Evaluation of the Durability of 100 Percent Fly Ash Concrete

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DISCLAIMER

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ABSTRACT

Building upon previous research conducted at Montana State University on concretes in which 100 percent of the binder is Class C fly ash from the Corette power plant in Billings, MT, the specific objectives of this project were threefold: 1) to identify additional fly ashes that could be used in 100 percent fly ash concretes, 2) to develop fly ash concrete mixtures with entrained air (which is a proven mechanism to improve freeze-thaw resistance in traditional concretes), and 3) to determine the durability of these concretes under various environments.

Three fly ashes similar in composition and production to the Corette fly ash were screened as potential binders in 100 percent fly ash concrete, namely, fly ashes from the Port Neal (Sioux City, IA), Dave Johnston (Glenrock, WY), and Council Bluffs (Council Bluffs, IA) power plants. Based on laboratory trial mixtures, concretes made with the Port Neal and Dave Johnston fly ashes had properties similar to those obtained using the Corette ash (e.g., 28-day compressive strength approaching 4,000 psi), and the Dave Johnston ash was selected for further consideration in addition to the Corette ash. Entrained air appeared to be readily induced in the Corette concrete using a commercial admixture. This entrained air had little effect on the workability of the fresh concrete, while it noticeably decreased the strength of the hardened concrete.

From a durability perspective, the freeze-thaw resistance of the Corette fly ash concrete (determined following ASTM C666) is promising, while there may be concerns about the performance of the Dave Johnston concrete (these tests are ongoing). Relative to ASR, both the Corette and the Dave Johnston concretes exhibited very little reactivity when tested following the test method described in ASTM C 1260. The sulfate resistance test (ASTM C1012) is of relatively long duration, and no meaningful results were obtained by the time this report was prepared (these tests are ongoing). Relative to hydrogen sulfide/microbial related deterioration of fly ash concrete, no significant corrosion was seen in samples exposed for approximately 2 ½ months to a sulfur enriched, wastewater-based microbial environment..

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1. INTRODUCTION

1.1. Background

For several years researchers at Montana State University have been investigating 100 percent fly ash based concretes—that is, concretes that use only fly ash (i.e., no Portland cement) as the binder. This work originally was motivated by an interest in minimizing the myriad of environmental impacts associated with traditional concrete by using a recycled byproduct for the binder, in this case, Class C fly ash from the Corette power plant in Billings, MT, rather than Portland cement. These impacts of Portland cement production range from disturbing virgin ground to extract the raw materials and fuels required in its production, to the CO_2 emitted during the manufacturing process, itself. In working with the Corette fly ash, it was quickly discovered that as binder in concrete it offered exceptional performance with respect to short term strength gain, long term ultimate strength, and workability relative to traditional Portland cement concrete. Mixtures similar to conventional concrete mixes routinely produced one-day strengths in excess of 2,900 psi and 28-day strengths in excess of 4,800 psi without extraordinary curing measures (i.e., at ambient temperatures and without chemical strength accelerators). Subsequent long term strengths have reached as high as 8,000 psi at one year of age. These results have been achieved with very workable mixtures (slump of 6 inches) without the use of sophisticated admixtures common in the concrete industry.

Recent work at MSU has focused on establishing the relationship between these various properties and the mixture proportions and mixing process, so that this new concrete can be reliably produced for practical applications using standard equipment. To further demonstrate the potential of this material, three large volume mixes were produced away from the controlled environment of the laboratory. These large volume mixes were made using ready mix equipment commonly available in the industry. In the first field trial, the raw materials were easily charged into a ready mix truck, mixed thoroughly, discharged, and cast into test specimens. Compressive strengths at 28 days and one year averaged 4,800 psi and 8,000 psi, respectively. This material was subsequently successfully used in two additional field trials in which precast wall panels on a small building structure and a cast-in-place building foundation were constructed (Cross, Stephens, and Vollmer, 2005).

The only impediments to increased use of 100 percent fly ash concretes in common construction applications is a) identification of specific ashes appropriate for this use, and b) the sparseness of information on their long term durability. Relative to availability of ash, every high calcium fly ash is unique and demonstrates a different degree of self-cementing behavior. Work completed to date has focused solely on the fly ash available from the Corette Power Plant in Billings, MT. Annual ash production at this plant is only 22,000 tons per year, and the plant is somewhat remote from major population centers. Efforts are necessary to identify additional sources of ash that possess the same desirable traits as the Corette ash. Relative to durability, in specifying and using building materials, knowledge of their durability is as important as understanding their strength characteristics to ensure that they offer the long service life typically expected by the end user. Conventional concrete structures are susceptible to both physical and chemical attack. The primary mechanism of physical degradation is prolonged exposure to cycles of freezing and thawing in a saturated state. As might be expected, as any water within the pores of the rigid concrete freezes, it expands and fractures the material. This damage, which can occur at both a microscopic and macroscopic level, accumulates over time, eventually contributing to failure of the structure. Some common forms of chemical attack ultimately degrade concrete in the same manner as freeze-thaw action. That is, in certain circumstances chemical reactions can occur over time after the concrete has hardened that produce expansive products. Once again, forces associated with this expansion lead to micro and/or macro cracking and ultimate failure of the structure. Common circumstances in which chemically initiated degradation can occur includes the use of aggregates that contain silica that reacts with alkalis in the binder (alkali-silica-reactivity, or ASR) and exposure to sulfates which react with various compounds in the hardened binder. Additionally, when used in wastewater applications, concrete structures have been known to degrade under the action of bacteria that grow in the sulfide-rich environment.

While based on its known properties, durability of this material is not expected be an issue (i.e., any more than the durability of Portland cement concrete is an issue), the chemistry and physical properties of 100 percent fly ash concretes are not identical to those of Portland cement concrete, and small differences in chemical composition, crystal structure, etc., have previously been observed to have a disproportionately large effect on the behavior of these types of materials. At present, the relatively simple and reasonably accurate and accepted method of establishing the durability of such materials is through testing, frequently done in an accelerated manner to generate over weeks, months, or years the expected exposure levels seen over years in actual practice.

1.2. Objectives and Scope

The objective of this project was to further develop and facilitate commercial use of 100 percent fly ash concrete in construction applications. This objective was realized by:

1) investigating additional fly ashes that are suitable for producing 100 percent fly ash concretes in addition to the ash from the Corette power plant in Billings, MT, which has already been found to be suitable in many aspects for construction applications;
2) developing fly ash concrete mixtures with entrained air, as air entrainment is the primary mechanism used in conventional concretes to improve their resistance to damage from freeze/thaw action; and
3) determining the durability of the concrete mixtures made with Corette and other candidate fly ashes identified in (1) above under various deleterious environments.

The characteristics of a given fly ash are primarily the result of the impurities in the coal being burned and the nature of the combustion and ash collection process. Plants similar to the Corette Plant in these respects may produce fly ash appropriate as the binder in 100 percent fly ash concretes. Correspondingly, a preliminary investigation was conducted on fly ash from three power plants in the western/central United States: the Port Neal Plant (Sioux City, IA), Dave Johnston Power Plant (Glenrock, WY), and the Council Bluffs Plant (Council Bluffs, IA). For each ash, concrete trial mixtures were determined based on previous experience with the Corette ash. In all cases, the goal was to produce a concrete for general construction purposes (i.e., footings, walls and slabs) with a slump of 4 to 6 inches, a set time of 1 to 3 hours, and an unconfined compression strength of at least 3,000 to 4,000 psi at 28 days. Trial concrete batches were subsequently prepared, and their workability (slump), set time, and unconfined compression strength were determined. Concretes made from the Dave Johnson fly ash best met the performance criteria of interest.

Air is entrained in concrete to improve its resistance to damage from repeated cycles of freezing and thawing in a wet environment. The microscopic bubbles of entrained air are produced by physically agitating the concrete in the presence of a chemical foaming agent. Historically, the amount of entrained air in a mixture has been difficult to control when a high volume of fly ash is present. Thus, a series of tests was done to determine appropriate admixture dosage rates to achieve target levels of air entrainment, as well as to qualitatively assess the uniformity of the level of entrained air obtained at a given rate.

The subsequent investigation of long term durability focused on concretes made with the Corette ash, with some preliminary tests also being performed on concretes made with the Dave Johnston Ash. Tests were performed to determine material performance when exposed to freeze-thaw cycles, sulfates, alkali silica reactive (ASR) aggregates, and hydrogen sulfide (sewer gas) in the presence of bacteria. These exposures, either singly or in combination, are typical of the environments in which concrete is used. Air commonly is entrained in concrete to improve its performance under freeze-thaw conditions. Thus, some of the above tests were conducted at different levels of entrained air. Note that absorption capacity often is a broad indicator of a concrete's resistance to degradation from these environmental exposures, and this property was evaluated as a possible indicator of durability. In all cases, the results of these tests were compared with those obtained from specimens made with traditional Portland cement based concretes.

2. EXECUTIVE SUMMARY

The objective of this project was to further investigate the properties of 100 percent fly ash concrete relative to its use in a wide range of construction applications (e.g., buildings, pavements, wastewater structures, etc.). The binder in traditional concretes for construction applications is Portland cement. While this binder offers excellent performance, its production is an energy intensive process. A material that resembles Portland cement is Class C fly ash, which is already being manufactured as a by-product of the combustion of coal to generate electricity. The cementitious nature of this material is well documented, and it routinely has been used to replace some of the Portland cement in conventional concrete. Some fly ashes, such as the fly ash produced at the Corette power plant in Billings, MT, however, are sufficiently cementitious to totally replace the Portland cement as the binder in concrete, and thus this ash along with other similar ashes are currently being underutilized relative to the full benefit that they have to offer.

Over the past several years, Montana State University (MSU) has been researching the role that Corette Class C fly ashes might have in concrete construction materials. In working with concretes made with only Corette ash as the binder, it was discovered that they offered exceptional performance with respect to short term strength gain (e.g., 2,900 psi at one day), long term strength (e.g., in excess of 4,500 psi at 28 days), and workability. Mix design procedures subsequently were developed for this concrete in ongoing projects at MSU, and its behavior in reinforced concrete elements was also investigated.

While work to date has focused on fly ash available from a single source (the Corette Power Plant), other fly ashes may also have the potential to serve as the sole binder in fly ash concrete. While fly ashes with physical and chemical properties similar to those of the Corette fly ash would be expected to perform well in this role, at the current state-of-the-art it is not possible to reliably predict the binding potential of a fly ash simply from its index properties (as they are currently being measured). In a more general sense, the properties of fly ash are dependent on the characteristics of the coal being burned and the nature of the combustion process. Therefore, in this investigation fly ashes were sought out that had both similar material properties and were produced in the same manner as the Corette fly ash (which is the result of burning Powder River Basin coal in a tangentially fired boiler). Within the available resources of the project, three such fly ashes were considered—specifically, ashes from the Port Neal (Sioux City, IA), Dave Johnston (Glenrock, WY), and Council Bluffs (Council Bluffs, IA) power plants.

Trial mortar and concrete mixtures were prepared with each of the three fly ashes identified above, with an additional Corette fly ash mixture serving as a control. The fly ash concretes made with the Port Neal and Dave Johnston fly ashes had 28-day compressive strengths of 100 and 93 percent, respectively, of the Corette fly ash control mixture (which had a 28-day compressive strength of 3870 psi). The Council Bluffs fly ash mixture, however, only achieved 33 percent of the Corette mixture's strength. The resources available in this project were only sufficient to move ahead and further investigate a single fly ash binder in addition to the Corette fly ash. The Dave Johnston fly ash was selected in this regard, although the Port Neal ash also performed very well, and should be further investigated when resources permit.

Long term durability is as important as basic strength for concretes used in general construction applications. Common and important durability issues in such applications include freeze-thaw resistance; alkali-silica reactivity, or ASR (i.e., alkalis in the cementing material react with silica in the aggregates to generate expansive and destructive forces in the concrete); sulfate resistance;

and hydrogen sulfide resistance. In this project, tests were conducted that addressed each of these durability concerns for concretes made with the Corette and Dave Johnston fly ashes. Note that absorption capacity is an indirect indicator

Prior to conducting the freeze-thaw tests, an investigation was done on entraining air in fly ash concretes, as air entrainment is the primary mechanism used in conventional concretes to improve their freeze-thaw resistance. While entraining air in Portland cement concretes that also contains fly ash has been problematic is some cases in the past, air was readily entrained in the Corette fly ash concrete using a commercial admixture (BASF's Micro-Air ®). Entrained air had little effect on the properties of the fresh concrete, but it did decrease the compressive strength of the hardened material (as is also observed in Portland cement concrete).

Thus far, following test method ASTM C666 in which concrete specimens are subjected to multiple cycles of freezing and thawing, the freeze-thaw resistance of the Corette fly ash concrete has been satisfactory and compares reasonably well with Portland cement concrete control mixtures. After 225 freeze-thaw cycles the relative dynamic modulus of the Corette concrete is 89 percent. A relative dynamic modulus of 80 percent or greater after 300 cycles of response is often assumed to indicate good freeze-thaw resistance. The performance of the air entrained and non-air entrained Corette concretes was similar. While the relative dynamic modulus of the Dave Johnston concrete is of this same magnitude, these specimens exhibited a distinct increase in their rate of weight loss after 144 freeze-thaw cycles, which could signal an impending significant change in their general condition.. Testing of all specimens will continue past the end of this project for at least 300 freeze-thaw cycles.

From an ASR perspective, all the fly ash mixtures exhibited similar behavior and significantly outperformed the Portland cement control mixtures. Following ASTM C1260, after 14 days of exposure to an alkali solution at elevated temperature, the fly ash mixtures expanded only 0.01 to 0.02 percent. The typical threshold at which a concrete is assessed as reactive is at an expansion of 0.10 percent to 0.20 percent; thus, the fly ash mixtures performed very well. The Portland cement control mixtures expanded 0.24 to 0.38 percent.

The sulfate resistance test (ASTM C1012) is of relatively long duration (minimum of 12 to 18 months), and no meaningful results were obtained by the time this report was prepared (these tests are ongoing).

Relative to hydrogen sulfide/microbial related deterioration of fly ash concrete, no significant corrosion was seen of samples exposed for approximately 2 ½ months to a sulfur enriched, wastewater-based microbial environment.

In summary, the results of this project have substantially increased the body of knowledge on 100 percent fly ash concretes relative to a) the availability of fly ashes that can be used as the binder in these concretes, and their durability over time relative to some of the common mechanisms of concrete deterioration. That being said, additional research is merited on both topics to further support the use of 100 percent fly ash concretes in common construction applications.

3. EXPERIMENTAL

To realize the objectives of this project, a suite of tests was conducted on specimens cast from mortar and concrete mixtures produced in the laboratory. The current state-of-the-art in cement chemistry and concrete technology is such that the performance of a given concrete cannot be definitively predicted based on the properties of its constituents. Therefore, the performance characteristics of "new" concrete mixtures typically are determined by conducting tests on trial batches of the mixtures made in the laboratory.

All sample preparation and laboratory testing was done substantially in accordance with applicable ASTM standards. All trial batches for laboratory testing were prepared following ASTM C 192, unless noted otherwise below. Note that independent of the specific aspect of response that a trial batch of concrete was made to investigate, its workability, set time, temperature, and unconfined compression strength generally were determined. These tests were accomplished following standard ASTM procedures (Slump—ASTM C143, Temperature—ASTM C1064, Unconfined Compression Strength—ASTM C39—4-in by 8-in test specimens).

Presented below is a brief description of the various constituents used in the 100 percent fly ash mortar and concrete mixtures produced in this investigation, followed by descriptions of the various test regimens these mixtures were subjected to. Note that the mortar mixtures generally were prepared using a bench top "bread" mixer, while concrete mixtures were prepared using a fixed vane, rotating drum floor mixer.

3.1. Materials

A combination of mortar and concrete mixtures was used for the experimental work completed for this investigation. In both cases, these mixtures resembled conventional Portland cement based mixtures except that 100 percent of the Portland cement was replaced with fly ash. Thus, the mortar mixtures were composed of fly ash, borax, water, and fine aggregate. The concrete mixtures were composed of fly ash, borax, water, and coarse and fine aggregate. An air entrainment admixture was used in selected mixtures. Many of the test suites included Portland cement based "control" specimens, in which, as the name implies, Portland cement rather than fly ash was used as the binder. These various materials are described in more detail in the following paragraphs.

By design, all the fly ashes used in this investigation were produced by burning the same type of coal—sub-bituminous coal from the Powder River Basin (PRB)—using the same combustion process—tangentially fired boiler (Vollmer, 2005). Fly ash from the Corette Power Plant produced from this coal and combustion process is known to produce competent 100 percent fly ash concrete, inferentially improving the likelihood that the fly ash from these plants (Port Neal, Dave Johnston, and Council Bluffs) would also perform well in this role. As would be expected, all these fly ashes have similar chemical and physical properties, as listed in Table 1. All these ashes would be considered "high calcium" Class C ashes, with a CaO content in excess of 25 percent. Note that all the fly ash used in the project was donated by Headwaters Resources, Inc. (South Jordan, UT), a major marketer of coal combustion byproducts.

Table 1. Fly Ash Properties (provided by Headwaters Resources, Inc)

Property	Fly Ash Source			
	Corette	Port Neal #3	Dave Johnston	Council Bluffs #3
Chemical				
Silicon Dioxide (%)	32.37	35.05	35.1	33.99
Aluminum Oxide (%)	17.52	18.63	18.4	21.39
Iron Oxide (%)	5.34	6.36	4.9	5.86
Sulfur Trioxide (%)	2.02	2.07	1.9	1.99
Calcium Oxide (%)	28.89	27.00	27.6	26.88
Loss on Ignition (%)	0.23	0.19	0.8	0.4
Physical				
Fineness, Retained on #325 Sieve (%)	12.10	13.27	20.2	13.7
Soundness, Autoclave Expansion (%)	0.17	0.07	0.04	0.05
Drying Shrinkage, Increase @ 28 days (%)	np	np	0.01	np
Density	2.72	2.60	2.65	2.59

np – not provided

The use of some form of set retarder with this type of concrete was found to be essential, in that in the absence of any such retarder the concrete has been observed to flash set in just a few minutes. Borax, a naturally occurring mineral composed of boron, sodium, oxygen and water, was previously found to be very effective for this purpose. Specifically, 20 Mule Team Borax ® (decahydrate borax) was used in this project. This product is a dry powder and is commercially marketed as a laundry detergent.

The mix water used was potable water obtained from a public water supply.

While a "standard" sand (notably, Ottawa sand) often is used in laboratory mortar mixtures to ensure better experimental control/uniformity in the attendant mortar specimens, 100 percent fly ash mortar mixtures made with Ottawa sand exhibited set times significantly different (up to 50 percent) from those made with local sands. While the cause of this variation in set behavior is unknown, it was believed that mortar mixtures made with local sand would be more reflective of the set behavior of the full concrete mixtures. Therefore, a local sand was used in the mortar mixtures. The concrete mixtures were also made with locally available materials (fine and coarse aggregates) that met the requirements of ASTM C 33. The coarse aggregate had a maximum size of ¾ inch.

A locally available Type I/II Portland cement manufactured by Holcim US (Waltham, MA) was used in the control mixtures.

Finally, the air entrainment admixture used in this effort was Micro Air ® produced by BASF (Florham Park, NJ). This liquid admixture is intended to be used to entrain air in Portland cement concrete; its effects in such applications includes, among other things, increasing freeze-thaw durability (the primary reason it is used), increasing workability (often considered a positive secondary outcome), and decreasing compressive strength (often considered a negative secondary outcome).

3.2. Evaluation of Fly Ash Binders

Work on this project began with the general evaluation of the workability, set time, and unconfined compression strength of concretes made with fly ashes from different sources (Port Neal No. 3, Dave Johnston, and Council Bluffs No. 3). As previously mentioned, the fly ashes for this effort were specifically selected based on their expected similarity to the Corette fly ash that has consistently shown good performance as the binder in 100 percent fly ash concrete. Both mortar and concrete mixtures were used in evaluating fly ash performance. In both cases, initial proportions for the trial mixtures were developed based on previous experience with the Corette ash.

Mortar mixtures have been found to be an efficient and effective method to determine the setting characteristics and relative strength of cementitious fly ash mixtures. The basic mortar proportions used in the initial investigation are shown in Table 2. Referring to Table 2, the mortar mixtures were made at a water-to-fly-ash ratio (w/fa) of 0.275, a paste-to-aggregate ratio of approximately 1, and retarder dosage rates from 0 to 0.5 percent by weight of fly ash. Mixes were made with various amounts of retarder to determine the amount of borax necessary to achieve a two-and-a-half-hour set time. The mortar mixes were prepared using a bench top mixer. Set time was judged as when the "bleed water" dissipated from the surface of the samples.

Table 2. Mix Proportions: Initial Mortar Mixtures used to Investigate the Set Time of Various Fly Ash Binders

Ingredient	Weight
Fly Ash[a], lbs	2.20
Sand, lbs	2.20
Water, lbs	0.62
Borax (retarder), lbs	variable – 0 to 0.011

[a] fly ashes used were from the Corette, Port Neal (#3), Council Bluffs (#3), and Dave Johnston Power Plants

In light of the limited resources available for this project, the decision was made at the outset to focus subsequent work on the Corette fly ash, with a proven history of good performance in 100 percent fly ash concrete, and on one additional fly ash believed to be promising based on the results of these initial trial mixtures. As discussed in the results section below, the Dave Johnston fly ash was selected as the additional fly ash to be further studied in the remainder of the project. The first step in this regard was to more systematically characterize the set time versus retarder dosage rate for the Corette and Dave Johnston fly ashes using additional mortar mixtures. The same basic mix proportions were used as are given in Table 2, with a slight reduction in the water content to provide a water-to-fly-ash ratio of 0.24. This water-to-fly-ash ratio was more consistent with that used in typical fly ash concrete mixtures, which generally are made at water-to-fly-ash ratios of 0.20 to 0.24.

The basic proportions used in the concrete trial mixtures made with each ash are shown in Table 3. These mixtures were used to characterize the relative compressive strengths of the different concretes over time (i.e., at 7, 14, 21, and 28 days). The concrete mixtures were made at a water-to-fly-ash ratio of 0.24, a paste-to-aggregate ratio of approximately 1:1.5, and retarder dosage rates to provide approximately a 2.5-hour set time (as determined from the mortar mixtures introduced above). This basic mixture previously has been shown to exhibit the workability and strength consistent with concretes used in common construction applications (Cross, Stephens, and Vollmer, 2005). When prepared at a w/fa ratio of 0.24, the mixture offers good workability and reasonable strength. When prepared at a w/fa ratio of 0.20, the mixture offers good strength and reasonable workability. At this point in this study, the decision was made to use the 0.24 mixture (although subsequently during the air entrainment investigation, the decision was made to use the 0.20 mixture for all subsequent work).

Table 3. Mix Proportions: Initial Concrete Mixtures used to Investigate the Compressive Strength of Various Fly Ash Binders (approximate yield of 1 cubic foot)

Ingredient	Weight
Fly Ash[a], lbs	40.9
Fine Aggregate, lbs	33.7
Coarse Aggregate, lbs	67.4
Water, lbs	9.8
Borax, lbs	as required for 2.5 hr set time[b]

[a] fly ashes used were from Corette, Port Neal (#3), Council Bluffs (#3), and Dave Johnston Power Plants
[b] see Table 5 for specific amount of retarder used in each mixture

3.3. Air Entrainment Investigation

No work has previously been done at MSU with air-entrained, 100 percent fly ash based concrete mixtures. As previously mentioned, the resistance of typical Portland cement based concretes to freeze-thaw deterioration has been found to substantially improve when microscopic air bubbles (10 to 100- µm in diameter) are entrained in the paste. This air entrainment typically is achieved using chemical admixtures introduced during the mixing process that promote the formation of stable bubbles in the fresh paste. Recommended dosage rates for the admixture used in this investigation, BASF's Micro Air, range from 0.125 to 1.50 ounces/hundred weight of cement, with the intent of producing up to approximately 7.5 percent air in the concrete mixture by volume. Note that controlling the volume of admixture entrained air in Portland cement based concretes that include fly ash has occasionally been problematic in the past. Unburned carbon in the fly ash (measured as loss on ignition) interacts with many air entraining admixtures, reducing their effectiveness (Hill and Folliard, 2006). This problem generally is more pronounced as the loss on ignition of the fly ash increases, with a 50 percent reduction or more in entrained air as the loss on ignition increases from 0 to approximately 3 percent. Whether or not this problem would be observed and would be further exaggerated in 100 percent fly ash concrete was uncertain at the beginning of this project. The loss on ignition for the ashes considered in this project are all less than 1 percent (see Table 1), which may minimize this problem. That being said, the concretes of interest use 100 percent fly ash as the binder, as opposed to a typical Portland cement concrete in which 5 to 15 percent of the cement is replaced by fly ash.

The specific objectives of this portion of the project were to a) establish the Micro Air dosage rates necessary to produce various amounts of entrained air in the concrete, and b) observe other effects this admixture and the presence of entrained air might have on the concrete in both the fresh and hardened state (i.e., set time and workability in the fresh state, and unconfined compression strength in the hardened state). These objectives were realized by determining the air content of concrete mixtures dosed at different rates with Micro Air. This work was done using Corette fly ash mixtures. Following Portland cement practice, dosage rate was expressed in terms of admixture amount per unit of cementititous material (i.e., ounces of admixture per hundred weight of fly ash), and rates in the range of 1.0 oz to 8 oz were initially considered. These mixtures were prepared following the proportions previously given in Table 3, with two adjustments: a) the mix water was reduced to 8.2 lbs, yielding a w/fa ratio of 0.20, and b) an admixture (Micro Air) was used to entrain air in the concrete. The decision was made to use a w/fa ratio of 0.20 rather than 0.24 based on the adverse effect that the entrained air was expected to have on the unconfined compressive strength of the concrete. In Portland cement concretes, entrained air reduces their compressive strength by approximately 2 to 9 percent for every percent of entrained air (Kosmatka, Kerkoff, and Panarese, 2002) . To offset this potential effect on the strength of the fly ash concretes, the decision was made to start with a concrete known to be initially stronger in the non-entrained air state—i.e., the 0.20 w/fa concrete—rather than the 0.24 w/fa concrete. Corette fly ash mixtures made a w/fa ratio of 0.20 typically are about 20 percent stronger than mixtures made with a w/fa of 0.24 (Cross and Stephens, 2005). This w/fa ratio (0.20) was used in all subsequent project work.

For each trial mixture, entrained air was measured following ASTM C231 (Pressure Type B Meter).

3.4. Durability Tests

To a large extent, each suite of durability tests was conducted on the same set of mixtures. This set consisted of:

- two mixtures with Corette fly ash as the binder, one without and one with entrained air (at 4.4 percent),
- one mixture with Dave Johnston fly ash as the binder, without entrained air, and
- two mixtures with Portland cement as the binder, one without and one with entrained air (at 5.8 percent).

The specimen sizes and shapes, as well as the nature of the material used for their construction (i.e., mortar or concrete) varied by test type, as is described in more detail in the sections below. The fundamental concrete and mortar mixtures used for the durability tests are presented in Table 4 and Table 5.

Table 4. Basic Mix Proportions and Properties: Mortar Mixtures Used for Durability Tests (ASR, Sulfate, and Hydrogen Sulfide)

	Mixture				
	w/fa =0.20			w/c = 0.40	
	Corette		Dave Johnson	Portland Cement	
	Air	No Air	No Air	Air	No Air
Ingredient	Quantity per 1 cubic foot				
Portland Cement, lbs	0	0	0	46.97	47.84
Fly Ash, lbs	64.0	64.21	60.32	0	0
Fine Aggregate, lbs	70.76	70.76	70.76	75.82	75.82
Water, lbs	12.40	12.84	12.06	18.79	19.13
Borax, lbs	0.71	0.74	0.39 lbs	0	0
Micro Air, fl oz	1.292	0	0	0.489	0
Properties	Measured Value				
Slump, in	6.5	6.5	1.0	8.25	9.75
Air Content, %	7.8	2.15	4.9	6.9	2.5
Set Time, min	180	180	156	240	240
2 day strength, psi	3415	4395	3241	3470	3807
Strength at the time of prep of this report (avg. 90 days), psi	6449	8140	7451	10028	13244

Table 5. Basic Mix Proportions and Properties: Concrete Mixtures Used for Durability Tests (Freeze-Thaw)

	Mixture				
	w/fa =0.20			w/c = 0.50	
	Corette		Dave Johnson	Portland Cement	
	Air	No Air	No Air	Air	No Air
Ingredient	Quantity per 1 cubic feet				
Portland Cement, lbs	0	0	0	20.61	25.19
Fly Ash, lbs	37.64	44.28	41.60	0	0
Coarse Aggregate, lbs	67.39	67.39	67.39	69.45	69.45
Fine Aggregate, lbs	33.70	33.70	33.70	41.34	41.24
Water, lbs	7.53	8.86	8.32	10.31	12.60
Borax, lbs	0.43	0.51	0.27	0	0
Micro Air, fl oz	2.26	0	0	1.24	0
Properties	Measured Value				
Slump, in	1.25	1	0.75	1	2.5
Air Content, %	4.4	2.3	2.9	5.8	2.1
Set Time, min	180	180	160	240	240
F/T Start strength, psi	2698	4289	3612	5326	6968
225 cycles (avg. 75 days)[a], psi	3073	5198	5177	5756	8801

[a] freeze-thaw specimens were exposed to 225 cycles at the time this report was prepared, testing will continue through 300 cycles

Absorption capacity often is a broad indicator of a concrete's resistance to degradation, as this degradation is influenced by the ability of aqueous solutions to move through the concrete matrix. Therefore, absorption was also evaluated as part of this investigation of fly ash concrete durability.

Note that some tests are expected to be continued past the end of the project and/or repeated after this project is concluded. In the past, a significant increase has been observed in the unconfined compressive strength of 100 percent fly ash concrete over time (e.g., a 100 percent increase from 28 days to one year). This increase has been attributed to further chemical reactions and changes in crystal structure of the concrete, which could affect its resistance to penetration by water and other contaminants (and thus indirectly its durability).

Absorption

The absorption properties of each mixture are being determined using the test methods outlined in ASTM C 642. This test involves submerging dry test specimens and monitoring their weight change, which corresponds to the water absorbed over time. The test specimens for this investigation are 4 in by 8 in cylinders that were cast from the same mix as the freeze thaw specimens. Tests were started after the freeze thaw test following a 28 day cure period.

Freeze-Thaw

Freeze-thaw resistance was quantified following the procedures in ASTM C 666 (Procedure A). This test method consists of subjecting concrete specimens to multiple freeze-thaw cycles while fully saturated (see Figure 1). Weight loss and change in dynamic modulus are monitored as a function of accumulated freeze-thaw cycles. As may be obvious, the degree of damage sustained by the concrete due to micro (as well as macro) cracking under freeze-thaw action is reflected by its attendant loss of weight and stiffness, where material stiffness can be non-destructively measured in terms of dynamic modulus. A durability factor can be calculated from the test results:

$$DF = \frac{P * N}{M}$$

where DF = durability factor,

PN = relative dynamic modulus at N cycles of response

$= \frac{n_1^2}{n^2} * 100$, where n1 and n are the transverse frequencies of natural vibration at N and 0 cycles of response, respectively

N = number of cycles of response at which P (the relative dynamic modulus) reaches the specified minimum value, or the specified number of cycles at which exposure is to be terminated (e.g., 300)

M = specified number of cycles at which exposure is to be terminated (e.g., 300)

As may be obvious, the relative dynamic modulus (PN) can also be used as a relative measure of performance of test specimens subjected to the same number of freeze-thaw cycles, with a value of 100 corresponding to no loss of stiffness, and decreasing values corresponding to increasing deterioration.

Concrete (as opposed to mortar) was used in the freeze-thaw tests, cast in rectangular prisms 3 inches by 4 in by 16 in. Three specimens from each concrete, Corette fly ash mixtures, without and with entrained air; Dave Johnston fly ash mixture, without entrained air; and Portland cement mixtures, without and with entrained air, were tested simultaneously. The specimens were exposed to six temperature cycles per day, and during each cycle, specimen temperatures were lowered from approximately 40 to 0 deg F, and then raised back up from 0 to 40 deg F.

Figure 1. Freeze-thaw Test Chamber

A sonometer was used to measure the frequencies of vibration required to calculate the dynamic moduli of the specimens (see Figure 2). The sonometer effectively functions as a frequency sweep tester, with the specimens resonating when the excitation frequency matches their natural frequencies. Dynamic modulus and weight loss tests were conducted on all specimens before testing began, and then after 35, 73, 144, 182, and 225 freeze-thaw cycles were experienced. Sonometer readings were repeated three times on each specimen during each round of measurements.

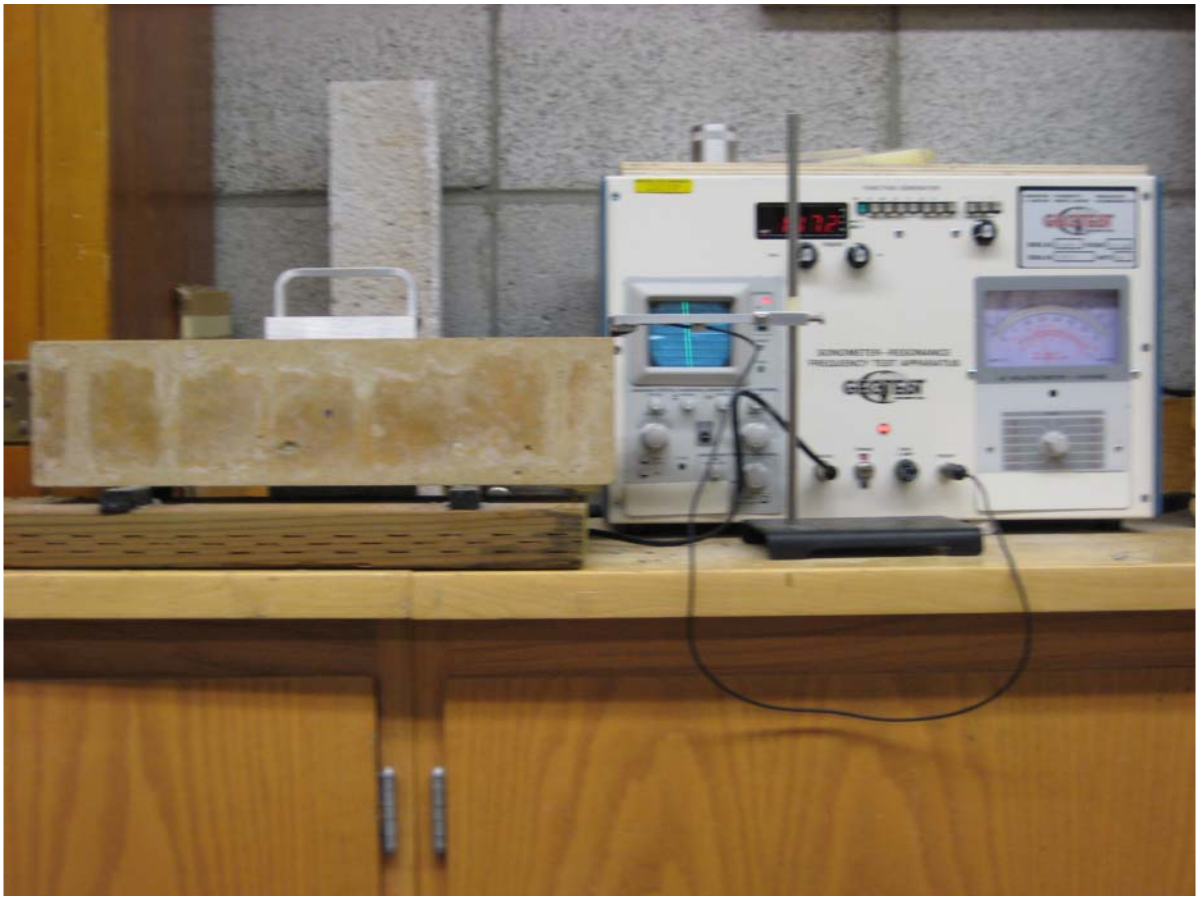


Figure 2. Sonometer Used in Determining Dynamic Modulus of Freeze-Thaw Test Specimens

Alkali Silica Reactivity (ASR)

The susceptibility of a particular concrete to ASR-related degradation is difficult to predict based simply on the properties of the cement and the aggregates themselves. Thus, this susceptibility is generally determined by testing. Several methods are available to investigate ASR, and initially it was proposed to perform a relatively simple stain test developed by Los Alamos National Laboratory (Powers, 1999) that detects the absence/presence of any alkali-silica reactions in a hardened concrete specimen. The opportunity developed to use instead a more sophisticated test, ASTM C 1260 Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), that involves immersing mortar bars in an alkaline solution at 80^{o} C for 14 days and monitoring their expansion. In using this test, it is important to note that the conditions the concrete is exposed to following this method are severe, and the test has indicated unacceptable performance for cement-aggregate combinations known to have performed well in actual applications.

ASTM C 1260 was designed for Portland cement based materials and was modified for this investigation in light of some differences in the properties of 100 percent fly ash versus Portland cement concretes. Notably, the test specifies a w/c ratio of 0.47 for the tested material. While this w/c ratio reasonably represents common Portland cement concrete mixtures, it is approximately twice the water-to-cementitious materials ratio used in general purpose 100 percent fly ash concrete mixtures. Correspondingly, the fly ash mortar specimens used in this investigation were made using a w/fa ratio of 0.20. Further note that this test is intended to be performed using the specific aggregate planned for a particular project. In this case, the test was performed using a locally available reactive aggregate.

Three mortar bars (1 in by 1 in by 10 in) from each of the five mixtures listed in Table 4 were submerged in alkali solution in the test apparatus shown in Figure 3. The subsequent change in length of the specimens was monitored at 2- to 3-day intervals throughout the duration of the test. The recommended limit of expansion to delineate potentially reactive aggregates is 0.2 percent (ASTM C 1260) over 14 days, although some agencies adopt a more conservative limit of 0.1 percent. In this case, testing was continued past the 14-day period as necessary until the specimens exhibited 0.1 percent expansion.

Figure 3. ASR Test Apparatus

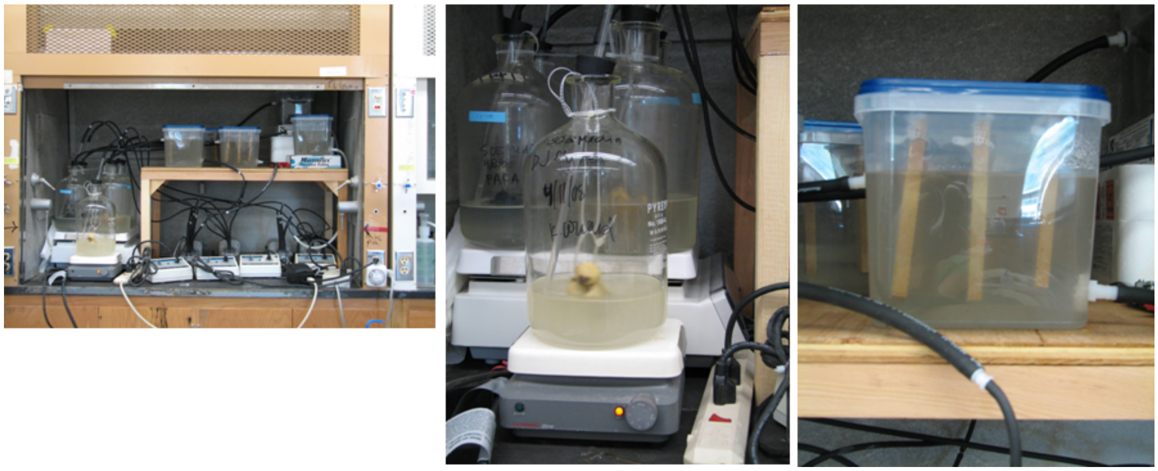
Sulfate Resistance

The sulfate resistance of 100 percent fly ash concrete is being determined using a modified version of ASTM test method C 1012. Similar to the requirements of ASTM C 1260, the mortar specimens used in this test are prepared at w/c ratios of 0.485 and 0.460, for non-air entrained and air entrained mixtures, respectively. As before, assuming the intent of this requirement is to replicate commonly used mixtures, the fly ash mortars used in these tests were made at a w/fa ratio of 0.20. The test itself consists of submerging test specimens (1 in by 1 in by 10 in) in a sulfate solution and periodically measuring their length change using a comparator as specified in ASTM C490. These measurements are generally taken over a period of time spanning at least one year and preferably 18 months and beyond. While initial measurements are made at relatively short intervals (weekly) subsequent measurements are taken less frequently (every two months).

Hydrogen Sulfide/Microbial Influenced Damage

The action of microbial sulfur oxidation in environments like the crown of a sewer pipe can produce prodigious amounts of acid that can react with the paste components in concrete, destroying the pipe. Unlike the other behaviors investigated in this project, no standard test methodology was available to investigate this type of concrete degradation. Testing was carried out using a modified version of a procedure described by Vincke and his associates (1999) that incorporates sulfide absorption, biodegradation and washing through several cycles. The goal was to use a mixed culture of microorganisms enriched from a concrete- corrosive environment to simulate the events in a sewer. This simulation was staged in a bench top reactor containing mortar coupons of the concretes of interest submerged in a medium produced by enriching wastewater samples from a treatment plant. Loss of mass due to corrosion and production of sulfuric acid and accompanying pH decrease was expected to provide a reasonable set of measurable parameters to distinguish any differences in behavior attributable to the type of concrete, while microbial community analysis was expected to ascertain whether the concrete type also selected for different microbial populations. An overview of the test methodology is presented below; additional details about all aspects of this methodology are presented in Appendix A.

The bench top reactors were designed to be large enough to hold 6 coupons (5 in by 1 in by 3/8 in) with ample space for the surrounding medium (see Figure 4). To mimic wastewater conditions, every evening at about 8 p.m., the medium in each reactor (described below) was drained to below the level of the coupons. At 7 a.m., the reactors were refilled with the medium, which was intermittently circulated through the reactors at 2 to 3 hour intervals until the system was again drained in the evenings. Each type of concrete was tested in its own isolated system. To ensure that the sulfur particles did not clog the reactor tubing, the sulfur was placed in cheesecloth and hung in the reactor medium. Following curing for 7 days, coupons were placed in an oven at 104ºC and then weighed before being suspended in the reactors. When the reactors were full, the coupons were submerged except for the top 1 in. Once placed into service, the reactors were operated continuously until sampled at the end of the run. Durations of exposure for each concrete type are shown in Table 6.



a) overview b) media bottles c) reactor with coupons

Figure 4. Reactors Used to Evaluate the Corrosion of Various Concrete Mixtures by Sulfur Oxidizing Bacteria

Table 6. Length of Time Reactors Were Run

Mortar Specimen	Days run
Portland cement, without entrained air	74
Portland cement, with entrained air	73
Corette, without entrained air	70
Corette, with entrained air	69
Dave Johnson, without entrained air	66

Biomass samples were obtained from the Bozeman, Montana Wastewater Treatment Plant. Samples were scraped from the gravity thickener where biofilms were perceived to be causing concrete corrosion. The samples were enriched for sulfur oxidizing bacteria on sulfur oxidizing bacterial medium (SOB medium). Elemental sulfur was added, and the medium was inoculated with the wastewater samples. The enrichment cultures were incubated at room temperature. The samples were monitored for a drop in pH, which corresponded to the production of sulfuric acid by the sulfur oxidizing bacteria. These SOB enriched cultures were then used as inoculum for the reactors.

At the end of the incubation periods shown in Table 6, four coupons were removed from each reactor. Three coupons were used for taking weight measurements to evaluate for corrosion. These three coupons were rinsed with tap water in attempt to remove salt and biofilm material. The coupons were dried at 104ºC for 168 hours and re-weighed. Note that a set of control coupons was used to determine the effect that just submerging concrete coupons in water had on their weight.

The surface of the fourth coupon was scraped and then rinsed (see Figure 5), and the rinse water was collected for biofilm bacterial community analysis.

Figure 5. Scraping Technique Used to Obtain Microbial Biomass from the Reactor Coupons

Additionally, ion chromatography (IC) was used to measure the amount of sulfate produced in the reactors. Finally, an indication of the predominant sulfur oxidizing bacterial groups present in a) the medium, b) the biofilm scrapings from the coupons, and c) the initial inocula used to spike the reactors was obtained using denaturing gradient gel electrophoresis (DGGE). DGGE is a bacterial community analysis technique. DGGE was done on all five reactors. The banding pattern produced by this methodology gives an indication of the microbial diversity in each of the reactor systems.

4. RESULTS AND DISCUSSION

4.1. Evaluation of Fly Ash Binders

Results from the initial evaluation of the Dave Johnston, Port Neal, and Council Bluff fly ashes as potential binders in 100 percent fly ash concrete are shown in Table 7. Also included in this table are results from tests conducted on a Corette fly ash mixture serving in the role of a control mixture. As previously stated, the Corette fly ash has consistently demonstrated the relatively high level of performance that can be achieved in a concrete that uses only fly ash as the binder. In this case, the Corette fly ash control mixture reached an unconfined compressive strength of 4,100 psi, with a retarder dosage of 0.45 percent by weight of fly ash required to produce a set time of 1 hour (these results are consistent with previous work done with this fly ash).

Table 7. Evaluation of Fly Ash Binders

Binder	Borax as a % of Weight of Fly Ash for 2.5 hr Set Time[a]	Slump[b] (in)	28 day Compressive Strength[b] (psi)
Port Neal	0.15	4	3870
Dave Johnston	0.38	4	3580
Council Bluffs	0.10	5	1270
Corette	0.45	5	3870

[a] from mortar mixtures
[b] from concrete mixtures

Referring to Table 7, the Dave Johnston and Port Neal mixtures achieved unconfined compression strengths at 28 days of the same order of magnitude as those of the Corette mixture (93 and 100 percent of control, respectively), while the strength of the Council Bluffs mixture was significantly lower than this value (only 33 percent of control). Therefore, the decision was made to suspend further work at this time with the Council Bluffs ash. Relative to the Dave Johnston and Port Neal mixtures, their strength behavior was subsequently scrutinized more closely by considering their strength gain as a function of time (see Figure 6). While the Port Neal mixture was stronger than the Dave Johnston mixture, the strength behavior of the Dave Johnston mixture as a function of time closely resembled that of the Corette mixture. Therefore, the decision was made to move ahead with additional development work with the Dave Johnston rather than the Port Neal fly ash. Nonetheless, the Port Neal fly ash arguably shows equivalent promise as the Dave Johnston fly ash as a binder in 100 percent fly ash concrete, and further work with this ash should be pursed as resources to do so become available.

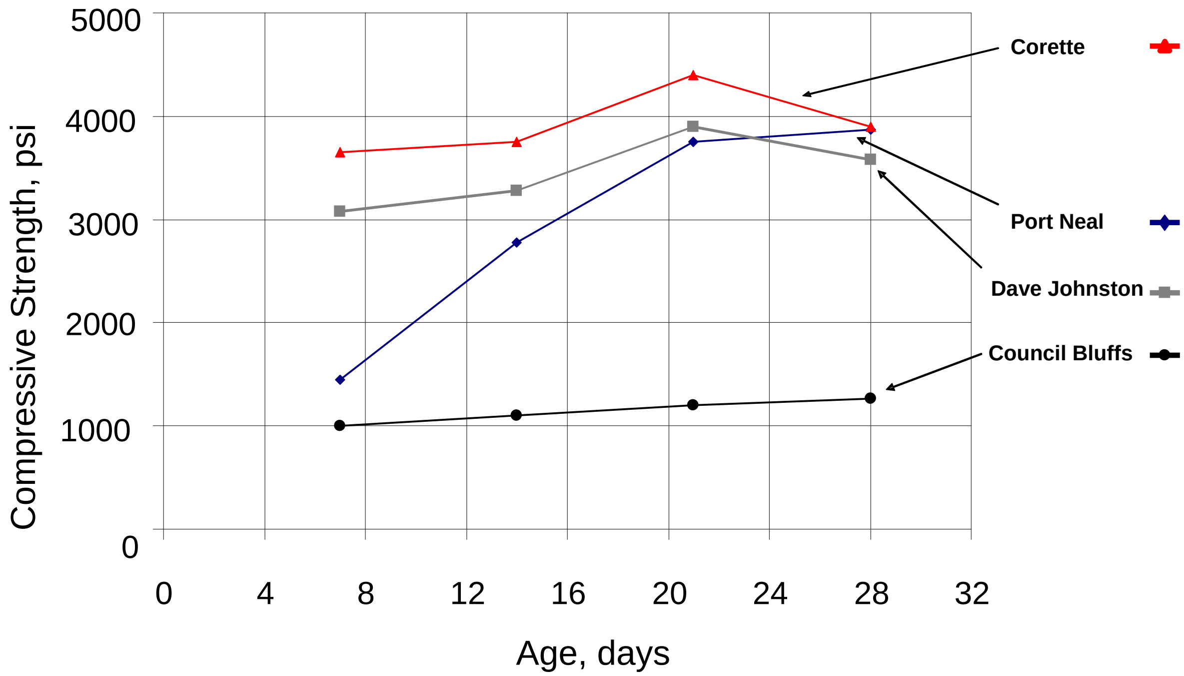


Figure 6. Compressive Strength Evaluation of Various Fly Ash Binders

The results of additional work that was subsequently done specifically on the set-time behavior of the Dave Johnston fly ash and the Corette fly ash control is summarized in Figure 7. This figure shows the relationship between set time, measured in minutes, and borax dosage rate, measured as a percent of fly ash by weight. The set time behavior of the Dave Johnston mixtures was similar to that of the Corette mixtures, with set time monotonically increasing as a function of retarder dosage rate, approximately following an exponential curve. However, mixtures with the Dave Johnston fly ash only required from 66 to 75 percent of the borax used with the Corette mixtures to achieve the same set time across the range of results of interest in this investigation (i.e., set times of 1/2 to 3 hours).

4.2. Air Entrainment Investigation

Entrained air appeared to be successfully introduced into the Corette fly ash concrete mixtures without difficulty using the air entrainment agent MicroAir. This conclusion is based on an obvious and predictable increase in the air content of trial concrete mixtures that were dosed with Micro Air. Additional work, however, needs to be done to make sure that this added air consists of micro bubbles with a size and dispersion appropriate to serve the intended function of entrained air. Nonetheless, relative to admixture dosage rate, it was found that the percent of entrained air was approximately linearly proportional to admixture amount, with 1.5 ounces per hundred weight of fly ash resulting in approximately 7 percent air in the mixture. This result is generally consistent with expectations based on the dosage rate/range provided by the manufacturer for Portland cement.

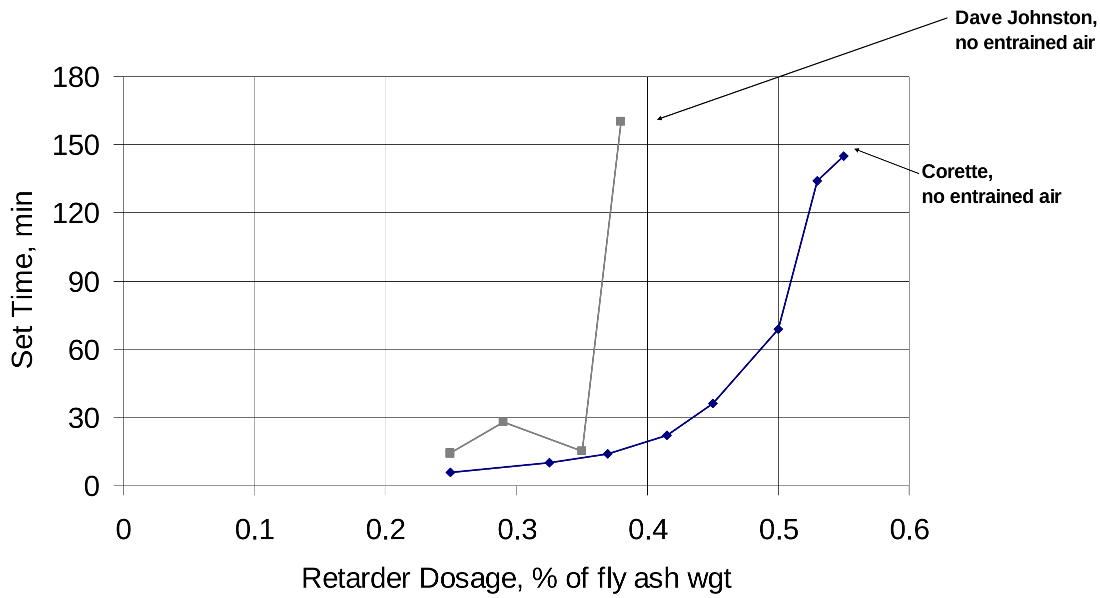


Figure 7. Results of Set Time Investigation, Dave Johnston and Corette Fly Ash Mixtures

In the fresh state, entrained air was found to increase the "stickiness" and decrease the bleed water in the fly ash concrete mixtures, similar to its effect on Portland cement concretes. Unlike Portland cement concretes, however, in which the workability of a mixture (measured by slump) typically increases with amount of entrained air, the workability of 100 percent fly ash concretes thus far has been found to be relatively unaffected by the presence of entrained air. Limited evidence indicates that air entrainment may actually decrease the workability of low w/fa ratio (i.e., w/fa of 0.18 and 0.20), low slump fly ash concrete mixtures. Set time appears to be unaffected by air entrainment, which once again is similar to the behavior of air-entrained Portland cement concretes.

In the hardened state, the compressive strength of 100 percent fly ash concretes was found to decrease with entrained air, as is also observed in Portland cement concretes. In Portland cement concretes, a 2 to 9 percent reduction in compressive strength is observed for every percent of entrained air in a mixture (Kosmatka, Kerkoff, and Panarese, 2002), with the larger reductions occurring in mixtures containing more cementitious material. The fly ash concrete mixtures developed to date are rich in paste (relatively high content of cementitious material) to maintain workability at the low water-to-cementitious materials ratios (w/c) being used (e.g., w/fa of 0.20, as opposed to w/c of 0.40 in Portland cement mixtures). Thus, it was both expected and observed that the strength loss for these concretes per percent of entrained air is toward the 9 percent end of the 2 to 9 percent range reported above. At a w/fa of 0.20, results to date indicate approximately a 7 percent reduction in compressive strength per percent of entrained air.

4.3. Durability Tests

Absorption

As previously mentioned, concrete durability is influenced by its absorption, as much of the degradation observed over time begins with fluid intrusion into the material. Work on the absorption tests was ongoing at the time this report was completed. Significant changes in material structure appear to occur for a considerable period after fly concrete is cast, i.e., well past the initial 28 day cure. Therefore, absorption tests will continue to be performed for at least a period of one year.

Freeze-Thaw

The results of the freeze-thaw tests, specifically the relative dynamic modulus and relative weight of each concrete mixture as a function of freeze-thaw cycles of exposure, are summarized in Figure 8 and Figure 9, respectively. These parameters were simply calculated as the ratio of their measured values at a given number of freeze-thaw cycles to their initial values before testing began. The reported results are the average values over three specimens. Note that due to the abbreviated project schedule, the test specimens had only accumulated 225 cycles of response at the time of this report. Testing subsequently will be continued until the specimens are subjected to at least 300 cycles of response. Continuing these tests to at least the full 300 cycle term is important, as a relatively sharp increase in rate of deterioration sometimes has been seen in between 200 and 300 cycles of exposure. In this case, the freeze-thaw performance is often judged acceptable if the relative dynamic modulus of the material is equal to or greater than 80 percent after 300 cycles of exposure. The dynamic modulus of the concretes investigated herein all exceeded this value after the 225 cycles of response completed to date.

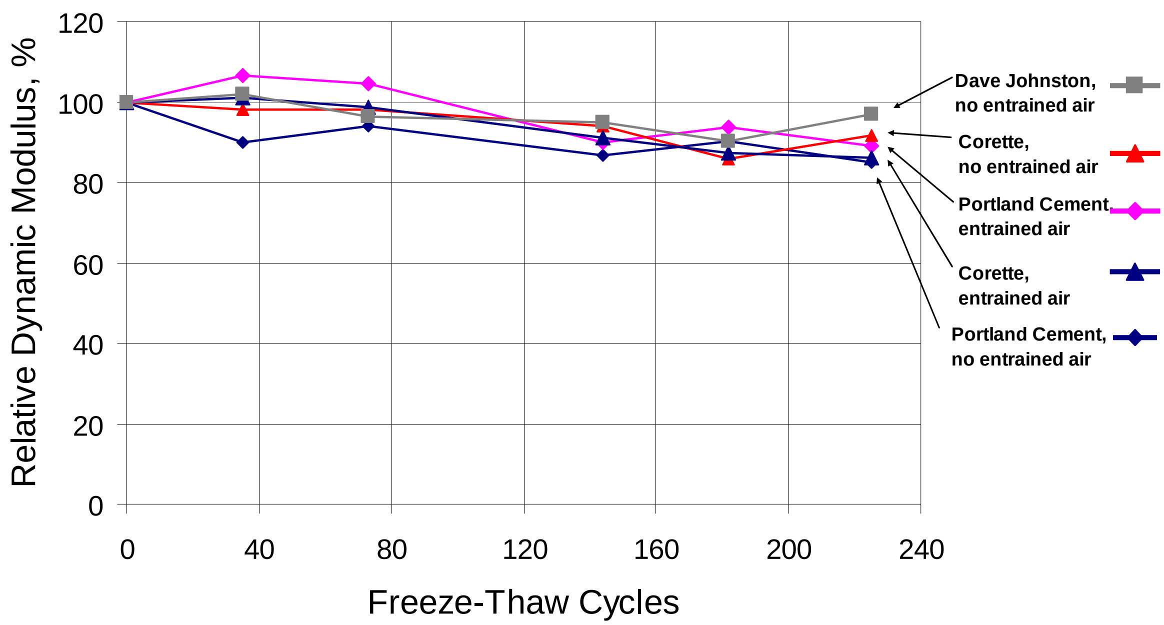


Figure 8. Freeze-Thaw Test Results, Relative Dynamic Modulus

With the exception of the Dave Johnston fly ash concrete, the fly ash and Portland cement concretes tested herein all exhibited similar behavior when exposed to repeated cycles of freezing and thawing. That being said, more detailed qualitative observations on the relative behavior of the various concretes are presented below; additional statistical analyses of these results will be performed in the future.

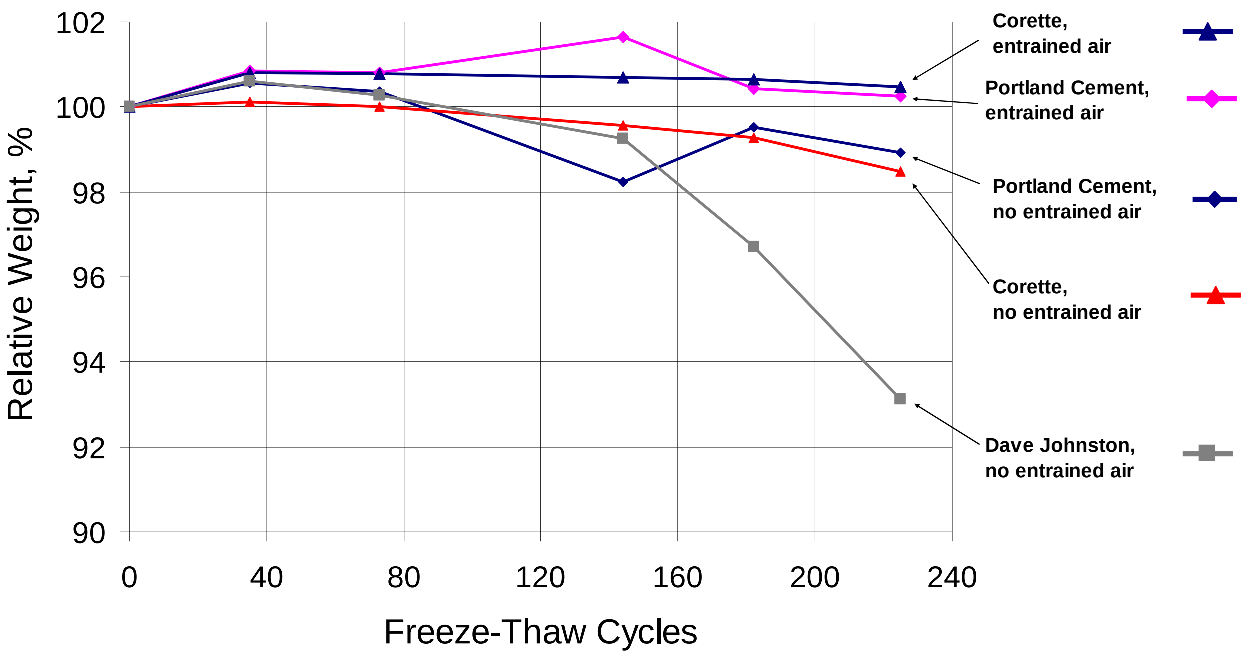


Figure 9. Freeze-Thaw Test Results, Relative Weight

Referring to Figure 8, the lowest relative dynamic modulus was fairly consistently seen for the Portland cement concrete without entrained air (85 percent at 225 cycles). The relatively poor performance of such concretes in saturated freeze-thaw environments is well documented. The performance of this mixture was actually better than expected based on results from other investigations (e.g., Pinto and Hoover, 2001; Tanesi and Meininger, 2006), in which low air content mixtures at comparable w/c ratios experienced a dramatic decrease (75 percent) in dynamic modulus at fewer than 100 freeze-thaw cycles. The comparatively positive performance of this mixture in this investigation was attributed primarily to its relatively high cement content (i.e., 680 lbs/cu yd) compared to standard mixes (i.e., 450 lbs/cu yd). Relative to the remaining concretes, the modulus values did generally decline as the number of exposure cycles increased, with calculated values of 86 to 95 percent at 225 cycles. To provide some perspective on these values, concretes with a minimum relative dynamic modulus of 60 percent after 300 freeze-thaw cycles have been considered to generally exhibit good freeze-thaw resistance (Mindess, Young, and Darwin, 2003).

The only obviously distinctive feature in the dynamic modulus and weight loss data was the acceleration in the weight loss seen in the Dave Johnston fly ash concrete that began between 144 and 182 cycles of exposure (see Figure 9). Starting in this interval, the relative weight of this concrete decreased from 99 to 93 percent. This apparent acceleration in the concrete's degradation was not coincidently seen in the dynamic modulus data for this concrete, although based on the experience of other researchers, it may soon manifest itself as the specimens are subjected to additional freeze-thaw cycles. Note that the other concretes experienced only nominal weight loss (less than 2 percent) through 225 cycles of exposure. While it is important in light of the variability in the individual data points not to attach too much significance to the exact values reported for these concretes in Figure 9, it is interesting to note that the two air-entrained concretes, which would be expected to offer the greater resistance to freeze-thaw, both experienced less weight loss than the non-air-entrained concrete.

Photographs of typical freeze-thaw test specimens from each type of concrete after 225 cycles of exposure are presented in Figure 10. The physical condition of the specimens was consistent with the relative dynamic modulus and relative weight data. That is, little deterioration was evident in the Corette fly ash and Portland cement concrete specimens, while substantial surficial spalling and cracking was observed in the Dave Johnston fly ash specimens.

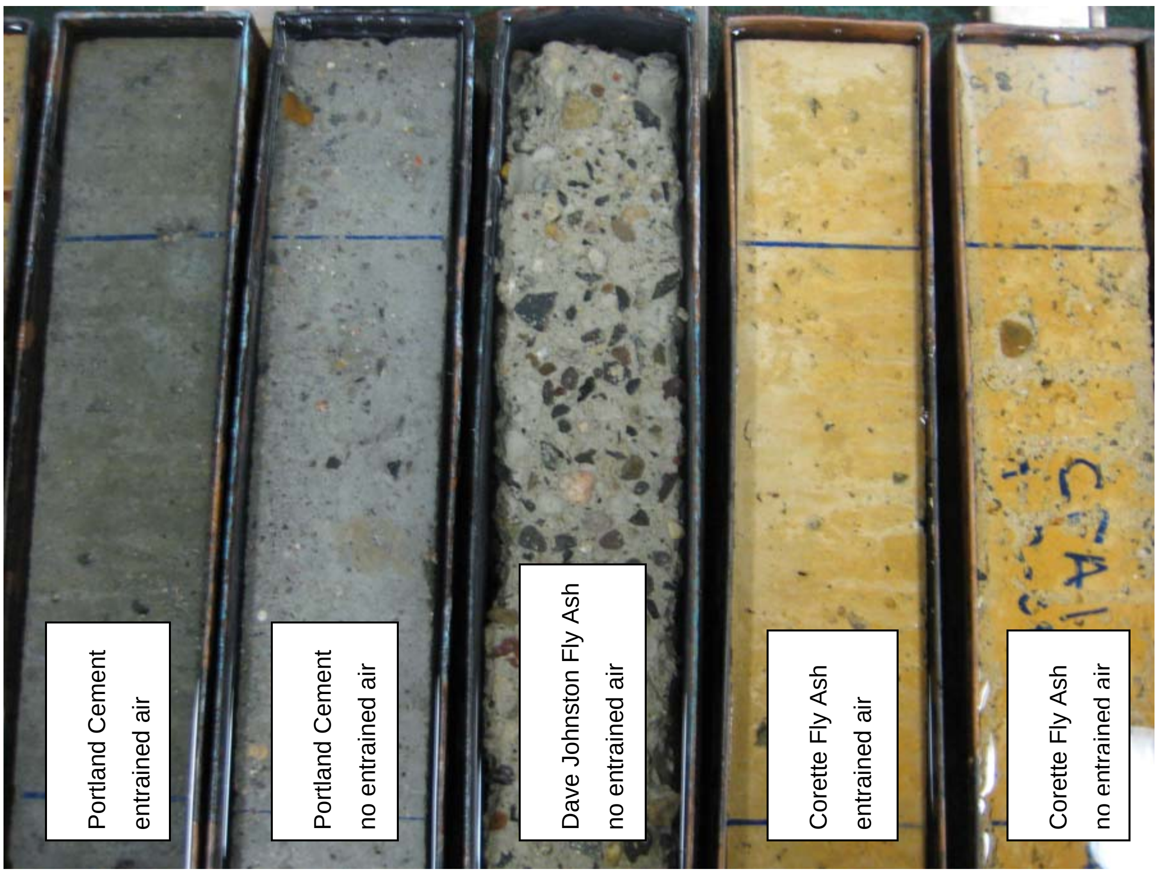


Figure 10. Condition of Freeze-Thaw Specimens Following 225 Cycles of Exposure

Alkali Silica Reactivity (ASR)

Results of the ASR test are summarized in Figure 11. All of the fly ash mixtures behaved similarly during the ASR test and exhibited significantly (i.e., an order of magnitude) less expansion than the Portland cement mixtures. After 14 days of exposure to the alkali solution, the fly ash mixtures expanded 0.01 to 0.02 percent, while the Portland cement mixtures with and without entrained air expanded 0.24 and 0.38 percent, respectively. Thus, using as a reaction threshold expansion of either 0.10 percent or 0.20 percent, the given aggregate would be judged non-reactive in a fly ash concrete, while it would be judged to be reactive in a Portland cement concrete. To some extent these results are not surprising, in that some researchers have reported that ASR problems can be mitigated by using Class C fly ash (e.g., Hicks, 2007), while other researchers have reported that high lime fly ashes (which often are Class C ashes) are ineffective (e.g., Rangaraju, 2007).

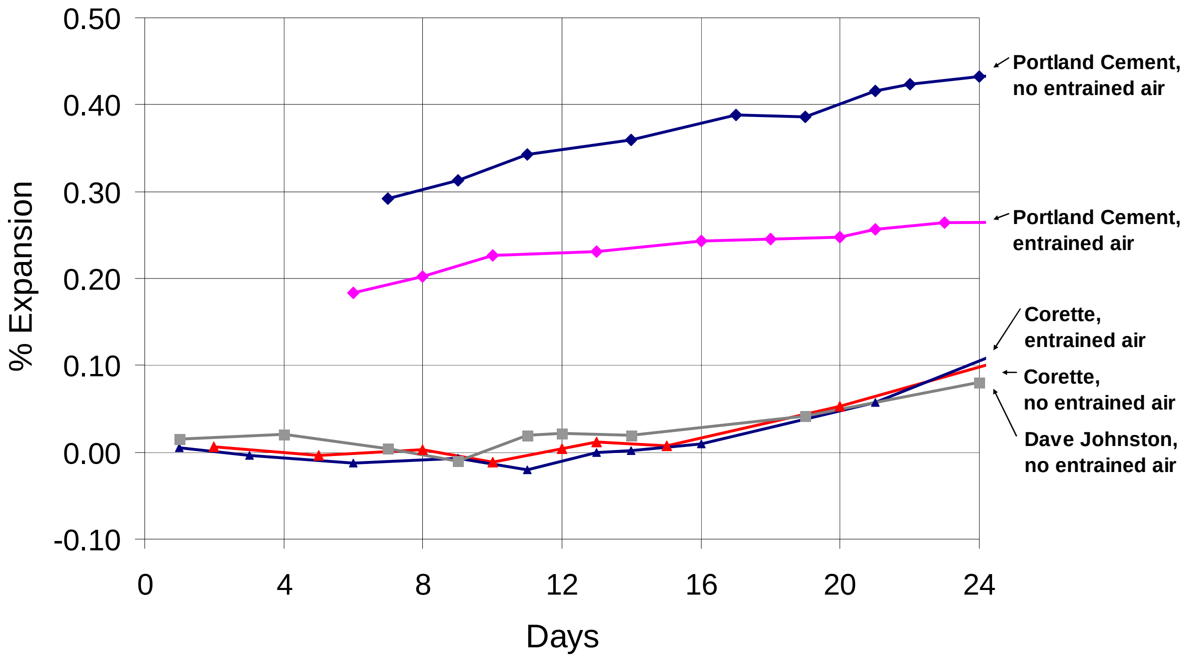


Figure 11. ASR Test Results

Sulfate

At this point in the project, the early age measurements made on the sulfate specimens offer little insight into the sulfate-related behavior of the various concretes. Recall that this test has at least a 12-month duration, and preferably 18 months. Monitoring of the test specimens will continue beyond this project and the final results will be disseminated at a later date.

Hydrogen Sulfide/Microbial Induced Damage

On all coupons from each reactor, the portion of the coupons that was submerged had a visible layer of precipitate (see Figure 12), perhaps struvite, that did not wash off in tap water. Nevertheless, the precipitate could be removed by mechanical scraping and produced a surface very similar to the original coupon. The Corette fly-ash coupons developed crystal growths above the medium line after approximately 70 days in the SOB medium; the crystalline growth contained some corroded fly-ash material. Similar observations were made when examining the

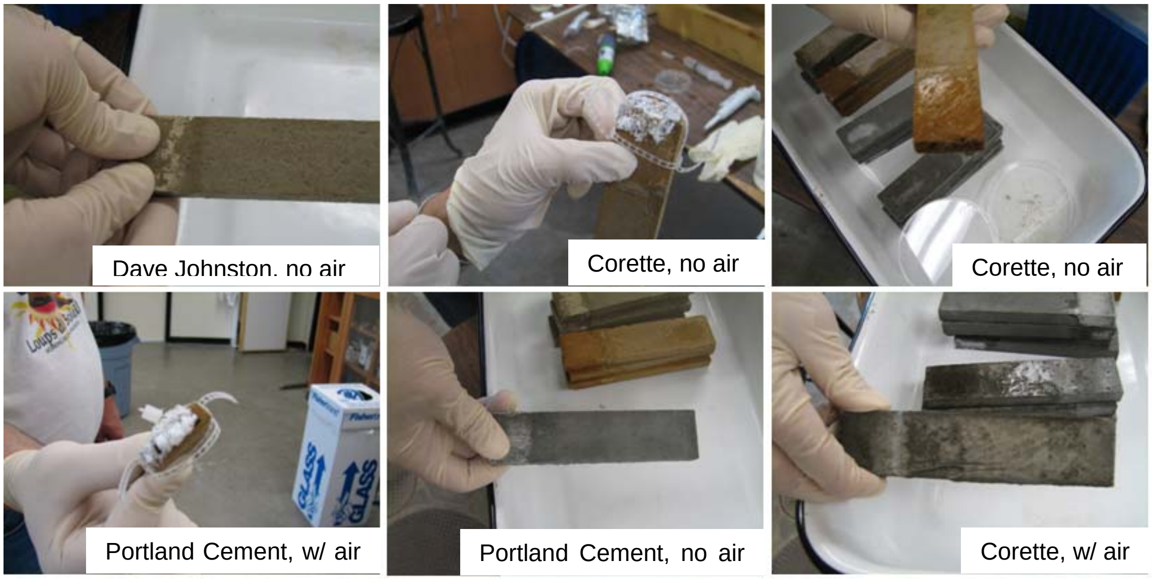


Figure 12. Mortar Coupons After Removal From the Reactors

Dave Johnston fly ash coupons. However, pieces of cement were not observed in the salt formation at the top of the Dave Johnston fly ash coupons. These data may indicate that the type and composition of fly-ash is important to preventing corrosion of concrete made from fly-ash cement. In general, the Portland cement coupons appeared to be visually unchanged from their original condition (see Figure 12). The Portland cement coupons did not have a crystalline growth above the liquid level.

The reactor with the Portland cement coupons was the only one where the pH decreased below the starting pH of 4.82, indicating the presence of sulfur oxidizing bacteria (see Table 8). The remainder of the reactors had pH values between 6 and 7 when the reactors were disassembled.

Table 8. pH Values Over the Course of the Experiment

Mixture	pH			
	Initial	13-May	2-Jun	17-Jun
Portland, without entrained air	4.82	3.88	4.44	4.65
Portland, with entrained air	4.82	6.97	7.00	6.81
Corette, without entrained air	4.82	6.84	6.77	6.44
Corette, with entrained air	4.82	6.82	6.84	6.87
Dave Johnston without entrained air	4.82	6.58	6.34	6.34

Ion chromatography (IC) was used to determine the amount of sulfate produced in the reactor systems. Table 3 provides the percent change in the amount of sulfate found in the original media, to the amount of sulfate found in the medium of each reactor after approximately 70 days. Each reactor was shown to produce sulfate, which indicated that the elemental sulfur originally placed in the reactors had been converted, by bacterial means, to sulfate. These data correlated with the pH data in Table 8. The pH in the Portland cement reactor dropped to 4.65, and the IC data indicated the largest percent change in sulfate production in this reactor.

Table 9. Percent Change in Sulfate in Each Reactor Over the Course of the Experiment

Mixture	% change in sulfate
Portland cement, without entrained air	314
Portland cement, with entrained air	13
Corette, without entrained air	29
Corette, with entrained air	25
Dave Johnston, without entrained air	26

Only nominal changes in mass were observed for the coupons during the course of the experiment (see Table 10). The control coupons (those retained in a beaker on the bench and not immersed until the end of the study) first lost mass upon drying at 104°C - about 1.0 g per coupon for the three fly ash samples, and over 1.5 g for the Portland cement coupons. After 24 hours of immersion in water at room temperature, these coupons were again dried (for 168 hours), whereupon they exhibited a net mass increase of between 0.11 and 0.26 grams (see rightmost column of Table 10). Total coupon masses, for comparison, ranged from 77 to 88 grams.

Table 10. Average Changes in Coupon Mass Following Incubation, Rinsing and/or Scraping and 168 hr Drying, and Mass Increase in Average Control (not incubated) Coupons

Mixture	Change in Coupon Mass (g)			
	Rinsed		Rinsed and Scraped	Control gain
	Mean gain	Std deviation		
Portland cement, without entrained air	0.744	0.097	0.591	0.256
Portland cement, with entrained air	1.313	0.025	1.236	0.195
Corette, without entrained air	0.719	0.261	0.465	0.145
Corette, with entrained air	0.431	0.060	0.128	0.107
Dave Johnston, without entrained air	0.548	0.054	0.384	0.171

The coupons removed from the reactors at the end of the incubation period were treated in two ways – a) rinsing and b) rinsing plus scraping. Regardless of treatment, all coupons gained weight (see Table 10), but significant amounts of salt were removed by scraping, and this is reflected in the smaller weight gains shown in Table 10 for the scraped coupons. When the hydration gain found in the control coupons is considered, the net amount of mass gain in the scraped coupons varied with coupon type, but as the difference is significantly less than a gram in most cases, it is likely due to variations in the success of the scraping step at removing salt. In the coupons that were only rinsed following removal from the reactor, all types showed nonzero mass increase, with the increase in the Portland cement (with entrained air) coupons being the largest. The remaining mass increases were not significantly different from each other.

Thus, corrosion from coupons of this size and type appears to be at a low enough rate to be virtually undetectable by mass. Further studies should utilize coupons with higher surface area to volume ratios, and ensure active sulfur oxidation in the reactors.

DGGE was performed on samples taken from both the medium and the coupon biofilm for every reactor. The DGGE indicated that the microbial community was different in each reactor. This could be due to varying environments based on the different coupons placed in each reactor system. The DGGE results are presented photographically in Figure 13. Each "Lane" corresponds to a sample being analyzed; each "Band" corresponds to a bacteria type. Lane 1 is a sample from the initial culture that was used to inoculate the reactors. The DGGE shows three strong bands in the initial culture. As the pH dropped significantly (pH 1.71) in this sample, these bands are likely indicators of sulfur oxidizing bacteria. The bands seen in the initial culture are labeled 1, 2, and 3, and appear in several of the reactors, as indicated in Table 11. Overall, this is an indication that the putative sulfur oxidizing bacteria are present in several of the reactors. Additionally, a drop in the pH in the reactor with PC coupons was recorded. Three bands in the Portland cement lane of the DGGE (Lane 2) correspond to the three bands seen in the initial culture, again indicating sulfur oxidizing bacteria. In addition, the biofilm samples are very similar to their corresponding medium samples in the Portland cement with entrained air and the Dave Johnston reactors. However, the rest of the reactors had significant differences in the microbial community between the biofilm and medium samples. A difference might be expected between biofilm communities on a coupon undergoing even slow corrosion and a suspended culture at the solution pH. Subsequent testing will be carried out with a higher inoculum strength to produce a more actively corroding environment.

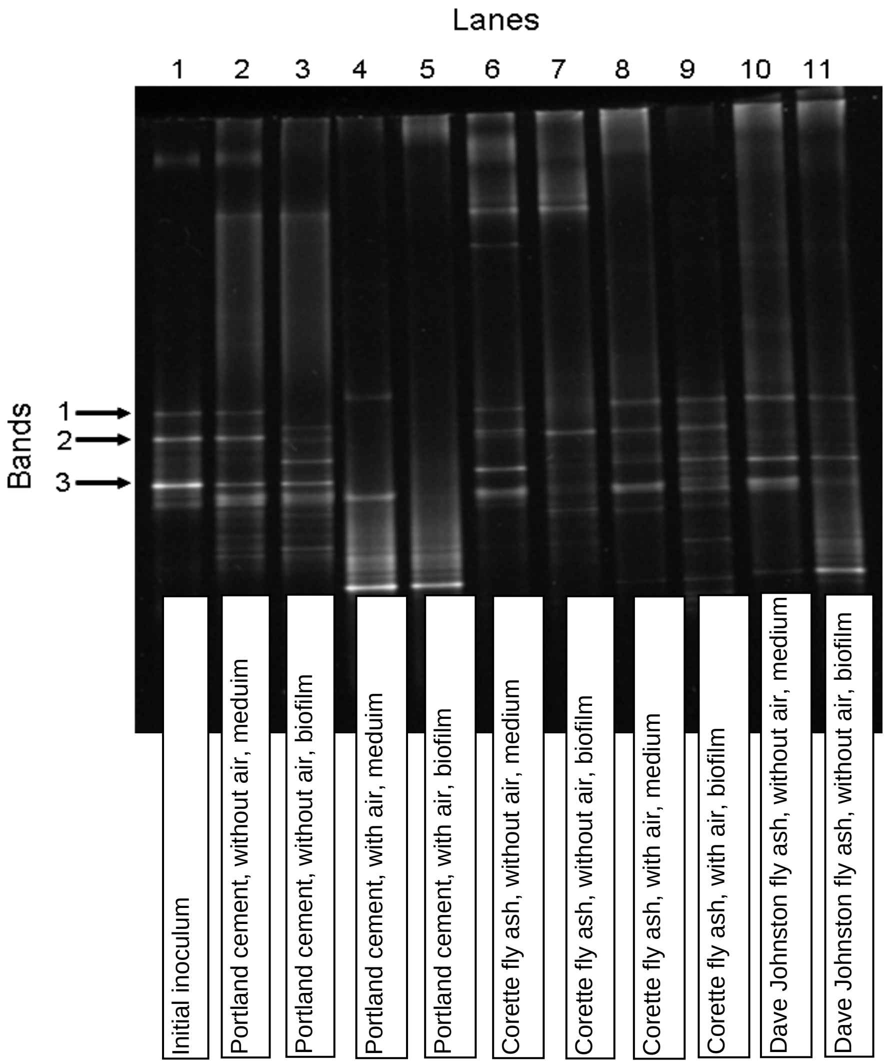


Figure 13. DGGE Comparison of the Microbial Communities of all Five Reactors

Table 11. Selected DGGE Results, Microbial Communities

Sample		Lane	Band Observed in Sample?		
			Band 1	Band 2	Band 3
Initial Inoculum		1	Yes	Yes	Yes
Portland cement, without air	Medium	2	Yes	Yes	Yes
	Biofilm	3			Yes
Portland cement, with air	Medium	4			
	Biofilm	5			
Corette fly ash, without air	Medium	6	Yes		
	Biofilm	7		Yes	
Corette fly ash, with air	Medium	8	Yes	Yes	
	Biofilm	9	Yes	Yes	
Dave Johnston fly ash, without air	Medium	10	Yes		
	Biofilm	11	Yes		

5. CONCLUSIONS

The results of this project have substantially increased the body of knowledge on 100 percent fly ash concretes. While the basic strength and other engineering properties of concretes made using just Class C fly ash from the Corette power plant in Billings, MT, as the binder (without any Portland cement) have been known for some time, little definitive information has been available on:

1) whether other similar fly ashes exhibit the same degree of cementing action as the Corette fly ash and can be used as the binder in fly ash concretes, and
2) whether these concretes offer acceptable durability for their intended application (e.g., construction of buildings, bridges, pavements, waste water structures, etc.).

The absence of information on these subjects has hindered use of this new material in the marketplace. The data obtained from this project should facilitate acceptance of this material across the design and construction community.

Relative to serving as the binder in fly ash concrete, three fly ashes believed to be similar in properties and manner of production to the Corette fly ash were investigated herein, namely fly ashes from the Port Neal (Sioux City, IA), Dave Johnston (Glenrock, WY), and Council Bluffs (Council Bluffs, IA) power plants. The Dave Johnston and Port Neal fly ashes were found to produce concretes with compressive strengths approaching those of Corette based mixtures (approximately 4,000 psi at 28 days). The Council Bluffs fly ash, however, only achieved approximately 33 percent of the fly ash control mixture (i.e., 1,260 psi at 28 days). Thus, of these three fly ashes, both the Dave Johnston and Port Neal ashes appeared promising as concrete binders. Based on available resources, only one of these ashes could be further investigated, and the decision was made to move ahead with the Dave Johnston in addition to the Corette ash. In subsequent mix development work with the Corette fly ash, it was further found that entrained air can be readily introduced into 100 percent fly ash concrete using a commercial admixture. Both non air entrained and air entrained mixtures were subsequently considered in the durability tests.

Prior to this test program, the durability of fly ash concretes could only be speculated on based on knowledge of, and past experience with, Portland cement concretes. In this project, performance data was collected on the freeze-thaw resistance, ASR sensitivity, and hydrogen sulfide/microbial resistance of these concretes. The tests conducted on freeze-thaw and hydrogen sulfide/microbial resistance are being continued beyond the end of this project to further increase the robustness of the data collected on these topics; additionally, work is continuing on the absorption and sulfate resistance tests that were started during this project, with the results to be reported at a later date.

Relative to freeze-thaw resistance, the performance of the Corette fly ash concrete has been satisfactory (relative dynamic modulus of 89 percent) through 225 cycles of exposure completed at the time this report was prepared. The performance of this concrete compares reasonably well with that of Portland cement concrete control mixtures. A relative dynamic modulus of 80 percent or greater after 300 cycles of response is often assumed to indicate good freeze-thaw resistance. The performance of the air entrained and non-air entrained Corette concretes was similar. While the relative dynamic modulus of the Dave Johnston concrete is of this same magnitude, these specimens exhibited a distinct increase in their rate of weight loss after 144 freeze-thaw cycles, which could signal a an impending significant change in their general condition..

From an ASR perspective, all the fly ash mixtures exhibited similar behavior and significantly outperformed the Portland cement control mixtures. Following ASTM C1260, after 14 days of exposure to an alkali solution at elevated temperature, the fly ash mixtures expanded only 0.01 to 0.02 percent. The typical threshold at which a concrete is assessed as reactive is at an expansion of 0.10 percent to 0.20 percent; thus, the fly ash mixtures performed very well. The Portland cement control mixtures expanded 0.24 to 0.38 percent.

Over the 2 ½ month duration of the hydrogen sulfide/microbial corrosion test, little deterioration was observed in the fly ash and Portland cement based concretes. Unlike the previous durability tests described above, no standard test protocol was available for studying this behavior. The test procedure developed herein involved cyclically exposing mortar coupons to a sulfur enriched, wastewater-based microbial medium in a series of independent reactors. Over the duration of the test, among other things, a) precipitates were noted on some of the specimens at the edge of their wetted zone, b) all the specimens nominally gained weight, c) the sulfate concentration increased in the exposure medium in each reactor, and d) some commonality was observed in the microbial communities that evolved in each reactor environment. In general, however, all activity was nominal in magnitude, and a longer test duration will be necessary to fully characterize the hydrogen sulfide/microbial resistance of these concretes.

While the data collected during this project will be very useful in further developing and moving ahead with commercial applications of fly ash concretes, it represents a relatively modest effort compared to the body of research conducted on Portland cement concretes. While it is both impossible and unnecessary to complete this same volume of research before fly ash concrete can be used in real life applications, certainly it would seem that some additional research on fly ash concrete is merited as this material moves into the marketplace. These future research needs are diverse, and include further durability testing both replicating and extending the work conducted herein, and further investigation of additional fly ashes to serve as the binder material in 100 percent fly ash concrete. One such potential binder identified herein, for example, is the fly ash from the Port Neal power plant, which performed as well as the Corette and Dave Johnston fly ashes in this preliminary investigation of its properties.

Interest in 100 percent fly ash concrete continues to grow, based on the many enquiries received by MSU concerning this material from around the country. Ideally, research on this material will continue so that design and construction industries have the information they need to use it.

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7. APPENDIX A

Hydrogen Sulfide/Microbial Induced Damage, Test Methodology

The action of microbial sulfur oxidation in environments like the crown of a sewer pipe can produce prodigious amounts of acid that can react with the paste components in concrete, destroying the pipe. Unlike the other behaviors investigated in this project, no standard test methodology was available to investigate this type of concrete degradation. Testing was carried out using a modified version of a procedure described by Vincke and his associates (1999) that incorporates sulfide absorption, biodegradation and washing through several cycles. The goal was to use a mixed culture of microorganisms enriched from a concrete- corrosive environment to simulate the events in a sewer. This simulation was staged in a bench top reactor containing mortar coupons of the concretes of interest submerged in a medium produced by enriching wastewater samples from a treatment plant. Loss of mass due to corrosion and production of sulfuric acid and accompanying pH decrease was expected to provide a reasonable set of measurable parameters to distinguish any differences in behavior attributable to the type of concrete, while microbial community analysis was expected to ascertain whether the concrete type also selected for different microbial populations. Details regarding this test methodology are presented below.

Reactor design

The reactors were designed to be large enough to hold 6 coupons (13 x 3 x 1 cm) with ample space for the surrounding medium. Each reactor was connected to a 4-liter medium bottle by an overflow line. An aliquot of the sulfur oxidizing culture was added to about 4 liters of medium (described below), and placed in the reactor systems. To mimic wastewater conditions, every evening at about 8 pm, each reactor was drained to below the level of the coupons by pumping all of the medium back into the media bottle. At 7 am, another set of pumps was used to refill and then re-circulate medium from the media bottle through the reactor. This was performed intermittently for 2 to 3 hour periods until the pump system was reversed in the evening. With the pumps and settings used, draining the reactor required about 7.58 minutes, while filling it required 24 minutes. Due to the small volume of water remaining in the bottom of the reactor overnight, the actual residence time during recirculation was about 37.5 minutes. Each type of concrete was tested in its own isolated system. Four liters of medium and 25g of sulfur were used per reactor. To ensure that the sulfur particles did not clog the reactor tubing, the sulfur was placed in cheesecloth and hung in the reactor medium.

Following curing for 7 days, coupons were placed in an oven at 104ºC and then weighed to 3 decimal points before being placed in the reactors. Coupons were suspended in the reactors by means of plastic ties wrapped around the top of the coupon and then looped through holes in the lid. When reactors were drained, coupons were completely out of the fluid. When the reactors were full, the coupons were submerged except for the top 3 cm. Once placed into service, the reactors were operated continuously until sampled at the end of the run. Durations of exposure for each concrete type are shown in Table 1.

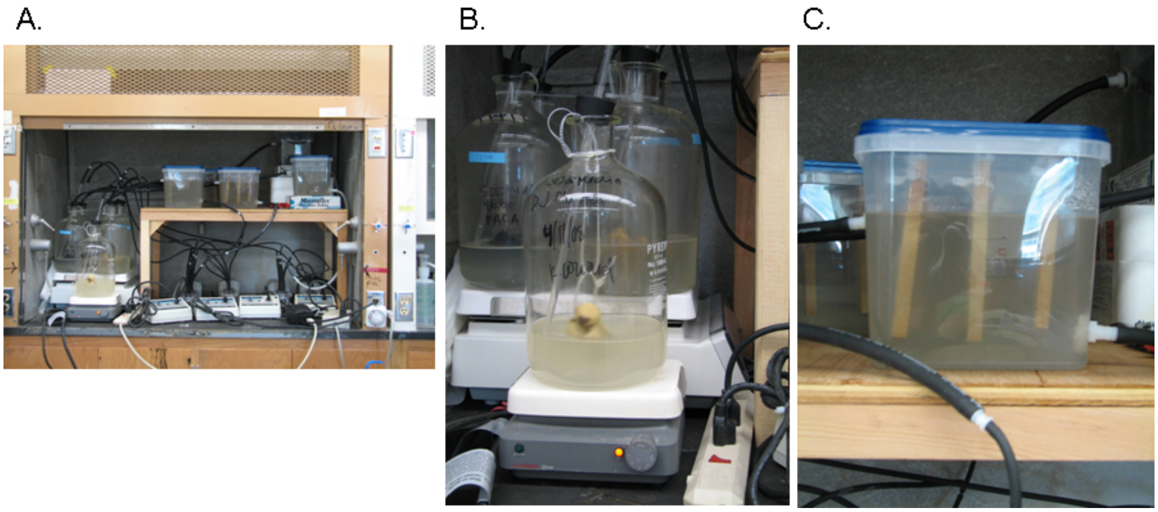

Fig 1. Pictures of the reactors used to evaluate the corrosion of various concrete mixtures by sulfur oxidizing bacteria. **A.** overview of the reactor system in chemical fume hood. **B.** Media bottles with stir motor. **C.** Reactor containers at full level with coupons.

Table 1. Length of time each individual reactor was run.

Reactor	**Reactor abbreviation**	**Days run**
Portland cement	PC	74
Portland cement – aerated	PCA	73
Curette plant fly ash	FAC	70
Curette plant fly ash – aerated	FACA	69
Dave Johnson fly ash	DJ	66

Bacterial inoculum

Biomass samples were obtained from the Bozeman, Montana Wastewater Treatment Plant. Samples were scraped from the gravity thickener where biofilms were perceived to be causing concrete corrosion. The wastewater treatment samples were enriched for sulfur oxidizing bacteria on sulfur oxidizing bacterial medium (SOB medium). SOB medium was composed of 22 mM KH_2PO_4, 4.2mM $MgSO_4$, 2.3mM $(NH_4)_2SO_4$, 2.3 mM $CaCl_2$ and 0.12mM $FeCl_3$, and adjusted to a pH of 4.82. Elemental sulfur (0.5g/75mls) was added, and the medium was inoculated with the wastewater treatment samples. The enrichment cultures were incubated at room temperature (25ºC) in baffle flasks at 200 rpm. Samples were monitored for a drop in pH, which corresponded to the production of sulfuric acid by the sulfur oxidizing bacteria. These SOB enriched cultures were then used as inoculum for the reactors.

Reactor sampling protocol

At the end of the incubation periods shown in the table above, four coupons were removed from each reactor. Three coupons were used for taking weight measurements to evaluate for corrosion. These three coupons were rinsed with tap water in attempt to remove salt and biofilm material. After the reactors had run for the number of days presented in Table 1, the coupons were removed, dried at 104ºC for 168 hours and re-weighed.

The surface of the fourth coupon was scraped with a wooden dowel, and then rinsed with sterile water (Fig 2). The water was collected for biofilm bacterial community analysis.

Fig. 2. Picture demonstrating the scraping technique used to obtain microbial biomass from the reactor coupons.

Coupon Control

A set of control coupons was used to determine the effect that just submerging concrete coupons in water had on mass measurements. Ten coupons, two of each type of cement, were dried for 24 hrs at 104°C, weighed, and subsequently partially submerged in water for 24 hours. The coupons were then rinsed with water from a squirt bottle to mock the removal of a biofilm. These coupons were again dried at 104°C. After 24 hours, the average weight difference between the initial drying step, and after being soaked in water and dried for 24 hours was 0.337g with a standard deviation of 0.0405. The average difference after 168 hrs was of drying at 104°C was 0.1997g with a standard deviation of 0.0517.

Ion Chromatography

Sulfate was measured using ion chromatography IC method. Samples were centrifuged at 5000xg and diluted by 1/10 (PC reactor effluent was diluted 1/100), then filtered through a 0.2 µm filter. Twenty-five µL samples were injected into a Dionex (Sunnyvale, CA) DX□500 chromatography system fitted with an IonPac AS9-HC column (4x200mm) and guard column. Detection was achieved using the suppressed conductivity (Dionex ASRS□ultra II) auto suppression, recycle mode. The mobile phase was 9 mM sodium carbonate (1.0ml/min).

Molecular Biology

Denaturing gradient gel electrophoresis (DGGE) is a bacterial community analysis technique. DGGE was done on all five reactors, both on samples from the medium and the biofilm scrapings, and from the initial inocula used to spike the reactors. The banding pattern gives an indication of the microbial diversity in each of the reactor systems. This technique provides an indication of the predominant sulfur oxidizing bacterial groups in the reactors. Further details on these methods are shown in the DGGE Section below.

Nested PCR

The reactors initially appeared to have an inhibitory substance which prevented the direct polymerase chain reaction (PCR) DNA amplification. Therefore, a nested PCR technique was utilized in order to amplify DNA from the reactor medium and biofilm scrapings. In this technique, the first set of primers is used to amplify a DNA sequence. In a second reaction, the second set of primers (located internally on the DNA sequence) is used to further amplify the template DNA (Fig 3). The advantage of this technique is allowing the first inhibitory reaction to minimally amplify the DNA of interest. This template, now enriched for the target, is then diluted (which further decreases inhibition) and DNA can then be amplified to a level conducive to downstream molecular work.

Fig. 3. Diagram of a nested PCR reaction. Primer set 1 is used first and amplifies template for the second reaction using primer set 2.

Specifically in this case, cell matter was used directly as DNA template for the first PCR reaction which used the 8F and 1492R primers. The product was subsequently used as template in the second PCR reaction, which utilized 1070F and 1492R-GC clamp primers (Ferris *et al.* 1996;Liu *et al.* 2002).

Reactions were done using a Mastercycler EP Gradient thermocycler (Eppendorf, Westbury, NY). Reaction mixture for PCR included GoTaq Green Mastermix (Promega, Madison, WI), 1 μM primer, and 0.2 mM dNTPs. 16S PCR: Amplification program; 94° for 10 min; with 25 cycles of 94° for 45s; 52° for 45s; 72° for 1.5 mins; finally 72° with 7 min extension. This program was used for both nested PCR reactions. This program was used with the universal 1070F and 1492R –GC clamp primers. Primers were synthesized by Integrated DNA Technologies (Coralville, IA).

DGGE

To gain an understanding of a bacterial community profile by DGGE, the first step is to PCR amplify the bacterial 16S gene in order to obtain sufficient quantities of DNA. The amplified 16S gene product is approximately the same length in every bacterial species; therefore electrophoresis of the 16S DNA on a typical agarose gel (which separates by size) does not give an indication of how many different 16S sequences (an indicator of species diversity) are present. In DGGE a denaturing gradient is established in the gel, as the 16S fragments migrate through the gel, due to electrophoresis, the double stranded 16S genes separate according to the strength of the bonds between the two strands. As GC bonds are stronger than AT bonds, differences in the nucleotide composition of any given 16S sequence will result in separation at a slightly different denaturant concentration in the gel. The 16S amplification is done with a primer which has a string of about 40 GC repeats that hold the gene product together at one end. The separation of 16S DNA from single to double stranded forms a Y shape molecule that retards the migration of the DNA through the gel, creating a distinct banding pattern. As different species have different 16S nucleotide sequences, the banding pattern is an indication of the species diversity in the bacterial community.

Denaturing gradient gel electrophoresis (DGGE) was done to evaluate the microbial community in the reactors. The DGGE had a gradient of acrylamide from 8 – 12% with a gradient of denaturant from 40% -70% (100% denaturant was composed of 7 M urea and 40% formamide, reagents were from Sigma-Aldrich, St. Louis, MO). The DGGE was run on a DCode system (Bio-Rad, Hercules, CA) for 16 hours at 60V. The gel was visualized by staining with SYBR Gold (Molecular Probes, Inc., Eugene, OR), and subsequently examined with a FluorChem 8800 fluorescence imager (Alpha Innotech, Inc., San Leandro, CA).

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