Glass Pozzolans in Marine Concrete

by Ashley Murr

Abstract: Marine concrete can be especially susceptible to chemical and physical deterioration, including corrosion of the reinforcement steel. For this reason, pozzolans such as fly ash, blast furnace slag, and silica fume, are commonly used to reduce corrosion in concrete subjected to marine environments by decreasing the permeability of the concrete matrix. The permeability of a concrete matrix is commonly used to indicate the susceptibility of a concrete to the corrosion of the steel reinforcement due to its effects on initial corrosion and subsequent corrosion. The water/cementitious materials (w/cm) ratio, binder type, curing conditions, and compaction factors can impact the level of permeability. A lower w/cm ratio can reduce the permeability, as does the addition of pozzolans. Ground glass is currently under intense scrutiny for its potential as a pozzolan in portland cement concrete, as it differs from other pozzolans due to its high alkali content. This research considers the potential for ground glass use as a pozzolan in marine concrete applications.

Marine Concrete

Concrete literally forms the foundations of our societies and supports our civilizations. In 2017, the world produced approximately 23 billion tons of concrete from 4.1 billion tons of cement (USGS, 2017). While most of the visible concrete is used in buildings and roadways, there are hidden tons of concrete beneath the ground and in the water. Any concrete that is in contact with water, almost exclusively in reference to seawater or the influence of seawater, is known as marine concrete (Alexander & Nganga, 2016). Such concrete is used for structures in marine environments.

Harsh mechanical and chemical wear warrants strict expectations to ensure that concrete in marine environments performs safely for its lifetime. In the United States, the American Concrete Institute (ACI), provides codes for concrete used in marine environments which prescribe safety and durability standards. Classifications defined by ACI detail specific exposure zones and subsequent composition and strength requirements for marine concrete. In general, marine concrete requires higher strength and lower w/cm ratios compared to concrete for ordinary purposes (ACI 318, 2014).

Deleterious Conditions

Specific threats posed to marine concrete include freeze thaw cycles, tidal erosion, and most notably, chloride penetration. These factors directly influence the design criteria for the concrete. To segregate the severity of these threats, three marine exposure are defined.

These distinct marine exposure zones affect the rate at which the concrete will erode and the mechanisms for chemical transport and deterioration (Otenio 2015; Jakobsen, et. al. 2016). There are three zones which are considered: 1) the atmospheric zone, 2) the splash zone, and 3) the submerged zone. Figure 1 illustrates the marine environment zones with the corresponding corrosion zones. Each zone exposes the concrete to unique conditions. The atmospheric zone raises concerns primarily regarding carbonation due to humidity and temperature (Santhanam & Otieno 2016).

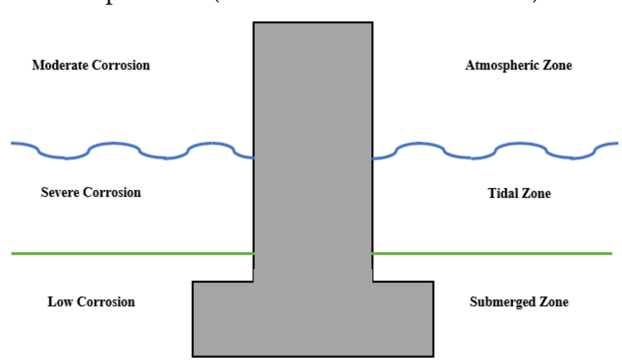

Figure 1. Marine environment zones and subsequent corrosion zones. Based on information from "1 - Introduction: Importance of marine concrete structures and durability design," by M. G. Alexander and G. Nganga, in M. G. Alexander (Ed.), *Marine Concrete Structures* (p. 1-13), 2016, Woodhead Publishing.

Concrete exposed to the splash and tidal zones encounter a vast range of physical mechanisms including abrasion, erosion, diffusion, sorption, wick action, and permeation which also worsen chemical mechanisms. Notably, the physical mechanisms significantly increase the transport of ions which cause chemical deterioration and corrosion. These zones are generally recognized as exhibiting the worst conditions (Santhanam & Otieno, 2016).

Most of the concern for submerged concrete is the permeation of chloride ions which corrode the reinforcing steel. Other ion absorption and sulfate attack are also of major concern in this zone. Supplementary cementitious materials combat the potential risks associated with this region and, to a lesser extent, the previous regions.

Specifications

The specifications regarding marine concrete are generally prescriptive-based but are increasingly becoming performance-based. In the United States, ACI 318 prescribes standards for water content, water/cementitious material ratios, and strength. Marine concrete typically must meet a w/cm ratio of 0.4 and a minimum 28-day strength of 5000 psi (ACI 318, 2014; Suprenant, 1991). Additional guidelines for marine concrete include CIRIA (Dupray et. al., 2010), PIANC (2015), and BS 6349-1-4 (2013). These guidelines offer recommendations for the materials and proportions used, techniques, and testing of the concrete.

Pozzolans

Although portland cement remains the binder of choice for the vast majority of concrete projects, pozzolans modify and enhance properties of portland cement concrete when added as supplementary cementitious materials (SCMs). Fly ash, slag, silica fume, metakaolin, and glass are among the common pozzolans. A pozzolan is a silica and/or alumina rich material that by itself possesses no cementitious properties but, when finely divided and reacted with water and calcium hydroxide, produces a binder with cementitious properties (ACI Concrete Terminology, 2017). Pozzolans contribute different properties based on physical and chemical characteristics. When added to marine concrete, pozzolans combat the deleterious conditions resulting from the harsh environments.

Pozzolans can be classified as natural or artificial depending on their source or origin. Current research is widely investigating the use of pozzolans in portland cement replacements, and a number of pozzolans are successfully employed in the field (Walker, et al., 2010; Tadayon, et al., 2016).

Use in Marine Concrete

Compressive strength and chloride ion resistivity are crucially important properties in marine concrete. The compressive strength indicates safety and varies by purpose, as specified by ACI. However, in the splash and submerged zones, the design standards revolve around the permeability of the concrete, as it indicates the resistivity to chloride ion penetration (Santhanam & Otieno, 2016; Allen & Moore, 2016). The penetration of chloride ions has the potential to corrode reinforcing rebar, compromising structural integrity (Kwon et al., 2017; Otieno, 2014).

Pozzolans may decrease the deleterious effects of seawater on concrete because of their chemical composition and microstructure. Fly ash, blast furnace slag, and silica fume are commonly used. One characteristic of successful pozzolans is fine particle size, which reduces the gaps between binder products and aggregates in addition to reducing the interstitial transition zone (ITZ), therefore decreasing weak spots and permeability. Additionally, higher alumina content increases reactions with the chloride ions. The chloride is then bound within the concrete matrix and does not reach the steel, thereby reducing corrosion. These pozzolans can also reduce the w/cm ratio which reduces permeability and absorption to reduce ions that enter the concrete matrix (Moffatt et al., 2017; Saha, 2017; Kouloumbi et al., 1994; Nath et al., 2018; Thomas, 1996)

Glass as a Pozzolan

Pozzolans are silica rich materials that exhibit cementitious properties when reacted with calcium hydroxide (ASTM C595, 2017). They can replace a portion of the portland cement as supplementary cementitious materials (SCMs). Historically, SCMs were added to enhance the properties of cement, where, for much of the twentieth century, fly ash and slag were used to increase flow and other properties. Today, however, natural pozzolans, such as waste glass, attract most of the research efforts (Shi & Zheng, 2007; Islam et al., 2016; Du & Tan, 2015; Shayan, 2005; Kamali & Ghahremaninezhad, 2016).

Glass Background

Bottles, windows, and electronics compose the vast majority of glass products with the largest sector being bottles, or what is more formally considered container glass. Container glass is also considered soda lime glass because of its composition and is typically designated as a nondurable good by the US Environmental Protection Agency (EPA). Approximately 11.5 million tons of waste glass is generated in the US each year. In 2014, nearly 3 million tons of that glass was recycled (U.S. Environmental Protection Agency, 2016). Bottle drops, curbside pick-ups, commingled municipal recycling facilities, and commercial waste transports all contribute to the pool of recycled glass, with each recycling facility varying in waste stream characteristics and end product. Generally, however, recycled glass is used to produce new glass. Once at the recycling facility, the glass is usually sorted by color for new glass products. Of the 3 million tons recycled, an additional 1.5 million tons fail to meet strict color or particle size standards, becoming destined instead for the landfill. These 1.5 million tons could have great potential and would not only improve the sustainability of the concrete industry, but would also divert a valuable resource from landfills.

Industry standards accept that for every ton of portland cement produced, 0.88 tons of carbon dioxide are produced and subsequently released into the atmosphere. In total, this amounts to between 5% and 8% of global carbon dioxide emissions each year. Using a process similar to the EPA's WARM Version 13 Model for the greenhouse gas emissions for fly ash, an estimation for greenhouse gas emissions for ground glass can be performed. Unlike portland cement, glass itself produces no excess carbon dioxide. Instead, the only source of greenhouse gas emissions originate from the energy required to grind the glass, which produces approximately 10.2 lbs of carbon dioxide for every ton of concrete. In other words, the ratio of carbon dioxide to concrete production is 0.005. Following the calculations, if a typical glass replacement rate of 20% is used, the resulting ton per ton carbon dioxide emissions decreases from 0.88 to a ratio of 0.705, yielding a total a reduction rate of 20%.

Structure and Composition

Glass is considered a pozzolan replacement due to its high silica content and amorphous, or noncrystalline, structure. Its basic molecular composition and structure lend to favorable properties for portland cement replacement. Additionally, the availability of waste glass suggests a reliable source and profitable market. When considering the market availability, economic viability, smaller carbon footprint, and both physical and chemical properties, evidence supports the investigation of using waste glass as a pozzolanic replacement in cement.

Compared to other pozzolans such as fly ash and slag, glass has a lower calcium content and higher silica content (see Figure 2).

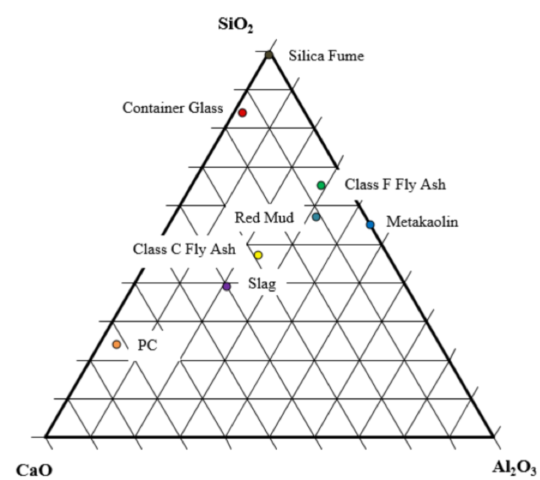

Figure 2. Ternary diagram comparison (Schlosser, 2017).

The high silica and alumina of ground glass has been suggested to reduce the chloride ion penetration in portland cement concrete (Omran & Tagnit-Hamou, 2015; Peyvandi et al., 2013; Du & Tan, 2017). As hydration occurs, silica and alumina become available in the concrete matrix. These available silica and alumina cations plausibly attract the negatively charged chloride ions, creating bonds which prevent the chloride ions from penetrating further into the matrix and corroding the reinforcing steel.

Since glass lacks calcium in comparison to portland cement and other pozzolans, concerns regarding compressive strength have historically been raised. However, this concern has been addressed and resolved through numerous studies on pozzolans. Because the pozzolanic reaction is slower than typical portland cement reactions, concretes using pozzolans may show lower early strength but eventually show higher late strengths. A multitude of studies support this trend and note that to attain adequate strength in portland cement concrete mixes, replacement rates should be around 20% by mass (Du et al., 2015; Shayan & Xu, 2005; Kamali et al., 2016; Knmiri et al., 2012; Aliabdo et al., 2016).

Current Use in Concrete

Although not yet widely used in the industry as a portland cement replacement, glass is attracting more investigative and implementation efforts. The ACI technical subcommittee on natural pozzolans continues to synthesize research efforts into a comprehensive document available for the industry. Current investigation regards the use of glass pozzolans for inland use and typical construction.

Research Gaps

While an abundance of research exists for glass pozzolan properties in standard concrete, no research exists for its properties in regard to its performance in marine concrete. Specifically, data regarding chloride resistivity is lacking. Future research should investigate the feasibility of using glass in marine concrete based on its chloride resistivity. These efforts would provide additional information on the chemical properties of glass pozzolans in portland cement concrete.

Summary

Marine concrete is subject to unique environments classified as marine exposure zones. Detailed specifications outline the performance for marine concretes, and pozzolans have successfully been used to meet these specifications. Pozzolans replace portions of portland cement in concrete, reducing the concrete's carbon footprint and also enhancing concrete properties.

Glass is a pozzolan under abundant investigation for its potential use in concrete. However, no research exists investigating its use in marine concrete. Data on its chloride resistivity will indicate its feasibility for use in marine concrete.

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