Use of Nano-Enhanced Plastic Based Cementitious Material [NPBC] to Improve Acid Resistance of Sewer Systems

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The main objective of the study is to assess the resistance of a new class of plastic-based cementitious material to sulfuric acid as a function of nanoparticle inclusion. Nano-Enhanced Plastic Based Cementitious Material (NPBC) is a product of the simultaneous combination of polyethylene Terephthalate (PET) plastic waste, sand and silicon oxide (SiO_2) nanoparticles. These elements combine to produce a specimen that has high strength, durability and resistance against sulfuric acid attack.

Key Words: Nano-Enhanced Plastic Based Cementitious Material (NPBC), Polyethylene Terephthalate (PET), Nanoparticle to Plastic Ratio (NPR), Plastic to Sand Ratio (PSR)

Introduction

Concrete sewer pipes are a major component of the United States' infrastructure; many of which are comprised of inadequacies. They are deteriorating and becoming vulnerable to failures. Based on initial conditions, several chemical reactions occur within a concrete sewer system where hydrogen sulfide in sewage is converted to sulfuric acid. Sulfuric acid is a highly corrosive acid that induces failure by reacting with the calcium hydroxide in concrete and results in volumetric expansion. The corrosive action of sulfuric acid is one of the primary causes for the distress and failure of concrete sewer pipes. This corrosion results in premature failures that are expensive to rehabilitate and poses significant environmental health hazards (Crayford, 2012). A damaged sewer system can lead to spills, bad odor and disease outbreaks. And the estimated cost for the restoration of these damaged systems is estimated at approximately \$390 billion dollars over the next 20 years (ASCE 2009). According to a recent study on the U.S underground infrastructure, about 40 percent of the 800,000 miles of concrete sewer pipes in the U.S are deteriorating (Sterling, 2009).

Discarded plastic waste presents another major concern for researchers, federal and state agencies and other professionals. The average American household used up to 42 pounds of PET bottles in 2005 and the U.S. collected approximately 5.7 billion pounds of PET for recycling in 2007 (NAPCOR, 2005). 1,500 plastic bottles are consumed every second in the U.S, and out of the 50 billion plastic bottles purchased each year, only 20 percent are recycled; the remaining 80 percent are sent to landfills to be incinerated, despite the existence of recycling programs (Scholtus, 2009). Plastic waste pollutes the air with numerous poisonous chemicals when incinerated. Both of these issues present major challenges to addressing environmental concerns and aging infrastructure in the U.S. NPBC presents a green and sustainable alternative that simultaneously addresses both of these concerns by 1) offering an alternative to concrete that has enhanced acid resistance, 2) making use of plastic waste thereby diverting plastic bottles from landfills and incinerators and 3) providing a versatile product that can be used in various commercial applications such as sewer pipe production and rehabilitation, manholes, wastewater treatment facilities, and acid containment and septic tanks, among others. Through investigation of the acid resistance and mechanics of deterioration of NPBC in a sulfuric acid environment, findings from this work will advance the state of knowledge of polymer-based solutions to concrete degradation under sulfuric acid corrosion.

Literature Review

Adequate realization of the capacities and capabilities of nanoparticles is a lowly ventured area; hence there is little documentation surrounding this topic. Some publications on the inclusion of nanoparticles have shown improvements in the mechanical properties of concrete (Nazari and Riahi 2011). Nazari and Riahi investigated the effects of different amounts of SiO_2 nanoparticles on the mechanical properties of high strength concrete and discovered that increases in nanoparticle percentages up to 4% by weight resulted in increased mechanical strength. When examined for permeability, their results showed that SiO2 nanoparticles are able to act as nanofillers that enhances the resistance of water infiltration. Several authors have documented on the effects of polymer addition to

concrete mixes on mechanical strength and acid resistance (Pacheco-Torgal, 2009; Reis and Carneiro, 2012; Pereira De Oliveira et al., 2011), but the use of PET and silicon nanoparticles in NPBC presents a definite distinction from past related publications. The plastic in NPBC is melted, whereas the mixing of plastic in concrete and mortars does not make use of the thermoplastic property of PET. Also, the inclusion of nanoparticles to the mixture of sand and plastic waste is a novel and uncharted territory in the field of engineering.

Materials and Methods

The three constituents used in this study included, shredded polyethylene terephthalate (PET) flakes from Greenpoint industries/Constar, Inc., sand conforming to ASTM C33 specification and silicon oxide nanopowder from Nanostructured & Ammorphous Materials Inc. Three mix design were used in this study, all with different nanoparticle to plastic ratio (NPR). All mix designs consisted of the same amount of sand and PET plastic waste. Also the plastic to sand ratio (PSR) was kept constant at 1 for all mixes. The NPR for the mix designs ranged from 0% to 1%. Refer to Table 1 for the mix design.

Table 1: Summary of the mix designs			
Material	Mix Design 1 (g)	Mix Design 2 (g)	Mix Design 3 (g)
Sand	1200	1200	1200
PET	1200	1200	1200
Nano-SiO2	0	1.2	12
PSR*	1	1	1
NPR**	0	0.1	1

*Plastic to Sand Ratio

**Nanoparticles to Plastic Ratio (%)

(1) Specimen Preparation

PET plastic flakes, sand and silicon oxide nanoparticles were used to prepare NPBC specimens. Prior to mixing all the different constituents, PET and sand was dried in an oven at a temperature of 110° C for a period of 24 hours. As depicted below in figure 1, the mixing procedure of NPBC is comprised of 3 steps: 1) simultaneous mixing of all the elements (PET, sand and nano-SiO₂) in a bowl; 2) melting the mixed composition in the oven at a temperature of 270 to 280 degree Celsius; and 3) thorough mixing of the PET-sand-nano SiO₂ mixture in its viscous form. After mixing, the composition is then pored into a Harvard miniature mold (33mm × 71mm) and cured at room temperature for 24 hours. Following the curing period, the specimens were weighed and the dimensions documented as well. A total of 3 mix designs, with a plastic to sand ratio (PSR) of 1 and varying amounts of silica nanoparticles were assessed. Table 4.2 shows the mix designs with a range of 0 to 1% nanoparticle to plastic ratio (NPR).



Figure 1: Sample Preparation of NPBC

(2) Sulfuric Acid Resistance of NPBC

The ASTM C 267 test method was employed in the testing of NPBC's resistance to sulfuric acid attack. After curing for 1 day, the specimens were weighed and then immersed in a 20% sulfuric acid solution. The specimens were then removed from the acid solution at intervals of 1 day, 7 days, 28 days and 84 days to assess the rate of sulfuric acid attack. Immediately following the removal of specimens, each sample was rinsed in water thoroughly and left to dry for a period of 30 minutes at room temperature. After the specimens were dry, they were analyzed by comparing the pre-exposure properties to the post exposure properties.

After sulfuric acid immersion, the weight of the specimen were determined and compared to pre-exposure weight of specimen. The percent loss or gain of each specimen was calculated and averaged for the set. A plot was then generated to depict the results.

 $\Delta W = [(W_2 - W_1)/W_1] \times 100$

Where: ΔW = Percent weight change W_I = Cured weight of specimen W_2 = Weight of specimen after sulfuric acid immersion

(3) Compression Testing of NPBC

Compressive strength tests were conducted in accordance with ASTM C 267 using a hydraulic MTS system such as the one in Figure 2. Specimens cured for periods of 1 day, 7 days, 28 days and 84 days were tested to determine the compression strength. For each mix design, a total of 18 samples were prepared. Each curing period was allocated 6 samples where only 3 of the 6 samples are exposed to sulfuric acid. The average of 3 samples per set of days curing and control was documented as the compression strength.



Figure 2: Hydraulic MTS System Used for Compression Testing

The compressive strength was calculated as follows:

$$f_C = (4P)/(\pi \times D^2)$$

Where:

 f_C = compressive strength, psi P = maximum load, lb D = measure diameter of sample

To analyze the degree of deterioration from immersion in sulfuric acid, a comparison was made between the exposed samples and the control samples. The percent decrease in compressive strength during immersion was calculated, taking the unexposed compressive strength as 100%.

$$\Delta f_{C} = \left[(f_{C(2)} - f_{C(1)}) / S_{1} \right] \times 100$$

Where:

 Δf_c = Percent change in compressive strength $f_{C(2)}$ = Average compressive strength of a set of specimens following sulfuric acid immersion $f_{C(1)}$ = Average compressive strength of a set of specimens following curing period

The percent increase or decrease of the compressive strength as a function of curing was then determine in the same manner where samples cured for 0 day will be taken as 100%. Following the preparation and testing of each set of specimen for compression, a plot was generated to determine the effect of sulfuric acid and curing time on strength. From this graph, the susceptibility of NPBC to sulfuric acid was determined.

Findings

(1) Changes in Sample Weight

Laboratory visual observation of all NPBC specimens revealed no surface cracks, or any type of discoloration after acid immersion periods of 1 day, 28 days and 84 days. Figure 3 shows specimens immersed in sulfuric acid beyond the period 84 days, without any compromise to their structural integrity.



Figure 3: View of NPBC specimens immersed in 20% sulfuric acid solution



Figure 4: Effect of Acid Immersion on Weight Changes of NPBC

The weight change results for NPBC specimens prepared with 0%, 0.1% and 1% nanoparticles are shown in figure 4. After 84 days of exposure, the control specimens (0% nanoparticles) had the highest weight change, approximately 1.6%, whereas specimens prepared with 0.1% and 1% nanoparticles had lower weight changes, 1% and 1.4% respectively. This phenomenon can be attributed to the ability of silicon nanoparticles to act as nanofillers that reduces permeability hence further enhancing the acid resistance of NPBC specimens (Nazari and Riahi 2011).



Figure 5: Effect of Nanoparticle on Strength

(2) Compression Test

In order to determine the optimal mix design for the addition of nanoparticles, compression test was conducted on specimen without sulfuric acid exposure. Figure 5 shows the variation of strength with differing nanoparticle percentages and from the plot, the specimen with 0.1% nanoparticle exhibited the highest strength. Following this observation, further comparison has been made only with 0% and 0.1% NPR specimens. Comparisons of compressive strength were made between the specimens prior to and after exposure to sulfuric acid; the results as shown in Figure 6 and figure 7. Due to inconsistencies in sample preparation from sample to sample, samples with the highest strength were selected because these samples represent achievable strengths using a definite controlled environment where mechanical methods are used for sample preparation. While the control specimen (0% NPR) exhibited a decrease in strength after 84 days of exposure in a sulfuric acid solution, specimens with 0.1% nanoparticles exhibited a slight increase in strength over the same period of time. This increase in strength can be attributed to several factor associated with the inclusion of nanoparticles.

According to Nazari and Riahi the inclusion of nanoparticles in cementitious materials improved their mechanical properties and durability characteristics. The improved strength and sulfuric acid resistance of nanoparticles can be attributed to 1) silica nanoparticles possessing a greater number of silanol groups available compared to sand particles, due to nanoparticles being characterized by a large specific surface area (Ke et al., 2005); and (2) chemical bonding between the silanol group from silica and carboxyl groups from PET in NPBC is supported at low pH, thus resulting in a stronger resistance to sulfuric acid attack (Ahimou et al., 2002 and Xu et al., 2005). The use of NPBC for rehabilitation of infrastructure such as sewer pipes promises to be a viable alternative as well. Due to its fast curing attributes, NPBC proves to have an advantage over most of the existing technologies used in the production and rehabilitation of sewer pipes.



Figure 6: Effect of Sulfuric Acid Exposure on NPBC [NPR 0%]



Figure 7: Effect of Sulfuric Acid Exposure on NPBC [NPR 0%]

Based on the test results, the following conclusions can be drawn. Data showed that NPBC specimens prepared with nanoparticles and subjected to an environment of sulfuric acid exhibited lower weight changes in relation to the control specimen (0% NPR). The optimum amount of nanoparticle inclusion required for benefit in both strength and acid resistance was determined to be a nanoparticle to plastic ration of 0.1%. This value of 0.1% is much different than the optimal value of 4% determine by Nazari and Riahi for use of nanoparticles in concrete. This can be attributed to the different constituent involved in both experiments as well as the method of preparation; NPBC

involves the melting at a relatively high temperature while concrete relies on the chemical reaction of cement and water. After the immersion period of 84 days in sulfuric acid solution, NPBC specimens prepared with 0.1% nanoparticles showed lower degradation in compressive strength. This can be attributed the silicon oxide nanoparticles acting as nanofillers (Nazari and Riahi 2011).

Discussions

These preliminary results shows NPBC to be a viable alternative that 1) has enhanced acid resistance; 2) can be used in various commercial applications such as sewer pipe production and rehabilitation, manholes, wastewater treatment facilities, acid containment and septic tanks; and 3) makes use of discarded plastic bottles that would otherwise be discarded. Although these results present an insight in the right direction to properly handle deteriorating sewers qualitatively, there are still several factors that have to be taken into consideration. Some of which are safety speculations of a cementitious material involving PET and nanoparticles. According to NAPCOR, PET does not leach noxious chemicals into their contents, but in the addendum for the future is to test the specimen for safety against contamination. This will determine if NPBC leaches any toxin and if so, are they within the acceptable limits. Also future plans include testing for the effect of abrasion and the use of a Fourier Transform Infrared Ray (FTIR) spectroscope to identify bonds in NPBC as well chemical reaction that are possibly taking place in the presence of sulfuric acid. As for now, NPBC signifies hope for the remediation of America's current underground infrastructure.

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