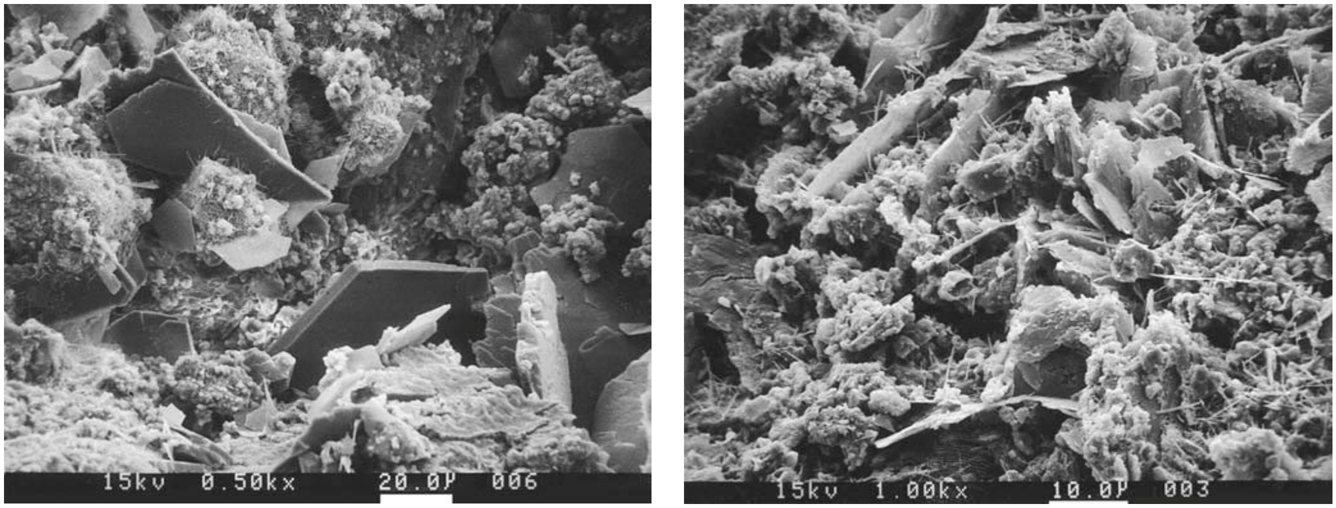

Figure 3-28. Scanning-electron micrographs of hardened cement paste at (left) 500X, and (right) 1000X.

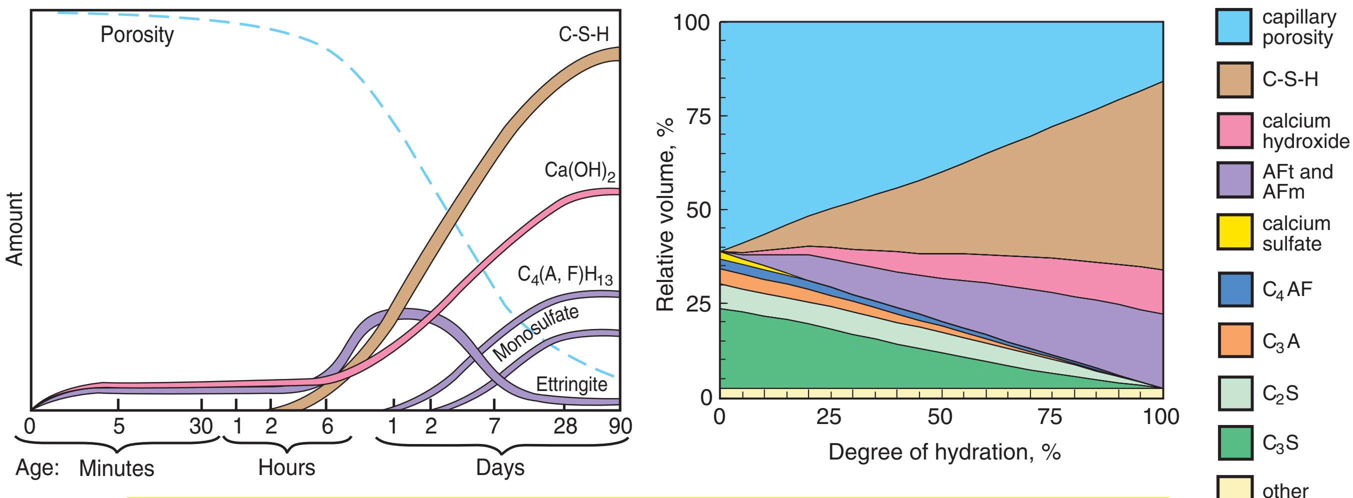

Figure 3-29. Relative volumes of the cement phases and hydration products in the microstructure of hydrating portland cement pastes (left) as a function of time (adapted from Locher, Richartz, and Sprung 1976) and (right) as a function of the degree of hydration as estimated by a computer model for a water to cement ratio of 0.50 (adapted from Tennis and Jennings 2000). Values are given for an average Type I cement composition (Gebhardt 1995): C_3S=55%, C_2S=18%, C_3A=10% and C_4AF=8%. "AFt and AFm" includes ettringite (AFt) and calcium monosulfoaluminate (AFm) and other hydrated calcium aluminate compounds. See Table 3-5 for cement phase reactions.

The percentage of each cement phase can be estimated from a chemical oxide analysis (ASTM C114, *Standard Test Methods for Chemical Analysis of Hydraulic Cement*, or AASHTO T 105) of the unhydrated cement using the Bogue equations, a form of which are provided in ASTM C150 (AASHTO M 85). X-ray diffraction (XRD) techniques (ASTM C1365, *Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis*) can generally be used to determine phase composition. Since the production of clinker depends on natural raw materials, there can be a significant level of trace elements in the major phases, which are not accounted for in the Bogue equations, Bogue calculations also assume a "perfect combination" (complete equilibrium) in the high temperature chemical reactions. XRD helps eliminate this bias. Table 3-6 shows typical oxide and phase composition and fineness for each of the principal types of portland cement.

Although elements are reported as simple oxides for consistency, they are usually not found in that oxide form in the cement. For example, sulfur from the gypsum is reported as SO_3 (sulfur trioxide), however, cement does not contain any sulfur trioxide. The amount of calcium, silica, and alumina establish the amounts of the primary phases in the cement and effectively the properties of hydrated cement. Sulfate is present to control setting, as well as drying shrinkage and strength gain (Tang 1992). Minor and trace elements and their effect on cement properties are discussed by Bhatty (1995) and PCA (1992). The primary cement phases have the following properties:

Tricalcium Silicate, C_3S, hydrates and hardens rapidly and is largely responsible for initial set and early strength (Figure 3-30). In general, the early strength of portland cement concrete is higher with increased percentages of C_3S.

Dicalcium Silicate, C_2S, hydrates and hardens slowly and contributes largely to strength increase at ages beyond one week.

Tricalcium Aluminate, C_3A, liberates a large amount of heat during the first few days of hydration and hardening. It also contributes slightly to early strength development. Cements with low percentages of C_3A are more resistant to soils and waters containing sulfates.

Tetracalcium Aluminoferrite, C_4AF, is the product resulting from the use of iron and aluminum raw materials to reduce the clinkering temperature during cement manufacture. It contributes little to strength. Most color effects that give cement its characteristic gray color are due to the presence of C_4AF and its hydrates.

Calcium Sulfate, as anhydrite (anhydrous calcium sulfate), gypsum (calcium sulfate dihydrate), or hemihydrate, (calcium sulfate hemihydrate, often called plaster of paris or bassanite) is added to cement during final grinding to provide sulfate to react with C_3A to form ettringite (calcium trisulfoaluminate). This controls the hydration of C_3A. Without sulfate, cement would set much too rapidly. In addition to controlling setting and early strength gain, the sulfate also helps control drying shrinkage and can influence strength through 28 days (Lerch 1946).

In addition to the above primary phases, portland cement may contain up to 5% limestone and numerous other lesser compounds (PCA 1997 and Taylor 1997).

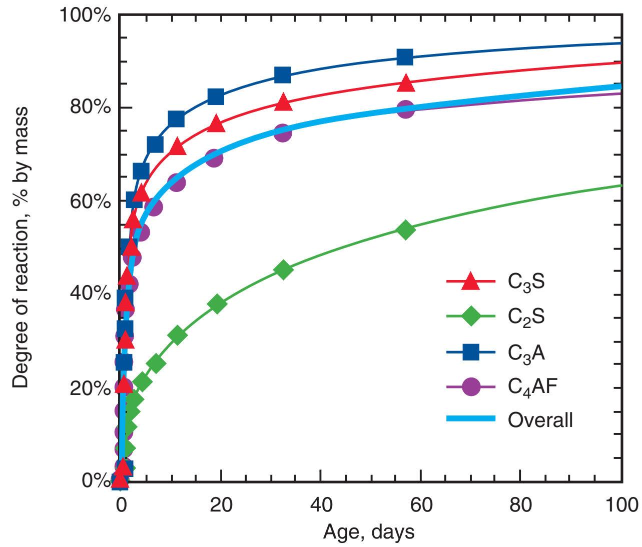

Figure 3-30. Relative reactivity of cement compounds. The curve labeled "Overall" has a composition of 55% C_3S, 18% C_2S, 10% C_3A, and 8% C_4AF, an average Type I cement composition (Tennis and Jennings 2000).

Water (Evaporable and Nonevaporable)

Water is a key ingredient of pastes, mortars, and concretes. The phases in portland cement must chemically react with water to develop strength. The amount of water added to a mixture controls the durability as well. The space initially occupied by water in a cementitious mixture is either partially or completely replaced over time as the hydration reactions proceed (Table 3-5). If more than about 35% water by mass of cement (a water to cement ratio of 0.35) is used,

Table 3-6. Composition and Fineness of Cements*

Type of portland cement	Chemical composition, %							Potential phase composition,%				Blaine fineness m^2/kg
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O eq	C_3O	C_2S	C_3A	C_4AF	
I (min-max) **I (mean)**	19.0-21.8 **20.2**	3.9-6.1 **5.1**	2.0-3.6 **2.7**	61.5-65.2 **63.2**	0.8-4.5 **2.5**	2.0-4.4 **3.3**	0.2-1.2 **0.7**	45-65 **57**	6-21 **15**	6-12 **9**	6-11 **8**	334-431 **384**
II (min-max) **II (mean)**	20.0-22.5 **20.9**	3.8-5.5 **4.6**	2.6-4.4 **3.3**	61.3-65.6 **63.7**	0.6-4.5 **2.0**	2.1-4.0 **2.9**	0.2-1.2 **0.56**	48-68 **57**	8-25 **17**	4-8 **7**	8-13 **10**	305-461 **377**
III (min-max) **III (mean)**	18.6-22.1 **20.4**	3.4-7.3 **4.8**	1.3-4.2 **2.9**	61.6-64.9 **63.3**	0.8-4.3 **2.2**	2.6-4.9 **3.6**	0.1-1.2 **0.61**	48-66 **56**	8-27 **16**	2-12 **8**	4-13 **9**	387-711 **556**
IV** (min-max) **IV** (mean)**	21.5-22.8 **22.2**	3.5-5.3 **4.6**	3.7-5.9 **5.0**	62.0-63.4 **62.5**	1.0-3.8 **1.9**	1.7-2.5 **2.2**	0.29-0.42 **0.36**	37-49 **42**	27-36 **32**	3-4 **4**	11-18 **15**	319-362 **340**
V** (min-max) **V** (mean)**	20.3-22.8 **21.6**	3.3-4.8 **3.8**	3.2-5.8 **3.9**	62.3-65.2 **63.9**	0.8-4.5 **2.2**	2.0-2.8 **2.3**	0.3-0.6 **0.45**	47-64 **58**	12-27 **18**	0-5 **4**	10-18 **12**	312-541 **389**
White** (min-max) **White** (mean)**	22.0-24.4 **22.7**	2.2-5.0 **4.1**	0.2-0.6 **0.3**	63.9-68.7 **66.7**	0.3-1.4 **0.9**	2.3-3.1 **2.7**	0.09-0.38 **0.18**	51-72 **64**	9-25 **18**	5-13 **10**	1-2 **1**	384-564 **482**

*Values represent a summary of combined statistics. Air-entraining cements are not included. For consistency in reporting, elements are reported in a standard oxide form. This does not mean that the oxide form is present in the cement. For example, sulfur is reported as SO_3, sulfur trioxide, but, portland cement does not have sulfur trioxide present. "Potential phase composition" refers to ASTM C150 (AASHTO M 85) calculations using an oxide analysis of the cement. The actual phase composition may differ due to incomplete or alternate chemical reactions.

**Type IV and White Cement data are based on limited data in Gebhardt (1995) and PCA (1996). Type IV is not commonly available. Adapted from Bhatty and Tennis (2008).

Table 9-7A. Observed Average Density of Fresh Concrete (SI Units)*

Maximum size of aggregate, mm	Air content, percent	Water, kg/m3	Cement, kg/m3	Density, kg/m3** Relative density of aggregate†				
				2.55	2.60	2.65	2.70	2.75
19	6.0	168	336	2194	2227	2259	2291	2323
37.5	4.5	145	291	2259	2291	2339	2371	2403
75	3.5	121	242	2307	2355	2387	2435	2467

* Source: Bureau of Reclamation 1981, Table 4.
** Air-entrained concrete with indicated air content.
† On saturated surface-dry basis. Multiply relative density by 1000 to obtain density of aggregate particles in kg/m3.

Table 9-7B. Observed Average Density of Fresh Concrete (Inch-Pound Units)*

Maximum size of aggregate, in.	Air content, percent	Water, lb/yd3	Cement, lb/yd3	Density, lb/ft3** Specific gravity of aggregate†				
				2.55	2.60	2.65	2.70	2.75
¾	6.0	283	566	137	139	141	143	145
1½	4.5	245	490	141	143	146	148	150
3	3.5	204	408	144	147	149	152	154

* Source: Bureau of Reclamation 1981, Table 4.
** Air-entrained concrete with indicated air content.
† On saturated surface-dry basis. Multiply specific gravity by 62.4 to obtain density of aggregate particles in lb/ft3.

Paste permeability is related to water-cement ratio, degree of cement hydration, and length of moist curing. A low-permeability concrete requires a low water-cement ratio and an adequate moist-curing period. Air entrainment aids watertightness but has little effect on permeability. Permeability increases with drying.

The permeability of mature hardened cement paste kept continuously moist ranges from 0.1×10^{-12} to 120×10^{-12} cm/s for water-cement ratios ranging from 0.3 to 0.7 (Powers and others 1954).The permeability of rock commonly used as concrete aggregate varies from approximately 1.7×10^{-9} to 3.5×10^{-13} cm/s. The permeability of mature, good-quality concrete is approximately 1×10^{-10} cm/s.

Test results obtained by subjecting 25-mm (1-in.) thick non-air-entrained mortar disks to 140-kPa (20-psi) water pressure are given in Figure 9-30. Mortar disks that had a water-cement ratio of 0.50 by weight or less and were moist-cured for seven days showed no water leakage. Where leakage occurred, it was greater in mortar disks made with high water-cement ratios. Also, for each water-cement ratio, leakage was less as the length of the moist-curing period increased. In disks with a water-cement ratio of 0.80, the mortar still permitted leakage after being moist-cured for one month. These results clearly show that a low water-cement ratio and a reasonable period of moist curing significantly reduce permeability.

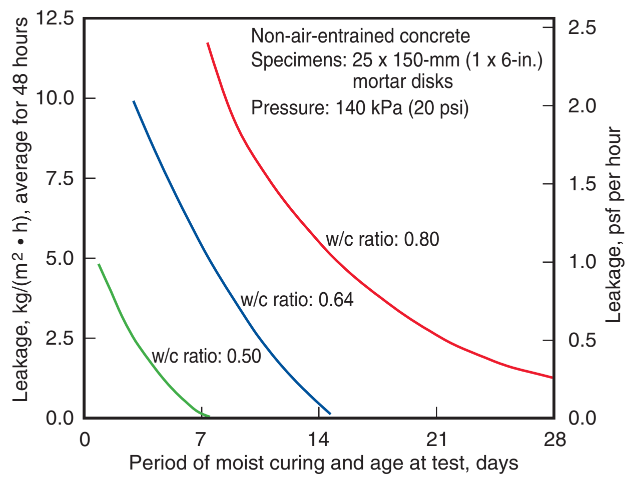

Figure 9-30. Effect of water-cement ratio (w/c) and curing duration on permeability of mortar. Note that leakage is reduced as the water-cement ratio is decreased and the curing period increased (McMillan and Lyse 1929 and PCA Major Series 227).

Figure 9-31 illustrates the effect of different water cement ratios on concrete's resistance to chloride ion penetration as indicated by electrical conductance. The total charge in coulombs was significantly reduced with a low water-cement ratio. Also, the results showed that a lower charge passed when the concrete contained a higher air content.

A low water-cement ratio also reduces segregation and bleeding, further contributing to watertightness. Of course watertight concrete must also be free from cracks, honeycomb, or other large visible voids.

Factors Affecting Durability

Permeability and Diffusion

Concrete subjected to severe exposure conditions should be highly impermeable. Permeability refers to the ease of fluid migration through concrete when the fluid is under pressure or to the ability of concrete to resist penetration by water or other substances (liquid, gas, or ions) as discussed in Chapter 9. Diffusivity refers to the ease with which dissolved ions move through concrete. Decreased permeability and diffusivity improves concrete's resistance to freezing-thawing cycles, resaturation, sulfate, and chloride-ion penetration, and other forms of chemical attack.

The size of the molecules or ions that are transported through the concrete, the viscosity of the fluid, and the valence of the ions can all affect the transport properties. Thus, permeability and diffusivity must be expressed in terms of the substance that is migrating through the concrete.

Permeability and diffusivity are influenced by porosity, but are distinct from porosity. Porosity is the volume of voids as a percent (or fraction) of the total volume. Permeability and diffusivity are affected by the connectivity of the voids. Figure 11-3 shows two hypothetical porous materials with approximately the same porosity. However, in one material the pores are discontinuous (as would be the case with entrained air bubbles), while in the other the pores are continuous. The latter material would be much more permeable than the former.

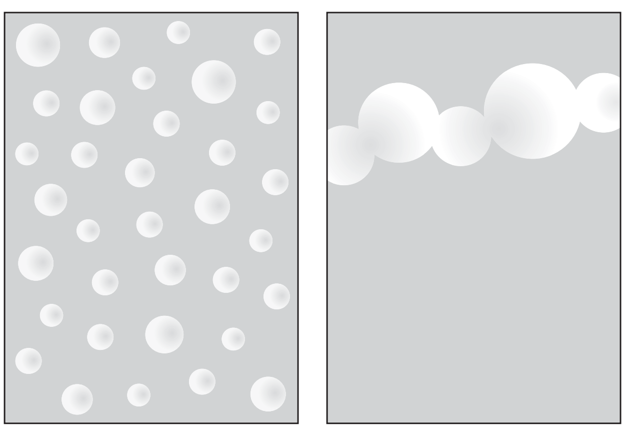

Figure 11-3. Porosity and permeability are related but distinct. The two hypothetical materials above have about the same porosity (total volume of pores), but very different permeabilities. Discrete pores have almost no effect on permeability, while interconnected pores increase permeability.

Figure 11-4 shows the relative sizes of the various pores and solids found in concrete. The capillary pores are primarily responsible for the transport properties. As a rough guide, Powers (1958) plotted the permeability versus capillary porosity for cement paste, as shown in Figure 11-5. It can be seen that as the porosity increases above about 30% (for example, due to a higher water-cement ratio), the permeability increases dramatically.

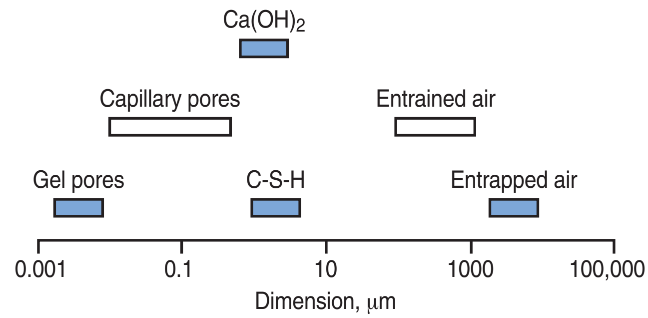

Figure 11-4. Relative sizes of different types of pores and other microstructural features.

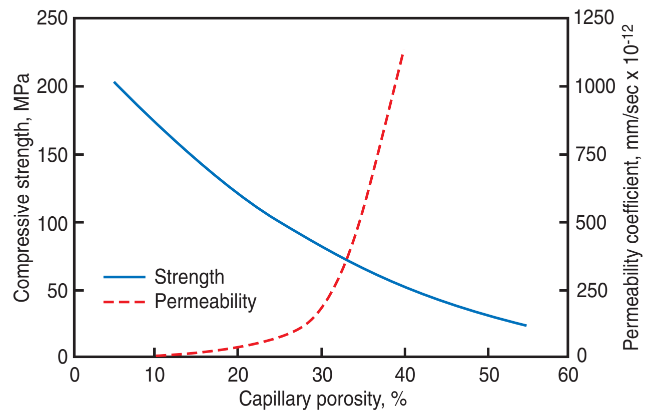

Figure 11-5. Both compressive strength and permeability are related to the capillary porosity of the cement paste, but in different ways. Above about 30% porosity, the permeability increases dramatically (adapted from Powers 1958).

Decreasing the porosity below 30% reduces the permeability, but any additional benefits obtained are relatively minor. The pore system of cement paste becomes discontinuous at about 30% porosity.

Powers and others (1959) calculated the time required for capillary pores to become discontinuous with increasing hydration of the cement, as shown in Table 11-1. It is notable that mixtures with a water-cement ratio greater than 0.7 will always have continuous pores. Figure 11-6 and Table 11-1 illustrate the relationship between water-cement ratio, permeability and curing. Observe the

Table 11-1. Approximate Age Required to Produce Maturity at Which Time Capillaries Become Discontinuous for Concrete Continuously Moist- Cured (Powers and others 1959)

Water-cement ratio by mass	Time required
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
Over 0.70	Impossible

KEYWORDS**:** admixtures, aggregates, air-entrained concrete, batching, cement, cold weather, curing, durability, fibers, finishing, high-performance concrete, hot weather, mixing, mixing water, mixture proportioning, placing, portland cement concrete, properties, special concrete, standards, supplementary cementing materials, sustainability, tests, and volume changes.

ABSTRACT**:** This book presents the properties of concrete as needed in concrete construction, including strength and durability. All concrete ingredients (cementing materials, water, aggregates, admixtures, and fibers) are reviewed for their optimal use in designing and proportioning concrete mixtures. Applicable ASTM, AASHTO, and ACI standards are referred to extensively. The use of concrete from design to batching, mixing, transporting, placing, consolidating, finishing, and curing is addressed. Concrete sustainability, along with special concretes, including high-performance concretes, are also reviewed.

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Cover photos show the world's tallest building, the Burj Khalifa in Dubai, U.A.E. The tower is primarily a concrete structure, with concrete construction utilized for the first 155 stories, above which exists a structural steel spire.

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WARNING: Contact with wet (unhardened) concrete, mortar, cement, or cement mixtures can cause SKIN IRRITATION, SEVERE CHEMICAL BURNS (THIRD-DEGREE), or SERIOUS EYE DAMAGE. Frequent exposure may be associated with irritant and/or allergic contact dermatitis. Wear waterproof gloves, a long-sleeved shirt, full-length trousers, and proper eye protection when working with these materials. If you have to stand in wet concrete, use waterproof boots that are high enough to keep concrete from flowing into them. Wash wet concrete, mortar, cement, or cement mixtures from your skin immediately. Flush eyes with clean water immediately after contact. Indirect contact through clothing can be as serious as direct contact, so promptly rinse out wet concrete, mortar, cement, or cement mixtures from clothing. Seek immediate medical attention if you have persistent or severe discomfort.