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14. ABSTRACT

The paper discusses the background of cementitious materials, and generally compares natural (Pozzolanic) cement to manufactured (Portland) cement. Fly ash is discussed as a common Pozzolan, and in particular, the low-energy requirement for fly ash as compared to Portland cement. Also, photomicrographs of fly ash particles and of chemically bonded fly ash are compared to a photomicrograph of Portland cement particles and a photograph of Portland cement concrete to dramatically illustrate the differences in the matrix formation of these cementitious materials.

Laboratory data is used to show that simply adding some fly ash to a Portland cement mix can greatly reduce the permeability of the concrete under certain curing conditions. In addition, laboratory data is used to show that chemically-bonded fly ash can be engineered so that its structural properties (i.e., compressive strength, flexural strength, modulus of elasticity, etc.) mimic those of Portland cement concrete. However, bonded fly ash has a far denser matrix than Portland cement, and that dense matrix, in turn, gives the bonded fly ash a relatively low permeability without significant curing. While not completely impermeable, as a structural material bonded fly ash is much more resistant to a chemical or biological intrusion than is Portland cement, when used as an expedient repair material, as demonstrated by laboratory comparison tests.

Finally, although bonded fly ash is denser than Portland cement mortar, but since it does not require rock aggregate, it actually has lower density that Portland cement concrete. This means that bonded fly ash can be used to decrease the total weight of a structure, while also reducing the energy requirements of the materials, and, at the same time, increasing the resistance to chemical or biological intrusion.

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Mark Anderson, Ph.D., P.E.[1] and Maj. Dov Dover, P.E.[2]

ABSTRACT

The paper discusses the background of cementitious materials, and generally compares natural (Pozzolanic) cement to manufactured (Portland) cement. Fly ash is discussed as a common Pozzolan, and in particular, the low-energy requirement for fly ash as compared to Portland cement. Also, photomicrographs of fly ash particles and of chemically bonded fly ash are compared to a photomicrograph of Portland cement particles and a photograph of Portland cement concrete to dramatically illustrate the differences in the matrix formation of these cementitious materials.

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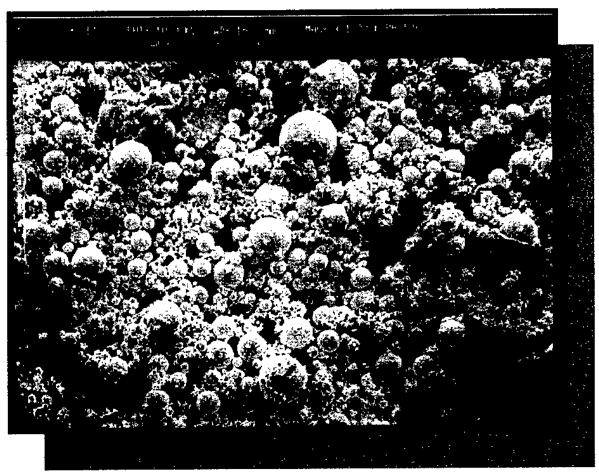
BACKGROUND

Basic Cement Types[3]

While there are some variations, cements can generally be separated into two major groups: "manufactured" cements and "natural" cements. The primary type of manufactured cement is Portland cement. The primary type of natural cement is Pozzolanic (or Pozzuolanic) cement.

Portland cement is made by kiln-firing limestone to produce "clinker," which is then pulverized to produce fine, cementitious particles. In a concrete or mortar made with Portland cement, the cement particles are generally the smallest particles. The Portland cement particles are extremely angular, due to the crushing action during manufacture. This particle angularity is illustrated in Figure 1(a), which is a photomicrograph of Portland cement particles. The effects of particle angularity are discussed in a subsequent section.

(a) Portland cement particles.



(b) Fly ash particles.

Figure 1. Photomicrographs of basic cement types.[4]

Pozzolanic (or Pozzuolanic) cement has been used since the days of the Roman Empire. In Roman times, the cement was made from volcanic ash taken from the island of Pozzoli (also spelled Pozzuoli, hence the two spellings of the cement's name). In modern times, Pozzolanic cement is made from fly ash, which is a waste product from the burning of coal (primarily from coal-fired utility plants). In the past, fly ash was released into the atmosphere via smoke stacks,

[3]Anderson, Mark, Ph.D., P.E., and Riley, Mike, *PaveMend™ as a Solution for Rapid Runway Repair*, **Proceedings**, 27th Annual International Air Transport Conference, American Society of Civil Engineers, Orlando, Florida, 2002.

[4] Photomicrograph prints used with the permission of ABC Cement, Inc.

but recent environmental regulations require collection and proper disposal of the fly ash (most often, into landfills). The combination of the ready availability of fly ash and a need for cements with improved properties for special tasks (such as airfield damage repair) has spurred development of products that utilize the special properties of fly ash to create high-strength, rapid-set materials.

Figure 1(b) shows a photomicrograph of fly ash (at the same scale as Figure 1(a)). Three important observations can be made readily from looking at Figure 1(b) (contrasted with Figure 1(a)). First, the shape of the fly ash particles is spherical. Second, the fly ash particles are poorly-graded (that is, the sizes of the particles are greatly varied). Third, even the large fly ash particles are far smaller than the Portland cement particles. The importance of these three observations will be discussed in the next section.

The shape and variation in size of the fly ash particles is due to a phenomenon not unlike the formation of hail (although the fly ash spheroids are composed mainly of SiO_2). Minuscule particles fly off the burning coal in minute molten bits that form round, glass balls as they tumble through the air. The heat waves cause more bits of molten glass to be carried upwards, some of which collide with other bits and become larger bits of molten glass that then tumble to form larger spheres. This process can continue with larger and larger spheres, until there are a wide variety of diameters of spheres. The glass spheroids are mainly composed of SiO_2, but have a number of other constituents, depending on the purity/impurity of the coal being burned.

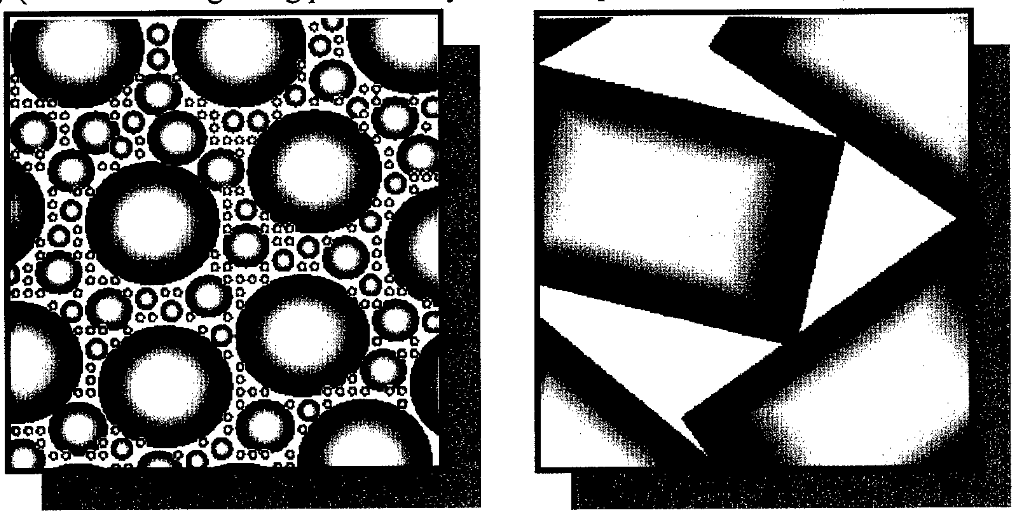
Matrix Density.

When considered independently from all other factors, rounded, poorly-graded particles (like fly ash), tend to form a denser matrix than angular, well-graded particles (like Portland cement). This phenomenon is illustrated in Figure 2. The actual differences may be even more dramatic than depicted in Figure 2, because the actual fly ash particles may be even smaller when compared to the actual Portland cement particles (see the photomicrographs in Figure 1).

The rounded shape of the fly ash particles also contributes indirectly to improved density through "workability." In a mix, the fly ash spheroids act as little "ball bearings" which make the mix workable (i.e., easy to mix and pour). In a Portland cement concrete mix, extra mix water, in addition to the water needed for the cement reaction, is almost always added for workability. This extra water tends to push the particles apart even more, which in turn creates void spaces between particles in the finished product.

Regardless of the mechanism of creating voids in concrete, the void spaces tend to form small, interconnected "tunnels" which attract nearby water by a phenomenon known as capillary action (similar to capillary action in small blood vessels). This, in turn, causes long-term durability problems that are an almost direct consequence of having water in the finished concrete. For example, in colder climates the action of freezing and thawing causes breakdown of the matrix (hence the term "freeze-thaw reaction"). Or, for example, extreme heat can cause water contained within the concrete matrix to be rapidly converted to steam that, in turn, causes a phenomenon similar to an explosion, again breaking down the concrete matrix.

Pozzolanic cements, which create denser matrices than Portland cements, are expected to have several benefits from the increased density. For example, it is expected that the permeability of the final matrix will be lower. The lowered permeability should, in turn, lead to improved durability, whether from freeze-thaw, jet blast, or other reactions that degrade the final product. In addition, the rounded shape and small size of the fly ash particles means that the addition of a small amount of fly ash to a Portland cement mix can do two important things: (1) improve the workability of the mix at the same water to cement (w/c) ratio; and (2) create a denser matrix. However, the addition of fly ash to a Portland cement concrete mix cannot be done "blindly," as the addition of Pozzolanic material to the mix can change the cement chemistry (as discussed regarding permeability in a subsequent section of this paper).



(a) Fly ash. (b) Portland cement.

Figure 2. Artist's conceptual view of cement matrices for basic cement types.

Chemically-Bonded Fly Ash as a "Quadruple-Green" Material.

Fly ash is definitely a "green" material, but particularly when compared to Portland cement. As previously discussed, the making of Portland cement is a "high energy" process, because the limestone must be kiln-fired to produce the "clinker" for crushing. Fly ash, on the other hand, is already a plentiful waste product, and one which usually must be discarded into land fills. In addition, Portland cement concrete generally utilizes aggregate which must be mined and crushed. Chemically-bonded fly ash can use waste materials as filler, such as harbor dredge or crushed glass. Therefore, chemically-bonded fly ash (which, obviously, uses fly ash as its major ingredient), and particularly when used as a replacement for Portland cement concrete, can be thought of as a "quadruple-green" material, because: (1) fly ash is a low-energy material (i.e., green due to energy savings, particularly when compared to Portland cement); (2) fly ash is a plentiful waste product (i.e., green due to waste product utilization); (3) chemically-bonded fly ash can use other waste materials as filler in the mix (i.e., green due to additional waste product utilization, particularly when compared to Portland cement mixes); and (4) fly ash is usually discarded into land fills (i.e., green due to land fill mitigation).

MECHANICAL PROPERTIES OF BONDED FLY ASH

Sample Density.

Figure 3 shows a test for density using a sample cube of chemically-bonded fly ash. Figure 4 compares actual density test results for chemically-bonded fly ash mortar with results for Portland cement mortar,[5] and also with a typical density value for Portland cement concrete.

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[5] The Portland cement mortar was made with a standard "off-the-shelf" mix.

As can be seen in Figure 4, the chemically-bonded fly ash mixed in a large (8 yd^3) mortar mixer was over 30% more dense than the standard Portland cement mortar. Also, the chemically-bonded fly ash mixed in small batches (5-gallon buckets) was almost 40% more dense than the standard Portland cement mortar. However, since the chemically-bonded fly ash does not require the addition of large aggregate, it still is significantly lighter than a typical Portland cement concrete mix. That is, the mortar portion of the mix is more dense than the mortar portion of the Portland cement concrete, but the finished product is still lighter than the finished Portland cement concrete. This means that the use of chemically-bonded fly ash could create a denser mix, but one which is still, in effect, a lightweight concrete (i.e., the best of both worlds).

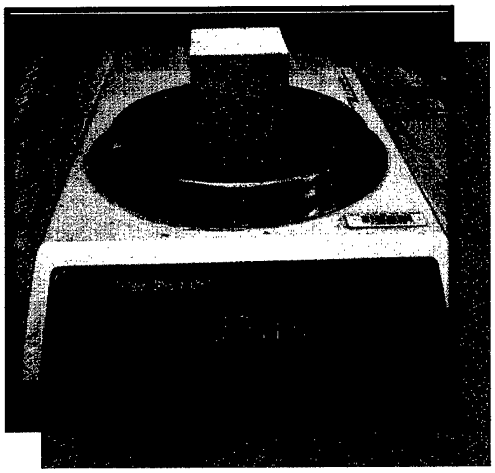


Figure 3. Density test setup for a sample of chemically-bonded fly ash.

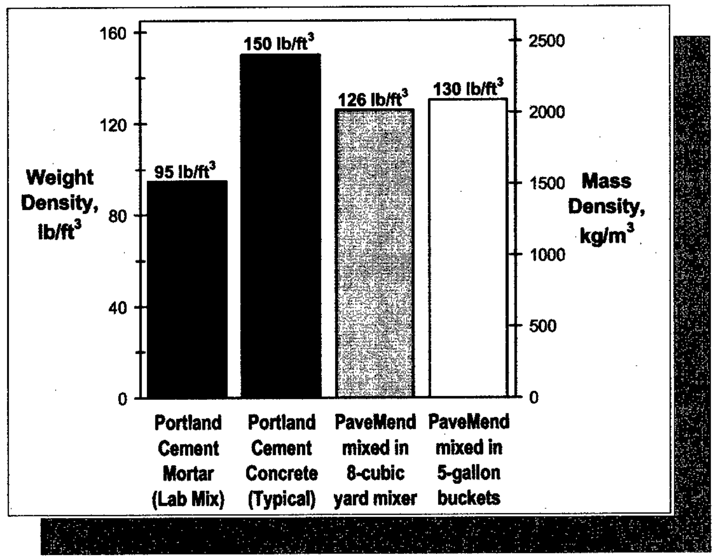
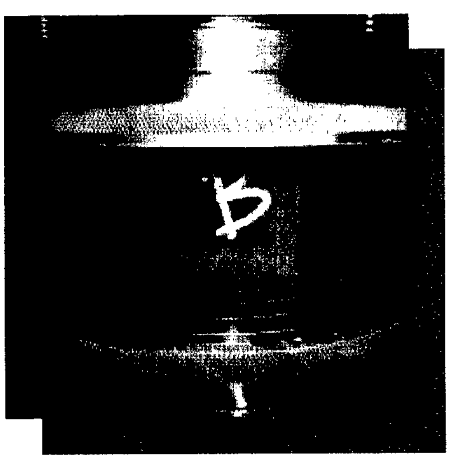


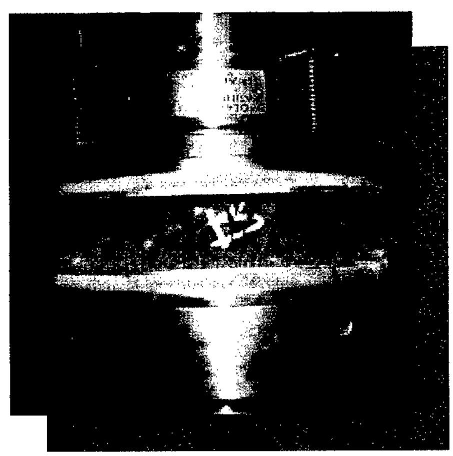
Figure 4. AFRL density test results.

Compressive Strength.

Figure 5 shows a compressive strength test of a chemically-bonded fly ash sample. The mortar cubes are standard cubes, with 2-inch (5-cm) sides.



(a) Test setup.



(b) Sample loaded to failure.

Figure 5. AFRL compressive strength test of a chemically-bonded fly ash sample

Figure 6 shows a compressive strength versus time curve for both chemically-bonded fly ash and standard Portland cement mortar. Figure 7 shows the exact same data as Figure 6, but with an expanded time line.

Of particular interest is the high early strength of the chemically-bonded fly ash. For example: (1) compressive strength of about 2,500-psi in about 1 hour (similar in strength to concrete used, e.g., for sidewalks); (2) compressive strength of about 3,500-psi in about 2 hours (similar in strength to high-quality highway paving concrete); (3) compressive strength of about 4,000-psi in about 4 hours (similar in strength to military runway quality concrete); and (5) ultimate compressive strength of about 5,000-psi (similar in strength to high-quality structural concrete).

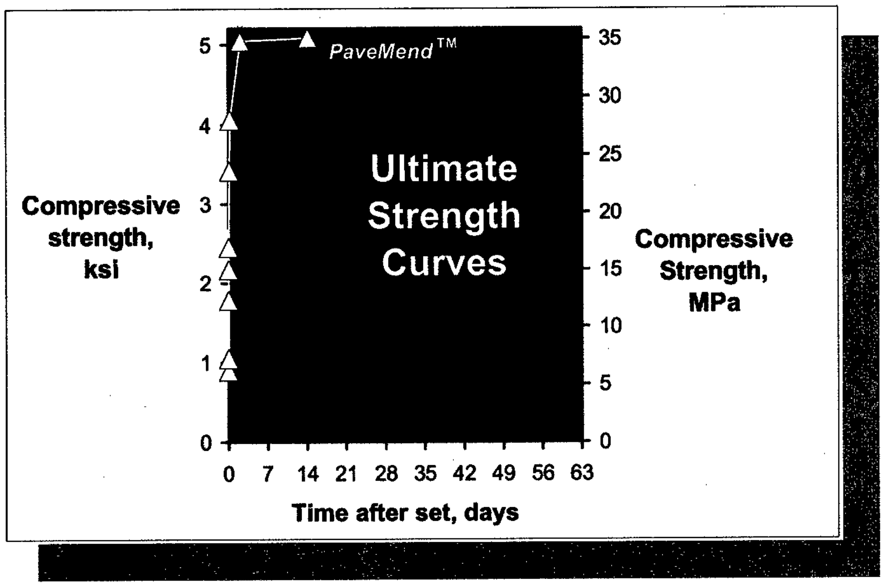


Figure 6. Results from AFRL compressive strength tests.

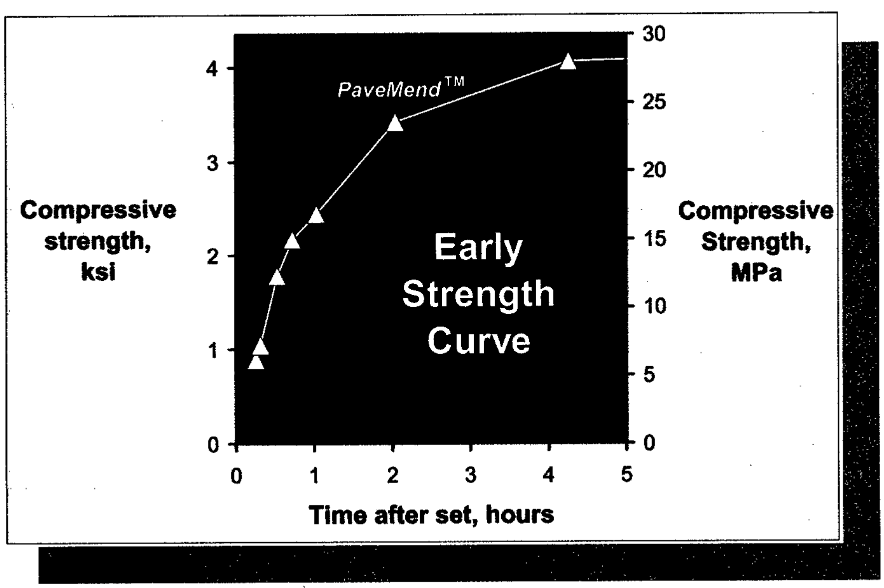


Figure 7. AFRL compressive strength results (expanded time line).

Modulus of Elasticity.

Figure 8 shows a modulus of elasticity test by the sonic method[6] being conducted by an AFRL / MLQD engineering aide. The sample being tested in Figure 8 is a 2-inch x 2-inch x 10-inch beam.

Figure 9 shows the results of AFRL sonic modulus of elasticity tests. Two different formulations of chemically-bonded fly ash were tested for modulus of elasticity. The key result from Figure 9 is that the modulus of elasticity of the chemically-bonded fly ash jumped almost immediately to a value of about 4-million psi (for both formulations), which is about the value expected for a fully-cured Portland cement concrete.

Figure 8. AFRL modulus of elasticity test performed by an AFRL/MLQD engineering aide.

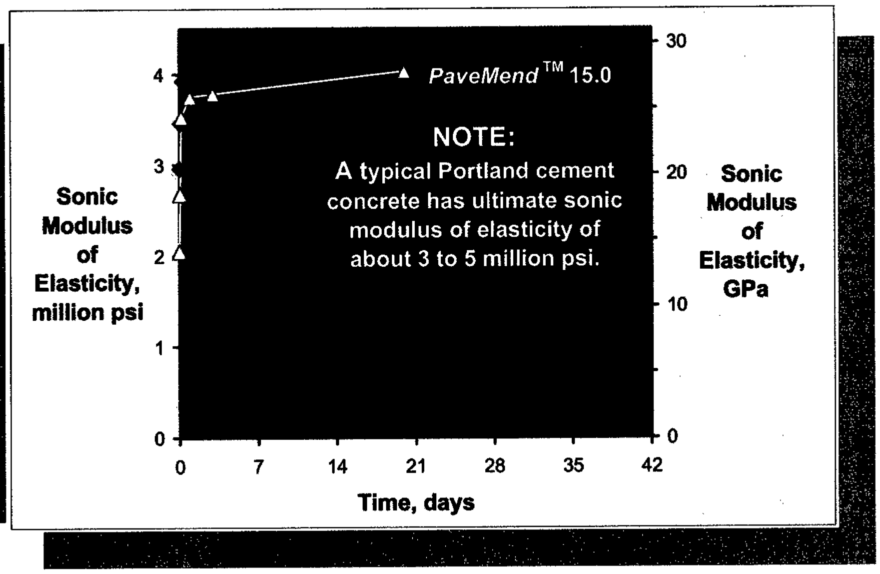


Figure 9. Results from AFRL sonic modulus of elasticity tests.

BONDED FLY ASH IN OPERATION ENDURING FREEDOM

Chemically-bonded fly ash was "battlefield tested" as an emergency repair material during Operation Enduring Freedom (OEF). Based on AFRL tests, the decision was made by Allied forces to purchase an undisclosed quantity of *PaveMend*,™ to be used at an undisclosed location during OEF, as an emergency airfield pavement repair material. To support the use of this material, AFRL / MLQD personnel traveled to the undisclosed location to train Air Force RED HORSE troops on the correct use of chemically-bonded fly ash for emergency repairs.

Figure 10 shows AFRL / MLQD personnel instructing an Air Force RED HORSE team on the use of *PaveMend*™ at an undisclosed location during OEF. Figure 11 shows an actual repair completed by the RED HORSE team at the undisclosed location.

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[6] Anderson, Mark, P.E., **A Guide for the Use of the James V-Meter to Determine the Modulus of Elasticity of Concrete Cores**, a manual prepared for the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida, July 1987; and subsequently adopted for worldwide use by the Air Force Airfield Pavement Evaluation (APE) teams.

A more complete description of the repairs performed during OEF is well beyond the subject and scope of this paper. However, this information is presented in summary form for two important reasons: (1) to emphasize that the use of chemically-bonded fly ash as a substitute for Portland cement concrete is not an untested idea at this point; (2) to emphasize that chemically-bonded fly ash has mechanical properties that, within hours, are similar to a fully-cured Portland cement concrete (which is exactly why it was used as an emergency repair material during OEF).

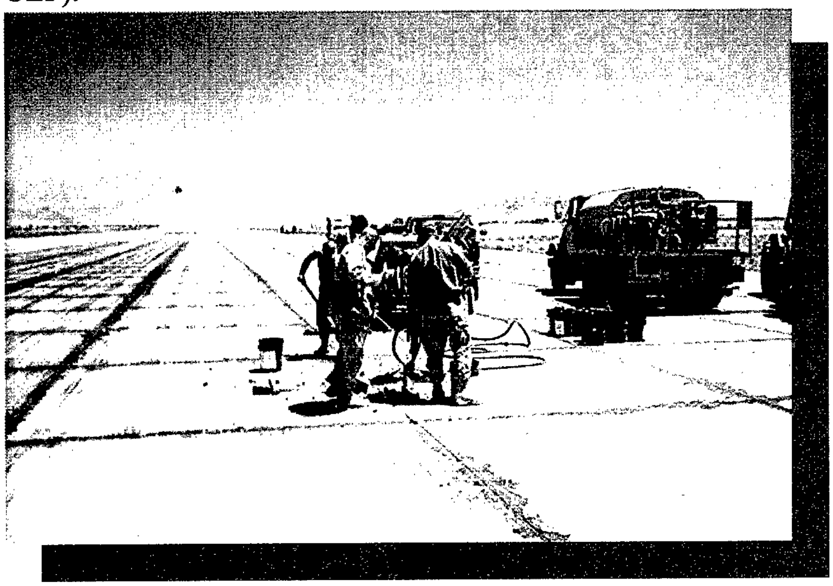

Figure 10. AFRL / MLQD personnel instruct an Air Force RED HORSE team on the use of *PaveMend*,™ a chemically-bonded fly ash repair material, at an undisclosed location during Operation Enduring Freedom.

(a) Before completion of emergency repair..

(b) After completion of emergency repair.

Figure 11. Emergency repair completed using *PaveMend*,™ a chemically-bonded fly ash repair material, at an undisclosed location during Operation Enduring Freedom.

PERMEABILITY TESTING

Test Apparatus.

The permeability tests performed by AFRL, and presented herein, are the constant head type, and were performed using a modified soil permeability test apparatus. The modifications included: (1) the attachment of an air compressor to the water tank to provide a relatively high pressure (i.e., 100-psi); and (2) replacing some of the original fittings with more sturdy ones, in order to withstand the higher pressure (i.e., 100-psi).

Figures 12 through 15 show the AFRL constant-head concrete permeability testing apparatus. Figure 12 shows the overall apparatus, including the three major components: (1) the permeameter, shown at left; (2) the constant-head water tank, shown in the center; and (3) the air compressor, shown at right. Figure 13 shows a close-up view of the permeameter. Of particular interest is the mounting of the test sample, which consists of a portion of a thin-walled soil sampling tube (i.e., a "Shelby" tube). For soil permeability testing, the thin-walled tube (which is about 3-feet long) is used to collect a soil sample *in situ*; then the sample tube, with sample inside, is sawed to a test length of about 3-inches. However, for concrete testing, the thin-walled sample tube is precut, and the concrete poured in. Figure 14 shows a close-up of the pressure gauge, showing the constant-head pressure of 100-psi. Figure 15 shows a close-up of the water collection from the bottom of the permeameter.

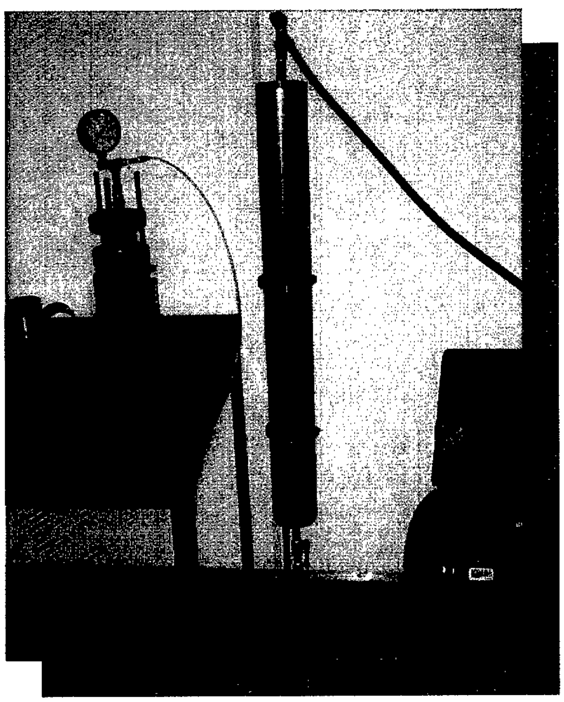

Figure 12. AFRL constant-head permeability test apparatus for concrete.

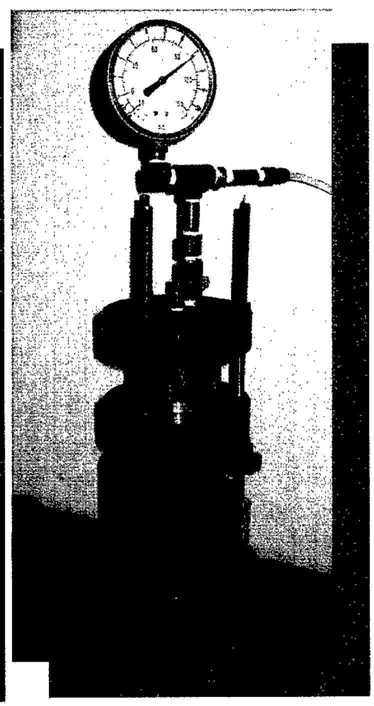

Figure 13. Close-up of AFRL concrete permeameter.

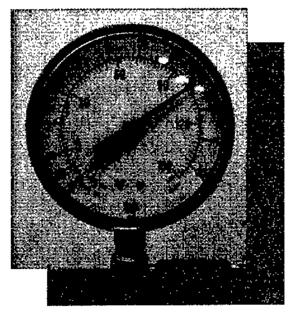

Figure 14. Close-up of pressure gauge.

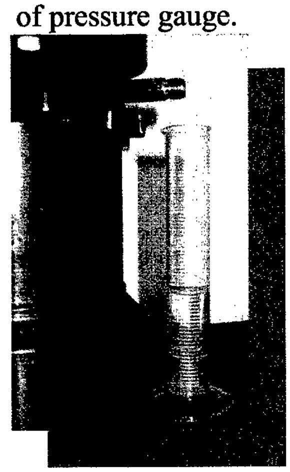

Figure 15. Close-up of water collection.

Permeability Samples.

Figures 16 through 18 show the sample molds, and example specimens of the types of material tested. Figure 16 shows the sample molds, which are 3-inch sections cut from a thin-walled soil sampler. Figure 17 shows a sample mold with red "bottom" cap installed. The red plastic cap is a standard moisture barrier which is sold as an accessory to the thin-walled sampler. However, on the standard thin-walled sampler, the cap does not fit completely flush with the metal. To insure uniform samples, one end of each "mold" was machined slightly to allow the red cap to fit completely flush with the metal (easily seen in Figure 16, on the left-most mold). In Figure 17, the red cap has been placed over the machined end, and the sample mold is ready to be turned upright and filled with concrete. Figure 18 shows actual samples, with the sample edges that were previously against the bottom of the molds facing upwards. As shown in Figure 18, the bottom edges are extremely flush, allowing for accurate length measurement and accurate permeability testing. The three sample types are shown in Figure 18, which are, from left to right: (1) standard Portland cement mortar; (2) standard Portland cement mortar plus 10% raw fly ash (by dry weight); and (3) chemically-bonded fly ash.

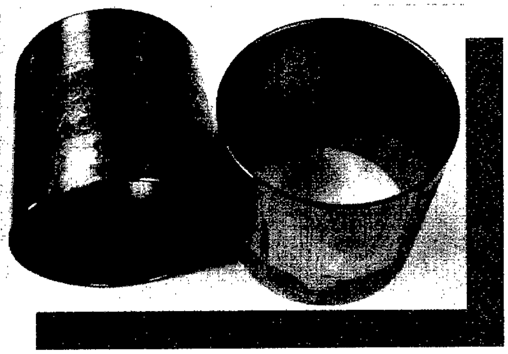

Figure 16. Sample molds for concrete permeability test.

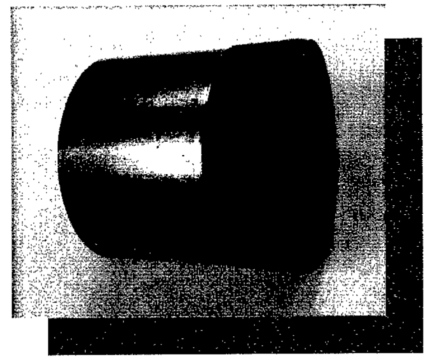

Figure 17. Sample mold with bottom cap installed.

Figure 18. Concrete permeability test specimens, from left to right: (1) standard Portland cement mortar; (2) standard Portland cement mortar plus 10% raw fly ash (by dry weight); and (3) chemically-bonded fly ash.

Curing Conditions.

Curing for the samples containing Portland cement were done two ways: wet-cured and dry-cured. For the wet-cured case, the "best-case" scenario of total immersion in water was used. The "worst-case" scenario was the dry-cure case, which was, as the name implies, an ambient cure at ambient temperature and humidity. The chemically-bonded fly ash samples were dry-cured only (since the chemically-bonded fly ash is being proposed here as an emergency repair material, it is most likely that a dry-cure is a realistic test for the material).

In effect, the two curing conditions provide insight into the two types of construction, with respect to permeability (and, therefore, the ability of the material to withstand chem-bio penetration). The wet-cured samples represent conventional construction, with proper curing of the concrete. In sharp contrast, the dry-cured samples represent concrete repairs (and, in particular, emergency repairs), where the curing is less likely to be done in an optimum fashion.

Permeability Results.

Figure 19 shows the results of the AFRL permeability tests. There are several important conclusions which can be drawn from Figure 19. The most important, in terms of the subject of this paper, is that chemically-bonded fly ash, dry-cured for 1-day, has an order of magnitude lower permeability than Portland cement mortar, dry-cured for 7-days (i.e., $7x10^{-8}$ cm/s and $7x10^{-7}$ cm/s, respectively). When the chemically-bonded fly ash is dry-cured for an equal amount of time (i.e., 7-days), the difference is even more pronounced (i.e., $4x10^{-8}$ cm/s compared to $7x10^{-7}$ cm/s). Perhaps more importantly, the chemically-bonded fly ash had lower permeability when dry-cured than the Portland cement mortar wet-cured the same amount of time (i.e., $4x10^{-8}$ cm/s and $5x10^{-8}$ cm/s, respectively).

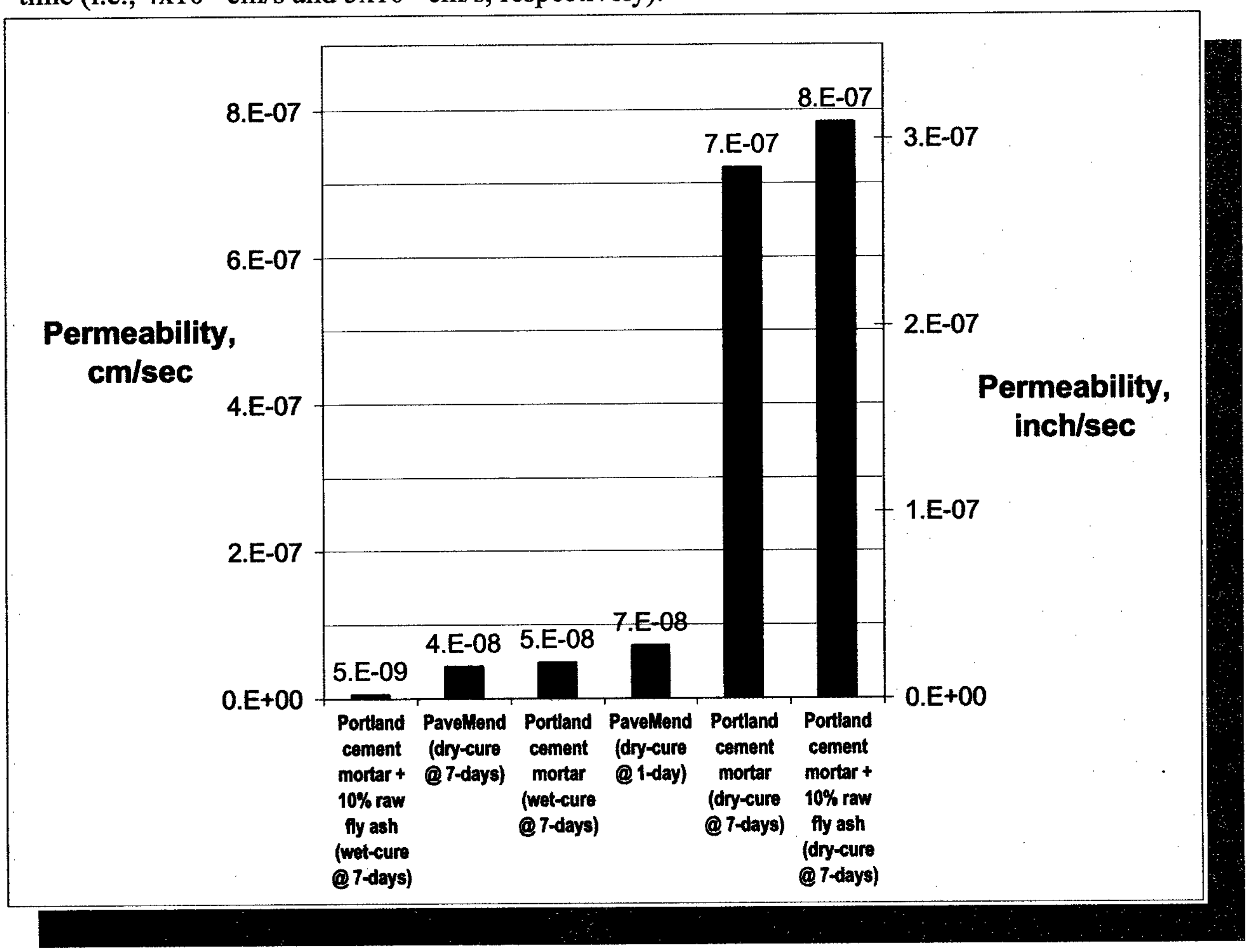

Figure 19. Results of AFRL permeability tests.

From a researcher's point of view, the addition of raw fly ash (10% by dry weight) to the Portland cement mortar produced the most interesting results. When wet-cured, the Portland cement mortar plus raw fly ash gave the lowest permeability of all the samples ($5x10^{-9}$ cm/sec); but, when dry-cured, the same mix gave the highest permeability of all the samples ($8x10^{-7}$ cm/sec). The first result is extremely important, because it shows that the addition of a small amount of fly ash to a Portland cement mortar mix can reduce the permeability by an order of magnitude, under optimum curing conditions (i.e., $5x10^{-9}$ cm/s and $5x10^{-8}$ cm/s, respectively). Conversely, the addition of a small amount of fly ash to a Portland cement mortar mix actually increases the permeability, when both samples are dry-cured (i.e., $7x10^{-7}$ cm/s and $8x10^{-7}$ cm/s, respectively). However, this small difference (about 8%) pales in comparison to the more than two orders of magnitude difference when the mortar plus fly ash is wet-cured. An 8% difference falls within the expected error for this test, so the question is open as to whether the addition of raw fly ash to the Portland cement mortar, with dry-curing, had essentially no effect – or had a deleterious effect. If, in fact, the effect was deleterious, the actual mechanisms causing this effect are unknown at this point, and beyond the scope of the research for this paper. Research is needed into the cement chemistry controlling the permeability for these mixes under differing curing conditions.

Finally, although slightly higher (about 30%), the chemically-bonded fly ash dry-cured for 1-day had permeability on the same order of magnitude as the Portland cement mortar wet-cured for 7-days (i.e., $7x10^{-8}$ cm/s and $5x10^{-8}$ cm/s, respectively). This is a key result because it indicates that chemically-bonded fly ash, used as a repair material, will almost immediately have permeability which approaches that of finished concrete, even when the chemically-bonded fly ash is cured under adverse curing conditions.

CONCLUSIONS

1. Chemically-bonded fly ash is a very "green" material (perhaps even "quadruple-green"), when compared to Portland cement concrete mixes.

2. Chemically-bonded fly ash has a denser matrix than Portland cement mortar.

3. Although chemically-bonded fly ash has a denser matrix than Portland cement mortar; as a repair material, it has a lighter weight than a typical Portland cement concrete mix.

4. Adding some fly ash to a Portland cement mix can greatly reduce the permeability of the concrete under certain curing conditions.

5. Chemically-bonded fly ash can be engineered so that its structural properties rapidly mimic those of fully-cured high-performance Portland cement concrete, even under adverse curing conditions.

6. **While not completely impermeable, chemically-bonded fly ash is much more resistant to a chemical or biological intrusion (compared to a Portland cement mix), when used as an expedient repair material, because of the low permeability it achieves almost immediately, even under adverse curing conditions.**